



Fragmentation reactions of realgar caused by early transition metal hydrides

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ABSTRACT

The reaction of realgar with $[\text{Cp}'_2\text{MH}_3]$ in boiling toluene gave $[\text{Cp}'_2\text{M}_2\text{As}_2\text{S}_6]$ ($\text{Cp}' = t\text{-BuC}_5\text{H}_4$; $\text{M} = \text{Nb}$: **1**; Ta : **2**), while $[\text{Cp}_2\text{WH}_2]$ ($\text{Cp} = \text{C}_5\text{H}_5$) reacted with As_4S_4 to give $[\text{Cp}_2\text{W}(\text{H})(\eta^1\text{-As}_5\text{S}_2)]$ (**6**). The structures were determined by X-ray crystallography. Compounds **1** and **2** are dimers in which two $\text{Cp}'\text{M}$ units are symmetrically bridged by a $\mu, \eta^{2:2}\text{-AsS}_3$ ligand, a sulfide ligand and a heteroallylic $\mu, \eta^{2:2}\text{-AsS}_2$ ligand. The structure of **6** belongs to the type of bent metallocenes in which tungsten is surrounded tetrahedrally by two Cp ligands, a crystallographically found hydride atom and the new As_5S_2 cage. The reaction of **1** with $\text{W}(\text{CO})_5\text{THF}$ gave $[\text{Cp}'_2\text{Nb}_2\text{As}_2\text{S}_6\text{W}(\text{CO})_5]$ (**3**) and $[\text{Cp}'_2\text{Nb}_2\text{As}_2\text{S}_6\text{W}(\text{CO})_3\text{W}(\text{CO})_5]$ (**4**). Compound **3** is a monoadduct of **1** bearing the $\text{W}(\text{CO})_5$ fragment at the As atom of the AsS_3 ligand. The structure of **4** contains a distorted cubane-like $\text{Nb}_2\text{WS}_4\text{As}$ cluster with an integrated $\text{W}(\text{CO})_3$ unit. A similar cluster **5** containing a CuI fragment instead of $\text{W}(\text{CO})_3$ was prepared from **1** and CuI. The structure is completed by an attached As_4S_3 cage, the As_3 basis of which is oriented towards iodide. Electrochemical investigations of **1**, **3**, and **4** shows for each compound quasi-reversible one-electron reductions with $E_{1/2} = -0.73$ V (**1**), -0.55 V (**3**) and -0.67 V (**4**), respectively.

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1. Introduction

The current interest in the chemistry of ligand complexes with mixed group 15 (E)/group 16 (Q) ligands is based on their potential ability as building blocks in coordination polymers. While the role of P_n ligand complexes in supramolecular chemistry has been summarized recently [1], that of As_n ligand complexes is still going to be explored [2]. A valuable source for the synthesis of As_n ligand complexes is realgar, As_4S_4 [3], which upon degradation of its cage by reactive organometallic complexes also forms metal complexes with heteroatomic As/S ligands [4]. These are stable hybrid clusters with inorganic cores and peripheral organometallic groups, which exhibit coordination properties corresponding to group 15 and/or group 16 ligand complexes [5].

Usual synthetic strategies for 15/16 ligand complexes include the reduction of binary E/Q phases by nucleophilic coordination compounds [6], the insertion of metal complex fragments into neutral or anionic cage molecules [7], and the thermal degradation of As_4S_4 by $[\text{Cp}^*\text{M}_2(\text{CO})_4]$ ($\text{M} = \text{Mo}$ [3], Fe [8], Ru [9]; $\text{Cp}^* = \text{C}_5\text{Me}_5$) or $[\text{Cp}^*\text{Co}_2(\text{CO})_2]$ [10] complexes. In this work we report on the fragmentation reactions of realgar with early transition metal hydrides, e.g. $[\text{Cp}'_2\text{NbH}_3]$ ($\text{Cp}' = t\text{-BuC}_5\text{H}_4$) and $[\text{Cp}_2\text{WH}_2]$ ($\text{Cp} = \text{C}_5\text{H}_5$), respectively. First attempts to prepare heterometallic clusters or

coordination polymers from the resulting As/S ligand complexes and copper(I) halides are described.

2. Results

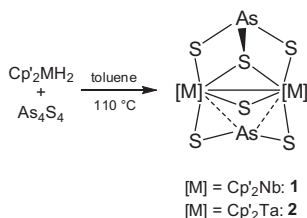
2.1. Reactions of As_4S_4 with $\text{Cp}'_2\text{MH}_3$ ($\text{M} = \text{Nb}$, Ta ; $\text{Cp}' = t\text{-BuC}_5\text{H}_4$)

The reaction of realgar with $[\text{Cp}'_2\text{NbH}_3]$ in boiling toluene gives after chromatographic workup violet $[\text{Cp}'_2\text{Nb}_2\text{As}_2\text{S}_6]$ (**1**) in nearly quantitative yield (Scheme 1). The composition of **1** was determined crystallographically and confirmed by elemental analysis. The field desorption mass spectrum (FDMS) in toluene contains the parent ion at $m/z = 770.2$. The ^1H NMR spectrum of **1** in C_6D_6 reveals a singlet at $\delta = 1.21$ ppm for the $t\text{-Bu}$ groups of the Cp' ligands and four multiplets at 5.97, 6.13, 6.18 and 6.28 ppm for the aromatic protons. The observed pattern is in agreement with the structure of the compound.

The analogous reaction of As_4S_4 and $[\text{Cp}'_2\text{TaH}_3]$ gives red $[\text{Cp}'_2\text{Ta}_2\text{As}_2\text{S}_6]$ (**2**) in 51% yield. The red solid transforms in the solid state slowly into golden leaves, which are no more soluble in any solvent. Single crystals of **2** were obtained by recrystallization of the red solid from toluene at -24 °C. The obtained red crystals also change their color at room temperature, but elemental analyses of the partially converted material confirm the composition found by X-ray crystallography. An explanation for this irreversible chromatic change cannot yet be given. The FD mass spectrum of **2** exhibits the parent ion at $m/z = 946.0$ and the ^1H NMR spectrum

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Scheme 1.

in C_6D_6 shows five signals in the ratio 9:1:1:1:1, what is in agreement with equivalent Cp' ligands in solution.

Crystal structure analyses of **1** and **2** show that in both complexes two Cp'M units ($M = \text{Nb}, \text{Ta}$) are symmetrically bridged by a $\mu, \eta^{2:2}\text{-AsS}_3$ ligand, a sulfide ligand (S5) and a $\mu, \eta^{2:2}\text{-AsS}_2$ ligand (Fig. 1). This description suggests a formal oxidation state for each metal atom of +4, diamagnetism may be achieved by formation of a metal–metal bond. The observed Nb–Nb (3.289 Å) and Ta–Ta distances (3.284 Å) (Table 1) do not exclude bonding interactions [11]. The As–S distances within the trigonal $\psi\text{-AsS}_3$ pyramid are inequivalent, so the distance As2–S3 is longer than the other ones. Organometallic complexes with the AsS_3^{3-} ligand are rare [12] because of the pronounced tendency of thioarsenate(III) solutions to oligomerize under loss of sulfur [4].

Of great interest is the new AsS_2 bridge. The small differences observed for the distances of the pairs As1–S1(S6) and M1(M2)–As1 are in agreement with an allylic character of the ligand, which may be described by the resonance formulas **A** and **B** (Scheme 2), in analogy with the NO_2^- ion. Contrary to the $\mu, \eta^{1:3}\text{-AsS}_2$ ligand in $[(\text{C}_5\text{Me}_5)_2\text{Mo}_2(\text{CO})_2\text{As}_2\text{S}_4 \cdot 2\text{Cr}(\text{CO})_5]$ [13] the central arsenic atom As1 interacts with the metal centers only weakly. The corresponding M–As bonds vary between 2.814(1) and 2.830(1) Å (Table 1).

2.2. Cluster formation reactions

The reaction of **1** with three equivalents of $\text{W}(\text{CO})_5\text{THF}$ in THF at room temperature gave after chromatographic workup and recrystallization brown crystals of $[\text{Cp}'_2\text{Nb}_2\text{As}_2\text{S}_6\text{W}(\text{CO})_5]$ (**3**) and red-brown needles of $[\text{Cp}'_2\text{Nb}_2\text{As}_2\text{S}_6\text{W}(\text{CO})_3\text{W}(\text{CO})_5]$ (**4**) (Scheme 3). Both samples were contaminated with $\text{W}(\text{CO})_6$, which could not be completely removed by high vacuum sublimation. X-ray diffraction analyses prove the composition of **3** and **4** and the FD mass spectrum of **4** exhibits the parent ion ($m/z = 1362.9$) and a weak peak at $m/z = 1037.2$. The latter can be assigned to the cluster core $[\text{Cp}'_2\text{Nb}_2\text{As}_2\text{S}_6\text{W}(\text{CO})_3]^+$. From the structural studies it is evident that compound **3** may be considered as intermediate monoadduct of **1**, which quickly reacts with $\text{W}(\text{CO})_5\text{THF}$ under formation of

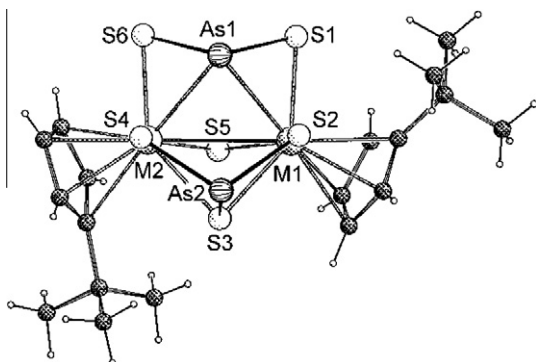
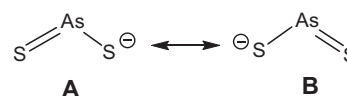
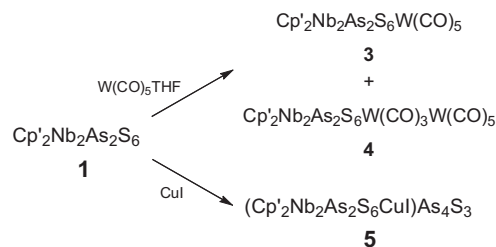
Fig. 1. Molecular structure of $[\text{Cp}'_2\text{M}_2\text{As}_2\text{S}_6]$ ($M = \text{Nb}$ (**1**), Ta (**2**)).

Table 1
Selected distances (Å) of $[\text{Cp}'_2\text{M}_2\text{As}_2\text{S}_6]$ [$M = \text{Nb}$ (**1**), $M = \text{Ta}$ (**2**)].

1		2	
Nb1–Nb2	3.289(1)	Ta1–Ta2	3.284(2)
Nb1–S1	2.372(1)	Ta1–S1	2.366(2)
Nb1–S2	2.532(1)	Ta1–S2	2.516(2)
Nb1–S3	2.556(1)	Ta1–S3	2.548(2)
Nb1–S5	2.420(1)	Ta1–S5	2.418(2)
Nb2–S3	2.569(1)	Ta2–S3	2.559(2)
Nb2–S4	2.550(1)	Ta2–S4	2.529(2)
Nb2–S5	2.386(1)	Ta2–S5	2.381(2)
Nb2–S6	2.383(1)	Ta2–S6	2.375(2)
As1–S1	2.271(1)	As1–S1	2.272(2)
As1–S6	2.257(1)	As1–S6	2.263(2)
As2–S2	2.250(1)	As2–S2	2.248(2)
As2–S3	2.289(1)	As2–S3	2.287(2)
As2–S4	2.260(1)	As2–S4	2.260(2)
Nb1...As1	2.830(1)	Ta1...As1	2.825(1)
Nb2...As1	2.821(1)	Ta2...As1	2.814(1)



Scheme 2.



Scheme 3.

cluster **4**. Attempts to increase the low yield of **3** by modifying the stoichiometry of the starting materials failed.

The IR spectrum of **3** shows $\nu(\text{CO})$ absorptions at 1933 and 2073 cm^{-1} typical of the $\text{W}(\text{CO})_5$ fragment. The CO absorptions in the spectrum of **4** at 1871, 1893, 1917, 1942 and 2077 cm^{-1} may be assigned to superposed patterns of $\text{W}(\text{CO})_5$ and $\text{W}(\text{CO})_3$ groups. The ^1H NMR spectra of **3** and **4** in C_6D_6 each show a singlet for the *t*-Bu groups at $\delta = 1.14$ (**3**) and 1.35 (**4**) ppm and four multiplets between $\delta = 4.4$ and 6.5 ppm. These patterns are in agreement with both structures (see below).

Layering of solutions of **1** in CH_2Cl_2 with the respective solution of CuX ($X = \text{Cl}, \text{Br}, \text{I}$) in acetonitrile gave after complete diffusion voluminous yellow precipitates and, in the case of CuI , dark rods of **5** (Scheme 3). These have according to X-ray diffraction analysis the composition $[\text{Cp}'_2\text{Nb}_2\text{As}_2\text{S}_6\text{CuI} \cdot \text{As}_4\text{S}_3]$.

2.2.1. Molecular structures of **3** and **4**

The molecular structure of **3** is closely related to that of **1**, except that As1 bears a $\text{W}(\text{CO})_5$ fragment (Fig. 2). Compared to the cluster core of **1** the distances and angles of **3** are nearly the same (Table 2). The observed As–W distance of $2.540(1)$ Å is typical of a coordinative As–W single bond [14].

The central feature of the structure of **4** is a distorted cubane-like $\text{Nb}_2\text{WS}_4\text{As}$ cluster, in which one metal atom is substituted by the main group element As [15]. However, the edge As2–S2 ($d = 3.691(2)$ Å) has clearly nonbonding character. This means that the adduct **3** acts as a 6e-tripod ligand which binds to a $\text{W}(\text{CO})_5$

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