ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2009, Vol. 35, No. 2, pp. 112–119. © Pleiades Publishing, Ltd., 2009.
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Heterometallic Heterochalcogenmethylarsenide Clusters: Synthesis, Molecular Structures, and Thermolysis

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Received August 5, 2008

Abstract—Reactions of the arsinechalcogenide complexes $[Fe_3(\mu_3\text{-}X)(\mu_3\text{-}AsCH_3)(CO)_9]$ (X = Se (**Ia**) or Te (**Ib**)) with $(PPh_3)_2Pt(PhC{\equiv}CPh)$ (transmetalation reaction) and $Cp_2Cr_2(SCMe_3)_2S$ (Cp = $\pi\text{-}C_5H_5$) (photochemical reaction) gave the heterometallic (heterochalcogen)(methylarsine) clusters $[(PPh_3)_2Pt(\mu_3\text{-}X)(\mu_3\text{-}AsCH_3)Fe_2(CO)_6]$ (**II** and **III**, respectively), as well as $Fe_3(\mu_3\text{-}X)(\mu_3\text{-}AsCH_3)(CO)_8(C_5H_5)_2Cr_2(\mu_3\text{-}S)(\mu_2\text{-}S^tBu)_2$ (**IV** and **V**, respectively). The structures of complexes **II, IV**, and **V** were determined by X-ray diffraction analysis. Thermolysis of all the complexes yielded no metal carbides or oxides.

DOI: 10.1134/S1070328409020055

The chemistry of organometallic clusters makes it possible to assemble atoms of dissimilar transition and main-group elements into a molecule. The atoms make up the molecule's framework and are surrounded by organic groups that easily eliminate during thermolysis. This allows targeted synthesis of nanosized particles of inorganic materials with the desired complex compositions, which otherwise are often inaccessible.

For instance, we have shown earlier that the platinum-iron-chalcogenide clusters $L_2Pt(\mu_3\text{-}X)_2Fe_2(CO)_6$ (L is cyclooctadiene (COD) or dicyclopentadiene (DCPD); X = S, Se, or Te) are the precursors of methanol-tolerant catalysts for oxygen reduction in methanol–air fuel cells [1, 2]. These clusters have been obtained by transmetalation of $Fe_3S_2(CO)_9$ with $LPtCl_2$ or by nucleophilic substitution of $(DCPD)PtCl_2$ for the halide anions in $[Fe_2S_2(CO)_6]^{2-}$ [3].

On the other hand, photochemical reactions of $Fe_3X_2(CO)_9$ with dichromium chalcogenide complexes $Cp_2Cr_2(XR)_2X$ (X = S, Se, or Te; R = CMe_3 or Ph) afforded not only heterometallic clusters (e.g., spirans $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S_2)Fe_3(\mu_3\text{-}S_2)(CO)_6$ [4]) but also heterochalcogenides (e.g. $(MeCp)_2Cr_2(\mu_3\text{-}SPh)_2(\mu_3\text{-}Se)Fe_3(\mu_3\text{-}Se_2)(CO)_8$ [5]).

It was interesting to obtain, by using analogous reactions, platinum or dichromium chalcogenide derivatives of the arsine(chalcogen)iron cluster $Fe_3(\mu_3\text{-}AsCH_3)(\mu_3\text{-}X)(CO)_9$ [6].

EXPERIMENTAL

All manipulations dealing with the synthesis and isolation of complexes were carried out under pure argon in dehydrated solvents. The starting complexes $Fe_3(\mu_3\text{-}X)(\mu_3\text{-}AsCH_3)(CO)_9$ (X = Se (**Ia**) or Te (**Ib**)) [6], $(PPh_3)_2Pt(PhC{\equiv}CPh)$ [7], $(C_5H_5)_2Cr_2(\mu_2\text{-}S)(\mu_2\text{-}SCMe_3)_2$ [8], and $(PPh_3)Fe_3(\mu_3\text{-}Te)_2(CO)_8$ [9] were prepared according to known procedures.

IR spectra were recorded on a Specord 75IR spectrophotometer for KBr pellets and solutions in ether. Elemental analysis was performed on a Carlo Erba CHNS analyzer at the Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences.

X-ray diffraction analysis of $(PPh_3)_2Pt(\mu_3\text{-}X)(\mu_3\text{-}AsCH_3)Fe_2(CO)_6$ (**II**) and $Fe_3(\mu_3\text{-}X)(\mu_3\text{-}AsCH_3)(CO)_8(C_5H_5)_2Cr_2(\mu_3\text{-}S)(\mu_2\text{-}S^tBu)_2$ (X = Se (**IV**) and Te (**V**)) were carried out with MoK_α radiation. Absorption corrections were applied in a semiempirical way from equivalent reflections for structures **II** and **V** and from ψ-curves for structure **IV**. All three structures were solved by the direct method and refined by the least-squares method in the anisotropic full-matrix approximation on F^2_{hkl}. Hydrogen atoms were located geometrically and refined in the rider model.

Crystallographic parameters and a summary of data collection and refinement for structures **II**, **IV**, and **V** are given in Table 1. Selected distances are given in the captions to Figs. 1–3. All calculations were performed with the SHELXTL PLUS program package [10]. The

Table 1. Selected crystallographic parameters and a summary of data collection and refinement for structures **II**, **IV**, and **V**

Parameter	Value		
	II	IV	V
Empirical formula	$C_{43}H_{33}AsFe_2O_6PtP_2Se$	$C_{27}H_{31}AsCr_2Fe_3O_8S_3Se$	$C_{27}H_{31}AsCr_2Fe_3O_8S_3Te$
M	1005.13	1211.39	1096.85
Diffractometer	Bruker SMART APEX II CCD	Bruker SMART 1000 CCD	Syntex $P2_1$
Scan mode	ω	ω	θ/2θ
T, K	100	120	297
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
Z	2	2	4
a, Å	9.8756(8)	10.1835(5)	14.104(3)
b, Å	13.9746(10)	13.8764(6)	22.631(5)
c, Å	14.5485(11)	17.5874(8)	15.371(3)
α, deg	104.383(2)	95.726(5)	90.00
β, deg	93.484(2)	92.422(5)	109.73(3)
γ, deg	109.688(2)	110.734(5)	90.00
V, Å^3	1808.1(2)	2304.67(18)	4618.2(19)
ρ_{calcd}, g/cm^{-3}	1.846	1.746	1.578
μ, cm^{-1}	38.88	52.66	28.79
F(000)	996	1182	2164
$2\theta_{max}$, deg	58	58	52
Number of measured reflections	21552	25535	9299
Number of independent reflections (N_1)	9532	12133	8932
Number of reflections with $I > 2\sigma(I)$ (N_2)	8012	8795	2318
Number of parameters refined	413	522	431
R_1 (for N_2)	0.0245	0.0336	0.0484
wR_2 (for N_1)	0.0580	0.0610	0.1232
GOOF	1.015	1.039	0.992
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.631/–0.622	1.253/–1.175	0.428/–0.433

atomic coordinates and other parameters for structures **II**, **IV**, and **V** have been deposited with the Cambridge Crystallographic Data Collection (nos. 697 390 (**II**), 697 389 (**IV**), and 697 388 (**V**)); see http://www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of complex II. A suspension of complex **Ia** (0.098 g, 0.167 mmol) and $(PPh_3)_2Pt(PhC{\equiv}CPh)$ (0.15 g, 0.167 mmol) was stirred in CH_3CN (25 ml) at room temperature for 20 h. The solution was evaporated to dryness in a water aspirator vacuum. The residue was washed with light petroleum (25 ml) and extracted with CH_2Cl_2 (30 ml). Heptane (15 ml) was added and the solution was concentrated to half its volume. The red-orange crystalline product that formed after three days at –18°C was filtered off, washed with hexane, and dried *in vacuo*. The yield was 0.10 g (51% with respect to $(PPh_3)_2Pt(PhC{\equiv}CPh)$).

IR (KBr, cm^{-1}): 2020 vs, 1970 vs, 1940 s, 1920 m, 1420 m, 1080 m, 740 w, 680 s, 600 m, 580 m, 530 m, 520 m, 500 m, 490 w.

For $C_{43}H_{33}AsFe_2O_6PtP_2Se$		
anal. calcd. (%):	C, 44.21;	H, 2.85.
Found (%):	C, 45.53;	H, 3.30.

Single crystals were used for X-ray diffraction analysis.

Synthesis of $(PPh_3)_2Pt(\mu_3\text{-Te})(\mu_3\text{-AsCH}_3)Fe_2(CO)_6 \cdot CH_2Cl_2$ (III). An analogous synthesis from complex **Ib** (0.10 g, 0.167 mmol) and $(PPh_3)_2Pt(PhC{\equiv}CPh)$ (0.15 g, 0.167 mmol) gave a red-orange crystalline product as a solvate with CH_2Cl_2. The yield was 0.12 g (55% with respect to $(PPh_3)_2Pt(PhC{\equiv}CPh)$).

IR (KBr, cm^{-1}): 2020 vs, 1970 vs, 1940 s, 1920 m, 1420 m, 1080 m, 740 w, 680 s, 600 m, 580 m, 530 m, 520 m, 500 m, 490 w.

For $C_{44}H_{35}AsCl_2Fe_2O_6PtP_2Te$		
anal. calcd. (%):	C, 40.59;	H, 2.71.
Found (%):	C, 40.87;	H, 1.63.

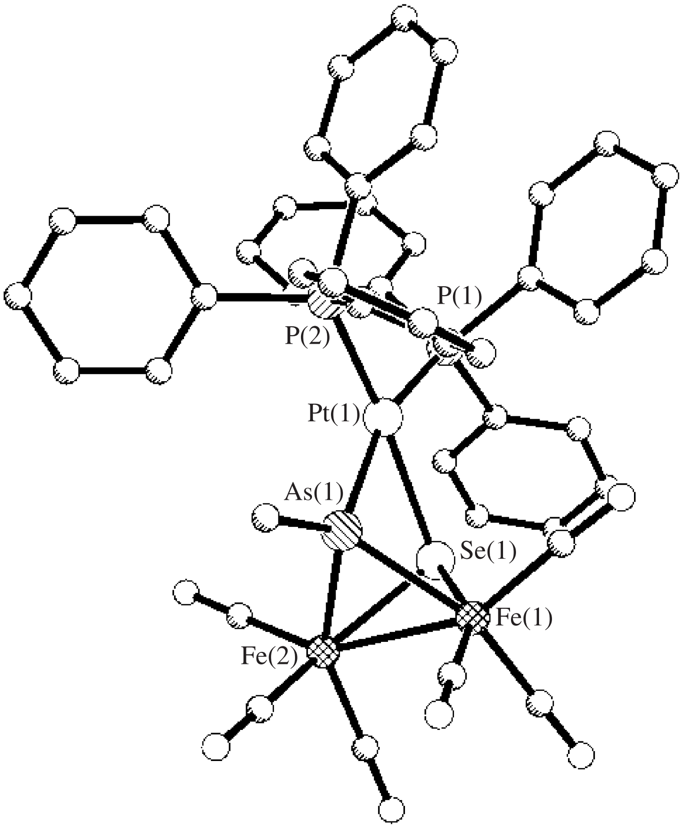


Fig. 1. Molecular structure of complex **II** in the crystal (hydrogen atoms are omitted). Selected bond lengths are Fe(1)–Fe(2) 2.599(1) Å, Fe(1)–Se(1) 2.426(1) Å, Fe(1)–As(1) 2.331(1) Å, As(1)–C 1.950(1) Å, As(1)–Pt(1) 2.414(2) Å, Pt(1)–Se(1) 2.491(1) Å, Pt(1)–P(2) 2.274(1) Å, and Pt(1)–P(2) 2.308(2) Å.

Synthesis of $(PPh_3)_2Pt(\mu_3\text{-}Te)_2Fe_2(CO)_6$. An analogous synthesis from $Fe_3Te_2(CO)_9$ (0.112 g, 0.167 mmol) and $(PPh_3)_2Pt(PhC{\equiv}CPh)$ (0.15 g, 0.167 mmol) produced a red-orange crystalline product. Recrystallization from CH_2Cl_2–hexane gave an orange needlelike precipitate. The yield was 0.11 g (52.5%). The IR spectrum of the complex is identical with the data cited in [11].

Synthesis of $Fe_3(\mu_3\text{-}Se)(\mu_3\text{-}AsCH_3)(CO)_8(\mu_3\text{-}S)Cr_2(C_5H_5)_2(\mu\text{-}S^tBu)_2$ (IV). A solution of complex **Ia** (0.15 g, 0.235 mmol) and $(C_5H_5)_2Cr_2(\mu\text{-}S)(\mu\text{-}S^tBu)_2$ (0.132 g, 0.296 mmol) in benzene (60 ml) was irradiated with UV light for 3.5 h, passed through a short column with silica gel, and concentrated to 10 ml. After heptane (15 ml) was added, the solution was concentrated to half its volume, kept at –18°C for a day, filtered, and concentrated to 2 ml. Dichloromethane (15 ml) was added and the solution was concentrated to 1/5 of its volume. Then heptane (15 ml) was added and the solution was concentrated to 1/5 of its volume. The black prisms that formed after four days were separated by decantation and dried *in vacuo*. The yield was 0.10 g (42% with respect to $Fe_3(\mu_3\text{-}Se)(\mu_3\text{-}AsCH_3)(CO)_9$).

IR (KBr, cm^{-1}): 2030 s, 1980 vs, 1960 vs, 1920 m, 1140 w, 800 w, 600 m, 590 m.

For $C_{27}H_{31}AsCr_2Fe_3O_8S_3Se$

anal. calcd. (%):	C, 32.26;	H, 3.11;	S, 9.57.
Found (%):	C, 32.29;	H, 2.70;	S, 9.75.

Single crystals were used for X-ray diffraction analysis.

Synthesis of $Fe_3(\mu_3\text{-}Te)(\mu_3\text{-}AsCH_3)(CO)_8(\mu_4\text{-}S)Cr_2(C_5H_5)_2(\mu\text{-}S^tBu)_2$ (V). An analogous synthesis from complex **Ib** (0.146 g, 0.229 mmol) and $(C_5H_5)_2Cr_2(\mu_2\text{-}S)\mu_2\text{-}S^tBu)_2$ (0.10 g, 0.224 mmol) gave complex **V** as black prisms. The yield was 0.06 g (25% with respect to $Cp_2Cr_2(\mu\text{-}S)(\mu\text{-}S^tBu)_2$).

IR (KBr, cm^{-1}): 2030 s, 1990 vs, 1960 vs, 1910 m, 1140 w, 800 w, 600 m, 590 m.

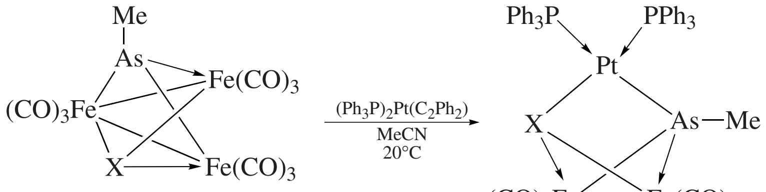
For $C_{27}H_{31}AsCr_2Fe_3O_8S_3Te$

anal. calcd. (%):	C, 30.77;	H, 2.97;	S, 9.13.
Found (%):	C, 30.51;	H, 2.50;	S, 8.85.

Single crystals for X-ray diffraction analysis were grown from benzene–hexane (1 : 1) as the solvate $\mathbf{V} \cdot C_6H_{14}$.

RESULTS AND DISCUSSION

Unlike dichalcogenide analogs, clusters **Ia** and **Ib** do not react with (DCPD)$PtCl_2$ in boiling THF in the presence of triethylamine. However, we found that they react with $(PPh_3)_2Pt(PhC{\equiv}CPh)$ in acetonitrile even at room temperature to give clusters **II** and **III**, which are isostructural with dichalcogenide analogs:



X = Se (**Ia**), Te (**Ib**) X = Se (**II**), Te (**III**)

Complexes **II** and **III** were isolated as red-orange crystals. They are stable in air and are soluble in THF, benzene, and CH_2Cl_2 but are poorly soluble in saturated hydrocarbons. According to X-ray diffraction data (Table 1, Fig. 1), the Pt atom in complex **II** has a square coordination with two P atoms (Pt–P 2.2741(10) and 2.3075(10) Å) and the bridges μ_3-Se and μ_3-$AsCH_3$ (Pt–Se 2.4912(4) Å, Pt–As 2.4138(4) Å), which are above and below the plane of the Pt and Fe atoms. The Fe–Fe bond is retained (Fe–Fe 2.5992(10) Å), but the Fe and Pt atoms are not bound to each other (Pt···Fe > 3.5 Å).

(Hexacarbonyl)(dichalcogenide)(diphosphine)diironplatinum clusters (e.g., $(PPh_3)_2Pt(\mu_3\text{-}S)_2Fe_2(CO)_6$) are structurally similar. They retain the Fe–Fe bond (2.504 Å) and the Pt atom is attached through two μ_3-sulfide bridges (Pt–S 2.305–2.334 Å). In these complexes, the square coordination typical of the Pt atom involves two ligands PPh_3 (Pt–P 2.311–2.348 Å) [11].

The absence of Pt–Fe bonds from such clusters is due to the repulsion between the CO group at each Fe atom and the phenyl groups at the P atoms [3]. If three CO groups at each Fe atom are replaced by two isoelectronic nitrosyl groups, the steric hindrances are eliminated and the cluster $(PPh_3)_2Pt(\mu_3\text{-}S)_2Fe_2(NO)_4$ contains the donor–acceptor bonds $Fe \longrightarrow Pt$ (2.8 Å) [12]. On the other hand, replacement of two triphenylphosphine molecules in the hexacarbonyl cluster by dicyclopentadiene, which has a larger cavity on the side of one CO group, allows the Fe atom bound to that carbonyl to approach the Pt atom as close as 3.0 Å [3].

Photochemical reactions of complexes **Ia** and **Ib** with $Cp_2Cr_2(\mu\text{-}S)(\mu\text{-}SCMe_3)_2$ give heterometallic heterochalcogenide methylarsine clusters **IV** and **V** resulting from replacement of only one CO group at the terminal Fe atom by a bridging S atom of the dichromium complex:

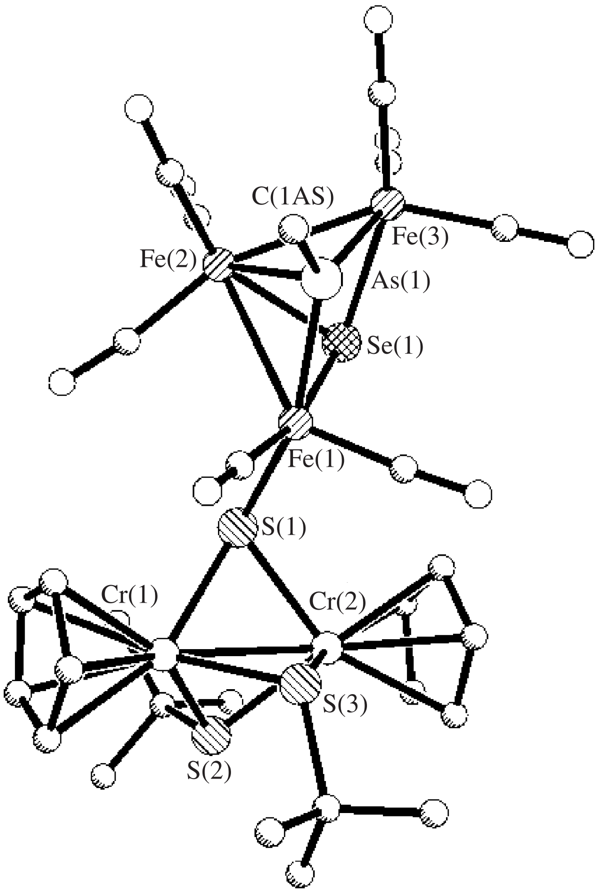
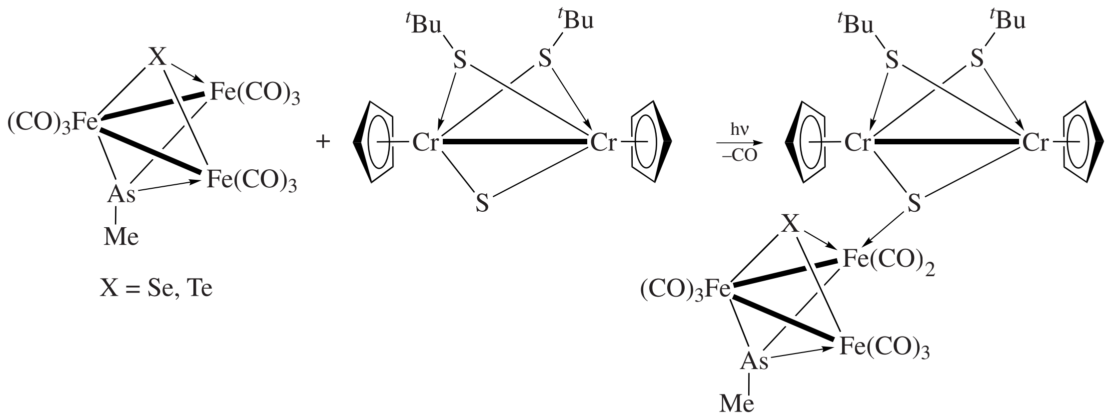


Fig. 2. Molecular structure of complex **IV** in the crystal (hydrogen atoms are omitted). Selected bond lengths are Cr(1)–Cr(2) 2.7004(4) Å, Cr(1)–S(1) 2.3200(6) Å, Cr(1)–S(2) 2.3594(6) Å, Cr(1)–S(3) 2.3502(6) Å, As(1)–C(1AS) 1.9481(19) Å, As(1)–Fe(1) 2.2568(4) Å, As(1)–Fe(3) 2.2947(4) Å, As(1)–Fe(2) 2.3541(4) Å, Se(1)–Fe(2) 2.3730(4) Å, Se(1)–Fe(1) 2.3978(4) Å, Se(1)–Fe(3) 2.4129(4) Å, Fe(1)–S(1) 2.3624(6) Å, Fe(1)–Fe(2) 2.7893(4) Å, and Fe(2)–Fe(3) 2.6655(4) Å.



X = Se (**Ia**), Te (**Ib**)

X = Se (**IV**), Te (**V**)

Clusters **IV** and **V** were isolated as black crystals. They are stable in air in the solid state but are unstable in solutions. The complexes are isostructural; their structure (**V**$\cdot$ C_6H_{14}) was determined by X-ray diffraction analysis (Table 1; Figs. 2, 3). The geometries of the triiron and dichromium fragments changes only slightly compared to the starting complexes **Ia** and **Ib** [6] and compared to $Cp_2Cr_2(\mu\text{-}S)(\mu\text{-}SCMe_3)_2$ [8]. The Cr–Cr bond lengthens insignificantly (from 2.689 to 2.7004(4) and 2.724(7) Å in complexes **IV** and **V**, respectively). However, the Cr–μ-S bond lengthens substantially (from 2.230 to 2.3200(6) and 2.313(21) Å, respectively) as the result of additional coordination of this bridge to the terminal Fe atom in the chain Fe_3 (S–Fe 2.3624(6) and 2.346(19) Å, respectively). Interestingly, this appreciably shortens the bond between this Fe atom and the methylarsine bridge (Fe(1)–As(1) 2.2568(4) and 2.255(7) Å, respectively) compared to the other two bonds (Fe(2)–As(1) 2.3541(4) and 2.358(20) Å, Fe(3)–As(1) 2.2947(4) and 2.299(20) Å, respectively), while the Fe–Se bonds in complex **IV** and the Fe–Te bonds in complex **V** differ only slightly

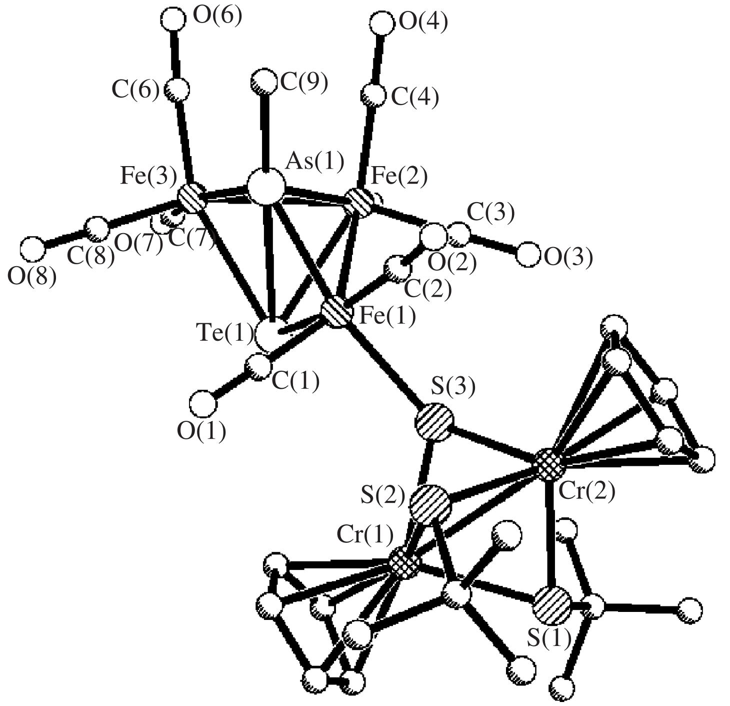
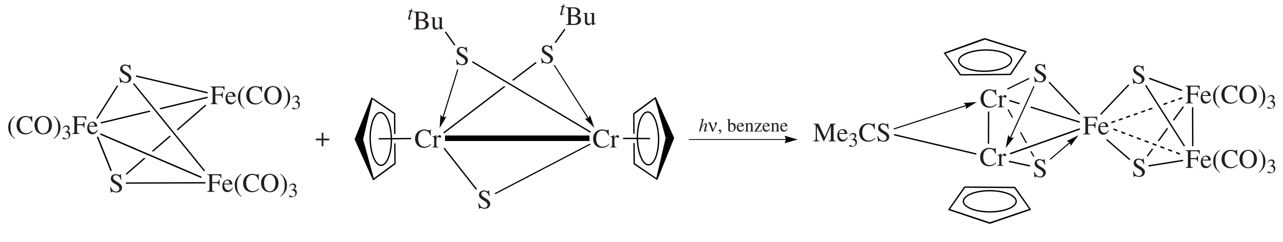


Fig. 3. Molecular structure of complex **V** in the crystal (hydrogen atoms and the solvate hexane molecule are omitted). Selected bond lengths are Cr(1)–Cr(2) 2.724(7) Å, Cr(1)–S(3) 2.313(21) Å, S(3)–Fe(1) 2.346(19) Å, Fe(1)–Fe(2) 2.838(54) Å, As(1)–C(9) 1.926(9) Å, Fe(1)–Te(1) 2.578(29) Å, Fe(1)–As(1) 2.255(7) Å, Fe(2)–As(1) 2.358(20) Å, and Fe(3)–As(1) 2.299(20) Å.

(2.3730(4)–2.4129(4) Å and 2.5494(16)–2.5771(17) Å). However, note that all the Fe–Se, Fe–Te, and Fe–As bonds in complexes **IV** and **V** are much shorter than the sums of the covalent radii of the elements (*r*(Fe) + *r*(Se) = 1.34 [12] + 1.17 [13] = 2.51 Å; *r*(Fe) + *r*(Te) = 1.34 + 1.37 [13] = 2.71 Å; *r*(Fe) + *r*(As) = 1.34 + 1.21 [14] = 2.55 Å). This is probably due to an additional dative interaction of the *d* electrons of iron with the vacant *d* orbitals of heavy main-group elements. In Fe–As bonding, the contribution from such an interaction is especially great for the Fe atom coordinated to the bridging S atom, which seems to be responsible for the greatest shortening of the Fe(1)–As(1) bonds.

Note that $Cp_2Cr_2(\mu\text{-}S)(\mu\text{-}SCMe_3)_2$ differently reacts with complexes **Ia** and **Ib** and with the earlier studied compound $Fe_3S_2(CO)_9$. In the latter reaction, one *tert*-butyl group eliminates from the S atom and three CO groups eliminate from one Fe atom to give a metal spiran [4].



This difference seemed strange because the earlier observed formation of an analog of clusters **IV** and **V** in a reaction of $(MeCp)_2Cr_2(\mu_3\text{-}SPh)_2(\mu_3\text{-}Se)$ with $Fe_3(\mu_3\text{-}Se_2)(CO)_9$ [5] could be easily explained by the larger Se bridge (compared to the S one) and by the more difficult cleavage of the S–Ph bond than the S–CMe_3 bond.

Apparently, the above difference is due to the fact that complexes **Ia** and **Ib** are more stable than dichalcogenide analogs. This was revealed in a DSC study of complexes **Ia** and **Ib** in an inert atmosphere. For instance, the earlier studied dichalcogenide clusters $Fe_3(\mu_3\text{-}X_2)(CO)_9$ (X = S, Se, and Te) undergo almost complete decarbonylation in the temperature range from 90 to 160°C [15]:

$$Fe_3S_2(CO)_9 \xrightarrow[-6CO]{110–138°C} Fe_3S_2(CO)_3 \xrightarrow[-2CO]{150–215°C} Fe_3S_2(C)(O),$$

$$Fe_3Se_2(CO)_9 \xrightarrow[-7CO]{90–150°C} Fe_3Se_2(CO)_3 \xrightarrow[-CO]{180–250°C} \xrightarrow[-CO]{180–250°C} Fe_3Se_2(C)(O),$$

$$Fe_3Te_2(CO)_9 \xrightarrow[-5CO]{110–160°C} Fe_3Te_2(CO)_3 \xrightarrow[-3CO]{150–210°C} \xrightarrow[-CO]{150–210°C} Fe_3Te_2(C)(O).$$

In contrast, thermolysis of complexes **Ia** and **Ib** does not begin below 150 and 160°C, the thermolysis is completed at 270 and 260°C without giving usual iron carbides and oxides; the methyl (or methylene) group is not detached from arsenic until CO eliminates completely:

$$Fe_3Se(AsMe)(CO)_9 \xrightarrow{150–270°C} Fe_3SeAs$$

(for weight loss, found: 44.8 ± 1.5%; calcd.: 45.4%),

$$Fe_3Te(AsMe)(CO)_9 \xrightarrow{160–260°C} Fe_3TeAs$$

(for weight loss, found: 41.9 ± 1.5%; calcd.: 41.9).

Unfortunately, the phase compositions of the samples were not determined because of their X-ray amorphous nature.

In [15], we have assumed that the formation of iron carbides and oxides is an electron-compensating process, when the electron deficiency arising during sequential decarbonylation is compensated by σ,π-coordination of the remaining CO groups with weakening and subsequent cleavage of the C–O bonds. The same occurs in the presence of π-ligands such as cyclooctadiene or dicyclopentadiene, which eliminate before CO groups; because of this, thermolysis of the clusters $LPt(\mu_3\text{-}X)_2Fe_2(CO)_6$ (X = S, Se, or Te; L = COD or DCPD) gives the compositions $PtX_2Fe_2(C)_2(O)_2$ [15]. However, if a complex contains firmly bound ligands (e.g., cyclopentadienyl), then they keep on compensating for the electron deficiency up to the loss of all CO groups, precluding the formation of metal carbides and oxides. Apparently, the methylidenearsine As=CH_2 can serve as such a stabilizing ligand in clusters **Ia** and **Ib**; the hydrocarbon fragment eliminates from it only at the end of the thermolysis.

Triphenylphosphine exhibits the same property; during thermolysis, $(PPh_3)Fe_3(\mu_3\text{-}Te)_2(CO)_8$ and $(PPh_3)_2Pt(\mu_3\text{-}Te)_2Fe_2(CO)_6$ do not lose this ligand until all carbonyl groups eliminate, thus preventing the formation of iron carbides and oxides:

$$((C_6H_5)_3P)Fe_3Te_2(CO)_8 \xrightarrow[-6CO]{116–203°} \{((C_6H_5)_3P)Fe_3Te_2\} \xrightarrow[-PPh_3]{237–340°} Fe_3Te_2,$$

$$(CO)_6Fe_2Te_2Pt(P(C_6H_5)_3)_2 \xrightarrow[-6CO]{210–231°} \{((C_6H_5)_3P)_2PtTeFe_2\} \xrightarrow[-2PPh_3]{240–350°} PtTe_2Fe_2.$$

According to X-ray powder diffraction data, $(PPh_3)Fe_3(\mu_3\text{-}Te)_2(CO)_8$ decomposes into iron ditellu-

Table 2. Phase composition of the final solid product of the decomposition of $(PPh_3)Fe_3(\mu_3\text{-}Te)_2(CO)_8$

Experiment 1		Experiment 2		$FeTe_2$ [16]		Fe [16]	
d, Å	*I*, %	*d*, Å	*I*, %	*d*, Å	*I*, %	*d*, Å	*I*, %
3.25	100	3.30	40	3.29	30		
		3.11	20	3.13	20		
2.81	100	2.79	100	2.81	100		
2.71	70	2.69	100	2.71	70		
2.655	20	2.64	40	2.650	10		
		2.43	10	2.450	5		
2.240	10	2.23	20	2.230	5		
2.065	20	2.060	80	2.070	50		
1.975	50	1.975	30			1.970	40
1.940	60	1.940	20	1.940	30		
1.855	20			1.846	40		
1.840	40	1.840	50			1.840	100
1.785	20	1.790	10	1.795	5		
1.755	10	1.730	10	1.744	10		
		1.695	10	1.704	5		
1.570	20	1.570	40	1.577	30		
1.560	10	1.560	10	1.558	10		
1.515	10			1.515	20		
		1.44	40			1.44	10
1.310	10	1.325	30	1.322	5		
		1.230	10			1.230	10

ride and metallic iron (Table 2) and $(PPh_3)_2Pt(\mu_3\text{-}Te)_2Fe_2(CO)_6$ decomposes into iron monotelluride and metallic platinum (Table 3).

Thermolysis of clusters **II** and **III** containing both triphenylphosphine and methylarsine proceeds through complete sequential elimination of CO, PPh_3, and CH_3 (or CH_2) to give the inorganic products $PtXAsFe_2$ (X = Se or Te):

$$(CO)_6Fe_2TeAs(CH_3)Pt(P(C_6H_5)_3)_2 \xrightarrow[-6CO]{90\text{–}234^\circ} \{((C_6H_5)_3P)_2PtTeAsFe_2\} \xrightarrow[-2PPh_3,\ -CH_3]{234\text{–}350^\circ} PtTeAsFe_2,$$

$$(CO)_6Fe_2SeAs(CH_3)Pt(P(C_6H_5)_3)_2 \xrightarrow[-6CO]{160\text{–}232^\circ} \{((C_6H_5)_3P)_2PtSeAsFe_2\} \xrightarrow[-2PPh_3,\ -CH_3]{232\text{–}330^\circ} PtSeAsFe_2.$$

Table 3. Phase composition of the final solid product of the decomposition of $(PPh_3)_2Pt(\mu_3\text{-}Te)_2Fe_2(CO)_6$

Experiment		FeTe [16]		Pt [16]	
d, Å	*I*, %	*d*, Å	*I*, %	*d*, Å	*I*, %
5.40 br	80				
3.45	5	3.500	20		
3.35	10	3.300	60		
2.92 br		2.90	60		
2.53					
2.26	5			2.265	100
2.10 br	20	2.092	100		
		2.005	100		
				1.962	53
1.865 br	20				
		1.795	20		
1.645 br	20				
1.270 br	10				

In conclusion, it should be noted that chalcogenmethylarsenide carbonyl iron clusters are convenient synthons for the preparation of clusters simultaneously containing various transition metals and various Groups 15 and 16 elements. In the resulting clusters, the formally single Fe–As and Fe–chalcogen bonds are substantially shorter than the sums of the covalent radii of the corresponding elements. This can be due to an additional dative interaction of the *d* electrons of iron with the vacant *d* orbitals of heavy main-group elements. The thermolysis of the clusters containing the methylarsenide or triphenylphosphine ligand gives complex inorganic products; the ratio of the heavy elements in the thermolysis products is identical with that in the starting cluster. The absence of iron carbides and oxides in these cases can be explained by the electron-compensating properties of the firmly bound ligands during decarbonylation processes.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 06-03-32891), the Division of Chemistry and Materials Sciences of the Russian Academy of Sciences (grant no. OKh 1.5), and the Presidium of the Russian Academy of Sciences (grant no. 8P15).

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