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**Preliminary communication**

# Synthesis of anionic antimony-iron and bismuth–iron clusters

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## Abstract

The anionic cluster $[ClSb\{Fe(CO)_4\}_3]^{2-}$ has been prepared by the reaction of $SbCl_3$ with $[HFe(CO)_4]^-$ and stabilized as its bis(triphenylphosphine)nitrogen(+1) ($PPN^+$) salt. The synthesis of the analogous bismuth complex is also reported.

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There is much current interest in the synthesis and reactions of transition-metal complexes containing atoms of the main-group elements. In the case of Group 5 elements, there is a very extensive chemistry involving phosphorus [1], but there are relatively few well-characterized carbonyl clusters containing the heavier members of the group especially antimony. To the best of our knowledge, the only structurally authenticated examples of iron-antimony compounds showing a nuclearity greater than two are the following; $[ClSb\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_3]_2\ [FeCl_4]\cdot CH_2Cl_2$ [2]; $[Cl_2Sb\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2][Sb_2Cl_7]$ [3]; $[Fe_2(CO)_8\{\mu\text{-}SbCH(SiMe_3)_2\}]$ [4]; $[Fe_2(CO)_8(\mu_4\text{-}Sb)]_2[Fe_2(CO)_6]$ [5a,b]; $[Et_4N][Fe_3(CO)_9(\mu\text{-}CO)\{\mu_3\text{-}SbFe(CO)_4\}]$, and $[Et_4N]_2[Fe_3(CO)_9\{\mu_3\text{-}SbFe(CO)_4\}_2]$ [6].

In continuation of our studies on (transition-metal)-main group complexes [7], we report here the synthesis of the first open anionic Fe/Sb cluster $(PPN)_2[ClSb\{Fe(CO)_4\}_3]$.

Treatment of $SbCl_3$ with $(PPN)[HFe(CO)_4]$ in a 1/3 mole ratio in THF at −40 °C affords a reddish-brown solution from which the complex $(PPN)_2[ClSb\{Fe(CO)_4\}_3]$ (**1**) can be isolated by evaporation of the solvent as red microcrystals in yields of about 55% based on antimony. A similar reaction involving $BiCl_3$ instead of $SbCl_3$ leads to bright black microcrystals of $(PPN)_2[ClBi\{Fe(CO)_4\}_3]$ (**2**). Both products are formed in lower yields if a smaller mole ratio is used. Complexes **1** and **2** have been characterized by elemental analyses and infrared spectra. The

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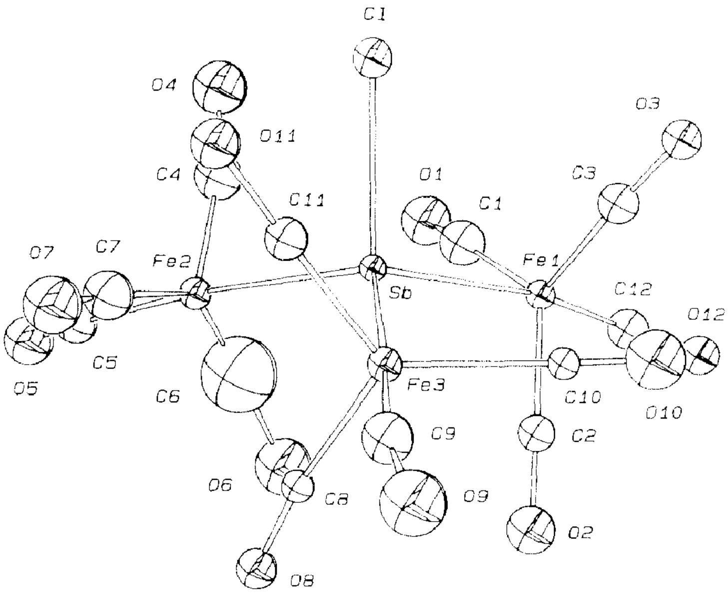

Fig. 1. Structure of the anion $[ClSb\{Fe(CO)_4\}_3]^{2-}$. Selected dimensions are as follows: Sb–Fe(1) 2.55, Sb–Fe(2) 2.54, Sb–Fe(3) 2.56, Sb–Cl 2.45 Å; Fe(1)–Sb–Fe(2) 114, Fe(1)–Sb–Fe(3) 115, Fe(2)–Sb–Fe(3) 116, Cl–Sb–Fe(1) 104, Cl–Sb–Fe(2) 102, Cl–Sb–Fe(3) 101°.

identical ν(CO) pattern of the two complexes as solids (KBr, **1**: 2015w; 1991vs; 1905vs,br; 1900sh; **2**: 2015w; 1985vs; 1905vs,br; 1895sh $cm^{-1}$) and in solution (THF, **1**: 2009w; 1989vs; 1922vs; 1906s; **2**: 2010w; 1985vs; 1920vs; 1905s $cm^{-1}$) indicates that they must be closely structurally related. The skeleton of **1** has been established by a preliminary X-ray crystal structure determination *. The structure of **1** consists of discrete $[ClSb\{Fe(CO)_4\}_3]^{2-}$ anions, $PPN^+$ cations, and solvent molecules. Figure 1 shows the structure of the anion, which has three iron atoms bonded to the central antimony atom in a distorted tetrahedral arrangement. The average Fe–Sb bond length of 2.55 Å is close to that in the triiron-antimony cluster cation $[ClSb\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_3]^+$ (2.54 Å) [2]. The Sb–Cl bond length (2.45 Å) is normal.

Interestingly, **1** was found to react with $[Cu(CH_3CN)_4]^+ BF_4^-$ to give the cluster $[Fe_2(CO)_8(\mu_4\text{-}Sb)]_2[Fe_2(CO)_6]$ (**3**), which was recently independently described by two groups [5]. Since in one of these reports [5b] **3** was obtained by adding $[Cu(CH_3CN)_4]^+ BF_4^-$ to an acetone solution produced by mixing $SbCl_3$ and $[Fe_2(CO)_8]^{2-}$, it was expected that the species present in that solution, and responsible for its dark colour, could be **1**. That this is the case is confirmed by the

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* Crystal data for **1**·THF, $Et_2O = C_{92}H_{78}ClN_2O_{14}P_4Fe_3Sb$, $M = 1884.29$, monoclinic, space group $P2_1/c$, $a$ 12.912(4), $b$ 27.567(4), $c$ 24.634(4) Å, $\beta$ 92.16(2)°, $U$ 8762 $Å^3$, $Z = 4$, $D_C$ 1.428 g $cm^{-3}$, $\mu$(Mo-$K_\alpha$) 9.57 $cm^{-1}$, $\lambda$(Mo-$K_\alpha$) 0.71069 Å. Intensities of 5130 reflections with $2 < \theta < 20°$ were measured on an Enraf–Nonius CAD4 diffractometer, $\theta/2\theta$ scan mode with $\omega$ scan width $= 1 + 0.343 \tan\theta$, scan speed 2.06 deg $min^{-1}$. One of the standard reflections showed a 49% loss in intensity and the data collection was therefore ended at this stage. The metal atoms were found by direct methods [8]. Calculations were performed by use of the Enraf–Nonius SDP/VAX package. The structure was refined by full matrix least squares using 2911 data with $I > 3\sigma(I)$ to $R = 0.13$. Isotropic thermal parameters were assigned to all atoms [9].

indentity of the IR spectra of $SbCl_3/[Fe_2(CO)_8]^{2-}$ and **1**. Further work in this area is in progress.

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