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

Lai Yoong Goh,*[a] Wei Chen[b] and Richard C. S. Wong[b]

[a] *Department of Chemistry, National University of Singapore, Kent Ridge, Singapore 119260.*
  E-mail: chmgohly@nus.edu.sg
[b] *Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia*

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
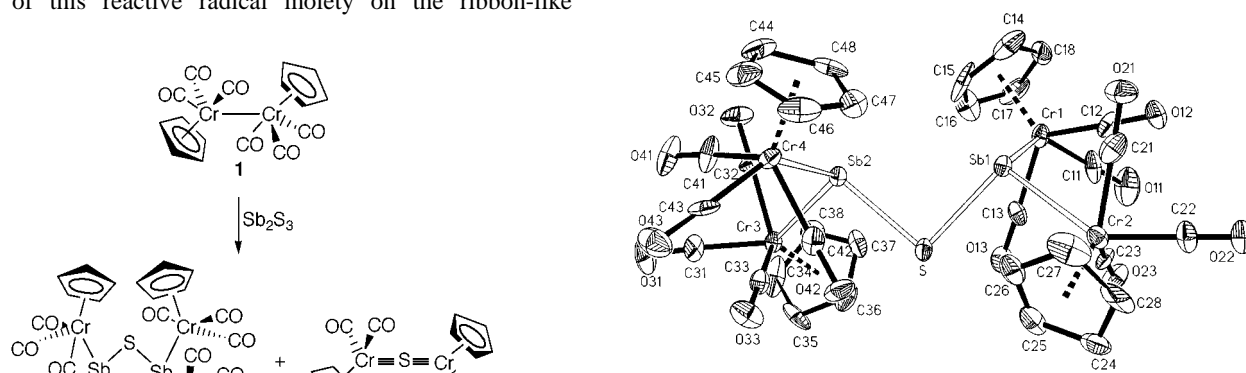
Scheme 1

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)$_5$Cr}$_n$[(Ph$_2$Sb)$_2$S] (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)$_4$Cr}[(Ph$_2$Sb)$_2$S] 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**.[4l] Somewhat related parallels are the Mn−E−Mn 'inidene' complexes [(MeCp)(CO)$_2$Mn]$_2$As$_2$E$^-$ (E = S, Se)[12] and the ruthenium complex (Cp*Ru)$_2$(As$_2$S)$_2$, the core structure of which consists of a Ru$_2$As$_4$ octahedron in which two edges are bridged by sulfur atoms.[13]

Notes and references

† *Experimental procedure*: a deep green suspension of [CpCr(CO)$_3$]$_2$ **1** (100 mg, 0.25 mmol) and Sb$_2$S$_3$ 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$_2$Cr$_2$(CO)$_4$S **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$_4$Cr$_4$(CO)$_{12}$Sb$_2$S **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$_6$D$_6$): δ 4.52 (s, η^5-Cp). ^{13}C NMR (100 MHz, C$_6$D$_6$): δ 89.61 (η^5-Cp). IR (cm^{-1}, Nujol): ν(CO) 1986s, 1954m, 1901vs; other bands, 1066vw, 1025vw, 840w, 722w. MS (EI, 70 eV): *m/z* 622 [Cp$_2$Cr$_2$(CO)$_4$Sb$_2$S], 468 [Cp$_2$Cr$_2$(CO)$_4$Sb], 417 [CpCr(CO)$_2$Sb$_2$], 346 [Cp$_2$Cr$_2$(CO)$_4$], 295 [CpCr(CO)$_2$Sb], 149 [CpCrS].

§ *Crystal data* for C$_{32}$H$_{20}$O$_{12}$SCr$_4$Sb$_2$ **2**: M_r = 1080.04, monoclinic, space group $P2_1/c$, a = 20.181(5), b = 12.400(4), c = 15.209(8) Å, $β$ = 106.26(3)°, V = 3653.7(24)° Å^3, D_c = 1.963 g cm^{-3}, Z = 4, $2θ_{max}$ = 24.99°, Mo-Kα = 0.71073 Å, ω-scan, T = 300 K. From 6413 reflections, 2446 were observed [I > 2σ(I)]. Lorentz-polarization and absorption corrections were applied (empirical), $μ$ = 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 = [σ^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.

1 L. Y. Goh, C. K. Chu, R. C. S. Wong and T. W. Hambley, *J. Chem.Soc., Dalton Trans.*, 1989, 1951; 1990, 977; L. Y. Goh, R. C. S Wong and E. Sinn, *J. Chem. Soc., Chem. Commun.*, 1990, 1484; *Organometallics*, 1993, **12**, 888; L. Y. Goh, R. C. S. Wong, W. H. Yip and T. C. W. Mak, *Organometallics*, 1991, **10**, 875.

2 L. Y. Goh, W. Chen and R. C. S. Wong, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1728; L. Y. Goh, W. Chen, R. C. S. Wong and K. Karaghiosoff, *Organometallics*, 1995, **14**, 3886; L. Y. Goh, W. Chen and R. C. S. Wong, *Phosphorus, Sulphur Silicon*, 1994, **93–94**, 209; L. Y. Goh, W. Chen, R. C. S. Wong, Z.-Y. Zhou and H. K. Fun, *Mendeleev Commun.*, 1995, 60; L. Y. Goh, W. Chen and R. C. S. Wong, *Organometallics*, 1999, **18**, 306.

3 For reviews, see: (*a*) O. J. Scherer, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1104; (*b*) J. Wachter, *Angew. Chem., Int. Ed.*, 1998, **37**, 750; (*c*) K. H. Whitmire, *Adv. Organomet.Chem.*, 1998, **42**, 1; (*d*) K. H. Whitmire, *J. Cluster Sci.*, 1991, **2**, 231.

4 Some references cited in ref. 3 above; also see for example: (*a*) M. Gorzellik, B. Nuber and M. L. Ziegler, *J. Organomet. Chem.*, 1992, **431**, 171; (*b*) N. C. Norman, N. L. Pickett, W. S. Storr, N. M. Boag and A. J. Goodby, *Polyhedron*, 1994, **13**, 2525; (*c*) W. Deck and H. Vahrenkamp, *Z. Anorg. Allg. Chem.*, 1991, **598/599**, 83; (*d*) W. Malisch and P. Panster, *J. Organomet. Chem.*, 1975, **99**, 421; (*e*) G. I. Nikonov, L. G. Kuzmina and J. A. K. Howard, *Organometallics*, 1997, **16**, 3723; (*f*) A.-M. Caminade, M. Veith, V. Huch and W. Malisch, *Organometallics*, 1990, **9**, 1798; (*g*) W. J. Evans, S. L. Gonzales and J. W. Ziller, *J. Chem. Soc., Chem. Commun.*, 1992, 1138; (*h*) J. Grobe, W. Golla, D. Le Van, B. Krebs and M. Läge, *Organometallics*, 1998, **17**, 5717; (*i*) J. Ellermann and A. Veit, *J. Organomet. Chem.*, 1985, **290**, 307; (*j*) H. J. Breunig and J. Pawlik, *Z. Anorg. Allg. Chem.*, 1995, **621**, 817; (*k*) H. J. Breunig, R. Rösler and E. Lork, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2819; (*l*) M. Wieber and N. Graf, *Z. Anorg. Allg. Chem.*, 1993, **619**, 1991, 2061.

5 J. R. Harper and A. L. Rheingold, *J. Organomet. Chem.*, 1990, **390**, C36.

6 S. Charles, B. W. Eichhorn and S. G. Bott, *J. Am. Chem. Soc.*, 1993, **115**, 5837.

7 G. W. Drake, G. L. Schimek and J. W. Kolis, *Inorg. Chem.*, 1996, **35**, 4534.

8 M. C. Baird, *Chem. Rev.*, 1988, **88**, 1217 and references cited therein; L. Y. Goh and Y. Y. Lim, *J. Organomet. Chem.*, 1991, **402**, 209 and references therein.

9 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley-Interscience, New York, 5th edn., 1988, p. 404.

10 G. Huttner, U. Weber, B. Sigwarth, O. Scheidsteger, H. Lang and L. Zsolnai, *J. Organomet. Chem.*, 1985, **282**, 331.

11 K. H. Whitmire, M. Shieh and J. Cassidy, *Inorg. Chem.*, 1989, **28**, 3164.

12 Ch. Emmerich, G. Huttner and A. Asam, *J. Organomet. Chem.*, 1993, **447**, 71.

13 H. Brunner, B. Nuber, L. Poll, G. Roidl and J. Wachter, *Chem. Eur. J.*, 1997, **3**, 57.