DALTON
FULL PAPER

Syntheses and structural properties of bis(hexacarbonyldicobalt) complexes from cyclic diynes

Bernhard J. Rausch, Rolf Gleiter * and Frank Rominger

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

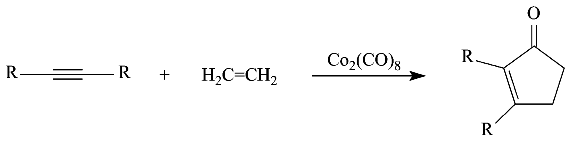
Received 4th January 2002, Accepted 5th March 2002
First published as an Advance Article on the web 17th April 2002

The bis(hexacarbonyldicobalt) complexes of nine ten- to fourteen-membered cyclic diynes (**1**–**3**, **5**, **6**, **8** and **10**–**12**) have been isolated. The structural parameters of the complexes have been examined by means of X-ray investigations on single crystals. It was found that the chair like conformation of the uncomplexed rings is changed into a twisted one upon complexation. In addition to the pure hydrocarbons the syntheses of the bis(hexacarbonyldicobalt) complexes of eight heterosubstituted cyclic diynes (**4**, **7**, **9**, **13**, **15**–**17**) and of a mono(hexacarbonyldicobalt) complex **18** are reported and their structural parameters are presented.

1 Introduction

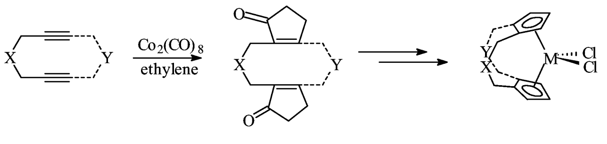
The reaction of alkynes with octacarbonyldicobalt is a widely used method in organometallic chemistry.[1] The resulting complexes are, for instance, used for the synthesis of polymers with transition metal backbones[2] and as protected alkyne equivalents.[3] In particular, the Nicholas reaction with propargylium–$Co_2(CO)_6$ complexes has been extensively investigated.[1,4]

The recent efforts in Pauson–Khand chemistry (Scheme 1)[5] especially on the development of photochemical versions[6] as well as recent quantum chemical investigations[7] on the Pauson–Khand mechanism demand an in depth study of the structural properties of the $C_2Co_2(CO)_6$-core. Even though there are many comprehensive reviews[5] on Pauson–Khand chemistry the structural details of the alkyne–$Co_2(CO)_6$ complexes as determined by X-ray crystallography are mostly scattered in many reports.[8,9]



Scheme 1 Pauson–Khand reaction to yield cyclopentenones.

We became interested in this field by carrying out two-fold Pauson–Khand reactions of acylic and cyclic diynes with ethylene[10] (Scheme 2) in order to obtain singly and doubly tethered cyclopentenones as starting materials for *ansa*-metallocenes.[11]



Scheme 2 Synthesis of *ansa*-metallocenes *via* two-fold tethered cyclopentenones.

During this research we noticed that for a deeper understanding of the mechanism of the cobalt mediated cyclization of the diynes a detailed knowledge of the structural features of the corresponding bis(hexacarbonyldicobalt) complexes is necessary. Therefore we have synthesized the bis(hexacarbonyldicobalt) complexes of 17 ten- to fourteen-membered cyclic diynes and scrutinized their structures by X-ray techniques. In this paper we report the results of this study.

2 Results

The two-fold tethered diynes were synthesized according to literature procedures.[10,12–19] They were reacted with $Co_2(CO)_8$ in light petroleum (30/40) or methylene chloride to afford the corresponding products after column chromatography. We have already published the syntheses of **1**, **2**, **10**–**12**[12] and **8**,[20] King *et al.* initially prepared **3** and **5**,[21] however, no crystal structures have been reported. The isolated yields obtained for the syntheses of **1**–**18** are given in Table 1.

A comparison shows that the yields are somewhat dependent on the ring size and functionality. We found good to excellent yields for the all-carbon membered rings **3**, **5**, **6** and **8** (about 90%). For the heterocyclic ten-membered rings the yields vary considerably: the yield is high for **9** (83%), but lower for **7**, **15**, **16** and **17** (47–69%). The cobalt complexes of the larger sulfur substituted rings **4**, **13** and **14** were isolated in very good yields (84–95%), however, the cyclophane diynes **1**, **2** and **10**–**12** afforded lower yields (30–67%).

To study the structural data of the bis(hexacarbonyldicobalt) complexes, single crystals could be obtained by solvent evaporation at room temperature except for the sole eleven membered ring **14**, which was isolated as a red powder. Cyclic diynes with an uneven number of CH_2 groups between the triple bonds tend to adopt a zig-zag arrangement of the chains. This leads to a chair conformation of the rings.[22] However, in the corresponding bis(hexacarbonyldicobalt) complexes the structure is dominated by the bulky complexed triple bonds. The repulsion between the $C_2Co_2(CO)_6$ units leads to a twisted conformation of the rings.

The fourteen-membered complexes **3**, **4** and **11** show very similar structural features (Table 2). They are able to form an unhindered staggered position of the $C_2Co_2(CO)_6$ units as shown in Fig. 1 for **3**. The axes of the complexed triple bonds are separated by about 580 ± 10 pm and twisted by about $66 \pm 2°$, giving rise to an ideal disposition of the alkyne units. Typical structural features of the pseudo-tetrahedral, C_2-symmetric Co_2C_2-cores were the planarity of the Co-coordinated fragments (1–2–3–4 in Scheme 3), the elongated complexed triple bonds (129–134 pm) and the bent geometry for the coordinated alkyne moieties (142–149°). Metal–carbonyl bond lengths vary between 177 and 184 pm. The CO-ligands *trans* to the acetylenic group have an average Co–C bond length of 183 pm, significantly longer than those of the CO-ligands in *cis* position (178 pm).

This can be attributed to differences in metal–ligand $d \longrightarrow \pi^*$ backbonding.[23] The six carbon monoxide ligands do not

DOI: 10.1039/b200195k

This journal is © The Royal Society of Chemistry 2002

Table 1 Cyclic $Co_2(CO)_6$ complexes **1**–**18** [$Co_2 = Co_2(CO)_6$]

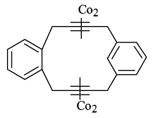
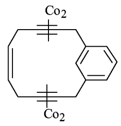
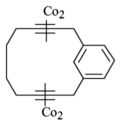
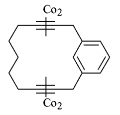
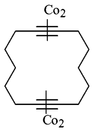
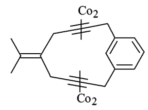
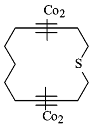
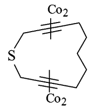
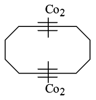
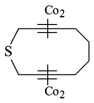
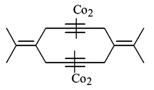
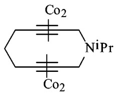
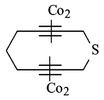
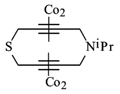
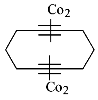
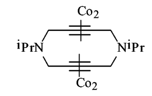
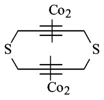
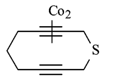
Compound		Yield (%)	Compound		Yield (%)
	**1**	64		**10**	34
	**2**	61		**11**	67
	**3**	91		**12**	30
	**4**	93		**13**	95
	**5**	87		**14**	84
	**6**	89		**15**	69
	**7**	47		**16**	59
	**8**	94		**17**	66
	**9**	83		**18**	57

Table 2 Selected transannular distances between the triple bonds, torsion angles between the triple bonds, bond distances and bond angles of the fourteen-membered cyclic complexes **3**, **4** and **11**

			Bond lengths/pm				
Compound	Distance d^a /pm Co_2C_2	Torsion γ^a /° Co_2C_2	C≡C	Co–CO	CoC≡O	OCCo–C	Angles/° C–C≡C
3	574.0	63.7	132.9–133.6	178.5–183.5	112.1–113.6	197.3–197.8	143.5–146.5
4	590.9	67.5	133.1–133.7	178.3–182.9	112.6–114.3	196.8–197.6	142.9–145.3
11	571.6	68.2	128.9–132.5	176.6–183.3	110.3–114.9	195.3–199.0	142.2–149.1

[a] See Scheme 3 for definition of distance d and torsion angle γ.

participate equally in the redistribution of electron density from the coordinated triple bond. The values obtained for **3**, **4** and **11** compare very well with those of simple dialkyl- and diarylacetylenes reported in the literature.[8] Further structural data are given in Table 2.

Shortening the ring size of **3**, **4** and **11** by one unit leads to unsymmetrically tethered thirteen-membered systems (*e.g.* **1**, **2**, **10**, Table 1 and Table 3). The chain in **2**, consisting of four methylene units, can be further shortened by introducing an aromatic (**1**) or olefinic (**10**) double bond into the cycle, causing a decrease of the separation between the Co_2C_2-cores down to 510 and 538 pm, respectively. The torsion angles of the unsymmetrically bridged complexes vary between 22 and 42° (Table 3).

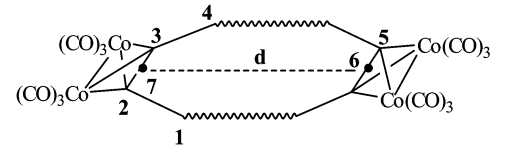
The symmetrically two-fold bridged twelve-membered ring **5** incorporates four methylene units on each side of the alkyne moiety. This leads to a separation between the triple bond centers of about 470 pm (Table 3). Unsymmetrically bent twelve-membered diynes form cobaltcarbonyl complexes (**12**, **13**) with similar structural features as seen for **1** and **10**. The additional structural features, for instance OCCo–C-bond lengths and C≡C–C-angles, obtained for the thirteen- to twelve-membered rings compare very well with those of simple dialkyl-and diarylacetylenes reported in the literature.[8] This is also the case for the bis(hexacarbonyldicobalt) complexes of the ten-membered cyclodiynes (**6**–**9**, **15**–**17**, Table 1 and Table 3).

A comparison of the torsion angles between the Co_2C_2-cores presented in Table 2 and Table 3 reveals for the symmetrically

Table 3 Transannular distances (pm) and torsion angles (°) of the complexed triple bonds in the thirteen- to ten-membered cycles **1**, **2**, **5**–**9**, **10**, **12**, **13**, **15**–**18**

Compound	Ring size	Co_2C_2-distance d^a	Co_2C_2-torsion γ^a	Compound	Ring size	Co_2C_2-distance d^a	Co_2C_2-torsion γ^a
1	13	509.7	41.6	**5**	12	469.5	0
2	13	576.9	21.9	**12**	12	489.9	38.7
10	13	538.2	38.3	**13**	12	500.2	46.8
7	10	355.9	62.6	**6**	10	343.9	58.2
8	10	347.7	61.3	**15**	10	344.4	55.6
9	10	363.5	64.2	**16**	10	352.0	60.2
18	10	344.6	26.0	**17**	10	406.5	0

[a] See Scheme 3 for definition of distance *d* and torsion angle *γ*.



Scheme 3 Definition of the triple bond distance *d* (the transannular distance between the triple bond centres) and the torsion angle *γ* (the angle between the triple bond centres 5–6–7–2) in cyclic bis(hexacarbonyldicobalt) complexes.

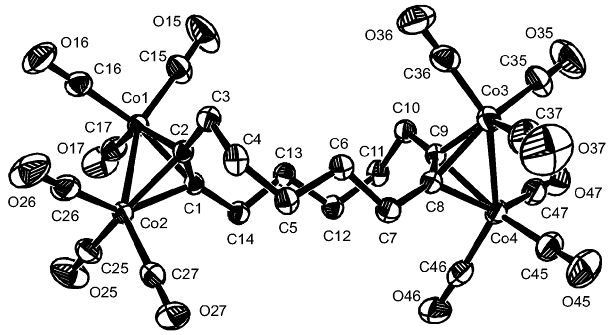


Fig. 1 Molecular structure of **3**. Hydrogen atoms are omitted for clarity. Ellipsoids are shown with 50% probability.

bridged fourteen- and ten-membered systems a twisting of about 60 ± 5°. However, the complexed triple bonds of the symmetrically tethered twelve-membered ring **5** is perfectly coplanar (Fig. 2). This exceptional conformational behavior was already observed in the study of the solid state structures of the corresponding cyclododeca-1,8-diyne.[15]

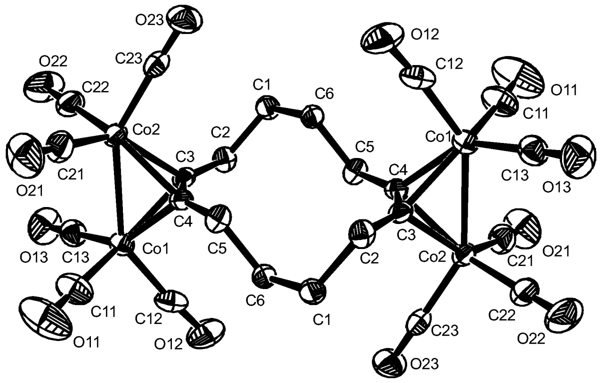


Fig. 2 Molecular structure of **5**. Hydrogen atoms are omitted for clarity. Ellipsoids are shown with 50% probability.

Ten-membered cyclic diynes often show special reactivities like transannular rearrangements[24] or metal-induced formation of CpCo-capped tricyclic cyclobutadienes.[25] Since those systems were also promising precursors for the construction of shortlinked two-fold bridged *ansa*-metallocenes (Scheme 2), they were intensively studied in this work. The structural analyses of the all-carbon rings (**6**, **8**) and their thia- and aza-derivatives (**7**, **9**, **15**, **16**, **17**) reveal a further decrease of the separation between complexed triple bonds to about 350 pm (Table 3). This leads to a close approach of the carbonyl-ligands of the Co_2C_2-cores, dramatically increasing their transannular interaction. As a consequence the ten-membered cycles are forced to twist by about 60°. Only in **17**, where the twisting is dominated by the interference of the isopropyl groups and the CO ligands, a tilting of 0° is encountered.

Since heteroatoms and especially sulfur atoms play an important role in Pauson–Khand reactions[5] and other cobalt-mediated cyclizations,[26] we scrutinized our data on **4**, **7**, **9**, **13**, **16** and **18** for any sulfur–cobalt interaction. However, no such interactions could be detected in the solid state.

A closer examination of the influence of transannular interactions of the Co_2C_2-cores can be done by comparing the transannular distances between the uncomplexed triple bonds (δ in Table 4) with the transannular distances between the complexed triple bonds (d in Table 4). Furthermore we list the ratio k between d and δ for compounds **3**–**5**, **7**–**9**, **13**, **15**, **17** and **18** from which both the X-ray structures of the cobalt complex and the corresponding diyne could be obtained.

Symmetrical tethering of the triple bonds by five (**3**, **4**) groups leads to a characteristic lengthening of the transannular distances *d* between the triple bonds in the carbonyl compounds by about 25%. This widening of the cyclic compounds upon coordination with octacarbonyldicobalt is about 17% in the case of symmetrical bridging with four (**5**) and three (**7**–**9** and **15**) groups. Only **17** shows a larger widening of 37%, probably due to the additional interaction of the isopropyl groups. Unsymmetrical linkage of the alkyne moieties reveals a rise in transannular ring size *d* by about 35% in the corresponding cobaltcarbonyls (**13**).

It is interesting to note, that this increase in transannular triple bond distance is already observed in the mono(hexacarbonyldicobalt) complex **18**. In Fig. 3 the structures of the mono- and the two-fold-coordinated species are presented. The comparison shows the transannular distance between the center of the uncomplexed triple bond and the complexed one in **18** to be 345 pm (k = 14%), whereas the consecutive complexation of the second triple bond moiety only increases the transannular distance between the coordinated triple bond centres up to 356 pm (additional 4%) for **7** (see Table 4).

3 Conclusions

Our systematic study of the structural features of cyclic bis(hexacarbonyldicobalt) complexes reveals that the geometry in the solid state depends on the interplay between the bulky $C_2Co_2(CO)_6$ units and on the conformational needs of the side chains. This leads to a widening of the transannular distance between the triple bond centres upon complexation of about 25% for fourteen-membered and about 17% for twelve- to ten-membered rings. Additionally it is found that the chair like

Table 4 Comparison between the ratios *k* of the transannular distances *δ* (pm) in cyclic diynes and their corresponding values *d* (pm) in the $Co_2(CO)_6$ complexes **3**–**5**, **7**–**9**, **13**, **15**, **17** and **18**

Compound	Ring size	Co_2C_2-distance d^a/pm	C≡C-distance δ^a	k^b	Compound	Ring size	Co_2C_2-distance d^a/pm	C≡C-distance δ^a/pm	k^b
3	14	574.0	464.0[15]	1.23	**5**	12	469.5	406.0[15]	1.17
4	14	590.9	472.6[27]	1.25	**13**	12	498.5	372.1[26]	1.34
7	10	355.9	302.2[28]	1.18	**15**	10	344.4	298.0[18]	1.15
8	10	347.7	299.1[15]	1.16	**17**	10	406.5	295.9[18]	1.37
9	10	363.5	310.2[28]	1.17	**18**	10	344.6	302.2[28]	1.14

[a] See Scheme 3 for definition of distance *d*, *δ* is defined as the corresponding value in the uncomplexed cyclic diynes. [b] *k* = distance *d*/distance *δ*.

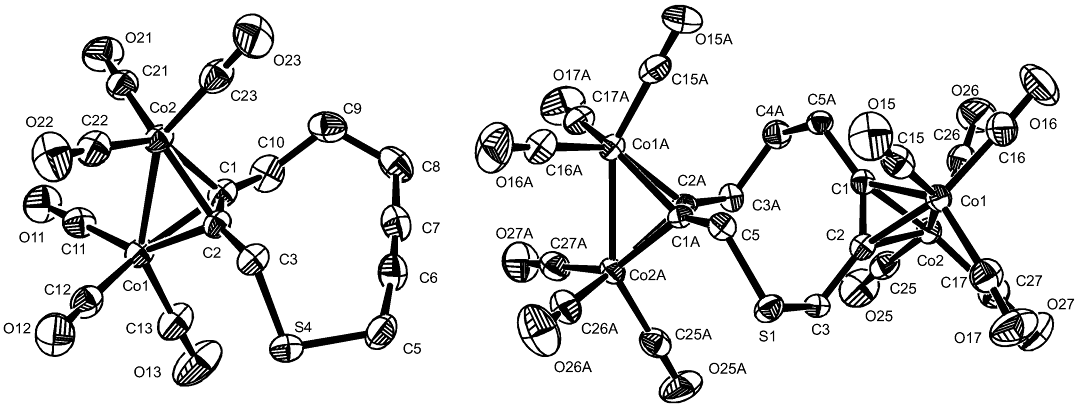


Fig. 3 Comparison between the molecular structures of **18** (left) and **7** (right). Hydrogen atoms are omitted for clarity. Ellipsoids are shown with 50% probability. Relevant structural parameters are given in Table 4.

conformation of the uncomplexed rings is changed into a twisted one. Our search to find any evidence for interactions between the heteroatoms and the $C_2Co_2(CO)_6$ unit in the solid state was in vain. This was unexpected since cobalt–heteroatom interactions, especially with sulfur centers, have been reported previously[29] and they play an important role in Pauson–Khand reactions.[5]

4 Experimental

4.1 General methods

All melting points are uncorrected. Elemental analyses were carried out by the Mikroanalytisches Laboratorium der Universität Heidelberg. UV light absorption data were recorded using a Hewlett Packard 8452A spectrometer. IR spectra were recorded with a Bruker Vector 22. The NMR spectra were measured with a Bruker WH 300 (^{1}H-NMR at 300 MHz; ^{13}C-NMR at 75.47 MHz) and a Bruker Avance 500 (^{1}H-NMR at 500 MHz; ^{13}C-NMR at 125.77 MHz) using the solvent as internal standard (*δ*). FD mass spectra refer to data from a Jeol JMS-700 instrument and were measured from methylene chloride solutions (c = 3–5 mg ml^{-1}) of the corresponding complexes. All reactions were carried out in dried glassware under nitrogen atmosphere using dried and oxygen-free solvents. Octacarbonyldicobalt was obtained from Strem and used without further purification. Materials used for column chromatography: neutral alumina (Merck), Celite (Fluka).

4.2 X-Ray crystallography and structure solution

The crystallographic data were recorded with a Bruker Smart CCD diffractometer at 200 K with Mo-K$_\alpha$ radiation (λ = 0.71073 Å). The structures were solved by using direct methods (except for **4** and **5**: Patterson-method), least-squares refinement, and Fourier techniques. Structure solution and refinement were performed with SHELXTL.[30] Hydrogen atoms were taken into account at calculated positions, except for **9** where they were refined isotropically. The X-ray structure of **7** has a crystallographic inversion center, so necessarily the sulfur atom is distributed over two positions with equal occupancy. There is also a little disordering in an isopropyl group of **16**. The asymmetric unit of **18** contains two independent molecules, in one of them the sulfur atom is disordered over two positions with almost equal occupancy. ORTEP drawings were obtained using the ORTEP-3 for Windows program.[31]

CCDC reference numbers 168766–168783.

See http://www.rsc.org/suppdata/dt/b2/b200195k/ for crystallographic data in CIF or other electronic format.

4.3 Standard procedure for preparation of bis(hexacarbonyldicobalt) complexes from cyclic diynes

To a solution of cyclic diyne in light petroleum (30/40) or methylene chloride was added solid octacarbonyldicobalt in one portion. The resulting red mixture was stirred in the dark over night. After rotary evaporation of the solvent the product was absorbed on Celite and purified by column chromatography on neutral alumina (grade III), eluting with mixtures of light petroleum (30/40) and diethyl ether.

4.3.1 (μ:μ-[4.4]Orthometacyclophan-2,12-diyne)bis(hexacarbonyldicobalt) 1. The synthesis of **1** has been reported previously.[12] Crystals were grown from light petroleum at 275 K.

Relevant structural parameters: chemical formula $C_{32}H_{16}Co_4O_{12}$; formula weight, 828.17; temperature, 293(2) K; crystal size, 0.50 × 0.35 × 0.10 mm; crystal system, triclinic; space group, $P\bar{1}$; Z, 4; a, 14.044(7); b, 16.345(9); c, 16.476(7) Å; α, 75.03(4); β, 70.57(3), γ, 72.45(4)°; absorption coefficient μ, 2.01 mm^{-1}; reflections collected/independent/observed, 11958/11804/5838; max/min transmission, 1.00 and 0.73; parameters, 865; goodness-of-fit on F^2, 1.10; $R(F)$, 0.096; $R_w(F^2)$, 0.138; $(\Delta\rho)$max, $(\Delta\rho)$min, 0.43 and −0.37 e Å^{-3}.

4.3.2 (μ:μ-[10]Metacyclophan-2,8-diyne)bis(hexacarbonyldicobalt) 2. The synthesis of **2** has been reported previously.[12] Crystals were grown from light petroleum at 275 K.

Relevant structural parameters: chemical formula $C_{28}H_{16}Co_4O_{12}$; formula weight, 780.13; temperature, 293(2) K; crystal size, 0.75 × 0.25 × 0.08 mm; crystal system, triclinic; space group,

$P\bar{1}$; Z, 2; a, 7.761(2); b, 12.608(5); c, 16.058(6) Å; α, 80.78(3); β, 87.97(3), γ, 86.97(3)°; absorption coefficient μ, 2.165 mm^{-1}; reflections collected/independent/observed, 6256/6256/3976; max/min transmission, 1.00 and 0.80; parameters, 398; goodness-of-fit on F^2, 1.09; $R(F)$, 0.064; $R_w(F^2)$, 0.115; ($\Delta\rho$)max, ($\Delta\rho$)min, 0.44 and −0.34 e Å^{-3}.

4.3.3 (μ:μ-Cyclotetradeca-1,8-diyne)bis(hexacarbonyldicobalt) 3. The synthesis of **3** has been reported previously.[21] Crystals were grown from light petroleum/diethyl ether (1 : 1) at 275 K.

Relevant structural parameters: chemical formula $C_{26}H_{20}Co_4O_{12}$; formula weight, 760.14; temperature, 200(2) K; crystal size, 0.30 × 0.28 × 0.18 mm; crystal system, triclinic; space group, $P\bar{1}$; Z, 2; a, 10.7821(2); b, 10.8413(2); c, 13.1236(2) Å; α, 93.192(1); β, 90.0893(3); γ, 96.513(1)°; absorption coefficient μ, 2.20 mm^{-1}; reflections collected/independent/observed, 15640/6919/6007; max/min transmission, 0.72 and 0.60; parameters, 379; goodness-of-fit on F^2, 1.04; $R(F)$, 0.025; $R_w(F^2)$, 0.063; ($\Delta\rho$)max, ($\Delta\rho$)min, 0.35 and −0.41 e Å^{-3}.

4.3.4 (μ:μ-1-Thiacyclotetradeca-4,11-diyne)bis(hexacarbonyldicobalt) 4. Starting materials: 335 mg (1.6 mmol) of 1-thiacyclotetradeca-4,11-diyne and 1.23 g (3.6 mmol) of octacarbonyldicobalt in 80 ml of light petroleum. Column chromatography with light petroleum/diethyl ether (50 : 1) as eluent afforded 1.18 g (93%) of **4** as a red solid. Needles were grown from light petroleum/diethyl ether (1 : 1) at 275 K. Mp 137 °C (decomp.). Elem. Anal.: Found: C, 38.47; H, 2.59; S, 4.12. $C_{25}H_{18}Co_4O_{12}S$ requires C, 38.59; H, 2.33; S, 4.12%. UV-vis (CH_2Cl_2), λ_{max}/nm (log ε): 250 (4.76), 350 (4.19), 408 (3.02). IR (KBr, cm^{-1}): 2930, 2090, 2040, 2015, 1988, 1629, 1434. ^{1}H-NMR (C_6D_6): δ 2.88–2.83 (m, 4H, CH_2), 2.69–2.65 (m, 4H, CH_2), 2.44–2.39 (m, 4H, CH_2), 1.40–1.35 (m, 4H, CH_2), 1.12–1.09 (m, 2H, CH_2). ^{13}C-NMR (C_6D_6): δ 28.4, 31.0, 31.7, 35.6, 35.7 (CH_2); 96.2, 99.6 (C); 200.5 (CO). FD-MS m/z 778 (M).

Relevant structural parameters: chemical formula $C_{25}H_{18}Co_4O_{12}S$; formula weight, 778.17; temperature, 200(2) K; crystal size, 0.46 × 0.16 × 0.14 mm; crystal system, triclinic; space group, $P\bar{1}$; Z, 2; a, 7.8123(1); b, 13.7006(2); c, 15.1082(2) Å; α, 105.367(1); β, 101.732(1); γ, 91.238(1)°; absorption coefficient μ, 2.27 mm^{-1}; reflections collected/independent/observed, 15418/6965/5825; max/min transmission, 0.77 and 0.52; parameters, 379; goodness-of-fit on F^2, 1.06; $R(F)$, 0.028; $R_w(F^2)$, 0.067; ($\Delta\rho$)max, ($\Delta\rho$)min, 0.40 and −0.55 e Å^{-3}.

4.3.5 (μ:μ-Cyclododeca-1,7-diyne)bis(hexacarbonyldicobalt) 5. The synthesis of **5** has been reported previously.[20] Crystals were grown from light petroleum/diethyl ether (1 : 1) at 275 K.

Relevant structural parameters: chemical formula $C_{24}H_{16}Co_4O_{12}$; formula weight, 732.09; temperature, 200(2) K; crystal size, 0.12 × 0.10 × 0.03 mm; crystal system, triclinic; space group, $P\bar{1}$; Z, 1; a, 7.6522(3); b, 9.5811(3); c, 9.9672(2) Å; α, 92.300(2); β, 98.951(1); γ, 104.569(1)°; absorption coefficient μ, 2.40 mm^{-1}; reflections collected/independent/observed, 7216/3174/2128; max/min transmission, 0.93 and 0.76; parameters, 181; goodness-of-fit on F^2, 0.97; $R(F)$, 0.038; $R_w(F^2)$, 0.071; ($\Delta\rho$)max, ($\Delta\rho$)min, 0.45 and −0.48 e Å^{-3}.

4.3.6 (μ:μ-4,9-Diisopropylidencyclodeca-1,6-diyne)bis(hexacarbonyldicobalt) 6. Starting materials: 212 mg (1.0 mmol) of 4,9-diisopropylidencyclodeca-1,6-diyne and 1.03 g (3.0 mmol) of octacarbonyldicobalt in 35 ml of methylene chloride. Column chromatography with light petroleum as eluent afforded 698 mg (89%) of **6** as a red solid. Crystals were grown from light petroleum at 275 K. Mp 170 °C (decomp.). Elem. Anal.: Found C, 42.86; H, 2.69. $C_{28}H_{20}Co_4O_{12}$ requires C, 42.89; H, 2.57%. UV-vis (CH_2Cl_2), λ_{max}/nm (log ε): 260 (4.43), 316 (3.77), 350 (3.70). IR (KBr, cm^{-1}): 2921, 2084, 2042, 2005, 1632, 1424. ^{1}H-NMR ($CDCl_3$): δ 3.79 (s, 8H, CH_2), 1.86 (s, 12H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 21.2 (CH_3); 35.9 (CH_2); 96.2 (C); 128.9 (C=C), 130.1 (C=C), 200.3 (CO). FD-MS m/z 784 (M).

Relevant structural parameters: chemical formula $C_{28}H_{20}Co_4O_{12}$; formula weight, 784.16; temperature, 200(2) K; crystal size, 0.40 × 0.24 × 0.14 mm; crystal system, monoclinic; space group, $C2/c$; Z, 4; a, 19.6831(5); b, 7.6322(2); c, 22.7230(6) Å; β, 111.922(1)°; absorption coefficient μ, 2.12 mm^{-1}; reflections collected/independent/observed, 15755/3623/3258; max/min transmission, 0.80 and 0.61; parameters, 201; goodness-of-fit on F^2, 1.10; $R(F)$, 0.022; $R_w(F^2)$, 0.055; ($\Delta\rho$)max, ($\Delta\rho$)min, 0.30 and −0.47 e Å^{-3}.

4.3.7 (μ:μ-1-Thiacyclodeca-3,8-diyne)bis(hexacarbonyldicobalt) 7. Starting materials: 50 mg (0.33 mmol) of 1-thiacyclodeca-3,8-diyne and 0.46 g (1.33 mmol) of octacarbonyldicobalt in 75 ml of methylene chloride. Column chromatography with light petroleum/diethyl ether (10 : 1) as eluent afforded 112 mg (47%) of **7** as a red solid. Plates were grown from methylene chloride/diethyl ether (1 : 3) at 275 K. Mp 143 °C (decomp.). Elem. Anal.: Found C, 34.75; H, 1.68; S 4.47. $C_{21}H_{10}Co_4O_{12}S$ requires C, 34.93; H, 1.40; S, 4.44%. UV-vis (CH_2Cl_2, λ_{max}/nm (log ε): 260 (4.33), 314 (3.81), 352 (3.73), 418 (3.03). IR (KBr, cm^{-1}): 2934, 2089, 2047, 2019, 1719, 1628, 1561, 1437, 1407. ^{1}H-NMR (CD_2Cl_2): δ 3.95 (s, 4H, CH_2), 3.02–3.06 (m, 4H, CH_2), 2.07–2.05 (m, 2H, CH_2). ^{13}C-NMR ($CDCl_3$): δ 32.1, 32.6, 34.5 (CH_2); 91.9, 96.6 (C); 199.6 (CO). FD-MS m/z 722 (M).

Relevant structural parameters: chemical formula $C_{21}H_{10}Co_4O_{12}S$; formula weight, 722.07; temperature, 200(2) K; crystal size, 0.22 × 0.20 × 0.01 mm; crystal system, monoclinic; space group, $C2/c$; Z, 4; a, 25.0971(6); b, 7.7272(2); c, 13.8406(2) Å; β, 107.601(1)°; absorption coefficient μ, 2.69 mm^{-1}; reflections collected/independent/observed, 8932/1832/1447; max/min transmission, 0.98 and 0.77; parameters, 192; goodness-of-fit on F^2, 1.06; $R(F)$, 0.030 $R_w(F^2)$, 0.059; ($\Delta\rho$)max, ($\Delta\rho$)min, 0.36 and −0.28 e Å^{-3}.

4.3.8 (μ:μ-Cyclodeca-1,6-diyne)bis(hexacarbonyldicobalt) 8. The synthesis of **8** has been reported previously.[20] Crystals were grown from light petroleum at 275 K.

Relevant structural parameters: chemical formula $C_{22}H_{12}Co_4O_{12}$; formula weight, 704.04; temperature, 200(2) K; crystal size, 0.30 × 0.21 × 0.09 mm; crystal system, monoclinic; space group, $C2/c$; Z, 4; a, 24.9890(5); b, 7.7330(2); c, 13.7310(3) Å; β, 107.517(1)°; absorption coefficient μ, 2.64 mm^{-1}; reflections collected/independent/observed, 10986/2885/2548; max/min transmission, 0.82 and 0.64; parameters, 172; goodness-of-fit on F^2, 1.09; $R(F)$, 0.022; $R_w(F^2)$, 0.056; ($\Delta\rho$)max, ($\Delta\rho$)min, 0.42 and −0.32 e Å^{-3}.

4.3.9 (μ:μ-1,6-Dithiacyclodeca-3,8-diyne)bis(hexacarbonyldicobalt) 9. Starting materials: 150 mg (0.89 mmol) of 1,6-dithiacyclodeca-3,8-diyne and 0.92 g (2.7 mmol) of octacarbonyldicobalt in 50 ml of methylene chloride. Column chromatography with light petroleum/diethyl ether (5 : 1) as eluent afforded 547 mg (83%) of **9** as a red solid. Plates were grown from methylene chloride at 275 K. Mp 150 °C (decomp.). Elem. Anal.: Found C, 32.39; H, 1.21; S, 8.61. $C_{20}H_8Co_4O_{12}S_2$ requires C, 32.46; H, 1.09; S, 8.66%. UV-vis (CH_2Cl_2), λ_{max}/nm (log ε): 264 (5.07), 354 (4.21). IR (KBr, cm^{-1}): 2921, 2090, 2048, 2021, 1630. ^{1}H-NMR (CD_2Cl_2): δ 3.99 (s, 8H, CH_2). ^{13}C-NMR (CD_2Cl_2): δ 34.2 (CH_2); 98.2 (C); 200.0 (CO). FD-MS m/z 740 (M).

Relevant structural parameters: chemical formula $C_{20}H_8Co_4O_{12}S_2$; formula weight, 740.10; temperature, 200(2) K; crystal size, 0.70 × 0.44 × 0.02 mm; crystal system, monoclinic; space group, $C2/c$; Z, 4; a, 25.1327(1); b, 7.7195(1); c, 13.8868(1) Å; β, 107.507(1)°; absorption coefficient μ, 2.76 mm^{-1}; reflections collected/independent/observed, 12658/2929/2651; max/min transmission, 0.96 and 0.62; parameters, 188; goodness-of-fit on F^2, 1.10; $R(F)$, 0.023; $R_w(F^2)$, 0.061; $(\Delta\rho)$max, $(\Delta\rho)$min, 0.40 and -0.35 e Å^{-3}.

4.3.10 (μ:μ-(*Z*)-[10]Metacyclophan-5-en-2,8-diyne)bis(hexacarbonyldicobalt) 10. The synthesis of **10** has been reported previously.[12] Crystals were grown from light petroleum at 275 K.

Relevant structural parameters: chemical formula $C_{28}H_{14}Co_4O_{12}$; formula weight, 778.11; temperature, 293(2) K; crystal size, 0.70 × 0.35 × 0.20 mm; crystal system, triclinic; space group, $P\bar{1}$; Z, 2; a, 7.830(4); b, 12.886(5); c, 16.209(6) Å; α, 91.32(3); β, 102.09(3), γ, 105.68(3)°; absorption coefficient μ, 2.19 mm^{-1}; reflections collected/independent/observed, 4787/4787/3391; max/min transmission, 1.00 and 0.81; parameters, 397; goodness-of-fit on F^2, 1.09; $R(F)$, 0.053; $R_w(F^2)$, 0.108; $(\Delta\rho)$max, $(\Delta\rho)$min, 0.64 and -0.41 e Å^{-3}.

4.3.11 (μ:μ-[11]Metacyclophan-2,9-diyne)bis(hexacarbonyldicobalt) 11. The synthesis of **11** has been reported previously.[12] Crystals were grown from light petroleum at 275 K.

Relevant structural parameters: chemical formula $C_{29}H_{18}Co_4O_{12}$; formula weight, 794.15; temperature, 293(2) K; crystal size, 1.10 × 0.30 × 0.10 mm; crystal system, triclinic; space group, $P\bar{1}$; Z, 2; a, 8.032(4); b, 14.263(7); c, 14.655(6) Å; α, 93.60(4); β, 95.73(4); γ, 102.93(4)°; absorption coefficient μ, 2.07 mm^{-1}; reflections collected/independent/observed, 4242/4242/3018; max/min transmission, 1.00 and 0.84; parameters, 407; goodness-of-fit on F^2, 1.15; $R(F)$, 0.058; $R_w(F^2)$, 0.122; $(\Delta\rho)$max, $(\Delta\rho)$min, 0.36 and -0.35 e Å^{-3}.

4.3.12 (μ:μ-5-Isopropyliden-[9]metacyclophan-2,7-diyne)bis(hexacarbonyldicobalt) 12. The synthesis of **12** has been reported previously.[12] Crystals were grown from light petroleum at 275 K.

Relevant structural parameters: chemical formula $C_{30}H_{18}Co_4O_{12}$; formula weight, 806.16; temperature, 200(2) K; crystal size, 0.85 × 0.75 × 0.25 mm; crystal system, monoclinic; space group, $P2_1/n$; Z, 2; a, 13.573(4); b, 10.648(3); c, 22.761(9) Å; β, 95.38(3)°; absorption coefficient μ, 2.05 mm^{-1}; reflections collected/independent/observed, 6767/6506/4254; max/min transmission, 1.00 and 0.54; parameters, 416; goodness-of-fit on F^2, 1.08; $R(F)$, 0.055; $R_w(F^2)$, 0.120; $(\Delta\rho)$max, $(\Delta\rho)$min, 0.36 and -0.65 e Å^{-3}.

4.3.13 (μ:μ-1-Thiacyclododeca-3,10-diyne)bis(hexacarbonyldicobalt) 13. Starting materials: 150 mg (0.84 mmol) of 1-thiacyclododeca-3,10-diyne and 0.63 g (1.8 mmol) of octacarbonyldicobalt in 50 ml of light petroleum. Column chromatography with light petroleum as eluent afforded 600 mg (95%) of **13** as a red solid. Needles of **13** were grown from light petroleum at 275 K. Mp 97 °C. Elem. Anal.: Found C, 36.90; H, 2.05; S, 4.34. $C_{23}H_{14}Co_4O_{12}S$ requires C, 36.83; H, 1.88; S, 4.27%. UV-vis (CH_2Cl_2), λ_{max}/nm (log ε): 258 (4.92), 310 (4.39), 352 (4.37), 414 (3.78). IR (KBr, cm^{-1}) 2087, 2049, 2021, 1627, 1438. ^{1}H-NMR (C_6D_6): δ 3.63 (s, 4H, CH_2), 2.66–2.64 (m, 4H, CH_2), 1.52–1.48 (m, 4H, CH_2), 1.28–1.26 (m, 2H, CH_2). ^{13}C-NMR (C_6D_6): δ 27.8, 29.2, 34.1, 37.8 (CH_2); 93.4, 97.8 (C); 200.2 (CO). FD-MS *m*/*z* 750 (M).

Relevant structural parameters: chemical formula $C_{23}H_{14}Co_4O_{12}S$; formula weight, 750.12; temperature, 200(2) K; crystal size, 0.36 × 0.08 × 0.07 mm; crystal system, monoclinic; space group, $P2_1/c$; Z, 8; a, 12.4898(2); b, 27.3932(4); c, 16.8607(2) Å; β, 100.645(1)°; absorption coefficient μ, 2.43 mm^{-1}; reflections collected/independent/observed, 38439/6925/5137; max/min transmission, 0.86 and 0.56; parameters, 721; goodness-of-fit on F^2, 1.06; $R(F)$, 0.036; $R_w(F^2)$, 0.064; $(\Delta\rho)$max, $(\Delta\rho)$min, 0.89 and -0.50 e Å^{-3}. Atom C8 in the first of the independent molecules is likely to be disordered.

4.3.14 (μ:μ-1-Thiacycloundeca-3,9-diyne)bis(hexacarbonyldicobalt) 14. Starting materials: 160 mg (0.98 mmol) of 1-thiacycloundeca-3,9-diyne and 0.93 g (2.7 mmol) of octacarbonyldicobalt in 80 ml of methylene chloride. Column chromatography with light petroleum/diethyl ether (25 : 1) as eluent afforded 573 mg (84%) of **14** as a red solid. Crystals were grown from light petroleum/diethyl ether (1 : 1) at 275 K. Mp 125 °C (decomp.). Elem. Anal.: Found C, 35.92; H, 1.87; S, 4.38. $C_{22}H_{12}Co_4O_{12}S$ requires C, 35.90; H, 1.64; S, 4.36%. UV-vis (CH_2Cl_2), $\lambda_{max/nm}$ (log ε): 256 (4.64), 312 (4.24), 316 (4.29), 352 (4.18). IR (KBr, cm^{-1}) 2927, 2858, 2473, 2087, 2050, 2015, 1624, 1435, 1344. ^{1}H-NMR ($CDCl_3$): δ 4.29 (s, 4H, CH_2), 3.11–3.07 (m, 4H, CH_2), 1.84–1.80 (m, 4H, CH_2). ^{13}C-NMR ($CDCl_3$): δ 29.5, 33.6, 40.3 (CH_2); 93.5, 97.9 (C); 199.4 (CO). FD-MS *m*/*z* 736 (M).

4.3.15 (μ:μ-*N*-Isopropyl-1-azacyclodeca-3,8-diyne)bis(hexacarbonyldicobalt) 15. Starting materials: 100 mg (0.57 mmol) of *N*-isopropyl-1-azacyclodeca-3,8-diyne and 0.49 g (1.4 mmol) of octacarbonyldicobalt in 70 ml of methylene chloride. Column chromatography with light petroleum/diethyl ether (50 : 1) as eluent afforded 290 mg (69%) of **15** as a red solid. Needles were grown from light petroleum/diethyl ether (1 : 1) at 275 K. Mp 127 °C (decomp.). Elem. Anal.: Found C, 38.57; H, 2.49; N, 1.93. $C_{24}H_{17}Co_4NO_{12}$ requires C 38.58, H 2.29, N 1.88%. UV-vis (CH_2Cl_2), λ_{max}/nm (log ε): 262 (4.56), 316 (4.02), 348 (4.02), 420 (3.40). IR (KBr, cm^{-1}) 2932, 2084, 2045, 2019, 1627, 1439, 1385. ^{1}H-NMR ($CDCl_3$): δ 4.04 (s, 4H, CH_2), 3.19–3.15 (m, 1H, CH), 3.01–2.96 (m, 4H, CH_2), 1.99–1.96 (m, 2H, CH_2), 1.14 (d, 6H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 21.8 (CH_3); 31.0, 32.2, 52.0 (CH_2); 53.7 (CH); 94.7, 97.7 (C); 200.2 (CO). FD-MS *m*/*z* 747 (M).

Relevant structural parameters: chemical formula $C_{24}H_{17}Co_4NO_{12}$; formula weight, 747.11; temperature, 233(2) K; crystal size, 0.50 × 0.17 × 0.08 mm; crystal system, monoclinic; space group, $P2_1/c$; Z, 4; a, 16.2075(5); b, 7.6766(1); c, 24.2396(9) Å; β, 108.594(1)°; absorption coefficient μ, 2.34 mm^{-1}; reflections collected/independent/observed, 10055/5772/3594; max/min transmission, 0.86 and 0.52; parameters, 387; goodness-of-fit on F^2, 1.02; $R(F)$, 0.063; $R_w(F^2)$, 0.163; $(\Delta\rho)$max, $(\Delta\rho)$min, 0.92 and -0.75 e Å^{-3}.

4.3.16 (μ:μ-*N*-Isopropyl-6-aza-1-thiacyclodeca-3,8-diyne)bis(hexacarbonyldicobalt) 16. Starting materials: 50 mg (0.57 mmol) of *N*-isopropyl-6-aza-1-thiacyclodeca-3,8-diyne and 0.27 g (1.4 mmol) of octacarbonyldicobalt in 35 ml of methyllene chloride. Column chromatography with light petroleum/diethyl ether (10 : 1) as eluent afforded 451 mg (59%) of **16** as a light red solid. Crystals were grown from diethyl ether/methylene chloride (1 : 1) at 275 K. Mp 150 °C (decomp.). Elem. Anal.: Found C, 36.05; H, 2.14; N, 1.88; S, 4.16. $C_{23}H_{15}Co_4NO_{12}S$ requires C, 36.10; H, 1.98; N, 1.83; S, 4.19%. UV-vis (CH_2Cl_2), λ_{max}/nm (log ε): 260 (4.32), 304 (3.83), 316 (3.77), 352 (3.68). IR (KBr, cm^{-1}) 2922, 2087, 2052, 2003, 1629, 1438, 1406. ^{1}H-NMR ($CDCl_3$): δ 4.12 (s, 4H, CH_2), 3.98 (s, 4H, CH_2), 3.31–3.22 (m, 1H, CH), 1.21 (d, 6H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 22.3 (CH_3); 34.2, 51.4 (CH_2); 53.7 (CH); 94.1, 95.4 (C); 199.8 (CO). FD-MS *m*/*z* 765 (M).

Relevant structure parameters: chemical formula $C_{23}H_{14}Co_4NO_{12}S$; formula weight, 765.14; temperature, 200(2) K; crystal size, 0.44 × 0.20 × 0.12 mm; crystal system, monoclinic; space group, $P2_1/n$; Z, 4; a, 16.8134(1); b, 7.6831(1); c, 23.1479(1) Å; β, 106.506(1)°; absorption coefficient μ, 2.41 mm^{-1}; reflections collected/independent/observed, 28495/6548/5455; max/min transmission, 0.81 and 0.38; parameters, 383; goodness-of-fit on F^2, 1.05; $R(F)$, 0.028; $R_w(F^2)$, 0.066; $(\Delta\rho)$max, $(\Delta\rho)$min, 0.42 and -0.47 e Å^{-3}.

4.3.17 (μ:μ-*N*,*N*′-Diisopropyl-1,6-diazacyclodeca-3,8-diyne)bis(hexacarbonyldicobalt) 17. Starting materials: 100 mg (0.46

mmol) of *N*,*N*′-diisopropyl-1,6-diazacyclodeca-3,8-diyne and 0.39 g (1.2 mmol) of octacarbonyldicobalt in 70 ml of methylene chloride. Column chromatography with light petroleum as eluent afforded 240 mg (66%) of **17** as a red solid. Needles were grown from light petroleum/diethyl ether (1 : 1) at 275 K. Mp 110 °C (decomp.). Elem. Anal.: Found C, 39.37; H, 2.94; N, 3.58. $C_{26}H_{22}Co_4N_2O_{12}$ requires C, 39.52; H, 2.81; N, 3.54%. UV-vis (CH_2Cl_2), λ_{max}/nm (log ε): 256 (4.50), 322 (3.92), 350 (3.91), 422 (3.22). IR (KBr, cm^{-1}) 2967, 2085, 2046, 2021, 1627, 1387. ^1H-NMR ($CDCl_3$): δ 4.05 (s, 8H, CH_2), 3.19 (m, 2H, CH), 1.10 (d, 6H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 19.9 (CH_3); 52.9 (CH); 53.4 (CH_2); 96.0 (C); 199.9 (CO). FD-MS *m*/*z* 791 (M + H).

Relevant structural parameters: chemical formula $C_{26}H_{22}Co_4N_2O_{12}$; formula weight, 790.18; temperature, 200(2) K; crystal size, 0.27 × 0.25 × 0.04 mm; crystal system, monoclinic; space group, $P2_1/n$; Z, 2; a, 12.6251(4); b, 7.7115(2); c, 16.0675(5) Å; β, 94.841(1)°; absorption coefficient μ, 2.15 mm^{-1}; reflections collected/independent/observed, 15325/3561/2720; max/min transmission, 0.93 and 0.76; parameters, 201; goodness-of-fit on F^2, 1.03; $R(F)$, 0.030; $R_w(F^2)$, 0.065; $(\Delta\rho)$max, $(\Delta\rho)$min, 0.45 and −0.44 e $Å^{-3}$.

4.3.18 (μ:μ-1-Thiacyclodeca-3,8-diyne)mono(hexacarbonyldicobalt) 18. To a mixture of 210 mg (1.4 mmol) of 1-thiacyclodeca-3,8-diyne in 50 ml methylene chloride was added dropwise a solution of 0.38 g (1.1 mmol) octacarbonyldicobalt in 30 ml methylene chloride over 6 h. The resulting red mixture was stirred over night. After rotary evaporation the product was absorbed on Celite and purified by column chromatography on neutral alumina (grade III). Eluting with light petroleum/diethyl ether (50 : 1) afforded 200 mg (57%) of **18** as a light red solid. Needles were grown from methylene chloride/diethyl ether at 275 K. Mp 74 °C. Elem. Anal.: Found C, 41.22; H, 2.46; N, 7.41. $C_{15}H_{10}Co_2O_6S$ requires C, 41.31; H, 2.31; S, 7.35%. UV-vis (CH_2Cl_2), λ_{max}/nm (log ε): 260 (4.18), 310 (3.64), 352 (3.65), 408 (2.82). IR (KBr, cm^{-1}) 2086, 2043, 2017, 1719, 1629, 1491, 1459, 1401. ^1H-NMR (C_6D_6): δ 3.97 (s, 2H, CH_2), 2.91–2.88 (m, 2H, CH_2), 2.83–2.79 (m, 2H, CH_2), 1.87–1.84 (m, 2H, CH_2), 1.43–1.35 (m, 2H, CH_2). ^{13}C-NMR (C_6D_6): δ 18.9, 21.5, 28.8, 35.3, 36.9 (CH_2); 77.7, 83.7, 99.1, 99.4 (C); 200.5 (CO). FD-MS *m*/*z* 436 (M).

Relevant structural parameters: chemical formula $C_{15}H_{10}Co_2O_6S$; formula weight, 436.15; temperature, 200(2) K; crystal size, 0.32 × 0.30 × 0.09 mm; crystal system, triclinic; space group, $P\bar{1}$; Z, 4; a, 7.7265(1); b, 14.0345(2); c, 16.1067(2) Å; α, 92.757(1); β, 96.672(1); γ, 90.312(1)°; absorption coefficient μ, 2.06 mm^{-1}; reflections collected/independent/observed, 17772/7845/6694; max/min transmission, 0.86 and 0.67; parameters, 452; goodness-of-fit on F^2, 1.19; $R(F)$, 0.034; $R_w(F^2)$, 0.084; $(\Delta\rho)$max, $(\Delta\rho)$min, 0.38 and −0.31 e $Å^{-3}$.

Acknowledgements

We are grateful to the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the BASF Aktiengesellschaft, Ludwigshafen, for financial support.

References and notes

1 G. G. Melikyan and K. M. Nicholas, in *Modern Acetylene Chemistry*, ed. P. J. Stang and F. Diederich, VCH, Weinheim, 1995, pp. 99–138.

2 M. G. Karpov, S. P. Tunik, V. R. Denisov, G. L. Starova, A. B. Nikolskii, F. M. Dolgushin, A. I. Yanovsky and Y. T. Struchkov, *J. Organomet. Chem.*, 1995, **485**, 219–225.

3 K. M. Nicholas and R. Pettit, *Tetrahedron Lett.*, 1971, **37**, 3475–3478.

4 Review: K. M. Nicholas, *Acc. Chem. Res.*, 1987, **20**, 207–214.

5 (*a*) I. U. Khand, G. R. Knox, P. L. Pauson and W. E. Watts, *Chem. Commun.*, 1971, 36; (*b*) I. U. Khand, G. R. Knox, P. L. Pauson and W. E. Watts, *J. Chem. Soc., Perkin Trans. 1*, 1973, 975–977; (*c*) P. L. Pauson, *Tetrahedron*, 1985, **41**, 5855–5860; (*d*) P. L. Pauson, in *Organometallics in Organic Synthesis*, ed. A. de Meijere and H. tom Dieck, Springer, Berlin, 1988, pp. 233–246; (*e*) N. E. Schore, in *Comprehensive Organic Synthesis*, ed. B. M. Trost, Pergamon, Oxford, 1991, vol. 5, pp. 1037–1062; (*f*) N. E. Schore, *Org. React.*, 1991, **40**, 1–90; (*g*) N. E. Schore, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford, 1995, vol. 12, pp. 703–739; (*h*) O. Geis and H. G. Schmalz, *Angew. Chem., Int. Ed.*, 1998, **37**, 911–915; (*i*) A. J. Fletcher and S. D. R. Christie, *J. Chem. Soc., Perkin Trans. 1*, 2000, 1657–1668; (*j*) Y. K. Chung, *Coord. Chem. Rev.*, 1999, **188**, 297–341; (*k*) K. M. Brummond and J. L. Kent, *Tetrahedron*, 2000, **56**, 3263–3283; (*l*) T. Sugihara, M. Yamaguchi and M. Nishizawa, *Chem. Eur. J.*, 2001, **8**, 1589–1595.

6 (*a*) C. M. Gordon, M. Kiszka, I. R. Dunkin, W. Kerr, J. S. Scott and J. Gebicki, *J. Organomet. Chem.*, 1998, **554**, 147–154; (*b*) S. M. Draper, C. Long and B. M. Myers, *J. Organomet. Chem.*, 1999, **588**, 195–199.

7 (*a*) M. Yamanaka and E. Nakamura, *J. Am. Chem. Soc.*, 2001, **123**, 1703–1708; (*b*) T. J. M. de Bruin, A. Milet, F. Robert, Y. Gimbert and A. E. Greene, *J. Am Chem. Soc.*, 2001, **123**, 7184–7185.

8 For X-ray structures of hexacarbonyldicobalt complexes of dialkyl- or diaryl-acetylenes see: (*a*) F. A. Cotton, J. D. Jamerson and B. R. Stults, *J. Am. Chem. Soc.*, 1976, **98**, 1774–1779; (*b*) F. Baert, A. Guelzim, J. M. Poblet, R. Wiest and J. Demuynck M. Benard, *Inorg. Chem.*, 1986, **25**, 1830–1841; (*c*) W. G. Sly, *J. Am. Chem. Soc.*, 1959, **81**, 18–20; N. A. Bailey and R. Mason, *J. Chem. Soc.*, 1968, 1293–1299; (*d*) D. Gregson and J. A. K. Howard, *Acta Crystallogr., Sect. C*, 1983, **39**, 1024–1027.

9 For X-ray structures of hexacarbonyldicobalt complexes of other acetylenes see: (*a*) M. Gruselle, B. Malezieux, J. Vaissermann and H. Amouri, *Organometallics*, 1998, **17**, 2337–2343; (*b*) S. J. Doig, R. P. Hughes, R. E. Davis, S. M. Gadol and K. D. Holland, *Organometallics*, 1984, **3**, 1921–1922; (*c*) M. Saha, S. Muchmore, D. van der Helm and K. M. Nicholas, *J. Org. Chem.*, 1986, **51**, 1960–1966; (*d*) M. I. Bruce, B. C. Hall, B. D. Kelly, P. J. Low, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1999, 3719–3728; (*e*) M. I. Bruce, B. D. Kelly, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 2000, **604**, 150–156; (*f*) M. A. Brook, J. Urschey and M. Stradiotto, *Organometallics*, 1998, **17**, 5342–5346; (*g*) A. M. Montana, K. M. Nicholas and M. A. Khan, *J. Org. Chem.*, 1988, **53**, 5193–5201; (*h*) J. Ju, B. R. Reddy, M. Khan and K. M. Nicholas, *J. Org. Chem.*, 1989, **54**, 5426–5428; (*i*) A. Gelling, J. C. Jeffery, D. C. Povey and M. J. Went, *J. Chem. Soc., Chem. Commun.*, 1991, 349–351; (*j*) B. Happ, T. Bartik, C. Zucchi, M. C. Rossi, F. Ghelfi, G. Palyi, G. Varadi, G. Szalontai, I. T. Horvath, A. Chiesi-Villa and C. Guastini, *Organometallics*, 1995, **14**, 809–819.

10 B. J. Rausch and R. Gleiter, *Tetrahedron Lett.*, 2001, **42**, 1651–1653.

11 H. H. Brintzinger, R. Fischer, R. Mülhaupt, B. Rieger and R. M. Waymouth, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1143–1170.

12 M. Ramming and R. Gleiter, *J. Org. Chem.*, 1997, **62**, 5821–5829.

13 R. Gleiter, R. Merger, B. Treptow, W. Wittwer and G. Pflaesterer, *Synthesis*, 1993, **6**, 558–560.

14 R. Gleiter, R. Merger and B. Nuber, *J. Am. Chem. Soc.*, 1992, **114**, 8921–8927.

15 R. Gleiter, M. Karcher, R. Jahn and H. Irngartinger, *Chem. Ber.*, 1988, **121**, 735–740.

16 R. Gleiter, S. Rittinger and H. Irngartinger, *Chem. Ber.*, 1991, **124**, 357–363.

17 K. C. Nicolaou, G. Zuccarello, C. Riemer, V. A. Estevez and W.-M. Dai, *J. Am. Chem. Soc.*, 1992, **114**, 7360–7371.

18 J. Ritter, R. Gleiter, H. Irngartinger and T. Oeser, *J. Am. Chem. Soc.*, 1997, **119**, 10599–10607.

19 R. Gleiter, J. Ritter, H. Irngartinger and J. Lichtentaehler, *Tetrahedron Lett.*, 1991, **32**, 2883–2886.

20 R. Gleiter, D. Kratz, W. Schäfer and V. Schehlmann, *J. Am. Chem. Soc.*, 1991, **113**, 9258–9264.

21 R. B. King, I. Haiduc and A. Efraty, *J. Organomet. Chem.*, 1973, **47**, 145–151.

22 (*a*) J. Dale, *Angew. Chem., Int. Ed. Engl.*, 1966, **5**, 1000–1021; (*b*) R. Gleiter, R. Merger, in *Modern Acetylene Chemistry*, ed. P. J. Stang and F. Diederich, VCH, Weinheim, 1995, pp. 285–319; (*c*) R. Gleiter, M. Ramming, H. Weigl, V. Wolfart, H. Irngartinger and T. Oeser, *Liebigs Ann./Recl.*, 1997, 1545–1550.

23 F. Robert, A. Milet, Y. Gimbert, D. Konya and A. E. Greene, *J. Am. Chem. Soc.*, 2001, **123**, 5396–5400.

24 R. Gleiter and J. Ritter, *Tetrahedron*, 1996, **52**, 10383–10388.

25 R. Gleiter and D. Kratz, *Tetrahedron Lett.*, 1990, **31**, 5893–5896.

26 R. Gleiter, J. Classen, B. J. Rausch, T. Oeser and F. Rominger, *J. Organomet. Chem.*, 2002, **641**, 3–8.

27 X-Ray structure of 1-thiacyclotetradeca-4,11-diyne deposited with the Cambridge Crystallographic Data Centre. Relevant structural parameters: chemical formula $C_{13}H_{18}S$; formula weight, 206.33; temperature, 200(2) K; crystal size, 0.29 × 0.24 × 0.15 mm; crystal system, orthorhombic; space group, *Pbca*; *Z*, 4; *a*, 9.0282(9); *b*, 9.4287(9); *c*, 13.6170(13) Å; absorption coefficient μ, 2.24 mm^{-1}; reflections collected/independent/observed, 2431/1187/865; max/min transmission, 0.97 and 0.74; parameters, 73; goodness-of-fit on F^2, 1.02; $R(F)$, 0.043; $R_w(F^2)$, 0.098; $(\Delta\rho)$max, $(\Delta\rho)$min, 0.22 and −0.17 e $Å^{-3}$.

28 R. Gleiter, S. Rittinger and H. Irngartinger, *Chem. Ber.*, 1991, **124**, 365–369.

29 J. E. Davies, L. J. Hope-Weeks, M. J. Mays and P. R. Raithby, *Chem. Commun.*, 2000, 1411–1412.

30 G. M. Sheldrick, Bruker Analytical X-ray Division, Madison, WI, 1997.

31 ORTEP-3 for windows – version of Ortep-III with a graphical user interface (GUI): L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **72**, 565.