

The Reaction of As_4S_n ($n = 3, 4$) and As_2S_3 with $(\text{C}_5\text{Me}_4\text{R})_2\text{Co}_2(\text{CO})_2$ ($\text{R} = \text{Me, Et}$): Fragmentation and Reassembling of Main-Group Ligands by Organometallic Complexes

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The reaction of $\text{Cp}^\#_2\text{Co}_2(\text{CO})_2$ **1** ($\text{Cp}^\# = \text{Cp}^* \text{ or } \text{Cp}^x$; $\text{Cp}^* = \text{C}_5\text{Me}_5$; **a**; $\text{Cp}^x = \text{C}_5\text{Me}_4\text{Et}$; **b**) with equimolar amounts of As_4S_n ($n = 3, 4$) and As_2S_3 was investigated at different temperatures. The formation of $\text{Cp}^\#_2\text{Co}_2(\text{CO})\text{As}_2\text{S}_2$ **3**, $\text{Cp}^\#_2\text{Co}_2\text{As}_2\text{S}_3$ **4**, $\text{Cp}^\#_3\text{Co}_3\text{As}_2\text{S}_4$ **5**, and $\text{Cp}^\#_3\text{Co}_3\text{As}_4\text{S}_2$ **6** was observed in ratios depending on the reaction conditions. Starting from As_4S_4 or As_4S_3 and **1b** insertion of a $\text{Cp}^x\text{Co}(\text{CO})$ fragment into one of the As–As bonds of the cages was

achieved in low yields leading to $\text{Cp}^x\text{Co}(\text{CO})\text{As}_4\text{S}_4$ **2b** and $\text{Cp}^x\text{Co}(\text{CO})\text{As}_4\text{S}_3$ **8**, respectively. Structures were studied by means of IR and ^1H -NMR spectroscopy and X-ray diffraction analyses. $\text{Cp}^\#_2\text{Co}_2(\text{CO})\text{As}_2\text{S}_2$ **3** may be supposed to be the key intermediate in the whole reaction sequence: On heating solutions of **3** complexes **4–6** of higher nuclearity and different connectivity within the inorganic ligand were formed.

There is a rich chemistry of organometallic compounds comprising unsubstituted ("naked") arsenic^[1] or sulfur^[1b,2] ligands. However, relatively little is known about compounds containing mixed ligands from group-15 and group-16 elements. Particular examples are organometallic arsenic sulfides which are composed of transition-metal centres containing organic π -ligands and As/S ligands of varying nuclearity. It was already established that the inorganic cage molecules realgar, As_4S_4 , and As_4S_3 may serve as sources for such ligands by extraction of fragments of any size up to " As_3S_3 "^[3,4]. In contrast to P_4S_3 ^[4–6], the complexation of the complete inorganic cages has not yet been realised. In preliminary work we showed that not only fragmentation reactions take place but that also recombination of small ligands up from atomic size occurs^[7]. However, as systematic investigation of the activation of distinct As_mS_n compounds by one and the same metal fragment was still necessary. In this study $\beta\text{-As}_4\text{S}_4$ ^[8–10] was employed in reactions with $\text{Cp}^\#_2\text{Co}_2(\text{CO})_2$ **1** ($\text{Cp}^\# = \text{Cp}^* \text{ or } \text{Cp}^x$; $\text{Cp}^* = \text{C}_5\text{Me}_5$; **a**; $\text{Cp}^x = \text{C}_5\text{Me}_4\text{Et}$; **b**). A completely different As–S connectivity is present in As_4S_3 ^[11] whereas As_2S_3 consists of a solid-state layer structure^[10b].

Preparative Results

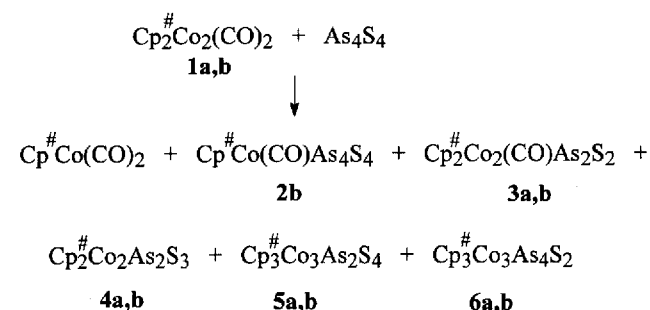
The System $\text{Cp}^\#_2\text{Co}_2(\text{CO})_2$ ($\text{Co}=\text{Co}$)/ As_4S_4

In the reactions of **1a, b** with realgar the introduction of the Cp^x ligand instead of Cp^* not only improved the crystallisation behaviour of the products but also affected the adsorption properties on SiO_2 such that better separations during column chromatography were achieved. For these reasons the reaction was systematically investigated

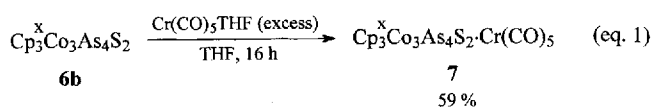
at different temperatures only in the case of **1b**, equimolar amounts of both starting materials being used in all cases.

At room temperature in toluene **1b** reacts rather slowly giving after 40 h compounds **3b–6b** in low yields along with $\text{Cp}^x\text{Co}(\text{CO})_2$ (Table 1). The latter arises from the addition of liberated CO to the Co–Co double bond of **1b**. Elemental analyses and mass spectroscopy are consistent with formulas $\text{Cp}^\#_2\text{Co}_2(\text{CO})\text{As}_2\text{S}_2$ **3b**, $\text{Cp}^\#_2\text{Co}_2\text{As}_2\text{S}_3$ **4b**, $\text{Cp}^\#_3\text{Co}_3\text{As}_2\text{S}_4$ **5b**, and $\text{Cp}^\#_3\text{Co}_3\text{As}_4\text{S}_2$ **6b** (Scheme 1). As **6b** did not crystallise well, the addition of $\text{Cr}(\text{CO})_5$ fragments was attempted. Even with a large excess of $\text{Cr}(\text{CO})_5(\text{THF})$, only the monoadduct **7** formed (Eq. 1) which was unequivocally characterised by means of elemental analyses and mass spectrometry. Single crystals suitable for X-ray crystallography could not be obtained.

Scheme 1



The reaction at 80°C was investigated for both **1a, b**. After 15 h in toluene **3a–6a** had formed. The yields of **3b–6b** increase considerably when compared to those obtained at ambient temperature (Table 1). Concomitantly,

Table 1. Product distribution in % yield as a function of reaction conditions for the reaction of As₄S₄ with **1a, b**

Conditions	Start. mater.	Cp [#] Co(CO) ₂	2a,b	3a,b	4a,b	5a,b	6a,b
Toluene, 80 °C, 15 h	1a	19	[a]	11	22	12	9
Toluene, 20 °C, 40 h	1b	9	[a]	6	2	2	1
Toluene, 80 °C, 15 h	1b	17	<1	10	10	11	13
<i>o</i> -Xylene, 144 °C, 15 h	1b	[a]	[a]	[a]	51	11	[a]

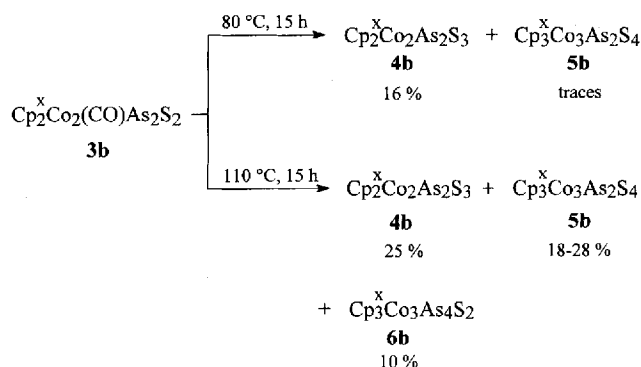
[a] Not observed.

the yield of Cp^xCo(CO)₂ increases from 9 to 17%. Whereas all compounds were separated by careful column chromatography, an additional product **2b** was isolated by means of fractional crystallisation from the second band along with some **6b**. Its identity was revealed by mass spectrometry and X-ray crystallography as Cp^xCo(CO)As₄S₄.

If **1b** reacts with realgar in boiling *o*-xylene only **4b** and **5b** are formed. It is striking that the yield of **4b** in this reaction is much higher than the total yields of **2b–6b** obtained when the reaction was carried out at 80 °C (Table 1). Control experiments with toluene solutions of Cp³Co₂(CO)As₂S₂ **3b** at 80 °C and 110 °C showed that at 80 °C Cp³Co₂As₂S₃ **4b** had formed along with traces of Cp³Co₃As₂S₄ **5b**, and starting material was recovered (Scheme 2). In boiling toluene, however, the latter completely disappeared, and the formation of **4b–6b** was observed. Addition of As₄S₄ did not affect the product distribution.

If **3b** reacts with elemental sulfur at room temperature its CO absorption in the IR spectrum disappears. The only well-defined product formed was Cp³Co₂S₄ which has been identified by comparison with an authentic sample^[12].

Scheme 2



The Reaction of **1b** with As₄S₃ and As₂S₃

Reaction of Cp³Co₂(CO)₂ with an equimolar amount of As₄S₃ afforded under analogous conditions (toluene, 80 °C,

17 h) compounds **3b–6b** in yields similar to those obtained from the reaction of **1b** with As₄S₄ (Table 2). In addition, brown Cp^xCo(CO)As₄S₃ **8** was formed in 3% yield. Compound **8** gave correct analyses; its structure is described below.

Table 2. Yields (%) of the reaction of **1b** with As₄S₄, As₄S₃, and As₂S₃ (toluene, 80 °C)

	As ₄ S ₄	As ₄ S ₃	As ₂ S ₃
Cp ^x Co(CO) ₂	17	10	6
Cp ^x Co(CO)As ₄ S ₄ , 2b	<1	–	–
Cp ^x ₂ Co ₂ (CO)As ₂ S ₂ , 3b	10	14	3
Cp ^x ₂ Co ₂ As ₂ S ₃ , 4b	6	8	19
Cp ^x ₃ Co ₃ As ₂ S ₄ , 5b	11	10	10
Cp ^x ₃ Co ₃ As ₄ S ₂ , 6b	13	12	4
Cp ^x Co(CO)As ₄ S ₃ , 8	–	3	–

With Cp³Co₂(CO)₂ under standard conditions (toluene, 80 °C, 17 h, equimolar ratio) As₂S₃ furnished the same compounds as As₄S₃ except for **8**^[13]. Compared to the reaction with As₄S₃ the yield of Cp³Co₃As₂S₄ remains constant whereas that of Cp³Co₂As₂S₃ increases considerably (Table 2). The yields of **3b** and **6b** are, however, lower.

Spectroscopic and Crystallographic Results

IR-Spectra

In the IR spectra (KBr disks) of compounds **2–8** only the absorptions of the CO ligands are of diagnostic value. Absorptions at 1998 (**2b**), 1987 (**3a**), 1987 (**3b**), and 2000 cm^{–1} (**8**) are characteristic of one terminal CO ligand for each complex. The ν(CO) frequency of **2b** is taken from its mixture with **6b**. The IR spectrum of **7** contains the absorption pattern typical of the Cr(CO)₅ fragment (2035 s, 1935 vs, 1895 s [cm^{–1}]).

¹H-NMR Spectra

The ¹H-NMR spectra of **3–8** are summarised in Table 3. Although they are rather complicated in the case of the C₅Me₄Et ligand, they support the crystallographic results. The resonances of **2b** could not be determined unequivocally for they are in part superposed by the signals of the very complex spectrum of **6b**.

The spectrum of **3a** contains two resonances originating from the Cp^{*} ligands. The set of the ring methyl resonances of **3b** is also in agreement with two different Cp^{*} ligands and, in addition, with a symmetry plane along the Co–Co axis bisecting both Cp^{*} ligands. The spectrum of **4a** exhibits only one resonance whereas four singlets for the ring methyl groups are in agreement with the crystallographic C₂ symmetry determined for this type of molecule^[3].

The spectrum of **5a** reveals two singlets for the ring methyl group ratio 1:2. This indicates the presence of two equivalent Cp^{*} rings, whereas the third one is slightly different. A similar situation was found for the solid-state structure of **5b** (see below)^[7]. The NMR spectrum of **5b** shows the pattern 2:2:2:4:2 for the ring CH₃ resonances. The spectra of **6a** and **6b** are indicative of three inequivalent Cp[#] ligands. Thus, three singlets in a ratio of 1:1:1 are

Table 3. ^1H -NMR spectroscopic data of **3–8** (CDCl_3 , i -TMS, 250 MHz)

	$\delta(\text{CH}_2\text{CH}_3)^{[a]}$	$\delta(\text{CH}_3)$	$\delta(\text{CH}_2\text{CH}_3)^{[a]}$
3a		1.67 (s, 15H), 1.92 (s, 15H)	
3b	0.93 (t, 3H), 1.11 (t, 3H)	1.64 (s, 6H), 1.71 (s, 6H), 1.92 (s, 6H), 1.93 (s, 6H)	2.26 (q, 2H), 2.36 (q, 2H)
4a		1.70 (s, 30H)	
4b	0.95 (t, 6H)	1.65 (s, 6H), 1.66 (s, 6H), 1.75 (s, 6H), 1.76 (s, 6H)	2.27 (q, 2H), 2.28 (q, 2H)
5a		1.51 (s, 15H), 1.59 (s, 30H)	
5b	0.95 (m, 9H) ^[d]	1.47 (s, 6H), 1.49 (s, 6H), 1.52 (s, 6H), 1.57 (s, 12H), 1.60 (s, 6H)	2.10 (m, 6H) ^[e]
6a		1.60 (s, 15H), 1.63 (s, 15H), 1.91 (s, 15H)	
6b	0.92 (m, 6H) ^[b] , 1.11 (t, 3H)	1.49 (s, 3H), 1.50 (s, 3H), 1.51 (s, 3H), 1.54 (s, 3H), 1.55 (s, 3H), 1.56 (s, 3H), 1.60 (s, 3H), 1.61 (s, 3H), 1.85 (s, 3H), 1.86 (s, 3H), 1.88 (s, 6H)	2.12 (m, 4H) ^[c] , 2.39 (q, 2H)
7	0.93 (m, 6H) ^[b] , 1.09 (t, 3H)	1.57 (s, 3H), 1.58 (s, 6H), 1.60 (s, 3H), 1.61 (s, 3H), 1.62 (s, 3H), 1.65 (s, 3H), 1.66 (s, 3H), 1.81 (s, 3H), 1.82 (s, 3H), 1.83 (s, 3H), 1.84 (s, 3H)	2.17 (m, 4H) ^[c] , 2.33 (q, 2H)
8	1.10 (t, 3H)	1.80 (s, 6H), 1.84 (s, 6H)	2.21 (q, 2H)

^[a] $^3J(\text{H-H}) = 7.5 \text{ Hz}$. – ^[b] Two superposed triplets. – ^[c] Two superposed quartets. – ^[d] Three superposed triplets. – ^[e] Three superposed quartets.

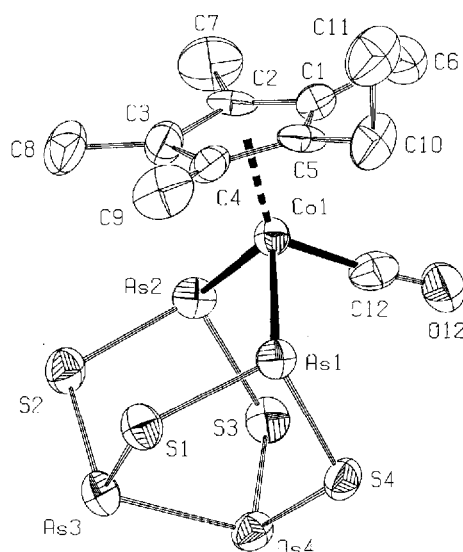
characteristic of **6a**. The much more complex spectrum of **6b** consists of eleven singlets, one of which exhibits a double intensity. The differences observed for the chemical shifts indicate two similar Cp^x rings, whereas the third ring seems to be significantly different. The spectrum of **7** is very similar to that of its precursor **6b**. This means that coordination of $\text{Cr}(\text{CO})_5$ does obviously not affect significantly the structure. Surprisingly, there is no indication of the presence of other isomers, but the spectroscopic data alone do not allow us to draw any as to the coordination site.

The spectrum of **8** shows two singlets for the ring methyl protons and one triplet and one quartet for the ethyl protons which is in agreement with a symmetry plane through the Cp^x ligand (see below).

X-ray Crystal Structures of **2b** and **8**

Single crystals of **2b** were obtained from a mixture of **2b** and **6b**. The structure of $\text{Cp}^x\text{Co}(\text{CO})\text{As}_4\text{S}_4$ **2b** may be derived from α - or β - As_4S_4 ^[9,10], a $\text{Cp}^x\text{Co}(\text{CO})$ fragment being inserted into one of the As–As bonds (Fig. 1). As a consequence, the four arsenic atoms form a considerably distorted tetrahedron. Compared to the structure of α - As_4S_4 one of the As–As distances increases from 2.566 to 3.714 Å, which is clearly nonbonding, whereas the other one is still of bonding nature [2.519(6) Å]. The nonbonding S–S distances and all As–S–As angles increase as well. This is also true for the S–As–S angles at As(3) and As(4), whereas the As–S distances do not change much.

The structure of **2b** is the first example of the insertion of a metal-complex fragment into the As_4S_4 cage. Similar

Figure 1. ORTEP Plot of the molecular structure of $\text{Cp}^x\text{Co}(\text{CO})\text{As}_4\text{S}_4$ (**2b**)

Selected bond lengths [Å] and angles [°]: Co–As(1) 2.369(6), Co–As(2) 2.383(6), Co–C(12) 1.740(18), As(3)–As(4) 2.519(6), As–S_{mean} 2.252(7), As(1)–S(1) 2.254(7), As(1)–S(4) 2.247(7), As(3)–S(1) 2.244(7), As(4)–S(4) 2.247(7), As(1)–As(2) 3.714(6), S(1)–S(2) 3.432(7), S(1)–S(4) 3.334(7); As(1)–Co–As(2) 102.8(2), As(1)–Co–C(12) 90.0(6), Co–As(1)–S(1) 113.1(2), S(1)–As(1)–S(4) 95.6(2), S(1)–As(3)–S(2) 100.1(2), As(1)–S(1)–As(3) 109.0(2), As(4)–As(3)–S(1) 100.6(2).

insertion reactions were already realised for the As_4 ^[14] and the P_4 molecule^[15].

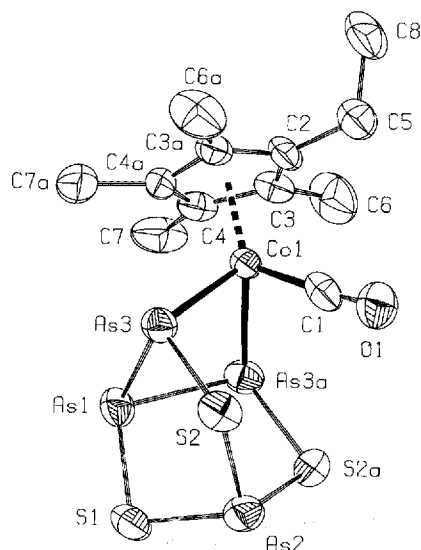
The crystal structure of $\text{Cp}^x\text{Co}(\text{CO})\text{As}_4\text{S}_3$ **8** can be described by the insertion of the $\text{Cp}^x\text{Co}(\text{CO})$ fragment into a basal As–As bond of As_4S_3 (Fig. 2). Obviously, in contrast to P_4S_3 ^[5,16], the apical position is less accessible to coordination. Compared to the structure of As_4S_3 ^[11] the distance As(3)–As(3a), which is 2.450 Å in the uncomplexed cradle, is considerably enlarged up to 3.251 Å. The nonbonding S(2)–S(2a) distance is 0.16 Å longer than that in As_4S_3 , whereas the S(2)–As(3) and S(2a)–As(3a) bonds are only 0.06 Å longer. As a consequence of the longer distances, some bond angles are also affected, e.g. As(3)–As(1)–As(3a) which increases from 60.2 to 82.3°.

The crystal structures of **3b**^[7], **4a**^[3], and **5b**^[7] were already determined and they are shown in Figures 3–5.

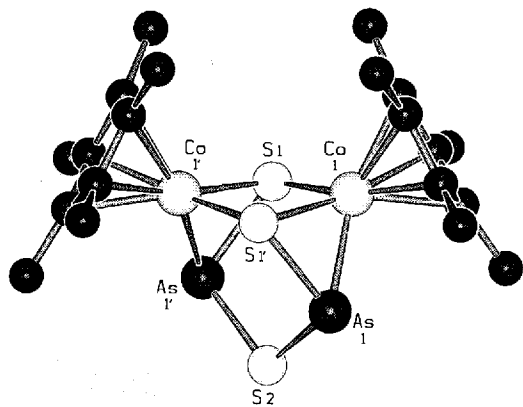
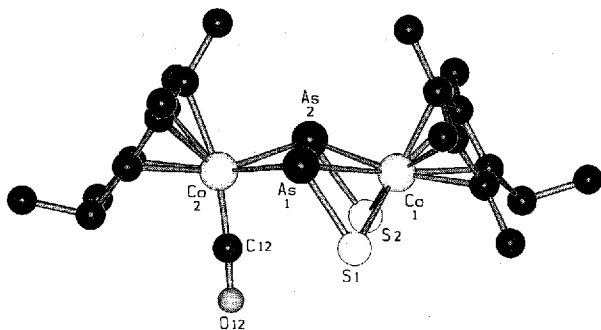
Discussion

The present study shows that peralkylated $\text{Cp}^x\text{Co}_2(\text{CO})_2$ reacts with As_4S_4 , As_4S_3 , and As_2S_3 to afford products containing As/S ligands of different size. The product distribution is influenced much more by the reaction conditions than by the nature of the employed As/S compounds.

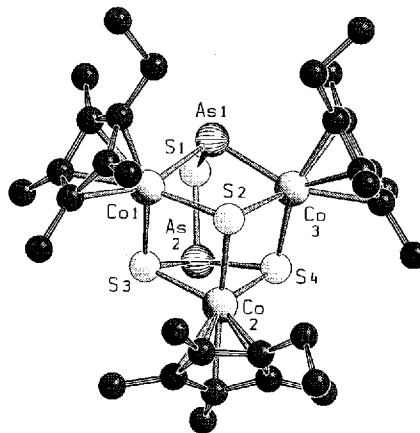
The isolation and characterisation of $\text{Cp}^x\text{Co}(\text{CO})\text{As}_4\text{S}_4$ and $\text{Cp}^x\text{Co}(\text{CO})\text{As}_4\text{S}_3$ provided for the first time evidence that the As_4S_4 and As_4S_3 cradles may be directly activated by a reactive complex fragment. In both cases insertion into As–As bonds was observed which indicates a nucleophilicity of the As coordination site superior to that of the S site. In this regard the reaction of **1b** with As_4S_4 and As_4S_3

Figure 2. ORTEP Plot of the molecular structure of $\text{Cp}^*\text{Co}(\text{CO})\text{As}_4\text{S}_3$ (**8**)

Selected bond lengths [Å] and angles [°]: Co–As(3) 2.375(1), Co–C(1) 1.750(14), As(1)–As(3) 2.470(1), As(1)–S(1) 2.209(4), As(2)–S(1) 2.252(4), As(3)–S(2) 2.263(3), As(3)–As(3A) 3.251(4), S(2)–S(2A) 3.511(4); As(3)–Co–As(3A) 86.4(1), As(3)–Co–C(1) 92.7(3), Co–As(3)–As(1) 90.1(1), As(3)–As(1)–As(3A) 82.3(1), S(2)–As(2)–S(2A) 103.9(1).

Figure 3. SCHAKAL Plot of $\text{Cp}_2^*\text{Co}_2(\text{CO})\text{As}_2\text{S}_2$ **3b**Figure 4. SCHAKAL Plot of $\text{Cp}_2^*\text{Co}_2\text{As}_2\text{S}_3$ **4a**

parallels that of $\text{Cp}_2^*\text{Co}_2(\text{CO})_2$ with As_4 ^[14] which proceeds by edge opening of the As_4 tetrahedron and insertion of a $\text{Cp}^*\text{Co}(\text{CO})$ fragment. As **2b** and **8** never exceed a low

Figure 5. SCHAKAL Plot of $\text{Cp}_3^*\text{Co}_3\text{As}_2\text{S}_4$ **5b**

concentration, it may be supposed that they are easily converted into other species.

One of these species may be a complex of the type $\text{Cp}_2^*\text{Co}_2(\text{CO})\text{As}_2\text{S}_2$ **3a, b** which contains two $\text{syn-}\eta^1:\eta^2\text{-AsS}$ bridges (Fig. 3). These are separated from each other by As–As [2.717(2) Å] distances which come relatively close to bonding character [e.g. $d(\text{As}–\text{As})$ in $\beta\text{-As}_4\text{S}_4 = 2.593(6)$ Å^[9]]. A terminal CO group at Co(2) formally saturates the metal and it probably facilitates the thermal conversion of **3a, b** in solution due to its liberation. In the new cage molecules $\text{Cp}_2^*\text{Co}_2\text{As}_2\text{S}_3$ **4b**, $\text{Cp}_3^*\text{Co}_3\text{As}_2\text{S}_4$ **5b**, and $\text{Cp}_3^*\text{Co}_3\text{As}_4\text{S}_2$ **6b**, stoichiometries are found which differ from that in **3b**. It is also evident that the connectivity of the main-group ligands has changed. Thus, a S–As–S–As–S chain (Fig. 4) is the substantial part of the $\text{Co}_2\text{As}_2\text{S}_3$ basket in **4a** (and consequently in **4b**). It is striking that in the reaction of **1b** with As_2S_3 the formation of $\text{Cp}_2^*\text{Co}_2\text{As}_2\text{S}_3$ is favoured, probably because the As_2S_3 structural unit already exists in the layered structure of the mineral. The structure of **5b** is characterised by a $\text{Co}_3\text{As}_2\text{S}_4$ cage which is held together by $\mu_3\text{-S}$ and $\mu_3\text{-As}_2\text{S}_3$ ligands (Fig. 5)^[7]. In this complex the As–S distances of the As_2S_3 ligand vary from 2.196(1) to 2.318(4) Å. The connectivity is As–S–As–(S,S). While **4b** and **5b** are more rich in sulfur compared to **3b**, the third degradation product, **6b**, is more rich in arsenic. Unfortunately, the connectivities in this compound are still unknown.

In conclusion, the formation of novel organometallic cobalt arsenic sulfides has been described to proceed via the activation of the inorganic cage molecules As_4S_4 and As_4S_3 by the reactive Co=Co bond. However, the key intermediate for the whole reaction sequence seems to be the dinuclear compound $\text{Cp}_2^*\text{Co}_2(\text{CO})(\mu, \eta^{1:2}\text{-AsS})_2$ **3**. This type of complex is also formed in the As_2S_3 reaction, and its diatomic AsS ligands are converted into ligands of higher nuclearity under thermal conditions.

We are grateful to Prof. G. Huttner for support of X-ray crystallographic measurement and to Dr. Manfred Zabel for performing the X-ray powder analyses of the employed As/S phases of As_4S_4 .

Experimental

All procedures were carried out under N_2 with dry solvents. Elemental analyses were performed by the Mikroanalytisches Laboratorium, Universität Regensburg (C, H) and Analytische Laboratorien Prof. Malissa und Reuter, D-51789 Lindlar (As, S). – IR spectra were measured with a Beckman 4240 spectrophotometer. – Molecular weights were determined by field desorption (FD) mass spectrometry in toluene solutions with a Finnigan MAT 95 instrument. – 1H -NMR spectra were recorded with a Bruker WM 250 instrument. – $Cp_2^*Co_2(CO)_2$ was prepared according to literature procedures^[17].

Preparation of As_4S_4 : As_4S_4 was prepared by melting of As powder (As_2O_3 was removed before by high-vacuum sublimation) with elemental sulfur in a molar ratio of 1.03:1^[8]. The melt was kept for 3 d at 440°C and then for 3 d at 300°C. Slow cooling to room temp. resulted in crystalline samples which gave the same X-ray powder diffraction pattern as β - As_4S_4 ^[8,9].

Preparation of As_4S_3 : As_4S_3 was prepared in a similar way as As_4S_4 , but the melt was kept for 7 d at 500°C and then placed in an ice bath. The vitreous sample melted at 198°C (201°C^[18]).

Reaction of $Cp_2^*Co_2(CO)_2$ with As_4S_4 : The reaction of **1a,b** with As_4S_4 was carried out at 20°C and 80°C, respectively, in toluene solution and at 144°C in *o*-xylene. Work-up of the reaction mixture was the same in all cases. Therefore, only the reaction performed at 80°C is described. Concerning the product distribution as a function of the reaction conditions see Table 1.

A suspension containing 1.90 mmol of **1a** or **1b** and 817 mg (1.90 mmol) of As_4S_4 in 50 ml of toluene was stirred for 15 h at 80°C. After evaporation of the solvent the oily brown residue was dissolved in toluene and prepurified on SiO_2 (column 10 × 3 cm). With toluene/ether (10:1) a broad red-brown band was eluted followed by a brown band. The latter contained $Cp_2^*Co_2(CO)As_2S_2$ **3a,b**. The first band was rechromatographed on a SiO_2 column (84 × 2.5 cm). With toluene/pentane (1:1) first orange-red $Cp^*Co(CO)_2$ and then green-brown $Cp_3^*Co_3As_4S_2$ **6a,b** was eluted. The latter contained in the case of **6b** some $Cp^*Co(CO)As_4S_4$ **2b**, which was separated by fractional crystallisation. The following bands contained red-brown $Cp_3^*Co_3As_2S_4$ **5a,b** and violet $Cp_2^*Co_2As_2S_3$ **4a,b**. Recrystallisation from toluene/pentane (1:1) (**3b**), toluene/pentane (3:1) (**4a,b**), pentane (**5b**), and toluene/pentane (3:1) (**6b**) gave crystalline products. The other samples were identified by analogy with their 1H -NMR spectra and by mass spectrometry.

2b: $C_{12}H_{17}As_4CoOS_4$ (664.1): Mol. mass 664.0 (FD-MS). – **3a:** $C_{21}H_{30}As_2Co_2OS_2$ (630.3): Mol. mass 630.3 (FD-MS). – **3b:** $C_{23}H_{34}As_2Co_2OS_2$ (658.4): calcd. C 41.96, H 5.21, S 9.74; found C 42.24, H 5.25, S 9.78. – Mol. mass 658.2 (FD-MS). – **4a:** $C_{20}H_{30}As_2Co_2S_3$ (634.3): calcd. C 37.87, H 4.77, As 23.62, S 15.16; found C 37.60, H 4.65, As 23.85, S 15.09. – Mol. mass 634.4 (FD-MS). – **4b:** $C_{22}H_{34}As_2Co_2S_3$ (662.4): calcd. C 39.89, H 5.17; found C 39.56, H 5.32. – Mol. mass 662.3 (FD-MS). – **5a:** $C_{30}H_{45}As_2Co_3S_4$ (860.6): calcd. C 41.87, H 4.09, S 14.90; found C 41.09, H 5.25, S 14.76. – Mol. mass 860.8 (FD-MS). – **5b:** $C_{33}H_{51}As_2Co_3S_4$ (902.7): calcd. C 43.92, H 5.70; found C 43.67, H 5.65. – Mol. mass 902.5 (FD-MS). – **6a:** $C_{30}H_{45}As_4Co_3S_2$ (946.3): Mol. mass 946.6 (FD-MS). – **6b:** $C_{33}H_{51}As_4Co_3S_2$ (988.4): calcd. C 40.10, H 5.20; found C 39.17, H 5.49. – Mol. mass 988.7 (FD-MS).

$Cp_3^*Co_3As_4S_2 \cdot Cr(CO)_5$ (7): A solution of 220 mg (0.22 mmol) of **6b** and of 6 equivalents of $Cr(CO)_5THF$ in 150 ml of THF was stirred for 16 h at ambient temp. After evaporation of the solvent, chromatography on SiO_2 (column 20 × 3 cm) gave upon elution

with toluene/pentane (1:1) an intensive brown band of $Cp_3^*Co_3As_4S_2 \cdot Cr(CO)_5$ **7** in 59% yield. Recrystallisation of **7** from toluene/pentane (1:1) afforded brown crystals. $C_{38}H_{51}As_4Co_3CrO_5S_2$ (1180.4): calcd. C 38.66, H 4.35; found C 38.81, H 4.24. – Mol. mass 1180.6 (FD-MS).

Thermolysis of $Cp_3^*Co_2(CO)As_2S_2$ at 110°C: A solution of 86 mg (0.13 mmol) of **3b** in 50 ml of toluene was refluxed for 15 h. After removal of the solvent the brown residue was dissolved in 5 ml of toluene/pentane (1:1) and the solution chromatographed on SiO_2 (column 15 × 3 cm). With toluene/pentane (1:1) traces of a green band, green-brown **6b** (10%), red-brown **5b** (18–28%), and violet **4b** (25% yield) were eluted successively.

Reaction of $Cp_2^*Co_2(CO)As_2S_2$ with Sulfur: A solution of 178 mg (0.27 mmol) of **3b** and 12 mg (0.37 mmol) of sulfur was stirred for 22 h at ambient temp. Chromatography on SiO_2 (column 15 × 3 cm) gave upon elution with toluene a small amount of green $Cp_2^*Co_2S_4$ ^[12] (FD-MS: Mol. mass calcd. 544.6, found 544.5) as the only well defined product.

Reaction of $Cp_3^*Co_2(CO)_2$ with As_4S_3 : A suspension of 902 mg (1.91 mmol) of **1b** and 756 mg (1.91 mmol) of As_4S_3 in 50 ml of toluene was stirred for 17 h at 80°C while the colour turned from bright green to dark brown. Work-up was the same as already described for the As_4S_4 reaction. The sequence of products in the second chromatography was $Cp^*Co(CO)_2$, brown $Cp^*Co(CO)As_4S_3$ **8**, **6b**, **5b**, and **4b**. Recrystallisation of **8** from toluene gave brown crystals. $C_{12}H_{17}As_4CoOS_3$ (632.1): calcd. C 22.80, H 2.71, S 15.22; found C 22.33, H 3.00, S 14.22. – Mol. mass 632.2 (FD-MS).

Reaction of $Cp_2^*Co_2(CO)_2$ with As_2S_3 : As suspension of 1101 mg (2.33 mmol) of **1b** and 573 mg (2.33 mmol) of As_2S_3 in 50 ml of toluene was stirred for 17 h at 80°C. Work-up of the brown solution was the same as described above for As_4S_4 . Yields of the products are given in Table 2.

X-ray Structure Determination^[19] of Complexes **2b** and **8**

$Cp^*Co(CO)As_4S_4$ (2b): Dark needles (0.10 × 0.15 × 0.6 mm³), monoclinic $C2h/5$, $P2_1/c$ (No. 14); cell: $a = 8.75(2)$, $b = 13.33(3)$, $c = 17.52(3)$ Å, $\beta = 91.6(2)^\circ$; $V = 2042.6$ Å³, $Z = 4$; $d_{\text{calcd.}} = 2.16$ g cm⁻³; empirical absorption correction: 6 reflections $6.5 < 2\theta < 40.0^\circ$. Transmission factor (min/max) 0.64/1.00, $\mu = 7.65$ mm⁻¹. $F(000)$ 1280, Syntex R3. Mo- K_α radiation, graphite monochromator, 3591 unique observed reflections, 1914 independent reflections [$I > 2.5\sigma(I)$]. Structure solution by means of Patterson and Fourier methods using the SHELXTL-Plus program package^[20]. Number of parameters = 200; $R = 0.064$, $R_w = 0.050$; residual electron density (max/min) 0.97/−0.96 e/Å³, shift/esd (max) 0.011, $GOOF = 2.15$.

$Cp^*Co(CO)As_4S_3$ (8): Dark red-brown plates (0.05 × 0.17 × 0.23 mm³), orthorhombic $D2h/16$, $Pcmm$ (No. 62); cell: $a = 9.870(6)$, $b = 10.904(5)$, $c = 18.14(1)$ Å; $V = 1952.3$ Å³, $Z = 4$; $d_{\text{calcd.}} = 2.11$ g cm⁻³; empirical absorption correction: 6 reflections $5.6 < 2\theta < 34.1^\circ$. Transmission factor (min/max) 0.52/1.00, $\mu = 7.9$ mm⁻¹. $F(000)$ 1192, Syntex R3. Mo- K_α radiation, graphite monochromator, 2810 unique observed reflections; 1217 independent reflections [$I > 2.5\sigma(I)$]. Structure solution by means of Patterson and Fourier methods using the SHELXTL-Plus program package^[20]. Number of parameters = 110. $R = 0.050$, $R_w = 0.039$; residual electron density (max/min) 0.74/−0.75 e/Å³, shift/esd (max) 0.003, $GOOF = 1.68$.

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