Nitrido-technetium and -rhenium Complexes with Chelating Phosphines: Synthesis, Reactivity and Crystal Structures†

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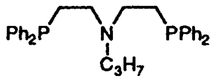
Nitrido-technetium(V) and -rhenium(V) complexes of general formula [MNCl$_2$L] [M = Tc or Re; L = bis(diphenylphosphinoethyl)propylamine (L^1), 1,8-bis(diphenylphosphino)-3,6-dioxaoctane (L^2) or 1,1,1-tris(diphenylphosphinomethyl)ethane (L^3)] have been synthesized and characterized. They were prepared by the reduction of [Tc^{VI}NCl$_4$]$^-$ or by the replacement of the two triphenylphosphines of [MNCl$_2$(PPh$_3$)$_2$] (M = Re or Tc) by bidentate or tripodal polyphosphine ligands L. Reaction of these complexes with an excess of potassium *O*-ethyl dithiocarbonate yields neutral dithiocarbonate compounds [MN(S$_2$CO)L], while cationic and neutral complexes [MN(S$_2$CNEt$_2$)L]$^+$ and [MN(S$_2$CNEt$_2$)$_2$] were obtained upon reaction with K(S$_2$CNEt$_2$). The crystal structures of [TcNCl$_2$L^1] and [TcNCl$_2$L^2] have been determined by X-ray crystallography; the complex [TcNCl$_2$L^1] shows square-pyramidal co-ordination at technetium with the Tc atom displaced from the basal plane towards the N atom by 0.410 Å. An unusual trigonal-bipyramidal geometry is observed for [TcNCl$_2$L^2]. The Tc≡N bond distances (1.60 Å) in both complexes are indicative of a strong triple bond.

It is well known that the great interest in the co-ordination chemistry of technetium is due to the availability in macroscopic amounts of the long-lived radionuclide ^{99}Tc and the widespread use in diagnostic nuclear medicine of the ^{99m}Tc isotope (140 keV, *ca.* 2.24 × 10^{14} J; $t_{\frac{1}{2}}$ = 6 h).

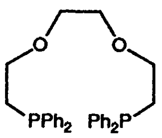
The chemistry of technetium with mono- and di-phosphine ligands in a variety of oxidation states has been explored extensively.[1] In particular, Deutsch and co-workers[2] have closely examined structural, electrochemical and kinetic aspects of technetium-(III) and -(II) complexes of the general formula [TcL'$_2$X$_2$]$^{+/0}$ (L' = chelating phosphine or arsine, X = halide or pseudohalide).

The synthesis and characterization of mixed-ligand technetium-(III) and -(II) complexes containing thiolate,[3] bipyridine,[4] phenanthroline,[4] *o*-mercaptophenol[5] or oxalic acid[6] have also been reported. Finally, mixed-ligand complexes containing technetium-(I)[7] or -(IV)[8] have been recently described. On the contrary, the chemistry of nitrido complexes of technetium with chelating phosphine ligands has remained overlooked. Nitridotechnetium(V) complexes with a series of mono-phosphines and -arsines,[9a,b] as well as complexes containing 1,2-bis(diphenylphosphino)ethane (dppe) have been synthesized and characterized.[10] More recently, cationic nitrido complexes with 1,2-bis(dimethylphosphino)ethane (dmpe) have been described and [TcN(dmpe)$_2$Cl]$^+$ has been characterized structurally.[11a,b]

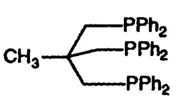
In this work we report the preparation, characterization and reactivity of complexes of the type [TcNCl$_2$L] [L = bis(diphenylphosphinoethyl)propylamine (L^1), 1,8-bis(diphenylphosphino)-3,6-dioxaoctane (L^2) or 1,1,1-tris(diphenylphosphinomethyl)ethane (L^3)] and the structural characterization of [TcNCl$_2$L^2] **1** and [TcNCl$_2$L^1] **2**. A comparison of the reactivity of the analogous rhenium complexes is made. The synthesis of the corresponding nitrido complexes with ^{99m}Tc is also described along with preliminary studies of their biodistribution in rats.



L^1



L^2



L^3

Results and Discussion

Neutral nitrido complexes of technetium [TcNCl$_2$L] (L = L^1–L^3) were prepared by a reduction–substitution route in which the starting material [AsPh$_4$][Tc^{VI}NCl$_4$] is both reduced and ligated by chelating phosphine ligands. These complexes, as well as the rhenium analogues, were also obtained starting from [MNCl$_2$(PPh$_3$)$_2$] (M = Tc or Re) by substitution of the two phosphine groups. This procedure however is slower and less efficient than the corresponding reduction–substitution reactions.

These complexes are readily soluble in CH$_2$Cl$_2$ and react with a wide range of ligands. Thus, reaction with an excess of potassium *O*-ethyl dithiocarbonate K$_2$(S$_2$COEt) yields neutral complexes of the general formula [MN(S$_2$CO)L] (M = Tc or Re, L = L^1–L^3) in which a dithiocarbonate anion, derived from hydrolysis of S$_2$COEt, replaces the two chlorine atoms. It appears however that the xanthate ‡ ligand is not able to replace a chelating phosphine to give K$_2$[TcN(S$_2$CO)$_2$].[12]

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

‡ Xanthate refers to alkyl or aryl dithiocarbonates.

In contrast to *O*-ethyl dithiocarbonate, diethylthiocarbamate reacts with $[MNCl_2L]$ (M = Tc or Re) to give either monosubstituted cationic complexes $[MN(S_2CNEt_2)L]^+$ or the known bisubstituted neutral species $[MN(S_2CNEt_2)_2]$ in good yields, depending on the stoichiometric ratio used.

The formulation of the complexes is supported by elemental analysis, IR and NMR spectroscopy. In addition, X-ray crystal structures of $[TcNCl_2L^2]$ **1** and $[TcNCl_2L^1]$ **2** were obtained.

Infrared and NMR data for the mixed-ligand rhenium complexes will be reported in detail elsewhere but are referred to here to enable comparisons to be made with the technetium complexes.

As expected, the IR spectra of the two series of technetium and rhenium complexes $[MNCl_2L]$ and $[MN(S_2CO)L]$ (M = Tc or Re, L = L^1–L^3) are virtually identical. The absorption of the M≡N multiple bond could not always be confidently assigned (see Experimental section) owing to the complexity of the spectra in the appropriate wavenumber range (1000–1100 cm^{-1}). For the complexes $[MNCl_2L]$ the only significant difference between the technetium and rhenium species is that the Re–Cl stretch is lower in energy (280–330 cm^{-1}) than the Tc–Cl stretch (305–350 cm^{-1}). Similarly no significant differences occur between the technetium and rhenium dithiocarbonate complexes. For these complexes, two strong bands in the range 1597–1610 and 1680–1695 cm^{-1} may be assigned to the C═O vibration and a single band at 835–850 cm^{-1} to the C–S single bond.[12] The IR spectra of the mixed-ligand cationic complexes $[MN(S_2CNEt_2)L][BPh_4]$ (M = Tc or Re, L = L^1–L^3) exhibit a single band in the range 1270–1285 cm^{-1} and a relatively weak stretching at *ca.* 840–850 cm^{-1}. We also observed these bands in the well known dithiocarbamate complexes of technetium and rhenium[9,10,13] but they were previously not assigned. The position of these bands points to a partial double-bond character for the CS_2^- group of the dithiocarbamate ligand. In the dithiocarbonate complexes here and previously discussed,[12] there are no absorptions in the range 1220–1280 cm^{-1}, while a single C═S band near 1235 cm^{-1} was found by Davison and co-workers[14] in technetium xanthate complexes.

We thus decided to synthesize $[Tc(PPh_3)(S_2COEt)_3]$ using $[TcCl_4(PPh_3)_2]$ as precursor. Its IR spectra showed a strong absorption at 1232 cm^{-1} indicative of the C═S bond. Our assignments above are supported if the C–S bond distances in the various species are considered. The C–S bond distance of 1.68 Å (average) in xanthate complexes[14] and 1.70–1.74 Å in dithiocarbamate derivatives[13a,b,d,15] reflect a degree of double-bond character and suggest a charge delocalization throughout the $X–CS_2^-$ (X = O or N) moiety and IR frequencies lie in the range 1230–1270 cm^{-1}. In the dithiocarbonate complex[12] $K_2[TcN(S_2CO)_2]\cdot 2H_2O$ we found a C–S bond distance of 1.78 Å and ν(C–S) 835–850 cm^{-1} indicative of a single bond.

Proton NMR Spectra.—The ^1H NMR spectra of the technetium and rhenium complexes are quite similar. A downfield shift of the signals of the nitridorhenium(V) species in comparison with the corresponding technetium complexes was observed.

The spectra of $[MNCl_2L]$ (M = Tc or Re, L = L^1–L^3) showed a complex multiplet in the range δ 6.8–8.0 assigned to the aryl protons and multiplets in the range δ 2.5–4.0 to the aliphatic CH_2 protons. In addition, the complexes containing L^1 showed multiplets at δ 1.3–1.35 and at δ 0.70–0.75 due to the CH_2 and CH_3 protons respectively of the propyl group. For $[MNCl_2L^3]$ a singlet at δ 0.40 (M = Tc) or δ 0.85 (M = Re) was attributed to the methyl group. The ^{31}P NMR spectra for $[MNCl_2L^3]$ showed signals at δ +26.25 and +28.50 (br) (M = Tc) or δ −28.20 and −28.60 (M = Re), but in neither case was a signal found near δ −27 characteristic of an unco-ordinated phosphine group. These data are comparable with those of other transition-metal complexes in which tripodal L^3 is three-co-ordinated to the metal.[11b,16]

In the mixed-ligand dithiocarbonate complexes $[MN(S_2CO)L]$ similar patterns were observed except that the signals were shifted to high-field relative to the $[MNCl_2L]$ complexes. The ^1H NMR spectra of the monosubstituted diethyldithiocarbamate compounds $[MN(S_2CNEt_2)L][BPh_4]$ are more difficult to interpret because the signals of the CH_2 and CH_3 protons of both ligands are situated in the range δ 2.3–4.0 and δ 1.0–1.5, respectively. Moreover, the methyl protons of the dithiocarbamate ligands in $[MN(S_2CNEt_2)L^2]^+$ (M = Tc or Re) were found at δ 1.05–1.40 similarly to other dithiocarbamate complexes.[13c,17] From these data, it is probable that both the technetium and rhenium complexes possess the same configuration.

Finally, the spectrum of the *O*-ethyl dithiocarbonate derivative $[Tc(PPh_3)(S_2COEt)_3]$ showed two quartets at δ 4.45 (CH_2, 4 H, *J* = 7.1) and 3.45 (CH_2, 2 H, *J* = 7.03) and two triplets at δ 1.35 (CH_3, 6 H, *J* = 7.1) and 1.15 (CH_3, 3 H, *J* = 7.03 Hz), the aryl protons of PPh_3 were assigned to a multiplet between δ 7.1 and 7.5. These data confirm the seven-co-ordinate geometry found by Davison and co-workers[14] for the corresponding *O*-isopropyl dithiocarbonate complex.

The results reported herein demonstrate the ability of the $[Tc{\equiv}N]^{2+,3+}$ and $[Re{\equiv}N]^{2+}$ cores to form neutral, lipophilic complexes with chelating phosphines. The new complexes are promising starting materials for preparing mixed-ligand compounds and may show potential use in radiopharmaceutical studies.

Structures of Complexes **1** *and* **2**.—The molecule of $[TcNCl_2L^2]$ **1** (Fig. 1) shows C_2 symmetry and is situated on a two-fold crystallographic rotation axis passing through the Tc and N atoms and the centre of the C(3)–C(3′) bond. The co-ordination around Tc^V is trigonal bipyramidal with the two P atoms in apical positions and N, Cl, Cl′ forming the basal plane. Such a co-ordination polyhedron for nitridotechnetium(V) compounds is quite unusual, the co-ordination geometries hitherto observed being octahedral or square pyramidal; moreover if we consider the two short contact distances of 3.190(2) Å between the central Tc atom and the two oxygens,

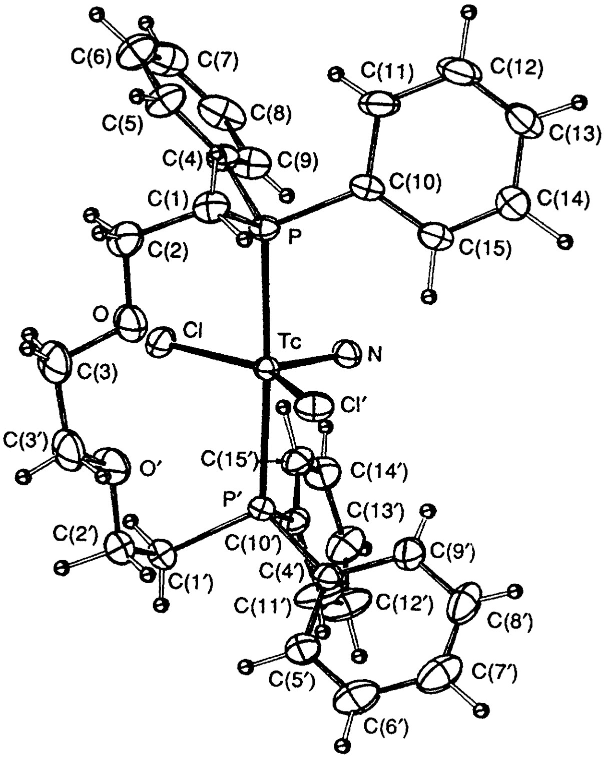

Fig. 1 View of the molecule of compound **1** showing the thermal ellipsoids at 30% probability

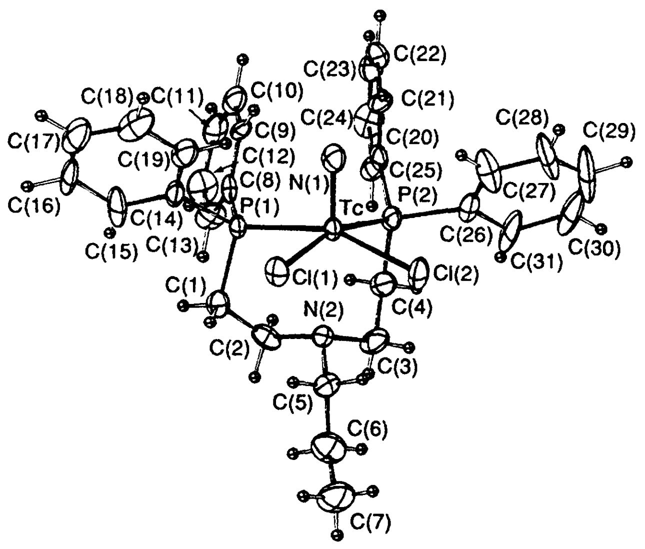

Fig. 2 View of the molecule of compound **2** showing the thermal ellipsoids at 30% probability

the Tc atom can be considered as seven-co-ordinated in a distorted pentagonal bipyramid. An interesting feature of this complex is that Tc^V assumes the more common octahedral co-ordination if we take, as the sixth co-ordination site, the mid-point of the two oxygen atoms which is, for symmetry reasons, in perfect *trans* position to the nitrido N atom. A similar situation has been found in the oxotechnetium(v) complex anion $[TcO(edta)]^-$ (H_4edta = ethylenediaminetetraacetic acid)[18] for which five vertices of the octahedron are occupied by oxygens and the sixth by the mid-point of two nitrogen atoms.

The structure of $[TcNCl_2L^1]$ **2** (Fig. 2) shows square-pyramidal co-ordination around Tc with the Tc atom displaced from the mean plane defined by Cl(1), Cl(2), P(1), P(2) towards the nitrogen atom N(1) by 0.410(2) Å. The Tc≡N bond distance of 1.60(1) Å is indicative of a strong triple bond [as also found in **1** where Tc≡N 1.601(4) Å]. The Tc • • • N(2) contact of 2.70(1) Å can be interpreted as an incipient increasing of the co-ordination from square pyramidal to octahedral. Owing to the strong *trans* influence exerted by the Tc≡N triple bond, five-co-ordinate square-pyramidal geometry is the most common co-ordination mode for this class of compound, however a few significant examples of pseudo-octahedral nitridotechnetium(v) compounds have been observed. These all show a strong *trans* influence exerted by the N^{3-} group, which is manifested by the lengthening of the Tc–X bond distances *trans* to the Tc≡N bond. For the only other reported compounds having nitrogen *trans* to the nitrido group the observed Tc–N(*trans*) bond distances are 2.491(4) Å in $[TcN(NCS)_2(MeCN)(PPh_3)]$,[19] 2.42(2) and 2.40(2) Å in $[TcNBr(bipy)_2]^+$ (bipy = 2,2′-bipyridine)[11b] and 2.45(5) Å in $[TcNCl(phen)_2]^+$ (phen = 1,10-phenanthroline).[20]

These distances are much longer than those (1.88–2.18 Å[21-23]) for nitrogens situated in basal positions for nitrido- and oxo-technetium derivatives. The wide variation of Tc–N(basal) in these complexes results from different charges and hybridization of the nitrogen atoms. Other pseudo-octahedral nitridotechnetium compounds have been observed with chlorine or oxygen in a *trans* position to the nitrido group. For these also the *trans* influence of the nitrido ligand causes bond lengthening. Thus Tc–Cl(*trans*) bond lengths of 2.7320(8) and 2.663(2) Å are observed in $[TcN(en)_2Cl]^+$ (en = ethylenediamine) and $[TcNCl(L^4)]^+$ (L^4 = 1,5,8,12-tetraazadodecane),[24] respectively, while Tc–Cl bond lengths, including those observed in the present compounds, in the absence of *trans* influences range from 2.32 to 2.43 Å.[18,24] For Tc–O bonds which are *trans* to the nitrido ligand the distances vary from 2.330(6) Å [Tc–O(carboxylate)] in $[TcN(en)_2L^5]^{2+}$ [L^5 = *N*-(2-aminoethyl)carbamic acid][25] to 2.688(4), 2.947(4) Å in $[TcN(L^6)]\cdot H_2O$ (H_2L^6 = 1,4,8,11-tetraazacyclotetradecane-5,7-dione)[26] and 2.560(2) Å in $[TcN(L^7)(H_2O)]^+$ (H_2L^7 = 1,4,8,11-tetraazacyclotetradecane-5-one),[22] where the *trans* position is occupied by a water molecule. By contrast when oxygen is in the equatorial plane of oxo- or nitrido-technetium(v) complexes, despite the large number of examples, no Tc–O distances greater than 2.16 Å have been observed.[18,21]

[^{99m}Tc≡N] *Complexes.—Radiopharmaceutical preparation.* Neutral monosubstituted complexes formulated as $[^{99m}TcNCl_2L]$ (L = L^1–L^3) were prepared following our previously established procedure[27] in which a solution of chelating phosphine (L) in ethanol (10^{-2} mol dm^{-3}) was employed instead of PPh_3, dmpe or dppe.[11b,27] The yields obtained were *ca.* 95%. The formulation of the technetium-99m complexes was confirmed by a comparison of the chromatographic behaviour of the compounds prepared in macroscopic amounts at the carrier-added (c.a.) level (characterized and discussed above) with that of the products obtained at the no carrier-added (n.c.a.) level.

In order to evaluate the ability of these derivatives towards substitution reactions a n.c.a. synthesis was carried out as follows. After completion of the procedure for the preparation of $[^{99m}TcNCl_2L]$ (L = L^1–L^3) the pH of the solution was adjusted to 7.5–8.0 using a 0.5 mol dm^{-3} HCO_3^-–CO_3^{2-} buffer. An ethanolic solution (0.5 cm^3, 2×10^{-2} mol dm^{-3}) of $K(S_2CNEt_2)$ was then added and the temperature raised to 75–80 °C for 15 min. The yield of product, $[^{99m}TcN(S_2CNEt_2)_2]$, was up to 95% when L^2 or L^3 were used to prepare the intermediate compounds but lower (85%) with L^1. The chromatographic analysis revealed the presence of only a single product corresponding to the well characterized $[^{99m}TcN(S_2CNEt_2)_2]$.[27,28]

Preliminary biodistribution studies on rats showed a higher liver and spleen uptake indicative of their lipophilic character.

The detailed synthesis and exchange reactions towards other ligands and biodistribution of these neutral technetium-99m complexes will be reported elsewhere.

Experimental

Materials.—Technetium-99 is a weak β^- emitter (0.292 keV, *ca.* 4.47×10^{-17} J; $t_{\frac{1}{2}} = 2.12 \times 10^5$ years) and all manipulations were performed in a laboratory approved for the handling of radioisotopes. Bremsstrahlung is not a significant problem due to the low energy of the β-particle emission. Normal radiation safety procedures must be used to prevent contamination.

Reagents and solvents were used as received without further purification, ammonium pertechnetate was purchased from Du Pont/Nen Products. The ligands L^1–L^3 were courteously supplied by C.N.R. Firenze, and the complexes $[AsPh_4][TcNCl_4]$, $[TcNCl_2(PPh_3)_2]$[29] and $[ReNCl_2(PPh_3)_2]$[30] were prepared according to the literature methods.

NMR spectra of CD_2Cl_2 and $CDCl_3$ solutions of the complexes were recorded on Varian Gemini 300 or Bruker AC 200P spectrometers with $SiMe_4$ (^1H) and 85% H_3PO_4 (^{31}P-{^1H}) as internal standards, infrared spectra on a Nicolet 510 P FTIR instrument in KBr using a Spectra-Tech collector diffuse reflectance accessory. Radioactive technetium was determined on a model TRICARB 300 C Packard liquid-scintillation instrument with Imstagel as scintillator after dissolution of the samples in nitric acid–hydrogen peroxide solutions; elemental analyses were performed on a model 1106 Carlo Erba elemental analyser.

Synthesis of the Nitrido Complexes $[MNCl_2L]$ (M = Tc *or* Re, L = L^1–L^3).—*Method* (*a*). The complex $[AsPh_4][TcNCl_4]$ (0.075 g, 0.0117 mmol) was dissolved in EtOH–CH_2Cl_2 (15 cm^3, 2:1), to which a solution of the appropriate ligand L (ratio 1:2) in ethanol was added with stirring at room temperature until the solution became yellow.

Crystals of the products were formed by slow evaporation of the organic solvent in air. Recrystallization from CH_2Cl_2–EtOH gave suitable crystals for X-ray diffraction of $[TcNCl_2L^1]$ and $[TcNCl_2L^2]$. Yield > 90%.

Method (*b*). The technetium, as well as the analogous rhenium complexes, were also prepared from $[MNCl_2(PPh_3)_2]$ (M = Tc or Re) by the same procedure. To a suspension of the starting complex (0.03 mmol) in CH_2Cl_2 (25 cm^3) a solution of the ligand in stoichiometric ratio (1:1) dissolved in EtOH (10 cm^3) was added with stirring at room temperature. The mixture was heated to 50 °C until the solution became yellow. By slow evaporation of the solvent, crystals of the products were collected. Yield $\geqslant$85%. The colour of the complexes ranges from pale yellow to orange.

$[TcNCl_2L^1]$ (Found: C, 55.60; H, 5.35; N, 4.15; Tc, 14.40. $C_{31}H_{35}Cl_2N_2P_2Tc$ requires C, 55.75; H, 5.30; N, 4.20; Tc, 14.90%); $\nu(Tc{\equiv}N)$ 1057, ν(Tc–Cl) 310–320 cm^{-1} (KBr). $\delta_H(CDCl_3)$ 2.9–2.75 (8 H, m, NCH_2CH_2P), 1.30 (4 H, q, $NC\mathit{H}_2C\mathit{H}_2CH_3$) and 0.75 (3 H, m, $NCH_2CH_2C\mathit{H}_3$).

$[TcNCl_2L^2]$ (Found: C, 53.60; H, 4.80; N, 2.00; Tc, 14.25. $C_{30}H_{32}Cl_2NO_2P_2Tc$ requires C, 53.55; H, 4.80; N, 2.10; Tc, 14.70%); ν(Tc–Cl) 350 cm^{-1} (KBr). $\delta_H(CDCl_3)$ 2.75–3.90 (12 H, m, CH_2CH_2).

$[TcNCl_2L^3]$ (Found: C, 60.90; H, 4.85; N, 1.60; Tc, 11.50. $C_{41}H_{39}Cl_2NP_3Tc$ requires C, 60.90; H, 4.85; N, 1.70; Tc, 12.25%); ν(Tc–Cl) 321–334 cm^{-1} (KBr). $\delta_H(CD_2Cl_2)$ 3.20–2.50 (6 H, m, CH_2) and 0.40 (3 H, s, CH_3); $\delta_P(CDCl_3)$ +26.25 (sp, 1 P) and +28.50 (br, 2 P).

$[ReNCl_2L^1]$ (Found: C, 49.10; H, 4.60; N, 3.65. $C_{31}H_{35}Cl_2N_2P_2Re$ requires C, 49.30; H, 4.70; N, 3.70%); $\nu(Re{\equiv}N)$(?) 1068, ν(Re–Cl) 315–289 cm^{-1} (KBr). $\delta_H(CDCl_3)$ 3.00–2.80 (8 H, m, NCH_2CH_2P), 1.35 (4 H, q, $NC\mathit{H}_2C\mathit{H}_2CH_3$) and 0.75 (3 H, m, $NCH_2CH_2C\mathit{H}_3$).

$[ReNCl_2L^2]$ (Found: C, 47.20; H, 4.20; N, 1.70. $C_{30}H_{32}Cl_2NO_2P_2Re$ requires C, 47.50; H, 4.25; N, 1.85%); ν(Re–Cl) 322 cm^{-1} (KBr). $\delta_H(CDCl_3)$ 4.00–2.80 (12 H, m, CH_2CH_2).

$[ReNCl_2L^3]$ (Found: C, 54.50; H, 4.35; N, 1.55. $C_{41}H_{39}Cl_2NP_3Re$ requires C, 54.95; H, 4.40; N, 1.60%); ν(Re–Cl) 314–323 cm^{-1} (KBr). $\delta_H(CD_2Cl_2)$ 3.60–2.50 (6 H, m, CH_2) and 0.85 (3 H, s, CH_3); $\delta_P(CD_2Cl_2)$ −28.20 (sp, 2 P) and −28.60 (w, 1 P).

Synthesis of Mixed-ligand Complexes.—The technetium and rhenium complexes were prepared using the same procedure.

Nitrido-dithiocarbonate and -diethyldithiocarbamate complexes. $[MN(S_2CO)L]$ *and* $[MN(S_2CNEt_2)L][BPh_4]$ (M = Tc *or* Re, L = L^1–L^3). The complex $[MNCl_2L]$ (60 mg) was dissolved in CH_2Cl_2 (10 cm^3) at room temperature and to it was added a three-fold molar excess of $K(S_2COEt)$ or $K(S_2CNEt_2)$ in stoichiometric ratio in EtOH (5 cm^3) and the solution gently warmed for a few minutes. A precipitate which formed upon slow evaporation of the organic solvent was collected by filtration, washed with small amounts of water and EtOH and dried with Et_2O. The colour of the compounds ranges from pale yellow to yellow. Yield 80–85%.

$[TcN(S_2CO)L^1]$ (Found: C, 55.25; H, 4.90; N, 3.95; S, 9.30; Tc, 15.10. $C_{32}H_{35}N_2OP_2S_2Tc$ requires C, 55.80; H, 5.10; N, 4.10; S, 9.30; Tc, 14.40%); ν(C=O) 1607, 1694, $\nu(Tc{\equiv}N)$ 1051, ν(C–S) 847 cm^{-1} (KBr). $\delta_H(CD_2Cl_2)$ 2.65–2.25 (8 H, m, NCH_2CH_2P), 1.25 (4 H, q, $NC\mathit{H}_2C\mathit{H}_2CH_3$) and 0.70 (3 H, m, $NCH_2CH_2C\mathit{H}_3$).

$[TcN(S_2CO)L^2]$ (Found: C, 52.70; H, 4.70; N, 1.90; S, 8.85; Tc, 13.85. $C_{31}H_{32}NO_3P_2S_2Tc$ requires C, 53.80; H, 4.70; N, 2.00; S, 9.25; Tc, 14.30%); $\nu(Tc{\equiv}N)$(?) 1061, ν(C=O) 1607, 1686, ν(C–S) 840 cm^{-1} (KBr). $\delta_H(CD_2Cl_2)$ 3.80–2.30 (12 H, m, CH_2CH_2).

$[TcN(S_2CO)L^3]$ (Found: C, 60.00; H, 4.70; N, 1.60; S, 7.35; Tc, 11.00. $C_{42}H_{39}NOP_3S_2Tc$ requires C, 60.80; H, 4.75; N, 1.70; S, 7.70; Tc, 11.95%); $\nu(Tc{\equiv}N)$(?) 1070, ν(C=O) 1611–1688, ν(C–S) 835 cm^{-1} (KBr).

$[TcN(S_2CNEt_2)L^1][BPh_4]$ (Found: C, 67.60; H, 6.20; N, 3.90; S, 6.30; Tc, 8.70. $C_{60}H_{65}BN_3P_2S_2Tc$ requires C, 67.70; H, 6.15; N, 3.95; S, 6.00; Tc, 9.30%); $\nu(Tc{\equiv}N)$ 1059, ν(C–S) 845, 1277 cm^{-1} (KBr). $\delta_H(CD_2Cl_2)$ 4.00–3.45 (4 H, m, $CH_3C\mathit{H}_2$, S_2CNEt_2), 3.00–2.70 (8 H, m, CH_2CH_2), 1.30–1.15 (6 H, m, $C\mathit{H}_3CH_2$, S_2CNEt_2), 1.25 (4 H, q, NCH_2CH_2) and 0.70 (3 H, m, $NCH_2C\mathit{H}_3$).

$[TcN(S_2CNEt_2)L^2][BPh_4]$ (Found: C, 66.30; H, 5.90; N, 2.70; S, 6.20; Tc, 9.00. $C_{59}H_{62}BN_2O_2P_2S_2Tc$ requires C, 66.40; H, 5.85; N, 2.60; S, 6.00; Tc, 9.30%); $\nu(Tc{\equiv}N)$(?) 1070, ν(C–S) 842, 1285 cm^{-1} (KBr). $\delta_H(CD_2Cl_2)$ 3.60–2.45 (12 H, m, CH_2CH_2), 3.90–3.35 (4 H, m, $NC\mathit{H}_2CH_3$) and 1.35–1.05 (6 H, m, $NCH_2C\mathit{H}_3$).

$[TcN(S_2CNEt_2)L^3][BPh_4]$ (Found: C, 69.60; H, 5.70; N, 2.25; S, 5.05; Tc, 7.85. $C_{70}H_{69}BN_2P_3S_2Tc$ requires C, 69.75; H, 5.80; N, 2.30; S, 5.30; Tc, 8.20%); ν(C–S) 845, 1277 cm^{-1} (KBr). $\delta_H(CDCl_3)$ 3.30–2.30 (6 H, m, CH_2), 3.80–3.40 (4 H, m, $C\mathit{H}_2CH_3$) and 1.40–1.00 (9 H, m, $CH_2C\mathit{H}_3$).

Crystallography.—*Crystal data.* $C_{30}H_{32}Cl_2NO_2P_2Tc$ **1**, M = 670.45, orthorhombic, space group $Fdd2$ (no. 43), a = 28.714(7), b = 23.915(5), c = 8.779(2) Å, U = 6028(2) Å^3 (by least-squares refinement on diffractometer angles for 25 automatically-centred reflections, in the range $9 < \theta < 12$, λ = 0.710 69 Å), Z = 8, D_c = 1.47 g cm^{-3}, μ = 7.8 cm^{-1}, F(000) = 2736, crystal dimensions 0.24 × 0.33 × 0.40 mm.

$C_{31}H_{35}Cl_2N_2P_2Tc$ **2**, M = 667.49, orthorhombic, space group $Pna2_1$ (no. 33), a = 11.650(3), b = 23.570(2), c = 13.003(2) Å, U = 3570(1) Å^3 (by least-squares refinement on diffractometer angles for 25 automatically-centred reflections in the range $8 < \theta < 12$, λ = 0.710 69 Å), Z = 4, D_c = 1.24 g cm^{-3}, μ = 6.52 cm^{-1}, F(000) = 1368, crystal dimensions 0.14 × 0.17 × 0.50 mm.

Data collection and processing. CAD4 diffractometer, ω–2θ scan mode, graphite-monochromated Mo-Kα radiation: compound **1**, 2947 unique reflections measured ($2 \leqslant \theta \leqslant 28$), giving 1765 with $I \geqslant 3\sigma(I)$, corrected for Lorentz, polarization and absorption (minimum transmission factor 0.89); compound **2**, 4479 unique reflections measured ($2 \leqslant \theta \leqslant 28$), giving 2168 with $I \geqslant 3\sigma(I)$, corrected for Lorentz, polarization and absorption (minimum transmission factor 0.98) effects.

Structure analysis and refinement. Solution by Patterson and Fourier methods. For compound **1**, full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and hydrogens isotropic. The weighting scheme $w = 4F_o^2/[\sigma^2(F_o^2) + (0.05F_o^2)^2]$ gave satisfactory agreement analyses. Final R =

Table 1 Fractional coordinates for compound **1** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Tc	0	0	0
Cl	0.071 86(3)	0.043 17(3)	−0.068 9(1)
P	0.040 51(2)	−0.091 20(3)	−0.008 7(1)
N	0	0	0.182 4(4)
O	0.031 0(1)	−0.043 1(1)	−0.328 6(3)
C(1)	0.074 6(1)	−0.105 6(1)	−0.180 2(4)
C(2)	0.046 2(1)	−0.098 9(2)	−0.324 0(5)
C(3)	0.004 9(2)	−0.030 3(2)	−0.459 9(4)
C(4)	0.003 0(1)	−0.152 1(1)	0.019 3(4)
C(5)	0.003 4(1)	−0.198 5(2)	−0.074 0(5)
C(6)	−0.026 8(2)	−0.242 5(2)	−0.048 7(7)
C(7)	−0.057 4(2)	−0.240 7(2)	0.072 3(7)
C(8)	−0.057 2(1)	−0.195 6(2)	0.166 2(6)
C(9)	−0.028 0(1)	−0.150 9(2)	0.139 6(5)
C(10)	0.083 4(1)	−0.099 2(1)	0.143 9(4)
C(11)	0.098 5(1)	−0.152 7(1)	0.185 3(6)
C(12)	0.130 4(1)	−0.160 0(2)	0.303 4(7)
C(13)	0.148 4(1)	−0.115 1(2)	0.375 4(5)
C(14)	0.133 9(1)	−0.062 1(2)	0.335 9(5)
C(15)	0.101 4(1)	−0.054 4(1)	0.221 3(4)

Table 2 Fractional coordinates for compound **2** with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Tc	0.234 14(8)	0.070 43(5)	0	C(13)	0.132 8(16)	0.083 8(8)	−0.347 5(14)
Cl(1)	0.064 1(3)	0.048 0(2)	0.100 2(3)	C(14)	−0.028 6(12)	0.126 4(7)	−0.110 6(13)
Cl(2)	0.336 2(4)	0.020 6(2)	0.133 1(4)	C(15)	−0.123 2(14)	0.120 4(11)	−0.177 3(18)
P(1)	0.097 2(3)	0.081 8(2)	−0.136 4(3)	C(16)	−0.216 5(13)	0.158 4(9)	−0.154 8(18)
P(2)	0.404 4(3)	0.061 6(2)	−0.105 4(4)	C(17)	−0.217 9(17)	0.199 4(10)	−0.080 6(21)
N(1)	0.254 1(9)	0.137 2(5)	0.012 8(14)	C(18)	−0.122 8(16)	0.202 6(9)	−0.016 6(19)
N(2)	0.215 4(10)	−0.034 0(5)	−0.083 9(11)	C(19)	−0.026 6(14)	0.166 6(8)	−0.033 8(15)
C(1)	0.042 2(13)	0.011 1(8)	−0.160 3(13)	C(20)	0.441 8(12)	0.116 1(7)	−0.202 7(13)
C(2)	0.136 0(16)	−0.030 7(8)	−0.175 5(13)	C(21)	0.448 7(13)	0.170 5(6)	−0.172 0(13)
C(3)	0.333 1(15)	−0.051 7(8)	−0.114 8(16)	C(22)	0.488 3(13)	0.212 2(8)	−0.239 4(16)
C(4)	0.395 5(14)	−0.003 7(8)	−0.174 6(17)	C(23)	0.515 4(14)	0.196 7(8)	−0.337 9(15)
C(5)	0.172 1(12)	−0.074 4(7)	−0.001 8(19)	C(24)	0.506 8(16)	0.144 9(10)	−0.370 5(15)
C(6)	0.171 9(19)	−0.136 0(10)	−0.037 6(22)	C(25)	0.469 1(14)	0.101 9(8)	−0.300 4(15)
C(7)	0.134 0(22)	−0.176 2(10)	0.046 7(21)	C(26)	0.539 3(12)	0.061 2(8)	−0.031 7(13)
C(8)	0.143 9(11)	0.111 4(7)	−0.260 3(12)	C(27)	0.553 8(17)	0.097 2(12)	0.050 0(17)
C(9)	0.186 8(12)	0.165 8(6)	−0.260 3(12)	C(28)	0.659 2(16)	0.102 4(13)	0.096 8(18)
C(10)	0.218 1(15)	0.190 6(8)	−0.343 9(16)	C(29)	0.744 5(15)	0.077 2(15)	0.076 4(24)
C(11)	0.208 3(16)	0.161 6(9)	−0.438 3(14)	C(30)	0.737 4(15)	0.038 0(10)	−0.001 8(28)
C(12)	0.164 2(18)	0.108 2(10)	−0.441 0(14)	C(31)	0.632 5(15)	0.028 4(11)	−0.062 2(22)

Table 3 Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses for compounds **1** and **2**

Compound **1**			
Tc–Cl	2.385(1)	C(1)–C(2)	1.511(5)
Tc–P	2.4730(8)	C(2)–O	1.405(5)
Tc–N	1.601(4)	C(3)–O	1.409(5)
P–C(1)	1.828(3)	C(3)–C(3′)	1.467(7)
Cl–Tc–P	88.11(3)	Tc–P–C(1)	116.3(1)
Cl–Tc–Cl′	150.62(4)	P–C(1)–C(2)	112.3(2)
Cl–Tc–P′	90.99(4)	C(1)–C(2)–O	107.0(3)
Cl–Tc–N	104.69(8)	C(2)–O–C(3)	113.3(3)
P–Tc–P′	176.46(4)	O–C(3)–C(3′)	108.4(3)
P–Tc–N	91.77(8)		
Compound **2**			
Tc–Cl(1)	2.429(4)	P(2)–C(4)	1.79(2)
Tc–Cl(2)	2.406(5)	C(1)–C(2)	1.48(2)
Tc–P(1)	2.401(4)	N(2)–C(2)	1.51(2)
Tc–P(2)	2.420(4)	N(2)–C(3)	1.49(2)
Tc–N(1)	1.60(1)	C(3)–C(4)	1.55(3)
P(1)–C(1)	1.81(2)		
Cl(1)–Tc–Cl(2)	84.9(2)	P(2)–Tc–N(1)	91.4(4)
Cl(1)–Tc–P(1)	83.0(1)	Tc–P(1)–C(1)	105.0(6)
Cl(1)–Tc–P(2)	162.4(2)	Tc–P(2)–C(4)	108.2(6)
Cl(1)–Tc–N(1)	106.1(4)	P(1)–C(1)–C(2)	112(1)
Cl(2)–Tc–P(1)	156.1(2)	C(1)–C(2)–N(2)	112(1)
Cl(2)–Tc–P(2)	87.7(2)	C(2)–N(2)–C(3)	111(1)
Cl(2)–Tc–N(1)	109.5(5)	N(2)–C(3)–C(4)	111(1)
P(1)–Tc–P(2)	97.8(2)	P(2)–C(4)–C(3)	114(1)
P(1)–Tc–N(1)	93.6(5)		

0.022 and $R' = 0.027$. Goodness of fit = 1.02. Final difference map peaks in the range −0.30 to +0.44 e Å^{-3}. Final atomic coordinates are given in Table 1 and a selection of bond distances and angles in Table 3. For compound **2**, full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and hydrogens in calculated positions. The weighting scheme $w = 4F_o^2/[\sigma^2(F_o^2) + (0.08F_o^2)^2]$ gave satisfactory agreement analyses. Final $R = 0.064$ and $R' = 0.083$. Goodness of fit = 1.48. Final difference map peaks in the range −0.55 to +0.88 e Å^{-3}. Final atomic coordinates are given in Table 2 and a selection of bond distances and angles in Table 3. Programs used and sources of scattering data are given in ref. 31 and the structures were drawn using ORTEP.[32]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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