Novel Inorganic Cage Structures Based on AsS Ligands and Cyclopentadienylruthenium Groups

Henri Brunner, Bernhard Nuber, Ludwig Poll, Gaby Roidl, and Joachim Wachter*

Abstract: The reaction of $[Cp_2^{(*)}Ru_2(CO)_4]$ [**a**: $Cp^{(*)} = Cp^*$ (η^5-C_5Me_5); **b**: $Cp^{(*)} = Cp^\times$ (η^5-C_5Me_4Et)] with β-realgar in boiling *n*-decane gives $[Cp_2^{(*)}Ru_2As_4S_4]$ (**1a,b**) in good yields along with some $[Cp_2^{(*)}Ru_2As_4S_2]$ (**2a,b**). According to X-ray diffraction analyses of **1b** and **2a**, their structures belong to two different types of inorganic clusters. Whereas **1b** has a cage structure in which the $Cp_2^{(*)}Ru_2$ unit is inserted into the As_4S_4 cradle, **2a** has a sandwich structure in which two coplanar η^2-As_2S ligands and the Cp* ligands are oriented parallel to one another. Analysis of the As–S connectivity in the core of **1b** reveals a structural relationship to the extremely rare form of arsenic sulfide As_4S_4(II), and not to the metastable high-temperature form β-As_4S_4 used in the synthesis. At lower temperatures (60, 115 °C) formation of CO-containing products is observed.

Keywords
clusters · ruthenium · sandwich complexes · arsenic sulfides

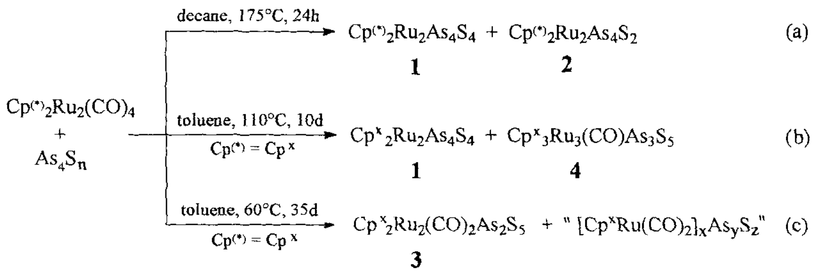
Introduction

Transition metal complexes with mixed As/S ligands are of particular interest because of their stoichiometric and structural diversity.[1] A useful source for such ligands is the mineral realgar As_4S_4[2] and its metastable high-temperature form β-As_4S_4.[3] The products isolated thus far from the reactions of realgar with reactive transition metal complexes have contained ligands that are smaller than the original cage molecule employed. This has led to the assumption that fragmentation reactions play a decisive role in the reaction pathways.[1, 4] Only recently it has been shown that small fragments or ligands (e.g., As, S, and AsS) can recombine to form larger (As_2S_2) or even three-dimensional (As_4S, AsS_3) structural units.[5, 6]

Insertion of realgar into the metal–metal bond of $[Cp^{(*)}{}_2Fe_2(CO)_4]$ under mild conditions gives complexes containing small As–S rings.[6] Their nature seem to be directly affected by the homolytic cleavage of the Fe–Fe bond.[7] Since a systematic investigation within one group of transition metals has not yet been carried out, we now wish to report on the reaction of As_4S_4 with related complexes of Ru, namely, $[Cp_2^*Ru_2(CO)_4]$ ($Cp^* = \eta^5$-C_5Me_5, **a**) and $[Cp_2^\times Ru_2(CO)_4]$ ($Cp^\times = \eta^5$-C_5Me_4Et, **b**). The influence of other sources for As–S ligands (e.g., As_4S_3 or As_2S_3) on the nature of the products will also be reported.

Results and Discussion

Preparation of $[Cp_2^{(*)}Ru_2As_4S_4]$ (1a,b) and $[Cp_2^{(*)}Ru_2As_4S_2]$ (2a,b): Reaction of $[Cp_2^{(*)}Ru_2(CO)_4]$ with one equivalent of β-As_4S_4[3] in boiling *n*-decane gave the red-orange compounds **1a,b** in moderate ($Cp^\times$) to good (Cp^*) yields along with minor amounts of **2a,b** (Scheme 1a).



Scheme 1. Reaction of $[Cp_2^{(*)}Ru_2(CO)_4]$ ($Cp^{(*)} = C_5Me_5$ (Cp^*) or C_5Me_4Et ($Cp^\times$)) with As_4S_n ($n = 3, 4$).

Reaction of $[Cp_2^{(*)}Ru_2(CO)_4]$ with As_4S_3 under analogous conditions gave similar results, although there was a slight sulfur deficiency in the inorganic starting material compared to As_4S_4. Complex **1a** also formed in the reaction of $[Cp_2^*Ru_2(CO)_4]$ with As_2S_3 (Table 1).

The mass spectra of the products allowed the assignment of the compositions as $[Cp_2^{(*)}Ru_2As_4S_4]$ for **1a,b** and $[Cp_2^{(*)}Ru_2$-

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Table 1. Yields [%] of the reaction of [$Cp_2^{(*)}Ru_2(CO)_4$] with As_4S_n ($n = 3, 4$) and As_2S_3 (decane, reflux).

Products	As_4S_4	As_4S_3	As_2S_3
[$Cp_2^*Ru_2As_4S_4$] (**1a**)	62	41	19
[$Cp_2^\times Ru_2As_4S_4$] (**1b**)	23	54	–
[$Cp_2^*Ru_2As_4S_2$] (**2a**)	6	9	[a]
[$Cp_2^\times Ru_2As_4S_2$] (**2b**)	5	7	–

[a] Not observed.

As_4S_2] for **2a,b**, which were confirmed by elemental analyses (**1a,b**, **2b**) and X-ray crystallographic studies (**1b**, **2a**). Isolation of analytically and spectroscopically pure **2a,b** was hampered by the difficult separation from the starting material [$Cp_2^{(*)}Ru_2(CO)_4$], because of very similar adsorption properties of the two compounds on SiO_2. Surprisingly, the ν(CO) IR absorptions of [$Cp_2^{(*)}Ru_2(CO)_4$] in the isolated mixture are significantly lower than the CO frequencies of pure *trans*-[$Cp_2^*Ru_2(CO)_4$][8] (Table 2a).

Table 2. Spectroscopic data of **1–4** and [$Cp_2^*Ru_2(CO)_4$].
a) IR data (KBr, cm^{-1}).

	$\tilde{\nu}$(CO)		$\tilde{\nu}$(CO)
trans-[$Cp_2^*Ru_2(CO)_4$]	1935, 1750	**3**	1945
2a·[$Cp_2^*Ru_2(CO)_4$]	1920, 1745	**4**	1938

b) ^1H NMR data ($CDCl_3$, i-TMS, 250 MHz) [a].

	$\delta(CH_2CH_3)$ [b]	$\delta(CH_3)$	$\delta(CH_2CH_3)$ [b]
1a		1.76 (s, 15H), 1.78 (s, 15H)	
1b	1.05 (m, 6H)	1.73 (s, 3H), 1.74 (s, 3H), 1.752 (s, 3H), 1.756 (s, 3H), 1.76 (s, 3H), 1.77 (s, 3H), 1.78 (s, 3H), 1.83 (s, 3H)	2.16 (m, 4H)
2a		1.54 (s, 30H)	
2b	1.18 (t, 6H)	1.99 (s, 12H), 2.01 (s, 12H)	2.29 (q, 4H)
3	1.07 (t, 6H)	1.75 (s, 6H), 1.77 (s, 6H), 1.80 (s, 6H), 1.82 (s, 6H)	2.23 (q, 4H)
4	1.05 (m, 9H) [c]	1.64 (s, 3H), 1.69 (s, 3H), 1.73 (s, 3H), 1.75 (s, 3H), 1.77 (s 3H), 1.78 (s, 3H), 1.79 (s, 3H), 1.82 (s, 3H), 1.83 (s, 6H), 1.84 (s, 3H), 1.85 (s, 3H)	2.19 (m, 6H) [d]

[a] Bruker WM250 instrument (24 °C). [b] $^3J(H-H) = 7.5$ Hz. [c] Three superposed triplets. [d] Three superposed quartets.

The ^1H NMR spectra of the dinuclear complexes **1a,b** (Table 2b) are characteristic of nonequivalent metal centers. The existence of eight ring methyl resonances in the spectrum of **1b** is in agreement with the asymmetric environment of each metal, which follows from the X-ray structure analysis (Figure 1, Table 3). In contrast the spectra for **2a,b** do not contain as many resonances.

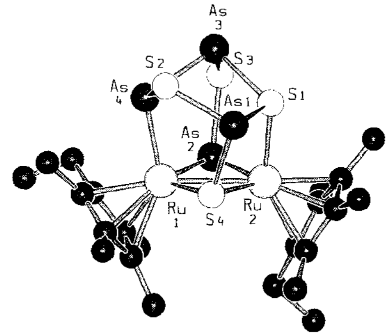

Fig. 1. Structure of [$Cp_2^\times Ru_2As_4S_4$] (**1b**) in the crystal (Schakal plot).

Table 3. Selected bond lengths [Å] and angles [°] for [$Cp_2^\times Ru_2As_4S_4$] (**1b**).

Ru1–Ru2	2.856(3)	As1–S2	2.181(7)
Ru1–As2	2.397(3)	As1–S4	2.311(6)
Ru1–As4	2.428(4)	As2–S3	2.313(6)
Ru1–S4	2.281(6)	As3–As4	2.413(4)
Ru2–As2	2.421(3)	As3–S1	2.330(6)
Ru2–S1	2.363(6)	As3–S3	2.188(7)
Ru2–S4	2.323(6)	As4–S2	2.282(8)
As1–S1	2.325(6)		
Ru2-Ru1-As2	54.0(1)	Ru1-As2-S3	113.8(2)
Ru2-Ru1-As4	100.8(1)	Ru2-As2-S3	106.9(2)
As2-Ru1-As4	91.6(1)	As4-As3-S1	94.7(2)
Ru2-Ru1-S4	52.3(2)	As4-As3-S3	95.7(2)
As2-Ru1-S4	106.0(2)	S1-As3-S3	96.1(3)
As4-Ru1-S4	94.9(2)	Ru1-As4-As3	109.2(1)
Ru1-Ru2-As2	53.3(1)	Ru1-As4-S2	108.5(2)
Ru1-Ru2-S1	93.9(2)	As3-As4-S2	87.2(2)
As2-Ru2-S1	94.4(2)	Ru2-S1-As1	92.9(2)
Ru1-Ru2-S4	51.0(2)	Ru2-S1-As3	113.4(2)
As2-Ru2-S4	103.9(2)	As1-S1-As3	102.1(2)
S1-Ru2-S4	84.2(2)	As1-S2-As4	101.6(3)
S1-As1-S2	101.2(3)	As2-S3-As3	102.8(3)
S1-As1-S4	85.3(2)	Ru1-S4-Ru2	76.7(2)
S2-As1-S4	99.2(3)	Ru1-S4-As1	113.7(2)
Ru1-As2-Ru2	72.7(1)	Ru2-S4-As1	94.3(2)

Cage (1b) and sandwich (2a) structure: The crystal structure of **1b** consists of a $Ru_2As_4S_4$ cage, which is shielded on one side by the sterically demanding C_5Me_4Et ligands (Figure 1). The structure may formally be derived from that of realgar(II)[9] by insertion of two $Cp^\times$Ru fragments into the As2–As4 and As2–S4 bonds (Figure 2). This means that **1b** is only the second complex with an As_4S_4 framework, after [$Cp^\times(CO)Co(\eta^2$-

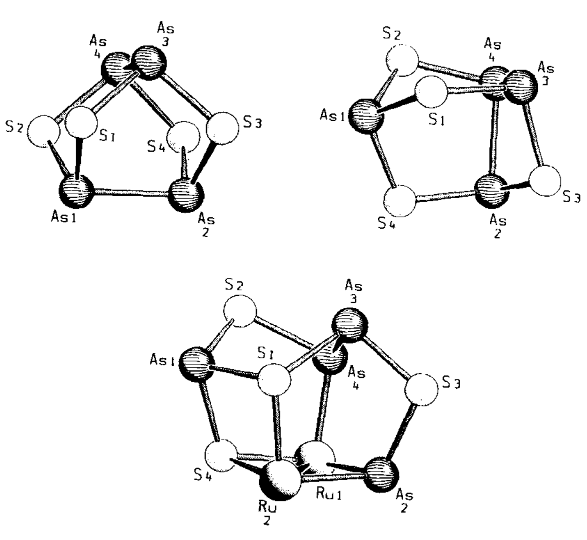

Fig. 2. Comparison of the structures of β-As_4S_4 [3] (top left) and As_4S_4(II) [9] (top right) with the core of [$Cp_2^\times Ru_2As_4S_4$] (**1b**, bottom) in Schakal views.

$\mathrm{As_4S_4})]$.[10] The latter was obtained in traces from the reaction of $[\{\mathrm{Cp}^\times(\mathrm{CO})\mathrm{Co}\}_2]$ with β-$\mathrm{As_4S_4}$. Compared to the As–As distance (2.519(6) Å) in the Co complex the distance As3–As4 (2.413(4) Å) in **1b** is remarkably short (Table 3). It is also shorter than the As–As distances in α-$\mathrm{As_4S_4}$ (2.566(1) Å),[2] β-$\mathrm{As_4S_4}$ (2.593(6) Å),[3] and $\mathrm{As_4S_4}$(II) (2.519(3) Å).[9] The As–S distances vary between 2.181(7) and 2.330(6) Å. In the valence electron count the inorganic ligand serves as an eight-electron donor. Together with the Ru–Ru bond (2.856(3) Å) a closed valence shell is achieved for each metal center.

Single crystals of "impure" $[\mathrm{Cp}^*_2\mathrm{Ru_2(CO)_4}]$ turned out to be a 1:1 mixture of *trans*-$[\mathrm{Cp}^*_2\mathrm{Ru_2(CO)_4}]$, which has already been structurally characterized,[11] and $[\mathrm{Cp}^*_2\mathrm{Ru_2As_4S_2}]$ (**2a**). Interestingly, crystallization of pure **2a** alone did not result in crystals of X-ray quality. Taking into account only the centers of each molecule the unit cell is composed of two *P* lattices: the origin of the $[\mathrm{Cp}^*_2\mathrm{Ru_2(CO)_4}]$ lattice is at 0,0,0, and that of **2a** at 1/2,1/2,1/2 (Figure 3). There are no intermolecular contacts that could explain the anomalous shift in the CO frequencies in the IR spectrum of $[\mathrm{Cp}^*_2\mathrm{Ru_2(CO)_4}]$ (see above).

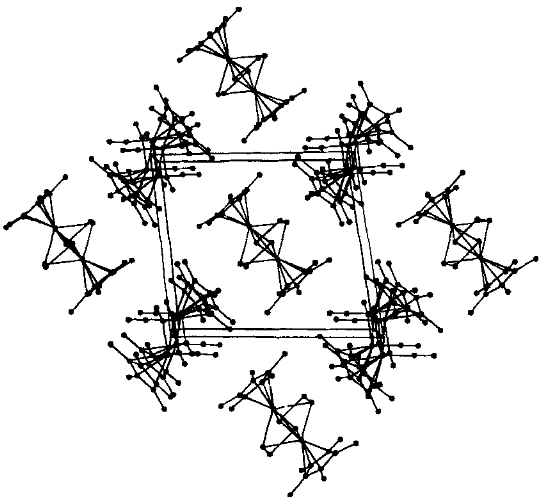

Fig. 3. View of the unit cell of $[\mathrm{Cp}^*_2\mathrm{Ru_2(CO)_4}]\cdot[\mathrm{Cp}^*_2\mathrm{Ru_2As_4S_2}]$ down the *a* axis. At the corners of the *P* lattice are $[\mathrm{Cp}^*_2\mathrm{Ru_2(CO)_4}]$ molecules.

The bond parameters of *trans*-$[\mathrm{Cp}^*_2\mathrm{Ru_2(CO)_4}]$ are identical with those of the previously determined structure.[11] The core of **2a** consists of a $\mathrm{Ru_2As_4}$ octahedron in which two edges are bridged by sulfur (Figure 4). The coplanar $\mathrm{As_2S}$ ligands are oriented parallel to the Cp* ligands, and a sandwich-like structure thus results. Obviously, there is a structural relationship between **2a** and the complex of type $[\mathrm{Cp}^*_2\mathrm{M}_2(\mu\text{-}\mathrm{As_2})_2]$, which has been synthesized for M = Co.[12] However, sulfur insertion into the As–As bonds has not yet been described.

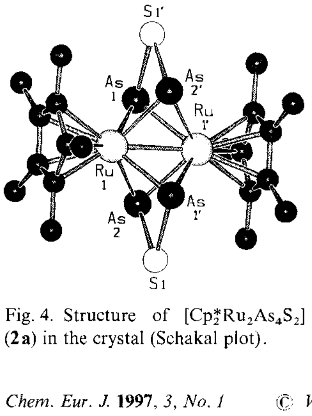

Fig. 4. Structure of $[\mathrm{Cp}^*_2\mathrm{Ru_2As_4S_2}]$ (**2a**) in the crystal (Schakal plot).

Although a similar $\mathrm{As_2S}$ bridge has been claimed for $[\mathrm{Cp}^*_2\mathrm{Mo_2As_2S_3}]$,[4a] complexes with $\mathrm{As_2S}$ ligands are still rare.[13] Extrusion of $\mathrm{As_2S}$ units from $\mathrm{As_4S}_n$ (n = 3, 4) by means of $\mathrm{Co^{II}}$ salts in the presence of triphos yields the (*cyclo*-)$\mathrm{As_2S}$ ligand.[14] The As–S distances in **2a** (mean 2.26 Å) are comparable to those in $\mathrm{As_4S_4}$.[2, 3] It is not yet clear whether the order of the relatively close As–As distances (2.824(2) and 3.065(3) Å) (Table 4) simply is a consequence of steric constraints imposed by the bridging ligands or whether it expresses some bonding interactions between all the As atoms. The latter cannot be excluded, because As–As bond lengths can vary widely, from 2.225(1) Å in $[\{\mathrm{Cp}^*(\mathrm{CO})_2\mathrm{Mn}\}_2\mathrm{As_2}]$[15] to 2.593(6) Å in β-$\mathrm{As_4S_4}$.[3b] The Ru–Ru distance decreases from 2.856(3) Å in **1b** to 2.752(1) Å in *trans*-$[\mathrm{Cp}^*_2\mathrm{Ru_2(CO)_4}]$ and 2.679(2) Å in **2a**.

Table 4. Selected bond lengths [Å] and angles [°] for $[\mathrm{Cp}^*_2\mathrm{Ru_2As_4S_2}]$ (**2a**).

Ru1–Ru1′	2.679(2)	As1′–S1	2.274(4)
Ru1–As1′	2.479(2)	As2–S1	2.286(4)
Ru1′–As1	2.479(2)	As1 ··· As2′	2.824(2)
Ru1′ As2′	2.467(2)	As1 ··· As2	3.065(4)
Ru1′–As2	2.482(2)	As1′ ··· As2	2.824(2)
Ru1-Ru1′-As1	57.4(1)	As1′-Ru1′-Ru1	57.3(1)
Ru1′-As1′-Ru1	65.4(1)	As1′-Ru1′-As1	114.6(1)
Ru1-As1′-As2	55.0(1)	As2′-Ru1′-As2	114.4(1)
Ru1′-As2′-S1′	98.2(1)	Ru1-As2′-S1′	96.9(1)
S1-As1′-Ru1	98.2(1)	As1-As2′-S1′	51.5(1)
Ru1-As2′-As1	55.3(1)	As1′-S1-As2	76.5(1)
Ru1′-As1′-S1	97.2(1)		

Ru-mediated skeletal isomerization of realgar or recombination of fragments? As has already been discussed above, the structure of **1b** may be derived from $\mathrm{As_4S_4}$(II) (Figure 2). However, this form of arsenic sulfide is not available on a preparative scale.[9] The material employed consists mainly of β-$\mathrm{As_4S_4}$ along with small quantities of other unidentified AsS phases as determined by X-ray powder diffraction. A phase transformation between $\mathrm{As_4S_4}$(II) and the metastable high-temperature form β-$\mathrm{As_4S_4}$ is not known.[3b]

The formation of **1b** starting from β-$\mathrm{As_4S_4}$ formally requires breaking of the As1–As2, As2–S4, and As4–S4 bonds and formation of the As1–S4 bond (Figure 2). These steps would lead to a slightly different As–S connectivity between the inorganic core of **1b** and the starting material. In addition the insertion of both $\mathrm{Cp}^\times\mathrm{Ru}$ fragments into the cradle would also require a severe distortion of its skeletal conformation.

As an alternative pathway to the Ru-mediated skeletal isomerization one might imagine that the inorganic cluster is formed by recombination of small fragments, provided a rapid fragmentation of realgar takes place.

In order to detect possible intermediates the reaction temperature was lowered. Therefore, reaction of $[\mathrm{Cp}^\times_2\mathrm{Ru_2(CO)_4}]$ (employed because of the better solubility of its products) with $\mathrm{As_4S_4}$ in toluene at 60 °C was monitored by IR spectroscopy. After 14 d there was evidence that several products bearing the 17-electron $\mathrm{Cp}^\times\mathrm{Ru(CO)_2}$ unit had been formed, but chromatographic separation into distinct products was impossible. After 35 d enrichment was observed of a red complex **3** in up to 15% yield (Scheme 1c). The composition $[\mathrm{Cp}^\times_2\mathrm{Ru_2(CO)_2As_2S_5}]$ was assigned by means of C,H analyses and mass spectrometry. The

IR spectrum exhibits only one absorption in the range of a terminal CO ligand ($\tilde{\nu}$(CO) = 1945 cm^{-1}); this may indicate the presence of two equivalent Ru centers. The ^{1}H NMR spectrum of **3** reveals four signals for the ring methyls (Table 2). A possible structure that is consistent with spectroscopic data can be derived from the β-As_4S_4 cage by substitution of two As atoms by two Ru centers (Figure 5).

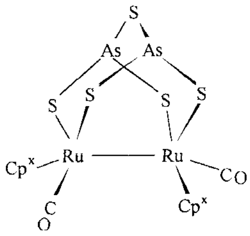

Fig. 5. Possible structure of **3**.

Reaction of [$Cp_2^x Ru_2(CO)_4$] with As_4S_4 in toluene at 110 °C gave two red products after 10 d, which were identified (C,H analyses, mass spectra) as **1b** (14% yield) and [$Cp_3^x Ru_3(CO)As_3S_5$] (**4**) (Scheme 1 b). The reaction did not take place in the dark. The IR spectrum of **4** exhibits one strong terminal ν(CO) frequency at 1938 cm^{-1}. The ^{1}H NMR spectrum (Table 2) is rather complex; it contains eleven singlets, which may indicate three inequivalent Ru centers. The ethyl resonances overlap and form broad multiplets. Single crystals of **3** and **4** are not yet available. Because various isomers are possible, the structures remain unclear.

The fact that **3** and **4** disappear at higher temperatures means that they are likely intermediates in the formation of **1** and probably **2**. However, the direct conversion of **3** or **4** into **1** or **2** has not yet been attempted.

Conclusion

The reaction of [$Cp_2^{(*)}Ru_2(CO)_4$] with equimolar amounts of As_4S_4 results in the formation of novel inorganic cage structures based on AsS ligands and peripheral organometallic groups. With increasing temperature, the content of CO ligands in the products decreases and selectivity increases: in boiling *n*-decane the formation of [$Cp_2^{(*)}Ru_2As_4S_4$] (**1a,b**) and [$Cp_2^{(*)}Ru_2As_4S_2$] (**2a,b**) is observed. From X-ray structure analysis of **1b** one might assume an isomerization of the β-As_4S_4 cage into that of As_4S_4(II), with concomittant insertion of CpRu fragments. However, the fact that **1a,b** are also formed from structurally and stoichiometrically different As–S compounds (e.g., As_4S_3 and As_2S_3) provides evidence for reaction pathways in which fragmentation into small units plays an important role. The recombination of the latter into new inorganic clusters seems to be typical for Ru chemistry; in the corresponding Fe system, fragmentation into relatively small fragments (e.g., $Fe_2As_2S_2$ and $Fe_2As_2S_3$) is the only reaction to be observed.[6, 16]

Experimental Section

The general methods and instruments that were used have been described elsewhere [10]. [$Cp_2^{(*)}Ru_2(CO)_4$] was prepared from $Ru_3(CO)_{12}$ [17] and C_5Me_4RH (R = Me, Et) [10,18]. β-As_4S_4 was prepared by fusing arsenic and sulfur powder in a molar ratio of 1.03:1 under vacuum (3 d, 440 °C) [3]. It was characterized by X-ray powder diffraction. Field desorption mass spectra were obtained from toluene solutions on a Finnigan MAT95 spectrometer.

Reaction of [$Cp_2^*Ru_2(CO)_4$] with As_4S_4 to give 1a and 2a: An orange suspension of [$Cp_2^*Ru_2(CO)_4$] (220 mg, 0.377 mmol) and As_4S_4 (161 mg, 0.377 mmol) in decane (30 mL) was refluxed for 24 h. The mixture turned slightly to brown. After distillation of the solvent, the brown residue was extracted with toluene (2 × 10 mL). The remaining residue was treated with CH_2Cl_2 (40 mL) giving 190 mg (56%) of crude **1a** in the soluble fraction. Crystals were obtained from toluene solutions at −20 °C. [$Cp_2^*Ru_2As_4S_4$] (**1a**): $C_{20}H_{30}As_4Ru_2S_4$ (900.5): calcd C 26.62, H 3.35; found C 26.07, H 4.27. FD-MS: *m/z* 902.0 (^{102}Ru).

The filtrate of the extraction was concentrated and then chromatographed on silica gel (column 20 × 5 cm). With toluene/pentane (1:1) an orange band was eluted containing **2a** in 6% yield. A second, yellow band (starting material) was not well separated and a following red band contained small amounts of **1a**. Crystallization of the first band from toluene/pentane mixtures gave crystalline [$Cp_2^*Ru_2(CO)_4$] along with single crystals of [$Cp_2^*Ru_2As_4S_2$](**2a**)·[$Cp_2^*Ru_2(CO)_4$] which were separated manually. $C_{20}H_{30}As_4Ru_2S_2$ (836.4): FD-MS: *m/z* 837.7 (^{102}Ru).

Reaction of [$Cp_2^xRu_2(CO)_4$] with As_4S_4:

175 °C: An orange suspension of [$Cp_2^xRu_2(CO)_4$] (649 mg, 1.06 mmol) and As_4S_4 (454 mg, 1.06 mmol) in *n*-decane (50 mL) was refluxed for 18 h. After distillation of the solvent the dark orange residue was extracted with toluene (2 × 10 mL). The combined extracts were chromatographed on silica gel (column 15 × 3 cm). With toluene/pentane (1:1) a red band containing **2b** was eluted followed by orange starting material. With toluene a red band containing 220 mg (23% yield) of **1b** was eluted. Recrystallization of **1b** from toluene/pentane gave dark brown prisms. **1b**: $C_{22}H_{34}As_4Ru_2S_4$ (928.0) calcd C 28.46, H 3.69, S 13.81; found C 28.57, H 3.65, S 12.81. FD-MS: *m/z* 928.5 (^{102}Ru). **2b**: $C_{22}H_{34}As_4Ru_2S_2$ (864.4): FD-MS: *m/z* 865.7 (^{102}Ru).

60 °C: The same reaction mixture as in the previous experiment was stirred at 60 °C for 35 d. After evaporation of the solvent, the dark orange residue was extracted with toluene (3 × 10 mL). The combined extracts were chromatographed on silica gel (column 10 × 3 cm). With toluene, orange starting material was recovered, and with toluene/ether (50:1) a red band eluted. Repeated chromatography of the latter on SiO_2 (column 7 × 3 cm, toluene) gave [$Cp_2^xRu_2(CO)_2As_2S_5$] (**3**) in 13% yield. $C_{24}H_{34}As_2O_2Ru_2S_5$ (867.2): calcd C 33.32, H 3.91; found C 33.25, H 3.95. FD-MS: *m/z* 867.2 (^{102}Ru).

110 °C: After 10 d in boiling toluene (stoichiometry and workup analogous to the 175 °C reaction) **1b** was isolated in 14% yield. With toluene/ether (10:1) [$Cp^x{}_3Ru_3(CO)As_3S_5$] (**4**) was eluted in 4% yield. $C_{34}H_{51}As_3ORu_3S_5$ (1164.1): calcd C 35.08, H 4.42; found C 34.92, H 4.40. FD-MS: *m/z* 1165.0 (center).

Table 5. Crystal structure data for complexes **1b** and **2a**·[$Cp_2^*Ru_2(CO)_4$].

	1b	**2a**·[$Cp_2^*Ru_2(CO)_4$]
formula	$C_{22}H_{34}As_4Ru_2S_4$	$C_{20}H_{30}As_4Ru_2S_2 \cdot C_{24}H_{30}O_4Ru_2$
mol. mass	928.0	1421.04
cryst. size [mm]	0.08 × 0.45 × 0.65	0.15 × 0.25 × 0.50
cryst. system	orthorhombic	triclinic
space group	*Pbcn* (no. 60)	$P\bar{1}$ (no. 2)
a [Å]	19.70(1)	8.473(4)
b [Å]	16.473(6)	11.679(5)
c [Å]	17.84(1)	12.714(8)
α [°]	90	81.04(4)
β [°]	90	82.25(4)
γ [°]	90	74.00(3)
V [Å]	5789.3	1189(1)
Z	8	1
ρ_{calcd} [g cm^{-3}]	2.13	1.99
radiation	$Mo_{K\alpha}$	$Mo_{K\alpha}$
μ [mm^{-1}]	5.84	4.14
scan mode	ω	ω
2θ (max) [°]	57.5	52.5
absorption corr. (ψ scans)	$5.0 < 2\theta < 43.0$ (7 refl.)	$5.0 < 2\theta < 40.0$ (7 refl.)
transmission (min/max)	0.29/1.00	0.76/1.00
total reflections	7883	4855
observed refl. [$I > 2.5\sigma(I)$]	2475	3183
parameters refined	180	263
R	0.085	0.058
R_w	0.064	0.048
resid. electron density [e Å^{-3}]	+2.00/−1.42	+0.94/−1.15
F(000)	3600	696

X-ray structure determination of complexes 1b and 2a·$[\mathrm{Cp}^{*}_{2}\mathrm{Ru}_{2}(\mathrm{CO})_{4}]$ [19]: Crystal data were collected on a Syntex R 3 diffractometer at room temperature. Relevant crystal and data collection parameters are summarized in Table 5. The structures were solved by using standard Patterson methods, least-squares refinement, and Fourier techniques. All calculations were performed with the SHELXTL Plus program package [20].

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[19] Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-405558 (**1b**) and 405559 (**2a**·$[\mathrm{Cp}^{*}_{2}\mathrm{Ru}_{2}(\mathrm{CO})_{4}]$).

[20] SHELXTL Plus, Siemens Analytical X-ray Instruments.