

Reactions of $[\text{Fe}_3(\mu_3\text{-Q})(\text{CO})_9]^{2-}$ (Q = Se, Te) with organic and organometallic dihalides of group 15 elements – an approach to functionalised clusters

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A number of novel *nido*-clusters of the type $[\text{Fe}_3(\mu_3\text{-SbR})(\mu_3\text{-Q})(\text{CO})_9]$ containing the heavier group 16 elements (Q = Se, Te) and Sb as group 15 element with attached functional groups (R = Cp*, $(\eta^5\text{-C}_5\text{H}_4\text{tBu})\text{Fe}(\text{CO})_2$) have been obtained by the reaction of $\text{K}_2[\text{Fe}_3(\mu_3\text{-Q})(\text{CO})_9]$ (Q = Se, Te) with RSbX_2 (X = Br, I). Furthermore, a first cluster $[\text{Fe}_3(\mu_3\text{-BiFe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_4\text{tBu}))(\mu_3\text{-Se})(\text{CO})_9]$ containing a Bi/Se combination has also been synthesised in a similar manner. The novel complexes were comprehensively characterised by various spectroscopic methods as well as by single crystal X-ray diffraction methods.

Introduction

Heteronuclear transition metal clusters with incorporated main group elements are interesting as precursors and molecular models of catalysts and functional solid state materials with well-defined composition and stoichiometry.¹ Thereupon compounds with different main group element combinations cause a particular interest, and development of convenient synthetic routes to such systems is desirable. Moreover, from the point of view of creation of materials and catalysts the synthetic routes must be supplemented by appealing approaches to the construction of larger aggregates (nano-sized giant clusters, inorganic polymers and supramolecular compounds) from the cluster building blocks and/or to supporting these species on a solid surface.

In this aspect, the idea of synthesising cluster complexes to which specific functional groups that can be used for the above mentioned purposes are attached, seems very fruitful. The most convenient means for its realisation are clusters with incorporated main group elements. Fortunately, their potential possibility of broad composition variation is supplemented by their high synthetic potential determined by the following roles which the main group elements play:

- a matrix for assembling a polynuclear cluster core;
- a stabilising component of the cluster core;
- a unit for further functionalisation of the cluster.

Our previous studies were mostly focused on the first two points,² as illustrated in Scheme 1: (a) a tetrahedral Fe_3Q core can be assembled using Q^{2-} as a matrix, (b) Q-atom-stabilised

clusters such as $[\text{Fe}_3(\mu_3\text{-Q})(\text{CO})_9]^{2-}$ (Q = Se (**1a**), Te (**1b**)) serve as entire building blocks for producing larger clusters incorporating both group 16 and group 15 elements. The reaction between $[\text{Fe}_3(\mu_3\text{-Q})(\text{CO})_9]^{2-}$ and CH_3AsI_2 or MesSbBr_2 (Mes = 2,4,6-Me₃C₆H₂) resembles an electrophilic addition in which an RE^{2+} moiety adds onto the initial cluster anions (Scheme 1).^{2e,3}

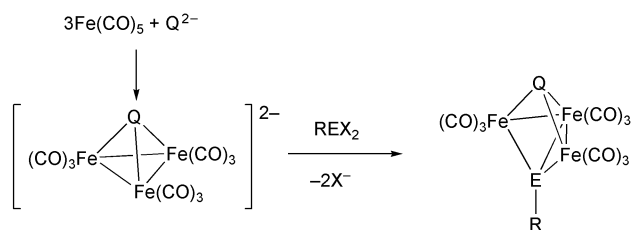
In this way the *nido* clusters containing mixed main group elements can be obtained in a relatively high yield (ca. 60%) and the reaction can be easily monitored.³ This allows one to propose it as a convenient route to a broad series of analogous *nido* clusters with different combinations of the main group elements. At the same time use of REX_2 with functionalised R-groups allows the creation of cluster complexes with attached functional groups.

Herein is presented the successful preparation of Cp* and Fp' (Cp* = $\eta^5\text{-C}_5\text{Me}_5$, Fp' = $(\eta^5\text{-C}_5\text{H}_4\text{tBu})\text{Fe}(\text{CO})_2$) substituted compounds containing both Sb and Q atoms: $[\text{Fe}_3(\mu_3\text{-SbCp}^*)(\mu_3\text{-Q})(\text{CO})_9]$ (Q = Se (**2a**), Te (**2b**)) and $[\text{Fe}_3(\mu_3\text{-SbFp}')(\mu_3\text{-Q})(\text{CO})_9]$ (Q = Se (**3a**), Te (**3b**)). The composition and the structure of the compounds lead us to expect further interesting reactivity patterns. Cp* is well-known as a reactive functional group which undergoes migration reactions thus causing different kinds of cluster core transformations.⁴ Moreover, Fp' is a typical example of a metal-containing functional group and, in principle, the use of analogous derivatives of other transition metals⁵ opens an opportunity for the preparation of various heterometallic clusters. Furthermore, reaction of **1** with $\text{Fp}'\text{BiCl}_2$ was successfully used for the preparation of $[\text{Fe}_3(\mu_3\text{-BiFp}')(\mu_3\text{-Se})(\text{CO})_9]$ (**4a**), which is the first example of a transition metal cluster containing a Bi/Se combination.⁶

Experimental

General

All manipulations were carried out under pre-purified nitrogen. All solvents were distilled from appropriate drying agents. The IR spectra were recorded on a Bruker IFS28 spectrometer. The NMR spectra were recorded on Bruker AC 250 (¹H: 250.133 MHz and ¹³C: 62.896 MHz) and AMX 300 (⁷⁷Se: 57.236 MHz and ¹²⁵Te: 94.696 MHz) spectrometers. Mass spectra were



Q = Se, Te; $\text{REX}_2 = \text{CH}_3\text{AsI}_2, \text{MesSbBr}_2$

Scheme 1

measured on a MAT 711 spectrometer (EI, 70 eV). The starting cluster compounds $K_2[Fe_3Q(CO)_9]$ ($K_2[1a]$, $Q = Se$ and $K_2[1b]$, $Q = Te$) were prepared by deprotonation of the corresponding $[H_2Fe_3Q(CO)_9]^-$ with KH. Cp^*SbBr_2 ,⁸ $Fp'SbI_2$ and $Fp'BiCl_2$ were prepared by the methods used previously for the synthesis of Cp^*SbCl_2 ,⁹ $CpFe(CO)_2SbI_2$ ¹⁰ and $CpFe(CO)_2BiCl_2$ ¹¹, respectively.

Synthesis of $[Fe_3(\mu_3-SbCp^*)(\mu_3-Q)(CO)_9]$ ($Q = Se$ (**2a**), Te (**2b**))

A solution of Cp^*SbBr_2 (0.3 mmol, 0.125 g) in 10 ml of CH_2Cl_2 was slowly added to a slurry of $K_2[Fe_3Q(CO)_9]$ (0.3 mmol; $K_2[1a]$: 0.173 g; $K_2[1b]$: 0.188 g) in 10 ml CH_2Cl_2 at $-60^\circ C$. After that the cooling bath was removed and the red–brown solution was allowed to reach room temperature. After 1 h of stirring at room temperature the dark red–brown solution was filtered from the brown precipitate and evaporated to dryness. The black solid thus obtained was extracted with hexane (2 \times 30 ml). The hexane extract contained almost pure **2a** or **2b**, respectively (TLC check, eluent hexane–toluene in different ratios). Crystalline **2a** (**2b**) was obtained by keeping the solution at $-24^\circ C$ overnight. Yield: **2a** 0.156 g (69%), **2b** 0.150 g (62%).

Compound 2a. Found (%): C, 29.9; H, 2.09. Calc. for $C_{19}H_{15}Fe_3O_9SbSe$ (%): C, 30.2; H, 2.00. IR (hexane, ν_{CO} , cm^{-1}): 2069 m; 2057 vw; 2040 vs; 2017 vs; 1997 m, sh; 1994 s; 1990 m, sh; 1979 m; 1959 w. 1H NMR (CD_2Cl_2 , δ , ppm, TMS): 1.88 (15H, CH_3). ^{13}C NMR (CD_2Cl_2 , δ , ppm, TMS): 12.3 (CH_3); 125.3 (C_5 ring); 207.6 (3CO); 213.6 (6CO). MS (EI, m/z): 756 (M^+); 621 ($[Fe_3SbSe(CO)_9]^+$); 593 ($[Fe_3SbSe(CO)_8]^+$); 565 ($[Fe_3SbSe(CO)_7]^+$); 537 ($[Fe_3SbSe(CO)_6]^+$); 369 ($[Fe_3SbSe]^+$).

Compound 2b. Found (%): C, 28.7; H, 2.04. Calc. for $C_{19}H_{15}Fe_3O_9SbTe$ (%): C, 28.4; H, 1.88. IR (hexane, ν_{CO} , cm^{-1}): 2063 m; 2035 s; 2013 s; 1990 s; 1977 m; 1957 w. 1H NMR (CD_2Cl_2 , δ , ppm, TMS): 1.93 (15H, CH_3). ^{13}C NMR (CD_2Cl_2 , δ , ppm, TMS): 12.3 (CH_3); 125.7 (C_5 ring); 208.9 (3CO); 214.7 (6CO). MS (EI, m/z): 806 (M^+); 671 ($[Fe_3SbTe(CO)_9]^+$); 643 ($[Fe_3SbTe(CO)_8]^+$); 615 ($[Fe_3SbTe(CO)_7]^+$); 587 ($[Fe_3SbTe(CO)_6]^+$); 419 ($[Fe_3SbTe]^+$).

Synthesis of $[Fe_3(\mu_3-SbFp')(\mu_3-Q)(CO)_9]$ ($Q = Se$ (**3a**), Te (**3b**))

A solution of $Fp'SbI_2$ (0.35 mmol, 0.213 g) in 10 ml of CH_2Cl_2 was slowly added to a slurry of $K_2[Fe_3Q(CO)_9]$ (0.35 mmol; $K_2[1a]$: 0.202 g; $K_2[1b]$: 0.219 g) in 10 ml of CH_2Cl_2 at $-60^\circ C$. After addition the cooling bath was removed and the brown–black mixture was allowed to reach room temperature. After 1 h of stirring at room temperature the solution was separated from the brown precipitate by filtration. The filtrate contained almost pure **3a** or **3b**, respectively (TLC check, eluent hexane–toluene in different ratios). The crude solid product obtained by evaporation of the solution was covered with 25 ml of hexane. A gradual addition of toluene (15 ml) to that mixture under ultrasonic agitation results in complete dissolution of the solid. Crystalline **3a** (**3b**) was obtained by keeping the solution at $-24^\circ C$ overnight. Yield: **3a** 0.240 g (78%), **3b** 0.255 g (93%).

Compound 3a. Found (%): C, 28.6; H, 1.63. Calc. for $C_{20}H_{13}Fe_4O_{11}SbSe$ (%): C, 28.1; H, 1.54. IR (CH_2Cl_2 , ν_{CO} , cm^{-1}): 2063 m; 2030 vs; 2008 s; 1978 m. 1H NMR (CD_2Cl_2 , δ , ppm, TMS): 1.27 (9H, CH_3); 5.07 (centre of multiplet, 4H, CH). ^{13}C NMR (CD_2Cl_2 , δ , ppm, TMS): 31.3, 83.1, 83.7 and 120.0 (Cp'); 208.7 (6CO); 210.7 (2CO); 213.7 (3CO). MS (EI, m/z): 854 (M^+); 826 (M^+-CO); 798 (M^+-2CO); 770 (M^+-3CO); 742 (M^+-4CO); 714 (M^+-5CO); 686 (M^+-6CO); 658 (M^+-7CO); 630 (M^+-8CO); 602 (M^+-9CO); 574 (M^+-10CO); 546 (M^+-11CO).

Compound 3b. Found (%): C, 27.0; H, 1.61. Calc. for $C_{20}H_{13}Fe_4O_{11}SbTe$ (%): C, 26.6; H, 1.45. IR (CH_2Cl_2 , ν_{CO} , cm^{-1}): 2059

m; 2025 vs; 2003 s; 1973 m. 1H NMR (CD_2Cl_2 , δ , ppm, TMS): 1.29 (9H, CH_3); 5.12 (centre of multiplet, 4H, CH). ^{13}C NMR (CD_2Cl_2 , δ , ppm, TMS): 31.3, 83.5, 83.7 120.1 (Cp'); 210.3 (6CO); 210.9 (2CO); 215.0 (3CO). MS (EI, m/z): 806 (M^+); 671 ($[Fe_3SbTe(CO)_9]^+$); 643 ($[Fe_3SbTe(CO)_8]^+$); 615 ($[Fe_3SbTe(CO)_7]^+$); 587 ($[Fe_3SbTe(CO)_6]^+$); 419 ($[Fe_3SbTe]^+$).

Synthesis of $[Fe_3(\mu_3-Fp'Bi)(\mu_3-Se)(CO)_9]$ (**4a**)

Solid $Fp'BiCl_2$ (0.350 mmol, 0.180 g) was added to a vigorously stirred slurry of $K_2[1a]$ (0.202 g, 0.350 mmol) in 10 ml of CH_2Cl_2 at $-60^\circ C$. 15 minutes later the mixture was allowed to warm up to room temperature. Subsequent 1 h stirring followed by filtration of the reaction mixture resulted in a brown–black solution containing almost pure **4a** (TLC check, eluent hexane–toluene in different ratios). Isolation of the product was carried out as described in the previous procedure, but larger amounts of solvents were used (50 ml of hexane and 30 ml of toluene). The compound **4a** crystallises as a **4a**·0.5(toluene) solvate. Yield of the solvate: 0.211 g (64%).

4a·0.5(toluene). Found (%): C, 28.5; H, 1.82. Calc. for $C_{23.5}H_{17}BiFe_4O_{11}Se$ (%): C, 28.6; H, 1.74. IR (CH_2Cl_2 , ν_{CO} , cm^{-1}): 2061 m; 2028 vs; 2005 s; 1971 m. 1H NMR (CD_2Cl_2 , δ , ppm, TMS): 1.21 (9H, CH_3); 5.07 (centre of multiplet, 4H, CH). ^{13}C NMR (CD_2Cl_2 , δ , ppm, TMS)*: 31.3, 83.3, 83.6 and 118.6 (Cp'); 209.0 (2CO); 209.6 (6CO); 212.4 (3CO). MS (EI, m/z): 942 (M^+); 914 (M^+-CO); 858 (M^+-3CO); 802 (M^+-5CO); 774 (M^+-6CO); 746 (M^+-7CO); 718 (M^+-8CO); 690 (M^+-9CO); 662 (M^+-10CO); 634 (M^+-11CO).

X-Ray crystal structure determination **2b**, **3a**, **3b**, **4a**

Crystallographic data and details of diffraction measurements are given in Table 1. Data were collected on a STOE IPDS diffractometer, except for **3b** for which a STOE STADI4 was used. The structures were solved by direct methods using the SHELXS-97 program^{12a} and refined by full-matrix least-squares method on F^2 using the SHELXL-97 program.^{12b} All non-hydrogen atoms were refined anisotropically (except those of the solvent molecule in **4a**).

CCDC reference numbers 196896–196899.

See <http://www.rsc.org/suppdata/dt/b2/b210839a/> for crystallographic data in CIF or other electronic format.

Results and discussion

Synthesis

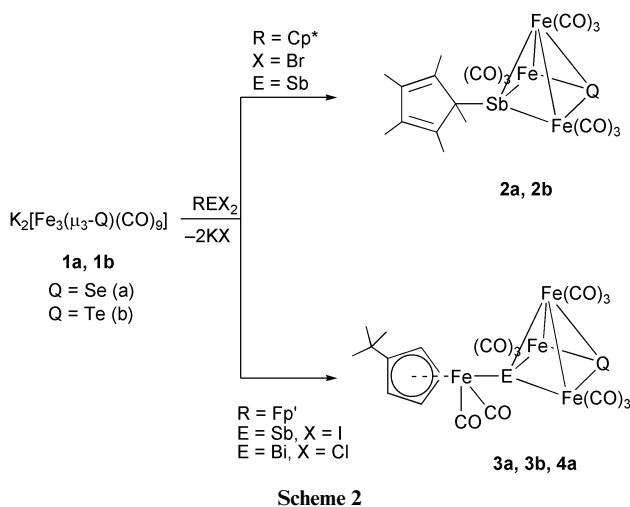
To prepare the compounds **2a**, **2b**, **3a**, **3b** and **4a** the reaction of $K_2[Fe_3(\mu_3-Q)(CO)_9]$ ($K_2[1a]$ or $K_2[1b]$) with the corresponding REX_2 has been performed (Scheme 2).

The use of the potassium salts of the starting cluster anions has significant advantages in comparison to the tetraethylammonium salts which we used in previous investigations.^{2e,3} For instance, the reactions of $[Et_4N]_2[1a]$ or $[Et_4N]_2[1b]$ with $MesSbBr_2$ in THF lead to $[Fe_3(\mu_3-SbMes)(\mu_3-Q)(CO)_9]$ in good yields ($\approx 50\%$), but the final reaction mixture contains several by-products with solubilities similar to that of $[Fe_3(\mu_3-SbMes)(\mu_3-Q)(CO)_9]$.³ To isolate the desired clusters chromatographic separation is necessary, which decreases the yields of the products. With the corresponding potassium salts the reactions proceed much more smoothly and the resulting CH_2Cl_2 solutions contain almost only the desired clusters. Thus, the use of the potassium salt $K_2[1a]$ was essential for the successful preparation of the Bi-containing cluster **4a**, which was obtained in 64% yield, whereas by using $[Et_4N]_2[1a]$ the synthesis failed. Unfortunately an analogous Bi/Te compound **4b** was not

* Signals for toluene are not reported.

Table 1 Crystallographic data for compounds **2b**, **3a**, **3b** and **4a**·0.5(toluene)

	2b	3a	3b	4a ·0.5C ₇ H ₈
Formula	C ₁₉ H ₁₅ Fe ₃ O ₉ SbTe	C ₂₀ H ₁₃ Fe ₄ O ₁₁ SbSe	C ₂₀ H ₁₃ Fe ₄ O ₁₁ SbTe	C _{23.5} H ₁₇ BiFe ₄ O ₁₁ Se
<i>M</i>	804.21	853.41	902.05	986.71
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>Pbcn</i>
<i>a</i> /Å	9.872(2)	9.819(2)	9.0904(18)	28.682(6)
<i>b</i> /Å	36.208(7)	18.667(5)	16.776(3)	11.118(2)
<i>c</i> /Å	14.072(3)	14.502(3)	17.831(4)	18.514(4)
β /°	102.73(3)	93.85(2)	103.56(3)	90
<i>V</i> /Å ³	4906.2(17)	2652.2(10)	2643.3(9)	5904(2)
<i>Z</i>	8	4	4	4
<i>D_s</i> /g cm ⁻³	2.178	2.137	2.267	2.220
<i>T</i> /K	200(1)	203(1)	200(1)	200(2)
Radiation	MoK α , λ = 0.71073 Å	MoK α , λ = 0.71073 Å	MoK α , λ = 0.71073 Å	MoK α , λ = 0.71073 Å
μ /mm ⁻¹	4.039	4.568	4.288	9.148
Diffractometer	STOE IPDS	STOE STADI4	STOE IPDS	STOE IPDS
Crystal size/mm	0.30 × 0.20 × 0.10	0.04 × 0.20 × 0.52	0.40 × 0.20 × 0.05	0.20 × 0.15 × 0.05
Total/unique refls.	27303/9214	7322/7068	10723/4030	14580/4625
<i>R</i> _{int}	0.0427	0.0241	0.0387	0.0533
Data/Parameters	9214/605	7068/335	4030/337	4625/361
<i>R</i> ₁ for <i>F</i> _{hkl} ≥ 4σ(<i>F</i>)	0.0324	0.0344	0.0249	0.0339
<i>wR</i> ₂ for all refls.	0.0851	0.0802	0.0633	0.0818
Goof for all refls.	0.937	1.134	0.966	0.917



obtained, even using this method. This reaction mixture shows at low temperature, by TLC control, a compound behaving in a manner similar to that of **4a**, but all attempts to isolate **4b** at ambient temperatures were unsuccessful.

The structure of compounds **2b**, **3a**, **3b** and **4a** were determined by single crystal X-ray diffraction. The compounds were further characterised by different spectroscopic methods (¹H, ¹³C and ⁷⁷Se or ¹²⁵Te NMR, EI mass and IR) and C, H-analysis. These methods were also used for the identification of **2a**, which shows an appropriate molecular ion peak and similar NMR data to those of the structurally characterised complex **2b**. Furthermore, the ¹H spectra of **2a** and **2b** reveal only one signal for the CH₃ protons of the η¹-bound Cp* group indicating a fluxional behaviour in solution. The corresponding ¹³C NMR spectra contain the signals expected for the CH₃ groups and for the carbon atoms of the C₅ ring, and two signals for the two non-equivalent groups of CO ligands. Based on these data a structure similar to that of **2b** can be suggested for **2a**.

The comparison of ⁷⁷Se and ¹²⁵Te NMR data of the [Fe₃(μ₃-ER)(μ₃-Q)(CO)₉] clusters is shown in Table 2 and reveals that selenium and tellurium chemical shifts are quite sensitive to the change of organic substituent bound to the Sb atom (compare Mes- and Cp*-substituted compounds). Approximately the same order of chemical shift change, but in the opposite direction, is observed for substitution of Sb with Bi (**3a** and **4a**).

Molecular structures of **2b**, **3a**, **3b** and **4a**

The complex **2b** crystallises in the monoclinic space group *P*2₁/*c* with two independent molecules, which differ only slightly in their bond distances and angles from each other. They differ only in the orientation of the Cp* moiety towards the cluster framework. In both molecules the Cp* rings are connected to the Sb atoms in a η¹ manner, but they are rotated around the C–Sb bond. The molecular structure of **2b** is depicted in Fig. 1. The molecular structure of **4a** is presented in Fig. 2. The structures of **3a** and **3b** are very similar to that of **4a** and have

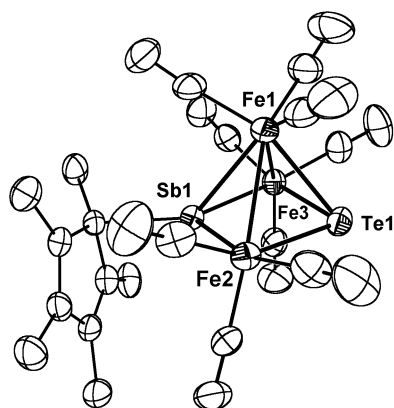


Fig. 1 Molecular structure of **2b** at 50% probability level with partial labeling scheme. H atoms are omitted for clarity.

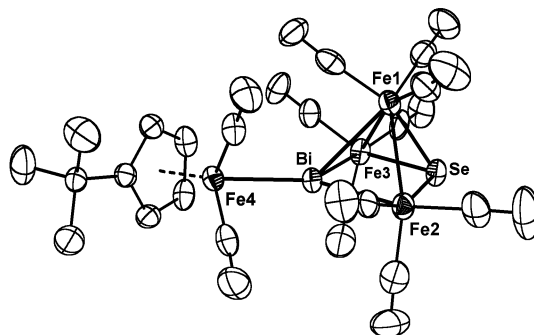


Fig. 2 Molecular structure of **4a** at 50% probability level with partial labeling scheme. H atoms are omitted for clarity.

Table 2 ^{77}Se and ^{125}Te NMR data for $[\text{Fe}_3(\mu_3\text{-ER})(\mu_3\text{-Q})(\text{CO})_9]$ clusters^a

$[\text{Fe}_3\text{Se}(\text{SbMes})(\text{CO})_9]^3$	634.1	$[\text{Fe}_3\text{Te}(\text{SbMes})(\text{CO})_9]^3$	751.9
$[\text{Fe}_3\text{Se}(\text{SbCp}^*)(\text{CO})_9]$ (2a)	540.7	$[\text{Fe}_3\text{Te}(\text{SbCp}^*)(\text{CO})_9]$ (2b)	593.2
$\text{Fe}_3\text{Se}(\text{SbFp}^*)(\text{CO})_9$ (3a)	676.8	$[\text{Fe}_3\text{Te}(\text{SbFp}^*)(\text{CO})_9]$ (3b)	823.5
$\text{Fe}_3\text{Se}(\text{BiFp}^*)(\text{CO})_9$ (4a)	792.6	—	—

^a CD_2Cl_2 , δ , ppm, referred to Me_2Se and Me_2Te respectively.

Table 3 Selected bond lengths, $\text{E} \cdots \text{Q}$ distances [\AA] and angles [$^\circ$] for compounds **2b**,^a **3a**, **3b**, **4a**

	2b Q = Te, E = Sb	3a Q = Se, E = Sb	3b Q = Te, E = Sb	4a Q = Se, E = Bi
Fe1–Fe2	2.7561(10)	2.7328(10)	2.7706(8)	2.7297(16)
Fe1–Fe3	2.7709(10)	2.7309(10)	2.7946(8)	2.7125(15)
Fe1–Q	2.5115(10)	2.3465(8)	2.5278(8)	2.3438(14)
Fe2–Q	2.5735(8)	2.3673(7)	2.5612(7)	2.3905(14)
Fe3–Q	2.5563(8)	2.3760(7)	2.5458(7)	2.3832(14)
Fe1–E	2.5912(9)	2.5737(8)	2.5555(8)	2.7128(11)
Fe2–E	2.4641(8)	2.4948(7)	2.5063(7)	2.5762(12)
Fe3–E	2.4677(8)	2.4947(7)	2.5012(6)	2.5970(12)
Fe4–E	—	2.5050(8)	2.5224(10)	2.6181(11)
$\text{E} \cdots \text{Q}$	3.1454(9)	3.121(1)	3.2764(11)	3.2418(9)
Q–Fe1–E	76.09(3)	78.59(3)	80.26(3)	79.38(4)
Q–Fe2–E	77.24(3)	79.82(2)	80.56(3)	81.40(4)
Q–Fe3–E	77.50(3)	79.66(2)	80.95(3)	81.10(4)
Fe2–E–Fe3	105.36(3)	96.61(3)	100.49(3)	93.37(3)
Fe2–Q–Fe3	99.74(3)	103.52(3)	97.84(3)	104.09(5)
Fe4–E–Fe1	—	132.44(2)	132.39(3)	126.29(4)
Fe4–E–Q	—	175.23(1)	173.396(14)	168.43(3)

^a The bond lengths and angles are given for one of two independent molecules. Corresponding parameters for the molecule B differ only slightly.

therefore been omitted. Selected bond lengths for all compounds with unified labelling are given in Table 3.

All molecules show the same topology of cluster framework: a distorted square pyramid with an almost planar FeEFeQ base (deviation of the atoms from the plane are for **2b**: 0.033 \AA (molecule A), 0.029 \AA (molecule B), **3b**: 0.032 \AA , **4a**: 0.032 \AA), which is slightly bent along the $\text{E} \cdots \text{Q}$ axis (folding angle for **2b**: 175.1 $^\circ$ (molecule A), 175.8 $^\circ$ (molecule B), **3a**: 175.0 $^\circ$, **3b**: 175.4 $^\circ$, **4a**: 179.0 $^\circ$). The complexes can be described as typical *nido* clusters containing 50 valence electrons. Cp^* in **2b** and Fp' in the other compounds play a role of terminal substituent attached to the corresponding group 15 element.

It should be mentioned that the distances between E and Q atoms in **2b**, **3a**, **3b**† and **4a** (Table 3) are less than the sums of the Van-der-Waals radii of the corresponding elements [4.00 \AA (Sb/Se), 4.40 \AA (Sb/Te), 4.40 \AA (Bi/Se)]. The distances differ only slightly from each other, which shows that they are determined rather by the requirements of the quite rigid cluster core than by E–Q bonding interactions. However, the latter should not be excluded, because the distances are comparable with E–Se bond lengths for compounds in which the Se-donor ligand $[\text{CH}_3\text{C}(\text{CH}_2\text{SeCH}_3)_3]$ is coordinated to Sb(III) or Bi(III) halides (3.187 and 3.157 \AA , respectively).¹³ Probably, for the analogous Bi/Te cluster, the requirements of the cluster framework geometry result in too short a Bi–Te contact, which can lead to a strong interaction between the elements followed by elimination of some inorganic bismuth tellurides or related materials. That might be the reason for the failure to obtain experimentally the Te/Bi complex (**4b**) by the reaction of **1b** with $[\text{Fp}'\text{BiCl}_2]$.

Some interesting features of the crystal packing of **3b** and **4a** were found. In **3b** the oxygen atom of one of the CO groups connected with Fe1 has a rather short contact with the same atom of the neighbouring cluster molecule. The $\text{O} \cdots \text{O}'$ distance (2.766(4)) is slightly less than the sum of Van-der-Waals radii of two oxygen atoms (2.80 \AA). Complex **4a** crystallises as a

solvate with toluene in a 2 : 1 ratio. The toluene molecules, which are disordered in two positions, form single layers lying between double layers of the cluster molecules (Fig. 3).

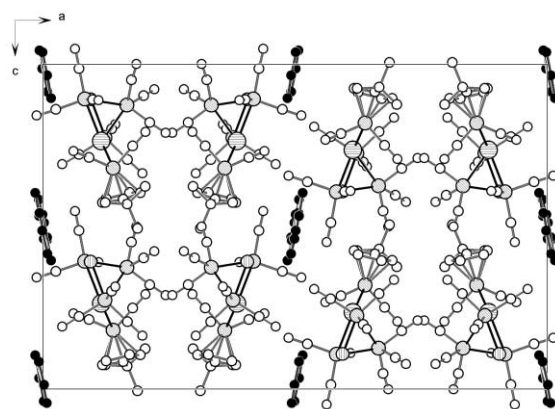


Fig. 3 Crystal packing of **4a**·0.5(toluene). Carbon atoms of disordered toluene molecules are shown as black balls. H atoms are omitted for clarity.

Conclusion

The results presented show that the reaction of $[\text{Fe}_3\text{Q}(\text{CO})_9]^{2-}$ with REX_2 serves as a convenient approach to a variety of cluster complexes, containing different group 15/16 element combinations as well as different functional substituents at the corresponding pnictide atoms. Further functionalisation of these substituents will open up a broad variety of possibilities for cluster aggregation as well as for the introduction of different reactive moieties.

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† Corresponding distances in $[\text{Fe}_3\text{Q}(\text{SbMes})(\text{CO})_9]$ have similar values: 3.226 \AA (Q = Te) and 3.091 \AA (Q = Se).³

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