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Dedicated to the memory of Professor A.A. Pasynskii

Complexes $[Fe_2(\mu\text{-}S_2ER_2)(CO)_6]$ (E = Si, Sn) as Reagents for the Synthesis of Heterometallic Clusters: Synthesis, Structure, and Reactions with Halogen-Containing Metal Complexes

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Abstract—Binuclear complexes $[Fe_2(\mu\text{-}S_2ER_2)(CO)_6]$ ($ER_2 = SiMe_2$ (**Ia**), $SiEt_2$ (**Ib**), $SnEt_2$ (**Ic**)), promising precursors of heterometallic clusters, were synthesized. Reactions of these complexes with transition metal halide complexes, $[Cp''RhCl_2]_2$ ($Cp'' = \eta^5\text{-}C_5H_3{}^tBu_2$), $[(Dppe)NiCl_2]$ ($Dppe = Ph_2PCH_2CH_2PPh_2$), $[(Ph_3P)AuCl]$, and $[Mn(CO)_5Cl]$, were studied. The reactions gave heterometallic clusters $[Fe_2Rh(\mu_3\text{-}S)_2(CO)_6Cp'']$ (**II**), $[Fe_2Ni(\mu_3\text{-}S)_2(CO)_6(Dppe)]$ (**III**), $[Fe_2(CO)_6(\mu\text{-}SSnClEt_2)(\mu\text{-}SAu(PPh_3))]$ (**IV**), $[Fe_2(CO)_6(\mu_4,\eta^2\text{-}S_2SnEt_2)\{Mn(CO)_4Cl\}_2]$ (**V**), and $[Fe_2Mn(CO)_9Mn(CO)_5(\mu_3\text{-}S)(\mu_4\text{-}S)]$ (**VI**). Cluster **V** was found to be converted to **VI** upon photochemical activation. The structures of compounds **I**–**VI** were determined by X-ray diffraction (CIF file CCDC nos. 751214 (**Ic**), 751215 (**III**·$0.5C_7H_8$), 2062206 (**V**), 2062207 (**Ib**), 2062208 (**Ia**), 2062209 (**IV**·$0.5CH_3C_5H_9$).

Keywords: coordination compounds, clusters, iron, sulfur, silicon, tin, *d*-metals, crystal structure, reactivity, synthesis

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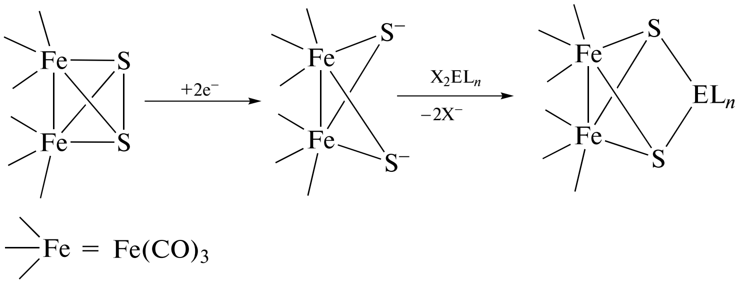
INTRODUCTION

Iron carbonyl chalcogenide clusters have been known for several decades and are classical objects used to study most of reactions of clusters and to systematize the targeted syntheses of more complex homo- and heterometallic derivatives [1, 2]. A considerable contribution to this research area was made by A.A. Pasynskii and his colleagues [3–7]. A special place among iron carbonyl chalcogenides belongs to easily accessible $[Fe_2(\mu\text{-}S_2)(CO)_6]$ known since the 1950s [8, 9]. The interest in this complex and its derivatives is due to the fact that cleavage of S–S and/or Fe–Fe bonds makes this complex a convenient source of {FeS} and $\{Fe_2S_2\}$ moieties for the design of larger clusters that are considered as abiological analogues of some enzyme active sites [10–12]. As a result, the chemistry of $[Fe_2(\mu\text{-}S_2)(CO)_6]$ has been studied rather comprehensively, but the interest in this subject has started to fade. Development of the chemistry of $[Fe_2(\mu\text{-}S_2)(CO)_6]$ and its analogues was stimulated once again by recently discovered activity of compounds with a $\{Fe_2S_2\}$ moiety in the photochemical reduction of proton to dihydrogen. Apart from molecular compounds, nanoparticles obtained by sorption of $[Fe_2(\mu\text{-}S_2)(CO)_6]$ on the surface of semiconductors, e.g., InP [13], CdTe [14], or ZnS [15, 16], proved to be active in these reactions. These results revived the interest in $[Fe_2(\mu\text{-}S_2)(CO)_6]$ [17–21] and stimulated us to address some problematic issues of the use of this complex for the synthesis of heterometallic clusters that preserve the $\{Fe_2S_2\}$ moiety.

One of such issues is related to the synthetic pathways that use the $[Fe_2(\mu\text{-}S)_2(CO)_6]^{2-}$ anion obtained in situ by the reduction of $[Fe_2(\mu\text{-}S_2)(CO)_6]$ [9]. It may seem that this dianion is similar to organic dithiolates. Being a chelating ligand with nucleophilic bridging sulfur atoms, it is expected to bind to the most positive atom or atoms of organic electrophiles via these sulfur atoms (Scheme 1).



Scheme 1.

Indeed, this scheme is applicable and, with an accuracy to the possible Fe–Fe bond cleavage, can be used to obtain clusters containing the $\{Fe_2S_2\}$ moiety, as was demonstrated by numerous examples [9, 22, 23]. However, the problem is that $[Fe_2(\mu\text{-}S)_2(CO)_6]^{2-}$ is unstable in solutions and undergoes further transformations, apparently related to the interaction between the anionic and the neutral form $[Fe_2(\mu\text{-}S_2)(CO)_6]$ [24, 25]. This eliminates the possibility for chemists to vary the synthetic conditions, e.g., use other reducing agents and solvents or higher temperature without the risk to get a number of anionic species of unknown composition in solution. In attempts to circumvent this problem, heterometallic clusters are synthesized using procedures based on the reduction of $[Fe_2(\mu\text{-}S_2)(CO)_6]$ under strictly specified conditions and subsequent use of $[Fe_2(\mu\text{-}S)_2(CO)_6]^{2-}$ anion without isolation. However, the amount of this anion cannot be determined with sufficient accuracy, because its exact yield is unknown. This considerably restricts the range of compounds that can be used in this synthesis.

This problem could be solved by replacing the unstable $[Fe_2(\mu\text{-}S)_2(CO)_6]^{2-}$ anion by neutral derivatives $[Fe_2(\mu\text{-}S_2ER_2)(CO)_6]$ (E = Si, Sn), which are stable under inert atmosphere at room temperature and readily soluble in all aprotic solvents. Presumably, they should be reactive towards transition metal halides, carboxylate, or alkoxides. This assumption is based on the fact that similar approaches using chalcogen-silylated and, to a lesser extent, -stannylated reagents are widely used in chemistry [26–29]. These approaches are based on the fact that the $\{R_3E\}^+$ and $\{R_2E\}^{2+}$ groups (E = Si, Sn) have a high affinity for a halide ion or an oxygen-containing acid residue ($X^- = Cl^-, Br^-, RCOO^-, RO^-$, etc.); therefore, the formation of R_3EX and R_2EX_2 ensures the driving force of the reaction. Furthermore, R_3EX and R_2EX_2 are relatively inert and can be easily separated from the target product of synthesis. In other words, R_3E and R_2E (E = Si, Sn) can be considered as good leaving groups in the reactions with transition metal halides, carboxylates, and alkoxides. These reactions should results in the formation of a chalcogen–metal bond and subsequently in the formation of the cluster core.

Compounds like $[Fe_2(\mu\text{-}S_2ER_2)(CO)_6]$ (E = Si, Sn) were prepared earlier [9], but their structure and reactivity were not investigated. Here we developed advanced procedures for the synthesis of $[Fe_2(\mu\text{-}S_2ER_2)(CO)_6]$ ($ER_2 = SiMe_2$ (**Ia**), $SiEt_2$ (**Ib**), and $SnEt_2$ (**Ic**)) and studied their structures by single crystal X-ray diffraction. Also, to confirm our assumption on the applicability of **Ia**–**Ic** for the synthesis of heterometallic clusters, we studied their reactions with transition metal halide complexes: $[Cp''RhCl_2]_2$ ($Cp'' = \eta^5\text{-}C_5H_3{}^tBu_2$), $[(Dppe)NiCl_2]$ ($Dppe = Ph_2PCH_2CH_2PPh_2$), $[(Ph_3P)AuCl]$, and $[Mn(CO)_5Cl]$, which resulted in the formation of $[Fe_2Rh(\mu_3\text{-}S)_2(CO)_6Cp'']$ (**II**), $[Fe_2Ni(\mu_3\text{-}S)_2(CO)_6(Dppe)]$ (**III**), $[Fe_2(CO)_6(\mu\text{-}SSnClEt_2)(\mu\text{-}SAu(PPh_3))]$ (**IV**), $[Fe_2(CO)_6(\mu_4,\eta^2\text{-}S_2SnEt_2)\{Mn(CO)_4Cl\}_2]$ (**V**), and $[Fe_2Mn(CO)_9Mn(CO)_5(\mu_3\text{-}S)(\mu_4\text{-}S)]$ (**VI**).

EXPERIMENTAL

All operations for the synthesis and product isolation were performed in an argon atmosphere using standard Schlenk technique. The solvents were refluxed with appropriate drying agents and distilled under argon to remove water and dissolved oxygen [30]. The compounds $[Fe_2(\mu\text{-}S_2ER_2)(CO)_6]$ ($ER_2 = SiMe_2$ (**Ia**), $SiEt_2$ (**Ib**), and $SnEt_2$ (**Ic**)) were synthesized using an approach described previously [9]. Single crystals for X-ray diffraction were selected from the isolated crystalline products. The complexes $[(Dppe)NiCl_2]$ [31], $[Mn(CO)_5Cl]$ [32], and $[(Ph_3P)AuCl]$ [33] were prepared by known procedures. The synthesis of $[Cp''RhCl_2]_2$ ($Cp'' = \eta^5\text{-}C_5H_3{}^tBu_2$) was carried out as described previously [34].

Elemental analysis was performed in laboratory No. 416 of the Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences. During elemental analysis, a short-term contact (several seconds) of the sample with air was allowed.

IR spectra (ν_{CO}, cm^{-1}) were measured on a Specord IR-75 spectrometer at room temperature for *n*-hexane solutions of compounds **I**, **II**, **IV**, and **V** and for CH_2Cl_2 solutions of clusters **III** and **VI**.

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at room temperature on a Bruker AC 250 spectrometer operating at 250.133 MHz (for ^{1}H), 62.896 MHz (for ^{13}C), and 101.256 MHz (for ^{31}P). The solvent signals (δ_H = 7.16 ppm for C_6D_6, δ_C = 77.0 ppm for $CDCl_3$) were used as the internal standards. A 85% aqueous solution of H_3PO_4 was used as the standard for ^{31}P NMR spectra. The spin–spin coupling constants are given in hertz.

Synthesis of $[Fe_2(CO)_6(\mu_3\text{-}S)_2SiMe_2]$ (Ia). A Na/K alloy (0.2 mL) (Na : K molar ratio of 2 : 3) was added to a solution of $[Fe_2(CO)_6(\mu\text{-}S_2)]$ (0.45 g, 1.31 mmol) in THF (15 mL) pre-cooled to 0°C. The mixture was stirred with cooling on a ice bath for 4 h. The resulting red solution was separated from the unreacted Na/K alloy and from the amorphous precipitate. The precipitate was washed with THF (15 mL). A solution of Me_2SiCl_2 (0.30 mL, 2.46 mmol) in THF (10 mL) was added to the combined solution. The reaction mixture was stirred at room temperature for 3 h and evaporated to dryness. The solid residue was dried in vacuum and extracted with two portions of hexane (30 and 15 mL). The resulting dark red solution was concentrated to one fourth its volume. Keeping the concentrated solution at –16°C resulted in precipitation of crystalline compound **Ia**. The yield was 0.33 g (50%).

IR (ν_{CO}, cm^{-1}): 2078 s, 2046 m, 2038 s, 2008 s, 1998 s, 1987 m, 1957 w.

Synthesis of $[Fe_2(CO)_6(\mu_3\text{-}S)_2SnEt_2]$ (Ic). A Na/K alloy (0.2 mL) (Na : K molar ratio of 2 : 3) was added to a solution of $[Fe_2(CO)_6(\mu\text{-}S_2)]$ (1.50 g, 4.37 mmol) in THF (35 mL) pre-cooled to 0°C. The mixture was stirred with cooling on a ice bath for 4 h. The resulting red solution was separated from the unreacted Na/K alloy and from the amorphous precipitate. The precipitate was washed with THF (15 mL). A solution of $[Et_2SnCl_2]$ (1.00 g, 4.03 mmol) in THF (40 mL) was added to the combined filtrate. The reaction mixture was stirred at room temperature for 3 h and evaporated to dryness. The solid residue was washed with hexane (15 mL) to remove the remaining starting $[Fe_2(CO)_6(\mu\text{-}S_2)]$ and then dried in vacuum. The resulting dark powder was extracted with two portions of CH_2Cl_2 (80 and 15 mL). The dark red solution was concentrated to one fourth its volume. Keeping the concentrated solution at –16°C resulted in precipitation of crystalline compound **Ic**. The yield was 1.14 g (50%).

IR (ν_{CO}, cm^{-1}): 2083 m, 2070 s, 2030 s, 2005 s, 2001s, 1990 sh, 1986 s, 1976 m.

Synthesis of $[Fe_2(CO)_6(\mu_3\text{-}S)_2SiEt_2]$ (Ib). The attempts to prepare **Ib** by the standard procedure described above for **Ia** and **Ic** gave the crystal phase of $[Fe_2(CO)_6(\mu_3\text{-}S)_2SiEt_2]\cdot[Fe_2(CO)_6(\mu\text{-}S_2)]$. Variation of the synthesis conditions did not solve the problem of formation of the co-crystallized product. Therefore, **Ib** was synthesized using a different procedure, namely $[Fe_2(CO)_6(\mu\text{-}S_2)]$ was reduced with $Li[BHEt_3]$ at low temperature.

A 1 M THF solution of $Li[BHEt_3]$ (3 mL) was added to a solution of $[Fe_2(CO)_6(\mu\text{-}S_2)]$ (0.50 g, 1.45 mmol) in THF (35 mL) pre-cooled to –80°C. The mixture was stirred at this temperature for 20 min. A solution of Et_2SiCl_2 (0.45 mL, 3.01 mmol) in THF (5 mL) was added dropwise to the obtained red solution. The reaction mixture was warmed up to room temperature, stirred for 3 h, and then evaporated to dryness. The solid residue was dried and extracted with two portions of hexane (40 and 5 mL). The resulting dark red solution was concentrated to one fourth its volume. Keeping the concentrated solution at –16°C resulted in precipitation of crystalline compound **Ib**. The yield was 0.49 g (78%).

IR (ν_{CO}, cm^{-1}): 2078 s, 2046 m, 2038 s, 2008 s, 1998 s, 1987 m, 1957 w.

Synthesis of $[Fe_2Rh(\mu_3\text{-}S)_2(CO)_6Cp'']$ (II) and $[Fe_2Ni(\mu_3\text{-}S)_2(CO)_6(Dppe)]$ (III). The reactions of **Ia**–**Ic** with $[Cp''RhCl_2]_2$ and $[(Dppe)NiCl_2]$ were carried out similarly using the following amounts of reactants: **II** was synthesized from **Ic** (0.049 g, 0.094 mmol) and $[Cp''RhCl_2]_2$ (0.034 g, 0.048 mmol); **III** was synthesized from **Ia** (0.025 g, 0.062 mmol) and $[(Dppe)NiCl_2]$ (0.033 g, 0.062 mmol); or from **Ib** (0.022 g, 0.051 mmol) and $[(Dppe)NiCl_2]$ (0.027 g, 0.051 mmol)); or from **Ic** (0.029 g, 0.056 mmol) and $[(Dppe)NiCl_2]$ (0.029 g, 0.055 mmol).

General procedure. Toluene (10 mL) was added to a mixture of solid reactants. The reaction mixture was stirred at room temperature for 12 h. The resulting dark red solution was filtered, a small amount of unidentified precipitate was washed with toluene (15 mL), and the combined filtrate was concentrated to half its volume and kept at –16°C, which resulted in the crystallization of phases **II** or **III**$\cdot 0.5C_7H_8$ in 70–80% yield.

Reaction products were identified using IR spectra [9, 23] (ν_{CO}, cm^{-1}): 2064 s, 2038 s, 1997 s, 1987 s (**II**); 2046 s, 2004 s, 1967 s, 1957 sh (**III**).

Synthesis of $[Fe_2(CO)_6(\mu\text{-}SSnClEt_2)(\mu\text{-}SAu(PPh_3))]$ (IV). Toluene (10 mL) was added to a mixture of solid **Ic** (0.062 g, 0.12 mmol) and $[(Ph_3P)AuCl]$ (0.54 g, 0.24 mmol). The reaction mixture was stirred at room temperature for 3 days, which resulted in the formation of a brown solution and a dark precipitate. The precipitate was collected on a filter and washed with toluene (15 mL). The combined filtrate contained several products (TLC data). The solution was evaporated to dryness and the residue was extracted with petroleum ether (20 mL). Keeping the resulting orange solution at –16°C gave crystals of the phase **IV**$\cdot 0.5CH_3C_5H_9$. The yield was 0.013 g (10%).

IR (ν_{CO}, cm^{-1}): 2073 s, 2064 s, 2045 m, 2033 s, 2027 s, 2004 s, 1988 s, 1978 s. ^{1}H NMR (C_6D_6; δ, ppm): 6.89 (s, 15H, PPh_3), 1.64 (q, 2H, CH_2, J_{SnH} = 58), 1.27 (t, 3H, CH_3). ^{31}P NMR (C_6D_6; δ, ppm): 36.1 (s, 1P, PPh_3).

Synthesis of $[Fe_2(CO)_6(\mu_4,\eta^2\text{-}S_2SnEt_2)\{Mn(CO)_4Cl\}_2]$ (V) and $[Fe_2Mn(CO)_6(\mu_3\text{-}S)(\mu_4\text{-}S)\{Mn(CO)_5\}]$ (VI). Toluene (10 mL) was added to a mixture of solid **Ic** (0.062 g, 0.12 mmol) and $[Mn(CO)_5Cl]$ (0.054 g, 0.24 mmol). The reaction mixture was stirred at room temperature for 2 weeks, which resulted in the formation of a brown solution and a dark precipitate. The precipitate was collected on a filter and washed with toluene (15 mL). The combined filtrate was evaporated to dryness. The solid residue was washed several times with hexane until the extract was colorless, and the residue insoluble in hexane was dissolved in toluene (30 mL). After the hexane extract was concentrated to 20 mL and kept at −16°C, crystals of compound **V** precipitated. The yield was 0.050 g (45%). Cooling of the toluene solution to −16°C resulted in crystallization of compound **VI**. The yield was 0.037 g (45%).

For $C_{18}H_{10}O_{14}S_2Cl_2Fe_2Mn_2Sn$ (**V**)

Anal. calcd., %	C, 23.4	H, 1.09
Found, %	C, 23.5	H, 1.1

IR spectrum of **V** (ν_{CO}, cm^{-1}): 2106 sh 2096 s, 2073 s, 2049 s, 2042 m, 2024 s, 2014 m, 2007 s, 1997 m, 1978 s. ^{1}H NMR (C_6D_6; δ, ppm): 1.87 (q., 2H, CH_2, J_{SnH} = 64.5), 1.36 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$; δ, ppm): 214.3–206.8 (m, 1C, CO), 29.5 (s., 1C, CH_2), 9.0 (s., 1C, CH_3).

Compound **VI** was identified using the IR spectrum [35] (ν_{CO}, cm^{-1}): 2137 w, 2072 s, 2058 s, 2030 s, 2014 s, 2004 sh 1998 m, 1994 sh 1938 w, 1917 w.

Synthesis of compound VI. Toluene (10 mL) was added to a solid mixture of **Ia** (0.075 g, 0.19 mmol) and $[Mn(CO)_5Cl]$ (0.089 g, 0.37 mmol), or **Ib** (0.065 g, 0.15 mmol) and $[Mn(CO)_5Cl]$ (0.70 g, 0.30 mmol). The reaction mixture was stirred at room temperature for 2 weeks, which resulted in the formation of a brown solution and a dark precipitate. The precipitate was collected on a filter and washed with toluene (15 mL). The combined filtrate was evaporated to dryness. The solid residue was washed with hexane (80 mL). The residue insoluble in hexane was dried in vacuum and dissolved in toluene. Keeping this solution at −16°C gave the crystals of compound **VI**. The yield was 0.038 g (30%) from **Ia** and 0.026 g (25%) from **Ib**.

X-ray diffraction study of the complexes was carried out at 150 K by the standard procedure on a Bruker-Nonius X8Apex automated four-circle diffractometer equipped with a CCD array detector using molybdenum radiation (λ = 0.71073 Å) and a graphite monochromator. The reflection intensities were measured in the φ-scan mode using narrow (0.5°) frames. Semiempirical absorption corrections were applied by the SADABS program [36]. The structures were solved by direct methods and refined by the full-matrix least squares method in the anisotropic approximation for non-hydrogen atoms using the SHELXTL software package [37]. The hydrogen atoms were refined in the rigid body approximation. The X-ray experiment details and structure refinement parameters are summarized in Table 1 and selected interatomic distances and bond angles are in Table 2.

The crystallographic parameters of the complexes are deposited with the Cambridge Crystallographic Data Center (CCDC nos. 751214 (**Ic**), 751215 (**III**·$0.5C_7H_8$), 2062206 (**V**), 2062207 (**Ib**), 2062208 (**Ia**), and 2062209 (**IV**·$0.5CH_3C_5H_9$)) and are available at the website www.ccdc.cam.ac.uk/data_reguest/cif.

RESULTS AND DISCUSSION

Complexes **Ia**–**Ic** were synthesized by successive reduction of $[Fe_2(\mu\text{-}S_2)(CO)_6]$ to $[Fe_2(\mu\text{-}S)_2(CO)_6]^{2-}$ in a THF solution and addition of the appropriate Cl_2ER_2 (ER_2 = $SiMe_2$, $SiEt_2$, $SnEt_2$). This pathway corresponds to Scheme 1 presented above. In the case of compounds **Ia** and **Ic**, the procedure in which the liquid Na/K alloy was used as the reducing agent proved to be optimal. Earlier, we proposed this approach for the synthesis of heterometallic clusters [23]. For unknown reason, this procedure was inapplicable for the preparation of **Ib**: the standard isolation procedure gave only the co-crystallization product $[Fe_2(CO)_6(\mu_3\text{-}S)_2SiEt_2]\cdot[Fe_2(CO)_6(\mu\text{-}S_2)]$. The procedure using $Li[BEt_3H]$ as the reducing agent was more effective in this case. This procedure described previously [9] was somewhat modified in the present study.

Compounds **Ia**–**Ic** were isolated in the crystalline state and studied by X-ray diffraction (Fig. 1, Tables 1 and 2). In the molecules of **Ia**–**Ic**, the $\{Fe_2S_2(CO)_6\}$ moiety is connected to the Sn or Si atoms via S atoms. The geometry of $\{Fe_2S_2(CO)_6\}$ is the same in all three cases. The replacement of silicon with tin has little effect on the Fe–Fe and Fe–S bond lengths. The expected slight decrease in the Fe–Fe distance and increase in the Fe–S distance do take place, but the difference does not exceed a few thousandths of angstrom. The S–Si and S–Sn bond lengths are in the same range as those in other currently known compounds with bridging stannothiolate and silicothiolate ligands [38].

Previously, heterometallic clusters **II** and **III** were prepared by successive reduction of $[Fe_2(\mu\text{-}S)_2(CO)_6]$ in toluene and addition of the complexes $[Cp''RhCl_2]_2$

Table 1. Crystallographic parameters and X-ray experiment details for compounds **Ia**–**Ic**, **III**·$0.5C_7H_8$, **IV**·$0.5CH_3C_5H_9$, and **V**

Parameter	Value					
	Ia	**Ib**	**Ic**	**III**·$0.5C_7H_8$	**IV**·$0.5CH_3C_5H_9$	**V**
M	402.04	430.09	520.69	847.05	1057.45	925.55
System	Triclinic	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group,	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a, Å	9.1326(3)	8.0113(2)	10.3807(3)	23.4098(8)	11.4668(4)	14.1917(2)
b, Å	9.2073(4)	9.8447(2)	9.2793(3)	12.4314(3)	13.2126(4)	11.0030(2)
c, Å	9.3959(4)	11.7599(2)	17.8586(7)	25.7385(9)	13.5206(4)	19.4710(4)
α, deg	88.903(1)	102.838(1)	90	90	77.8150(10)	90
β, deg	64.930(1)	102.838(1)	105.661(1)	107.463(1)	68.5180(10)	90.1480(10)
γ, deg	85.186(1)	104.465(1)	90	90	72.5010(10)	90
V, Å^3	713.00(5)	798.68(3)	1656.38(10)	7145.1(4)	1806.14(10)	3040.41(9)
Z	2	2	4	8	2	4
ρ(calcd.), g/cm^3	1.873	1.788	2.088	1.575	1.944	2.022
F(000)	400	432	1008	3448	1020	1792
μ(radiation), mm^{-1}	2.425	2.171	3.494	1.574	5.793	2.923
Crystal size, mm	0.24 × 0.15 × 0.14	0.32 × 0.31 × 0.28	0.08 × 0.07 × 0.04	0.40 × 0.12 × 0.08	0.27 × 0.11 × 0.02	0.30 × 0.17 × 0.14
T, K	100.0(2)	100.0(2)	100.0(2)	150(2)	100.0(2)	100.0(2)
2θ$_{max}$, deg	62.86	63.80	56.54	55.16	62.56	62.74
Ranges of reflection indices	$-13 \le h \le 9$, $-12 \le k \le 13$, $-13 \le l \le 12$	$-11 \le h \le 11$, $-13 \le k \le 13$, $-11 \le l \le 17$	$-9 \le h \le 13$, $-10 \le k \le 12$, $-23 \le l \le 23$	$-30 \le h \le 30$, $-14 \le k \le 15$, $-33 \le l \le 33$	$-16 \le h \le 13$, $-18 \le k \le 18$, $-19 \le l \le 13$	$-20 \le h \le 14$, $-14 \le k \le 14$, $-27 \le l \le 15$
Number of measured reflections	8185	9372	13273	61587	34957	17438
Number of unique reflections (R_{int})	3800 (0.0244)	4379 (0.0195)	4112 (0.0371)	16209 (0.0447)	9765 (0.0291)	8088 (0.0198)
Number of reflections with $I \ge 2\sigma(I)$	3126	3993	3288	11038	8728	6916
Number of refined parameters	174	192	192	875	444	372
R-factors for $I \ge 2\sigma(I)$	$R_1 = 0.0373$, $wR = 0.0848$	$R_1 = 0.0228$, $wR_2 = 0.0473$	$R_1 = 0.0333$, $wR_2 = 0.0789$	$R_1 = 0.0365$, $wR_2 = 0.0826$	$R_1 = 0.0211$, $wR_2 = 0.0471$	$R_1 = 0.0228$, $wR_2 = 0.0437$
R-factors for all reflections	$R_1 = 0.0495$, $wR_2 = 0.0907$	$R_1 = 0.0261$, $wR_2 = 0.0486$	$R_1 = 0.0478$, $wR_2 = 0.0836$	$R_1 = 0.0771$, $wR_2 = 0.1015$	$R_1 = 0.0278$, $wR_2 = 0.0498$	$R_1 = 0.0309$, $wR_2 = 0.0464$
GOOF on F^2	1.029	1.039	1.034	1.018	1.043	1.029
Residual electron density (min/max, e Å^{-3})	–0.459/0.962	–0.248/0.389	–0.556/3.948	–0.391/0.489	–0.811/1.159	–0.471/0.686

Table 2. Selected bond lengths (Å) and angles (deg) for complexes **Ia**–**Ic**, **III**·$0.5C_7H_8$, **IV**·$0.5CH_3C_5H_9$, **V**

Bond	**Ia** (E = Si)	**Ib** (E = Si)	**Ic** (E = Sn)	**III**·$0.5C_7H_8$ (M = Ni)*	**IV**·$0.5CH_3C_5H_9$ (M = Au, E = Sn)	**V** (M = Mn, E = Sn)
	d, Å					
Fe(1)–Fe(2)	2.4823(5)	2.4863(3)	2.4928(8)	2.4944(6)	2.4968(5)	2.5303(4)
Fe(1)–S(1)	2.3103(8)	2.3140(4)	2.3032(11)	2.2834(9)	2.2844(7)	2.2651(5)
Fe(1)–S(2)	2.3114(7)	2.3074(4)	2.2987(11)	2.2872(9)	2.2934(7)	2.2681(5)
Fe(2)–S(1)	2.3132(7)	2.3123(4)	2.3064(11)	2.2896(9)	2.2666(7)	2.2663(5)
Fe(2)–S(2)	2.3090(7)	2.3054(4)	2.3017(11)	2.2857(8)	2.2973(7)	2.2635(5)
E(1)–S(1)	2.1530(9)	2.1507(5)	2.4762(10)			2.5494(5)
E(1)–S(2)	2.1537(10)	2.1501(5)	2.4714(10)		2.4648(6)	2.5448(5)
M–P		2.2662(6)		2.1757(8), 2.1836(8)	2.2662(6)	
M–S(1)		2.3110(6)		2.1888(8)	2.3110(6)	2.3456(5)
M–S(2)		2.8718(6)		2.1893(8)	2.8718(6)	2.3421(5)
Sn(1)–Cl(1)					2.4270(7)	3.0481(5)
Sn(1)–Cl(2)						2.8635(5)
Mn(1)–Cl(1)						2.3903(5)
Mn(2)–Cl(2)						2.3953(6)
Angle	ω, deg					
S(1)Fe(1)Fe(2)	57.59(2)	57.457(11)	57.30(3)			
S(1)Fe(1)S(2)	80.56(3)	80.777(14)	81.59(3)	76.91(3)	79.45(2)	75.648(18)
S(1)Fe(2)S(2)	80.55(3)	80.854(14)	81.45(3)			
Fe(1)S(1)Fe(2)	64.94(2)	65.018(11)	65.49(3)	66.11(3)	66.54(2)	67.888(16)
Fe(1)S(2)Fe(2)	64.99(2)	65.232(11)	65.63(3)	66.12(3)	65.90(2)	67.885(16)
E(1)S(1)Fe(1)	86.25(3)	86.530(17)	91.99(3)			
E(1)S(1)Fe(2)	87.03(3)	85.864(16)	90.51(3)			
E(1)S(2)Fe(1)	86.20(3)	86.711(16)	92.22(3)		100.38(2)	97.752(18)
E(1)S(2)Fe(2)	87.12(3)	86.047(17)	90.71(3)		102.31(3)	97.683(18)
S(1)E(1)S(2)	87.87(4)	88.255(19)	74.85(3)		65.975(19)	66.146(14)
S(1)MS(2)				80.97(3)		
MS(1)Fe(1)				92.55(3)	116.03(3)	137.97(2)
MS(1)Fe(2)				90.16(3)	120.08(3)	132.18(2)
MS(2)Fe(2)				90.25(3)		136.27(2)
MS(2)Fe(1)				92.43(3)		138.28(2)
S(1)Sn(1)Cl(1)					159.77(2)	68.150(14)
S(2)Sn(1)Cl(2)						70.689(14)
Cl(1)Sn(1)S(2)					95.20(2)	134.001(14)
MS(1)Sn(1)					144.61(3)	112.110(19)

* Data are given for one of two independent molecules.

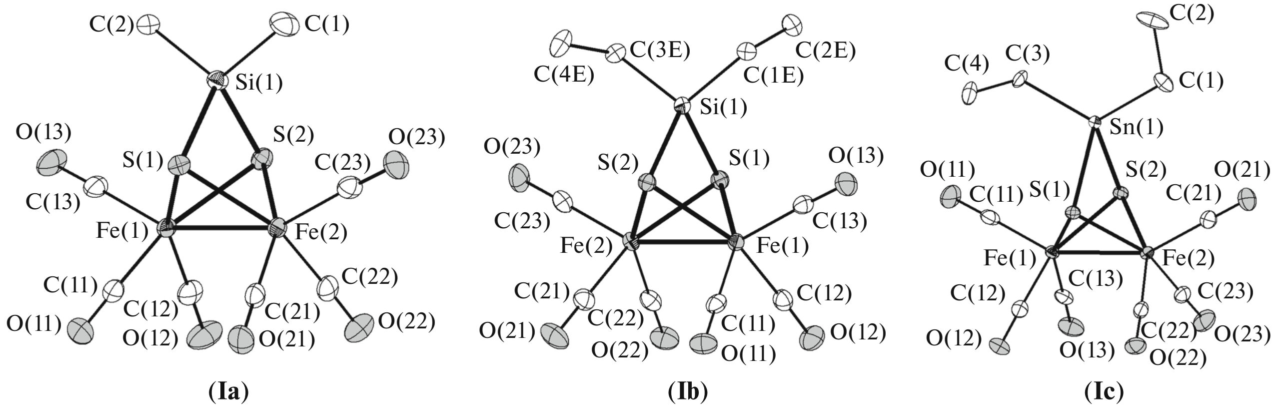
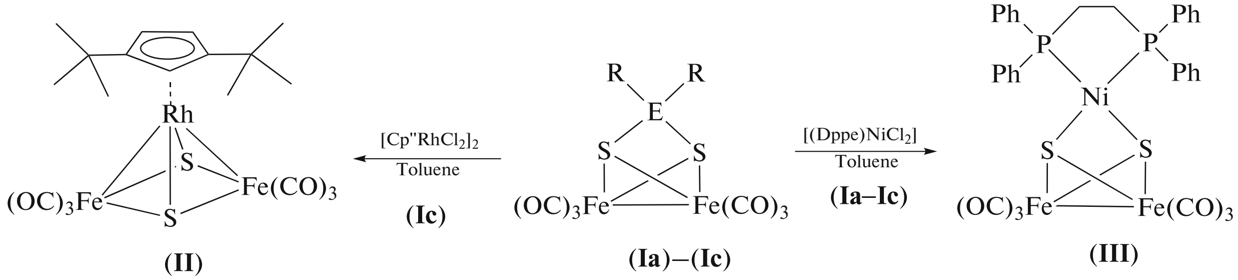


Fig. 1. Structure of molecules of compounds **Ia**–**Ic** in the crystal. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted.

or $[(Dppe)NiCl_2]$, respectively, as shown in Scheme 1 [23, 39]. To verify the applicability of this approach for the preparation of the same compounds using silyl and stannyl reagents, we performed reactions of **Ic** with $[Cp''RhCl_2]_2$ and reactions of **Ia**–**Ic** with $[(Dppe)NiCl_2]$. We found that elimination of Cl_2ER_2 to give complexes **II** and **III** actually took place (Scheme 2).

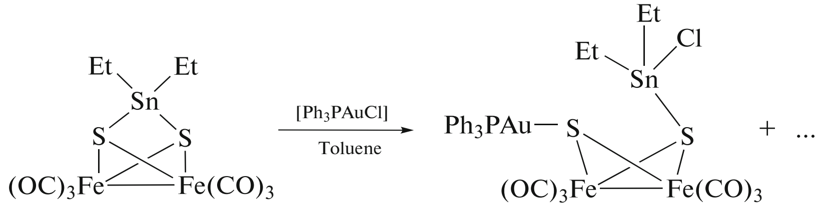


Scheme 2.

The yields of crystalline products in these reactions are 70–80%, which is comparable with the yields in the reactions of $[Fe_2(\mu\text{-}S)_2(CO)_6]^{2-}$ with $[Cp''RhCl_2]_2$ and $[(Dppe)NiCl_2]$. However, a benefit of using **Ia**–**Ic** is that the reacting species are stable neutral complexes that exist in a pure state and are easily taken in appropriate amounts for the synthesis, unlike the $[Fe_2(\mu\text{-}S)_2(CO)_6]^{2-}$ anions, which are formed in situ, are unstable in solution, and cannot be isolated as solids. In addition, the use of $[Fe_2(\mu\text{-}S)_2(CO)_6]^{2-}$ restricts the choice of solvents: so far, all reactions with this anion were carried out in THF. The reactions with silylated and stannylated clusters proceed at room temperature even in a non-polar solvent, for example, toluene. Thus, this offers some freedom in planning and choice of optimal conditions of synthesis and simplifies the product isolation procedure. For example, when toluene is used as the solvent, the procedure is reduced to mere concentration and cooling of the reaction mixture.

The structure of cluster **II** was described previously [23]; therefore, it was identified by comparing its IR spectrum with that of an authentic sample. Cluster **III** was previously structurally characterized as a diethyl ether solvate: **III**·$0.5Et_2O$ [39]. In our case, crystallization from toluene affords solvate **III**·$0.5C_7H_8$. The crystal of the solvate contains two independent $[Fe_2Ni(\mu_3\text{-}S)_2(CO)_6(Dppe)]$ molecules whose structures have only minor differences in bond lengths and angles, probably caused by specific features of the crystal packing. The incorporated toluene molecules are ordered. Generally, the molecules of cluster **III** virtually coincide with those in solvate **III**·$0.5Et_2O$ [39].

The reactions of **Ia**–**Ic** with $[Cp''RhCl_2]_2$ and $[(Dppe)NiCl_2]$ can be considered as test reactions, since their outcomes were beyond doubt. They were studied, most of all, in order to compare the new synthetic approach with that used previously. The subsequent reactions with other transition metal halide complexes were accomplished with the goal to obtain new, previously unknown heterometallic clusters. For example, the reaction of **Ic** with [(Ph_3P)AuCl] was expected to give an iron/gold cluster. Indeed, compound **IV** was isolated from the reaction mixture (Scheme 3), but in a yield of only 10%. The TLC and ^{31}P NMR monitoring of the reaction indicates that actually a product mixture is formed, and compound **IV** is the only product that can be isolated, while other products decompose during isolation. Moreover, isolation of compound **IV** also was a lucky chance. Attempted crystallization from pure hexane did not meet with success. However, when light petroleum ether was used instead of hexane, crystals with solvation molecules of methylcyclopentane $CH_3C_5H_9$, present in a minor amount in the solvent, were formed. Most likely, exactly this hydrocarbon is best suited for co-crystallization with "branched" molecules of cluster **IV**.



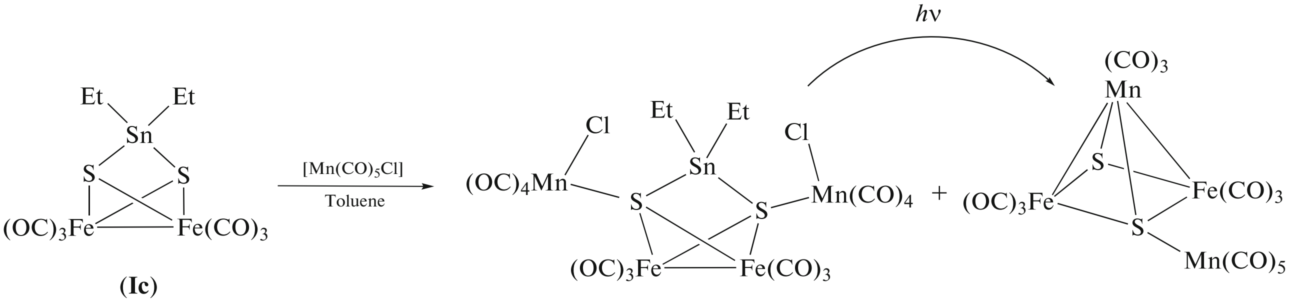
(**Ic**) (**IV**)

Scheme 3.

The structure of solvate **IV**·0.5$CH_3C_5H_9$ was determined by single crystal X-ray diffraction (Fig. 2). The molecule contains both the {Au(PPh_3)} moiety linked to a sulfur atom and the {$SnEt_2Cl$} moiety linked to the second sulfur atom. In other words, the $\{SnEt_2\}^{2+}$ moiety is not eliminated as the corresponding chloride. The reaction product can rather be described as the result of addition of [(Ph_3P)AuCl] to the S–Sn bond. Attempts to vary the reaction conditions (reactant ratio, temperature, solvent) or replacement of stannylated complex **Ic** with silylated analogues **Ia** and **Ib** did not result in isolation and characterization of any other coordination compounds.

Compound **IV** forms a molecular crystal structure in which the cluster moiety is described as [Fe_2(μ-SSnClEt$_2$)(μ-SAuPPh$_3$)(CO)$_6$]. The Sn(1)–S(1) distance markedly increases (up to 2.8718(6) Å) and the Sn(1)–S(2) distance somewhat decreases (down to 2.4648(6) Å) with respect to those in cluster **Ic**, in which the Sn–S distances are 2.4757(9) and 2.4713(9) Å. The FeSAu bond angles are 116.03(3)° and 120.08(3)°. They are virtually equal to the FeSHg bond angles (116(1)°) in [Fe_2(μ-CH_3HgS)$_2$(CO)$_6$] [40].

The first attempt to carry out the reaction of **Ic** with [Mn(CO)$_5$Cl] in 1 : 2 ratio in toluene at room temperature gave two products **V** and **VI** in approximately equal yields (Scheme 4).



(**Ic**) (**V**) (**VI**)

Scheme 4.

In the synthesis of **V** and **VI**, concentration and cooling of the solution leads to crystallization of both compounds, **V** as coarse light red crystals and **VI** as fine dark green crystals. Cluster **VI** was described previously [35]. It was identified by X-ray diffraction and IR spectroscopy. Compound **V** was obtained for the first time. The products were separated owing to different solubilities in hexane. The structure of cluster **V** was established by X-ray diffraction (Fig. 3). In the molecule of **V**, the {Mn(CO)$_4$Cl} moieties are linked to the S atoms. The Cl atoms are coordinated to manganese and to tin in the μ-fashion. The Sn(1)–Cl(1) and Sn(1)–Cl(2) distances are rather long (3.0481(5) and 2.8635(5) Å, respectively) and are typical of chloride

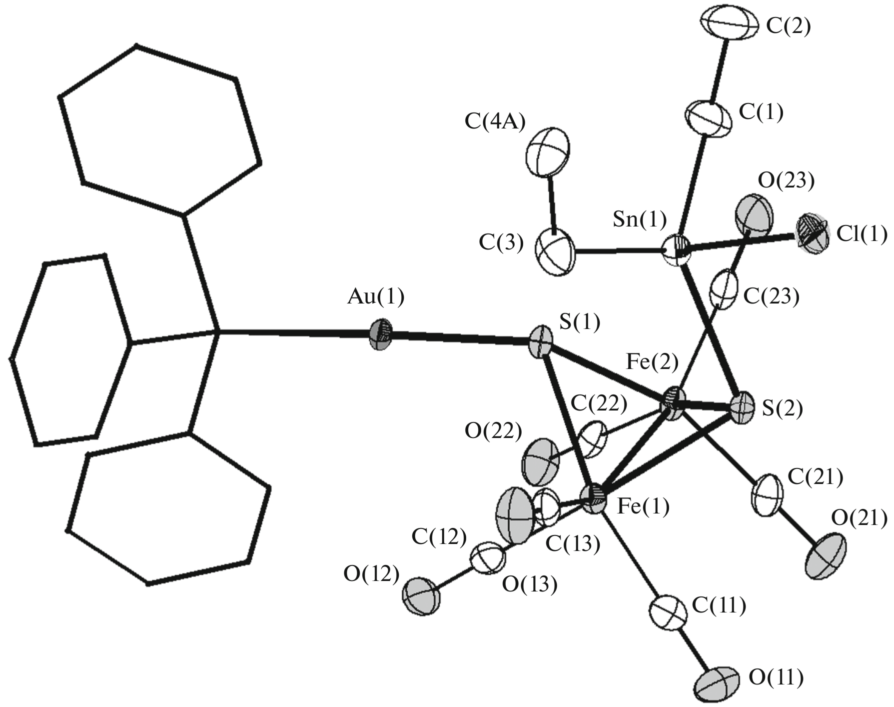


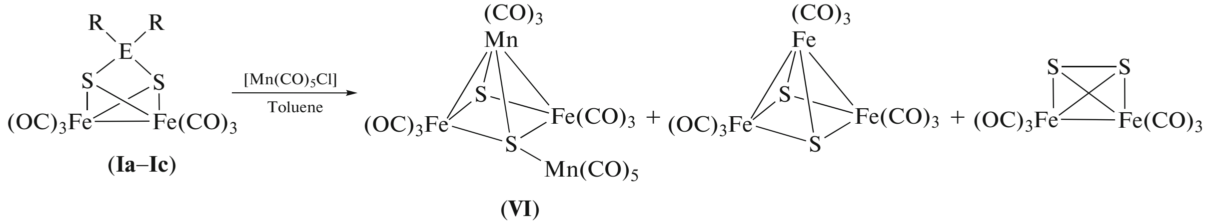
Fig. 2. Structure of cluster **IV** in the crystal. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted, phenyl groups are shown in the simplified form.

bridges in polynuclear homo- and heterometallic tin compounds, e.g., 2.920(1) to 3.097(1) Å in [$(\eta^6\text{-}C_6H_6)Sn(AlCl_4)_2{\cdot}C_6H_6]_n$ [41]. The increase in the tin coordination number leads to some elongation of the Sn–S bonds (by ~0.07 Å) (Table 2).

The ^{1}H NMR spectrum of cluster **V** in solution exhibits signals for ethyl hydrogen atoms: a triplet for CH_3 at 1.36 ppm and a quartet for CH_2 at 1.87 ppm, and also satellites of CH_2 proton splitting on ^{117}Sn and ^{119}Sn nuclei with spin–spin coupling constants J_{SnH} = 64.5 Hz. The ^{13}C NMR spectrum of cluster **V** shows a multiplet for the carbon atoms of CO ligands (206.8–214.3 ppm), CH_2 groups (29.8 ppm), and CH_3 groups (9.0 ppm).

A comparison of clusters **V** and **VI** indicates that their molecules differ by the {Et_2SnCl_2} moiety, which has not been eliminated from **V**. It is reasonable to assume that cluster **V** is an intermediate that should be converted to compound **VI** via elimination of Et_2SnCl_2, but this process is kinetically retarded. To verify this assumption, we attempted to initiate this elimination. We found that photochemical initiation (daylight irradiation of a solution of **V** in toluene or benzene) actually results in complete transformation of **V** into cluster **VI**, but thermal initiation (heating of a solution of **V** in dichloromethane) does not cause this transformation.

Unlike **Ic**, clusters **Ia** and **Ib** react with [$Mn(CO)_5Cl$] to give **VI** as the major product. The reaction mixture also contains minor amounts of [$Fe_2(CO)_6(\mu\text{-}S_2)$] and [$Fe_3(CO)_9(\mu_3\text{-}S)_2$] (Scheme 5).



Scheme 5.

Meanwhile, no Si-containing compound structurally similar to cluster **V** was observed. If the reaction of **Ia** and **Ib** with [$Mn(CO)_5Cl$] follows the same pathway, the second step is not kinetically retarded and R_2SiCl_2 is readily eliminated without additional activation. Most likely, this is due to the fact that silicon,

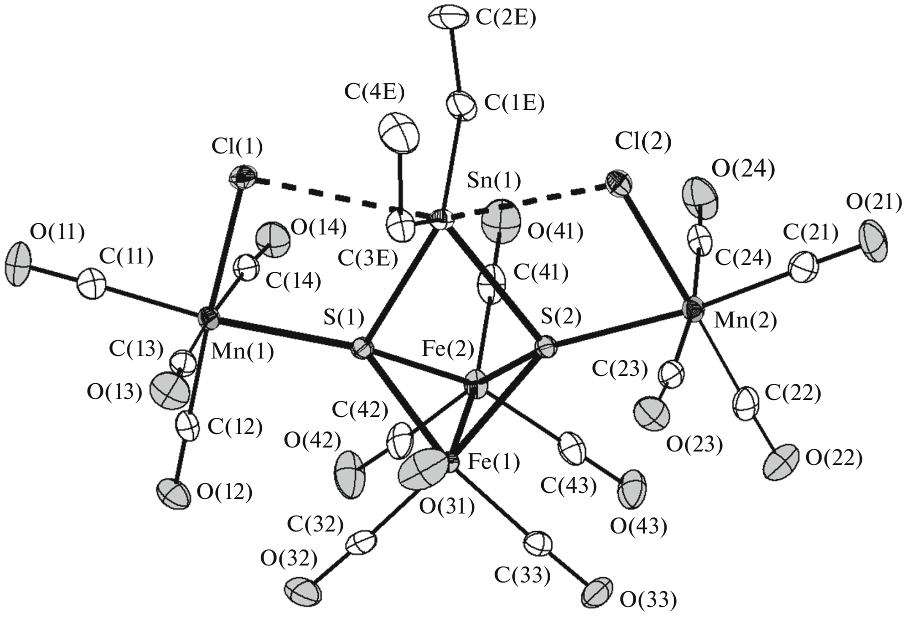


Fig. 3. Structure of cluster **V** in the crystal. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted.

unlike tin, does not tend to have coordination numbers above 4. The presence of the clusters $[Fe_2S_2(CO)_6]$ and $[Fe_3S_2(CO)_9]$ in the reaction mixture is attributable to partial decomposition of reaction intermediates to give thermodynamically more stable complexes.

Thus, we have shown that the reactions of silylated and stannylated complexes $[Fe_2(\mu\text{-}S_2ER_2)(CO)_6]$ (E = Si, Sn) with halogen-containing *d*-metal complexes actually lead to heterometallic clusters and could be used as a new synthetic approach to these clusters. These reactions afford clusters similar to the clusters formed by the conventional pathway: reduction of $[Fe_2(CO)_6(\mu\text{-}S_2)]$ to the dianion and the subsequent treatment of the dianion with electrophilic agents. The advantage of the proposed approach is the possibility of accurate dosing of $[Fe_2(\mu\text{-}S_2ER_2)(CO)_6]$ and their solubility in all organic solvents. However, some specific features should be addressed for carrying out synthetic experiments. For example, in the case of stannylated compounds, it is necessary to take into account that the elimination of R_2SnCl_2 is retarded; therefore, the elimination of this moiety from the intermediate may require photochemical initiation.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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