The Chemistry of Heteroallyl Derivatives of Technetium. Reactivity of $[TcNCl_2(PPh_3)_2]$ and $[Tc(CO)_3Cl(PPh_3)]$ with Thiazetidine Ligands, Crystal Structures of $[Tc(CO)_2(PPh_3)_2\{PhN{=}C(OEt)S\}]$ and $[TcN(Cl)(PPh_3)\{PhN{=}C(OEt)S\}]$†

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The complex $[Tc(CO)_3Cl(PPh_3)]$ reacts with the sodium salt of PhNC(OEt)SH to give the thiazetidine complex $[Tc(CO)_2(PPh_3)_2\{PhN{=}C(OEt)S\}]$ (**1**). The complex $[TcNCl_2(PPh_3)_2]$ reacts with an excess of the neutral ligand to give $[TcN(Cl)(PPh_3)\{PhN{=}C(OEt)S\}]$ (**2**). When the reaction is carried out in presence of the ligand salt the disubstituted complex $[TcN\{PhN{=}C(OEt)S\}_2]$ (**3**) is obtained. The crystal structures of (**1**) and (**2**) were determined by *X*-ray crystallography and refined to conventional *R* factors of 0.0295 and 0.0649 respectively. Compound (**1**) is monoclinic, space group $P2_1$, with a = 12.825(5), b = 16.713(5), c = 9.480(5) Å, β = 94.29(3)°, and Z = 2. The technetium environment is distorted octahedral. Selected bond distances are: Tc–P(1) 2.423(1) Å, Tc–P(2) 2.456(1), Tc–S 2.529(1), Tc–N 2.228(5), and Tc–C 1.89(1) Å (mean). Compound (**2**) is triclinic, space group $P\bar{1}$, with a = 9.428(5), b = 10.237(5), c = 15.603(5) Å, α = 89.29(3), β = 102.74(3), γ = 115.61(3)°, and Z = 2. The environment of Tc is distorted square pyramidal with the nidrido N atom as apex. Selected bond distances are: Tc–N (nitrido) 1.615(7), Tc–N (ligand) 2.135(7), Tc–S 2.375(3), Tc–Cl 2.366(2), and Tc–P 2.429(2) Å.

The chemistry of technetium is an active research area, with emphasis on the production of new compounds for use in diagnostic nuclear medicine. Recently rhenium chemistry has also been investigated with regard to the potential use of its radioactive isotope, ^{186}Re, in nuclear medicine.[1] The chemistries of Tc and Re are quite similar due to their relative positions in the Periodic Table and the lanthanide contraction, even if they show salient differences in redox behaviour.

We have previously reported the synthesis and characterization by *X*-ray diffraction of rhenium(I) and technetium(I) complexes with π-acceptor pseudoallyl ligands.[2] The present paper reports the synthesis of pseudoallyl (S,N) metal-bonded complexes of Tc^I and Tc^V containing the $[Tc{\equiv}N]^{2+}$ core. Recently thiazetidine rhenium compounds with the metal in oxidation states I and V have been published by us.[3] These derivatives were obtained by using the preformed ligand or by insertion reactions of the heteroallene RNCS molecule.

Results and Discussion

The reaction of $[Tc(CO)_3Cl(PPh_3)]$ in tetrahydrofuran (thf) solution with the ligand PhNC(OEt)SH in the deprotonated form gives rise to the thiazetidine technetium(I) complex $[Tc(CO)_2(PPh_3)_2\{PhN{=}C(OEt)S\}]$ (**1**). A toluene solution of $[TcNCl_2(PPh_3)_2]$ reacts with an excess of the ligand at reflux to give orange crystals of the thiazetidine complex $[TcN(Cl)(PPh_3)\{PhN{=}C(OEt)S\}]$ (**2**). No reaction is observed when the starting technetium compound is $[TcNCl_4]^-$. However the addition of free PPh_3 to the reaction mixture gives the product (**2**). The disubstituted complex $[TcN\{PhN{=}C(OEt)S\}_2]$ (**3**) is obtained when the reaction is carried out in thf and in the presence of the ligand salt.

The characterization of the complexes was achieved by elemental analysis, i.r. and ^{1}H n.m.r. spectra (see Experimental section). For the technetium(I) complex (**1**) the i.r. spectrum shows the phosphine band at 1 090 cm^{-1} and two strong bands at 1 930 and 1 860 cm^{-1} as expected for two *cis* terminal carbonyl groups. These values are closely related to those of the corresponding technetium(I) and rhenium(I) pseudoallyl complexes.[2] The C=N vibration of the co-ordinated thiazetidine moiety is found at 1505 cm^{-1}; the occurrence of a band in this region is usually considered as evidence of partial double-bond character of the C–N group.[4] No significant bands are observed in the ν(CS) region (1 000—900 cm^{-1}), while a band of medium intensity, at 1 220 cm^{-1}, seems to be related to the ethoxo group of the ligand. For the technetium(V) complex (**2**) no changes in the absorption bands of PPh_3 and Tc≡N stretching vibrations were observed with respect to $[TcNCl_2(PPh_3)_2]$ (1 090 and 1 100 cm^{-1}). For the disubstituted complex (**3**) only the band at 1 100 cm^{-1} due to the Tc≡N group is present. There is an increase in the values [ν(CN) *ca.* 1 535; ν(C–O–C) *ca.* 1 260 cm^{-1}] with respect to those of the corresponding technetium(I) complex. The proton n.m.r. spectra show the expected signals due to the ethoxo group, and moreover the chemical shift values for the technetium(V) complexes are present at lower field than those of the technetium(I) compound. This behaviour can be explained by a higher electron-accepting capacity of the metal

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† Dicarbonyl [*O*-ethyl (phenylimino)thiocarbonato-*NS*]bis(triphenylphosphine)technetium(I) and chloro [*O*-ethyl (phenylimino)thiocarbonato-*NS*]nitrido(triphenylphosphine)technetium(V).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

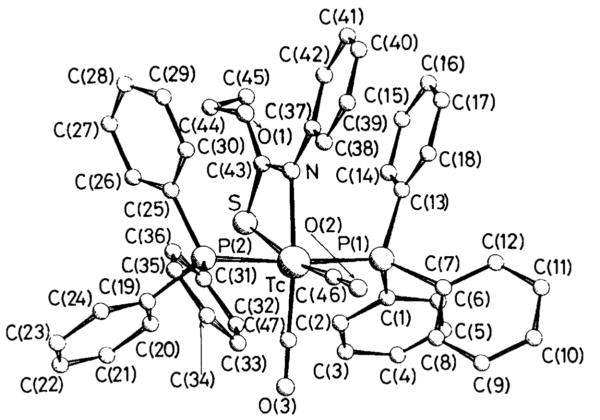

Figure 1. The molecular structure and atomic labelling for $[Tc(CO)_2(PPh_3)_2\{PhN{=}C(OEt)S\}]$ (**1**)

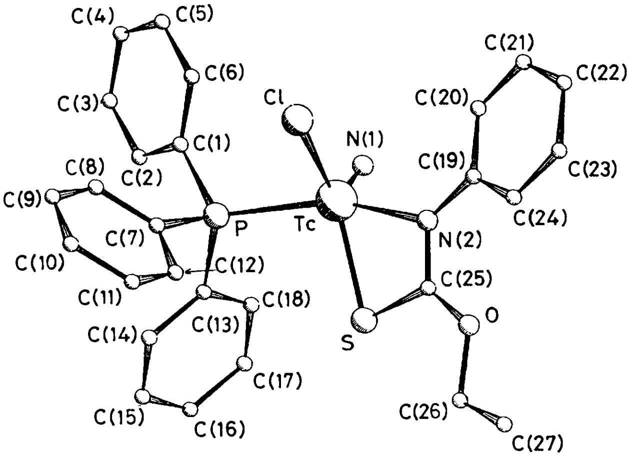

Figure 2. The molecular structure and atomic labelling for $[TcN(Cl)(PPh_3)\{PhN{=}C(OEt)S\}]$ (**2**)

in the higher oxidation state, as also observed for analogous rhenium compounds.[3]

Structural studies were carried out on the complexes $[Tc(CO)_2(PPh_3)_2\{Ph{=}NC(OEt)S\}]$ (**1**) and $[TcN(Cl)(PPh_3)\{PhN{=}C(OEt)S\}]$ (**2**) (see Figures 1 and 2). The technetium atom of (**1**) has a six-co-ordinate distorted octahedral geometry, while the technetium atom in (**2**) has a distorted square pyramidal geometry with the nitrido N atom as apex. The chemistry of the $Tc^V{\equiv}N$ is characterized by the formation of square-pyramidal complexes having an apical technetium-nitrido multiple bond. The $Tc{\equiv}N$ bond distance of 1.615(7) Å in compound (**2**) is consistent with $Tc{\equiv}N$ and $Re{\equiv}N$ distances found in all complexes presently known:[2,5–10] 1.611(3) Å in $[TcN(C_{27}H_{23}N_2OPS_2)]$ and 1.613(3) Å in $[TcN(C_{10}H_{18}N_4S_3)]$,[2] 1.604(6) Å in $[TcN(S_2CNEt_2)_2]$,[9] 1.623(4) Å in $[TcN(C_9H_6NS)_2]$,[5] 1.629(4) Å in $[TcN(NCS)_2(MeCN)(PPh_3)_2]$,[10] as well with 1.602(9) Å in $[ReNCl_2(PPh_3)_2]$,[11] and 1.660(8) and 1.614(13) Å in the octahedral complexes $[ReNCl_2(PPhMe_2)_3]$[12] and $K_2[OsNCl_5]$.[13] Among all these structures only that of $[TcN(NCS)_2(MeCN)(PPh_3)_2]$ shows the Tc atom in a distorted octahedral co-ordination,[10] the others being square-pyramidal. Very recently we have investigated an homogeneous class of technetium(v) nitrido complexes with chelating amines, $[TcN(Cl)L_2]^+$ [L = ethylenediamine (en), propylenediamine, or 1,5,8,12-tetra-azadodecane (tadd)],[14] all possessing a distorted pseudo-octahedral structure, with a sixth, negatively charged ligand, in *trans* position to the $Tc{\equiv}N$ bond. However, the strong *trans* influence and large steric requirements of the nitrido-ligand result in an extreme lengthening of the Tc–Cl *trans* bond distances in these complexes, which are the longest Tc–Cl bond distances ever observed in technetium complexes {2.7320(8) Å for $[TcN(Cl)(en)_2]^+$ and 2.663(2) Å for $[TcN(Cl)(tadd)]^+$}. The $Tc{\equiv}N$ bond distances of 1.603(3) Å for $[TcN(Cl)(en)_2]^+$ and 1.626(6) Å for $[TcN(Cl)(tadd)]^+$ are of the same order of magnitude as those referred to above. The situation is quite different to that observed with the isoelectronic $[Tc{=}O]^{3+}$ core in that this moiety occurs in two limiting types of complex, square-pyramidal oxo-complexes and nearly regular octahedral dioxo-complexes (the Tc atom lying on the same plane of the *cis* ligands as the $Tc{=}O$),[15,16] encompassing the formation of distorted pseudo-octahedral species having a weakly bonded ligand *trans* to the $Tc{=}O$ group.[15,17] The N^{3-} group is considered the strongest known π-electron donor,[18] and thus it is likely to exert a *trans* influence greater than that of the oxo-group. As a consequence of the $Tc{\equiv}N$ multiple bond the square-pyramidal geometry is highly preferred and only greatly distorted octahedral geometries with a marked lengthening of the metal–ligand bond distance of the substituent (usually negatively charged) *trans* to the nitrido group are expected.

X-Ray Structures of $[Tc(CO)_2(PPh_3)_2\{PhN{=}C(OEt)S\}]$ (**1**) *and* $[TcN(Cl)(PPh_3)\{PhN{=}C(OEt)S\}]$ (**2**).—As shown in Figure 1, in complex (**1**) the Tc atom is six-co-ordinate. Distortions from the idealized octahedral geometry are almost localized in the equatorial plane where the bidentate ligand subtends an angle of only 64.7° to the metal and makes therefore large angles with the adjacent carbonyl groups. Inspection of the co-ordination bonds shows that: (*i*) both Tc–S and Tc–N bonds are significantly longer than the sum of the covalent radii, these distances being probably determined by the geometrical constraints of the bidentate ligand and by the relatively strong *trans* influence of the CO groups; (*ii*) the Tc–CO bonds are significantly shorter than the sum of the covalent radii because of the double-bond character induced by the back-donation effect; (*iii*) bond distances involving Tc compare very favourably with the corresponding distances found in a series of rhenium complexes with the same or with similar ligands, which is not surprising when one considers that the same atomic and very similar covalent radii are assigned to these elements. In particular this structure can be compared with that, recently determined, of the congeneric complex $[Re(CO)_2(PPh_3)_2\{PhN{=}C(OEt)S\}]$[3] [Re–P 2.420 (mean), Re–S 2.548(4), Re–N 2.20(1), and Re–C 1.86 Å (mean)]. Even if the compounds are not isomorphous, the two molecules are isostructural, in terms of their stereochemical features. The five equatorial atoms Tc, S, N, C(46), and C(47) are essentially coplanar (within 0.006 Å). The plane of the chelate moiety defined by S,N,C(43),O(1) is inclined by 6° to the equatorial plane, and the attached phenyl ring is rotated somewhat round the N–C(37) axis. As already found in the rhenium compound, the C–O–C angle of about 119° indicates that the O atom is sp^2 hybridized. The C–O(1) bond lengths agree with those expected for a $C(sp^3)$–O–$C(sp^2)$ system.[19] Moreover the C–S bond of 1.727(6) Å is single,[20] whereas a strong double-bond character can be attributed to N–C(43) [1.290(7) Å]; therefore the negative charge of the ligand seems to be mainly localized on the sulphur atom.

As shown in Figure 2, in complex (**2**) the Tc atom is five-co-ordinate. As expected, the metal atom is displaced (by 0.78 Å) toward the nitrido-nitrogen N(1) from the mean plane defined by the four base atoms, three of which are coplanar within 0.1 Å while N(2) is significantly displaced (by 0.6 Å), also toward N(1). Also in this compound major distortions with respect to the idealized square-pyramidal geometry arise from the geometrical constraints of the bidentate ligand which subtends an angle of only 68.1° to the metal. The four atoms S, N(2), C(25), and O are exactly coplanar, and the phenyl ring makes with this plane an angle of only 17° so that entire bidentate ligand can be considered as approximately planar. We observe that, whereas the Tc–P bond distance is of the same order as that in complex (**1**), both the Tc–S and Tc–N distances within the bidentate ligand are significantly shorter. This feature, which could appear to be a contradiction, is not surprising when considering the combined effect of a stronger σ bond from the ligand to a metal ion which is in (**2**) in a higher oxidation state, as well the very different influence exerted by the *trans* ligands, because of their different type, and of the different co-ordination geometry. Other structural details involving the bidentate ligand itself are not remarkably different from those found in complex (**1**).

Experimental

Materials.—Technetium-99 is a β^- emitter ($t_{\frac{1}{2}} = 2.1 \times 10^5$ years). All manipulations of solutions and solids were performed in a laboratory approved for the handling of radioisotopes with monitored heads and glove-boxes. The preparation of the starting material [Tc(CO)$_3$Cl(PPh$_3$)$_2$] was performed as reported in the literature.[13] However, the addition of an excess of PPh$_3$ to the reaction mixture shortens the reaction time from 20 to 8 h (yield >90%). The compound [TcNCl$_2$(PPh$_3$)$_2$] was obtained by reaction of [NH$_4$][TcO$_4$] with hydrazine dihydrochloride and triphenylphosphine,[7] while [AsPh$_4$][TcNCl$_4$] was prepared by reaction of [NH$_4$][TcO$_4$] with NaN$_3$ in the presence of concentrated HCl and of the corresponding cation.[5] The ligand PhNC(OEt)SH was prepared by adding PhNCS to dried EtOH.[21] The solution was evaporated to dryness and the residue was treated with n-hexane; the white product was recovered by filtration, dried *in vacuo*, identified by elemental analysis and its ^{1}H n.m.r. spectrum, and used without further purification. Other materials were reagent grade.

Infrared and ^{1}H n.m.r. spectra were recorded on Perkin-Elmer and WP80-MHz Bruker spectrometers, respectively. Elemental analyses were performed on a Carlo Erba model 1106 elemental analyser.

Synthesis of the Complexes.—Complex [Tc(CO)$_2$(PPh$_3$)$_2$-{PhN=C(OEt)S}] (**1**) was obtained by adding [Tc(CO)$_3$Cl-(PPh$_3$)] to an anhydrous thf solution of the salt of the ligand generated *in situ* by treating an excess of PhNC(OEt)SH with NaH. The mixture (25 cm^3) was refluxed for 20 min and then evaporated to one-third of its volume. The white product was obtained upon addition of EtOH and crystallized from CH$_2$Cl$_2$–EtOH, yield 60% (Found: C, 65.9; H, 4.8; N, 1.6; S, 3.9. Calc. for C$_{47}$H$_{40}$NO$_3$P$_2$STc: C, 65.6; H, 4.7; N, 1.6; S, 3.7%). Infrared data (Nujol): ν(C≡O) 1 930 and 1 860; ν(C$\overset{\cdots}{-}$N) 1 505; ν(C–O–C) 1 220 cm^{-1}. ^{1}H N.m.r. (CDCl$_3$): δ 6.87 (m, NC$_6$H$_5$), 3.47 (q, CH$_2$), and 0.85 (t, CH$_3$).

[TcN(Cl)(PPh$_3$){PhN=C(OEt)S}] (**2**). An excess of the ligand was added to a toluene solution (25 cm^3) of [TcNCl$_2$-(PPh$_3$)$_2$] (0.166 mmol). The mixture was refluxed for 2 h and the solid orange product was obtained by adding EtOH to the concentrated solution. The same compound was also prepared using [AsPh$_4$][TcNCl$_4$] as starting material in the presence of an excess of free PPh$_3$. The orange complex was crystallized from CH$_2$Cl$_2$–EtOH, yield 70% (Found: C, 54.4; H, 4.2; N, 4.4; S, 4.9. Calc. for C$_{27}$H$_{25}$ClN$_2$OPSTc: C, 54.9; H, 4.3; N, 4.7; S, 5.4%). Infrared data (Nujol): ν(C$\overset{\cdots}{-}$N) 1 540; ν(C–O–C) 1 265; ν(Tc≡N) 1 100 cm^{-1}. ^{1}H N.m.r. (CDCl$_3$): δ 4.47 (q, CH$_2$) and 1.38 (t, CH$_3$).

[TcN{PhN=C(OEt)S}$_2$] (**3**). The starting compound [TcNCl$_2$(PPh$_3$)$_2$] (0.166 mmol) was added to an anhydrous thf solution of the salt of the ligand generated *in situ* by treating an excess of PhNC(OEt)SH with NaH. The mixture (25 cm^3) was refluxed for 20 min and the solid product was obtained by adding EtOH to the concentrated solution. The orange complex

Table 1. Atomic co-ordinates of the complex [Tc(CO)$_2$(PPh$_3$)$_2${PhN=C(OEt)S}] (**1**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Tc	0.866 52(3)	0.0	0.136 02(4)	C(21)	1.161 6(2)	−0.134 5(2)	0.460 7(4)
P(1)	0.682 8(1)	−0.034 3(1)	0.101 5(1)	C(22)	1.269 6(2)	−0.123 7(2)	0.464 2(4)
P(2)	1.048 9(1)	0.042 1(1)	0.186 5(1)	C(23)	1.311 3(2)	−0.063 7(2)	0.383 1(4)
S	0.845 3(1)	0.009 0(1)	0.398 6(1)	C(24)	1.244 9(2)	−0.014 4(2)	0.298 4(4)
O(1)	0.805 6(3)	0.165 7(3)	0.437 6(4)	C(25)	1.064 2(3)	0.135 7(3)	0.287 8(4)
O(2)	0.877 0(4)	0.020 0(3)	−0.181 2(4)	C(26)	1.080 0(3)	0.132 9(3)	0.434 9(4)
O(3)	0.929 4(4)	−0.173 8(3)	0.093 5(6)	C(27)	1.085 3(3)	0.203 7(3)	0.513 0(4)
N	0.818 9(3)	0.119 6(3)	0.212 7(4)	C(28)	1.074 8(3)	0.277 3(3)	0.444 0(4)
C(1)	0.634 3(2)	−0.124 1(2)	0.191 5(4)	C(29)	1.058 9(3)	0.280 1(3)	0.296 9(4)
C(2)	0.698 9(2)	—0.166 2(2)	0.290 4(4)	C(30)	1.053 6(3)	0.209 3(3)	0.218 8(4)
C(3)	0.660 6(2)	−0.233 3(2)	0.357 3(4)	C(31)	1.127 3(3)	0.057 1(3)	0.031 9(4)
C(4)	0.557 7(2)	−0.258 1(2)	0.325 3(4)	C(32)	1.112 7(3)	0.001 7(3)	−0.077 8(4)
C(5)	0.493 1(2)	−0.216 0(2)	0.226 3(4)	C(33)	1.169 3(3)	0.008 8(3)	−0.197 2(4)
C(6)	0.531 5(2)	−0.148 9(2)	0.159 4(4)	C(34)	1.240 4(3)	0.071 3(3)	−0.207 0(4)
C(7)	0.632 7(3)	−0.057 8(3)	−0.082 6(4)	C(35)	1.255 0(3)	0.126 8(3)	−0.097 3(4)
C(8)	0.695 2(3)	−0.107 3(3)	−0.159 5(4)	C(36)	1.198 4(3)	0.119 6(3)	0.022 1(4)
C(9)	0.662 1(3)	−0.129 2(3)	−0.297 7(4)	C(37)	0.795 4(3)	0.194 1(2)	0.142 8(4)
C(10)	0.566 6(3)	−0.101 5(3)	−0.359 0(4)	C(38)	0.834 8(3)	0.206 4(2)	0.011 3(4)
C(11)	0.504 2(3)	−0.051 9(3)	−0.282 1(4)	C(39)	0.810 8(3)	0.276 5(2)	−0.063 9(4)
C(12)	0.537 2(3)	−0.030 1(3)	−0.143 9(4)	C(40)	0.747 3(3)	0.334 4(2)	−0.007 7(4)
C(13)	0.594 7(3)	0.043 5(2)	0.161 5(4)	C(41)	0.707 9(3)	0.322 1(2)	0.123 7(4)
C(14)	0.557 8(3)	0.036 7(2)	0.295 7(4)	C(42)	0.731 9(3)	0.251 9(2)	0.199 0(4)
C(15)	0.492 9(3)	0.095 9(2)	0.345 1(4)	C(43)	0.820 6(4)	0.106 7(3)	0.347 0(5)
C(16)	0.464 9(3)	0.161 8(2)	0.260 2(4)	C(44)	0.812 9(6)	0.148 8(4)	0.589 2(6)
C(17)	0.501 8(3)	0.168 5(2)	0.126 0(4)	C(45)	0.705 2(6)	0.130 4(6)	0.635 8(8)
C(18)	0.566 7(3)	0.109 4(2)	0.076 6(4)	C(46)	0.873 2(4)	0.014 0(4)	−0.059 8(6)
C(19)	1.136 9(2)	−0.025 1(2)	0.294 9(4)	C(47)	0.906 5(4)	−0.108 0(4)	0.109 2(6)
C(20)	1.095 2(2)	−0.085 1(2)	0.376 0(4)				

Table 2. Atomic co-ordinates of the complex [TcN(Cl)(PPh$_3$){PhN=C(OEt)S}] (**2**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Tc	0.257 16(9)	0.241 16(8)	0.192 98(6)
P	0.344 5(2)	0.135 5(2)	0.322 2(2)
Cl	0.469 3(3)	0.471 9(2)	0.252 7(2)
S	0.231 5(3)	0.061 5(2)	0.087 9(2)
O	0.273 1(8)	0.207 5(6)	−0.059 4(5)
N(1)	0.085 8(9)	0.210 8(9)	0.213 8(5)
N(2)	0.252 4(8)	0.313 7(7)	0.063 9(4)
C(25)	0.255 5(10)	0.206 9(8)	0.020 4(8)
C(26)	0.290 3(14)	0.086 7(10)	−0.097 7(7)
C(27)	0.343 1(15)	0.136 7(12)	−0.180 5(8)
C(2)	0.238 7(7)	0.065 4(4)	0.479 0(4)
C(3)	0.208 7(7)	0.099 6(4)	0.557 3(4)
C(4)	0.235 0(7)	0.241 3(4)	0.579 2(4)
C(5)	0.291 2(7)	0.348 7(4)	0.522 7(4)
C(6)	0.321 3(7)	0.314 5(4)	0.444 3(4)
C(1)	0.295 0(7)	0.172 8(4)	0.422 5(4)
C(8)	0.655 6(6)	0.252 0(6)	0.437 4(3)
C(9)	0.823 1(6)	0.301 5(6)	0.455 4(3)
C(10)	0.896 8(6)	0.297 5(6)	0.387 8(3)
C(11)	0.803 0(6)	0.243 9(6)	0.302 2(3)
C(12)	0.635 5(6)	0.194 4(6)	0.284 1(3)
C(7)	0.561 8(6)	0.198 4(6)	0.351 7(3)
C(14)	0.357 8(5)	−0.134 0(5)	0.330 0(4)
C(15)	0.289 2(5)	−0.285 3(5)	0.315 4(4)
C(16)	0.124 0(5)	−0.363 9(5)	0.277 4(4)
C(17)	0.027 5(5)	−0.291 2(5)	0.254 0(4)
C(18)	0.096 1(5)	−0.139 9(5)	0.268 6(4)
C(13)	0.261 3(5)	−0.061 3(5)	0.306 6(4)
C(20)	0.203 8(7)	0.522 2(7)	0.075 8(3)
C(21)	0.201 3(7)	0.650 4(7)	0.046 0(3)
C(22)	0.254 4(7)	0.701 7(7)	−0.029 8(3)
C(23)	0.310 1(7)	0.624 9(7)	−0.075 8(3)
C(24)	0.312 6(7)	0.496 7(7)	−0.046 0(3)
C(19)	0.259 5(7)	0.445 4(7)	0.029 8(3)

Table 3. Bond distances (Å) and angles (°) for complex (**1**) with estimated standard deviations (e.s.d.s)

Tc–P(1)	2.423(1)	O(1)–C(44)	1.461(7)
Tc–P(2)	2.456(1)	C(44)–C(45)	1.51(1)
Tc–S	2.529(1)	O(2)–C(46)	1.159(7)
Tc–N	2.228(5)	O(3)–C(47)	1.14(9)
Tc–C(46)	1.880(6)	P(1)–C(1)	1.856(8)
Tc–C(47)	1.900(7)	P(1)–C(7)	1.857(8)
N–C(37)	1.432(6)	P(1)–C(13)	1.841(8)
N–C(43)	1.290(7)	P(2)–C(19)	1.849(8)
S–C(43)	1.727(6)	P(2)–C(25)	1.838(9)
O(1)–C(43)	1.332(7)	P(2)–C(31)	1.855(8)
P(1)–Tc–P(2)	175.3(1)	C(43)–O(1)–C(44)	119.3(5)
S–Tc–N	64.7(1)	O(1)–C(44)–C(45)	109.5(6)
S–Tc–C(47)	103.8(2)	Tc–P(1)–C(1)	119.0(1)
N–Tc–C(46)	104.1(2)	Tc–P(1)–C(7)	116.2(1)
C(46)–Tc–C(47)	87.4(3)	Tc–P(1)–C(13)	113.8(2)
Tc–S–C(43)	78.9(2)	C(1)–P(1)–C(7)	99.0(2)
Tc–N–C(43)	100.8(4)	C(1)–P(1)–C(13)	101.3(2)
Tc–C(46)–O(2)	177.7(6)	C(7)–P(1)–C(13)	105.2(2)
Tc–C(47)–O(3)	179.0(6)	Tc–P(2)–C(19)	117.8(1)
Tc–N–C(37)	133.0(3)	Tc–P(2)–C(25)	114.1(2)
S–C(43)–N	115.3(4)	Tc–P(2)–C(31)	116.7(1)
S–C(43)–O(1)	123.4(4)	C(19)–P(2)–C(25)	100.9(2)
N–C(43)–O(1)	121.3(5)	C(19)–P(2)–C(31)	100.2(2)
C(37)–N–C(43)	126.1(5)	C(25)–P(2)–C(31)	104.8(2)

Table 4. Bond distances (Å) and angles (°) for complex (**2**) with e.s.d.s

Tc–Cl	2.366(2)	N(2)–C(19)	1.42(1)
Tc–N(1)	1.615(7)	C(25)–O	1.29(1)
Tc–N(2)	2.135(7)	O–C(26)	1.47(1)
Tc–S	2.375(3)	C(26)–C(27)	1.49(2)
Tc–P	2.429(2)	P–C(1)	1.817(6)
S–C(25)	1.78(1)	P–C(7)	1.810(5)
N(2)–C(25)	1.31(1)	P–C(13)	1.817(6)
N(1)–Tc–Cl	113.9(3)	S–C(25)–N(2)	109.5(9)
N(1)–Tc–N(2)	106.9(3)	S–C(25)–O	125.5(7)
N(1)–Tc–S	112.3(3)	N(2)–C(25)–O	125.1(8)
N(1)–Tc–P	94.9(3)	C(25)–O–C(26)	119.7(8)
S–Tc–N(2)	68.1(2)	O–C(26)–C(27)	105.4(9)
S–Tc–P	95.9(1)	Tc–P–C(1)	115.7(2)
Cl–Tc–N(2)	89.6(2)	Tc–P–C(7)	112.2(3)
Cl–Tc–P	89.4(1)	Tc–P–C(13)	113.2(2)
Tc–S–C(25)	80.3(4)	C(1)–P–C(7)	104.9(3)
Tc–N(2)–C(25)	101.3(6)	C(1)–P–C(13)	105.1(3)
Tc–N(2)–C(19)	132.7(5)	C(7)–P–C(13)	104.8(2)
C(19)–N(2)–C(25)	125.7(8)		

was crystallized from CH_2Cl_2–EtOH, yield 40% (Found: C, 46.0; H, 4.2; N, 8.6; S, 12.2. Calc. for $C_{18}H_{20}N_3O_2S_2Tc$: C, 45.6; H, 4.3; N, 8.9; S, 13.5%). Infrared data (Nujol): ν(C$\cdots$N) 1 530; ν(C–O–C) 1 260; ν(Tc≡N) 1 100 cm^{-1}. ^1H N.m.r. ($CDCl_3$): δ 7.32 (m, NC_6H_5), 4.52 (q, CH_2), and 1.42 (t, CH_3).

X-*Ray Crystallography*.—Well formed crystals of maximum dimension 0.2 mm were chosen for the *X*-ray work. Cell constants for both compounds were determined by accurate settings of least 25 medium-angle reflections.

Crystal data. [Tc(CO)$_2$(PPh$_3$)$_2${PhN=C(OEt)S}] (**1**), $C_{47}H_{40}NO_3P_2STc$, *M* 857, monoclinic, space group $P2_1$, a = 12.825(5), b = 16.713(5), c = 9.480(5) Å, β = 94.29(3)°, U = 2 026 Å^3, D_c = 1.40 g cm^{-3} for Z = 2, μ(Mo-K_α) = 5.6 cm^{-1}. F(000) = 884.

[TcN(Cl)(PPh$_3$){PhN=C(OEt)S}] (**2**), $C_{27}H_{25}ClN_2OPSTc$, *M* 591, triclinic, space group $P\bar{1}$, a = 9.428(5), b = 10.237(5), c = 15.603(5) Å, α = 89.29(3), β = 102.74(3), γ = 115.61(3)°, U = 1 319 Å^3, D_c = 1.49 g cm^{-3} for Z = 2, μ(Mo-K_α) = 7.2 cm^{-1}. F(000) = 600.

Intensities for both compounds were measured to θ = 25° on a four-circle Philips diffractometer using graphite-monochromatized Mo-K_α radiation (λ = 0.7107 Å). Both crystals are stable under irradiation. A total of 4 333 reflections were recorded for (**1**) of which 3 414 with $I > 3\sigma(I)$ were considered as 'observed' and used in subsequent calculations. A total of 3 672 reflections were recorded for (**2**), of which 2 913 were 'observed'. The intensities were corrected for Lorentz polarization and for absorption.[22] The structures were solved by standard methods and refined to final conventional *R* factors of 0.0295 for (**1**) and 0.0649 for (**2**), when the maximum shift in the refined parameters was 0.1σ in both cases. Phenyl groups were refined as rigid bodies (C–C 1.395, C–H 1.08 Å) with fixed isotropic thermal parameters for the H atoms (U_{iso} = 0.07 Å^2). Phenyl carbon atoms in complex (**2**) were refined isotropically. The quantity minimized in the refinement was $\Sigma w(\Delta F)^2$ with w = 1. Scattering factors for Tc were taken from ref. 23, corrected for the anomalous dispersion; those for the other atoms were supplied internally by SHELX.[24] Final atomic parameters are listed in Tables 1 and 2, bond distances and angles in Tables 3 and 4.

Additional material available from the Cambridge Crystallographic data centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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