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**Reactions of Distibanes with  $[\text{Fe}_2(\text{CO})_9]$ : Synthesis, Structure and DFT calculations of  $[(\text{Et}_2\text{Sb})_4\text{Fe}_4(\text{CO})_{14}]$ ,  $[(n\text{-Pr}_2\text{Sb})_4\text{Fe}_3(\text{CO})_{10}]$ ,  $[(\text{Me}_3\text{SiCH}_2)_2\text{Sb}_4\text{Fe}_2(\text{CO})_6]$ , and  $[2\text{-(Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\text{SbFe}_2(\text{CO})_8]$**

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**Reactions of Distibanes with [Fe<sub>2</sub>(CO)<sub>9</sub>]: Synthesis,  
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 [(n-Pr<sub>2</sub>Sb)<sub>4</sub>Fe<sub>3</sub>(CO)<sub>10</sub>], [{(Me<sub>3</sub>SiCH<sub>2</sub>)<sub>2</sub>Sb}<sub>4</sub>Fe<sub>2</sub>(CO)<sub>6</sub>],  
 and [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>SbFe<sub>2</sub>(CO)<sub>8</sub>]**

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## ARTICLE

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# Reactions of Distibanes with $[\text{Fe}_2(\text{CO})_9]$ : Synthesis, Structure and DFT calculations of $[(\text{Et}_2\text{Sb})_4\text{Fe}_4(\text{CO})_{14}]$ , $[(n\text{-Pr}_2\text{Sb})_4\text{Fe}_3(\text{CO})_{10}]$ , $[\{(\text{Me}_3\text{SiCH}_2)_2\text{Sb}\}_4\text{Fe}_2(\text{CO})_6]$ , and $[2\text{-(Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_4\text{SbFe}_2(\text{CO})_8]$

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*Dedicated to Prof. U. Rosenthal on the Occasion of his 60<sup>th</sup> birthday*

**Keywords:** Antimony; Iron; Heterometallic complexes; X-ray diffraction; Density functional calculations.

Syntheses of  $[(\text{Et}_2\text{Sb})_4\text{Fe}_4(\text{CO})_{14}]$  (**1**),  $[(n\text{-Pr}_2\text{Sb})_4\text{Fe}_3(\text{CO})_{10}]$  (**2**),  $[\{(\text{Me}_3\text{SiCH}_2)_2\text{Sb}\}_4\text{Fe}_2(\text{CO})_6]$  (**3**), and  $[2\text{-(Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_4\text{SbFe}_2(\text{CO})_8]$  (**4**) by reactions of distibanes with  $\text{Fe}_2(\text{CO})_9$ , crystal structures of **1–4** and DFT calculations of **1** are reported.

## Introduction

In a previous investigation we found that the tetraorganodistibanes  $\text{R}_2\text{Sb-SbR}_2$  ( $\text{R} = \text{Et}, \text{tBu}, \text{Ph}$ ) react with  $\text{Fe}_2(\text{CO})_9$  with elimination of  $\text{Fe}(\text{CO})_5$  and CO and formation of  $\text{R}_2\text{Sb-SbR}_2\text{Fe}(\text{CO})_4$  (**A**),  $(\text{CO})_4\text{FeR}_2\text{Sb-SbR}_2\text{Fe}(\text{CO})_4$  (**B**) or  $(\text{CO})_3\text{Fe}(\text{R}_2\text{Sb})_2\text{Fe}(\text{CO})_3$  (**C**) [1]. These results were not surprising and analogous phosphorus or arsenic compounds are also well known [2–4]. The complexes **A–C** were characterized by mass spectra and  $^1\text{H-NMR}$ - and IR-measurements [1]. In the present second study with focus on crystal structure determinations we used  $\text{R}_2\text{SbSbR}_2$  ( $\text{R} = \text{Et}, n\text{-Pr}, \text{Me}_3\text{SiCH}_2, 2\text{-(Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_4$ ) for the reactions with  $\text{Fe}_2(\text{CO})_9$  and report here on novel antimony iron clusters:  $[(\text{Et}_2\text{Sb})_4\text{Fe}_4(\text{CO})_{14}]$  (**1**),  $[(n\text{-Pr}_2\text{Sb})_4\text{Fe}_3(\text{CO})_{10}]$  (**2**),  $[\{(\text{Me}_3\text{SiCH}_2)_2\text{Sb}\}_4\text{Fe}_2(\text{CO})_6]$  (**3**), and  $[2\text{-(Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_4\text{SbFe}_2(\text{CO})_8]$  (**4**). **1–4** represent novel types of compounds in the chemistry of iron complexes with pnictogen ligands. The closest related compounds are dimethylarsenic bridged iron complexes [5]. **4** is a stibinidene complex [6] stabilized by intramolecular coordination of the pendant dimethylamino group. Related to **4** is the tungsten complex  $\text{RSb}[\text{W}(\text{CO})_5]_2$  [ $\text{R} = 2\text{-(Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_4$ ] [7].

## Results and Discussion

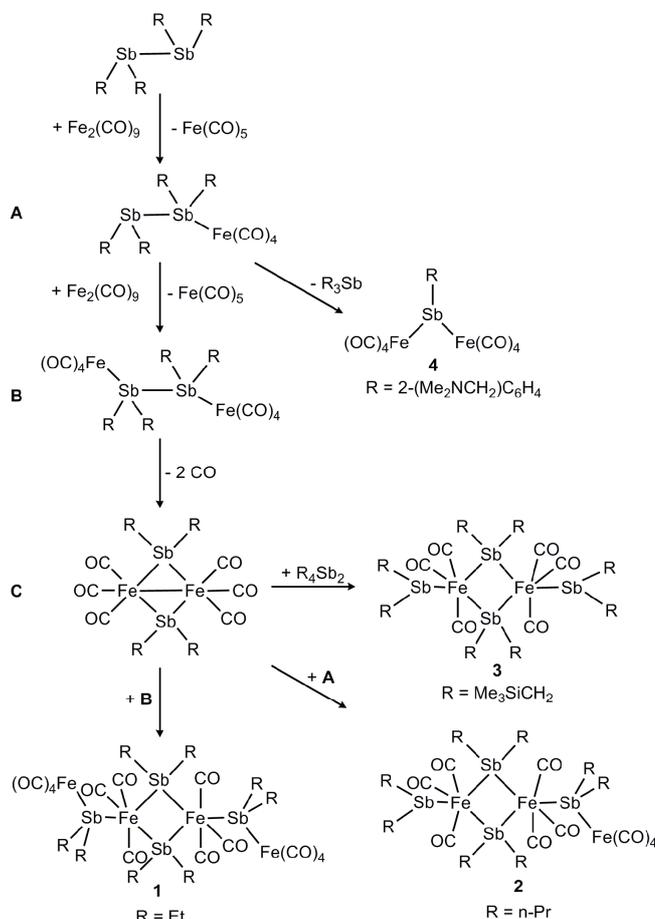
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The reactions between the distibanes and  $\text{Fe}_2(\text{CO})_9$  were carried out in n-hexane at ambient temperature in the 1:1 molar ratio for the synthesis of **1–3**. In the case of **4** a 1 : 3 ratio was used. Possible synthetic pathways are described in Scheme 1.



Scheme 1. Preparation of **1–4**.

The formation of **1–3** can be explained by addition of distibane, or of the previously described distibane complexes of the types **A** and **B** to the central Fe–Fe-bond in an antimonido complex of type **C**. The formation of **1** and **2** can however also result from reactions of  $\text{Fe}_2(\text{CO})_9$  with analogues of **3**. The complexes **1** and **3** were isolated in about 50 % yield. A small crop of crystals was obtained in the case of **2** and **4**. Only in the case of **3** the composition of the product represents the initial stoichiometry of the reagents. For **1** and **2** the stoichiometry corresponds to excess  $\text{Fe}_2(\text{CO})_9$ . The formation of **4** probably results from the elimination of  $\text{R}_3\text{Sb}$  from the corresponding distibane complex **B**.

**1–3** are obtained as red air sensitive crystals. The colour of **4** is orange and the crystals are stable in air. The structures of **1–4** were determined by single crystal X-ray diffractometry. They are shown in the Figures 1–4. A common feature of **1–3** is the central framework with two bridging  $\text{R}_2\text{Sb}$  groups between  $\text{Fe}(\text{CO})_3\text{SbR}_2$  fragments. In **1** and **2** the external  $\text{R}_2\text{Sb}$  groups are coordinated to  $\text{Fe}(\text{CO})_4$  groups. The central  $\text{Fe}_2\text{Sb}_2$  ring and also the antimony atoms in the periphery lie in a plane. The four coordinate antimony atoms in the center and in the periphery of **2** and **3** have tetrahedral environments. The antimony centers of the  $\text{R}_2\text{SbFe}$  units are pyramidal. The central iron atoms have octahedral environments with the ligands in meridional positions. The coordination of the iron atoms is trigonal bipyramidal with the antimony atoms in axial positions. The trans-annular Fe–Fe distances in **1–3** range between 3.95 and 3.99 Å. These values are much longer than Fe–Fe bonds in analogues of type **C** complexes like  $(\text{CO})_3\text{Fe}(\text{AsMe}_2)_2\text{Fe}(\text{CO})_3$  (Fe–Fe 2.73 Å) [8] and prove the absence of bonds between the iron atoms. In contrast the transannular Sb...Sb distances in **1–3** with values in the range 3.28 – 3.29 Å correspond to relatively close interactions. They lie between the values for the sum of van der Waals radii of two antimony atoms (4.4 Å [9]) and a true Sb–Sb single bond (e.g.  $\text{Me}_2\text{Sb–SbMe}_2$  Sb–Sb, 2.862 (2) Å [10]).

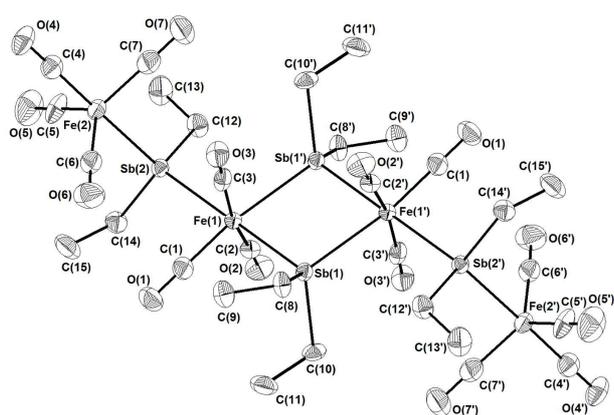


Figure 1. Molecular structure of  $[(\text{Et}_2\text{Sb})_4\text{Fe}_4(\text{CO})_{14}]$  (**1**). The thermal ellipsoids are represented in 50% probability. The hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ): Fe(1)–Sb(1) 2.5577(13), Fe(1)–Sb(2) 2.5946(13), Fe(1)–Sb(1') 2.6122(15), Fe(2)–Sb(2) 2.5288(14), Sb(1)–Sb(1') 3.2891(10), C(10)–Sb(1)–C(8) 101.9(4), Sb(1)–Fe(1)–Sb(2) 178.91(6), Sb(1)–Fe(1)–Sb(1') 79.01(4), Sb(2)–Fe(1)–Sb(1') 101.31(5), Fe(1)–Sb(1)–Fe(1') 100.99(4), Fe(1)–Sb(1)–Sb(1') 51.23(3), Fe(1')–Sb(1)–Sb(1') 49.76(3), C(14)–Sb(2)–C(12) 96.3(4), Fe(2)–Sb(2)–Fe(1) 119.56(5), Sb(2)–Fe(1)–Sb(1)–Fe(1') 178.9(1), Sb(1')–Fe(1)–Sb(1)–Fe(1') 0, Sb(1)–Fe(1)–Sb(2)–Fe(2) 7(3), Sb(1')–Fe(1)–Sb(2)–Fe(2) 99.50(5).

The Fe–Sb bond lengths in **1–3** despite the different nature of the bonds lie in the relatively small range between 2.53 and 2.61 Å. Similar values were found for  $\text{Ph}_3\text{SbFe}(\text{CO})_4$  (Sb–Fe 2.472(1) Å [11]) or  $\text{Fe}_2(\text{CO})_8\text{SbCH}(\text{SiMe}_3)_2$  (Sb–Fe 2.641(1), 2.663(1) Å [12]).

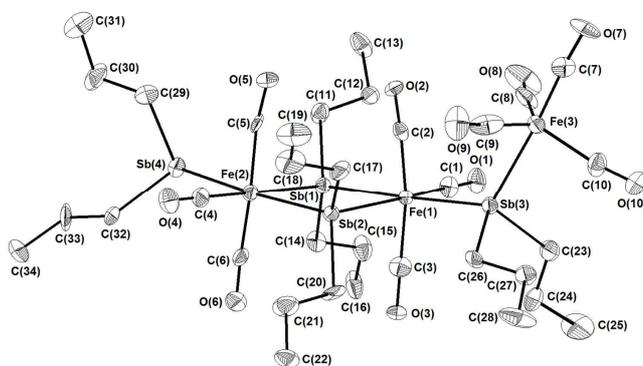


Figure 2. Molecular structure of  $[(n\text{-Pr}_2\text{Sb})_4\text{Fe}_3(\text{CO})_{10}]$  (**2**). The thermal ellipsoids are represented in 25% probability. The hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ): Fe(1)–Sb(1) 2.551(4), Fe(1)–Sb(2) 2.626(3), Fe(1)–Sb(3) 2.584(4), Fe(2)–Sb(2) 2.537(4), Fe(2)–Sb(1) 2.567(3), Fe(2)–Sb(4) 2.659(4), Fe(3)–Sb(3) 2.537(3), Sb(1)–Sb(2) 3.2848(16), Sb(1)–Fe(1)–Sb(2) 78.75(10), Sb(1)–Fe(1)–Sb(3) 177.65(14), Sb(2)–Fe(1)–Sb(3) 101.24(11), Sb(1)–Fe(2)–Sb(2) 80.13(10), Sb(2)–Fe(2)–Sb(4) 170.72(13), Sb(1)–Fe(2)–Sb(4) 90.67(11), Fe(1)–Sb(1)–Fe(2) 100.95(11), Fe(1)–Sb(1)–Sb(2) 51.64(7), Fe(2)–Sb(1)–Sb(2) 49.53(8), Fe(1)–Sb(2)–Fe(2) 99.72(10), Sb(1)–Sb(2)–Fe(2) 50.34(7), Fe(1)–Sb(2)–Sb(1) 49.60(8), Fe(3)–Sb(3)–Fe(1) 119.77(11).

Crystals of **4** contain two independent molecules with similar structures, which consist of the aryl-antimony unit between two  $\text{Fe}(\text{CO})_4$  groups. The pendant dimethylamino group is coordinated to the antimony center through a short  $\text{N}\cdots\text{Sb}$  bond (2.283(7) Å). The coordination of the nitrogen atom to the antimony atom induces planar chirality (the nitrogen atom acts as the pilot atom and the phenyl ring as the chiral plane). **4** crystallizes as a racemate, the isomer pairs being generated by symmetry with respect to the inversion centre of the unit cell. The  $R_N$  isomer of molecule containing Sb(1) is depicted in Figure 4. The Sb–Fe bond lengths range between 2.4816 (1) and 2.4878(1) Å. The coordination geometry around the iron atoms is trigonal bipyramidal with the Sb atoms in axial positions. The antimony atom lies slightly above the  $\text{Fe}_2\text{C}(\textit{ipso})$  plane (sum of angles  $\text{SbFe}_2$ ,  $\text{SbFeC}$  352.92  $^\circ$ ) and with the nitrogen atom the coordination polyhedron around Sb is trigonal pyramidal. All these structural features correspond to the description of **4** as complex of a stibinidene ligand with dative bonds through the lone pairs of electrons in  $sp^2$  orbitals of antimony to the  $\text{Fe}(\text{CO})_4$  fragments and intramolecular coordination of the nitrogen lone pair of the dimethylamino group to the empty  $p$ -orbital at antimony.

The identity of **1–4** is confirmed by the mass spectra. Molecular ions (**3**, **4**), or characteristic fragments (**1**, **2**) were observed using electron impact or chemical ionization. The fragments result from the loss of CO, organic groups or  $\text{Fe}(\text{CO})_4$  units. Particularly intense signals result from ions of the composition  $[\text{R}_4\text{Sb}_2\text{Fe}_2(\text{CO})_6]^+$  which correspond to the previously reported antimonido complexes of type **C** [1]. NMR studies were performed for **1–3**. The  $^1\text{H-NMR}$  spectra

in  $C_6D_6$  are very complex. They show more signals than expected and some signals are very broad. **1** contains two pairs of diastereotopic  $Et_2Sb$  groups and therefore signals of two  $ABX_3$  spin systems can be expected. The observed spectrum however shows more signals. In the methyl region it contains two well resolved triplet signals and three unresolved broad signals. One well resolved multiplet and three broad signals appear for the methylene groups. An unambiguous assignment of these signals was not achieved. Very broad overlapping  $^1H$ -NMR signals were observed also for **2**.

More informative is the  $^1H$ -NMR spectrum of **3** where three singlet signals appear in the region of the  $Me_3Si$  groups and 14 singlet signals in the region of the  $CH_2$  groups. One methyl-signal and four signals of the AB system for the  $CH_2$  groups can be assigned to the distibine  $R_2SbSbR_2$  [13]. The remaining signals probably stem from **3** and the corresponding type C complex.

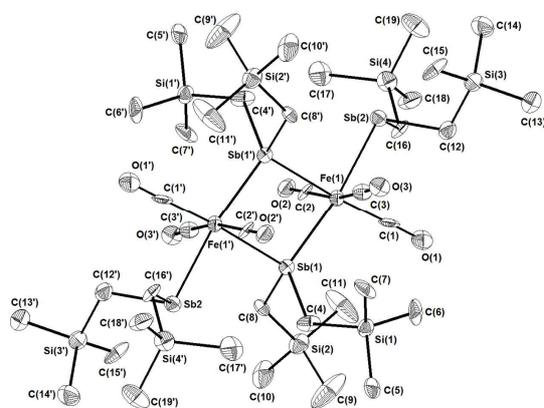


Figure 3. Molecular structure of  $[(Me_3SiCH_2)_2Sb]_4Fe_2(CO)_6$  (**3**). The thermal ellipsoids are represented in 30% probability. The hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ): Fe(1)–Sb(1) 2.552(4), Fe(1)–Sb(1') 2.622(4), Fe(1)–Sb(2) 2.661(4), Sb(1)–Fe(1') 2.622(4), Sb(1)–C(4) 2.16(2), Sb(1)–C(8) 2.14(2), Sb(2)–C(12) 2.16(2), Sb(2)–C(16) 2.19(2), C(4)–Sb(1)–C(8) 97.9(8), C(12)–Sb(2)–C(16) 94.3(9), Fe(1)–Sb(1)–Fe(1') 99.56(12), Sb(1)–Fe(1)–Sb(2) 172.19(16), Sb(1')–Fe(1)–Sb(2) 91.92(13), Sb(1)–Fe(1)–Sb(1') 80.44(12).

Theoretical calculations were carried out on compound **1** using ADF2008.1e software package [14–16]. The starting geometries used were those found by X-ray diffraction. The optimizations were done using the BLYP functional and TZ2P basis set, using a medium frozen core. The geometry optimization was performed using the  $C_i$  point group symmetry, as found in the crystal structure. The energy minimum of the calculated geometries was confirmed by frequency calculations. Further information regarding the DFT calculations can be found as ESI.

In order to benchmark the results of the calculated structure of **1** a geometry optimization and a frequency calculation were carried out on the well studied  $Fe(CO)_5$ . The results compare well with experimental and theoretical results performed with different functionals and basis sets (ESI, Table S2 and ESI, Table S3) [17–19]. Our calculations

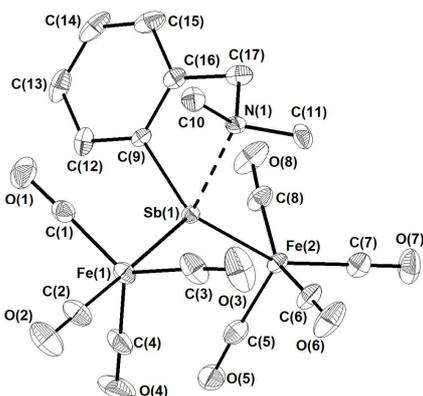
with BLYP functional and TZ2P basis set on  $Fe(CO)_5$  gave bond lengths with deviations between 1.8 – 3.0 % with respect to the values found by X-ray diffraction on single crystal [19]. This result is consistent with calculations reported before [17,18]. The vibrational frequencies calculated for the CO stretching vibrations have errors ranging from 2.1 to 2.6 %, compared to experimental values [19]. These errors are comparable to those reported by Schaefer III et al. [17], and by Jonas and Thiel [18].

In the calculated structure of **1** the Sb–Fe bond lengths are in the range 0.14 to 0.20 Å longer than those found by X-ray diffraction. The calculated C–Sb–C and Sb–Fe–Sb bonding angles are less than  $1^\circ$  different from the measured values. A large difference ( $1.67^\circ$ ) between measured and calculated values was found for the Fe1–Sb2–Fe2 bond angle. The CO bond lengths of the  $Fe(CO)_3$  fragment have deviations ranging from 0.3 to 4.4 %, whereas those of the  $Fe(CO)_4$  fragment range from -1.2 to 1.7 %. The Fe–C bond lengths display deviations between the theoretical and experimental spectrum ranging from 0.6 to 4.4 %. Both, the Fe–C and CO bonds have relative errors on larger domain than those found for  $Fe(CO)_5$ , indicating that for complex **1** the geometry is not so well described.

The calculated infrared spectrum of **1** contains seven signals for the valence vibrations of the  $Fe(CO)_3$  and  $Fe(CO)_4$  fragments. It reproduces only partially the experimental spectrum of a nujol emulsion of **1**, where only six signals are visible and the intensities are different. Both spectra and a list of the IR frequencies with assignments based on the  $C_i$  symmetry of **1** are presented as ESI. The assignments are based on the assumption that the calculated signal of lowest intensity is not observed in the experimental spectrum. The deviations between calculated and experimental frequencies range between 3.1 and 5.1 %. They are larger than the deviations found for  $Fe(CO)_5$ . This is probably a consequence of the larger differences in bond lengths calculated for **1**.

## Conclusions

The present study that had aimed at a crystallographic confirmation of our earlier results revealed that reactions between distibanes (and probably also other dipnictides) are more versatile than we knew before and unexpected new complexes were obtained. Nevertheless the formation of the novel multinuclear complexes **1–3** can easily be explained by reactions between previously reported compounds, i.e. distibanes or distibane complexes with antimonido complexes  $(CO)_3Fe(SbR_2)_2Fe(CO)_3$ . Although new products obtained from the system  $Fe_2(CO)_9 / R_2SbSbR_2$  ( $R = \text{alkyl}$ ) are presented here, still many questions are open and for a full understanding of this chemistry more detailed studies are required. Of particular importance in this context are studies of the behaviour of **1–3** in solution and the unambiguous characterization including crystallography of a complex of the type  $(CO)_3Fe(SbR_2)_2Fe(CO)_3$ . With view on the present results we cannot exclude that our previously reported  $(CO)_3Fe(SbEt_2)_2Fe(CO)_3$  was in fact complex **1**.

Figure 4. Molecular structure of the isomer  $R_{N1}$  molecule **1** of [2-

( $\text{Me}_2\text{NCH}_2$ ) $\text{C}_6\text{H}_4\text{SbFe}_2(\text{CO})_8$ ] (**4**). The thermal ellipsoids are represented in 30% probability. The hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ): Fe(1)–Sb(1) 2.4878(11), Fe(2)–Sb(1) 2.4701(11), Fe(3)–Sb(2) 2.4681(10), Fe(4)–Sb(2) 2.4816(11), C(9)–Sb(1) 2.127(7), C(26)–Sb(2) 2.138(6), N(1)–Sb(1) 2.283(7), N(2)–Sb(2) 2.299(7), C(9)–Sb(1)–N(1) 77.8(3), C(9)–Sb(1)–Fe(2) 111.78(19), N(1)–Sb(1)–Fe(2) 106.48(15), C(9)–Sb(1)–Fe(1) 115.0(2), N(1)–Sb(1)–Fe(1) 108.03(16), Fe(2)–Sb(1)–Fe(1) 126.14(4), C(26)–Sb(2)–N(2) 77.2(2), C(26)–Sb(2)–Fe(3) 108.53(18), N(2)–Sb(2)–Fe(3) 106.73(14), C(26)–Sb(2)–Fe(4) 116.71(18), N(2)–Sb(2)–Fe(4) 107.05(14), Fe(3)–Sb(2)–Fe(4) 127.98(4).

## Experimental Section

The reactions and manipulations of the compounds were performed under an atmosphere of argon. All solvents were dried and freshly distilled prior to use.  $\text{Fe}_2(\text{CO})_9$ ,  $\text{Et}_4\text{Sb}_2$ ,  $n\text{-Pr}_4\text{Sb}_2$ , and  $(\text{Me}_3\text{SiCH}_2)_4\text{Sb}_2$  were prepared according to the literature [20–25]. The NMR spectra were recorded on Bruker AVANCE DPX-200 and the  $^1\text{H}$  chemical shifts are reported in  $\delta$  units (ppm) relative to the residual peak of solvent ( $\text{C}_6\text{D}_5\text{H}$ ,  $^1\text{H}$ , 7.15 ppm). Mass spectra were recorded on a Finnigan MAT 95 and the IR spectra were recorded from Nujol mulls on a Perkin-Elmer FT-IR SPEKTRUM 1000 spectrometer.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 753157 - 753160. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax.: (internat.) + 44 1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

### [( $\text{Et}_2\text{Sb}$ ) $_4\text{Fe}_4(\text{CO})_{14}$ ] (**1**)

2.0 g (5.5 mmol)  $\text{Et}_4\text{Sb}_2$  in 20 ml  $n$ -hexane were added dropwise to 2.0 g (5.5 mmol)  $\text{Fe}_2(\text{CO})_9$  in 80 ml  $n$ -hexane and the mixture was stirred at ambient temperature for 12 h. The red brown solution was filtered through a frit. The solution was concentrated at reduced pressure and kept at  $-28^\circ\text{C}$  when 0.9 g (49 %) red crystals of **1** (m.p. 105 – 110  $^\circ\text{C}$ ) formed.

$^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.10 (t,  $\text{CH}_3$ ), 1.30 (t,  $\text{CH}_3$ ), 1.8 – 1.95 (m,  $\text{CH}_2$ ),  $^3\text{J} = 7.3$  Hz; 0.8 – 1.0, 2.0 – 2.2, 2.3 – 2.5 (broad unresolved signals). MS (EI, 70eV): 1192 (2) [ $M - 5\text{CO}$ ] $^+$ , 1080 (1) [ $\text{R}_8\text{Sb}_4\text{Fe}_3(\text{CO})_9$ ] $^+$ , 655 [ $\text{Sb}_4\text{Fe}_3$ ] $^+$ , 640 (20) [ $\text{R}_4\text{Sb}_2\text{Fe}_2(\text{CO})_6$ ] $^+$ , 273 (20) [ $\text{RSb}_2$ ] $^+$ , 208 (15) [ $\text{SbR}_3$ ] $^+$ , 151 (30) [ $\text{RSb}$ ] $^+$ , 28 (100) [ $\text{CO}$ ] $^+$ ,  $\text{R} = \text{C}_2\text{H}_5$ . IR Nujol:  $\nu$  (CO) 2066, 2042, 2030, 1986, 1965, 1950  $\text{cm}^{-1}$ .

### [( $n\text{-Pr}_2\text{Sb}$ ) $_4\text{Fe}_3(\text{CO})_{10}$ ] (**2**)

2.28 g  $n\text{-Pr}_4\text{Sb}_2$  (5.5 mmol) were added through a syringe to 2.0 g (5.5 mmol)  $\text{Fe}_2(\text{CO})_9$  in 70 mL  $n$ -hexane. The mixture was stirred

at ambient temperature for 16 h. After filtration and removal of the solvent 1.73 g (74%) of a red brown viscous liquid remained. Several air sensitive red crystals of **2** (m.p. 215  $^\circ\text{C}$ , dec.) formed when the liquid was kept for 3 months at  $-28^\circ\text{C}$ .

$^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.88 ( $\text{CH}_3$ ), 1.23 ( $\text{CH}_2$ ), 1.5 – 1.6 ( $\text{CH}_2$ ). MS (CI negative,  $\text{NH}_3$ ) 1251 (20) [ $\text{R}_8\text{Sb}_4\text{Fe}_3(\text{CO})_9$ ] $^+$ , 1225 (20) [ $\text{R}_8\text{Sb}_4\text{Fe}_3(\text{CO})_8$ ] $^+$ , 1139 (80) [ $\text{R}_8\text{Sb}_4\text{Fe}_3(\text{CO})_5$ ] $^+$ , 653 (100) [ $\text{R}_3\text{Sb}_2\text{Fe}_2(\text{CO})_6$ ] $^+$ ; (CI positive,  $\text{NH}_3$ ) 1165 (4) [ $\text{R}_8\text{Sb}_4\text{Fe}_3(\text{CO})_6$ ] $^+$ , 697 (40) [ $\text{R}_4\text{Sb}_2\text{Fe}_2(\text{CO})_6\text{H}$ ] $^+$ , 417 (80) [ $\text{R}_4\text{Sb}_2$ ] $^+$ , 251 (100) [ $\text{R}_3\text{Sb}$ ] $^+$ ; MS (EI, 70eV) 696 (5) [ $\text{R}_4\text{Sb}_2\text{Fe}_2(\text{CO})_6$ ] $^+$ , 686 (2) [ $\text{R}_4\text{Sb}_2\text{Fe}_2(\text{CO})_5$ ] $^+$ , 572 (6) [ $\text{R}_3\text{Sb}_2\text{Fe}_2(\text{CO})_3$ ] $^+$ , 516 (5) [ $\text{R}_3\text{Sb}_2\text{Fe}_2(\text{CO})$ ] $^+$ , 446 (3) [ $\text{R}_3\text{Sb}_2\text{Fe}_2\text{H}$ ] $^+$ , 416 (25) [ $\text{R}_4\text{Sb}_2$ ] $^+$ , 402 (20) [ $\text{RSb}_2\text{Fe}_2$ ] $^+$ , 347 (40) [ $\text{R}_2\text{SbFe}(\text{CO})_3$ ] $^+$ , 305 (50) [ $\text{RSbFe}(\text{CO})_3$ ] $^+$ , 250 (20) [ $\text{R}_3\text{Sb}$ ] $^+$ , 207 (10) [ $\text{R}_2\text{Sb}$ ] $^+$ , 165 (100) [ $\text{RSbH}$ ] $^+$ ; ( $\text{R} = \text{C}_3\text{H}_7$ ). IR Nujol:  $\nu$  (CO) 2040, 2005, 1994, 1950, 1932  $\text{cm}^{-1}$ .

### [( $(\text{Me}_3\text{SiCH}_2)_2\text{Sb}$ ) $_4\text{Fe}_2(\text{CO})_6$ ] (**3**)

0.81 g (1.37 mmol) [ $(\text{Me}_3\text{SiCH}_2)_2\text{Sb}$ ] $_2$  in 10 mL  $n$ -hexane were added dropwise to 0.5 g (1.37 mmol)  $\text{Fe}_2(\text{CO})_9$  in 50 ml  $n$ -hexane and the brown mixture was stirred 12 h at ambient temperature. After filtration and concentration at reduced pressure the remaining solution was stored at  $-10^\circ\text{C}$  for 1 d and 1.1 g (50 %) red crystals of **3** formed.

$^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.12 (s, ( $\text{CH}_3$ ) $_3\text{Si}$ ), 1.9 (s, ( $\text{CH}_3$ ) $_3\text{Si}$ ), 0.5 – 1.6 (m,  $\text{CH}_2$ ); 0.17 (s, 36 H,  $\text{Me}_3\text{Si}$ ), AB spin system with A: 0.67, B: 0.96,  $^2\text{J} = 13$  Hz (8H,  $\text{CH}_2$ ) ( $\text{Me}_3\text{SiCH}_2$ ) $_4\text{Sb}_2$ . MS-EI 70eV (186  $^\circ\text{C}$ )  $m/z$  (rel. int. %), 1464 (0.2) [ $M$ ] $^+$ , 1449 (0.2) [ $M - \text{Me}$ ] $^+$ , 1171 (2) [ $M - \text{R}_2\text{Sb}$ ] $^+$ , 1139 (2), 872 (8) [( $\text{R}_2\text{Sb}$ ) $_2\text{Fe}_2(\text{CO})_6$ ] $^+$ , 857 (4), 844 (6) [( $\text{R}_2\text{Sb}$ ) $_2\text{Fe}_2(\text{CO})_5$ ] $^+$ , 788 (18) [( $\text{R}_2\text{Sb}$ ) $_2\text{Fe}_2(\text{CO})_3$ ] $^+$ , 704 (40) [( $\text{R}_2\text{Sb}$ ) $_2\text{Fe}(\text{CO})_2$ ] $^+$ , 592 (20) [ $\text{R}_4\text{Sb}_2$ ] $^+$ , 295(50) [ $\text{R}_2\text{Sb}$ ] $^+$ , 145 (60) [( $\text{Me}_3\text{Si}$ ) $_2$ ] $^+$  73 (100) [ $\text{Me}_3\text{Si}$ ] $^+$ ;  $\text{R} = \text{Me}_3\text{SiCH}_2$ . IR Nujol:  $\nu$  (CO) 2043, 2007, 1992, 1962, 1932, 1877  $\text{cm}^{-1}$ .

### [ $\text{RSb}\{\text{Fe}(\text{CO})_4\}_2$ ] ( $\text{R} = 2\text{-}(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4$ ) (**4**)

1.0 g (1.2 mmol)  $\text{R}_4\text{Sb}_2$  ( $\text{R} = 2\text{-}(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4$ ) were added to 1.4 g (3.8 mmol)  $\text{Fe}_2(\text{CO})_9$  in 100 mL tetrahydrofuran and the mixture was stirred 24 h at ambient temperature. After filtration and removal of the solvent an oily liquid remained. This liquid was extracted with tetrahydrofuran. Several orange crystals of **7** (m.p. 150 – 160  $^\circ\text{C}$ , dec.) formed at  $-10^\circ\text{C}$  in a few days. The liquid phase contained  $\text{R}_3\text{Sb}$ .

MS-EI (70 eV, 170  $^\circ\text{C}$ ): 591 (2.2) [ $M$ ] $^+$ , 563 (1) [ $M - \text{CO}$ ] $^+$ , 507 (4) [ $M - 3\text{CO}$ ] $^+$ , 479 (2) [ $M - 4\text{CO}$ ] $^+$ , 451 (3) [ $M - 5\text{CO}$ ] $^+$ , 423 (10) [ $M - 6\text{CO}$ ] $^+$ , 395 (18) [ $M - 7\text{CO}$ ] $^+$ , 367 (17) [ $M - 8\text{CO}$ ] $^+$ , 339 (16) [ $\text{RSbFeCO}$ ] $^+$ , 311 (10) [ $\text{RSbFe}$ ] $^+$ , 255 (2) [ $\text{RSb}$ ] $^+$ , 135 (81) [ $\text{R} + \text{H}$ ] $^+$ , 91 (85) [ $\text{R-NMe}_2$ ] $^+$ , 58 (100) [ $\text{CH}_2\text{NMe}_2$ ] $^+$ ,  $\text{R} = 2\text{-}(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4$ .

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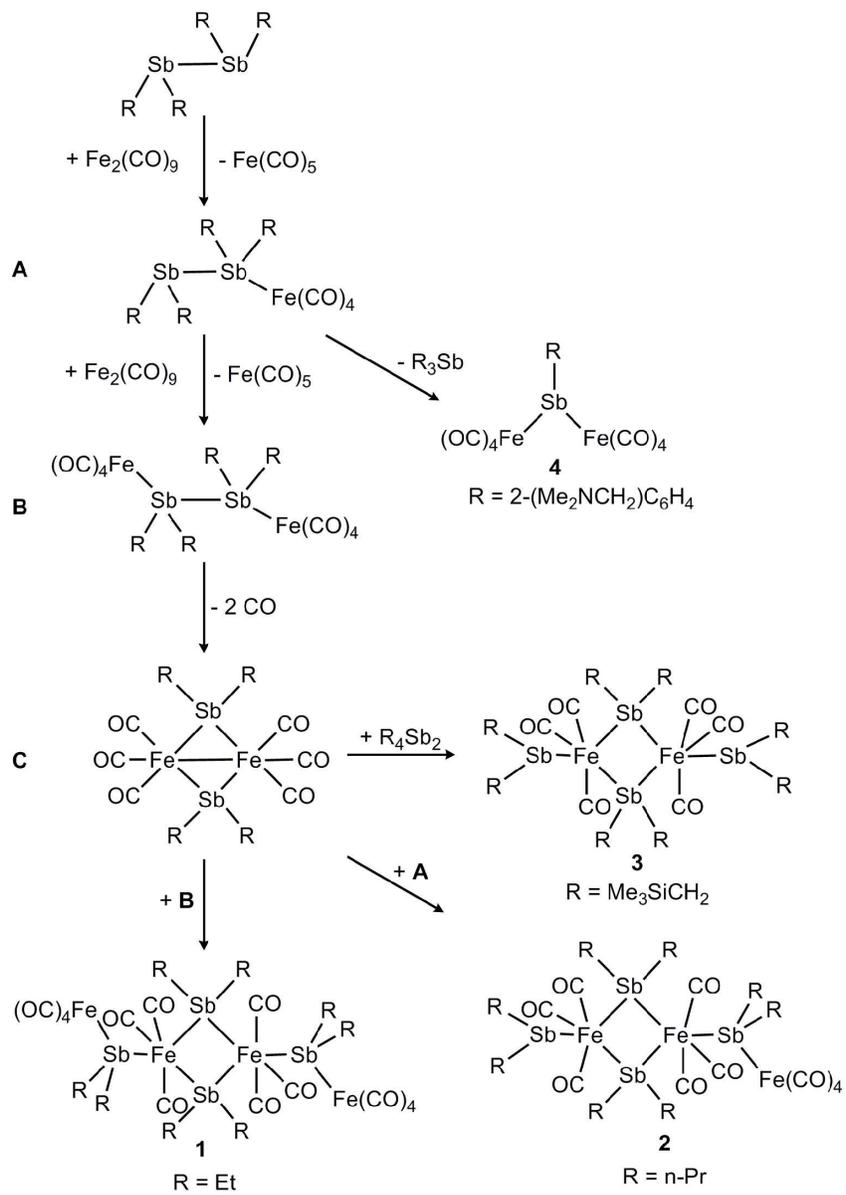
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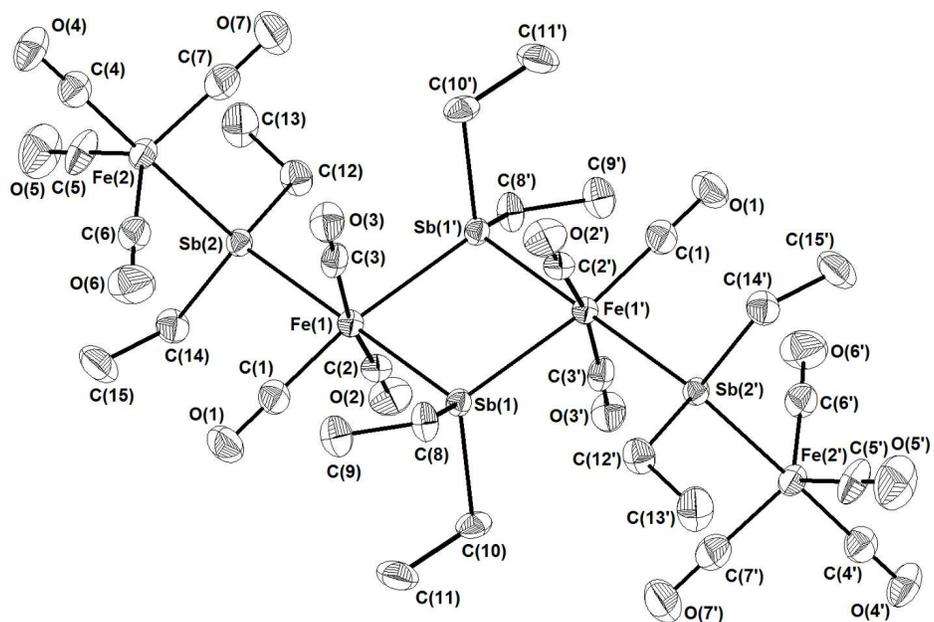
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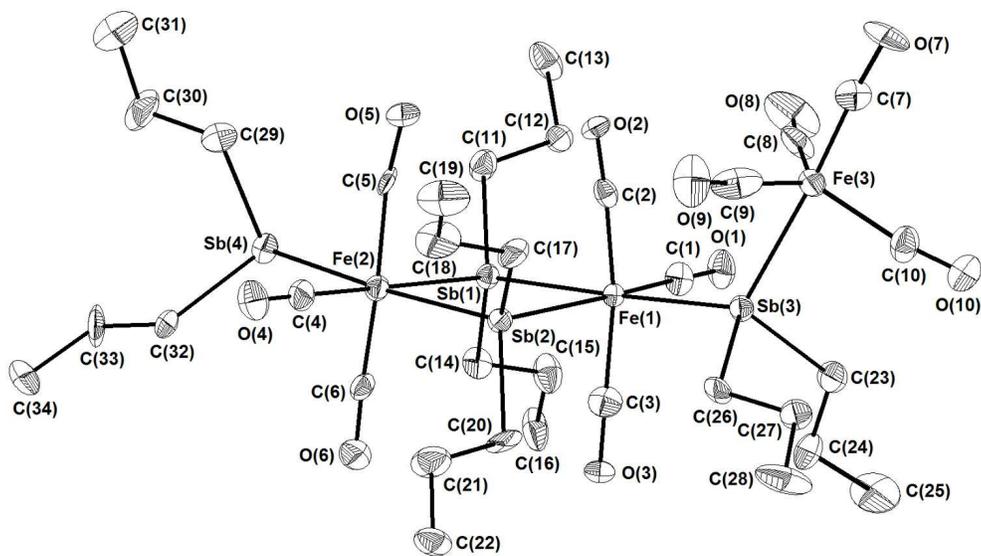
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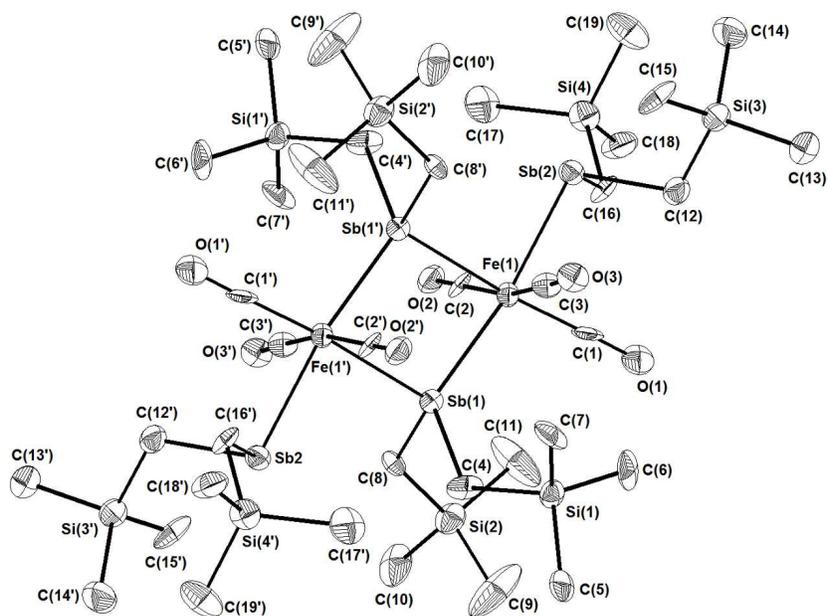
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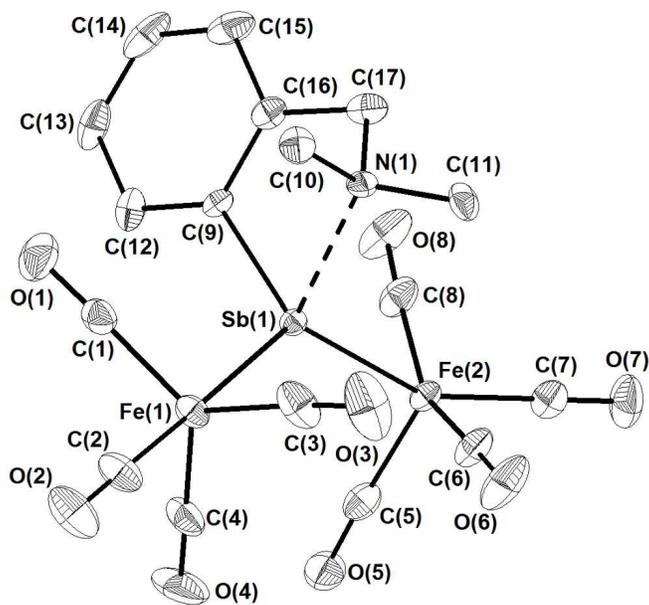
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