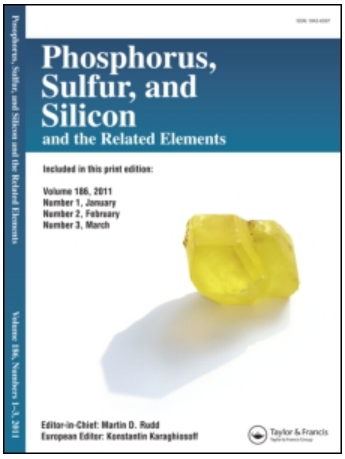

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Wagner, Christoph and Merzweiler, Kurt(2001) 'Synthesis, Structure and Reactivity of Novel Clusters with Tetrahedral Mo_2SbE Core (E = S, Se)', Phosphorus, Sulfur, and Silicon and the Related Elements, 168: 1, 199 — 203
To link to this Article: DOI: 10.1080/10426500108546554
URL: http://dx.doi.org/10.1080/10426500108546554

Phosphorus Sulfur and Silicon, 2001, Vol. 168, pp. 199-203
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Synthesis, Structure and Reactivity of Novel Clusters with Tetrahedral Mo_2SbE Core (E = S, Se)

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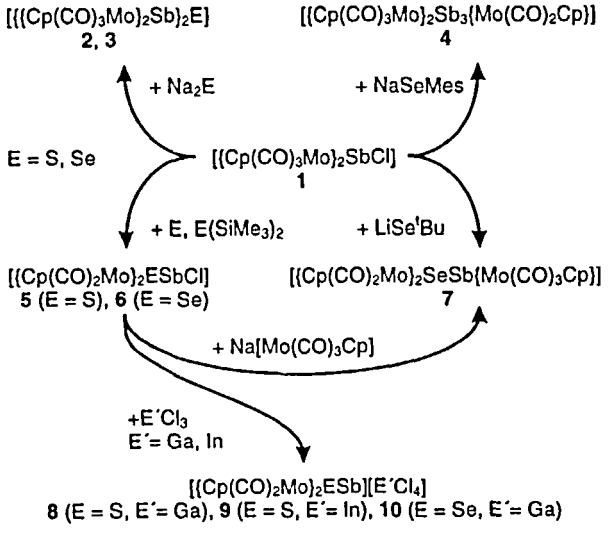
$[\{Cp(CO)_3Mo\}_2SbCl]$ **(1)** [1] reacts with elemental chalcogens E (E = S, Se) and various chalcogen compounds like $E(SiMe_3)_2$, Na_2E, NaSeMes and $LiSe^tBu$ to form a variety of new cluster compounds.

Keywords: Antimony; Cluster compounds; Chalcogens; Crystal Structure

2. RESULTS

Scheme 1 summarizes the reactions of **1** with different chalcogen reagents.



SCHEME 1

[{Cp(CO)$_3$Mo}$_2$SbCl] (**1**) reacts with Na_2E (E = S, Se) to form [{{Cp(CO)$_3$Mo}$_2$Sb}$_2$E] (**2**, **3**). The X-ray crystal structure determination [2a] revealed, that **2** contains two {Cp(CO)$_3$Mo}$_2$Sb-moieties which are bridged by a sulfur atom (Fig. 1). **2** is the second structurally characterised compound containing an Sb-S-Sb chain with organometal units attached to antimony. The first example [(CO)$_5$CrPh$_2$SbSSbPh$_2$] [3] and **2** show comparable bond parameters.

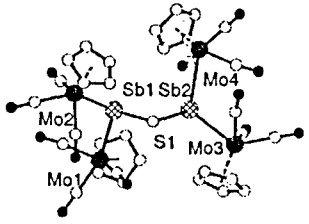


FIGURE 1
The molecular structure of **2** (H atoms omitted for clarity). Selected bond lengths (pm) and angles (°): Sb-S 246.5(2), 248.3(2), Sb-Mo 292.3(2)-293.8(2), Sb(1)-S(1)-Sb(2) 93.5(1), Mo-Sb-Mo 116.6(1), 117.2(1), S(1)-Sb-Mo 97.6(1)-107.7(1).

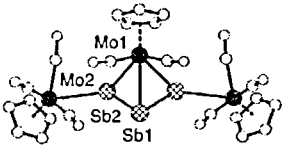


FIGURE 2
The molecular structure of **4** (H atoms omitted for clarity). Selected bond lengths (pm) and angles (°): Sb(1)-Sb(2) 277.0(1), Sb(1)-Mo(1) 293.2(2), Sb(2)-Mo(1) 290.3(1), Sb(2)-Mo(2) 295.5(1), Sb(2)-Sb(1)-Mo(1) 61.1(1), Sb(2)-Sb(1)-Sb(2') 74.9(1), Sb(1)-Sb(2)-Mo(1) 62.2(1), Sb(1)-Sb(2)-Mo(2) 110.8(1), Mo(1)-Sb(2)-Mo(2) 119.4(1), Sb(2)-Mo(1)-Sb(2') 70.9(1), Sb(1)-Mo(1)-Sb(2) 56.7(1).

2.2 Synthesis of [{Cp(CO)$_3$Mo}$_2$Sb$_3$[Mo(CO)$_2$Cp]] (4)

The redox reaction of **1** with NaSeMes leads to [{Cp(CO)$_3$Mo}$_2$Sb$_3${Mo(CO)$_2$Cp}] (**4**) in a remarkable high yield (20%). Additionally $(SeMes)_2$ is formed in a stoichiometric amount. A probable pathway for the formation of **4** could be:

$$[\{Cp(CO)_3Mo\}_2SbCl] + 2\ NaSeMes \longrightarrow [\{Cp(CO)_3Mo\}Sb\{SeMes\}_2] + NaCl + [Na\{Mo(CO)_3Cp\}]$$

$$3\ [\{Cp(CO)_3Mo\}Sb\{SeMes\}_2] \longrightarrow 4 + 3\ (SeMes)_2 + 3\ CO$$

According to the X-ray crystal structure determination [2b], **4** contains an angular Sb_3-unit (Fig. 2). **4** can be compared with [R_2As_3{Mo(CO)$_2$Cp}] (R = Me, Ph) [4], which are As analogues of π-allylic complexes. [{$(C_5Me_5)_2Sm$}$_3$Sb$_3$]·thf contains an allyl like Sb_3 fragment with an Sb-Sb-Sb angle of 114.5° and a trigonal planar coordination around the Sb_3 unit [5]. But in **4** the Sb-Sb-Sb angle of 74.9°

and the trigonal-pyramidal coordination of the Sb atoms are not in agreement with an allylic character.

2.3 Synthesis of [{Cp(CO)$_2$Mo}$_2$ESbCl] (E = S, Se)

[{Cp(CO)$_2$Mo}$_2$SeSbCl] (6) and the sulfur-analogue 5 can be obtained by the reaction of 1 with elemental chalcogens or with the silylated chalcogens E(SiMe$_3$)$_2$ (E = S, Se) [6]. 5 and 6 are cluster compounds with a distorted tetrahedral Mo$_2$ESb core (Fig. 3). The Sb-Cl distances are unusually long (264.8 and 272.7 pm) and indicate a considerable ionic character of these bonds.
According to the Pauling concept, the Sb-Cl bond orders lie between 0.47 and 0.39 [7]. Therefore, it is reasonable to consider 5 and 6 as close ion pairs, consisting of [{Cp(CO)$_2$Mo}$_2$ESb]$^+$ cations and Cl$^-$ anions. On the basis of this assumption, the electron count for the cluster core leads to 40 electrons, which is in accordance with the required value for a closed tetrahedron.

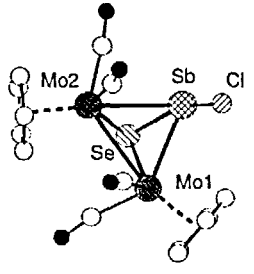


FIGURE 3
Molecular Structure of 6
(H atoms omitted for clarity).

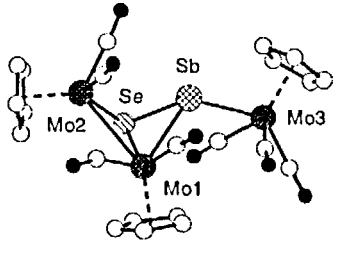


FIGURE 4
Molecular Structure of 7
(H atoms omitted for clarity).

2.4 Synthesis of [{Cp(CO)$_2$Mo}$_2$SeSb{Mo(CO)$_3$Cp}] (7)

The reaction of 6 with Na[Mo(CO)$_3$Cp] leads to [{Cp(CO)$_2$Mo}$_2$SeSb{Mo(CO)$_3$Cp}] 7, which also contains an Mo$_2$SbSe core, but with butterfly geometry, Mo(1) and Se forming the hinge bond (Fig. 4) [6]. In addition to the formation of an exocyclic Sb-Mo bond, a cluster Sb-Mo bond is cleaved. This structural change can be attributed to the increase of the number of cluster valence electrons by two from 40 (tetrahedral core) in 6 to 42 (butterfly core) in 7. Therefore, 7 can be described formally as an electron precise cluster with single bonds between the core atoms.
The reaction of 1 with LiSe^{t}Bu leads to a mixture of 7 and [{Mo(CO)$_2$Cp}$_2$SeSbCl] 6 in a yet unknown way.

5 and **6** react with the Lewis acids $E'Cl_3$ (E' = Ga, In) under abstraction of the weakly bonded chloride ion to give the cationic cluster species $[\{Cp(CO)_2Mo\}_2ESb]^+$ and anions of the type $[E'Cl_4]^-$ (Fig 5).
In the crystal structures both of the sulfur derivatives $[\{Cp(CO)_2Mo\}_2SSb][E'Cl_4]$ (E' = Ga **8**, In **9**) and $[\{Mo(CO)_2Cp\}_2ScSb][GaCl_4]$ **10** no interactions between the cations and the anions can be found[6]. The shortest distances (Sb-Cl) are 343 to 388 pm.

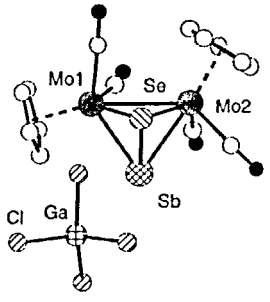


FIGURE 5
The molecular structure of **10** (H atoms omitted for clarity).

Acknowledgement
This work was supported by the Fonds der Chemischen Industrie and the DFG.

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[2] Crystal structure determinations: The data collections were performed on a Stoe IPDS image plate diffraction system at 293 K with MoK_α-radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using SHELXL-97 and refined with SHELXL-97 [8]. The molecular drawings were generated with DIAMOND [9]. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ UK, (fax: +44 1223 336033 or email: deposite@ccdc.cam.ac.uk). a) **1** $C_{32}H_{20}Mo_4O_{12}SSb_2$, triclinic, $P\bar{1}$, a; b; c [pm]: 1262.3(7); 1580.1(5); 2060.8(7), α; β; γ [°]: 105.89(3); 91.32(4); 91.04(4) V = 3951(3)·10^6pm^3, 48245 reflections collected in the 2θ-range 4.90–56.18 °, 17682 unique reflections (R_{int} = 0.0883), 9838 with $F_o > 4\sigma(F_o)$, 919 parameters, R_1 ($I > 2\sigma(I)$) 0.0487, wR_2 (all data) 0.1144. CCDC = 147368 b) 2 $C_{23}H_{15}Mo_3O_8Sb_3$, orthorhombic, P nma, a; b; c [pm]: 1301.1(4); 2825.5(6); 774.4(2) V = 2846.8(12)·10^6 pm^3, 17365 reflections collected in the 2θ-range 5.46–49.98°, 2558 unique reflections (R_{int} = 0.1494), 1654 with $F_o > 4\ \sigma\ (F_o)$. 172 parameters, R_1 ($I > 2\sigma(I)$) 0.0432, wR_2(all data) 0.0924. CCDD = 147369.

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