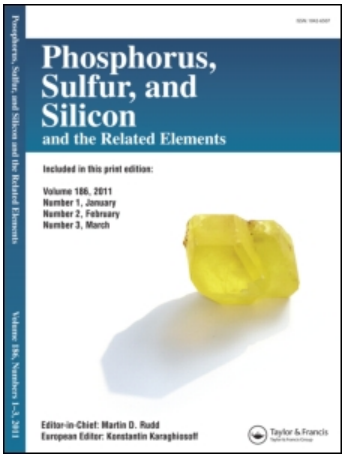

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COMPLEXES WITH *cyclo*-Sb_n LIGANDS

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The four membered organoantimony ring (*t*BuSb)$_4$ (**1**) reacts with $[(C_5R_5)Mo(CO)_3]_2$, (R = H, Me) to form the tetrahedrane derivatives $[(C_5H_5)Mo(CO)_2]_2Sb_2$ (**2**), $(C_5H_5)Mo(CO)_2Sb_3$ (**3**), $[(C_5Me_5)Mo(CO)_2]_2Sb_2$ (**4**), and $[(C_5Me_5)Mo(CO)_2Sb_3]$ (**5**). An organo antimony ring, $(C_5Me_5)Mo(CO)_3(tBu_3Sb_4)$ (**6**), is also formed. In the crystalline state both *cyclo*-Sb_3 complexes, **3** and **5** are associated through close intermolecular Sb···Sb contacts to form supramolecular layers.

Keywords: antimony ligands; organoantimony compounds; molybdenum complexes; supramolecular chemistry

INTRODUCTION

The chemistry of complexes with substituent-free („naked") P_n or As_n ligands containing element-element bonds has developed considerably during the last decade. The main pnicogene sources for these complexes were white phosphorus P_4 or yellow arsenic As_4 [1, 2], but also organo phosphorus or arsenic rings were used[3]. Little is known

of complexes with naked antimony ligands, probably due to the absence of versatile antimony sources. Anionic complexes with the ligand Sb_7^{3-} were prepared by complexation of the corresponding alkali metal antimonide[4]. Important diantimony complexes resulted from the reduction of antimony trichloride with anionic metal carbonyls[5]. The thermal reaction of metallic antimony with $[(C_5H_5)Mo(CO)_3]_2$ gave $[(C_5H_5)Mo(CO)_2]_2Sb_2$ (**2**), however in a rather low yield[6].

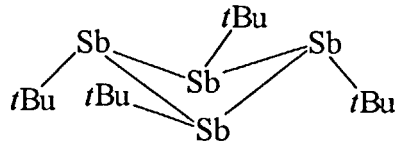
Our intention was to find suitable antimony sources for the generation of „naked" *cyclo*-Sb_n ligands. As the Sb_4 molecule is not available in condensed states, we considered organoantimony rings as reagents, in analogy to arsenic chemistry. Such rings should be easy to prepare and to handle and possess organo substituents that eliminate easily. A similar approach had been made before in a study of the reaction between $[(C_5Me_5)Sb]_4$ and $[(C_5H_5)Mo(CO)_3]_2$ however only known compounds including **2** were isolated[7].

RESULTS AND DISCUSSIONS

Reactions of (*t*BuSb)$_4$ (1) with $[(C_5H_5)Mo(CO)_3]_2$

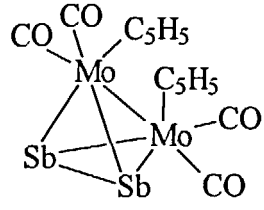
We chose (*t*BuSb)$_4$ (**1**), first reported in 1965 by Issleib et al.[8], as reagent. **1** is reasonably easy to prepare in an amount of grams by magnesium reduction of the corresponding organoantimony dichloride, after published procedures[8-11]. Purification is possible by preparative chromatography or by vacuum sublimation, the latter method leading to a yellow crystalline product which can be stored

for years when protected against light and stored in an inert atmosphere.



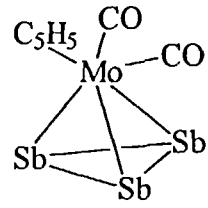
(1)

Reactions between **1** and $[(C_5H_5)Mo(CO)_3]_2$ were carried out at boiling temperatures in various solvents. The main products were **2** (yield up to 89%), and elemental antimony (black powder and antimony mirror).



(2)

In high boiling solvents like decaline or mesitylene, **2** was the only soluble reaction product and therefore these solvents should be used for an efficient synthesis of this compound. In toluene, as additional product, the first *cyclo*-Sb_3 complex **3** was formed. **3** was isolated together with **2** in a fraction which solves in toluene, but not in petroleum ether. Further separation was done by preparative column chromatography on aluminium oxide, having a toluene - petroleum ether mixture as moving phase. **3** crystallises easily to form thin dark red needles, with metallic aspect, and solves in hydrocarbon solvents



(3)

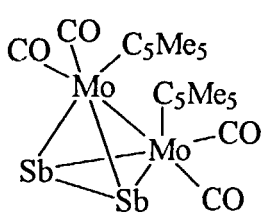
to give yellow solutions. Similar colour changes also occur with thermochromic distibines and dibismuthines displaying strong intermolecular interactions in the crystal.

The use of even lower boiling solvents, like petroleum ether, to conduce the reaction between **1** and $[(C_5H_5)Mo(CO)_3]_2$ resulted in an increase of the reaction time, but did not lead to the formation of other products.

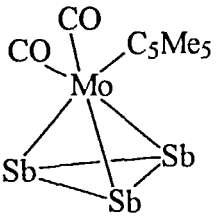
The mass spectra of pure **2** and **3** at oven temperatures above 300 °C present intensive signals of $[(CpMo)_2Sb_5]$. This compound is probably generated by thermal rearrangement in the melt.

Reactions of (*t*BuSb)$_5$ (1) with $[(C_5Me_5)Mo(CO)_3]_2$

In order to increase the relative yield of the *cyclo*-Sb_3 complex, we chose $[(C_5Me_5)[Mo(CO)_3]_2$ as starting material and used again column chromatography for separation. As expected, the bulky pentamethyl cyclopentadienyl group influenced favourably the formation of the Sb_3 complex **5**, which became the main antimony containing product (yield 27%). The separation by column chromatography afforded also the Sb_2 complex **4** and a novel organometal antimony ring **6**. The isolation of **6** gives some indications about a possible reaction pathway leading to the formation

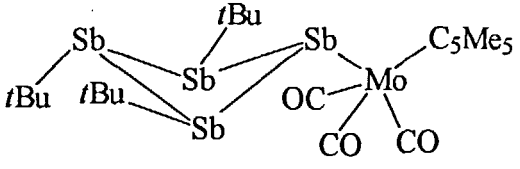


(4)



(5)

of **5**. Both reagents, the molybdenum complex and the *tert*-butyl antimony ring are candidates for the formation of radicals by homolytical splitting of the Mo-Mo, Sb-Sb, or Sb-C bonds, respectively.



(6)

The reaction conditions, boiling in toluene for some hours, are favourable for a radical mechanism. A possible way for the formation of **6** could be the combination of the radical $C_5Me_5(CO)_3Mo\cdot$ resulting from the cleavage of the molybdenum dimer, with the antimony radical $tBu_3Sb_4\cdot$ produced by elimination of a *tert*-butyl radical from **1**. Such a radical pathway might also lead to other combination products, e.g. the dimer tBu_3Sb_4-Sb_4tBu_3. Our search for this bicycle has not yet led to positive results. It is however interesting in this context, that the analogous arsenic derivative tBu_3As_4-As_4tBu_3 has recently [12] been synthesised by reaction of $(tBuAs)_4$ with

$Co_2(CO)_8$. As for the cyclopentadienyl analogues, the mass spectra of **4**, **5** and **6** present at higher temperature intensive signals for $[(Cp^*Mo)_2Sb_5]$. Our attempt to synthesise this compound by heating **5** in decaline failed. After 4 hours refluxation, only the most stable compound **4**, and metallic antimony formed. $[(Cp^*Mo)_2Sb_5]$ is supposed to posses a triple decker sandwich structure.

Structures of 3, 5, and 6

X-ray crystal structure analyses have been carried out for the complexes **3**, **5**, and **6**. The structures of **1** [11] and **2** [6] have been described before. The molecular structures of the Sb_3 complexes **3** and **5** are depicted in the Figures 1 - 2.

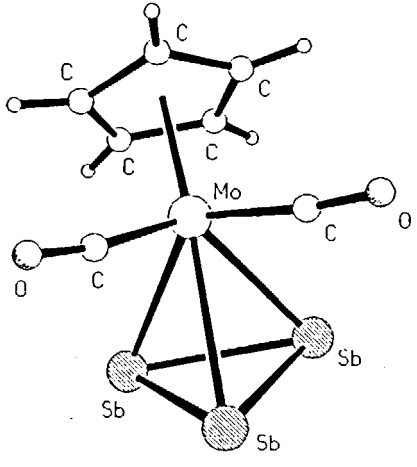


FIGURE 1 Molecular Structure of $[(C_5H_5)Mo(CO)_2Sb_3]$ (**3**) Sb-Sb 273.5(1) - 278.1(1) pm, Mo-Sb 286.1(1) - 294.9(1) pm

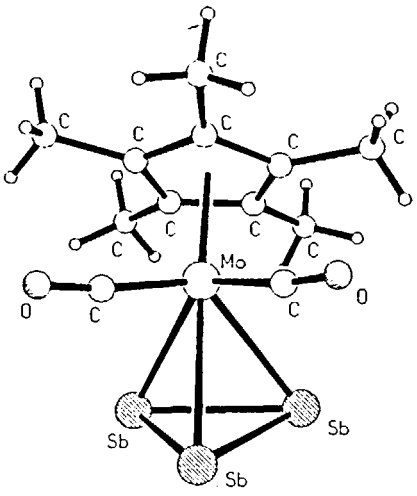


FIGURE 2 Molecular Structure of $[(C_5Me_5)Mo(CO)_2Sb_3]$ (**5**) Sb-Sb 273.97(9) - 276.82(8) pm, Mo-Sb 285.12(8) - 292.52(9)

In both complexes there are almost tetrahedral $MoSb_3$ units similar to the analogous MoP_3 or $MoAs_3$ complexes. In the crystal the molecules of **3** and **5** are associated to supramolecular layers through close intermolecular Sb···Sb contacts between the atoms of the Sb_3 ligands. The relevant contact distances are shorter than the sum of the van der Waals radii of two Sb atoms (440 pm), they range from 384 to 428 pm for **3** and from 374.5 to 383.4 pm for **5**. The shortest contact distances of **3** and **5** and the intermolecular separations in analogous phosphorus and arsenic complexes are listed in Table 1. When the ratio of the intermolecular and the intramolecular distances between the pnicogen atoms is used as measure only E···E/E-E ratios beneath 1.4 indicate relevant intermolecular interactions. The

comparison of the data in table 1 reveals that only in the case of the antimony compounds relevant associations to supramolecular entities occur, whereas in the case of the phosphorus and arsenic derivatives the packing of the molecules does not lead to significant associations.

TABLE 1 Intramolecular (E-E) and intermolecular E···E distances in complexes with E_3-ligands (E = P, As, Sb)

Compound	mean E-E	shortest E···E	E···E/E-E	ref.
$[C_5H_5Cr(CO)_2P_3]$	213	356	1.67	[13]
$[C_5H_5Mo(CO)_2P_3]$	213	360	1.69	[14]
$[C_5H_5Cr(CO)_2As_3]$	234	352	1.51	[15]
$[C_5Me_5Cr(CO)_2As_3]$	235	375	1.56	[16]
$[C_5Me_5Mo(CO)_2As_3]$	238	378	1.59	[17]
$[C_5H_5Mo(CO)_2Sb_3]$	275	384	1.40	
$[C_5Me_5Mo(CO)_2Sb_3]$	275	375	1.36	

The structure of **6** is depicted in Fig. 3. The compound consists of a folded stibetane ring with three *tert*-Butyl substituents and one $(C_5Me_5)Mo(CO)_3$ group in trans positions. The inspection of the Sb-Sb distances reveals some interesting details. Three Sb-Sb bond lengths are almost equal (281.45 - 282.4 pm) and compare very well with the distances in **1** (Sb-Sb 281.4(2) - 282.1(2))[11]. The fourth Sb-Sb bond length is longer (285,38(8)), the difference being small but significant. Also the Mo-Sb bond length is a little longer than expected. These unspectacular deviations may be caused by a certain

steric hindrance between bulky substituents in the molecule.

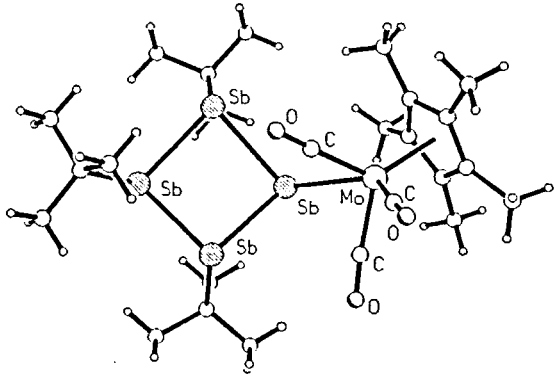


FIGURE 3 Molecular Structure of $(C_5Me_5)Mo(CO)_3(tBu_3Sb_4)$ (**6**) Sb-Sb 281.45(5), 2 × 282.42(6), 285.38(8), Sb-Mo 288.39(6) pm

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