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Preliminary communication

Synthesis and molecular structure of $[\eta^5\text{-}C_5H_5Mo(CO)_2]_2(\mu,\eta^2\text{-}Sb_2)$. Formation of an Sb=Sb double bond from metallic antimony

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Abstract

The complex $\{[\eta^5\text{-}C_5H_5Mo(CO)_2]_2(\mu,\eta^2\text{-}Sb_2)\}$ (1), synthesized from the thermolytic reaction of $[\eta^5\text{-}C_5H_5Mo(CO)_3]_2$ and elemental antimony, is the first example of μ,η^2 coordination of a four-electron diantimony fragment to a transition metal dimer. As determined by X-ray crystallography, 1 is a tetrahedral cluster characterized by a very short Sb–Sb bond of 2.678(1) Å bound side-on to form a plane nearly perpendicular to an elongated Mo–Mo bond of 3.114(1) Å.

The interactions of the Group-15 metalloids (E = P, As) with isoelectronic 15-electron transition-metal centers have generated a number of novel complexes [1]. For example, the thermolytic reactions of $[\eta^5\text{-}C_5H_5Mo(CO)_3]_2$ and the *cyclo*-organopolyarsines $[(RAs)_n$ where R = Me, $n = 5$; R = Ph, $n = 6]$, have resulted in the sequential replacement of As by $CpMo(CO)_2$ (Cp = $\eta^5\text{-}C_5H_5$) in the tetrahedrane framework and the formation of $CpMo(CO)_2(\eta^3\text{-}As_3)$ [2], $\{[CpMo(CO)_2)_2](\mu,\eta^2\text{-}As_2)\}$ (2) [3,4] and $\{[CpMo(CO)_2]_3(\mu_3\text{-}As)\}$ [5] (realgar, As_4S_4, as the arsenic source). More recently yellow arsenic, As_4, has been used in the synthesis of arsenic-containing clusters [6].

We have now extended this mode of reactivity to antimony and report the synthesis and molecular structure of $\{[CpMo(CO)_2)_2]\}(\mu,\eta^2\text{-}Sb_2)\}$ (1), which represents the first example of a four-electron donor diantimony fragment coordinating in a side-on, μ,η^2 fashion to a transition-metal dimer. Complex **1** is synthesized from the reaction of $[\eta^5\text{-}C_5H_5Mo(CO)_3]_2$ (0.752 g, 1.535 mmol) and elemental (metallic) antimony (1.871 g, 15.37 mmol) in 15 ml of toluene in a sealed Carius tube heated in a sand bath (180 °C, 5 d). The filtrate of the cooled reaction mixture was chromatographed on an alumina column and **1** was isolated (Et_2O, 10% CH_2Cl_2) in low yield (4.3%) [7*]. Recrystallization in toluene produced red, nearly isometric crystals suitable for X-ray diffraction [8*].

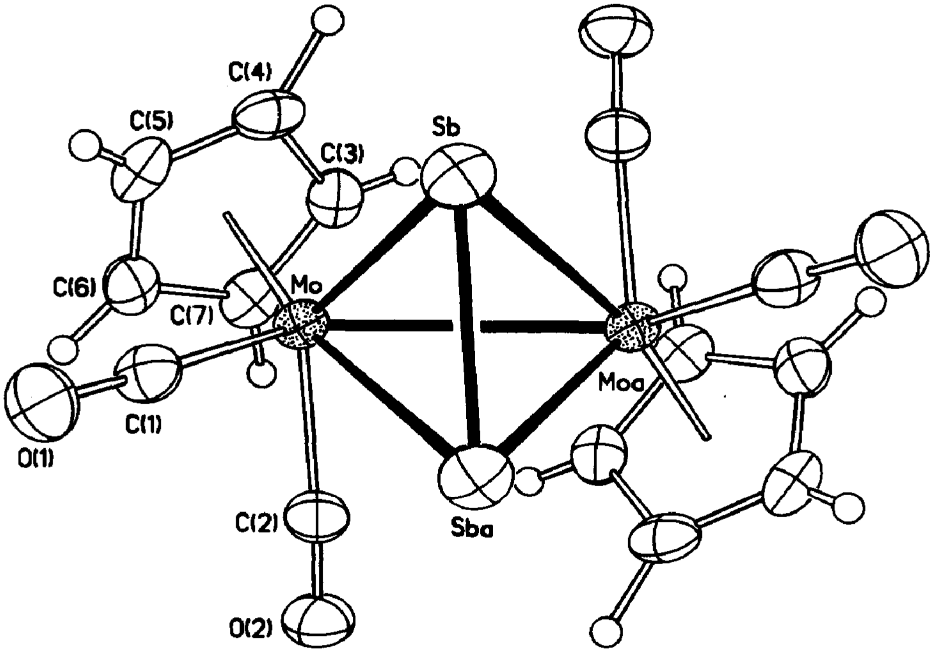

Fig. 1. Molecular structure and labelling scheme for **1**. (CNT–Mo, 2.027(3); Mo–Mo(a), 3.114(1); Mo–Sb, 2.762(1); Mo–Sb(a), 2.854(1); Sb–Sb(a), 2.678(1) Å; Mo–C(1)–O(1), 176.1(4); Mo–C(2)–O(2), 172.5(4)°. CNT(1)–Mo–Mo(a)–CNT(2), −78.2°. Mo–Sb–Sb(a)–Mo(a), 86.5°.

The molecular structure of **1** as determined by X-ray crystallography is shown in Fig. 1. The midpoints of the Mo–Mo and Sb–Sb vectors lie on a crystallographic two-fold axis. This distorted tetrahedral cluster framework is structurally analogous to the previously reported diarsenic complex (**2**) [3]. The side-on diantimony (and diarsenic) fragments form a plane which is nearly perpendicular with the Mo–Mo (a) bond (deviation = 3.5°). The cyclopentadienyl ligands are arranged in a staggered, *cis-gauche* arrangement (torsion angle = −78.2°). Complex **1** possesses an extremely short Sb–Sb bond (2.678(1) Å). Previous examples of multiple Sb–Sb bonds include: the triangular pinwheel complex $\{[W(CO)_5]_3(\mu_3,\eta^2\text{-}Sb_2)_2\}$ (**3**), Sb–Sb = 2.663(3) Å [9] (the shortest Sb–Sb we are aware of), where the diantimony fragment acts as a six-electron donor; the stibinidene complexes $\{[M(CO)_5]_3(\mu_3,\eta^2\text{-}RSb_2)_2\}$ (M = W, R = Ph, Sb–Sb = 2.706(4) Å) [9]; M = Cr, R = t-Bu, Sb–Sb = 2.720(3) Å) [10]; the metallocyclopropane analogue $\{Fe(CO)_4[\eta^2\text{-}(SiMe_3)_2CHSb]_2\}$, Sb–Sb = 2.774(1) Å [11]; the tetraphenyltristibine anion $Ph_4Sb_3^-$, Sb–Sb = 2.761(1)Å [12]; and interspersed short distances in the Zintl anions Sb_7^{3-} (Sb–Sb range = 2.717(2) to 2.906(2) and 2.692(4) to 2.880(4) Å, respectively) [13,14] and Sb_4^{2-} (Sb–Sb ave = 2.750(1) Å) [13]. In comparison, representative distances for an Sb–Sb single bond are 0.15–0.20 Å longer as demonstrated in: *cyclo*(t-BuSb)$_4$, 2.818(2) [15]; *cyclo*(PhSb)$_6$, 2.837(3)[16]; and $\{[(CH_3)_3Si]_2Sb\}_2$, 2.867(1) Å [17].

The nature of the bonding of the "naked" diantimony fragments in **1** and in **3** can be assessed through a comparison of Sb–Sb and M–Sb distances in the two complexes. The Sb–Sb distance is 0.015 Å longer in **1**, in which the Sb$_2$ group is a

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* Reference number with asterisk indicates a note in the list of references.

four-electron donor, compared to **3** where the group is an apparent six-electron donor; corresponding Mo–Sb distances (2.762(1) and 2.854(1) Å) are skewed to accommodate the Cp rings (cf. 3.5° deviation from perpendicularity) and considerably shorter than the nearly equivalent W–Sb distances (3.016(3) Å) found in **3**. The Mo–Mo distance, 3.114(1) Å, is longer in **1** than in its As_2 analogue, 3.039(2) Å, reflecting the approximately 0.5 Å increase in the pnictogen–pnictogen bond.

Several other products accompany the formation of **1**. We find mass spectrometric evidence for $[CpMo(CO)]_2(\mu,\eta^2\text{-}Sb_2)_2$ (for which the As analogue is known) [16], and crystallographic evidence for the formation of various fulvalene-substituted products, i.e., $\{\eta^5:\eta^5\text{-}C_{10}H_8[Mo_2(CO)_6]\}$ and $[(\eta^5\text{-}C_5H_5)(\eta^5:\eta^5\text{-}C_{10}H_8)Mo_3(CO)_6(\mu_3\text{-}Sb)]$. In the presence of $Mo(CO)_6$, an $Mo(CO)_5$ group caps Sb in the Mo_3Sb tetrahedral complex $\{(\eta^5\text{-}C_5H_5Mo(CO)_2)_3(\mu_3\text{-}Sb)[Mo(CO)_5]\}$. The formation of the fulvalene products is particularily intriguing, and a more complete study of reaction conditions and pathways leading to its formation is currently underway.

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7 ^{1}H NMR (250 MHz, C_6D_6): δ 4.367 (5H). IR (CH_2Cl_2): ν_{CO} 1936, 1885 cm^{-1}. M.p. 252°C. HRMS: 677.6705 (calcd. 677.676 amu).

8 *Crystal data*: (23°C) for **1**, monoclinic, $I2/a$, a 14.457(9), b 7.627(7), c 16.865(11) Å, β 115.86(5)°, V 1673.4(22) Å^3, $Z = 4$, D_c 2.765 g cm^{-3}, μ(Mo-K_α) 46.62 cm^{-1}. A Nicolet R3m/μ diffractometer was used to collect 2125 data ($4° \leqslant 2\theta \leqslant 55°$) of which 1916 were independent ($R_{int} = 2.10\%$) and 1599 with $F_o \leqslant 6\sigma(F_o)$ were observed. The intensity data were corrected for absorption ($T_{max}/T_{min} =$ 0.275/0.178). The structure was solved by direct methods. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were located and refined isotropically. At convergence $R(F)$ 2.62%, $R_w(F)$ 3.24%, GOF 1.081, Δ/σ 0.04, $\Delta(\rho)$ 0.629 e Å^{-3}, $N_o/N_v = 13.2$. Atomic coordinates, bond distances and angles, and thermal parameters may be obtained from one of the authors (ALR).

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