Remetalation processes upon the formation of magnetically active heterometallic sulfide-bridged clusters

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The processes of formation of antiferromagnetic heterometallic trinuclear clusters $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)_2ML_n$ (ML_n = Re(CO)(NO), $W(NO)_2$, W(NO)Cl, and $W(NO)(SCMe_3)$) from the antiferromagnetic binuclear chromium(III) complex $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (**1**) and nitrosyl-containing halide derivatives of Re^I and W^0 were considered. It is shown that adducts of **1** with ML_m (ML_m = $Re(NO)(CO)_2Cl_2$, $W(NO)_2Cl_2 \cdot$ **1**, and $W_2(NO)_2(CO)_4I_2$) are formed at the first stage. Then they loose the $CpCrHal_2$ moiety and transform into the reactive remetalation products, $CpCr(\mu\text{-}SCMe_3)_2(\mu\text{-}S)ML_x$ (M = Re and W). The latter complexes join the electron-deficient CpCrS moiety to generate triangular clusters. The magnetic behavior of antiferromagnetic adducts and triangular clusters is discussed, and the existence of correlations between the energy of spin-spin exchange ($-2J$(Cr—Cr)) and Cr—Cr and Cr—S(sulfide) bond lengths is mentioned.

Key words: magnetically active clusters, sulfur-containing ligands.

1. Introduction

Sulfide- and thiolate-bridged heterometallic clusters are the subjects of numerous studies devoted to the modeling of metal-containing enzymes or magnetic materials.[1] However, despite ever-increasing interest in the compounds of this class, the accessibility of the clusters remains to a great extent limited due to synthetic difficulties. The most efficient method for the preparation of sulfide-bridged heteronuclear clusters is the so-called chemical assembling, when, for example, a binuclear complex (a "block" containing sulfur atoms with lone electron pairs) is used as a ligand with respect to an electron-deficient metal-containing ML_n fragment generated from low-valent cyclopentadienyl- or carbonyl-containing transition metal complexes on heating or under UV irradiation. In principle, this method could solve the problem of synthesis of clusters with almost any set of metals in the framework, but, unfortunately, the limited choice or insufficient stability of the initial "blocks" prevent its wide application. For example, only some compounds, $Fe_2S_2(CO)_6$,[2—6] $Cp_2V_2S_4$,[7—9] $Cp_2Mo_2S_4$,[10—12] $Cp_2Cr_2S_5$,[13,14] and $L_4Pt_2S_2$ (L = PR_3),[15,16] were successfully used for designing heterometallic clusters. In addition, it is noteworthy that none of the sulfide- and/or thiolate-bridged heterobinuclear complexes known so far has been applied in cluster synthesis.

Another promising method for the preparation of heteronuclear cluster compounds is remetalation of electron-saturated or electron-excessive homonuclear clusters, when isoelectronic metal-containing fragments are substituted to form a new heterometallic sulfide-containing framework. For example, this method is used for synthesizing neutral $HFe_2CoS(CO)_9$ and $Fe_2CoS(CO)_9(NO)$ and anionic $Fe_2CoS(CO)_9^-$ clusters from $Fe_3S_2(CO)_9$ and $Co_2(CO)_8$ [17] or $(Ph_3P)_2MFe_2S_2(CO)_6$ (M = Pd and Pt) by the reaction of $Fe_3S_2(CO)_9$ with $(Ph_3P)_2MCl_2$.[18,19] The subsequent substitution of metal-containing moieties in heterobimetallic clusters results in the formation of chiral compounds with three and four different metal atoms. Such compounds were obtained by Richter and Vahrenkamp by remetalation of the clusters with the MM'_2S core upon the reaction with Me_2As-containing complexes.[20—22] However, it should be mentioned that in this case the initial homonuclear clusters do not always exchange metal-containing fragments, and the yields of clusters thereby formed are low.

It has been shown previously that the use of the antiferromagnetic binuclear chromium(III) thiolate-sulfide complex, $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (**1**), or its methylcyclopentadienyl analog as a "unit" for the growing of the cluster core in reactions with carbonyl-containing metal complexes results in the formation of unusual magnetically active heterometallic sulfide-bridged clusters. The

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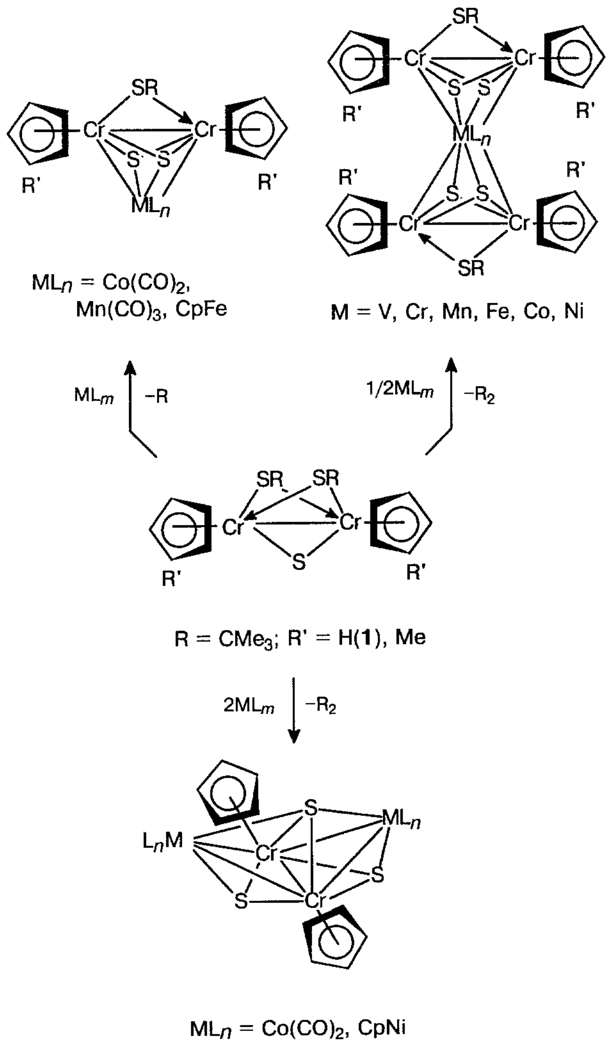
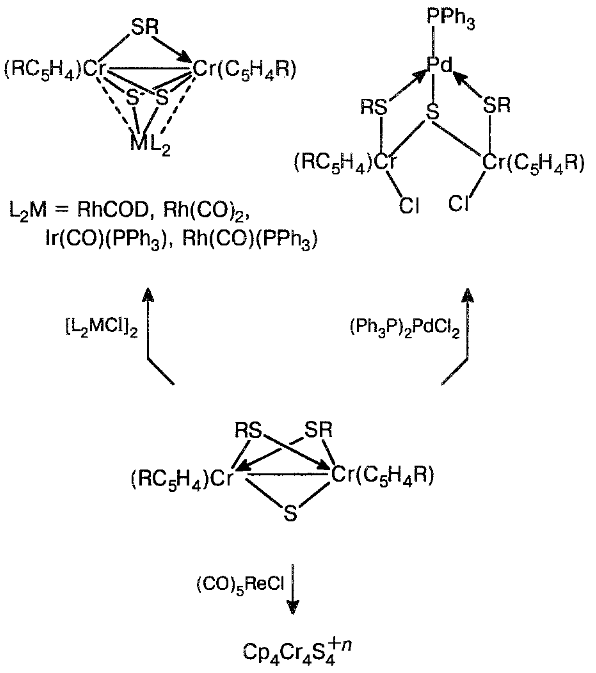
Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2337—2348, December, 1995.

variation of the ratio between **1** and ML_n makes it possible to synthesize triangular $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2ML_n$ clusters, $[Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2]_2M$ metal spirans, or $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)(ML_n)_2$ clusters with the "butterfly" metal core[23] (Scheme 1). In this case, however, when halogen-containing transition metal compounds are used for the generation of the ML_n fragments, the results can be unpredictable. For example, complex **1** reacts with Rh^I- and Ir^I-containing $[L_2MCl]_2$ compounds (L_2M = $Rh(CO)_2$, [24] $Rh(CO)(PPh_3)$, [25] CODRh, [24] or $Ir(CO)(PPh_3)$ [25]) to form triangular antiferromagnetic clusters $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2ML_2$, while the reaction with $Re(CO)_5X$ (X = Cl and Br) results only in homonuclear cubans $Cp_4Cr_4S_4{}^n$ (n = 0, +1).[26] On the other hand, the reaction of **1** (or its methylcyclopentadienyl analog) with $(Ph_3P)_2PdCl_2$ unexpectedly resulted in the formation of ferromagnetic compounds $(RC_5H_4)_2Cr_2(Cl)_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)Pd(PPh_3)_2$, in which halogen atoms are bonded to Cr^{III} atoms and metal—metal bonds are absent[27] (Scheme 2).

Scheme 1



Scheme 2



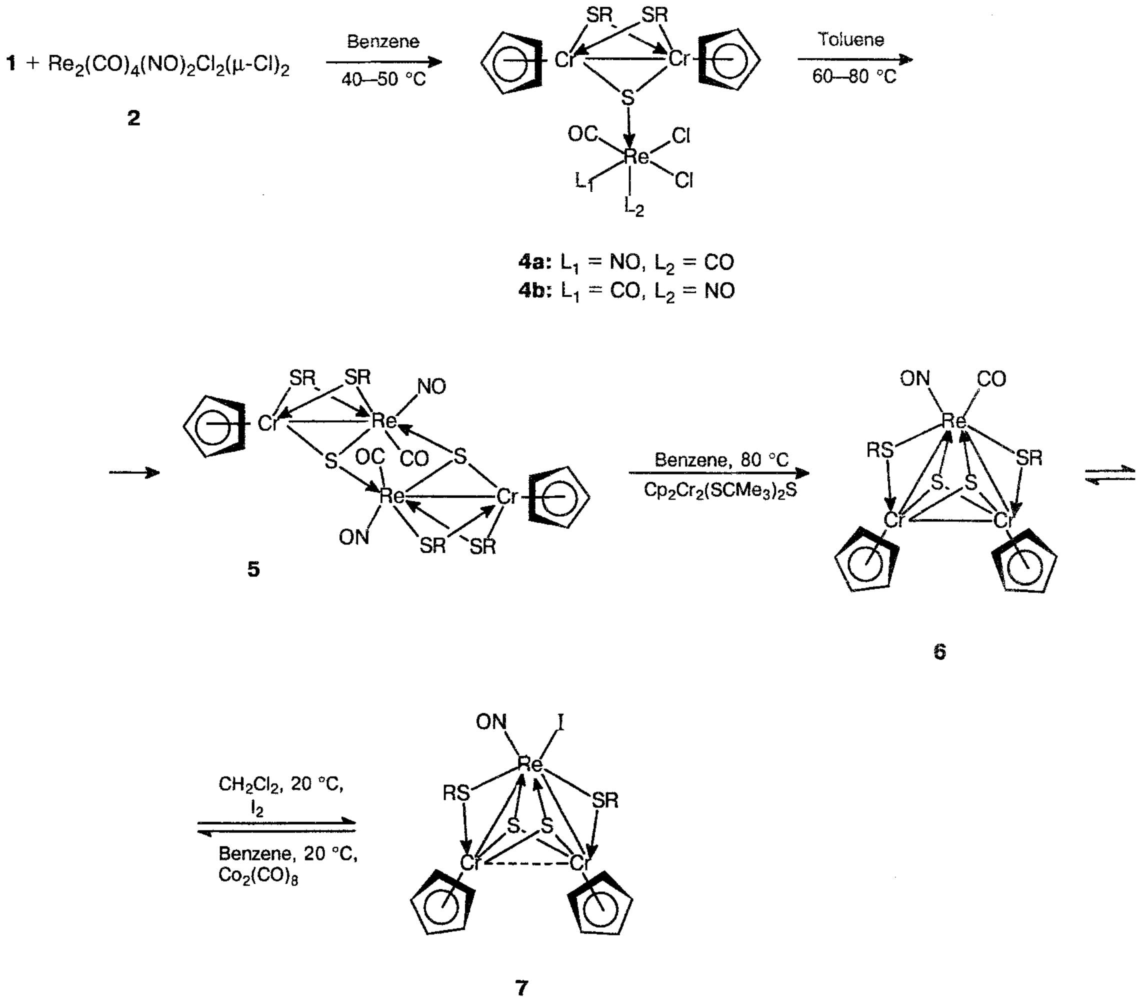
This substantial difference in the character of the products formed indicates an important role of halogen atoms in the formation of the cluster core. Therefore, taking into account interest to the search of new ways of synthesis and for development of the main principles of the chemical assembling of heteronuclear sulfide-bridged clusters, we performed a detailed study of reactions of **1** with halide derivatives of Re^I and W^0 containing carbonyl and nitrosyl ligands and studied the effects of the steric and electron factors on the process of cluster formation. The results of these studies are summarized in this work.

2. Remetalation processes upon the formation of triangular clusters with the Cr_2M (M = Re, W) core

2.1. Chromium- and rhenium-containing clusters

The binuclear diamagnetic rhenium(I) complex $Re_2(CO)_4(NO)_2Cl_2(\mu\text{-}Cl)_2$ (**2**) readily reacts with N- and P-donors to give $LRe(CO)_2(NO)Cl_2$ or $L_2Re(CO)(NO)Cl_2$ monomers.[28,29] Taking into account the ability of **1** to act as a donor ligand on binding with a metal-containing fragment due only to the lone electron pair of the sulfide bridge (for example, in the formation of the $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)Re_2(CO)_9$(**3**) cluster[30]), we performed the reaction between **1** and **2** (the 2 : 1 ratio of the reagents) under mild conditions (benzene, 40—50 °C). It turned out that this reaction results in the formation of antiferromagnetic (magnetic properties of all antiferromagnetic clusters are considered below) adducts

Scheme 3



$Cp_2Cr_2(SCMe_3)_2(\mu_3\text{-}S)Re(CO)_2(NO)Cl_2$ (**4**), which differ only in the configuration of the μ_3-SReNO fragment (*cis* in **4a** and *trans* in **4b**),[31] the ratio between isomers **4a** and **4b** being ~3 : 1 (Scheme 3). The X-ray diffraction study of both adducts shows that **1** does not basically change its structure upon the coordination with the rhenium atom. However, there is a noticeable shortening of the Re—S bonds in adducts **4** (**4a**: 2.502(9), **4b**: 2.461(3) Å), which contain strong acceptor NO groups bound to the Re^I atom, compared to the value of 2.555(2) Å observed in **3**, having the metal-carbonyl group $Re_2(CO)_9$.[30] In addition, the Cr—Cr bonds in isomers **4** (**4a**: 2.777(6), **4b**: 2.788(3) Å) are longer than in **3** (2.732(2) Å).

Further heating of adducts **4** (individual isomers or their mixture, 60—80 °C, toluene) results in the elimination of the $CpCrCl_2$ fragment (probably in the form of the known low-soluble dimer[32] or insoluble polymer) and one CO group and formation of tetranuclear cluster $[CpCr(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)Re(CO(NO)]_2$ (**5**) as the main reaction product[31] (see Scheme 3). Compound **5** is the dimerized product of remetalation of the initial complex **1**, in which one CpCr fragment is replaced for Re(CO)(NO). The 18-electron environment of the rhenium(I) atom in **5** is achieved due to the additional coordination with the sulfide bridge of the adjacent Cr,Re fragment. Therefore, bonding between the electron-saturated Re atom and electron-deficient Cr^{III} atom (15-electron environment) can take place in cluster **5** only by overlapping of the half-occupied orbital (from the Cr^{III} atom) and occupied orbital (from the Re^I atom), which results in the appearance of the one-electron Cr—Re bond, whose length (3.126(3) Å) in the linear Cp(center)CrRe (178.7(2)°) fragment is considerably greater than the sum of covalent radii of Cr (1.45 Å) and Re (1.56 Å).[33]

It is noteworthy that the presence of two paramagnetic Cr^{III} centers in a molecule of **5** determine the magnetic properties of the cluster. Its effective magnetic moment calculated per one chromium atom (4.04 μ_B) is close to the purely spin value (3.96 μ_B) and is temperature independent in the 296—77 K range. Such behavior indicates the absence of spin-spin exchange interactions between paramagnetic atoms *via* the complex system of bridges.

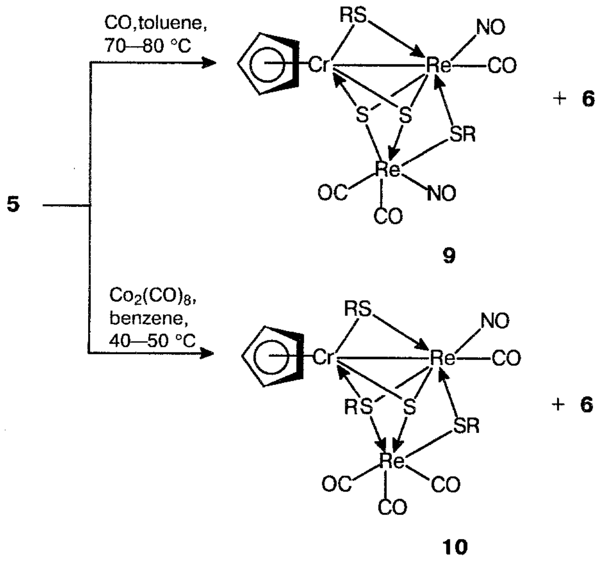
Finally, the addition of the CpCrS fragment generated from **1** in the thermal reaction between **1** and **5** (a 1 : 2 ratio, benzene, 80 °C) to the binuclear Cr,Re species results in the formation of the antiferromagnetic triangular cluster $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)_2Re(CO)(NO)$ (**6**, yield 59 %)[31] (see Scheme 3). Complex **6** also can be obtained in a 52 % yield from **4** and **1** (2 : 1 ratio, benzene, 80 °C) or by the direct reaction between **1** and **2** (3 : 1 ratio, MeCN, 80 °C, yield 63 %). An interesting feature of **6** is the fact that this cluster exists as two crystalline forms: **6a** (crystals obtained from a CH_2Cl_2/C_6H_6 mixture or toluene)[31] and **6b** (crystals grown from MeCN).[34] These forms differ substantially in the values of the bond lengths (**6a**: 2.940(5), **6b**: 3.080(2) Å for Cr—Re and **6a**: 2.759(9), **6b**: 2.367(5) Å for $Cr—SCMe_3$), although the Cr—Cr bond lengths are almost equal (3.010(5) and 3.002(4) Å in **6a** and **6b**, respectively). One cannot exclude the effect of crystallization conditions (different solvents) or packing effects on the formation of the forms with similar spectral (ν(CO) and ν(NO) are 1951 and 1683 cm^{-1} in **6a** and 1950 and 1685 cm^{-1} in **6b**) and magnetic parameters (see below), but the possible reason for this nonequivalence can be the difference in the electron nature of bonding of the $Re(CO)(NO)(SCMe_3)_2$ fragment with magnetic $Cp_2Cr_2(\mu\text{-}S)_2$ group (in this case, the rhenium atom is diamagnetic), containing a nonlinear Cp(center)CrCrCp(center) fragment (the angles Cp(center)CrCr are 126.5 and 127.0° in **6a** and **6b**, respectively, and the torsion angles Cp(center)CrCrCp(center) in **6a** and **6b** are equal to 3.6 and 3.1°). Two bridging sulfur atoms of the $Cp_2Cr_2(\mu\text{-}S)_2$ group are bound to Re^I due to lone electron pairs, resulting in the 18-electron environment of the rhenium atom. In turn each Cr^{III} atom in this fragment has three orbitals for bonding with the Re and S atoms of the thiolate-bridged ligand (the remaining six orbitals participate in bonding with CpCr (three orbitals), Cr—μ-S (two bonds, two orbitals), and Cr—Cr (one orbital)), two of which are half-occupied and one orbital is vacant. Thus, each Cr—Re bond formally can be formed by overlapping of the occupied orbital from the Re atom and by the half-occupied or empty orbital of the Cr atom. This should result in the appearance of one- or two-electron metal—metal bonds, respectively. The lone electron pair of the SR group can interact with the orbitals of the Cr atom in a similar way.

The suggested qualitative scheme of bonding is rather rough and is based on a simple electron counting that is often used for the description of the metal—metal bonding in the cluster chemistry. This scheme does not take into account the effects of electron density delocalization in the metal sulfide core of the cluster and the influence of the additional π-interaction of lone electron pairs of sulfide bridges with the electron-deficient chromium atoms, giving, as a rule, the orbital mixing. As a result, the metal—metal bonding turns out to be a complex function depending on many parameters. On the other hand, it can be noticed that the Cr—Re distance (3.080 Å) in **6b** is close to that of the similar one-electron metal—metal bond observed in **5** (*R*(Cr—Re), 3.126 Å). In this case, assuming that the nature of bonding between chromium and rhenium atoms in these clusters is similar, removal of one electron from the antibonding orbital of the Cr—Re bond (as a rule, energy levels of orbitals of metal—metal bonds are the highest) should result in the appearance of a strong two-electron Cr—Re bond. This occurs upon the oxidation of **6** by iodine in CH_2Cl_2 (20 °C), when the CO group (two-electron ligand) bonded with the rhenium atom is substituted for the iodine atom (one-electron ligand). In the isolated cluster $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)_2Re(NO)I$ (**7**) (yield 87 %), one Cr—Re bond is short (2.744(5) Å), while the second bond is lengthened (3.034(5) Å) and close to that observed in form **6b**. However, the Cr—Cr bond becomes noticeably antibonding (**7**: *R*(Cr—Cr) 3.139(6) Å), and the $Cr—SCMe_3$ bonding remains almost unchanged (*R*(Cr—SR) 2.364(9)—2.399(9) Å).[35] Complex **7** readily transforms into **6** by the reaction with a small excess (10—15 %) of $Co_2(CO)_8$, and the reaction proceeds in nearly quantitative yield.

In fact, the sequence of chemical transformations studied demonstrates the formation of triangular clusters with Cr_2Re cores (**6** and **7**) from binuclear chromium complex **1** and the $Re(CO)_2(NO)Cl_2$ metal-containing fragment generated from **2**. In this case, the remetalation of the initial complex-"block" **1** to the heterobimetallic Cr,Re-containing species, which is able to subsequently join the electron-deficient species (for example, CpCrS), is a new and the most important stage. This type of transformations has been previously unknown for electron-unsaturated clusters containing electron-deficient metal centers. Therefore, the ligand environment of the metal atom in the ML_n fragment is of special significance. In fact, it can be noticed that hard Cr^{III} atoms in adducts **4** are bound to soft sulfur-containing bridges, while the soft Re^I atom contains hard chlorine atoms in the coordination sphere. As a result, an increase in temperature induces the ligand exchange, according to the Pearson principle,[36] followed by the elimination of the $CpCrCl_2$ species. It is noteworthy that similar transfer of Cl atoms from the soft Pd^{II} atom to the hard Cr^{III} atoms has previously been observed in the formation of stable $(RC_5H_4)_2Cr_2(Cl)_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)Pd(PPh_3)$ clusters[27] mentioned (see Introduction). However, no products of remetalation of **1** with the formation of a complex containing Cr and Pd atoms have not been obtained yet.

Isolated dimerized complex **5** contains Cr and Re atoms and can be obtained upon the elimination of a CO molecule from the binuclear complex $CpCr(\mu\text{-}SCMe_3)_2(\mu\text{-}S)Re(CO)_2(NO)$ (**8**), which appeared at one of the stages of pyrolysis of adducts **4**. It is evident that **8** can be used as a unique heteronuclear "block" for the chemical design of asymmetric clusters. Therefore, an attempt to synthesize **8** by carbonylation of **5** has been undertaken. However, the reaction of **5** with CO, occurring at 70—80 °C in toluene (no reaction is observed for 2 days at 20—60 °C), results in the formation of two trinuclear clusters, **6** and $CpCr(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Re(CO)(NO)(\mu\text{-}SCMe_3)Re(CO)_2(NO)$ (**9**), in similar yields (36.3 and 43.2 %, respectively) (Scheme 4). It can easily be noticed that **9** is the product of the formal addition of the $Re(CO)_2(NO)(SCMe_3)$ fragment instead of one CMe_3 group to the bimetallic $CpCr(\mu\text{-}SCMe_3)_2(\mu\text{-}S)Re(CO)(NO)$ unit containing the one-electron Cr—Re bond (3.068(2) Å, Cp(center)CrRe angle 176.8(2)°) due to bonding of the peripheral rhenium atom with two sulfide bridges (*R*(Re—S) = 2.484(2), 2.499(2) Å) and formation of a thiolate bridge between two Re atoms. Although no metal—metal bonding between the peripheral Re atom and the Cr and Re atoms exists in the heterobinuclear fragment (Cr···Re 3.391(2) Å, Re···Re 3.317(1) Å) of **9**, the compound can be considered as the first cluster derivative of heterometallic "block" **8**. The failure to obtain **8** by this method stimulated study of a reaction of **5** with another carbonylating agent, $Co_2(CO)_8$. In this case, the reaction also resulted in the formation of two compounds: clusters **6** and $CpCr(\mu\text{-}SCMe_3)(\mu_3\text{-}SCMe_3)(\mu_3\text{-}S)Re(CO)(NO)(\mu\text{-}SCMe_3)Re(CO)_3$ (**10**)[35] (see Scheme 4). A molecule of **10** contains the unchanged heterometallic $CpCr(SCMe_3)_2(S)Re(CO)(NO)$ fragment (*R*(Cr—Re) 3.150(2) Å, Cp(center)CrRe angle 178.3(2)°), which exists in the initial compound **5** bonded to the $Re(CO)_3(SCMe_3)$ fragment by tridentate thiolate and sulfide bridges and by the bridged SR group between the Re atoms (it is likely that the NO group is accepted by the Co atom to form the volatile $Co(NO)(CO)_3$ complex). As **9**, compound **10** contains no metal—metal bonds between the peripheral Re atom and the Cr and Re atoms of the binuclear fragment (Cr···Re 3.668(2) Å, Re···Re 3.454(1) Å). The existence of only one paramagnetic center in **9** and **10** determines magnetic properties of the clusters. Their effective magnetic moments (3.80 and 3.68 μ_B for **9** and **10**, respectively) are close to the pure spin value and are temperature-independent in the 289—79 K range. It thus turned out that the carbonylation of **5** by various agents results in formal disproportionation of the cluster with the Cr_2Re_2 core to the triangles with the Cr_2Re (in **6**) and $CrRe_2$ (in **9** or **10**) cores.

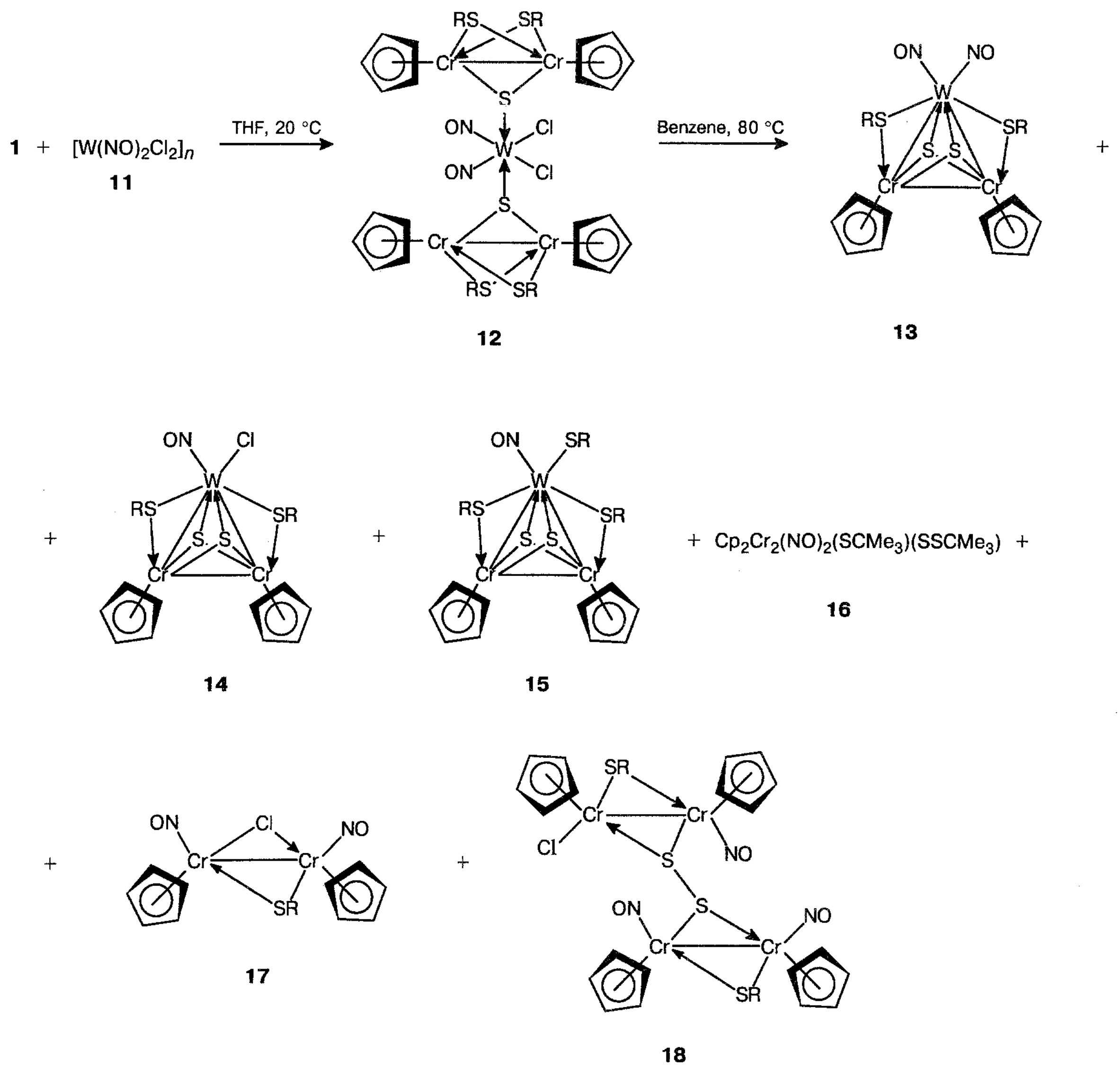
Scheme 4



2.2. Clusters with chromium and tungsten atoms

As shown above, the main stages of the preparation of triangular clusters with Cr and Re atoms are as follows: (1) the formation of adduct **1** containing the metal halide fragment; (2) the remetalation of **1** involving the transfer of halogen atoms from M to hard Cr^{III} atoms followed by the elimination of the $CpCrCl_2$ species; and (3) the addition of the CpCrS species generated from the second molecule of **1** to the transmetallated complex. It could be expected that this scheme of transformations is general for the formation of chromium-containing clusters with various metal-containing moieties. Therefore, other low-valent halogen-containing derivatives, in particular, $[W(NO)_2Cl_2]_n$ (**11**), were used in reactions with **1**. Similar to **2**, complex **11** readily reacts with phosphines to give $L_2W(NO)_2Cl_2$ complexes[37,38] that are isoelectronic to compounds $L_2Re(CO)(NO)Cl_2$.[28,29] Therefore, it is not surprising that the reaction of **1** with **11** (a 2 : 1 ratio) occurs even at room temperature in THF to form black needle-like crystals of the antiferromagnetic adduct $[Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)]_2W(NO)_2Cl_2$ (**12**: μ_{eff} = 1.69 to 0.58 μ_B (290—79 K)) in an almost quantitative yield[34] (Scheme 5). Complex **12**, characterized by chemical analysis and IR and mass spectra (FAB), contains two coordinated molecules **1**, one of which is necessary for the remetalation, while the second is necessary for the generation of CpCrS. As a result, heating of **11** in benzene (80 °C) immediately results in the formation of the antiferromagnetic triangular cluster $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)_2W(NO)_2$ (**13**), which is isoelectronic to the rhenium-containing analog **6**. Independently of the method of crystallization and the type of solvent (toluene, benzene, CH_2Cl_2, THF, and MeCN were used), complex **13** was isolated in the form of one compound, which is almost isostructural to isomer **6b** (the values of the covalent radii of rhenium and tungsten are similar[33]). For example, the Cr—W bonds in **13** are elongated (3.088(3) Å) and, probably, of the one-electron type, while the $Cr—SCMe_3$ bonds (2.374(3) Å) have normal lengths typical of similar type clusters.[23—25,27,30] In addition, the Cr—Cr bond length

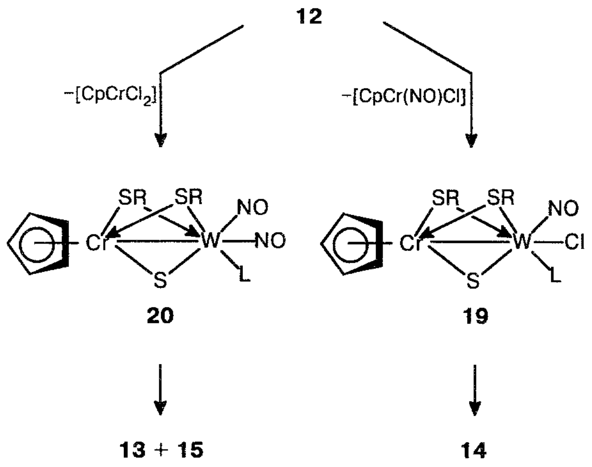
Scheme 5



of the bent CpCrCrCp fragment (Cp(center)CrCr angle 124.2(4)°) is noticeably increased (3.088(3) Å, the torsion angle Cp(center)CrCrCp(center) is equal to 3.9°) compared to the value in the linear fragment (Cp(center)CrCr angle 179.4(5)°) in complex **1** (2.689(6) Å).[39] However, cluster **13** is formed in a relatively low yield of 27.8 %. In addition, trinuclear clusters $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)_2W(NO)Cl$ (**14**, yield 16.6 %) and $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)_2W(NO)(SCMe_3)$ (**15**, yield 30.9 %) and the products of nitrosylation and nitrosylhalogenation of **1** (total yield 17 %) were isolated from the reaction mixture: previously known $Cp_2Cr_2(NO)_2(\mu\text{-}SCMe_3)(\mu\text{-}SSCMe_3)$ (**16**: *R*(Cr—Cr) 2.906(2) Å [40]) and the new $Cp_2Cr_2(NO)_2(\mu\text{-}SCMe_3)(\mu\text{-}Cl)$ (**17**: *R*(Cr—Cr) 2.959(2) Å) and $Cp_4Cr_4(NO)_3(Cl)(\mu\text{-}SCMe_3)_2(\mu_4\text{-}S_2)$ (**18**: *R*(Cr—Cr) 2.681(2) Å) complexes (see Scheme 5).

Unlike the 18-electron W^0 atom in **13**, trinuclear clusters **14** and **15** contain 16-electron W^{II} atoms. In this case, according to the model mentioned above, the Cr—W bonds are formed due to overlap of half-occupied orbitals from the W and Cr atoms and turn out to be two-electron. In fact, the Cr—W bond lengths (2.843(3)—2.889(3) Å) in **14** are noticeably shorter than in **13** with approximately equal Cr—Cr distances (3.036(4)—3.068(4) Å) in the bent Cp_2Cr_2 system (Cp(center)CrCr angle 124.2(5)—127.9(5)°). In this situation, a sharp lengthening of the Cr—W bonds (3.090(1) Å) observed in a molecule of cluster **15** (*R*(Cr—Cr) 3.027(1) Å, Cp(center)CrCr angle 126.9(1)°), which is an isoelectronic analog of **14**, was quite unexpected. The possible reason for this distinction can be the difference in the contributions of the additional π-interaction of lone electron pairs of the terminal

Scheme 6

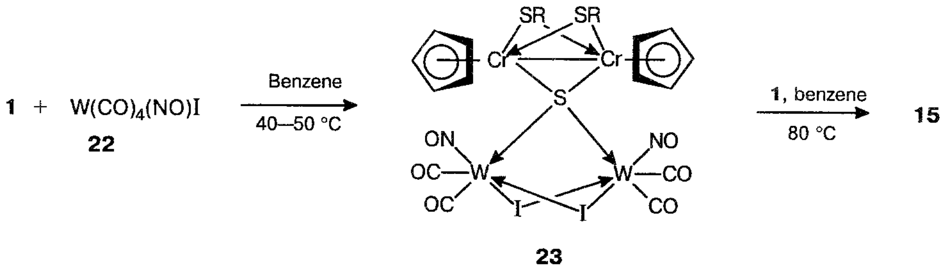


donor ligand (Cl in **14** and SR in **15**) with the electron-deficient W^{II} atom, which is competing relative to the Cr—W bonding. As a result, the $W—SCMe_3$ bond (2.323(2) Å) in **15** is considerably shortened compared to the sum of covalent radii of the elements[33] than the W—Cl bond (2.424(5)—2.434(4) Å) in **14**. In addition, one should take into account the steric effect of the bulky *tert*-butyl substituent of the terminal SR group at the W atom in **15**, which results in a specific "withdrawal" of the metal-containing W(NO)(SR) fragment from the binuclear $Cp_2Cr_2S_2$ fragment (the W—μ_3-S bonds (2.582(2)—2.590(2) Å) in **15** are somewhat lengthened compared to similar bonds in **14** (2.447(5)—2.559(5) Å)).

The formation of clusters **14** and **15** and nitrosyl-containing chromium complexes **16—18** unambiguously indicates occurrence of the parallel processes of Cl and SR exchange and transfer of NO to Cr upon the thermolysis of **12**. The smooth elimination of the NOCl fragment from the molecular ion is observed in the mass spectrum of the cluster (FAB, 70 eV, 20—40 °C).[34] Therefore, it can be supposed that the elimination (or transfer) of NO and Cl from the W atom under the conditions of thermal reaction results in the formation of the transmetallated complex $CpCr(SCMe_3)_2(S)W(NO)(Cl)L$ (**19**), where L is the coordinated molecule of **1**. Cluster **19** is further transformed into cluster **14**. Cluster **13** with the $W(NO)_2$ fragment is formed from the remetalation product $CpCr(SCMe_3)_2(S)W(NO)_2L$ (L is coordinated **1**) (**20**) obtained upon the transfer of two halogen atoms and elimination of $CpCrCl_2$. It should be mentioned that **1**, which is the fragment of cluster **20**, can be a source of CpCrS that is necessary for the formation of triangular cluster **13** and can generate the thiolate group that substitutes one NO ligand in **20** or **13**. This results in the formation of cluster **15** (Scheme 6). Eliminated molecules of NO and, probably, NOCl are nitrosylating reagents, and, hence, the formation of nitrosyl chromium-containing complexes **16**, **17**, and **18** is not surprising. It fact, it has been shown previously that **16** is formed due to the reaction between NO and **1** (see Ref. 40). We have also analyzed the composition of the products of the reaction of **1** with NOCl and isolated complexes **16**, **17**, and $Cp_2Cr_2(NO)(Cl)(\mu\text{-}SCMe_3)_2$ (**21**, *R*(Cr—Cr) 3.071(8)—3.116(8) Å). In the absence of halogen atoms, when $[(NO)_2W(MeCN)_4](PF_6)_2$ is used as the initial complex, the thermal reaction with **1** (a 1 : 2 ratio of the reagents, benzene, 50 °C) results in the formation of **13**, **15**, and **16**.

Like **2** and **11**, complex $W(CO)_4(NO)I$ (**22**)[41] reacts with phosphines to give $L_2W(CO)_2(NO)I$ adducts[41] but contains only one halogen atom. In this situation, heating of **1** and **22**, independently of the ratio of reagents (it varied from 2 : 1 to 1 : 2), gives only one compound, antiferromagnetic adduct $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_4\text{-}S)W_2(CO)_4(NO)_2(\mu\text{-}I)_2$ (**23**)[42]. A molecule of **1** (*R*(Cr—Cr) 2.764(4) Å) in **23** serves as a specific bridge between two W atoms (W···W 3.559(1) Å) due to using two lone electron pairs of the sulfide atom. The subsequent reaction of **23** with **1** as the temperature increases (1 : 1 ratio, toluene, 80 °C) results in the formation of triangular cluster **15** as the main soluble reaction product (yield 47.7 %) (Scheme 7). Cluster **15** can also be obtained by the thermal reaction between **1** and **22** in a 79.6 % yield (a 3 : 1 ratio, toluene, 80 °C). The mechanism of formation of **15** is not quite clear in this case; however, one can expect the formation of the intermediate $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)_2W(NO)(CO)$ cluster (**24**), whose composition is similar to that of **6**, but contains the 17-electron W^I atom. It is likely that its W—CO bond is somewhat destabilized and cleaved in the presence of an excess of **1** as a source of SR groups.

Scheme 7



This results in the substitution of CO for the thiolate ligand, whose bonding with the W^{II} atom is strengthened by an additional π-interaction of the lone electron pairs of the sulfur atom with the half-occupied orbitals of the metal atom.

The considered examples of the formation of antiferromagnetic triangular clusters $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)_2M(NO)L$ (ML = Re(CO) (**6a,b**); W(NO) (**13**); WCl (**14**); $W(SCMe_3)$ (**15**)) from the antiferromagnetic $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ "block" (**1**) and nitrosyl-halide rhenium and tungsten derivatives various in structure illustrate basically new possibilities for synthesizing heteronuclear sulfide-bridged clusters. The most important stage of formation of the triangular Cr_2M core is the remetalation of the electron-deficient fragment in **1**, which has not been observed previously. It can be assumed that a similar mechanism is also possible when using other polynuclear complexes-"blocks" in cluster assembling.

3. Factor preventing remetalation of a dichromium fragment

Unlike $Re_2(CO)_4(NO)_2Cl_4$ (**2**) containing labile carbonyl groups, mononuclear $(PR_3)_2Re(CO)(NO)Cl_2$ complexes (**25**) are very strong and do not decompose even upon boiling in xylene.[29] This behavior affects their reactivity toward **1** in such a way that **25** (R = Et (**a**), OMe (**b**), and OPr^i (**c**)) forms no adducts with the dichromium complex at 20—80 °C in various solvents (benzene, toluene, CH_2Cl_2, THF, and MeCN). In this case, an increase in temperature (toluene, 110 °C) results only in the formation of the known tetrahedral $Cp_4Cr_4S_4$ cluster, while the rhenium-containing reagent remains unchanged.

The substitution of Cl atoms for triflate groups (otf = O_3SCF_3) in **25** results in the formation of $(PR_3)_2Re(CO)(NO)(otf)_2$ complexes (**26a,b**) in which aniono ligands can be replaced by coordinated MeCN molecules to form the corresponding cations.[43] However, unlike the reaction of $[(NO)_2W(NCMe)_4]^{2+}$ mentioned, the reaction between **26** and **1** in boiling acetonitrile does not result in the formation of stable adducts or heterometallic clusters. For example, only the cationic paramagnetic tetrahedral $[Cp_4Cr_4S_4][otf]$ cluster (**27**, μ_{eff} = 1.78 μ_B (295—78 K), *R*(Cr—Cr) 2.726(2)—2.804(2) Å (monoclinic modification) and 2.748(3)—2.780(3) Å (orthorhombic modification), yield 83.9 %) was isolated in the case of triethylphosphine derivative **26a**, while the antiferromagnetic methylated $[Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}SMe)][otf]$ complex (**28**, *R*(Cr—Cr) 2.766(2) Å)[44] was formed in the case of **26b** (the methylation occurs due to the methyl group of the phosphite ligand, and a yield of **28** is 86.3 %) (Scheme 8). Thus, the use of complexes with strongly bonded ligands in reactions with **1** prevents the formation of adducts and, hence, transmetallated complexes and heterometallic clusters.

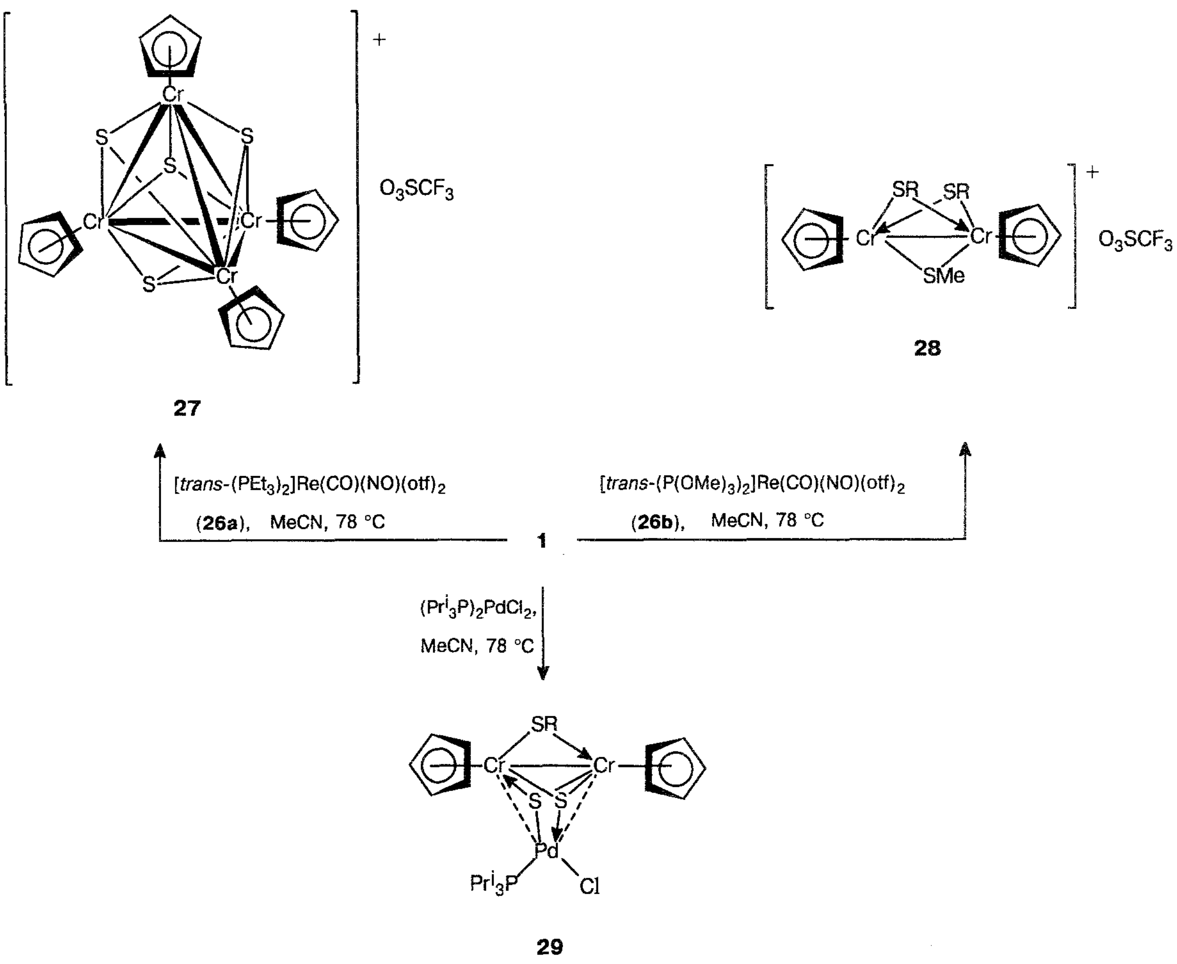
It has already been mentioned that the reaction of **1** with $(Ph_3P)_2PdCl_2$ (benzene, 20 °C) is accompanied by the exchange of acido ligands at Cr^{III} and Pd^{II} atoms to form the trinuclear ferromagnetic $Cp_2Cr_2(Cl)_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)Pd(PPh_3)$ cluster.[27] Unlike this cluster, the $(Pr^i_3P)_2PdCl_2$ complex containing bulky strongly bonded triisopropylphosphine groups does not react with **1** under these conditions and upon boiling in benzene. However, the presence of acetonitrile (a 1 : 1 MeCN—benzene mixture, 60—80 °C) in the reaction medium favors the elimination of one phosphine ligand and Cl atom from the Pd^{II} atom and the *tert*-butyl radical from the thiolate bridge in **1**. This results in the formation of the antiferromagnetic triangular $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Pd(PPr^i_3)Cl$ cluster (**29**) (see Scheme 8), which contains the linear Cp_2Cr_2 group (Cp(center)CrCr angle 174.2(5)°) with the short Cr—Cr bond (2.690(14) Å). The type of cluster **29** differs from the described triangles obtained by the reactions of **1** with rhenium and tungsten nitrosyl-halide derivatives. The structure of **29** is similar to those of products of the reactions of the dichromium complex with Rh- and Ir-containing compounds $[L_2MCl]_2$ and $L_2(CO)MCl$, $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2ML_2$ clusters (ML_2 = $Rh(CO)_2$,[24] $Rh(CO)(PPh_3)$,[25] RhCOD,[24] $Ir(CO)(PPh_3)$[25]). Compound **29** is probably formed due to the elimination of *tert*-butyl chloride from the dichromium fragment. In fact, it has been shown previously that prolonged boiling of monomers **25** in MeCN results in a partial exchange of Cl atoms for MeCN molecules.[43] Therefore, it can be expected that under similar conditions MeCN facilitates the elimination of Cl^- ions from the Pd-containing complex and its reaction with **1**, and due to the coordinational saturation of Cr atoms the eliminated Cl^- anions are bonded to the C atom of the *tert*-butyl radical of the thiolate group without involving Cr^{III} atoms. Although this results finally in the formation of heteronuclear cluster **29**, the process of its formation differs from those of triangles **6**, **13**, **14**, and **15** containing rhenium and tungsten atoms and does not involve the stage of remetalation. Thus, the failure to obtain adducts with **1** or the difficulty of transferring halogen atoms to chromium atoms prevents the formation of Cr,M-transmetallated derivatives.

4. Magnetic properties of antiferromagnetic adducts and heterometallic triangular clusters with nitrosylated metal-containing moieties

The adducts $Cp_2Cr_2(SCMe_3)_2(\mu_3\text{-}S)M(NO)L_n$ (ML_n = $Re(CO)_2Cl_2$ (**4a,b**, *cis*- and *trans*-isomers), $W_2(CO)_4(NO)I_2$ (**23**)) and triangular clusters $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)_2M(NO)L$ (ML = Re(NO) (**6a,b**), ReI (**7**), W(NO) (**13**), WCl (**14**), $W(SCMe_3)$ (**15**)) considered above exhibit antiferromagnetic properties characterized by temperature dependences of the magnetic susceptibility (χ_m) and magnetic moment (μ_{eff}):

$$\mu_{eff} = \sqrt{8\chi_m T}\ .$$

Scheme 8



It is noteworthy that peripheral metal-containing moieties are electron-saturated and diamagnetic almost in all adducts and, therefore, the use of the dimeric Heisenberg—Dirac—Van Vleck (HDVV) model[45] according to which

$$H = -2JS_1S_2 + g\beta\mathbf{H}(S_{1z} + S_{2z}),$$

where H is the Hamiltonian, $-2J$ is the exchange parameter, S are the spins of intereacting ions, g is the isotropic g-factor, β is the Bohr magneton, and $\mathbf{H}$ is the vector of magnetic field strength, makes it possible to sufficiently correctly calculate $-2J$ from the experimental temperature dependence of the magnetic susceptibility.[46] The value of the isotropic exchange parameter ($-2J$) serves as an energy criterion for the estimation of the spin-spin interaction between paramagnetic centers. It also should be taken into account that the exchange parameter in the binuclear three-bridged Cr_2S_3 fragment is the complex function and, as shown previously,[46,47] is the sum of the values that characterize the exchange *via* the direct (by the metal—metal bond) and indirect (due to bridge ligands) mechanisms.

The analysis of the magnetic data for adducts of **1** with various metal-containing moieties allows one to notice that the values of exchange interaction ($-2J$) for nitrosyl-containing compounds **4a,b** and **23** ($-2J$ = 328, 328, and 338 cm^{-1}, respectively) are considerably lower than those for initial compound **1** ($-2J$ = 430 cm^{-1}) or adducts of **1** with metal-containing carbonyl "ears", $Cp_2Cr_2(SCMe_3)_2(\mu_3\text{-}S)M(CO)_n$ (**3**: $M(CO)_n = Re_2(CO)_9$, $-2J$ = 424 cm^{-1}; **30**: $M(CO)_n = Mn_2(CO)_9$, $-2J$ = 440 cm^{-1}; **31**: $M(CO)_n = W(CO)_5$, $-2J$ = 440 cm^{-1}; **32**: $M(CO)_n = Mo(CO)_5$, $-2J$ = 440 cm^{-1}).[30,48,49] The similar decrease in $-2J$ is observed for methylated complexes $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}SMe)^+X^-$ (**28**: X = O_3SCF_3, $-2J$ = 313 cm^{-1}; **33**: X = I, $-2J$ = 350 cm^{-1}) (Table 1). Some geometric parameters of the three-bridged dichromothiolate sulfide fragment in molecules of adducts with nitrosyl-containing metal moieties **4a,b** and **23** and methylated cation in **28** noticeably differ from the corresponding values for **1**, **3**, **30**, **31**, and **32**. For example, the Cr—Cr (2.764—2.788 Å) and Cr—S(sulfide) (2.32—2.36 Å) distances for the first group of compounds are higher than similar distances in **1** (*R*(Cr—Cr) 2.689 Å, *R*(Cr—S(sulfide))

Table 1. Structural and magnetic parameters of adducts $Cp_2Cr_2(SCMe_3)_2(\mu_3\text{-}S)ML_n$

Compound	ML_n	*R*(Cr—Cr) /Å	φ(Cp(c)CrCr) /deg	*R*(M—μ_3-S) /Å	*R*(Cr—μ-S) /Å	φ(Cr(μ-S)Cr) /deg	*R*(Cr—SR) /Å	φ(Cr(SR)Cr) /deg	μ_{eff} /μ_B (*T*/K)	−2*J* /cm^{-1}
1	—	2.689(8)	177.5(9)	—	2.24(1)	74.1(5)	2.38(1)	68.3(4); 69.3(4)	0.98—0.02 (297—79)	430
3	$Re_2(CO)_9$	2.732(2)	176.7(1)	2.555(2)	2.318(2)— 2.329(2)	72.01(5)	2.330(1)— 2.356(1)	71.28(6); 71.32(6)	1.29—0.32 (296—77)	424
30	$Mn_2(CO)_9$	2.739(8)	176.2(4)	2.448(9)	2.31(1)	72.7(3)	2.35(1)	71.4(3)	1.26—0.65 (295—80)	440
31	$W(CO)_5$	2.73(1)	178.2(9)	2.57(2)	2.27(2)	73.7(5)	2.35(2)	71.7(6)	1.09—0.04 (295—77)	440
32	$Mo(CO)_5$	2.73(1)	178.3(8)	2.58(2)	2.28(2)	73.9(5)	2.37(2)	70.3(7)	1.08—0.02 (295—77)	440
4a	$Re(CO)_2(NO)$—Cl_2(*cis*-isomer)	2.777(6)	177.0(5)	2.502(9)	2.338(9)— 2.313(9)	73.3(3)	2.343(9); 2.384(9)	72.2(3); 73.3(3)	1.36—0.60 (291—79)	328
4b	$Re(CO)_2(NO)$—Cl_2(*trans*-isomer)	2.788(3)	179.3(1)	2.461(3)	2.332(2)	73.4(1)	2.358(3); 2.361(3)	72.4(1); 72.5(1)	1.39—0.62 (291—79)	328
23	$W_2(CO)_4$—$(NO)_2I_2$	2.764(4)	179.3(1)	2.551(5); 2.566(5)*	2.357(5)	71.8(2)	2.351(5)— 2.362(5)	71.6(2); 72.0(2)	1.42—0.56 (291—79)	338
28	CH_3^+	2.766(2)	178.9(1)	—	2.357(3)**	71.9(1)***	2.347(3)— 2.361(3)	71.8(1); 72.1(1)	1.42—0.34 (294—79)	313

* The W—μ_4-S bond. ** The Cr—SMe bond. *** The Cr(SMe)Cr angle.

2.24 Å) and carbonyl-containing adducts (*R*(Cr—Cr) 2.73 Å, *R*(Cr—S(sulfide)) 2.27—2.32 Å). At the same time, the values of the Cr—SR bond lengths are very similar (2.34—2.38 Å) in all compounds (see Table 1). The probable reason for the noticeable weakening of metal—metal and metal—sulfide bonds, which appears in the case of nitrosyl-containing adducts and methylated complexes, can be the weakening of the additional π-interaction between lone electron pairs of the sulfide bridge and half-occupied orbitals of Cr^{III} atoms due to withdrawal of the electron density from the S atom bonded to the strongly accepting $M(NO)L_n$ moieties or CH_3^+ substituent. This effect is especially noticeable in $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_4\text{-}S)W_2(CO)_4(NO)_2(\mu\text{-}I)_2$ (**23**), in which both electron pairs of the sulfide bridge participate in binding with two tungsten atoms, and thus, the possibility of an additional bonding is excluded (the Cr—S(sulfide) equal to 2.357 Å is nearly equivalent to the Cr—SR distance of 2.351—2.362 Å). On the contrary, the Cr—S(sulfide) bonds are the strongest (2.24 Å) in free **1**, whose structure possesses the maximum possibility for this π-interaction. However, according to the quantum chemical calculations for Mo- and Cr-containing sulfide-bridged clusters,[50] similar compounds are typical of the substantial mixing of molecular orbitals of M—S and M—M bonds. It can be assumed that in adducts **3**, **30**, **31**, and **32** the effect of metal-containing carbonyl moieties bonded to the sulfide bridge in the dichromium fragment is reduced only to the inconsiderable weakening of Cr—S(sulfide) and Cr—Cr bonds (see Table 1), and the value of exchange parameter −2*J* remains unchanged, while stronger acceptors (nitrosyl-containing metal moieties and CH_3^+) noticeably weaken the corresponding bonds and exchange interactions *via* both channels (*via* the metal—metal bond and the bridge S atom).

It should be mentioned in this connection that the values of CrSCr angles are rather close for the compounds listed and do not correlate with −2*J*, and the Cp(center)CrCrCp(center) system remains linear to provide formally the best conditions for overlapping of half-occupied orbitals of Cr^{III} atoms and formation of the metal—metal bond (see Table 1). If the Cp_2Cr_2 fragment is bent, the Cr—Cr bonding is strongly weakened, which results in the fact that in triangular $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)_2M(NO)L$ (ML = Re(NO) (**6a,b**), W(NO) (**13**), WCl (**14**), $W(SCMe_3)$ (**15**)) clusters, in which the magnetic $Cp_2Cr_2S_2$ system contains the bent Cp(center)CrCrCp(center) fragment, the Cr—Cr distances substantially increase (>3.0 Å), and exchange parameters −2*J* calculated in terms of the dimeric HDVV model (M(NO)L metal-containing moieties are diamagnetic) are noticeably lower than those in **1** or its adducts and range from 231 to 272 cm^{-1} (Table 2). The −2*J* values are close for triangular clusters, despite the difference in electron configurations of M (Re and W atoms have 18-electron configurations in **6** and **13**, while **14** and **15** contain 16-electron W atoms).

Table 2. Geometric parameters and magnetic properties of clusters $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu\text{-}SCMe_3)_2M(NO)L$

Compound	M, L	Geometric parameters of the $Cp_2Cr_2S_2$ fragment				R(M—Cr) /Å	μ_{eff}* /μ_B (T/K)	$-2J$ /cm^{-1}
		Cr—Cr /Å	Cr—S(sulf) /Å	Cp(c)CrCr /deg	Tors. angle, ω Cp(c)CrCrCp(c) /deg			
6a	Re, CO	3.010(6)	2.344(6)	126.5(6)	3.6	2.940(5)	1.65—0.55 (288—79)	231
6b	Re, CO	3.002(4)	2.335(5)	127.0(5)	3.1	3.080(5)	1.67—0.58 (296—82)	228
13	W, NO	3.025(4)	2.343(4)	124.2(4)	3.3	3.088(3)	1.61—0.74 (290—79)	272
14	W, Cl**	3.036(4); 3.068(4)	2.288(5)— 2.317(5)	124.2(5)— 127.9(5)	3.6; 1.6	2.843(3)— 2.889(3)	1.49—0.40 (290—79)	270
15	W, SR	3.027(1)	2.338(2)	126.9(1)	0	3.090(2)	1.52—0.59 (291—79)	246

* Calculated per Cr atom. ** Two independent molecules in the block cell.

Probably, this means that magnetic parameters of these clusters are mainly determined by electron and geometric parameters of the magnetic $Cp_2Cr_2S_2$ fragment, which are close for the compounds studied (see Table 2).

However, the appearance of the third paramagnetic Re^{II} atom in the $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)_2Re(NO)I$ cluster (**7**) results in the distortion of the metal core, and the Cr—Cr distance increases to 3.123 Å. This affects exchange interactions, and the $-2J$(Cr—Cr) value decreases to 70 cm^{-1} ($-2J$(Re—Cr) = 320 cm^{-1}). The Cr—Cr bond cleavage can be the possible reason for this weakening of the exchange. It is noteworthy that a similar change in magnetic properties due to the metal—metal bond cleavage has been observed previously for alkoxide $Cp_2Cr_2(\mu\text{-}OCMe_3)_2X_2$ complexes with close geometric parameters of the $Cp_2Cr_2O_2$ fragment.[47] At the same time, one cannot rule out the effect of the third paramagnetic center (Re^{II}, $S = 1/2$), whose appearance results in an increase in the ferromagnetic contribution to the antiferromagnetic exchange and, as shown previously,[51] decreases antiferromagnetic type spin-spin interactions. Both factors result in a decrease in the value of exchange parameter $-2J$ (see Table 2). Thus, the observed dependences of the energy parameter of the spin-spin interaction on electron and geometric factors demonstrate the possibilities to control magnetic properties of clusters at the molecular level.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 93-03-5394) and the Swiss National Science Foundation. The authors are grateful to Prof. A. A Pasynskii for useful discussions.

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Received June 27, 1995;
in revised form July 27, 1995