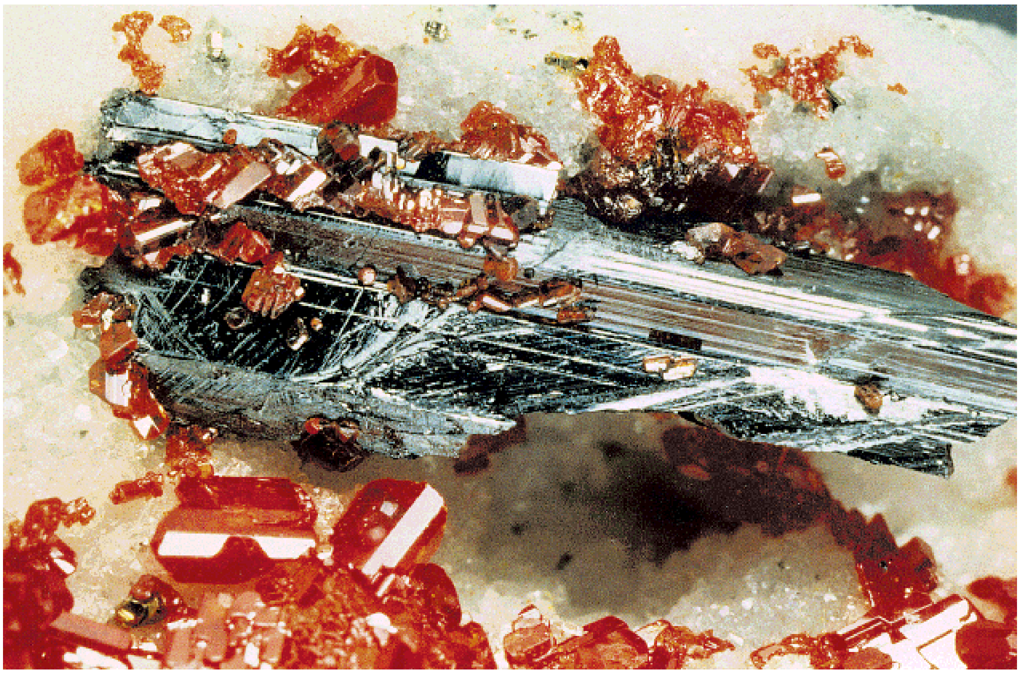
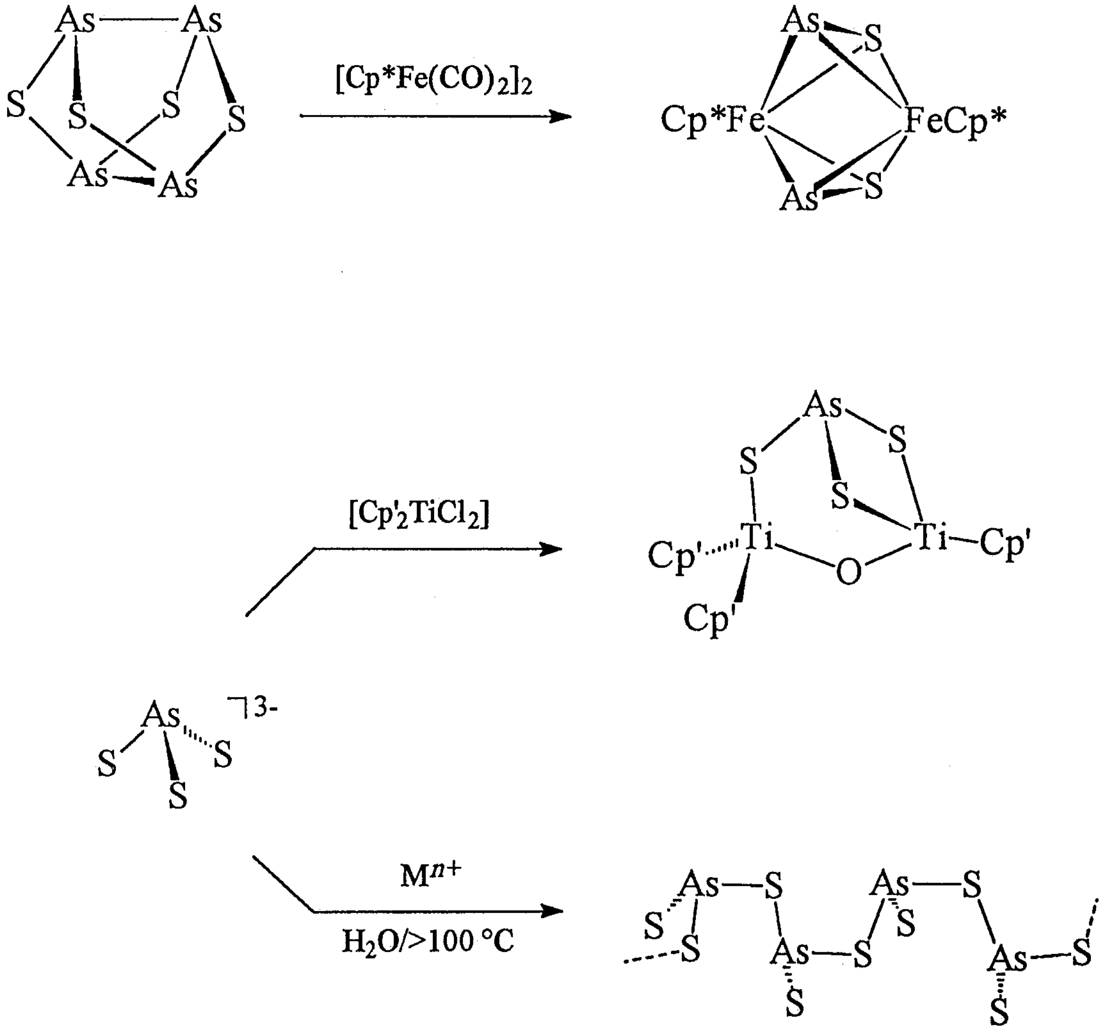


“AsS” (from As_4S_4) and AsS_2^- (from AsS_3^{3-}) are the smallest building blocks, which form the molecular cage of realgar (red) and the infinite $PbAs_2S_4$ chains in the sulfosalt mineral sartorite (black shining).

Examples of the compounds that are accessible in the laboratory from the above starting materials are illustrated below.



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Mixed Ligands from Group 15/16 Elements: Interface of Solid-State and Molecular Chemistry

Joachim Wachter*

Heteroatomic ligands E/X containing the elements P, As, Sb (E) and S, Se, Te (X) span the wide range from simple salts through to neutral and anionic cage molecules and on to solids. Their coordination chemistry with numerous metals, ranging from the formation of diatomic ligands in organometallic complexes to extended solid-state structures is currently the focus of a great deal of attention. Besides neutral clusters such as $E_4X_{3(4)}$, Zintl phases and covalent solids play an increasing role in the development of new E/X ligands. Typical synthetic strategies are the reduction of binary phases by nucleophilic complexes and the introduction of organometallic complex fragments ML_n (L = CO, cyclopentadienyl) into neutral and anionic cage molecules. The ligands can be classified into three groups: a) small, covalently bonded E/X ligands with different π-bond participation and a pronounced tendency for "self-condensation", b) heteroatomic Zintl anions, which are incorporated into electron precise complexes under partial fragmentation, and c) neutral cage molecules, which are useful for studying fragmentation mechanisms and for the construction of new hybride clusters with inorganic cores and peripheral organometallic groups. In this context labile "primary complexes" that still contain the intact inorganic cage are of particular interest. Structural and other aspects of the degradation and rearrangement of these clusters are discussed in terms of the main group and transition elements employed and the reaction conditions.

Keywords: main group elements · ligands · solid–state chemistry · transition metals

1. Introduction

Thiosalts of arsenic and antimony should be familiar to chemists from their earlier experiences in classical analytical chemistry; however, very few students realize at this stage the manifold varieties of these compounds in Nature. The building blocks are flat trigonal pyramids that condense under the influence of metal ions to give chain, band, and ring structures; thus, there is a certain resemblance to silicate chemistry. In this way the family of sulfosalts,[1] which are a structurally and optically fascinating class of compounds, has been established. Another natural product is the red realgar As_4S_4,[2] which is built up in a very different manner as a molecular cage, and which is frequently employed as ligand supplier for transition metal complexes. Synthetic solid-state compounds containing Group 15 thioanions are realized in the laboratory by means of hydro- and solventothermal procedures. This aspect is summarised in a topical review.[3]

Molecular sections of solid-state structures produced in this way occur in mixed polyatomic anions, the nature of which ranges from centered anions (e. g. phosphate type) to main group element clusters, and in transition metal complexes. Syntheses and structural chemistry of mixed anions with respect to the Zintl ion concept have alreay been thoroughly summarized.[4] In addition to the stabilization of discrete anions by suitable cations, the synthesis of "transition metal carbonyl main group hybrid clusters"[5] is becoming increasingly important. Hereby covalent bonds between main group and transition elements are formed, which are similar to those typically found for complexes with unsubstituted ("naked") homoatomic ligands of Groups 15 and 16.

The quest for novel structures with pnicogen ligands "E" has been influenced in a decisive manner by the isolobal relationship P(As) $\overset{\circ}{\longleftrightarrow}$ CH.[6] In contrast, for the heavier homologues antimony and bismuth far fewer results are available.[7] The complex chemistry of chalcogen ligands "X" has been reviewed under different aspects: They tend, particularly in the case of the heavier elements, to oligomerize,[8] which gives rise to different chain lengths and manifold coordination properties and results in a wide structure chemistry.[9] The number of known complexes with homo-

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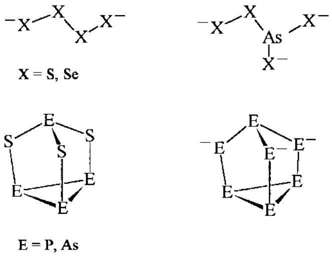
atomic ligands is considerably greater than that of transition metal complexes with mixed ligands.

According to a proposal by Kanatzidis et al.,[10] the advantage of introducing trivalent E^- building blocks into polychalcogenide skeletons lies primarily in the additional branching possibilities offered (Scheme 1 top). On the other hand the substitution of sulfur by E^- in neutral, mixed cage molecules, such as E_4S_3, provides a relationship to Zintl ions and their complexes (Scheme 1 bottom).[11] Extension of these formalisms gives rise to the question of how combinations from mE and nX ligands to mixed ligands E_mX_n may express the different coordinative and electronic properties of both element groups under the influence of reactive metal fragments.



Scheme 1. Substitution of an atom X by E^- in polychalcogenides provides a branching site (top), similar substitution in neutral sulfur-containing cage molecules gives Zintl ions (bottom).

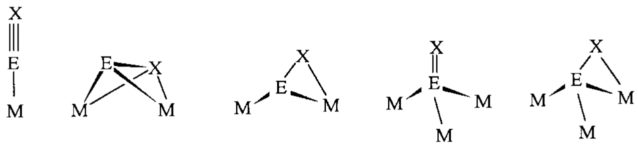
The primary goals of this article are to summarize the rapidly growing body of knowledge on transition metal complexes with mixed ligands of the heavier elements—excluding NO and NS ligands[12,13]—and to find trends within a group of the periodic table. In addition to carbonyl complex fragments,[4,5] the role of cyclopentadienyl[*] and of other complexes in the stabilization of molecular aggregates will be examined. Examples from thioarsenate(III) chemistry will show that there is a steady transition from low molecular weight main group clusters to covalent solid-state structures, with and without incorporation of transition metals. Building blocks that are common or similar to polymeric solids and molecular compounds should stimulate the interest of the complex chemist in this ligand pool, which is at the interface of solid-state and molecular chemistry.

2. Synthetic and Structure Chemistry of Di- to Tetratomic Ligands

The simplest mixed ligands may be expressed by the combinations EX, E_2X, EX_2, E_2X_2, and EX_3. The coordination behavior of these ligands is correspondingly rich, and, apart from PS[14] and some EX_3 species (see Section 2.4), they do not exist in the free state nor in solution. The transition from discrete ions to extended structures is such a fluid one especially in the thioarsenite system that it seems appropriate to also treat its condensation reactions. Preferred methods for the syntheses of transition metal complexes are the fragmentation of E_4X_n cages ($n = 3,4$) and the chalcogenation of pnicogen ligands. In contrast extraction of binary or ternary chalcogenide/pnictide phases in polar solvents, for example ethylenediamine and in the presence of large organic cations, and reactions in superheated or supercritical aqueous and nonaqueous solvents[3] give, depending on the conditions, discrete ions or more or less extended structures.

2.1. EX Ligands

Diatomic ligands exist in the coordination forms **I**–**IV** (Scheme 2); it is noticable that with the exception of one complex of type **II** (in which X = Se) sulfur has been employed as chalcogen X. In contrast to ligands containing one of the lighter elements N and O (one should note the rich complex chemistry of NO and NS,[12] but also the exotic PO[15]), there is a preferred tendency of the heavier elements for bridge formation. Semiempirical calculations[16] for the free molecules PO, PS, AsS, and AsSe indicate the following order for donor ability of the unpaired π electron located in the π* HOMO: PO > PS > AsS > AsSe. The energies of the two filled π bonding orbitals decrease in the reverse order AsSe > AsS > PS > PO; thus, better π-ligand-to-metal interactions are expected for AsSe, AsS, and PS than for PO.



I **II** **III** **IVa** **IVb**

Scheme 2. Different coordination types for diatomic EX ligands.

Joachim Wachter was born in 1945. After studying chemistry at the Universität München he received his Ph.D. in 1976 under the supervision of Prof. Dr. H. Brunner at the Universität Regensburg. In 1978/79 he spent a year as a postdoctoral researcher with Prof. J. G. Riess in Nice, in 1987 and 1992 he was invited to the University of Dijon as professeur associé. Since 1977 he has headed a research group at the Universität Regensburg. His main scientific interests are the organometallic chemistry of the chalcogens and the mixed ligands of Group 15/16 elements, and the cluster chemistry of highly reactive tellurium.

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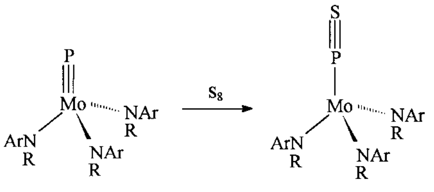
[*] Abbreviations used throughout the text: Cp = η^5-cyclopentadienyl, $Cp^{(*)}$ = any substituted Cp ligand, Cp* = C_5Me_5 and/or EtC_5Me_4, en = ethylenediamine, triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane, np_3 = tris(2-diphenylphosphinoethyl)amine, PPN = bis(triphenylphosphane)iminium.

The only example of coordination type **I** known to date is complex **1**. The existence of the terminal PS ligand was deduced from spectroscopic data and from the synthetic method [Eq. (1)]. Structural parameters are not yet available.[17]



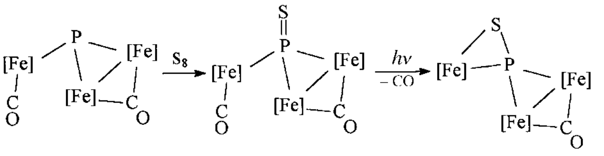
1

(1)

R = tBu, Ar = 3,5-$Me_2C_6H_3$

The symmetrical bridge of the coordination type **II** belongs to the large family of diatomic η^2 ligands, which are formed from homonuclear E_2 (E = P, As)[6] and X_2 (X = S, Se)[9,18] ligands. Homonuclear examples for the η^1:η^2 coordination type **III** are thus far only found in chalcogenide complexes (X = S,[19] Se[20]), a heteronuclear example will be given in Section 2.1.1.

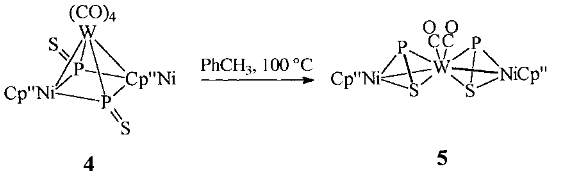
The coordination type **IVa** (X = S, E = P) is accessible by oxidative addition of sulfur to μ_3-P ligands (**2**, **4**).[21] This method should be more widely applicable because of the frequency of μ_3-E ligands (see also Eq. (6)). The μ_3-PS ligand ($d_{P\text{-}S}$ = 2.008(5) Å) in **2** is capable of eliminating CO under formation of **3**, in which a five-electron donor of coordination type **IVb** is present [Eq. (2)]; however, structural data are not yet available.[21a] Whereas in the latter ligand all valence electrons of phosphorus are used for coordination, the bis(dimetallatetrahedrane) **5** contains two η^2-PS ligands. These are formed from the μ_3-PS bridges of cluster **4** by a rearrangement of the skeleton and a redistribution of the electrons in the ligand [Eq. (3)].[21c]



2 **3**

(2)

[Fe] = $C_5H_5Fe(CO)$



4 **5**

(3)

Cp" = $C_5H_iPr_4$

A comparison of the P–S distances in **2**, **4**, and **5** allows a cautious assignment of single- and double-bond regions (Table 1). The value found for the PS radical[14] is even shorter than these values, and in this regard it is of interest that the unpaired π* electron is preferentially located at phosphorus.[16]

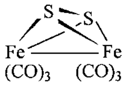
Table 1. Classification of diatomic EX ligands in transition metal complexes.

Ligand	Complex	$d_{E\text{-}X}$ [Å]	n[a]	BO[b]	Ref.
PS[c]	–	1.8977	–	2.5	[14]
μ_3-PS	**2**	2.008(5)	3	2	[21a]
μ_3-PS	**4**	1.952(2)	3	2	[21c]
μ,η^2-PS	**5**	2.092(2)	5	1	[21c]
μ,η^2-AsS	**7**	2.227(2)	5	1	[23]
μ,η^2-AsS	**8**(S)	2.165(2)	5	1	[24]
μ,η^2-AsSe	**8**(Se)	2.281(3)	5	1	[25]
μ,η^1:η^2-AsS	**14**	2.170(4)	3	1	[31]

[a] Number of valence electrons. [b] Formal bond order. [c] Obtained from a $PSCl_3$/He discharge.

2.1.1. η^2-Bridging Ligands (Type II)

The η^2-EX ligands have one less valence electron than the X_2 ligands; thus, in isostructural complexes with the same central metal an additional negative charge is required. This formalism can be illustrated with the pair of complexes $[Fe_2(S_2)(CO)_6]$ (**6**)[22] and $[Fe_2(AsS)(CO)_6]^-$ (**7**).[23] Complex **7** is formed by reductive coupling of $S_2O_4^{2-}$ and AsO_2^{2-} by $[Fe_3(CO)_{12}]$ under hydrothermal conditions, and serves as one of the first examples for the application of hydrothermal methods in organometallic chemistry.



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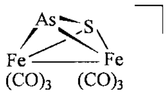
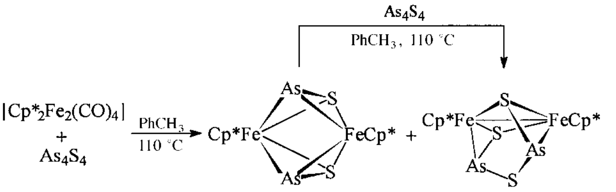


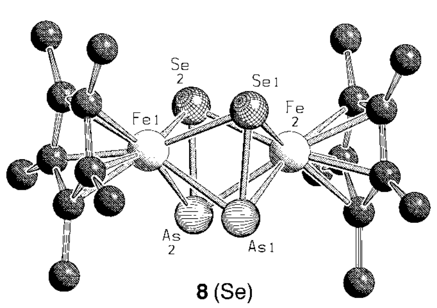
7

Two η^2-EX ligands form the core of the sandwichlike Cp*Fe complex **8**(S), which is obtained together with the topologically completely different complex **9** in the reaction of $[Cp^*_2Fe_2(CO)_4]$ with As_4S_4 in boiling toluene [Eq. (4)].[24] In contrast, the analogous reaction with As_4Se_4 gives exclusively $[Cp^*_2Fe_2As_2Se_2]$ (**8**(Se)) (Figure 1).[25]



8(S) **9**

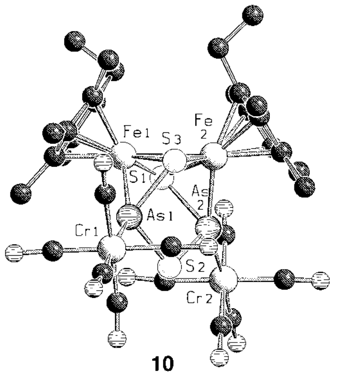
(4)



8 (Se)

Figure 1. Molecular structure of **8**(Se) in the crystal.

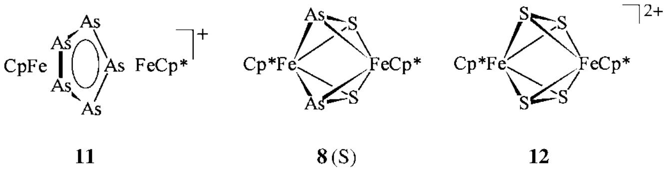
The structures of complexes **8** are characterized by two coplanar η^2-AsX bridges, whereas that of **9** contains a "basket" with an alternating AsS chain. Complex **8**(S) can be converted into **9** by reaction with mild sulfur donors [Eq. (4)]; the cage structure of **9** has been confirmed through the determination of the structure of the $Cr(CO)_5$ bisadduct **10** (Figure 2).[24] Although the incoming sulfur atom is incorporated between the two As atoms, a planar As_2S_3 ring is not formed (similar to the As_5 ring in **11**, see Scheme 3), but instead a five-membered twisted As–S chain. The $Cr(CO)_5$ groups in **10** are coordinated to both As atoms under considerable distortion of the tetrahedral geometry (angle Fe-As-Cr 145.8°). Further consequences of their steric interactions with the C_5Me_4Et ligands are the hindrance of free rotation of the cyclopentadienyl rings and the reformation of **9** by dissociation of the $Cr(CO)_5$ groups upon warming in solution.[24]



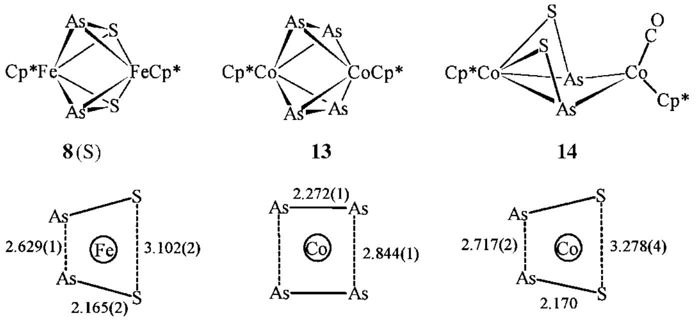
10

Figure 2. Molecular structure of $[(C_5Me_4Et)_2Fe_2As_2S_3\{Cr(CO)_5\}_2]$ (**10**) in the crystal.

Similar to the dication $[Cp^*_2Fe_2S_4]^{2+}$ (**12**),[26] complexes **8** possess 36 valence electrons (VE). From a structural point of view one may consider the "mixed" complex **8**(S) as a link between the "pure" sandwich complexes $[CpCp^*Fe_2As_5]^+$ (**11**)[27] (30 VE) and **12** (Scheme 3). The exclusive *cis* arrangement of the trapezoid-arranged AsS ligands gives rise to As–As distances in the range for single bonds (Scheme 4). The values of 2.629(1) Å (**8**(S)) and 2.587(3) Å (**8**(Se)), respectively, are at the upper limit of values determined to date for As–As bonds (e.g. 2.593(6) Å in β-As_4S_4[28] and 2.602(3) Å in diarsadisilabicyclo[1.1.0]butane[29]). In comparison the As_4 ligand plane in $[Cp^*_2Co_2As_4]$ (**13**) forms a rectangular middle deck in which the As_2 bridges are significantly separated from each other.[30]



Scheme 3. Examples for cyclopentadienyliron sandwich complexes containing homo- and heteroatomic ligands.



Scheme 4. Comparison of the structures of complexes **8**(S), **13**, and **14** made by slicing through the ligand plane.

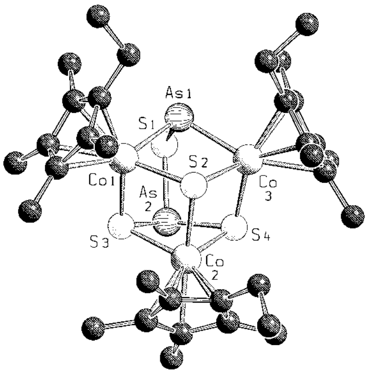
2.1.2. The η^1:η^2 Coordination Type III

Only one example is known for this coordination type thus far: In $[Cp^*_2Co_2(CO)(AsS)_2]$ (**14**) two η^1:η^2-AsS ligands form a trapezoid plane that is tilted towards one metal center.[31] The As–As distance is slightly longer than those in complexes **8** (see Scheme 4); in contrast, the As–S distances remain practically unchanged although each ligand now acts as a three-electron donor. A significantly longer As–S distance has been found in **7** (Table 1), which may be indicative of the π-acceptor properties of the EX ligands by increased back-donation through negative charge. Generally, all As–S distances discussed thus far are shorter than those reported for the trigonal AsS_3 pyramid (see Section 2.4.1).

Complex **14** is formed from $[Cp^*_2Co_2(CO)_2]$ and As_4S_4 as the main product in a relatively narrow temperature range around 80 °C. At higher temperatures formation of complexes **15**–**17** is favored, in which the As/S ratios deviate considerably from that in the starting material [Eq. (5)].[31] The structure of **15**[32]

$$[Cp^*_2Co_2(CO)_2] + As_4S_4 \xrightarrow{PhCH_3} \underset{\mathbf{14}}{[Cp^*_2Co_2(CO)As_2S_2]} + \underset{\mathbf{15}}{[Cp^*_2Co_2As_2S_3]} + \underset{\mathbf{16}}{[Cp^*_3Co_3As_2S_4]} + \underset{\mathbf{17}}{[Cp^*_3Co_3As_4S_2]} \qquad (5)$$

is analogous to that of **9**, apart from the lack of the metal–metal bond. Complex **16** also possesses an As_2S_3 core , but here a trigonal-pyramidal AsS_3 center acts as a triply bridging ligand; one arm of this is lengthened by one As (Figure 3). The structure of the arsenic-rich cluster **17** has not yet been determined.

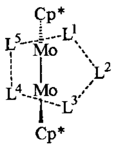


16

Figure 3. Molecular structure of $[(C_5Me_4Et)_3Co_3As_2S_4]$ (**16**) in the crystal.

2.1.3. Organometallic Sandwich Complexes

Sandwich complexes containing cyclopentadienyl Group 6 metal fragments and in particular their bonding have already been reviewed in detail, and thus they are mentioned only briefly here.[6]. In the combination with E/S ligands dimers of type **18** (M = Mo) are formed, in which parallel five-membered rings are the dominating structural element. Starting from *cyclo*-E_5^-[27] the substitution of E by S leads to increasing distortion within the central five-membered ring. As a consequence first separation into a pair of ES/E_3 and then S_2/E_2S bridging ligands is observed, accompanied by a continuous decrease of π bonding[6] from **18a, b**[33,34] ("(P/As)$_4$S") to **18c, d**[34] ("(P/As)$_2S_3$" rings).



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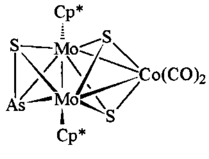


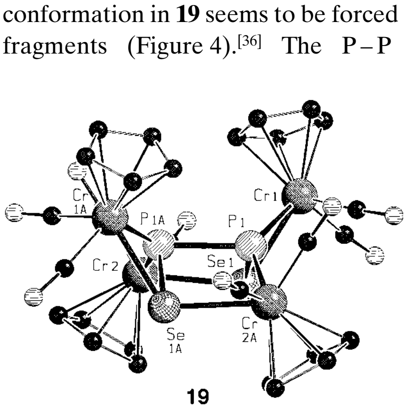
18e

	L¹	L²	L³	L⁴	L⁵
a	P	P	P	P	S
b	As	As	As	As	S
c	P	S	P	S	S
d	As	S	As	S	S

Formation of the 48-electron cluster **18e** from **18d** and $[Co_2(CO)_8]$ demonstrates that a main group ligand may be replaced by a complex fragment. All metal atoms achieve a closed valence shell in that the $Co(CO)_2$ fragment and the AsS ligand serve as 13-electron and 5-electron building blocks, respectively. The As–S distance in **18e**, the first example for an AsS ligand, is 2.237(3) Å.[35] As may also be replaced by P.

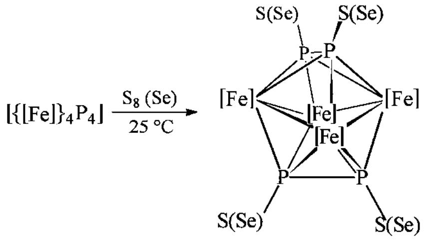
2.2. E_2X_2 Ligands

Whereas **8**(S) and **14** may be regarded at best as borderline cases for As_2S_2 ligands, a "real" P_2Se_2 ligand forms the backbone in $[\{CpCr(CO)_2\}_4P_2Se_2]$ (**19**), one of the many fragmentation products of the P_4Se_3 cage in its reactions with $[CpCr(CO)_3]_2$ (see Section 4.1.1). The approximate *Z*-like conformation in **19** seems to be forced by the four $CpCr(CO)_2$ fragments (Figure 4).[36] The P–P and P–Se distances (2.237(5) and 2.250(3) Å, respectively) are both in the ranges for single bonds. Nearly planar P_2X_2 ligands (X = S, Se) form the characteristic units in the clusters **20**.[37] They have been synthesized by chalcogen addition to the E_2 ligands in $[Cp_4Fe_4P_4]$ [Eq. (6)]; the overall geometry of the clusters does not alter. The P–P distances (av 2.38 Å) are not affected by the oxidation, whereas the P–S (av 1.965(8) Å) and P–Se distances (av 2.10 Å) are typical for double bonds (Table 1).



19

Figure 4. Molecular structure of $[\{CpCr(CO)_2\}_4P_2Se_2]$ (**19**) in the crystal.[36]



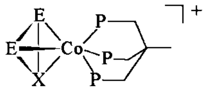
(6)

[Fe] = C_5H_5Fe

20

2.3. E_mX_{3-m} Ligands (m = 1,2; E = P, As; X = S, Se, Te)

The pseudo-tetrahedral clusters $[(triphos)Co(\eta^3\text{-}E_2X)]^+$ (**21**) contain the ligand combinations **a**–**e**, which are the preferred structural elements among triatomic E/X ligands.



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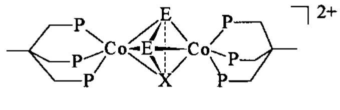


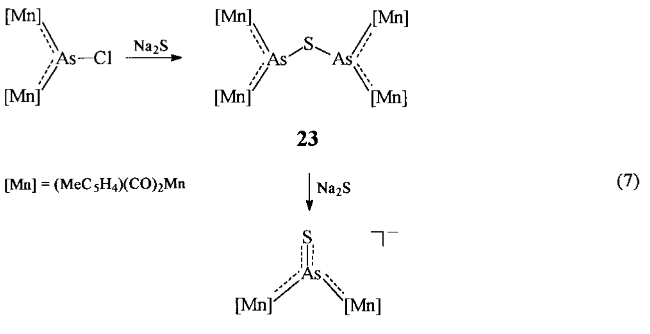
22 a, c

E	P	P	As	As	As
X	S	Se	S	Se	Te
	a	**b**	**c**	**d**	**e**

This class of compounds combines Co^{II} salts and triphos with the corresponding four-electron ligands, which arise from the fragmentation of E_4X_3 cage molecules (see Scheme 7) or As_2X_3 layers (X = Se, Te). Syntheses, structures, and reactions of these complexes have already been reviewed.[38] The electronic situation of the employed complex fragment determines whether heteroatomic (as in **21**) or homoatomic three-membered cycles (as in $[(triphos)Ni(P_3)]^+$[39] and $[Cp^*(CO)_2Mo(E_3)]$ (E = P, As)[34]) are extracted from the mixed E_4X_3 cage units.

Compounds **21a, c** react with (triphos)Co^{II} to form the salts **22a, c**. These compounds belong to the class of 32-electron triple deckers. In contrast to their η^3-P_3 analogues[40] the ligand plane in these complexes is strongly distorted as shown by two rather different As–S distances (2.336(5) and 3.099(6) Å).[41]

Complex **23** may be described as a bis(diarsinidene) compound in which sulfur functions as a bridge [Eq. (7)].[42] The trigonal-planar As atoms of the As_2S ligand are part of



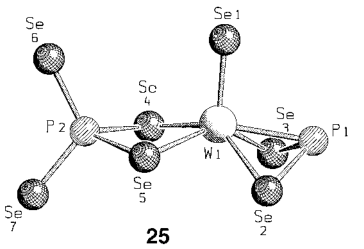
23

24

(7)

the original 4π-electron system together with all the Mn centers. Complex **23** reacts with excess sulfide under cleavage of the S bridge to give **24**, the four-center 6π-electron system of which exhibits a relatively short (Table 1) As–S distance of 2.123(3) Å.[42]

The only known example for an EX_2 ligand is in $[W(=Se)PSe_4(PSe_2)]^{2-}$ (**25**) (Figure 5), which crystallizes as a PPh_4 salt.[43] The structural parameters are in agreement with a side-on coordinated heteroallyl ligand of the formal charge −1, making it isoelectronic with NO_2^-. The selenophosphate ligand will be commented on in more detail in Section 3.1.



25

Figure 5. Structure of the dianion of $(PPh_4)_2$ **25** in the crystal.[43]

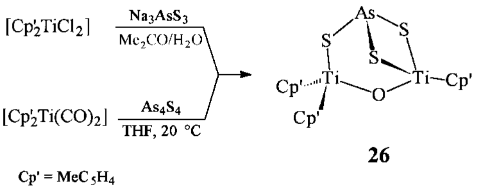
2.4. How Useful Are EX_3 Building Blocks as Ligands?

EX_3 building blocks are the only species among the di- to tetratomic element combinations that may be stabilized as ions in aqueous and nonaqueous solutions, though with some restrictions. In Nature they play an important role as the structure-determining component of the extensive mineral class of sulfosalts:[1] Trigonal ψ-EX_3 pyramids (E = As, Sb, Bi; X = S, Se, Te) with a stereochemically active lone pair of electrons (ψ) either form isolated EX_3 units or are "condensed" through common X bridges to give polymeric units of chains, bands, and rings.[44] As highly charged ligands they form mainly covalent solids with metals like Tl, Pb, Cu, Ag, Zn, Hg, Mn, Co, and Ni. For the complex and solid-state chemist, aspects of mineral genesis, that is the mobilization of thioarsenite, thioantimonite, and thiobismutite ions in the melt or in hydrothermal solutions as well as their conversion into the crystal lattice upon cooling[45] may be of interest in terms of the development of model systems based on soluble compounds as a means to understanding these processes. In the following it will be shown that through these efforts the number of potential ligands is growing rapidly.

2.4.1. *Chemistry of Discrete Thioarsenate(III)*

The simplest discrete thioanion of trivalent arsenic is obtained as Na_3AsS_3 by melting together Na_2S and As_2S_3.[46] Modern variants prefer the reaction of As_2S_3 with M_2S (M = K, Rb, Cs) in liquid NH_3.[47] Reaction of As_2S_3 with Na_2S in aqueous medium results in an unstable yellow solution, from which $(PPN)_3[AsS_3]$ may be isolated upon addition of (PPN)Cl.[48] Warming of such solutions leads under loss of sulfide and condensation to one-dimensional $NaAsS_2$ chains containing corner-linked AsS_3 pyramids (see Scheme 5).[49] In this context the question arises if and under what conditions the single steps of the condensations can be detected.

Initially, the first organometallic complex comprising an AsS_3 unit is presented: Complex **26** is formed in a metathesis reaction from $(PPN)_3[AsS_3]$ and $[(MeC_5H_4)_2TiCl_2]$ [Eq. (8)].[48] The only "flaw" is a μ-oxo ligand, which probably serves to stabilize the molecule. The same product is also obtained from the mild degradation of realgar As_4S_4 [Eq. (8)],[48] but it should be noted here that the starting material and the product possess different As–S connectivities (see Section 4.3). The electronically unequal Ti centers in **26** make the As–S distances in the AsS_3 bridge significantly different ($\Delta d = 0.07$ Å). In contrast to this the trigonal AsS_3 pyramid generally has equidistant As–S distances and equivalent S-As-S angles. An analysis of structural parameters of synthetic and natural sulfosalts reveals a range of 2.26–2.36 Å for d(As–S) and 98.0 ± 2° for the angles at As.[46, 50]

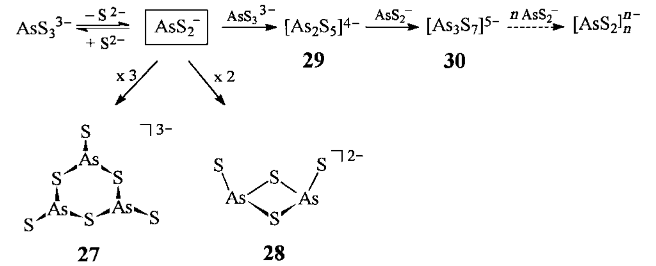


26

(8)

2.4.2. *Polymetathioarsenite Compounds*

AsS_3^{3-} solutions in liquid ammonia readily dissociate to give S^{2-} and metathioarsenite AsS_2^-.[51] Already in 1960 the investigation of the system AsO_2^-/HS^- under alkaline conditions led to the proposal of a trimerization of AsS_2^- to *cyclo*-$As_3S_6^{3-}$ (**27**) (Scheme 5).[52] Anion **27** is isolable in the form of $[As_3S_6]_2(enH_2)_3$,[53] by dissolving As_2S_3 in ethylendiamine;



29 **30**

27 **28**

Scheme 5. Partial steps of the metathioarsenite oligomerization realized under laboratory conditions.

the latter also provides the necessary protons for cation formation. In the chairlike **27** the exocyclic As–S bonds are about 0.15 Å shorter than the other As–S bonds.

The formally simplest oligomerization of AsS_2^- would lead to the dimer **28**. However, this ion has been synthesized only indirectly from As_4S_4 and potassium in the presence of 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane ([2.2.2]cryptand). Noteworthy in the structure of **28**[54] are the two edge-sharing AsS_3 pyramids; this building principle is not often observed in As/S sulfosalt chemistry.

The coordination potential of the anionic ligands is used in hydrothermal syntheses. In general a metal salt and a thioarsenate(III) substrate are heated under conditions given in Table 2.[3] The degree of condensation as well as the conformation of the chains are determined by the metal cations. Eventual excess of negative charge is compensated by large organic cations (e.g. Ph_4P^+, Me_4N^+), which can thus function as spacers between the anionic chains.

The simplest species in the metathioarsenite oligomerization (Scheme 5) is $[As_2S_5]^{4-}$ (**29**), which is realized in the reduction of MoO_3 by K_3AsS_3 (Table 2) as infinite sinusoidal chains in $[Mo_2O_2As_2S_7]_n^{2n-}$ (**31**) (Scheme 6).[55] In this compound **29** acts as a double chelate bridging two molecular $[Mo_2O_2S_2]^{2+}$ units. The thiophilic character of the latter is well documented in many coordination compounds with sulfides and polysulfides.[56] If, however, the original building blocks are connected in an all-*cis* configuration formation of soluble cyclic compounds should be possible, such as $[Mo_2O_2As_2S_7]_2^{4-}$ (**32**). The synthesis of this compound was postulated 13 years ago by Rauchfuss by an alternative route (see Section 3.4).[48]

The combination $BiCl_3/Rb_3AsS_3$ (Table 2) yields a two-dimensional network composed of the cyclic anion **27** and octahedrally coordinated Bi^{3+} ions. The layers are separated from each other by Me_4N^+ and Rb^+ ions.[47] The following member in the series is $[As_3S_7]^{5-}$ (**30**) (see Scheme 5), which may be realized by reaction of $InCl_3$ with K_3AsS_3 (Table 2). The insertion of an additional AsS_2 unit provides a further coordination site; thus, In^{3+} achieves the coordination number 5 (Figure 6).[47] In the dianion $[Hg_2As_4S_9]^{2-}$ (**33**) trigonal-planar Hg^{II} forms with the As_4S_9 chain eight-membered rings, which function as subunits of a one-dimensional structure.[57] At the end of the reaction sequence polymeric chains, such as in $NaAsS_2$[49b, c] or $TlAsS_2$[58] are obtained. Common to all these compounds are edge-linked AsS_3 pyramids, the formation of which may be explained by "condensation" of AsS_3^{3-} under loss of sulfide.

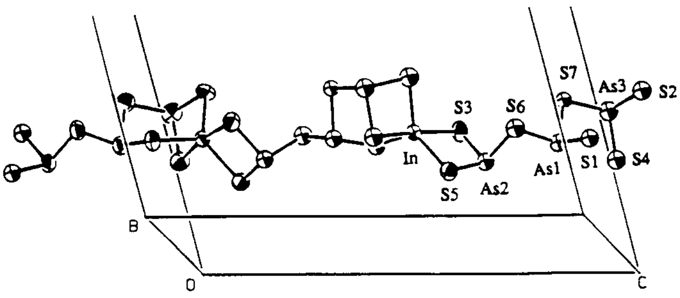
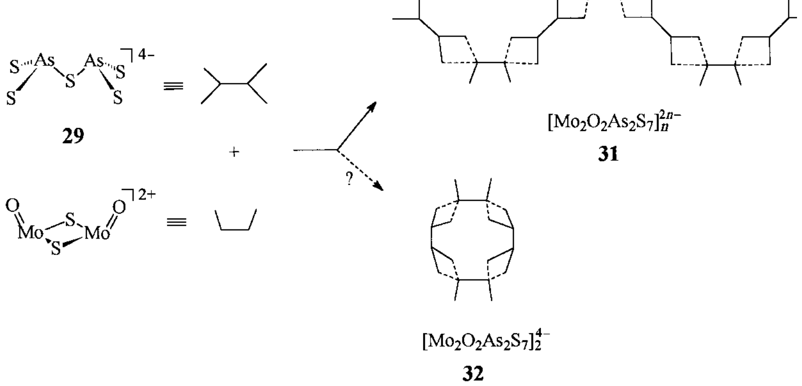


Figure 6. View of an $InAs_3S_7$ chain in the lattice of $(Ph_4P)_2[InAs_3S_7]$.[47]

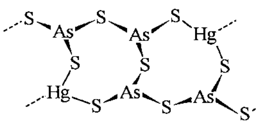
Table 2. Routes to thioarsenate(III) and selected polymetathioarsenite compounds.

Compound	As/S structural element	Starting materials	Reaction conditions	Ref.
M_3AsS_3	ψ-pyramid	As_2S_3, S_8, M (M = K, Rb, Cs)	NH_3 (liq)	[47]
Na_3AsS_3	ψ-pyramid	As_2S_3, Na_2S	melt	[46]
$(PPN)_3[AsS_3]$	ψ-pyramid	As_2S_3, Na_2S, (PPN)Cl	H_2O/EtOH	[48]
$[Cp'_3Ti_2(AsS_3)O]$ **26**[a]	ψ-pyramid	$[Cp'_2TiCl_2]$, Na_3AsS_3	acetone/H_2O	[48]
$[K(crypt)]_2[As_2S_4]$	**28**	As_4S_4, K, [2.2.2]cryptand	NH_3 (liq); CH_3CN	[54]
$(enH_2)_3[As_3S_6]_2$	**27**	As_2S_3, en	en, 20 °C	[53]
$(Me_4N)_2Rb[BiAs_6S_{12}]$	**27**	$BiCl_3$, Rb_3AsS_3, Me_4NCl	H_2O, 120 °C	[47]
$(Me_4N)_2[Mo_2O_2As_2S_7]$	**29**	MoO_3, K_3AsS_3, Me_4NCl	H_2O, 110 °C	[55]
$(Ph_4P)_2[InAs_3S_7]$	**30**	$InCl_3$, K_3AsS_3, Ph_4PBr	H_2O, 120 °C	[47]
$(Ph_4P)_2[Hg_2As_4S_9]$	**33**	$HgCl_2$, K_3AsS_3, Ph_4PBr	H_2O, 130 °C	[57]
$NaAsS_2$	$[AsS_2]_\infty$	As_2S_3, Na_2S	H_2O, 80 °C	[49]
$TlAsS_2$	$[AsS_2]_\infty$	As_2S_3, Tl_2S	H_2O, 225–340 °C	[58]

[a] $Cp' = MeC_5H_4$.



Scheme 6. Schematic representation of the synthesis of one-dimensional **31**[55] and cyclic **32**[48] from $[As_2S_5]^{4-}$ (**29**) and $[Mo_2O_2S_2]^{2+}$.

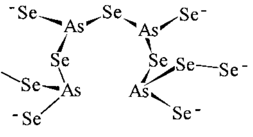


33

Although the anions shown in Scheme 5 are preferentially incorporated into covalent lattices, **27** and **28** may also be obtained in discrete form. The single steps represented by the anionic ligands **27**–**30** may be considered as a model for the formation of sulfosalt minerals. Indeed *cyclo*-$[As_3S_6]^{3-}$ (**27**) exists as the essential unit in trechmannite, $AgAsS_2$,[59] and in axial conformation of the exocyclic sulfur atoms in smithite, $AgAsS_2$.[60] In contrast baumhauerite, $Pb_3As_4S_9$, is composed of As_3S_7 (**30**), As_4S_9, and As_5S_{11} chain fragments.[61] Examples for naturally occurring infinite chains are $TlAsS_2$ (lorandite),[62] which is also the first sulfosalt synthesized in the laboratory[58] (Table 2), and $PbAs_2S_4$[63] (sartorite).

2.4.3. Sulfosalt Compounds of the Heavier Homologues Sb, Bi and Se, Te

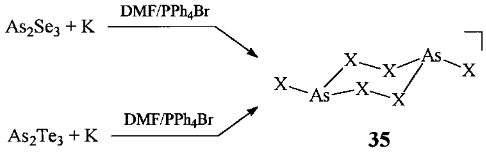
Compounds of the heavier homologues Sb, Bi, and Se, Te exhibit an increasing tendency for the formation of complex anions with a cage structure.[4, 64] Some of these anions have already been tested successfully as ligands in transition metal complexes (see Section 3). The following examples comprising structural elements analogous to the sulfosalts in Scheme 5 warrant mention in this context: the Se analogue of **27**[65] and the Sb/Se analogue of **28**[54] as discrete anions as well as the Se analogue of **29**[55] and the Sb analogue of **30**[66] in low dimensional structures ($[Mo_2O_2(\mu\text{-}Se_2)As_2Se_5]^{2-}$ and $[Ag_3Sb_3S_7]^{2-}$, respectively). However, analogies between the chemistry of thio- and selenoarsenates cannot always be drawn. For instance, the system $HgCl_2/K_2AsSe_3/Me_4NCl$ forms the novel structural unit **34** under conditions given in Table 2, and not the expected anion $[As_4Se_9]^{6-}$ (**33**):[67] Self-condensation of $AsSe_3^{3-}$[10] leads in this case to an $AsSe_4$ subspecies containing Se–Se bonds (see Section 3.2).



34

Like the As sulfosalts, ternary phases of the composition $MAsSe_2$ (M = Na, K, Rb, Cs) also consist of infinite chains,[68] as does $(NEt_4)[BiSe_2]$, which is very sensitive to hydrolysis.[69] The first selenobismutate is soluble in ethylendiamine and CH_3CN, probably under chain fragmentation. In contrast, the anionic $SbSe_2$ chains in $KSbSe_2$ consist of edge-sharing ψ-$SbSe_4$ tetrahedra.[70]

It is expected that anionic clusters, extracted from binary phases in strongly basic solvents and in the presence of suitable cations,[4] may be good candidates for ligands. How such compounds might appear is demonstrated by the cyclic dianions **35**, which have already gained some importance as ligand precursors (see Section 3.2). Formally, they may be formed by oxidative cyclization according to $2\,EX_3^{3-} \rightarrow E_2X_6^{2-} + 4\,e^-$, but actually the best synthesis is reduction of As_2Se_3[71] or As_2Te_3 [72,73] with potassium in DMF [Eq. (9)]. The system is very sensitive towards solvent effects, as has been reported elsewhere in detail.[74]



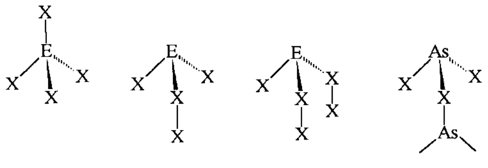
(9)

35
(X = Se, Te)

3. Mixed Zintl Anions as Ligands

In the synthesis of the molecular sulfosalt compounds **27** and **28** it has already been pointed out that basic solvents are able to convert binary E/X phases by electron transfer reactions under mild conditions into complex Zintl anions. This action is enhanced by working in polar solvents (e.g. DMF, en) and in the presence of alkali metals. The stabilization of the cluster anions is achieved by using large counterions, such as Me_4N^+ and Ph_4P^+, or by the addition of cryptands.[4,5]

For the application as ligands in transition metal complexes the mixed main group clusters prepared in this way must be selectively accessible and soluble in organic solvents. These conditions are best fulfilled by the cyclic anions $[As_2X_6]^{2-}$ (**35**) and $[P_2Se_8]^{2-}$ (**36**) (see Section 3.1), but it must be noted that these have never been incorporated completely into transition metal complexes; instead they are fragmented into penta- or hexaatomic E/X ligands. Pentaatomic E/X ligands may be divided into the subgroups **V** (central atom E with coordination number 4) and **VIa** (a trigonal-pyramidal structure type closely related to the sulfosalts, coordination number 3). Formally both structure types are related by the redox equation $\mathbf{V}^{3-} + 2\,e^- \rightleftharpoons \mathbf{VIa}^{3-}$. The examples realized thus far demonstrate that the equilibrium in the presence of transition metal complexes is on the right-hand side for arsenic chalcogenides, which favors the formation of X–X bonds. Heavier chalcogenides may form another dichalcogenido arm (**VIb**). If at the end of the side chain of **VIa** X is replaced by As, **VIc** is obtained; this structure type is realized for X = S in the μ_3-As_2S_3 ligand of **16**. Similar to tetrachalcogenido ligands[9c, 75] the dichalcothioarsenites **VIa**, **b** preferentally form five-membered chelate rings with metal ions of mostly covalent nature.



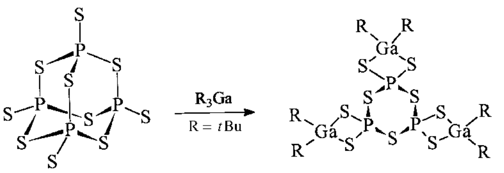
a **b** **c**

V **VI**

3.1. Thio- and Selenophosphate Complexes

In contrast to the abundance of ternary and quaternary solid-state compounds with anionic P/S and P/Se ligands,[76] molecular complexes with P/X ligands are still relatively rare. This is evidently related to the difficulties arising from the transfer of discrete PX_4^{3-} ions into compounds that are soluble in organic solvents, although they may be isolated from aqueous solutions as hydrates.[4]

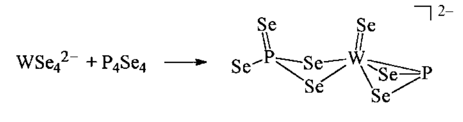
The first molecular example of a cyclic phosphorus(v) sulfide is **37**, which is obtained in the reaction of P_4S_{10} with tBu₃Ga [Eq. (10)] upon formally removing a P=S group from the top of the adamantane skeleton. The core of the molecule is a twisted P_3S_3 ring in which the integrated thiophosphate groups now function as chelate agents.[77]



(10)

37

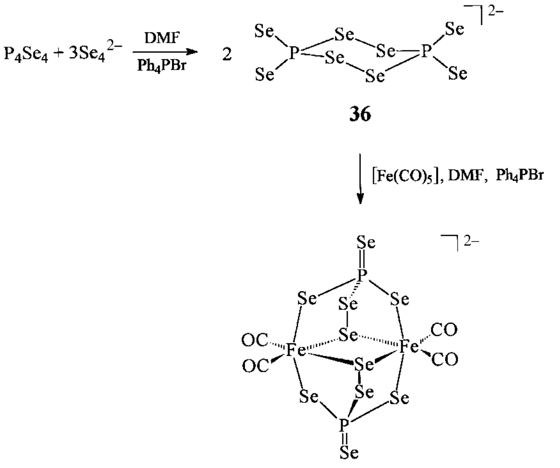
The only known molecular example for a complex with the PSe_4 unit is $[W(=Se)PSe_4(PSe_2)]^{2-}$ (**25**).[43] This compound is obtained from vitreous P_4Se_4 and $(Ph_4P)_2[WSe_4]$ [Eq. (11)]. It contains along with the side-on coordinated PSe_2 ligand a bidentate PSe_4 group, which most likely arises from oxidative Se addition at trivalent phosphorus (see Figure 5).



(11)

25

The usefulness of selenophosphates as ligands is documented by the cyclic phosphorus selenide **36**, which reacts with $[Fe(CO)_5]$ to give the dinuclear Fe^{II} complex **38** [Eq. (12)].[78]



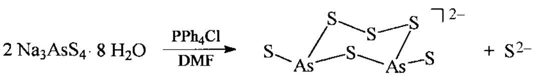
(12)

38

The original geometry around the P atom is maintained, but there is an increased amount of Se found in the two perselenophosphate ligands, which may indicate an intermediate existence of free selenium.

3.2. Dichalcoarsenate(III) Complexes

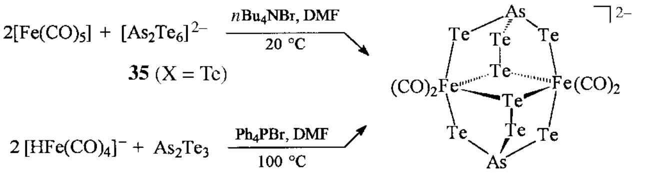
The lability of pentavalent thioarsenate is evident from the problems that arise when trying to convert Na_3AsS_4 hydrate into a salt soluble in organic solvents [Eq. (13)]: Upon loss of sulfide the six-membered ring **39** is formed, which is isomeric with **35** (X = S).[79] [Eq. (13)]. It contains two sulfur segments of different length and two As^{III} centers. In contrast to this system, solutions of SbS_4^{3-} in ethylenediamine seem to be sufficiently stable.[69]



(13)

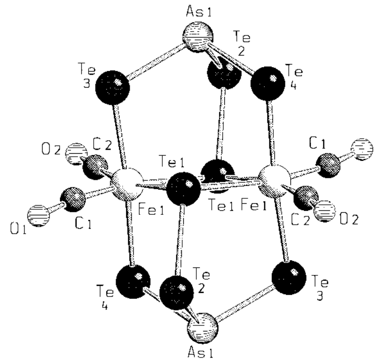
39

Whereas the ligand ability of **39** has not yet been tested, the cyclic dianion **35** (Te) reacts with $[Fe(CO)_5]$ to give **40** [Eq. (14)], which exibits a geometry comparable to that of **38** (Figure 7).[73] This means that also in this reaction dichalcogen side arms are formed contrary to the original stoichiometry. Interestingly the same result is obtained upon reduction of As_2Te_3 glass with $[HFe(CO)_4]^-$ [Eq. (14)], demonstrating that binary E/X phases may also be converted into mixed anionic cage ligands by means of nucleophilic transition metal complexes.



(14)

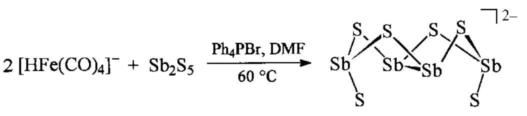
40



40

Figure 7. Structure of the dianion of $(nBu_4N)_2$-**40** in the crystal.[73]

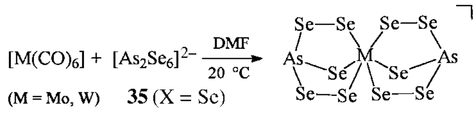
In contrast, base reduction of Sb_2S_5 with the same carbonyl reagent does not lead to a novel complex, but instead to the new main group cluster $[Sb_4S_6]^{2-}$ (**41**) with SbS wingtips in an unusual conformation [Eq. (15)].[80]



(15)

41

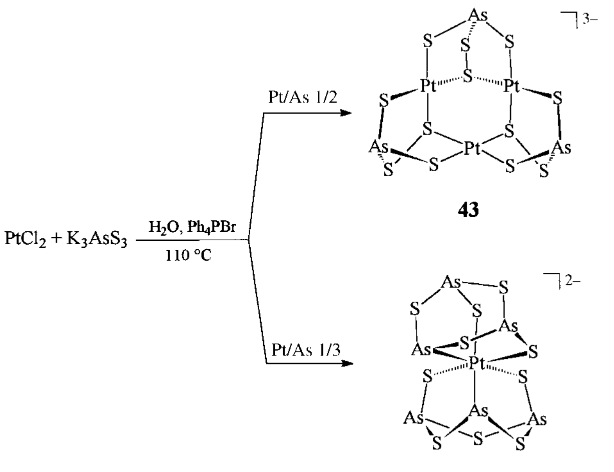
In principle the trigonal As^{III} pyramid is maintained during the reactions described by Equations (14) and (16) (see below). This means that liberated chalcogen, which is obtained from partial decomposition of the ligand, is employed for the construction of new X–X bonds. Unusual large Se/metal ratios characterize the complexes **42** that are synthesized by complete decarbonylation of $[M(CO)_6]$ (M = Mo, W) under mild conditions [Eq. (16)].[81] The coaxial arrangement in the two $AsSe_5$ cages is striking, and may be explained by weak contacts (Se ··· Se 2.702–3.017 Å) between opposite Se atoms. The reaction type described in Equations (12), (14), and 16 resembles, in principle, the oxidative decarbonylation of metal carbonyls by polyselenides and polytellurides.[75] However, the creation of a new branching point by incorporation of the trivalent arsenic into the MX_4 ring causes a new electronic situation for the central metal.



42

(16)

Under hydrothermal conditions AsS_3^{3-} buildung blocks may undergo not only condensation reactions but also the formation of discrete clusters [Eq. (17)]. Depending on the Pt/As ratio $[Pt_3(AsS_4)_3]^{3-}$ (**43**) and $[Pt(As_3S_5)_2]^{2-}$ (**44**) are formed from $PtCl_2$ and K_3AsS_3, both of which differ in terms of the oxidation states of Pt.[82] The dominating structural element in **43** (planar environment for Pt^{II}) are three AsS_4 groups of type **VIa**. The structure of **44** is characterized by two As_3S_3 rings, which with one of the As atoms and as well as two additional S atoms generate an octahedral environment at the Pt^{IV} center. This might indicate a possible participation of *cyclo*-$[As_3S_6]^{3-}$ (**27**), which would then be reduced by the originally present Pt^{II} to give $[As_3S_5]^{3-}$ and sulfide.[82]

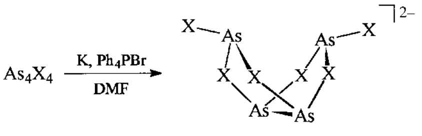


44

(17)

3.3. Stabilization of Cage Anions in Metal Carbonyl Complexes

The $[As_4X_6]^{2-}$ compounds **45**[54, 71b, 83] are mixed cluster anions in which the basic realgar framework is still recognizable [Eq. (18)]. The nucleophilic AsX wingtips and the lone pairs of electrons of the cradle should increase the reactivity. Indeed reactions of **45**(Se) with transition metal carbonyl complexes exhibit reactivities between that of polychalcogenides[9c,75] and that of classical Zintl anions like E_7^{3-},[84] since depending on the metal carbonyl used not only M–X, but M–E bonds are formed.

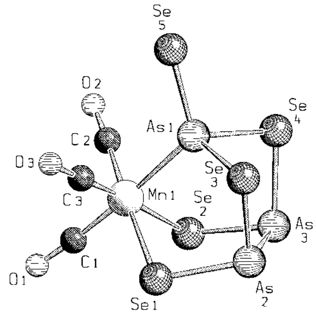


X = S, Se **45**

(18)

To date, all investigations have been carried out with $[As_4Se_6]^{2-}$ (**45**(Se)), which reacts with $[Mn_2(CO)_{10}]$ to give the cluster **46** [Eq. (19)]. The core of the molecule may formally be derived from the realgar cradle in that an As atom is replaced by a $Mn(CO)_3$ fragment (Figure 8).[73] Thus **45**(Se) already contains most of the preformed building blocks, since only the elimination of terminal "AsSe" seems to be necessary, whereas the final cyclization is achieved by coordination of As1 at Mn1. The As–Se distances in **46** may be divided into three categories: As1–Se5 (2.254(4) Å) is 0.07 Å shorter than As2–Se1 and 0.16 Å shorter than As1–Se3. The average As–Se distance of 2.354(4) Å is in a good agreement with the length expected for As–Se single bonds. Overall the ligand may be regarded as a six-electron donor of the formal charge −3, which results in a Mn^I center with 18 valence electrons.

$$[Mn_2(CO)_{10}] + \underset{\mathbf{45}\,(Se)}{[As_4Se_6]^{2-}} \xrightarrow[100\ °C]{Ph_4PBr,\ DMF} \underset{\mathbf{46}}{[Mn(CO)_3(As_3Se_5)]^{2-}} \qquad (19)$$



46

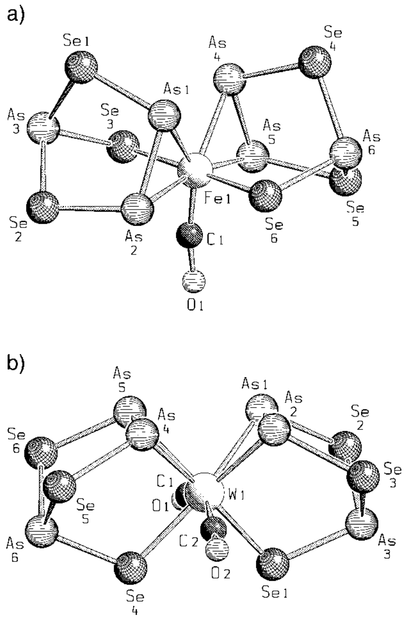
Figure 8. Structure of the dianion of $(Ph_4P)_2$-**46** in the crystal.[73]

The complexes **47**[73] and **48**[81] are formed in the oxidative decarbonylation reaction of $[Fe(CO)_5]$ or $[M(CO)_6]$ (M = Mo, W) with **45**(Se) [Eq. (20)]. They may also be derived from known E/X cage structures, since they belong to the type of metal-substituted E_4X_3 cages in which one basal E atom is replaced by a ML_n fragment (see Section 4.2). In **47** and **48** two As_3Se_3 building blocks share a metal center as common corner. Although different conformations of the cages relative

$$\underset{\mathbf{45}(\mathrm{Se})}{[\mathrm{Fe(CO)_5}] + [\mathrm{As_4Se_6}]^{2-}} \xrightarrow[100\ ^\circ\mathrm{C}]{\mathrm{DMF}} \underset{\mathbf{47}}{[\mathrm{Fe(CO)(As_3Se_3)_2}]^{2-}} \qquad (20\mathrm{a})$$

$$\begin{tikzcd} \underset{\mathbf{45}(\mathrm{Se})}{[\mathrm{M(CO)_6}] + [\mathrm{As_4Se_6}]^{2-}} \arrow[r, "\mathrm{DMF}", "100\ ^\circ\mathrm{C}"'] & \underset{\mathbf{48}}{[\mathrm{M(CO)_2(As_3Se_3)_2}]^{2-}} \arrow[d, "\mathrm{Se_8}"] \\ \mathrm{M = Mo, W} & \underset{\mathbf{42}}{[\mathrm{M(AsSe_5)_2}]^{2-}} \end{tikzcd} \qquad (20\mathrm{b})$$

to each other are possible only those with neighboring arsenic atoms are observed; slight differences in the arrangement of such As atoms are apparent in **47** and **48** (Figure 9). There is no explanation for the comparably short As–As distances (e.g. 2.381(4) Å in **47**) within the cage ligands (see Table 3).



47

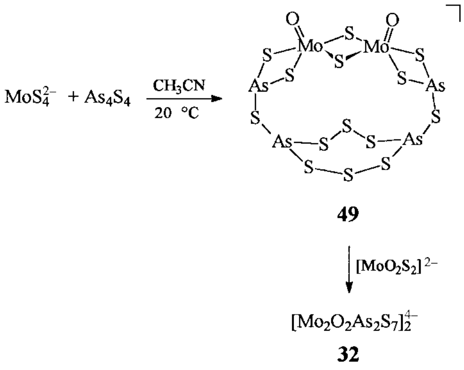
48

Figure 9. The different conformations of the As_3Se_3 cages in a) **47**[73] and b) **48**[81] (Schakal plots). Counterion in the crystallographically investigated salts is $[Ph_4P]^+$.

Complex **47** may also be obtained by reduction of As_4Se_4 with $[HFe(CO)_4]^-$ in DMF at 100°C. By contrast, under similar conditions As_2Te_3 gives the completely different structure **40** (see Eq. (14)). This difference might be a consequence of the different structures of the binary phases. The As_3Se_3 subunits in **48** can be transformed into polyselenidearsenate(III) ligands of type **VIb** in **42** by reaction of **48** with red selenium under elimination of CO [Eq. (20b)]. Notably, there is no oxidative addition of Se to arsenic under formation of structure type **V**, but a substitution of all As by Se atoms, which, in turn, reduces the degree of branching in the cradle.[81]

3.4. Cage Building Blocks Based on Tetrathio and Tetraseleno Metalates

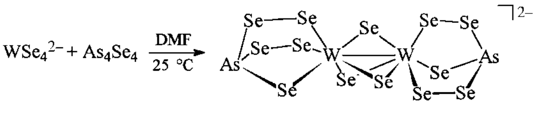
Neutral cage molecules like As_4S_4 can be converted into mixed E/X cluster anions by alkali metal chalcogenides.[4] Similar nucleophilic effects are exerted by tetrathio and tetraselenometalates. The first reaction in this sense was that of MoS_4^{2-} with As_4S_4 [Eq. (21)] , in which the product **49** is a combination of the complex fragment $[Mo_2O_2S_2]^{2+}$ and an $As_4S_{12}^{4-}$ chelate ligand.[48] The origin of the oxygen ligand is unclear. The close relationship to complexes containing sulfosalt units is demonstrated by the reaction of **49** with $[MoO_2S_2]^{2-}$ in which the excess sulfur is eliminated.[48] It is very likely that **32** possesses a cyclic structure in which $As_2S_5^{4-}$ units (**29**) may function as tetradentate chelate ligands (see Scheme 6).



(21)

In contrast, tetraselenometalates MSe_4^{2-} (M = Mo, W) form with As_4Se_4 clusters like **42** and **50** [Eq. (22)], which both contain $AsSe_5^{3-}$ ligands but have metals in different oxidation states. In the dinuclear tungsten(V) complex **50** a $W_2Se_3^{4+}$ core links the "terminal" cage ligands, which are slightly twisted towards each other.[85] Another method for the preparation of **42** (M = Mo) is the decarbonylation of $[Mo(CO)_6]$ with $[As_2Se_6]^{2-}$ (see Equation (16)). The reaction of WSe_4^{2-} with P_4Se_4 belongs to the same reaction type, and has already been outlined in Equation (11), but it gives a completely different result.

$$MoSe_4{}^{2-} + As_4Se_4 \xrightarrow[25\ ^\circ\mathrm{C}]{\mathrm{DMF}} \underset{\mathbf{42}}{[\mathrm{Mo(AsSe_5)_2}]^{2-}} \qquad (22\mathrm{a})$$



(22b)

50

4. Activation of Neutral Cage Molecules

Among the mixed neutral main group clusters, the coordination chemistry of the cage molecules E_4X_n (n = 3,4; E = P, As; X = S, Se) has been investigated in detail.[38, 86] In contrast to mixed complex anions, "primary" complexes can be isolated under mild conditions with reactive transition metal complexes, that is intact inorganic cages stabilized by Lewis acidic complex fragments or peripheral sterically demanding groups from organometallic components or multidentate phosphane chelates. Their stability is a function of the reaction partners and reaction conditions, which gives rise to very diverse fragmentation patterns and thus to the formation of ligand fragments of different size. As it is evident that all fragmentation reactions proceed via primary products, these will be discussed first.

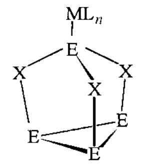
4.1. Primary Complexation

4.1.1. E_4X_3 Cages (E = P, As; X = S, Se) as Ligands

E_4X_3 compounds exist as molecular cradles that are derived from the tetrahedron.[86] The compounds are easily synthesized by fusing together the elements, they are sufficiently soluble in organic solvents, and most importantly they possess reactive centers the nucleophilicity of which differ considerably.

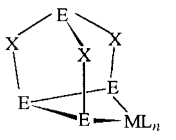
Sterically demanding Lewis acidic complex fragments like $[M(CO)_5]$ (M = Mo, W) [87] and $[(np_3)M]$ (M = Ni, Pd)[88] coordinate to P_4X_3 (X = S, Se) to give complexes of the apical type **51**. The coordination pattern is in agreement with the electronic structure of P_4S_3, which predicts donor properties for the apical phosphorus comparable to those of tertiary phosphanes. The basal P_3 unit, however, should behave more like P_4.[89] Indeed edge-opening reactions are typical for P_4[90] and As_4.[30] Thus, oxidative addition of Ir^I or Pt^0 metal fragments to P_4S_3 leads to the complex type **52**.[91] The electronically unsaturated products dimerize or trimerize to yield stable aggregates (see Scheme 7, Section 4.2).

The complexation of intact As_4S_3 seems to be much more difficult, since to date there is only proof for one example each of η^1 (**51d**)[92] and η^2 coordination (**52c**) (Table 3).[31] Apical coordination as well as insertion into the base do not significantly influence the distances within the E_4X_3 cage, with the exception of the cleaved E–E bonds, which are clearly elongated.



51

E = P, As; X = S, Se

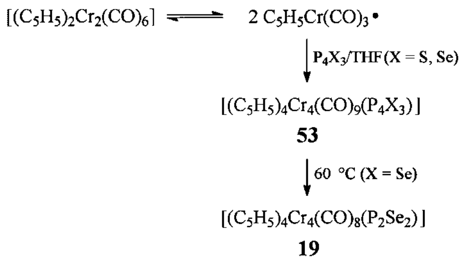


52

ML$_n$: see Table 3

Curiously, for a definite metal fragment there exists only one corresponding complex type. Therefore it is not yet known if there is any link between both forms **51** and **52**; for instance, in the form of a migration of a metal from the top to the base, and what role the X atoms might play in this. It would be important in this context to prove coordination to the sulfur bridge atoms, which in principle might be expected because of the excellent suitability of sulfur ligands as nucleophiles with respect to 16-electron complex fragments.[93] A first indication for the participation of bridging sulfur is the addition of up to four $M(CO)_5$ fragments (M = Mo, W) to P_4S_3. Nevertheless, there is only spectroscopic evidence and the structures have not been cofirmed.[86]

The role of organometallic radicals in the activation of the cages has still not been investigated in detail. A first example is the reaction of P_4X_3 (X = S, Se) with $(C_5H_5)Cr(CO)_3$ radicals arising from $[(C_5H_5)_2Cr_2(CO)_6]$ [Eq. (23)]. The for-



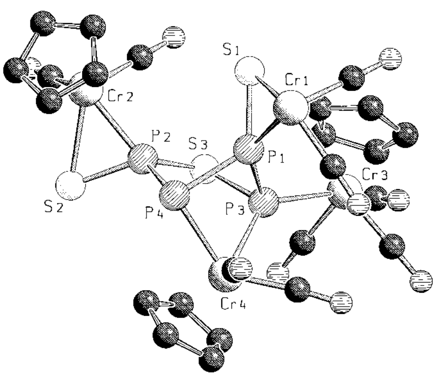
(23)

Table 3. E–E and E–X distances in complexes with $E_4X_{4(3)}$ and E_3X_3 building blocks and in the inorganic precursor cages.

Complex	n[a]	d(E–E) [Å]	d(E···E) [Å]	d(E_{bas}–X) [Å]	d(E_{ap}–X) [Å]	Ref.
$[(CO)_5Mo(P_4S_3)]$ **51a**	0	2.24(1)		2.12(4)	2.13(1)	[87]
$[(np_3)Ni(P_4S_3)]$ **51b**	0	2.23(1)		2.09(1)	2.12(1)	[88a]
$[(np_3)Ni(P_4Se_3)]$ **51c**	0	2.21(1)		2.238(5)	2.280(3)	[88b]
$[(CO)_5Cr(As_4S_3)]$ **51d**	0	2.484(5)		2.21(1)	2.21(1)	[92]
$\{IrCl(CO)(P_4S_3)(PPh_3)\}_2$ **52a**	1	2.265(5)[c]	3.055(5)			[91a]
$[Pt(P_4S_3)(PPh_3)]_3$ **52b**	1	2.22(1)	3.03(3)	2.11(2)[c]	2.10(2)[c]	[91b]
$[(C_5Me_4Et)Co(CO)(As_4S_3)]$ **52c**	1	2.470(1)	3.251(4)	2.209(4), 2.263(3)[b]	2.252(4)	[31]
$[(C_5H_5)_4Cr_4(CO)_9(P_4S_3)]$ **53a**	3	2.201(5)[c]		2.001(4)[d]		[94a, c]
$[(C_5H_5)_4Cr_4(CO)_9(P_4Se_3)]$ **53b**	3	2.237(5)[c]		2.250(3)[d]		[94b]
$[(C_5Me_4Et)Co(CO)(As_4S_4)]$ **54a**	1	2.519(6)	3.714(6)	2.252(7)[c]		[31]
$[(triphos)Rh(P_3S_3)]$ **57a**		2.165(6)				[100]
$[(triphos)Ir(P_3S_3)]$ **57b**		2.164(7)				[100]
$[(triphos)Rh(P_3Se_3)]$ **57c**		2.15(1)				[100]
$[Fe(CO)(As_3Se_3)_2]^{2-}$ **47**		2.381(4)		2.403(5)[c]	2.358(5)[c]	[73]
$[W(CO)_2(As_3Se_3)_2]^{2-}$ **48** (M = W)		2.356(7)[c]		2.440(7)[c]	2.354(8)[c]	[81]
P_4S_3		2.23(1)		2.09(1)	2.09(1)	[105]
P_4Se_3		2.22(1)		2.24(1)	2.24(1)	[106]
As_4S_3		2.45(1)		2.20(1)	2.22(1)	[107]
As_4S_4		2.569(1)[c]		2.237(2)[c]		[2, 28]
As_4Se_4[e]		2.57(1)		2.38(1)		[108]

[a] Number of edge openings. [b] Metal-coordinated As. [c] Average value. [d] $P-X_{terminal}$. [e] Structural parameters of As_4Se_3 are not known.[109]

mation of $[(C_5H_5)_4Cr_4(CO)_9(P_4X_3)]$ (**53a**) (X = S) and **53b** (X = Se) requires the cleavage of P–P *and* P–X cage bonds. As consequence of the formation of a new P–P bond in **53a** a central P_4S ring, in which all P atoms are linked to each other, is the characteristic feature (Figure 10).[94] The Cr centers are either directly attached to the ring or coordinated to the peripheral P/X groups. Complexes **53a** and **53b** are thermally unstable, and lead to a series of fragmentation products (see below). The first isolable intermediate product in the case of **53b** is $[(C_5H_5)_4Cr_4(CO)_8(P_2Se_2)]$ (**19**) (see Equation (23) and Figure 4).



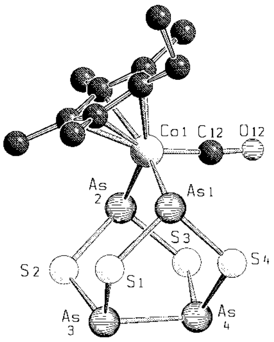
53a

Figure 10. Molecular structure of $[Cp_4Cr_4(CO)_9(P_4S_3)]$ (**53a**)[94] in the crystal. The Cp ring at Cr1 is omitted for clarity.

Only a few studies are known concerning the numerous other phosphorus sulfides that are derived from the P_4 tetrahedron. For example, the $P_4S_7/Mo(CO)_6$ system is handicapped by the low solubility of the inorganic cage and light sensitivity of the products.[86]

4.1.2. *Complexes with As_4S_4 Ligands*

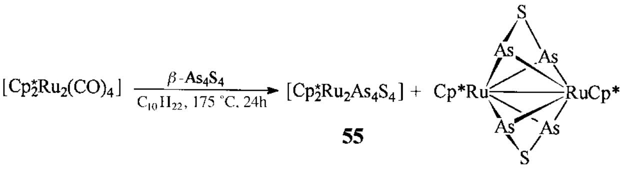
Whereas the coordination behavior of E_4X_3 cage molecules has already been relatively well investigated, there are comparatively few results on E_4X_4 compounds.[95] A first hint for the possible activation of the complete realgar molecule by a complex is the insertion of "Cp*Co(CO)" (from [Cp*Co(CO)]$_2$) into one of the two As–As bonds to give [Cp*Co(CO)As_4S_4] (**54a**) (Figure 11).[31] As in the E_4X_3 complexes of type **52** insertion of the Co fragment leads to considerable widening of the relevant As–As distance and angle; the other distances resemble those in the free ligand (Table 3). However, **54a** is only a by-product (the main products are **14**–**17**; see Eq. (5)); the same is also true for its homologue [Cp*Ir(CO)As_4S_4] (**54b**), which is formed from $[Cp^*_2Ir_2(CO)_3]$ and As_4S_4.[96] Thus, the systematic activation of realgar by coordinatively unsaturated transition metal fragments as well as their use in organometallic synthesis remains a desirable goal.



54a

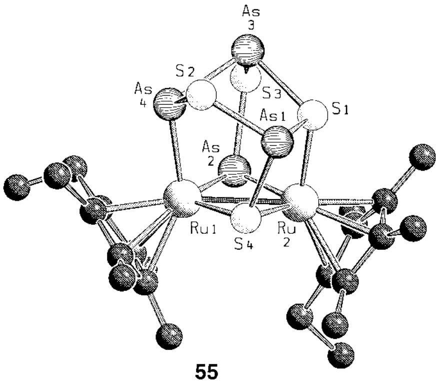
Figure 11. Molecular structure of $[(C_5Me_4Et)Co(CO)(\eta^2\text{-}As_4S_4)]$ (**54a**) in the crystal.

Reaction of $[Cp^*_2Ru_2(CO)_4]$ with β-As_4S_4[97] in boiling decane [Eq. (24)] gives $[Cp^*_2Ru_2As_4S_4]$ (**55**), which contains an As_4S_4 cage that is enlarged by two metal atoms (Figure 12). $[Cp^*_2Ru_2As_4S_2]$ (**56**) is formed as by-product in this reaction, and may be considered as a "classical" fragmentation product.[98] A comparison of the As–S connectivities in **55** with those in known As_4S_4 forms reveals a structural relationship rather to the extremely rare $As_4S_4(II)$,[99] since in this case it would only require insertion of both Cp*Ru fragments into the bonds As2–As4 and As2–S4 (Figure 13). However, a



$$[Cp^*_2Ru_2(CO)_4] \xrightarrow[C_{10}H_{22},\ 175\,^\circ C,\ 24h]{\beta\text{-}As_4S_4} \underset{\mathbf{55}}{[Cp^*_2Ru_2As_4S_4]} + \mathbf{56} \qquad (24)$$

56



55

Figure 12. Molecular structure of $[(C_5Me_4Et)_2Ru_2As_4S_4]$ (**55**) in the crystal.

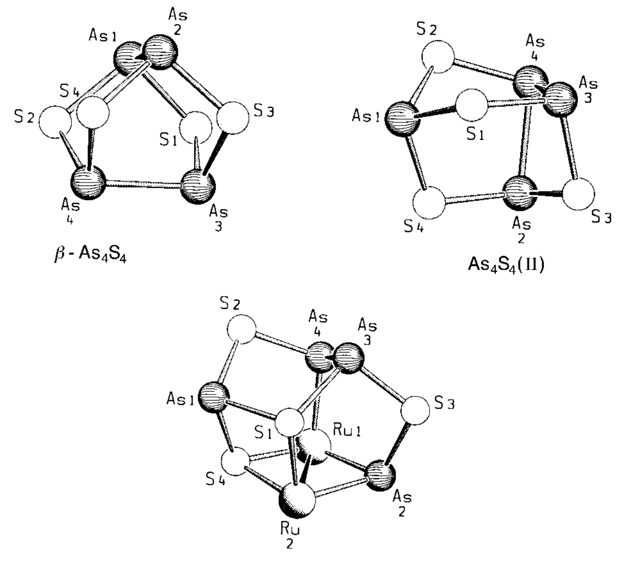
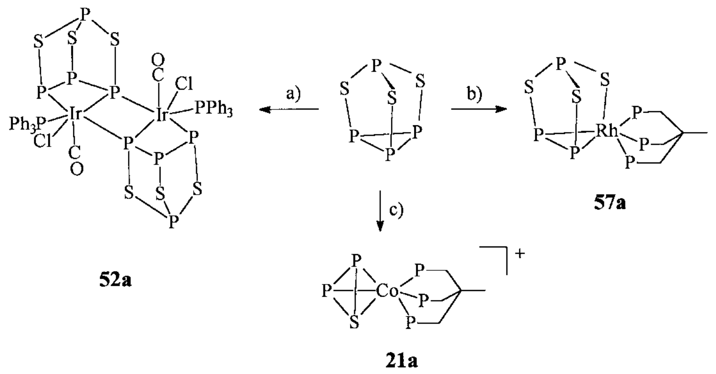


Figure 13. Comparison of the molecular structures of β-As_4S_4[2] and $As_4S_4(II)$[99] with the core of **55** (bottom) (Schakal plots).

phase transformation of β-As_4S_4 into As_4S_4(II) has been excluded;[28] thus **55** is more likely to be a recombination product of smaller intermediate building blocks. This hypothesis is also supported by the formation of **55** from phases that have lower sulfur contents such as As_4S_3 and As_2S_3.[98]

The sandwichlike structure of **56** is a result of the coplanar arrangement of the two As_2S ligands. The As atoms form an approximate square; the distances between 2.824(2) and 3.065(4) Å may indicate weak bonding interactions. Although S insertions into As–As bonds have not yet been described, the structural relationship to $[Cp^*_2Co_2(\mu\text{-}As_2)_2]$ (**13**) (see Scheme 4) is evident.[30]



Scheme 7. Representation of some of the different reaction modes of P_4S_3. a) Opening of a basal edge with $[IrCl(CO)(PPh_3)_2]$; b) substitution of one of the atoms in the base with $[\{RhCl(cod)\}_2]$/triphos; c) fragmentation of the cage with $Co(BF_4)_2$/triphos.

4.2. Metal-Substituted E_4X_3 Cages

Formal substitution of a P atom from the base of P_4X_3 (X = S, Se) by a ML_n fragment results in the complex type $ML_n(P_3X_3)$. In practice the neutral complexes $[(triphos)M(P_3X_3)]$ (**57**) are formed by reaction of $[MCl(cod)]_2$ (M = Rh, Ir; cod = 1,5-cyclooctadiene) with P_4X_3[100] in the presence of triphos (Scheme 7). The interplay between the steric demand of the supporting ligands (triphos, np_3) and the electron configuration of the metal determines whether the cage is incorporated only by opening of a basal edge (**52a**) or if it is fragmented in a mild way to give the three-electron ligand present in **57**.[38] If, however, Co^{II} or Ni^{II} salts are used, P_2X or P_3 fragments are extruded from the base and transformed into η^3-ligands as in **21a** (Scheme 7).[38]

A comparison of the structure of complexes **57** with those of the initial cages reveals a slight but significant shortening of the basal P–P bonds. This is even more pronounced for the As–As bonds in the structurally related anionic As_3Se_3 clusters **47** and **48** (see Table 3).

The reaction of As_4S_4 with $(triphos)M^I$ complexes (M = Rh, Ir) under comparable reaction conditions leads to $[(triphos)M(As_3S_3)]$ (**57b**), which is analogous to **57a**. Thus, in this case "AsS" elimination and a rearrangement of the cage skeleton are required.[101] Interaction of realgar with $(triphos)M^{II}$ complexes (M = Co, Ni) leads to an even more drastic "decomposition" of the molecule, yielding $[(triphos)M(\eta^3\text{-}As_2S)]$ (M = Co, **21c**).[38]

4.3. Fragmentation and Recombination Reactions in Organometallic Complexes

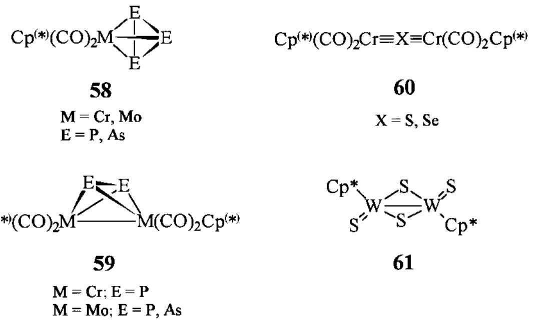
For many years the basic idea of the reactions of organometallic complexes with E/X cages was to obtain complexes as stable as possible under thermal conditions, despite the obvious risk of fragmentations. Dimeric, CO-containing cyclopentadienyl complexes with metal–metal multiple bonds or labile metal–metal single bonds have been employed as substrates. Modifying the reaction conditions has allowed more of the intermediate products to be isolated and their decomposition into the stable final products to be investigated systematically. Apart from the realization of new structures, this clearly shows the significance of small mixed ligands, which recombine under suitable conditions to give larger aggregates.

The dimers $[Cp^*_2M_2(CO)_4]$ ($M{\equiv}M$; M = Cr, Mo, W) preferentially react with $E_4X_{3(4)}$ to give products containing the E/X components of the original cage in separated form (Table 4, Scheme 8). The only exception are the mixed sandwich complexes $[Cp^*_2Mo_2P_4S]$ (**18a**) and $[Cp^*_2Mo_2E_2S_3]$ (**18c,d**). Little attention has been paid to the mechanism of formation of the metallatetrahedranes **58**, which reflect the simplest case of a recombination of atomic fragments. As possible intermediates one may consider complexes like **19** and **53**, which are formed in reactions with $CpCr(CO)_3$ radicals [Eq. (23)], but which fragment at higher temperatures to give **58**–**60**.[94] This system has allowed the activation and degradation of an inorganic cage to be investigated from the very beginning of the processes for the first time. Recent investigations in our group have shown that the fragmentation rate may be

Table 4. Product spectrum of the reactions of $[Cp^{(*)}_2M_2(CO)_{4(6)}]$ (M = Cr, Mo, W) with $E_4X_{3(4)}$ cage molecules.

Reactands	T [°C]	Intermediate products	E/X separated products[a]	Ref.
$[Cp_2Cr_2(CO)_6]/P_4S_3$	20–60	$[Cp_4Cr_4(CO)_9P_4S_3]$ **53a**	$[Cp(CO)_2CrP_3]$ **58a** $[\{Cp(CO)_2Cr\}_2P_2]$ **59a** $[\{Cp(CO)_2Cr\}_2S]$ **60a**	[94c]
$[Cp_2Cr_2(CO)_6]/P_4Se_3$	60	$[Cp_4Cr_4(CO)_9P_4Se_3]$ **53b** $[Cp_4Cr_4(CO)_8P_2Se_2]$ **19**	$[Cp(CO)_2CrP_3]$ **58a** $[\{Cp(CO)_2Cr\}_2P_2]$ **59a** $[\{Cp(CO)_2Cr\}_2Se]$ **60b**	[94b]
$[Cp^*_2Cr_2(CO)_6]/As_4S_4$	20		$[\{Cp^*(CO)_2Cr\}_2S]$ **60c**	[96]
$[Cp^*_2Cr_2(CO)_4]/As_4S_4$	110		$[Cp^*(CO)_2CrAs_3]$ **58b**	[96]
$[Cp^*_2Mo_2(CO)_4]/P_4S_3$	110		$[Cp^*(CO)_2MoP_3]$ **58c** $[\{Cp^*(CO)_2Mo\}_2P_2]$ **59b**	[34b]
$[Cp^*_2Mo_2(CO)_4]/As_4S_4$	100		$[Cp^*(CO)_2MoAs_3]$ **58d** $[\{Cp^*(CO)_2Mo\}_2As_2]$ **59c**	[34a]
$[Cp^*_2W_2(CO)_4]/As_4S_4$	110		$[Cp^*_2W_2S_4]$ **61**	[32]

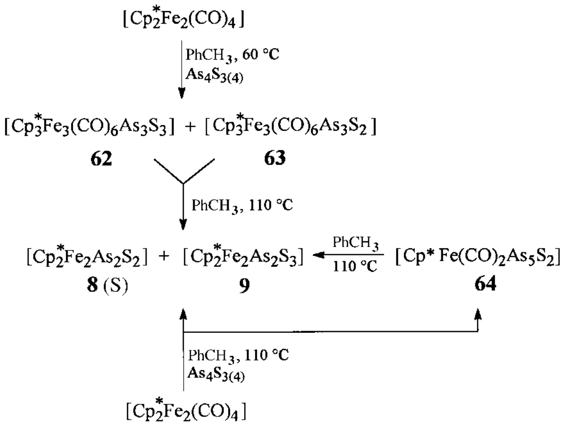
[a] Only in the reactions described in reference [34] were E/X mixed products obtained: $[Cp^*_2Mo_2P_4S]$ **18a**, $[Cp^*_2Mo_2P_2S_3]$ **18c** and $[Cp^*_2Mo_2As_2S_3]$ **18d**.



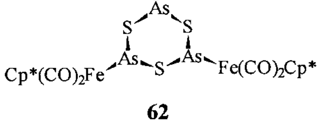
Scheme 8. Stable end products of the reactions of P_4X_3 (X = S, Se) and As_4S_4 with $[Cp^*_2M_2(CO)_{4(6)}]$ (M = Cr, Mo, W).

increased by the use of electron-rich ligands (Cp*) and slowed by employing relatively bulky $As_4S_4 \cdot Cr(CO)_5$ adducts.

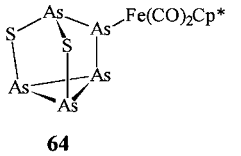
The AsS and As_2S_3 ligands in **8**(S) and **9** (see Eq. (4)) also do not stem directly from the inorganic cages, but from the intermediate products **62**–**64** that are characterized by very different As/S ratios. The complexes are stabilized by the 17-electron fragment $Cp^*Fe(CO)_2^{\bullet}$, and degradation to stable products containing comparatively slow ligands requires more drastic reaction conditions (Scheme 9).[102] The structures of the iron complexes **62** and **64** may be derived by analogies: complex **62** may be regarded as an As-metalated As_3S_3 ring resembling *cyclo*-$As_3S_6^{3-}$ (**27**),[53] whereas **64** may be formulated as a metalated derivative in the series E_4S_3, $E_5S_2^-$, E_6S^{2-}, and E_7^{3-} (see Scheme 1).



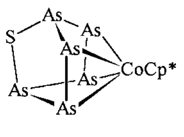
Scheme 9. The stepwise reaction of $[Cp^*_2Fe_2(CO)_4]$ with $As_4S_{3(4)}$.



62



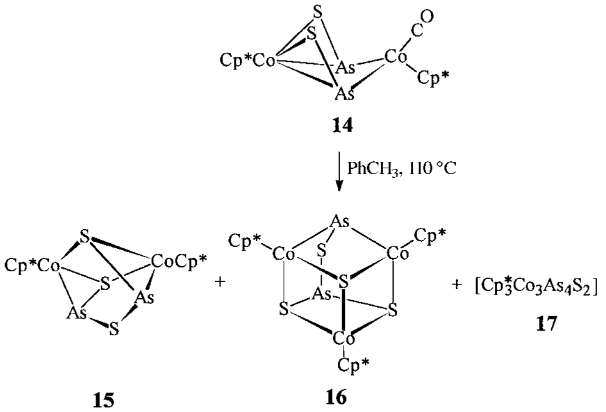
64



65

Complex **64** belongs to the structurally characterized class of Zintl ion complexes $[P_7\{Fe(CO)_2Cp\}_3]$,[11a] $[(P_7H)\{Mo(CO)_4\}]^{2-}$,[11b] and $[As_7\{Cr(CO)_3\}]^{3-}$.[103] A further member of this family is the Co complex **65**,[104] in which formally two As^- units replace two sulfur bridges in As_4S_3. As the base forms part of the bonding system (cleavage of one As–As bond), all As atoms are coordinated to the Cp*Co fragment, which achieves a closed valence shell.

Complex **65** arises from the system $[Cp^*_2Co_2(CO)_2]/As_4S_4$ (see Eq. (5)), which has been modified by addition of "$Cr(CO)_5$". The intermediary formed $As_4S_4 \cdot Cr(CO)_5$ adduct influences the nature of the products such that preferentially compounds rich in arsenic, such as **65** or $[Cp^*_2Co_2As_6]$,[30] are formed. In the original reaction sequence shown in Equation (5) complex **14** plays the key role, because controlled thermolysis of a solution of **14** in toluene results in products of different As/S stoichiometry and connectivity [Eq. (25)]. The As-rich cluster **17** evidently serves to help maintain the As/S balance.[31] This reaction provided evidence for the first time for the synthesis of new organometallic main group clusters by the recombination of smaller ligand fragments.



(25)

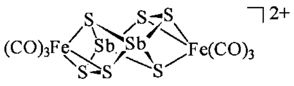
In a certain way this behavior reflects the self-condensation of metathioarsenites. In agreement with this supposition, CO-containing intermediate products with smaller inorganic building blocks are precursors in the formation of the Ru cluster **55**; however, the structures of these are not yet clear.[98]

5. Summary and Outlook

The chemistry of mixed ligands from Group 15/16 elements represents a rapidly growing modern field, ranging from diatomic ligands, which are unstable in the free state or nonexistent, to polymers in natural and synthetic solids. In between are anionic and neutral main group clusters, which either serve as ligand precursors or (less frequently) are directly incorporated into metal complexes.

Discrete anions may form solids by condensation, a process that can be controlled by metal ions. The aggregates that are formed by recombination of ligand fragments require less space. Conversely, sections of solid-state structures are realized by introduction of negative charge and large counterions or of organometallic complex fragments containing CO and Cp ligands. Whereas hydro- and solventothermal syntheses are already established as standard methods for the preparation of ternary and quaternary phases, their transfer to soluble complexes has, unlike the synthesis of polychalcogenido complexes[110] and in spite of preliminary successes, attracted little interest to date.

The focus of many studies are ligands based on As/S(Se). The use of the heavier pnicogens Sb and Bi should be stimulated by the fact that the classical Zintl ions Sb^{3-}[111] and Sb^{7-}[84b] can be incorporated into organometallic complexes. Promising candidates might be $Sb_6S_6^{2-}$,[80] $Sb_{12}Se_{20}^{4-}$,[112] $Sb_2S_{15}^{2-}$,[113] or fragments out of them. A first step in this direction might be the cationic cluster $[Fe_2(Sb_2S_6)(CO)_6]^{2+}$ (**66**), which represents a completely new type of compound. Furthermore it demonstrates impressively, that the development of new synthetic methods seems to have no limits: the cationic cluster **66** is formed as the SbF_6 salt from $[Fe(CO)_5]$ and $S_8(Sb_2F_{11})_2$ in liquid SO_2 by Sb transfer from the anion into a cationic sulfur complex.[114]



66

Although the presented area of research is mainly motivated by the fascination for the unusual and surprising structures, one should also always bear in mind the mechanisms and reaction pathways. Thus, metathesis reactions of mixed anions with transition metal halide complexes—the only example is shown in Equation (8)—represent an astonishingly neglected route, which might even be used for the incorporation of intact anionic clusters. In this way it should be possible to study the fragmentation mechanism as a function of the metal center, as has already been carried out for neutral cage molecules.

There are only a few indications of cage-opening reactions induced by radicals; these are mainly based on the one-electron fragments $CpCr(CO)_3^{\bullet}$ and $Cp^*M(CO)_2^{\bullet}$ (M = Fe, Ru). As this reaction type seems to be responsible for rearrangements, recombinations to new ligands, and even cage-expansion reactions, photochemical investigations should be intensified. In this context it is of great interest that realgar undergoes a light-induced rearrangement into para-realgar, which takes place even in the solid-state and which involves the cleavage of As–As bonds.[115]

I wish to thank my co-workers for their numerous contributions to this review. Dr. B. Nuber from the research groups of Prof. Dr. M. L. Ziegler and later Prof. Dr. G. Huttner (Heidelberg) is acknowledged for the numerous X-ray structure investigations. I am particularly indebted to Prof. Dr. H. Brunner for generous support, and to the Deutsche Forschungsgemeinschaft. I thank Prof. M. M. Kubicki (Dijon) for the semiempirical calculations of the free EX ligands, and W. Gabriel and B. Hofmann, Naturhistorisches Museum Bern for the photo used in the frontispiece.

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