Novel Main Group-Transition Metal Cluster Compounds Incorporating Antimony, Iron and Cobalt

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Dedicated to Professor Herbert W. Roesky on the occasion of his 65th birthday

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The reaction of [{$Cp^x(CO)_2Fe$}$SbCl_2$] [**1a**: $Cp^x = \eta^5$-$C_5H_3tBu_2$-1,3 (Cp"); **1b**: $Cp^x = \eta^5$-C_5Me_5 (Cp*)] with $Na_2[Fe(CO)_4]$ or $K[Co(CO)_4]$ affords the novel antimony-transition metal cluster compounds [{μ_3-$SbFe(CO)_2Cp"$}$_3${$Fe(CO)_3$}$_4$] **(2)**, [{$Fe_3(CO)_9$}{μ_3-$SbFe(CO)_2Cp"$}$_2$] **(3)** and [{μ_4-$SbFe(CO)_2$-Cp*}$_2${$Co_4(CO)_{10}(\mu$-CO)}] **(4)**. All products were characterised by X-ray structure analyses and other methods. Cluster **2** reveals a novel Sb_3Fe_4 core, which does not follow the Wade–Mingos rules. Cluster **3** forms a square-pyramidal *nido*-cluster. The Sb_2Co_4 cluster core of **4** derives from a pentagonal bipyramid and consists of apical Sb and equatorial Co atoms with one missing pentagonal core atom.

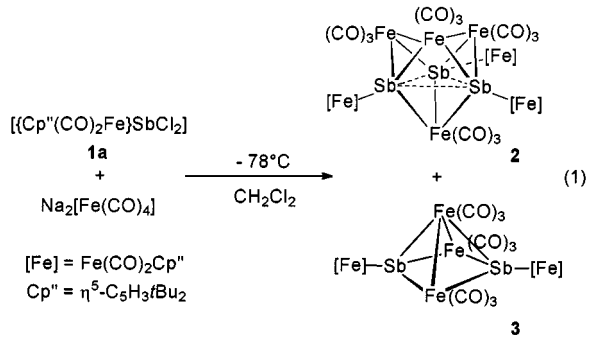
Introduction

Clusters which incorporate main group elements and transition metals together in a core framework have been of wide interest in the last years.[1] We are particularly interested in complexes which contain the heavy group 15 elements Sb and Bi. Amongst those, only a few examples of antimony-rich complexes have been prepared, e.g. [{$Mo(CO)_3Cp^x$}$_2$(μ,η^2-Sb_2)] (Cp^x = Cp,[2] Cp*[3]) [(μ,η^2-Sb_2){$W(CO)_5$}$_3$],[4] and [{$Mo(CO)_2Cp^x$}(η^3-Sb_3)][3] (Cp^x = Cp, Cp*). The synthetic approach to these clusters is versatile: they can be prepared either by metalation of $SbCl_3$, reaction of elemental antimony with transition metal complexes or from cyclic organo-antimony precursors.

Even though there is a large variety of synthetic methods to yield these cluster compounds, a rational way of preparing them is still missing. Recently, we reported the synthesis and structure of transition metal-substituted dichlorides of antimony and bismuth of the formula [{$Cp"(CO)_2Fe$}ECl_2] [E = Sb **(1a)**, Bi].[5] These complexes have interesting properties for the building-up of main group element-transition metal clusters of varying composition in a straightforward manner. This might be feasible by either using reducing agents (e.g. Mg) to yield (μ_3-E) bridged binary compounds[5] or by incorporating other transition metals from a reaction with metalates. This latter reaction was successfully used to prepare phosphorus rich complexes starting from $[Cp(CO)_3WPCl_2]$.[6] We herein report the synthesis and structures of novel antimony-containing main group-transition metal cluster compounds.

Results and Discussion

The reaction of [{$Cp"(CO)_2Fe$}$SbCl_2$] **(1a)** with $Na_2[Fe(CO)_4]$ yields the novel cluster compound [{μ_3-$SbFe(CO)_2Cp"$}$_3${$Fe(CO)_3$}$_4$] **(2)** as the main product and smaller amounts of [{μ_3-$SbFe(CO)_2Cp"$}$_2${$Fe_3(CO)_9$}] **(3)** [Equation (1)]. While it was possible to isolate **2** as a pure compound by fractional crystallisation, the minor product **3** always co-crystallises with **2**. Attempts to separate these mixtures by column chromatography on silica gel or aluminium oxide failed due to the decomposition of the products. The complex [{$Cp^*(CO)_2Fe$}$SbCl_2$] **(1b)** reacts with two equivalents of $K[Co(CO)_4]$ to form [{μ_4-$SbFe(CO)_2$-Cp*}$_2${$Co_4(CO)_{10}(\mu$-CO)}] **(4)** [Equation (2)] and some $[Cp^*(CO)Fe(\mu\text{-}CO)_2Co(CO)_3]$ **(5)**. The occurrence of **5** is a hint that, as a side-reaction, a metal-antimony bond cleavage occurs — as it was also reported for the reaction of **1a** with magnesium.[5] Complex **5** has already been structurally characterised,[7] and our X-ray[8] and spectroscopic data are similar to the reported values.



All complexes were isolated as red crystalline compounds, which are readily soluble in *n*-hexane or toluene. In the IR spectra of compounds **2**–**4**, the CO stretching frequencies for terminal CO groups are detected, whereas for cluster **4** an addition band at 1779 cm^{-1} for a bridging

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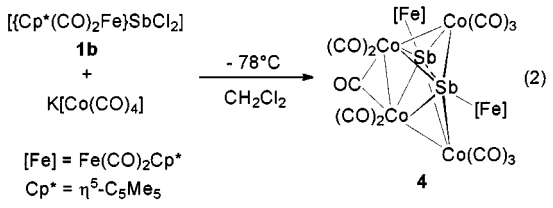

CO group is found. In the ^{1}H NMR spectrum of **2** at ambient temperature the *t*Bu groups and the protons on the Cp" rings are inequivalent. At a temperature of 368 K the two signals of the methyl protons coalesce indicating the free rotation of the Cp" ligands. The free activation enthalpy of this process at the coalescence temperature (T_c = 368 K) is calculated to be $\Delta G^{\#}_{Tc}$ = 80 kJ/mol.

An X-ray structure analysis of **2** reveals a central Sb_3Fe tetrahedron, the Sb_3 and two Sb_2Fe planes of which are capped by three $Fe(CO)_3$ groups (Figure 1). The Fe atom of the tetrahedron additionally coordinates to three carbonyl ligands, whereas each antimony atom binds to an $Fe(CO)_2Cp"$ fragment. Within the Sb_3 unit two different kinds of Sb···Sb distances are observed: long distances are found around the Sb(3) atom [3.2412(9) and 3.2574(10) Å] and are much longer than known Sb−Sb single bonds as, for example, in Sb_7^{3-} [2.717(2)−2.906(2) Å],[9] [{Mo(CO)$_2$Cp*}(η^3-Sb$_3$)][3] [2.7397(9)−2.7682(8) Å], (*t*BuSb)$_4$ [2.822(1)−2.878(1) Å[10a]] or in [(Me$_3$Si)$_2$CHSb]$_3$ [2.8188(6)−2.8453(6) Å].[10b] However, the shortest distance in **2** [Sb(1)−Sb(2) = 3.0259(9) Å] is still within the range of long, bonding Sb−Sb distances as found in the compound [{Cp(CO)$_2$Fe}{Cr(CO)$_5$}SbBr]$_2$,[11] possessing the longest known Sb−Sb single bond length of 3.069(6) Å. Intermolecular Sb···Sb distances within the structure of **2** are in the range of 3.678(1)−4.271(1) Å, as found for Me_4Sb_2 [12] and [(η^3-Sb$_3$){Mo(CO)$_2$Cp^x}] (Cp^x = Cp, Cp*).[3]

The Sb_3Fe_4 cluster core of **2** is close to C_s symmetry with the symmetry plane defined by the atoms Sb(3), Fe(6) and Fe(7), which becomes evident by the similarity in the bond lengths of Fe(6)−Sb(1) and Fe(6)−Sb(2) [2.6686(14) vs. 2.6672(15) Å], and Fe(6)−Fe(5) and Fe(6)−Fe(4) [2.844(2) vs. 2.8466(18) Å] (Figure 2). Due to the steric hindrance of the bulky Cp" ligands, the molecule might not be able to adopt an overall C_s symmetry. Describing the Sb_3Fe_4 cluster core of the 20 skeletal electrons by the Wade−Mingos rules does not lead to a satisfactory explanation of the adopted polyhedron. An explanation can be given using the concept of "Topological Electron Counting" (TEC), as suggested by Teo[13] for the relation between cluster geometry and valence electrons in transition metal clusters. Using this relation with mixed transition metal-main group element clusters, the number of bonding orbitals (CVMO) will count to $CVMO = 8X + 3N - F + 2$ (X = number of transition elements; N = number of main group elements; F = number of polyhedral faces). In the case of the cluster core in compound **2** this results in a CVMO of 34 on assuming bonding Sb−Sb interactions. Calculating the number of cluster electrons by EAN rules leads to 68, which fits with the number of bonding cluster orbitals. To the best of our knowledge this polyhedron is so far unique for a main group transition metal cluster.

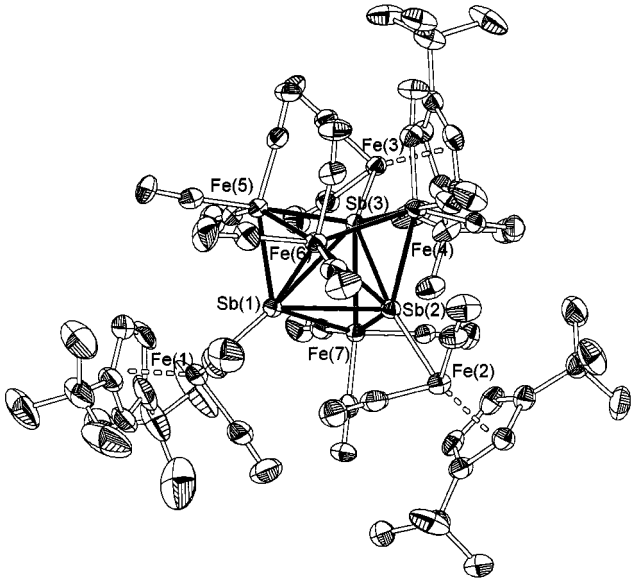

Figure 1. Molecular structure of [{μ_3-SbFe(CO)$_2$Cp"}$_3${Fe(CO)$_3$}$_4$] **(2)** showing 30% probability ellipsoids; hydrogen atoms are omitted for clarity; selected bond lengths [Å]: Sb(1)−Sb(2) 3.0259(9), Sb(1)−Sb(3) 3.2412(9), Sb(2)−Sb(3) 3.2574(10), Sb(1)−Fe(1) 2.5917(14), Sb(1)−Fe(5) 2.5170(14), Sb(1)−Fe(6) 2.6686(14), Sb(1)−Fe(7) 2.6337(13), Sb(2)−Fe(2) 2.5921(16), Sb(2)−Fe(4) 2.5311(13), Sb(2)−Fe(6) 2.6672(15), Sb(2)−Fe(7) 2.6076(14), Sb(3)−Fe(3) 2.6415(14), Sb(3)−Fe(4) 2.6312(14), Sb(3)−Fe(5) 2.6157(13), Sb(3)−Fe(7) 2.6833(12), Fe(6)−Fe(5) 2.844(2), Fe(6)−Fe(4) 2.8466(18)

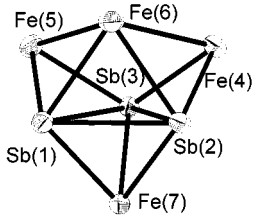

Figure 2. Sb_3Fe_4 cluster core in **2**

The structure of the compound [{μ_3-SbFe(CO)$_2$Cp"}$_2${Fe$_3$(CO)$_9$}] **(3)** is built up of a tetragonal pyramid of three Fe and two Sb atoms, with the two Sb and two of the Fe atoms alternately building the base square (Figure 3). The third Fe atom is at the top of the pyramid. Each Sb atom is additionally bound to a $Fe(CO)_2Cp"$ moiety. On using the Wade−Mingos rules on the Sb_2Fe_3 cluster core, an electron count comes to 14 skeletal electrons, which is the same number as in *nido*-pentaborane B_5H_9, which also forms a square pyramid. A similar cluster framework has been found for the lighter congeners of Sb within [{Fe$_3$(CO)$_9$}{μ_3-PFe(CO)$_2$Cp}$_2$][14] and [{Fe$_3$(CO)$_9$}{μ_3-AsMo(CO)$_3$Cp}$_2$].[15] The Fe−Fe distances within the $Fe_3(CO)_9$ fragment in **3** are 2.823(2) Å and 2.814(2) Å. The Fe−Fe bond length is dependent on the atomic radius of the pnicogenido atom, and decreases from **3** through [{Fe$_3$(CO)$_9$}{μ_3-AsMo(CO)$_3$Cp}$_2$] [2.726(2) and 2.750(2) Å] to [{Fe$_3$(CO)$_9$}{μ_3-PFe(CO)$_2$Cp}$_2$] [2.704(3) and 2.718(4) Å]. In compound **3** there is no bonding interaction

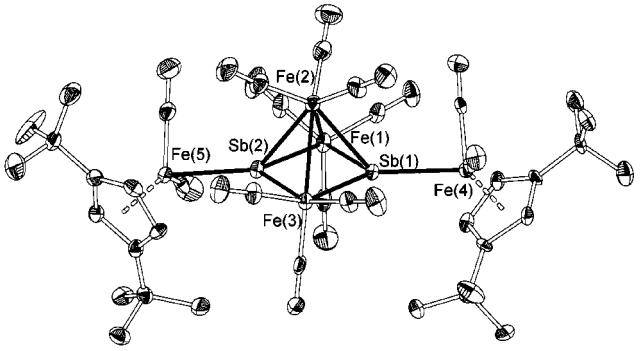

Figure 3. Molecular structure of $[\{\mu_3\text{-SbFe}(CO)_2Cp''\}_2\{Fe_3(CO)_9\}]$ **(3)** showing 30% probability ellipsoids; hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: Sb(1)−Fe(1) 2.5075(19), Sb(1)−Fe(2) 2.543(2), Sb(1)−Fe(3) 2.530(2), Sb(1)−Fe(4) 2.5518(19), Sb(2)−Fe(1) 2.512(2), Sb(2)−Fe(3) 2.5240(18), Sb(2)−Fe(2) 2.5529(18), Sb(2)−Fe(5) 2.5607(18), Sb(1)···Sb(2) 3.1705(15), Fe(1)−Fe(2) 2.823(2), Fe(2)−Fe(3), 2.814(2); Fe(1)−Sb(1)−Fe(3) 101.94(7), Fe(1)−Sb(2)−Fe(3) 101.97(7), Sb(1)−Fe(1)−Sb(2) 78.34(6), Sb(2)−Fe(3)−Sb(1) 77.71(6), Fe(1)−Sb(1)−Fe(4) 121.74(6), Fe(3)−Sb(1)−Fe(4) 136.28(6), Fe(2)−Sb(1)−Fe(4) 128.54(6), Fe(1)−Sb(2)−Fe(5) 125.27(6), Fe(2)−Sb(2)−Fe(5) 135.23(7), Fe(3)−Sb(2)−Fe(5) 131.87(6), Fe(3)−Fe(2)−Fe(1) 87.92(7)

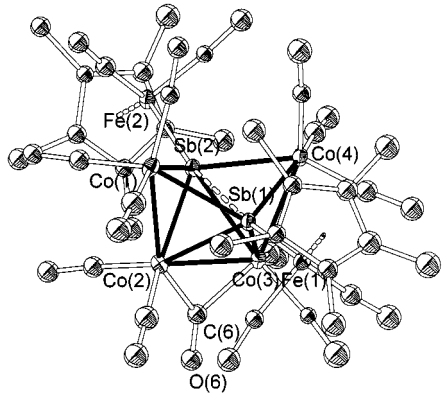

Figure 4. Molecular structure of $[\{\mu_4\text{-SbFe}(CO)_2\text{-}Cp^*\}_2\{Co_4(CO)_{10}(\mu\text{-}CO)\}]$ **(4)** showing 30% probability ellipsoids; hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: Sb(1)−Sb(2) 2.986(2), Sb(1)−Fe(1) 2.599(4), Sb(2)−Fe(2) 2.606(3), Co(1)−Co(2) 2.658(5), Co(2)−Co(3) 2.598(5), Co(3)−Co(4) 2.683(4), Sb(1)−Co(1) 2.628(3), Sb(1)−Co(2) 2.653(4), Sb(1)−Co(3) 2.605(4), Sb(1)−Co(4) 2.608(4), Sb(2)−Co(1) 2.611(4), Sb(2)−Co(2) 2.614(3), Sb(2)−Co(3) 2.651(3), Sb(2)−Co(4) 2.621(4), Co(2)−C(6) 1.84(3), Co(3)−C(6) 1.93(3), C(6)−O(6) 1.20(3); Sb(1)−Co(2)−Sb(2) 69.07(9), Sb(1)−Co(3)−Sb(2) 69.23(10), Co(1)−Co(2)−Co(3) 104.78(15), Co(2)−Co(3)−Co(4) 104.47(15)

between Fe(1) and Fe(3) [Fe(1)···Fe(3) = 3.913(2) Å]. All Sb−Fe bond lengths are within the small range of 2.5075(19) [Sb(1)−Fe(1)] and 2.5607(18) Å [Sb(2)−Fe(5)] and are therefore shorter than the Sb−Fe bond lengths in **2**. The Sb···Sb distance is 3.1705(15) Å. The folding angle between the two planes defined by Sb(1), Fe(1) and Sb(2), and Sb(1), Fe(3) and Sb(2), respectively, is 178.29(2)° and hence close to planarity. It is similar to that of the dianionic *nido*-cluster $[\{Fe_3(CO)_9\}(\mu_3\text{-SbFe}(CO)_4)_2]^{2-}$ [174.54(3)°].[16a] At first sight, the structures of this compound and of its homologues $[\{Fe_3(CO)_9\}(\mu_3\text{-EFe}(CO)_4)_2]^{2-}$ (E = As,[16b] Bi[16c]) seem to be similar to **3**; however, in these dianionic complexes the lone pair of the pnicogens coordinates to an exocyclic $Fe(CO)_4$ group,[16d] whereas in **3** a σ-bond exists to exocyclic $CpFe(CO)_2$ moieties.

The X-ray structure analysis of **4** (Figure 4) shows a central Sb_2Co_2 tetrahedron, two planes of which are capped by one $Co(CO)_3$ group each. The Co−Co edge of the tetrahedron is bridged by a carbonyl ligand. Each antimony atom additionally binds to an $Fe(CO)_2Cp^*$ fragment. The Sb−Sb distance in **4** is 2.986(2) Å and hence is shorter than the distances in compound **2** [3.0259(9)−3.2574(10) Å]. The Sb−Co bond lengths [2.605(4)−2.651(3) Å] are in the known range for single bonds [2.480(1)−2.690(1) Å].[17−19]

The anionic cluster compounds $[E_2Co_4(CO)_{10}(\mu\text{-}CO)]^{n-}$ (E = Sb, Bi; n = 1, 2), possessing a E_2Co_4 core similar to **4**, were first described by Whitmire[20] and Martinengo,[21] respectively. In contrast to these compounds, compound **4** is uncharged, and the electrons of the charges in the former compounds are in **4** formally located in the Sb−Fe bonds to the $Fe(CO)_2Cp^*$ fragments. This results in a longer Sb−Sb distance in **4** [2.986(2) Å] than that in $[Sb_2Co_4(CO)_{10}(\mu\text{-}CO)]^{2-}$ [2.882(2) Å] and a concomitant shortening of the Co−Co bond lengths within the cluster core [2.598(5)−2.683(4) Å] compared to those in $[Sb_2Co_4(CO)_{10}(\mu\text{-}CO)]^{2-}$ [2.645(5)−2.717(5) Å]. The same tendency is visible for the Sb−Co bond lengths [2.605(4)−2.653(4) Å in **4** compared to 2.616(4)−2.676(4) Å]. The Sb−Sb bond length in the monoanionic compound $[Sb_2Co_4(CO)_{10}(\mu\text{-}CO)]^-$ [2.911(1) Å][20] is still shorter than in **4**, whereas the Co−Co distances in $[Sb_2Co_4(CO)_{10}(\mu\text{-}CO)]^-$ tend to fall in a wider range [2.510(3)−2.725(3) Å], as do Sb−Co distances [2.605(2)−2.692(2) Å]. As for the Sb_3Fe_4 polyhedron in **2**, a description of the Sb_2Co_4 cluster core of **4** following the Wade−Mingos rules fails. A thorough MO-theoretical discussion of charged 18-electron clusters of this type and a discussion as to whether $[E_2Co_4(CO)_{10}(\mu\text{-}CO)]^{2-}$ clusters are best expressed as a bicapped tetrahedron or derived from a pentagonal bipyramid was previously described by Whitmire and co-workers.[20] On this basis, for **4** we tend towards the explanation of the pentagonal bipyramid with a missing pentagonal core atom. Assuming that the structure of **4** derives from a bicapped tetrahedron, angles of 109.5° are expected, whereas only 108° is necessary for a pentagonal bipyramid. Angles of 104.78(15) and 104.47(15) for Co(1)−Co(2)−Co(3) and Co(2)−Co(3)−Co(4), respectively, are found within **4** and are even smaller than necessary, whereas the angles of the tetrahedral faces Sb(1)−Co(2)−Sb(2) [69.07(9)°] and Sb(1)−Co(3)−Sb(2) [69.23(10)°] are larger than the expected 60° for a bicapped tetrahedron.

Conclusions

In contrast to reactions of $[\{Cp^x(CO)_2Fe\}SbCl_2]$ [Cp^x = Cp" **(1a)**; Cp^x = Cp* **(1b)**] with magnesium, which yield (μ_3-Sb) bridged binary antimony-transition metal complexes, these compounds react with transition metalates

with incorporation of a main group element moiety within a transition metal cluster framework. Only a small tendency to Sb−Sb bond formation was observed, as found for the complexes **2** and **4**. For similar reactions of phosphorus-containing starting materials of the formula $[L_nMPCl_2]$,[6] a higher tendency of P−P bond formation was discovered. The reason for this can probably be found in the stronger metallic character of Sb, and hence in the higher tendency of element−metal bond formation.

Generally, the compounds **1a,b** open a facile and rational way to generate novel main group-transition metal clusters. Starting from halogenated main group elements which already bear a transition metal function, they might even serve as a good starting point for preparing cluster compounds with different main group elements and different transition metals in a specific manner.

Experimental Section

General Techniques: All manipulations were performed under an atmosphere of dry Ar using standard Schlenk techniques. All solvents were dried by common methods and freshly distilled prior to use. NMR spectra were recorded on a Bruker AC 250 using TMS as external standard. Mass spectra were done with a Varian MAT 711. IR spectra were recorded on a Bruker IFS 28 FT-IR spectrometer. Elemental analyses were performed on a Elementar Vario EL of the institute.

Reagents: $K[Co(CO)_4]$[22] and $Na_2[Fe(CO)_4]$[23] were prepared according to literature methods. The synthesis of $[\{Cp^x(CO)_2Fe\}SbCl_2]$ (**1a:** $Cp^x = \eta^5$-$C_5H_3tBu_2$-1,3; **1b:** $Cp^x = \eta^5$-C_5Me_5) has been described previously.[5]

Synthesis of $[\{\mu_3$-$SbFe(CO)_2Cp''\}_3\{Fe(CO)_3\}_4]$ (2) and $[\{\mu_3$-$SbFe(CO)_2Cp''\}_2\{Fe_3(CO)_9\}]$ (3). To a solution of $[\{Cp''(CO)_2Fe\}SbCl_2]$ **(1a)** (0.42 g, 0.87 mmol) in 50 mL of THF at −78 °C was added $Na_2[Fe(CO)_4]$ (0.19 g, 0.87 mmol in one portion). After one hour, the solution was allowed to warm up to room temperature. The solvent was then evaporated in vacuo. Subsequently, the brown residue was dissolved in 50 mL of hexane and filtered through a column of dry SiO_2 (10 cm × 2 cm). The solution was concentrated to 30 mL and red crystals of **2** (120 mg, 23%) were obtained at 0 °C. Further concentration of the solution to 10 mL gave a mixture of **2** and **3** (457 mg).

2: IR (KBr): ν̃(CO) = 2012(m), 1997(vs), 1985(s), 1961(m), 1942(m), 1932(m), 1925(m), 1911 (m), 1897(m), 1879(s). − ^{1}H NMR (C_7D_8, 300 K): δ = 1.05 (s, 9 H), 1.10 (s, 9 H), 4.10 (dd, J = 1.9 Hz, 1 H) 5.17 (dd, J = 1.9 Hz, 1 H), 5.53 (dd, J = 1.9 Hz, 1 H); 368 K: 1.10 (s, 9 H), 4.20 (br, 1 H) 5.13 (br, 1 H), 5.30 (br, 1 H). − $C_{57}H_{63}Fe_7O_{18}Sb_3$ (1792.30): calcd. C 38.20, H 3.54; found C 37.94, H 3.23.

Synthesis of $[\{\mu_4$-$SbFe(CO)_2Cp^*\}_2\{Co_4(CO)_{10}(\mu$-$CO)\}]$ ($Cp^* = \eta^5$-C_5Me_5) (4): To a solution of $[\{Cp^*(CO)_2Fe\}SbCl_2]$ **(1b)** (0.44 g, 1 mmol) in 50 mL of THF at −78 °C was added $K[Co(CO)_4]$ (0.42 g, 2 mmol) at one go. After 1 h of stirring at this temperature the solution was allowed to warm up to room temperature. After another hour of stirring at room temperature all volatiles were evaporated in vacuo. The brown residue was dissolved in 20 mL of CH_2Cl_2 and subsequently filtered through a column of dry SiO_2 (10 cm × 2 cm). The resulting solution was reduced in vacuo to 10 mL. At 0 °C red crystals of **4** were obtained. Isolated yield: 860 mg (67%, based on **1b**). After reducing the solution to a volume of 2 mL 50 mg of $[Cp^*(CO)Fe(\mu$-$CO)_2Co(CO)_3]$ **(5)** was isolated.

4: IR (KBr): ν̃(CO) = 2004(vs), 1971(s), 1949(sh), 1779(m). − ^{1}H NMR ($CDCl_3$, 300 K): δ = 1.90 (s, 15 H). − EI-MS (70 eV): *m/z* (%) = 1281.6 (1.4) [M^+], 494.1 (10.6) [$Cp^*_2Fe_2(CO)_4^+$], 341.0 (3.3)

Table 1. Crystallographic Data for 2−4

	2	**3**	**4**
empirical formula	$C_{57}H_{63}Fe_7O_{18}Sb_3$	$C_{39}H_{42}Fe_5O_{13}Sb_2$	$C_{35}H_{30}Co_4Fe_2O_{15}Sb_2$
M_r	1792.27	1241.48	1281.51
T [K]	200(1)	200(1)	200(1)
Crystal size	0.30 × 0.20 × 0.16	0.20 × 0.08 × 0.01	0.10 × 0.10 × 0.02
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Crystal system	monoclinic	triclinic	triclinic
a [Å]	10.319(2)	9.6577(19)	10.928(2)
b [Å]	26.876(5)	9.793(2)	14.194(2)
c [Å]	26.411(5)	27.484(6)	15.792(3)
α [°]	92.67(3)	82.57(3)	67.62(3)
β [°]	90	80.45(3)	73.45(3)
γ [°]	90	63.76(3)	69.31(3)
V [Å^{-3}]	7316(3)	2294.8(8)	2086.7(7)
Z	4	2	2
d_c [g cm^{-3}]	1.627	1.797	2.040
μ_c [mm^{-1}]	2.491	2.753	3.562
2θ range [°]	4.24 ≤ 2θ ≤ 51.68	4.52 ≤ 2θ ≤ 51.82	3.56 ≤ 2θ ≤ 51.68
hkl range	−11 ≤ *h* ≤ 12	−11 ≤ *h* ≤ 11	−13 ≤ *h* ≤ 8
	−33 ≤ *k* ≤ 32	−11 ≤ *k* ≤ 11	−17 ≤ *k* ≤ 17
	−30 ≤ *l* ≤ 29	−33 ≤ *l* ≤ 30	−19 ≤ *l* ≤ 17
Data/restraints/parameters	48806/0/784	16159/0/544	8128/0/283
No. of unique data	13250 (R_{int} = 0.0986)	8252 (R_{int} = 0.1204)	6059 (R_{int} = 0.1721)
Independent reflections [$I > 2\sigma(I)$]	9503	3820	2100
Goodness-of fit on F^2	1.047	0.771	0.781
R_1,[a] wR_2[b] [$I > 2\ \sigma(I)$]	0.0609, 0.1537	0.0540, 0.0909	0.0835, 0.1828
R_1,[a] wR_2 [b] [all data]	0.0849, 0.1667	0.1356, 0.1110	0.2006, 0.2311
Largest diff. peak/hole [e·Å^{-3}]	1.059, −0.637	0.805, −1.273	1.174, −1.817

[a] $R = |F_0| - |F_c||/|F_0|$. − [b] $wR_2 = [\omega(F_0^2 - F_c^2)^2]/[(F_0^2)^2]^{1/2}$.

$[Co_2(CO)_8^+]$, 134.1 (100) $[Cp^{*+}]$. – $C_{35}H_{30}Co_4Fe_2O_{15}Sb_2$ (1281.54): calcd. C 32.80, H 2.36; found C 32.09, H 2.44.

X-ray Structure Determination and Details of Refinement: Data were collected on a STOE IPDS area-detector diffractometer using Mo-K_α (λ = 0.71069 Å) radiation. Machine parameters, crystal data and data collection parameters are summarised in Table 1. The structures were solved by direct methods using SHELXS-86,[24a] full-matrix least-squares refinement on F^2 in SHELXL-97[24b] with anisotropic displacement for non-H atoms (**2** and **3**), hydrogen atoms placed in idealised positions and refined isotropically according to the riding model. Due to the low crystal quality of **4**, only the heavy atoms Fe, Co and Sb were anisotropically refined, which causes relatively large values for R_1 and wR_2.

Crystal Data for [Cp*(CO)Fe(μ-CO)$_2$Co(CO)$_3$] (5): Cell dimensions: a = 8.1836(16) Å, b = 9.1759(18) Å, c = 12.139(2) Å, α = 90.51(3)°, β = 90.67(3)°, γ = 110.50(3)°, V = 853.7(3) Å^3, Z = 2, $d_{calcd.}$ = 1.626 g cm^{-3}, μ = 1.848 mm^{-1}, space group $P\bar{1}$, 6655 reflection collected, of which 3082 independent (R_{int} = 0.0389), 2656 with $I > 2\sigma(I)$. $R1$ = 0.0289, $wR2$ = 0.0789, max./min. residual electron densities 0.455 and −0.496 e Å^{-3}.

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-143869 to -143871 (**2**–**4**) and CCDC-143985 for **5**. 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].

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