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# A facile reaction of $Sb_2S_3$ with $[CpCr(CO)_3]_2$: formation of a novel tetrachromium complex $[CpCr(CO)_3]_4(Sb_2S)$

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**The reaction of $[CpCr(CO)_3]_2$ with $Sb_2S_3$ under mild reaction conditions led to the isolation of $[CrCp(CO)_2]_2S$ 4 and the new tetrachromium complex $[CpCr(CO)_3]_4(Sb_2S)$ 2, which has been characterized *via* a single crystal X-ray diffraction analysis.**

Our earlier work has demonstrated the role of the 17-electron $CpCr(CO)_3^{\cdot}$ species in the cleavage of the pnictogen tetrahedra $P_4$ and $As_4$,[1] and of mixed element $P_4X_3$ (X = S, Se) cages,[2] to generate complexes possessing a variety of geometries and structures. This communication reports the results from an extension of the investigation to $Sb_2S_3$.

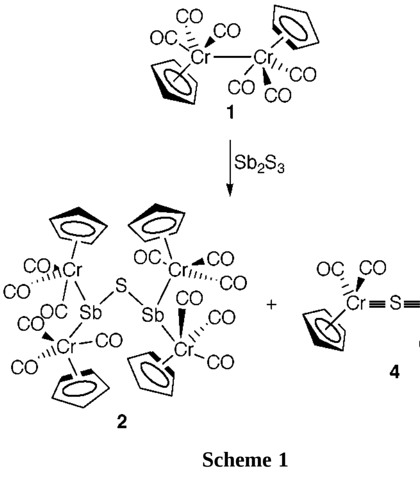
In comparison to the organotransition metal complexes of the lighter elements of Group 15, those of antimony are scarce.[3] Most of the reported complexes derived from the reactions of the trihalo compounds $SbX_3$ or their alkyl derivatives, *e.g.* $RSbX_2$, $R_2SbX$, $R_3Sb$, $MeC(CH_2Sb)_3$ and $(Bu^tSb)_4$, with the anions of metal carbonyls, metal carbonyl clusters or cyclopentadienylmetal carbonyl fragments, as well as neutral transition metal fragments.[4] A few unique reactions generated antimony ligands from the reactions of elemental antimony with $[CpMo(CO)_3]_2$,[5] of the nortricyclic Zintl ion $Sb_7^{3-}$ with $Ni(CO)_2(PPh_3)_2$[6] and of $S_8(Sb_2F_{11})$ with $Fe(CO)_5$.[7]

The reaction of $[CpCr(CO)_3]_2$ **1** with 6 mol equiv. of $Sb_2S_3$ in toluene under ultrasonication at ambient temperature for 48 h, led to the isolation of $[CpCr(CO)_3]_4(Sb_2S)$ **2** (19.3%), $[CpCr(CO)_2]_2(Cr{\equiv}Cr)$ **3** (5.8%) and $Cp_2Cr_2(CO)_4S$ **4** (46.6%) from the product mixture.† The tetrachromium complex **2** has been characterized spectroscopically‡ and by a single crystal X-ray diffraction analysis.§ Thermolysis of **2** at 80 °C, monitored by proton NMR spectral analysis, showed total degradation after 2 h to give **4** (28%), $Cp_4Cr_4S_4$ **5** (13%) and an insoluble as-yet-unidentified precipitate.

The reaction is represented in Scheme 1. In view of the facile dissociation of **1** into the 17-electron $CpCr(CO)_3^{\cdot}$ monomeric species,[8] it is conceivable that the reaction proceeds *via* the attack of this reactive radical moiety on the ribbon-like polymeric structure of $Sb_2S_3$, cleaving the interlocking $SbS_3$ and $SSb_3$ tetrahedra in the structure,[9] producing the $Cr_4Sb_2S$ complex **2** together with the $Cr{\equiv}S{\equiv}Cr$ complex **4**, into which **2** also degrades under thermolytic conditions. Such reactions of $Sb_2S_3$ with an organometallic fragment under the mild conditions as utilised here is unprecedented, demonstrating the efficiency of the $CpCr(CO)_3^{\cdot}$ species in the cleavage of the antimony–sulfur bonds of the polymeric structure of $Sb_2S_3$, as in the case of the cage molecules of the lighter elements of Groups 15/16.[1,2]

An ORTEP plot of **2** is shown in Fig. 1. The molecule possesses an approximate $C_2$ symmetry with a butterfly configuration about the central sulfur atom. Each of the Sb atoms is coordinated to one S and two Cr atoms which form the base of a trigonal pyramid [angles ranging from 98.5(1) to 115.07(9)° at Sb1 and 98.8(1) to 114.83(9)° at Sb2]. Each Cr atom in turn is coordinated to one Cp ring and three CO ligands in a four-legged piano stool configuration. The $Cr_2SbS$ fragments in the molecule belong to the electron precise pyramidal $EM_2Y$ type[3c] [E = Sb, M = the 17-electron $CpCr(CO)_3$ fragment, Y = S]; the structure can be envisaged as the product of 'fusion' of two such units with the extrusion of a S atom, resulting in a bent Sb–S–Sb bridge [angle 93.9(3)°]. The Sb–Cr bond distances in **2** (2.837–2.849 Å) are longer than those found in $[\{Cr(CO)_5\}_3(\mu_3\text{-}Sb)]^-$ (2.624–2.636 Å)[10] and in $[Sb(Fe(CO)_4)_3\{Cr(CO)_5\}]^-$ (2.638 Å).[11] The Cr–Sb–Cr angles (115.07, 114.83°) are smaller than those in $[\{Cr(CO)_5\}_3(\mu_3\text{-}Sb)]^-$ (118.9, 122.2°).[10]

The new complex **2** is the first example of a transition metal complex containing a 'bare' antimony–sulfur bridging ligand with each antimony atom bonded to two metal atoms. The only other reported instance of such antimony–sulfur ligands, *viz.* the $Sb_2S_6$ ligand in the cationic cluster $[Fe_2(Sb_2S_6)(CO)_6]^{2+}$ is bonded to the Fe atoms only *via* its six S atoms.[7] The closest analogues to **2** are complexes containing an organoantimony–sulfur ligand, $\{(CO)_4Cr\}_n[(Ph_2Sb)_2S]$ and



**Scheme 1**

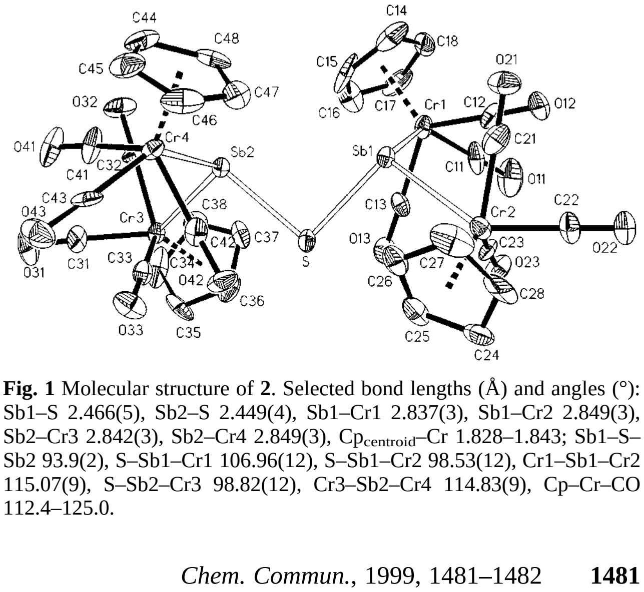


**Fig. 1** Molecular structure of **2**. Selected bond lengths (Å) and angles (°): Sb1–S 2.466(5), Sb2–S 2.449(4), Sb1–Cr1 2.837(3), Sb1–Cr2 2.849(3), Sb2–Cr3 2.842(3), Sb2–Cr4 2.849(3), $Cp_{centroid}$–Cr 1.828–1.843; Sb1–S–Sb2 93.9(2), S–Sb1–Cr1 106.96(12), S–Sb1–Cr2 98.53(12), Cr1–Sb1–Cr2 115.07(9), S–Sb2–Cr3 98.82(12), Cr3–Sb2–Cr4 114.83(9), Cp–Cr–CO 112.4–125.0.

$\{(CO)_5Cr\}_n[(Ph_2Sb)_2S]$ ($n$ = 1 or 2, depending on whether one or both Sb atoms are linked to Cr carbonyl fragments). Compared to **2**, the crystallographically characterized $\{(CO)_4Cr\}[(Ph_2Sb)_2S]$ complex possesses an Sb–S–Sb angle of 96.7(5)° and a Sb–Cr distance of 2.598(3) Å, much shorter than in **2**.[4*l*] Somewhat related parallels are the $\mathrm{Mn}\overset{..}{-}\mathrm{E}\overset{..}{-}\mathrm{Mn}$ 'inidene' complexes $[(MeCp)(CO)_2Mn]_2As_2E^-$ (E = S, Se)[12] and the ruthenium complex $(Cp^*Ru)_2(As_2S)_2$, the core structure of which consists of a $Ru_2As_4$ octahedron in which two edges are bridged by sulfur atoms.[13]

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## Notes and references

† *Experimental procedure*: a deep green suspension of $[CpCr(CO)_3]_2$ **1** (100 mg, 0.25 mmol) and $Sb_2S_3$ powder (503 mg, 1.48 mmol) in toluene (20 ml) was ultrasonicated at ambient temperature for 48 h. The resultant orange–green reaction mixture was filtered through Celite (2 × 1 cm disc, *ca.* 1.5 g) and concentrated to *ca.* 20 ml. The filtrate was absorbed onto Celite (*ca.* 2 g) and concentrated to dryness before loading onto a silica gel column (2 × 10 cm) prepared in *n*-hexane–toluene (1 : 1). Elution gave four fractions: (i) a brownish green eluate in *n*-hexane–toluene (1 : 1, 25 ml), which on concentration gave deep green crystals of $Cp_2Cr_2(CO)_4S$ **4** (43 mg, 0.11 mmol, 46.6% yield). (ii) A deep green eluate in *n*-hexane–toluene (1 : 1, 10 ml), from which was obtained lustrous deep green crystals of the starting dimer **1** (23 mg, 0.057 mmol, 23.0% recovery). (iii) A dark green eluate in *n*-hexane–toluene (1:2, 20 ml) which yielded fine dark green crystalline $[CpCr(CO)_2]_2$ **3** (5 mg, 0.014 mmol, 5.8% yield). (iv) A dark brown eluate in THF (15 ml), which on concentration yielded fine black crystalline $Cp_4Cr_4(CO)_{12}Sb_2S$ **2** (26 mg, 0.024 mmol, 19.3% yield). Elemental analyses. Calc. C, 35.56; H, 1.85; Cr, 19.26; O, 13.33; Sb, 22.59; S, 2.96. Found: C, 35.0; H, 2.27; Cr, 19.03; Sb, 22.88; S, 2.95%.

‡ *Selected spectroscopic data*: $^1$H NMR (100 MHz, $C_6D_6$): $\delta$ 4.52 (s, $\eta^5$-Cp). $^{13}$C NMR (100 MHz, $C_6D_6$): $\delta$ 89.61 ($\eta^5$-Cp). IR (cm$^{-1}$, Nujol): $\nu$(CO) 1986s, 1954m, 1901vs; other bands, 1066vw, 1025vw, 840w, 722w. MS (EI, 70 eV): *m/z* 622 $[Cp_2Cr_2(CO)_4Sb_2S]$, 468 $[Cp_2Cr_2(CO)_4Sb]$, 417 $[CpCr(CO)_2Sb_2]$, 346 $[Cp_2Cr_2(CO)_4]$, 295 $[CpCr(CO)_2Sb]$, 149 [CpCrS].

§ *Crystal data* for $C_{32}H_{20}O_{12}SCr_4Sb_2$ **2**: $M_r$ = 1080.04, monoclinic, space group $P2_1/c$, $a$ = 20.181(5), $b$ = 12.400(4), $c$ = 15.209(8) Å, $\beta$ = 106.26(3)°, $V$ = 3653.7(24)° Å$^3$, $D_c$ = 1.963 g cm$^{-3}$, $Z$ = 4, $2\theta_{max}$ = 24.99°, Mo-K$\alpha$ = 0.71073 Å, $\omega$-scan, $T$ = 300 K. From 6413 reflections, 2446 were observed [$I > 2\sigma(I)$]. Lorentz-polarization and absorption corrections were applied (empirical), $\mu$ = 53.073 cm$^{-1}$, transmission$_{max./min.}$ = 99.93/61.12. The structure was solved by the direct method (SHELXS86) and refined on $F^2$ (SHELXL93). All non-hydrogen atoms (except C38 and C47) were refined anisotropically; C38 and C47 were refined isotropically as their temperature factors became non-positive. H atoms were generated geometrically and were allowed to ride on their respective carbon atoms. The final $R$ and $wR$ {w = $[\sigma^2(F_o^2) + (0.0139P)^2]^{-1}$ where $P = 1/3(F_o^2 + 2F_c^2)$} are 0.0836 and 0.1011, respectively, for 450 variables. The maximum residual peak is 0.945 e Å$^{-3}$. Diffraction-quality crystals of **2** were obtained as brownish black polyhedra from a saturated solution in THF after a week at −28 °C. A selected crystal was coated in epoxy glue, and X-ray diffraction measurements were made on a CAD4 diffractometer. CCDC 182/1303. See http://www.rsc.org/suppdata/cc/1999/1481/ for crystallographic files in .cif format.

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