Formation and Structure of $[(CO)_4Mo(Et_4Sb_2)]_2$

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The formation and the structure of $[(CO)_4Mo(Et_4Sb_2)]_2$ (**1**) and of a complex with distibane and distibane oxide ligands (**2**) are reported.

Key words: Antimony, Chromium, Molybdenum

Introduction

Distibanes, R_4Sb_2, and distibane oxides, R_4Sb_2O, have been used as monodentate or bidentate bridging antimony ligands [1]. Previous work has shown that cyclic complexes of the types $[(CO)_4M(R_4Sb_2)]_2$ (M = Cr, R = Me [2]) and $[(CO)_4M(R_4Sb_2O)]_2$ (M = Cr, R = Me [3], 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 $[(CO)_4Mo(Et_4Sb_2)]_2$ (**1**), a cyclic complex with the tetraethyl distibane ligand and of a complex with distibane and distibane oxide ligands (**2**).

Results and Discussion

$[(CO)_4Mo(Et_4Sb_2)]_2$ (**1**) is formed by the ligand exchange reaction between excess Et_4Sb_2 and [*cis*-(piperidine)$_2$Mo(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 $[(CO)_4Cr(Me_4Sb_2)]_2$ was obtained serendipitously from 2,6-$Mes_2C_6H_3Sb(SbMe_2)_2$ (Mes = 2,4,6-$Me_3C_6H_2$) and [Cr(nbd)(CO)$_4$] (nbd = norbornadiene) [2]. The reaction between Me_4Sb_2 and [Cr(nbd)(CO)$_4$] gave the polymer $[(CO)_4Cr(Me_4Sb_2)]_n$ [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 ^{1}H NMR spectrum at 200 MHz in C_6D_6 contains a triplet signal for the methyl groups (δ = 1.23 ppm) and broad multiplet signals (δ = 1.71 – 1.84 ppm) for the diastereotopic protons of the methylene groups. The signals of complex **1** are considerably shifted from those of the free ligand Et_4Sb_2 (CH_3: δ = 1.33 ppm; CH_2: δ = 1.6 – 1.7 ppm) [6]. The ^{13}C NMR spectrum of **1** contains all the expected signals for the carbon atoms of the ethyl and CO groups. The mass spectrum shows the signals of the molecular ion and characteristic fragments. Three of the expected four signals can be distinguished in the IR spectrum for the ν(CO) streching vibrations of the Mo(CO)$_4$ groups. The crystal structure of **1** was determined by single-crystal X-ray diffraction. The molecular structure is depicted in Fig. 1.

The structure of **1** is composed of two tetracarbonyl molybdenum groups connected by two bridging tetraethyldistibane ligands in *cis* positions to each other. The resulting central Mo_2Sb_4 heterocycle adopts a chair conformation. The value for the Sb–Sb bond length in **1** is very similar to the corresponding values reported for other complexes or adducts with distibane ligands, as, *e. g.* $[(CO)_5Cr]_2(R_4Sb_2)$ (R = Me 2.810(1) Å [7]; R = Ph 2.865(4) Å [8]), $[(CO)_4Cr(Me_4Sb_2)]_2$ (2.816(1) Å [2]), $[tBu_3M]_2(Et_4Sb_2)$ (M = Al 2.838(1), Ga, 2.839(1) Å [10]). The Sb–Mo bonds in **1** are a little longer than the corresponding bond in $Ph_3SbMo(CO)_5$ (2.756(1) Å [9]). The geometry of the Mo(CO)$_4$ fragments is normal with bond angles close 90°. The sum of the C–Sb–Sb and C–Sb–C bond angles in **1** (295.5°) is similar to analogous sums of angles in the adducts $[tBu_3M]_2(Et_4Sb_2)$ (M = Al 292.9°; Ga, 291.1° [10]) and in $[(CO)_4Cr(Me_4Sb_2)]_2$ (294.8° [2]). These sums of angles are between the values expected for a p^3 configuration (270°) and a sp^3 hybridization (328°) of the coordinating antimony atoms. The distibane fragments in **1** adopt a synclinal

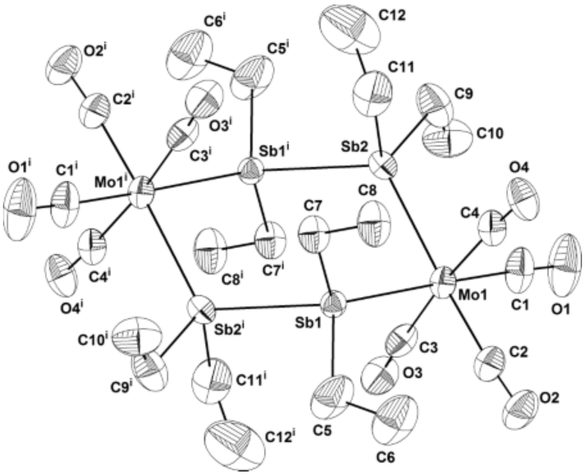

Fig. 1. Molecular structure of $[(CO)_4Mo(Et_4Sb_2)]_2$ (**1**) in the crystal (displacement ellipsoids at the 20 % probability level; hydrogen atoms omitted for clarity). Selected bond lengths (Å) and bond angles (deg): C5–Sb1 2.180(13), C7–Sb1 2.185(10), C9–Sb2 2.150(12), C11–Sb2 2.25(2), Mo1–Sb1 2.800(2), Mo1–Sb2 2.768(2), Sb1–Sb2^{i} 2.817(2); C5–Sb1–C7 97.8(6), C5–Sb1–Mo1 117.5(4), C7–Sb1–Mo1 120.0(3), C9–Sb2–C11 102.9(7), C9–Sb2–Mo1 118.5(5), C11–Sb2–Mo1 108.9(6), Sb1–Mo1–Sb2 89.4(1).

conformation, with a Mo–Sb–Sb–Mo torsion angle of 72.1(2)°. This value is similar to the Cr–Sb–Sb–Cr torsion angle in $[(CO)_4Cr(Me_4Sb_2)]_2$ (66.8(1)° [2]).

Complex **2** was isolated from a product mixture formed by reacting $[Cr(nbd)(CO)_4]$, Me_4Sb_2 and the ethyl antimony polymer $(EtSb)_x$. Mass spectrometry revealed that the target molecule *cyclo*-$[Cr(CO)_4(Me_2Sb(SbEt)_2SbMe_2)]$ 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_4Sb_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_6D_6 shows two singlet signals ($\delta = 0.88$, 0.93 ppm) of almost equal intensity for the bridging Me_4Sb_2 and Me_4Sb_2O ligands. These data are different from the value of the known complex with two distibane oxide ligands $[(CO)_4Cr(Me_4Sb_2O)]_2$ ($\delta = 1.00$ 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 $[(CO)_4Cr(Me_4Sb_2)]_2$, 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 $[(CO)_4Cr(Me_4Sb_2)]_2$ (Sb–Cr 2.6205(9) Å, Sb–C (2.122(10), 2.096(13) Å [2]) and $[(CO)_4Cr(Me_4Sb_2O)]_2$ (Sb–Cr 2.573 (4), 2.566 (3) Å; Sb–C 2.076(18) – 2.131(15) Å [3]).

Conclusion

The synthesis of $[(CO)_4Mo(Et_4Sb_2)]_2$ (**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 $[(CO)_4Cr(Me_4Sb_2)]_2$ and $[(CO)_4Cr(Me_4Sb_2O)]_2$ 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 $[(CO)_4Cr(Me_4Sb_2O)(Me_4Sb_2)Cr(CO)_4]$.

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. $(EtSb)_x$ [14], Me_4Sb_2, Et_4Sb_2 [15], $[(nbd)Cr(CO)_4]$ [16], and [*cis*-(piperidine)$_2Mo(CO)_4$] [17] were prepared as described in the literature.

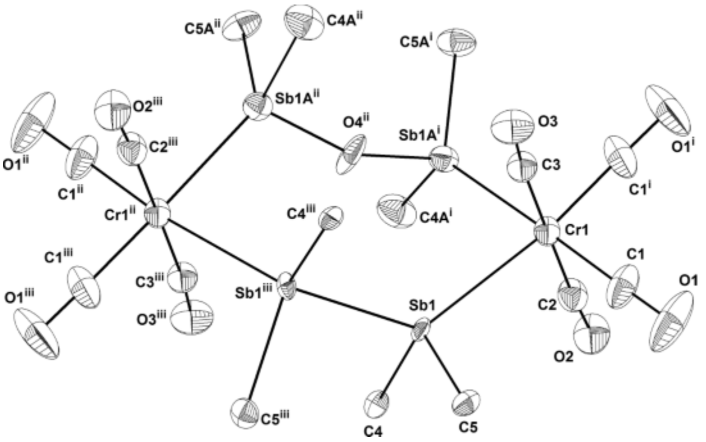

Fig. 2. Molecular structure of a molecule selected from the disordered structure of **2** (displacement ellipsoids at the 25 % probability level; hydrogen atoms omitted for clarity). Selected bond lengths (Å) and bond angles (deg): C4–Sb1 2.16(3), C5–Sb1 2.30(6), C4A^{i}–Sb1A^{i} 2.105(15), C5A^{i}–Sb1A^{i} 2.089(19), Cr1–Sb1 2.773(8), Cr1–Sb1A^{i} 2.540(4); C4–Sb1–C5 112.6(15), C4–Sb1–Cr1 113.2(9), C5–Sb1–Cr1 106.6(14), C4A^{i}–Sb1A^{i}–C5A^{i} 96.6(7), C4A^{ii}–Sb1A^{ii}–Cr1^{ii} 121.6(4), Cr5A^{ii}–Sb1A^{ii}–Cr1^{ii} 125.0(7).

*Synthesis of [Mo(CO)$_4$(Et$_2$SbSbEt$_2$)]$_2$ (**1**)*

A solution of 1.0 g (2.6 mmol) of [*cis*-(piperidine)$_2$Mo(CO)$_4$] and 1.5 g (4.1 mmol) of Et$_4$Sb$_2$ 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}. – ^{1}H NMR (200.1 MHz, C$_6$D$_6$): $\delta = 1.23$ (t, 6H, C*H*$_3$, $J = 8$ Hz), 1.71 – 1.84 (m, 4H, C*H*$_2$). – ^{13}C NMR (50.3 MHz, C$_6$D$_6$): $\delta = 7.48$ (*C*H$_3$), 12.69 (*C*H$_2$), 212.18 (*C*O), 214.35 (*C*O). – MS (EI; 70 eV): m/z (%) = 1138 (9) [M]$^{+}$, 900 (9), 707 (9), 680 (17), 463 (10), 360 (55) [Et$_4$Sb$_2$]$^{+}$, 303 (54) [Et$_3$Sb$_2$]$^{+}$, 275 (52) [Et$_2$Sb$_2$]$^{+}$, 245 (28), 208 (27), 179 (18) [Et$_2$Sb]$^{+}$, 151 (65) [EtSbH]$^{+}$, 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 (EtSb)$_x$ in 20 mL toluene and 0.5 g (2 mmol)

Table 1. Crystal structure data and numbers pertinent to data collection and structure refinement for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{24}H_{40}Mo_2O_8Sb_4$	$C_{16}H_{24}Cr_2O_{8.75}Sb_4$
Formula weight, g mol^{-1}	1135.44	947.33
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/m$
a, Å	10.9705(15)	13.251(3)
b, Å	14.0618(13)	11.259(3)
c, Å	12.3199(13)	10.447(3)
β, deg	107.057(9)	116.68(3)
Volume, Å^3	1816.9(4)	1392.7(7)
Z	2	2
Calculated density, Mg m^{-3}	2.08	2.25
Absorption coefficient, mm^{-1}	3.6	4.6
$F(000)$, e	1072	884
Crystal size, mm^3	0.3 × 0.4 × 0.6	0.2 × 0.3 × 0.4
θ range for data collection, deg	2.62 – 27.50	2.5 – 27.48
Index ranges *hkl*	±14, ±18, −16 → 15	−11 → 16, −14 → 13, ±13
Reflections collected / unique / R_{int}	4159 / 3133 / 0.0308	1680 / 1211 / 0.0439
Completeness to θ_{max}, %	99.7	99.6
Max. and min. transmission	0.061, 0.496	0.081, 0.533
Data / parameters / restraints	4159 / 196 / 17	1680 / 113 / 14
Goodness-of-fit on F^2	1.029	1.049
Final $R1$ / $wR2$ [$I > 2\sigma(I)$]	0.0503 / 0.1401	0.0396 / 0.0914
Final $R1$ / $wR2$ (all data)	0.0674 / 0.1544	0.0643 / 0.1017
Extinction coefficient	0.0011(3)	–
Largest difference hole / peak, e Å^{-3}	−1.44 / 1.01	−0.79 / 0.72

of Me_4Sb_2 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 Kieselgur, 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 **2**. – ^{1}H NMR (200.1 MHz, C_6D_6): δ = 0.88 (s, 12 H, Cr-$(CH_3)_2$Sb-Sb$(CH_3)_2$-Cr), 0.93 (s, 12 H, Cr–$(CH_3)_2$SbOSb$(CH_3)_2$-Cr). – MS (EI, 70 eV): m/z (%) = 952 (40) $[M]^+$, 840 (40) $[M–Me–4CO]^+$, 756 (40) [M–Me–7CO], 728 (70) $[M–Me–8CO]^+$, 668 (40) $[M–5Me–8CO]^+$, 304 (80) $[Me_3Sb_2O]^+$, 151 (100) $[Me_2Sb]^+$.

Crystal structure determinations

Data were collected at 173(2) K on a Siemens P4 diffractometer using Mo K_α 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 **1** were found to be disordered over two positions. The refinement was carried out using free variables. The ratio of the disorder components is 0.85 to 0.15. In order to obtain normal C–C bond lengths for the ethyl groups, C5, C6, and C11, C12 were restrained to a value of 1.54 Å within a standard uncertainty of 0.02 Å. In order to fix the orientation of the methyl group containing C12, the Sb2···C12 distance was restrained to a value of 3.1 Å within a standard uncertainty of 0.02 Å. Rigid bond restraints were applied to C5–C6 and C11–C12 bonds. For the C5, C6, C11, and C12 atoms a restraint for the isotropic displacement parameters was applied.

The structure of **2** was refined using free variables for the antimony atoms and for the O4 atom. The center of the molecule is located on a C_2 axis. The crystal structure can be described as composed of the complexes $[(CO)_4CrMe_2SbSbMe_2]_2$, $[(CO)_4CrMe_2SbOSbMe_2]_2$ and $(CO)_4Cr(Me_2SbSbMe_2)(Me_2SbOSbMe_2)Cr(CO)_4$. The ratio of the disordered components containing antimony and carbon atoms is 0.26 : 0.74. The O4 atom is located on a C_2 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 *via* www.ccdc.cam.ac.uk/data_request/cif.

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