**Inorganica Chimica Acta**

LETTER

# Lipophilic Technetium Complexes IX. The Reduction of (3-Oxapentane-1,5-dithiolato)-(*p*-carbmethoxybenzenethiolato)oxotechnetium(V) by Tertiary Phosphines

HANS-JUERGEN PIETZSCH, HARTMUT SPIES* and STEFFEN HOFFMANN

*Central Institute of Nuclear Research, Rossendorf, 8051 Dresden, PSF 19 (G.D.R.)*

(Received October 20, 1989)

Recently we described the preparation of a new class of oxotechnetium complexes derived from tridentate/monodentate thiol ligands TcO(SXS)SR, (HSXSH = HS–$CH_2$–$CH_2$–X–$CH_2$–$CH_2$–SH with X = O, S, RSH = monothiols) [1, 2]. A special question of interest is the stability of the oxotechnetium group in this coordination environment towards reducing agents, in particular, tertiary phosphines. Additional impetus for investigating the system TcO(SXS)SR/phosphines comes from the increasing interest in the coordination chemistry of Tc with joint sulfur/phosphorus coordination.

The present paper describes the reduction of complexes of the type TcO(SXS)(SR) by tertiary phosphines and a new complex with thiol/thioether/phosphine coordination synthesized by facile reduction of (3-oxapentane-1,5-dithiolato)(4-carbmethoxybenzenethiolato)oxotechnetium(V) with triphenylphosphine as well as by ligand-exchange reaction on $TcCl_4(PPh_3)_2$.

## Experimental

*Methods*

UV–Vis spectra were recorded on a Specord M 40 from Carl-Zeiss Jena (solvent, chloroform). Infrared spectra were measured on KBr discs on a UR 20 spectrometer and $^1$H NMR spectra on a WH 90 DS Bruker Spectrospin spectrometer (solvent, chloroform). The content of technetium was determined by liquid-scintillation counting.

*Synthesis of (3-Oxapentane-1,5-dithiolato)(p-carbmethoxybenzenethiolato)oxotechnetium(V) (1)*

This was prepared as described in ref. 2. $TcCl_4(PPh_3)_2$ was synthesized according to ref. 3.

*Synthesis of (3-Oxapentane-1,5-dithiolato)(p-carbmethoxybenzenethiolato)(triphenylphosphine)-technetium(III) (2)*

*By reduction with triphenylphosphine*

Compound **1** (42 mg; 100 μmol) and 105 mg (400 μmol) triphenylphosphine were dissolved in 4 ml acetone. After addition of 4 ml acetic acid the mixture was stirred at room temperature for 45 min. The colour of the solution turned from yellow to violet. The volume was reduced to 5 ml, methanol was added until the solution became turbid and the mixture was allowed to stand overnight in the refrigerator. The precipitate formed was dissolved in 2 ml chloroform and, after addition of 1 ml methanol, violet crystals precipitated; yield, 43 mg (65% rel. to compound **1**).

*By ligand exchange reaction*

$TcCl_4(PPh_3)_2$ (50 mg; 65 μmol), 17 mg (98 μmol) HS–$C_6H_4$–$COOCH_3$ (*para*), 9 mg (65 μmol) HS–$CH_2$–$CH_2$–O–$CH_2$–SH and 5 ml ethanol were boiled under reflux for 2 h. $TcCl_4(PPh_3)_2$ dissolved and the colour of the solution turned to violet. The volume of the mixture was reduced to 2 ml; subsequent isolation and purification of the complex followed the procedure as described above. Yield, 17 mg (40% rel. to compound **1**); melting point 199–200 °C.

*Anal.* Calc. for $C_{30}H_{30}O_3S_3PTc$: C, 54.22; H, 4.52; S, 14.45; Tc, 14.9. Found: C, 54.20; H, 4.62; S, 14.91; Tc, 14.5%.

$^1$H NMR ($CDCl_3$): 3.0m (4H) and 3.4m (4H) S–$CH_2$–$CH_2$–O–$CH_2$–$CH_2$–S; 3.9s (3H) $OCH_3$; 7.48–7.84 AA′BB′ (4H) 1,4-subst. $C_6H_4$; 7.4m (15H) $P(C_6H_5)_3$. IR (KBr): 2880–3080 $cm^{-1}$ aliph. CH; 1720 $cm^{-1}$ C=O; 705, 770 $cm^{-1}$ arom. CH; 1105 $cm^{-1}$ $OCH_3$. UV–Vis ($CHCl_3$) ($\lambda_{max}$ (log ε): 578nm (2.7).

## Results and Discussion

TcO(SOS)(S-$C_6H_4$-$COOCH_3$) (**1**) is reduced by triphenylphosphine in acetone/acetic acid (1:1), as indicated by the change of colour of the reaction mixture to deep violet. Figure 1 illustrates the spectrophotometric changes: the wavelength of maximum

*Author to whom correspondence should be addressed.

0020-1693/90/$3.50

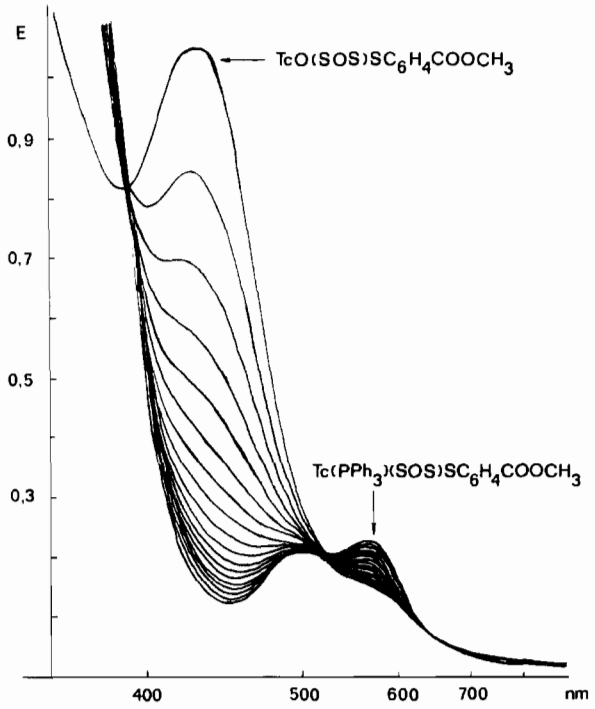


Fig. 1. Sequential scans of the UV–Vis spectrum of $5 \times 10^{-4}$ M complex **1** and $2.5 \times 10^{-3}$ M $PPh_3$ in acetone at ambient temperature (path length 1 cm; approximately 3 min between each scan).

TABLE 1. UV–Vis data of products formed by the reduction of compounds of type **1** with tertiary phosphines (in acetone/acetic acid)

| X in SXS | S–R | $PR_3$ | $\lambda_{max}$ (nm) |
|---|---|---|---|
| O | $S-C_6H_4-COOCH_3$ | $PPh_3$ | 498sh, 566 |
| O | $S-C_4H_9$ | $P(CH_2-CH_2-CN)_3$ | 495sh, 540 |
| S | $S-C_6H_4-OCH_3$ | $PPh_3$ | 495, 557 |
| O | $S-C_6H_5$ | $PBu_3$ | 497, 582 |

absorption shifts from 435 to 578 nm, while isosbestic points are maintained at 384 and 525 nm.

The reaction is not limited to triphenylphosphine. $PMe_2Ph$, $PBu_3$, and $P(CH_2-CH_2-CN)_3$ react with compound **1** in a similar manner, as shown by the UV–Vis data of the reaction products (Table 1). Furthermore, compounds of the type **1** containing mercaptan and thiophenol anions as co-ligands (compounds described in ref. 2) show an analogous change of colour in the presence of tertiary phosphines. The reaction is carried out at a concentration level of about 100 μmol of the Tc precursor in the same solvent as used above, to yield a violet microcrystalline compound (2).

The spectrum of compound **2** is identical to that obtained in the last scan (Fig. 1). Analytical data of this complex correspond to $Tc(SOS)(SR)(PPh_3)$ formed according to

$$TcO(SOS)SR\ (1) \xrightarrow{PPh_3} Tc(SOS)(SR)(PPh_3)\ (2)$$

This formulation is confirmed by spectroscopic data. Figure 2 shows the $^1H$ NMR spectrum of **2**. There are signal groups which can be clearly assigned to the individual ligands. From the integral, it follows that the ligand ratio in the complex is 1:1:1. The IR spectrum shows no Tc=O band, but the C=O vibration is observed at 1730 $cm^{-1}$. The compound is easily soluble in benzene with decreasing solubility in the order: chloroform, ethanol, methanol; it is practically insoluble in water.

Complex **2** is also readily obtained from the precursor $Tc(PPh_3)_2Cl_4$ [3] by treatment with 3-oxapentane-1,5-dithiol/monothiol in a ratio of 1:1:1.5 (Tc-precursor:SXS:S-ligand). However, the latter reaction is much more complicated than the above-described oxygen abstraction reaction, in which the SOS/S coordination stays complete, because the exchange of all chlorine atoms and one phosphine ligand of the precursor by the two different thiol ligands is required. As expected, the yield of compound **2** is lower than that starting

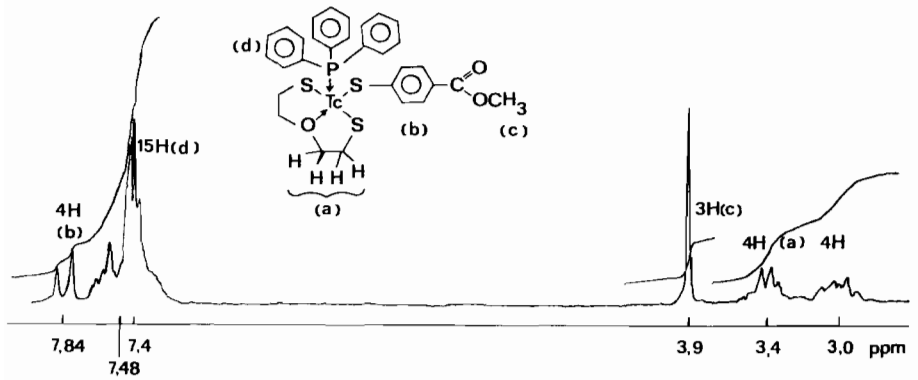


Fig. 2. Room temperature 90 MHz $^1H$ NMR spectrum of **2** (in $CDCl_3$).

from the oxotechnetium(V) complex **1**, and formation of by-products is observed. There is some evidence that compound **2** is also formed as a minor product among other undefined species when pertechnetate reacts with a mixture of the three ligands.

The general ability of tertiary phosphines to reduce oxotechnetium(V) complexes to the corresponding Tc(III) compounds has been shown for Schiff base ligand complexes [4, 5]. Compounds of type **1** show a remarkably facile abstraction of oxygen by triphenylphosphine. This could either be due to the presence of the thioether moiety in the coordination sphere or to the fact that there are less steric requirements in the $SOS/S_1$ ligand set compared to the systems mentioned above. The new complex should be able to adopt a trigonal-bipyramidal geometry, thus minimizing the steric hindrance between the bulky triphenylphosphine and the thiol ligands. Regarding the facility, the reduction of complexes of type **1** is comparable, for example, to the reduction of five-coordinated complexes TcOCl(L) (L = *N*-(2-oxidophenyl)-salicylideneiminate or *N*-(2-sulfidophenyl)salicylideneiminate) by phosphine ligands [6]. However, this reaction gives, in contrast to our results, the unusual corresponding Tc(III) dimer complexes $\mu$-O(Tc(L)$P_2$)$_2$ [6].

## References


1 H.-J. Pietzsch, H. Spies, S. Hoffmann and J. Stach, *Inorg. Chim. Acta, 161* (1989) L15.
2 H.-J. Pietzsch, H. Spies and S. Hoffmann, *Inorg. Chim. Acta, 165* (1989) 163.
3 U. Mazzi, G. de Paoli, P. di Bernardo and L. Magon, *J. Inorg. Nucl. Chem., 38* (1976) 721.
4 A. Duatti, A. Marchi, S. A. Luna, G. Bandoli, U. Mazzi and F. Tisato, *J. Chem. Soc., Dalton Trans.*, (1987) 867.
5 U. Mazzi, F. Refosco, F. Tisato, G. Bandoli and M. Nicolini, *J. Chem. Soc., Dalton Trans.*, (1988) 847.
6 F. Tisato, F. Refosco, U. Mazzi, G. Bandoli and M. Nicolini, *Inorg. Chim. Acta, 157* (1989) 227.