Formation and Structure of 
\([\text{CO}_4\text{Mo(ET}_4\text{Sb})_2]\) 

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Formation and Structure of \([\text{CO}_4\text{Mo(ET}_4\text{Sb})_2]\) (1) and of a complex with distibane and distibane oxide ligands (2) are reported.

**Key words:** Antimony, Chromium, Molybdenum

**Introduction**

Distibanes, \(\text{R}_4\text{Sb}_2\), and distibane oxides, \(\text{R}_4\text{Sb}_2\text{O}\), have been used as monodentate or bidentate bridging antimony ligands [1]. Previous work has shown that cyclic complexes of the type \([\text{CO}_4\text{M(R}_4\text{Sb}_2)]_2\) \((\text{M} = \text{Cr}, \text{R} = \text{Me}[2])\) and \([\text{CO}_4\text{M(R}_4\text{Sb}_2\text{O})]_2\) \((\text{M} = \text{Cr}, \text{R} = \text{Me}[3], \text{Ph}[4])\) are formed, when two distibane or distibane oxide molecules occupy bridging positions between two 14-electron transition metal tetracarbonyl fragments. We report here the synthesis and the structure of \([\text{CO}_4\text{Mo(ET}_4\text{Sb})_2]\) (1), a cyclic complex with the tetrathyl distibane ligand and of a complex with distibane and distibane oxide ligands (2).

**Results and Discussion**

\([\text{CO}_4\text{Mo(ET}_4\text{Sb})_2]\) (1) is formed by the ligand exchange reaction between excess ET\(_4\)Sb\(_2\) and \([\text{cis}-(\text{piperidine})_2\text{Mo(\text{CO})}_4]\) in toluene. This reaction represents a direct synthesis for a complex containing two bridging distibane ligands between transition metal carbonyl fragments. The analogous complex \([\text{CO}_4\text{Cr(Me}_4\text{Sb}_2)]_2\) was obtained serendipitously from 2,6-Mes\(_2\)C\(_6\)H\(_4\)Sb(SbMe\(_2\)\(_2\)) \((\text{Mes} = 2,4,6-\text{Me}_3\text{C}_6\text{H}_2)\) and \([\text{Cr(nbd)(\text{CO})}_4]\) (nbd = norbornadiene) [2]. The reaction between Me\(_4\)Sb\(_2\) and \([\text{Cr(nbd)(\text{CO})}_4]\) gave the polymer \([\text{CO}_4\text{Cr(Me}_4\text{Sb}_2)]_n\) [5] instead of a cyclic dimer.

Compound 1 is a yellow crystalline compound, soluble in organic solvents and sensitive to air. The complex was characterized by spectroscopic methods and X-ray crystallography. The molecular structure is depicted in Fig. 1.

**Note**

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conformation, with a Mo–Sb–Mo torsion angle of 72.1(2)°. This value is similar to the Cr–Sb–Cr–Cr torsion angle in [(CO)$_4$Cr(Me$_2$Sb)$_2$]$_2$ (66.8(1)° [2]).

Complex 2 was isolated from a product mixture formed by reacting [Cr(nbd)(CO)$_4$], Me$_2$Sb$_2$ and the ethyl antimony polymer (EtSb). Mass spectrometry revealed that the target molecule cyclo-

[Cr(CO)$_4$(Me$_2$Sb(SbEt)$_2$SbMe$_2$)] was present in the product mixture, but attempts to isolate and fully characterize this tetrastibane complex failed [11]. However, analogous complexes are known from our previous work [12, 13]. The formation of 2 can easily be explained by reactions of the components [Cr(nbd)(CO)$_4$], Me$_2$Sb$_2$ and traces of oxygen from the environment which lead to a partial oxidation of the distibane ligands. Complex 2 was characterized by NMR spectroscopy, mass spectrometry and single-crystal X-ray crystallography. The $^1$H NMR spectrum of 2 in C$_6$D$_6$ shows two singlet signals (δ = 0.88, 0.93 ppm) of almost equal intensity for the bridging Me$_3$Sb$_2$ and Me$_4$Sb$_2$O ligands. These data are different from the value of the known complex with two distibane oxide ligands [(CO)$_4$Cr(Me$_2$Sb$_2$O)$_2$] (δ = 1.00 ppm [3]), which shows up as an impurity in the spectrum. It would be of interest to compare the spectra of 2 and of the known distibane complex [(CO)$_4$Cr(Me$_2$Sb)$_2$]$_2$, but no NMR data are available for the latter. The EI mass spectrum of 2 contains an intense peak for the molecular ion and peaks for fragments resulting from the loss of CO groups. Single crystals of 2 were analyzed by X-ray diffraction. The determination of the molecular structure revealed fixed positions for the Cr(CO)$_4$ groups and pair-wise disordered positions for the carbon and antimony atoms of the distibane and distibane oxide bridges. A model of a molecule selected from the disordered structure of 2 is shown in Fig. 2. The geometry of the Cr(CO)$_4$ groups is as expected. Due to the disorder, the geometric parameters of the antimony ligands, and particularly the position of the bridging oxygen atom, are not well defined. The values for the Sb–Cr and Sb–C bond lengths in 2 are similar to those for [(CO)$_4$Cr(Me$_2$Sb)$_2$]$_2$ (Sb–Cr 2.6205(9) Å, Sb–C (2.122(10), 2.096(13) Å [2]) and [(CO)$_4$Cr(Me$_2$Sb$_2$O)$_2$] (Sb–C 2.573 (4), 2.566 (3) Å; Sb–C 2.076(18) – 2.131(15) Å [3]).

Conclusion

The synthesis of [(CO)$_4$Mo(Et$_2$Sb)$_2$]$_2$ (1) from appropriate precursors is important for the development of the chemistry of cyclic complexes with distibane ligands. Complex 2 is an example of a cyclic complex with two different ligands between transition metal atoms. The crystal structure determination of 2 reveals disorder of the positions of the ligands, and based on crystallographic data the presence of [(CO)$_4$Cr(Me$_2$Sb)$_2$]$_2$ and [(CO)$_4$Cr(Me$_4$Sb$_2$O)$_2$] in the crystal cannot be ruled out. The $^1$H NMR data and the mass spectra are in favor of a description of 2 as the complex [(CO)$_4$Cr(Me$_2$Sb$_2$O)(Me$_4$Sb$_2$)Cr(CO)$_4$].

Experimental Section

The operations were performed in an inert atmosphere using dry solvents distilled under argon. The NMR spectra were recorded on a Bruker Avance DPX-200 spectrometer operating at 200.1 MHz ($^1$H), and 50.3 MHz ($^{13}$C). The infrared spectrum was recorded from Nujol mull on a Perkin-Elmer Spectrum 1000 instrument. Mass spectra were recorded on a Finnigan MAT 8200 spectrometer. (EtSb)$_2$ [14], Me$_4$Sb$_2$, Et$_2$Sb$_2$ [15], [nbd]Cr(CO)$_4$ [16], and [cis-(piperidine)$_2$Mo(CO)$_4$] [17] were prepared as described in the literature.
Fig. 2. Molecular structure of a molecule selected from the disordered structure of 2 (displacement ellipsoids at the 25% probability level; hydrogen atoms omitted for clarity). Selected bond lengths (Å) and bond angles (deg): C4–Sb1 2.16(3), C5–Sb1 2.30(6), C4A–Sb1A 2.105(15), C5A–Sb1A 2.089(19), Cr1–Sb1 2.773(8), Cr1–Sb1A 2.540(4); C4–Sb1–C5 112.6(15), C4–Sb1–Cr1 113.2(9), C5–Sb1–Cr1 106.6(14), C4A–Sb1A–C5A 96.6(7), 4A–Sb1A–Cr1I 121.6(4), Cr5A–Sb1A–Cr1I 125.0(7).

Synthesis of [Mo(CO)4(ET2SbSbET2)]2 (1)

A solution of 1.0 g (2.6 mmol) of [cis-(piperidine)2Mo(CO)4] and 1.5 g (4.1 mmol) of ET2Sb2 in 90 mL toluene was heated to reflux for 1 h and stirred at ambient temperature for 12 h. Crystallization from n-hexane gave 0.17 g (20%) of yellow crystals of 1. Single crystals were obtained by recrystallization from toluene/petroleum ether (1/1) at −28 °C. M. p. 180 °C. – IR (Nujol): ν(CO) = 2011, 1909, 1875 cm−1. – 1H NMR (200.1 MHz, C6D6): δ = 1.23 (t, 6H, CH3, J = 8 Hz), 1.71 – 1.84 (m, 4H, CH2). – 13C NMR (50.3 MHz, C6D6): δ = 7.48 (CH3), 12.69 (CH2), 212.18 (CO), 214.35 (CO). – MS (EI; 70 eV): m/z (%) = 1138 (9) [M]+, 900 (9), 707 (9), 680 (17), 463 (10), 360 (55) [ET4Sb2]+, 303 (54) [ET2Sb2]+, 275 (52) [ET2Sb2]+, 245 (28), 208 (27), 179 (18) [ET2Sb]+, 151 (65) [ET2SbH]+, 28 (100) [CO]+.

Formation of 2

Cr(CO)4(nbd) (0.4 g, 2 mmol) in 20 mL toluene, 0.5 g (3 mmol) of (ET4Sb)x in 20 mL toluene and 0.5 g (2 mmol) of...
of Me₄Sb₂ in 10 mL toluene were combined, and the resulting mixture was heated to reflux for 1 h and stirred at ambient temperature for 12 h. Removal of the solvent under reduced pressure, extraction of the oily residue with toluene/petroleum ether (1/1), filtration through a frit covered with Kieselgel, and removal of the solvents gave 0.8 g of a red viscous liquid. Dissolving this product in toluene/petroleum ether and crystallization at −28 °C gave several crystals of \( \text{Sb}_2 \text{(CO)}_6 \text{Me}_4 \text{Cr} \). 

Crystal structure determinations

Data were collected at 173(2) K on a Siemens P4 diffractometer using MoKα radiation (λ = 0.71073 Å) and corrected for absorption effects using DIFABS [18]. The structures were solved by Direct Methods [19]. Structure solutions and refinements were performed using the WinGX software package [20].

The antimony atoms in the structure of \( \text{Me}_4\text{Sb}_2 \text{Cr} \) were found to be disordered over two positions. The refinement was carried out using free variables. The ratio of the disorder components containing antimony and carbon atoms is 0.26 : 0.74. The O4 atom is located on a C2 axis. The crystal structure can be described as composed of the complexes \([\text{(CO)}_4\text{CrMe}_2\text{SbShMe}_2]_2\), \([\text{(CO)}_4\text{CrMe}_2\text{SbOShMe}_2]_2\); and \([\text{(CO)}_4\text{Cr}(\text{SbShMe}_2)(\text{SbOShMe}_2)\text{Cr}])_2\). The ratio of the disordered components containing antimony and carbon atoms is 0.26 : 0.74. The O4 atom is located on a C2 axis with a site occupation factor of 0.37. The Sb1–C5 and Sb1A–O4 bonds were the subject of the rigid bond restraint with the standard uncertainty for the anisotropic displacement parameters at 0.1 and 0.5, respectively. For Sb1A–O4 also a restraint for the isotropic displacement parameters was applied. The C4 and C5 atoms were restrained to have an isotropic behavior, approximated with a standard uncertainty of 0.01.

Crystallographic data are summarized in Table 1. The representations of the molecular structures were created using the DIAMOND software package [21].

CCDC 830725 and 830726 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre \textit{via} www.ccdc.cam.ac.uk/data_request/cif.