Synthesis and Structure of a Novel Antimony–Iron Cluster

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The cluster $[Fe_2(CO)_8(\mu_4\text{-}Sb)]_2[Fe_2(CO)_6]$, **(1)**, has been prepared by the reaction of $SbCl_3$ with $Na_2[Fe(CO)_4]$ and the structure of **(1)** has been determined by *X*-ray crystallography.

Considerable interest is now apparent in hybrid clusters in which substituent-free (bare) main-group elements are incorporated into transition metal frameworks.[1] In the context of group 5, several clusters have been reported featuring phosphorus,[1] arsenic,[1] and bismuth.[1,2] However, much less is known about antimony-containing clusters. In fact, to the best of our knowledge $[Rh_{12}Sb(CO)_{27}]^{3-}$ and $Sb_2[W(CO)_5]_3$ constitute the only structurally authenticated examples of such compounds.[3,4]

Previously it has been demonstrated that the reaction of PCl_3 or $AsCl_3$ with $Fe_2(CO)_9$ results in chloride-containing clusters, $[Fe_2(CO)_8EFe_2(CO)_6Cl]$ (E = P or As).[5] Interestingly, we find that the same compounds are produced when PCl_3 or $AsCl_3$ is treated with an excess of $Na_2[Fe(CO)_4]$ in the presence of $Fe_2(CO)_9$ in tetrahydrofuran solution. However, a comparable reaction with $SbCl_3$ results in a new type of main-group–transition metal cluster, $[Fe_2(CO)_8(\mu_4\text{-}Sb)]_2[Fe_2(CO)_6]$ **(1)**. Purification of **(1)** was effected by column chromatography (silica gel–n-hexane) and dark green *X*-ray quality crystals (m.p. 230 °C, decomp.) were grown from n-hexane solution at −20 °C.†

The solid state structure of **(1)** comprises individual molecules with no significantly short intermolecular contacts.‡

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† Compound **(1)** had satisfactory analytical and spectroscopic characteristics.

‡ *Crystal data for* **(1)**: $C_{22}O_{22}Fe_6Sb_2$, $M = 1194.81$, monoclinic, $C2/c$ (No. 15), $a = 44.809(7)$, $b = 9.362(2)$, $c = 17.670(3)$ Å, $\beta = 111.53(2)°$, $U = 6895.6$ Å^3, $Z = 8$, $D_c = 2.302$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 40.90$ cm^{-1}. A total of 5706 unique reflections was measured on an Enraf-Nonius CAD-4 diffractometer over the range $3.0 \leqslant 2\theta \leqslant 48.0°$ ($\theta/2\theta$ scan mode). An empirical absorption correction was applied, but no correction was made for decay (<1%). The structure was solved by direct methods and refined (difference Fourier, full-matrix, least squares) using 2812 reflections with $I > 3.0\sigma(I)$. The final residuals were $R = 0.0377$ and $R_w = 0.0461$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

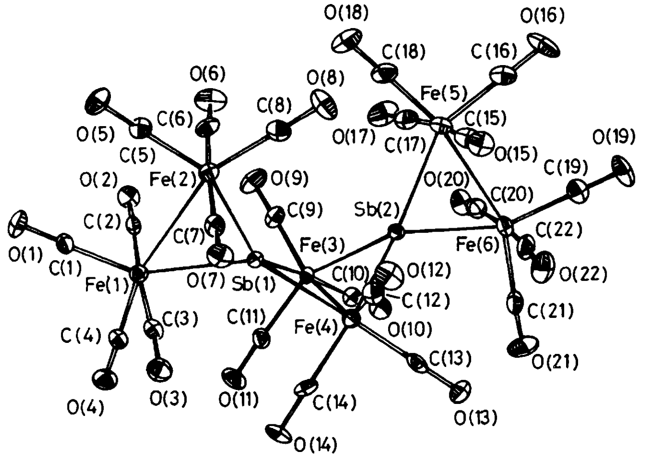
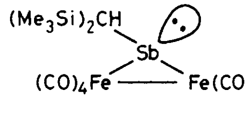


Figure 1. View (ORTEP) of $[Fe_2(CO)_8(\mu_4\text{-}Sb)]_2[Fe_2(CO)_6]$, (**1**), showing the atom numbering scheme. Important bond lengths (Å) and angles (°) are as follows: Fe(1)–Fe(2) 2.846(2), Fe(1)–Sb(1) 2.557(1), Fe(2)–Sb(1) 2.551(1), Fe(3)–Sb(1) 2.504(1), Fe(4)–Sb(1) 2.493(1), Fe(3)–Sb(2) 2.471(1), Fe(4)–Sb(2) 2.508(1), Fe(3)–Fe(4) 2.857(2), Fe(5)–Sb(2) 2.555(1), Fe(6)–Sb(2) 2.566(2), Fe(5)–Fe(6) 2.840(2); Fe(1)–Sb(1)–Fe(2) 67.73(7), Fe(3)–Sb(1)–Fe(4) 69.74(6), Fe(3)–Sb(2)–Fe(4) 70.02(6), Fe(5)–Sb(2)–Fe(6) 67.40(6), Sb(1)–Fe(1)–Fe(2) 56.03(4), Sb(1)–Fe(2)–Fe(1) 56.23(4), Sb(2)–Fe(5)–Fe(6) 56.50(4), Sb(2)–Fe(6)–Fe(5) 56.12(4).

The antimony–iron skeleton possesses approximately C_{2v} symmetry, the C_2 axis lying on the mid-point of the Fe(3)–Fe(4) axis (Figure 1). The structure consists of a central Fe_2Sb_2 butterfly arrangement which is similar in conformation to those of bis(μ-phosphido) or bis(μ-arsenido)$Fe_2(CO)_6$ complexes.[6] In turn, each antimony atom is involved in an Fe_2Sb ring, thereby achieving a μ_4-spiro geometry. These $SbFe_2(CO)_8$ moieties are reminiscent of the 'closed' stibinidene complex (**2**).[7]



(**2**)

As in the case of (**2**), the Fe–Fe bond lengths are somewhat long [average 2.843(2) Å] but nevertheless consistent with single bonding. The Sb–Fe bond lengths in the $Sb[Fe(CO)_4]_2$ moieties [average 2.555(1) Å] are also consistent with a bond order of unity. Note, however, that the Sb–Fe bond lengths in the Sb_2Fe_2 core are somewhat shorter [2.494(1) Å], thus suggesting that each Sb atom donates three electrons to the butterfly subunit and two electrons to the $SbFe_2$ triangles. Each Sb atom is co-ordinated to four Fe atoms, and all the iron atoms exhibited distorted octahedral geometries. The dihedral angle between the Fe(1)–Fe(2)–Sb(1) and Fe(3)–Fe(4)–Sb(1) planes is 72.4° and the fold angle along Fe(3)–Fe(4) is 109.3°.

Finally, we note that although it is possible to prepare bismuth–tungsten clusters by treatment of $[W(CO)_5]^{2-}$ with bismuth chlorides,[8] the reaction of $[Fe(CO)_4]^{2-}/Fe_2(CO)_9$ mixtures with $BiCl_3$ failed to produce bismuth–iron clusters.

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