Pergamon

PII: S0277–5387(98)00169–7

Polyhedron Vol. 17, No. 21, pp. 3711–3720, 1998
© 1998 Elsevier Science Ltd
All rights reserved. Printed in Great Britain
0277–5387/98 \$19.00+0.00

A mixed-ligand P,S,N-*cis*-dioxorhenium(V) complex by ligand exchange reactions on *trans*-monooxo-trichlorobis(triphenylphosphine)rhenium(V): formation and structural studies

Matthias Friebe,[a]* Ruediger Jankowsky,[a] Hartmut Spies,[a] Wilhelm Seichter,[b] Minas Papadopoulos,[c] Efstratios Chiotellis[c] and Bernd Johannsen[a]

[a] Forschungszentrum Rossendorf, Institut für Bioanorganische und Radiopharmazeutische Chemie, Postfach 510119, 01314 Dresden, Germany

[b] Institut für Organische Chemie, TU-Bergakademie Freiberg, Leipziger Straße 29, 09596 Freiberg, Germany

[c] Institutes of Radioisotopes-Radiodiodiagnostic Products and Material Science, NCSR "Demokritos", P.O. Box 60228, 15310 Ag. Paraskevi, Athens, Greece

(Received 11 February 1998; accepted 20 April 1998)

Abstract—In the course of our efforts to synthesize rhenium(V) complexes for potential use in nuclear medicine, tridentate dithiolate ligands were combined with (dialkylamine) ethylene thiols [HS–$(CH_2)_2$–NR'_2] (R′ = alkyl, alkoxy) to form amine group bearing mixed-ligand complexes [ReO(SNS)(S)]. The reaction of HS–CH_2–CH_2–N–(CH_2–CH_2–N$(C_2H_5)_2$)CH_2–CH_2–SH (*N*,*N*-bis(2-mercaptoethyl)-*N′*,*N′*-diethylethylenediamine, **2**, as a tris-chelating ligand and 1,4-dioxa-8-azaspiro-*N*-2-mercaptoethylene-[4,5]-decane, **3**, with the neutral Re(V) complex [$ReOCl_3(PPh_3)_2$], **1**, yields, in addition to the expected square-pyramidal "**3**+**1**" compound (1,4-dioxa-8-azaspiro-*N*-2-thiolatoethylene-[4,5]-decane)*N*,*N*-bis(2-mercaptoethyl)(*N′*,*N′*-di-ethyl-ethylenediamine) oxorhenium(V), **4**, the new five-coordinated complex [1,4-dioxa-8-azaspiro-*N*-2-mercaptoethylene-[4,5]-decane(triphenylphosphinato)dioxorhenium(V)], **5**. Being the only product in the absence of the tridentate component, **5** has a trigonal–bipyramidal structure, where the coordination sphere is formed by two oxo groups in an uncommon *cis*-arrangement, S and N from the aminothiolate and by the phosphorus atom from the phosphine group originating from the precursor molecule. The structure was verified by mass, ^{1}H NMR, IR spectroscopy as well as by XRD. In addition, extended x-ray absorption spectroscopy (EXAFS) was applied to both the precursor and the resulting compound **5** to compare the complex structures in the solid and the soluted state. Experiments with ^{18}O labelled water added to the reaction mixture led to ^{18}O in the dioxo core, showing that water is the origin of the additional oxo group. © 1998 Elsevier Science Ltd. All rights reserved. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: rhenium(V) mixed ligand complexes; *cis*-dioxo; trigonal–bipyramidal; X-ray structure; XANES; EXAFS

INTRODUCTION

There is great interest in the chemistry of technetium and rhenium [1] because of the high significance that the radioactive nuclides ^{99m}Tc and ^{186}Re/^{188}Re have in nuclear medicine. Our special attention is focused on the so-called "3+1" mixed-ligand complexes, a class of compounds useful for the design of new radiotracer molecules [2, 3], where the MO^{3+} core is coordinated by both a tridentate and a monodentate ligand.

We were particularly interested in "3+1" com-

---

* Author to whom correspondence should be addressed. Fax: +49-351-260-3232; E-mail: friebe@fz-rossendorf.de.

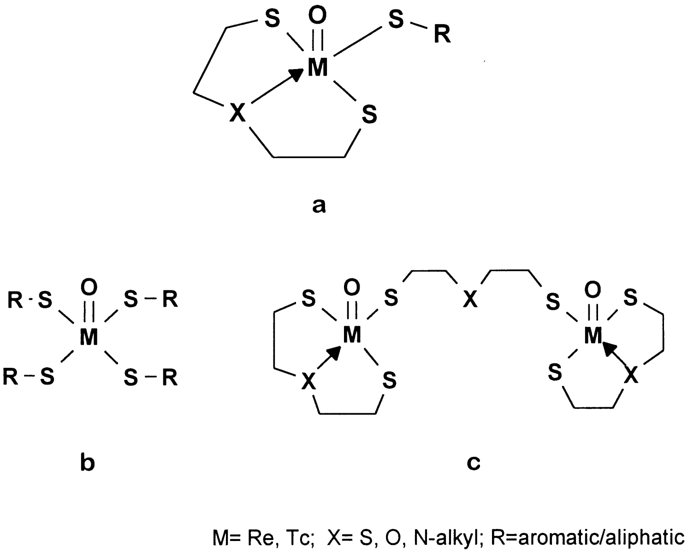


Fig. 1. A selection of known oxometal(V) complexes as the results of ligand exchange reactions on oxometal(V) precursors.

plexes in which dialkylaminothiolates are the monodentate ligands, since some of the "3 + 1" complexes are of interest with respect to brain imaging agents [4, 5] and play an important role in the search for neuroreceptor–affine complexes.

The involvement of two competing ligands in the formation of the mixed-ligand complexes gives rise to various species (Figure 1). Depending on the stoichiometric ratios of the ligands, not only the desired "3 + 1" compound (a) but also complexes of only the monodentate ligands having a formal S_4 coordination (b) [6] and dinuclear complexes (c) containing only the tridentate ligand may be formed [7, 8].

In order to optimize the reaction conditions for the preparation of such a complex **4** (Figure 2) by ligand exchange reactions, we studied the reaction of $[ReOCl_3(PPh_3)_2]$ (**1**) with the tridentate ligand $[HS–(CH_2)_2–N(CH_2–CH_2NEt_2)–(CH_2)_2–SH]$ (**2**) [9, 10] and dialkylaminothiolates such as **3** Fig. 2. When the tridentate ligand was used as the minor compound versus one to one ratios of the dialkylaminothiolate and the metal precursor in reaction mixtures in order to avoid the formation of dinuclear bridged complex products, two compounds were obtained. One consists of the expected "3 + 1"-product **4** while the other is a hitherto unknown type of a *cis*-dioxorhenium(V) complex, **5**.

Here we describe the formation and structural characterization of these new compounds. Structure investigations in solution using EXAFS were performed in addition.

RESULTS AND DISCUSSION

Starting from *trans*-monooxotrichlorobis-(triphenylphosphine)rhenium(V) $[ReOCl_3(PPh_3)_2]$ (**1**) as a rhenium(V) precursor [11] with a mixture of **2** [SNS] and **3** [S(N)], the reactants **1**, **2** and **3** were used in various stoichiometric amounts (1:1:2, 1:0.5:1 or 1:1:1). In all cases the expected "3 + 1" mixed-ligand complex **4** was formed and a second neutral rhenium(V) complex **5** was observed with an excess of **3** over **1** and **2** or with the tridentate ligand as a minor compound Fig. 2. **5** became the major product and could be isolated as a dark red, stable, crystalline solid in a 49 percent yield (Figure 2, route b) when **2** was omitted in the reaction mixture. A base such as sodium acetate or triethyl amine in the reaction mixture seems to be essential for the formation of **4** and **5**. No formation of **5** and less yields for **4** are observed after refluxing in methanol for one hour [12] without addition of the described bases. **5** was also formed in oxygen free solvents such as dichloromethane or acetonitrile (Figure 3).

Complexes **4** and **5** are readily soluble in organic solvents. Elemental analysis shows that **4**, as expected, contains both the tridentate ligand **2** and the monodentate ligand **3,** while complex **5** contains ligand **3** and one triphenylphosphane.

^{1}H *NMR spectroscopy*

^{1}H NMR studies of **4** show signals with chemical shifts identical to those found for the O-methylene-bound protons of ligand **3** as well as the typical signal pattern of the two ethyl groups bound to the ethylene diamine fragment. All this verifies the presence of the tris chelating ligand **2** in the complex. In order to identify the other protons of the coordinated ligand **2**, NOESY spectra of a similar compound [9] bearing **2** were used for comparison.

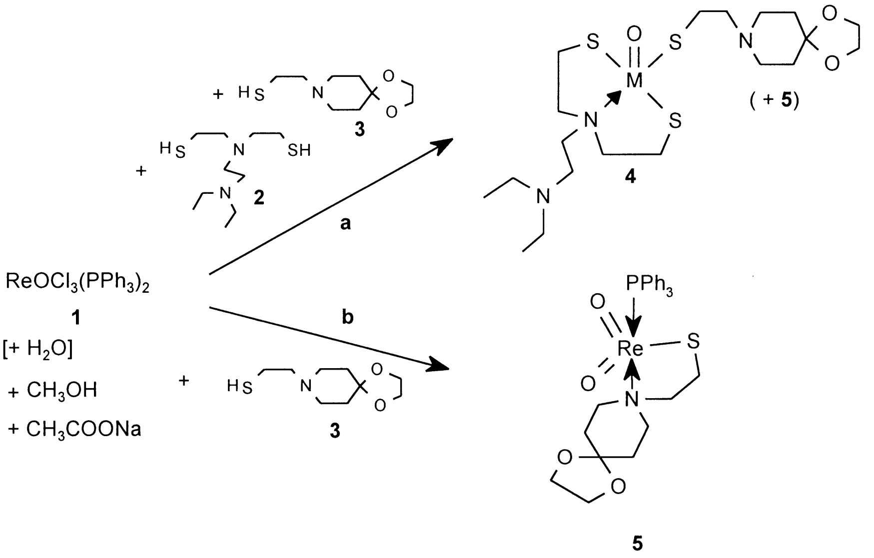


Fig. 2. Reaction scheme of the formation of the mono-oxo rhenium(V) complex **4** and the *cis*-dioxo rhenium(V) complex **5**.

^{1}HNMR investigations of **5** confirm the formulation, showing a signal pattern typical of phosphorus bound to arylic protons and a defined multiplet signal of four O-methylene bound protons in the expected range. Due to the bound nitrogen of the ring system of **3** in case of **5**, the symmetry of the O-methylene protons is disturbed and shows the splitting of the signal pattern as expected. The measured intensities of the arylic/aliphatic signals yield a 1:1 ratio corresponding to **3**/PPh_3.

IR spectroscopy

The IR spectrum of **5** did not show the intensive signal at $\nu = 945\,cm^{-1}$ for Re═O as observed for **4**. Two intense bands shifted to shorter wave numbers at $\nu = 836$ and $907\,cm^{-1}$ were detected. These values are typical of the *cis*-O═Re═O group as recorded for postulated [13] or established [14] *cis*-dioxorhenium(V) coordinated complexes.

Unlike **4**, **5** needs the attack of an oxygen donor on **1** for its formation. We assume that traces of water are the source of the second oxygen in the *cis*-dioxo arrangement of **5**. To prove this assumption, [${}^{18}O$] water was added to the reaction mixture. As described in literature [15] the increased mass of the (${}^{18}O$)-oxygen in the molecule should effect a noticeable shift of the obtained O═Re═O signals to shorter wave numbers. The resulting **5** shows a modified IR spectrum [Fig. 4(a)], where the oxo-rhenium stretches were shifted to $\eta = 798\,cm^{-1}$ and $\eta = 856\,cm^{-1}$ and the exactly identical fingerprint range clearly revealed the formation of an [${}^{18}O$]-containing compound **5**. The found shifts are in a comparable range to IR data of (${}^{18}O$)–CO vs (${}^{16}O$)–CO [15] studies.

X-ray crystal structure

Crystals of **5** suitable for X-ray diffraction studies were obtained by recrystallization from ether/*n*-heptane. The structure determination clearly reveals the formation of a trigonal bipyramid. As already anticipated from IR data, the O-donors are arranged in a *cis* configuration and form a plane with the S-atom. The phosphorus and nitrogen donors compose the apices of the trigonal P–Re–N bipyramid. The small distortion of the ideal 180° P–Re–N angle is caused by the S-donor in the trigonal plane. In contrast to a *trans*-dioxo configuration, the O–Re–O angle is decreased to 135°. Due to the O_x–Re–S angles of about 112° and to P,N donors being perpendicular to the trigonal plane, a distorted trigonal bipyramid is formed. The parameter τ, introduced to classify five coordinated complexes to square–pyramidal ($\tau = 0$) or trigonal–bipyramidal geometry ($\tau = 1$) [16], was determined as 0.64. Discrepancies concerning the ideal trigonal bipyramid can be explained by the O_3–Re–O_4 angle of oxygen coordination in the equatorial plane. In accordance with theory, the bond length found for the dioxo core increases to 1.73 Å, compared with 1.65 Å for the mono-oxo core (Re═O, **4**) [10]. The bond lengths of the other donors show no significant differences between structures [10] such as **4** and **5** (Table 1).

The occurrence of a dioxo core shows a remarkable parallel to *trans*-dioxorhenium(V) compounds containing [P, N, Cl] or [P, I] chelating systems [14, 17]. We assume that this phenomenon results from the tendency of the metal core to become neutral. The *cis*-dioxo configuration of **5** is obviously influenced by the steric effects of the ligand **3**. The C_2 distance of

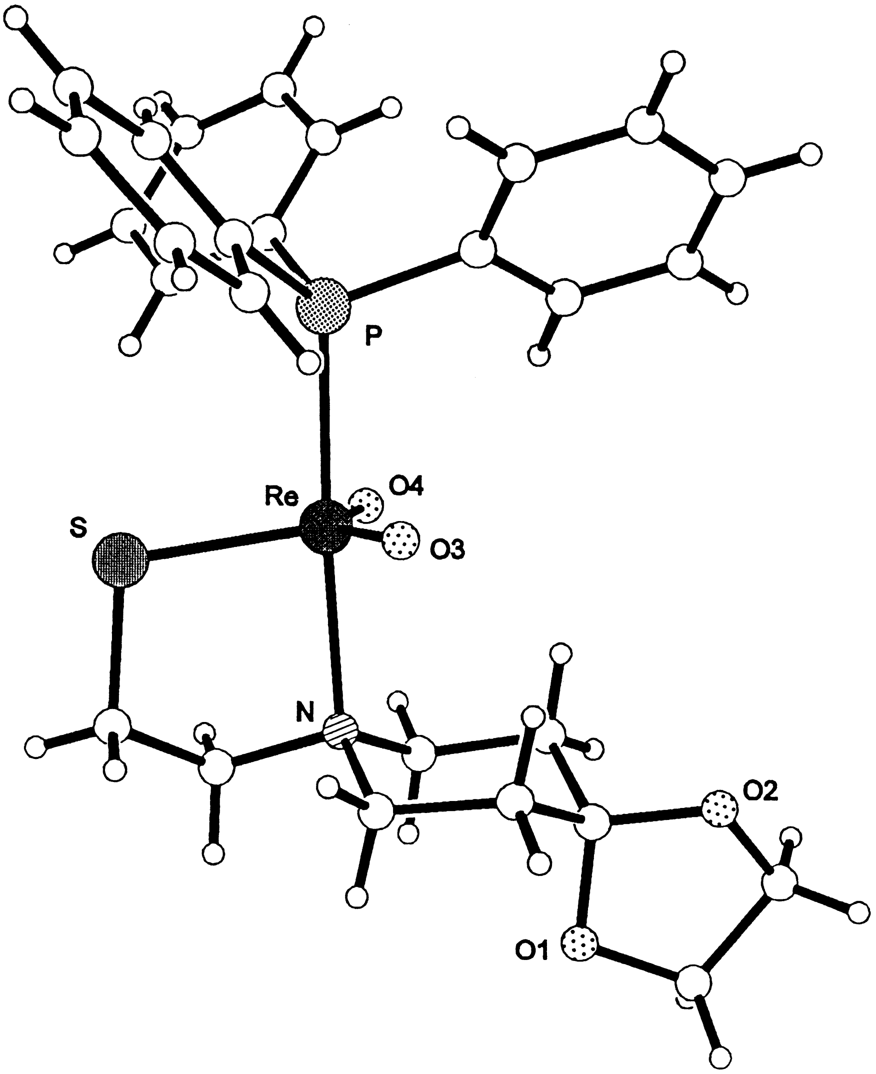


Fig. 3. X-ray crystallographic structure of **5**.

both the nitrogen and sulphur donors affects the arrangement out of the trigonal equatorial plane. This is caused by the intramolecular tension in **5** in opposition to the coordination mode in the base plane of a square pyramidal complex such as **4**. That fact excludes the *trans*-configuration of the dioxo core.

XANES/EXAFS measurements

To better understand the changes in the atomic environment of the central atom associated with the formation of the *cis*-dioxo compound, investigations of the rhenium coordination sphere at the precursor state and the final *cis*-dioxo complex state appeared to be helpful. Therefore, EXAFS measurements were applied to deliver atomic radial distributions of the ligand atoms around the rhenium central atom. EXAFS investigations made it possible to trace the structural relationships in the reaction mixture by considering the neighbourhood closest to rhenium in the solid (suspended) precursor state as well as in the soluted *cis*-dioxo compound state, which are both present in the reaction mixture. A comparison of the clarified crystal structure of **5** with its rhenium coordination sphere in a non-crystalline state was of special interest from a nuclear medical point of view.

XANES data

A strong white line as typical of measurements at the rhenium L_{III} absorption edge [16] was observed for both complexes under investigation. The absorption edge position of complex **1** was determined to be 10533 eV, that of complex **5** was 10535 eV. The differ-

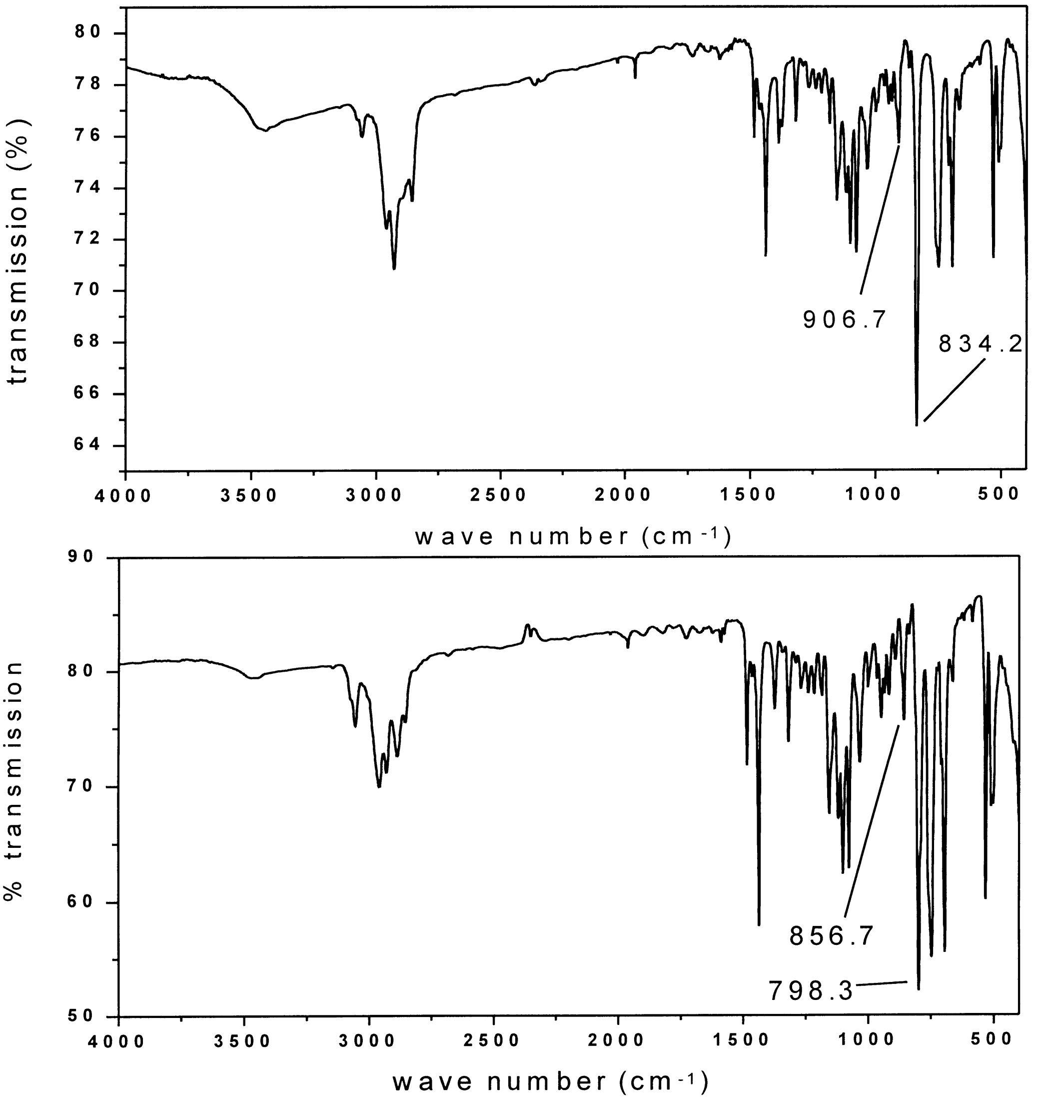


Fig. 4. IR spectrum of **5** obtained by the reaction without addition of water (measured in $CHCl_3$). (a) IR spectrum of **5** obtained by addition of [^{18}O] water to the reaction mixture (measured in $CHCl_3$).

Table 1. Selected bond distances (Å) and angles (°) of **5**

Atoms	Bond length (Å) and angles (°)	Atoms	Bond length (Å) and angles (°)
Re–O(3)	1.736(5)	O(3)–Re–N	87.6(3)
Re–O(4)	1.735(5)	O(4)–Re–N	93.0(2)
Re–S	2.269(2)	S(1)–Re–N	85.5(2)
Re–N	2.280(6)	O(3)–Re–P	86.5(2)
Re–P	2.403(2)	O(4)–Re–P	90.7(2)
O(3)–Re–O(4)	135.9(3)	S(1)–Re–P	97.43(8)
O(3)–Re–S	111.1(2)	N(1)–Re–P	174.0(2)
O(4)–Re–S	113.0(2)		

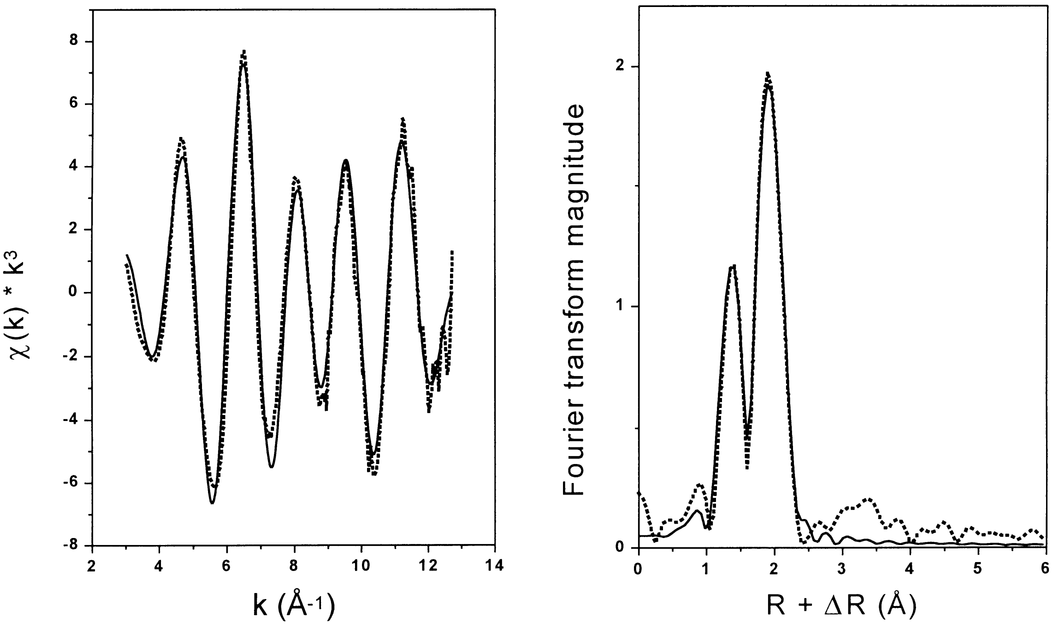


Fig. 5. (a) EXAFS data of complex **1**. Dotted lines, experimental data; solid lines, fit data. (b) Fourier transform corresponding to (a).

Table 2. EXAFS fit results for complex **1**

Shell	N	R^a (Å)	σ^2 (Å^2)
O	1.1(1)	1.70(1)	0.001(1)
P/Cl	5.2(4)	2.41(1)	0.005(1)

N is the number of coordinating atoms. R: distance to rhenium central atom. σ^2: Debye–Weller factor. Fit mode: Marquardt algorithm using least squares method. Calculated resolution in distance: 0.16 Å. The theoretical resolution in distance is given by the formula $\Delta R = 2\pi/k_{\max}$ [19] ΔE_0: -8 eV.

a Distance to the rhenium central atom.

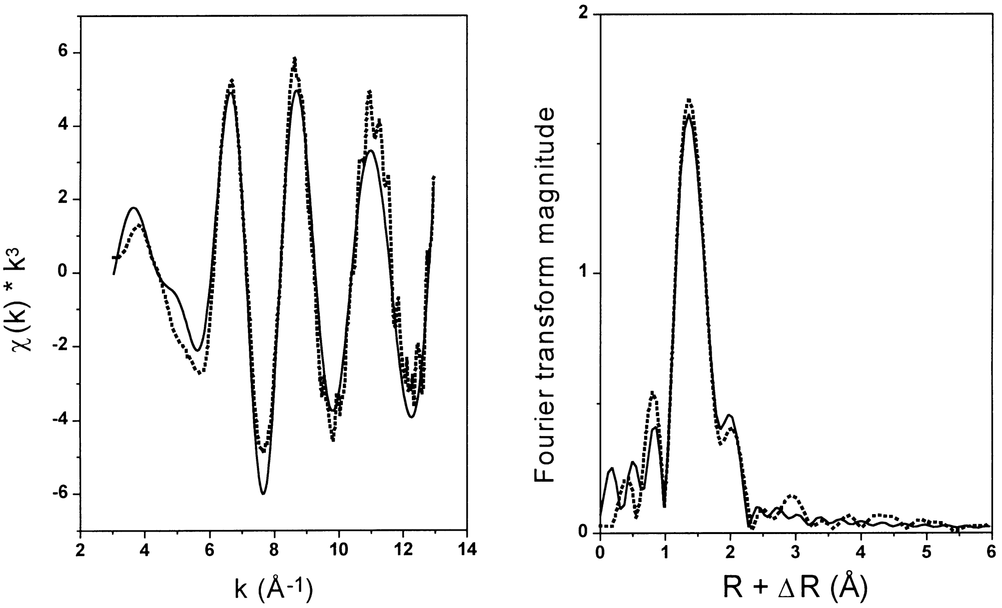
ence in the absorption edge position suggests different electron densities at both complex central atoms.

EXAFS data of ***1***

The Fourier transform of the complex **1** EXAFS data consists of two coordination shells which are well resolved. Figure 5(a) and (b) show the EXAFS data, their Fourier transforms and the corresponding fit data of complex **1**.

The peak at 1.4 Å in the Fourier transform (not corrected for scattering phase-shift) is thought to represent the short-bound oxygen atom, the large peak at 1.9 Å is probably generated by the mixed chlorine/phosphorus coordination shell. Taking this model as a default to fit the data, the EXAFS fit data shown in Table 2 were obtained.

A short-bound oxygen atom is detected at a distance of 1.70 Å as is typical of a rhenium central atom with a formal oxidation state of +5. The second coordination shell was fitted with a backscattering function of the atomic number 16 as the mean number of phosphorus (atomic number 15) and chlorine (atomic number 17), since EXAFS functions for the latter are not expected to be resolvable. As the fit result for this shell, five P/Cl atoms at a mean distance of 2.41 Å were found. The Debye–Weller factor of 0.005 Å^2 suggests a distribution of the backscattering atoms over a distance range within the coordination shell. On the one hand, this may be due to the difference in distance between the chlorine and the phosphorus atoms, on the other, the relatively high coordination number of five may also lead to increased Debye–Weller terms. As described elsewhere [20], the precursor complex **1** may occur in various forms of the general constitution $ReOCl_3(PPh_3)_2$. These conformation isomers are mainly characterized by differences in the PPh_3 ligand conformation and crystal packing patterns (monoclinic and triclinic), which lead to changes in the rhenium–ligand distances. The rhenium–oxygen bond distances as elucidated by XRD analysis are 1.66 Å for one monoclinic (A) and one triclinic isomer (B) and 1.73 Å for the other triclinic monomer (C). EXAFS analysis of the precursor showed a rhenium–oxygen distance of 1.70 Å, which is regarded as a mean value of various isomers, including the triclinic isomer C and one or both other isomers. The EXAFS value of the bond distance of the P/Cl coordination shell also seems to represent a mean value of various isomers, since the mean value of this shell as shown



6. (a) EXAFS data of complex **5**. (b) Fourier transform corresponding to (a).

by XRD analysis was 2.45, 2.40 and 2.44 Å for isomers A, B and C. Hence, an unambiguous assignment of the analyzed isomers is not possible, although the existence of the triclinic isomer C can be assumed. However, the constitutional identity of the precursor could be proven by EXAFS.

EXAFS data of ***5***

Complex **5** exhibits a significantly different radial distribution function around the rhenium central atom. Figure 6(a) and (b) show the EXAFS data and their Fourier transform of complex **5**. Dotted lines represent the experimental data, solid lines the best fit.

A strong Fourier transform amplitude is detected at 1.3 Å (not corrected for scattering phase-shift) suggesting a remarkably changed first coordination shell with respect to the rhenium precursor. A second peak occurs at 2.1 Å, obviously caused by the second coordination shell. Taking the complex structure as elucidated by XRD analysis as a default to fit the data, the results presented in Table 3 were obtained.

Table 3. EXAFS fit results for complex **5**

Shell	N	R^a (Å)	σ^2 (Å^2)
O	2.2(4)	1.74(1)	0.001(1)
P/S	1.8(3)	2.33(1)	0.006(1)

N is the number of coordinating atoms. R: distance to rhenium central atom. σ^2: Debye–Weller factor. Fit mode: Marquardt algorithm using least squares method. Calculated resolution in distance: 0.16 Å. The theoretical resolution in distance is given by the formula $\Delta R = 2\pi/k_{\max}$ [19].ΔE_0: -9 eV.

a Distance to the rhenium central atom.

A substantial increase in the coordination number of the oxygen shell as well as an increase in its mean bond distance to rhenium were observed. This strongly suggests the existence of a dioxo rhenium core. The bond distance is in excellent agreement with the value determined by XRD analysis of the crystalline complex. Considering the second coordination shell, two sulphur backscatterers were used to fit the data and gave results of two backscattering atoms with a mean distance of 2.33 Å. It is noteworthy that the Debye–Weller factor of this coordination shell is increased, probably caused by two distant backscatterers which were fitted within one coordination shell. These two atoms are thought to be a sulphur atom at a distance of around 2.27 Å and a phosphorus backscatterer located at around 2.40 Å. The detected bond length seems likely to represent the mean distance between these two atoms. The results obtained are in good agreement with the values determined by XRD analysis of the complex. However, there is a discrepancy in view of the comparison of the crystal and the solution structure. The nitrogen atom located at 2.28 Å as determined in crystal is not detectable. Attempts to include it in the EXAFS fit gave unreasonable results and thus failed. This problem is obviously caused by the strong dominance of the phosphorus/sulphur shell contribution in the complex EXAFS. The relatively weak backscattering contribution of the amine nitrogen atom at the expected distance of 2.28 Å is therefore not believed to be resolvable. Similar phenomena were observed on other systems [21, 22]. However, it can be stated that the unexpected complex as determined in XRD analysis is also existent in solution and seems therefore to represent a relatively stable coordination.

CONCLUSIONS

The described ligand exchange reaction procedure resulted in **4** and the new complex species **5** with the remarkable configuration of the O-donor atoms and an unexpected bidentate coordination of one mercaptoethylene amine derivative. ^{1}H NMR, FAB/CI mass spectroscopy investigations and the elemental analysis suggest a 1:1:1 ratio of **3**, a triphenylphosphane and a dioxo metal core. The *cis*-arrangement of the dioxo core could be proved by IR investigations. The completely trigonal–bipyramidal structure was elucidated by XRD measurements. The origin of the second short-bound oxygen proved to be water present in the reaction mixture, as shown by ^{18}O labelling studies. Even at 1:1 to 1:3 ratios of the reactants **1**/**3** no formation of further compounds analogous to that shown in Fig. 1 was observed.

Five-fold coordinated compounds of trigonal–bipyramidal O-coordination [23], S, or bis-alkyl coordination [24] and *cis*-configuration of the oxo groups have previously been described mainly for rhenium(VII) compounds. For the oxidation state of +5, however, only the *trans*-configuration has been published, with the exceptions of one P,P,I *cis*-dioxo complex characterized [14] by XRD, as well as two complexes containing bipyridyl compounds and a *cis*-dioxo structure characterized by IR data [13].

XRD and EXAFS studies of **5** showed that the coordination of the *cis*-dioxo compound is nearly identical in the solid and in the soluted state.

The formation of the *cis*-dioxo complex is not specific to the applied amine thiol **3**. Products containing other amino alkyl thiols which were obtained further show almost the same UV-spectra and was characterized by XRD in one special case (part of a further publication).

Regarding the "3 + 1" approach it has to be remarked the reactants should be used strictly in a 1:1:1 ratio in cases of such potentially bidentate ligands. A compensation of the higher reactivity of the tris chelating unit by the use of an excess of the "monodentate" co-ligand **3** is impossible.

EXPERIMENTAL SECTION

Materials and instrumentation

Elemental analyses were performed on a LECO CHNS-932 elemental analyser. Infrared spectra (KBr pellets, in $CHCl_3$) were measured on a Specord M80 or on a Perkin Elmer FT-IR Spectrum 2000. Proton NMR investigations were carried out on a Varian Inova-400 device (solvent $CDCl_3$). Mass spectrometry was done using a Finnigan MAT 95 mass spectrometer. Column chromatography was done using Silica gel 60 (0.04–0.063 mm) from Merck.

Preparation of ligands and the precursor

The *trans*-mono-oxotrichlorobis(triphenylphosphine)rhenium(V) was prepared starting from perrhenate as described in the literature [11].

To prepare the ligands *N*,*N*-bis(2-mercaptoethyl)-*N′*,*N′*-diethylethylenediamine **2** and 1,4-dioxa-8-aza-spiro-*N*-2-mercaptoethylene-[**4**,**5**]-decane **3**, a published procedure was applied [25].

*Preparation of compounds **4** and **5***

The precursor **1** (166.0 mg, 0.2 mmol) was suspended in 20 ml of methanolic sodium acetate solution (0.15 N) by gentle stirring. The ligand **2** (17.9 mg, 0.1 mmol) and the co-ligand **3** (40.7 mg, 0.2 mmol) were dissolved in dichloromethane/methanol and added as a mixture. The resulting suspension was heated at 70°C for 30 min and a change of colour from yellowish green to greenish brown was observed. The reaction mixture was diluted with 10 ml of dichloromethane, washed twice with 10 ml of water and the organic phase was extracted with 10 ml of 0.1 N hydrochloric acid. A dark red organic phase (**5**) and a dark green aqueous phase ("3 + 1" product **4**) were obtained. The organic portion was dried over sodium sulphate, filtered, reduced in volume by evaporation and purified by chromatography over silica gel 60 with trichloromethane as the liquid phase. The eluate was evaporated to dryness and the precipitate dissolved in diethyl ether. After adding a mixture of ether/n-heptane (1:1), dark red, analytically pure crystals were obtained by slow evaporation of the solvents. Yield: 67 mg (*ca.* 49%, referred to **1**); m.p. 172–174°C. - IR(KBr): $\nu = 836$; 907 cm^{-1} (O=Re=O). Mass spectrum: (FAB pos.) *m*/*z* 681(32)/683(78) $[M]^+$; 682(62)/684(100) $[M+H]^+$; ^{1}H NMR($CDCl_3$): δ 3.943 [m, 4H, O–CH_2–CH_2–O (3)], δ 3.366 [m, 2H, N–CH_2–CH$_2$–S (3)], δ 2.700 [m, 2H, S–CH_2–CH$_2$ (3)], δ 2.660; 2.345 [2m, 4H, N–CH_2–CH$_2$ (3)], δ 1.696; 1.528 [2m, 4H, C–CH_2–CH$_2$ (3)].

A quantity of dichloromethane was added to the dark green aqueous phase and the pH was increased to 10 by adding a small volume of sodium hydroxide in order to re-extract compound **4**. The organic portion was dried over sodium sulphate, filtered and reduced in volume by evaporation. Compound **4** was purified by chromatography as described above and eluted by using a mixture of dichloromethane/methanol (19:1). The solvent mixture was removed by allowing to stand overnight and crude green crystals were obtained. Yield: 40 mg (*ca.* 62%, referred to **2**); m.p. 134–136°C. IR(KBr): $\nu = 945$ cm^{-1}

(Re=O). Mass spectrum: (CI neg.) *m*/*z* 637(58)/639(100) $[M]^+$. ^{1}H NMR ($CDCl_3$): δ 3.953 [s, 4H, O–CH_2–CH_2–O (**3**)], δ 2.721 [m, 4H, N–CH_2–CH_2 (*3*)], δ 1.805 [t, 4H, N–CH_2–CH_2–C (**3**)], δ 3.872 [t, 2H, N–CH_2–CH_2–NEt_2 (**2**)], δ 3.626; 3.584; 3.292; 2.971 [m, 8H, N–CH_2–CH_2–S (**2**)], δ 2.860 [t, 2H, N–CH_2–CH_2–NEt_2 (**2**)], δ 2.602 [m, 2H, S–CH_2–CH_2–N (**2**)], δ 2.566 [q, 4H, N–CH_2–CH_3 (**2**)], δ 1.061 [t, 6H, N–CH_2–CH_3 (**2**)].

Preparation of the [^{18}O]*-bearing complex* **5**

The precursor **1** (166.0 mg, 0.20 mmol) was suspended in a mixture of 1 ml of [^{18}O] water and 5 ml dried methanol which contained water-free sodium acetate (0.15 N). After addition of **3** (47.8 mg, 0.24 mmol) dissolved in 0.5 ml of dried methanol the reaction mixture was stirred and refluxed for 30 min. The dark reddish solution obtained was reduced in volume by evaporation to give a final volume of approximately 2 ml. The solution was applied to a silica gel column and purified by eluting with chloroform. The dark reddish chloroformic solution obtained was used for IR measurements.

X-ray crystal structure analysis of **5**

The structure was determined using a single crystal, obtained by slow evaporation of an ether/*n*-heptane solution of **5**. $C_{27}H_{31}N_1O_4P_1S_1Re_1$ ($M = 682.79$). The intensity data for compound **5** were collected on a ENRAF-NONIUS CAD4 diffractometer. The reflections were performed by the ω–2θ scan method, using graphite monochromated CuK_α radiation ($\lambda = 1.5418$ Å) at $T = 296(2)$ K. Triclinic space group P-1 (No. 2), $a = 9.323(3)$ Å, $b = 15.438(3)$ Å, $c = 20.671(3)$ Å, $\alpha = 103.18(3)^\circ$, $\beta = 100.39(3)^\circ$, $\gamma = 105.39(3)^\circ$, $V = 2699.6(11)$ Å^3, $Z = 4$, $D_c = 1.677$ g cm^{-3}, $\mu = 10.355$ mm^{-1}. The number of totally measured reflections was 11077, of which 9947 were considered to be significant and were used for the structure determination. The refinement procedure was carried out by full-matrix least-squares, where the minimized function was $\omega(|F_0| - |F_c|)^2$. Refinement converged at $R = 0.0514$ and $R_w = 0.1521$.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Center. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: +44-1223-336-033; e-mail: teched@chemcrys.cam.ac.uk) (CCDC-No. 100471).

EXAFS measurements of **1** *and* **5**

Rhenium L_{III} edge data were collected in transmission mode using ionization chambers at beamline X1.1 of the HASYLAB synchrotron, Hamburg, Germany. To monochromatize the synchrotron beam, a monochromator system consisting of a Si(211) double-crystal monochromator was used. The DORIS III storage ring was operated at 3 GeV at ring currents between 40 and 70 mA during measurements. Higher harmonics were rejected by detuning the monochromator crystals to 50% of the incident beam intensity. A rhenium(V) complex served as a reference for energy calibration of the monochromator. Three scans were used per sample on average. A check for anomalies was carried out after each scan. Data were energy-calibrated using the first derivative method, where the first inflected point in the reference derivative was set to 10535 eV. Sample absorption edge positions were determined by derivatizing the sample spectra and detecting the first inflected points. Data processing and analysis were performed using the program package EXAFSPAK [26]. The experimental data were analyzed by being fitted with theoretical EXAFS functions generated by the FEFF6.01a program [27]. Since phosphorus, sulphur and chlorine produce very similar backscattering functions, mixed-atom coordination shells consisting of these atoms were fitted with EXAFS functions for sulphur backscatterers. To fit the data, coordination numbers were at first kept constant. When constant values for DE_0 and distances were obtained, coordination numbers were allowed to float.

Acknowledgements—We are grateful to S. Machill of the Technische Universität Dresden for measuring the FAB/CI mass spectra.

REFERENCES

1. Yoshihara, K., Baldas, J., Johannsen, B., Spies, H., Volkert, W., Jurisson, S., Alberto, R., Kryutchkov, S., Omori, T. and Hashimoto, K., *Topics in Current Chemistry*. Springer-Verlag, Berlin/Heidelberg/New York, 1996.
2. Pietzsch, H.-J., Spies, H., Hoffmann, S. and Stach, J., *Inorg. Chim. Acta*, 1989, **161,** 15.
3. Spies, H., Syhre, R. and Pietzsch, H.-J., *Plzen Lek. Sb.*, 1990, **62,** 85.
4. Johannsen, B., Scheunemann, M., Spies, H., Brust, P., Wober, J., Syhre, R. and Pietzsch, H.-J., *Nucl. Med. Biol.*, 1996, **23,** 429–438.
5. Meegalla, S., Plössl, K., Kung, M.-P., Chumpradit, S., Stevenson, C., Frederick, D. and Kung, H. F., *Bioconj. Chem.*, 1996, **7,** 421–429.
6. Mc Donell, A. C. *et al.*, *Aust. J. Chem.*, 1983, **36,** 253.
7. Pietzsch, H.-J., Spies, H. and Hoffmann, S., *Inorg. Chim. Acta*, 1989, **165,** 163.
8. Papadopoulos, M. *et al.*, Private communication (submitted).
9. Spyriounis, D. M., Pelecanou, M., Stassinopoulou, C. I., Raptopoulou, C. P., Terzis, A.

and Chiotellis, E., *Inorg. Chem.*, 1995, **34,** 1077–1082.

10. Papadopoulos, M. S., Pirmettis, I. C., Pelecanou, M., Raptopoulou, C. P., Terzis, A., Stassinopoulou, C. I. and Chiotellis, E., *Inorg. Chem.*, 1996, **25,** 7377–7383.
11. Johnson, N. P., Lock, C. J. and Wilkinson, G., *J. Chem. Soc.* 1964, 1064.
12. Gerber, T. I., Perils, J., Du Perez, J. G. and Bandoli, G., *Acta Cryst. C*, 1997, **53,** 217–219.
13. Ram, M. S. and Hupp, J. T., *Inorg. Chem.*1991, **30**(1), 130–133.
14. Ciani, G. F., D'Alfonso, G., Romiti, G. F., Sironi, A. and Freni, M., *Inorg. Chim. Acta*, 1983, **72,** 29–37.
15. Brodsky, A. E., *Isotopenchemie*. Akademie-Verlag, Berlin, 1961, pp. 291–299.
16. Addison, A. W., Rao, T. N., Reedijk, J., van Run, J. and Verschoor, G. C., *J. Chem. Soc. Dalton Trans.*, 1984, 1349.
17. Bolzati, C., Tisato, F., Refosco, F., Bandoli, G. and Dolmella, A., *Inorg. Chem.*, 1996, **35,** 6221–6229.
18. Fröba, M. and Lochte, K., Metz, W., *J. Phys. Chem. Solids*, 1996, **57,** 635–641.
19. Koningsberger, D. C. and Prins, R. (eds.), *X-ray Absorption Spectroscopy. Principles, Applications, Techniques of EXAFS, SEXAFS and XANES*. John Wiley and Sons, New York, 1988.
20. Lebuis, A.-M. and Beauchamp, A. L., *Can. J. Chem.*, 1993, **71,** 441–449.
21. Chance, M. R., Sagi, I., Wirt, M. D., Frisbie, S. M., Scheuring, E., Chen, E., Bess, J. W., Henderson, L. E., Louis, E. and Arthur, L. O., *Proc. Natl. Acad. Sci. U.S.A.*, 1992, **89,** 10041–10045.
22. Summers, M. F., Henderson, L. E., Chance, M. R., Bess, J. W., Julian, W., South, T. L., Blake, P. R. and Sagi, I., *Protein Sci.*, 1992, **1,** 563–574.
23. Herrmann, W. A., Wojtczak, W. A., Artus, G. R., Kühn, F. E. and Mattner, M. R., *Inorg. Chem.*, 1997, **36,** 465–471.
24. Shiang, Cai, Hoffmann, D. M. and Wierda, D. A., *Inorg. Chem.*, 1989, **28,** 3784–3786.
25. Marabella, C., Enemark, J., Miller, A., Bruce, A., Parayadath, N., Corbin, J. and Stiefel, E., *Inorg. Chem.*, 1983, **22,** 3456.
26. George, G. G. and Pickering, I. J., *EXAFSPAK, A Suite of Computer Programs for Analysis of X-ray Absorption Spectra*. Stanford Synchrotron Radiation Laboratory, Stanford, U.S.A., 1995.
27. Zabinsky, S., Rehr, J., Ankudinov, A., Albers, R. C. and Eller, M. J., *Phys. Rev. B*, 1995, **52,** 2995–3009.