Synthesis, Structure and Reactivity of Sulfur-Rich Cyclopentadienyl-Transition Metal Complexes: Sulfur Chemistry from an Organometallic Point of View

By Joachim Wachter*

Metal-sulfur centers play an important role in the activity of metalloproteins in enzymatic catalysis and the activity of metal sulfides as heterogeneous catalysts. The systematic search for M–S model compounds led to the discovery of an interesting and novel structural chemistry, which stems from the numerous coordination possibilities of sulfur ligands. The intention of this review article is to present and outline new approaches to sulfur chemistry from the organometallic point of view. Reactive cyclopentadienyl-transition metal fragments incorporate elemental sulfur to give polynuclear sulfur-rich complexes, which can contain either mono-, di- or polysulfido ligands or several such ligands in combined form. The versatile structural chemistry of the complexes formed and their reactivity towards organic, inorganic and organometallic compounds are discussed, and examples of some simple and rational procedures for their synthesis starting from cyclopentadienylcarbonyl- and cyclopentadienylhydrido-complexes are outlined. Their reactivity is manifested in numerous metal- and ligand-centered reactions. Finally the, albeit far less extensive, complex chemistry of the other chalcogens (O, Se, Te) is also considered for comparison, thus providing a more detailed survey of particular aspects of this area of chemistry.

1. Introduction

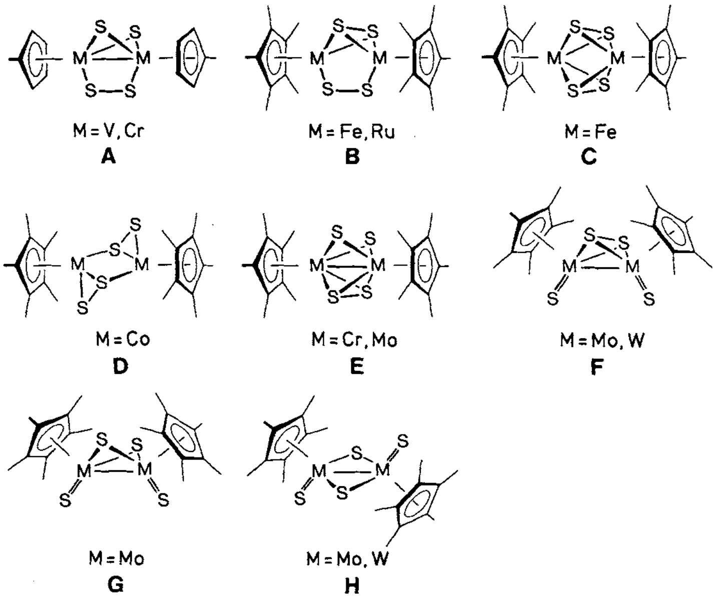
The chemistry of soluble transition metal sulfides is virtually inexhaustible. Whether one is considering the stabilization of unusual bonding systems or molecular model compounds, the immense range of possibilities available to sulfur in metal complex ligands is impressive.

Metal–sulfur complexes are, for example, of special interest with regard to the modes of action and the structures of many enzymes. The as yet unsolved problem of the structure of the active center of nitrogenase—the enzyme system that converts atmospheric nitrogen into ammonia—is often cited as example to demonstrate just how difficult it is to obtain structural information of biological centers indirectly using even the best possible model complexes.[1]

Metal sulfides also play a role in the desulfurization of fossil fuels by hydrogenation (e.g. hydrodesulfurization, HDS).[2] Utilization of the worlds sulfur-containing resources in an economic and environmentally unobjectionable way demands that basic research be carried out on soluble model systems—the HDS process actually occurs on a heterogeneous metall sulfide surface.

It is obvious from the examples already quoted that simple model systems in the form of soluble transition metal sulfides are required in order to extend our existing knowledge of sulfur coordination chemistry. The effort being made in this direction is reflected in the number of reviews of complexes with mono-,[3] di-[4] and polysulfido ligands.[5] Parallel to these investigations a new research area has been opened up with the chemistry of polynuclear sulfur-rich transition metal complexes. The addition of elemental sulfur to reactive cyclopentadienylmetal fragments and subsequent fragmentation of the generally unisolable primary products leads predominantly to binuclear complexes. The advantages offered by this chemistry are the generally uncomplicated synthetic strategies, the good solubility of the products, and the readiness of the products to undergo further reactions. The use of cyclopentadienyl carbonyl complexes often enables the spectroscopic observation and isolation of intermediates that can provide valuable information about the degradation of the S_8 ring.

As already demonstrated in an earlier review of the structures of binuclear sulfur-rich cyclopentadienyl complexes,[6] the sulfur: metal ratio varies from 1:2 to 10:2. The structure



Scheme 1. Examples of possible structure types (A–H) for [$Cp_2^{(*)}M_2S_4$] complexes.

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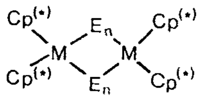
of the relatively simple molecules $[Cp_2^{(*)}M_2S_4]$[*] has alone been formulated in eight different ways to date (Scheme 1). This immediately calls for a clarification and comparison of the background information concerning the formation, structure and reactivity of all these complexes in relation to the nature of the central metal and to the influence of the substituents in the $Cp^{(*)}$ ligand.

The number of analogous Se- and Te-complexes is still relatively small, but nevertheless the existing results allow a comparison to be made between the differing reactivities of the chalcogens and a given CpM fragment. Oxygen is an exception since there already exists an extensive V-complex and Re-complex chemistry.[7] Even so, a discussion of the structural peculiarities of its complexes in comparison to the complexes of its higher homologues would appear stimulating.

2. Syntheses and Structures

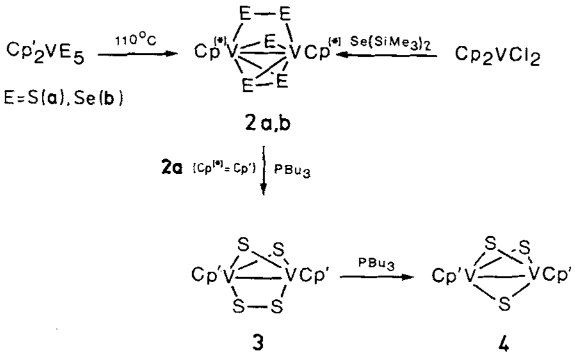
2.1. Cyclopentadienyl Sulfides and Selenides of the Electron-Deficient Transition Metals

Rings with an even number of members in which two $Cp_2^{(*)}M$ fragments are present but do not directly interact with each other, are characteristic of the complexes **1** of the group 4 metals. There are many diverse methods available for the synthesis of such complexes. Ti-complexes **1**, for example, are accessible by desulfurization of $Cp_2^{(*)}TiS_5$ with PR_3 (the number n of bridging chalcogen atoms in the product depends on the nucleophilicity of the phosphane[8]) or by the reaction of Cp'_2TiCl_2 with Li_2Se_2 (n = 2).[9] Reaction of carbonyl derivatives such as $Cp_2^{(*)}Ti(CO)_2$ with H_2S[10] or H_2Se[11] yields the kinetically labile complexes **1** (n = 1). These form symmetrical clusters at higher temperatures, e.g. $[Cp_4Ti_4Se_4]$. A less pungent and less toxic way to complexes of type **1** is via the reaction of Cp'_2Zr, prepared in situ, with elemental S or Se.[12] Two different sorts of chalcogen bridges can be found in $[Cp_4Hf_2(\mu\text{-}O)(\mu\text{-}Se_4)]$,[13] the only known binuclear hafnium compound. It is formed from Cp_2HfSe_5 by exposure to air.



1, M = Ti, Zr
E = S, n = 1-3; E = Se, n = 1,2

The sulfur-rich vanadium complexes $[Cp_2^{(*)}V_2E_n]$ **2**–**4** (E = S, Se; n = 3–5) are structurally completely different from the binuclear complexes **1**. The diamagnetic compounds **2** can be prepared either by thermolysis of Cp'_2VE_5[14, 15] or by dehalogenation of Cp_2VCl_2 with $Se(SiMe_3)_2$[16]. Since these reactions occur with the elimination of a $Cp^{(*)}$ ligand from each metal atom, the products strive to overcome their electron deficiency by utilizing three different chalcogen bridges as well as a metal–metal interaction (d_{V-V} 2.66–2.77 Å). An interesting and recurring phenomenon in complexes of the general composition $[Cp_2^{(*)}M_2S_n]$ ($n \geq 4$) is the stabilization of unusual electron configurations at the metal by M–E d_π–p_π interactions.[*] Such stabilizations may be the driving force for the unusual sulfur abstraction from **2a** ($Cp^{(*)} = Cp'$) by PBu_3 with formation of the 26e complexes **3**[18] and **4**.[17] Due to the very short V–S distances ($\bar{d}_{V-S}$ 2.23 Å) for *all* sulfur atoms, an alternative view of the general system of **3** and **4** with 34 valence electrons was suggested.[18]



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[*] If not otherwise indicated the following abbreviations for the cyclopentadienyl ligands apply: $Cp = C_5H_5$, $Cp' = MeC_5H_4$, $Cp^* = C_5Me_5$, $Cp^{(*)}$ = any other substituted cyclopentadienyl ring. These ligands are η^5-coordinated in all cases.

[*] With a neutral charge distribution the contribution of the chalcogen ligands to the electron count of **2** is $2(\mu\text{-}E) + 2(\mu,\eta^1\text{-}E_2) + 6\ (\mu,\eta^2\text{-}E_2)$ electrons, which together with the 2 × 10 electrons from the two $Cp^{(*)}V$ units adds up to 30e [3, 4]. The alternative view with $\mu\text{-}E^{2\ominus}$, $\mu,\eta^1\text{-}E_2^{2\ominus}$, and $\mu,\eta^2\text{-}E_2^{2-}$ ligands (4+4+8) and two $V^{4\oplus}$ centers leads to a similar result.

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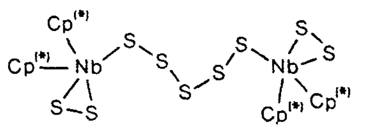
The examples of sulfur-rich CpNb dimers known to date apparently show more similarities to Ti-complexes than to V-complexes. Thus, in principle, $[Cp_4Nb_2S_2]$[19] belongs to the same structure type as **1**, despite its weak Nb–Nb interaction (d_{Nb-Nb} 3.23 Å). A mixture of most likely very similar polysulfido complexes is formed upon reaction of $(tBuC_5H_4)_2NbH_3$ with S_8. The structure of **5**, in which the



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two $(tBuC_5H_4)_2Nb(\eta^2\text{-}S_2)$ units are connected by an S_5-chain, was determined by an X-ray crystallographic analysis.[20] The above-mentioned mixture of polysulfido complexes can, depending on the large number of S–S bonds, be converted in toluene at 100 °C into three trinuclear clusters of slightly less sulfur content, of which **6** and **7** have been fully characterized (Fig. 1). The niobium-sulfur skeleton of **6** shows not less than five different ligand types (Scheme 2).[20] The core of the molecule (Fig. 1 a) is a much flattened Nb_3S tetrahedron, whose base is spanned by a triply bridging S_2 group. Two Nb–Nb bonds are each bridged by an $\eta^1, \eta^2\text{-}S_2$ ligand. In contrast, Nb1–Nb2 is bridged by an $\eta^1, \eta^2\text{-}S_3$ ligand. The coordination sphere of Nb3 is completed by a terminal $\eta^2\text{-}S_2$ ligand.

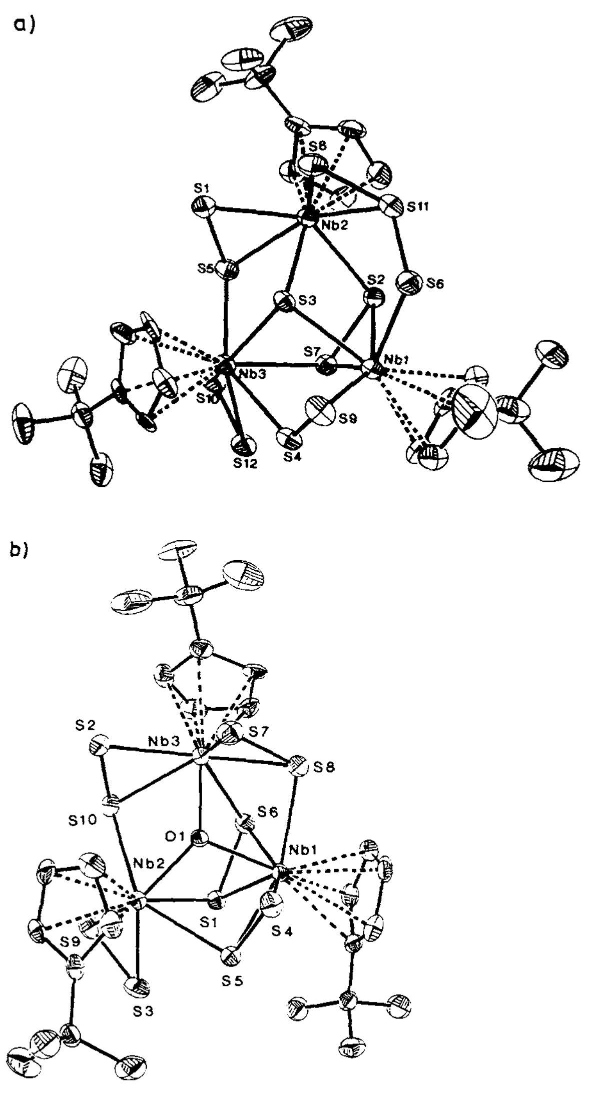
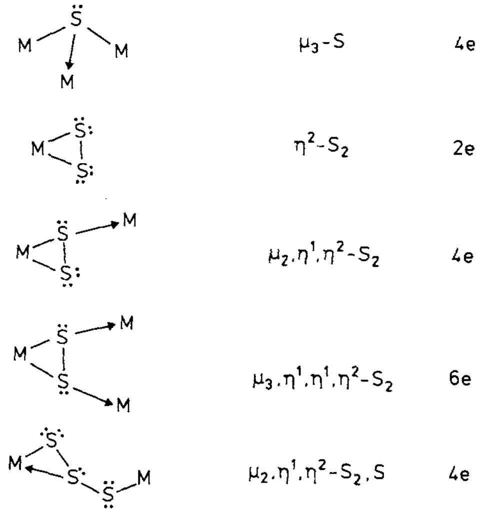


Fig. 1. a) Structure of $[(tBuC_5H_4)_3Nb_3S_{12}]$ **6** in the crystal. The S_2 ligand S4-S9 is bound η^2 to Nb1. b) Structure of $[(tBuC_5H_4)_3Nb_3S_{10}O]$ **7** in the crystal.



Scheme 2. Overview of representative sulfur ligand types found in **6**, their bonding, and the number of electrons which they—assumed as neutral—contribute to the bonding.

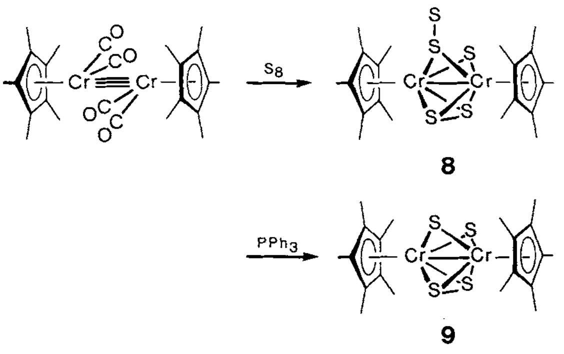
The structure of **7** (Fig. 1 b), which can also be prepared directly from **6** by heating for a longer time in toluene solution, is closely related to that of **6**. At the apex of the central tetrahedron there is an oxygen atom, however, and instead of the S_3 ligand there is now only an $\eta^1,\eta^2\text{-}S_2$ ligand. This has no electronic consequences, but as a first principle of order a uniform orientation of the points of the edge-bridging S_2 ligands towards the top of the tetrahedron can be seen. This means that the compounds **6** and **7** differ in a remarkable way from the sulfur-bridged, but still halogen-containing clusters formed on reaction of $CpMHal_4$ (M = Nb, Ta) with $S(SiMe_3)_2$.[16]

The sulfurization of Cp-carbonyl-Nb derivatives has until now only been investigated sporadically, although this entry to sulfur-rich cyclopentadienyl complexes has proven very successful for the later transition metal elements. Thus, reaction of $[CpNb(CO)_3(thf)]$ with S_8 leads to the CO-free complex of the composition $[Cp_2Nb_2S_5]$. Its structure, however, is still unclear.[21] It therefore remains to be seen whether the complexes $[\{CpNb(CO)_2\}_2(\mu\text{-}S)_n]$ (n = 2,3) are formed as intermediates en route to complexes with less CO- but a higher sulfur-content upon reaction of H_2S or MeSH and $[CpNb(CO)_3(thf)]$.[21]

2.2. Binuclear Cyclopentadienyl Chalcogenides of the Chromium Triad

2.2.1. Complexes of the Type [$Cp_2^{(*)}Cr_2S_n$] (n = 4,5)

Due to the reactivity of their M–M triple bonds the complexes $[Cp^{(*)}M(CO)_2]_2$ are generally the most suitable starting materials for the synthesis of sulfur-rich binuclear complexes of the Cr triad. Thus for example, reaction of $[Cp^*Cr(CO)_2]_2$ and S_8 affords the complex **8**,[22] which in turn reacts with PPh_3 with elimination of sulfur to give **9**.[23] The complexes **8** and **9** are isoelectronic (each possessing 32 valence electrons) and therefore have similar structural frameworks resembling those of triple-decker compounds[22, 24] in which all bridging ligands lie in a plane perpendicular to the Cr–Cr vector and parallel to the Cp* rings. It is worth pointing out that **8** contains an η^1-S,S bridge, in which only one S atom is coordinated to both Cr atoms (Fig. 2). The bent character of this moiety (S5 is orientated towards the η^2-S_2 ligand) suggests a 2e donor (Scheme 3, **J** and **K**) and therefore not the valence tautomer **I**, in which the η^1-S_2 ligand would effectively be a 4e donor. In contrast its SO homologue $[\{Cp(CO)_2Mn\}_2(\mu\text{-}SO)]$ has the structure corresponding to **I**.[25] A participation of the resonance structure **K** explains the relatively long S–S bond (2.101 Å) and the higher nucleophilicity of the terminal sulfur atom.[23, 24] The formation of the η^1-S_2 ligand is surprising, since it does not differ electronically from a μ-S ligand.



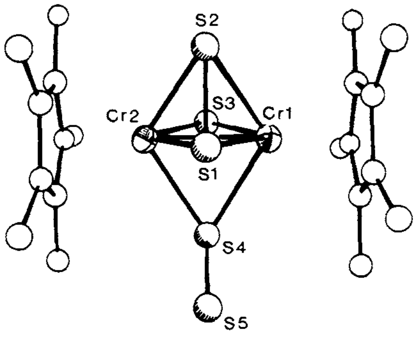
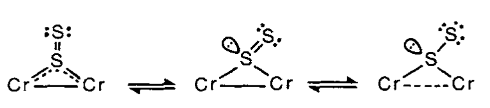
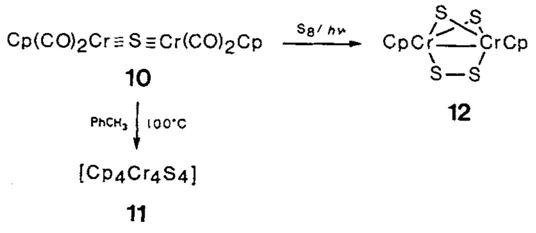


Fig. 2. Structure of **8** in the crystal.

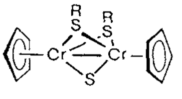


Scheme 3. Possible valence tautomerism of the μ,η^1-S,S ligand of **8**.

The reaction of $[CpCr(CO)_3]_2$ with S_8 is of a completely different character, since a relatively labile Cr–Cr single bond makes the insertion of sulfur possible. Other than in the case of dimers of the iron triad (see, for example, **36** and **41** in Section 2.4) with a Cr dimer maximally S_2 units are inserted into the M–M bond and only two CO ligands are substituted.[26] The main product **10** contains an almost linear CrSCr multiply bonded system.[27] Thermally, this readily undergoes cleavage of CO to give the 60e pseudocubane **11**. Photochemically, however, it can be transformed in the presence of sulfur into **12**.[28] From a structural point of view complex **12** has the same ligand set as the vanadium complex **3**. Formally, **12** (structure type **A** in Scheme 1) is related to **9** (structure type **E**) through a 90° rotation of the S_2 bridge (in contrast to the analogously built Mo sulfides (see Section 2.2.2) **9** and **12** are configurationally stable). Although the two complexes differ in their total electron count by four electrons, their magnetic behavior is very similar.



Also conceivable would be the existence of $[Cp_2Cr_2(\mu_1,\eta^2\text{-}S_2)(\mu\text{-}S)]$, an even more sulfur-deficient compound than **9**. The isoelectronic dimethylthiolato complex **13** is already known. It shows antiferromagnetic behavior and serves as starting material for the synthesis of numerous S-bridged cluster compounds.[29]



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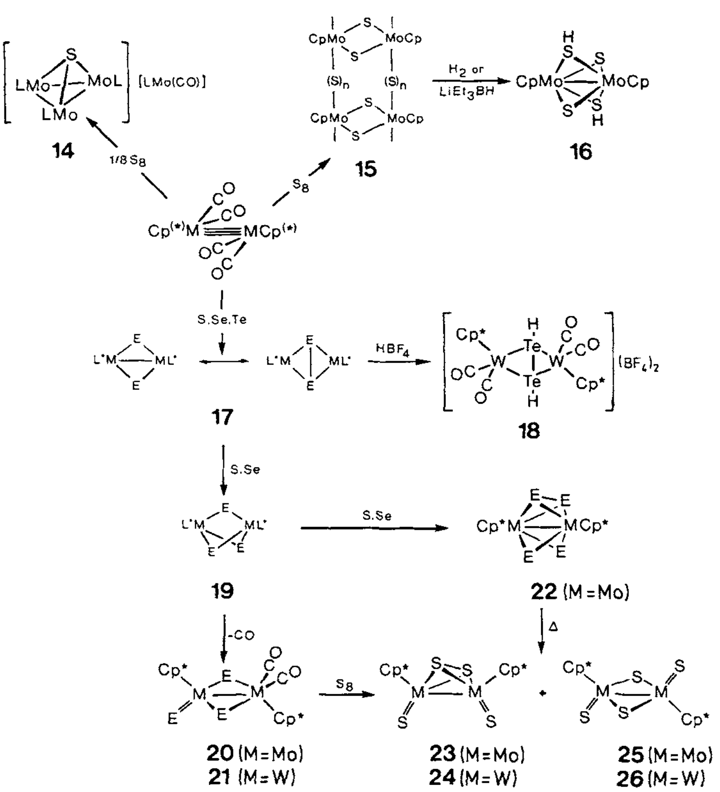
2.2.2. *Cyclopentadienyl Sulfides and Selenides of Mo and W*

Since the M–M triple bond in $[Cp^{(*)}M(CO)_2]_2$ when M = Mo and W is generally more reactive than that when M = Cr,[30] the 'harvest' of sulfur-containing compounds is naturally richer. In contrast to the Cr system, even Se- und Te-containing compounds are occasionally isolated. As far as results up to now indicate, there are parallels between the reactivity of S and Se, while Te is distinctly less reactive. Particularly striking is the control of the course of reaction by the nature of the cyclopentadienyl ligand (Scheme 4), whereby steric effects may largely be decisive.

$[CpMo(CO)_2]_2$ reacts with substoichiometric amounts of sulfur to give **14**, whose cation contains an Mo_3S tetrahedron.[31] In contrast, with sulfur in excess the insoluble compound **15** is formed.[31–33] The formulation of **15** as a polymer would appear justified insofar as it can be converted under mild conditions with H_2[34] or $LiEt_3BH$ into the soluble hydrogensulfido-complex **16**.[35]



Scheme 4. Overview of the reactions of the chalcogens S,Se and Te with $[\mathrm{Cp}^{(*)}\mathrm{M(CO_2)}]_2$ (M = Mo, W; L = Cp(CO)$_2$, L* = Cp*(CO)$_2$). **19**–**22**: **a**, E = S; **b**, E = Se. X-ray structurally characterized complexes shown in bold print.

As demonstrated by the occurrence of the kinetically labile di- and tri-chalcogen products **17** and **19** in the reaction of $[\mathrm{Cp^*M(CO)_2}]_2$ (M = Mo, W) with condensed sulfur or selenium vapor at low temperatures, there must be a stepwise addition of chalcogen fragments to the M ≡ M bonds.[36] In contrast, in order to introduce the much less reactive Te the reaction must be carried out at the temperature of boiling THF. The intermediate **17**, for which there are two conceivable isomeric forms, can in the case of the W–Te compound be captured as a stable complex salt **18** by double protonation. This contains the unusual $\mathrm{Te_2H_2}$ ligand.[36]

The formation of the complexes **20** and **21** from **19** can be interpreted in terms of an intramolecular rearrangement of the E-ligand framework with partial CO elimination and formation of an M–M bond. **21a** is the first structurally characterized complex whose sulfur bridges are not symmetrical owing to the unusual polarization of the molecule.[37] Whereas the CO ligands of the Mo-intermediates **19** (M = Mo) and **20** are relatively easily substituted by sulfur or selenium (45 °C, toluene), the W-complex **21a** reacts only with $\mathrm{S_8}$ under substantially more drastic conditions (115 °C) to give well defined complexes.[37, 38] **23**–**26** are the thermally most stable complexes of the whole synthetic sequence. In agreement with this, **22a** isomerizes in solution to give **23** and **25**.[37] Whereas the transformation **22a** → **23** can be described as an opening of both monosulfur bridges, the reaction **22a** → **25** requires the additional cleavage of the η^2-bridge.[39] Interestingly, the entire process is photochemically reversible, since irradiation of any one isomer gives the two other isomers.[40]

Although even more $[\mathrm{Cp}_2^{(*)}\mathrm{Mo_2S_4}]$ isomers are conceivable (cf. Scheme 1 and Ref. [41]), the reaction products derived from the reaction of $[\mathrm{CpMo(CO)_3H}]$ with methylthiirane[42] or $[\mathrm{Cp^*Mo(CO)_3H}]$ with $\mathrm{S_8}$[33] belong, just like $[\mathrm{Cp'_2Mo_2S_4}]$[33] to structural type **H** (Scheme 1), which is also realized in **25**.

A comparison of the structures of **22a**[37] and **25**[33] reveals a 'clamping' effect of the bridging ligands in **22a**: the formal Mo–Mo bond orders (2 for **22a**, 32 valence electrons (VE) and 3 for **25**, 30 VE) contradict the observed Mo–Mo distances of 2.599 and 2.905 Å, respectively. On the other hand, the Mo–S bridging bonds of **25** are on average ca. 0.06 Å shorter than in **22a**, which could point to a delocalization of the electrons of the bridging sulfur atoms in **25**. Such a delocalization is further supported by the distinctly lower nucleophilicity found for **25**[23] compared to that for **22a**.[23]

An interesting by-product of the reaction of $[\mathrm{Cp^*Mo(CO)_3H}]$ with $\mathrm{S_8}$ is **27**, which contains three different types of $\mathrm{S_2}$ ligands (Fig. 3),[33] including the seemingly rare nonplanar η^1–$\mathrm{S_2}$ bridge[4] (Mo-S1-S1'-Mo').

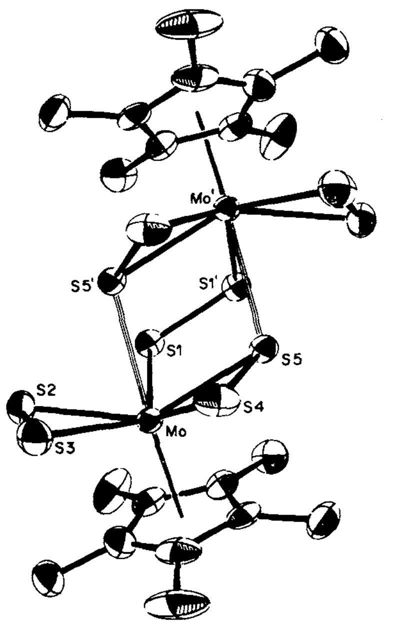
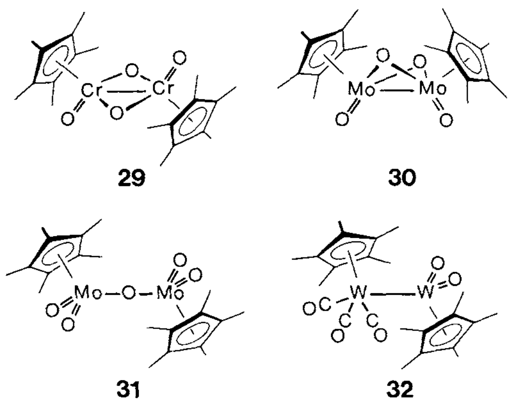


Fig. 3. Structure of $[\mathrm{Cp_2^*Mo_2S_{10}}]$ **27** in the crystal [33].

2.2.3. Cyclopentadienyl Oxo Complexes

Even from the relatively few examples presented here (see Scheme 5) it can be seen that—with the exception of $[\mathrm{Cp_4Cr_4O_4}]$[43] prepared by *E. O. Fischer* et al.—Cp-complexes of the Cr triad containing exclusively O-ligands have the same composition $[\mathrm{Cp}_2^{(*)}\mathrm{M_2E}_n]$ (n = 4,5) as their S-homologues. However, they differ considerably in many structural respects. One reason for this could be that the formal oxidation state of the metal center in the complexes with oxo ligands ($\mathrm{Cr^V}$ in **29**[45], $\mathrm{Mo^{VI}}$ in **31**,[45–47]) is frequently higher than in the complexes of the usual chalcogens. The only compound which can be directly derived from an already known sulfur complex, namely **25**, is $[\mathrm{Cp_2Mo_2(\mu\text{-}O)_2O_2}]$ **28** with the structural type **H** (Scheme 1).[44]



Scheme 5. Examples for the structures of dinuclear $Cp^{(*)}$ oxo complexes of the chromium triad.

The absence of complexes with $O_2^{2\ominus}$ ligands is remarkable. Thus, e.g., the transfer of the peroxo ligand of $(t\mathrm{BuNC})_2\mathrm{Ni}(O_2)$ is only possible with the rupture of the O–O bond by the Mo≡Mo triple bond of $[Cp^*Mo(CO)_2]_2$.[48] The resulting complex **30** shows a folded Mo_2O_2 core like that of type **G** (Scheme 1). No structural equivalent in the $[Cp_2^{(*)}Mo_2S_4]$ system exists for the Cp^*MoO_2 moieties present in **31** and the nearly linear $O^{2\ominus}$ ligand that is linking them.[47]

There have been contradictory reports on the reaction of $[Cp^*W(CO)_2]_2$ with O_2: At first two products of the composition $[Cp_2^*W_2(CO)_2O_2]$ and $[Cp_2^*W_2O_4]$ were reported,[49] but then, in another experiment, the substitution of only one CO group could be established.[50] The X-ray structural analysis of **32** shows that, owing to the mixed oxidation states of its W atoms, this complex has a structure to some extent related to that of $[Cp_2^*W_2(CO)_2S_3]$ **21a**.[37]

Complexes which contain both oxo and thio ligands are accessible by reaction of the $[Cp_2^*Mo_2S_4]$ isomers **22a**, **23** and **25** with atmospheric oxygen.[33, 51, 52] The progress of the reaction can be monitored quite well by ^{95}Mo-NMR spectroscopy, since the molybdenum centers suffer a shielding effect of $\Delta\delta = 400-600$ by introduction of oxygen.[53] The final products **33** are, according to X-ray structural analyses, clearly of the structural types **G** and **H** (Scheme 1). The oxo ligands are always terminal, i.e. there are always two $S^{2\ominus}$ bridges present. Prerequisite for such a reaction with oxygen at the metal center (examples for an oxidation of the sulfur ligands have been well documented[54]) is obviously the presence of terminal sulfido or selenido ligands. Consistent with the course of the reaction of **22a** with O_2 is that the dioxo complex *syn*-$[Cp_2^*Mo_2(\mu\text{-}Se)_2O_2]$ can be structurally characterized (type **G**), whereas this has not been possible for complexes with terminal Mo=Se moieties.[36, 38]

$$\underset{\mathbf{22a}}{[Cp_2^*Mo_2S_4]} \xrightarrow{O_2} \underset{\mathbf{33}, n=1,2}{[Cp_2^*Mo_2S_{4-n}O_n]} + \underset{\mathbf{34}}{[Cp_2^*Mo_2S_4]\cdot SO_3}$$

The sulfur released in the reaction of **22a**, **23** and **25** with O_2 can be isolated in the form of an SO_3-adduct to the starting compound. It is assumed, however, that in such a reaction the complex with the most nucleophilic sulfur bridges, **22a**, is employed. Consistent with the comparatively large S–S distance (2.168(2) Å), **34** also chemically resembles an SO_3-adduct of the $S^{2\ominus}$ bridge rather than a complex with an η^1-thiosulfato bridge.[52a, 55] Further information about the mechanism of the reaction can be found in Section 3.4.

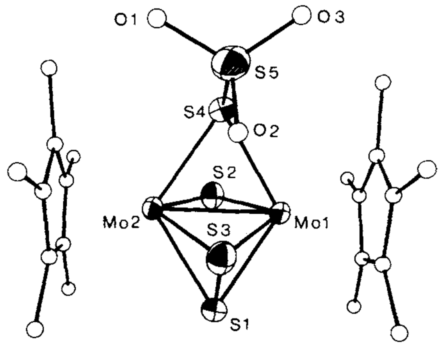


Fig. 4. Structure of **34** in the crystal.

2.3. Cyclopentadienyl Chalcogenides of Mn and Re

Generally applicable methods for the preparation of chalcogen-rich complexes of Mn and Re have not yet been developed. Thus, the reaction of S, Se and Te with $[Cp(CO)_2ML]$ (M = Mn, Re; L = thf, Et_2O) leads only to mono- and dichalcogen-bridged products of the $CpM(CO)_2$ fragment.[56] With regard to the subject of this review these complexes are somewhat of a 'dead end', since they do not react any further with chalcogens. The only structurally characterized complex with a higher sulfur content is $[\{CpRe(CO)\}_2S_5]$, **35**. This contains a puckered seven-membered ring (Fig. 5), in which an S_2 bridge and an S_3 bridge connect two CpRe(CO) moieties.[57] Thus, each Re center has only 16 valence electrons.

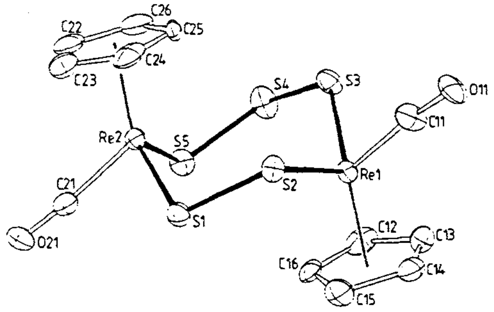
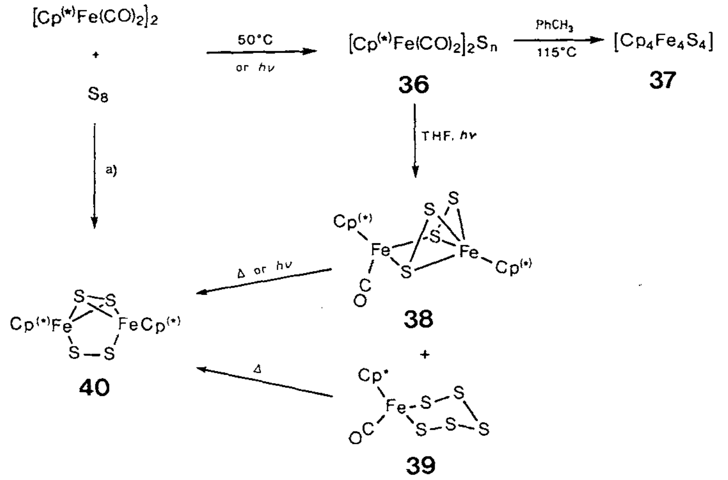


Fig. 5. Structure of **35** in the crystal [57].

Two CO-free dinuclear complexes of the composition $[Cp_2^*Mn_2S_4]$ have been prepared from the reactions of Cp_2^*Mn and $Cp_2^*Mn_2(\mu\text{-}CO)_3$ (*Mn≡Mn*), respectively, with S_8. The elucidation of the structures of these extremely air-sensitive compounds still proves to be quite a challenge.[6] $[Cp_2^*Re_2S_4]$ is reported to be obtained upon reaction of Cp^*ReOCl_2 with $(Me_3Si)_2S$, but this too requires better structural characterization.[7c] The oxygen homologue [$Cp^*_2Re_2O_4$] (structural type **H**, Scheme 1) is a typical example of how the chemistry exhibited by O- and S-complexes differs. It can be obtained by careful deoxygenation of Cp^*ReO_3 and represents a preparatively important and very reactive intermediate.[7c, 58]

2.4. Cyclopentadienyl Sulfides of Fe and Ru

Sulfur-rich cyclopentadienyliron complexes have so far only been prepared from [$Cp^{(*)}Fe(CO)_2]_2$ and elemental sulfur. Scheme 6 covers the differing types of influence exhibited by the substituents on the $Cp^{(*)}$ ring in the thermal reaction: when $Cp^{(*)}$ = Cp the 60e heterocubane **37**[32, 59] is obtained, whereas when $Cp^{(*)}$ = Cp* one obtains the complex **40**(Cp*)[60]. **40**(Cp) can, in contrast, only be prepared photochemically.[61] Both complexes **40** exhibit an interesting structural feature in that two η^1-S_2 and η^2-S_2 bridges are found perpendicular to each another.[60, 61] These diamagnetic molecules (34 valence electrons from 2$Cp^{(*)}$ + η^1-S_2 and η^2-S_2 bridges + 2 Fe = 10 + 2 + 6 + 16) have relatively large Fe–Fe distances (ca. 3.50 Å) and shortened Fe–S distances. The latter fact in particular proves that there is increased π-donation from the η^1-S_2 ligand coplanar to the Fe–Fe vector. The mixing of the sulfur p_x-orbitals perpendicular to the Fe_2S_2 plane with a set of metal d-orbitals of suitable symmetry may explain this effect.[62]

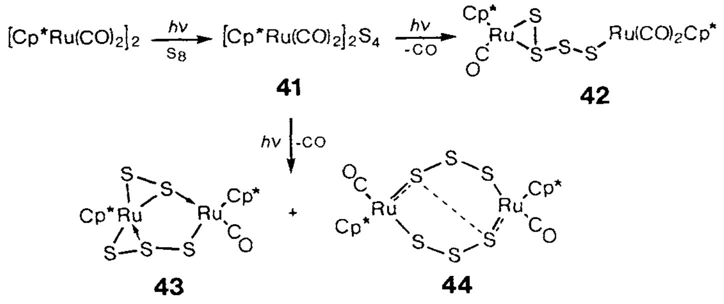


Scheme 6. Overview of the reactions in the system [$Cp^{(*)}Fe(CO)_2]_2$/sulfur. a) Toluene, 115 °C, only starting from [$Cp^*Fe(CO)_2]_2$.

The products **36** derived from insertion of sulfur into the Fe–Fe bond are of intermediate character, of which the derivatives with $Cp^{(*)}$ = Cp can even be isolated. **36**(Cp, n = 3) can be converted into **37** in boiling toluene,[63] **36**(Cp, n = 5) reacts photochemically in THF solution to give **38**(Cp), which in solution exists in three isomeric forms, of which that given in Scheme 6 has been characterized by an X-ray structure analysis.[61a]

Recently, the permethylated intermediates **38**(Cp*) and **39** formed during the photolytic preparation of **40**(Cp*) could also be isolated.[64] In contrast to **40**, **39** is paramagnetic (ESR signal at g = 2.056(3)).

Since [$Cp^*Ru(CO)_2]_2$ dissociates easily under photochemical conditions to give reactive 17e fragments,[65] it seems likely that the mechanism for the uptake of S_8 is radical in nature.[66] The primarily formed compound is the tetrasulfido-bridged complex **41** (Scheme 7). This is either stabilized intramolecularly in the form of **42** with elimination of CO or reacts further to give the sulfur-rich compounds **43** and **44**.[67] In the course of the latter process an S_4 bridge is broken down and the sulfur fragments that are released are apparently so reactive that they recombine to form a second bridging ligand. In this sense the formation of **43** and **44** is favored by the addition of S_8. Under thermal conditions (toluene 115 °C) only **41** and **43** are formed. The structure of **43** can be described as a Ru_2S_3-ring with two sulfur atoms bridging two adjacent Ru–S bonds (Fig. 6), i.e. the sulfur bridges are effectively pure σ-donors. The assumption of a folded eight-membered ring in **44**, in which two S_3-ligands bridge the Cp*(CO)Ru centers, is based on an analogy to the structurally characterized [{Cp'RuPPh$_3$}$_2$S$_6$], which can be prepared from [$Cp'_2Ru_2(PPh_3)_4S_2]^{2\oplus}$ and $S_6^{2\ominus}$.[68] Compared to **43**, there are rather different bonding modes, e.g. a bicyclic Ru_2S_6 core as a consequence of relatively important transannular S–S interactions (d_{S-S} 2.77 Å). Concomittantly, the different Ru–S distances (Δd = 0.11 Å) prove that there is an additional π-donor stabilization of the Ru centers by one S-atom in each case.



Scheme 7. Overview of the reactions in the system [$Cp^*Ru(CO)_2]_2$/sulfur.

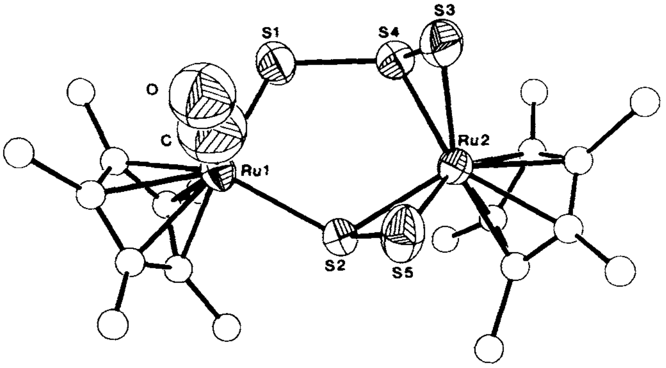


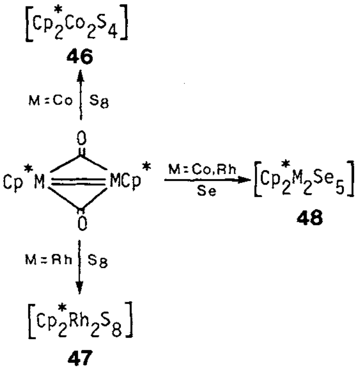
Fig. 6. Structure of **43** in the crystal.

With **36**(Cp, n = 4) and **5** as examples it could be shown that complexes with polysulfido ligands tend to undergo thermal decomposition with the formation of clusters. In contrast to this the metal-sulfur rings in **43** and **44** are so stable that up to now no way has been found to convert them, e.g., into the Ru-analogue of **40**. In this connection it is hard to explain why just a slight modification of the substituents of the Cp ring has such a large effect on the reaction: $[(EtC_5Me_4)_2Ru_2(CO)_4]$ reacts with S_8 in boiling toluene to give $[(EtC_5Me_4)_2Ru_2S_4]$ **45** (structure type **B**) and other still not fully characterized CO-free products.[69]

It is known from the higher sulfur homologues, that Se can be inserted into the Fe–Fe bond of $[CpFe(CO)_2]_2$. The number of bridging members in the products $[\{CpFe(CO)_2\}_2(\mu\text{-}Se)_n]$ appears, however, to be limited to n = 1 and 2, respectively.[70] An excess of Se leads to the 60e heterocubane $[Cp_4Fe_4Se_4]$.[71]

2.5. Cyclopentadienyl Chalcogenides of Co and Rh

The substrates from the Co triad that were chosen for reactions with chalcogens were the M = M double bonded dimers $[Cp^*M(CO)]_2$ (M = Co, Rh). These react with sulfur and selenium but not Te under mild conditions, finally giving CO-free products which have different structures (**46**–**48**), depending on the chalcogen and the metal. **46** has the structure type **D** (Scheme 1), in which the two η^1,η^2-S_2 bridges each act as 4e donors. (Fig. 7a).[60] In contrast, the molecular structure of **47** contains two RhS_4 chelates, which are coupled with formation of a slightly puckered Rh_2S_3 five-membered ring (Fig. 7b).[72] This asymmetric method of coordination allows the donation of four electrons per ligand and is thus quite interesting, since up to now all bridging S_4 ligands have been found to act as 6e donors coordinated via their terminal atoms.[5] In contrast, two non-bridging S_4 chelating ligands are present in **51** (see Scheme 8), which is the precursor of **47**. The elimination of sulfur from **47** to give a complex analogous to **46** with a $Rh_2S_4{}^{2\oplus}$ core has not yet been successfully carried out—although a core of this type is found in $[(triphos)_2Rh_2S_4](BPh_4)_2$ **54**.[73]



The 36e complexes **48** (M = Rh, Co) may be regarded as triple-decker complexes of a special kind.[74] The middle deck is a planar pseudo-five-membered ring which is σ-bound through three coordination sites and consists of a $Se^{2\ominus}$ ligand and a $Se_4^{2\ominus}$ ligand (Fig. 7c). The relatively short intramolecular Se···Se distances of about 3.10 Å could be responsible for the stabilization of this bonding system. Weaker intermolecular Van-der-Waals interactions ($d_{Se\cdots Se}$ 3.50 Å) seem to be responsible for the anisotropic orienta-

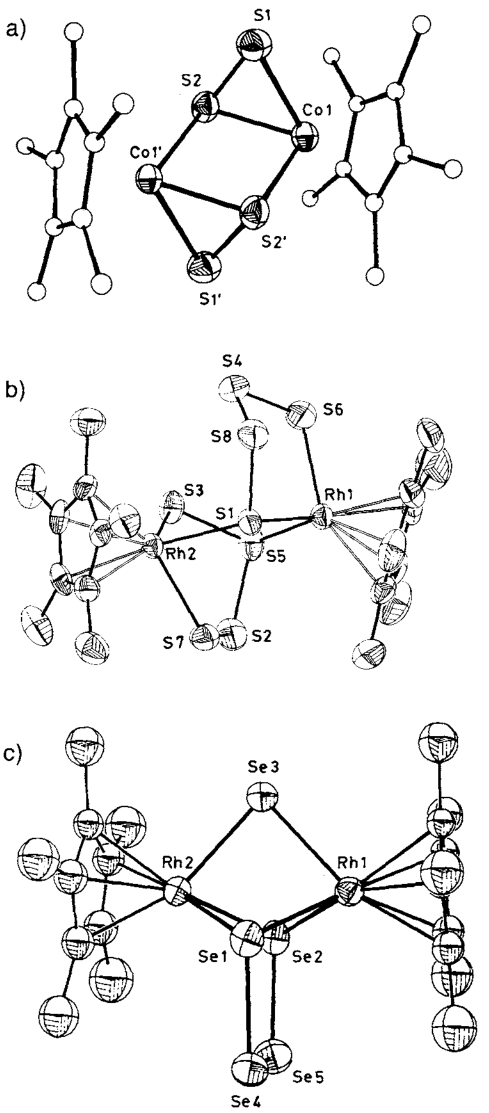


Fig. 7. Structures of a) **46**, b) **47** and c) **48** (M = Rh) in the crystal.

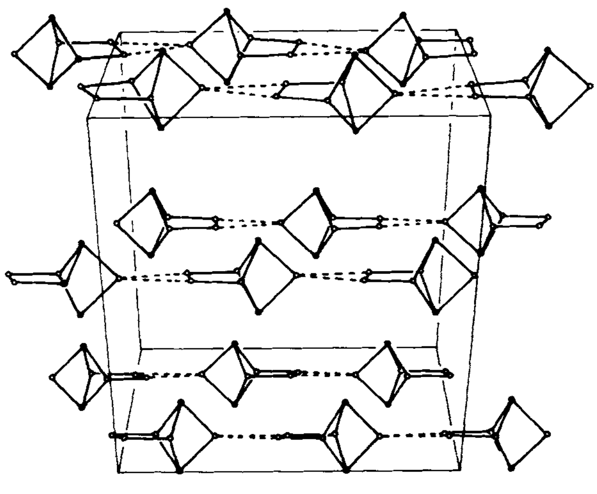
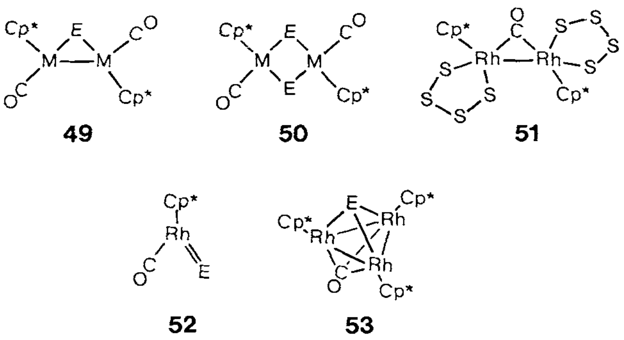


Fig. 8. Unit cell of **48** (M = Rh) (○ = Se atoms, ● = Rh atoms; the Cp* ligands have been omitted for clarity).

tion of the molecules in the crystal lattice. This is unusual for cyclopentadienyl complexes. All Se atoms lie in one plane, which, due to the parallel Cp* rings, gives it a compact layer structure (Fig. 8).

Investigations of the mechanism whereby the complexes **46**–**48** are formed must concentrate above all on evidence for and characterization of the mono- and dichalcogenide adducts at the M = M bond, **49** and **50** (Scheme 8), since the incorporation and fragmentation of the chalcogen units occurs so quickly that they can hardly be followed, even by low-temperature IR spectroscopy.[74b] The stability of these complexes can certainly be traced to the influence of the central metal (some of the cobalt complexes are so labile that they can only be characterized by IR spectroscopy), but the reactivity of the chalcogen employed is also an important factor. The order of reactivity is $S_8 \approx Se_8 > Se_x > Te$. Due to oxidative addition of sulfur or selenium respectively (tellurium is not sufficiently reactive) at the metal centers of **49** and **50**, ME_4 chelating rings are ultimately formed. Only in the case of the Co/S system (**46**) does the degradation of the S_8 ring ultimately give an MS_2 unit. A further intermediate **51**[74b] with a symmetrically bridging CO ligand has been isolated in the Rh/S system. Solutions of **51** eliminate CO at room temperature with the formation of **47**.



Scheme 8. Intermediates of the reactions of $[Cp^*M(CO)]_2$ (M = Co, Rh) with the chalcogens E (S, Se, Te).

Although it has not yet been directly proved, mononuclear complexes with metal-sulfur double bonds play a key role in the formation of sulfur-bridged binuclear complexes—this is at least true in the case of the $Cp^{(*)}(CO)_2M/S_8$ (M = Mn, Re) systems.[56] The complexes **52**, with noble gas configurations, also come into this category—indirect evidence for their existence has been obtained by studying the manner in which the complex **49** (M = Rh; E = S, Se) disproportionates to give the structurally characterized 48e clusters **53**.[64]

3. Reactions

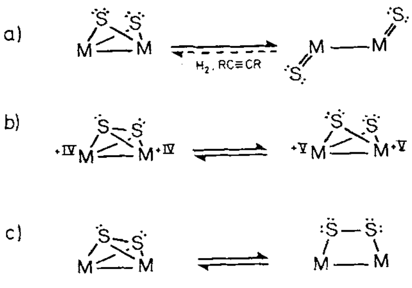
3.1. Tranformations of Mono- and Disulfido Ligands

Due to their clear structures the complexes of the type $[Cp_2^{(*)}M_2S_4]$ are especially suitable for the study of ligand transformations. A special case, limited as yet to Mo and W complexes, is the opening of a pair of monosulfido bridges to two terminal M = S units (Scheme 9). The reverse reaction is not only photochemically possible, it is also induced by H_2 or unsaturated organic molecules, giving complexes such as **16**[33].

During the course of the isomerization **22a** → **25**[37] (Scheme 4) a reductive opening of the η^2-S_2 bridge with consequent flattening of the folded Mo_2S_2 four-membered ring was also observed. According to recent experimental findings this reaction could even proceed via a dissociative mechanism.[52b] The bridge opening occurs formally with a change in the metal oxidation state [b) in Scheme 9] represented by Equation (a):

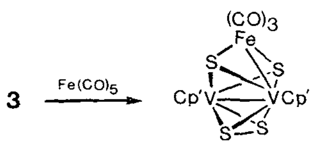
$$2\,Mo^{IV} + S_2^{2\ominus} \rightarrow 2\,Mo(V) + 2S^{2\ominus} \qquad (a)$$

The reverse reaction, whose inorganic equivalent is the redox-condensation reaction of oxothiomolybdates and -tungstates $[MO_nS_{4-n}]^{2\ominus}$ (M = Mo, W; n = 0–2),[75] can be carried out photochemically.



Scheme 9. Transformations of sulfur ligands in $[Cp_2^{(*)}M_2S_4]$ complexes. a) and b) M = Mo, W. c) M = V, Fe.

An elegant possibility of removing any electron deficiency arising at the metal centers, is the rearrangement of a μ,η^1-S_2 ligand to a μ,η^2-S_2 ligand [(c) in Scheme 9 from right to left]. This 90° rotation, which theoretically ought to be symmetry forbidden,[39] effectively gives the complex four more valence electrons. This explains, for example, why the 26e complex $[Cp'_2V_2S_4]$ **3** undergoes such a transformation to give the 48e trinuclear cluster **55** upon addition of an $Fe(CO)_3$ fragment at the monosulfido bridges.[76] In contrast to such chemically induced isomerizations[77] the electron-transfer induced η^1-$S_2 \rightarrow \eta^2$-S_2 isomerization of $[Cp^*_2Fe_2S_4]$ **40**(Cp*, structure type **B**) on oxidation is reversible — oxidation can be achieved with Br_2, I_2, $[Cp_2Fe]PF_6$ or even electrochemically, giving the dication **56** with an inert gas configuration. As in **40**(Cp*), the Fe–Fe distance in **56**, although



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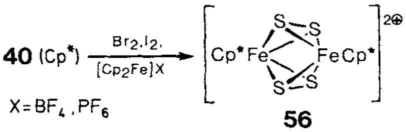

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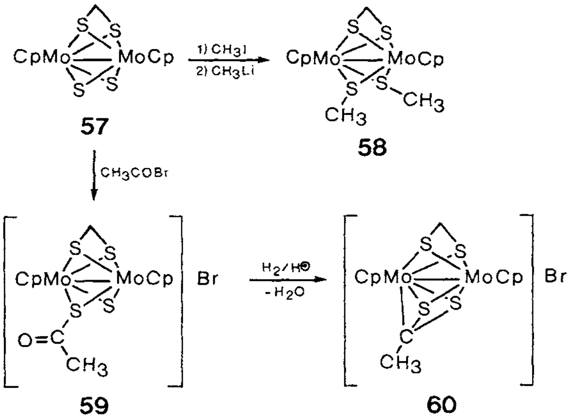
shortened by ca. 0.7 Å by the clamping effect of the two η^2-S_2 bridges, is non-bonding in nature.[78] Careful electrochemical investigations revealed the existence of an intermediate monocation, which quickly disproportionates to give **40**(Cp*) and **56**. Also remarkable is the stabilization of the S_2-bridges by the $Cp^{(*)}$-ligands, which, in principle, counteracts their possible elimination.[62]

3.2. Formation of S–C Bonds

3.2.1. The Alkylation of Sulfur Bridges

All sulfur ligands of the $Cp_2^{(*)}M_2S_4$ complexes presented in this paper have lone electron pairs and thus possess nucleophilic properties. Reaction with CH_3I leads predominantly to alkylation of the monosulfido bridges, whose nucleophilicity is only exceeded by the μ,η^1-S,S ligand in $[Cp^*_2Cr_2S_5]$ **8**.[23] Sulfur ligands whose lone pairs are withdrawn in order to stabilize the unsaturated metal centers via π-donation (e.g. in **2**, **3**, **40**, **45**), are, in contrast, inert to alkylation by CH_3I. The monocationic complexes formed by such alkylation reactions are then susceptible to attack by nucleophiles, e.g. CH_3Li.[79] By such a reaction sequence, for example, the *cis*-dithiolato complex **58** is accessible from **57** (Scheme 10).[80]

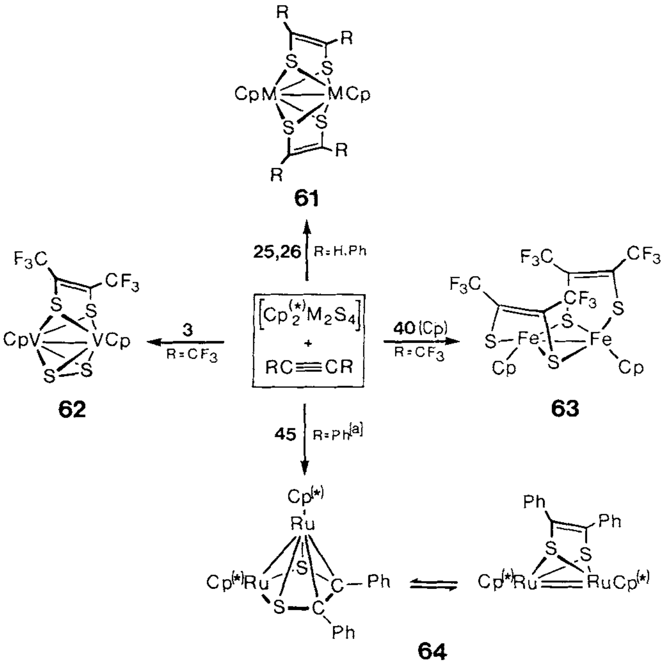


Scheme 10. Alkylation and acylation reactions at sulfur bridges using **57** as example.

In the complex **57**, which is accessible by reaction of the bis(hydrogensulfido) complex **16** with $CH_2Br_2/NaOCH_3$, two sulfur bridges are connected by a methylene bridge.[80] Owing to the two remaining cisoid $S^{2\ominus}$ bridges, **57** is without doubt a good model system for the molybdenum sulfide surfaces of commercial hydrotreating catalysts. Examples of alkylation reactions of **57** include, inter alia, the reductive cleavage of the C–Hal bonds of haloesters, acyl halides and vinyl bromides.[81] Of the complexes formed in this way the acetyl complex **59** is especially interesting, since it is able to activate H_2 with HHal elimination and then eliminate water in a complicated reaction sequence after addition of further acid. The complex salt **60** finally formed by this reaction contains a μ,η^2,η^3-dithioacetato ligand. Completely analogous to this C=O bond cleavage is the evolution of NH_3 from CH_3CN, whereby **60** is again formed.[82] Such reactions with expansion of the metal coordination sphere are very rare for the $[Cp_2^{(*)}M_2S_4]$-system. However, they show that, under certain circumstances, the central metal can act as a Lewis base.

3.2.2. Alkenedithiolato Complexes

It is impossible to arrange the reactions of complexes of the type $[Cp^*_2M_2S_4]$ with alkynes in a systematic scheme. This is again a consequence of the various reactivities of the sulfur ligands (Scheme 11).



Scheme 11. Overview of the formation of complexes with alkenedithiolato bridges from $[Cp_2^{(*)}M_2S_4]$ complexes ($Cp^{(*)}$ in **64** = η^5-C_5Me_4Et). [a] Reaction only in the presence of PBu_3.

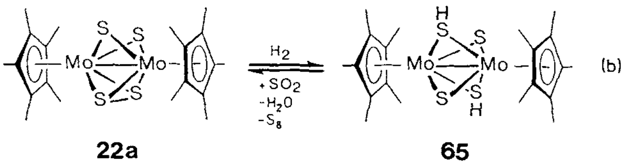
Only the Mo and W complexes **25** and **26**[33, 83] react with unactivated alkynes. The bis(alkenedithiolato) complexes **61** thereby obtained can be reversibly hydrogenated under mild conditions to give bis(alkanedithiolato) complexes. The organic component of the dithiolato ligands is able to undergo exchange reactions with unsaturated hydrocarbons[41, 83].

Complexes with π-donor sulfur ligands react only with electrophilic alkynes. Thus, $[Cp'_2V_2S_5]$, **2a**(Cp') reacts with hexafluorobutyne to give the mononuclear bischelate complex $[Cp'V\{SC(CF_3)=C(CF_3)S\}_2]$,[15] whereas $[Cp'_2V_2S_4]$ **3**, with 90° rotation of the η^1-S_2 ligand, affords **62** with a symmetrical alkenedithiolato bridge.[18] $[Cp_2Fe_2S_4]$ **40**(Cp) reacts with $CF_3C\equiv CCF_3$ with cleavage of both S_2 bridges to give the bisadduct **63**, in which the two μ,η^1,η^2-alkenedithiolato ligands are 4e donors. Of the two possible isomers only *cis*-**63** has been structurally characterized.[61b] The Ru-complex **45**, which is isostructural with **40**, (Section 2.4) reacts with $PhC\equiv CPh$ only in the presence of the sulfur abstracting reagent PBu_3 to give the pentagonal-pyramidal *nido*-cluster **64**. ^1H-NMR spectroscopic findings in solution indicate that the equilibrium between the unusual μ,η^2,η^4-coordination and a symmetrically bridging η^2-coordination shown in Scheme 11 can be assumed for the cluster **64**.[69]

3.3. Formation of S–H Bonds

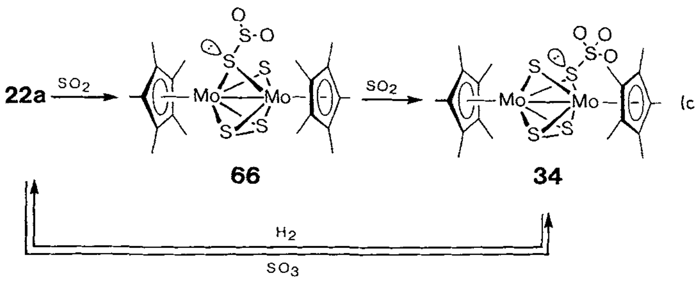
As long ago as 1949 it was shown that chemisorption of H_2 on MoS_2 occurs with the formation of SH ligands.[84] One such activation of H_2 on heterogeneous metal sulfide surfaces has been discussed as a possible step in the mechanism of the HDS catalysis.[85] In this context the complex $[Cp_2^{(*)}Mo_2S_2(SH)_2]$ (**16**; for synthesis see Scheme 4) is of special importance owing to the concomitant presence of sulfido- and mercapto-bridging ligands. For example **16** catalyzes the H/D exchange in a H_2D_2 mixture,[34] it hydrogenates N=N and C=N bonds under mild conditions[86] and adds thiols with elimination of H_2 to give thiolato complexes, and it reacts with C_2H_4 and C_2H_2, forming alkane- and alkenedithiolato complexes (e.g. **61**).[34]

An interesting reaction is the reduction of SO_2 with **65** to give H_2O and S_8 [Eq. (b)] which may proceed with formation of labile S–S bonds (see Section 3.4). The complex **22a** thus formed reacts with H_2 with cleavage of the disulfido bridge to give **65** again. The overall process can thus be formulated as a metal-catalyzed SO_2 reduction.[87] Attempts to hydrogenate the S_2 ligands in other $[Cp_2^{(*)}M_2S_4]$ complexes reveal that Mo is by a long way the most favorable center for such reactions. Thus, reactions of the Cr-complex **9**, which is isolobal with **22a**, and its more sulfur-rich precursor **8** with H_2 only proceed under high pressure and then with the formation of $[Cp_4^*Cr_4S_4]$. (Although the mechanism of this reaction is still not clear, it could be confirmed that the presence of H_2 is essential.)[23] In contrast, $[Cp_2^*Fe_2S_4]$ **40**(Cp*) is inert to H_2 up to 250 bar.[60]



3.4. Formation of S–S Bonds

As already indicated in Section 2.2.3 one of the products (**34**) formed upon reaction of **22a** with atmospheric oxygen contains a coordinated SO_3 ligand on the monosulfido bridge. The same product could be synthesized in much better yield by the direct reaction of SO_3·pyridine with **22a** [Eq. (c)].[88] This reaction can also be used to synthesize new unusual ligands such as μ,η^1-S_3O_3 in **8**·SO_3[24] and μ,η^1-$SeSO_3$ in **49**·SO_3 (M=Rh, E=Se).[89]

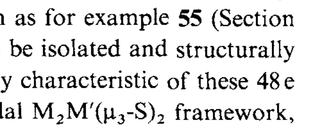


34 can also be prepared in a two-step reaction from **22a** and SO_2 [Eq. (c)]. Remarkably the initially formed SO_2-adduct **66** is oxidized to **34** by SO_2 and not by O_2—this has been proved using ^{18}O-labeling experiments.[90]. During the oxidation elemental sulfur is formed. Results so far would suggest that the oxidation proceeds with inversion at the S-atom, thus indicating the existence of further as yet unidentified intermediates. For the air "oxidation" of **22a** and similar complexes (above all **8**) the presence of sulfur, which is easily activated, is essential.[24] The oxidation of SO_2 to SO_3 by excess SO_2 can be assumed not only to occur on the complex but also in solution by a disproportionation reaction. In solution the SO_3 being a very strong electrophile is an excellent coordination reagent not only for sulfur but also for other chalcogen ligands as well.[24, 88]

Since **34** can be reduced to **22a** with H_2 [Eq. (c)] and since an excess of H_2 causes the formation of **65**, it has been suggested that the processes in Equations (b) and (c) can be summarized in a cycle,[87, 90] that is as an organometallic variant of the Claus process (oxidation of H_2S to S with atmospheric oxygen).

3.5. Synthesis of Tri- and Tetranuclear Clusters

A further outstanding property of a large number of the $[Cp_2^{(*)}M_2S_4]$ complexes is their ability to coordinate reactive or unsaturated metal fragments using the lone pairs of the sulfur ligands. Thus, the sulfur ligands enlarge their connectivity from μ_2 to μ_3 and exceptionally to μ_4. Whereas simple adducts can only as a rule be characterized with difficulty, the 48e trinuclear clusters such as for example **55** (Section 3.1) or **68** are stable enough to be isolated and structurally characterized.[76, 91] Particularly characteristic of these 48e clusters is a trigonal-bipyramidal $M_2M'(\mu_3\text{-}S)_2$ framework, the M–M edge of which is spanned by a μ,η^2-S_2 ligand. This arrangement is of special interest as a building block for the construction of multimetallic chains. It is also capable of oxidatively adding a further metal fragment, striving for a cubane type structure with a $M_2M'_2S_4$ core.[91, 92]



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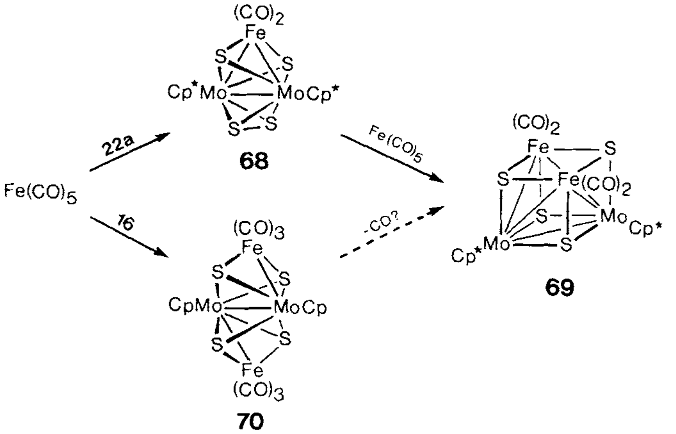
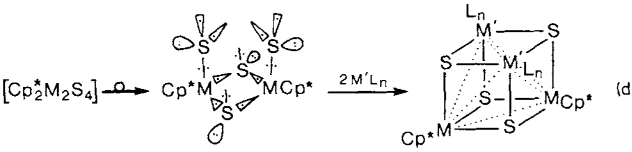
A simple and efficient concept for the synthesis of homo- and heterometallic clusters containing an $M_2M'_2S_4$ core is that developed on the basis of $[Cp_2^*Cr_2S_5]$ **8** (which loses its labile S atom on reaction) and $[Cp_2^*Mo_2S_4]$ presented in Equation (d). Starting from any structural framework (**E**, **G** or **H**) the Cr and Mo dimers can, after transformation of all mono- and disulfido-ligands into four-electron donors,[93] function as potential 38e substrate (2Cp*M + 4μ_3-S =



$2 \times 11 + 4 \times 4$). These give 60e and 62e clusters with formation of M–S and M–M bonds on addition of two 11e or 12e $M'L_n$ fragments respectively.



(d)

Typical examples of directed syntheses of homo- and bimetallic clusters are listed in Table 1. $Cp^{(*)}M$ (M = Cr, Mo),[94] Fe(NO)[95] and Co(CO)[96] can serve as 11e fragments, i.e. also complex-fragments with easily substituted ligands, so that ligand substitutions in the clusters are possible without destroying the cluster skeleton. Thus, e.g., the CO ligands in $[Cp^*_2Cr_2Co_2(CO)_2S_4]$ can be successively substituted by $P(OMe)_3$ without fragmentation of the cluster framework.[97]

All the 60e $M_2M'_2S_4$ clusters possess a distorted cubic ('pseudocubane') structure with incorporated M_4 and S_4 tetrahedra—they have six M–M bonds for electronic reasons.[29, 97, 98] The attainment of the same cubic structure is also the motive behind the formation of the 56e, 58e, and 60e clusters, even if the presence of the vanadium atoms provokes magnetic anomalies. All Vanadium clusters are accessible from the 36e building block **3** (Table 1).

Addition of the 12e fragments $Mo(CO)_3$, $Fe(CO)_2$ or CuCl to **22a** leads ultimately to stable 62e heterocubanes (Table 1) containing only five M–M bonds.[91, 100] Clusters with both oxo- *and* thio-ligands can be prepared in the same way. Thus, for example, the cluster $[Cp^*_2Mo_2Cr_2(CO)_6O_2S_2]$ can be isolated from the reaction of $[Cp^*_2Mo_2O_2S_2]$ with $[Cr(CO)_3(MeCN)_3]$.[52a]

The results obtained from the analogous reactions with **16** are less consistent. The reaction with $Ni(CO)_4$ is the only reaction which gives a product, namely $[Cp_2Mo_2Ni_2(CO)_2S_4]$, with the expected 62e pseudocubane type structure.[101] In contrast, $Co_2(CO)_8$ reacts with **16** not only with elimination of CO but also of H_2S, thus yielding **67**. Two edge-sharing Mo_2CoS tetrahedra spanned by a μ_4-S ligand are characteristic of this cluster.[101] The reaction of **16** with $Fe(CO)_5$[102] or $Fe_2(CO)_9$[101] also yields a completely different sort of product, the 66e cluster **70**. This has only 3 M–M bonds, all metal atoms lying in one plane. Whether **70** can be converted into a cluster of the type **69**, has evidently not been investigated.

It is not the SH ligands that are responsible for the differing behavior of **16**, but rather the $Cp^{(*)}$ ligands: the permethylated derivative **65** reacts with $Co_2(CO)_8$ to give $[Cp^*_2Mo_2Co_2(CO)_2S_4]$, which has a 'normal' 60e M_4S_4 core.[103]

4. Conclusion and Perspectives

This review should hopefully have illustrated the appeal of the extremely variable structural chemistry of sulfur ligands from the organometallic point of view with particular reference to the dimeric cyclopentadienyl-transition metal complexes. The reactivity potential of these complexes has also been outlined. The unpredictable coexistence of mono-, di- and polysulfur ligands as well as the abilities to undergo ligand transformations and to be effective π-donor ligands, guarantee future developments in the structural chemistry and reactivity of these complexes. Although it is relatively difficult to present rigid principles, it was possible to show by

Table 1. Overview of the syntheses of homo- and heteronuclear clusters with the $M_2M'_2$ core from $[Cp^{(*)}_2M_2S_n]$ complexes (n = 4,5).

Substrate	Reactant	Conditions	Cluster	n [a]	Ref.
$[Cp'_2V_2S_4]$ **3**	$[Cp'_2V_2S_4]$	PBu_3; 20 °C	$[Cp'_4V_4S_4]$	56	[99]
	$Hg[Fe(CO)_3(NO)]_2$	toluene; 115 °C	$[Cp'_2V_2Fe_2(NO)_2S_4]$	58	[76b]
	$[Co(CO)_3(NO)]$	CH_2Cl_2; 20 °C	$[Cp'_2V_2Co_2(NO)_2S_4]$	60	[76b]
$[Cp^*_2Cr_2S_5]$ **8**	$[Cp_2Cr_2(CO)_4]$	THF; *hv*	$[Cp^*_2Cp_2Cr_4S_4]$	60	[94]
	$[Cp^*_2Cr_2S_5]$	H_2; 150 bar, 80 °C	$[Cp^*_4Cr_4S_4]$	60	[23]
	$[Fe(CO)_3(NO)][(Ph_3P)_2N]$	THF; *hv*	$[Cp^*_2Cr_2Fe_2(NO)_2S_4]$	60	[95]
	$Co_2(CO)_8$	toluene; 20 °C	$[Cp^*_2Cr_2Co_2(CO)_2S_4]$	60	[96]
$[Cp^*_2Mo_2S_4]$ **22a**	$[Cp_2Cr_2(CO)_4]$	THF; *hv*	$[Cp^*_2Mo_2Cp_2Cr_2S_4]$	60	[94]
	$[Cp_2Mo_2(CO)_4]$	toluene; 115 °C	$[Cp^*_2Cp_2Mo_4S_4]$	60	[94]
	$[Fe(CO)_3(NO)][(Ph_3P)_2N]$	THF; *hv*	$[Cp^*_2Mo_2Fe_2(NO)_2S_4]$	60	[95]
	$Co_2(CO)_8$	toluene; 20 °C	$[Cp^*_2Mo_2Co_2(CO)_2S_4]$	60	[96]
	$Mo(CO)_6$	toluene; 115 °C	$[Cp^*_2Mo_4(CO)_6S_4]$	62	[91]
	$Fe(CO)_5$	THF; 25 °C	$[Cp^*_2Mo_2Fe_2(CO)_4S_4]$ **69**	62	[91]
	CuCl	CH_2Cl_2; 20 °C	$[Cp^*_2Mo_2Cu_2(Cl)_2S_4]$	62	[100]
$[Cp_2Mo_2S_2(SH)_2]$ **16**	$Ni(CO)_4$	THF; 25 °C	$[Cp_2Mo_2Ni_2(CO)_2S_4]$	62	[101]

[a] Number of valence electrons in the cluster.

means of thermal, photochemical or electrochemical investigations that some relationships exist within groups of certain complex types. Above all, it would appear that electrochemistry will play an important role in the future, for such investigations should not only make up for the general lack of redox-active inorganic metal–sulfur complexes[104] but also open up the possibility of investigating new reaction types.[78, 80, 83]

The search for mixed chalcogen–pnicogen ligands could be a particularly fruitful field in which to extend our present knowledge of complexes of Cp with O, Se and Te ligands. This is immediately apparent on comparing the structural relationships between, e.g., **48** and [$Cp_2^*Cr_2P_5$][105] or [$Cp_2Mo_2As_5$][106] despite their differing bonding systems. In this connection, the first success in this search may have been the formal substitution of one and of three P atoms of the *cyclo*-P_5 ligand of [$Cp_2^*Mo_2P_5$] by sulfur atoms.[107]

Because of the nucleophilicity of their monosulfido ligands the sulfur-rich complexes of the vanadium and chromium triads exhibit model character for the study of heterogeneous metal sulfide surfaces in commercially important hydrodesulfurization catalyses.[108] However, with regard to the excellent HDS properties of RuS_2 and Rh_2S_3[109] the suitability of sulfur-rich Ru- and Rh-complexes described in this contribution would be well worth investigation.

Since the active centers of commercial HDS catalysts also consist of MoM'S phases (M' = Fe, Co, Ni)[110] the preparation of heteronuclear clusters with an M_4S_4 core [Eq. (d)] using the synthetic concepts developed for the complexes [$Cp_2^{(*)}M_2S_4$] could be of some importance. Actually, novel sulfur-resistant CO hydrogenation and HDS catalysts can be prepared[111] from **67** and **70** by coating them on oxidic supports which are then calcinated in an H_2 atmosphere. It should also be pointed out that striving for a high Fe:M ratio (particularly when M = Mo) or replacing the Cp ligands by, e.g., dithiocarbamato ligands could lead to the creation of clusters of physiological importance.[112]

I should once again thank my own co-workers cited in the reference section for their engaged contribution. Since conventional spectroscopic data on the compounds mentioned do not lead to a definite structural conclusion because of the very simple ligand situation, X-ray structural analysis has been of considerable importance. I would therefore particularly like to thank Prof. Dr. M. L. Ziegler (Universität Heidelberg) and his co-workers for their continued support since the very early stages of this work, and Dr. U. Klement (Universität Regensburg). I am particularly indebted to Prof. Dr. H. Brunner for generous material support and for the goodwill this work required and to Frau Karin Kilgert for the preparation of the manuscript.

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