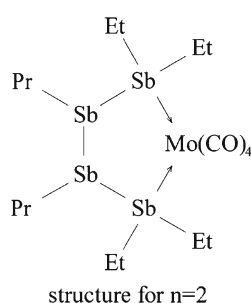


APPLICATION NOTE

Liquid Injection Field Desorption Ionization Mass Spectrometry of Cyclic Metal Carbonyl Complexes with Tetra-Antimony Ligands

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Abstract. Reactions of (norbornadiene)Cr(CO)₄ or *cis*-(piperidine)₂Mo(CO)₄ with R₂Sb-SbR₂, and *cyclo*-(R'Sb)_n (R' = Et, *n*-Pr; *n* = 4, 5) give the complexes *cyclo*-[M(CO)₄(R₂Sb-SbR'-SbR'-SbR₂)] (**1**: M = Cr, R = Me, R' = Et; **2**: M = Mo, R = Et, R' = Et; **3**: M = Mo, R = Et, R' = *n*-Pr). Not accessible to established characterization methods, the oily, extremely reactive unpurified mixture of **3** with scrambled ligands was characterized by mass spectrometry using liquid injection field desorption ionization (LIFDI).

Key words: Tetrastibane, Tetra-antimony ligand, Cyclic metal carbonyl complex, Liquid injection field desorption ionization (LIFDI)

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Introduction

Inspired by the pioneering work of Rheingold [1] on the famous ladder polymer *catena*-(MeAs)_x and on related antimony compounds, the study of the multifold chemistry of polystibanes has been in the focus of our research for many years [2–6]. In a preceding communication, we reported that distibanes R₂Sb-SbR₂ (R = Me, Ph) react with stable antimony rings (R'Sb)_n (R' = Me₃SiCH₂, *n* = 4, 5) forming of ring-chain equilibria mainly with tri-stibanes R₂Sb-SbR'-SbR₂ [3]. Although tetrastibanes are not major components of these equilibria they are trapped in reactions with (norbornadiene)Cr(CO)₄. The complexes *cyclo*-[Cr(CO)₄(R₂Sb-SbR'-SbR'-SbR₂)] form in good yield and the structures were determined by X-ray crystallography [4, 5].

In contrast to the well-established ring structures of (R'Sb)_n (R' = Me₃SiCH₂, *n* = 4, 5 [7]), much less is known of the chemistry of the ethyl and *n*-propyl polystibane system [2]. These sterically less protected polystibanes exist in the solid state as insoluble polymers *catena*-(R'Sb)_x (R' = Et, *n*-Pr, *x* >> 5), which as analogues of *catena*-(MeAs)_x are of particular interest [2]. Addition of benzene to *catena*-(R'Sb)_x and heating leads to ring chain equilibria. Faint yellow solutions of tetramers and pentamers *cyclo*-(R'Sb)_n (R' = Et,

n-Pr, *n* = 4, 5) form in very low concentrations. NMR-tube experiments revealed that also these rings react in solution with excess R₂Sb-SbR₂ (R = Me, Et) forming the tristibanes R₂Sb-SbR'-SbR₂ (R = Me, Et; R' = Et, *n*-Pr) [3].

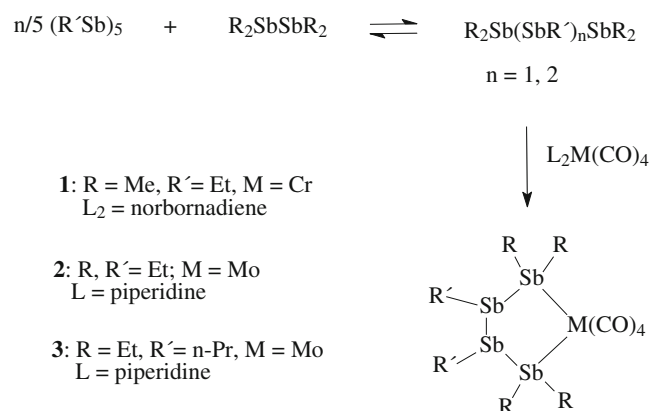
In continuation of these investigations, we have now studied the reactions of ethyl and *n*-propyl antimony polymers with distibanes using (norbornadiene)Cr(CO)₄ or *cis*-(piperidine)₂Mo(CO)₄ as trapping reagents. Here, we report on novel cyclic complexes with tetrastibane ligands.

Experimental

Sample Preparation

The operations were carried out in an argon atmosphere using dried solvents distilled under argon. (EtSb)_x [2], (*n*-PrSb)_x [2], Me₂Sb-SbMe₂ [8], Et₂Sb-SbMe₂ [8], (norbornadiene)Cr(CO)₄ [9], and *cis*-(C₅H₁₁N)₂Mo(CO)₄ [10] were prepared as described in the literature.

To prepare *cyclo*-[Cr(CO)₄(Me₂Sb-SbEt-SbEt-SbMe₂)] (**1**), 0.4 g (1.6 mmol) Cr(CO)₄(nbd) in 20 mL toluene, 0.5 g (3.3 mmol) (EtSb)_x in 20 mL toluene and 0.5 g (1.6 mmol) Me₂Sb-SbMe₂ in 10 mL toluene were combined. The resulting mixture was heated to reflux for 1 h and stirred at ambient temperature for 12 h. Removal of the solvent at reduced pressure, extraction of the oily residue with toluene/



Scheme 1. The shown structure applies to **2** and corresponds to the predominant component of **3** which is a mixture of homologues with scrambling alkane ligands of formula $Mo(CO)_4[Sb_4Et_{(6-n)}Pr_n]$ with $1 \leq n \leq 6$

petroleum ether (1/1), filtration through a frit covered with diatomaceous earth, and removal of the solvents gave 0.8 g of a red viscous liquid containing **1**.

Synthesizing *cyclo*-[$Mo(CO)_4(Et_2Sb-SbEt-SbEt-SbEt_2)$] (**2**), 2.0 g (13 mmol) $(EtSb)_x$, 2.5 g (8 mmol) *cis*-[$(C_5H_{11}N)_2Mo(CO)_4$], and 2.4 g (7 mmol) Et_4Sb_2 in 90 mL toluene were reacted as described above for **1**; 3.2 g of a red viscous oil containing **2** were obtained.

Preparing *cyclo*-[$Mo(CO)_4(Et_2Sb-PrSb-PrSb-SbEt_2)$] (**3**), 1.0 g (6 mmol) $(n-PrSb)_x$, 1.1 g (3 mmol) *cis*-[$(C_5H_{11}N)_2Mo(CO)_4$], and 1.1 g (3 mmol) Et_4Sb_2 in 60 mL toluene were reacted as described above for **1**. 2.0 g of a red viscous oil containing **3** were obtained.

Mass Spectrometry

LIFDI spectra were recorded with an AccuTOF instrument (JEOL, Tokyo, Japan) equipped with a LIFDI source

(LINDEN CMS, Leeste/Weyhe, Germany). Sample solutions were provided in capped autosampler vials sealed with a rubber septum. Ca. 40 nL of the toluene solutions of ca. 0.1–1 mMol/L were loaded to the LIFDI source via a fused silica capillary. The capillary was punched through the septum without breaking the inert environment as described elsewhere [11, 12].

Results and Discussion

The distibanes $R_2Sb-SbR_2$ (R = Me, Et) react with the polymers $(R'Sb)_x$ (R' = Et, n-Pr) and $(norbornadiene)Cr(CO)_4$, or *cis*- $(piperidine)_2Mo(CO)_4$ in refluxing toluene forming the tetrastibane complexes *cyclo*-[$M(CO)_4(R_2Sb-SbR'-SbR'-SbR_2)$] (**1**: M = Cr, R = Me, R' = Et; **2**: M = Mo, R = Et, R' = Et; **3**: M = Mo, R = Et, R' = n-Pr). An overview of the reaction pathway is given in Scheme 1. Like in previous experiments [4, 5], we found that tetrastibanes are coordinated as ligands in **1–3** although in the equilibria reactions between R_4Sb_2 (R = Me, Et) and $(RSb)_n$ (R = Et, n-Pr, Me_3SiCH_2) in benzene only tristibanes and no tetrastibanes were detected. Tetrastibanes are far better ligands forming five-membered heterocycles on coordination to Cr or Mo. Apparently they are trapped preferentially by reactions with the $M(CO)_4$ fragments.

The complexes **1–3** are initially formed as components of red liquid product mixtures. Attempts to crystallize these products failed. Separation by chromatographic methods led to decomposition. The established characterization methods X-ray, NMR, and elemental analysis failed to a large extent. The identification of **1–3** is, therefore, mainly based on mass spectrometry. The EI-spectra of **1** and **2** contain molecular ions and characteristic fragments resulting from the loss of CO molecules and alkyl groups:

Seventy eV MS (EI) of **1** exhibited peaks at the following m/z (%) [formula]: 798 (20) [$Me_2Et_4Sb_4Cr(CO)_4$]⁺⁺, 770 (40) [M]⁺⁺, 686 (40) [$M-3CO$]⁺⁺, 658 (40) [$M-4CO$]⁺⁺, 600

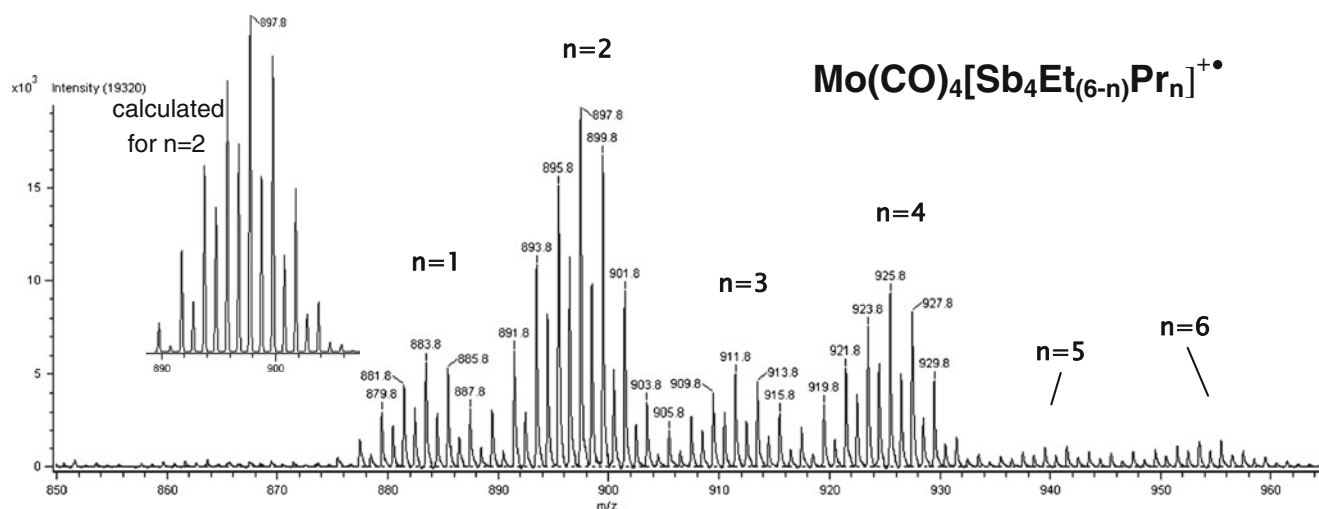


Figure 1. LIFDI spectrum of **3**. The molecular ion isotopic patterns exhibit a series of homologues with scrambled ethyl and propyl ligands. Substantial loss of ligands from the main component $Mo(CO)_4[Sb_4Et_4Pr_2]^{++}$ is not observed: $(M-CO)^+$, $(M-Et)^+$, and $(M-Pr)^+$ are absent at m/z 870, m/z 869, and m/z 855 respectively. The inset shows the calculated isotopic pattern of $Mo(CO)_4[Sb_4Et_4Pr_2]^{++}$

(40), 585 (20) $[M-4CO-2Et-Me]^+$, 555 (20) $[MeSb_4Cr]^+$, 540 (70) $[Sb_4Cr]^+$, 432 (40) $[MeSb_3Cr]^+$, 417 (30) $[Sb_3Cr]^+$, 28 (100) $[CO]^+$.

Seventy eV MS (EI) of **2** exhibited peaks at the following m/z (%) [formula]: 870 (43) $[M]^+$, 842 (6) $[M-CO]^+$, 814 (19) $[M-2CO]^+$, 785 (6) $[M-2CO-Et]^+$, 756 (13), 728 (19), 699 (18), 642 (46), 613 (49) $[MoSb_4Et]^+$, 585 (20) $[MoSb_4H]^+$, 360 (55) $[Et_4Sb_2]^+$, 301 (54) $[Et_2Sb_2]^+$, 273 (47) $[EtSb_2]^+$, 208 (40) $[Et_3Sb]^+$, 150 (88) $[EtSb]^+$, 28 (100) $[CO]^+$.

1H -NMR (C_6D_6) 0.9–2.0 (m). IR Nujol: 2012 (st), 1940 (st), 1908 (st) cm^{-1} ν (CO).

Meaningful EI mass spectra of the propyl compound **3** were not obtained. However with the liquid injection field desorption ionization (LIFDI) technique [11], molecular ions not only of **3** but also of the series of $Mo(CO)_4Sb_4Et_{(6-n)}Pr_n$ complexes with $1 \leq n \leq 6$ are observed:

MS (LIFDI) m/z (rel. int. %) [formula]: 954 (6) $[Mo(CO)_4Pr_6Sb_4]^+$, 940 (5) $[Mo(CO)_4EtPr_5Sb_4]^+$, 926 (50) $[Mo(CO)_4Et_2Pr_4Sb_4]^+$, 912 (20) $[Mo(CO)_4Et_3Pr_3Sb_4]^+$, 898 (100) $[Mo(CO)_4Et_4Pr_2Sb_4]^+$, 884 (30) $[Mo(CO)_4Et_5PrSb_4]^+$. 1H -NMR (C_6D_6) 0.6–2.0 m. IR Nujol: 2012.5 (st), 1930.5 sh, 1909 (st) ν (CO) cm^{-1} .

The LIFDI spectrum of **3** is shown in Figure 1. In contrast to the EI spectra of **1** and **2**, the LIFDI spectra do not exhibit loss of CO molecules or alkyl groups, the base peaks of which would appear at m/z 870 (loss of CO), 869 (loss of Et), or 855 (loss of Pr), respectively, from the main component of **3**. The absence of CO loss convincingly proves the unprecedented softness of the LIFDI technology compared with other ionization methods including electrospray ionization (ESI) [13], matrix assisted laser desorption ionization (MALDI), and fast atom bombardment (FAB) [14].

Mixed species are also observed in the electron impact spectrum of **1**. Apparently, scrambling of the alkyl groups accompanies the formation of **1** and **3** and hampers the crystallization and structural analysis by X-ray methods. Structures of related complexes are, however, well known. There is little doubt that the *catena*-tetrastibanes coordinate through the terminal antimony atoms to the transition metal centers [4, 5].

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