Polyhedron Vol. 11, No. 17, pp. 2151–2155, 1992
Printed in Great Britain

0277–5387/92 $5.00+.00

THE PREPARATION AND ELECTROCHEMISTRY OF TECHNETIUM AND RHENIUM COMPLEXES OF 2-(DIPHENYLPHOSPHINO)BENZENETHIOL. THE CRYSTAL AND MOLECULAR STRUCTURES OF [$Re(2-Ph_2PC_6H_4S)_3$] AND [$Tc(2-Ph_2PC_6H_4S)_3$]

JONATHAN R. DILWORTH,* ANTONY J. HUTSON
and STEPHEN MORTON

Department of Chemistry and Biological Chemistry, University of Essex,
Wivenhoe Park, Colchester, Essex CP4 3SQ, U.K.

and

MARY HARMAN and MICHAEL B. HURSTHOUSE

School of Chemistry and Applied Chemistry, University of Wales, College of Cardiff,
P.O. Box 912, Cardiff CF1 3TB, U.K.

and

JON ZUBIETA

Department of Chemistry, Syracuse University, New York, NY 13244-4100, U.S.A.

and

COLIN M. ARCHER and J. DUNCAN KELLY

Amersham International plc, White Lion Road, Amersham, Bucks HP7 9LL, U.K.

(*Received* 18 *March* 1992; *accepted* 19 *May* 1992)

Abstract—Reaction of a variety of rhenium(III) or (V) precursors with the bidentate (1 −) mixed phosphino-thiol ligand 2-(diphenylphosphino)benzenethiol (DPPBTH) in mildly alkaline methanol leads to the formation of the 16-electron complex [$Re(DPPBT)_3$] (**I**). With technetium [$Tc(DPPBT)_3$] (**II**), [$TcOCl(DPPBT)_2$] (**III**) or [$TcN(DPPBT)_2$] (**IV**) may be obtained depending on the conditions and starting material. The X-ray crystal and molecular structures of **I** and **II** show very similar distortions from ideal geometry due to *intra*ligand interactions. The complexes have been further studied by cyclic voltammetry and UV–vis spectroscopy.

The coordination chemistry of mono- and polydentate thiols with both nitrogen and sulphide co-donor atoms has been thoroughly investigated.[1-10] There are many examples of complexes containing both thiolate and tertiary phosphine donor sets, however, chelating ligands containing both phosphorus and sulphur as the donor atoms have not been studied to any great extent.[11-14]

The coordination chemistry of the mixed thiol-phosphine aliphatic ligands $Ph_2PCH_2CH_2SH$[15] and $PhP(CH_2CH_2SH)_2$[16] has been investigated to a comparatively limited extent.[17,18] More recently the aromatic mixed thiol-phosphine ligands [$P(C_6H_4SH)_3$], [$PhP(C_6H_4SH)_2$] and [$Ph_2P(C_6H_4SH)$] have

---

* Author to whom correspondence should be addressed.

Abbreviations: [$Re(2-Ph_2PC_6H_4S)_3$] = tris-[2-(diphenylphosphino)benzenethiolate]rhenium(III). [$Tc(2-Ph_2PC_6H_4S)_3$] = tris-[2-(diphenylphosphino)benzenethiolato]technetium(III).

been reported,[19–22] together with a limited amount of their coordination chemistry. Within group VIII the complexes $[ReOCl\{2\text{-}Ph_2PC_2H_4S\}_2]$[17] and $[Tc(MeCN)(PPh_3)\{P(C_6H_4S)_3\}]$ and some derivatives of the latter have been described.[30] We report here on the coordination chemistry of rhenium and technetium with the mixed phosphine-thiol bidentate ligand $2\text{-}Ph_2PC_6H_4SH$ (DPPBTH).

RESULTS AND DISCUSSION

Synthesis of the neutral rhenium(III) complex $[Re(DPPBT)_3]$ (**I**) can be achieved by several synthetic routes. Reaction of the rhenium(III) precursors $[ReBr_2(N_2COPh)(PPh_3)_2]$ and $[ReCl_3(MeCN)(PPh_3)_2]$ with DPPBTH methanol under reflux in the presence of base leads to the formation of $[Re(DPPBT)_3]$ (**I**) in fair to good yield, irrespective of the quantity of ligand used. Reaction of the rhenium(V) precursors $[ReOCl_3(PPh_3)_2]$ and $[Bu^n{}_4N][ReOCl_4]$ under the same conditions also gives **I**. This is in contrast with the behaviour of the analogous aliphatic mixed phosphine-thiol $Ph_2PCH_2CH_2SH$.[17] Reaction of this ligand with $[Re(OCl_3(PPh_3)_2]$ leads to the formation of $[ReOCl(Ph_2PCH_2CH_2S)_2]$. Here the presence of the apparently more reducing phosphine and aromatic thiol donor set leads to the further reduction of rhenium(V) to rhenium(III).

By contrast, whereas reaction of $[TcCl_4(PPh_3)_2]$ with an excess of DPPBTH in ethanol leads to a high yield of $[Tc(DPPBT)_3]$ (**II**), use of only three equivalents of HDPPBT gives a mixture of **II** and a second technetium containing species, as shown by HPLC (β detection). These two species could not be separated by recrystallization, but if $[Bu^n{}_4N][TcOCl_4]$ in dichloromethane is treated with exactly two equivalents of HDPPBT at −80°C the new species $[TcOCl(DPPBT)_2]$ (**III**) is obtained in high yield, and shows no tendency to disproportionate. Addition of methanol to a dichloromethane solution of **III** results in the bleaching of the initially purple solution to a pale straw colour, presumably due to ionization of the chloride ion in the more polar solvent, but after a few minutes unchanged purple **III** precipitates. It did not prove possible to isolate $[TcO(DPPBT)_2]^+$ by addition of a suitable large counter-ion. Reaction of $[TcNBr_2(PPh_3)_2]$ with HDPPBT results in the formation of $[TcN(DPPBT)_2]$ in high yield.

The crystal structures of I *and* II

The complexes **I** and **II** are isostructural and show great similarities in their structures. A view of **II** is shown in Fig. 1, and important bond lengths and angles are given in Table 1. In each case the structure is $[M\,mer\text{-}P_3mer\text{-}S_3]$, with one ligand showing very significantly longer M—P and M—S bonds than the other two. At first it was believed that this might be due to the correct formulation

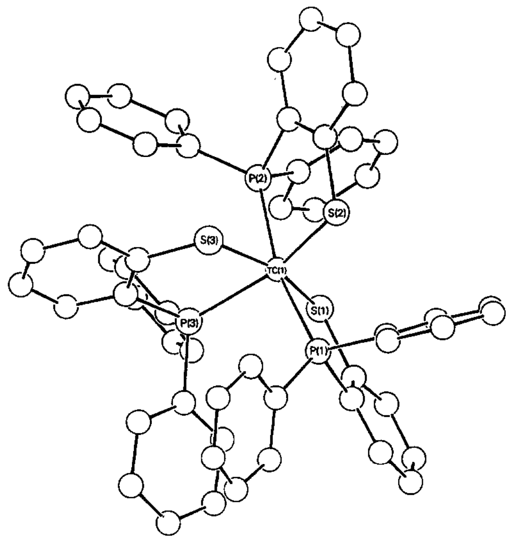

Fig. 1. A graphical representation of the structure of complex **II**, with a partial atom labelling scheme.

Table 1. Important bond lengths and angles for **I** and **II**

(i) Bond lengths		
M =	Re	Tc
M—S(1)	2.269(5)	2.256(2)
M—S(2)	2.303(5)	2.293(2)
M—S(3)	2.477(5)	2.486(3)
M—P(1)	2.391(5)	2.399(2)
M—P(2)	2.411(5)	2.423(2)
M—P(3)	2.473(5)	2.472(2)
(ii) Bond angles		
M =	Re	Tc
S(1)—M—S(2)	113.0(2)	114.25(9)
S(1)—M—S(3)	166.4(1)	165.70(9)
S(1)—M—P(1)	84.3(2)	84.43(9)
S(1)—M—P(2)	91.7(2)	91.84(9)
S(1)—M—P(3)	87.4(2)	86.85(9)
S(2)—M—S(3)	80.6(2)	80.05(8)
S(2)—M—P(1)	86.0(2)	86.03(8)
S(2)—M—P(2)	83.9(2)	83.92(8)
S(2)—M—P(3)	159.6(1)	158.89(9)
S(3)—M—P(1)	96.4(2)	96.55(8)
S(3)—M—P(2)	90.4(2)	90.20(9)
S(3)—M—P(2)	79.0(2)	78.85(8)
P(1)—M—P(2)	166.7(1)	166.75(8)
P(1)—M—P(3)	96.0(2)	95.94(8)
P(2)—M—P(3)	96.5(2)	96.55(8)

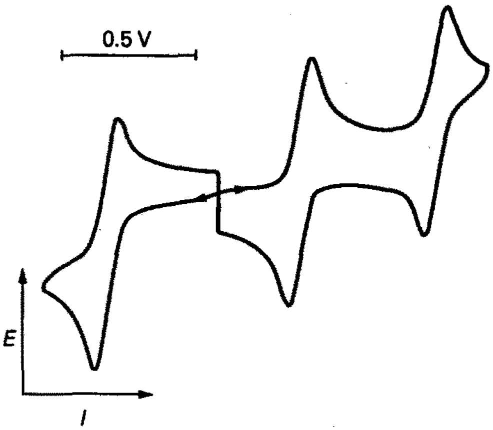

Fig. 2. The cyclic voltammogram of complex **II** in dichloromethane at a platinum working and auxilliary electrode, silver wire pseudo-reference electrode, with a [$Bu^n{}_4N$][BF_4] support electrolyte, showing the three reversible redox processes.

being [M$(DPPBT)_2$(HDPPBT)], however, FAB-mass spectral, electrochemical and other chemical data make this seem very unlikely. In addition, there is no evidence for ν(SH) in the IR spectra of either complex, and **I** is EPR silent and diamagnetic in solution as evidenced from the NMR spectra, nor do the complexes show any sign of deprotonation on reaction with strong base. A number of close *intra*ligand contacts in the crystal structure suggest that steric crowding is responsible for the differences in bond length, and each PS ligand is in a distinct environment and therefore subject to different steric repulsions.

Electrochemistry

Both **I** and **II** show two reversible oxidations and one reversible reduction by cyclic voltammetry in dichloromethane at a platinum electrode (Fig. 2). All three processes conformed to the conventional criteria for Nernstian diffusion-controlled, one-electron, reversible electron transfers. As would be expected the rhenium complex is slightly harder to reduce than its technetium analogue (see Table 2). The variety of oxidation states available to rhenium or technetium in this ligand environment (from M^{II} to M^{V}) is indicative of the ability of the phosphinothiolate ligand to delocalize electron density in an analogous manner to dithiolenes.

Complex **III** shows no oxidation processes from 0 to +1 V in dichloromethane, but reduces irreversibly at *ca* −0.7 V at room temperature. At −80°C this reduction becomes reversible (Table 2). The irreversibility at room temperature is possibly due to the loss of chloride ions from the reduced species. The nitrido-complex **IV** is rather surprisingly electrochemically inactive over the range ±1.5 V.

EXPERIMENTAL

WARNING! Technetium-99 is a weak β emitter and should be handled in a properly equipped radiochemical laboratory.

All manipulations were carried out under an inert atmosphere of dry dinitrogen gas. Standard Schlenk tube–vacuum line and syringe techniques were utilized throughout where appropriate. Elemental analyses were performed by Medac Ltd, University of Brunel, U.K., for the rhenium compounds, or by Butterworth Laboratories Ltd, Teddington, U.K., for technetium samples. FAB-mass spectra were performed by the SERC Mass Spectrometry Service Centre at the University College of Swansea, U.K., for rhenium samples or Amersham International plc, Cardiff, U.K., for technetium samples. ^{1}H and ^{31}P NMR were measured using an EX270 Jeol (270

Table 2. Electrochemical data for **I**, **II** and **III**[a]

Complex	Couple	$E_p{}^a$ (V)	$E_p{}^c$ (V)	ΔE_p
[Re$(DPPBT)_3$]	M^{III}–M^{II}	−0.990	−1.059	0.069
	M^{III}–M^{IV}	+0.229	+0.172	0.057
	M^{IV}–M^{V}	+1.013	+0.938	0.075
[Tc$(DPPBT)_3$]	M^{III}–M^{II}	−0.581	−0.694	0.113
	M^{III}–M^{IV}	+0.506	+0.408	0.098
	M^{IV}–M^{V}	+1.266	+1.161	0.105
[TcOCl$(DPPBT)_2$][b]	M^{V}–M^{IV}	−0.497	−0.682	0.185

[a] In 0.2 M [$NBu^n{}_4$][BF_4] in dichloromethane.
[b] At −80°C.

MHz) NMR spectrometer in $CDCl_3$ solutions. UV–vis data were recorded on a Phillips PU8730 UV–vis spectrophotometer in the range 190–630 nm using dichloromethane solutions in quartz cells. Methanol was dried by the standard method and distilled under dinitrogen before use.[23] Cyclic voltammetry measurements were made on an EG and G PAR model 362 scanning potentiostat, using the "Condecon" family of programs and an IBM PCII computer for evaluation. Dichloromethane was used as an electrochemical solvent because the compounds failed to dissolve in other solvents. A three-electrode cell configuration was used, with a platinum wire working electrode, platinum wire secondary electrode and a silver wire reference electrode. Potentials are quoted relative to the ferrocene/ferrocenium couple (+0.54 V vs SCE electrode in THF at a platinum electrode).

$[ReOCl_3(PPh_3)_2]$,[24] $[Bu^n{}_4N][ReOCl_4]$,[25] $[ReCl_3(MeCN)(PPh_3)_2]$,[26] $[ReBr_2(N_2COPh)(PPh_3)_2$,[27] $[TcCl_4(PPh_3)_2]$[28] and $[TcNBr_2(PPh_3)_2]$[29] were prepared according to the literature methods. The ligand DPPBTH[19] was also synthesized according to the literature method.

X-ray structure analysis

Crystals of **I** were grown from dichloromethane/methanol, those of **II** from dichloromethane/isopropanol.

The structure of **I** was determined on an Enraf–Nonius CAD4 diffractometer using Mo-K_α radiation, and solved by the Patterson method. 6729 reflections with $I \geqslant 4\sigma(I)$ were used in a full-matrix least-squares refinement. Crystal data: $C_{54}H_{42}P_3ReS_3$, monoclinic, space group $P2_1/n$, $a = 10.43(2)$, $b = 17.29(1)$, $c = 26.02(1)$ Å, $\beta = 100.94(2)°$, $Z = 4$, $V = 4602.65$ Å^3, $D_{calc} = 1.54$ g cm^{-3}, $F(000) = 2136$, final $R = 0.048$, $R_w = 0.068$.

The structure of **II** was determined using a Rigaku AFC5S diffractometer using Mo-K_α radiation and solved by the Patterson method and full-matrix least-squares refinement using 3915 reflections with $I \geqslant 3\sigma(I)$. $C_{54}H_{42}P_3S_3Tc$, monoclinic, space group $P2_1/n$, $a = 10.415(2)$, $b = 17.302(3)$, $c = 26.042(4)$ Å, $\beta = 100.91(1)°$, $Z = 4$, $D_{calc} = 1.44$ g cm^{-3}, $F(000) = 2008$, final $R = 0.054$, $R_w = 0.063$.

Tris{2-diphenylphosphinobenzenethiolato}-rhenium(III), [Re(DPPBT)$_3$]

(a) To a suspension of $[ReOCl_3(PPh_3)_2]$ (0.1 g, 0.12 mmol) in methanol (25 cm^3) was added DPPBTH (0.11 g, 0.36 mmol) and triethylamine (0.7 cm^3). The solution was heated to reflux for 30 min to give a dark burgundy precipitate. This was filtered and washed with diethylether and ethanol and dried *in vacuo*. Yield, 0.08 g (63%). Found: C, 60.4; H, 3.8. Calc. for $C_{54}H_{42}P_3S_3Re$: C, 60.8; H, 4.0%.

(b) As above using $[ReBr_2(N_2COPh)(PPh_3)_2]$ (0.1 g, 0.1 mmol) and DPPBTH (0.09 g, 0.3 mmol). Yield, 0.07 g (66%). Found: C, 60.6; H, 3.9. Calc. for $C_{54}H_{42}P_3S_3Re$: C, 60.8; H, 4.0%.

(c) As above using $[ReCl_3(MeCN)(PPh_3)_2]$ (0.1 g, 0.17 mmol) and DPPBTH (0.15 g, 0.5 mmol). Yield, 0.07 g (66%). Found: C, 60.4; H, 3.9. Calc. for $C_{54}H_{42}P_3S_3Re$: C, 60.8; H, 4.0%.

(d) As above using $[Bu^n{}_4N][ReOCl_4]$ (0.1 g, 0.16 mmol) and DPPBTH (0.14 g, 0.48 mmol). Yield, 0.12 g (70%). Found: C, 60.8; H, 3.9. Calc. for $C_{54}H_{42}P_3S_3Re$: C, 60.8; H, 4.0%.

The compound showed the expected mass ion (1066) and isotope distribution in the FAB-mass spectrum. The UV–vis spectrum showed peaks at $\lambda_{max} = 323$ and 534 nm.

Tris{2-diphenylphosphinobenzenethiolato}-technetium(III), [Tc(DPPBT)$_3$]

A suspension of $[TcCl_4(PPh_3)_2]$ (0.142 g, 0.186 mmol) and HDPPBTH (0.204 g, 0.693 mmol) in ethanol (10 cm^3) was refluxed for 2 h. The very dark, blue–green product was removed by filtration and recrystallized from dichloromethane/isopropanol, washed with ether and dried. Yield, 0.157 g (86%). Found: C, 65.7; H, 4.7. Calc. for $C_{54}H_{42}P_3S_2Tc$: C, 66.2; H, 4.3%. The FAB–mass spectrum showed the expected mass ion (979). The UV–vis spectrum showed a strong absorption at 600 nm with a much weaker band at 420 nm.

Oxochlorobis{2-diphenylphosphinobenzenethiolato}-technetium(V), [TcOCl(DPPBT)$_2$]

A solution of $[Bu^n{}_4N][TcOCl_4]$ (0.100 g, 0.200 mmol) in dichloromethane was cooled in a dry-ice/acetone bath and HDPPBT (0.106 g, 0.361 mmol) in dichloromethane was added. After stirring for a few minutes the solution was allowed to warm to room temperature, and was then evaporated to dryness. The purple product was triturated with methanol, and recrystallized from dichloromethane/diethylether. Yield, 0.059 g (40%). Found: C, 58.2; H, 4.1; Cl, 4.3. Calc. for $C_{36}H_{28}ClOP_2S_2Tc$: C, 58.7; H, 3.8; Cl, 4.8%. The product gave a very strong Tc=O stretch at 940 cm^{-1} and had a broad visible absorption at 550 nm in dichloromethane.

Nitridobis{*2-diphenylphosphinobenzene-thiolato*}*technetium*(V), [TcN(DPPBT)$_2$]

A suspension of [$TcNBr_2(PPh_3)_2$] (0.080 g, 0.100 mmol) and HDPPBT (0.088 g, 0.299 mmol) in acetone was refluxed for 0.5 h to give a yellow solid in a pale green solution. The bright yellow product was recrystallized from dichloromethane/heptane. Yield, 0.041 g (59%). Found: C, 60.9; H, 4.1; N, 2.0. Calc. for $C_{36}H_{28}NP_2S_2Tc$: C, 61.8; H, 4.0; N, 2.0%. A medium intensity Tc≡N stretch was observed at 1070 cm^{-1}.

Acknowledgements—We would like to thank Dr D. J. Lowe at the University of Sussex for obtaining the EPR spectra, Dr J. A. Ballantine at the University College of Swansea for the mass spectra results and Dr J. R. Miller, University of Essex, for the mass spectra Isotope Splitting Pattern computer programme. Two of us (AJH and SM) would like to thank the SERC for the funding. We gratefully acknowledge the Herman Stark Company, Germany, for their gift of rhenium metal, and Amersham International plc, U.K., for the supply of ammonium pertechnetate.

REFERENCES

1. P. J. Blower and J. R. Dilworth, *Coord. Chem. Rev.* 1987, **76**, 121.
2. D. Sellman, M. Geck, F. Knoch, G. Ritter and J. Dengler, *J. Am. Chem. Soc.* 1991, **113**, 1819.
3. D. Sellman, P. Lechner, F. Knoch and M. Moll, *Angew. Chem., Int. Edn Engl.* 1991, **30**, 552.
4. D. Sellman and I. Barth, *Z. Anorg. Allg. Chem.* 1989, **557**, 234.
5. D. Sellman, G. Binker, M. Moll and E. Herdtweck, *J. Organomet. Chem.* 1987, **327**, 403.
6. D. Sellman and O. Kaeppler, *Z. Naturforsch. B. Chem. Sci.* 1987, **42**, 1291.
7. D. Sellman, U. Reineke, G. Huttner and L. Zsolani, *J. Organomet. Chem.* 1986, **310**, 83.
8. D. Sellman, G. Binker, M. Moll and C. E. Campana, *Inorg. Chim. Acta* 1987, **130**, 221.
9. A. E. Ogilvy and T. B. Rauchfuss, *Organometallics* 1988, **7**, 1884.
10. D. Sellman and E. Boehlen, *Z. Naturforsch. B.* 1982, **37b**, 1026.
11. V. K. Issleib and W. Gans, *Z. Anorg. Allg. Chem.* 1982, **491**, 163.
12. V. K. Issleib and D. Wienbeck, *Z. Anorg. Allg. Chem.* 1978, **440**, 5.
13. M. Savignac, P. Cadiot and F. Mathey, *Inorg. Chim. Acta* 1980, L43.
14. V. K. Issleib and W. Gans, *Z. Anorg. Allg. Chem.* 1981, **475**, 116.
15. J. Chatt, J. R. Dilworth, J. A. Schmutz and J. A. Zubieta, *J. Chem. Soc., Dalton Trans.* 1979, 1595.
16. J. R. Geigy, F.P. 1,401,930/1965.
17. P. J. Blower, J. R. Dilworth, G. J. Leigh, B. D. Neaves, F. B. Normanton, J. Hutchinson and J. A. Zubieta, *J. Chem. Soc., Dalton Trans.* 1985, 2647.
18. D. W. Stephen, *Inorg. Chem.* 1984, **23**, 2207.
19. E. Block, G. Ofori-Okai and J. A. Zubieta, *J. Am. Chem. Soc.* 1989, **111**, 2327.
20. D. F. Garret, K. L. Cynthia and J. C. Marton, *J. Am. Chem. Soc.* 1989, **111**, 654.
21. E. Block, V. Eswarakrishnan, M. Gernon, G. Ofori-Okai, C. Saha, K. Tang and J. A. Zubieta, *J. Am. Chem. Soc.* 1989, **111**, 658.
22. J. R. Dilworth, Y. Zheng, S. Lu and Q. Wu, *J. Chem. Soc., Dalton Trans.* 1992, 1757.
23. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, 3rd edn, p. 217. Pergamon Press, London (1988).
24. N. P. Johnson, C. J. L. Lock and G. Wilkinson, *J. Chem. Soc.* 1964, 1054.
25. J. R. Dilworth, W. Hussain, A. J. Hutson, C. J. Jones and F. S. McQuillan, *Inorg. Synth.* 15-31-5.
26. G. Rouschias, *Chem. Rev.* 1974, **74**, 531.
27. J. Chatt, J. R. Dilworth, G. J. Leigh and R. J. Paske, in *Progress in Coordination Chemistry* (Edited by M. Cais), p. 246. Elsevier, Amsterdam (1968).
28. J. E. Fergusson and J. H. Hickford, *J. Inorg. Nucl. Chem.* 1966, **28**, 2293.
29. U. Abram, B. Lorenz, L. Kaden and D. Scheller, *Polyhedron* 1988, **4**, 285.
30. N. de Vries, A. Davison and A. G. Jones, *Inorg. Chim. Acta* 1989, **165**, 9.