Technetium Diazenido Complexes. Part 1. Syntheses and Structures of [$TcCl(NNC_6H_4Cl\text{-}4)_2(PPh_3)_2$] and [$TcCl(NNPh)(Ph_2PCH_2CH_2PPh_2)_2$][$PF_6$]·$H_2O$†

Colin M. Archer,[a] Jonathan R. Dilworth,*,[a] Panna Jobanputra,[a] Russell M. Thompson,[a] Mary McPartlin[b] and Wolfgang Hiller[c]

[a] *Department of Chemistry and Biological Chemistry, University of Essex, Wivenhoe Park, Colchester, Essex CO4 3SQ, UK*

[b] *School of Chemistry, University of North London, Holloway Road, London N7 8DB, UK*

[c] *Anorganische Chemisches Institut, Technische Universitat Munich, Chemiegebaude, Lichtenburger Str. 4, D-8048, Garching, Germany*

Reaction of [NBu_4][$TcOCl_4$] with monosubstituted organohydrazines $RNHNH_2$ (R = aryl) in methanol leads to red solutions of technetium diazenido species. These species may be derivatised with the monotertiary phosphine PPh_3 to give the khaki to orange bis(diazenido) complexes [$TcCl(NNR)_2(PPh_3)_2$] (R = Ph **1**, C_6H_4Cl-4 **2** or C_6H_4Me-4 **3**) and the lime-green monodiazenido complex [$TcCl_2(NNC_6H_4NO_2\text{-}4)(PPh_3)_2$] **4**. These triphenylphosphine derivatives are also easily prepared directly from [NH_4][TcO_4]. An X-ray crystal structure of one of the bis(diazenido) complexes [$TcCl(NNC_6H_4Cl\text{-}4)_2(PPh_3)_2$] shows the Tc to be trigonal bipyramidal with axial PPh_3 ligands. Derivatisation of the red technetium diazenido containing solutions with the bidentate ditertiary phosphine ligand $Ph_2PCH_2CH_2PPh_2$ (dppe) gives the orange cationic complexes [$TcCl(NNR)(dppe)_2$]$^+$ (R = Ph **5**, C_6H_4Cl-4 **6** or $C_6H_4NO_2$-4 **7**) isolated as hexafluorophosphate or tetraphenylborate salts in good yield. These cationic monodiazenido complexes may also be prepared by substitution reactions of complexes **1**–**4** with dppe, or directly from [NH_4][TcO_4]. X-Ray structure details for **5**: monoclinic, space group *C*2/*c* with $Z = 4$ in a unit cell of dimensions $a = 23.808(5)$, $b = 13.830(3)$, $c = 17.452(4)$ Å, $\beta = 92.53(2)°$. Complex **5** has slightly distorted *trans* octahedral geometry with two co-ordinated dppe ligands surrounding both axial phenyldiazenido and chloride ligands. The angle at the α nitrogen Tc–N(1)–N(2) is 163(2)° with Tc–N(1) 1.917(19) and N(1)–N(2) 1.25(4) Å. The phenyldiazenido(1−) ligand therefore bonds formally as a singly bent three-electron donor giving complex **5** an overall valence electron count of eighteen. A most important development of this work is that these technetium complexes are directly accessible from ammonium pertechnetate [NH_4][TcO_4], the chemical form of technetium used in preparation of radiopharmaceuticals.

We are currently exploring the chemistry of complexes of technetium containing technetium–nitrogen multiple bonds.[1] Our interests arise not only from the importance of technetium chemistry in the radiopharmaceuticals industry, but also as part of a program to explore the similarities and differences between such technetium complexes and the already well known rhenium, molybdenum and tungsten complexes. Recent publications explored the chemistry of technetium–nitrido (Tc≡N),[1c] -hydrazido(2−) (Tc=NNR) (R = alkyl or aryl)[1d] and -imido complexes (Tc=NR)[1e] (R = aryl). Here we present our initial efforts towards the elucidation of the chemistry of technetium complexes containing diazenido ligands, Tc–N=NR (R = aryl). Parts of this work have have communicated previously,[1b] and the syntheses of [$TcCl(NNR)_2(PPh_3)_2$] (R = aryl) has also been independently reported during the preparation of this paper.[2] In the work presented herein the high-yield syntheses of complexes containing bis- and mono-diazenido cores are reported from the common starting material [NBu_4][$TcOCl_4$] *and* directly from [NH_4][TcO_4], the chemical form of technetium used in radiopharmaceutical synthesis. We also report the crystal structure determinations of examples of a bis- and a mono-diazenido-complex of technetium.

Results and Discussion

The most straightforward method for the synthesis of transition-metal diazenido complexes is the reaction of a monosubstituted organohydrazine with a high-valent metal halogeno or metal oxo precursor.[3] In particular the synthesis of rhenium diazenido complexes is easily achieved by this route.[4] One readily available class of rhenium diazenido complexes is of the type [$ReCl(NNR)_2(PPh_3)_2$] (R = aryl). These complexes are easily prepared by the reaction of [$ReOCl_3(PPh_3)_2$] with an excess of a monosubstituted arylhydrazine in the presence of PPh_3 in alcohol under reflux [equation (1)]. The organodiazenido metal core is a robust functional unit synthetically accessible through a condensation type reaction to yield intermediate complexes of type M=N–NHR which then give the organodiazenido core MNNR *via* an internal redox step which removes the remaining H atom.

$$[ReOCl_3(PPh_3)_2] + RNHNH_2\ (\text{excess}) \xrightarrow[\text{heat}]{\text{MeOH, PPh}_3} [ReCl(NNR)_2(PPh_3)_2] \qquad (1)$$

These rhenium bis(diazenido) complexes [$ReX(NNR)_2(PPh_3)_2$] (X = Cl or Br) are known to undergo facile protonation at the β nitrogen of one of the -NNR units on treatment with HX (X = Cl or Br) to yield the corresponding rhenium diazenido–hydrazido(2−) complexes [$ReX_2(NNR)(NNHR)(PPh_3)_2$].[5]

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

The reaction of $[NBu_4][TcOCl_4]$ in dry methanol at room temperature with an excess of phenylhydrazine gives a deep red reaction solution. The addition of an excess of triphenylphosphine to the reaction mixture yields the insoluble khaki-green complex formulated as $[TcCl(NNPh)_2(PPh_3)_2]$ **1**. The complex precipitates from the methanol solution and is practically insoluble in most organic solvents. It is however, partially soluble in CH_2Cl_2 and $CHCl_3$, and high performance liquid chromatography (HPLC) analysis (β^- particle detection) confirms it as a single species. Complex **1** exhibits a single resonance at δ 29.3 in its $^{31}P-\{^1H\}$ NMR spectrum. The infrared spectrum of **1** contains bands at 1601, 1543 and 1475 cm^{-1} which may be assigned to the diazenido ligands. There are no infrared bands in the 3000–3500 cm^{-1} region assignable to ν(N–H). The ^1H NMR spectrum of the sparingly soluble product shows no evidence of protonation of the co-ordinated diazenido residues. Complex **1** could not be satisfactorily recrystallised owing to its poor solubility. This unsubstituted phenyldiazenido complex thus appears to be dimeric or even polymeric, possibly with chloro bridges and perhaps should be more correctly formulated as $[\{TcCl(NNPh)_2(PPh_3)_2\}_n]$. In any case it is not a particularly convenient starting material with which to investigate substitution chemistry. The formation of a halogeno-bridged structure requires one of the diazenido ligands to be doubly bent for the metal to conform to the eighteen-electron role. However, the observed infrared spectra are not sufficient to determine the geometry of the diazenido ligands.

Use of 4-substituted hydrazine hydrochlorides $4\text{-}XC_6H_4NHNH_2\cdot HCl$ (X = Cl or Me) has led to the preparation of the analogous bis(diazenido) complexes $[TcCl(NNC_6H_4X\text{-}4)_2(PPh_3)_2]$ (X = Cl **2** or Me **3**) from $[NBu_4][TcOCl_4]$. These air-stable orange crystalline solids are reasonably soluble and consequently are much superior starting materials than **1**. Compound **2** in particular has proved to be the most suitable for a systematic investigation of the substitution chemistry of technetium bis(diazenido) complexes, giving relatively clean products on reaction with the appropriate ligands.[6] The crystal structure of **2** has been determined.

The bis(diazenido) complexes $[TcCl(NNR)_2(PPh_3)_2]$ can also be synthesised directly from $[NH_4][TcO_4]$ in high yield. Reaction of $[NH_4][TcO_4]$ with $4\text{-}ClC_6H_4NHNH_2\cdot HCl$ and PPh_3 in dry methanol under reflux gives a good (60–70%) yield of **2**. This exciting result suggests that all TcNNR complexes may be synthesised in good yield directly from pertechnetate, the chemical form of technetium used in the preparation of radiopharmaceuticals.

The addition of the bidentate ditertiary phosphine 1,2-bis(diphenylphosphino)ethane (dppe) to the red reaction mixtures generated from $PhNHNH_2$ and $[NBu_4][TcOCl_4]$, or $PhNHNH_2$ and $[NH_4][TcO_4]\cdot HCl$, in methanol gives the orange cationic product $[TcCl(NNPh)(dppe)_2]^+$ **5** isolated as its hexafluorophosphate salt. This cation is diamagnetic and sharply defined ^1H NMR spectra are obtained for this complex. This shows two equivalent doublets at δ 5.60 (J = 8) and 6.66 (J = 8 Hz). Decoupling experiments demonstrated that these two protons are not coupled to each other and therefore these resonances are assigned to the two *ortho*-phenyl protons of the single diazenido ligand. The room-temperature $^{31}P-\{^1H\}$ NMR spectrum of **5** exhibits a broad signal ($w_{\frac{1}{2}} \approx 300$ Hz) at δ 38. The signal sharpens at lower temperatures and at 243 K a single slightly broadened peak is observed ($w_{\frac{1}{2}} = 30$ Hz). This phenomenon has been observed with technetium complexes previously and is due to quadrupolar relaxation interactions of the P-donor atoms with the ^{99}Tc nucleus ($I = \frac{9}{2}$). No ν(NH) band is observed in the infrared spectrum of this complex nor is NH evident in the ^1H NMR spectrum indicating that the complex does not contain a hydrazido(2–) ligand (Tc=N–NHPh). A band at 1680 cm^{-1} is assigned to ν(NN) of the diazenido ligand. The crystal structure of the hexafluorophosphate salt of **5** has been determined. Complexes of the type $[TcCl(NNR)(dppe)_2]^+$ may also be prepared either directly from $[NH_4][TcO_4]$ and the appropriate hydrazine or by substitution of the bis(diazenido) starting materials $[TcCl(NNR)_2(PPh_3)_2]$. Thus reaction of **2** with an excess of dppe in methanol–toluene under reflux leads to pure orange crystalline $[TcCl(NNC_6H_4Cl\text{-}4)(dppe)_2]^+$ **6** isolated as hexafluorophosphate or tetraphenylborate salts. However, complex **6** is also more conveniently prepared in high yield directly from $[NH_4][TcO_4]$, $4\text{-}ClC_6H_4NHNH_2\cdot HCl$, and dppe in methanol under reflux. The routes to technetium diazenido complexes are thus quite versatile. Reaction of the bis(diazenido) complex **2** to give the monodiazenido complex **6** suggests that one of the hydrazine derived ligands is much more labile than the other, and is lost upon reaction with the sterically demanding dppe ligand. In order to investigate this and to elucidate the validity of both $[Tc(NNR)_2]^+$ and $[Tc(NNR)]^{2+}$ as new cores for the development of technetium-based radiopharmaceutical products it was felt necessary to investigate the lability of the –NNR unit on reaction with other ligands. Detailed HPLC experiments (β^- detection) were performed to see if a bis(diazenido) intermediate was formed in the preparation of the cation $[TcCl(NNC_6H_4Cl\text{-}4)(dppe)_2]^+$ **6** (retention time 14 min) from the $[TcCl(NNC_6H_4Cl\text{-}4)_2(PPh_3)_2]$ **2** starting material (retention time 9.4 min). The HPLC results showed that the cation formed after only 15 min stirring at room temperature, and that no other technetium-containing intermediate was detected. This proves that one –NNR moiety is very labile, and is easily lost in solution at room temperature in the presence of an appropriate ligand, to give the monodiazenido complex. The facile protonation chemistry of these technetium bis(diazenido) species observed previously is probably a preliminary process leading to the eventual loss of one –NNR unit.[2]

In contrast to this behaviour, the bis(aryldiazenido) cores of molybdenum, $[Mo(NNR)_2]^{2+}$ and rhenium, $[Re(NNR)_2]^+$ are considerably more robust moieties than that of $[Tc(NNR)_2]^+$ to further ligand substitution reactions.

Complexes $[ReCl(NNR)_2(PPh_3)_2]$ (R = aryl) undergo substitution upon treatment with an excess of dppe in methanol under reflux to yield the novel formally twenty-electron *trans*-bis(diazenido) complex $[Re^{III}(NNR)_2(dppe)_2]^+$ with retention of both multiply bonded nitrogen containing ligands.[7]

The *cis* bis(diazenido) molybdenum unit, $[Mo(NNR)]^{2+}$ is also a chemically robust core that persists in a variety of solvents and synthetic conditions and even provides a nucleus for aggregation in cluster formation.[3] However, both of these cores may also undergo considerable chemistry such as protonation, alkylation or N–N bond cleavage, leading to a variety of products.[3]

The preparation of technetium–diazenido complexes containing more reducing alkyl-substituted tertiary phosphines proved to be much more elusive. Reaction of **2** with $Me_2PCH_2CH_2PMe_2$ (dmpe) in methanol under reflux led to the isolation of a pale pink complex (HPLC retention time 10 min, single species) containing no nitrogen. This product could not be isolated in pure form, but is tentatively formulated as $[Tc^I(dmpe)_3][BPh_4]$. The analogous reaction under less forcing conditions at room temperature was thought to lead to the desired cation $[TcCl(NNC_6H_4Cl\text{-}4)(dmpe)_2]^+$ isolated as its hexafluorophosphate salt (retention time 9.6 min, single species). However, this product could not be isolated in pure form. Similar attempts to substitute **1** and **3** with both dppe and dmpe did not give clean products. Substitution reactions of complexes **2** and **3** with an excess of the less sterically bulky monotertiary phosphines PMe_2Ph or $PMePh_2$ gave single species in solution (HPLC). However, high solubility precluded further work-up of these apparently cationic species. Direct reaction of $[NBu_4][TcOCl_4]$, hydrazine, and the appropriate phosphine also led to these highly soluble species.

Reaction of $4\text{-}O_2NC_6H_4NHNH_2$ with $[NBu_4][TcOCl_4]$ and PPh_3 in methanol led to the isolation of the lime-green technetium(III) monodiazenido complex $[TcCl_2(NNC_6H_4NO_2\text{-}4)(PPh_3)_2]$ **4** in very good yield. Apparently a bis(diazenido)

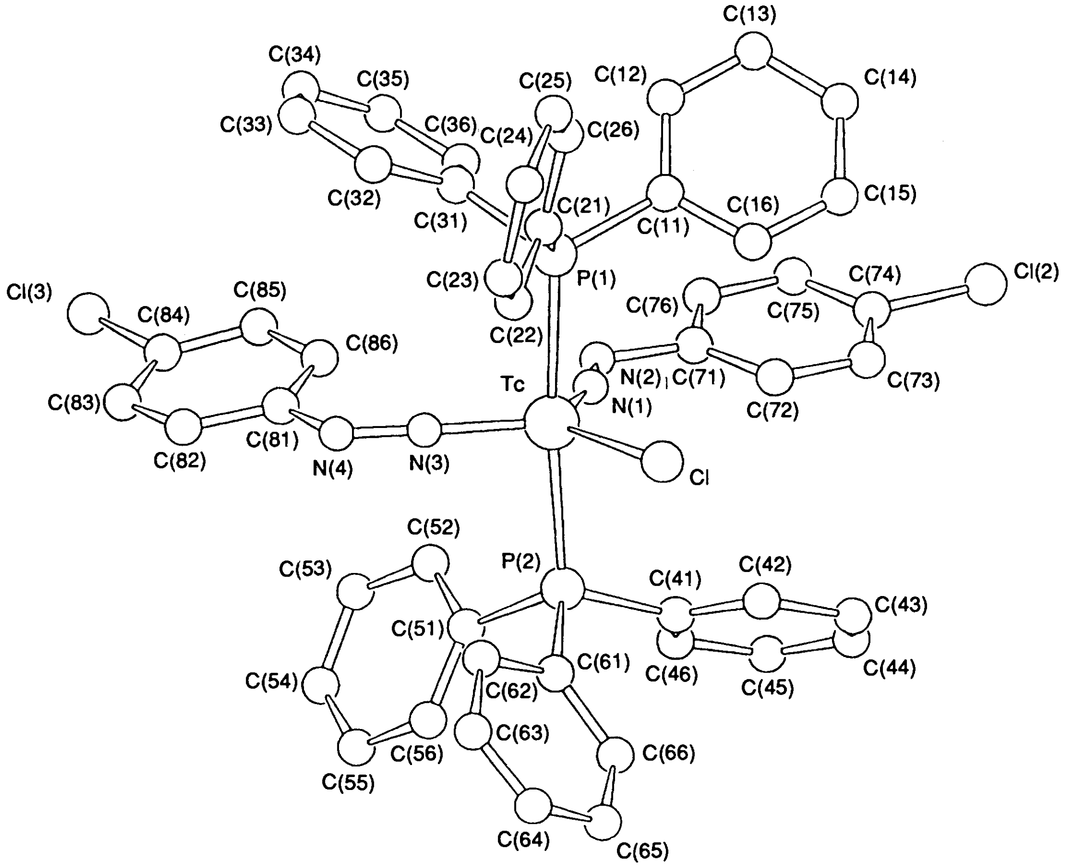

Fig. 1 A representation of the molecular structure of $[TcCl(NNC_6H_4Cl\text{-}4)_2(PPh_3)_2]$ **2**

Table 1 Selected bond lengths (Å) and bond angles (°) for $[TcCl(NNPh)(dppe)_2][PF_6]\cdot H_2O$ **5**

Tc–Cl	2.342(8)	Tc–N(1)	1.917(19)
Tc–P(1)	2.460(4)	Tc–P(2)	2.506(4)
N(1)–N(2)	1.25(4)	N(2)–C(201)	1.29(3)
C(201)–C(202)	1.395	C(201)–C(206)	1.395
C(202)–C(203)	1.395	C(203)–C(204)	1.395
C(204)–C(205)	1.395	C(205)–C(206)	1.395
N(1)–Tc–Cl	177.3(6)	P(1)–Tc–Cl	85.3(2)
P(1)–Tc–N(1)	92.6(6)	P(2)–Tc–Cl	90.2(2)
P(2)–Tc–N(1)	91.1(6)	P(2)–Tc–P(1)	81.5(1)
N(2)–N(1)–Tc	163(2)	C(201)–N(2)–N(1)	130(3)
C(202)–C(201)–N(2)	117(2)	C(206)–C(201)–N(2)	122(2)

complex is not formed from reaction of this 4-nitro-substituted phenylhydrazine. Complex **4** promises to be a useful starting material for the preparation of a variety of monodiazenido complexes as it has two potentially replaceable chloride ligands. In the presence of an excess of dppe in methanol–toluene under reflux, complex **4** gives the orange crystalline $[TcCl(NNC_6H_4\text{-}NO_2\text{-}4)(dppe)_2]^+$ **7** isolated as its tetraphenylborate salt in high yield.

Description of the Molecular Structure of Complex **2**.—The crystal and molecular structure of **2** is essentially identical to that of the previously structurally determined complex $[TcCl(NNC_6H_4Br\text{-}4)_2(PPh_3)_2]$[2] and thus will only be discussed briefly and the crystallographic data are not included. A representation of the structure of complex **2** is given in Fig. 1. The co-ordination sphere contains mutually *trans* PPh_3 ligands in the axial positions of a trigonal bipyramid with the chloride and *cis* aryldiazenido ligands occupying the equatorial positions. The $-NNC_6H_4Cl\text{-}4$ moieties exhibit essentially linear M–N–N angles and bond lengths which suggest extensive delocalisation and multiple bonding throughout the moieties with significant metal-to-metal back bonding. An observation confirming this is the virtual planarity of the entire $Tc\text{–}NNC_6H_4Cl\text{-}4$ unit. The diazenido ligands adopt singly bent geometry and are formally three-electron donors giving complexes of the type $[TcCl(NNR)_2(PPh_3)_2]$ a formal valence electron count of eighteen.

Description of the Molecular Structure of Complex **5**.—The X-ray single-crystal analysis of **5** confirms the formulation as $[TcCl(NNPh)(dppe)_2][PF_6]$ and the complex cation has the structure illustrated in Fig. 2. One molecule of water of crystallisation is also present. Selected bond lengths and interbond angles for **5** are given in Table 1 and atomic coordinates in Table 2. The closest approaches of the complex cation and the anion are shown in Fig. 3.

The complex cation, $[TcCl(N_2Ph)(dppe)_2]^+$ **5**, has a slightly distorted *trans*-octahedral geometry (Fig. 2). As is usual in complexes with two bidentate ligands, the main deviation from regular co-ordination is a result of the steric requirements of the two symmetry-related five-membered chelate rings which in this structure have a P–Tc–P angle of 81.5(1)°. This is similar to the value of 80.8(1)° for the two symmetry-related P–Tc–P angles in the related complex $[TcBr_2(dppe)_2]^+$[8] and 80.6(3)° for those in $[TcCl(NO)(dppe)_2]Cl\cdot H_2O$.[9]

Computed space-filling models show that the co-ordinated dppe ligands provide a centrosymmetric envelope that surrounds both the axial phenyldiazenido (Fig. 4) and chloride ligands (Fig. 5). The phenyl ring of the former ligand protrudes only slightly above the protection of the bulky organophosphine ligands, giving a short intermolecular contact with a neighbouring complex cation [H(204) ··· H(14″) 2.10 Å]. As in the structure of $[TcCl(NO)(dppe)_2]^+$[9] crystal packing would

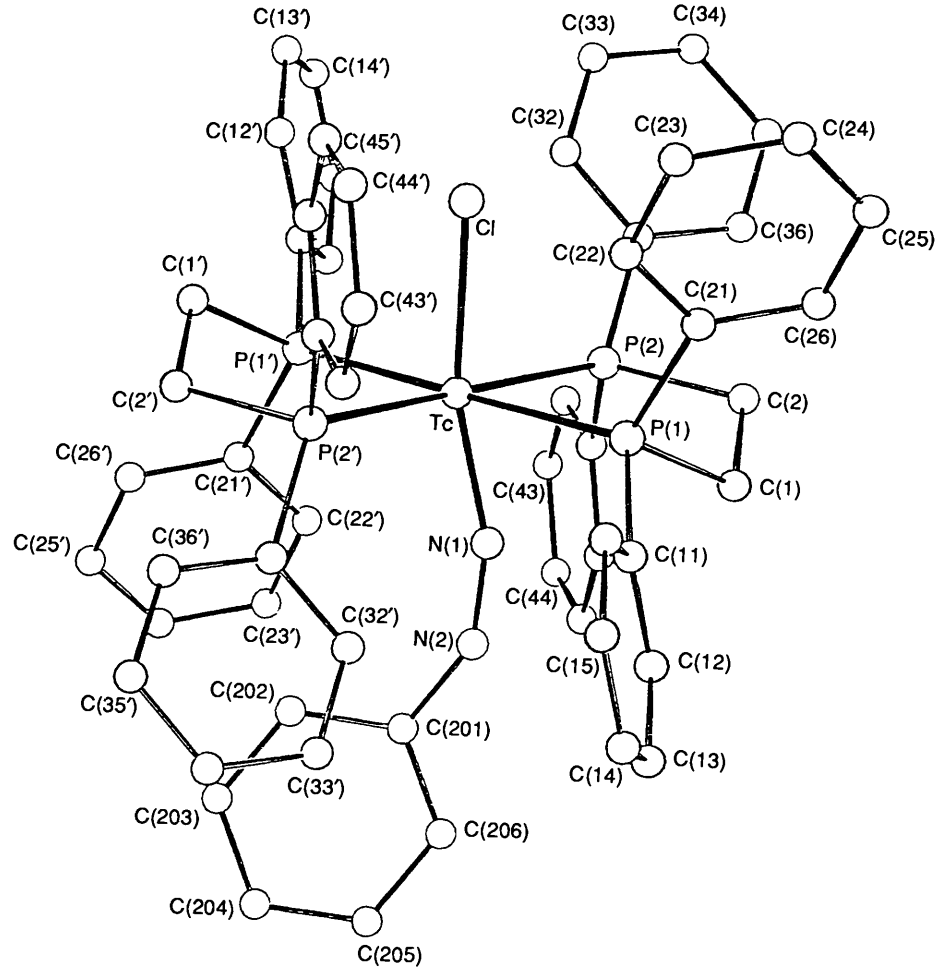

Fig. 2 A perspective view of the complex cation $[TcCl(NNPh)(dppe)_2]^+$ of **5** showing the numbering scheme used in the X-ray structural analysis

Table 2 Fractional atomic coordinates for $[TcCl(NNPh)(dppe)_2][PF_6]\cdot H_2O$ **5**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Tc	0.250 00	0.250 00	0.000 00	C(15)	0.138 1(4)	−0.041 7(7)	−0.185 7(5)
Cl	0.153 4(3)	0.272 7(6)	0.012 6(5)	C(16)	0.181 1(4)	0.024 7(7)	−0.169 6(5)
N(1)	0.328 3(8)	0.226 2(14)	−0.013 3(11)	C(21)	0.279 7(3)	0.166 0(6)	−0.195 6(5)
N(2)	0.380 6(13)	0.222 1(21)	−0.002 3(17)	C(22)	0.316 8(3)	0.095 9(6)	−0.166 1(5)
P(1)	0.224 4(2)	0.207 6(3)	−0.133 9(2)	C(23)	0.361 1(3)	0.064 1(6)	−0.209 4(5)
P(2)	0.257 6(2)	0.414 9(3)	−0.058 1(2)	C(24)	0.368 2(3)	0.102 5(6)	−0.282 2(5)
P(3)	0.500 2(6)	0.128 5(7)	0.275 9(6)	C(25)	0.331 2(3)	0.172 7(6)	−0.311 7(5)
F(1)	0.558 5(9)	0.121 4(16)	0.302 6(14)	C(26)	0.286 9(3)	0.204 4(6)	−0.268 4(5)
F(2)	0.498 8(12)	0.211 6(19)	0.327 2(16)	C(31)	0.321 6(4)	0.479 2(7)	−0.067 5(6)
F(3)	0.503 9(12)	0.031 0(16)	0.220 8(12)	C(32)	0.368 1(4)	0.461 7(7)	−0.018 0(6)
F(4)	0.515 8(12)	0.222 0(19)	0.223 3(15)	C(33)	0.416 8(4)	0.516 9(7)	−0.023 8(6)
F(5)	0.476 0(11)	0.073 7(19)	0.341 1(16)	C(34)	0.418 9(4)	0.589 6(7)	−0.079 0(6)
F(6)	0.438 5(10)	0.139 7(18)	0.259 4(14)	C(35)	0.372 4(4)	0.607 1(7)	−0.128 5(6)
C(201)	0.420 3(6)	0.228 5(11)	−0.050 2(9)	C(36)	0.323 7(4)	0.551 9(7)	−0.122 7(6)
C(202)	0.406 7(6)	0.270 6(11)	−0.121 2(9)	C(41)	0.212 6(4)	0.507 1(7)	−0.021 3(5)
C(203)	0.449 2(6)	0.294 8(11)	−0.170 4(9)	C(42)	0.234 7(4)	0.584 9(7)	0.020 9(5)
C(204)	0.505 2(6)	0.276 8(11)	−0.148 5(9)	C(43)	0.198 8(4)	0.651 2(7)	0.053 8(5)
C(205)	0.518 9(6)	0.234 6(11)	−0.077 5(9)	C(44)	0.140 7(4)	0.639 7(7)	0.044 4(5)
C(206)	0.476 4(6)	0.021 4(11)	−0.028 3(9)	C(45)	0.118 5(4)	0.561 9(7)	0.002 2(5)
C(11)	0.168 3(4)	0.122 1(7)	−0.159 0(5)	C(46)	0.154 4(4)	0.495 6(7)	−0.030 7(5)
C(12)	0.112 6(4)	0.153 1(7)	−0.164 7(5)	C(1)	0.196 4(7)	0.322 1(11)	−0.177 5(9)
C(13)	0.069 5(4)	0.086 7(7)	−0.180 8(5)	C(2)	0.236 1(7)	0.404 8(11)	−0.160 3(9)
C(14)	0.082 3(4)	−0.010 7(7)	−0.191 4(5)				

largely be determined by the organophosphine ligands, so that a random orientation of the cationic complex in the crystal might be expected; this is consistent with the disordered model adopted in the refinement. The space-filling models illustrate the very close contacts between a phenyl ring hydrogen atom and atoms of the axial ligands, [N(2) • • • H(46′) 2.51] and [Cl • • • H(46) 2.63 Å]. These distances are less than the sum of the respective van der Waals radii of the atoms involved (H, 1.2; N, 1.5; Cl, 1.8 Å), and that involving the chlorine atom may indicate some degree of hydrogen bonding. Similar very short

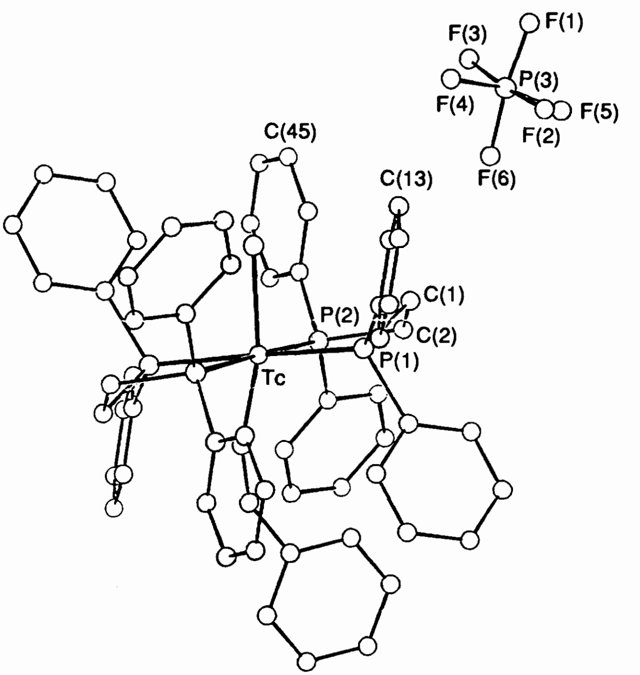

Fig. 3 A view of part of the crystal structure of complex **5** showing the relative orientation of the complex cation and the $[PF_6]^-$ anion

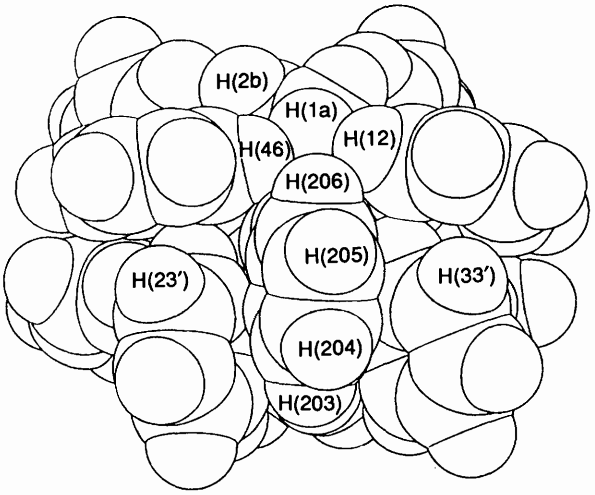

Fig. 4 A computed space-filling model of the complex cation $[TcCl(NNPh)(dppe)_2]^+$ of **5**, viewed onto one side of the co-ordination plane of the four phosphorus atoms, showing the envelopment of the diazenido ligand by the two bulky dppe ligands

contacts, between phenyl-ring H atoms and highly electronegative axial ligands, are present in the reported structures of $[TcBr_2(dppe)_2]^+$ [8] and $[TcCl(NO)(dppe)_2]^+$.[9]

The arrangement of the axial ligands is nearly linear [Cl-Tc-N(1) 177.3(6)°]. Due to the disorder, the parameters associated with these ligands have relatively highly estimated standard deviations, so that detailed discussion of their geometry is of limited value.

Organodiazenido ligands have been shown to adopt several different bonding modes in metal complexes with 'singly bent',[10] 'doubly bent'[11] and bridging[12] modes all common. In formal terms the singly bent mode may be regarded as 'isoelectronic' with the better known NO^+ ligand. The metal–nitrogen bond distance in **5** of 1.917(19) Å is significantly longer than the values of 1.75–1.80 Å normally found for transition-metal diazenido complexes.[3] This probably reflects the steric repulsion exerted by the bulky organodiphosphine ligands in the equatorial plane. In **5** the angle at the α nitrogen, Tc–N(1)–N(2) of 163(2)° is significantly different to the exactly linear value of 180°, but is very much larger than the value of 120° expected for a 'doubly bent' co-ordination. The diazenido ligand is thus formally singly bent indicating that it is acting as a three-electron donor, which confers an overall eighteen-electron valence shell configuration on the technetium in **5**. The Tc–N(1)–N(2) bond angle compares reasonably with the two slightly different Tc–N–N bond angles of 166.1(6) and 172.1(7)° for the formally linear singly bent $-NNC_6H_4Cl$-*p* ligands in the bis(diazenido) complex **2** determined in this work. In the structures of bis(organo-diazenido)rhenium complexes reported recently, $[Re(NNC_6H_4Br\text{-}4)_2(SC_6H_4Br\text{-}4)(PPh_3)_2]$ and $[Re(NNC_6H_4Br\text{-}4)_2Cl(PPh_3)_2]$, two different angles at the formally linear (singly bent) diazenido-α-nitrogen atom were observed [172(3) and 165(2)° for the former and 160.9(2) and 178.1(2)° for the latter[4d]]. Theoretical studies of metal carbonyl complexes show that the angle of the C atom would be exactly linear only in a perfectly symmetrical environment,[13] and in practice angles in the range 160–180° are observed for terminal CO ligands. The present Tc–N(1)–N(2) angle does not differ significantly from the Tc–N–O angle of 166(4)° in the closely analogous nitrosyl complex $[TcCl(NO)(dppe)_2]^+$.[9] In both these complexes a more 'bent' configuration of the N atom may be precluded by repulsive interactions with the surrounding phenyl rings of the organodiphosphine ligands (see above).

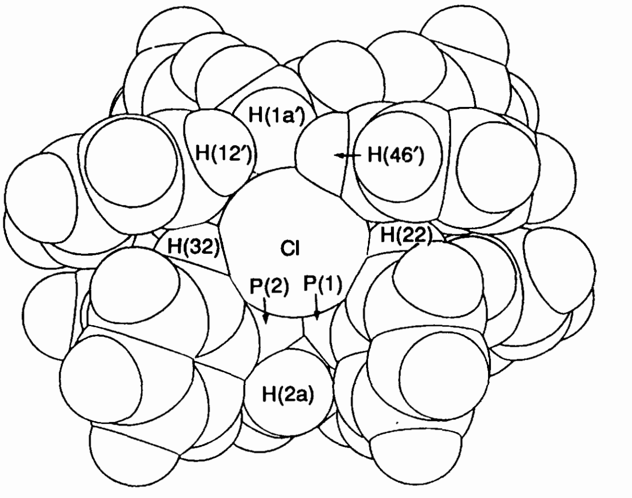

Fig. 5 A computed space-filling model of the complex cation $[TcCl(NNPh)(dppe)_2]^+$ of **5** viewed onto the second side of the co-ordination plane of the four phosphorus atoms, showing the envelopment of the chloride ligand by the two bulky dppe ligands

In the recently structurally characterised rhenium monodiazenido analogue, $[ReCl(NNC_6H_4Me\text{-}4)(dmpe)_2]^+$, the bond length of Re–N 1.784(5) Å and Re–N–N bond angle of 165.4(4)° are much more normal for the singly bent -NNR moiety.[7] In respect of this evidence it may be that the steric bulk of the two dppe ligands accounts for the extremely long Tc–N bond length in **5**. In fact this very long bond is much more like the observed metal–nitrogen bond lengths in the two recently structurally characterised formally twenty-electron *trans* bis(diazenido) rhenium cations $[Re(NNC_6H_4Me\text{-}4)_2(dppe)_2]^+$ [Re–N 1.908(2) Å and Re–N–N 162.7(2)°] and $[Re(NNC_6H_4Cl\text{-}4)_2(dmpe)_2]^+$ [Re–N 1.928(4) and 1.920(4) Å; Re–N–N 147.3(5) and 149.0(4)°].[7] These pseudo-octahedral complexes have *trans* bis -NNR moieties that may be functioning as less than three-electron donors in order to reduce the electron density at rhenium to eighteen. However, again steric effects cannot be ruled out.

The equivalent bond lengths in the two bidentate dppe ligands of **5** are equal by space-group symmetry. The two independent Tc–P lengths within each ligand are significantly different in length [Tc–P(1) 2.460(4), Tc–P(2) 2.506(4) Å]. The mean Tc–P length of 2.483(4) Å is shorter than that of 2.502 Å reported for the analogous dibromotechnetium(III) complex, $[TcBr_2(dppe)_2]^+$, in which the two chemically equivalent Tc–P bond lengths, within each of the symmetry related dppe ligands, were also significantly different [2.488(1) and 2.513 Å].[10] The differences in Tc–P lengths may arise from steric factors associated with the accommodation of the axial groups in the restricted space left by the bulky phenyl groups of the two organodiphosphine ligands. The mean Tc–P bond length in the related cationic complex $[TcCl(NO)(dppe)_2]^+$, in which a very similar disorder is observed, is 2.464(7) Å; although this appears rather shorter than that observed here, the difference is not significant due to the relatively high standard deviations obtained for the former structure.[9]

Conclusion

We have synthesised and characterised some new mono- and bis-diazenido complexes of technetium. These complexes show considerable promise as useful starting materials for a range of technetium diazenido complexes. Systematic substitution chemistry of these and related complexes with technetium–nitrogen multiple bonds are in progress to assess their potential for preparation of new diagnostic reagents.

Preliminary steps have also been taken towards derivatising the diazenido phenyl groups with functional substituents. These could be used to provide highly specific targeting properties or perhaps the covalent attachment of technetium complexes to biological materials.

Significantly, the synthesis of the technetium diazenido complexes has been successfully extrapolated to the ^{99m}Tc level used in radiopharmaceutical preparation, and this will be reported in detail elsewhere.[14]

Experimental

Technetium-99 Complexes.—**CAUTION**: Technetium-99 is a low-energy β^- particle emitter [292 keV ($\approx 4.67 \times 10^{-17}$ J, $t_{\frac{1}{2}} = 2.14 \times 10^5$ y). Normal radiation safety procedures were followed at all times. All manipulations of solutions and solids were performed in an efficient fumehood to prevent contamination and inadvertent inhalation. When handled in milligram quantities these compounds do not present a serious health hazard since common laboratory glassware provides adequate shielding. Bremsstrahlung radiation is not a significant problem due to the low energy of the β^- particle emission.

All reactions were performed under an atmosphere of dinitrogen using predried, distilled solvents unless noted otherwise. The salt $[NBu_4][TcOCl_4]$ was prepared by the literature procedure.[15] All other reagents used were obtained from commercial sources and used as received. Solutions of 0.343 mmol dm^{-3} $[NH_4][TcO_4]$ in 0.1 mol dm^{-3} aqueous ammonia were obtained from Amersham.

Infrared spectra were recorded as Nujol mulls (KBr) on a Perkin Elmer 257 spectrometer, NMR spectra on a Bruker WP-80 spectrometer with synthesiser frequencies of 80.13 and 32.44 MHz for ^{1}H and ^{31}P, respectively. Elemental analyses were performed by Butterworth Laboratories Ltd., Teddington, Middlesex.

Preparation of the Diazenido Complexes.—$(Tc(NNPh)_2Cl(PPh_3)_2]$ **1**. The complex $[NBu_4][TcOCl_4]$ (0.070 g, 0.14 mmol), $PhNHNH_2$ (0.60 cm^3, 6.1 mmol) and PPh_3 (0.222 g, 0.88 mmol) in methanol (5 cm^3) were stirred under reflux for 1 h. After cooling to room temperature overnight the resultant yellow-gold precipitate was collected by filtration, washed with methanol (5 cm^3) and diethyl ether (10 cm^3) and then dried *in vacuo* to give **1** (yield 0.094 g, 0.11 mmol, 80% based on technetium). This material is only partially soluble in halogenated solvents and insoluble in alcohols. Hence, attempts to purify the complex by recrystallisation were only partially successful (Found: C, 64.25, 63.90, 65.25; H, 4.30, 4.50, 4.50; N, 4.85, 6.20, 6.55. $C_{48}H_{40}ClN_4Tc$ requires C, 66.30; H, 4.65; N, 6.45%); ν_{max}(KBr) 1601, 1543 and 1475 (NN) cm^{-1}; ^{31}P-{^{1}H} NMR ($CDCl_3$) δ 29.3.

$[TcCl(NNC_6H_4Cl\text{-}4)_2(PPh_3)_2]$ **2**. *Method 1. From* $[NBu_4][TcOCl_4]$. The complex $[NBu_4][TcOCl_4]$ (0.134 g, 0.268 mmol), p-$ClC_6H_4NHNH_2{\cdot}HCl$ (0.120 g, 0.67 mmol), NEt_3 (0.09 cm^3, 0.67 mmol) and PPh_3 (0.211 g, 0.804 mmol) in methanol (5 cm^3) were stirred at room temperature for 2 h to give a khaki suspension. The solid product was collected by filtration and washed with methanol, then diethyl ether and dried (yield 0.134 g, 53%). The product could be recrystallised from CH_2Cl_2–MeOH yielding bright orange crystals (Found: C, 61.25; H, 4.00; Cl, 11.75; N, 6.05. $C_{48}H_{38}Cl_3N_4P_2Tc$ requires C, 61.45; H, 4.10; Cl, 11.35; N, 5.95%); HPLC(thf) 9.4 min, single species; ν_{max}(KBr) 1600 and 1555 (NN) cm^{-1}; ^{31}P-{^{1}H} NMR ($CDCl_3$) δ 30.27.

Method 2. Directly from $[NH_4][TcO_4]$. Aqueous $[NH_4][TcO_4]$ (1 cm^3, 0.343 mmol) was evaporated to dryness *in vacuo*. The compound $4\text{-}ClC_6H_4NHNH_2{\cdot}HCl$ (0.260 g, 1.45 mmol) in absolute ethanol (5 cm^3) was added with stirring to give an orange solution after 10 min. Solid PPh_3 (0.380 g, 1.45 mmol) was added and the mixture heated under reflux for 1.5 h. After cooling to room temperature the khaki solid was collected by filtration and washed with diethyl ether (yield 0.249 g, 74%). The product could be recrystallised from CH_2Cl_2–MeOH to yield an orange crystalline solid which has an identical IR spectrum to that of an authentic sample of **2** prepared from $[NBu_4][TcOCl_4]$ in method 1. Similar reaction in methanol solvent resulted in a 67% yield of **2**.

$[TcCl(NNC_6H_4Me\text{-}4)_2(PPh_3)_2]$ **3**. The complex $[NBu_4][TcOCl_4]$ (0.178 g, 0.356 mmol), $4\text{-}MeC_6H_4NHNH_2{\cdot}HCl$ (0.282 g, 1.78 mmol), NEt_3 (0.25 cm^3, 1.78 mmol) and PPh_3 (0.280 g, 1.07 mmol) were stirred overnight at room temperature in methanol (5 cm^3) to give a khaki-green suspension. The product was collected by filtration, washed with diethyl ether and dried (yield, 0.122 g, 40%). HPLC(thf) 10.4 min, single species (Found: C, 64.1; H, 4.6; Cl, 3.55; N, 5.9. $C_{50}H_{44}ClN_4P_2Tc$ requires C, 66.95; H, 4.95; Cl, 3.95; N, 6.25% for the crude material); ν_{max}(KBr) 1620, 1570 and 1535 (NN) cm^{-1}. NMR ($CDCl_3$): ^{1}H, δ 2.29 (6 H, 5, 2 × CH_3), 6.5–8.0 (38 H, m, phenyl H); ^{31}P-{^{1}H}, δ 28.6. The product may be recrystallised from CH_2Cl_2–MeOH.

$[TcCl_2(NNC_6H_4NO_2\text{-}4)(PPh_3)_2]$ **4**. The complex $[NBu_4][TcOCl_4]$ (0.52 g, 0.304 mmol), $4\text{-}O_2NC_6H_4NHNH_2$ (0.116 g, 0.76 mmol) and PPh_3 (0.239 g, 0.912 mmol) in methanol (5 cm^3) were stirred overnight at room temperature to give a pale orange solid which was collected by filtration, washed with diethyl ether, and dried (yield 0.223 g, 77%). The product could be recrystallised from CH_2Cl_2–MeOH to give a lime-green solid (0.151 g, 52%). HPLC(thf) 10.4 min, single species (Found: C, 57.65, 57.40; H, 4.20, 4.25; Cl, 8.60, 7.95; N, 4.9, 4.95. $C_{43}H_{38}Cl_2N_3O_4P_2Tc$ requires C, 58.90; H, 4.35; Cl, 8.10; N, 4.80%); ν_{max}(KBr) 1620 and 1600 (NN), 1555s (NO_2) and 1335s (NO_2) cm^{-1}. NMR ($CDCl_3$): ^{1}H, δ 3.4 (MeOH), 7.0–8.0 (phenyl H); ^{31}P-{^{1}H}, δ 30.0.

$[TcCl(NNPh)(dppe)_2][PF_6]$ **5**. *Method 1. From* $[NBu_4][TcOCl_4]$. Phenylhydrazine (52 μl, 0.53 mmol) was added to a stirred solution of $[NBu_4][TcOCl_4]$ (0.080 g, 0.16 mmol) in methanol (5 cm^3). After 5 min solid dppe (0.253 g, 0.064 mmol) was added and the reaction mixture was heated under reflux 1 h. After cooling to room temperature, the mixture was filtered, and an excess of $[NH_4][PF_6]$ (1 g, 6.1 mmol) in water (3 cm^3) was added to precipitate the orange product **5**. This was collected by filtration, washed with methanol (15 cm^3) and dried in air (yield 0.095 g, 0.08 mmol, 50%). The complex could be recrystallised from CH_2Cl_2–ethanol (Found: C, 58.90; H, 4.70; N, 2.70. $C_{58}H_{53}ClF_6N_2P_5Tc$ requires C, 58.95; H, 4.60; N, 2.25%).

Method 2. Directly from $[NH_4][TcO_4]$. Phenylhydrazine (50 μl, 0.51 mmol) was added to a stirred solution of 0.29 mol dm^{-3} aqueous $[NH_4][TcO_4]$ (0.5 cm^3, 0.15 mmol) in reagent grade methanol (3 cm^3). No reaction appeared to take place until concentrated hydrochloric acid (0.1 cm^3) was added to the reaction mixture 5 min later. This was followed immediately by the addition of solid dppe (0.241 g, 0.81 mmol) and the reaction mixture was heated under reflux for 1 h. After cooling to room temperature and filtering to remove excess of unreacted dppe, an excess of solid [NH$_4$][PF$_6$] was added to the mixture which was then stirred at room temperature overnight. The orange precipitate was collected by filtration, washed with propan-2-ol and diethyl ether and dried *in vacuo* to give **5** (yield 0.108 g, 0.09 mmol, 60%). The product was identified by comparison of its IR and ^{1}H NMR spectra with those obtained from the authentic sample of **5** prepared by method 1.

[TcCl(NNC$_6$H$_4$Cl-4)(dppe)$_2$][PF$_6$] **6**. *Method 1*. From [TcCl(NNC$_6$H$_4$Cl-4)$_2$(PPh$_3$)$_2$] **2**. Complex **2** (0.101 g, 0.107 mmol) and dppe (0.107 g, 0.269 mmol) in methanol–toluene (1 : 1, 4 cm^3) were heated under reflux for 1 h to give a dark orange solution. Solid [NH$_4$][PF$_6$] (0.018 g, 0.110 mmol) was added with stirring to the filtered reaction mixture to give the orange solid **6** (yield: 0.059 g, 43%), HPLC(thf) 13.6 min, single species. This compound could be recrystallised from CH$_2$Cl$_2$–MeOH (Found: C, 55.45; H, 4.25; N, 2.50. C$_{58}$H$_{52}$Cl$_2$F$_6$N$_2$P$_5$Tc·0.67CH$_2$Cl$_2$ requires C, 55.40; H, 4.20; N, 2.20%).

Method 2. From [NH$_4$][TcO$_4$]. Complex **6** was also prepared from [NH$_4$][TcO$_4$] (0.29 mmol), 4-ClC$_6$H$_4$NHNH$_2$·HCl (0.129 g, 0.72 mmol), and dppe (0.561 g, 1.41 mmol) in methanol under reflux. The hexafluorophosphate salt was recrystallised from CH$_2$Cl$_2$–MeOH (yield, 0.298 g, 0.24 mmol, 84%) (Found: C, 55.75; H, 4.35; N, 1.95%).

[TcCl(NNC$_6$H$_4$Cl-4)(dppe)$_2$][BPh$_4$] **6a**. Complex **6a** was similarly prepared from **2** (0.098 g, 0.104 mmol) and dppe (0.104 g, 0.26 mmol) in methanol–toluene (1 : 1, 4 cm^3) under reflux for 3 h. The orange product was precipitated with solid Na[BPh$_4$] (0.035 g, 0.102 mmol) and recrystallised from CH$_2$Cl$_2$–diethyl ether. HPLC(thf) 14.0 min, single species.

[TcCl(NNC$_6$H$_4$NO$_2$-4)(dppe)$_2$][BPh$_4$] **7**. Complex **4** (0.051 g, 0.06 mmol) and dppe (0.060 g, 0.151 mmol) in methanol–toluene (1 : 1, 3 cm^3) were heated under reflux for 1 h to give an orange-red solution. Solid Na[BPh$_4$] (0.02 g, 0.058 mmol) was added with stirring to the cooled filtered reaction mixture to precipitate an orange solid. This was recrystallised from CH$_2$Cl$_2$–diethyl ether to yield orange crystals (yield 0.06 g, 72%). HPLC(thf) 14.2 min, single species (Found: C, 67.80; H, 5.20; Cl, 4.15; N, 3.15. C$_{82}$H$_{72}$BCl$_2$N$_3$O$_2$P$_4$Tc·0.5 CH$_2$Cl$_2$ requires C, 68.60; H, 5.10; Cl, 4.90; N, 2.90%); ν_{max}(KBr) 1640, 1600 (NN), 1570s (NO$_2$) and 1340s (NO$_2$) cm^{-1}.

Crystal Structure Determination of Complex **5**.—*Crystal data*. C$_{58}$H$_{53}$ClF$_6$N$_2$P$_5$Tc, M = 1181.29, monoclinic, space group $C2/c$, a = 23.808(5), b = 13.830(3), c = 17.452(4) Å, β = 92.53(2)°, U = 5740.71 Å^3, F(000) = 2416, μ(Mo-Kα) = 4.30 cm^{-1}, Z = 4, D_c = 1.367 g cm^{-3}.

Data collection and processing. Data were collected using a crystal of dimensions 0.37 × 0.32 × 0.17 mm on a Philips PW1100 diffractometer with a constant scan width of 0.80° in the range θ 3–25°, using graphite crystal-monochromated Mo-Kα radiation. A θ–2θ scan mode was used, and during data collection no significant change in intensity occurred in three reference reflections which were checked every 5 h. Lorentz-polarisation correlations were applied to the data and equivalent reflections were merged to give a total of 2419 unique reflections with $I/\sigma(I)$ > 3.0.

Structure analysis and refinement. The existence of a c-glide in the crystal was indicated by characteristic systematic absences ($h0l$, $l = 2n + 1$), in addition to those caused by the C-face centred lattice (hkl, $h + k = 2n + 1$). The presence of only four molecules in the unit cell, shown by the calculated density, indicated that the technetium atom was either located on a site of special symmetry in the centrosymmetric space group $C2/c$ or that it was in a general position of the equivalent non-centrosymmetric space group Cc. The Patterson synthesis showed a centrosymmetric distribution of four phosphorus atoms round the technetium atom so that the Fourier synthesis based on these atoms had exact inversion symmetry. This map showed clear images of superimposed Cl and –NNPh groups occupying both axial sites of an approximately octahedral metal co-ordination sphere. In addition, there was a peak, attributed to the phosphorus atom of the counter ion, with coordinates very close to 0.50, y, 0.25; this was nearly, but not exactly on the two-fold symmetry axis of the centrosymmetric space group. The atoms of the phenyl rings were located as well defined maxima of virtual centrosymmetric distribution round the technetium atom. Initial refinement of the atomic parameters was attempted in space group Cc, with the two halves of the molecules in separate blocks, and full occupancy assigned to the one Cl atom and one –NNPh group in opposite axial sites, and to the seven atoms of the PF$_6^-$ counter ion. The standard of refinement achieved in this way was not satisfactory due to the large number of parameters involved, most of which were related in pairs of virtual inversion symmetry in the crystal. Better refinement was obtained using a disordered model in the centrosymmetric space group $C2/c$, and assigned half occupancy to all the atoms of the axial ligands and counter ion. Satisfactory convergence was achieved by keeping the parameters of the –NNPh ligand and those of the Cl donor in separate blocks, and applying a 'damping' factor to the shifts. Absorption corrections using the empirical method of Walker and Stuart[16] were applied, after initial refinement of all atomic parameters. Anisotropic thermal parameters were assigned to all atoms, except carbon and hydrogen, in the final cycles of refinement. The H atoms were included at calculated positions with fixed isotropic thermal parameters of 0.08 Å^2. Weights were applied to the individual reflections as $1/\sigma^2(F)$ and refinement converged at R 0.0988 and R' 0.104.[17] The relatively high final R value may be attributed to the disorder present in the structure. Neutral-atom scattering factors, corrected for the real and imaginary parts of the anomalous scattering, were used for all atoms and were taken from ref. 18.

The final refined fractional coordinates for the atoms are given in Table 2.

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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