Technetium and Rhenium Complexes with Thioether Ligands, 6[◇]

Synthesis and Structural Characterization of Mixed-Ligand Oxorhenium(V) Complexes Containing Bidentate Dithioethers and Monothiolato Ligands

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Neutral oxorhenium(V) complexes with dithioether ligands of the general formula $[ReOX_3(RS[CH_2]_2SR)]$, X = Cl, Br, R = *n*Bu, Et, Bzl were synthesized. Ammonium perrhenate reacts in concentrated hydrochloric acid with dithiaalkanes ($RS[CH_2]_2SR$, R = *n*Bu, Et, Bzl) dissolved in glacial acetic acid to give octahedral complexes of the type $[ReOCl_3(RS[CH_2]_2SR)]$ (**1a**–**c**). In concentrated hydrobromic acid, *n*Bu–S$(CH_2)_2$S–*n*Bu leads to the corresponding tribromo complex (**2**). The X-ray structure of **2** shows a distorted octahedron with facial coordination of the bromide ligands. The sulfur atoms are *cis* coordinated to the terminal oxygen. Dissolution of **1a** (R = *n*Bu) in methanol leads to the substitution of the chloride *trans* to the oxo ligand by a methoxy group. The resultant complex $[ReOCl_2(MeO)(n\text{-}Bu{-}S[CH_2]_2S{-}n\text{Bu})]$ (**3**) is stable and can be isolated from methanolic solution, but changes to the μ-oxo-bridged dirhenium complex μ-oxobis[dichloro(5,6-dithiadodecane)oxorhenium(V)] (**4**) when dissolved in other organic solvents. **1a** reacts with an excess of benzenethiol by substitution of two chlorides to give the mixed-ligand complex bis(benzenethiolato)chloro(5,8-dithiadodecane)oxorhenium(V) (**5a**). The related 4-methylbenzenethiolato complex **5b** was synthesized starting from the μ-oxo complex **4**. X-ray crystal structure determination of **5b** shows the equatorial arrangement of the sulfur atoms. The *trans* position to the oxygen atom is occupied by a chloride ion.

Introduction

Knowledge of the coordination chemistry of rhenium and technetium is of great importance for the design of radiopharmaceuticals based on 186/188-Re and 99m-Tc. Taking rhenium as a substitute for radioactive technetium, we particularly explored the coordination ability of thioether ligands at the metal oxidation state +5, +3, and +1[2–5].

Thioether compounds offer access to new small neutral complexes of rhenium and technetium, which are of interest in the design of radiopharmaceuticals.

Here we report on the reaction of dithioether ligands of the type $RS[CH_2]_2SR$ (R = *n*Bu, Et, Bzl) with ammonium perrhenate(VII) or tetrachlorooxorhenate(V) to give a series of mononuclear $[ReOX_3(RS[CH_2]_2SR)]$ and binuclear $[ReOCl_2(RS[CH_2]_2SR)]_2O$ complexes. One representative of this class of complexes, $[ReCl_3O(EtS[CH_2]_2SEt)]$ (**1b**), was already described by Kotegov who suggested for it a structure in accordance with IR data[6]. The mononuclear species are related to the oxobridged complex **4** that was recently described by us[2] and can be converted into it in a solvent-dependent reaction.

The chloro ligands in the complexes gave rise to exchange reactions with thiols such as benzenethiol.

Results and Discussion

In acetone/methanol solution, tetrachlorooxorhenate(V) salts react with bidentate dithioether ligands, such as 5,8-dithiadodecane, to oxobridged binuclear complexes $[ReCl_2ORS(CH_2)_2SR]_2O$, as described elsewhere[2] for R = *n*Bu, **4**. With glacial acetic acid as the solvent, the reaction produces the mononuclear complexes $[ReCl_3O(RS[CH_2]_2SR)]$ (**1a**–**c**). These compounds can also be synthesized in a one-pot reaction starting from a mixture of ammonium perrhenate and conc. HCl and the ligand dissolved in glacial acetic acid. The reaction can be considered as reduction of $[ReO_4]^-$ by conc. HCl to give intermediate tetrachlorooxorhenate(V) in the formation of **1a**–**c**. In this respect the reaction is comparable to those starting from $[ReCl_4O]^-$. All complexes obtained are turquoise microcrystals, which are stable to air and moisture. Using hydrobromic acid instead of HCl the related tribromooxorhenium complex **2** could be synthesized. Slow evaporation of the reaction mixture yields yellowish green crystals suitable for X-ray analysis. Infrared spectra, elemental analysis, and NMR spectra of the trihalogenooxorhenium

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complexes **1a**–**c** and **2** verify the structure that was deduced for **1b** from infrared data by Kotegov[6].

The presence of halogen atoms in both the *trans* and the *cis* position may give rise to subsequent substitution by nucleophilic agents.

Alcoholate ligands are able to substitute the less nucleophilic chloride in the *trans* position[7] to the double bonded oxygen. One example is known from Lock and co-workers, who reported the formation of the pyridyl complex [$ReOCl_2(OEt)py_2$] starting from [$ReOCl_3py_3$][8]. We observed halogen exchange when trichlorooxorhenium complexes **1a**–**c** were dissolved in methanol. **1a** is only slightly soluble in methanol, but within ten minutes the colour of the heterogeneous mixture changed from green to violet. The violet *trans* methoxy complex **3** can be separated from the solution, while the undissolved solid undergoes a further change in colour to dark green due to the conversion to **4**. The same conversion to **4** occurs by dissolution of solid **3** in organic solvents other than methanol. A similar phenomenon in reverse direction was described by Lock et al. for another type of oxobridged dinuclear rhenium complex. The bipyridine complex [$ReOCl_2bipy]_2O$ was converted by ethanol to the mononuclear species.

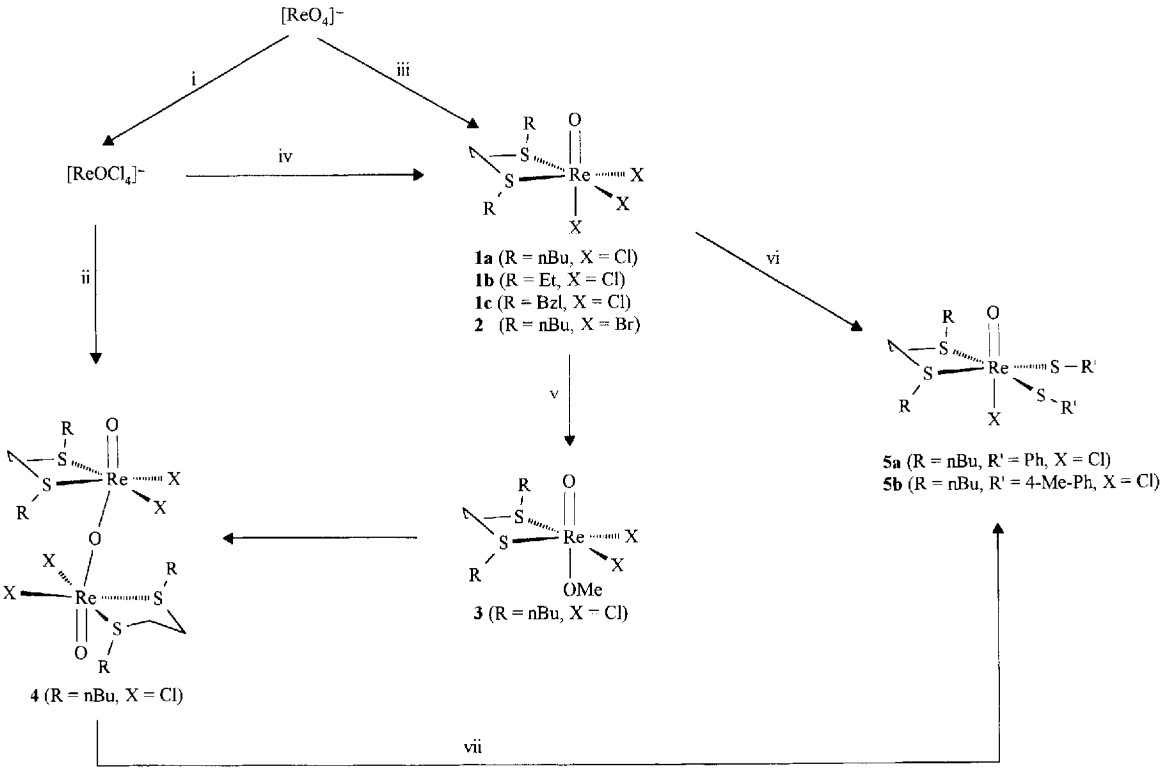
The infrared spectrum of **3** shows a Re–O vibration band at 936 cm^{-1} characteristic of the $Re{=}O^{3+}$ moiety with a *trans*-coordinated alkoxy ligand[1,9]. An ^1H-NMR spectrum of the fresh $CDCl_3$ solution of **3** shows a broad singlet at $\delta = 3.31$. Both the IR and the ^1H-NMR spectra support the assumption that the *trans*-chloro ligand was substituted by the more nucleophilic methoxy group. In the ^1H-NMR spectrum of the same solution taken 24 h later the peak at $\delta = 3.31$ has dissappeared, which indicates the cleavage of the Re–OMe bond to form the dinuclear complex **4**. A direct conversion of **1a**–**c** to the μ-oxo-bridged dirhenium complex **4** was achieved in other organic solvents. Traces of water may be the origin of the bridging oxygen.

Further experiments referred to substitution reactions of the equatorial sulfur and chlorine ligands with thiolato ligands. Reaction of **1a** with benzenethiol in tetrahydrofuran leads to the brown complex **5a**. The same products have been obtained by reaction of **4** with benzenethiol. X-ray structure analysis of **5b** shows that two benzenethiolate molecules occupy the equatorial positions of the chlorines. One of the halogen ligands displaces the bridging oxygen *trans* to the Re=O core. The band at ca. 940 cm^{-1} in the infrared spectrum and elemental analysis support the structure of **5a** as well as those of **5b**. The ^1H-NMR spectra for **5a** and **5b** exhibit all resonances associated with the benzenethiol and dithioether ligands. There is no indication of a substitution of the thioether ligands under moderate reaction conditions, which demonstrates the stability of the rhenium sulfur bond of coordinated thioether ligands.

The molecular structures of **2** and **5b** have been determined by X-ray crystal analysis and are depicted in Figures 1–4. Selected bond lengths and angles are listed in Table 1.

In the crystal of **2** a statistical disorder of the butyl groups is observable. This affects various positions of the carbons C(4), C(5), C(6), and C(10) of structure **A** (Figure 1) and C(4′), C(5′), C(6′), and C(10′) of structure **B** (Figure 2). The mean probability of structure **A** and **B** is 49 and

Scheme 1. i: According to[12]; ii: $RS[CH_2]_2SR$, acetone/methanol[2]; iii: HCl (for **1a**–**c**), HBr (for **2**); $RS[CH_2]_2SR$/AcOH; iv: $RS[CH_2]_2SR$/AcOH; v: Methanol; vi: PhSH, acetone; vii: 4-Me-C_6H_4SH, chloroform/methanol; viii: Aprotic organic solvents



51%. The distorted octahedral coordination sphere of the rhenium is formed by the terminal oxygen, the dithioether ligand and the three bromides. S(1), S(2), Br(1), Br(2) are positioned in the equatorial plane *cis* coordinated to the oxygen and Br(3).

The angle of the O–Re–Br(3) axis is 163.8(2)°. With 2.421(2) and 2.453(3) Å the Re–S bonds are in the expected range[10,11]. While the equatorial distances Re–Br(1) and Re–Br(2) are 2.4860(14) and 2.490(3) Å, the bond length of Re–Br(3) is elongated by 2.5969(13) Å. This fact is attributed to the *trans* influence of the oxo ligand.

Figure 1. Molecular structure of tribromooxorhenium(V) **2**, structure **A**

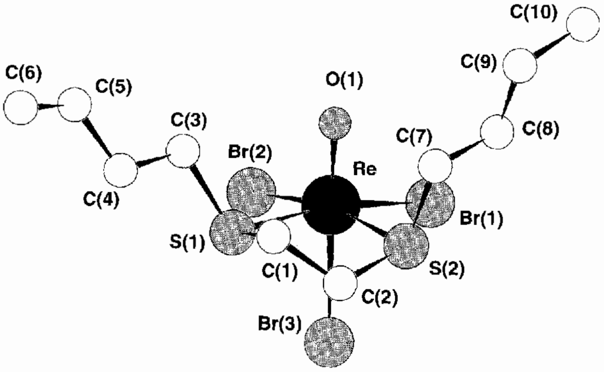


Figure 2. Molecular structure of tribromooxorhenium(V) **2**, structure **B**

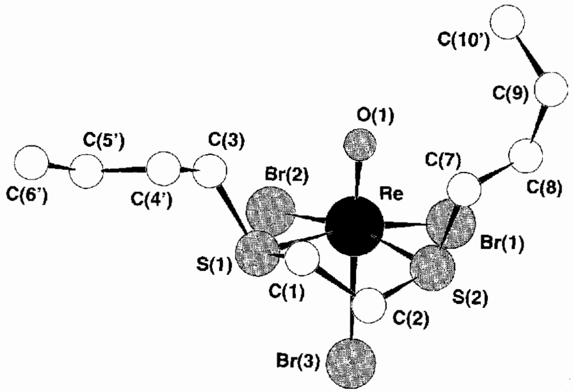


Figure 3 shows the crystal structure of complex **5b**. As illustrated by the perspective view of the molecule, **5b** consists of a discrete monomolecular unit of the rhenium atom in an octahedral environment.

Figure 4 represents the structure after a rotation around the Re–O bond by 90°. All atoms of both the benzenethiol ligands are in one common plane, i.e. the rings are not stacked. The *n*-butyl groups are positioned parallel to this plane.

In the complex **5b** the O–Re–Cl angle of 158.4(3)° is reduced, the opening faces the thioether ligand (Figure 4). The Re–S bonds of 2.291(4) Å and 2.318(4) Å of the benzenethiols are in the reported range[10,11]. Likewise in complex **2** the elongation of the Re–halogen bond by 2.453(4) Å is attributed to the *trans* effect of the oxygen.

Figure 3. Molecular structure of **5b**

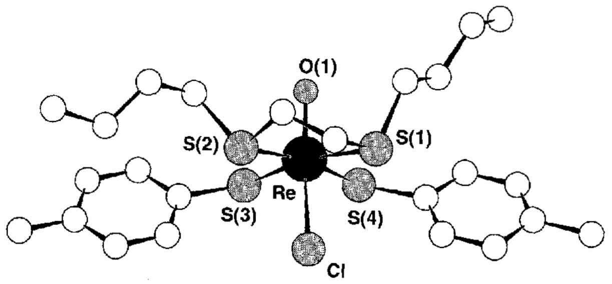


Figure 4. View of the molecular structure of **5b** turned around the Re–O bond by 90°

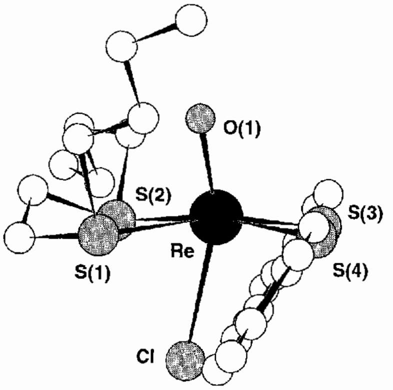


Table 1. Selected bond lengths and angles of complexes **2** and **5b**

2					
Re–O(1)	1.667(5)	Re–S(2)	2.453(3)	Re–Br(2)	2.490(3)
Re–S(1)	2.421(2)	Re–Br(1)	2.4860(14)	Re–Br(3)	2.5969(13)
O(1)–Re–S(1)	90.2(2)	S(1)–Re–S(2)	86.09(9)	S(2)–Re–Br(2)	167.61(7)
O(1)–Re–Br(1)	100.8(2)	S(1)–Re–Br(1)	168.86(7)	S(2)–Re–Br(3)	76.94(8)
O(1)–Re–S(2)	89.0(2)	S(1)–Re–Br(3)	80.97(7)	Br(1)–Re–Br(2)	89.10(6)
O(1)–Re–Br(2)	102.8(2)	S(1)–Re–Br(2)	90.11(7)	Br(1)–Re–Br(3)	87.93(5)
O(1)–Re–Br(3)	163.8(2)	S(2)–Re–Br(1)	92.35(7)	Br(2)–Re–Br(3)	90.83(6)
5b					
Re–O(1)	1.680(10)	Re–S(1)	2.534(4)	Re–S(3)	2.291(4)
Re–Cl	2.453(4)	Re–S(2)	2.483(4)	Re–S(4)	2.318(4)
O(1)–Re–S(1)	86.5(3)	S(1)–Re–Cl	75.71(14)	S(1)–Re–S(3)	168.83(14)
O(1)–Re–S(2)	87.6(3)	S(2)–Re–Cl	78.51(14)	S(2)–Re–S(4)	169.53(14)
O(1)–Re–S(3)	104.6(3)	S(3)–Re–Cl	93.5(2)	S(1)–Re–S(4)	98.51(14)
O(1)–Re–S(4)	102.7(3)	S(4)–Re–Cl	92.1(2)	S(2)–Re–S(3)	96.97(14)
O(1)–Re–Cl	158.4(3)	S(1)–Re–S(2)	83.88(14)	S(3)–Re–S(4)	78.73(14)

We found that the product formed in the reaction of ammonium perrhenate and tetrachlorooxorhenate(V) with thioether ligands depends on the solvent used. In strong acids the trihalogenooxorhenium(V) complexes [ReX$_3$O(RS-[CH$_2$]$_2$SR)] **1a–c** and **2** were obtained, while in neutral protic organic solvents the oxobridged dirhenium complexes [ReCl$_2$O(RS[CH$_2$]$_2$SR)]$_2$O (**4**) were formed. During the reaction of **1a** with methanol the halogen in *trans* position to the Re–O core is substituted and the intermediate **3** is obtained. The complex is stable in solid and in methanolic solution, but in other organic solvents immediately converts to the oxobridged dinuclear complex.

Further, substitution reactions of the trichlorooxorhenium(V) complex **1a** and the dinuclear complex **4** with benzenethiol lead to the same mixed-ligand complexes **5a**, **b**. A replacement of the dithioether ligand does not occur under these reaction conditions.

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Experimental Section

General: All solvents and commercially available substances like $(NH_4)[ReO_4]$ were of analytical grade. $(AsPh_4)[ReOCl_4]$ was prepared according to a literature procedure[12]. All thioether ligands were synthesized by a common reaction described by Fehér and Vogelbruch[13]. – IR spectra were measured in KBr discs on a Specord M 80 spectrometer from Carl Zeiss Jena.

X-ray Crystallographic Study[14]: The X-ray data were collected at room temperature (296 K) on an ENRAF-NONIUS CAD 4 diffractometer, using graphite monochromatized Mo-K_α radiation (λ = 0.71073 Å). A summary of the crystallographic data is given in Table 2. The positions of the non-hydrogen atoms were determined by the heavy atom technique. After anisotropic refinement of the positions of these, the hydrogen positions were calculated according to ideal geometries. Empirical absorption corrections with the program DIFABS[15] were made at two stages during the structure refinement. Most of the calculations were carried out in the ENRAF-NONIUS SDP system with some local modifications. Selected bond lengths and angles are contained in Table 1. Atomic positional and thermal parameters, full lists of bond lengths and angles, and F_o/F_c values have been deposited as supplementary material.

Table 2. Crystal structure parameters of complexes **2** and **5b**

	2	**5b**
Empirical formula	$C_{10}H_{22}Br_3OReS_2$	$C_{24}H_{36}ClOReS_4$
Formular weight	648.33	690.42
Crystal system	monoclinic	triclinic
Space group	C12 1/n1	P –1
a [Å]	24.167(9)	7.866(2)
b [Å]	12.257(4)	11.037(3)
c [Å]	14.04(2)	16.137(3)
α [°]	90.00	88.380(10)
β [°]	119.50(5)	78.020(10)
γ [°]	90.00	85.390(10)
Volume [$Å^3$]	3619(4)	1365.9(6)
Z	8	2
Temperature [K]	293(2)	293(2)
δ [g/cm^3]	2.380	1.679
Absorption coefficient [mm^{-1}]	13.556	4.867
F(000)	2416	688
μ (MoKα) [Å]	0.71069	0.71070
Crystal size [mm^3]	$0.72 \times 0.14 \times 0.14$	$0.45 \times 0.22 \times 0.04$
θ range	1.92 – 24.98	1.85 – 21.98
Index ranges	$0 \le h \le 28$	$0 \le h \le 6$
	$0 \le k \le 14$	$-11 \le k \le 11$
	$-16 \le l \le 14$	$-16 \le l \le 16$
Reflections collected	3264	3059
Independent reflections	3180	3044
GOF on F^2	0.696	1.219
Final R indices [$I > 2\sigma(I)$]	$R1 \approx 0.0349$	$R1 = 0.0576$
	$wR2 = 0.0997$	$wR2 = 0.1516$
R indices (all data)	$R1 \approx 0.0456$	R1 = 0.0689
	$wR2 = 0.1099$	$wR2 = 0.1558$
Largest diff. peak	1.216	1.244
Largest diff. hole	–0.521	–1.147

Preparation of **1a**: 41.3 mg (200 μmol) of 5,8-dithiadodecane, dissolved in 1 ml of glacial acetic acid, was added to 40.2 mg (150 μmol) of $(NH_4)[ReO_4]$, dissolved in 1.5 ml of concentrated HCl. After 20 min the precipitate was filtered off and washed three times with glacial acetic acid and then three times with diethylether, yielding 65 mg (85%) of **1a**, turquoise microcrystals, m.p. 117–118°C. – IR (KBr): $\tilde{\nu}$ = 2960 (C–H), 2936 (C–H), 2872 (C–H), 976 (Re=O). – ^1H NMR ($CDCl_3$): δ = 0.99 (t, J = 7.2 Hz, 6H, $CH_3CH_2CH_2CH_2S$), 1.56 (sext, J = 7.3 Hz, 4H, $CH_3CH_2CH_2CH_2S$), 1.94 (br, 4H, $CH_3CH_2CH_2CH_2S$), 2.9–3.7 (m, 8H, $CH_2SCH_2CH_2SCH_2$). – $C_{10}H_{22}Cl_3OReS_2$ (515): calcd. C 23.32, H 4.31, S 12.45; found C 23.25, H 4.39, S 12.31.

Preparation of **1b**: The preparation is similar to that of **1a** except for the ligand 3,6-dithiaoctane. Yield: 54 mg (79%) turquoise-green powder, m.p. 163°C. – IR (KBr): $\tilde{\nu}$ = 2952 (C–H), 2928 (C–H), 984 (Re=O). – ^1H NMR ($CDCl_3$): δ = 1.63 (br, 6H, CH_3CH_2S), 3.35 and 3.47 (br, 4H, CH_3CH_2S), 3.60 and 3.75 (4H, SCH_2CH_2S). – $C_6H_{14}Cl_3OReS_2$ (459): calcd. C 15.71, H 3.08, S 13.98, Cl 23.18; found C 15.74, H 3.14, S 13.75, Cl 23.61.

Preparation of **1c**: The preparation is similar to that of **1a**. The ligand is 1,6-diphenyl-2,5-dithiahexane. Yield: 50 mg (57%) turquoise-green powder, m.p. 120–121°C. – IR (KBr): $\tilde{\nu}$ = 2928 (C–H), 976 (Re=O), 768 (Ph). – ^1H NMR ([D_6]acetone): δ = 3.50 and 3.62 (br, 4H, SCH_2CH_2S), 4.39 and 4.81 (d, J = 13.0 Hz, 4H, C_6H_5-CH_2), 7.48 (dd, J = 7.1 Hz, 2H, p-H), 7.52 (dd, J = 7.1 Hz, J = 7.3 Hz, 4H, m-H), 7.63 (d, J = 7.3 Hz, 4H, o-H). – $C_{16}H_{18}Cl_3OReS_2$ (583): calcd. C 32.96, H 3.11, S 11.00, Cl 18.24; found C 32.65, 2.94, S 11.17, Cl 18.52.

Preparation of **2**: The preparation is similar to that of **1a**. Instead of hydrochloric acid hydrobromic acid was used. Slow evaporation of the reaction solution led to 29 mg (30%) of **2**, yellowish green needles, m.p. 145°C. – IR (KBr): $\tilde{\nu}$ = 2960 (C–H), 2928 (C–H), 2872 (C–H), 976 (Re=O). – ^1H NMR ($CDCl_3$): δ = 1.00 (t, J = 7.2 Hz, 6H, $CH_3CH_2CH_2CH_2S$), 1.59 (sext, J = 7.3 Hz, 4H, $CH_3CH_2CH_2CH_2S$), 1.88 (br, 4H, $CH_3CH_2CH_2CH_2S$), 2.6–3.6 (m, 8H, $CH_2SCH_2CH_2SCH_2$). – $C_{10}H_{22}Br_3OReS_2$ (648): calcd. C 18.53, H 3.39, S 9.89, Br 36.97; found C 18.40, H 3.25, S 9.83, Br 37.18.

Preparation of **3** *and* **4**: The preparation of **4**, starting from tetrachlorooxorhenate, was published elsewhere[2].

3: 50 mg (100 μmol) of **1a** were suspended in methanol. After a few minutes the colour of the precipitate and the solution turned from green to violet. The violet solution was filtered and kept in the refrigerator to separate a violet precipitate (**3**). It was possible to dissolve the complex in chloroform or acetone, but this changed the colour again to green. Removing of the solvent led to complex **4**. Yield of **3**: 6.1 mg (12%) violet microcrystals, m.p. 137°C. – IR (KBr): $\tilde{\nu}$ = 2960 (C–H), 2936 (C–H), 2872 (C–H), 1116 (O–Me), 936 (Re=O). – ^1H NMR ($CDCl_3$): δ = 0.99 (t, J = 7.4 Hz, 6H, $CH_3CH_2CH_2CH_2S$), 1.54 (sext, J = 7.4 Hz, 4H, $CH_3CH_2CH_2CH_2S$), 1.92 (quint, J = 7.4 Hz, 4H, $CH_3CH_2CH_2CH_2S$), 3.31 (br, 3H, OCH_3), 2.7–3.5 (m, 8H, $CH_2SCH_2CH_2SCH_2$). – $C_{11}H_{25}Cl_2O_2ReS_2$ (511): calcd. C 25.88, H 4.94, S 12.56, Cl 13.89; found C 25.64, H 4.67, S 12.73, Cl 15.2.

4: Yield: 44.2 mg (86%), m.p. 209°C. – IR (KBr): $\tilde{\nu}$ = 2960 (C–H), 2928 (C–H), 2872 (C–H), 688 (Re=O). – ^1H NMR ($CDCl_3$): δ = 0.97 (t, J = 7.2 Hz, 6H, $CH_3CH_2CH_2CH_2S$), 1.52 (sext, J = 7.2 Hz, 4H, $CH_3CH_2CH_2CH_2S$), 1.87 (quint, J = 7.2 Hz, 4H, $CH_3CH_2CH_2CH_2S$), 3.48 (s, 2H), 2.7–3.6 (m, 8H, $CH_2SCH_2CH_2SCH_2$). – $C_{20}H_{44}Cl_4O_3Re_2S_4$ (511): calcd. C 25.88, 4.94, S 12.56, Cl 13.89; found C 25.64, H 4.67, S 12.73, Cl 15.2.

Preparation of **5a**: A solution of 45 mg (88 μmol) of **1a** in 1 ml of acetone was cooled to 5°C. 22 mg (200 μmol) of benzenethiol were added and the mixture was stirred while the reaction temperature rose to room temperature. The colour of the solution immediately turned to dark brown. After an hour the solvents were removed in vacuo, the residue was washed three times with a small amount of diethylether to remove the excessive benzenethiol and then dissolved in 1 ml of acetone. Slow evaporation gave 49.5 mg (85%) of **5a**, brown crystals, m.p. 144°C. − IR (KBr): $\tilde{\nu}$ = 2960 (C−H), 2928 (C−H), 2872 (C−H), 940 (Re=O), 744 (Ph). − ^1H NMR ($CDCl_3$): δ = 0.81 (t, *J* = 7.3 Hz, 6H, $C\mathit{H}_3CH_2CH_2CH_2S$), 1.1−1.5 (br, 8H, $CH_3C\mathit{H}_2C\mathit{H}_2CH_2S$), 2.39 (br, 4H, $CH_3CH_2CH_2C\mathit{H}_2S$), 2.9−3.4 (br, 8H, SCH_2CH_2S), 7.16 (dd, *J* = 7.6 Hz, *p*-H), 7.39 (dd, *J* = 7.6 Hz, *J* = 8.0 Hz, *m*-H), 7.63 (d, *J* = 8.0 Hz, *o*-H). − $C_{22}H_{32}ClOReS_4$ (662): calcd. C 39.89, H 4.78, S 19.36, Cl 5.35; found C 39.41, H 4.74, S 19.15, Cl 6.20.

Preparation of **5b**: A solution of 56 mg (450 μmol) of 4-methylbenzenethiol in 2 ml of chloroform was added to 98 mg (100 μmol) of **4**, dissolved in 3 ml of chloroform. The mixture was stirred for 30 min. During this time the colour changed from turquoise to reddish brown. Addition of 2 ml of methanol to the mixture and slow evaporation of most of the solvent gave 96 mg (70%) of **5b**, dark brown needles, m.p. 142−143°C. − IR (KBr): $\tilde{\nu}$ = 2960 (C−H), 2928 (C−H), 2872 (C−H), 936 (Re=O), 808 (Ph). − ^1H NMR ($CDCl_3$): δ = 0.81 (t, *J* = 7.2 Hz, 6H, $C\mathit{H}_3CH_2CH_2CH_2S$), 1.1−1.5 (m, 8H, $CH_3C\mathit{H}_2C\mathit{H}_2CH_2S$), 2.39 (br, 4H, $CH_3CH_2CH_2C\mathit{H}_2S$), 2.43 (s, 6H, C_6H_4-$C\mathit{H}_3$), 2.8−3.4 (br, 8H, SCH_2CH_2S), 7.21 (d, *J* = 7.8 Hz, *m*-H), 7.63 (d, *J* = 7.8 Hz, *o*-H). − $C_{24}H_{36}ClOReS_4$ (690): calcd. C 41.77, H 5.22, S 18.56, Cl 5.15; found C 41.56, H 5.24, S 18.61, Cl 5.50.

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