Synthesis of Technetium-99 Nitrido Complexes with Chelating Diphosphine and Diimine Ligands *

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The reaction of $[TcNCl_4]^-$ with bidentate diphosphines P–P gives the cationic complexes $[TcNCl(P\text{–}P)_2]^+[A]^-$ [P–P = $Ph_2PCH_2CH_2PPh_2$ or $Me_2PCH_2CH_2PMe_2$ (dmpe), A = BPh_4 or PF_6] in good yield. An analogous complex was prepared with $Me_2PCH_2CH_2NMe(CH_2)_3NMeCH_2CH_2PMe_2$ whereas the bulky $Pr^i_2PCH_2CH_2PPr^i_2$ (dippe) gave a binuclear complex $[Tc_2N_2Cl_4(dippe)_2]$ which on the basis of ^{31}P NMR spectroscopy has bridging chloride groups. An X-ray crystal structure of $[TcNCl(dmpe)_2][BPh_4]$ revealed a distorted *trans*-octahedral geometry about technetium with an exceptionally long Tc=N bond distance of 1.853(6) Å. Reaction of $[TcNBr_4]^-$ with 2,2′-bipyridyl (bipy) in ethanol gives $[TcNBr(bipy)_2]_2[TcBr_4]$. An X-ray crystal structure revealed a *cis*-octahedral structure for the nitrido-cation [Tc=N 1.621(20) Å] with the novel tetrahedral tetrabromotechnetate(II) dianion.

There is increasing interest in the co-ordination chemistry of technetium because of its use in radiodiagnostic imaging. Recent studies of the complex chemistry of this element have led to the development of new and clinically useful radiopharmaceuticals.[1]

The best studied area of technetium chemistry is that of compounds containing the technetyl core, $[Tc^V{=}O]^{3+}$, with a wide variety of ligands. By comparison, the chemistry of technetium with core configurations other than $[Tc{=}O]^{3+}$ has not been as well described.

The syntheses of complexes containing the technetium–nitride core $[Tc^V{=}N]^{2+}$ have been reported in the literature.[2] In many ways the chemistry of the technetium nitride core parallels that of the technetyl core and isostructural pairs of oxo and nitrido-complexes with equivalent sets of ancillary ligands are now known.[3]

In an effort further to elucidate the chemistry of the technetium nitrido-core we have explored the reactions of the tetrahalogenonitridotechnetate anions, $[TcNX_4]^-$ (X = Cl or Br), with multidentate ligands having phosphorus and nitrogen donor atoms. Parts of this work have been communicated elsewhere.[4]

Results and Discussion

Reactions with Phosphines.—The reactions of the technetium(VI) nitrides, $[TcNX_4]^-$ (X = Cl or Br), with reducing ligands containing soft donor atoms such as phosphorus or sulfur are known to give stable species containing the $[Tc^V{=}N]^{2+}$ core [equation (1)].[2] The synthesis of $[TcNCl_2(PPh_3)_2]$ from $[TcNCl_4]^-$ is an example of such a reaction.[5,6] The reaction of $[TcNCl_4]^-$ with 1,2-bis(diphenylphosphino)ethane (dppe) yields the six-co-ordinate cationic complex, *trans*-$[TcNCl(dppe)_2]^+$ **1**, which can be isolated as a salt with $[PF_6]^-$ or $[BPh_4]^-$ anions. This complex has been reported by Abram *et al.*[6] but was erroneously described as a five-co-ordinate dication with no chloride ions co-ordinated *trans* to the nitride nitrogen atom. Reaction of 1,2-bis(dimethylphosphino)ethane (dmpe) with $[TcNCl_4]^-$ yields the analogous complex, *trans*-$[TcNCl(dmpe)]^+$ **2**. This was isolated as its $[BPh_4]^-$ salt and was recrystallised from CH_2Cl_2–pentane. Likewise $[TcNCl_4]^-$ reacts with the novel tetradentate ligand *N*,*N*′-(2′-dimethylphosphinoethyl)-*N*,*N*′-dimethylpropylenediamine L to give the cationic complex, *trans*-$[TcNCl(L)]^+$ **3**.

$$[Tc^{VI}NX_4]^- + \text{excess L} \longrightarrow [Tc^{V}LN_n]^{m} \qquad (1)$$

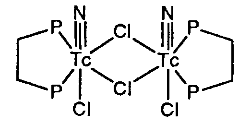

Fig. 1 Proposed structure for complex **4**

Ligand L was synthesised in a multistage synthesis involving the novel addition of $Me_2P(S)CH{=}CH_2$ to *N*,*N*′-dimethylpropylenediamine, $MeNH(CH_2)_3NHMe$. Full details of this synthesis appear in the Experimental section, and the extension to other novel polydentate phosphorus-containing ligands will be reported elsewhere.

The reaction of $[TcNCl_4]^-$ with the bulky diphosphine ligand 1,2-bis(diisopropylphosphino)ethane (dippe) gives only a neutral species with a stoichiometry of one dippe ligand per technetium. Presumably the bulky isopropyl groups prevent formation of a bis-ligand complex analogous to compounds **1**–**3**. Fast atom bombardment (FAB) mass spectral analysis of this complex (positive-ion mode) showed the compound to be the dimeric species, $[\{TcNCl_2(dippe)\}_2]$ **4**. Prominent peaks due to $[M + H]^+$ (m/z = 889), loss of chlorine (m/z = 817), and cleavage of the dimer (m/z = 482) are observed in the mass spectrum. The structure of **4** (Fig. 1) is assigned on the basis of its ^{31}P NMR spectrum in $CDCl_3$ which exhibits a single, quadrupole-broadened and temperature-invariant, resonance at δ_P = 88.4. Alternative structures would exhibit more complex NMR spectra.

The X-Ray Crystal Structure of **2**.—The X-ray single crystal structure analysis of the sample confirms the formulation as

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Non-SI unit employed: mmHg ≈ 133 Pa.

Table 1 Selected bond lengths (Å) and angles (°) for $[TcNCl(dmpe)_2][BPh_4]$

Tc-P(1)	2.447(2)	Tc-P(2)	2.448(2)
Tc-P(3)	2.443(2)	Tc-P(4)	2.453(2)
Tc-Cl	2.608(3)	Tc-N	1.853(6)
P(2)-Tc-P(1)	81.5(1)	P(3)-Tc-P(1)	170.5(1)
P(3)-Tc-P(2)	98.8(1)	P(4)-Tc-P(1)	96.9(1)
P(4)-Tc-P(2)	172.1(1)	P(4)-Tc-P(3)	81.4(1)
Cl-Tc-P(1)	87.9(1)	Cl-Tc-P(2)	85.1(1)
Cl-Tc-P(3)	82.7(1)	Cl-Tc-P(4)	87.1(1)
N-Tc-P(1)	91.7(2)	N-Tc-P(2)	92.5(1)
N-Tc-P(3)	97.8(2)	N-Tc-P(4)	95.3(1)
N-Tc-Cl	177.6(1)		

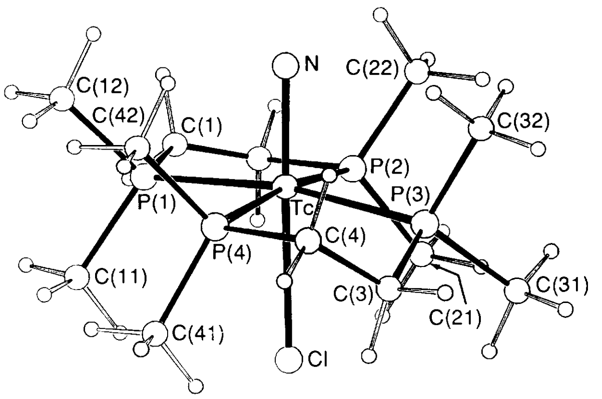

Fig. 2 A perspective view of the cationic complex $[TcNCl(dmpe)_2]^+$, showing one component of the disorder and the numbering scheme used in the X-ray structure analysis

$[TcNCl(dmpe)_2][BPh_4]$ and shows the complex cation to have the structure illustrated in Fig. 2; principal bond lengths and angles are given in Table 1.

The complex cation $[TcNCl(dmpe)_2]^+$ **2** has a slightly distorted octahedral geometry. The main deviation from regular co-ordination is a result of the steric requirements of the two five-membered chelate rings giving angles P(1)-Tc-P(2) 81.5(1) and P(3)-Tc-P(4) 81.4(1)°. These are closely similar to the mean value of 81.43(7)° for the equivalent angles in the analogous dichloro complex $[TcCl_2(dmpe)_2]^+$.[7] The chloride and nitride ligands occupy *trans* sites with a Cl-Tc-N angle of 177.6(1)°.

The Tc-P bond lengths are in the range 2.443-2.453(2) Å, and the individual values are not significantly different from the mean value of 2.448(1) Å. However, they are markedly shorter than the mean value of 2.501(11) Å reported for the dibromo complex of the related bis(diphenylphosphino)ethane ligand, $[TcBr_2(dppe)_2]^+$,[8] an observation that may be explained by the increase in metal covalent radius resulting from the decrease in oxidation state from Tc^V in **2** to Tc^{III} in $[TcBr_2(dppe)_2]^+$. Unexpectedly, the Tc^V-P bond lengths in the nitrido complex **2** are significantly longer than the mean Tc^{III}-P length of 2.436 Å in the dichloro analogue.[7] This appears to indicate greatly enhanced π-back bonding from Tc to P on replacement of a nitrido by a chloro ligand.

The Tc-Cl bond distance of 2.608(2) Å is the longest so far reported being 0.071 Å longer than the value of 2.527(4) Å observed for the very elongated Tc^V-Cl bond *trans* to the co-ordinated oxygen atom in the oxotechnetium(v) complex of *N,N'*-ethylenebis(acetylacetoneimine)(H_2 acacen).[9,*] It is also 0.275 Å longer than the mean *trans* Tc^{III}-Cl bond length in the cation $[TcCl_2(dmpe)_2]^+$,[7] and 0.290 Å longer than that in the *o*-phenylenebis(dimethylarsine) complex $[TcCl_2(pdma)_2]^+$.[10] The Tc^{III}-Cl bond length in both the latter cations would be expected to be longer than in **2** on the basis of oxidation state. This is further evidence of the strong *trans* influence of the N^{3-} ligand in technetium complexes, previously noted in the structure of acetonitrile(isothiocyanato)(nitrido)bis(triphenylphosphine)technetium(v),[2b] where a Tc-N length of 2.491(4) Å to acetonitrile was reported *trans* to the nitrido ligand. An extremely long Re^V-Cl bond was also observed *trans* to the nitrido ligand in $[ReNCl_2(PEt_2Ph)_2]$, Re-Cl 2.563 Å.[11]

The most interesting feature in the structure of $[TcNCl(dmpe)_2]^+$ is the observation of a very long Tc-N bond of length 1.853(6) Å.* The first structural characterisation of a technetium nitrido species was of bis(diethyldithiocarbamato)nitridotechnetium(v) in which a Tc-N bond length of 1.604 Å was reported for the five-co-ordinate complex.[12] In the more recent structure analysis of the six-co-ordinate isothiocyanato complex a slightly longer technetium-nitrido distance of 1.629 Å was reported.[2b] For complexes of the closely related metal, rhenium, similar marked differences between metal-nitride bonds have been observed[13] with Re-N bond lengths varying from 1.53 Å[14] in $K_2[ReN(CN)_4]$ to 1.788 Å[11] in $[ReNCl_2(PEt_2Ph)_3]$. The wide range of Re^V-N bond lengths has been attributed to steric factors.[13]

In the $[TcNCl(dmpe)_2]^+$ cation the technetium and four phosphorus donor atoms (see Supplementary data) show marked deviations from exact planarity with the Tc atom lying 0.148 Å above the best-fit plane in the direction of the nitrido ligand and the four phosphorus donors lying on the other side with deviations in the range 0.020-0.054 Å. Similar deviation of the technetium atom from the equatorial plane occurs in octahedral oxotechnetium(v) complexes.[15] For example in (*N*-2-oxidophenyl)salicylideneiminato-*NOO'*)oxo(quinolin-8-ato)technetium(v) the technetium atom is displaced by 0.08 Å in the direction of the co-ordinated oxygen atom[16] and in [TcO(acacen)Cl] a deviation of 0.37 Å is observed.[9] The TcP_2 planes of the two bidentate ligands are at an angle of 11.4° to each other. The two carbon atoms of each ligand ethylene bridge lie on opposite sides of the corresponding plane. For the disordered chelate ring atoms C(1) and C(2') are 0.63 and 0.49 Å, respectively, below the TcP(1)P(2) plane (towards the chloro ligand) and atoms C(2) and C(1') lie 0.30 and 0.11 Å, respectively, above the plane (towards the nitrido ligand). For the second chelate ring these deviations are C(3) (0.51 Å below) and C(4) (0.27 Å above) the plane TcP(3)P(4).

Reactions with N-Donor Ligands.—Unlike phosphines, nitrogen donor ligands are generally not regarded as reducing ligands. However, aromatic imines such as 2,2'-bipyridyl (bipy) and 1,10-phenanthroline (phen) are well known as ligands for transition metals in low oxidation states. The reactions of these ligands with the tetrahalogenonitridotechnetate anions, $[TcNX_4]^-$ (X = Cl or Br), were pursued with a view to comparing the products **1**-**4** obtained with the phosphine compounds.

The reactions of $[TcNCl_4]^-$ and $[TcNBr_4]^-$ with bipy and phen in alcohol are highly dependent on the alcohol used. The complexes are only partially soluble in ethanol and can be isolated as precipitates from this solvent as their simple chloride or bromide salts, **5**-**7**. However, the complexes are soluble in methanol and if these reactions are performed in this solvent the cations can be isolated as the salts of other anions (*e.g.* **8**).

The compounds are diamagnetic and are assigned as the *cis*-nitridohalogeno isomers, **A**, rather than the *trans* isomer **B** (Fig. 3) on the basis of ^1H NMR spectroscopy. The ^1H NMR spectra of compounds **5**-**8** exhibit very complex patterns of signals in the aromatic region which are assigned to the bipy ligand protons. The ^1H NMR spectrum of **5** is shown in Fig. 4. If

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* Some caution is required in considering the bond lengths in **2** because of the pseudo-symmetry arising from the siting of the Tc, Cl and N atoms close to the *n*-glide plane which caused problems in refinement.

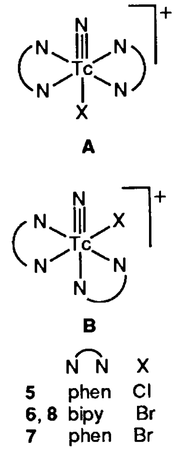


Fig. 3 Possible isomers of complexes **5**–**8**

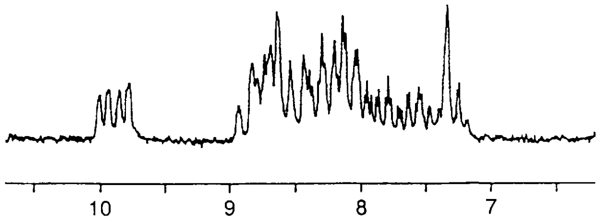


Fig. 4 ^{1}H NMR spectrum of complex **5** in [$^2H_6$]dmso

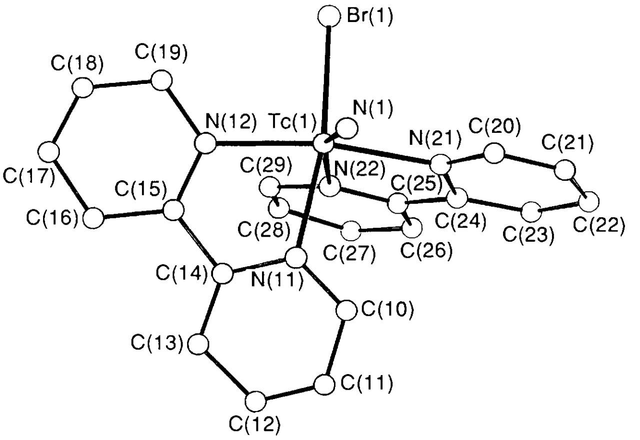
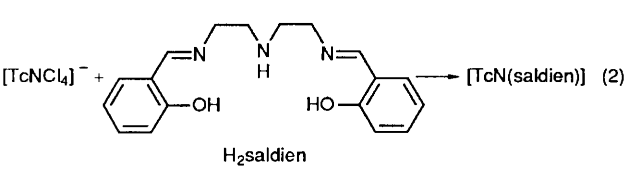


Fig. 5 A perspective view of the structure of one of the cations [TcNBr(bipy)$_2$]$^+$, showing the numbering scheme used in the X-ray structure analysis

5–**8** were the *trans* isomers, **B**, the ^{1}H NMR spectrum would contain only four resonances due to four sets of equivalent ligand protons on either bipy or phen. For the *cis* isomers, **A**, the ligand protons are each in unique environments and therefore magnetically inequivalent, giving rise to the complex spectra observed.

The reaction of [TcNCl$_4$]$^-$ with the pentadentate Schiff base ligand bis(salicylidene)diethylenetriamine(H$_2$saldien) gives the expected product [TcN(saldien)] **9** in 72% yield [equation (2)].



As precipitated from ethanol, compounds **5**–**7** gave poor elemental analyses, even after extensive drying *in vacuo*, although NMR, fast atom bombardment mass spectrometry (FABMS) and the elemental analysis of **8** all confirmed the complexes to be as assigned. In an effort to obtain good analytical data for one of these, **6**, a new batch was recrystallized from acetone–diethyl ether. However, recrystallization had the opposite effect to that desired and the analytical data for the recrystallized material diverged more from the expected values than that for the originally isolated material. Therefore a crystal structure determination for the recrystallized material was undertaken, and it proved to be a new compound [TcNBr(bipy)$_2$]$_2$[TcBr$_4$]·0.5MeOH.

Table 2 Selected bond lengths (Å) and angles (°) for [TcNBr(bipy)$_2$]$_2$[TcBr$_4$]·0.5MeOH **10**

Tc(1)–Br(1)	2.529(4)	Tc(1)–N(1)	1.621(20)
Tc(1)–N(11)	2.129(17)	Tc(1)–N(12)	2.104(19)
Tc(1)–N(21)	2.161(18)	Tc(1)–N(22	2.415(19)
Tc(2)–Br(2)	2.521(4)	Tc(2)–N(2)	1.598(20)
Tc(2)–N(31)	2.109(18)	Tc(2)–N(32)	2.127(18)
Tc(2)–N(41)	2.150(20)	Tc(2)–N(42)	2.396(18)
Tc(3)–Br(3)	2.399(4)	Tc(3)–Br(4)	2.401(5)
Tc(3)–Br(5)	2.417(4)	Tc(3)–Br(6)	2.388(4)
N(1)–Tc(1)–Br(1)	102.2(7)	N(11)–Tc(1)–Br(1)	158.9(5)
N(11)–Tc(1)–N(1)	98.1(8)	N(12)–Tc(1)–Br(1)	92.1(6)
N(12)–Tc(1)–N(1)	103.8(9)	N(12)–Tc(1)–N(11)	77.1(7)
N(21)–Tc(1)–Br(1)	91.6(5)	N(21)–Tc(1)–N(1)	90.6(9)
N(21)–Tc(1)–N(11)	94.2(7)	N(21)–Tc(1)–N(12)	164.0(7)
N(22)–Tc(1)–Br(1)	84.5(4)	N(22)–Tc(1)–N(1)	161.6(8)
N(22)–Tc(1)–N(11)	78.1(6)	N(22)–Tc(1)–N(12)	93.0(7)
N(22)–Tc(1)–N(21)	71.9(7)	N(21)–Tc(2)–Br(2)	96.7(7)
N(31)–Tc(2)–Br(2)	161.8(5)	N(31)–Tc(2)–N(2)	100.7(8)
N(32)–Tc(2)–Br(2)	93.5(5)	N(32)–Tc(2)–N(2)	106.1(8)
N(32)–Tc(2)–N(31)	76.7(7)	N(41)–Tc(2)–Br(2)	86.2(5)
N(41)–Tc(2)–N(2)	95.3(9)	N(41)–Tc(2)–N(31)	97.4(7)
N(41)–Tc(2)–N(32)	158.5(8)	N(42)–Tc(2)–Br(2)	87.9(4)
N(42)–Tc(2)–N(2)	166.9(8)	N(42)–Tc(2)–N(31)	76.2(6)
N(42)–Tc(2)–N(32)	85.8(7)	N(42)–Tc(2)–N(41)	72.6(7)
Br(4)–Tc(3)–Br(3)	109.9(2)	Br(5)–Tc(3)–Br(3)	112.1(2)
Br(5)–Tc(3)–Br(4)	106.1(2)	Br(6)–Tc(3)–Br(3)	109.6(2)
Br(6)–Tc(3)–Br(4)	106.9(2)	Br(6)–Tc(3)–Br(5)	111.9(2)

The detailed electrochemistry of these complexes and the biodistribution of the ^{99m}Tc analogues of these nitride cations will be reported elsewhere.

X-Ray Crystal Structure of **10**.—The X-ray structure determination of the recrystallized compound **6** showed it to have transformed into the complex salt *cis*-[TcNBr(bipy)$_2$]$_2$-[TcBr$_4$] **10** for which a preliminary report has been published.[4]

In the structure of **10** there are two crystallographically independent *cis*-[Tc^{V}NBr(bipy)$_2$]$^+$ cations with the distorted *cis*-octahedral co-ordination geometry shown in Fig. 5. There are no significant structural differences between the two cations. Selected bond lengths and angles are given in Table 2. In both cations the bipyridine ligands are displaced from regular octahedral geometry in a direction away from the *cis*-[TcN(Br)]$^+$ unit. The dihedral angles between the best-fit planes for the two bipyridine ligands in the cations are 70.6 and 71.1° which represent significant deviations from the ideal 90° angle. In both cations the Tc=N bond between technetium and the bipyridine nitrogen ligated *trans* to the nitrido atom [mean 2.400(18) Å] is significantly longer than the other Tc–bipy nitrogen distances [mean = 2.130(18) Å]. This is a further reflection of the strong *trans* influence of the nitride ligand.[2b] The Tc≡N and Tc–Br bond lengths of the cations [1.621(20), 2.598(20) and 2.529(4), 2.521(4) Å respectively] compare well with the Tc≡N and Tc–Br bond lengths found in other such systems.[2b,12]

The most unusual part of the structure is the presence of the [Tc^{II}Br$_4$]$^{2-}$ anion (Fig. 6), a hitherto unknown species exhibiting virtually regular tetrahedral symmetry. The Br–Tc–Br

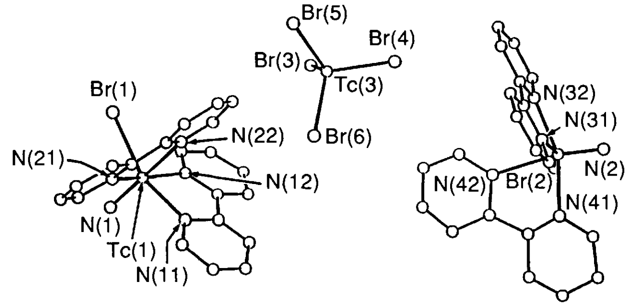


Fig. 6 A view of part of the structure of $[TcNBr(bipy)_2]_2[TcBr_4]$, showing the nitride cations and the $[TcBr_4]^{2-}$ dianion together with a partial atom numbering scheme

angles vary between 106.1(2) and 112.1(2)° [mean = 109.4(2)°]. The Tc–Br bond lengths in the anion do not differ significantly from the mean value of 2.401(4) Å. This anion is isoelectronic and isostructural with the well known first-row transition metal d^5 tetrahedral tetrahalogenometalate anions, $[Mn^{II}X_4]^{2-}$ and $[Fe^{III}X_4]^-$. Second-row transition element analogues have not previously been structurally characterised.

This unusual dianion presumably arises from the loss of the nitride ligand in $[TcNBr_4]^-$, although a disproportionation reaction involving *cis*-$[TcNBr(bipy)_2]^+$ cannot be excluded on the basis of the evidence presented here. The loss of nitride ligands in technetium–nitride chemistry, while unusual, is not without precedent.[17] The observation of $[TcBr_4]^{2-}$ in the solid state also leaves open the question of whether or not this species may be synthesized more directly in the future, for instance by the hypothetical route indicated in equation (3).

$$[Tc^{IV}Br_6]^{2-} + 2e^- \longrightarrow [Tc^{II}Br_4]^{2-} + 2Br^- \qquad (3)$$

Experimental

Since ^{99}Tc is a long-lived radionuclide all work was carried out with the appropriate care and precautions. Aqueous solutions of $NH_4{}^{99}TcO_4$ were supplied by Amersham International; $[NBu_4][TcNCl_4]$ and $[NBu_4][TcNBr_4]$ were prepared according to the literature procedure.[3] The ligands dippe[18] and saldien[19] were prepared according to literature procedures. All other reagents were commercially available and used as received unless noted otherwise.

Proton, ^{13}C and $^{31}P-\{^1H\}$ NMR spectra were obtained on a Bruker WP 80 spectrometer. IR spectra were obtained as Nujol mulls on KBr discs using a Beckman IR spectrometer. Elemental analyses were performed by Butterworth Laboratories Ltd., Teddington, Middlesex. Fast atom bombardment mass spectra were performed by M-Scan Ltd, Ascot, Berkshire using the positive-ion mode and glycerol as the matrix.

Syntheses.—N,N′-(2′-*Dimethylphosphinothioylethyl*)-N,N′-*dimethylpropylenediamine.* *N,N*′-Dimethylpropylenediamine (4 g) (prepared by reaction of methylamine with 1,3-dibromopropane) and dimethylvinylphosphine sulfide[1] (9.4 g) were dissolved in ethanol (200 cm^3) and the mixture heated under reflux for 72 h. The solvent was removed under reduced pressure (60 °C at 18 mmHg) and the residue dissolved in chloroform (400 cm^3). The chloroform solution was washed with aqueous sodium hydroxide solution (50 cm^3, 2 mol dm^{-3}), then with water (50 cm^3), and finally dried ($MgSO_4$). Removal of the solvent under reduced pressure gave a residue which was recrystallised from ethyl acetate to give the pure product (7.48 g, 56%) (Found: C, 45.7; H, 9.35; N, 8.20. $C_{13}H_{32}N_2P_2S_2$ requires C, 45.6; H, 9.4; N, 8.2%). NMR ($CDCl_3$): $^{31}P-\{^1H\}$, δ 36.0; ^{13}C, δ 21.3 (d, J_{PC} 54), 25.1, 31.9 (d, J_{PC} 52 Hz), 41.6, 51.2 and 55.4.

N,N′-(2′-*Dimethylphosphinoethyl*)-N,N′-*dimethylpropylenediamine.* The reduction procedure and subsequent work-up were carried out in an inert atmosphere of dinitrogen using degassed solvents. To a suspension of lithium aluminium hydride (1.2 g) in dry dioxane (125 cm^3) was added *N,N*′-(2′-dimethylphosphinothioylethyl)-*N,N*′-dimethylpropylenediamine (3.34 g) and the mixture heated under reflux for 36 h. (NB after a short initiation period a vigorous exothermic reaction often occurs which may necessitate cooling the reaction mixture). The mixture was allowed to cool and the excess lithium aluminium hydride decomposed by the careful addition of aqueous dioxane (12 cm^3, 30% water), then aqueous sodium hydroxide (3 cm^3, 2 mol dm^{-3}), and finally water (2 cm^3). The resulting mixture was filtered through a glass sinter under reduced pressure and the solvent then removed under reduced pressure (50 °C at 50 mmHg) to give the pure phosphine (2.54 g, 90%), NMR ($CDCl_3$): $^{31}P-\{^1H\}$, δ −53.6; ^{13}C, δ 13.5 (d, J_{PC} 13.5), 24.8, 29.2 (d, J_{PC} 10.5), 41.2, 53.8 (d, J_{PC} 18 Hz) and 54.8.

$[TcNCl(dppe)_2][BPh_4]$ **1**. $[NBu_4][TcNCl_4]$ (126 mg, 0.25 mmol) and dppe (364 mg, 0.91 mmol) were heated under reflux in dry MeOH (5 cm^3) for 30 min. The reaction mixture was cooled to room temperature. The excess dppe was filtered off, and $NaBPh_4$ (145 mg, 0.42 mmol) was added as a solid to the stirred filtrate. After one hour the orange precipitate which formed was collected by filtration and recrystallised from CH_2Cl_2–EtOH to give 57% (180 mg, 0.14 mmol) of $[TcNCl(dppe)_2][BPh_4]$ (Found: C, 71.1; H, 5.2; N, 0.6. Calc. for $C_{76}H_{68}BClNP_4Tc$: C, 72.2; H, 5.4; N, 1.1%). $^{31}P-\{^1H\}$ NMR: δ 35.0. IR: 1091 cm^{-1} ν(Tc–N).

$[TcNCl(dmpe)_2][BPh_4]$ **2**. 1,2-Bis(dimethylphosphino)ethane (0.20 cm^3, 1.2 mmol) was added to a stirred solution of $[NBu_4][TcNCl_4]$ (0.10 g, 0.20 mmol) in MeCN (3 cm^3) under an atmosphere of dinitrogen and the reaction mixture stirred at room temperature for 30 min. The MeCN was removed *in vacuo*, the oily residue washed with Et_2O, and then taken up in CH_2Cl_2 (3 cm^3). The salt $NaBPh_4$ (0.34 g, 1.0 mmol) was then added as a solid and the CH_2Cl_2 solution was layered with light petroleum (b.p. 40–60 °C). This gave 30 mg of product. A second recrystallisation of the mother-liquor yielded an additional 82 mg of material (yield: 0.12 mmol, 60%) (Found: C, 55.3; H, 6.9; N, 1.6. Calc. for $C_{36}H_{52}BClNP_4Tc$: C, 56.4; H, 6.8; N, 1.8%). NMR: $^{31}P-\{^1H\}$ (CH_2Cl_2), δ 42.4. ^1H ($[^2H_6]$acetone), δ 1.36–2.40 (broad multiplets, PCH and CH_3) and 6.5–8.0 (m, phenyl). FABMS (*m/z*): 448 (M^+), 413 (M^+ − Cl) and 298 (M^+ − dmpe).

$[TcNCl(L)][BPh_4]$ **3**. The complex $[NBu_4][TcNCl_4]$ (110 mg, 0.22 mmol) was dissolved in CH_2Cl_2 (5 cm^3) and a solution of the ligand *N,N*′-(2′-dimethylphosphinoethyl)-*N,N*′-dimethylpropylenediamine in dioxane (29% w/w, 0.40 cm^3, 0.44 mmol) was added to the stirred solution. The reaction mixture was stirred at room temperature for 1 h. The solvents were removed *in vacuo*, and the oily residue was redissolved in MeOH (0.5 cm^3); $NaBPh_4$ (80 mg, 0.23 mmol) in MeOH (1 cm^3) was added to the product and the yellow precipitate was collected and washed with methanol, diethyl ether and light petroleum. This gave, after drying *in vacuo*, $[TcNCl(L)][BPh_4]$ (12.0 mg, 0.17 mmol) in 78% yield. The product could be recrystallised from CH_2Cl_2 solutions layered with light petroleum (Found: C, 53.9; H, 6.7; Cl, 12.9; N, 4.9. Calc. for $C_{37}H_{54}BCl_3N_3P_2Tc$: C, 54.5; H, 6.2; Cl, 13.0; N, 5.2%). ^1H NMR ($[^2H_6]$acetone): δ 0.80–4.50 (complex m), 2.42 (s, NCH_3), 5.58 (s, CH_2Cl_2), and 6.71–8.04 (m, phenyl). FABMS (*m/z*): 412 (M^+). IR: 1056 cm^{-1} ν(Tc–N)?

$[\{TcNCl_2(dippe)\}_2]$ **4**. The phosphine dippe (200 μl, 0.76 mmol) was added to a stirred solution of $[NBu_4][TcNCl_4]$ (93 mg, 0.19 mmol) in McCN (5 cm^3) and the reaction mixture was heated to reflux for 45 min, cooled to room temperature and the MeCN removed *in vacuo*. The residue was taken up in a minimum of CH_2Cl_2, the solution filtered and heptane layered onto the solution and allowed to diffuse into the CH_2Cl_2 layer. This gave 31 mg of an orange product. A second reiteration of this procedure yielded a further 14 mg of product. The overall yield of $[\{TcNCl_2(dippe)\}_2]$ (45 mg, 0.10 mmol) was

54% (Found: C, 37.8; H, 3.1; Cl, 15.8; N, 3.1. Calc. for $C_{14}H_{32}Cl_2NP_2Tc$: C, 37.8; H, 7.2; Cl, 15.9; N, 3.2%). NMR ($CDCl_3$): ^1H, δ 0.69–1.62 (m, sharp, CH_3) and 3.17 (m, CH + CH_2); $^{31}P-\{^1H\}$, δ 88.4. IR: 1078 cm^{-1} ν(Tc–N)?

$[TcNCl(phen)_2]Cl$ **5**. 1,10-Phenanthroline (0.20 g, 1.11 mmol) was added as a solid to a stirred solution of $[NBu_4][TcNCl_4]$ (0.15 g, 0.30 mmol) of reagent grade EtOH (5 cm^3). The reaction solution was stirred at room temperature for two hours and then filtered. Diethyl ether (10 cm^3) was added to the filtrate and the mixture was covered and left to stand overnight. The dark red crystalline product was then collected, washed with 25 cm^3 of Et_2O–EtOH (10:1, v/v) and dried *in vacuo*. The yield of *cis*-$[TcNCl(phen)_2]Cl\cdot H_2O$ (76 mg, 0.14 mmol) was 47% (Found: C, 49.5; H, 3.2; N, 12.1. Calc. for $C_{24}H_{18}Cl_2N_5OTc$: C, 51.3; H, 3.2; N, 12.5%). ^1H NMR ([$^2H_6$]dmso): 6.5–10.4 (m).

cis-$[TcNBr(bipy)_2]Br$ **6**. The complex $[NBu_4][TcNBr_4]$ (0.105 g, 0.16 mmol) and 2,2′-bipyridyl (0.156 g, 1.00 mmol) were heated in EtOH (3 cm^3) at reflux for 1 h. The solvents were removed *in vacuo* and the solids taken up in CH_2Cl_2 (2 cm^3) and precipitated by the addition of Et_2O until the solution started to become cloudy. This solution was cooled to −30 °C for 2 d and red crystals of product were collected, washed with EtOH (2 × 5 cm^3) and dried *in vacuo*. The yield of *cis*-$[TcNBr(bipy)_2]$-Br (0.76 g; 0.13 mmol) was 81% (Found: C, 39.4; H, 3.4; N, 11.4. Calc. for $C_{20}H_{18}Br_2N_5OTc$: C, 39.9; H, 3.0; N, 11.6%). FABMS (*m/z*): 504 ([^{79}Br] M^+), 506 ([^{81}Br] M^+). IR: 1050 cm^{-1} ν(Tc–N)?

cis-$(TcNBr(phen)_2]Br$ **7**. Prepared as for $[TcNBr(bipy)_2]Br$ from $[NBu_4][TcNBr_4]$ (0.100 g, 0.15 mmol) and 1,10-phenanthroline (0.20 g, 1.11 mmol) in EtOH (4 cm^3). The yield of *cis*-$[TcNBr(phen)_2]Br$ (65 mg, 0.10 mmol) was 67% (Found: C, 43.3; H, 2.8; Br, 23.5; N, 10.7. Calc. for $C_{24}H_{16}Br_2N_5Tc\cdot H_2O$: C, 44.3; H, 2.8; Br, 24.5; 10.9%). ^1H NMR: δ 7.18–10.42 (m). IR: 1046 cm^{-1} ν(Tc–N)?

cis-$[TcNBr(bipy)_2][BPh_4]$ **8**. A solution of bipy (0.18 g, 1.17 mmol) in anhydrous MeOH (2 cm^3) was added to a stirred solution of $[NBu_4][TcNBr_4]$ (0.11 g, 0.16 mmol) in dry MeOH (5 cm^3). The solution was stirred at room temperature for 1 h and then $NaBPh_4$ (0.24 g, 0.70 mmol) was added as a solid to the reaction mixture. The dark red solution yielded a large amount of a pale orange solid which was contaminated with $[NBu_4][BPh_4]$. The mixture was recrystallised from dmf–EtOH to give 0.08 g (1.10 mmol, 62%) of orange, crystalline *cis*-$[TcNBr(bipy)_2][BPh_4]$ (Found: C, 64.6; H, 4.3; N, 8.7. Calc. for $C_{44}H_{36}BBrN_5Tc$: C, 64.2; H, 4.4; N, 8.5%). ^1H NMR ([$^2H_6$]dmso): δ 6.75–10.00 (complex, m). IR: 1063 cm^{-1} ν(Tc–N)?

[TcN(saldien)] **9**. A solution of H_2saldien (101 mg, 0.33 mmol) in tetrahydrofuran (thf) (5 cm^3) was prepared and NaOMe (0.40 cm^3, 1.7 mol dm^{-3} in MeOH, 0.68 mmol) was added. After 5 min a solution of $[NBu_4][TcNBr_4]$ (145 mg, 0.22 mmol) in thf (5 cm^3) was added. The reaction mixture turned red-brown immediately. It was heated to reflux for 1 h, cooled to room temperature, filtered and the solvents were removed *in vacuo*. The residue was taken up in a minimum of CH_2Cl_2 and chromatographed on a column of silica gel (75 × 25 mm) which had been prepared in MeOH and then washed with CH_2Cl_2 (200 cm^3). Elution with CH_2Cl_2 eluted a major red fraction. This was concentrated *in vacuo* to *ca.* 3 cm^3 and the product was precipitated by the addition of diethyl ether. This gave [TcN(saldien)] (65 mg, 0.15 mmol) as a red-brown powder in 72% yield (Found: C, 51.2; H, 4.6; N, 12.9. Calc. for $C_{18}H_{19}N_4O_2Tc$: C, 51.3; H, 4.5; N, 13.3%). FABMS (*m/z*): M^+ (423). ^1H NMR ($CDCl_3$): δ 1.75–5.00 (broad m, 8 H, aliphatic), 6.00–8.00 (broad m, 10 H, aromatic and imine CH) and 12.9 (br, NH). IR: 1592 and 1622 cm^{-1} ν(C=N).

$[TcNBr(bipy)_2]_2[TcBr_4]$ **10**. Preparation carried out as for **6** but using methanol as reaction solvent. The complex precipitated as a reddish orange solid which was recrystallised from acetone–diethyl ether.

The Crystal Structures of **2** *and* **10**.—*Crystal data*. **2** $[C_{36}H_{52}BClNP_4Tc]$, M = 743.43, monoclinic, space group $P2_1/n$ (alt. no. 14), a = 19.862(4), b = 12.983(3), c = 15.919(3) Å, β = 107.11(2)°, U = 3923.4 Å^3, F(000) = 1600, μ(Mo-Kα) = 5.52 cm^{-1}, Z = 4, D_c = 1.240 g cm^{-3}; **10** $C_{40}H_{32}Br_6N_{10}Tc_3\cdot 0.5CH_4O$, M = 1148.23, monoclinic, space group $P2_1/c$ (no. 14), a = 9.143(2), b = 35.014(7), c = 15.581(3) Å, β = 105.96(2)°, U = 4795.7 Å^3, F(000) = 2760, μ = 57.07 cm^{-1}, Z = 4, D_c = 1.590 g cm^{-3}.

Data were collected using crystals of **2** (dimensions 0.34 × 0.29 × 0.19 mm) and **10** (dimensions 0.25 × 0.25 × 0.12 mm) on a Philips PW1100 diffractometer with a constant scan width of 0.80° in the θ range 3–25°, using graphite crystal-monochromated Mo-Kα radiation. A θ–2θ scan mode was used, and no significant change occurred in three reference reflections which were checked every 5 h. Lorentz polarization corrections were applied to the data and equivalent reflections were merged to give totals of 4382 and 2598 unique reflections with $I/\sigma(I) > 3.0$ for **2** and **10** respectively. For **2** scans round the diffraction vector of several strong reflections showed no significant variation in intensity, indicating that absorption corrections were not necessary. For both **2** and **10** the SHELX program[20] was used to solve the structures.

The relatively low number of significant data for **10** were due to the poor diffraction by the crystal at high angles. For **2** the solution of the structure was relatively difficult due to the siting of the technetium atom exactly on the *n*-glide (y = 0.25). The metal and two phosphorus atoms were located from a Patterson synthesis. A subsequent observed Fourier synthesis showed a double image of the molecule generated by a pseudo mirror plane at y = 0.25, from which the remaining phosphorus atoms and one phenyl ring of the anion were identified. A Fourier synthesis phased on these atoms showed very little pseudosymmetry and the positions of most of the non-hydrogen atoms were located. After four cycles of refinement of the parameters of these atoms a difference-Fourier synthesis gave reliable coordinates for the chlorine and nitrogen atom lying slightly above and below the technetium position in the b direction. The ethylene group of one of the diphosphine ligands is disordered, two distinct sites for atoms C(1) and C(2) being identified, and these refined satisfactorily with fixed occupancies of 0.5. All the non-hydrogen atoms except those of half occupancy were assigned anisotropic thermal parameters in the final cycles of blocked full-matrix refinement. The Tc, N and Cl atoms, which all lay close to the glide plane, were refined in different cycles. The relatively high anisotropic thermal parameters of the methyl carbon atoms C(11), C(12) and C(21), C(22), bonded to P(1) and P(2), are consistent with some disorder of these atoms corresponding to the two orientations of the ethylene bridge. Although a difference-Fourier synthesis had shown rather extended regions of electron density at the sites of these atoms it did not prove possible to resolve them into separate components. All H atoms were included at calculated positions and were assigned isotropic thermal parameters; those of the ordered ethylene groups were constrained to be equal (final values 0.087 Å^2) as were those of the methyl groups (final value 0.143 Å^2), and the H atoms of the disordered ethylene group (of half occupancy) were assigned fixed values of 0.08 Å^2. Weights were applied to the individual reflections as $1/\sigma^2(F)$ and refinement converged at R 0.0548 and R' 0.0593 with 146 parameters.

For **10** the positions of the remaining non-hydrogen atoms were located from subsequent difference-Fourier syntheses, and the hydrogen atoms of the bipyridyl rings were included at calculated positions. Two residual peaks of *ca.* 3 e Å^{-3} were attributed to solvent molecule, MeOH, occupying two related sites near a crystallographic inversion centre. They were included as C and O atoms of half occupancy. After initial refinement of the atomic parameters using isotropic thermal parameters absorption corrections were applied to the data using the empirical method of Walker and Stuart.[21] Anisotropic

Table 3 Fractional atomic coordinates for $[TcNCl(dmpe)_2][BPh_4]$ **2**

Atom	*x*	*y*	*z*
Tc	0.107 49(3)	0.245 39(4)	0.383 79(3)
P(1)	0.071 30(10)	0.067 85(14)	0.342 33(12)
P(2)	0.183 85(10)	0.158 33(14)	0.513 41(11)
P(3)	0.127 32(11)	0.423 13(14)	0.435 50(12)
P(4)	0.0179 8(9)	0.329 52(13)	0.263 49(11)
Cl	0.015 40(11)	0.248 77(18)	0.471 56(13)
N	0.175 5(3)	0.240 0(4)	0.325 3(3)
C(3)	0.049 0(4)	0.495 5(5)	0.374 2(5)
C(4)	0.031 3(4)	0.469 5(5)	0.277 4(5)
C(11)	−0.013 9(5)	0.025 0(7)	0.345 4(7)
C(12)	0.074 7(6)	0.024 9(6)	0.236 8(6)
C(21)	0.175 2(5)	0.178 9(8)	0.621 3(5)
C(22)	0.275 6(4)	0.171 1(9)	0.528 2(7)
C(31)	0.140 5(5)	0.458 2(7)	0.549 9(5)
C(32)	0.198 4(4)	0.486 2(7)	0.407 0(6)
C(41)	−0.073 9(3)	0.313 0(7)	0.258 5(5)
C(42)	0.018 5(4)	0.303 6(6)	0.151 3(4)
B	0.116 7(3)	0.250 8(6)	−0.092 6(4)
C(1)	0.143 4(6)	−0.014 6(9)	0.408 0(8)
C(2)	0.155 0(8)	0.020 4(10)	0.506 7(9)
C(1′)	0.119 6(10)	−0.016 2(15)	0.436 8(13)
C(2′)	0.186 3(10)	0.020 2(14)	0.485 7(12)
C(51)	0.123 6(2)	0.125 7(2)	−0.066 6(3)
C(52)	0.144 4(2)	0.055 2(2)	−0.120 3(3)
C(53)	0.140 1(2)	−0.050 3(2)	−0.105 9(3)
C(54)	0.115 1(2)	−0.085 2(2)	−0.037 8(3)
C(55)	0.094 4(2)	−0.014 7(2)	0.015 9(3)
C(56)	0.098 6(2)	0.090 7(2)	0.001 5(3)
C(61)	0.034 5(1)	0.260 3(3)	−0.162 5(2)
C(62)	0.022 9(1)	0.252 6(3)	−0.253 1(2)
C(63)	−0.045 7(1)	0.251 0(3)	−0.309 5(2)
C(64)	−0.102 8(1)	0.257 3(3)	−0.275 4(2)
C(65)	−0.091 1(1)	0.265 0(3)	−0.184 9(2)
C(66)	−0.022 5(1)	0.266 5(3)	−0.128 4(2)
C(71)	0.179 2(2)	0.292 5(3)	−0.135 8(3)
C(72)	0.246 2(2)	0.248 4(3)	−0.107 4(3)
C(73)	0.301 1(2)	0.289 6(3)	−0.134 7(3)
C(74)	0.289 2(2)	0.374 9(3)	−0.190 3(3)
C(75)	0.222 3(2)	0.419 1(3)	−0.218 7(3)
C(76)	0.167 3(2)	0.377 9(3)	−0.191 4(3)
C(81)	0.129 4(2)	0.329 6(3)	−0.004 9(2)
C(82)	0.094 0(2)	0.423 6(3)	−0.013 0(2)
C(83)	0.111 5(2)	0.494 2(3)	0.056 0(2)
C(84)	0.164 5(2)	0.471 0(3)	0.133 2(2)
C(85)	0.199 9(2)	0.377 0(3)	0.141 3(2)
C(86)	0.182 4(2)	0.306 3(3)	0.072 2(2)

Table 4 Fractional atomic coordinates for $[TcNBr(bipy)_2]_2[TcBr_4]\cdot 0.5\ MeOH$ **10**

Atom	*x*	*y*	*z*
Tc(1)	0.1902(2)	0.4191(1)	0.5513(1)
Br(1)	0.0883(3)	0.4586(1)	0.4117(2)
Tc(2)	1.0489(3)	0.1044(1)	0.3590(1)
Br(2)	0.7998(4)	0.0688(1)	0.3115(2)
Tc(3)	0.5278(3)	0.3073(1)	0.2544(2)
Br(3)	0.2716(4)	0.2907(1)	0.1757(2)
Br(4)	0.7018(4)	0.2623(1)	0.2201(2)
Br(5)	0.5996(4)	0.3692(1)	0.2107(2)
Br(6)	0.5593(4)	0.3035(1)	0.4115(2)
N(1)	0.0585(22)	0.4242(6)	0.6019(13)
N(11)	0.3256(19)	0.3781(5)	0.6390(12)
N(12)	0.1326(22)	0.3677(5)	0.4802(13)
N(21)	0.3122(21)	0.4676(5)	0.6225(12)
N(22)	0.4302(21)	0.4241(6)	0.5153(13)
C(10)	0.4116(26)	0.3852(7)	0.7195(16)
C(11)	0.5050(29)	0.3576(7)	0.7695(18)
C(12)	0.5086(30)	0.3246(8)	0.7372(18)
C(13)	0.4146(29)	0.3157(8)	0.6504(18)
C(14)	0.3220(25)	0.3429(7)	0.6049(15)
C(15)	0.2116(26)	0.3369(7)	0.5183(16)
C(16)	0.1827(28)	0.3008(8)	0.4783(17)
C(17)	0.0686(28)	0.2978(8)	0.3994(18)
C(18)	−0.0109(28)	0.3284(7)	0.3656(17)
C(19)	0.0195(27)	0.3635(7)	0.4034(16)
C(20)	0.2526(29)	0.4890(7)	0.6772(17)
C(21)	0.3330(31)	0.5174(8)	0.7236(18)
C(22)	0.4766(29)	0.5257(7)	0.7265(16)
C(23)	0.5443(26)	0.5040(7)	0.6695(15)
C(24)	0.4638(24)	0.4735(6)	0.6215(14)
C(25)	0.5171(26)	0.4514(6)	0.5593(15)
C(26)	0.6568(27)	0.4579(7)	0.5474(16)
C(27)	0.7002(31)	0.4356(7)	0.4850(17)
C(28)	0.6076(27)	0.4080(7)	0.4370(17)
C(29)	0.4706(28)	0.4029(7)	0.4557(16)
N(2)	1.1518(22)	0.0713(6)	0.3354(13)
N(31)	1.2096(21)	0.1488(5)	0.3957(13)
N(32)	0.9918(20)	0.1413(5)	0.2463(12)
N(41)	1.0642(22)	0.0839(6)	0.4914(13)
N(42)	0.9250(20)	0.1504(5)	0.4289(12)
C(30)	1.3235(28)	0.1493(7)	0.4722(17)
C(31)	1.4209(28)	0.1809(7)	0.4928(17)
C(32)	1.4043(29)	0.2112(8)	0.4363(18)
C(33)	1.2895(29)	0.2097(8)	0.3574(18)
C(34)	1.1972(25)	0.1786(7)	0.3394(15)
C(35)	1.0737(25)	0.1734(7)	0.2542(16)
C(36)	1.0407(27)	0.2012(8)	0.1880(17)
C(37)	0.9258(26)	0.1951(7)	0.1139(16)
C(38)	0.8486(28)	0.1616(7)	0.1066(17)
C(39)	0.8849(27)	0.1347(7)	0.1735(16)
C(40)	1.1245(31)	0.0505(8)	0.5204(20)
C(41)	1.1267(34)	0.0324(10)	0.6005(22)
C(42)	1.0679(36)	0.0558(10)	0.6546(27)
C(43)	1.0098(35)	0.0897(10)	0.6306(22)
C(44)	1.0062(26)	0.1039(7)	0.5426(17)
C(45)	0.9336(29)	0.1413(7)	0.5188(18)
C(46)	0.8821(30)	9.1684(8)	0.5731(21)
C(47)	0.8206(28)	0.1998(8)	0.5344(19)
C(48)	0.8101(29)	0.2106(8)	0.4481(19)
C(49)	0.8655(26)	0.1840(7)	0.4013(17)
O	0.4726(65)	−0.0132(16)	0.5049(44)
C	0.5707(38)	0.0556(9)	0.4952(23)

thermal parameters were assigned to the metal and bromine atoms in the final cycles of refinement, and the H atoms were assigned common isotropic thermal parameters (one for each bipyridyl ligand, final values 0.05, 0.11, 0.08 and 0.11 Å^2). Weights were applied to the individual reflections as $1/\sigma^2(F)$ and refinement converged at *R* 0.0655 and *R′* 0.0613 with 298 parameters.

The final refined fractional coordinates for the atoms in **2** and **10** are given in Tables 3 and 4 respectively. The final estimated standard deviations are relatively high due to the low number of observed data.

Neutral scattering factors, corrected for the real and imaginary parts of the anomalous scattering, were used for all atoms and were taken from ref. 22.

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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