Organometallic Chemistry

Formation of antiferromagnetic thiolate-bridged and sulfide-bridged complexes

5.* Interactions of phosphinehalide complexes of Re^{I} and Pd^{II} with antiferromagnetic $Cp_2Cr_2(SCMe_3)_2S$ and diamagnetic $Fe_3S_2(CO)_9$ compounds

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Reactions of $Cp_2Cr_2(SCMe_3)_2S$ (**1**) with rhenium complexes $(CO)(NO)Re(PR_3)_2X_2$ [R = Et, X = Cl (**7a**); R = Et, X = O_3SCF_3 (**7b**); R = OMe, X = O_3SCF_3 (**7c**)] containing strongly bound phosphine ligands and with $Pd(PPr^i_3)_2Cl_2$ (**8**) containing bulky P donors were studied. The reaction between compounds **1** and **7a** does not occur in various solvents within a temperature range of 22—80 °C. Interaction of **1** with triflat derivatives **7b** and **7c** yields the paramagnetic tetrahedral homonuclear cationic cluster $Cp_4Cr_4S_4{}^{+}O_3SCF_3{}^{-}$ (**10**) and the binuclear methylated complex $Cp_2Cr_2(SCMe_3)_2(SMe)^{+}O_3SCF_3{}^{-}$ (**11**), respectively. The reaction of compound **1** with **8** affords the antiferromagnetic heteronuclear cluster $Cp_2Cr_2(SCMe_3)S_2PdCl(PPr^i_3)$ (**12**). The structure of the core of **12** is analogous to the structures of the rhodium-containing complexes $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2RhL_2$. Although compound **8** reacts with $Fe_3S_2(CO)_9$ (**5**), the major products are the homometallic trinuclear clusters $Fe_3S_2(CO)_8(PPr^i_3)$ (**14**) (as a mixture of isomers) and $Fe_3S_2(CO)_7(PPr^i_3)_2$ (**15**), whereas the heteronuclear complex $(CO)_6Fe_2S_2Pd(PPr^i_3)_2$ (**16**) was found only in trace amounts. The reasons for the difference in the reactivities of the rhenium and palladium derivatives toward compounds **1** and **5** are discussed. The structures of complexes **10** (two crystal modifications), **11**, **12**, **15**, and **16** were established by X-ray structural analysis of the single crystals.

Key words: phosphinehalide complexes of Re^{I} and Pd^{II}; sulfur-containing clusters, synthesis, structure; magnetic properties.

Recently,[1,2] we have found that the binuclear antiferromagnetic complex $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (**1**) reacts with carbonylnitrosyl compounds of Re^{I} and W^{0}, $Re_2(CO)_4(NO)_2Cl_4$ and $W(CO)_4(NO)I$, to form the antiferromagnetic triangular heteronuclear clusters $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)_2M(NO)X$ [M = Re and X = CO (**2a**); or M = W and X = $SCMe_3$ (**2b**)] containing the nonlinear magnetic $Cp_2Cr_2(\mu\text{-}S)_2$ system. The pro-

* For Part 4, see I. L. Eremenko, S. E. Nefedov, H. Berke, B. I. Kolobkov, and V. M. Novotortsev, *Organometallics*, 1995, **14**, 1132.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 1, pp. 141—152, January, 1997.

1066-5285/97/4601-0137 $18.00

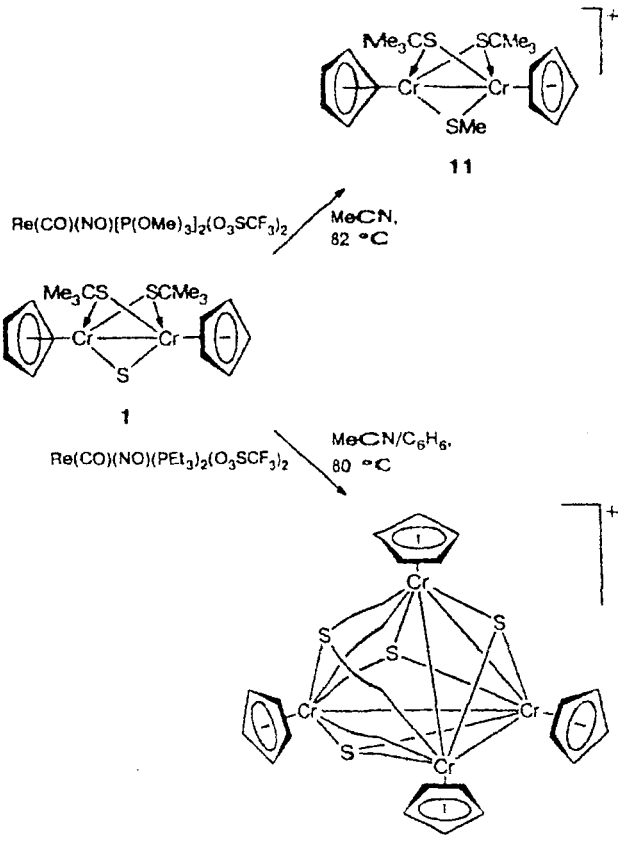
cess of formation of the clusters involves the transfer of a halide atom from "soft" Re or W atoms to "harder" Cr atoms followed by elimination of $CpCrHal_2$ and formation of the heterometallic reactive intermediate $CpCr(\mu\text{-}SCMe_3)_2(\mu\text{-}S)M(NO)L_n$. The latter compound accepts the CpCrS particle generated from complex **1** to yield product **2**.

The analogous Cl/SR exchange was also observed in the reaction of complex **1** with $(Ph_3P)_2PdCl_2$ (**3**). In this case, stable $(CpCrCl)_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)Pd(PPh_3)$ (**4a**) and $(MeC_5H_4CrCl_2)(\mu\text{-}SCMe_3)_2(\mu\text{-}S)Pd(PPh_3)$ (**4b**) clusters were isolated. Unexpectedly, these clusters appear to be ferromagnetics [$2J = +28$ cm^{-1} (**4a**), $+11$ cm^{-1} (**4b**)], and they do not contain metal—metal bonds [**4b**: Cr...Cr, 4.079(1) Å; Pd...Cr, 3.230(1) and 3.380(1) Å].[3] Note that transmetallation, which involved ligand exchange, with the participation of compound **3** and the triangular cluster $Fe_3S_2(CO)_9$ (**5**), yielded the heteronuclear cluster $(CO)_6Fe_2(\mu_3\text{-}S)_2Pd(PPh_3)_2$ (**6**) and $FeCl_2$ precipitated from the reaction mixture.[4] Therefore, the stage of the transfer of a halide atom from the "softer" metal center to the "harder" center is very important in transmetallation and, apparently, should produce stable complexes readily removed from the reaction medium (for example, insoluble $Cp_2Cr_2Cl_4$ [1] or $FeCl_2$ [4]). However, the ligand exchange is most convenient in the case of the previous formation of an adduct, in which metal centers and halide and sulfur atoms (of thiolate ligands) belonging to one molecule are rather close to each other. Therefore, reagents can be chosen that hinder the formation of adducts with compounds **1** or **3** and, therefore, excludes the ligand exchange. This prevents the subsequent transmetallation and, therefore, the formation of heteronuclear clusters analogous to the compounds with Cr_2Re and Cr_2W cores isolated previously.[1,2] In this work, we use the rhenium complexes, which contain strongly bound phosphine ligands $Re(CO)(NO)(PR_3)_2X_2$ [R = Et, X = Cl (**7a**); R = Et, X = O_3SCF_3 (**7b**); and R = OMe, X = O_3SCF_3 (**7c**)], and the palladium complex $(PPr^i_3)_2PdCl_2$ (**8**), in which phosphine ligands contain bulky substituents. In both cases the conditions that prevent the formation of adducts are formally fulfilled, which makes it possible to verify the assumption made.

Results and Discussion

Interaction of $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ with $Re(CO)(NO)(PR_3)_2X_2$. As expected, the mononuclear complex $Re(CO)(NO)(PEt_3)_2Cl_2$ (**7a**) does not react with compound **1** in various solvents (benzene, MeCN, or THF) within the temperature range of 22—80 °C. Boiling of the reagents in toluene resulted only in transformation of complex **1** into the diamagnetic neutral tetrahedral cluster $Cp_4Cr_4S_4$ (**9**), which was obtained previously in the absence of rhenium-containing agents.[5] In this case, compound **7a** remained completely unconsumed in the reaction mixture. In complexes **7b** and **7c**, the triflat O_3SCF_3 ligands are rather labile and can be replaced by N donors, for example, by molecules of pyridine or even acetonitrile.[6] However, complex **7b** appeared to be inactive toward compound **1** in benzene (20—80 °C), whereas when MeCN (MeCN : C_6H_6 = 1 : 1) is present in the reaction mixture, compound **7b** forms the ionic paramagnetic tetranuclear cluster $Cp_4Cr_4S_4^+O_3SCF_3^-$ (**10**, μ'_{eff} = 1.78 μ_B in the temperature range of 295—78 K) (Scheme 1).

Scheme 1



After recrystallization, monoclinic or orthorhombic crystals of complex **10** (as the solvate with CH_2Cl_2) were obtained. In both cases, the results of X-ray structural analysis (Fig. 1, Table 1) indicate to the formal strengthening of the tetrahedral metal Cr_4 core of the cation [the Cr—Cr distances are 2.726(2)—2.804(2) Å (monoclinic modification) and 2.748(3)—2.780(3) Å (orthorhombic modification)] compared to the neutral analog **9** [Cr—Cr, 2.818(3)—2.891(6) Å].[7] Previously, an analogous effect has been observed for the paramagnetic

Table 1. Principal bond lengths (d) and bond angles (ω) in the structures of tetranuclear cations **10** (the monoclinic and orthorhombic modifications)

Bond	d/Å	Angle	ω/deg
	Monoclinic modification		
Cr(1)—Cr(2)	2.750(2)	Cr(1)—S(1)—Cr(2)	78.6(1)
Cr(1)—Cr(3)	2.741(2)	Cr(1)—S(1)—Cr(3)	77.5(1)
Cr(1)—Cr(4)	2.804(2)	Cr(2)—S(1)—Cr(3)	77.9(1)
Cr(2)—Cr(3)	2.726(2)	Cr(2)—S(2)—Cr(3)	76.9(1)
Cr(2)—Cr(4)	2.756(2)	Cr(2)—S(2)—Cr(4)	78.0(1)
Cr(3)—Cr(4)	2.754(2)	Cr(3)—S(2)—Cr(4)	78.2(1)
Cr(1)—S(1)	2.193(4)	Cr(1)—S(3)—Cr(3)	75.0(1)
Cr(1)—S(3)	2.248(2)	Cr(1)—S(3)—Cr(4)	77.6(1)
Cr(1)—S(4)	2.246(2)	Cr(3)—S(3)—Cr(4)	75.8(1)
Cr(2)—S(1)	2.149(3)	Cr(1)—S(4)—Cr(2)	75.5(1)
Cr(2)—S(2)	2.199(3)	Cr(1)—S(4)—Cr(4)	77.1(1)
Cr(2)—S(4)	2.245(3)	Cr(2)—S(4)—Cr(4)	75.6(1)
Cr(3)—S(1)	2.184(3)		
Cr(3)—S(2)	2.184(3)		
Cr(3)—S(3)	2.256(3)		
Cr(4)—S(2)	2.181(4)		
Cr(4)—S(3)	2.227(2)		
Cr(4)—S(4)	2.255(2)		
	Orthorhombic modification		
Cr(1)—Cr(2)	2.777(3)	Cr(1)—S(1)—Cr(2)	76.6(1)
Cr(1)—Cr(3)	2.748(3)	Cr(1)—S(1)—Cr(4)	76.6(1)
Cr(1)—Cr(4)	2.774(3)	Cr(2)—S(1)—Cr(4)	76.8(1)
Cr(2)—Cr(3)	2.766(4)	Cr(2)—S(2)—Cr(3)	76.4(1)
Cr(2)—Cr(4)	2.780(4)	Cr(2)—S(2)—Cr(4)	76.8(1)
Cr(3)—Cr(4)	2.777(3)	Cr(3)—S(2)—Cr(4)	76.6(1)
Cr(1)—S(1)	2.241(4)	Cr(1)—S(3)—Cr(2)	77.7(2)
Cr(1)—S(3)	2.227(5)	Cr(1)—S(3)—Cr(3)	76.1(2)
Cr(1)—S(4)	2.213(5)	Cr(2)—S(3)—Cr(3)	77.3(2)
Cr(2)—S(1)	2.238(5)	Cr(1)—S(4)—Cr(3)	76.7(2)
Cr(2)—S(2)	2.229(5)	Cr(1)—S(4)—Cr(4)	78.1(2)
Cr(2)—S(3)	2.201(5)	Cr(3)—S(4)—Cr(4)	78.2(2)
Cr(3)—S(2)	2.242(4)		
Cr(3)—S(3)	2.229(5)		
Cr(3)—S(4)	2.213(6)		
Cr(4)—S(1)	2.236(5)		
Cr(4)—S(2)	2.240(5)		
Cr(4)—S(4)	2.189(5)		

cluster $(MeC_5H_4)_4Cr_4S_4^+Sn(THF)Cl_5^-$ and the antiferromagnetic cluster $(MeC_5H_4)_4Cr_4S_4^+(MeC_5H_4)CrBr_3^-$.[8]

According to the results of calculations and the data of photoelectron spectroscopy, in neutral molecule **9**, the highest occupied level is $1t_2^6$. In this case, removal of one electron ($1t_2^5$) results in the fact that the lone electron pairs of the bridging S atoms are involved in bonding of the metal core.[9] Therefore, the total delocalization of the electron density is enhanced, and the core contracts. This effect is well illustrated by the data of the precision determination of the difference electron density obtained for the 60-electron cluster $(MeC_5H_4)_4Cr_4S_4$ (HOMO $1t_2^6$)[10] and the 56-electron vanadium analog $(MeC_5H_4)_4V_4S_4$ (HOMO $1t_2^2$).[11] For example, in the electron-deficient vanadium-containing cluster, the lone electron pairs on the S atoms are

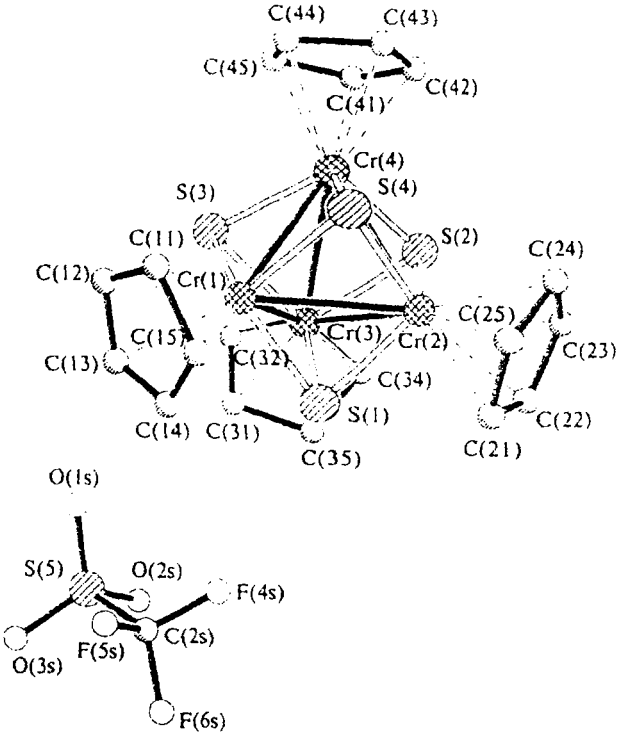


Fig. 1. Molecular structure of the complex $Cp_4Cr_4S_4^+O_3SCF_3^-$ (**10**).

substantially delocalizied over the metal centers, and the electron density on the V—S and V—V bonds is substantially increased.

Analog of **7b**, $Re(CO)(NO)[P(OMe)_3]_2(O_3SCF_3)_2$ (**7c**), also did not react with compound **1** in benzene (20—80 °C), whereas in MeCN, the complex $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}SMe)^+O_3SCF_3^-$ (**11**) formed. According to the data of X-ray structural analysis (Fig. 2, Table 2), the cation of molecule **11** contains two *tert*-butylthiolate [Cr—S, 2.347(3)—2.361(3) Å] and one methylthiolate bridges [Cr—S, 2.353(3) and 2.357(3) Å] between two equivalent CpCr fragments. The occurrence of the third SMe bridge results in strengthening of intramolecular nonbonded interactions [C(R)...C(R'), 3.0—3.1 Å]. The Cr—Cr bond length [2.766(2) Å] in the cation is substantially longer than the analogous value in neutral complex **1** [2.698(8) Å].[5] Such weakening of the metal—metal bond manifests itself in the energy of spin-spin exchange interactions. For compound **11**, the value of $-2J$ (313 cm^{-1}) calculated within the framework of the Heisenberg—Dirac—Van Vleck dimeric model[12,13] is substantially smaller than the value of $-2J$ (430 cm^{-1}) observed for complex **1**. However, the magnetic behavior of **11** is analogous to the behavior of $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}SMe)^+I^-$ ($-2J$ = 350 cm^{-1}), which we obtained previously[14] by the reaction of MeI with **1**, and to the behavoir of the isomeric adducts $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)Re(CO)_2(NO)Cl_2$

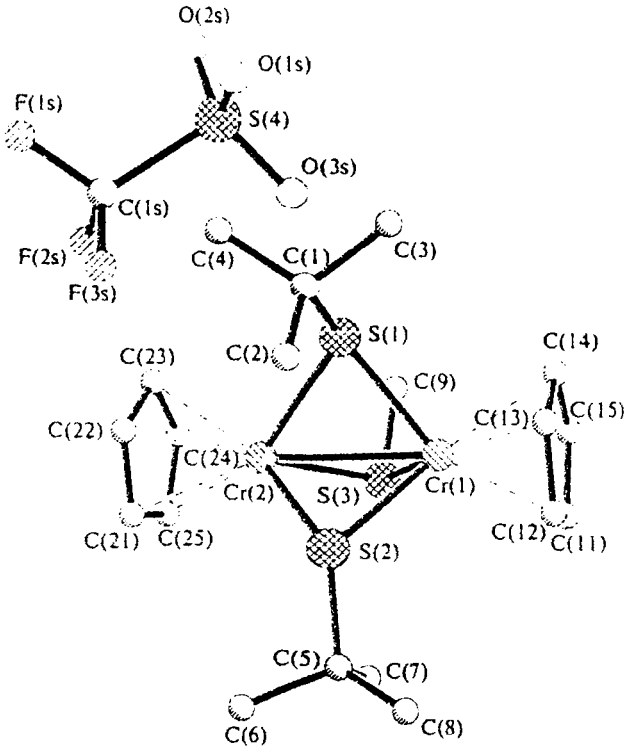


Fig. 2. Structure of the binuclear ionic complex $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}SMe)^+O_3SCF_3^-$ (**11**).

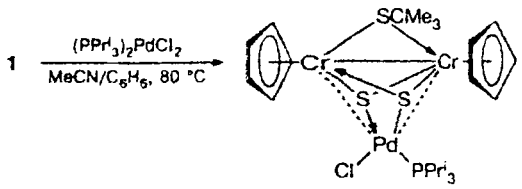
Table 2. Principal bond lengths (d) and bond angles (ω) in the structure of binuclear methylated cation **11**

Bond	d/Å	Angle	ω/deg
Cr(1)—Cr(2)	2.766(2)	Cr(1)—S(1)—Cr(2)	72.1(1)
Cr(1)—S(2)	2.361(3)	Cr(1)—S(3)—Cr(2)	71.9(1)
Cr(2)—S(1)	2.347(2)	Cr(1)—S(2)—Cr(2)	71.8(1)
Cr(2)—S(3)	2.353(3)		
Cr(1)—S(1)	2.355(3)		
Cr(1)—S(3)	2.357(3)		
Cr(2)—S(2)	2.356(3)		

($-2J$ = 328 cm^{-1}) containing the elongated Cr—Cr bond [2.788(3) and 2.777(6) Å for the compounds with the *trans*- and *cis*-S—Re—NO fragments, respectively].[1]

Interaction of $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ with $(PPr^i_3)_2PdCl_2$. As in the case of rhenium-containing complexes **7a—c**, $(PPr^i_3)_2PdCl_2$ (**8**) did not react with compound **1** in benzene or toluene within the temperature range of 20—80 °C. However, when MeCN (MeCN : C_6H_6 = 1 : 1) was added, the triangular cluster $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2PdCl(PPr^i_3)$ (**12**) formed (Scheme 2). Complex **12** is rather stable in air in the solid state, but it readily decomposes in solution. According to the data of X-ray structural analysis, this compound contains the binuclear fragment $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu\text{-}S)_2$ [Cr—Cr, 2.690(14) Å, the

Scheme 2



12

Cp_c—Cr—Cr angle is 174.2(3)°]. Two sulfide bridges of this fragment are bonded to the Pd atom [Pd—S, 2.314(6) and 2.370(6) Å] (Fig. 3, Table 3). The Pd—Cr distances [3.112(8) Å] correspond to the one-electron bond between metal atoms, which occurs through overlapping of half-occupied orbitals of the Cr^{III} atoms and occupied (or unoccupied) orbitals of the Pd atom (16-electron environment). As a result, the Pd^{II} atom in the cluster is in a planar-square ligand environment (except for the Cr—Pd bonds). This situation is similar to that observed previously for the Rh-containing clusters $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2RhL_2$ [L_2 = $(CO)_2$ (**13**): Cr—Cr, 2.708(1) Å; Cr—Rh, 3.010(1) and 3.134(1) Å [15]; L_2 is cyclooctadiene: Cr—Cr, 2.686(1) and 2.688(1) Å, Cr—Rh, 3.064(1)—3.009(1) Å in two independent molecules[16]]. Therefore, it is not surprising that the magnetic properties of these compounds are also similar [$-2J$ = 570 cm^{-1} (**12**), 592 and 568 cm^{-1} (**13**)]. It should be noted that although heterometallic cluster **12** with the Cr_2Pd core forms in this case, its structural type differs from that found for the heterometallic triangular clusters, the products of the interactions of compound **1** and rhenium-containing and tungsten-containing reagents with halide atoms.[1,2] Therefore, the preferential formation of cluster **12** in the reaction under study (the yield of the product was 60%) indicates, apparently, that the conditions for the transfer of Cl atoms to Cr atoms, which are necessary for transmetallation, are absent. It can be suggested that, as in the case of formation of the rhodium-containing clusters,[15,16] the halide atom is eliminated from compound **8** as Bu^tCl. By contrast, the interaction of the triphenylphosphine complex of palladium **3**, which involves the ligand exchange, affords ferromagnetic clusters **4** in high yields (~90%).[3]

The difference in the steric effects of phosphine ligands may be responsible for the difference in the reactivity of palladium reagents **3** and **8** toward complex **1**. Because the Tolman angle in the trisisopropylphosphine molecule is substantially larger (160°) than that in PPh_3 (144°),[17] the formation of an intermediate adduct in the reaction of compound **1** with **8** is hindered, which more likely leads to the cleavage of the Pd—Cl bond in the presence of polar molecules of acetonitrile and to the outer-sphere attack of the Cl^-

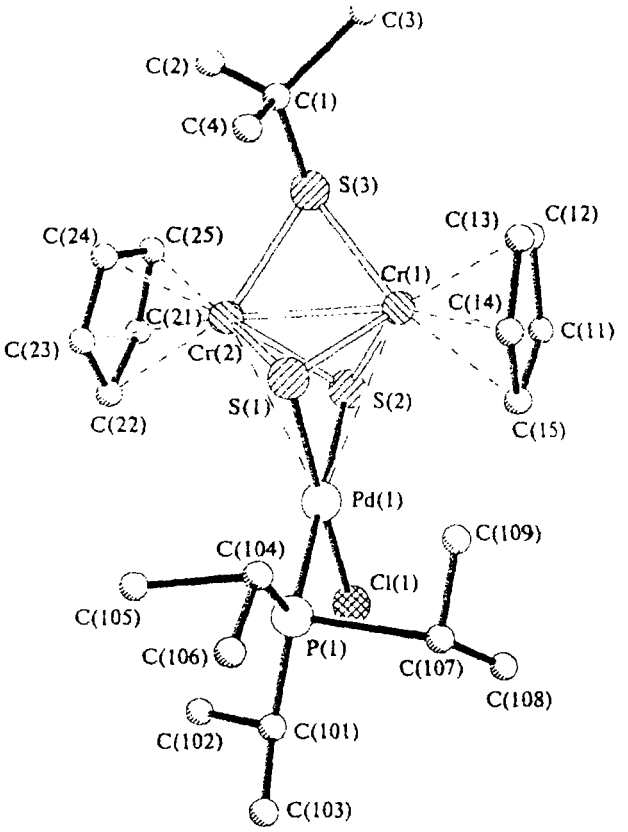


Fig. 3. Structure of the heteronuclear cluster $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2PdCl(PPr^i_3)$ (**12**).

ion on the tertiary C atom of the Bu^{t}Cl bridge. As a result, the *tert*-butylchloride is eliminated, and the binuclear particle $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu\text{-}S)_2^-$ that forms attacks $(PPr^i_3)_2PdCl(MeCN)^+$, followed by elimination of one phosphine ligand and formation of cluster **12**.

Interaction of $Fe_3S_2(CO)_9$ with $(PPr^i_3)_2PdCl_2$. The reaction of compound **5** with **8** proceeds in benzene only upon heating. In this case, the major products of the reaction were the products of neutral ligand exchange, the trinuclear iron complexes containing one or two phosphine ligands [$Fe_3S_2(CO)_8(PPr^i_3)$ (**14**) and $Fe_3S_2(CO)_7(PPr^i_3)_2$ (**15**), respectively], whereas the heteronuclear cluster $(CO)_6Fe_2S_2Pd(PPr^i_3)_2$ (**16**) was observed only in trace amounts (<1%) (Scheme 3). Compounds **14** (as a mixture of isomers), **15**, and **16** were separated by column chromatography. The struc-

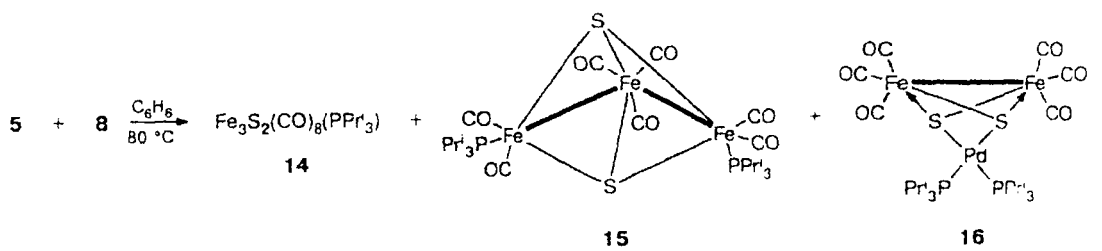
Table 3. Principal bond lengths (d) and bond angles (ω) in the heteronuclear core of cluster **12**

Bond	d/Å	Angle	ω/deg
Pd(1)—S(1)	2.314(6)	S(1)—Pd(1)—S(2)	82.6(2)
Pd(1)—P(1)	2.318(7)	S(2)—Pd(1)—P(1)	177.6(2)
Cr(1)—Cr(2)	2.690(14)	S(2)—Pd(1)—Cl(1)	90.5(2)
Cr(1)—S(2)	2.267(13)	Pd(1)—S(1)—Cr(1)	85.1(3)
Cr(2)—S(1)	2.325(14)	Pd(1)—S(2)—Cr(1)	84.6(3)
Cr(2)—S(3)	2.284(14)	Cr(1)—S(1)—Cr(2)	71.0(4)
Pd(1)—S(2)	2.370(6)	Cr(1)—S(3)—Cr(2)	96.7(4)
Pd(1)—Cl(1)	2.350(6)	S(1)—Pd(1)—P(1)	95.0(2)
Cr(1)—S(1)	2.305(14)	S(1)—Pd(1)—Cl(1)	172.9(3)
Cr(1)—S(3)	2.418(15)	P(1)—Pd(1)—Cl(1)	92.0(2)
Cr(2)—S(2)	2.363(14)	Pd(1)—S(1)—Cr(2)	85.8(3)
		Pd(1)—S(2)—Cr(2)	83.7(3)
		Cr(1)—S(2)—Cr(2)	71.0(4)

Table 4. Principal bond lengths (d) and bond angles (ω) in the iron-sulfide core of diphosphine cluster **15**

Bond	d/Å	Angle	ω/deg
	Molecule A		
Fe(1)—Fe(2)	2.566(2)	S(1)—Fe(1)—P(1)	109.0(1)
Fe(2)—Fe(3)	2.641(2)	S(2)—Fe(1)—P(1)	107.1(1)
Fe(1)—S(1)	2.263(3)	S(1)—Fe(3)—P(2)	171.2(1)
Fe(1)—S(2)	2.251(3)	S(2)—Fe(3)—P(2)	94.5(1)
Fe(2)—S(1)	2.268(3)	Fe(1)—S(1)—Fe(2)	69.0(1)
Fe(2)—S(2)	2.282(3)	Fe(1)—S(1)—Fe(3)	100.2(1)
Fe(3)—S(1)	2.268(3)	Fe(2)—S(1)—Fe(3)	71.2(1)
Fe(3)—S(2)	2.236(3)	Fe(1)—S(2)—Fe(2)	68.9(1)
Fe(1)—P(1)	2.255(4)	Fe(1)—S(2)—Fe(3)	101.6(1)
Fe(1)—P(2)	2.318(3)	Fe(2)—S(2)—Fe(3)	71.5(1)
	Molecule B		
Fe(4)—Fe(5)	2.630(2)	S(3)—Fe(4)—P(3)	94.6(1)
Fe(5)—Fe(6)	2.569(2)	S(4)—Fe(4)—P(3)	169.1(1)
Fe(4)—S(3)	2.238(3)	S(3)—Fe(6)—P(4)	103.8(1)
Fe(4)—S(4)	2.263(3)	S(4)—Fe(6)—P(4)	108.4(1)
Fe(5)—S(3)	2.271(3)	Fe(4)—S(3)—Fe(5)	71.4(1)
Fe(5)—S(4)	2.266(3)	Fe(4)—S(3)—Fe(6)	101.8(1)
Fe(6)—S(3)	2.255(3)	Fe(5)—S(3)—Fe(6)	69.2(1)
Fe(6)—S(4)	2.255(3)	Fe(4)—S(4)—Fe(5)	71.0(1)
Fe(4)—P(3)	2.330(3)	Fe(4)—S(4)—Fe(6)	101.0(1)
Fe(6)—P(4)	2.241(4)	Fe(5)—S(4)—Fe(6)	69.3(1)

Scheme 3



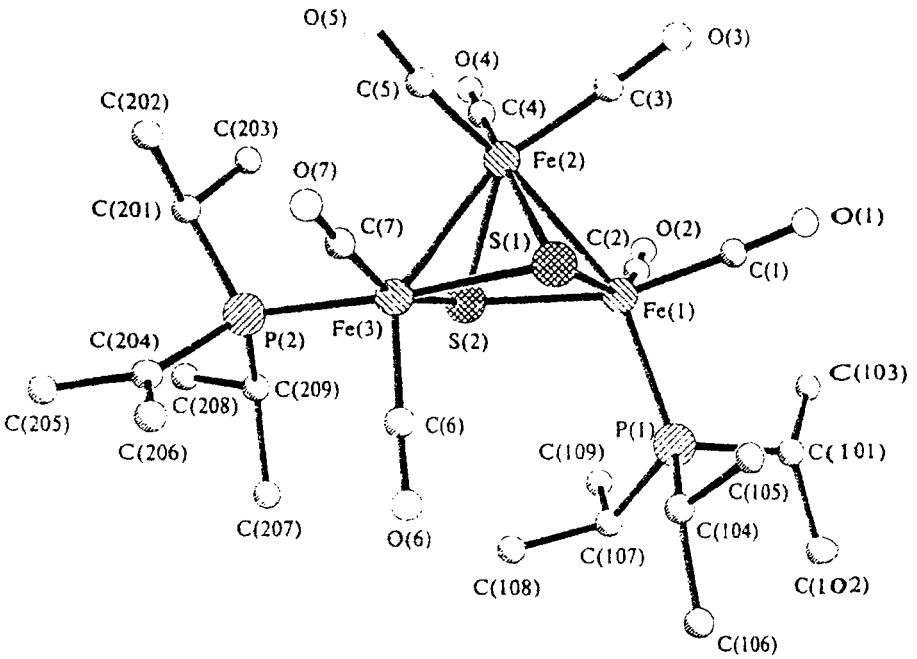


Fig. 4. Structure of one independent $Fe_3S_2(CO)_7(PPr^i_3)_2$ molecule (**15**).

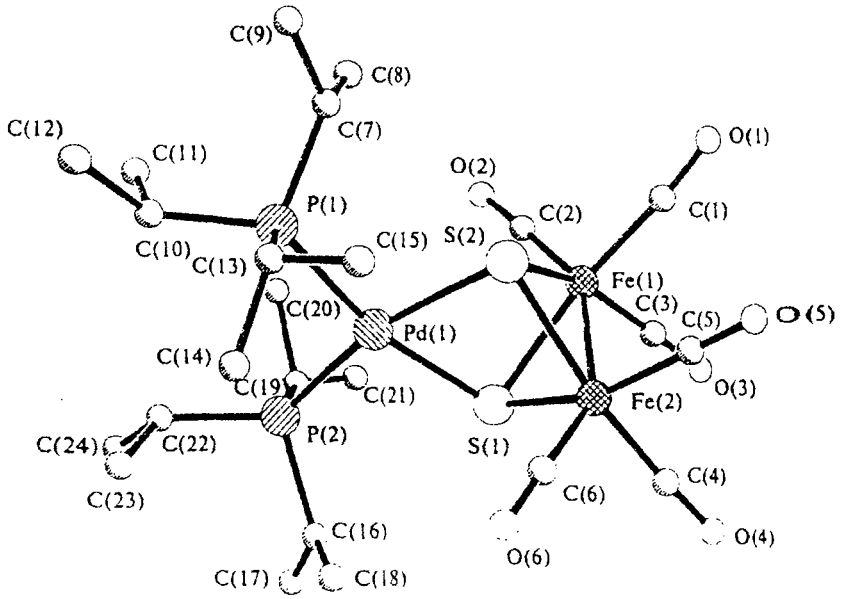


Fig. 5. Structure of the heteronuclear cluster $(CO)_6Fe_3S_2Pd(PPr^i_3)_2$ (**16**).

tures of **15** and **16** were established by X-ray structural analysis (Figs. 4, 5 and Tables 4, 5, respectively). Similar to the known structure of **5**,[18] diphosphine cluster **15** has the triangular Fe_3 core with two metal—metal bonds [2.566(2), 2.641(2) Å and 2.569(2), 2.630(2) Å in two independent molecules A and B, respectively], whereas the third Fe—Fe distance is nonbonding (>3.2 Å). The tridentate S atoms are located above and below the plane of the metal triangle [Fe—S, 2.236(3)—2.282(3) Å and 2.238(3)—2.271(3) Å in two independent molecules A and B, respectively] and form an almost planar Fe_2S_2 fragment containing Fe atoms, which are not bonded to each other. Each Fe atom of this ring has two carbonyl groups and one phosphine ligand [Fe—P, 2.255(4), 2.318(3) Å and 2.241(4), 2.350(4) Å], unlike the central Fe atom, which is

Table 5. Principal bond lengths (d) and bond angles (ω) in the structure of heteronuclear cluster **16**

Bond	d/Å	Angle	ω/deg
Pd(1)—S(1)	2.332(7)	S(1)—Pd(1)—S(2)	74.3(2)
Pd(1)—P(1)	2.362(7)	S(2)—Pd(1)—P(1)	89.4(2)
Fe(1)—Fe(2)	2.508(4)	S(2)—Pd(1)—P(2)	162.7(2)
Fe(1)—S(2)	2.275(7)	Pd(1)—S(1)—Fe(1)	93.9(2)
Fe(2)—S(2)	2.264(7)	Pd(1)—S(2)—Fe(1)	93.9(2)
Pd(1)—S(2)	2.330(7)	Fe(1)—S(1)—Fe(2)	66.8(2)
Pd(1)—P(2)	2.356(7)	S(1)—Pd(1)—P(1)	163.7(2)
Fe(1)—S(1)	2.274(7)	S(1)—Pd(1)—P(2)	88.5(2)
Fe(2)—S(1)	2.281(7)	P(1)—Pd(1)—P(2)	107.8(2)
		Pd(1)—S(1)—Fe(2)	94.1(2)
		Pd(1)—S(2)—Fe(2)	94.6(2)
		Pd(1)—S(2)—Fe(2)	67.1(2)

bonded to three carbonyl groups. The phosphine ligands in the molecule are in different orientations: one ligand lies almost in the Fe_2S_2 plane, and the second ligand is located above this plane. Based on the structural data of disubstituted derivative **15**, the isomeric composition of monophosphine complex **14** can be suggested. As in the case of the selenium-containing cluster $(CO)_6Fe_3Se_2(PR_3)_2$,[19] at least three positional isomers can occur for compound **14**: two isomers with the phosphine groups, which are bonded to only one terminal Fe atom and have different orientations with respect to the Fe_3 plane (as, for example, in compound **15**), and the third isomer in which the PR_3 group is coordinated to the central Fe atom. This agrees with the ^{31}P NMR spectra of a solution of compound **14** in toluene at −100 °C (three signals at δ 96.0, 79.0, and 51.1 with the intensity ratio of 2 : 1 : 1).

Molecule **16** contains the binuclear fragment $(CO)_6Fe_2S_2$ [Fe—Fe, 2.508(4) Å; Fe—S, 2.264(7)—2.281(7) Å] with the eclipsed orientations of the $Fe(CO)_3$ groups, which manifests themselves in the IR spectrum as three ν(CO) bands at 2043, 1998, and 1956 cm^{-1}. Two sulfide bridges of the diiron disulfide system are bonded to the Pd atom of the $Pd(PPr^i_3)_2$ fragment [Pd—S, 2.330(7) and 2.332(7) Å; Pd—P, 2.356(7) and 2.362(7) Å]. However, the Pd—Fe distances are nonbonding (Pd...Fe >3.2 Å). The general geometric parameters of molecule **16** are very close to those for the $(CO)_6Fe_2(\mu_3\text{-}S)_2Pd(PPh_3)_2$ cluster (**6**) [Fe—Fe, 2.504(5) Å; Fe—S, 2.266(8)—2.299(8) Å; Pd—S, 2.311(7)—2.348(7) Å; Pd—P, 2.305(7)—2.334(7) Å].[3]

Therefore, studies of the reactivities of rhenium and palladium complexes with strongly bound ligands (in the case of the Re complexes) and with bulky ligands (the Pd compound) under conditions that hinder the formation of intermediate adducts with complexes **1** and **5** demonstrated that the intramolecular transfer of halide atoms to the Cr or Fe atoms does not occur. As a result, transmetallation and, therefore, formation of a new cluster heterometallic core with the nonlinear magnetic $Cp_2Cr_2S_2$ system, which were observed previously for rhenium and tungsten complexes with the readily eliminated carbonyl groups, are unfavorable.[1,2]

Experimental

The initial reagents and the final products were synthesized under an atmosphere of pure nitrogen. Benzene, toluene, THF, and diethyl ether were purified by distillation with sodium benzophenone ketyl. Hexane and heptane were distilled over a sodium dispersion under a concurrent flow of nitrogen or argon. MeCN and CH_2Cl_2 were twice distilled over P_2O_5. The course of the reaction was monitored by TLC (Merck, 5×7.5 cm, Kieselgel 60, 70 F_{254}). Wherever possible, the mixtures of the compounds formed were separated by column chromatography (Merck, Kieselgel 60, 70—230 ASTM). The IR spectra were recorded on a BIO-RAD FTS-45 instrument (as KBr pellets). The mass spectra were measured on a Finnigan MAT 8320 spectrometer (70 eV). The ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 instrument (at 300.1 and 75.5 MHz, respectively). The ^{31}P NMR spectra were recorded at 121.5 MHz, the chemical shifts were measured relative to 85% H_3PO_4 (the external standard). The temperature dependence of the magnetic susceptibility was measured using the Faraday method in the range of 79—296 K.

Reaction of compound 1 with complex 7b. A solution of compounds **1** (360 mg, 0.81 mmol) and **7b** (622 mg, 0.80 mmol) in a 1 : 1 benzene—MeCN mixture (50 mL) (violet) was boiled for 18 h. The brown solution that formed was concentrated to dryness at 60 °C (0.1 Torr). The solid residue was extracted with a 1 : 1 benzene—CH_2Cl_2 mixture (40 mL). The extract was concentrated to 15 mL and cooled to 5 °C. The brown crystals (plates, the monoclinic modification) that precipitated were separated, washed with hexane, and dried *in vacuo*. The yield of $Cp_4Cr_4S_4^+O_3SCF_3^-$ (**10**) obtained as a solvate **10** · CH_2Cl_2 was 280 mg (0.34 mmol, 83.9%). Found (%): C, 31.41; H, 3.11; S, 19.48. $C_{22}H_{22}Cl_2Cr_4F_3O_3S_5$. Calculated (%): C, 31.81; H, 2.65; S, 19.30. IR, ν/cm^{-1}: 3099 m, 2954 m, 2852 m, 1460 w, 1429 m, 1377 w, 1362 w, 1263 s, 1223 m, 1147 m, 1066 w, 1027 m, 1007 w, 823 m, 754 w, 727 w, 636 m, 570 w, 516 w, 475 w.

Recrystallization of compound **10** from a CH_2Cl_2—heptane mixture (2 : 1) afforded brown prisms belonging to the orthorhombic system. Both crystal modifications were studied by X-ray structural analysis.

Reaction of compound 1 with complex 7c. A solution of compounds **1** (190 mg, 0.44 mmol) and **7c** (320 mg, 0.44 mmol) in MeCN (30 mL) (violet) was boiled for 12 h. The dark-violet solution, which contained no initial reagents (according to the TLC data), was chromatographed on a silica gel layer (5×20 cm, THF), and the violet zone was separated. The eluate was concentrated to 10 mL. Then heptane (1 mL) was added, and the solution was cooled to −10 °C. The needle-like black-violet crystals that formed were decanted from the solution, washed with hexane, and dried *in vacuo*. The yield of $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}SMe)^+O_3SCF_3^-$ (**11**) was 230 mg (0.38 mmol, 86.3%). Found (%): C, 39.24; H, 4.88. $C_{20}H_{31}Cr_2F_3O_3S_4$. Calculated (%): C, 39.47; H, 5.10. IR, ν/cm^{-1}: 3081 m, 2984 m, 2959 m, 2854 w, 1468 w, 1456 w, 1431 w, 1064 w, 1028 s, 1006 w, 821 s, 748 w, 636 s, 591 w, 575 w, 515 m, 417 w.

Table 6. Crystallographic data for the compounds studies

Parameter	**10** (monoclinic)	**10** (orthorhombic)	**11**	**12**	**15**	**16**
Molecular formula	$C_{21}H_{20}Cr_4F_3O_3S_5 \cdot CH_2Cl_2$	$C_{21}H_{20}Cr_4F_3O_3S_5 \cdot CH_2Cl_2$	$C_{20}H_{31}Cr_2F_3O_3S_4$	$C_{29}H_{40}Cr_2ClPPdS_3 \cdot C_6H_6$	$C_{25}H_{42}Fe_3O_7P_2S_2$	$C_{24}H_{42}Fe_2O_6P_2PdS_2$
Space group	$P2_1/n$	$P2_12_12_1$	$P2_1/c$	$Pna2_1$	$P\bar{1}$	$P2_1/n$
a/Å	17.343(5)	9.579(3)	14.869(5)	29.443(15)	13.061(5)	11.241(4)
b/Å	9.585(3)	16.555(7)	14.567(4)	12.040(5)	15.222(5)	17.397(6)
c/Å	18.508(5)	17.978(6)	13.357(3)	9.927(5)	16.970(5)	18.404(8)
α/deg					85.57(2)	
β/deg	108.21(2)		113.76(2)		89.94(2)	107.44(2)
γ/deg					86.96(2)	
V/Å^3	2922(1)	2852(2)	2648(1)	3581(3)	3360(2)	3433(2)
Z	4	4	4	4	4	4
d_{calc}/g cm^{-3}	1.883	1.934	1.527	1.438	1.491	1.458
μ/cm^{-1}	20.33	20.83	11.77	14.28	15.99	15.35
θ/2θ scanning range	3–52°	4–56°	3–52°	3–52°	3–48°	3–48°
Number of measured reflections	5758	3829	5188	3684	8839	4806
Number of reflections with $I > 4.0\sigma(I)$	3400	1919	2359	1065	4191	1853
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.010F^2$	$w^{-1} = \sigma^2(F) + 0.001F^2$	$w^{-1} = \sigma^2(F) + 0.018F^2$	$w^{-1} = \sigma^2(F) + 0.0353F^2$	$w^{-1} = \sigma^2(F) + 0.0011F^2$	$w^{-1} = \sigma^2(F) + 0.0029F^2$
R	0.055	0.061	0.048	0.059	0.070	0.049
R_w	0.084	0.053	0.062	0.073	0.078	0.061

Table 7. Atomic coordinates ($\times 10^4$) and isotropic temperature factors (U_{eq}) for cluster **10** (the monoclinic modification)

Atom	x	y	z	$U_{eq}/Å^2$
Cr(1)	3039(1)	1758(1)	6543(1)	35(1)
Cr(2)	3245(1)	2552(1)	5187(1)	42(1)
Cr(3)	2621(1)	−11(1)	5318(1)	39(1)
Cr(4)	1691(1)	2335(1)	5273(1)	37(1)
S(1)	3812(2)	860(3)	5923(2)	91(1)
S(2)	2177(2)	1514(3)	4405(2)	79(1)
S(3)	1877(1)	552(2)	6081(1)	49(1)
S(4)	2686(1)	3792(2)	5925(1)	46(1)
C(11)	3209(13)	2860(16)	7619(6)	154(9)
C(12)	2927(7)	1517(22)	7692(5)	111(7)
C(13)	3467(8)	611(12)	7617(5)	83(4)
C(14)	4082(6)	1269(13)	7535(5)	77(4)
C(15)	3975(9)	2625(14)	7521(6)	105(6)
C(21)	4480(7)	3076(21)	5197(9)	120(8)
C(22)	4084(9)	2454(17)	4511(9)	113(8)
C(23)	3483(8)	3270(13)	4142(6)	85(5)
C(24)	3456(8)	4449(11)	4561(6)	88(5)
C(25)	4087(10)	4312(18)	5229(8)	116(7)
C(31)	2932(8)	−2196(9)	5656(6)	82(5)
C(32)	2129(8)	−2185(10)	5347(7)	86(5)
C(33)	1945(7)	−1754(11)	4614(7)	91(5)
C(34)	2641(11)	−1530(11)	4421(6)	98(7)
C(35)	3307(7)	−1794(11)	5104(10)	106(7)
C(41)	432(6)	2130(13)	4486(7)	88(5)
C(42)	735(6)	3306(15)	4310(6)	82(5)
C(43)	899(6)	4173(11)	4940(11)	126(8)
C(44)	680(7)	3394(19)	5518(7)	104(6)
C(45)	377(6)	2196(14)	5215(7)	88(5)
S(5)	4777(1)	−3475(2)	7588(1)	50(1)
O(1s)	4071(4)	−2700(8)	7572(5)	88(3)
O(2s)	4695(5)	−4248(8)	6892(4)	95(3)
O(3s)	5163(4)	−4214(7)	8280(4)	71(2)
C(2s)	5508(5)	−2147(9)	7578(5)	57(3)
F(4s)	5265(4)	−1344(7)	6961(4)	97(3)
F(5s)	5648(4)	−1311(6)	8172(3)	94(3)
F(6s)	6216(3)	−2717(7)	7591(4)	94(3)
Cl(1)	1148(3)	2977(4)	2208(3)	123(2)
Cl(2)	2325(2)	742(4)	2461(2)	106(1)
C(1s)	1315(7)	1168(12)	2353(10)	113(7)

Table 8. Atomic coordinates ($\times 10^4$) and isotropic temperature factors (U_{eq}) for cluster **10** (the orthorhombic crystals)

Atom	x	y	z	$U_{eq}/Å^2$
Cr(1)	1586(2)	6597(1)	9032(1)	23(1)
Cr(2)	2170(3)	7609(1)	7841(1)	33(1)
Cr(3)	−244(2)	6692(2)	7859(1)	27(1)
Cr(4)	2325(3)	5943(1)	7668(1)	29(1)
S(1)	3599(4)	6737(3)	8411(2)	34(1)
S(2)	1290(4)	6852(3)	6929(2)	39(1)
S(3)	417(5)	7675(3)	8630(2)	45(1)
S(4)	604(5)	5599(3)	8404(3)	53(1)
C(11)	1047(17)	7040(11)	10157(8)	57(2)
C(12)	485(17)	6300(9)	10064(8)	52(2)
C(13)	1442(21)	5739(12)	9959(9)	81(2)
C(14)	2728(20)	6104(14)	10008(9)	119(2)
C(15)	2506(15)	6968(13)	10103(8)	77(2)
C(21)	3524(23)	8607(11)	8109(13)	123(2)
C(22)	2263(25)	8913(9)	8011(11)	153(2)
C(23)	1905(20)	8824(11)	7281(11)	92(2)
C(24)	2961(18)	8466(10)	6955(9)	67(2)
C(25)	4012(19)	8334(14)	7460(12)	120(2)
C(31)	−2456(13)	6624(11)	8232(9)	48(2)
C(32)	−2280(13)	7305(11)	7833(11)	59(2)
C(33)	−1856(15)	6229(14)	7107(9)	82(2)
C(34)	−1882(16)	7060(14)	7089(14)	114(2)
C(35)	−2178(15)	6000(11)	7761(12)	70(2)
C(41)	3170(20)	5349(15)	6661(11)	136(2)
C(42)	2181(16)	4929(13)	6863(12)	99(2)
C(43)	2727(21)	4663(9)	7616(12)	96(2)
C(44)	3991(17)	5041(12)	7692(12)	92(2)
C(45)	4177(19)	5495(14)	7080(13)	108(2)
S(5)	6390(4)	5109(2)	9986(2)	38(1)
F(1)	8681(10)	4480(7)	9466(5)	70(2)
F(2)	8559(9)	4528(6)	10648(5)	58(2)
F(3)	7363(10)	3653(5)	10080(6)	67(2)
O(1)	5599(10)	4917(7)	10638(6)	49(2)
O(2)	5741(11)	4906(7)	9289(6)	60(2)
O(3)	7034(12)	5892(7)	10003(6)	60(2)
C(1s)	7803(14)	4427(10)	10039(9)	39(2)
C(2s)	3803(20)	3270(15)	9844(11)	137(2)
Cl(2s)	4476(11)	2673(8)	9239(9)	249(2)
Cl(1s)	2063(11)	3495(5)	9614(6)	201(2)

Crystals suitable for X-ray structural analysis were obtained by recrystallization of the complex from a benzene—CH_2Cl_2 mixture (2 : 1).

Complex $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2PdCl(PPr^i_3)$ (12). A solution of compounds **1** (880 mg, 2 mmol) and **8** (960 mg, 1.98 mmol) in a 1 : 1 benzene—MeCN mixture (70 mL) (violet) was boiled for 5 h. The black-violet solution, which contained only one product (according to the TLC data), was chromatographed on a column (5×30 cm); the black-violet zone was eluted with a 1 : 1 : 1 benzene—CH_2Cl_2—Et_2O mixture. The eluate (50 mL) was concentrated to 10 mL and cooled to 5 °C. The needle-like crystals of **12** that precipitated were separated from the solution, washed with hexane, and dried *in vacuo*. The yield of complex **12** was 780 mg (1.13 mmol, 60%). Found (%): C, 40.08; H, 5.55; Cl, 5.45. $C_{29}H_{40}ClCr_2PPdS_3$. Calculated (%): C, 40.00; H, 5.80; Cl, 5.15. MS (FAB), *m/z*: 690 [M^+]. IR, ν/cm^{-1}: 3084 m, 2970 m, 2955 m, 2920 m, 2869 m, 1467 m, 1453 m, 1438 m, 1386 m, 1362 m, 1297 w, 1241 m, 1157 m, 1092 w, 1060 w, 1020 m, 657 m, 530 m, 417 w. μ_{eff} (292—87 K): 1.16—0.57 μ_B.

Reaction of compound 5 with complex 8. A solution of compounds **5** (500 mg, 1.03 mmol) and **8** (510 mg, 1.03 mmol) in benzene (50 mL) (cherry-red) was boiled for 5 h. The brown solution did not contain initial reagents (according to the TLC data) and contained three products, which were separated by column chromatography (5×50 cm) by elution of three zones.

1. The red-brown zone was eluted with heptane (50 mL). The red solution that obtained was concentrated to 10 mL and cooled to −30 °C. The $Fe_3S_2(CO)_8(PPr^i_3)$ compound (**14**) (as a mixture of isomers) was obtained in a yield of 360 mg (0.58 mmol, 56.3%) as red-brown platelet-like crystals. Found (%): C, 33.56; H, 3.52. $C_{17}H_{21}Fe_3O_8PS_2$. Calculated (%): C, 33.12; H, 3.41. MS (EI), *m/z*: 616 [M^+].

Table 9. Atomic coordinates ($\times 10^4$) and isotropic temperature factors (U_{eq}) for cluster **11**

Atom	x	y	z	U_{eq}/Å^2
Cr(1)	3388(1)	3231(1)	393(1)	23(1)
Cr(2)	2074(1)	4576(1)	−783(1)	26(1)
S(1)	3479(1)	4803(1)	836(2)	25(1)
S(2)	1691(1)	3265(2)	0(2)	27(1)
S(3)	3066(2)	3691(2)	−1411(2)	27(1)
C(1)	3320(6)	5157(6)	2118(7)	32(4)
C(2)	2509(7)	4634(7)	2259(8)	49(4)
C(3)	4304(6)	4962(7)	3072(7)	44(4)
C(4)	3102(8)	6179(7)	2016(9)	58(5)
C(5)	906(7)	2378(7)	−956(8)	46(4)
C(6)	−143(7)	2725(8)	−1380(9)	63(5)
C(7)	1197(13)	2183(14)	−1870(15)	239(18)
C(8)	1002(10)	1520(7)	−310(13)	130(9)
C(9)	4082(7)	4412(7)	−1364(8)	44(4)
C(11)	4003(8)	1834(7)	384(8)	49(4)
C(12)	3681(7)	1865(6)	1224(8)	44(4)
C(13)	4224(7)	2541(6)	1983(7)	39(4)
C(14)	4899(7)	2911(7)	1596(8)	47(4)
C(15)	4777(7)	2472(7)	614(8)	48(4)
C(21)	557(8)	5119(8)	−1604(12)	73(6)
C(22)	1103(9)	5757(7)	−867(9)	57(5)
C(23)	1840(8)	6066(7)	−1134(11)	61(6)
C(24)	1759(10)	5627(9)	−2083(11)	68(7)
C(25)	984(10)	5039(9)	−2386(9)	71(6)
S(4)	3059(2)	6052(2)	5485(2)	45(1)
O(1s)	3172(6)	5935(8)	6572(6)	97(5)
O(2s)	3513(7)	6846(7)	5266(9)	118(7)
O(3s)	3188(6)	5225(6)	5012(8)	97(5)
F(1s)	1528(6)	7061(5)	5070(10)	134(7)
F(2s)	1507(8)	6333(10)	3738(8)	187(7)
F(3s)	1196(5)	5681(5)	4953(7)	101(4)
C(1s)	1790(8)	6294(8)	4774(10)	58(6)

588 [M$^+$−CO], 560 [M$^+$−2CO], 504 [M$^+$−2CO−Fe], 476 [M$^+$−3CO−Fe], 448 [M$^+$−4CO−Fe], 420 [M$^+$−5CO−Fe], 392 [M$^+$−6CO−Fe], 232 [M$^+$−6CO−Fe−PPr$^i_3$]. IR, ν/cm^{-1}: 2966 w, 2934 w, 2875 w, 2068 s, 2024 sh.s, 2021 sh.s, 2006 v.s, 1982 sh.s, 1969 s, 1949 s, 1461 w, 1394 w, 1370 w, 1259 w, 1241 w, 1155 w, 1082 w, 1071 w, 1052 w, 1028 w, 926 w, 878 w, 654 w, 605 m, 568 m, 537 m, 514 w, 476 w.

2. The brown fraction was eluted with heptane (50 mL). The brown solution obtained was concentrated to 10 mL and cooled to −10 °C. The $Fe_3S_2(CO)_7(PPr^i_3)_2$ compound (**15**) was obtained in a yield of 210 mg (0.28 mmol, 27.3%) as brown prismatic crystals. Found (%): C, 40.41; H, 5.65. $C_{25}H_{42}Fe_3O_7P_2S_2$. Calculated (%): C, 40.11; H, 5.61. MS (EI), *m/z*: 748 [M$^+$], 720 [M$^+$−CO], 560 [M$^+$−CO−PPr$^i_3$], 504 [M$^+$−2CO−Fe−PPr$^i_3$], 476 [M$^+$−3CO−Fe−PPr$^i_3$], 448 [M$^+$−4CO−Fe−PPr$^i_3$], 420 [M$^+$−5CO−Fe−PPr$^i_3$], 392 [M$^+$−6CO−Fe−PPr$^i_3$], 232 [M$^+$−6CO−Fe−2PPr$^i_3$]. IR, ν/cm^{-1}: 2999 w, 2988 m, 2963 m, 2935 m, 2876 m, 2033 s, 1990 v.s, 1975 v.s, 1964 v.s, 1940 s, 1924 s, 1462 w, 1448 m, 1385 w, 1367 w, 1259 w, 1243 w, 1154 w, 1077 w, 1059 w, 1032 m, 924 w, 878 m, 804 w, 660 m, 641 m, 614 w, 592 m, 574 m, 520 w, 487 w. ^{1}H NMR (C_6D_6), δ: 2.16 (m, 6 H, CH); 1.09 (dd, 32 H, CH_3, $^3J_{H-H}$ = 7.1 Hz, $^3J_{P-H}$ = 14.0 Hz). ^{13}C{^{1}H} NMR (C_6D_6), δ: 219.3 (d, 2 CO, $^2J_{P-C}$ = 21.0 Hz); 215.0 (s, CO); 211.3 (d, 2 CO, $^2J_{P-C}$ = 16.0 Hz); 208.6 (s, CO); 207.0 (s, CO); 26.7 (d, 12 CH_3, $^1J_{P-C}$ = 17.9 Hz); 19.8 (s, 6 CH). ^{31}P{^{1}H} NMR (C_6D_6), δ: 91.2 (s, br); 77.2 (s).

Table 10. Atomic coordinates ($\times 10^4$) and isotropic temperature factors (U_{eq}) for cluster **12**

Atom	x	y	z	U_{eq}/Å^2
Pd(1)	1763(1)	5455(1)	200	62(1)
Cr(1)	2700(3)	5897(6)	1573(11)	55(2)
Cr(2)	2718(3)	5910(7)	−1136(9)	49(2)
S(1)	2243(2)	6977(4)	215(18)	53(2)
S(2)	2458(2)	4464(4)	277(17)	47(2)
S(3)	3364(2)	5947(5)	139(19)	55(2)
P(1)	1101(2)	6494(5)	134(27)	121(2)
Cl(1)	1356(2)	3777(5)	134(27)	112(2)
C(1)	3671(7)	7285(17)	82(40)	73(3)
C(2)	3908(9)	7166(24)	−958(34)	104(3)
C(3)	4057(11)	7418(20)	1458(32)	91(3)
C(4)	3356(8)	8268(16)	33(38)	102(3)
C(11)	2632(11)	5021(27)	3564(27)	99(3)
C(12)	3051(11)	5683(22)	3584(21)	52(3)
C(13)	2896(11)	6751(19)	3661(20)	52(3)
C(14)	2423(14)	6748(23)	3498(31)	80(3)
C(15)	2213(9)	5515(22)	3308(26)	55(3)
C(21)	2816(16)	4838(21)	−2995(30)	108(3)
C(22)	2381(8)	5679(31)	−3067(22)	92(3)
C(23)	2572(23)	6512(27)	−3143(31)	192(3)
C(24)	3005(13)	6588(33)	−2790(24)	117(3)
C(25)	3028(26)	5397(26)	−2950(33)	248(3)
C(101)	598(11)	5881(24)	−367(36)	147(3)
C(102)	720(11)	5356(21)	−1658(40)	240(3)
C(103)	165(10)	6316(25)	−322(44)	310(3)
C(104)	1188(12)	7968(23)	174(44)	182(3)
C(105)	1178(11)	7839(24)	−1635(42)	276(3)
C(106)	780(8)	8726(21)	108(42)	158(3)
C(107)	940(14)	6771(33)	2431(36)	249(3)
C(108)	862(17)	5775(27)	3104(38)	396(3)
C(109)	1358(12)	7403(34)	2861(37)	204(3)
C(1s)	−106(23)	1413(42)	11315(43)	223(5)
C(2s)	−394(13)	911(28)	10654(32)	111(5)
C(3s)	−268(16)	664(32)	9335(36)	123(5)
C(4s)	41(19)	1401(35)	8779(38)	160(5)
C(5s)	270(12)	2177(25)	9712(29)	95(5)
C(6s)	377(14)	1777(29)	11046(34)	112(5)

3. The brown fraction was eluted with benzene (30 mL), and a brown solution was obtained. Heptane (5 mL) was added, and the solution was concentrated to 8 mL and cooled to 5 °C. The $(CO)_6Fe_3S_2Pd(PPr^i_3)_2$ complex (**16**) was obtained in a yield of 10 mg (~1%) as brown prismatic crystals. Found (%): C, 37.12; H, 5.23. $C_{24}H_{42}Fe_2O_6P_2PdS_2$. Calculated (%): C, 37.40; H, 5.45. MS (EI), *m/z*: 770 [M$^+$], 742 [M$^+$−CO], 714 [M$^+$−2CO]. IR, ν/cm^{-1}: 2963 m, 2927 m, 2835 m, 2853 w, 2043 s, 1998 v.s, 1956 v.s, 1464 w, 1449 w, 1385 w, 1366 w, 1261 m, 1093 m, 1053 m, 1025 m, 924 w, 879 w, 800 m, 664 w, 645 w, 617 w, 575 m, 567 m, 526 w, 501 w. ^{1}H NMR (C_6D_6), δ: 2.10 (m, 6 H, CH); 1.02 (m, 32 H, CH_3).

X-ray structural study of complexes 10, 11, 12, 15, and 16. The crystals of **10** (both modifications), **11**, **15**, and **16**,

Table 11. Atomic coordinates ($\times 10^4$) and isotropic temperature factors (U_{eq}) for cluster **15**

Atom	*x*	*y*	*z*	U_{eq}/Å^2
Fe(1)	1173(1)	6427(1)	2410(1)	48(1)
Fe(2)	−317(1)	6605(1)	3381(1)	49(1)
Fe(3)	−1407(1)	7026(1)	2084(1)	42(1)
S(1)	−352(2)	5801(2)	2312(2)	47(1)
S(2)	66(2)	7614(2)	2374(2)	45(1)
P(1)	1965(2)	6448(2)	1228(2)	54(1)
P(2)	−2355(2)	8361(2)	2010(2)	48(1)
O(1)	2197(6)	4726(5)	2912(6)	103(1)
O(2)	2576(7)	7445(6)	3247(6)	106(1)
O(3)	653(7)	5071(6)	4287(5)	106(1)
O(4)	322(7)	7875(6)	4459(5)	100(1)
O(5)	−2308(7)	6322(6)	4088(5)	96(1)
O(6)	−1324(6)	6883(5)	402(5)	82(1)
O(7)	−3251(6)	6027(5)	2314(5)	93(1)
C(1)	1795(8)	5413(7)	2704(7)	65(1)
C(2)	2046(8)	7038(7)	2885(7)	65(1)
C(3)	300(9)	5688(8)	3925(7)	77(1)
C(4)	66(9)	7375(7)	4051(7)	70(1)
C(5)	−1571(8)	6462(7)	3756(7)	66(1)
C(6)	−1363(8)	6969(6)	1056(6)	53(1)
C(7)	−2533(8)	6463(7)	2224(7)	64(1)
C(101)	3301(8)	5953(8)	1280(7)	77(1)
C(102)	3935(9)	6107(9)	528(8)	112(1)
C(103)	3943(9)	6204(8)	1967(8)	104(1)
C(104)	1287(9)	5767(7)	548(6)	75(1)
C(105)	1265(9)	4804(7)	841(7)	97(1)
C(106)	1632(10)	5838(9)	−324(8)	129(1)
C(107)	2050(8)	7536(6)	670(6)	60(1)
C(108)	1029(8)	7951(8)	371(7)	89(1)
C(109)	2561(9)	8174(7)	1141(7)	87(1)
C(201)	−2877(8)	8783(8)	2931(7)	72(1)
C(202)	−3708(9)	8243(8)	3294(8)	108(1)
C(203)	−2054(9)	8873(8)	3548(7)	84(1)
C(204)	−3446(9)	8399(8)	1345(8)	103(1)
C(205)	−4121(9)	9251(7)	1244(7)	91(1)
C(206)	−3735(10)	7787(9)	917(8)	136(1)
C(207)	−1367(9)	9271(7)	706(7)	83(1)
C(208)	−1915(9)	10212(6)	1804(7)	77(1)
C(209)	−1569(8)	9273(6)	1617(6)	60(1)
Fe(4)	−6403(1)	11219(1)	2912(1)	42(1)
Fe(5)	−5538(1)	11900(1)	1621(1)	46(1)
Fe(6)	−4376(1)	12603(1)	2589(1)	47(1)
S(3)	−6101(2)	12647(2)	2659(2)	43(1)
S(4)	−4701(2)	11159(2)	2658(2)	44(1)
P(3)	−8179(2)	11456(2)	2952(2)	47(1)
P(4)	−3887(2)	12941(2)	3790(2)	53(1)
O(8)	−6282(7)	10922(6)	4607(5)	90(1)
O(9)	−6394(6)	9340(5)	2665(5)	85(1)
O(10)	−6529(6)	10492(5)	893(5)	81(1)
O(11)	−6433(7)	13417(6)	654(5)	92(1)
O(12)	−3738(7)	11669(6)	624(5)	97(1)
O(13)	−4462(7)	14351(6)	1747(6)	105(1)
O(14)	−2289(7)	12255(5)	2046(5)	93(1)
C(8)	−6346(8)	11073(7)	3926(6)	57(1)
C(9)	−6443(8)	10077(7)	2755(6)	62(1)
C(10)	−6181(8)	11037(7)	1226(6)	56(1)
C(11)	−6092(8)	12796(7)	1031(6)	60(1)
C(12)	−4438(8)	11792(7)	1015(7)	63(1)
C(13)	−4401(8)	13683(7)	2115(7)	72(1)
C(14)	−3092(9)	12400(7)	2271(7)	67(1)
C(301)	−8548(8)	12588(7)	3235(7)	62(1)
C(302)	−8225(9)	12736(7)	4079(7)	85(1)
C(303)	−9630(9)	12963(8)	3073(8)	103(1)
C(304)	−8799(8)	10732(7)	3734(7)	77(1)
C(305)	−8435(10)	9807(8)	3820(8)	115(1)
C(306)	−9951(9)	10781(8)	3730(8)	105(1)
C(307)	−8940(9)	11374(7)	2048(7)	75(1)
C(308)	−8674(9)	12043(8)	1404(7)	89(1)
C(309)	−8880(9)	10429(7)	1777(7)	89(1)
C(401)	−3511(11)	11937(9)	4452(9)	121(1)
C(402)	−2303(16)	11611(15)	4116(14)	148(1)
C(42a)	−2914(13)	11258(11)	4157(11)	58(1)
C(403)	−3771(15)	12011(14)	5343(13)	105(1)
C(43a)	−4021(13)	11284(12)	4762(12)	75(1)
C(404)	−4858(12)	13600(10)	4327(9)	136(1)
C(405)	−4844(15)	13236(14)	5393(14)	128(1)
C(45a)	−5690(13)	13323(12)	4498(11)	63(1)
C(406)	−5687(15)	14123(14)	4116(13)	104(1)
C(46a)	−4875(13)	14652(11)	3763(11)	65(1)
C(407)	−2464(15)	13339(14)	3728(14)	124(1)
C(47a)	−2949(13)	13772(12)	3889(12)	69(1)
C(408)	−2345(11)	13826(10)	4627(9)	124(1)
C(409)	−2307(9)	14042(8)	3123(7)	84(1)

which were used for X-ray structural analysis, were mounted on glass sticks with the use of epoxide resin. Unstable compound **12** was mounted under an atmosphere of argon. The unit cell parameters were determined and refined using 24 equivalent reflections, which were measured in the range $2\theta = 22-26°$ on an automated four-circle Nicolet R3 diffractometer (the orthorhombic modification of **10**, **12**, **15**, and **16**) or on a Siemens R3m/v diffractometer (the monoclinic modification of **10** and **11**) (Mo-Kα radiation, $\lambda = 0.710703$ Å). All structures were solved by the direct methods, which revealed the positions of the Pd, Fe, Cr, S, P, and Cl atoms. The positions of other nonhydrogen atoms were revealed from the subsequent difference Fourier maps. All nonhydrogen atoms were refined anisotropically by the full-matrix least-squares method. For the structures of **12** and **16**, absorption corrections were applied using the DIFABS program.[20] The hydrogen atoms of the Cp rings, *tert*-butyl substituents of the thiolate groups, and isopropyl fragments were generated geometrically, and their positions were not refined. In the structure of **15**, the PPr^i_3 ligand of one independent molecule was disordered. Both positions of this group were revealed, and their occupation factors were close to 0.5. All calculations were carried out on a Pentium 100/8/860 computer with the use of the SHELXTL PLUS program package.[21] The crystallographic parameters of the compounds and the details of the refinement are given in Table 6. The atomic coordinates are given in Tables 7—12.

Table 12. Atomic coordinates ($\times 10^4$) and isotropic temperature factors (U_{eq}) for cluster **16**

Atom	x	y	z	U_{eq}/Å^2
Pd(1)	1843(2)	2714(1)	7890(1)	48(1)
Fe(1)	2557(3)	2500(2)	6252(2)	62(1)
Fe(2)	4422(3)	2897(2)	7324(2)	65(1)
S(1)	3113(5)	1925(3)	7415(3)	58(2)
S(2)	2542(5)	3482(3)	7065(3)	55(2)
P(1)	750(5)	3779(3)	8168(3)	52(2)
P(2)	1453(6)	1652(3)	8580(3)	57(2)
O(1)	2427(17)	3560(11)	5024(10)	116(3)
O(2)	33(18)	1913(11)	5720(10)	121(3)
O(3)	3858(18)	1367(11)	5626(11)	134(3)
O(4)	6250(18)	1805(12)	7106(13)	149(3)
O(5)	5410(16)	4085(9)	6566(10)	100(3)
O(6)	5594(15)	3361(11)	8897(10)	116(3)
C(1)	2517(21)	3137(14)	5501(14)	87(3)
C(2)	1074(22)	2167(14)	5932(13)	86(3)
C(3)	3280(22)	1814(15)	5866(14)	97(3)
C(4)	5536(23)	2226(15)	7223(15)	105(3)
C(5)	5010(20)	3617(14)	6868(13)	75(3)
C(6)	5109(22)	3167(14)	8253(14)	89(3)
C(7)	−23(21)	4309(13)	7293(13)	85(3)
C(8)	−839(20)	3815(13)	6647(12)	97(3)
C(9)	−585(24)	5049(14)	7322(15)	139(3)
C(10)	−404(20)	3677(13)	8695(13)	79(3)
C(11)	−1557(20)	3257(15)	8259(14)	120(3)
C(12)	−807(22)	4398(13)	9014(13)	106(3)
C(13)	1791(23)	4463(15)	8777(15)	108(3)
C(14)	2611(25)	4170(16)	9525(15)	159(3)
C(15)	2695(28)	4789(19)	8531(19)	203(3)
C(16)	2915(21)	1090(14)	9052(15)	101(3)
C(17)	2844(28)	358(16)	9264(17)	183(3)
C(18)	3953(19)	1661(14)	9460(13)	103(3)
C(19)	562(23)	976(15)	7946(15)	111(3)
C(20)	−767(22)	1223(15)	7420(14)	132(3)
C(21)	635(30)	601(19)	7376(18)	210(3)
C(22)	609(20)	1703(14)	9291(13)	84(3)
C(23)	1319(23)	2109(15)	9980(13)	130(3)
C(24)	70(23)	949(15)	9484(14)	127(3)

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-33171) and the Switzerland National Science Foundation.

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Received July 2, 1996;
in revised form October 11, 1996