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Synthesis and structure of the novel mixed Sb/Se and Sb/Te containing iron carbonyl clusters $[Fe_3(\mu_3\text{-}Y)(\mu_3\text{-}SbMes)(CO)_9]$ $(Y = Se, Te)$ and $[Fe_3(\mu_3,\eta^2{:}\eta^1\text{-}SeSbMes)(\mu_3\text{-}SbMes)(CO)_{10}]$

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Abstract

The reaction between the cluster dianion $[Fe_3(\mu_3\text{-}Y)(CO)_9]^{2-}$ (**1**) (Y = Se (**a**), Te (**b**)) and $MesSbBr_2$ leads to the formation of $[Fe_3(\mu_3\text{-}Y)(\mu_3\text{-}SbMes)(CO)_9]$ (**2a**,**b**) (Mes = 2,4,6-$Me_3C_6H_2$). The molecular structures of both compounds were established by single crystal X-ray diffraction and reveals *nido* cluster cores containing square pyramidal FeSbFeY units capped by a third Fe carbonyl fragment as an apical vertex. The novel compound $[Fe_3(\mu_3,\eta^2{:}\eta^1\text{-}SeSbMes)(\mu_3\text{-}SbMes)(CO)_{10}]$ (**3**) was obtained by a similar reaction via slightly modified reaction conditions. This molecule contains a $Fe(CO)_4$ and a $Fe_2(CO)_6$ fragment, respectively, which are connected by a μ_3-SbMes and a novel $\mu_3,\eta^2{:}\eta^1$-SeSbMes ligand. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Cluster; Carbonyl complexes; Iron; Antimony; Selenium; Tellurium

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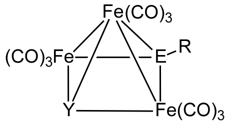
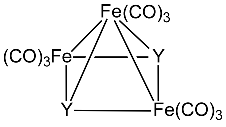
1. Introduction

Chemistry of heteronuclear transition metal clusters with incorporated main group elements is a highly attractive area owing to their relationship to a number of areas ranging from bioinorganic chemistry of metalloenzymes to synthesis of functional solid state materials with well-defined composition and stoichiometry [1]. To a large extent, that causes an unflagging interest in the development of appealing general synthetic routes to a large variety of such cluster systems, particularly of compounds with new combinations of different main group elements.

In the course of a systematic investigation of the reactivity of cluster dianions $[Fe_3(\mu_3\text{-}Y)(CO)_9]^{2-}$ (Y = Se, Te) and their protonated derivatives we have found that reaction of $[Fe_3(\mu_3\text{-}Se)(CO)_9]^{2-}$ (**1a**) with CH_3AsI_2 results in good yields ($\approx 60\%$) of $[Fe_3(\mu_3\text{-}Se)(\mu_3\text{-}AsCH_3)(CO)_9]$ corresponding to the structural type **A** [2]. That makes the latter compound a convenient object for further research, particularly for comparison of chemistry of mixed Group 15/16 type **A** clusters with their well-known type **B** analogues (Y = Group 16 element or RE, where E = Group 15 element). Our preliminary investigations have shown that in some cases the chemistry can be quite different [3].



A



B

Presently, transition metal clusters with incorporated Group 15/16 elements are primarily represented by the light Group 15 elements as the Y/N, Y/P and Y/As combinations [4], and only two structurally characterized complexes with Sb/Se and Sb/Te combinations are known; $[PPh_4][Fe_2(CO)_4\{\mu,\eta^3\text{-}SbSe_2(Se_2)\}]$ [5] and $[NEt_4][Cu_4(\mu_3,\eta^3\text{-}Te_7)(\mu_3,\eta^3\text{-}SbTe_5)]$ [6], both containing antimony polychalcogenides as ligands.

To prepare new examples of clusters with Sb/Se and Sb/Te combinations a reaction of $[Et_4N]_2[Fe_3(\mu_3\text{-}Y)(CO)_9]$ (Y = Se (**1a**), Te (**1b**)) with $MesSbBr_2$ was

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investigated in the present work. For heavy Group 15 elements a priori one could expect two possible results: formation of type **A** clusters—as observed for CH_3AsI_2—or compounds with a direct Sb–Y bond—if an Sb containing electrophile attacks the Y atom. We have found that both variants are possible. The type **A** clusters $[Fe_3(\mu_3\text{-}Y)(\mu_3\text{-}SbMes)(CO)_9]$ (Y = Se (**2a**), Te (**2b**)) were obtained in high yields, and for Y = Se the modification of the reaction conditions results in a compound containing a Se–Sb bond: $[Fe_3(\mu_3,\eta^2{:}\eta^1\text{-}SeSbMes)(\mu_3\text{-}SbMes)(CO)_{10}]$ (**3**).

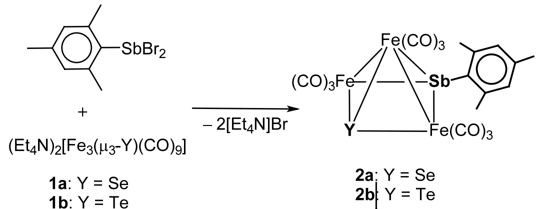
2. Results and discussion

2.1. Synthesis

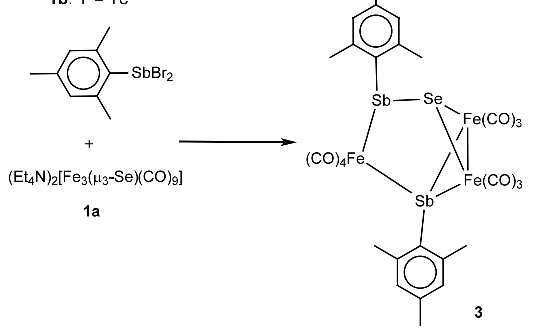
The reaction depicted in Eq. (1) can be formally described as the result of nucleophile–electrophile interaction of $[Fe_3(\mu_3\text{-}Y)(CO)_9]^{2-}$ and $[RSb]^{2+}$ species. In principle such consideration gives opportunity to choose more or less optimal reaction conditions following our general knowledge of this type of reaction. Thus, for example, to obtain $[Fe_3(\mu_3\text{-}Y)(\mu_3\text{-}SbMes)(CO)_9]$ (Y = Se (**2a**), Te (**2b**)) as major products of the reaction of $MesSbBr_2$ with **1a** or **1b**, respectively, the following circumstances have to be considered: (i) in principle, $[Fe_3(\mu_3\text{-}Y)(CO)_9]^{2-}$ and $MesSbBr_2$ cannot react exclusively via metathesis reaction but also via a redox process; (ii) only a stoichiometric 1:1 reaction of $[Fe_3(\mu_3\text{-}Y)(CO)_9]^{2-}$ with $MesSbBr_2$ results in the desired compounds, but 1:2 or 2:1 reaction can take place too if one of the reagents is in excess. Both redox and non-stoichiometric reactions have to be minimized in this case.

Reaction (1) was carried out via dropwise addition of a THF solution of $MesSbBr_2$ to a slurry of **1a** or **1b**, respectively, in THF at −60 °C. The low temperature conditions were primarily used to minimize redox processes. The solvent and the order of addition of reagents were chosen to minimize reactions which are different from the 1:1 nucleophile–electrophile procedure: if the reactions do proceed in solution, dropwise addition of $MesSbBr_2$ to slurries [7] of **1a** and **1b**, respectively, decreases the probability that more than two reacting particles interact with each other due to their low concentration. Via this procedure the novel complexes **2a** and **2b** were obtained in reproducible good yields.

Attempts to modify the reaction conditions to increase the yields of the products were unsuccessful, but in one case, Eq. (2), we succeeded in the isolation of a novel and structurally interesting compound $[Fe_3(\mu_3,\eta^2{:}\eta^1\text{-}SeSbMes)(\mu_3\text{-}SbMes)(CO)_{10}]$ (**3**). Here, **2a** was only detected in trace amounts by TLC [8].



(1)



(2)

The neutral compound **3** contains two MesSb moieties without any Br atoms; therefore, this cluster results from a complex reaction including probably both metathesis and redox processes. This product was obtained when a solid mixture of **1a**, $MesSbBr_2$ and THF, cooled by liquid nitrogen, was allowed to warm up to room temperature with stirring. Probably, in this case the reaction starts when the first drops of THF are melting and well-soluble $MesSbBr_2$ is formed in an extremely concentrated solution [9]. This provides a 2:1 reaction between $MesSbBr_2$ and **1a** which probably leads to an unknown intermediate, which is subsequently reduced by iron carbonyl species, e.g. **1a**. Moreover, it cannot be excluded that the reduction proceeds at elevated temperature during the isolation procedure. Unfortunately, it was neither possible to isolate an intermediate nor to obtain **3** in higher yield. But indirect evidence for the proposed reaction pathway lies in the fact that the same result was obtained when a few drops of THF were added to a solid consisting of **1a** and $MesSbBr_2$ at −60 °C, and this reaction mixture was worked up as described in the Section 4.

2.2. Molecular structures of **2a, 2b** and **3**

The molecular structures of **2a** and **2b** are depicted in Figs. 1 and 2, respectively. Selected bond lengths and angles are listed in Table 1. The cluster cores of **2a** and **2b** can be described as distorted square pyramids with a slightly distorted FeSbFeY base and are, therefore, examples representing a type **A** core. In this case the Y and Sb atoms are four-electron donors, hence the compounds **2a** and **2b** possess 50 valence electrons typical for *nido* cluster cores (14 skeletal electrons) without a third Fe–Fe bond between the atoms Fe_1 and Fe_3. In both products the FeSbFeY planes are

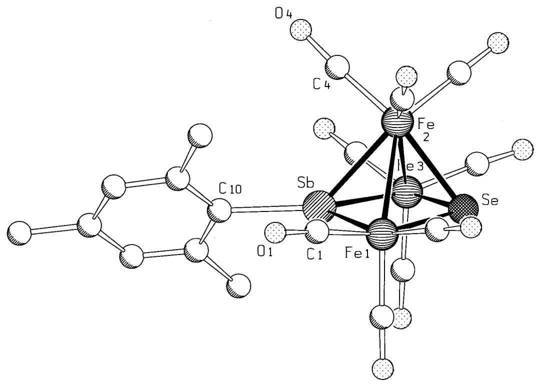


Fig. 1. Molecular structure of [$Fe_3(\mu_3$-Se)(μ_3-SbMes)$(CO)_9$] (**2a**) in the crystal and selected atom labeling scheme (hydrogen atoms are omitted for clarity).

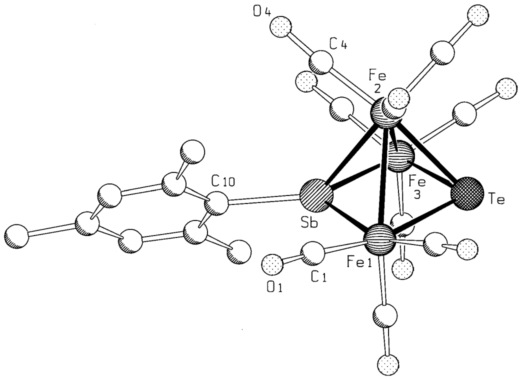


Fig. 2. Molecular structure of [$Fe_3(\mu_3$-Te)(μ_3-SbMes)$(CO)_9$] (**2b**) in the crystal and selected atom labeling scheme (hydrogen atoms are omitted for clarity).

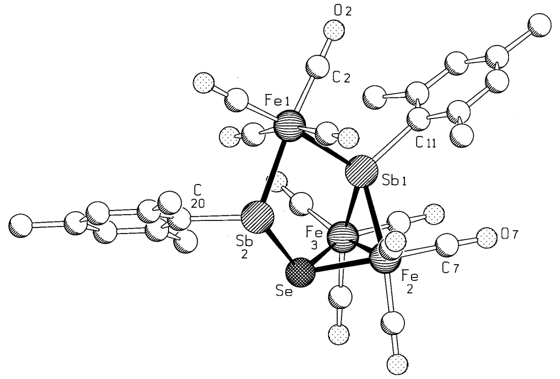


Fig. 3. Molecular structure of [$Fe_3(\mu_3,\eta^2{:}\eta^1$-SeSbMes)($\mu_3$-SbMes)$(CO)_{10}$] (**3**) in the crystal and selected atom labeling scheme (hydrogen atoms are omitted for clarity).

Table 1
Selected bond lengths (Å) for [$Fe_3(\mu_3$-Y)(μ_3-SbMes)$(CO)_9$] **2a** and **2b**

	2a (Y = Se)	**2b** (Y = Te)
Y–Fe_1	2.3906(10)	2.5466(9)
Y–Fe_2	2.3567(9)	2.5171(7)
Y–Fe_3	2.3976(10)	2.5563(8)
Sb–C_{10}	2.130(4)	2.135(3)
Sb–Fe_1	2.4638(8)	2.4637(7)
Sb–Fe_2	2.5521(9)	2.5324(8)
Sb–Fe_3	2.4714(9)	2.4653(9)
Fe_1–C_1	1.790(5)	1.787(4)
Fe_1–Fe_2	2.7685(10)	2.8210(9)
Fe_2–C_4	1.779(5)	1.778(4)
Fe2–Fe3	2.7278(11)	2.7573(10)
C_1–O_1	1.133(6)	1.129(5)
C_4–O_4	1.145(7)	1.137(5)
$Fe_1\cdots Fe_3$	3.745	3.836

slightly bent along the $Fe_1\cdots Fe_3$ axis leading to a folding angle of 7.9° in **2a** and 5.8° in **2b**, respectively.

The molecular structure of **3** is depicted in Fig. 3; selected bond lengths and angles are listed in Table 2. In complex **3**, the $Fe(CO)_4$ and the $Fe_2(CO)_6$ fragments are connected by a μ_3-SbMes ligand as well as by an unusual $\mu_3,\eta^2{:}\eta^1$-SeSbMes moiety. The Se atom of the SeSbMes ligand occupies a bridging position on the Fe_2–Fe_3 edge. The atom Sb_2 has an almost tetrahedral coordination polyhedron (c.f. angles in Table 2). Thus, all three Se–Sb_2, Fe_1–Sb_2 and C_{20}–Sb_2 bonds have to be described as ordinary, regardless of the lengthened Se–Sb_2 bond in **3**, which is with 2.6005(6) Å longer than Se–Sb bonds found e.g. in [PPh_4][$Fe_2(CO)_4\{\mu,\eta^3$-$SbSe_2(Se_2)\}$] (**4**) (2.520–2.549 Å) [5]. The latter fact is probably a result of the steric influence of the mesityl group in **3**. Additionally, counting MesSb as a four-electron donor and MesSbSe also as a four-electron donor, all Fe containing fragments fulfill the EAN rule. In an isoelectronic point of view the novel MesSbSe fragment can be considered as a heavy element analogue of

Table 2
Selected bond lengths (Å) and angles (°) for [$Fe_3(\mu_3,\eta^2{:}\eta^1$-SeSb-Mes)($\mu_3$-SbMes)$(CO)_{10}$] (**3**)

Bond lengths	
Sb_1–C_{11}	2.146(2)
Sb_1–Fe_1	2.6512(7)
Sb_1–Fe_2	2.5207(11)
Sb_1–Fe_3	2.5235(8)
Sb_2–C_{20}	2.175(3)
Sb_2–Se	2.6005(6)
Sb_2–Fe_1	2.7046(12)
Se–Fe_2	2.3847(8)
Se–Fe_3	2.3625(10)
Fe_1–C_2	1.829(3)
Fe_2–C_7	1.778(3)
Fe_2–Fe_3	2.6478(8)
C_2–O_2	1.124(4)
C_7–O_7	1.140(3)
$Fe_1\cdots Fe_2$	4.491
$Fe_1\cdots Fe_3$	4.502
Bond angles	
C_{20}–Sb_2–Se	105.03(7)
C_{20}–Sb_2–Fe_1	106.03(7)
Se–Sb_2–Fe_1	103.97(4)

thionitrosoaryls or—alkyls, RNS, which can coordinate in a similar mode to three or four metals [10]. Furthermore, the novel RSbSe ligand in **3** is the first example for the heavier Group 15 homologues, which are up to now only known for RPS ligands [11].

3. Conclusions

The results have shown that the reaction of the chalcogenide iron cluster anions $[Fe_3(\mu_3\text{-}Y)(CO)_9]^{2-}$ (**1**) (Y = Se, Te) containing a Fe_3Y tetrahedral core with electrophilic organic derivatives of Group 15 element halides represents an efficient way to novel clusters incorporating heavier Group 16 and 15 elements. Even thought that the isolated yield of complex **3** is low, however, its formation justifies further detailed investigations of this general reaction concept. It is anticipated that by tuning the reaction conditions this synthetic concept may allow the controlled preparation of clusters with direct bonds between different main group elements to generate novel types of mixed main group element ligands.

4. Experimental

4.1. General procedures

All manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. All solvents were dried by common methods and freshly destined prior to use. The compounds **1a** and **1b** were prepared according to the described procedure [12]. The IR spectra were recorded on a Bruker IFS28 spectrometer. The NMR spectra were recorded on a Bruker AC 250 (^{1}H: 250.133 MHz) and AMX 300 (^{77}Se: 57.236 MHz and ^{125}Te: 94.696 MHz). Mass spectra were measured on a MAT 711 spectrometer (electron impact, 70 eV).

4.2. Synthesis of $[Fe_3(\mu_3\text{-}Y)(\mu_3\text{-}SbMes)(CO)_9]$ (Y = Se (**2a**), Te (**2b**))

A solution of $MesSbBr_2$ (0.30 mmol, 0.120 g) in 10 ml of THF was slowly added to a slurry of **1a** (**1b**) (0.30 mmol) in 10 ml of THF at −60 °C. The mixture was allowed to warm up and after 1 h stirring at room temperature (r.t.) was filtered. Evaporation of the solution resulted in a dark brown solid, which was dissolved in a few ml of CH_2Cl_2 and mixed with 3 ml of silca gel. A powder obtained by drying of the mixture in vacuum was transferred to a chromatography column (2 × 20 cm) containing silica gel and chromatographed: Fraction 1 (hexane–toluene, 1/1), dark brown band: **2a** (**2b**). Dark brown crystals of **2a** (**2b**) were obtained by slow diffusion of hexane into the toluene solution at 8 °C. Yields: **2a** −0.104 g (47%), **2b** −0.125 g (53%). Fraction 2 (CH_2Cl_2), black–brown broad band; compound decomposes during the isolation process.

4.2.1. Compound **2a**

Found: C, 30.1; H, 2.01. Calc. for $C_{18}H_{11}Fe_3O_9SbSe$: C, 29.2; H, 1.50%. IR (hexane, ν_{CO}, cm^{-1}): 2073 w; 2043 s; 2022 s; 2004 w, sh; 1999 m; 1994 w; 1986 w, sh; 1962 vw. ^{1}H-NMR (CD_2Cl_2, δ, ppm, TMS): 2.30 (3H, p-CH_3); 2.56 (6H, o-CH_3); 7.03 (2H, m-H). ^{77}Se-NMR (CD_2Cl_2, δ, ppm, Me_2Se): 634.1. MS (EI, m/z): 740 (13) [M^+]; 712 (46) [M^+ −CO]; 684 (2) [M^+ −2CO]; 656 (12) [M^+ −3CO]; 628 (29) [M^+ −4CO]; 600 (2) [M^+ −5CO]; 572 (58) [M^+ −6CO]; 544 (35) [M^+ −7CO]; 516 (58) [M^+ −8CO]; 488 (100) [M^+ −9CO]; 369 (38) [Fe_3SbSe].

4.2.2. Compound **2b**

Found: C, 28.3; H, 2.06. Calc. for $C_{18}H_{11}Fe_3O_9SbTe$: C, 27.4; H, 1.41%. IR (hexane, ν_{CO}, cm^{-1}): 2067 w; 2047 w; 2038 s; 2027 w; 2016 s; 2007 w; 1996 m; 1989 w; 1983 w, sh; 1961 vw. ^{1}H-NMR (CD_2Cl_2, δ, ppm, TMS): 2.31 (3H, p-CH_3); 2.62 (6H, o-CH_3); 7.06 (2H, m-H). ^{125}Te-NMR (CD_2Cl_2, δ, ppm, Me_2Te): 751.9. MS (EI, m/z): 790 (20) [M^+]; 762 (22) [M^+ −CO]; 734 (5) [M^+ −2CO]; 706 (15) [M^+ −3CO]; 678 (29) [M^+ −4CO]; 650 (4) [M^+ −5CO]; 622 (65) [M^+ −6CO]; 594 (28) [M^+ −7CO]; 566 (60) [M^+ −8CO]; 538 (100) [M^+ −9CO]; 419 (25) [Fe_3SbTe].

4.3. Synthesis of $[Fe_3(\mu_3,\eta^2:\eta^1\text{-}SeSbMes)(\mu_3\text{-}SbMes)(CO)_{10}]$ (**3**)

THF (25 ml) was condensed onto the mixture of solid **1a** (1.782 g, 2.35 mmol) and $MesSbBr_2$ (0.941 g, 2.35 mmol) cooled by liquid nitrogen. The mixture was slowly allowed to warm up and after 1 h stirring at r.t. was filtered. The dark brown, viscous solution was evaporated to dryness in vacuum without heating. The residue was washed with octane at 50–70 °C and then extracted with toluene (100 ml) at 50–70 °C. The toluene extract was kept at 0 °C and filtered to remove a fine amorphous solid. The filtrate was evaporated to dryness and the residue was dissolved in CH_2Cl_2 (5 ml). Octane (25 ml) was layered onto the CH_2Cl_2 solution. Keeping this mixture at 0 °C resulted in some additional portion of the amorphous solid and few large dark brown crystals (2 mg, 0.2%) of **3** which were manually separated under a microscope. By TLC only traces of **2a** have been detected. Since **3** decomposes on the TLC plate the actual yield of **3** is not completely known.

Compound **3**: MS (EI, m/z): 1008 (13) [M^+], 980 (14) [M^+ −CO], 924 (26) [M^+ −3CO], 889 (100) [M^+ −C_9H_{11}], 868 (38) [M^+ −5CO].

Table 3
Crystallographic data for **2a**,**b** and **3**

	2a	**2b**	**3**
Empirical formula	$C_{18}H_{11}Fe_3O_9SbSe$	$C_{18}H_{11}Fe_3O_9SbTe$	$C_{28}H_{22}Fe_3O_{10}Sb_2Se$
Formula weight	739.53	788.17	1008.47
Temperature (K)	203(2)	203(2)	203(2)
λ (Ag–K_α)	0.56087	0.56087	0.56087
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a (Å)	8.7760 (17)	8.7210(17)	11.000(2)
b (Å)	9.0100(18)	9.0910(18)	11.609(2)
c (Å)	29.650(6)	29.507(6)	14.037(3)
α (°)	90	90	93.45(3)
β (°)	97.10(3)	96.98(3)	112.39(3)
γ (°)	90	90	90.13(3)
V (Å^3)	2326.5(8)	2322.1(8)	1653.7(6)
Z	4	4	2
μ (mm^{-1})	2.411	2.237	2.131
D_{calc} (g cm^{-3})	2.111	2.255	2.025
F(000)	1416	1488	968
θ Range (°)	2.62 25.84	2.56 25.96	2.07 25.90
Index ranges	$-12 \le h \le 12$, $-14 \le k \le 9$, $-45 \le l \le 45$	$-13 \le h \le 12$, $-12 \le k \le 14$, $-45 \le l \le 32$	$-17 \le h \le 17$, $-18 \le k \le 17$, $-21 \le l \le 20$
R_{int}	0.0845	0.0301	0.0286
Reflections measured	21917	14258	25693
Independent reflections	8191	8779	12084
Parameters	292	292	403
Goodness-of-fit on F^2	1.049	1.044	1.018
Reflections with $I > 2\sigma(I)$	6037	6943	9566
Final R_1, wR_2 ($I > 2\sigma(I)$)	0.0504, 0.1226	0.0386, 0.0912	0.0299, 0.0700
R indices (all data)	0.0755, 0.1402	0.0548, 0.1024	0.0443, 0.0758
Largest difference peak and hole (e Å^{-3})	1.669, −1.077	0.951, −1.068	0.642, −0.622

5. X-ray crystal structure determinations of complexes 2a, 2b and 3

Single crystals of the compounds **2a**, **2b** and **3** were mounted at low temperature in inert oil on a glass fiber. Data were collected on a STOE IPDS diffractometer at 203(2) K using Ag–K_α radiation ($\lambda = 0.56087$). The structures were solved by direct methods using the SHELXS-97 computer program [13] and refined on F^2 by full-matrix least-squares (SHELXL-97) [14]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in calculated positions and were refined with an overall isotropic temperature factor using a riding model. Crystallographic data are given in Table 3.

6. Supplementary material

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-183878–183880 for the compounds **2a**, **2b** and **3**. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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[7] Complexes **1a** and **1b** are poorly soluble in THF, therefore, the slurries of **1a** and **1b** in THF are actually a mixture of a solid and a saturated solution.

[8] Several attempts to separate other products from this reaction mixture besides of **3** and **2a** failed due to the decomposition of these compounds, inclusive **3**, even at TLC plates in a glove box.

[9] Attempts to carry out a reaction of $MesSbBr_2$ and the well soluble $K_2[Fe_3(\mu_3\text{-}Se)(CO)_9]$ in THF in a 2:1 stoichiometry at moderate concentrations of reagents leads only to the isolation of **2a** in high yields (80%). A corresponding Te containing analogue of **3** was not detected when the reaction of **1b** with $MesSbBr_2$ was carried out under similar conditions as shown in Eq. (2). **2b** in trace amounts is the only soluble and, therefore, by NMR detectable product in this case.

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