

Technetium complexes of capped tetradentate ligands Part II. The synthesis and electrochemistry of technetium(III) and (V) complexes of 2-diphenylphosphino-*N,N*-bis(2- diphenylphosphinoethyl)ethaneamine (NP₃) and tris-2- diphenylphosphinoethylphosphine (PP₃)

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(Received October 21, 1991)

Abstract

A series of cationic technetium complexes *cis*-[TcXY(L)]⁺ has been prepared for X=Y=Cl; X=N, Y=Br and X=Cl, Y=NNC₆H₄Cl, and L=NP₃ and PP₃ and isolated as their tetraphenylborate or hexafluorophosphate salts. The *cis*-dichlorides show reversible one-electron reductions at -0.13 V versus SCE in dimethylformamide for both ligands whereas the other complexes are more difficult to reduce. Attempts to prepare *cis*-[TcO₂(L)]⁺ were not successful, but the novel complex [TcOCl₂(L)][BPh₄] (L=NP₃) was isolated and complexes formulated as [Tc(SO₄)₂(L)][BPh₄] (L=NP₃ and PP₃) were prepared using H₂SO₄ as the acid.

Introduction

Since the introduction of the potentially tetradentate tripodal capped ligands NP₃ and PP₃ in 1967 [1] and 1969 [2] the chemistry of their transition metal complexes has been extensively examined. So far however the only report of the chemistry of either ligand with technetium concerns ^{99m}Tc labelling and biodistribution studies of PP₃ [3]. Complexes of the type [TcXY(diphosphine)₂]⁺ (X=Y=O [4]; X=Y=Cl [4]; X=Cl, Y=N [5]) adopt a *trans* configuration for X and Y and the ligand *trans* to nitride is strongly destabilised. We were interested to know, as part of our ongoing study of capped tetradentate ligands, if the chemistry of complexes of NP₃ and PP₃, with their obligately *cis*-XY geometry, would differ significantly from that of their *trans* analogues.

Results and discussion

Treatment of [TcCl₄(PPh₃)₂] with an excess of NP₃ under reflux in ethanol results in the formation of an

orange solution from which orange [TcCl₂(NP₃)]Cl can be precipitated by addition of ether. More conveniently the cation can be isolated by addition of Na[BPh₄] or [NH₄][PF₆] as the tetraphenylborate or hexafluorophosphate salts. The analogous reaction with PP₃ gives pale pink [TcCl₂(PP₃)] [BPh₄] in high yield. In a similar way the off-white [TcNBr(PP₃)] [Y] and pale yellow [TcNBr(NP₃)] [Y] were readily prepared from [NBu₄][TcNBr₄] or from [TcNBr₂(PPh₃)₂] in acetone. Satisfactory proton NMR spectra were obtained for the nitrides, and [TcCl₂(PP₃)] [PF₆] gives a somewhat broadened spectrum, but [TcCl₂(NP₃)]Cl and the corresponding [BPh₄]⁻ salt show the classic signs of temperature independent paramagnetism, with a sharp line spectrum from +16 to -6 ppm. In the case of [TcNBr(NP₃)] [BPh₄] it was possible to observe the expected two phosphorus environments at +42 and +37 ppm with relative intensity 2:1, although the signals were much broadened by the technetium quadrupole. It is impossible to say whether the amine nitrogen or a PPh₂ unit is *trans* to the nitride (Fig. 1), though in the latter case the phosphine might be expected to be weakly bound to technetium, or even dangling, and to give a sharp NMR signal. In addition to the *trans* influence steric crowding of the phenyl groups, as in

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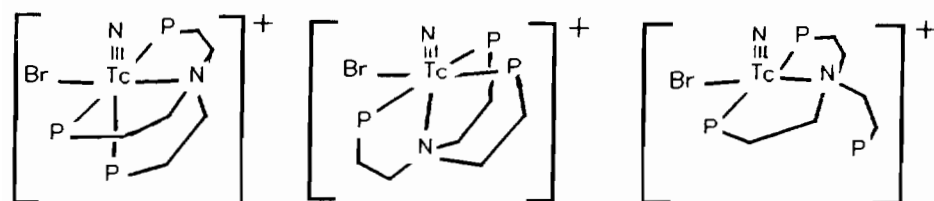


Fig. 1. The possible structures for $[\text{TcNBr}(\text{NP}_3)]^+$.

$[\text{CoCl}_2(\text{NP}_3)][\text{BF}_4]$ [6], would tend to encourage five coordination.

The use of a precursor derived from ammonium pertechnetate and 4-chlorophenylhydrazine hydrochloride in the preparation of technetium diazenides has been described [7, 8]. Reaction of this precursor with NP_3 or PP_3 results in the speedy formation of *cis*- $[\text{TcCl}(\text{NNR})(\text{L})]^+$, which can be obtained as purple-pink (PP_3) or green (NP_3) solids by addition of suitable counterions. Both of these complexes are diamagnetic, and in the case of the PP_3 derivative the four required ^{31}P NMR signals were observed at -13 , $+32$ and $+45$ ppm, again greatly broadened by the technetium quadrupole. Further confirmation of the diazenide structures was provided by FAB-mass spectroscopy.

Attempts to obtain *cis*-dioxo complexes were not successful. Reaction of ammonium pertechnetate with NP_3 or PP_3 in aqueous ethanol under mildly basic conditions gives a black, insoluble product which was not further characterised. Under mildly acidic conditions the product depends on the nature of the acid. With HCl , NP_3 gave a product analysing as $[\text{TcOCl}_2(\text{NP}_3)][\text{BPh}_4]$ and showing the expected parent ion at 838 with a two chlorine isotope pattern in the FAB-MS. Sulfuric acid gave a species analysing as the sulfato complex $[\text{Tc}(\text{SO}_4)_2(\text{L})]^+$, whereas no clean species were isolated using fluoroboric acid.

The product of the reaction of $[\text{TcCl}_2(\text{NP}_3)]\text{Cl}$ with azide ion in methanol depends upon conditions, an azide being obtained under neutral conditions ($\nu = 2040 \text{ cm}^{-1}$) but the *cis*-nitride-chloride was obtained under acidic conditions, both in very low yields and of low purity. Reaction with 1,1- and 1,2-dialkylhydrazines yielded materials of low carbon and nitrogen content which were not further characterised. Other simple metathesis reactions of the halide ligands in the complexes $[\text{TcCl}_2(\text{L})]^+$ are in progress and will be reported elsewhere.

In view of the obligately *cis* geometry of these complexes we were interested to know whether their electrochemical behavior would differ significantly from related *trans* complexes.

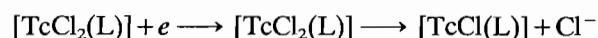
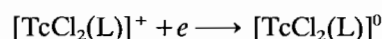
Electrochemical data were obtained for the dichlorides, nitride-bromides and chloride-diazenides in dimethylformamide, and are summarised in Table 1.

TABLE 1. Reduction and oxidation potentials^a for $[\text{TcXYL}]^+$

| Complex | Process | E_{pa} | E_{pc} E_{pi} | ΔE_p^b |
|---|-----------|-----------------|------------------------------------|----------------|
| $[\text{TcCl}_2(\text{NP}_3)]^+$ | reduction | -0.10 | -0.16 | 61(R) |
| | reduction | | $-1.23(\text{I})$ | |
| $[\text{TcCl}_2(\text{PP}_3)]^+$ | reduction | -0.09 | -0.18 | 84(R) |
| | reduction | | $-1.32(\text{I})$ | |
| $[\text{TcNBr}(\text{NP}_3)]^+$ | reduction | | $-1.13(\text{I})$ | |
| | oxidation | | $+0.86(\text{I})$ | |
| $[\text{TcNBr}(\text{PP}_3)]^+$ | reduction | | $-1.07(\text{I})$ | |
| | reduction | | -1.22 | 84(Q) |
| $[\text{TcCl}(\text{NNR})(\text{dppe})_2]^{+\text{c, d}}$ | reduction | -1.14 | -1.22 | |
| | reduction | | $-1.50(\text{I})$ | |
| $[\text{TcCl}(\text{NNR})(\text{NP}_3)]^+$ | reduction | | $-1.23(\text{I})$ | |
| | oxidation | | $+0.95(\text{I})$ | |
| $[\text{TcCl}(\text{NNR})(\text{PP}_3)]^{+\text{d}}$ | reduction | | $-1.13(\text{I})$ | |
| | oxidation | | $+0.98(\text{I})$ | |

^aIn dimethylformamide/0.2 M $[\text{NBu}_4][\text{BF}_4]$ vs. SCE. ^bR = reversible, I = irreversible; Q = quasireversible. ^cR = 4-chlorophenyl; the dppe complex is from ref. 8. ^dAs the tetraphenylborate salt, all other complexes are hexafluorophosphates.

The dichlorides behave in a similar way to that reported for $[\text{TcCl}_2(\text{dmpe})_2]^+$ and $[\text{TcCl}_2(\text{depe})_2]^+$ [8], in that a reversible reduction is followed by a further irreversible reduction, the second step probably being irreversible due to rapid loss of chloride ion (eqn. (1)), the reductions occurring at slightly less negative potentials than those reported for the *trans* complexes.



(1)

For $[\text{TcCl}_2(\text{PP}_3)]^+$ a second, weaker, reversible reduction was always observed at -0.31 V (Fig. 2), probably due to material adsorbed on the electrode, while for $[\text{TcCl}_2(\text{NP}_3)]^+$ irreversible product waves from the second reduction were observed at -0.91 and $+0.17$ V and a reversible couple due to adsorbed material slowly builds up at $+0.12$ V.

There is some ambiguity concerning the electrochemical behaviour of $[\text{TcNCl}(\text{diphosphine})_2]^+$, Dilworth *et al.* [10] report that reduction only occurs at potentials more negative than -1.0 V, whereas Bishop

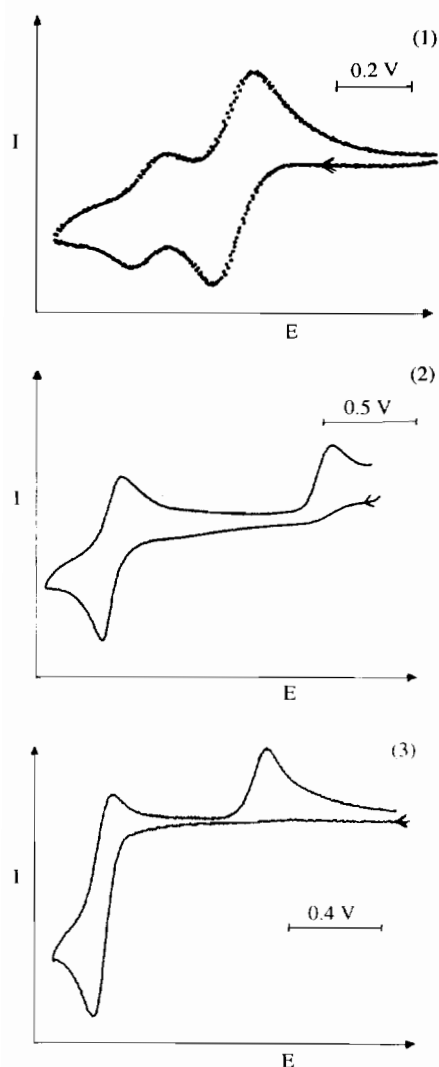
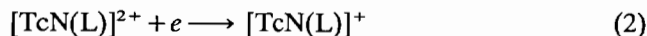
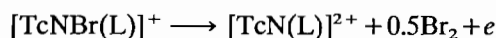


Fig. 2. Cyclic voltammograms for $[\text{TcCl}_2(\text{PP}_3)]^+[\text{PF}_6]^-$ (1), $[\text{TcNBr}(\text{NP}_3)]^+$ (2), and $[\text{TcCl}(\text{NNPh})(\text{dppe})_2]^+$ (3); scan rate 0.5 V/s. All in DMF solvent with Pt working electrode, Ag pseudo reference, and $[\text{Bu}_4\text{N}][\text{BF}_4]$ as support electrolyte.

[11] reports a reversible couple at +0.09 V which we now believe may be due to traces of hydrolysis products or the *trans* dichloride, as well as irreversible processes at -1.33 and +0.43 V. In our nitride-bromides no reduction is observed until below -1.0 V (see Table 1), and then is irreversible. Oxidation occurs irreversibly for $[\text{TcNBr}(\text{NP}_3)]^+$ at +0.86 V and this oxidation results in a near reversible product wave at -0.30 V (Fig. 2). The slight irreversibility in this reduction is due to an as yet unidentified chemical reaction of the reduced species. Although the corresponding oxidation wave was not clearly visible against the background for the PP_3 analogue, a similar product wave was observed at -0.43 V. One possibility is that the oxidation is accompanied by loss of the bromide ligand as 0.5Br_2 and that the resulting $[\text{TcNL}]^{2+}$ and $[\text{TcNL}]^+$ complexes

have some stability (eqn. (2)). However at this stage we cannot rule out the possibility of attack by fluoride on the dication, or some form of disproportionation reaction to give one electroactive product. Whatever the identity of the product resulting from the irreversible step, it evidently still contains the tetradentate ligand, as the secondary process occurs at different potentials for NP_3 and PP_3 .



No data were available for *trans*-chloride-diazenides, so an examination of $[\text{TcCl}(\text{NNR})(\text{dppe})_2][\text{BPh}_4]$, available in these laboratories [7], was carried out. This compound reduced quasireversibly at -1.18 V, the product decomposing with a rate constant of about $1.8(1) \text{ s}^{-1}$ probably to $[\text{Tc}(\text{NNR})(\text{dppe})_2]^+$ with loss of chloride. An irreversible product peak was observed (Fig. 2) at -0.39 V, and further irreversible reductions follow the first beyond -1.50 V. These have not yet been studied further, but may well involve simultaneous reduction and protonation of the NNR ligand, as has been noted for the isoelectronic Mo and W dialkylhydrazido complexes derived from ligated dinitrogen. Interestingly the neutral diazenido complexes $[\text{MBr}(\text{NNEt})_2](\text{dppe})_2$ ($\text{M}=\text{Mo}, \text{W}$) demonstrate reversible oxidations in the range -0.1 to +0.4 V [12]. Even allowing for the presence of an alkyl rather than phenyl diazenide substituent this shows the dramatic effect on the LUMO of introducing a positive charge on the isoelectronic Tc complexes.

For $[\text{TcCl}(\text{NNR})(\text{NP}_3)]^+$ and $[\text{TcCl}(\text{NNR})(\text{PP}_3)]^+$ irreversible reduction occurs at -1.23 and -1.13 V, respectively, producing product waves at -0.35 and -0.40 V respectively, both being irreversible.

The redox potentials and behaviour observed for all the complexes show remarkable similarities both between the NP_3 and PP_3 complexes and also between analogous *cis* and *trans* complexes.

Experimental

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

Reaction mixtures were monitored by anisocratic HPLC (Gilson) employing ultraviolet and β detection. NMR spectra were obtained on a JEOL EX270 spectrometer operating at 270 MHz for protons. Electrochemical data were obtained and treated using the CONDECON program operating on an IBM PC OPU-SII computer with an EG and G CONDECON analogue-digital convertor and EG and G modal 620 potentiostat.

Platinum working and auxiliary and silver reference electrodes were employed, and voltammograms were calibrated using the ferrocene/ferrocenyl couple (+0.38 V [13] versus SCE).

Microanalyses were carried out by Butterworths Laboratories Ltd, Teddington, UK, and FAB-MS data were kindly obtained by Amersham International plc, Cardiff Laboratories, Cardiff, UK.

Technetium-99 was supplied as an aqueous solution of ammonium pertechnetate by Amersham International plc.

$[\text{TcCl}_4(\text{PPh}_3)_2]$, $[\text{TcNBr}_4][\text{PPh}_4]$ and $[\text{TcNBr}_2(\text{PPh}_3)_2]$ were prepared as described in the literature [14–16].

Dichloro-2-diphenylphosphino-N,N-bisdiphenylphosphinoethylethaneamine technetium(III) chloride, $[\text{TcCl}_2(\text{NP}_3)]\text{Cl}$

A suspension of $[\text{TcCl}_4(\text{PPh}_3)_2]$ (0.180 g; 0.235 mmol) and NP_3 (0.257 g; 0.393 mmol) in ethanol (5 cm³) was heated to reflux for 2 h. The solution was allowed to cool, filtered, and treated with diethyl ether (15 cm³), the product was collected by filtration, recrystallised from dichloromethane/ether and dried. Yield 0.084 g; 42% orange solid.

Anal. Found: C, 58.32; H, 4.97; N, 1.69. Calc. for $\text{C}_{42}\text{H}_{42}\text{Cl}_3\text{NP}_3\text{Tc}$: C, 58.72; H, 4.93; N, 1.63%.

Dichloro-2-diphenylphosphino-N,N-bisdiphenylphosphinoethylethaneamine technetium(III) hexafluorophosphate, $[\text{TcCl}_2(\text{NP}_3)][\text{PF}_6]$

This compound was prepared as above using $[\text{TcCl}_4(\text{PPh}_3)_2]$ (0.172 g; 0.224 mmol) and NP_3 (0.252 g; 0.385 mmol). After filtering the ethanol solution $[\text{NH}_4][\text{PF}_6]$ (0.170 g; 1.04 mmol) was added. The solids were collected after 1 h and recrystallised from dichloromethane/ether and dried. Yield 0.152 g; 78% orange solid.

Anal. Found: C, 51.60; H, 4.71; N, 1.21. Calc. for $\text{C}_{42}\text{H}_{42}\text{Cl}_2\text{F}_6\text{NP}_4\text{Tc}$: C, 52.08; H, 4.37; N, 1.45%.

Dichlorotriscis-2-diphenylphosphinoethylphosphine technetium(III) hexafluorophosphate, $[\text{TcCl}_2(\text{PP}_3)][\text{PF}_6]$

This compound was prepared as the NP_3 analogue using $[\text{TcCl}_4(\text{PPh}_3)_2]$ (0.084 g; 0.110 mmol), PP_3 (0.148 g; 0.221 mmol) and $[\text{NH}_4][\text{PF}_6]$ (0.211 g; 1.29 mmol). Yield 0.102 g; 94% pale pink solid.

Anal. Found: C, 51.53; H, 4.77. Calc. for $\text{C}_{42}\text{H}_{42}\text{Cl}_2\text{F}_6\text{P}_5\text{Tc}$: C, 51.19; H, 4.29%.

Bromonitrido-2-diphenylphosphino-N,N-bisdiphenylphosphinoethylethaneamine technetium(V) tetraphenylborate, $[\text{TcNBr}(\text{NP}_3)][\text{BPh}_4]$

A suspension of $[\text{TcNBr}_2(\text{PPh}_3)_2]$ (0.152 g; 0.191 mmol) and NP_3 (0.170 g; 0.260 mmol) in acetone (5 cm³) was heated under reflux for 2 h. The solution

was cooled and filtered, then evaporated to dryness *in vacuo*. After redissolving the residue in ethanol (5 cm³) and treating with $\text{Na}[\text{BPh}_4]$ (0.172 g; 0.503 mmol) in ethanol (2 cm³) the product was isolated by filtration, recrystallised from dichloromethane/ether, and dried. Yield 0.172 g; 78% pale yellow solid.

The same material could be obtained directly from $[\text{PPh}_4][\text{TcNBr}_4]$ and NP_3 in acetone.

Anal. Found: C, 66.91; H, 5.37; N, 2.34. Calc. for $\text{C}_{66}\text{H}_{62}\text{BBrN}_2\text{P}_3\text{Tc}$: C, 67.99; H, 5.36; N, 2.40%.

Bromonitridotriscis-2-diphenylphosphinoethylphosphine technetium(V) hexafluorophosphate, $[\text{TcNBr}(\text{PP}_3)][\text{PF}_6]$

This compound was prepared as above using $[\text{TcNBr}_2(\text{PPh}_3)_2]$ (0.152 g; 0.191 mmol), PP_3 (0.172 g; 0.261 mmol) and $[\text{NH}_4][\text{PF}_6]$ (0.15 g; 0.92 mmol). Yield 0.164 g; 85% off-white solid.

Anal. Found: C, 50.39; H, 4.46; N, 1.59. Calc. for $\text{C}_{42}\text{H}_{42}\text{BrF}_6\text{NP}_5\text{Tc}$: C, 50.02; H, 4.20; N, 1.39%.

Chloro-4-chlorophenyldiazenido-2-diphenylphosphinobis-2-diphenylphosphinoethylethaneamine technetium(III) hexafluorophosphate, $[\text{TcCl}(\text{NNR})(\text{NP}_3)][\text{PF}_6]$

A 'diazenide precursor' was prepared [7] using $[\text{NH}_4][\text{TcO}_4]$ (0.50 cm³; 0.166 mmol) and $[\text{H}_2\text{NNHR}] \cdot \text{HCl}$ ($\text{R} = \text{C}_6\text{H}_4\text{Cl}$, 0.147 g; 0.821 mmol) in methanol. The solution was treated with NP_3 (0.198 g; 0.303 mmol) and refluxed for 1 h. After cooling the solution was treated with $[\text{NH}_4][\text{PF}_6]$ (0.160 g; 0.98 mmol), and the solids were collected by filtration. After recrystallisation from dichloromethane/diethyl ether, the green solid was obtained in 20% yield (0.035 g).

Anal. Found: C, 54.02; H, 4.57; N, 3.71. Calc. for $\text{C}_{48}\text{H}_{46}\text{Cl}_2\text{F}_6\text{N}_3\text{P}_4\text{Tc}$: C, 53.74; H, 4.32; N, 3.92%.

FAB-MS: found, 926 (2 chlorine atoms); calc. for $\text{C}_{48}\text{H}_{46}\text{Cl}_2\text{N}_3\text{P}_4\text{Tc}$, 926.

Chloro-4-chlorophenyldiazenidotris-2-diphenylphosphinoethylphosphine technetium(III) tetraphenylborate, $[\text{TcCl}(\text{NNR})(\text{PP}_3)][\text{BPh}_4]$

The preparation was carried out as above using $[\text{NH}_4][\text{TcO}_4]$ (0.166 mmol), $[\text{H}_2\text{NNHR}] \cdot \text{HCl}$ (0.142 g; 0.792 mmol), PP_3 (0.209 g; 0.132 mmol) and $\text{Na}[\text{BPh}_4]$ (0.220 g; 0.643 mmol) to give the product (0.222 g; 90%) as a dusty-pink solid.

Anal. Found: C, 67.40; H, 5.25; N, 2.06. Calc. for $\text{C}_{72}\text{H}_{66}\text{BCl}_2\text{N}_2\text{P}_4\text{Tc}$: C, 68.42; H, 5.26; N, 2.22%.

FAB-MS: found, 943 (2 chlorine atoms); calc. for $\text{C}_{48}\text{H}_{46}\text{Cl}_2\text{N}_2\text{P}_4\text{Tc}$, 943.

Oxodichloro-2-diphenylphosphino-N,N-bis-2-diphenylphosphinoethylethaneamine technetium(V) tetraphenylborate, $[\text{TcOCl}_2(\text{NP}_3)] [\text{BPh}_4]$

A solution of $[\text{NH}_4][\text{TcO}_4]$ (0.375 cm³; 0.125 mmol) in ethanol (5 cm³) was treated with 32% hydrochloric

acid (0.236 g) and NP_3 (0.102 g; 0.156 mmol) and brought briefly to reflux. After cooling and filtering the solution it was treated with $\text{Na}[\text{BPh}_4]$ (0.158 g; 0.462 mmol), and the solids collected by filtration. Recrystallisation gave 0.058 g (40%) of orange product.

Anal. Found: C, 68.37; H, 5.62; N, 1.45. Calc. for $\text{C}_{66}\text{H}_{62}\text{BCl}_2\text{NOP}_3\text{Tc}$: C, 68.40; H, 5.39; N, 1.21%.

Bis(sulfato)tris(2-diphenylphosphinoethyl)phosphine technetium(V) tetraphenylborate

Ammonium pertechnetate (0.25 cm³, 0.083 mmol) was added to a suspension of PP_3 (0.107 g; 0.160 mol) in ethanol (5.0 cm³). A few drops of dilute (2 N) sulfuric acid were added and the solution stirred at room temperature for 2 h. A small amount of white precipitate was filtered off and the product precipitated by the addition of sodium tetraphenylborate (0.114 g) in ethanol. The product was recrystallised from acetone-ether. Yield 0.062 g, 58%.

Anal. Found: C, 62.25; H, 5.17. Calc. for $\text{C}_{66}\text{H}_{62}\text{O}_8\text{P}_4\text{S}_2\text{Tc}$: C, 61.88; H, 4.87%.

The NP_3 complex was prepared analogously, but satisfactory analyses were not obtained. Neither complex showed any IR bands assignable to $\text{Tc}=\text{O}$.

Acknowledgements

We are grateful to Amersham International plc for the provision of ammonium pertechnetate and to SERC for financial support of S.M.

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