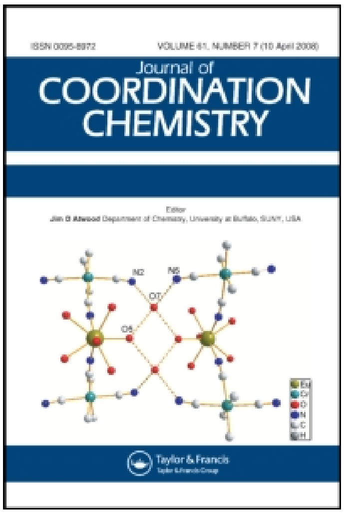

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BIS(CYCLOPENTADIENYL TRANSITION METAL) COMPLEXES RICH IN SULFUR

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BIS(CYCLOPENTADIENYL TRANSITION METAL) COMPLEXES RICH IN SULFUR

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Synthetic techniques for the incorporation of elemental sulfur into dimeric cyclopentadienyl transition metals are reported. The resulting sulfur rich complexes (S/M ratio $\geq$ 2:1) differ significantly in their structures, depending on the nature of the metal. With the exception of the chromium triad only 3d elements are concerned. The reactivity of the dicyclopentadienyl dimetal sulfides is localized both on the sulfur ligands and at the metal center as demonstrated by isomerization reactions and reactions with organic molecules. Some of these processes are of catalytic interest. The complexes $(MeC_5H_4)_2V_2S_4$, $(C_5Me_5)_2Cr_2S_5$ and $(C_5Me_5)_2Mo_2S_4$ are useful substrates for the synthesis of tri- and tetra-nuclear clusters, the latter being first representatives of mixed metal heterocubanes with a $M_2M'_2S_4$ core. In a short chapter the present knowledge on cyclopentadienyl complexes containing other chalcogenides is summarized.

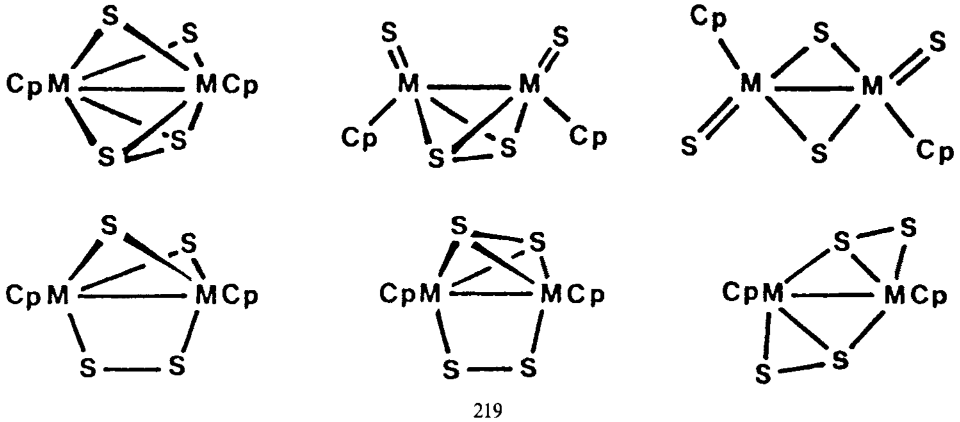
Key words: Sulfur complexes, synthesis, structure, reactivity

1. INTRODUCTION

Inorganic chalcogen ligands have become very attractive in transition metal chemistry during the last few years. Whereas the incorporation of the elements oxygen, selenium and tellurium seems to be at the very beginning, the coordination chemistry of sulfur ligands is already well developed. Several reviews dealing with mono-, di-, and polysulfur ligands have already been published.[1-3]

A new field in this chemistry involves the combination of mono- and disulfur ligands by cyclopentadienyl transition metal fragments, leading in most cases to the formation of dinuclear compounds comprising four or five sulfur atoms. In spite of their rather simple formulas these compounds exhibit interesting structural aspects as shown in Scheme 1. Their structures as well as the reactivity of the sulfur ligands vary significantly with the nature of the metal. In this review the syntheses and structures of these compounds will be described along with some chemical aspects, e.g. isomerization reactions, reactions with organic molecules, and the easy and systematic access of polynuclear sulfide clusters.

Scheme 1. Various Structure Types of $Cp_2M_2S_4$-Complexes



2. SYNTHESES AND STRUCTURES

Various organic and inorganic sulfur containing compounds have been used as sulfur transfer reagents to transition metal carbonyls,[1] but in most cases they work accidentally and often lead to unexpected products. The most suitable substrates for the synthesis of $Cp_2M_2S_x$ complexes are dimeric cyclopentadienyl carbonyl complexes in their reaction with elemental sulfur. First attempts to introduce elemental sulfur into such compounds led to insoluble products when $C_5H_5V(CO)_4$ or $[C_5H_5Mo(CO)_3]_2$ were used as starting material.[4] Somewhat more promising seemed to be the reaction of $[C_5H_5Fe(CO)_2]_2$ with S_8 in boiling toluene, which led to the cubane-like cluster $(C_5H_5)_4S_4$.[4] In the following years it was shown that these reactions could be optimized by the introduction of substituents at the cyclopentadienyl rings or by a modification of the reaction conditions. A summary of all sulfur rich Cp dimers cited in this article, along with the sulfur ligand set typical for each compound, is given in Table I.

2.1 *Vanadium and Niobium Compounds*

Two vanadium containing complexes of formulas $Cp_2V_2S_4$ and $Cp_2V_2S_5$ are known, the latter of which is directly accessible from the thermal desulfurization of Cp_2VS_5.[5] Their structural characterization is only possible in the case of alkyl-substituted cyclopentadienyl rings.[6] As it has been shown by thermolytic studies on the related Cp_2TiS_5 complex, it is likely that this reaction proceeds via organosulfur intermediates.[7] The molecular structure of $(MeC_5H_4)_2V_2S_5$ consists of equivalent $(MeC_5H_4)V$ units bridged by three different types of sulfur ligands (Figure 1). The electronic contribution of these μ-S, μ,η^1-S_2, and μ,η^2-S_2 ligands results in a total of 30-32 electrons, depending on whether one regards the η'-S_2 ligand as a 2 or 4 electron ligand. Although the molecule is electron deficient, one sulfur atom can be abstracted by PBu_3 to give the still more unsaturated complex $(C_5H_4R)_2V_2S_4$ (R = Me, i-prop), in which the V atoms are bridged by one μ,η^1-S_2 and two μ-S ligands (Figure 2).[8] The driving force for this reaction may be the achievement of a closed shell configuration for the metal atoms by π-interactions of

TABLE I
Ligand assemblies for bis(cyclopentadienyl transition metal) sulfides

Compound	no of isomers	ligand types	
$(MeC_5H_4)_2V_2S_4$	1	μ-S; syn-μ-η^1-S_2	(8)
(i-prop $C_5H_4)_2V_2S_4$	1	μ-S; syn-μ-η^1-S_2	(8)
$(MeC_5H_4)_2V_2S_5$	1	μ-S; μ-η^2-S_2	(6)
(i-prop $C_5H_4)_2V_2S_5$	1	μ-S; μ-η^2-S_2	(8)
$(C_5H_5)_2Nb_2S_5$	1	?	(9)
$(C_5Me_5)_2Cr_2S_4$	1	μ-S; μ-η^2-S_2	(12)
$(C_5Me_5)_2Cr_2S_5$	1	μ-S; iso-μ-η^1-S_2; μ-η^2-S_2	(10)
$(C_5H_5)_2Mo_2S_4$	1	μ-S; S_{ter}	(18)
$(MeC_5H_4)_2Mo_2S_4$	1	μ-S; S_{ter}	(20)
$(C_5Me_5)_2Mo_2S_4$	3	μ-S; μ-η^2-S_2 μ-η^2-S_2; S_{ter} μ-S; S_{ter}	(13,20)
$(C_5Me_5)_2Mo_2S_{10}$	1	μ-η^1,η^2-S_2; skew-μ-η^1-S_2; η^2-S_2	(20)
$(C_5H_5)_2W_2S_4$	1	μ-S; S_{ter}	(18)
$(C_5Me_5)_2W_2S_4$	2	μ-η^2-S_2; S_{ter} μ-S; S_{ter}	(13)
$(C_5Me_5)_2Mn_2S_4$	2	?	(28)
$(C_5H_5)_2Fe_2S_4$	2(?)	syn-μ-η^1-S_2; μ-η^2-S_2	(31,32)
$(C_5Me_5)_2Fe_2S_4$	1	syn-μ-η^1-S_2; μ-η^2-S_2	(33)
$(C_5Me_5)_2Co_2S_4$	1	μ-η^1,η^2-S_2	(33)

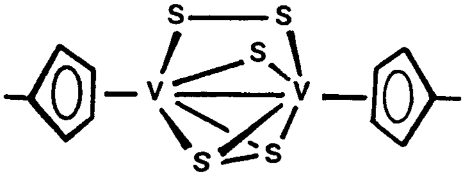


FIGURE 1 Molecular structure of $(MeC_5H_4)_2V_2S_5$.

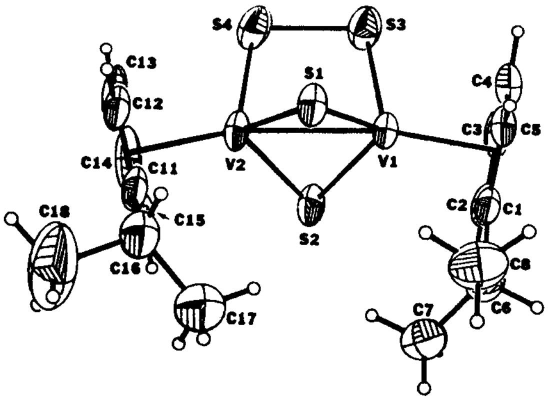


FIGURE 2 ORTEP drawing of $(i\text{-}propC_5H_4)_2V_2S_4$.

all sulfur ligands with the vanadium centers as indicated by very short V-S bonding distances.

$(C_5H_5)_2Nb_2S_5$, which is formed from $C_5H_5Nb(CO)_3THF$ and S_8,[9] might have a structure closely related to $(C_5H_4R)_2V_2S_5$.[8] The desulfurization of H_2S or CH_3SH, respectively, by $C_5H_5Nb(CO)_3THF$ only leads to $[C_5H_5Nb(CO)_2]_2\text{-}(\mu\text{-}S)_2$ and $[C_5H_5Nb(CO)_2]_2(\mu\text{-}S)_3$.[9]

2.2 The Chromium Triad

For the preparation of sulfur rich chromium cyclopentadienides the M-M triply bonded $[C_5Me_5Cr(CO)_2]_2$ seems to be the only suitable substrate. Apparently, the methyl substituents at the cyclopentadienyl ligand favor the reaction, for $[C_5H_5Cr(CO)_2]_2$ does not react at all.[10] By contrast, the reaction of $[C_5H_5Cr(CO)_3]_2$ with S_8 results in the insertion of a mono- or disulfur ligand into the relatively labile Cr-Cr bond.[11] Complete CO-substitution was not observed in this reaction.

The molecular structure of $(C_5Me_5)_2Cr_2S_5$ (Figure 3) contains a $\mu\text{-}S\text{-}$, a $\mu,\eta^2\text{-}S_2\text{-}$, and a $\mu(\eta^1\text{-}S_2)$ ligand, the latter representing a novel type of disulfur bridge in which only one sulfur atom is coordinated to both Cr atoms, whereas the other S atom is uncoordinated.[10] The unique nature of this ligand is further documented by Cr-S-S angles of about 109°, corresponding to sp^3 hybridization, and a rather long S-S bond length of 2.10 Å when compared to other $\mu,\eta^2\text{-}S_2$ ligands. A still longer S-S distance (2.15 Å) is found for the $\eta^2\text{-}S_2$ ligand. These findings suggest, in particular for the $\eta^2\text{-}S_2$ ligand, a back donation from occupied metal-d-orbitals into vacant π^* orbitals of the S_2 ligands. This explanation would be in contrast to the expectation that transition metal atoms in a low d configuration prefer stabilization by disulfur ligand orbitals.[2]

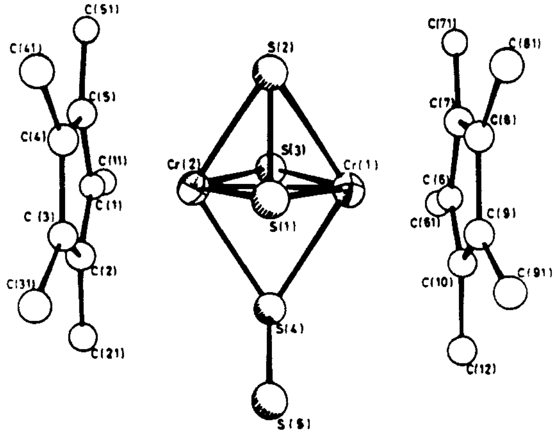


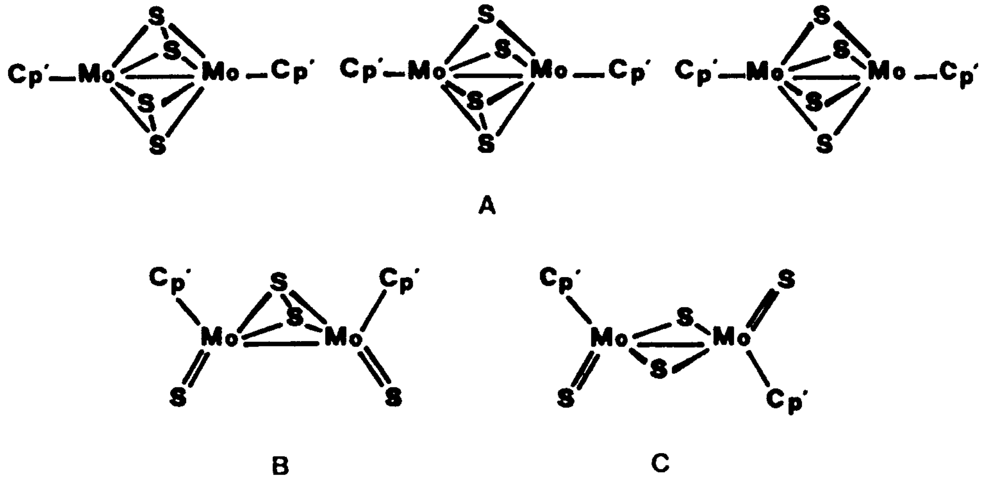
FIGURE 3 View of $(C_5Me_5)_2Cr_2S_5$.

$(C_5Me_5)_2Cr_2S_5$ can easily be transferred into $(C_5Me_5)_2Cr_2S_4$ by abstraction of the uncoordinated sulfur atom of the η^1-S_2 ligand by means of PPh_3.[12] The latter complex should have a structure similar to $(C_5Me_5)_2Mo_2(\mu\text{-}S_2)\text{-}(\mu\text{-}S)_2$,[13] as suggested by spectral data.

Two methods have been developed to transfer the insoluble polymer $[(C_5H_5)_2Mo_2S_x]_n$, which results from the reaction of S_8 with $[C_5H_5Mo(CO)_3]_2$[4] and $[C_5H_5Mo(CO)_2]_2$,[14] respectively, into the soluble complex $(C_5H_5)_2Mo_2\text{-}(\mu\text{-}S)_2(\mu\text{-}SH)_2$; the hydrosulfido complex is either formed by hydrogenation with H_2 under mild conditions[15] or by reduction with $LiEt_3BH$.[16] In this complex two isomers exist showing a relatively slow cis-trans isomerization.[17]

The mononuclear hydrosulfido complexes $C_5H_5M(CO)_3SH$ (M = Mo, W) are formed from the reaction of $C_5H_5M(CO)_3H$ with methylthiirane; they give the carbonyl free dinuclear compounds $(C_5H_5)_2M_2S_4$ on thermal decomposition.[18] An excess of methylthiirane leads to the bis-dithiolato complex $(C_5H_5)_2\text{-}(\mu\text{-}SCH_2CHMeS)$, which releases the olefin part at elevated temperatures.[19] $(MeC_5H_4)_2Mo_2S_4$ is formed in low yields from $[MeC_5H_4Mo(CO)_3]_2$ and S_8.[20]

Scheme 2. Possible Isomers in the $(C_5Me_5)_2Mo_2S_4$-System



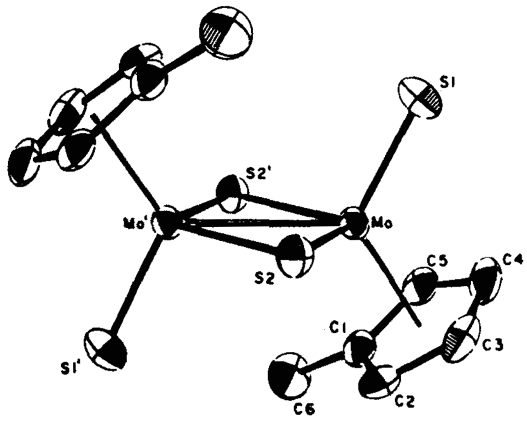


FIGURE 4 ORTEP drawing of $(MeC_5H_4)_2Mo_2(\mu\text{-}S)_2S_2$.

Much better yields of soluble compounds can be obtained when starting from the permethylated complex $C_5Me_5Mo(CO)_3H$ and S_8: In boiling THF $(C_5Me_5)_2Mo_2S_4$ can be isolated along with $(C_5Me_5)_2Mo_2S_{10}$ as a byproduct.[20] The structures of the three $Cp_2Mo_2S_4$ compounds mentioned above all belong to the same type C (Scheme 2).[18,20] As shown for $(MeC_5H_4)_2Mo_2S_4$ in Figure 4 they are characterized by a planar $Mo_2(\mu\text{-}S)_2$ unit, to which terminal sulfido ligands are attached in an anti configuration, leaving the Mo(V)centers in an electron deficient situation. $(C_5Me_5)_2Mo_2S_{10}$ contains three types of S_2 ligands (Figure 5), involving the rather rare example of a non-planar $\eta^1\text{-}S_2$ bridge. This compound is easily desulfurized by H_2 with the formation of H_2S and $(C_5Me_5)_2Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2$.[15]

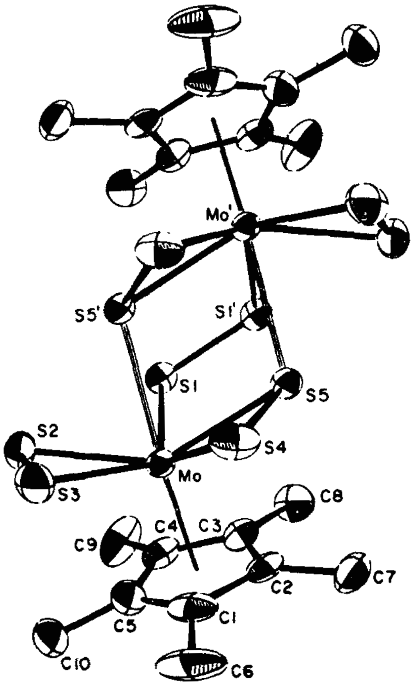
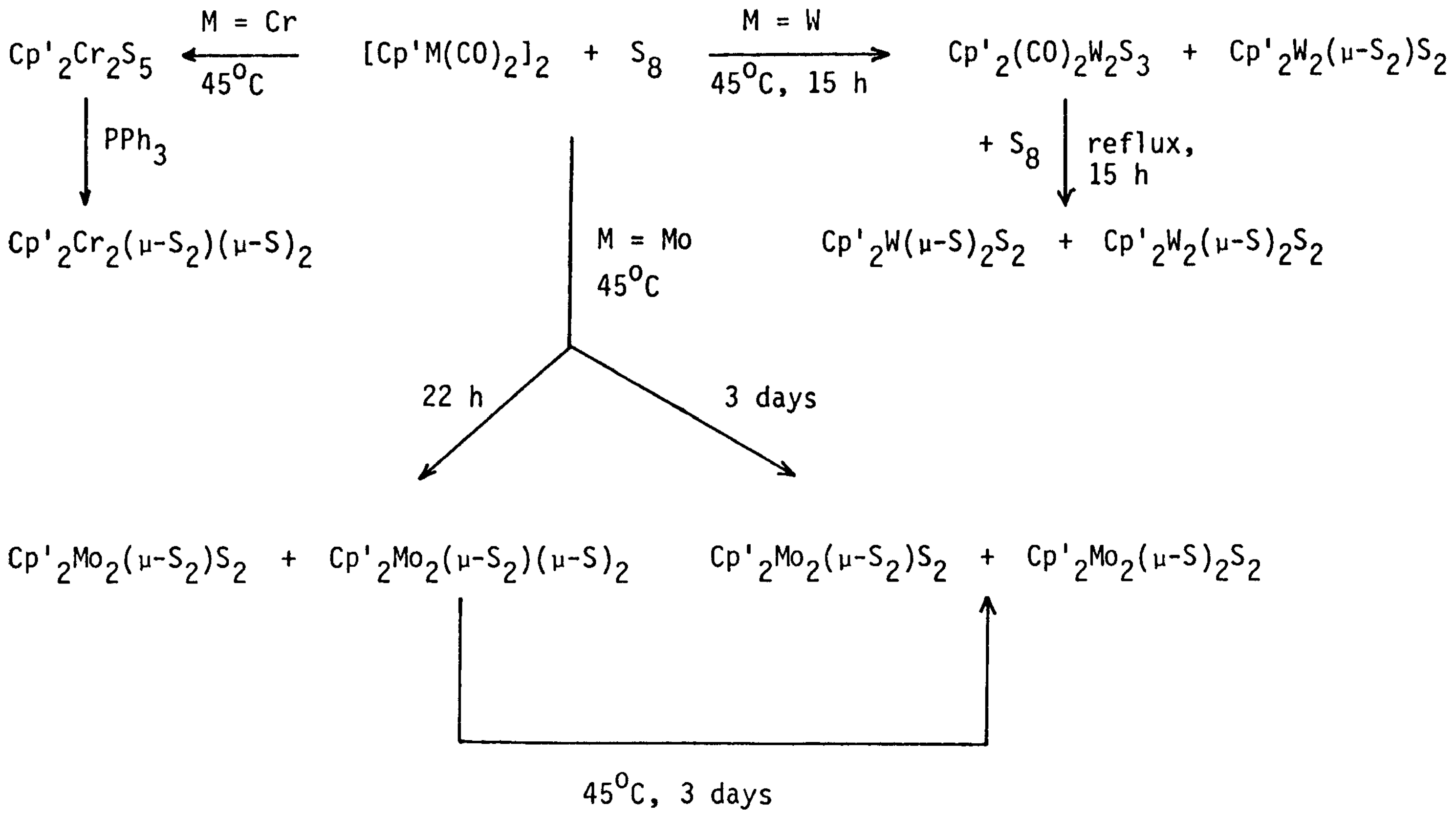


FIGURE 5 Perspective drawing of $(C_5Me_5)_2Mo_2S_{10}$.

Scheme 3. Synthesis of $Cp'_2M_2S_4$-Isomers ($Cp' = \eta^5$-C_5Me_5; M = Cr, Mo, W) from $[Cp'M(CO)_2]_2$ and S_8



Replacement of the Cp ring in $CpMo(CO)_3H$ by the isoelectronic trispyrazolylborato group drastically changes the reactivity, for the reaction with S_8 stops at $[HBpz_3Mo(CO)_2]_2S$, which is characterized by a linear $Mo{\equiv}S{\equiv}Mo$ unit.[21]

The high reactivity of the metal-metal triple bond in $[CpMo(CO)_2]_2$ derivatives can also be used for the incorporation of sulfur, but with different results depending on the nature of the Cp ring. Thus, $[C_5H_5Mo(CO)_2]_2$ reacts with S_8 (1:1 molar ratio) with formation of the trimolybdenum cluster $[(C_5H_5)_3Mo_3\text{-}(CO)_6(\mu_3\text{-}S)][C_5H_5Mo(CO)_3$.[14] In the $(C_5H_5)_3Mo_3(CO)_6S$ cation of this cluster the trigonal plane of three $C_5H_5(CO)_2Mo$-units is capped by a μ_3-S atom.

These results are in contrast to the reaction behavior of $[C_5Me_5Mo(CO)_2]_2$, which gives with elemental sulfur three different isomers A-C (Scheme 2) of the general formula $(C_5Me_5)_2Mo_2S_4$, no stable CO containing complex could be obtained.[13] It has been shown that the isomer ratio depends on the reaction conditions. Thus, isomer A is less stable and can thermally be converted into B and C (Scheme 3),[13] whereas preliminary photochemical investigations have shown that irradiation of any isomer eventually yields the other two isomers.[22] The molecular structure of A resembles that one of the above mentioned $(C_5Me_5)_2Cr_2S_5$ (Figure 3) with the only exception that the $\eta^1(\mu\text{-}S,S)$ ligand is replaced by a mono-sulfur bridge.[13] Further structural possibilities especially for Mo(V) dimers have been discussed elsewhere.[20,23]

Although the W-S-W bridged compound $[C_5H_5(CO)_3W]_2S$ has already been prepared from $C_5H_5W(CO)_3H$ and $S(NMe_2)_2$ [24] or SO_2,[25] the W-W bond of $[CpW(CO)_3]_2$ (Cp = C_5H_5 or C_5Me_5) is inert towards the insertion of sulfur. On the other hand, $[C_5Me_5W(CO)_2]_2$ reacts with S_8 with formation of a stable carbonyl-containing complex along with two $(C_5Me_5)_2W_2S_4$ isomers.[13] $(C_5Me_5)_2(CO)_2W_2S_3$ consists of a planar $W_2(\mu\text{-}S)_2$ core which is polarized by the coordination of two terminal CO groups to one W atom and of one terminal S ligand to the other W atom (Figure 6). Both CO groups can be replaced by sulfur, leading to two isomers of $(C_5Me_5)_2W_2S_4$ which are related to the corresponding Mo isomers B and C.[13]

An increased reactivity has been found for condensed sulfur vapor, allowing the access to thermally unstable, still CO containing products.[26] However, this stepwise oxidation of the metal-metal triple bond of $[C_5Me_5M(CO)_2]_2$ (M = Mo, W) ends up in each case in the formation of the thermally more stable $(C_5Me_5)_2M_2S_4$ complexes.

The different results obtained from the $[C_5Me_5M(CO)_2]_2$ series (M = Cr, Mo, W) are summarized in Scheme 3 and may be in part explained by differences in the reactivity of the metal-metal triple bond.[27] Thus, it is known that $[C_5Me_5Cr(CO)_2]_2$ is much less reactive than its Mo and W homologues. On the other hand, it is not yet clear why the coordination of a $\eta^1(\mu\text{-}S,S)$ disulfur ligand is preferred to a simple, electronically

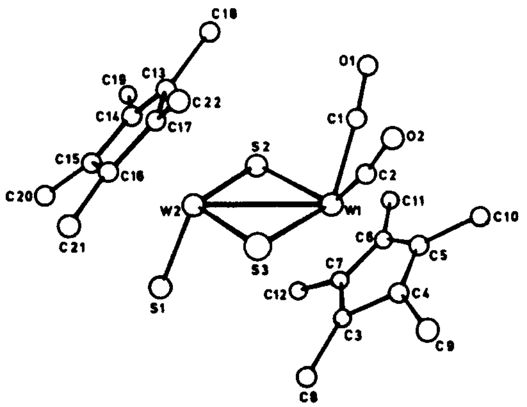


FIGURE 6 Molecular structure of $(C_5Me_5)_2W_2(CO)_2S_3$.

equivalent μ-S ligand in $(C_5Me_5)_2Cr_2S_5$, whereas in the Mo or W case only "conventional" mono- and disulfur ligands exist.

2.3 *Manganese and Rhenium Sulfides*

No sulfur rich Mn and Re cyclopentadienides are known so far. The incorporation of elemental sulfur into $Cp(CO)_2M(solv)$ complexes (M = Mn, Re; solv = THF or ether) does not lead to a complete CO substitution. Instead, a series of interesting CO containing compounds with different assemblies of mono-, di-, or trisulfur ligands can be isolated.[28] We found the reaction of $(C_5Me_5)_2Mn$ with S_8 to be a promising entry to dimeric sulfides. A green and a blue isomer of formula $(C_5Me_5)_2Mn_2S_4$ could be isolated, but their structures are still unknown.[29]

2.4 *Iron and Cobalt Sulfides*

The only hitherto employed cyclopentadienyl iron substrate is $[CpFe(CO)_2]_2$, which in the case of $Cp{=}C_5H_5$ reacts with S_8 in boiling toluene with formation of the cubane-like cluster $(C_5H_5)_4Fe_4S_4$.[4,30] As an intermediate in this reaction the polysulfur bridged complex $[C_5H_5Fe(CO)_2]_2(\mu\text{-}S_3)$ was established, which is formed in boiling THF and which can be decarbonylated at elevated temperatures.[31] By contrast, the photolytic reaction of $[C_5H_5Fe(CO)_2]_2$ with S_8 gives $(C_5H_5)_2Fe_2(CO)S_4$ which can be converted into two isomers of formula $(C_5H_5)_2Fe_2S_4$ by further irradiation.[32] The structure of one of these isomers is characterized by symmetrically bridging η^1-S_2 and η^2-S_2 ligands being perpendicularly oriented to each other.[33]

Only one isomer is formed in a good yield in the reaction of $[C_5Me_5(CO)_2Fe]_2$ with an excess of sulfur in boiling toluene.[34] $(C_5Me_5)_2Fe_2S_4$ has the same structure as the unsubstituted compound. Both compounds are distinguished by short S-S distances, e.g. 2.01 Å near the average for the η^1-S_2 ligand.[33,34] A relatively long Fe-Fe distance (ca. 3.50 Å) outside the range of metal-metal interaction may be indicative of enhanced donor electronic activities of the η^1-S_2 ligand, so that it can be regarded as a 4 rather than a 2 electron ligand. A similar situation has been found in $(C_5H_5)_2Fe_2(\eta^1\text{-}S_2)(\mu\text{-}SR)_2$.[35]

Although the tendency of the C_5H_5Co-fragment to form sulfide clusters is well established with the clusters $(C_5H_5)_3Co_3S_2$ [36] and $(C_5H_5)_4Co_4S_4$,[37] the first dinuclear compound was discovered only very recently. $(C_5Me_5)_2Co_2S_4$ is synthesized from $[C_5Me_5Co(CO)]_2$ and sulfur under mild conditions.[34] It represents a new structural type,

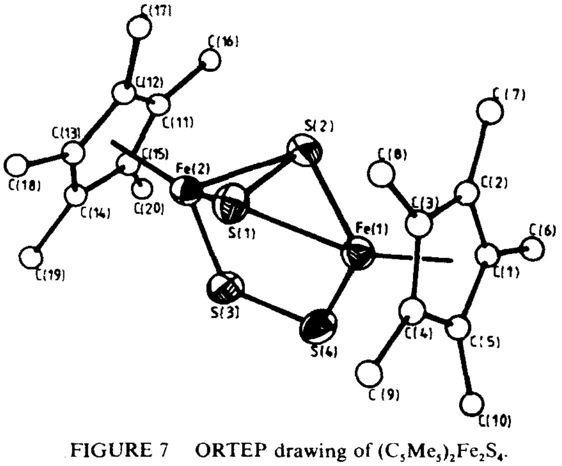


FIGURE 7 ORTEP drawing of $(C_5Me_5)_2Fe_2S_4$.

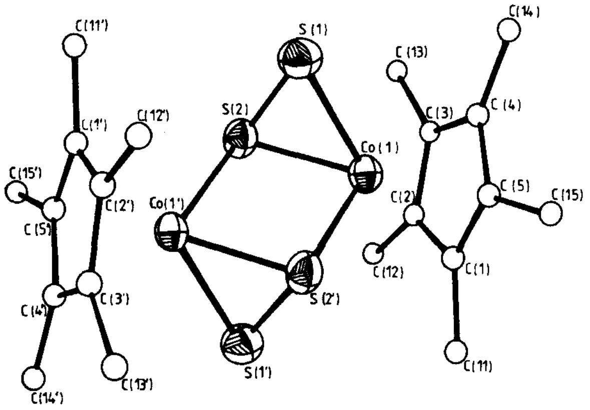


FIGURE 8 View of $(C_5Me_5)_2Co_2S_4$.

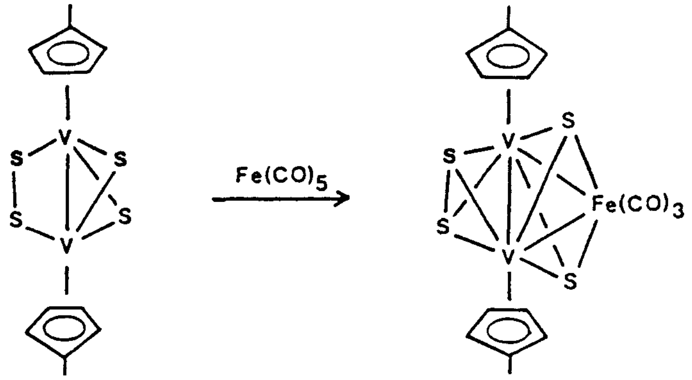
although it contains two already known η^1,η^2-disulfur bridges, contributing four electrons to each metal atom (Figure 8). Characteristic of the molecule is a Co_2S_2 plane, one further S-atom is located above and the other one below this plane. The Co-Co distance of 3.38 Å, precluding any metal-metal interaction, is in agreement with the diamagnetic character of the molecule.

3. REACTIONS

3.1 Sulfur Ligand Transformations

Sulfur ligand transformations are often combined with changes in the oxidation state of the metal center. An intramolecular redox process, which is symbolized by the equation $2\,S^{2-} + 2\,Mo(V) \rightleftharpoons S_2^{2-} + 2\,Mo(IV)$ may be responsible for the interconversion of the Mo and W isomers A-C (Scheme 2). Additionally, such isomerizations involve the transformation of a monosulfur bridge into a terminal ligand or vice versa dependent on the reaction conditions.[13,22]

The electron deficient complex $Cp_2V_2S_4$ (Figure 2) represents a system of particular interest: Electrophilic diazenes promote the oxidative coupling of two S^{2-} ligands into a η^2-disulfide bridge, when the triazoline ligand acts as a bridge itself.[38] This example further demonstrates that the reactivity of transition metal sulfides needs not be localized exclusively on the sulfur ligands but may also incorporate the metal as a center of reactivity. In order to compensate for the electron deficient character of the metal center a "rotation" of the μ,η^1-S_2 ligand into a η^2-S_2 bridge takes place.[38] A similar process also occurs in the addition of $Fe(CO)_3$- or $Fe(NO)_2$-fragments to $Cp_2V_2S_4$,[39,40] thus allowing the resulting trinuclear clusters to obey the EAN rule (Equation 1).



(1)

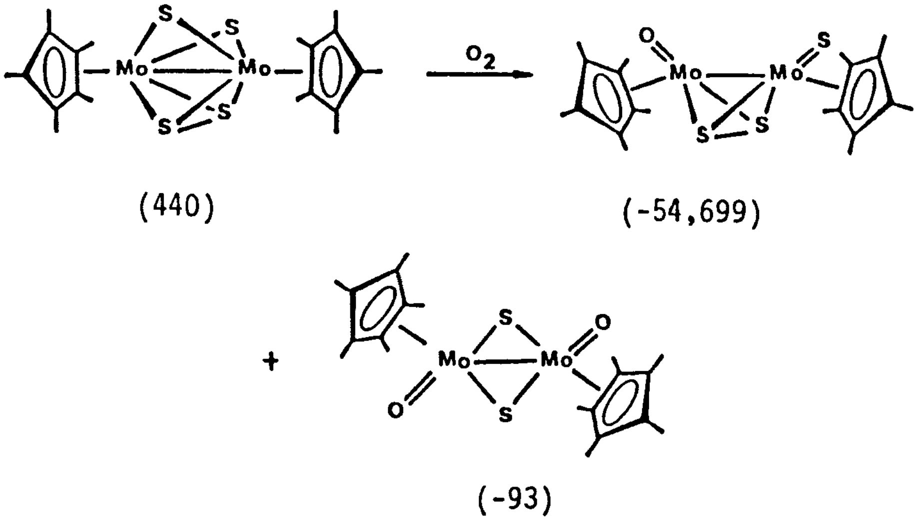
No isomerization reactions have been detected for the chromium compounds $(C_5Me_5)_2Cr_2S_4$ and $(C_5Me_5)_2Cr_2S_5$, but they react under H_2 pressure with formation of the cubane-like cluster $(C_5Me_5)_4Cr_4S_4$.[12] A mechanism for this reaction has not yet been established, but it is very likely, that the presence of H_2 is essential for this reaction. In this regard it may be of interest that $(C_5Me_5)_2Fe_2S_4$ is obviously inert towards H_2, even at a pressure of 250 bar.[34]

A rearrangement of terminal into bridging sulfide ligands is facilitated by hydrogen or unsaturated organic molecules.[20] However, the formation of $(C_5Me_5)_2Mo_2(\mu\text{-}SH)_2(\mu\text{-}S)_2$ is also possible upon insertion of hydrogen into the η^2-disulfur bridge of the Mo(IV) isomer A (Scheme 2).[12] This observation suggests that apart from redox reactions homolytic cleavage of the S-S bond may be involved in such processes. A similar bridge cleavage is part of a catalytic cycle in which SO_2 is reduced by $(C_5Me_5)_2Mo_2(SH)_2S_2$ to give sulfur and water under mild conditions.[41]

An opening of the "closed" isomer A into the "open" isomers B and C can be observed on exposure of $(C_5Me_5)_2Mo_2S_4$ to air.[13] This reaction is accompanied by the substitution of one or two terminal sulfur ligands by oxygen (Scheme 4). The progress of such an oxidation reaction can easily be monitored by ^{95}Mo nmr spectroscopy, for the chemical shifts are very sensitive to the sulfur to oxygen ratio in the coordination sphere of the metal atom.[42] It has also been shown that $(C_5Me_5)_2Mo_2(\mu\text{-}S)_2S_2$ can be transferred to $(C_5Me_5)_2Mo_2(\mu\text{-}S)_2O_2$ on exposure to air.[20] The structure of this compound is analogous to $(C_5H_5)_2Mo_2(\mu\text{-}S)_2O_2$, which was the first example of an organometallic compound containing doubly briding S atoms between two transition metal atoms.[43]

The interaction of oxygen with $Cp_2M_2S_4$-complexes has only been investigated for the Mo derivatives, in which the metal center seems to be the only reaction site. However, several examples have been provided recently in which μ-S- as well as η^2-S_2-ligands have been oxidized to μ-SO-,[44,45] η^2-S_2O-,[45,46] and η^2-S_2O_2-[45] ligands. These results should encourage the quest for new mixed chalcogen ligands in cyclopen-

Scheme 4. Oxidation of $(C_5Me_5)_2Mo_2S_4$ by air (δ ^{95}Mo values in parentheses)

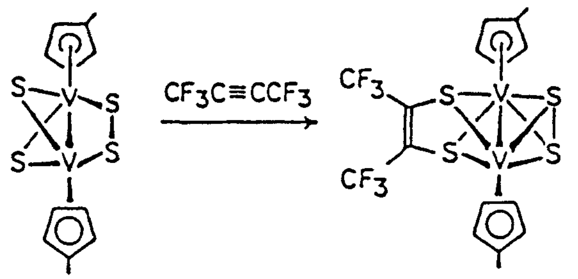


tadienyl complexes. In the same sense the stabilization of Lewis acids by basic sulfide bridges should be possible. As a first example a bis-SO_2-adduct of $[C_5Me_5W(CO)_2]_2[\mu\text{-}S]_2$ has been characterized.[25]

3.2 *Reactions with Organic Molecules*

As established by the results of the crystallographic studies the sulfur ligands may be expected to have a more or less nucleophilic character. Thus, they react with CF_3CO_2H or CH_3I and electrophilic alkynes or alkines. For the ligand set present in $(C_5Me_5)_2Cr_2S_5$ and $(C_5Me_5)_2Mo_2S_4$ a decrease in nucleophilicity in the order $\eta^1\text{-}(\mu\text{-}S,S) > \mu\text{-}S > (\eta^2\text{-}S_2)$ has been found.[12]

Different results are obtained when $Cp_2M_2S_x$ (x = 4,5) complexes react with electrophilic acetylenes. A mononuclear bischelate complex, $(MeC_5H_4)V(S_2C_2R_2)_2$, is formed from $(MeC_5H_4)_2V_2S_5$ and $CF_3C{\equiv}CCF_3$,[6] whereas the formation of a symmetric dithiolene bridge is accompanied by a $\eta^1\text{-}S_2 \rightarrow \eta^2\text{-}S_2$ rearrangement[8] (Equation 2).



(2)

In general, the vanadium dimers appear to be less reactive than the corresponding Mo and W dimers. Thus, $(MeC_5H_4)_2Mo_2S_4$ in both isomeric forms A and C reacts with C_2H_4 and C_2H_2 to give Cp dimers containing symmetrically bridging alkane- or alkenedithiolato bridges.[20,47]

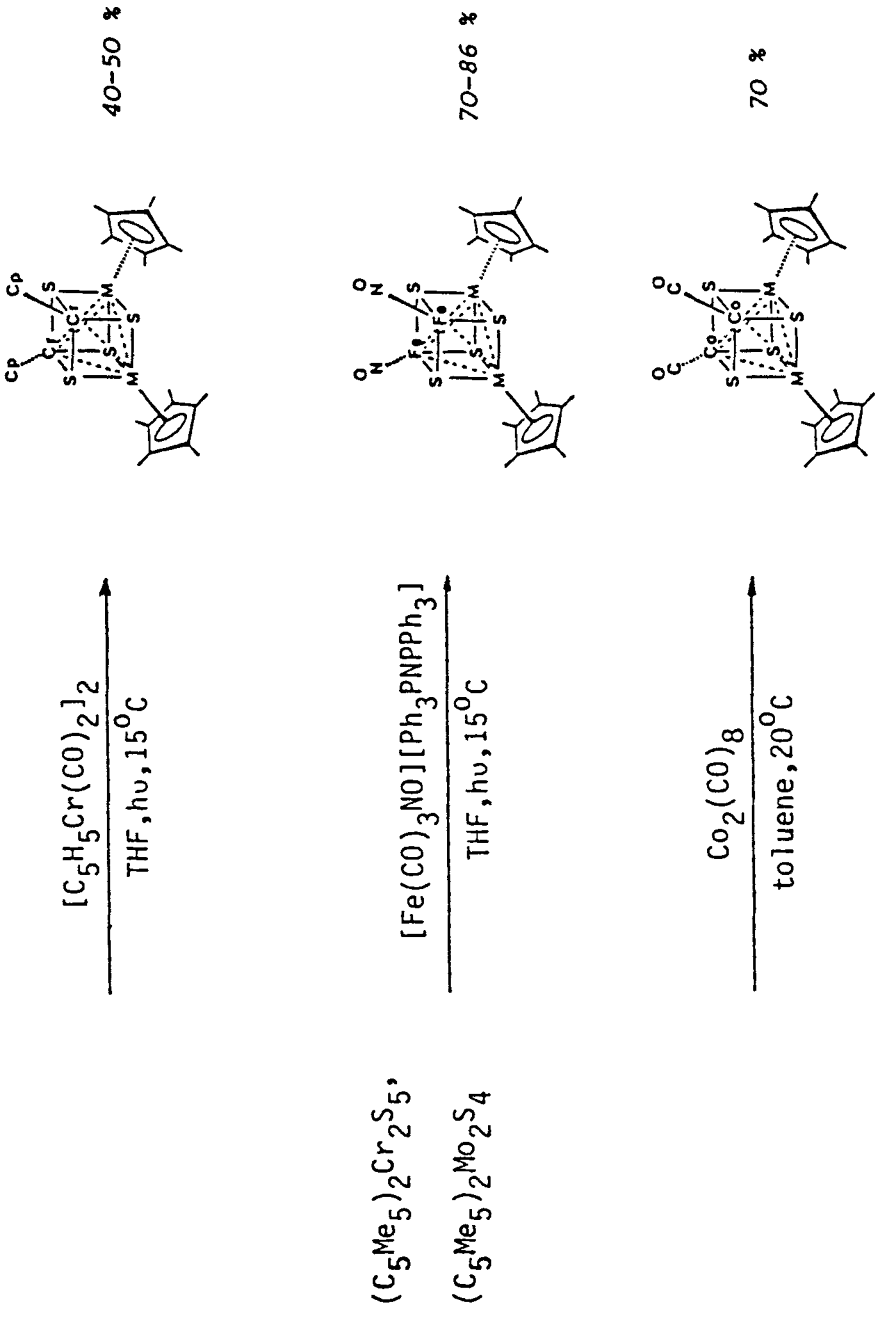
The reaction of C_2H_2 with $(C_5H_5)_2W_2(\mu\text{-}S)_2S_2$ gives dimers with terminal coordinated alkene dithiolate chelates.[47] Some of these compounds are of special interest for they undergo hydrocarbon exchange reactions as well as hydrogenation under mild conditions.[17,47] New dithiocarbonimidate bridges are formed in the reversible reaction of isocyanides with dithiolato complexes.[48] Further investigations comprising monosulfur bridges in a fixed cis position[49] have been directed towards the homogeneous hydrolysis of CS_2.[50]

$(C_5H_5)_2Fe_2S_4$ gives upon reaction with $CF_3C{\equiv}CCF_3$ a mono- as well as a bis-adduct, in which the bidentate 2,3-dithiolatobutene ligands are coordinated through one bridging and one terminal sulfur atom.[33]

Practically no attention has been paid to the nucleophilic cleavage of the S-S bond by e.g. Na/Hg, $LiEt_3BH$ or RLi. These reactions lead in the case of organic disulfides or $Fe_2(CO)_6(\mu\text{-}S_2)$ to highly reactive anions with versatile properties.[51]

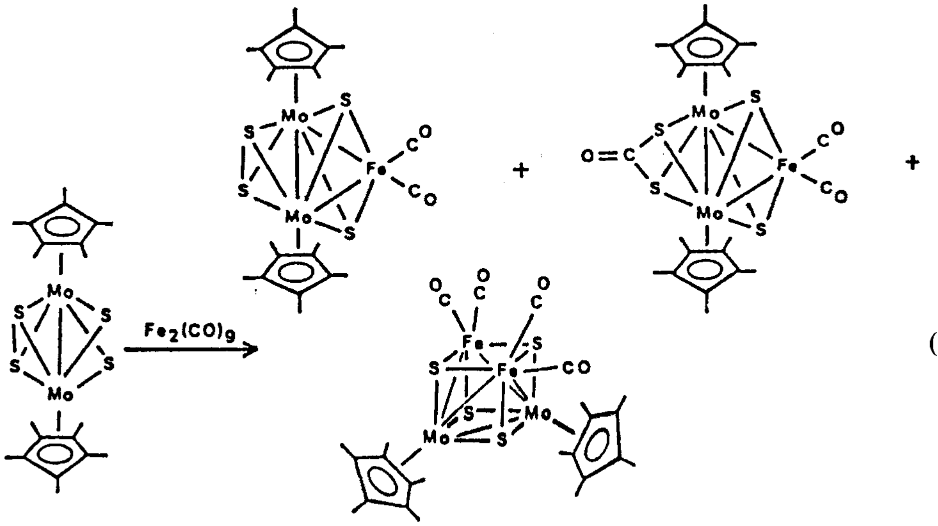
3.3 *Synthesis of Tri- and Tetranuclear Clusters*

$Cp_4M_4S_4$ clusters can be divided into subunits consisting of one $Cp_2M_2S_4$-and two CpM-fragments. The hitherto developed routes for the synthesis of e.g. $(MeC_5H_4)_4Cr_4S_4$,[52] $(i\text{-}propC_5H_4)_4Mo_4S_4$,[53] $(C_5H_4)_4Fe_4S_4$,[30] and $(C_5H_5)_4Co_4S_4$ [37] do not refer to this consideration, for they have been obtained more or less accidentally. A general concept for the synthesis of homo- and heterometallic M_4S_4-clusters has been elaborated on the basis of $(C_5Me_5)_2Cr_2S_5$ and $(C_5Me_5)_2Mo_2S_4$, regardless of the isomeric nature of the Mo compound. From Scheme 5 one may deduce that the Cr and Mo dimers serve as potential 38-e precursors which are expanded by two each of the 11-e fragments MCp (M = Cr, Mo),[54] Fe(NO),[55] or Co(CO)[56] into 60-electron clusters. These compounds belong to the cubane-like clusters as established by the presence of six metal-metal bonds in $(C_5Me_5)_2Cr_2Co_2\{P(OMe)_3\}_2(\mu_3\text{-}S)_4$.[57]



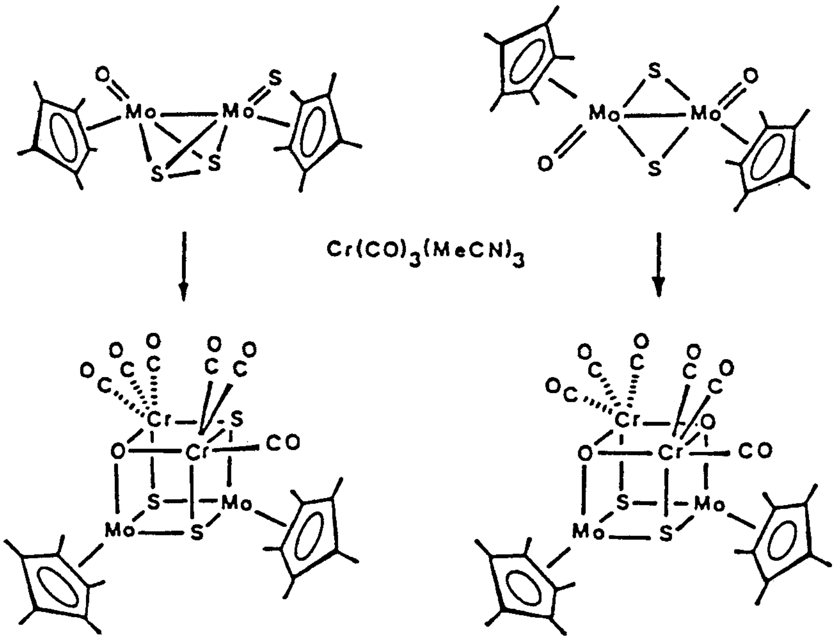
Scheme 5. Synthesis of 60-e $M_2M'_2S_4$-Clusters

When the 12-e fragments $Mo(CO)_3$ or $Fe(CO)_2$ are added to $(C_5Me_5)_2Mo_2S_4$, 62-e heterocubanes along with two Mo_2FeS_4 complexes (Equation 3) are formed.[58] It has not been established whether the trinuclear clusters can be regarded as intermediates in the formation of the tetranuclear clusters. The remarkably mild insertion of a CO ligand into the η^2-S_2 bridge of the dinuclear substrate cannot be achieved by a high pressure reaction of carbon monoxide with $(C_5Me_5)_2Mo_2S_4$.



(3)

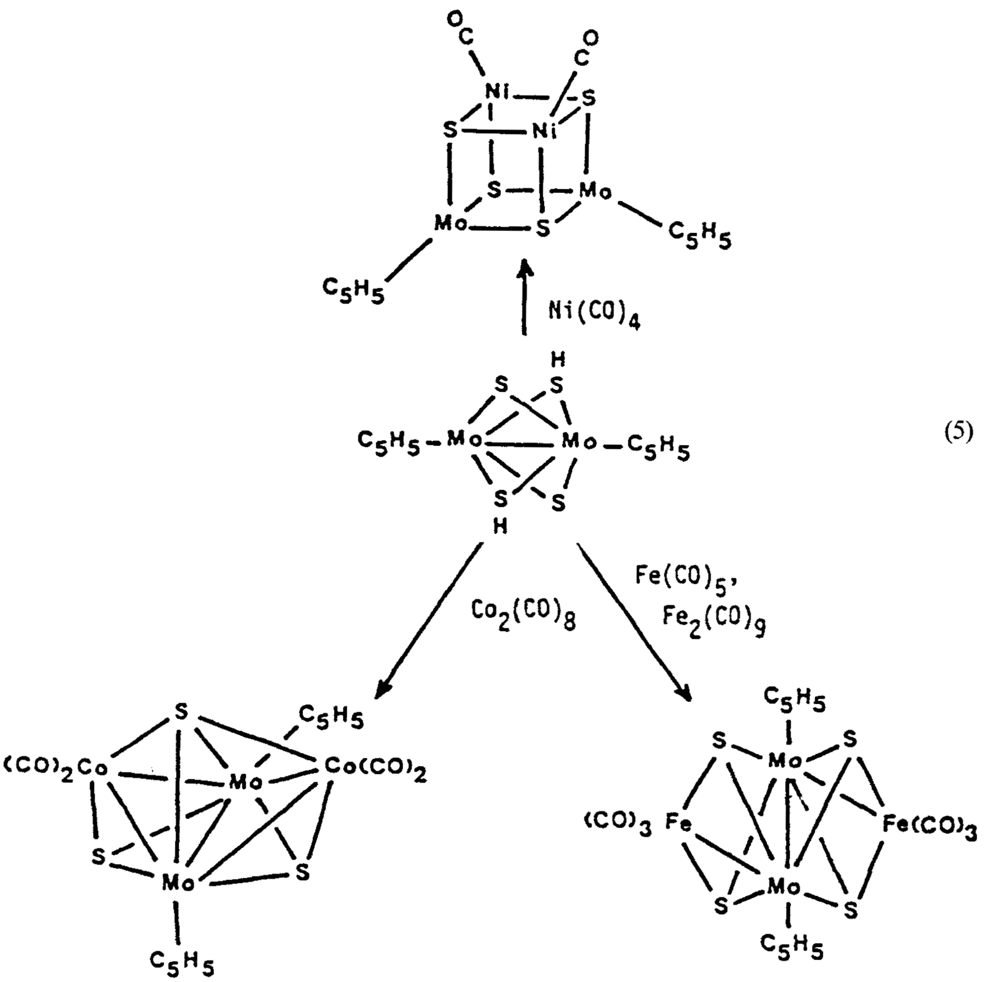
The construction of mixed oxo/thio-clusters follows the same principle as discussed above. Thus, 62-e heterocubanes can be isolated from the reaction of $(C_5Me_5)_2Mo_2O_xS_{(4-x)}$ ($x = 1, 2$) with $Cr(CO)_3(CH_3CN)_3$ [59] (Equation 4).



(4)

(MeC$_5$H$_4$)$_2$V$_2$S$_4$ [8] represents a potential 36-e building block for heterocubane cluster synthesis. This complex reacts with Hg[Fe(CO)$_3$(NO)]$_2$ or Co(CO)$_3$(NO) with formation of (MeC$_5$H$_4$)$_2$V$_2$Fe$_2$(NO)$_2$S$_4$ (58-e) and (MeC$_5$H$_4$)$_2$V$_2$Co$_2$(NO)$_2$S$_4$ (60-e), respectively.[39] In one of these reactions the closo cluster (MeC$_5$H$_4$)$_2$V$_2$Fe(NO)$_2$S$_4$ can be isolated at intermediate. Like (MeC$_5$H$_4$)$_2$V$_2$Fe(CO)$_3$S$_4$ (Equation 1)[40] it contains a side-on coordinated η^2-S$_2$ bridge. This disulfur ligand either inserts a (PPh$_3$)$_2$Pt-fragment or eliminates one sulfur atom by the interaction with PBu$_3$.[40] A similar S-abstraction has also been observed in the conversion of (MeC$_5$H$_4$)$_2$V$_2$S$_5$ into (MeC$_5$H$_4$)$_2$V$_2$S$_5$ into (MeC$_5$H$_4$)$_2$V$_2$S$_4$, but seems to be limited to the vanadium dimers only.[8]

It is of interest to compare these rather homogeneous results with cluster formation reactions of (C$_5$H$_5$)$_2$Mo$_2$(μ-SH)$_2$(μ-S)$_2$ [15,16] which is structurally closely related to (C$_5$Me$_5$)$_2$Mo$_2$(μ-S$_2$)(μ-S)$_2$. However, the reactions of the hydrosulfide complex with Fe(CO)$_5$, Co$_2$(CO)$_8$, and Ni(CO)$_4$ proceed in different ways (Equation 5). (C$_5$H$_5$)$_2$Mo$_2$Fe$_2$(CO)$_6$S$_4$ represents a 66e-cluster containing a planar Mo$_2$Fe$_2$ core,[16,60] whereas (C$_5$H$_5$)$_2$Mo$_2$Co$_2$(CO)$_4$S$_3$ involves a μ_4-S bridge[16] as the characteristic feature. Only (C$_5$H$_5$)$_2$Mo$_2$Ni$_2$(CO)$_2$S$_4$[16] corresponds to the predicted 62-e cubane-like cluster type.[58]



(5)

4. DINUCLEAR CYCLOPENTADIENYL COMPLEXES OF THE OTHER CHALCOGENIDES

It may be of interest to compare the chemistry of the bis(cyclopentadienyl transition metal) sulfides with that of the other calcogenides. Among these selenium shows ligating properties closely related to sulfur. Thus, examples for mono- and di-selenium ligands are known from the literature which might also occur in hypothetical $Cp_2M_2Se_4$- or $-Se_5$ complexes: μ-Se-,[61,62] μ,η^1-Se_2-,[28] μ,η^2-Se_2-[63] and $\mu(\eta^1,\eta^2)$-Se_2-ligands.[64] Combinations of these ligands are found in $(C_5Me_5)_2Mo_2(\mu\text{-}Se_2)(\mu\text{-}Se)_2$, $(C_5Me_5)_2Mo_2(\mu\text{-}Se)_2O_2$, and $(C_5Me_5)_2(CO)_2W_2(\mu\text{-}Se)_2Se$, which are accessible from $(C_5Me_5)_2M_2(CO)_4$ (M = Mo, W) and elemental selenium.[65] A complex of composition $(C_5Me_5)_2Co_2Se_5$ has also been reported, but not structurally characterized.[66] Condensed selenium vapor can also be used to synthesize thermally unstable, still CO containing complexes of Mo and W.[26]

Efforts for the incorporation of elemental tellurium have been so far directed towards metal carbonyl derivatives only. The stabilization of several (although limited) examples of μ-Te ligands with nucleophilic character[67] as well as Te_2-ligands[68] may be indicative of the existence of tellurium complexes fulfilling the conditions for this review.

As already described in section 3.1 oxygen is able to displace terminal S^{2-} ligands from Mo centers. Although the complexes $(C_5H_5)_2Mo_2(\mu\text{-}O)_2O_2$ and $(C_5H_5)_2Mo_2(\mu\text{-}O)O_4$ synthesized some years ago,[69] a systematic oxidation reaction of Cp metal carbonyls has been initiated only very recently, leading to $(C_5H_5)_2Cr_2O_4$,[70] $(C_5Me_5)_2Mo_2O_4$,[71] $(C_5Me_5)_2$-Mo_2O_5,[70] and $(C_5Me_5)_2Re_2O_4$.[72] The results of crystallographic studies (Scheme 6) show that oxygen ligands induce higher oxidation states at the metal centers than sulfur ligands and that new structural types can be realized which have not vet been found for $Cp_2M_2S_4$ compounds.

Scheme 6

M = Cr, Re

Cp = C_5H_5, C_5Me_5

5. FINAL REMARKS

Rational, general synthetic techniques have been developed for the stabilization of mono- and disulfur ligands in dinuclear cyclopentadienyl transition metal complexes. These compounds differ significantly in their structures and exhibit interesting reactivity patterns. Most of the sulfur-rich transition metal cyclopentadienides presented in this review belong to first row transition metals. However, the results obtained in the chromium triad indicate that changes in structures and reactivity may be expected when going from 3d to 4d and 5d elements.

Whereas the synthesis of new sulfur ligands[3] or the realization of new coordination modes for already known ligands appears to be more and more difficult, a transfer of this knowledge to the other chalcogenes should be attempted. Another motivation for the synthesis of new ligands being unstable under normal conditions may arise from several new exciting Cp complexes containing "inorganic" phosphorus or arsenic ligands.[73] Some of these molecules resemble in their structures Cp_2M_2 sulfides. As a first impulse in this direction the stabilization of AsS_3-,[74] AsS-,[75] As_2S-[76] or As_2S_3-ligands[77] from As_4S_4 by different CpM fragments may be considered.

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