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Note

Five-coordinate rhenium(III)-thiolato complexes: the structure of $[Re(SCH_2PhOCH_3)_3(PPh_3)_2]$

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Abstract

A novel five-coordinate rhenium(III)-thiolato complex, $Re(SCH_2C_6H_4OCH_3\text{-}p)_3(PPh_3)_2$ has been isolated during the reaction of *trans*-$ReOCl_3(PPh_3)_2$ with *p*-methoxybenzyl mercaptan. In the unexpected structure that was acquired, the central metal has undergone a reduction from Re(V) to Re(III). The five-coordinate Re(III) complex has been characterized by spectroscopic methods, elemental analysis and X-ray crystallography. X-ray crystallographic studies showed the coordination geometry around rhenium to be that of a trigonal bipyramid. The basal plane is defined by three sulfur atoms of the monodentate ligand, while the two apical positions are occupied by two phosphines of the precursor. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The coordination chemistry of technetium and rhenium has attracted much attention due to the widespread use of ^{99m}Tc in diagnostic imaging and ^{186}Re and ^{188}Re in radiotherapy [1]. Rhenium is technetium's third row congener, thus exhibiting similar chemical properties to technetium. Minor chemical differences between complexes of these two isotopes can result in different biological behavior. The most pronounced of these is the redox potential of the central metal. Complexes of rhenium are more difficult to reduce than the analogous technetium complexes [2].

As part of our investigations into thiolato complexes of rhenium, we have looked into the side products of different reaction systems involving a variety of thiols as coligands [3–6]. In the course of a systematic study, we reacted *trans*-$ReOCl_3(PPh_3)_2$ with an excess of *p*-methoxybenzyl mercaptan, *p*-$CH_3OC_6H_4CH_2SH$. Surprisingly, we obtained a complex with the unexpected structure $[Re(SCH_2C_6H_4OCH_3\text{-}p)_3(PPh_3)_2]$, where the central rhenium atom had undergone a reduction from Re(V) to Re(III). So far, the acquisition of pentacoordinate Re(III) complexes has been described in the literature only a few times [7,8]. The Re(III) products might be thermodynamically more stable, thus more favorable than the Re(V) products [9].

This report presents the complex $[Re(SCH_2C_6H_4OCH_3\text{-}p)_3(PPh_3)_2]$ as the major reaction product, while among the minor products we can find the pentavalent Re(V) anion $[ReO(SCH_2C_6H_4OCH_3\text{-}p)_4]^-$, where the central metal is surrounded by four thiolato groups.

2. Experimental

2.1. Materials and methods

IR spectra were recorded as KBr pellets in the range 4000–500 cm^{-1} on a Perkin-Elmer 1600 FT-IR spec-

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trophotometer and were referenced to polystyrene. Elemental analyses were performed on a Perkin-Elmer 2400/II automatic analyzer.

All laboratory chemicals were reagent grade. The *p*-methoxybenzyl mercaptan used as coligand was purchased from Fluka. The $ReOCl_3(PPh_3)_2$ precursor was prepared according to literature [10].

2.2. Synthesis of $[Re(SCH_2PhOCH_3\text{-}p)_3(PPh_3)_2]$

2.2.1. Method A

To a stirred suspension of trichlorobis(triphenylphosphine)rhenium(V) oxide, $ReOCl_3(PPh_3)_2$ (166 mg, 0.2 mmol) in methanol (10 ml), 1 M CH_3COONa in methanol was added. 123.2 mg of *p*-methoxybenzyl mercaptan dissolved in dichloromethane (5 ml) were added under stirring. The reactants are in a 1:4 molar ratio, and were heated under reflux for approximately 1 h, after which the solution turned to a dark greenish-brown color. After being cooled to room temperature, water was added and the complex was extracted with CH_2Cl_2. The organic extract was dried over $MgSO_4$, the volume of the solution was reduced to 10 ml and then 2–3 ml of methanol were added. Slow evaporation of the solvents at room temperature afforded the major product of the reaction, $[Re(SCH_2PhOCH_3)_3(PPh_3)_2]$, as brown crystals. Yield 45%. $R_f = 0.80$ (silica gel, 2/1/1 benzene/CH_3CN/$CHCl_3$). *Anal.* Calc. for $C_{60}H_{57}O_3P_2S_3Re$: C, 61.53; H, 4.91; S, 8.20. Found: C, 61.50; H, 4.77; S, 7.76%.

2.2.2. Method B

Potassium perrhenate (19 mg), *p*-methoxybenzyl mercaptan (50 mg) and triphenylphosphine (86.56 mg) were refluxed in methanol, in a 1:5:5 molar ratio. After the addition of excess $SnCl_2$ (38 mg), the solution became a light olive–green color, which eventually became dark brown. The resulting suspension was filtered, in order to eliminate the SnO_2, and consequently allowed to crystallize. Yield 40%.

2.3. X-ray crystallography

The crystals of the complex were of poor quality and the only reason for collecting data was to establish the connectivity of the molecule. A brown crystal (0.10 × 0.10 × 0.60 mm) was mounted in air on a Crystal Logic Dual Goniometer diffractometer using graphite-monochromated Mo radiation. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the range $11 < 2\theta < 23°$ and they appear in Table 1. Intensity data were recorded using a θ–2θ to $2\theta_{max} = 47$ with scan speed 2.2 min^{-1} and scan range $2.4 + \alpha_1\alpha_2$ separation. Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorentz, polarization and absorption corrections were applied using Crystal logic software.

Symmetry equivalent data were averaged with $R_{int} = 0.0568$ to give 3926 independent reflections from a total 4068 collected. The structure was solved with SHELXS-86 [11] and refined by full-matrix least-squares techniques on F^2 with SHELXS-93 [12] using 3926 reflections and refining 288 parameters. All hydrogen atoms of the ligands (except those of the symmetric thiol) were introduced at calculated positions as riding on bonded atoms. All non-hydrogen atoms (except O_2 and C_{38}) were refined anisotropically.

The final values of R_1, wR_2 for observed data are given in Table 1 and for all data they are 0.0940 and 0.1938, respectively. The maximum and minimum residual peaks in the final difference map were 2.595 and 2.771 e $Å^{-3}$ in the vicinity of the heavy metal. The largest shift/e.s.d in the final cycle was 0.147.

3. Results and discussion

trans-$ReOCl_3(PPh_3)_2$ is one of the most versatile precursor compounds in Re(V) chemistry [13]. Mild reduction of monooxo Re(V) species leads to mononuclear Re(III) with removal of terminal oxide. This provides the usual synthetic route to octahedral complexes of Re(III) [14]. A series of *trans*-octahedral Re(III) complexes has recently been reported, which can be useful precursors for the preparation of mixed-ligand complexes [15]. Another series of five-coordinate rhenium(III) has been synthesized, starting from pre-reduced $Re^{III}Cl_3(MeCN)(PPh_3)_2$ by substitution reactions with mixed bidentate and monodentate thiol ligands [7]. All attempts to obtain $Re^{III}P_2S_3$ compounds starting from Re(VII) or Re(V) precursors by reduction/substi-

Table 1
Summary of crystal, intensity collection and refinement data

Empirical formula	$C_{60}H_{57}O_3P_2ReS_3$
Formula weight	1170.46
Temperature	298
Wavelength	Mo Kα 0.71070
Space group	*I*2/*a*
a (Å)	17.88(1)
b (Å)	16.47(1)
c (Å)	18.48(1)
β (°)	102.44(2)
V (°)	5313(1)
Z	4
D_{calc}/D_{meas} (Mg m^{-3})	1.463/1.44
Absorption coefficient *μ* (mm^{-1})	2.510
F(000)	2376
Goodness-of-fit on F^2	1.185
R indices [2747 reflections $I > 2\sigma(I)$]	$R_1 = 0.0659$[a], $wR_2 = 0.1678$[b]

[a] R_1 based on *F* values.

[b] wR_2 based on F^2.

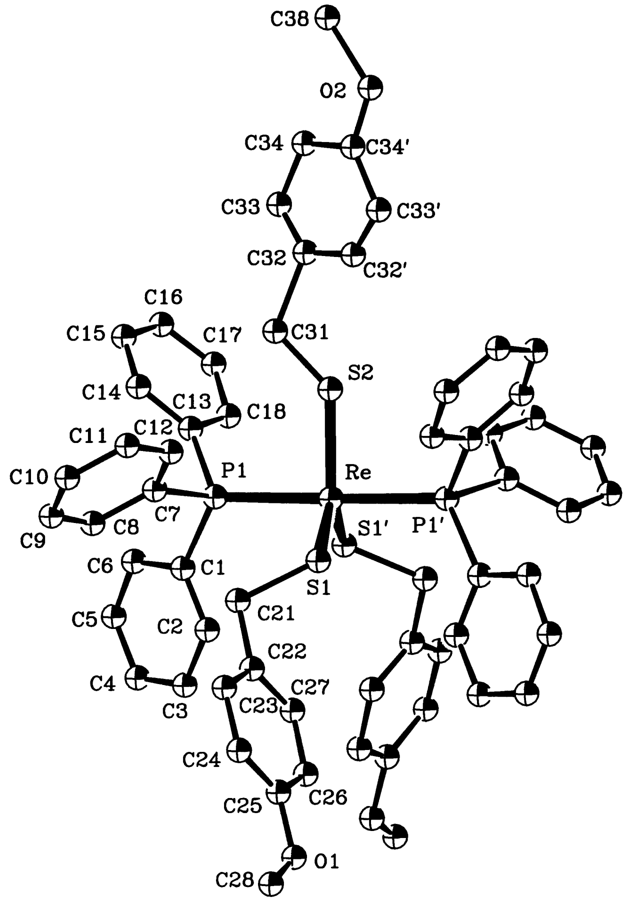

Fig. 1. ORTEP diagram of [Re($SCH_2C_6H_4OCH_3$-*p*)$_3$(PPh_3)$_2$]. Atoms are presented isotropically, labels of some symmetrical atoms and H-atoms have been omitted for clarity.

tution reactions involving the above-mentioned thiol ligands failed. Here we describe the successful synthesis of a trigonal bipyramidal, five-coordinate Re(III) complex, *trans*-Re^{III}($SCH_2C_6H_4OCH_3$-*p*)$_3$(PPh_3)$_2$, along with its crystal structure. The complex resulted from the in situ reduction of *trans*-$Re^VOCl_3(PPh_3)_2$ precursor in the presence of an excess of *p*-methoxybenzyl mercaptan, *p*-$CH_3OC_6H_4CH_2SH$, in a neutral methanolic solution. The same complex was also formed by reacting $KReO_4$, *p*-methoxybenzyl mercaptan and triphenylphosphine in the presence of stannous chloride.

TLC is used to monitor the reaction and check for the existence of other products in the crude reaction mixture. Another product of the above reaction is the anion $[Re^VO(SCH_2PhOCH_3\text{-}p)_4]^-$, which has been isolated as the tetraphenylphosphonium salt [16].

The infrared spectrum of *trans*-Re^{III}($SCH_2C_6H_4$-OCH_3-*p*)$_3$(PPh_3) is free of any IR band in the ν(Re=O) region, suggesting the absence of the Re=O core. The PPh_3 derivatives show a P-sensitive absorption at 1088 cm^{-1}. Furthermore, the peaks found at 1247 and 816 cm^{-1} are indicative of the existence of the methoxybenzyl moiety.

Table 2
Selected bond distances (Å) and angles (°) for **1**

Re–P(1)	2.421(3)
Re–S(1)	2.256(3)
Re–S(2)	2.243(5)
S(2)–Re–S(1)	119.4(1)
S(1)–Re–S(1′)[a]	121.3(2)
S(2)–Re–P(1)	89.6(1)
S(1)–Re–P(1)	83.7(1)
S(1)–Re–P(1′)	96.7(1)
P(1)–Re–P(1′)	179.2(1)

[a] The primed atoms are generated by the symmetry operation: 1/2 − *x*, *y* 1 − *z*.

An ORTEP diagram of the complex is given in Fig. 1 and selected bond distances and angles are listed in Table 2. The coordination sphere around rhenium is comprised of three sulfur atoms of monodentate thiols and two phosphorus atoms of triphenyl phosphines in a trigonal bipyramidal geometry. The three sulfur atoms define the basal plane of the trigonal bipyramid and the two phosphines of the precursor occupy the apical positions. There is a C_2 symmetry axis passing through Re, and atoms S(2) and C(38) of one of the thiol ligands, and as a result, atoms C(31) and O(2) were found disordered and refined with occupation factors fixed at 10.50. The trigonal bipyramidal geometry of rhenium is almost ideal (trigonality index, $\tau = 0.96$), due to the symmetry of the molecule. The bond distances in the coordination sphere are consistent with those found in other complexes [7,8,16]. The angles between the atoms of the basal plane are close to the ideal value of 120° (119.4(1)–121.3(2)°), while P(1)–Re(1)–P(1′) is almost 180° (179.2(1)°).

4. Supplementary material

Tables of crystallographic data, fractional atomic coordinates and anisotropic thermal parameters and a full listing of bond distances and angles are available upon request. A CIF in ASCII format is also available.

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