Polynuclear nitrosyl carbonyl Re^I complexes with thiolate and sulfide bridges

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The reaction of the complex $Re_2(CO)_4(NO)_2Cl_4$ (**1**) with $NaSCMe_3$ (**2**) (in THF or MeCN, 65—80 °C, 24 h) was studied at different ratios of the reagents (from 1 : 2 to 1 : 6). At the reagent ratio of 1 : 2, the binuclear complex $Re_2(CO)_4(NO)_2Cl_2(\mu\text{-}SCMe_3)_2$ (**3**) was obtained as a mixture of *syn* and *anti* isomers (**3a** and **3b**, respectively) containing Re_2S_2 fragments with different structures (the butterfly-like structure in **3a** and the planar fragment in **3b**). When the initials were taken in ratios from 1 : 4 to 1 : 6, two compounds were isolated: the binuclear complex $Re_2(CO)_4(NO)_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ **4** (cocrystallized as a mixture of *syn* and *anti* isomers, **4a** and **4b**, respectively) and the triangular cluster $Re_3(CO)_3(NO)_3(\mu\text{-}SCMe_3)_3(\mu_3\text{-}S)(\mu_3\text{-}Cl)$ (**5**). Apparently, complex **4** is formed in the course of isolation as a result of elimination of SR_2 from the unstable tetrathiolate dimer $Re_2(CO)_4(NO)_2(SCMe_3)_2(\mu\text{-}SCMe_3)_2$ (**6**). Cluster **5** is the product of the reaction between compounds **3** and **4**. Products of interaction of compound **6** with silica gel upon column chromatography of the reaction mixture were studied. Four complexes containing hydroxy and oxo bridging groups, $(CO)_2(NO)Re(\mu\text{-}SCMe_3)_2(\mu\text{-}OH)Re(SCMe_3)(CO)(NO)$ (**7**), $(CO)_3(NO)_3Re_3(\mu\text{-}SCMe_3)_3(\mu_3\text{-}SCMe_3)(\mu_3\text{-}O)$ (**8**), $[(CO)_2(NO)_2Re_2(SCMe_3)_2(\mu\text{-}SCMe_3)_2(\mu\text{-}OH)][Na(THF)(Et_2O)]$ (**9**), and $[(CO)_2(NO)_2Re_2(SCMe_3)_2(\mu\text{-}SCMe_3)_2(\mu\text{-}OH)]_2[Na(H_2O)_6][H_5O_2]$ (**10**), were isolated. The structures of complexes **3**, **4**, **5**, **7**, **8**, **9**, and **10** were established by X-ray diffraction study.

Key words: rhenium complexes, rhenium clusters, nitrosyl ligands, thiolate and sulfide bridges; X-ray analysis.

Thiolate and thiolate sulfide complexes of transition metals[1] attract attention as catalysts of redox reactions[2] and also as models of metal-containing enzymes.[3] However, the corresponding Re^I compounds are poorly studied. Only several carbonyl-containing dimers of composition $(CO)_6L_2Re_2(\mu\text{-}SR)_2$ (R = Bu^t and L = CO;[4] and R = Bu^t and L = MeCN[5]) are known. Their structures are similar to those of the corresponding halogen-containing derivatives. Recently, we reported[6—8] procedures for the chemical assembly of clusters with Cr and Re atoms in which metal atoms are bonded *via tert*-butylthiolate and sulfide bridging ligands. In these compounds, the terminal nitrosyl and carbonyl groups are coordinated to the Re^I atoms. This fact suggests that it is possible to synthesize "pure" carbonylnitrosyl rhenium clusters containing thiolate and thiolate sulfide fragments. One would expect that the reaction with the use of the binuclear complex $Re_2(CO)_4(NO)_2Cl_2(\mu\text{-}Cl)_2$ (**1**)[9] as the starting material will afford the intermediate thiolate halide complexes $Re_2(CO)_4(NO)_2Cl_2(\mu\text{-}SR)_2$, which are promising compounds as matrices in studies of unsaturated organic molecule transformations occurring between two rhenium metal centers (analogously to the known ruthenium complexes $Cp_2Ru_2(Cl)_2(\mu\text{-}SR)_2$).[10]

In this work, we studied the synthesis, chemical properties, and stability of new bi- and trinuclear thiolate and thiolate sulfide rhenium complexes with nitrosyl ligands.

Results and Discussion

The chemical properties of the binuclear complex $Re_2(CO)_4(NO)_2Cl_2(\mu\text{-}Cl)_2$ (**1**) have been studied in detail.[11—15] In particular, it was demonstrated that the CO groups in complex **1** are readily replaced by the N- and P-donors,[11—15] THF,[14] or cyclooctadiene.[13] In all the cases, except for the last-mentioned, the mononuclear complexes $L_{n+1}Re(CO)_{2-n}(NO)Cl_2$ (n = 0 or 1) were formed. The halogen atoms in these mononuclear complexes can be replaced by tosylate[15] or triflate[13,14] groups, acetylenide fragments,[11] or an *ortho*-metallated azobenzene ligand using exchange reactions.[15]

Formation of thiolate and thiolate sulfide rhenium(I) complexes

Complex **1** reacts with $NaSCMe_3$ (**2**) in polar solvents (THF or MeCN). It is difficult to perform the

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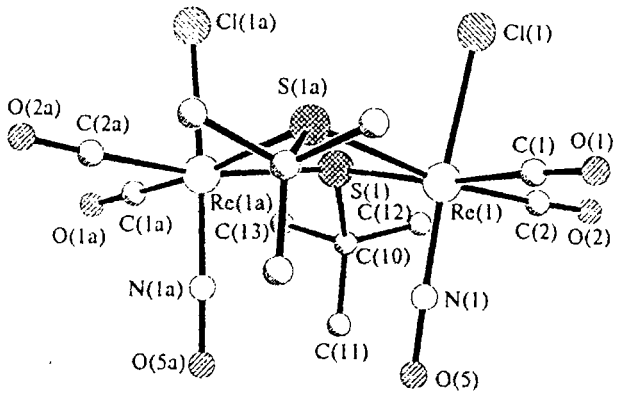


Fig. 1. Structure of *syn*-$Re_2(CO)_4(NO)_2Cl_2(\mu\text{-}SCMe_3)_2$ (**3a**) in the crystals of **3** and **3a**.

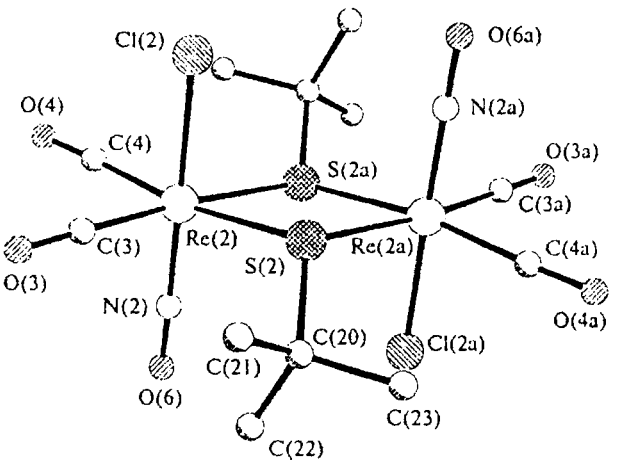


Fig. 2. Structure of *anti*-$Re_2(CO)_4(NO)_2Cl_2(\mu\text{-}SCMe_3)_2$ (**3b**) in the crystal of **3**.

reaction of compound **2** in benzene or toluene because of poor solubility of **2** in these solvents. The reaction products are very sensitive to moisture and are readily converted into polynuclear hydroxides. When the starting compounds were taken in a ratio of 1 : 2, the major products were the *syn* and *anti* isomers of the complex $Re_2(CO)_4(NO)_2Cl_2(\mu\text{-}SCMe_3)_2$ (**3a** and **3b**, respectively) (Scheme 1). These isomers were isolated from the reaction mixture by fractional crystallization as crystals of **3** containing both isomers in a ratio of 1 : 1. We failed to separate stereoisomers by crystallization (only several crystals of the *syn* isomer were isolated). It was impossible to use preparative thin-layer or column chromatography on SiO_2 or Al_2O_3 due to rapid hydrolysis of compound **3** even under an inert atmosphere.

X-ray diffraction study of complex **3** (Figs. 1 and 2, Table 1) demonstrated that the cyclic Re_2S_2 fragment (Re...Re, 3.790(1) Å; Re—S, 2.491(4) Å) in *syn* isomer **3a** is nonplanar. The folding angle along the Re...Re line is 34.8(1)°. The NO groups are in cisoid positions (Re—N, 1.785(13) Å; N—O, 1.19(2) Å), and the ClReNO groups are linear (Re—Cl, 2.418(5) Å, the Cl—Re—NO angle is 176.4(3)°). In *anti* isomer **3b**, the cyclic Re_2S_2 fragment is planar (Re...Re, 3.822(1) Å; Re—S, 2.478(5) Å), and the NO ligands are in *trans* positions with respect to each other (Re—NO, 1.84(2) Å; N—O, 1.18(2) Å). As a result of this arrangement, the angle between the linear ClReNO group (Re—Cl, 2.419(6) Å; the Cl—Re—NO angle is 177.7(5)°) and the metal—metal line is close to the right angle (91.8(1)°), unlike molecule **3a** in which a substantial distortion from the orthogonal arrangement is observed (the ClReNO/Re...Re angle is 99.2(1)°). It should be noted that the conformation of the $Re_2(SR)_2$ ring in molecule **3b** is similar to the conformations observed in the struc-

Table 1. Selected bond lengths (*d*) and bond angles (ω) in the binuclear *syn* and *anti* isomers of complex **3**

Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
Re(1)—S(1)	2.494(4)	S(1)—Re(1)—Cl(1)	86.2(1)	Cl(2)—Re(2)—C(3)	89.5(5)
Re(1)—Cl(1)	2.418(5)	S(1)—Re(1)—N(1)	96.7(4)	N(2)—Re(2)—C(3)	91.6(7)
Re(1)—N(1)	1.785(13)	Cl(1)—Re(1)—N(1)	176.4(3)	S(2)—Re(2)—C(4)	171.2(6)
Re(1)—C(1)	1.972(18)	S(1)—Re(1)—C(1)	170.3(5)	Cl(2)—Re(2)—C(4)	88.3(6)
Re(1)—C(2)	1.944(17)	Cl(1)—Re(1)—C(1)	85.7(5)	N(2)—Re(2)—C(4)	89.7(8)
Re(1)—S(1a)	2.491(4)	N(1)—Re(1)—C(1)	91.6(6)	C(3)—Re(2)—C(4)	86.9(8)
Re(2)—S(2)	2.478(5)	S(1)—Re(1)—C(2)	98.6(4)	S(2)—Re(2)—S(2a)	79.8(2)
Re(2)—Cl(2)	2.419(6)	Cl(1)—Re(1)—C(2)	83.7(5)	Cl(2)—Re(2)—S(2a)	93.6(2)
Re(2)—N(2)	1.840(18)	N(1)—Re(1)—C(2)	93.7(6)	N(2)—Re(2)—S(2a)	85.5(4)
Re(2)—C(3)	1.913(18)	C(1)—Re(1)—C(2)	85.9(6)	C(3)—Re(2)—S(2a)	173.9(5)
Re(2)—C(4)	1.932(20)	S(1)—Re(1)—S(1a)	76.8(2)	C(4)—Re(2)—S(2a)	98.4(6)
Re(2)—S(2a)	2.505(4)	Cl(1)—Re(1)—S(1a)	86.0(1)	Re(1)—S(1)—Re(1a)	98.9(2)
S(1)—Re(1a)	2.491(4)	N(1)—Re(1)—S(1a)	96.8(4)	Re(2)—S(2)—Re(2a)	100.2(2)
S(2)—Re(2a)	2.505(4)	C(1)—Re(1)—S(1a)	97.3(5)	Re(1)—N(1)—O(5)	177.0(14)
N(1)—O(5)	1.187(18)	C(2)—Re(1)—S(1a)	168.9(5)	Re(2)—N(2)—O(6)	177.1(14)
N(2)—O(6)	1.182(23)	S(2)—Re(2)—Cl(2)	83.2(2)	Re(1)—C(1)—O(1)	174.2(16)
O(1)—C(1)	1.141(22)	S(2)—Re(2)—N(2)	98.7(5)	Re(1)—C(2)—O(2)	177.6(14)
O(2)—C(2)	1.156(21)	Cl(2)—Re(2)—N(2)	177.7(5)	Re(2)—C(3)—O(3)	177.5(18)
O(3)—C(3)	1.121(24)	S(2)—Re(2)—C(3)	95.3(6)	Re(2)—C(4)—O(4)	176.4(15)
O(4)—C(4)	1.141(25)				

Scheme 1

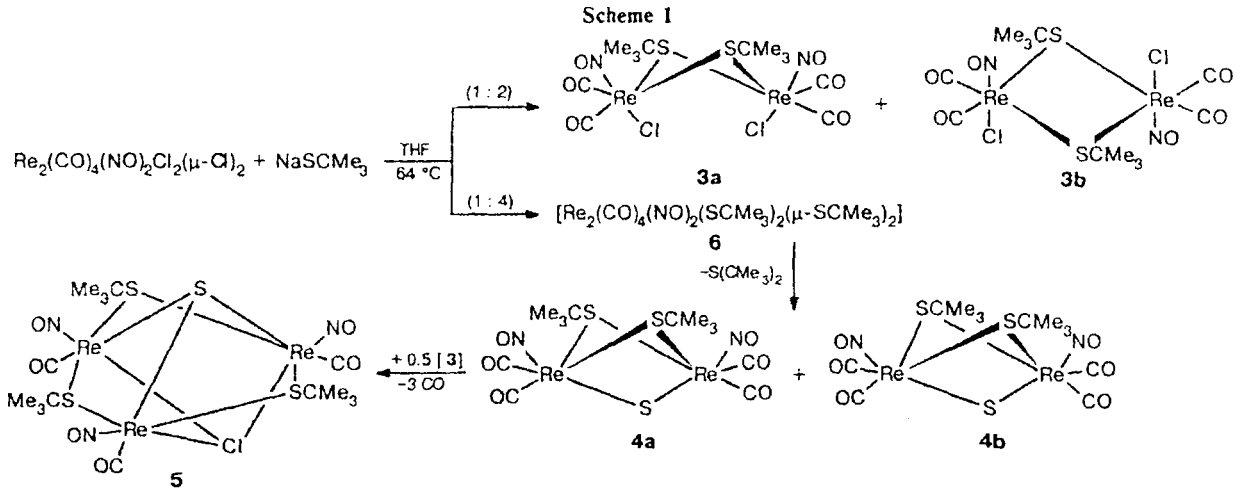


Table 2. Selected bond lengths (d) and bond angles (ω) in the molecule of thiolate sulfide complex **4**

Bond	d/Å	Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
Re(1)—S(1)	2.444(13)	S(1)—Re(1)—S(2)	87.3(5)	C(1)—Re(1)—C(2)	90.5(16)	S(3)—Re(2)—C(4)	101.0(15)
Re(1)—S(2)	2.463(17)	S(1)—Re(1)—S(3)	64.0(6)	S(1)—Re(2)—S(2)	85.9(4)	N(2)—Re(2)—C(4)	85.4(19)
Re(1)—S(3)	2.546(22)	S(2)—Re(1)—S(3)	78.3(6)	S(1)—Re(2)—S(3)	62.8(5)	C(3)—Re(2)—C(4)	89.6(16)
Re(1)—N(1)	1.861(28)	S(1)—Re(1)—N(1)	89.9(11)	S(2)—Re(2)—S(3)	77.5(6)	Re(1)—S(1)—Re(2)	88.8(4)
Re(1)—C(1)	1.833(37)	S(2)—Re(1)—N(1)	121.4(14)	S(1)—Re(2)—N(2)	113.8(11)	Re(1)—S(2)—Re(2)	88.8(6)
Re(1)—C(2)	1.947(40)	S(3)—Re(1)—N(1)	147.6(12)	S(2)—Re(2)—N(2)	95.0(17)	Re(1)—S(3)—Re(2)	84.8(7)
Re(2)—S(1)	2.495(10)	S(1)—Re(1)—C(1)	166.5(15)	S(3)—Re(2)—N(2)	171.8(16)	Re(1)—N(1)—O(3)	169.7(33)
Re(2)—S(2)	2.477(19)	S(2)—Re(1)—C(1)	80.5(11)	S(1)—Re(2)—C(3)	146.8(16)	Re(2)—N(2)—O(4)	172.0(33)
Re(2)—S(3)	2.577(22)	S(3)—Re(1)—C(1)	118.5(11)	S(2)—Re(2)—C(3)	103.8(12)	Re(1)—C(1)—O(1)	167.5(37)
Re(2)—N(2)	1.793(51)	N(1)—Re(1)—C(1)	91.5(15)	S(3)—Re(2)—C(3)	88.0(14)	Re(1)—C(2)—O(2)	177.5(29)
Re(2)—C(3)	1.908(31)	S(1)—Re(1)—C(2)	102.9(13)	N(2)—Re(2)—C(3)	97.1(16)	Re(2)—C(3)—O(5)	174.5(34)
Re(2)—C(4)	1.983(42)	S(2)—Re(1)—C(2)	143.2(10)	S(1)—Re(2)—C(4)	81.5(9)	Re(2)—C(4)—O(6)	176.0(37)
S(1)—C(5)	1.916(47)	S(3)—Re(1)—C(2)	74.9(12)	S(2)—Re(2)—C(4)	166.4(9)		
S(2)—C(9)	1.860(34)	N(1)—Re(1)—C(2)	94.2(13)				
S(3)—C(5a)	1.930(54)						
C—O(aver.)	1.18(5)						
N—O(aver.)	1.21(5)						

tures of the above-mentioned carbonylthiolate dimers when only *anti* isomers (with the planar rhenium-containing ring) were isolated (in $(CO)_6L_2Re_2(\mu\text{-}SR)_2$: R = Bu[t] and L = CO;[4] Re...Re, 3.808(1)A; Re—S, 2.507(3) Å; and R = Bu[t] and L = MeCN;[5] Re...Re, 3.882(1) Å; Re—S, 2.522(3)—2.534(4) Å). However, an important characteristic feature of complex **3b** in this series is a substantial shortening of the Re—S bonds (see Table 1) owing to the presence of nitrosyl strong acceptor substituents.

At the reagent ratio of 1 : 4, all halogen atoms in molecule **1** should be substituted. Refluxing of this mixture in THF afforded an orange solution from which two diamagnetic compounds were isolated by fractional crystallization: the binuclear thiolate sulfide complex $Re_2(CO)_4(NO)_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (**4**) (as a mixture of *syn* (**4a**) and *anti* isomers (**4b**), in low yield) and the trinuclear cluster $Re_3(CO)_3(NO)_3(\mu\text{-}SCMe_3)_3(\mu_3\text{-}S)(\mu_3\text{-}Cl)$ (**5**) as the major product (see Scheme 1). The IR spectrum of complex **4** has four bands characterizing CO stretching vibrations (2072, 2010, 1992, and 1896 cm^{-1}) and one band corresponding to the NO groups (1765 cm^{-1}). Ac-

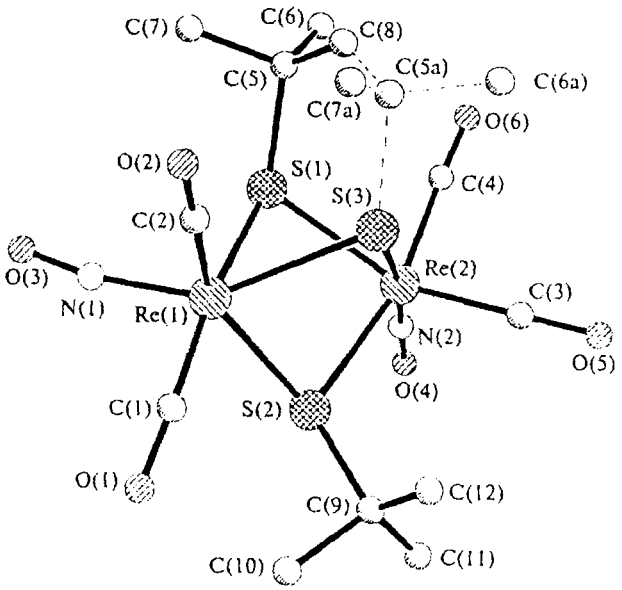


Fig. 3. Structures of *syn* and *anti* isomers of $Re_2(CO)_4(NO)_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (**4**).

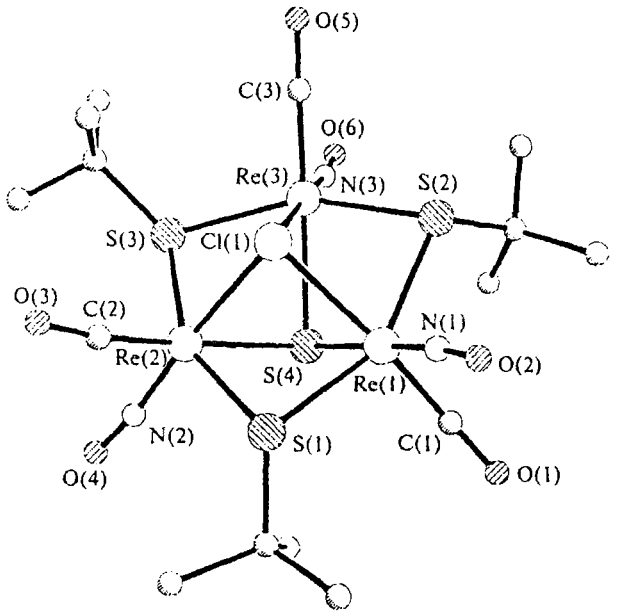


Fig. 4. Structure of the trinuclear cluster $Re_3(CO)_3(NO)_3(\mu\text{-}SCMe_3)_3(\mu_3\text{-}S)(\mu_3\text{-}Cl)$ (**5**).

cording to the data of X-ray analysis, the asymmetric unit contains two isomers with the *syn* and *anti* arrangements of the *tert*-butyl substituents in the thiolate bridges (Fig. 3, Table 2), which differ in the orientation of the alkyl radicals (disorder) at the adjacent sulfur atoms (occupancies of the C atoms of the *tert*-butyl groups at two of three S atoms are 0.5, see Fig. 3), unlike complex **3**, whose crystals contain both isomers as independent molecules. Therefore, it is impossible to determine accurate geometric characteristics of the metal core of each isomer of complex **4** (Re...Re, 3.451(1) Å; Re—SR, 2.444(18)—2.495(16) Å; Re—S, 2.456(22) and 2.577(22) Å; Re—N, 1.79(5) and 1.86(3) Å; Re—C, 1.94(4) and 1.98(4) Å; the Re—SR—Re angles are 88.8(4)° and 88.4(6)°) although, similar to molecule **3**, the Re—SR bonds are substantially strengthened due to the high metal center accepting ability being enhanced by the nitrosyl ligands.

The IR spectrum of triangular cluster **5** has one stretching band of the CO ligands and one stretching band of the NO ligands (1980 and 1721 cm^{-1}, respectively). The X-ray data demonstrated that the core of the molecule is the Re_3 triangle with the nonbonded metal—metal distances (Re...Re, 3.335(1), 3.346(1), and 3.313(1) Å) (Fig. 4, Table 3). The tridentate S (Re—S, 2.565(8)—2.573(9) Å) and Cl (Re—Cl, 2.476(9)—2.508(9) Å) atoms are located above and below the plane of this triangle. All sides of this triangle are supplemented with the *tert*-butylthiolate bridging fragments (Re—S, 2.433(9)—2.440(10) Å). Each Re atom is bonded to the terminal CO and NO groups (Re—C, 1.89(3), 1.84(3), and 1.94(3) Å; Re—N, 1.70(3), 1.81(3), and 1.81(3) Å). As a result, in complex **5** the metal atoms have 18-electron configurations and a distorted octahedral environment.

To increase the solubility of compound **2**, we carried out the reaction in MeCN (the ratio of the reagents was 1 : 4), the nature of the resulting products remained virtually unchanged. In this case, only an insignificant change in the ratio of complexes **4** and **5** was observed, while we failed to isolate the expected tetrathiolate dimer $Re_2(CO)_4(NO)_2(SR)_2(\mu\text{-}SR)_2$ (**6**, R = CMe_3), which is the product of complete dehalogenation. It can be suggested that dimer **6** was formed in the presence of an excess of compound **2**, however, because of rather severe conditions, it underwent thermolysis with elimination of R_2S to form complex **4**, as was observed previously[16] in the synthesis of $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$. In addition,

Table 3. Selected bond lengths (d) and bond angles (ω) in the molecule of triangular cluster **5**

Bond	d/Å	Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
Re(1)—S(1)	2.440(10)	S(1)—Re(1)—S(2)	151.3(3)	S(4)—Re(2)—Cl(1)	81.0(3)	S(2)—Re(3)—C(3)	95.3(14)
Re(1)—S(2)	2.433(9)	S(1)—Re(1)—S(4)	83.6(3)	S(1)—Re(2)—N(2)	102.9(10)	S(3)—Re(3)—C(3)	103.4(14)
Re(1)—S(4)	2.576(10)	S(2)—Re(1)—S(4)	82.8(3)	S(3)—Re(2)—N(2)	95.6(9)	S(4)—Re(3)—C(3)	174.5(11)
Re(1)—Cl(1)	2.476(9)	S(1)—Re(1)—Cl(1)	76.8(3)	S(4)—Re(2)—N(2)	95.4(10)	Cl(1)—Re(3)—C(3)	93.3(11)
Re(1)—N(1)	1.704(27)	S(2)—Re(1)—Cl(1)	76.3(3)	Cl(1)—Re(2)—N(2)	176.3(11)	N(3)—Re(3)—C(3)	88.8(14)
Re(1)—C(1)	1.885(31)	S(4)—Re(1)—Cl(1)	81.5(3)	S(1)—Re(2)—C(2)	94.7(11)	Re(1)—S(1)—Re(2)	86.0(3)
Re(2)—S(1)	2.451(10)	S(1)—Re(1)—N(1)	94.9(9)	S(3)—Re(2)—C(2)	102.1(10)	Re(1)—S(2)—Re(3)	86.6(3)
Re(2)—S(3)	2.420(8)	S(2)—Re(1)—N(1)	100.2(9)	S(4)—Re(2)—C(2)	170.9(12)	Re(2)—S(3)—Re(3)	85.9(3)
Re(2)—S(4)	2.573(8)	S(4)—Re(1)—N(1)	175.9(8)	Cl(1)—Re(2)—C(2)	89.9(13)	Re(1)—S(4)—Re(2)	80.8(2)
Re(2)—Cl(1)	2.508(10)	Cl(1)—Re(1)—N(1)	101.8(9)	N(2)—Re(2)—C(2)	93.7(16)	Re(1)—S(4)—Re(3)	81.1(3)
Re(2)—N(2)	1.813(35)	S(1)—Re(1)—C(1)	100.2(9)	S(2)—Re(3)—S(3)	153.3(3)	Re(2)—S(4)—Re(3)	80.2(2)
Re(2)—C(2)	1.936(35)	S(2)—Re(1)—C(1)	104.8(8)	S(2)—Re(3)—S(4)	82.9(3)	Re(1)—Cl(1)—Re(2)	84.0(3)
Re(3)—S(2)	2.439(11)	S(4)—Re(1)—C(1)	89.5(10)	S(3)—Re(3)—S(4)	76.8(3)	Re(1)—Cl(1)—Re(3)	84.3(3)
Re(3)—S(3)	2.437(11)	Cl(1)—Re(1)—C(1)	170.8(11)	S(2)—Re(3)—Cl(1)	75.7(3)	Re(2)—Cl(1)—Re(3)	82.7(3)
Re(3)—S(4)	2.565(9)	N(1)—Re(1)—C(1)	87.1(13)	S(3)—Re(3)—Cl(1)	84.2(3)	Re(1)—N(1)—O(2)	177.8(25)
Re(3)—Cl(1)	2.504(8)	S(1)—Re(2)—S(3)	154.1(3)	S(4)—Re(3)—Cl(1)	81.2(3)	Re(2)—N(2)—O(4)	175.7(33)
Re(3)—N(3)	1.815(29)	S(1)—Re(2)—S(4)	83.4(3)	S(2)—Re(3)—N(3)	101.9(11)	Re(3)—N(3)—O(6)	174.3(30)
Re(3)—C(3)	1.838(37)	S(3)—Re(2)—S(4)	76.9(3)	S(3)—Re(3)—N(3)	97.5(12)	Re(1)—C(1)—O(1)	172.7(29)
C—O(aver.)	1.16(4)	S(1)—Re(2)—Cl(1)	76.0(3)	S(4)—Re(3)—N(3)	96.7(9)	Re(2)—C(2)—O(3)	175.5(39)
N—O(aver.)	1.18(4)	S(3)—Re(2)—Cl(1)	84.4(3)	Cl(1)—Re(3)—N(3)	177.0(10)	Re(3)—C(3)—O(5)	176.2(35)

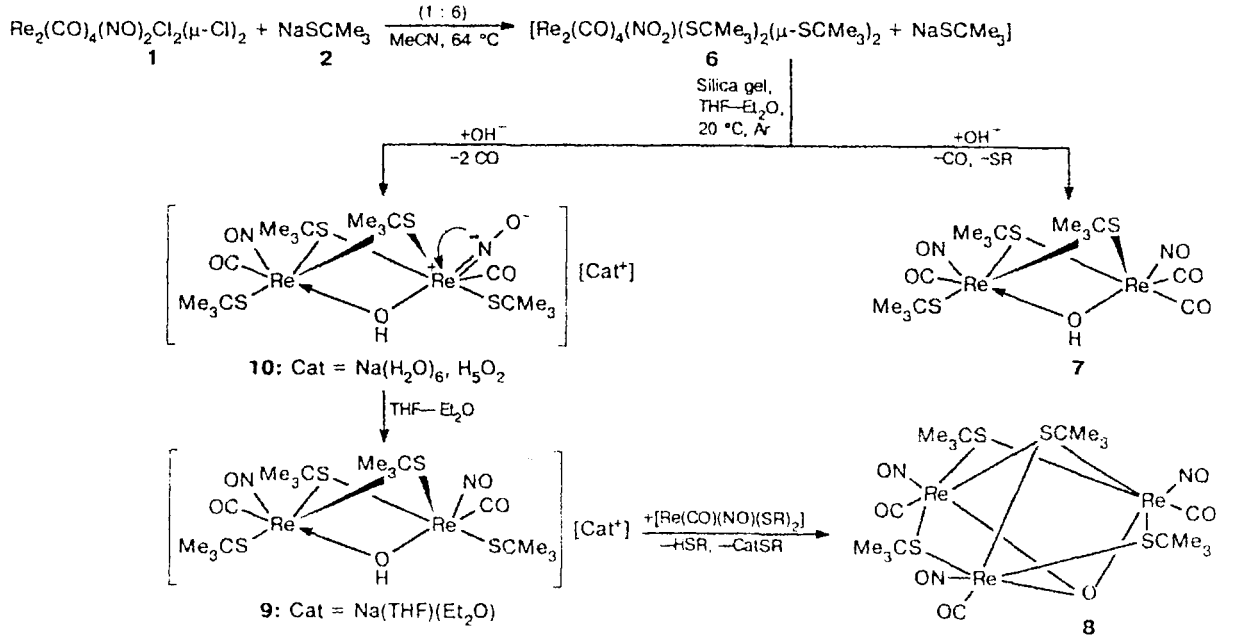
complex **4** containing a sulfide bridge with two lone electron pairs, reacts readily with intermediate halogen-containing thiolate **3** (analogously to the reaction of the dichromium complex with compound **1**, which we have studied previously[6]) and forms cluster **5** after partial decarbonylation. According to the scheme suggested, when the reaction was carried out with the reagents taken in a ratio of 1 : 4 upon heating, complex **1** and intermediate compounds **3**, **4**, and **6** were consumed in the course of the reaction, and therefore, it is not surprising that triangular cluster **5** was the major product. To increase the concentration of dimer **6** in the reaction mixture, we increased the concentration of sodium thiolate (to the ratio of 1 : 6) and used MeCN in which the solubility of $NaSCMe_3$ is substantially higher. However, in this case, only compounds **4** and **5** were isolated (by concentrating the reaction solution *in vacuo* upon heating). As was mentioned above, we could not use chromatography for separating the reaction products because they readily underwent hydrolysis even under an inert atmosphere. However, in this case *tetrathiolate* hydroxo complexes would be expected to be isolated, which would be indirect evidence in favor of the suggested scheme of conversions.

Interaction of thiolate rhenium(I) complexes with silica gel

The interaction of compound **1** with **2** at a reagent ratio of 1 : 6 (in boiling MeCN for 24 h) leads to complete disappearance of complex **1** and to the absence of complex **3** in the solution (when using IR spectroscopy for monitoring the course of the reaction, we could detect only compound **1** and **3** because the positions of their CO and NO stretching bands differ substantially from the absorption bands of the other reaction products). In this case, the amount of NaCl that precipitated corresponded to complete substitution of the halogen atoms in the initial rhenium dimer. After removal of MeCN at reduced temperatures (from −10 to −15 °C), the reaction mixture in THF was chromatographed on silica gel (the best result was obtained when Kieselgel 60 was used) in Ar atmosphere. In this case, the following diamagnetic complexes were obtained: **4** (in low yield), $(CO)_2(NO)Re(\mu\text{-}SCMe_3)_2(\mu\text{-}OH)Re(SCMe_3)(CO)(NO)$ (**7**), $(CO)_3(NO)_3Re_3(\mu\text{-}SCMe_3)_3(\mu_3\text{-}SCMe_3)(\mu_3\text{-}O)$ (**8**), $[(CO)_2(NO)_2Re_2(SCMe_3)_2(\mu\text{-}SCMe_3)_2(\mu\text{-}OH)][Na(THF)(Et_2O)]$ (**9**), and $[(CO)_2(NO)_2Re_2(SCMe_3)_2(\mu\text{-}SCMe_3)_2(\mu\text{-}OH)]_2[Na(H_2O)_6][H_5O_2]$ (**10**) (Scheme 2). It should be noted that we failed to separate the last two mentioned ionic compounds either by chromatography or by fractional crystallization. However due to the different habitus of the crystals (the major product, complex **9**, was obtained as yellow-green prismatic crystals, while compound **10** was obtained as yellow-orange plates in an insignificant amount), they were separated mechanically.

All the compounds obtained are air-stable in the solid state. The IR spectrum of binuclear complex **7**, which was isolated as thin needle-like orange-yellow crystals, shows three stretching bands of the CO groups (2088, 2014, and 1959 cm^{-1}) and two bands corresponding to the NO groups (1771 and 1724 cm^{-1}). The mass spectrum of complex **7** has the molecular ion peak $[M]^+$. According to the data of chemical analysis, this complex contains only three thiolate groups and a hydroxy group (3210 cm^{-1}). Actually, complex **7** is the

Scheme 2



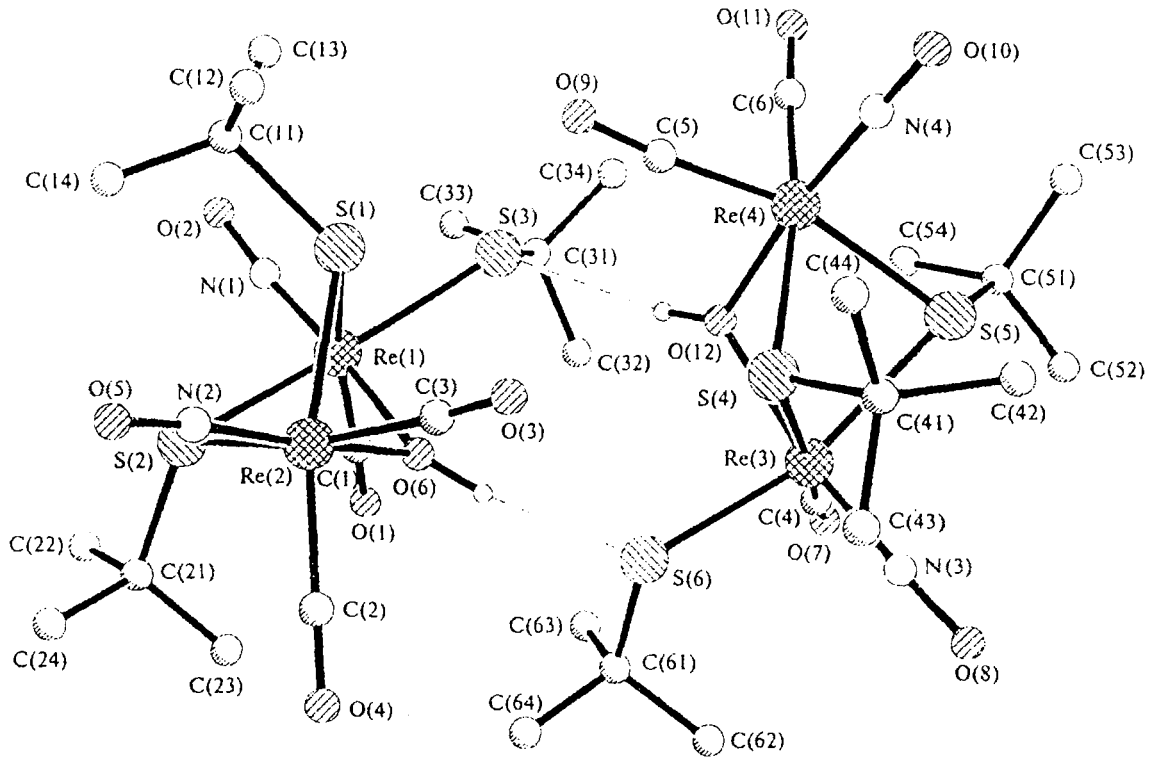


Fig. 5. Two independent molecules of the hydroxo complex $(CO)_3(NO)_2Re_2(SCMe_3)(\mu\text{-}SCMe_3)_2(\mu\text{-}OH)$ (**7**).

Table 4. Selected bond lengths (d) and bond angles (ω) in the molecule of complex **7**

Bond	d/Å	Bond	d/Å	Angle	ω/deg	Angle	ω/deg
Re(1)—S(1)	2.488(6)	Re(3)—O(12)	2.124(9)	S(1)—Re(1)—S(2)	79.0(2)	S(4)—Re(3)—O(12)	73.0(4)
Re(1)—S(2)	2.475(5)	Re(3)—N(3)	1.752(15)	S(1)—Re(1)—S(3)	80.0(2)	S(5)—Re(3)—O(12)	76.0(3)
Re(1)—S(3)	2.434(5)	Re(3)—C(4)	1.955(30)	S(2)—Re(1)—S(3)	158.3(2)	S(6)—Re(3)—O(12)	89.6(3)
Re(1)—O(6)	2.129(11)	Re(4)—S(4)	2.474(5)	S(1)—Re(1)—O(6)	73.1(3)	S(4)—Re(4)—S(5)	80.4(2)
Re(1)—N(1)	1.744(14)	Re(4)—S(5)	2.449(5)	S(2)—Re(1)—O(6)	77.7(3)	S(4)—Re(4)—O(12)	74.8(3)
Re(1)—C(1)	1.901(23)	Re(4)—O(12)	2.055(12)	S(3)—Re(1)—O(6)	89.0(3)	S(5)—Re(4)—O(12)	77.6(3)
Re(2)—S(1)	2.483(5)	Re(4)—N(4)	1.761(20)	S(1)—Re(2)—S(2)	78.9(6)	Re(3)—S(4)—Re(4)	81.0(2)
Re(2)—S(2)	2.448(5)	Re(4)—C(5)	1.902(25)	S(1)—Re(2)—O(6)	73.7(3)	Re(3)—S(5)—Re(4)	82.2(1)
Re(2)—O(6)	2.099(12)	Re(4)—C(6)	1.966(24)	S(2)—Re(2)—O(6)	78.9(3)	Re(3)—O(12)—Re(4)	101.4(4)
Re(2)—N(2)	1.808(21)	N(1)—O(1)	1.175(20)	Re(1)—S(1)—Re(2)	81.4(2)	Re(1)—N(1)—O(1)	177.1(15)
Re(2)—C(2)	1.937(21)	N(2)—O(5)	1.131(29)	Re(1)—S(2)—Re(2)	82.4(1)	Re(2)—N(2)—O(5)	174.4(17)
Re(2)—C(3)	1.968(25)	N(3)—O(8)	1.188(20)	Re(1)—O(6)—Re(2)	100.1(4)	Re(3)—N(3)—O(8)	178.0(17)
Re(3)—S(4)	2.506(6)	N(4)—O(10)	1.155(28)	S(4)—Re(3)—S(5)	79.4(2)	Re(4)—N(4)—O(10)	176.9(18)
Re(4)—S(5)	2.470(5)	C—O(aver.)	1.15(3)	S(4)—Re(3)—S(6)	81.2(2)	Re—C—O(aver.)	175.6(2)
Re(4)—S(6)	2.424(6)			S(5)—Re(3)—S(6)	158.5(2)		

product of replacement of one CO group and the terminal SR ligand in molecule **6** by a three-electron hydroxy bridge. This formally does not change the configuration of the Re^I atoms but leads to a three-bridged structure, as in the case of complex **4**. X-ray diffraction study (Fig. 5, Table 4) showed that this complex was actually formed as a result of hydrolysis of one Re—SR bond in dimer **6** and elimination of the CO group. As a result, the 18-electron metal atoms in the three-bridged $Re_2(SR)_2(OH)$ fragment are located at a nonbonded distance (Re...Re, 3.235(1) and 3.241(1) Å in two independent molecules). This separation is, however, substantially smaller than the corresponding distances in binuclear complexes **3** and **4** due, apparently, to the tightening effect of the hydroxy bridge (Re—OH, 2.129(11), 2.099(12) Å and 2.124(9), 2.055(12) Å in two independent molecules, respectively). The Re—OH distances are slightly different due, apparently, to the difference in the ligand environment around the metal centers in the molecule. Thus, one Re atom in molecule

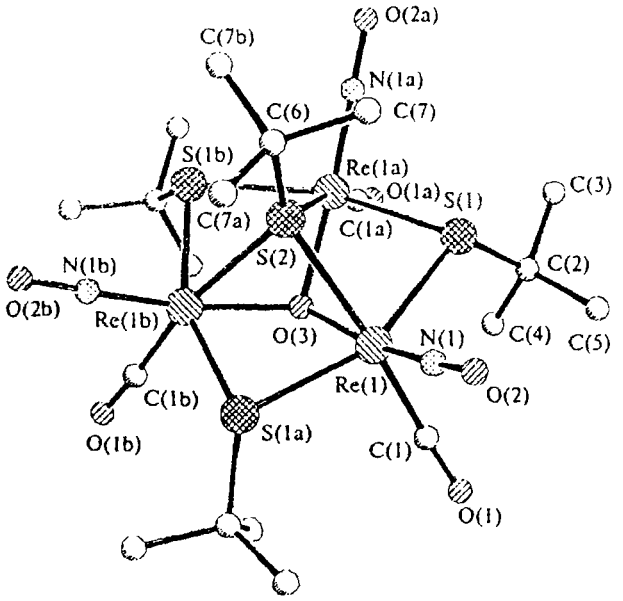


Fig. 6. Structure of the trinuclear oxo cluster $(CO)_3(NO)_3Re_3(\mu\text{-}SCMe_3)_3(\mu_3\text{-}SCMe_3)(\mu_3\text{-}O)$ (**8**).

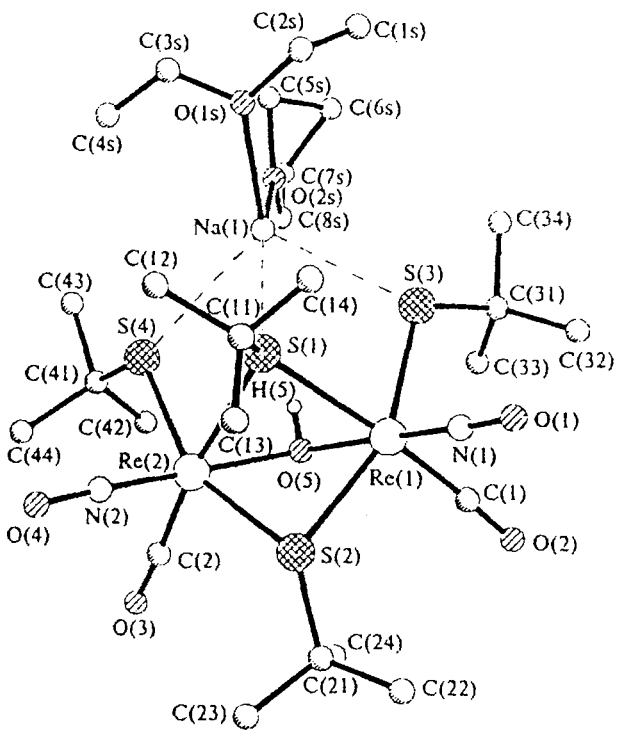


Fig. 7. Structure of ionic complex $[(CO)_2(NO)_2Re_2(SCMe_3)_2(\mu\text{-}SCMe_3)_2(\mu\text{-}OH)][Na(THF)(Et_2O)]$ (**9**).

7 is bonded to two terminal carbonyl groups and one nitrosyl group, while the second Re atom bears the carbonyl, nitrosyl, and thiolate ligands (see Table 4).

Trinuclear oxo cluster **8** is isoeletronic to sulfide halide analog **5**. Molecule **8** contains a symmetrical triangle formed by the Re atoms in which the equivalent Re(CO)(NO) fragments (ν(CO) 1992 cm^{-1}, ν(NO) 1724 cm^{-1}) are held together *via* the bidentate thiolate bridges (Re—S, 2.446(5)—2.452(5) Å), the μ_3-$SCMe_3$ ligand (Re—S, 2.505(1) Å), and the μ_3-oxo group (Re—O, 2.030(1) Å) (Fig. 6, Table 5). As a result, the metal atoms are electron-saturated, and no direct metal—metal bonding is observed in the cluster (all three Re...Re distances are equal to 3.252(1) Å). The nitrosyl ligands in molecule **8** are in *trans* positions with respect to the O atom (Re—N, 1.759(16) Å; N—O, 1.204(22) Å; the N—Re—O angle is 167.7(5)°), whereas the CO groups are in *trans* positions with respect to the S atom of the tridentate thiolate bridge (Re—C, 1.939(23) Å; C—O, 1.141(28) Å, the C—Re—S angle is 166.7(5)°).

The dirhenium tetrathiolate fragment was found in the anions of compounds **9** and **10** containing cations of different compositions. In both cases, the $[(CO)_2(NO)_2Re_2(SCMe_3)_2(\mu\text{-}SCMe_3)_2(\mu\text{-}OH)]^-$ contains two bridging (Re—S are 2.455(4)—2.522(4) Å in **9** and 2.450(9)—2.512(7) and 2.445(6)—2.524(8) Å in two

Table 5. Selected bond lengths (*d*) and bond angles (ω) in the molecule of trinuclear cluster **8**

Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
Re(1)—S(1)	2.446(5)	S(1)—Re(1)—S(2)	79.3(1)	Re(1)—S(1)—C(2)	116.7(7)
Re(1)—S(2)	2.505(1)	S(1)—Re(1)—O(3)	80.5(1)	Re(1)—S(1)—Re(1b)	83.2(2)
Re(1)—O(3)	2.030(1)	S(2)—Re(1)—O(3)	63.8(1)	C(2)—S(1)—Re(1b)	114.6(7)
Re(1)—N(1)	1.759(16)	S(1)—Re(1)—N(1)	97.5(5)	Re(1)—S(2)—C(6)	131.5(1)
Re(1)—C(1)	1.939(23)	S(2)—Re(1)—N(1)	103.8(5)	Re(1)—S(2)—Re(1a)	81.0(1)
Re(1)—S(1a)	2.452(5)	O(3)—Re(1)—N(1)	167.7(5)	C(6)—S(2)—Re(1a)	131.4(1)
S(1)—C(2)	1.888(23)	S(1)—Re(1)—C(1)	98.8(7)	Re(1)—S(2)—Re(1b)	81.0(1)
S(1)—Re(1b)	2.452(5)	S(2)—Re(1)—C(1)	166.0(6)	C(6)—S(2)—Re(1b)	131.5(1)
S(2)—C(6)	1.857(1)	O(3)—Re(1)—C(1)	102.2(6)	Re(1a)—S(2)—Re(1b)	81.0(1)
S(2)—Re(1a)	2.505(1)	N(1)—Re(1)—C(1)	90.2(8)	Re(1)—O(3)—Re(1a)	106.4(1)
S(2)—Re(1b)	2.505(1)	S(1)—Re(1)—S(1a)	155.9(2)	Re(1)—O(3)—Re(1b)	106.4(1)
O(1)—C(1)	1.141(28)	S(2)—Re(1)—S(1a)	79.2(1)	Re(1a)—O(3)—Re(1b)	106.4(1)
O(2)—N(1)	1.204(22)	O(3)—Re(1)—S(1a)	80.3(1)	Re(1)—N(1)—O(2)	176.1(16)
O(3)—Re(1a)	2.030(1)	N(1)—Re(1)—S(1a)	98.1(6)	Re(1)—C(1)—O(1)	174.5(19)
O(3)—Re(1b)	2.030(1)	C(1)—Re(1)—S(1a)	99.4(6)		

Table 6. Selected bond lengths (d) and bond angles (ω) in complex **9**

Bond	d/Å	Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
Re(1)—S(1)	2.521(5)	S(1)—Re(1)—S(2)	79.1(1)	S(1)—Re(2)—O(5)	75.5(3)	Re(1)—S(2)—Re(2)	82.6(1)
Re(1)—S(2)	2.463(4)	S(1)—Re(1)—S(3)	80.2(2)	S(2)—Re(2)—O(5)	76.4(3)	Re(1)—S(3)—Na(1)	105.6(2)
Re(1)—S(3)	2.421(5)	S(2)—Re(1)—S(3)	155.8(2)	S(4)—Re(2)—O(5)	86.4(3)	Re(2)—S(4)—Na(1)	104.9(2)
Re(1)—O(5)	2.097(9)	S(1)—Re(1)—O(5)	75.8(3)	S(1)—Re(2)—N(2)	100.2(4)	S(1)—Na(1)—O(1s)	102.8(4)
Re(1)—N(1)	1.742(14)	S(2)—Re(1)—O(5)	76.4(3)	S(2)—Re(2)—N(2)	100.0(5)	S(3)—Na(1)—O(1s)	115.3(5)
Re(1)—C(1)	1.892(22)	S(3)—Re(1)—O(5)	86.4(3)	S(4)—Re(2)—N(2)	96.0(5)	S(4)—Na(1)—O(1s)	123.6(5)
Re(2)—S(1)	2.522(4)	S(1)—Re(1)—N(1)	101.6(6)	O(5)—Re(2)—N(2)	174.8(5)	S(1)—Na(1)—O(2s)	162.5(6)
Re(2)—S(2)	2.454(4)	S(2)—Re(1)—N(1)	99.5(4)	S(1)—Re(2)—C(2)	169.4(5)	S(3)—Na(1)—O(2s)	105.8(6)
Re(2)—S(4)	2.424(5)	S(3)—Re(1)—N(1)	96.9(5)	S(2)—Re(2)—C(2)	99.0(5)	S(4)—Na(1)—O(2s)	107.6(5)
Re(2)—O(5)	2.112(10)	O(5)—Re(1)—N(1)	175.4(5)	S(4)—Re(2)—C(2)	98.9(5)	O(1s)—Na(1)—O(2s)	94.6(7)
Re(2)—N(2)	1.802(14)	S(1)—Re(1)—C(1)	169.7(6)	O(5)—Re(2)—C(2)	93.9(6)	Re(1)—O(5)—Re(2)	100.9(4)
Re(2)—C(2)	1.891(15)	S(2)—Re(1)—C(1)	99.7(5)	N(2)—Re(2)—C(2)	90.4(6)	Re(1)—O(5)—H(5)	112.3(35)
S(1)—Na(1)	3.037(8)	S(3)—Re(1)—C(1)	98.4(5)	Re(1)—S(1)—Re(2)	80.1(1)	Re(2)—O(5)—H(5)	106.7(40)
S(3)—Na(1)	2.890(10)	O(5)—Re(1)—C(1)	94.0(6)	Re(1)—S(1)—Na(1)	99.0(2)	Re(1)—N(1)—O(1)	176.6(13)
S(4)—Na(1)	2.954(9)	N(1)—Re(1)—C(1)	88.6(8)	Re(2)—S(1)—Na(1)	100.1(2)	Re(2)—N(2)—O(4)	176.9(13)
Na(1)—O(1s)	2.304(17)	S(1)—Re(2)—S(2)	79.2(1)	Re(1)—S(1)—C(11)	117.8(6)	Re(1)—C(1)—O(2)	177.5(14)
Na(1)—O(2s)	2.292(18)	S(1)—Re(2)—S(4)	80.1(1)	Re(2)—S(1)—C(11)	118.7(5)	Re(2)—C(2)—O(3)	176.4(14)
O(1)—N(1)	1.181(19)	S(2)—Re(2)—S(4)	155.8(1)	Na(1)—S(1)—C(11)	129.2(6)		
O(2)—C(1)	1.165(28)						
O(3)—C(2)	1.163(20)						
O(4)—N(2)	1.168(20)						
O(5)—H(5)	0.872(70)						

Table 7. Selected bond lengths (d) and bond angles (ω) in the anions and cations of compound **10**

Bond	d/Å	Bond	d/Å
$[(CO)_2(NO)_2Re_2(SCMe_3)_2(\mu\text{-}SCMe_3)_2(\mu\text{-}OH)]^-[Na(H_2O)_6]^+$			
Re(1)...Re(2)	3.219(2)	Re(1)—S(1)	2.450(9)
Re(1)—S(2)	2.508(9)	Re(1)—S(3)	2.420(9)
Re(1)—O(5)	2.131(20)	Re(1)—N(1)	1.717(30)
Re(1)—C(1)	1.798(43)	Re(2)—S(1)	2.436(9)
Re(2)—S(2)	2.512(7)	Re(2)—S(4)	2.416(8)
Re(2)—O(5)	2.092(24)	Re(2)—N(2)	1.670(37)
Re(2)—C(2)	1.758(34)	O(1)—N(1)	1.207(43)
C—O(aver.)	1.189(56)	O(4)—N(2)	1.234(50)
O(4)—Na(1)	2.927(31)	O(5)—H(5)	0.686(69)
Na(1)—O(1w)	2.435(20)	Na(1)—O(2w)	2.365(25)
Na(1)—O(3w)	2.335(31)	Na(1)—O(4w)	2.352(30)
Na(1)—O(5w)	2.352(30)	Na(1)—O(6w)	2.314(27)
$[(CO)_2(NO)_2Re_2(SCMe_3)_2(\mu\text{-}SCMe_3)_2(\mu\text{-}OH)]^-[H_5O_2]^+$			
Re(3)...Re(4)	3.240(2)	Re(3)—S(5)	2.446(8)
Re(3)—S(6)	2.524(8)	Re(3)—S(8)	2.428(8)
Re(3)—O(10)	2.142(17)	Re(3)—N(3)	1.667(30)
Re(3)—C(3)	1.959(36)	Re(4)—S(5)	2.445(6)
Re(4)—S(6)	2.516(10)	Re(4)—S(7)	2.427(6)
Re(4)—O(10)	2.110(17)	Re(4)—N(4)	1.750(24)
Re(4)—C(4)	1.886(36)	O(6)—N(3)	1.303(45)
C—O(aver.)	1.12(4)	O(9)—N(4)	1.165(34)
O(10)—H(10)	0.783(77)		

Angle	ω/deg	Angle	ω/deg
$[(CO)_2(NO)_2Re_2(SCMe_3)_2(\mu\text{-}SCMe_3)_2(\mu\text{-}OH)]^-[Na(H_2O)_6]^+$			
S(1)—Re(1)—S(2)	79.5(3)	S(2)—Re(1)—S(3)	80.7(3)
S(1)—Re(1)—S(3)	155.9(3)	S(1)—Re(1)—O(5)	75.9(5)
S(2)—Re(1)—O(5)	76.7(6)	S(3)—Re(1)—O(5)	86.4(5)
S(2)—Re(1)—N(1)	96.1(14)	S(1)—Re(1)—N(1)	99.6(11)
O(5)—Re(1)—N(1)	172.1(16)	S(3)—Re(1)—N(1)	96.0(9)
S(1)—Re(1)—C(1)	96.6(11)	S(2)—Re(1)—C(1)	168.5(10)
S(3)—Re(1)—C(1)	100.2(12)	O(5)—Re(1)—C(1)	91.8(11)
N(1)—Re(1)—C(1)	95.2(17)	S(1)—Re(2)—S(2)	79.7(2)
S(2)—Re(2)—S(4)	82.6(3)	S(1)—Re(2)—S(4)	156.3(3)
O(5)—Re(2)—N(2)	178.3(10)	S(2)—Re(2)—O(5)	77.3(5)
S(1)—Re(2)—O(5)	76.9(5)	S(2)—Re(2)—N(2)	101.0(9)
S(4)—Re(2)—O(5)	84.0(5)	S(1)—Re(2)—C(2)	91.4(13)
S(1)—Re(2)—N(2)	102.7(10)	S(4)—Re(2)—C(2)	104.1(13)
S(4)—Re(2)—N(2)	95.9(9)	N(2)—Re(2)—C(2)	87.2(21)
S(2)—Re(2)—C(2)	168.9(17)	Re(1)—S(2)—Re(2)	79.8(2)
O(5)—Re(2)—C(2)	94.4(20)	Re(1)—O(5)—Re(2)	99.3(9)
Re(1)—S(1)—Re(2)	82.4(2)	Re(2)—O(5)—H(5)	107.9(86)
N(2)—O(4)—Na(1)	143.4(18)	Re(2)—N(2)—O(4)	170.2(24)
Re(1)—O(5)—H(5)	116.9(66)	Re(1)—N(1)—O(1)	172.2(35)
$[(CO)_2(NO)_2Re_2(SCMe_3)_2(\mu\text{-}SCMe_3)_2(\mu\text{-}OH)]^-[H_5O_2]^+$			
S(5)—Re(3)—S(6)	78.5(3)	S(5)—Re(3)—O(10)	77.3(5)
S(5)—Re(3)—S(8)	156.4(2)	S(8)—Re(3)—O(10)	85.1(5)
S(6)—Re(3)—O(10)	75.6(5)	S(6)—Re(3)—N(3)	102.5(11)
S(5)—Re(3)—N(3)	99.0(9)	O(10)—Re(3)—N(3)	176.0(10)
S(8)—Re(3)—N(3)	98.2(9)	S(6)—Re(3)—C(3)	167.3(10)
S(5)—Re(3)—C(3)	100.8(9)	O(10)—Re(3)—C(3)	91.8(12)
S(8)—Re(3)—C(3)	95.3(8)	N(3)—Re(3)—C(3)	90.1(15)
S(5)—Re(4)—S(6)	78.7(3)	S(6)—Re(4)—S(7)	80.2(3)
S(5)—Re(4)—S(7)	156.2(3)	S(5)—Re(4)—O(10)	77.8(4)
S(6)—Re(4)—O(10)	76.4(6)	S(7)—Re(4)—O(10)	86.7(4)
S(6)—Re(4)—N(4)	101.4(9)	S(5)—Re(4)—N(4)	96.4(6)
O(10)—Re(4)—N(4)	174.1(7)	S(7)—Re(4)—N(4)	98.4(6)
S(5)—Re(4)—C(4)	101.2(7)	S(6)—Re(4)—C(4)	166.7(9)
S(7)—Re(4)—C(4)	96.8(6)	O(10)—Re(4)—C(4)	90.5(10)
N(4)—Re(4)—C(4)	91.8(13)	Re(3)—S(5)—Re(4)	83.0(2)
Re(3)—S(6)—Re(4)	80.0(3)	Re(3)—O(10)—Re(4)	99.3(7)
Re(4)—O(10)—H(10)	95.1(62)	Re(3)—N(3)—O(6)	175.3(24)
Re(4)—N(4)—O(9)	178.9(23)	Re(3)—C(3)—O(7)	169.6(28)
Re(4)—C(4)—O(8)	177.4(14)		

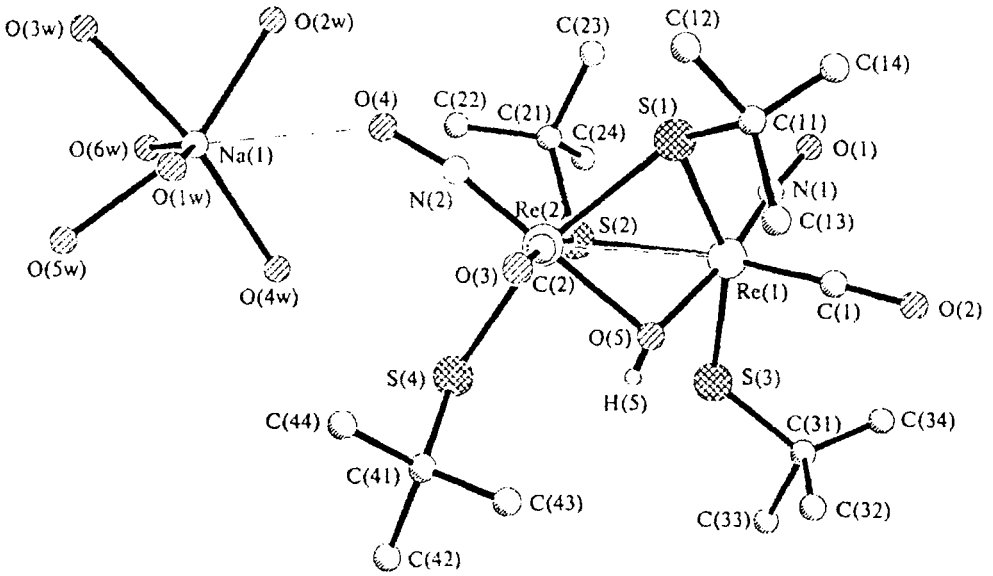


Fig. 8. Structure of the ionic complex $[(CO)_2(NO)_2Re_2(SCMe_3)_2(\mu\text{-}SCMe_3)_2(\mu\text{-}OH)][Na(H_2O)_6]$ in the crystal of **10**.

independent anions in the crystal of **10**) and two terminal (Re—S are 2.420(5) and 2.426(4) Å in **9** and 2.420(9), 2.416(8) Å and 2.427(6), 2.428(8) Å in two independent anions in the crystal of **10**) thiolate groups (Figs. 7—9, Tables 6 and 7), while the Re—Re bond is absent (Re...Re are 3.246(1) Å in **9** and 3.219(2) and 3.240(2) Å in **10**). Apparently, these anions were formed as a result of replacement of two CO groups in molecule **6** by the four-electron OH^- bridging ligand (Re—O are 2.107(10) and 2.117(10) Å in **9** and 2.131(20), 2.092(24) Å and 2.142(17), 2.110(17) Å in two independent anions in the crystal of **10**). Therefore, each metal atom is bonded to only one terminal carbonyl group and one nitrosyl group. The latter is retained in the anions (as well as in neutral molecules **7** and **8**) after chromatography. The structures of the cations in the crystals of **9** and **10** are different. In the first compound (the major product), the sodium ion is coordinated by the THF and ether molecules (Na—O, 2.302(17) and 2.292(9) Å, respectively) and is weakly bonded to three S atoms of the two terminal and one bridging thiolate groups of the anion (Na—S, 2.891(10), 2.954(9), and 3.039(9) Å, respectively). In the crystal of compound **10**, the Na^+ cation is coordinated by six water molecules (Na—O, 2.314(27)—2.435(20) Å) and is weakly bonded to the O atom of the nitrosyl group of the Re(CO)(NO) fragment (Na...ON, 2.93(3) Å) of one of the two independent anions. This has a substantial effect on its geometric parameters (Re—N, 1.670(30) Å, N—O, 1.24(5) Å). An analogous elongation of one of the N—O bonds (1.30(4) Å) and the strengthening of the Re—N bond (1.667(30) Å) are observed in the second independent binuclear anion of **10** (the bond lengths in the second Re—NO group have standard values: Re—N, 1.750(24) Å; N—O, 1.17(3) Å). However, this anion is not affected by the H_5O_2 cation (O...O, 2.12(4) Å; O...HO, 1.60(8) Å; the O—H—O angle is 109(2)°; the positions of all hydrogen atoms were located from electron density syntheses and then refined). This effect is

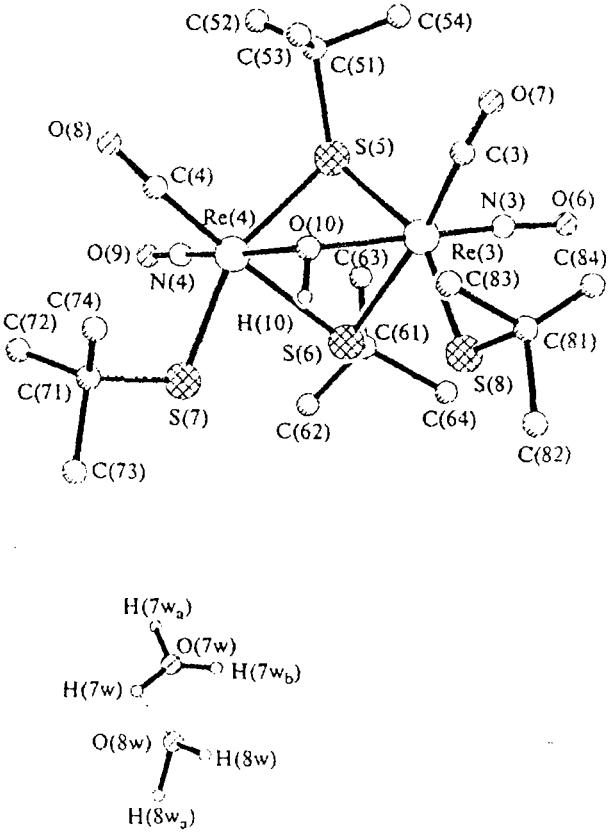


Fig. 9. Structure of the ionic complex $[(CO)_2(NO)_2Re_2(SCMe_3)_2(\mu\text{-}SCMe_3)_2(\mu\text{-}OH)][H_5O_2]$ in the crystal of **10**.

Table 8. Crystallographic parameters of structures

Parameter	3 · CH_2Cl_2	3a	4	5	7	8	9	10
Molecular formula	$C_{12}H_{18}Cl_2N_2O_6Re_2S_2$ · · CH_2Cl_2[a]	$C_{12}H_{18}Cl_2N_2O_6Re_2S_2$	$C_{12}H_{18}N_2O_6Re_2S_3$	$C_{15}H_{27}ClN_3O_6Re_3S_4$	$C_{15}H_{28}N_2O_6Re_2S_3$	$C_{19}H_{36}N_3O_7Re_3S_4$	$C_{36}H_{79}N_4$+ +$NaO_{18}Re_4S_4$	$C_{26}H_{55}N_2$+ +$NaO_7Re_2S_4$
Space group	$C2/c$	$Cmc2_1$	$P2_1$	$P2_1/c$	$P\bar{1}$	$Pa\bar{3}$	$P\bar{1}$	$P2_1/c$
a/Å	27.293(13)	14.364(5)	8.963(3)	19.570(7)	11.594(4)	18.614(3)	16.081(5)	14.620(5)
b/Å	11.796(5)	12.504(5)	16.088(7)	9.383(3)	13.091(4)	18.614(3)	16.218(4)	12.314(3)
c/Å	17.254(8)	12.233(5)	9.967(4)	16.565(7)	18.105(6)	18.614(3)	16.432(4)	23.728(8)
α/deg	—	—	—	—	95.22(2)	—	116.26(2)	—
β/deg	112.22(2)	—	111.53(2)	106.31(2)	93.29(2)	—	106.83(2)	106.70(2)
γ/deg	—	—	—	—	108.29(2)	—	92.25(2)	—
V/Å^3	5142(4)	2197(2)	1337.0(9)	2919(2)	2588(1)	6449(3)	3608(2)	4092(2)
Z	8[b]	4[c]	2	4	4[b]	8[d]	2	4[e]
μ/cm^{-1}	100.15	114.68	93.01	128.18	96.18	115.31	69.79	61.63
d_{calc}/g cm^{-3}	2.270	2.345	1.875	2.345	2.056	2.277	1.731	1.674
θ/2θ scan range	3—52	3—48	3—6	4—46	3—50	3—50	3—54	3—54
Number of observed reflections	3668	1063	3361	5054	6396	1911	9236	7255
Number of reflections with $I > 4\sigma$	3586	667 ($I > 3\sigma$)	3361	5054	3257	1085	4691	2499
Weighting scheme	Unit weights	$w^{-1} = \sigma^2(F) + 0.0010F^2$	Unit weights	$w^{-1} = \sigma^2(F) + 0.0050F^2$	$w^{-1} = \sigma^2(F) + 0.0003F^2$	$w^{-1} = \sigma^2(F) + 0.0001F^2$	$w^{-1} = \sigma^2(F) + 0.0013F^2$	$w^{-1} = \sigma^2(F) + 0.0011F^2$
R	0.037	0.073	0.055	0.068	0.032	0.067	0.059	0.036
R_w	0.041	0.075	0.067	0.092	0.036	0.041	0.075	0.042

[a] The asymmetric unit contains two independent molecules of the isomers and one CH_2Cl_2 molecule of solvation.
[b] The asymmetric unit contains two independent molecules located in inversion centers.
[c] The molecule is located on a crystallographic plane m.
[d] The molecule is located on a crystallographic threefold axis.
[e] The asymmetric unit contains two independent anions and two different cations.

revealed in the IR spectra of compound **10**, which have three stretching bands of the CO groups (1975, 1966, and 1953 cm^{-1}) and three bands corresponding to the NO groups (1718, 1667, and 1658 cm^{-1}). The last two mentioned bands should be, apparently, assigned to the distorted NO fragments. It should be noted that, unlike complex **10**, the spectrum of the symmetrical anion of compound **9** shows only one CO stretching band and one NO stretching band (1966 and 1705 cm^{-1}, respectively). Although we failed to obtain complex **10** in high yield and to study it in more detail (as was mentioned above, complex **10** was present as a small admixture along with compound **9**, and it is, apparently, an intermediate product), it is believed (based on the available data) that **10** is a primary product, which was formed after addition of OH^- to tetrathiolate complex **6**. As a result, the electron density in one of the Re—NO fragments is redistributed to form the zwitterionic $Re^+{=}N{-}O^-$ group. This group was transformed into the initial state in the course of elution of the complex with a THF—ether mixture due to the appearance of the softer $Na(THF)(Et_2O)$ cation bonded to the S atoms. In this case, trinuclear cluster **8** can be considered as the product of formal replacement of the Na-containing cation by the soft $[Re(CO)(NO)]^+$ fragment followed by deprotonation of the OH group. However, the details of this process are not clear yet.

Table 9. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (B_{eq}) in the structure of $3 \cdot CH_2Cl_2$

Atom	x	y	z	$B_{eq}/Å^2$
Re(1)	656(1)	2006(1)	3425(1)	40(1)
Re(2)	2216(1)	6020(1)	4661(1)	48(1)
S(1)	297(2)	2412(3)	1892(2)	41(1)
S(2)	2550(2)	7662(3)	4113(3)	49(2)
Cl(1)	788(2)	4029(4)	3616(3)	55(2)
Cl(2)	3113(2)	5344(4)	5048(4)	81(3)
Cl(3)	784(5)	4536(9)	5887(8)	196(8)
Cl(4)	286(4)	3136(12)	6735(6)	186(6)
N(1)	596(5)	500(11)	3340(8)	45(6)
N(2)	1531(7)	6506(13)	4405(8)	68(7)
O(1)	1059(5)	1853(13)	5365(8)	83(7)
O(2)	1849(5)	2029(11)	3726(7)	67(5)
O(3)	1878(7)	4625(13)	3067(10)	101(9)
O(4)	1966(5)	3869(12)	5448(9)	83(7)
O(5)	557(5)	−503(11)	3320(9)	74(7)
O(6)	1093(5)	6798(13)	4274(10)	91(7)
C(1)	886(6)	1934(14)	4653(11)	47(7)
C(2)	1405(6)	1995(13)	3618(8)	38(6)
C(3)	2011(7)	5152(15)	3652(11)	53(7)
C(4)	2068(8)	4682(16)	5182(12)	63(9)
C(5)	386(14)	4479(26)	6424(24)	169(23)
C(10)	619(8)	1606(18)	1288(11)	67(9)
C(11)	596(14)	391(21)	1343(18)	163(25)
C(12)	1177(9)	2039(24)	1576(13)	113(13)
C(13)	329(9)	1974(21)	353(10)	96(11)
C(20)	2131(7)	8170(15)	3042(9)	53(7)
C(21)	2257(9)	7411(18)	2431(12)	90(11)
C(22)	1545(8)	8095(21)	2879(12)	93(11)
C(23)	2291(9)	9397(15)	2971(12)	84(11)

In conclusion, note that the existence of tetrathiolate anions in complexes **9** and **10** supports strongly the scheme of conversions of thiolate rhenium complexes with the participation of unstable intermediate **6**. It is interesting that hydrolysis of the thiolates under study upon chromatography was accompanied by elimination

Table 10. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (B_{eq}) for *syn* isomer **3a**

Atom	x	y	z	$B_{eq}/Å^2$
Re(1)	0	1155(2)	1260	44(1)
Re(2)	0	3381(2)	3348(2)	42(1)
S(1)	1025(8)	1961(8)	2662(6)	43(3)
Cl(1)	0	−392(18)	2347(13)	78(5)
Cl(2)	0	2442(18)	5035(15)	81(5)
O(1)	1506(26)	29(32)	−215(20)	68(7)
O(2)	0	2729(65)	−138(49)	126(11)
O(3)	0	4769(75)	1479(56)	180(12)
O(4)	1416(21)	4953(29)	4428(22)	61(6)
N(1)	0	2150(97)	357(90)	255(12)
N(2)	0	4267(33)	1974(28)	34(7)
C(1)	851(45)	418(58)	379(49)	127(11)
C(2)	879(32)	4304(39)	4059(30)	70(8)
C(11)	2226(30)	2358(34)	2247(28)	55(8)
C(12)	2824(47)	1320(38)	1829(43)	90(10)
C(13)	2632(71)	2835(60)	3237(58)	161(11)
C(14)	2255(45)	3204(40)	1283(34)	86(9)

Table 11. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (B_{eq}) for binuclear complex **4**

Atom	x	y	z	$B_{eq}/Å^2$
Re(1)	8623(2)	5009(11)	2272(1)	39(1)
Re(2)	4762(2)	5001(11)	2259(1)	39(1)
S(1)	7482(12)	5247(13)	4121(11)	53(3)
S(2)	6167(14)	4226(13)	925(13)	50(3)
S(3)	6492(14)	6138(13)	1724(14)	54(3)
O(1)	9504(34)	4210(26)	−71(34)	101(3)
O(2)	10456(33)	6670(25)	2347(30)	86(3)
O(3)	11477(34)	4227(26)	4686(32)	93(3)
O(4)	2994(35)	3436(26)	2670(34)	103(3)
O(5)	1727(35)	5717(26)	−129(32)	99(3)
O(6)	3688(33)	5927(25)	4518(30)	91(3)
N(1)	10389(32)	4493(23)	3636(31)	53(3)
N(2)	3765(40)	4107(32)	2607(39)	118(3)
C(1)	9174(33)	4613(25)	792(33)	48(3)
C(2)	9757(33)	6043(24)	2285(32)	42(3)
C(3)	2947(35)	5468(28)	772(35)	65(3)
C(4)	4106(36)	5564(29)	3725(36)	72(3)
C(5)	7928(37)	6302(29)	5079(35)	11(3)
C(6)	7007(39)	6285(32)	6072(37)	25(3)
C(7)	9686(39)	6286(32)	5946(38)	25(3)
C(8)	7536(30)	7007(20)	4265(28)	26(3)
C(5a)	6993(43)	7118(35)	2925(41)	40(3)
C(6a)	5405(42)	7611(36)	2291(41)	47(3)
C(7a)	8193(43)	7501(37)	2470(42)	58(3)
C(9)	5291(37)	4222(27)	−1081(34)	61(3)
C(10)	6640(38)	3842(31)	−1520(37)	87(3)
C(11)	3879(38)	3720(29)	−1533(37)	78(3)
C(12)	4970(33)	4962(38)	−1689(30)	61(3)

Table 12. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (B_{eq}) for triangular cluster 5

Atom	x	y	z	$B_{eq}/Å^2$
Re(1)	2008(1)	1577(2)	768(1)	40(1)
Re(2)	3311(1)	64(2)	133(1)	41(1)
Re(3)	1646(1)	−175(1)	−1060(1)	37(1)
S(1)	3277(5)	1241(10)	1442(5)	48(3)
S(2)	904(5)	904(10)	−264(6)	43(3)
S(3)	2786(5)	−838(9)	−1274(5)	39(3)
S(4)	2422(5)	2032(9)	−555(5)	38(3)
Cl(1)	2216(5)	−927(9)	428(5)	43(3)
O(1)	1877(19)	4875(26)	895(21)	91(5)
O(2)	586(19)	1200(29)	2316(18)	85(5)
O(3)	4185(19)	−2415(31)	985(21)	108(5)
O(4)	4570(18)	1328(36)	−254(21)	102(5)
O(5)	803(17)	−2895(27)	−1437(18)	89(5)
O(6)	973(18)	761(32)	−2814(15)	85(5)
N(1)	1764(15)	1387(28)	1672(13)	38(5)
N(2)	4073(17)	889(37)	−99(18)	65(5)
N(3)	1224(18)	461(28)	−2117(19)	53(5)
C(1)	1933(16)	3561(33)	903(18)	35(5)
C(2)	3852(20)	−1562(38)	688(21)	63(5)
C(3)	1118(22)	−1817(37)	−1317(24)	55(5)
C(11)	3859(20)	2825(38)	1749(24)	60(5)
C(12)	3683(27)	3497(41)	2553(26)	95(5)
C(13)	4648(24)	2239(44)	2093(28)	87(5)
C(14)	3726(23)	3878(39)	983(26)	79(5)
C(21)	277(21)	2350(39)	−841(23)	58(5)
C(22)	−325(23)	1641(43)	−1515(26)	89(5)
C(23)	−1(25)	3037(42)	−90(25)	75(5)
C(24)	665(25)	3509(35)	−1182(24)	72(5)
C(31)	2919(20)	−2763(37)	−1471(18)	45(5)
C(32)	2556(28)	−3050(44)	−2278(27)	107(5)
C(33)	2800(20)	−3817(39)	−823(23)	64(5)
C(34)	3737(23)	−2846(41)	−1412(29)	84(5)

of the CO groups (apparently, first) and the terminal SR fragments, while the thiolate bridges and the nitrosyl ligands were retained under these conditions. These transformations of rhenium thiolates differ from the conversions, which we have observed previously upon chromatography of thiolate molybdenum complexes and chromium and rhenium clusters in which S atoms were oxidized to form S(O)R bridges.[6,17]

Experimental

All operations associated with the synthesis of the starting and final compounds and purification of the solvents were carried out under dry oxygen-free nitrogen or argon. Acetonitrile and CH_2Cl_2 (Merck) were purified by double distillation over P_2O_5. Diethyl ether, THF, and acetone were dehydrated by distillation over sodium benzophenone ketyl. The hydrocarbon solvents were distilled over dispersed sodium. Silica gel (Kieselgel 60, Merck, 70–230 mesh ATSM), which was preliminarily dried *in vacuo* (4–6 h, 60 °C, 0.1 Torr) and applied to a column in anhydrous heptane under argon, was used for column chromatography (5×25 cm column). Chromatography was carried out under an atmosphere of argon or nitrogen.

Table 13. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (B_{eq}) for compound 7

Atom	x	y	z	$B_{eq}/Å^2$
Re(1)	3988(1)	945(1)	2391(1)	39(1)
Re(2)	2543(1)	2405(1)	3224(1)	47(1)
Re(3)	7974(1)	5500(1)	2931(1)	43(1)
Re(4)	6653(1)	5430(1)	1295(1)	50(1)
S(1)	2691(4)	1957(4)	1877(3)	49(2)
S(2)	2265(4)	467(4)	3179(3)	47(2)
S(3)	5376(4)	1973(4)	1564(3)	42(2)
S(4)	6138(5)	6008(4)	2539(3)	51(2)
S(5)	8698(5)	6492(4)	1861(3)	54(2)
S(6)	6548(4)	4433(4)	3713(3)	43(2)
O(1)	5800(14)	191(11)	3306(8)	72(7)
O(2)	3171(14)	−1063(12)	1382(8)	82(8)
O(3)	3074(16)	4802(13)	2947(12)	118(11)
O(4)	3045(17)	3096(13)	4898(9)	97(10)
O(5)	−58(16)	2114(14)	3318(11)	111(10)
O(6)	4335(10)	2396(8)	3125(6)	45(5)
O(7)	10051(15)	4537(14)	3166(10)	90(9)
O(8)	9248(14)	7280(12)	4094(9)	93(8)
O(9)	3913(18)	4139(14)	997(8)	87(9)
O(10)	6179(17)	7096(13)	477(8)	98(10)
O(11)	7259(17)	4358(14)	−174(9)	101(10)
O(12)	7051(10)	4402(8)	1987(5)	42(5)
N(1)	3519(15)	−266(12)	1799(8)	53(7)
N(2)	937(18)	2232(14)	3245(9)	66(9)
N(3)	8735(15)	6548(14)	3632(9)	62(8)
N(4)	6389(18)	6432(14)	787(10)	71(9)
C(1)	5124(19)	483(16)	2958(10)	52(10)
C(2)	2859(21)	2826(18)	4288(12)	65(11)
C(3)	2930(21)	3938(19)	3061(12)	70(12)
C(4)	9268(23)	4855(20)	3078(14)	81(13)
C(5)	4973(25)	4589(20)	1140(12)	68(13)
C(6)	7055(22)	4700(17)	396(13)	68(12)
C(11)	1246(19)	1143(20)	1256(11)	67(11)
C(12)	689(23)	2017(20)	1105(14)	112(16)
C(13)	1787(17)	794(21)	553(10)	103(14)
C(14)	419(19)	228(19)	1589(11)	83(12)
C(21)	2492(22)	−57(16)	4084(13)	65(11)
C(22)	2471(21)	−1220(16)	3874(12)	88(12)
C(23)	3663(22)	567(18)	4541(10)	76(13)
C(24)	1383(19)	−66(16)	4499(11)	77(11)
C(31)	6632(17)	1457(15)	1365(12)	50(9)
C(32)	7614(18)	1725(17)	2026(12)	76(12)
C(33)	6191(19)	251(14)	1112(12)	78(11)
C(34)	7169(17)	2022(16)	718(11)	69(11)
C(41)	6111(23)	7438(14)	2734(12)	61(10)
C(42)	7297(21)	8277(16)	2518(12)	80(12)
C(43)	6036(24)	7596(17)	3563(11)	95(14)
C(44)	5034(26)	7501(19)	2281(12)	107(17)
C(51)	10043(19)	6212(18)	1417(12)	70(10)
C(52)	11085(22)	6783(18)	1966(13)	99(14)
C(53)	10128(22)	6803(18)	712(12)	99(14)
C(54)	9836(21)	5022(17)	1243(12)	82(12)
C(61)	7204(17)	3839(14)	4434(9)	44(8)
C(62)	8282(19)	4699(17)	4882(10)	74(11)
C(63)	7587(22)	2909(16)	4126(12)	89(13)
C(64)	6243(18)	3433(17)	4944(10)	67(11)

The IR spectra (as KBr pellets) were recorded on a Bio-Rad FTS-45 instrument. The mass spectra (EI) were obtained on a Finnigan MAT 8320 instrument (70 eV).

Table 14. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (B_{eq}) for trinuclear cluster **8**

Atom	x	y	z	B_{eq}/Å^2
Re(1)	495(1)	3264(1)	6725(1)	26(1)
S(1)	759(3)	2429(3)	5745(3)	29(2)
S(2)	1833	3167	6833	28(1)
O(1)	−1075(9)	3613(9)	6345(10)	66(7)
O(2)	−8(9)	2187(8)	7782(8)	51(6)
O(3)	1079	3921	6079	32(3)
N(1)	172(9)	2629(9)	7345(9)	34(6)
C(1)	−483(12)	3511(11)	6464(12)	45(8)
C(2)	65(11)	2356(12)	5010(12)	42(9)
C(3)	439(14)	1924(12)	4408(12)	64(10)
C(4)	−215(11)	3061(11)	4751(10)	40(8)
C(5)	−544(12)	1906(13)	5355(12)	58(10)
C(6)	2409	2591	7409	26(5)
C(7)	2160(13)	1816(11)	7319(12)	60(10)

Complex $Re_2(CO)_4(NO)_2Cl_2(\mu\text{-}SCMe_3)_2$ (*syn* and *anti* isomers, 3a and 3b). A yellow solution of $Re_2(CO)_4(NO)_2Cl_4$ (**1**) (1 g, 1.4 mmol) in THF (30 mL) containing a suspension of NaSR (**2**) (350 mg, 3.1 mmol) was refluxed for 24 h. The yellow-orange solution that formed was filtered off from a white precipitate, and the solvent was evaporated to dryness at 22 °C (0.1 Torr). The oily precipitate that formed was washed with cold pentane (from −10 to −15 °C) and extracted with diethyl ether (45 mL). The extract was filtered off, concentrated to 5–7 mL, and cooled to −30 °C. The finely crystalline precipitate of isomers **3** that formed was separated from the solution, washed with cold pentane, and dried *in vacuo*. The yield was 750 mg (0.94 mmol, 64%). Recrystallization of complex **3** from a 1 : 1 : 2 CH_2Cl_2—Et_2O—pentane mixture gave yellow-orange prismatic crystals of $3 \cdot CH_2Cl_2$ suitable for X-ray diffraction study. Repeated recrystallization of single crystals from a 1 : 1 Et_2O—pentane mixture gave a small amount (<3 mg) of needle-like crystals of **3a** (*syn* isomer), which were also studied by X-ray analysis. Found (%): C, 19.00; H, 2.34; N, 3.55. $C_{12}H_{18}Cl_2N_2O_6Re_2S_2$. Calculated (%): C, 18.20; H, 2.20; N, 3.50. MS, *m/z*: 680 $[Re_2(CO)_2(NO)_2Cl_2(SCMe_3)S]^+$, 652 $[Re_2(CO)(NO)_2Cl_2(SCMe_3)S]^+$, 624 $[Re_2(NO)_2Cl_2(SCMe_3)S]^+$, 567 $[Re_2(NO)_2Cl_2S_2]^+$, 475 $[Re_2Cl_2S]^+$, 253 $[ReClS]^+$. IR, ν/cm^{-1}: 3010 m, 2921 m, 2871 w, 2095 v.s, 2088 v.s, 2026 v.s, 2017 v.s, 1785 v.s, 1779 v.s, 1479 m, 1451 m, 1393 w, 1362 w, 1157 m, 1019 w, 804 w, 606 w, 558 w, 484 m.

Complex $Re_2(CO)_4(NO)_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (*syn* and *anti* isomers of 4) and cluster $Re_3(CO)_3(NO)_3(\mu\text{-}SCMe_3)_3(\mu_3\text{-}S)(\mu_3\text{-}Cl)$ (5). A yellow solution of complex **1** (800 mg, 1.17 mmol) in THF (30 mL) containing a suspension of NaSR (**2**) (550 mg, 4.91 mmol) was refluxed for 24 h. The resulting yellow-orange solution was filtered off and concentrated to dryness *in vacuo* at 20 °C. The solid residue formed was extracted with pentane (4×10 mL) until the extract became colorless. Then the residue was extracted with diethyl ether (4×10 mL). The pentane extract was concentrated to 5 mL at 20 °C (0.1 Torr) and cooled to +5 °C. The yellow prismatic crystals of compound **4** that precipitated were separated from the solution by decantation, washed with cold pentane (−40 °C), and dried *in vacuo*. The yield of complex **4** was 60 mg (6.7%). Found (%): C, 19.81; H, 2.45. $C_{12}H_{18}N_2O_6Re_2S_3$. Calculated (%): C, 19.07; H, 2.38. MS, *m/z*: 754 $[M]^+$, 726 $[M-CO]^+$, 669 $[M-CMe_3-CO]^+$, 640 $[M-2CMe_3]^+$, 612 $[M-2CMe_3-CO]^+$, 584 $[M-2CMe_3-2CO]^+$, 556 $[M-2CMe_3-3CO]^+$, 554 $[M-2CMe_3-2CO-NO]^+$, 526 $[M-2CMe_3-3CO-NO]^+$, 528 $[M-2CMe_3-4CO]^+$, 498 $[M-2CMe_3-4CO-NO]^+$, 468 $[Re_2S_3]^+$. IR, ν/cm^{-1}: 2964 m, 2926 m, 2904 m, 2072 v.s, 2010 v.s, 1906 v.s, 1891 v.s, 1765 v.s, 1459 m, 1363 m, 1260 w, 1150 m, 1018 w, 806 w, 627 w, 595 w, 473 m.

The ethereal extract was concentrated to 10 mL and cooled to −10 °C. Orange prismatic crystals of **5** were washed with cold pentane (−10 °C) and dried *in vacuo*. The yield of cluster **5** was 380 mg (45.2%). Found (%): C, 17.03; H, 2.78; N, 3.67. $C_{15}H_{27}ClN_3O_6Re_3S_4$. Calculated (%): C, 16.86; H, 2.53; N, 3.93. MS, *m/z*: 1066 $[M]^+$, 1038 $[M-CO]^+$, 952 $[M-3CO-NO]^+$, 895 $[M-CMe_3-3CO-NO]^+$, 865 $[M-CMe_3-3CO-2NO]^+$, 838 $[M-2CMe_3-3CO-NO]^+$, 808

Table 15. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (B_{eq}) for compound **9**

Atom	x	y	z	B_{eq}/Å^2
Re(1)	2456(1)	4046(1)	7021(1)	48(1)
Re(2)	2558(1)	5984(1)	6113(1)	47(1)
S(1)	3737(3)	4491(3)	6537(2)	47(1)
S(2)	2564(3)	6032(3)	7148(2)	50(1)
S(3)	2528(3)	2337(3)	6531(2)	62(2)
S(4)	2674(3)	5147(4)	5212(2)	61(1)
Na(1)	3203(5)	2867(6)	5533(3)	79(2)
O(1)	3586(11)	3322(12)	8185(6)	124(2)
O(2)	651(10)	3650(10)	7395(7)	111(2)
O(3)	887(10)	7516(10)	5594(6)	98(2)
O(4)	3856(11)	7833(10)	6100(7)	117(2)
O(5)	1701(7)	4644(8)	6189(4)	50(2)
N(1)	3134(11)	3647(11)	7720(7)	75(2)
N(2)	3367(10)	7087(11)	6110(6)	72(2)
C(1)	1341(14)	3776(12)	7251(9)	81(2)
C(2)	1502(11)	6905(12)	5792(7)	55(2)
C(11)	4960(11)	4873(13)	7029(7)	60(2)
C(12)	5523(14)	5136(19)	6611(9)	143(2)
C(13)	4957(14)	5769(16)	7416(10)	135(2)
C(14)	5352(13)	3932(14)	7346(10)	121(2)
C(21)	1507(13)	6695(13)	7304(8)	71(2)
C(22)	1579(13)	6427(14)	7940(7)	85(2)
C(23)	1693(14)	7922(12)	7258(8)	87(2)
C(24)	534(12)	6372(14)	6904(8)	83(2)
C(31)	1561(12)	1342(12)	6521(9)	73(2)
C(32)	1601(15)	1029(14)	7142(8)	103(2)
C(33)	621(11)	1781(14)	6222(9)	93(2)
C(34)	1816(14)	349(12)	6195(9)	102(2)
C(41)	1800(14)	5580(15)	4529(8)	83(2)
C(42)	774(10)	5362(14)	4509(7)	76(2)
C(43)	2069(13)	4938(17)	4034(7)	109(2)
C(44)	1946(12)	6831(14)	4425(8)	96(2)
O(1s)	4656(10)	2124(11)	5548(6)	104(3)
O(2s)	2342(13)	1794(14)	4776(8)	147(3)
C(1s)	4783(21)	428(22)	5898(14)	279(4)
C(2s)	5223(21)	1351(21)	5960(15)	233(4)
C(3s)	5264(17)	2556(19)	5282(11)	153(4)
C(4s)	4789(18)	3348(20)	4848(12)	194(4)
C(5s)	2741(23)	967(22)	4474(16)	275(4)
C(6s)	1944(19)	226(20)	4468(13)	195(4)
C(7s)	1133(23)	1123(22)	4071(16)	278(4)
C(8s)	1384(19)	1844(21)	4494(13)	196(4)
H(5)	1712(36)	4195(37)	5907(33)	80(4)

Table 16. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (B_{eq}) for compound **10**

Atom	*x*	*y*	*z*	$B_{eq}/Å^2$
Re(1)	−4060(1)	8243(1)	1259(1)	54(1)
Re(2)	−5772(1)	8132(1)	1873(1)	47(1)
S(1)	−5175(6)	6906(5)	820(5)	63(3)
S(2)	−4156(5)	8634(5)	2882(5)	48(3)
S(3)	−3289(6)	9860(7)	2154(6)	74(3)
S(4)	−5819(6)	9711(6)	2978(5)	57(3)
O(1)	−2488(19)	7402(21)	1379(19)	140(5)
O(2)	−4215(18)	7921(18)	−740(19)	110(5)
O(3)	−7682(19)	7599(19)	491(16)	117(5)
O(4)	−6462(18)	7368(17)	2893(17)	117(5)
O(5)	−5249(12)	8783(11)	1229(12)	48(4)
N(1)	−3128(17)	7766(20)	1396(24)	132(5)
N(2)	−6158(18)	7616(20)	2409(18)	85(4)
C(1)	−4209(17)	8020(24)	47(26)	87(5)
C(2)	−6829(23)	7715(28)	978(32)	198(5)
C(11)	−5824(20)	6244(18)	−480(17)	55(4)
C(12)	−6606(24)	5584(22)	−497(25)	140(5)
C(13)	−6229(20)	6882(21)	−914(18)	79(5)
C(14)	−5334(23)	5675(23)	−982(21)	90(5)
C(21)	−3683(21)	7902(19)	3471(24)	106(5)
C(22)	−4092(26)	8000(25)	4225(19)	116(5)
C(23)	−3844(23)	6832(20)	2726(22)	93(5)
C(24)	−2691(21)	8350(21)	3916(25)	111(5)
C(31)	−3003(22)	10323(27)	1427(25)	106(5)
C(32)	−3858(23)	10405(29)	756(26)	133(5)
C(33)	−2550(25)	11414(25)	2270(25)	127(5)
C(34)	−2434(21)	9913(26)	946(26)	123(5)
C(41)	−6797(25)	10185(23)	2524(22)	87(5)
C(42)	−6538(26)	11335(29)	3269(26)	148(5)
C(43)	−6902(26)	10064(26)	1533(22)	131(5)
C(44)	−7612(19)	9682(29)	2565(27)	136(5)
Na(1)	−6886(5)	8067(5)	4671(6)	21(3)
O(1w)	−5901(14)	8752(13)	6342(14)	77(4)
O(2w)	−5944(14)	6969(14)	4566(16)	83(4)
O(3w)	−7634(15)	7093(14)	5043(15)	84(4)
O(4w)	−6066(16)	9317(16)	4697(15)	95(5)
O(5w)	−7670(19)	9136(16)	5503(19)	121(5)
O(6w)	−8245(19)	7743(17)	3493(18)	119(5)
Re(3)	−9617(1)	4421(1)	2388(1)	48(1)
Re(4)	−7815(1)	3832(1)	3292(1)	36(1)
S(5)	−9099(5)	2937(5)	1821(5)	46(3)
S(6)	−8033(5)	4963(5)	2619(5)	45(3)
S(7)	−6820(5)	5230(5)	4665(5)	47(3)
S(8)	−9505(5)	6087(5)	3390(7)	63(3)
O(6)	−10592(18)	4365(20)	524(20)	152(4)
O(7)	−11378(14)	3756(14)	2417(17)	81(4)
O(8)	−7857(13)	2681(14)	4311(16)	70(4)
O(9)	−6500(14)	2905(15)	2512(15)	75(4)
O(10)	−8857(10)	4444(11)	3708(10)	33(4)
N(3)	−10172(18)	4347(17)	1322(19)	81(5)
N(4)	−7027(14)	3269(13)	2826(15)	40(4)
C(3)	−10733(19)	4035(20)	2497(22)	68(5)
C(4)	−7828(17)	3130(19)	3948(17)	46(4)
C(51)	−9771(18)	1874(17)	1720(20)	53(5)
C(52)	−9281(22)	1117(18)	1436(23)	85(5)
C(53)	−9995(19)	2089(20)	2514(22)	71(5)
C(54)	−10597(18)	1701(20)	824(22)	76(5)
C(61)	−7719(21)	4605(24)	1457(22)	82(5)
C(62)	−6705(17)	4921(23)	1820(22)	82(5)
C(63)	−7983(20)	3629(21)	732(21)	75(5)
C(64)	−8105(22)	5373(23)	1136(21)	99(5)
C(71)	−6383(18)	5193(18)	5845(19)	50(4)
C(72)	−5743(21)	4463(26)	5690(23)	111(5)
C(73)	−5792(21)	6196(21)	6528(18)	76(5)
C(74)	−7029(16)	5000(20)	6155(18)	52(5)
C(81)	−10478(21)	6403(23)	3814(29)	102(5)
C(82)	−10098(20)	7494(22)	4485(29)	144(5)
C(83)	−10369(24)	5981(21)	4663(24)	107(5)
C(84)	−11244(19)	6158(25)	3168(32)	196(5)
O(7w)	125(32)	8304(31)	2132(39)	384(5)
O(8w)	140(34)	9542(34)	3364(38)	378(5)
H(5)	−5204(50)	9258(50)	1500(50)	25(6)
H(10)	−9202(52)	3972(52)	3429(52)	49(6)
$H(7w_b)$	−318(53)	8543(53)	1869(53)	81(6)
H(7w)	475(52)	8605(52)	2797(52)	43(6)
$H(7w_a)$	443(52)	7519(52)	1326(51)	46(6)
$H(8w_a)$	712(53)	10137(53)	3722(53)	79(6)
H(8w)	−414(52)	9973(52)	3708(51)	46(6)

$[M-2CMe_3-3CO-2NO]^+$, 778 $[M-2CMe_3-3CO-3NO]^+$, 721 $[Re_3S_4Cl]^+$. IR, ν/cm^{-1}: 2964 w, 2923 w, 1980 v.s, 1721 v.s, 1452 w, 1389 w, 1358 m, 1156 w, 1136 w, 800 w, 590 w, 510 w, 473 w.

Products of the reaction of complex 1 with NaSR isolated after chromatography of the reaction mixture on silica gel. A yellow solution of complex **1** (500 mg, 0.708 mmol) and compound **2** (500 mg, 4.464 mmol) in MeCN (30 mL) was refluxed for 24 h until the absorption bands of the CO and NO groups of complexes **1** and **3** disappeared in the IR spectrum. The resulting orange solution was filtered off from a white precipitate of NaCl and concentrated to dryness *in vacuo* at temperatures from −10 to −15 °C until an orange oil was formed. Then the oily residue was dissolved in THF (20 mL) and applied to a column with silica gel under argon. Chromatography was carried out under argon to elute four bands:

a. A yellow solution in pentane (50 mL), which was concentrated to 10 mL and cooled to +5 °C to afford yellow prismatic crystals of $(CO)_3(NO)_3Re_3(\mu\text{-}SCMe_3)_3(\mu\text{-}SCMe_3)(\mu_3\text{-}O)$ (**8**) in a yield of 100 mg (15.0%). Found (%): C, 20.63; H, 3.51; N, 3.70; S, 10.99. $C_{19}H_{36}N_3O_7Re_3S_4$. Calculated (%): C, 20.65; H, 3.26; N, 3.80; S, 11.59. MS, *m/z*: 1020 $[M-3CO]^+$, 990 $[M-3CO-NO]^+$, 960 $[M-3CO-2NO]^+$. IR, ν/cm^{-1}: 2962 m, 2921 m, 2855 w, 1992 v.s, 1724 v.s, 1452 m, 1390 m, 1367 m, 1157 w, 1144 m, 549 m, 493 m, 482 w, 443 w.

b. A yellow solution in pentane (30 mL), which was concentrated to 5 mL and cooled to −5 °C to give complex **4** in a yield of 14 mg (~2%).

c. A yellow-orange solution in CH_2Cl_2 (50 mL), which was concentrated to 10 mL and cooled to −5 °C to afford orange needle-like crystals of $(CO)_2(NO)Re(\mu\text{-}SCMe_3)_2(\mu\text{-}OH)Re(SCMe_3)(CO)(NO)$ (**7**) in a yield of 280 g (48.2%). Found (%): C, 22.48; H, 3.55; N, 3.40; S, 11.86. $C_{15}H_{28}N_2O_6Re_2S_3$. Calculated (%): C, 22.50; H, 3.50; N, 3.50; S, 12.00. MS, *m/z*: 800 $[M]^+$, 772 $[M-CO]^+$, 716 $[M-3CO]^+$, 659 $[M-3CO-CMe_3]^+$, 602 $[M-3CO-2CMe_3]^+$, 672 $[M-3CO-NO-2CMe_3]^+$, 615 $[M-3CO-NO-3CMe_3]^+$, 452 $[Re_2S_2O]^+$. IR, ν/cm^{-1}: 3210 w, 2960 m, 2918 m, 2859 m, 2088 v.s, 2014 v.s, 1959 v.s, 1771 v.s, 1724 v.s, 1648 m,

1553 w, 1503 w, 1455 m, 1359 m, 1241 w, 1150 m, 1016 w, 541 w, 471 w.

d. A yellow-green solution in a THF—Et_2O mixture (70 mL). The solution was concentrated to 20 mL, heptane (5 mL) was added, and the solution was cooled to −5 °C. A mixture of crystals of $[(CO)_2(NO)_2Re_2(SCMe_3)_2(\mu\text{-}SCMe_3)_2(\mu\text{-}OH)][Na(THF)(Et_2O)]$ (**9**) and $[(CO)_2(NO)_2Re_2(SCMe_3)_2(\mu\text{-}SCMe_3)_2(\mu\text{-}OH)]_2[Na(H_2O)_6][H_5O_2]$ (**10**) was obtained in a yield of 180 mg (24.7%). Orange platelet-like crystals of **10** (<2 mg) were separated mechanically from the major portion of green-yellow prismatic crystals of **9** and were used for X-ray diffraction study. For complex **9**, found (%): C, 30.29; H, 4.92; N, 2.76; Na, 2.51; Re, 38.05; S, 12.43. $[C_{18}H_{37}N_2O_5Re_2S_4][C_8H_{18}O_2Na]$. Calculated (%): C, 30.29; H, 5.34; N, 2.72; Na, 2.23; Re, 38.05; S, 12.43. IR spectrum of compound **9**, ν/cm^{-1}: 3200 w, 2956 m, 2922 m, 2890 m, 2858 m, 1966 v.s, 1705 v.s, 1471 w, 1455 m, 1389 w, 1364 m, 1153 m, 1094 m, 1052 w, 1020 w, 899 w, 829 m, 570 w, 544 m, 496 m, 448 w. IR spectrum of compound **10**, ν/cm^{-1}: 3340 br.m, 3190 w, 2957 m, 2920 m, 2891 m, 2875 m, 1975 v.s, 1966 v.s, 1953 v.s, 1718 v.s, 1667 v.s, 1658 v.s, 1634 m, 1456 m, 1385 m, 1362 m, 1261 w, 1152 m, 1100 m, 1017 w, 831 m, 759 m, 541 m, 488 w.

X-ray diffraction study of complexes. Crystals of **3** (a mixture of the *syn* and *anti* isomers) and **4** (a mixture of the *syn* and *anti* isomers) and single crystals of **3a** (the *syn* isomer), **5**, **7**, **8**, **9**, and **10** were prepared as described above. The crystals (all mounted in air) were glued to glass fibers using epoxy resin and transferred on a diffractometer. The X-ray intensity data sets ($\theta/2\theta$ scanning technique, Mo-Kα radiation, λ = 0.71073 Å) were collected on automated four-circle Nicolet R3 (for **3**, **3a**, **4**, **5**, **7**, **9**, and **10**, T = 22 °C) and Siemens R3m/v (for **8**, T = −40 °C) diffractometers. The unit cell parameters were determined and refined using 24 equivalent reflections with $2\theta < 24-28°$. In all the cases, three strong reflections with $0 < \chi < 60°$ were used as the standards. No significant variation in these standards was observed, and therefore, no correction was applied. All structures were solved by direct methods to locate the Re, S, and Cl atoms and most of the C, O, and N atoms (as well as the Na atoms in the structures of **9** and **10**). The positions of the remaining nonhydrogen atoms were located from subsequent difference Fourier maps. For the disordered *tert*-butylthiolate ligand in the structure of **4**, both positions with occupancies of approximately 0.5 were determined. All nonhydrogen atoms in the structures were refined anisotropically. The hydrogen atoms of all the organic ligands were generated geometrically and refined using the riding model. The positions of the hydrogen atoms of the bridging OH groups in complexes **7**, **9**, and **10** and the positions of the H atoms in the H_5O_2 cation in complex **10** were revealed from difference Fourier maps and refined isotropically. At the stage of isotropic refinement, for all the compounds under study absorption corrections were applied using the DIFABS program.[18] All calculations were carried out with the use of the SHELXTL PLUS program package (PC version).[19] The crystallographic parameters of the compounds under study and selected details of the refinement are given in Table 8. The selected geometric characteristics of the molecules are given in Tables 1—7. The atomic coordinates are listed in Tables 9—16. For the structure of "pure" *syn* isomer **3a**, only the atomic coordinates are listed. The bond lengths and bond angles are not reported because they are virtually identical to the values observed in the structure of **3**.

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