APPLICATIONS OF LIGAND EXCHANGE REACTIONS OF TECHNETIUM COMPLEXES

by

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To Mom, Dad, and Bubby

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ABSTRACT

Chapter 1

Two general routes for the preparation of technetium complexes with aromatic amine, chloride, and alkoxide ligands are presented. The reactions of tetrachloro(oxo)technetate(V) anion ((n-Bu_4N)[$TcOCl_4$]) with pyridine in tetrahydrofuran/alcohol solvent or of dioxotetrakis(pyridine)technetium(V) cation ([$TcO_2(py)_4$]Cl) with LiCl in sulfuric acid/alcohol both yield a neutral alkoxydichloro(oxo)bis(pyridine)technetium(V) complex. The same isomer appears to result from either route. The analogous thiazole derivatives may be prepared in a like manner. The complex chloro(1,2-ethanediolato)oxo(1,10-phenanthroline)technetium(V), $TcOCl(C_2H_4O_2)(C_{12}H_8N_2)$ is prepared from (n-Bu_4N)[$TcOCl_4$] with 1,2-ethanediol and 1,10-phenanthroline in methanol. Further insight into the bonding in this complex comes from the single crystal X-ray structure determination. The space group is monoclinic, $P2_1/c$ with a = 7.440(2) Å, b = 8.928(3) Å, c = 21.355(4) Å, β = 92.48(2)°, V = 1417.2(7) $Å^3$, and Z = 4. The structure was solved by standard methods and refined to R = 0.051, R_w = 0.036 based on 1859 reflections. The oxo and chloride ligands are mutually *cis* in the highly distorted octahedral coordination sphere. The unusually long Tc-Cl bond length (2.418(2) Å) is attributed to a *trans* influence exerted by the coordinated diolate. This effect combined with short lengths for the C-C bond (1.491(1) Å) and for the O-Tc-O linkage (1.924(4) Å, 1.902(3) Å) suggest partial multiple bonding between the technetium and the diolate.

Chapter 2

The trioxotechnetium(VII) complexes $TcO_3Cl(AA)$ (AA = phen, bpy, 5-NO_2-phen, 3,4,7,8-Me_4-phen) cleanly oxidize olefins (C_2R_4) in solution at 22° C, forming in high

yields the corresponding oxotechnetium(V) diolate complexes, $TcOCl(OCR_2CR_2O)(AA)$. The complexes have been characterized by ^1H NMR, IR, elemental analysis, and fast atom bombardment mass spectrometry. The free diols isolated by hydrolysis of these diolate complexes with HCl were shown by capillary gas chromatography to represent *syn* addition of the two hydroxyl groups across the double bond. The related rhenium complex, $ReOCl(OCH_2CH_2O)(phen)$ undergoes the reverse reaction when thermalized, releasing ethene and producing $ReO_3Cl(phen)$.

Attempted hydrolysis with HBr causes reduction of the metal and the complex $TcBr_4(C_{12}H_8N_2)\cdot 1/2CH_2Cl_2$ is isolated. A single crystal X-ray structure was performed on a small plate-like crystal. The space group is orthorhombic, *Pbca* with a = 18.504(4) Å, b = 14.427(3) Å, c = 12.640(2) Å, V = 3374(2) $Å^3$, and Z = 8. The structure was solved by standard methods and refined to R = 0.097, R_w = 0.109 based on 859 observations with some disorder noted in the lattice solvent. The molecule has distorted octahedral geometry primarily imposed by the N-Tc-N bite angle of 78(1)°. The average Tc-Br bond length is 2.453(7) Å and the average Tc-N distance is 2.14(3) Å.

Chapter 3

The preparation and characterization of (acetonitrile)trichlorobis(triphenylphosphine)technetium(III) from $(n\text{-}Bu_4N)[TcOCl_4]$ with triphenylphosphine in acetonitrile solvent is described. The analogy of this complex to $ReCl_3(PPh_3)_2(MeCN)$ is discussed in terms of their rich substitution chemistry. Reactions of $TcCl_3(PPh_3)_2(MeCN)$ with CO and NO are described. Characterization of the products, carbonyltrichlorobis(triphenylphosphine)technetium(III) and trichloronitrosylbis(triphenylphosphine)technetium(II) is also described.

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PREFACE:

Technetium is the element of lowest atomic number which has no stable isotopes. Since the half life of its longest lived isotope (^{98}Tc, $t_{1/2} = 4.2 \cdot 10^6$ y) is short on the geological timescale,[1] there is virtually no terrestrial abundance of this element. The widespread use of uranium fission as a source of energy, however, leads to the general availability of technetium isotopes. Approximately 30 kg of technetium is produced annually at typical nuclear generating stations.[1] Technetium-99 as ammonium pertechnetate may be purchased by holders of Nuclear Regulatory Commission licenses at a cost[2] of approximately $58.00 per gram of metal. This price essentially reflects the cost of separating the isotope from spent uranium fuel rods since there is little commercial demand.[3]

The principal use of technetium involves technetium-99m, the metastable nuclear excited state of technetium-99. This nuclear isomer is widely used as a tracer in diagnostic nuclear medicine[4] owing to its nearly ideal decay properties ($t_{1/2}$ = 6.0 h, γ = 143 keV) . The main motivation for studying the chemistry of technetium-99, therefore, has been to model coordination compounds of technetium-99m which differentially localize in various tissues. Although this area of research has been extremely fruitful, the non-medical applications of technetium chemistry should not be overlooked. In particular, the central position of technetium in the transition series makes this element an excellent tool for studying aspects of both 'early' and 'late' transition metal chemistry

In this thesis, rational ligand exchange reactions of molecular (e.g. pyridine, acetonitrile) and atomic (ie. oxo) ligands on technetium are described; also discussed are some applications of these reactions.

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Chapter 1

Ligand Substitution Reactions Involving Aromatic Amines on Technetium(V)

INTRODUCTION:

Since the discovery[1] of *trans*-$[TcO_2(py)_4]^+$, there has been considerable interest in oxotechnetium(V) complexes with aromatic amine ligands. Some of these compounds have been investigated as potential ^{99m}Tc diagnostic radiopharmaceutical agents[2] and they have been used as ligand substitution reagents for the preparation of novel species.[3]

Clarke[4] prepared a series of mixed ligand complexes with stoichiometry $TcOX_2A_2(OR)$ (X = Cl, Br; A = 4-cyanopyridine, 4-nitropyridine; R = Me, Et) related to the compound $TcOCl_2(bpy)(OEt)$[5]. It had been postulated that these complexes can only be isolated when an electron-withdrawing amine is used. It was speculated, however, that similar complexes with unsubstituted pyridine were reaction intermediates in the formation of $[TcO_2(py)_4]^+$ and a series of μ-oxo dimers.[6]

The use of diolate ligands to substitute for the chlorides on (n- $Bu_4N)[TcOCl_4]$ has been well established for Tc(V) complexes such as $Na[TcO(eg)_2]$[7] (eg = 1,2-ethanediolate), $(n\text{-}Bu_4N)[TcO(catecholate)_2]$,[7] and $Na_3[TcO(glucoheptanate)_2]$.[8] The oxotechnetium-bis(diol) complexes have proven extremely useful as a source of the TcO^{3+} core for ligand exchange under mild conditions.[9] Other examples of technetium diolate complexes include the recently described[10] series of complexes TcO(eg)L, prepared by treating $NaTcO(eg)_2$ with L (where L is a polyaminecarboxylate ligand, e.g. EDTA). The exact coordination environment of these characteristically pale-blue species remains unclear since they do not form single crystals suitable for X-ray diffraction.

Since the non-oxo ligands of dioxotetrakis(pyridine)technetium(V) and oxotetrachlorotechnetate(V) had been shown to be labile, it was reasonable to expect that under appropriate conditions a variety of mixed ligand complexes with a combination of halides, alkoxides, and aromatic amines could be prepared. Herein we report the preparation of a number of such complexes: $TcOCl_2(A)_2(OR)$ (A = py, thiazole (tz); R =

Et, Me), $TcOCl(AA)(OCH_2CH_2O)$ (AA = bpy, phen). The former series can be prepared without the need for electronegative substituents on the ligands via two different routes, substitution of Cl^- for A in [*trans*-$TcO_2(A)_4$]Cl with alcohol solvent, and substitution of A for Cl^- on (n-Bu_4N)[$TcOCl_4$] in THF/alcohol.

EXPERIMENTAL:

Instrumentation:

Fourier transform IR spectra were measured from 4800 to 400 cm^{-1} on an IBM IR/30S spectrometer with DTGS detector and 2 cm^{-1} bandwidth. Infrared absorptions from 400 to 200 cm^{-1} were measured on a Perkin-Elmer 1430A grating spectrometer. ^{1}H NMR spectra were recorded at 250 MHz on a Bruker WM-250 or at 90 MHz on a JEOL FX-90Q.

Technetium-99 NMR spectra were recorded at 90.232 MHz using a Varian XL-400 instrument. A 15 μs pulse width and 0.15 s acquisition time were used. The spectral width was set at 10^5 Hz using 30016 data points in the FID weighted with 100 Hz Gaussian line broadening. Since the reference sample ($NH_4[^{99}TcO_4]$ in D_2O = 0 ppm) resonates at 90.032 MHz in this spectrometer, a difference greater than the maximum spectral width (10^5 Hz) obtainable, chemical shifts were calculated manually based on the spectrometer frequency, transmitter offset, transmitter base offset, and relative shift within the spectral window. The resulting uncertainty in chemical shift is estimated at ± 2 ppm.

Fast atom bombardment mass spectra were measured on samples dissolved in a 3-nitrobenzyl alcohol matrix using a MAT 731 mass spectrometer operating at an accelerating voltage of 8 kV. The source was equipped with an Ion Tech B11N FAB gun producing a beam with 6-8 keV xenon neutrals.

Ultraviolet and visible absorption spectra were recorded on a Hewlett Packard 8451A photodiode array spectrophotometer. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA.

Syntheses:

Caution! ^{99}Tc is a β^- emitter ($t_{1/2} = 2.1 \cdot 10^5$ y). All manipulations of solutions

and solids were performed in a laboratory approved for the handling of radioisotopes using precautions outlined elsewhere.[11]

All solvents were of at least reagent grade and used as received,except for MeOH, which was distilled from I_2 activated Mg turnings. Water was passed though a Barnstead Ultrapure ion-exchange column and distilled using a Corning AG-1 glass still. The complexes $(n\text{-}Bu_4N)[TcOCl_4]$[11b,12] and $[TcO_2(py)_4]Cl$[6] were prepared by literature methods.

Preparation of $TcOCl_2(py)_2(OMe)$: Method 1:

Into a disposable vial was weighed 52.94 mg $(n\text{-}Bu_4N)[TcOCl_4]$ (0.106 mmol), followed by 1 ml THF to dissolve. Upon addition of 3 drops of pyridine, an intense green color formed. After adding 0.25 ml MeOH, a green precipitate gradually formed. The precipitate was redissolved by warming and adding an additional 1.5 ml of THF. The reaction mixture was cooled to -20°C where the product crystallized as small plates. The crystals (30.13 mg, 76%) were filtered in a medium porosity fritted glass funnel, washed with cold THF, H_2O, and hexanes; and were dried in vacuo at room temperature. This product is soluble with gradual decomposition in CH_2Cl_2 and $CHCl_3$.

Method 2:

Into a disposable vial was weighed 22.00 mg $[TcO_2(py)_4]Cl$ (0.046 mmol) followed by 1.50 ml of 0.71 *M* LiCl (Mallinckrodt) in MeOH. To the resulting orange-brown solution was added with stirring 2 drops conc. H_2SO_4 (Mallinckrodt). The blue-green precipitate (12.62 mg, 74%) that formed immediately was filtered in a fine porosity fritted glass funnel and rinsed with MeOH, H_2O, and hexanes; then dried in vacuo at room temperature. The infrared spectrum of this product is identical to that made by method 1.

Anal. Calcd. for $C_{11}H_{13}Cl_2N_2O_2Tc$: C, 35.11%; H, 3.58; Cl, 18.66; N, 7.36. Found:

C, 35.23%; H, 3.49; Cl, 18.91; N, 7.47.

IR (KBr): 3113 cm^{-1}(w), 2907(w), 2813(w), 1607(s), 1483(m), 1451(s), 1444(s), 1352(w), 1244(w), 1208(m), 1159(m), 1120(s), 1071(m), 1064(s), 1048(m), 1017(m), 954(s), 939(s), 931(s), 769(s), 753(m), 695(s), 684(s), 644(m), 505(m), 458(w), 340(m), 330(m). ^1H NMR (CD_2Cl_2): δ 8.95(d, 4H), 7.95(m, 2H), 7.55(t, 4H), 3.43(s, bound MeO-), 3.35(s, free MeOH). UV-vis (CH_2Cl_2): $\lambda max(\varepsilon)$ 308 nm(6,500 $l \cdot mol^{-1} \cdot cm^{-1}$), 650(100).

Preparation of $TcOCl_2(py)_2(OEt)$: Method 1:

Into a disposable vial was weighed 22.56 mg (n-Bu_4N)[$TcOCl_4$] (0.045 mmol) followed by 1.5 ml THF to dissolve. Three drops of pyridine were added with stirring followed by an equal volume of absolute EtOH. Some yellow needles, presumably [$TcO_2(py)_4$]Cl, which formed on cooling to -20°C were removed by filtration through paper. A mixture of $CHCl_3$ and EtOH (2:1) was added to the green filtrate and the resulting solution was concentrated by evaporation. On subsequent cooling to -20°C, silvery-green plates (5.36 mg, 40%) formed which were filtered in a medium porosity fritted glass funnel, rinsed with EtOH and hexanes, and dried in vacuo at room temperature. The product is slightly soluble in alcohol and soluble in CH_2Cl_2.

Method 2:

Into a disposable vial was weighed 17.76 mg [$TcO_2(py)_4$]Cl (0.037 mmol) followed by 2 ml of 0.16 *M* LiCl in absolute EtOH. To the resulting brown solution was added with stirring 2 drops conc. H_2SO_4. Within one minute, small green crystals formed (4.07 mg, 38%) which were filtered in a medium porosity fritted glass funnel and rinsed with EtOH, MeOH, H_2O, and hexanes; then dried in vacuo at room temperature. The infrared spectrum of this product is identical to that made by method 1.

Anal. Calcd. for $C_{12}H_{15}Cl_2N_2O_2Tc$: C, 37.22%; H, 3.99; N, 7.28. Found: C, 37.04%; H, 3.89; N, 7.20.

IR (KBr): 3098 cm^{-1}(w), 3076(w), 3031(w), 2977(w), 2929(w), 2859(w), 1608(m), 1484(w), 1452(s), 1355(w), 1345(w), 1240(w), 1215(m), 1103(s), 1071(s), 1049(m), 1016(w), 947(s), 939(m), 919(s), 877(w), 765(s), 693(s), 646(m), 578(w), 463(w), 411(w), 401(w). ^1H NMR (CD_2Cl_2): δ 9.07(d, 4H), 8.01(m, 2H), 7.61(t, 4H), 3.79(q, 2H), 1.02(t, 3H). UV-vis (CH_2Cl_2): $\lambda max(\varepsilon)$ 646 nm(70 $l \cdot mol^{-1} \cdot cm^{-1}$).

Preparation of TcOCl(eg)(phen):

To 51.61 mg (n-Bu_4N)[$TcOCl_4$] (0.103 mmol) in a disposable vial was added 2.5 ml MeOH and 1.5 ml 1,2-ethanediol (Fisher). The resulting blue solution[13] was stirred for several minutes before adding 32 mg of crystalline 1,10-phenanthroline monohydrate (Baker, 0.162 mmol) with vigorous stirring. The solution immediately became bright green and a green microcrystalline precipitate gradually formed. The solid (29.87 mg, 73%) was collected on a medium porosity fritted glass funnel and rinsed with methanol and hexanes, then dried in vacuo at room temperature. The product is soluble in $CHCl_3$, CH_2Cl_2, and MeCN; it dissolves with decomposition to a purple product in water.

Anal. Calcd. for $C_{14}H_{12}ClN_2O_3Tc$: C, 43.05%; H, 3.10; Cl, 9.08; N, 7.17. Found: C, 42.14%; H, 3.03; Cl, 8.95; N, 7.04.

IR (KBr): 3435 cm^{-1}(s), 3050(m), 2909(m), 2888(m), 2838(m), 1628(w), 1579(w), 1518(m), 1496(w), 1457(w), 1429(s), 1416(w), 1343(w), 1322(w), 1226(w), 1205(w), 1156(w), 1112(w), 1024(s), 1006(w), 980(w), 952(vs), 909(s), 873(w), 854(s), 781(w), 741(w), 722(s), 656(m), 614(s), 539(m), 511(w), 458(w), 430(w), 419(m), 411(w). ^1H NMR ($CDCl_3$): δ 10.32(dd, 1H), 8.98(dd, 1H), 8.46(dd, 1H), 8.35(dd, 1H), 7.98(m, 1H), 7.92(s, 2H), 7.66(m, 1H), 5.99(ddd, H_d: J_{ad} = 3.93 Hz, J_{bd} = 6.08, J_{cd} = -11.47), 5.65(ddd, H_c: J_{ac} = 6.08,

J_{bc} = 3.16), 5.37(ddd, H_b: J_{ab} = -10.96), 4.61(ddd, H_d). ^{99}Tc NMR ($CDCl_3$): δ 1960 ppm ($\Delta\nu 1/2$ = 29104 Hz). UV-vis (MeCN): $\lambda max(\varepsilon)$ 206 nm(29,900 $l \cdot mol^{-1} \cdot cm^{-1}$), 222(32,400), 268(26,600), 422(2,170), 640(36). Conductivity (MeCN): 20 $cm^2 \cdot \Omega^{-1} \cdot eq^{-1}$. FABMS(+): m/z [ion, abundance] = 745 [$(2M-Cl)^+$, 0.12%] ;726 [$(2M+O-2Cl)^+$, 0.09%]; 390 [$(M)^+$, 2.0%]; 355 [$(M-Cl)^+$, 100%]; 330 [$(M-eg)^+$, 27%]; 327 $(M-Cl-C_2H_4)^+$, 28%]; 311 [$(M-Cl-C_2H_4-O)^+$, 47%].

Preparation of TcOCl(eg)(bpy):

Using the procedure above, but substituting 2,2'-bipyridine (Aldrich, 99.5%) for the 1,10-phenanthroline; 65.98 mg (n-Bu_4N)[$TcOCl_4$] (0.132 mmol) was converted to 38.71 mg chlorooxo(1,2-ethanediolato)(2,2'-bipyridine)technetium(V) (80% yield).

Anal. Calcd. for $C_{12}H_{12}ClN_2O_3Tc$: C, 39.32; H, 3.30; N, 7.64. Found: C, 38.97; H, 3.35; N, 7.78.

IR (KBr): $\nu Tc{=}O$ 956 cm^{-1}. ^1H NMR ($CDCl_3$): δ 10.07(d, 1H), 8.64(d, 1H), 8.2-7.8(overlapping multiplets, 4H), 7.64(m, 1H), 7.33(m, 1H), 5.82(ddd, 1H), 5.61(ddd, 1H), 5.40(ddd, 1H), 4.56(ddd, 1H). UV-vis (MeCN): $\lambda max(\varepsilon)$ 200 nm(20,200 $l \cdot mol^{-1} \cdot cm^{-1}$), 242(11,000), 296(14,100), 422(1,730), 640(30), 800(30). Conductivity (MeCN, 0.0914 m*M*): 27 $cm^2 \cdot \Omega^{-1} \cdot eq^{-1}$.

Preparation of TcOCl(catecholate)(phen):

To 27.44 mg (n-Bu_4N)[$TcOCl_4$] (0.055 mmol) in a disposable vial was added 45 mg pyrocatechol (Mallinckrodt, 0.41 mmol) dissolved in 3.5 ml MeOH. To the resulting red solution was added with stirring 50 mg 1,10-phenanthroline monohydrate (0.25 mmol). A red precipitate which rapidly forms was filtered in a fritted glass funnel and washed with methanol. The precipitate recrystallizes from hot benzene giving red-brown needles.

IR (KBr): 3056 cm^{-1}(w), 1630(w), 1606(w), 1580(w), 1518(m), 1495(w),

1463(s), 1429(s), 1344(w), 1320(w), 1238(s), 1213(m), 1146(w), 1097(w), 1019(w), 939(s), 912(m), 874(w), 861(w), 849(s), 801(s), 778(w), 744(m), 719(s), 672(m), 655(m), 649(m), 562(w), 543(m), 456(w), 448(w),430(w). ^1H NMR ($CDCl_3$): δ 10.05(dd, 1H), 8.80(dd, 1H), 8.55(dd, 1H), 8.37(dd, 1H), 8.02(m, 1H), 7.98(s, 2H), 7.61(dd, 1H), 7.46(dd, 1H), 6.9(m, ~3H), 3.5(br, ~1H). FABMS(+): m/z [ion, abundance] = 403 [$(M-Cl)^+$, 100%].

Preparation of $[TcO_2(tz)_4]Cl{\cdot}3H_2O$:

To 76.9 mg (n-Bu_4N)[$TcOCl_4$] (0.154 mmol) was added with magnetic stirring 150 µl thiazole (Aldrich) and 300 µl MeOH. To the resulting brown solution was added three drops H_2O, causing the appearance of a tan precipitate. The precipitate was redissolved by gently heating with additional MeOH. On cooling to -20° C orange crystals formed (63.75 mg, 74%) which were filtered in a fritted glass funnel and rinsed with $CHCl_3$, $(CH_3)_2CO$, and hexanes. The residual solvent was removed in vacuo for <5 min since prolonged evacuation causes the crystals to desolvate. This product is unstable in solution in the absence of excess thiazole ligand.

Anal. Calcd. for $C_{12}H_{18}ClN_4O_5S_4Tc$: C, 25.33%; H, 2.98; N, 9.97; S, 22.69. Found: C, 25.69%; H,3.23; N,9.99; S, 22.86.

IR (KBr): 3416 cm^{-1}(s), 3100(s), 3061(s), 1653(m), 1505(m), 1383(m), 1320(w), 1246(m), 1217(m), 1123(w), 1092(w), 1071(m), 1051(m), 922(m), 876(m), 843(s), 822(vs), 789(m), 756(m), 629(s), 554(w). ^1H NMR (CD_3OD/thiazole): δ 9.48(d, 1H), 8.24(d, 1H), 7.76(m, 1H). UV-vis (MeOH/thiazole): λmax 468 nm.

Preparation of $TcOCl_2(tz)_2(OMe)$:

To 49.45 mg (n-Bu_4N)[$TcOCl_4$] (0.099 mmol) was added with magnetic stirring 100

μl thiazole, 100 μl THF, and 100 μl MeOH. The green precipitate which formed immediately was redissolved by adding 3 ml THF and heating to boiling. On cooling to -20° C, green crystals formed (23.17 mg, 60%) which were filtered in fine porosity fritted glass funnel, rinsed with H_2O and hexanes; then dried in vacuo at room temperature. The product is soluble in Me_2SO, in which it gradually decomposes.

Anal. Calcd. for $C_7H_9Cl_2N_2O_2S_2Tc$: C, 22.04; H, 2.39; Cl, 18.68; N, 7.34; S, 16.84. Found: C, 21.72%; H, 2.34; Cl, 18.32; N, 7.24; S, 16.57.

IR (KBr): 3443(m), 3117(m), 3110(m), 3102(m), 2808(w), 1621(w), 1506(m), 1444(w), 1424(w), 1388(m), 1318(w), 1239(m), 1234(m), 1102(s), 1060(m), 933(vs), 923(s), 885(m), 817(m), 740(w), 731(m), 624(m), 613(w), 525(m). ^1H NMR ($(CD_3)_2CO$): δ 9.70(d, 2H), 8.35(d, 2H), 8.15(m, 2H), 3.42(s, <3H). UV-vis (Me_2SO): λmax 644 nm (ε>70 $l \cdot mol^{-1} \cdot cm^{-1}$). Conductivity ($Me_2SO$): <23 $cm^2 \cdot \Omega^{-1} \cdot eq^{-1}$.

Collection of X-ray data for TcOCl(eg)(phen):

The product isolated from the reaction medium was not suitable for single crystal structure determination. Suitable crystals were grown by slow vapor diffusion of hexane into a CH_2Cl_2 solution of the complex. Precession photographs revealed the symmetry of the crystal. Unit cell parameters were obtained from a least squares fit of χ, φ, and 2θ for 15 reflections in the range 19.1° < 2θ < 25.7°, recorded on a Syntex $P2_1$ diffractometer with use of Mo Kα radiation (λ = 0.71069Å). Crystal data and other parameters related to collection are summarized in Table 1.I. The density was obtained by suspension in a carbon tetrachloride-methylene bromide mixture. Intensities were measured on the $P2_1$ diffractometer with a coupled θ(crystal) - 2θ(counter) scan. The methods of selection of scan rates and initial data treatment have been described.[14] Corrections were made for Lorentz and polarization effects, but not for absorption. This will make the maximum error in F_o <1.7%.

Solution of structure:

The technetium atom was found from a three-dimensional Patterson map, and refinement with electron density difference syntheses revealed all of the other atoms. At this stage, the temperature factors of the non-hydrogen atoms were made anisotropic. Further refinement by full-matrix least squares, which minimized $\Sigma(|F_o| - |F_c|)^2$, varied all parameters and was terminated when the maximum shift/error was roughly 0.25. Reflections with $3\sigma_I > I > -3\sigma_I$ were treated by the method of French and Wilson.[15] Corrections were made for secondary extinctions by the SHELX method.[16] Scattering curves were from the International Tables[17], as were the anomalous dispersion corrections applied to the scattering curves for Tc and Cl.[18] The atom parameters are listed[19] in Table 1.II.

RESULTS AND DISCUSSION:

The reaction of alcoholic solutions of (n-Bu_4N)[$TcOCl_4$] with excess pyridine generally yields $[TcO_2(py)_4]^+$. It has been noted,[20] however, that some water is required to supply the second oxo ligand. When this reaction is performed with scrupulously dried pyridine and alcohol, an unidentified dark green-brown intermediate is formed which will further react with water to produce the dioxotechnetium complex. In tetrahydrofuran, however, the reaction of (n-Bu_4N)[$TcOCl_4$] with pyridine gives a bright emerald green solution which precipitates on addition of ROH (R = Me, Et) as $TcOCl_2(py)_2(OR)$. The significantly lower dielectric constant of THF compared to methanol is probably of prime importance in favoring formation of the neutral species, since solvents less polar than THF, such as CH_2Cl_2 and $CHCl_3$, cause the same color change.

Trop[21] noted that solutions of $[TcO_2(py)_4]^+$ had the distinctive aroma of pyridine. Furthermore, these solutions gradually decompose unless free ligand is added to the solution, further suggesting that the pyridine ligands of these complexes are labile. In order to better understand the ligand exchange properties of this complex, solution Raman spectra of $[TcO_2(py)_4]Cl$ were recorded in differing concentrations of pyridine in methanol. Figure 1.1 shows the region of the spectra where technetium-oxygen stretching modes ν(O=Tc=O) are found. As the concentration of pyridine in solution is decreased, the intensity of the band at 860 cm^{-1} decreases relative to two new bands at 800 cm^{-1} and 895 cm^{-1}. The solid state Raman spectrum[21] of $[TcO_2(py)_4](ClO_4)$ also shows a band at 860 cm^{-1} which was assigned as ν_{sym}(O=Tc=O). The two new bands which intensify when the free pyridine concentration is decreased may be assigned as ν_{asym} and ν_{sym}(O=Tc=O) of a non-centrosymmetric molecule. The $[TcO_2(py)_4]^+$ ion, with D_{4h} coordination symmetry, has only the symmetric stretch allowed in the Raman spectrum. A similar molecule not possessing an inversion center might be expected to have both of the O=Tc=O

stretching modes allowed in the Raman and in the infrared spectra. A possible equilibrium reaction explaining these results is shown in Scheme 1.I.

The Raman results did not provide any information regarding the rate of ligand dissociation from the complex. Proton NMR experiments, however, allowed for a rough estimate of the exchange lifetime. Distinct resonances for both coordinated and free pyridine are observed separated by approximately 70 Hz in the 90 MHz NMR spectrum of $[TcO_2(py)_4]Cl$ combined with four equivalents of pyridine. Therefore, the minimum lifetime can be calculated[22] from Equation 1. Substituting for the minimum separation observed ($\Delta\nu$), the exchange lifetime (τ) for the pyridine ligands must be greater than three milliseconds.

$$\tau > \frac{\sqrt{2}}{2\pi\Delta\nu} \qquad (1.I)$$

In a separate experiment, a large excess of perdeuteropyridine (C_5D_5N, Aldrich, 99% deuterated) was added to a methanolic solution of $[TcO_2(py)_4]Cl$ and its ^1H NMR spectrum was measured immediately. The spectrum showed the residual protons on the pyridine-d5 superimposed with the spectrum of free proteopyridine. The appearance of the spectrum did not change over the following 30 minutes. These results suggest that the coordinated proteopyridine molecules rapidly equilibrate with the free deuteropyridine in solution, roughly on the timescale of mixing. Confirmation of this hypothesis comes from the FAB mass spectrum of the NMR sample which was isolated from solution 30 minutes following the addition of C_5D_5N. The only ions observed corresponded to $[TcO_2(C_5D_5N)_4]^+$ and two sequential losses of 84 mass units (C_5D_5N) indicating that the NMR spectrum observed immediately after mixing reflects complete equilibration of the pyridine molecules. It may be concluded that the value for the dissociation lifetime of the first pyridine ligand must fall between three milliseconds and tens of seconds. Very likely, therefore, this dissociation

step will be rate limiting in substitution reactions of $[TcO_2(py)_4]^+$.

The reaction of $[TcO_2(py)_4]^+$ with chloride ion in alcohol to form $TcOCl_2(py)(OR)$ is interesting for several reasons. This reaction requires the addition of concentrated sulphuric acid,[23] presumably in order to doubly protonate one oxo ligand, thereby labilizing it. The ability of the alcohol to deprotonate and coordinate under such acidic conditions is quite remarkable, and reflects the high electrophilicity of technetium(V). This discovery of a second route to these bis(amine)-dichloride complexes provides mechanistic insight which was heretofore unavailable. As evidenced by their identical IR and NMR spectra, the same geometrical isomer is formed by both routes shown in Scheme 1.II. This demonstrates that the *trans*-labilizing effect is probably unimportant in the determination of geometry which must therefore be controlled by rearrangements to the thermodynamic product.

Thiazole derivatives $TcO_2(tz)_4^+$ and $TcOCl_2(tz)_2(OR)$ were prepared demonstrating the generality of the reaction conditions. The similarity of the thiazole and pyridine derivatives suggest that thiazole is acting as an N donor only. This assumption is confirmed by the proton NMR spectra which show a larger shift from free ligand of the protons α to the nitrogen. Bonding of thiazole through the nitrogen is seen[24] for the divalent ions of Co, Ni, Cu, and Zn.

There is evidence[25] that bleomycin (shown in Figure 1.2) binds Mn^{2+} in part through the 2,4'-bithiazole moiety on this anti-tumor antibiotic. The donor atoms of this potentially ambidentate ligand which participate in manganese binding could not, however, be uniquely determined. Technetium has been used to radiolabel bleomycin[26] though the chemical nature of this complex also has not been determined. The formation of the relatively stable Tc(V) thiazole complexes suggests that the bithiazole moiety may also play a role in the binding of technetium to bleomycin.

Although the complexes $TcOCl_2(py)_2(OR)$ are hydrolytically unstable in solution, they are apparently more robust than the analogous complexes made[4] with the poorer donors 4-

nitropyridine and 4-cyanopyridine or the thiazole complex reported here. The NMR spectra (Figure 1.3) for the pyridine complexes in $CDCl_3$ or CD_2Cl_2 show a small resonance corresponding to free alcohol, suggesting that loss of the alkoxide ligand is at least one step in the decomposition process. As expected, the complexes with a chelating diolate ligand, e.g. $TcOCl(OCH_2CH_2O)(phen)$ have enhanced solution stability making it possible to recrystallize the complex to form single crystals suitable for X-ray diffraction. The diolate derivatives, however, could only be prepared with the bidentate amines 2,2'-bipyridine and 1,10-phenanthroline.

Unlike the mono-alcoholate complexes, the diolate species gave readily interpretable positive mode fast atom bombardment mass spectra. The mass spectra not only confirm the identity of the complexes, but also give insight into the hydrolysis products. Since the complex was dissolved in an undried nitrobenzyl alcohol matrix before acquiring the spectra, some hydrolysis could take place on the probe. The low abundance peak at m/z = 726 ($Tc_2O_3(eg)_2(phen)_2$) corresponds to hydrolysis of both chloride ligands. All attempts to isolate this compound from the dark purple hydrolysis mixture have been unsuccessful. The other ion in this mass region with m/z = 745 ($Tc_2ClO_2(eg)_2(phen)_2$) may correspond to a cluster of two molecules with one of the chlorine atoms dissociated.

Further information on the reactivity of this complex comes from the fragmentation patterns in the molecular ion region of the mass spectrum. The most abundant ion in this region corresponds to the loss of the chloride ligand which is expected considering the unusually long Tc-Cl bond length (vide infra). A more interesting fragment is the one of mass 327 ($TcO_3(phen)^+$) corresponding to loss of chloride and ethene from the molecule. This ion is reminiscent of the known Tc(VII) species[5] $TcO_3Cl(phen)$, suggesting that these two isolable species might be interrelated. Furthermore, the mass spectra of substituted vicinal diolate complexes described in Chapter 2 similarly show losses of the corresponding alkene.

As shown in Figure 1.4, the NMR spectrum of TcOCl(eg)(phen) has seven distinct aromatic proton resonances and four distinct ethanediolate signals. This evidence suggests that the O and Cl atoms have a mutually *cis*- conformation yielding a completely asymmetrical environment (point group C_1). It was unclear, however, whether a nitrogen or oxygen donor was *trans*- to the oxo ligand. Evidence for the former comes by comparison of the Tc=O stretching frequency (952 cm^{-1}) to that of TcO(eg)(HB(pyz)$_3$)[28] (pyz = pyrazole) (953 cm^{-1}) which must have a *trans*- nitrogen.

A single crystal X-ray structure was obtained in order to understand the structural features of the diolate mixed-ligand complexes. The molecule is shown in Figure 1.5 and bond lengths and angles are given in Table 1.III. The technetium atom is six-coordinate but is significantly distorted from normal octahedral geometry. In part this is because the 1,10-phenanthroline ligand enforces a small N1-Tc-N2 angle (72.7(2)°) and in part it is the effect of the strongly bonded O3 atom (Tc-O3, 1.661(4)Å) repelling the remaining equatorial ligands (O3-Tc-Cl,O1,O2 angles 95.8(2), 105.0(2), 112.0(2)°). The Tc-N2 bond (2.268(4)Å) is longer than the normal range of Tc-N distances (2.055(6)-2.209(6)Å)[29] because of the *trans* influence of the oxo group O3 on N2. Furthermore, Tc-N1 (2.173(4)Å) is at the upper limit of normal Tc-N distances and Tc-Cl (2.418(2)Å) is longer than Tc-Cl bonds normally found in Tc(V) compounds where the chlorine is not *trans* to the oxo group (range 2.291-2.359Å, average 2.324Å).[30-35] This lengthening is due to the *trans* influence of the strongly bonded O^- groups of the ethanediolato moiety. The Tc-O(diol) distances are normal for an RO^- group bonded to technetium,[30-31,34,36] but the two differ significantly (Tc-O1, 1.924(4); Tc-O2, 1.902(3)Å). The difference is consistent with Cl having a stronger *trans* influence than an amine.

Because of the strong *trans* influence imparted by the ethanediolato group, its bonding might be visualized as shown in Scheme 1.III as a resonance hybrid involving primarily a

singly bonded 1,2-ethanediolate, but also, to a lesser extent, two doubly bonded oxygens and ethene. The C1'-C2' distance of the diolate at 1.491(1) Å is shorter than expected for a single bond, but significantly longer than for a double bond. This carbon- carbon bond length is slightly shorter than the equivalent bond (1.498(5) Å) in $(C_5Me_5)ReO(eg)$,[37] which loses ethene on heating to 150°C in vacuo. The bond lengths and angles within the 1,10-phenanthroline group agree well with the averages calculated previously.[38,39] The ligand is significantly non-planar, being folded about a line passing through the centers of the C5-C6 and C11-C12 bonds. The fold is more pronounced at the C11-C12 end. The dihedral angle between the two pyridine rings is 6.5(2), made up of dihedral angles of about 3° between the pyridine rings and the central ring. We assume this fold is to accommodate bonding to the technetium atom which lies 0.376(4)Å out of the best plane through the phenanthroline ligand in the same direction as the nitrogen atoms. Non-planarity of 1,10-phenanthroline ligands has been observed previously, but there appears to be no regular trend in the distortions. Bending of the type observed here has also been observed previously,[38] but in those cases the metal atoms (Na^+, Rb^+) lie out of the plane of the ligand in the direction opposite that of the nitrogen atoms.

The ethanediolato ligand is twisted such that both carbon atoms lie on the same side of the Tc,O1,O2 plane: C1' by 0.16(1)Å and C2' by 0.58(1)Å. Although this effect may simply be due to intramolecular repulsions, the partial multiple bonding between the carbons as discussed above may be responsible for this distortion. As shown in the packing diagram (Figure 1.6), pairs of molecules related by a center of symmetry are arranged to overlap the 1,10-phenanthroline rings and maximize $\pi-\pi$ interactions, though the contacts between adjacent molecules are van der Waals.

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Table 1.I: Crystal Data

compound	$C_{14}H_{12}ClN_2O_3Tc$
f.w.	390.6
morphology	needle
crystal size, mm	0.10 x 0.10 x 0.35
systematic absences	h0l, l = 2n+1; 0k0, k = 2n+1
space group	$P2_1/c$, #14
unit cell (Å and °)	a = 7.440(2) b = 8.928(3) β = 92.48(2) c = 21.355(4)
volume, $Å^3$	1417.2(7)
Z	4
r_{obs}, r_{calc}, $g \cdot cm^{-3}$	1.81(2), 1.830
T, °C	22
linear abs. coeff., cm^{-1}	11.97
abs. corr. factor	1.11-1.16
max 2θ, reflectns meas	45°; h, k, ±l
standard reflectns (σ(I))	1 0 6 (0.014), 0 1 -6 (0.018)
no. of reflectns meas	2157
R_{int}	0.0197
no. of unique reflectns	1859
final R, R_w	0.051, 0.036
final Δ/σ; max, ave	0.25, 0.069
final difference map; max, min $eÅ^{-3}$	0.49, -0.47
secondary extinction, x	-0.00026
weighting	$w = ((\sigma F)^2 + 0.000206F_o^2)^{-1}$
F(000)	770.2
number of variables	239
error in obs of unit weight	1.114

$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2\}^{1/2}$

Table 1.II: Atomic Positional Parameters ($X10^4$) and Temperature Factors ($Å^2$)$X10^3$

	X	Y	Z	U_{eq}*
Tc	1853(1)	1642(1)	3687.3(2)	38
Cl	4964(2)	850(2)	3731(2)	47
O(1)	-234(5)	2842(4)	3478(2)	50
O(2)	1911(5)	1434(4)	2802(2)	51
O(3)	1061(6)	116(4)	4025(2)	64
N(1)	1997(6)	2689(5)	4606(2)	36
N(2)	3170(5)	3913(4)	3579(2)	31
C(1)	1523(8)	2042(7)	5131(2)	44
C(2)	1385(8)	2803(8)	5695(3)	53
C(3)	1786(7)	4287(8)	5723(3)	43
C(4)	2365(6)	5025(6)	5190(2)	35
C(5)	2865(7)	6560(7)	5170(3)	41
C(6)	3472(8)	7187(7)	4644(3)	48
C(7)	3618(7)	6329(5)	4079(2)	36
C(8)	4323(8)	6874(6)	3522(3)	45
C(9)	4484(8)	5934(7)	3032(3)	46
C(10)	3881(7)	4467(6)	3068(3)	40
C(11)	3074(6)	4833(6)	4083(2)	31
C(12)	2442(6)	4170(5)	4642(2)	40
C(1')	-1061(10)	2422(11)	2894(3)	68
C(2')	388(10)	2047(11)	2459(3)	75

*$U_{eq} = 1/3(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta)$

Table 1.III: Selected Interatomic distances (Å) and angles (°).

Tc-O(1)	1.924(4)	Tc-O(2)	1.902(3)	Tc-O(3)	1.661(4)
Tc-N(1)	2.173(4)	Tc-N(2)	2.268(4)	Tc-Cl	2.418(2)
N(1)-C(1)	1.322(7)	C(1)-C(2)	1.390(8)	C(2)-C(3)	1.36(1)
N(2)-C(10)	1.328(7)	C(10)-C(9)	1.388(8)	C(9)-C(8)	1.352(8)
C(3)-C(4)	1.398(8)	C(4)-C(5)	1.422(8)	C(4)-C(12)	1.401(7)
C(8)-C(7)	1.407(8)	C(7)-C(6)	1.437(8)	C(7)-C(11)	1.396(7)
N(1)-C(12)	1.365(7)	C(5)-C(6)	1.350(9)	O(1)-C(1')	1.418(8)
N(2)-C(11)	1.359(6)	C(11)-C(12)	1.429(7)	O(2)-C(2')	1.431(9)
C(1')-C(2')	1.491(1)				

O(3)-Tc-Cl	95.8(2)	O(3)-Tc-O(1)	105.0(2)
O(3)-Tc-O(2)	112.0(2)	O(3)-Tc-N(1)	88.0(2)
O(3)-Tc-N(2)	160.1(2)	Cl-Tc-O(1)	159.0(1)
Cl-Tc-O(2)	87.0(1)	Cl-Tc-N(1)	94.7(1)
Cl-Tc-N(2)	81.3(4)	O(1)-Tc-O(2)	82.9(2)
O(1)-Tc-N(1)	88.7(2)	O(1)-Tc-N(2)	80.0(2)
O(2)-Tc-N(1)	159.7(2)	O(2)-Tc-N(2)	87.6(2)
N(1)-Tc-N(2)	72.7(2)	Tc-N(1)-C(2)	125.0(4)
Tc-N(1)-C(12)	118.0(3)	C(12)-N(1)-C(1)	116.7(4)
Tc-N(2)-C(10)	127.3(3)	Tc-N(2)-C(11)	115.0(3)
C(11)-N(2)-C(10)	117.5(4)	N(1)-C(1)-C(2)	123.6(6)
C(1)-C(2)-C(3)	119.3(6)	C(2)-C(3)-C(4)	119.9(5)
N(2)-C(10)-C(9)	122.6(5)	C(10)-C(9)-C(8)	120.2(6)
C(9)-C(8)-C(7)	119.2(5)	C(3)-C(4)-C(5)	124.7(5)
C(3)-C(4)-C(12)	116.7(5)	C(12)-C(4)-C(5)	118.6(5)
C(8)-C(7)-C(6)	124.7(5)	C(8)-C(7)-C(11)	117.1(5)
C(11)-C(7)-C(6)	118.2(5)	C(4)-C(5)-C(6)	121.5(5)
N(1)-C(12)-C(4)	123.7(5)	N(1)-C(12)-C(11)	116.3(4)
C(7)-C(6)-C(5)	121.2(5)	N(2)-C(11)-C(7)	123.3(4)
N(2)-C(11)-C(12)	116.2(4)	C(11)-C(12)-C(4)	120.0(5)
Tc-O(1)-C(1')	111.8(4)	O(1)-C(1')-C(2')	108.1(6)
C(12)-C(11)-C(7)	120.5(4)	Tc-O(2)-C(2')	114.8(4)
O(2)-C(2')-C(1')	110.2(6)		

Figure 1.1: Raman spectra of $[TcO_2(py)_4^+]$ in varying concentrations of pyridine. [Tc] = 14 m*M*. (a) 100% MeOH, 0% pyridine. (b) 99.75% MeOH, 0.25% pyridine. (c) 97.5% MeOH, 2.5% pyridine. (d) 90% MeOH, 10% pyridine.

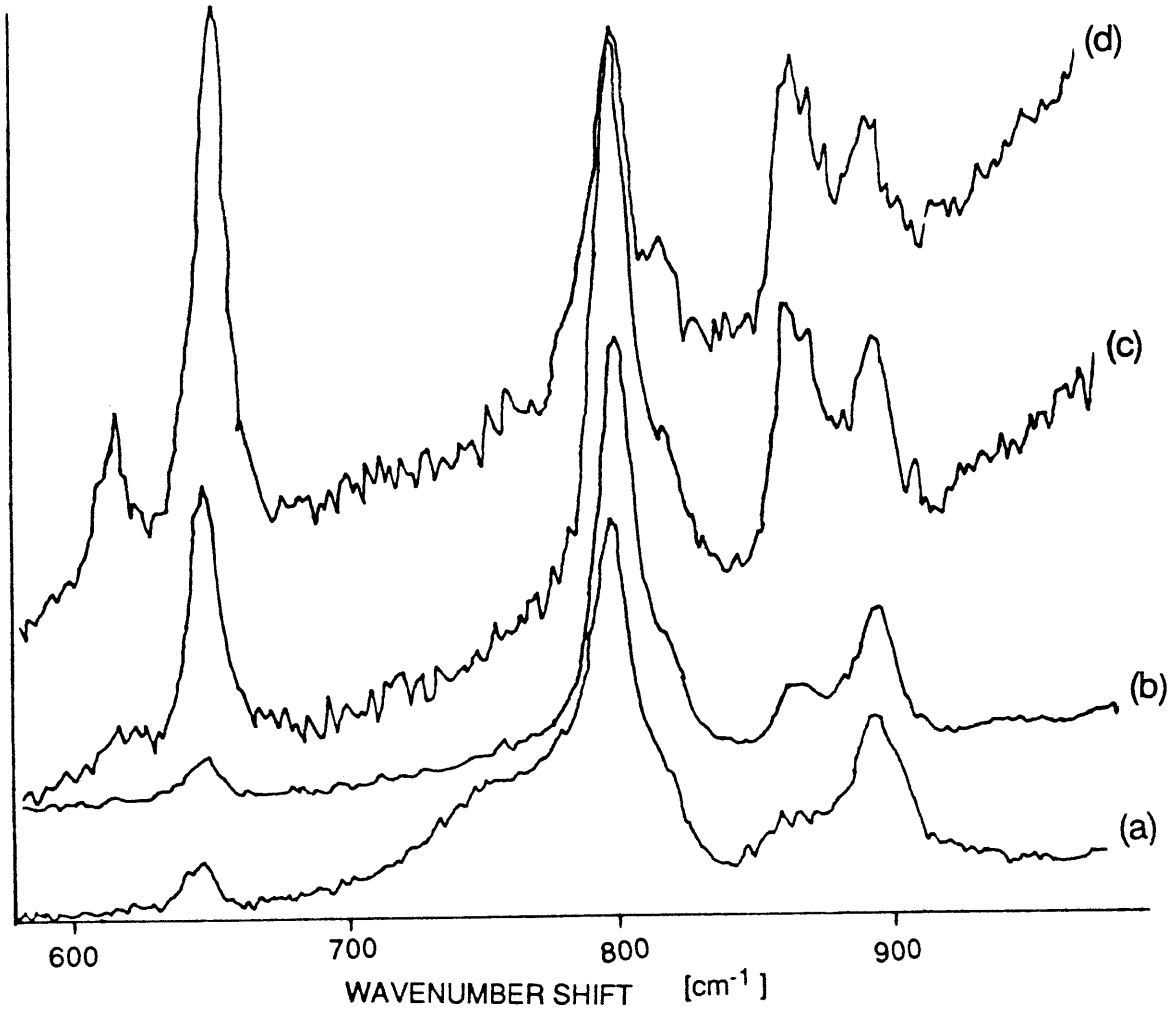

(d)
(c)
(b)
(a)
600
700
800
900
WAVENUMBER SHIFT [cm-1]

Figure 1.2: Bleomycin A2. The bithiazole moiety is outlined by a box.

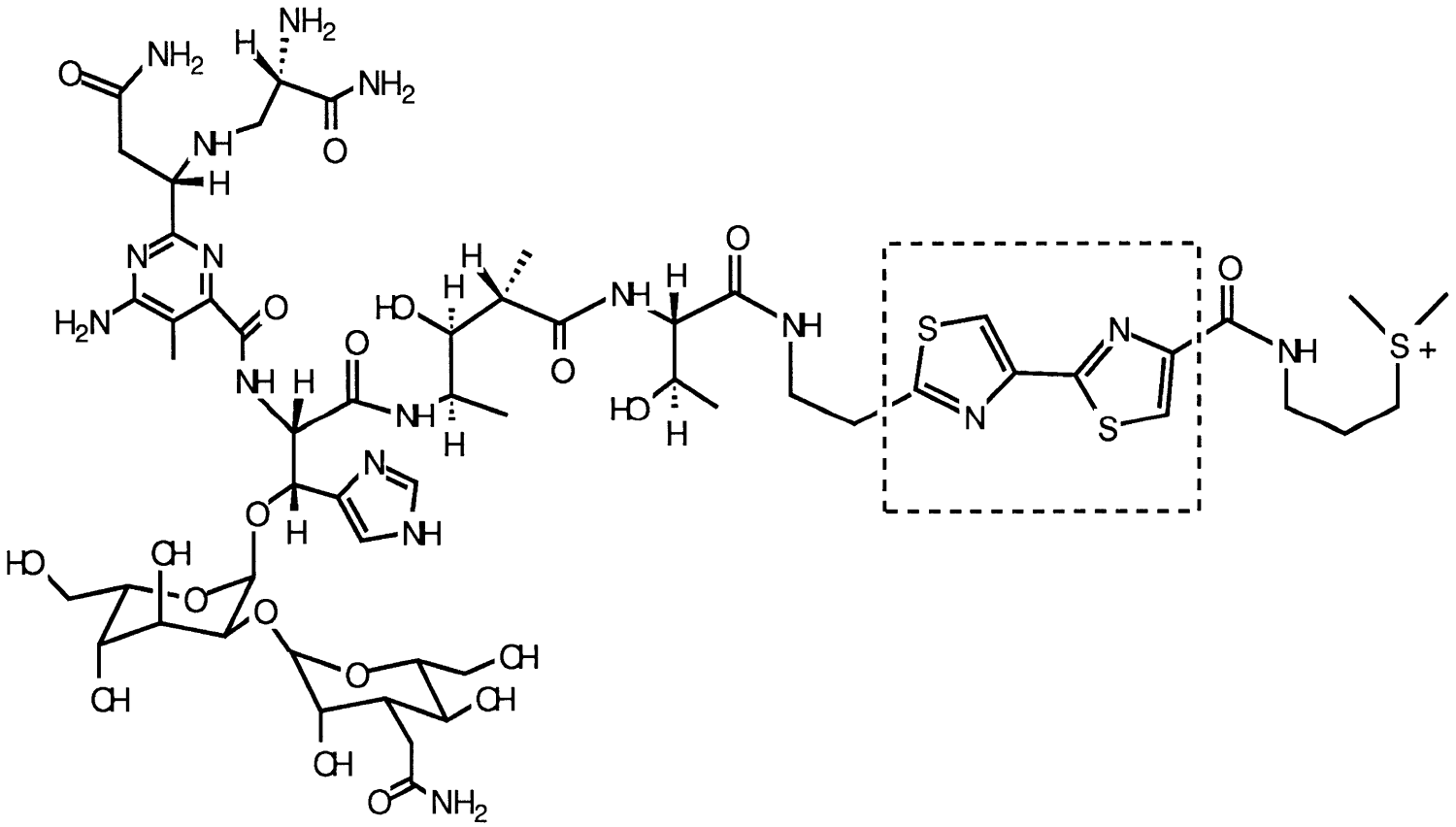


Figure 1.3: Proton NMR spectrum (300 MHz) of $TcCl_2(py)_2(OMe)$ showing a small resonance due to dissociated methanol.

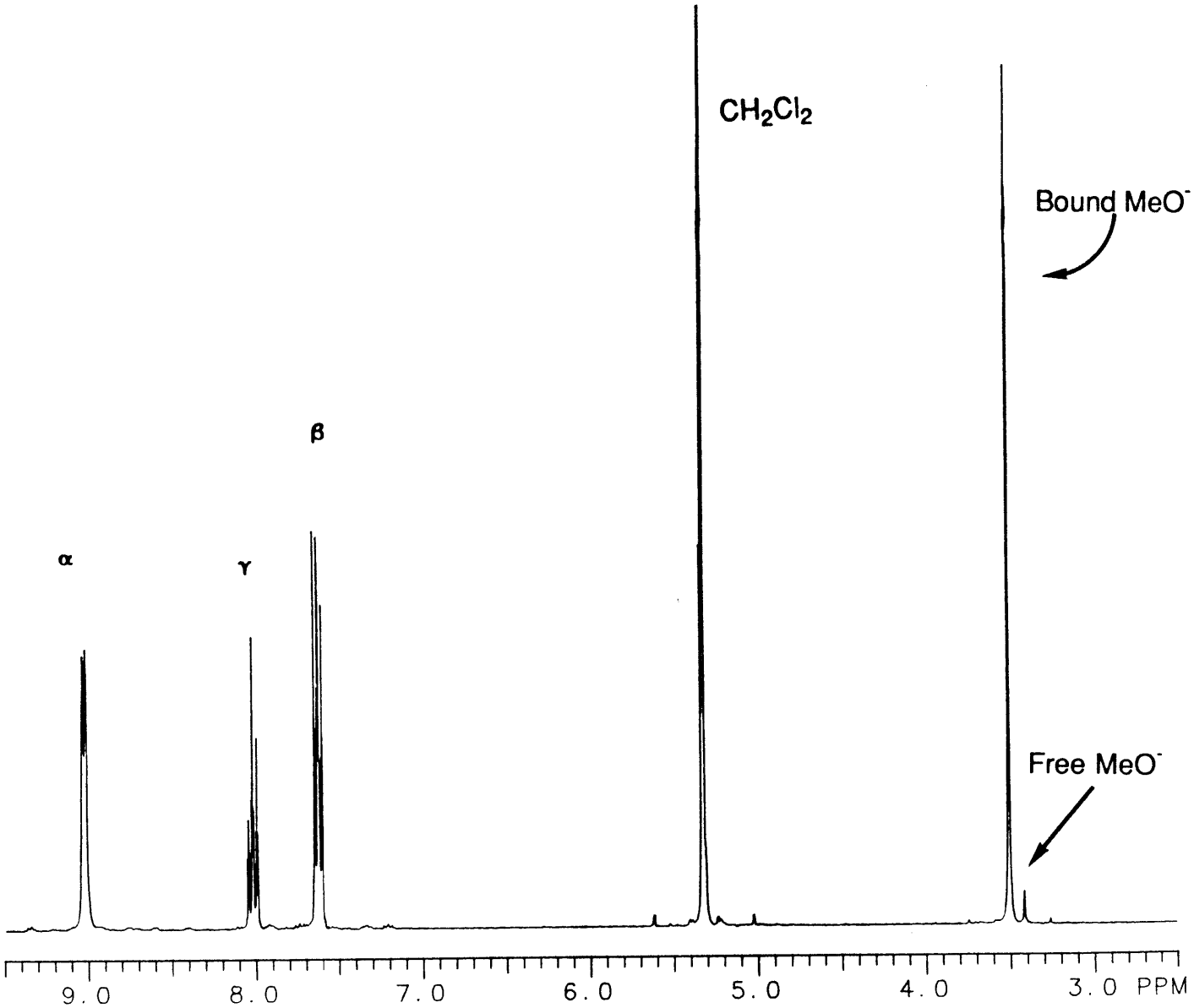

CH_2Cl_2
Bound MeO⁻
β
α
γ
Free MeO⁻
9.0
8.0
7.0
6.0
5.0
4.0
3.0 PPM

Figure 1.4: Proton NMR spectrum (300 MHz) of TcOCl(eg)(phen). Inset, ethylene glycol region expanded to show eight line multiplets.

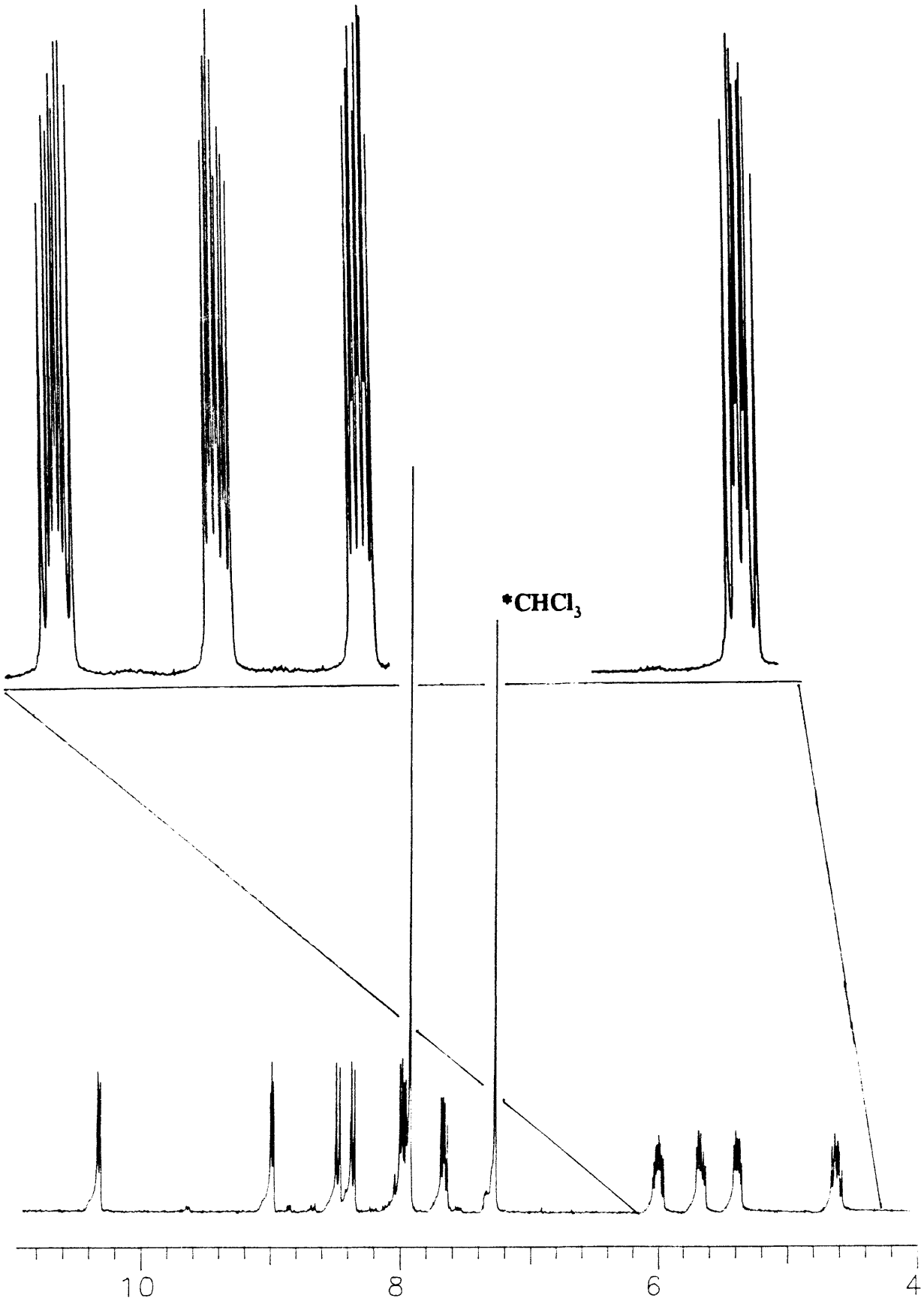

*CHCl3
10
8
6
4

Figure 1.5: SNOOPI drawing of TcOCl(eg)(phen) showing atom numbering scheme.

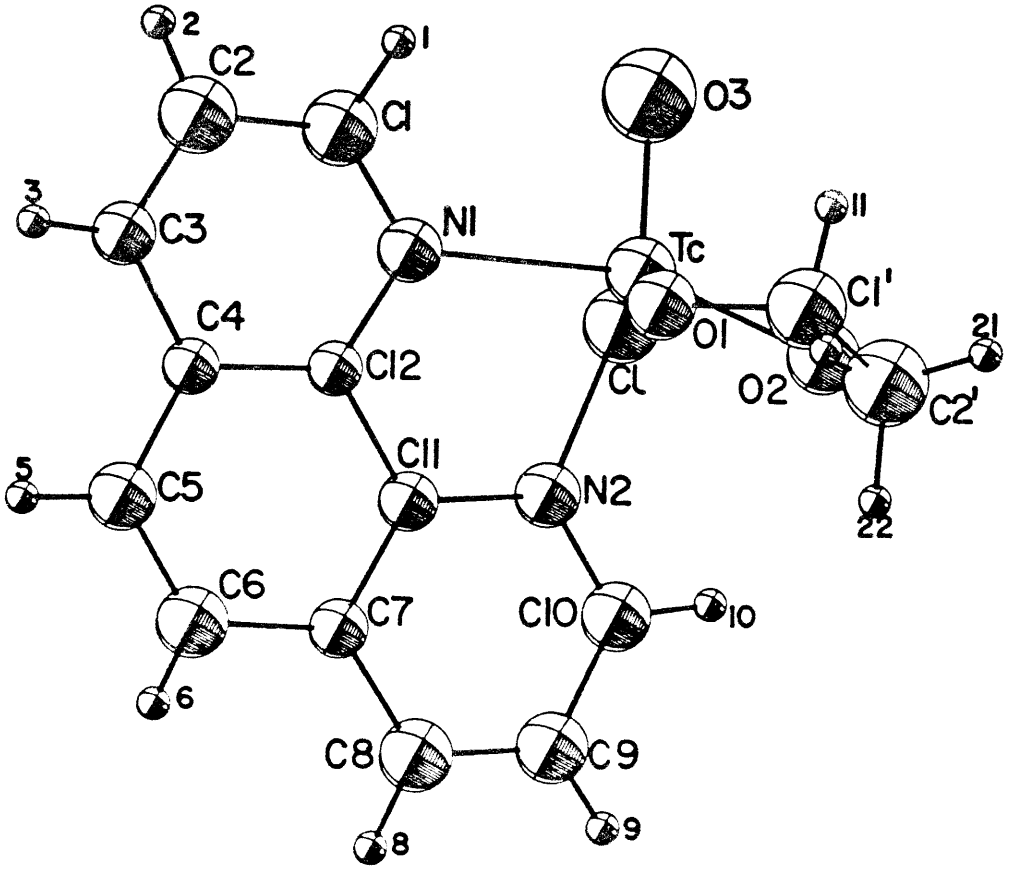
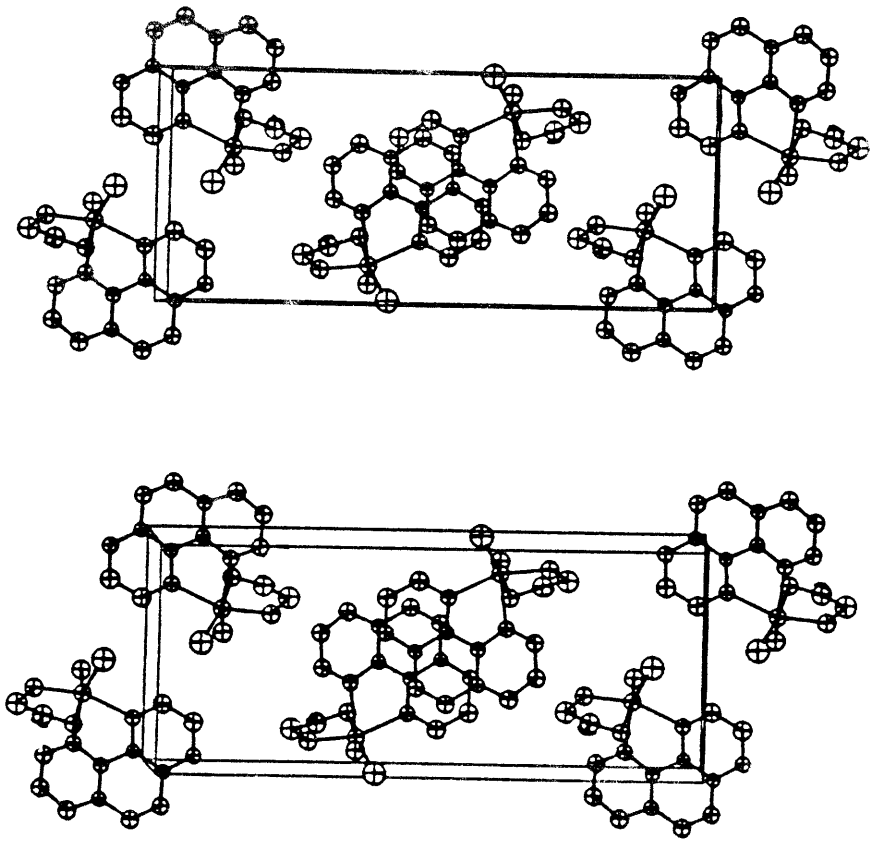
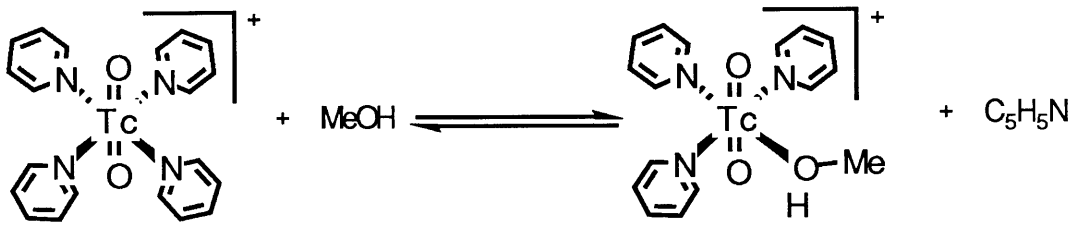

2
C2
1
C1
O3
3
C3
N1
Tc
11
Cl'
C4
O1
21
C12
Cl
O2
C2'
C11
5
C5
N2
22
C6
C7
C10
10
6
C8
C9
9
8

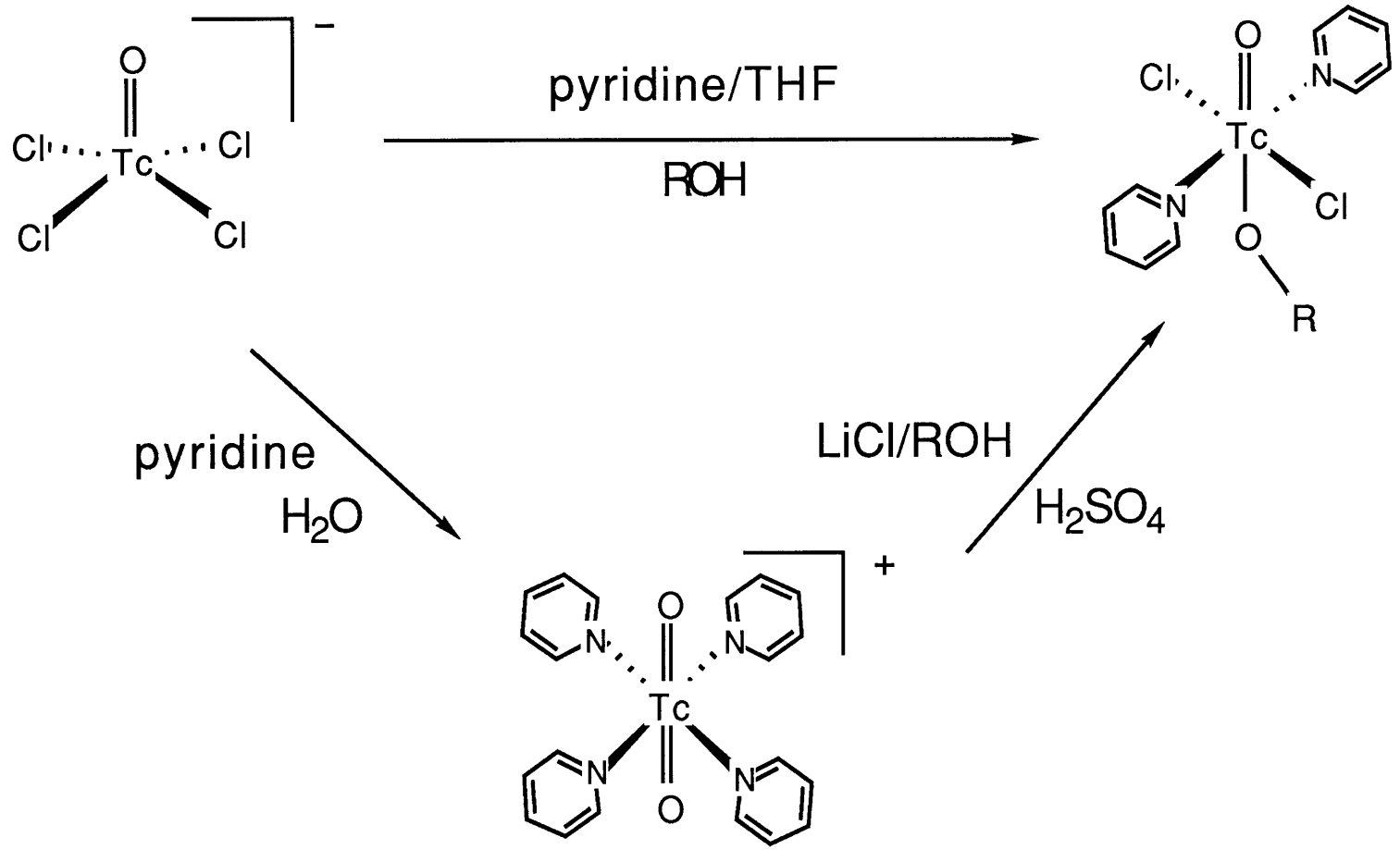
Figure 1.6: Packing diagram for TcOCl(eg)(phen).



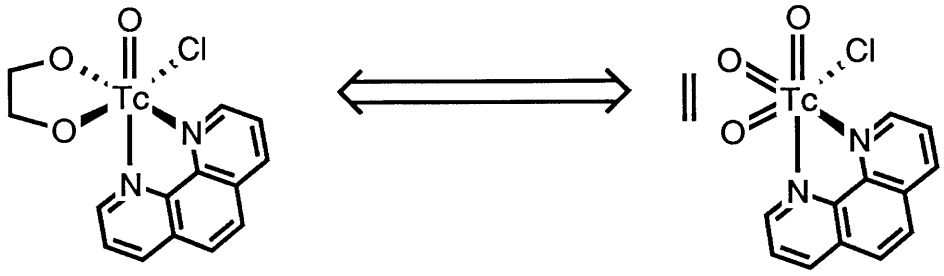
Scheme 1.I



Scheme 1.II



Scheme 1.III



Chapter II

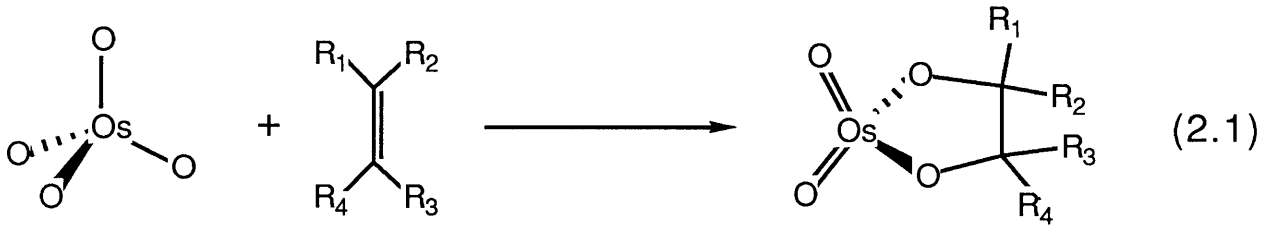
Alkene-Diol Interconversion

with

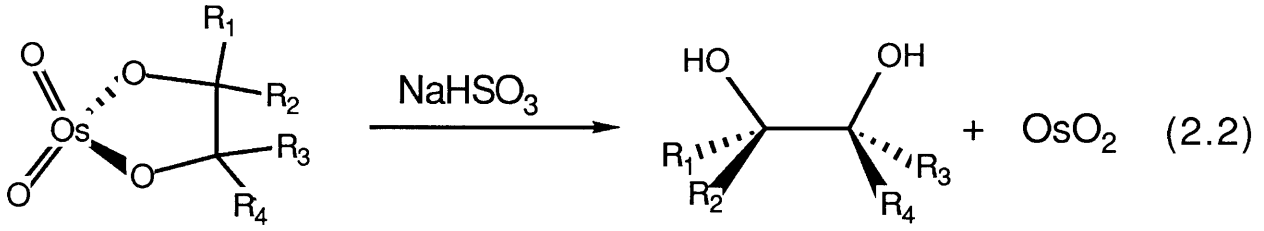
Technetium and Rhenium Complexes

INTRODUCTION:

Among the most selective and reliable organic transformations are those which involve the transfer of an oxygen atom from a metal complex to a carbon atom. Reagents often used in these reactions include[1] CrO_2Cl_2, MnO_4^-, OsO_4, and SeO_2. The reaction of OsO_4 with alkenes[2], for example, (Reactions 2.1-2.2) is the most reliable route available for the *cis*-dihydroxylation of alkenes to give the corresponding diols. The high cost of osmium tetroxide (≈$66/g) as well as its high toxicity has motivated the search for alternative methods for *cis*-dihydroxylation of alkenes.



(2.1)



(2.2)

Reactions of alkenes with the oxides of metals other than osmium have been investigated for potential *cis*-dihydroxylating ability. The tetraoxide of ruthenium, the less expensive and less toxic second row congener of osmium, does yield[3] vicinal diols when reacted with

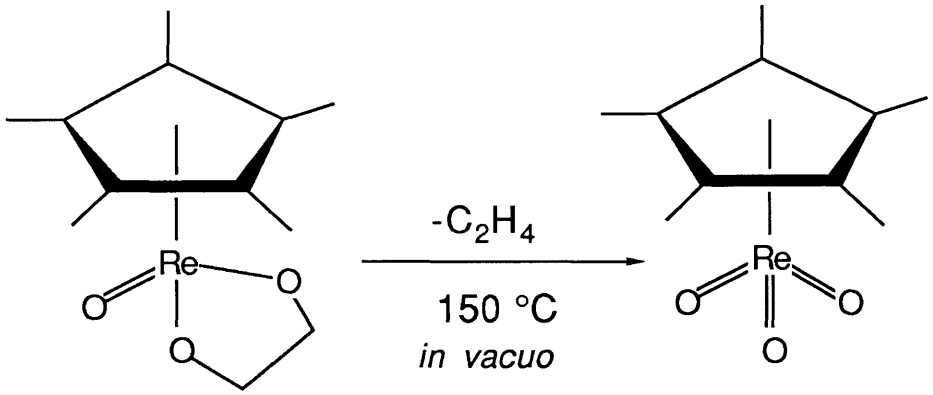
alkenes at low temperature, but its extremely strong oxidation potential leads to poor yields. Since permanganate is capable of *cis*-dihydroxylation of alkenes under certain conditions (although overoxidation is common)[4], the reaction of perrhenyl chloride, ReO_3Cl with alkenes has been attempted[5] but no diols were formed. This Re(VII) compound, however, was shown capable of oxidizing alkenes,[5] with the most predominant product being the corresponding chlorohydrin.

The other approach taken to overcome the cost and toxicity limitations of osmium tetroxide is the application of oxidative cleavage to the resulting osmate esters, leading to a catalytic role for the osmium. Oxidizing agents used for this purpose include metal chlorates, hydrogen peroxide, *tert*-butyl hydroperoxide, dioxygen, and tertiary amine N-oxides. Under ordinary conditions, best results are achieved with the last of these reagents, giving yields[6] comparable to those obtained by stoichiometric oxidation with OsO_4.

Homogeneous catalysis by technetium has been little studied, presumably due to fear of its radioactivity. Nevertheless, catalytic activity for hydrogenation,[7] epoxidation,[8] and metathesis[9] of alkenes has been noted for various complexes of this element. The epoxidation reaction of alkenes with ^tBuOOH catalyzed[8] by soluble technetium complexes with oxidation states ranging from 0 to +5 is germane to the present discussion because epoxides can be readily converted into diols. The stereochemistry of the epoxide products, however, is virtually independent of the stereochemistry of the starting alkene and the selectivities for the epoxide are poor.

The loss of C_2H_4 from the technetium(V) complexes with diolate ligands TcOCl(eg)(AA) (AA=bpy, phen), which is observed in the mass spectrometer and noted in Chapter 1, is very reminiscent of the thermolysis reaction[10] of $Cp^*ReO(OCH_2CH_2O)$ (Reaction 2.3). The technetium diolate complexes do not lose ethene under similar conditions, though the reverse reaction, ie. oxidation of alkenes to diolates, is plausible considering the relatively stronger oxidizing ability of technetium compared to rhenium, ceteris paribus. The

technetium(VII) complexes, $TcO_3Cl(AA)$ (AA=phen, bpy), were first prepared by Davison, Abrams and Jones, who noted[11] their instability toward reduction. In this chapter, the use of these trioxotechnetium(VII) complexes for the *cis*-dihydroxylation of alkenes is described.



(2.3)

EXPERIMENTAL:

Instrumentation:

Fourier transform IR spectra were measured from 4800 to 400 cm^{-1} on an IBM IR/30S spectrometer with DTGS detector and 2 cm^{-1} bandwidth. ^{1}H NMR spectra were recorded at 250 MHz on a Bruker WM-250, or at 300 MHz on a Varian XL-300.

Fast atom bombardment mass spectra were measured on samples dissolved in a 3-nitrobenzyl alcohol matrix using a MAT 731 mass spectrometer operating at an accelerating voltage of 8 kV. The source was equipped with an Ion Tech B11N FAB gun producing a beam with 6-8 keV xenon neutrals.

Technetium-99 NMR spectra were recorded at 67.524 MHz using a Varian XL-300 instrument. A 34 μs pulse width and 0.41 s acquisition time were used. The spectral width was set at 37 kHz using 30016 data points in the FID weighted with 10 Hz Gaussian line broadening.

Ultraviolet and visible absorption spectra were recorded on a Hewlett Packard 8451A photodiode array spectrophotometer. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA.

Gas chromatography was performed using a HP-5890A capillary gas chromatograph equipped with a flame ionization detector. Separation of diols was performed with a 28.5 m long, 0.317 mm ID J&W fused silica column supporting a 0.25 μ film of DB-5 (5% phenylmethyl silicone). The temperature programmer held the column at 50°C for four minutes then ramped at eight degrees per minute to a maximum temperature of 250°C.

Syntheses:

Caution! ^{99}Tc is a β^- emitter ($t_{1/2} = 2.1 \cdot 10^5$ y). All manipulations of solutions and solids were performed in a laboratory approved for the handling of radioisotopes using

precautions outlined elsewhere.[12]

All solvents were of at least reagent grade and used as received unless otherwise noted. Dichloromethane (EM Science), preserved with 70 ppm of isopentene, was stirred overnight with conc. H_2SO_4, washed with saturated aqueous Na_2CO_3, and predried over anhydrous $CaCl_2$. It was then distilled under N_2 from P_4O_{10} and stored in the dark under N_2. Water was passed though a Barnstead Ultrapure ion-exchange column and distilled using a Corning AG-1 glass still. TcO_3Cl(phen) and TcO_3Cl(bpy) were prepared by literature methods.[11] $(Ph_4As)[ReOCl_4]$ was prepared by the method of Cotton and Lippard.[13] Styrene (Aldrich, 99+%, stabilized with 10-15 ppm ^{t}Bu-catechol) was vacuum distilled (bp 45-48 °C) using a vacuum insulated, glass bead packed column. Dibutyl fumarate (*trans*-$C_4H_9OC(O)CH{:}CHC(O)OC_4H_9$) was prepared by condensation of ^{n}BuOH (Mallinckrodt) with fumaryl chloride (Aldrich, 95%) in Et_2O using pyridine to scavenge generated HCl.

Preparation of $TcO_3Cl(5\text{-}NO_2\text{-phen})$:

To 0.109 g 5-nitro-1,10-phenanthroline (G. F. Smith) was added 10 ml MeOH. The ligand was dissolved by gentle heating and the resulting solution cooled to ambient temperature before adding 0.5 ml of 0.385 *M* $(NH_4)[TcO_4]$ (0.193 mmol). The solution was stirred and 1.5 ml conc. HCl was added dropwise. An olive-green precipitate formed almost immediately. After cooling the reaction mixture to -20 °C, the product was collected on a medium porosity fritted glass funnel. After washing well with MeOH, the product was dried in vacuo overnight. Yield: 77.90 mg (99%).

Anal. Calcd. for $C_{12}H_7ClN_3O_5Tc$: C, 35.36%; H, 1.73; Cl, 10.31; N, 10.31. Found: C, 35.80%; H, 1.94; Cl, 8.83; N, 10.57.

IR (KBr): 3057 cm^{-1}(w), 3086(w), 1535(s), 1516(s), 1489(w), 1456(w), 1430(m), 1419(m), 1386(m), 1354(m), 1330(s), 1297(w), 1254(w), 1222(w),

1202(w), 1180(w), 1149(w), 1119(w), 899(vs), 872(s), 839(m), 824(m), 756(m), 737(w), 721(m), 654(w). FABMS(+): m/z 373 $(M+H-Cl)^+$, 357 $(M+H-Cl-O)^+$, 340 $(M-Cl-2O)^+$.

Preparation of $TcO_3Cl(3,4,7,8\text{-}Me_4\text{-}phen)$:

To 0.109 g 3,4,7,8-tetramethyl-1,10-phenanthroline (G. F. Smith) was added 15 ml EtOH to dissolve. To the resulting solution was added 0.5 ml of 0.3 *M* $(NH_4)[TcO_4]$ followed by 1.5 ml conc. HCl. A white precipitate (presumably Me_4-phen·HCl) formed immediately and became yellow after stirring overnight. The mixture was filtered in a fritted glass funnel and rinsed well with MeOH, EtOH, and acetone, then dried in vacuo overnight. Yield: 32.66 mg (52%).

IR (KBr): νTc=O 892. cm^{-1}(s), 874(m). FABMS(+): m/z [ion, abundance] 441 $[(M+Na)^+$, 31%], 386 $[(MH_3\text{-}Cl)^+$, 31%], 383 $[(M-Cl)^+$, 19%], 367 $[(M-Cl-O)^+$, 100%], 351 $[(M-Cl-2O)^+$, 29%].

Preparation of $TcO_4H(2,9\text{-}Me_2\text{-}phen)$:

To 0.2 g 2,9-dimethyl-1,10-phenanthroline (neocuproine, Aldrich, 0.96 mmol) was added 10 ml MeOH to dissolve. The solution was stirred and 0.65 ml 0.3 *M* $(NH_4)[TcO_4]$ was added, followed by 2 ml conc HCl. An off-white solid formed gradually after scratching the wall of the glass vial containing the reaction mixture. Further precipitation was afforded by cooling to -20 °C. The solid product was isolated on a fritted glass funnel and rinsed with MeOH, then dried in vacuo overnight. Yield: 46.36 mg, 64%.

Anal. Calcd. for $C_{14}H_{13}N_2O_4Tc$: C, 45.18%; H, 3.52; Cl, 0.0; N, 7.53. Found: C, 45.39%; H, 3.61; Cl, 0.0; N, 7.65.

IR (KBr): νTc=O 906. cm^{-1}(s), 893(s), 878(s). ^1H NMR ($(CD_3)_2CO$): δ 8.98(d, 2H), 8.32(s, 2H), 8.16(d, 2H), ~3.7(broad), 3.18(s, 6H). ^{99}Tc NMR ($CDCl_3$): δ +17

ppm relative to external TcO_4^-; $\Delta\nu_{1/2}$ = 20 Hz.

Reaction of $Na[HB(pyz)_3]$ with TcO_4^- and H_2SO_4:

To 15 ml EtOH in a disposable vial was added 0.14 g $Na[HB(pyz)_3]$ (0.6 mmol) and 0.67 ml of 0.30*M* $(NH_4)[TcO_4]$. The mixture was stirred and two drops conc. H_2SO_4 were added causing an immediate flocculent white precipitate to form. The suspension was filtered and the filtrate was chilled to -20 °C for two days. Clusters of yellow-brown needles formed which were filtered and dried in vacuo overnight.

IR (KBr): 3122 cm^{-1}(w), 2488(w), 1511(w), 1404(s), 1388(m), 1313(s), 1223(s), 1167(w), 1120(s), 1072(m), 1050(s), 990(w), 919(w), 888(vs), 818(w), 794(m), 766(s), 722(w), 710(m), 657(w), 616(m). ^1H NMR ($CDCl_3$): δ 8.21 (d, 3H), 7.65 (d, 3H), 6.32 (t, 3H), trace impurities at 7.98, 7.73, 6.61, 6.42. ^{99}Tc NMR ($CDCl_3$): δ +196 ppm relative to internal TcO_4^-; $\Delta\nu_{1/2}$ = 789 Hz. FABMS(+): m/z [ion, abundance] 672 $[(Tc_2O_3(HB(pyz)_3)_2)^+$, 5%], 559 $[(Tc(OH)_2(HB(pyz)_3)_2)^+$, 21%], 344 $[(TcO_2(HB(pyz)_3))^+$, 38%], 328 $[(TcO(HB(pyz)_3))^+$, 100%].

Reaction of TcO_3Cl(AA) with alkenes in CH_2Cl_2:

Preparation of TcOCl(*dl*-4,5-octanediolate)(phen):

Into a 50 ml Erlenmeyer flask was added 0.38 g *trans*-4-octene (3.39 mmol), 40 ml purified CH_2Cl_2, and 76.67 mg chlorotrioxo(1,10-phenanthroline)technetium(VII) (0.212 mmol). The resulting yellow slurry was magnetically stirred vigorously for approximately 30 minutes. The reaction mixture became a homogeneous green solution which was filtered through a medium porosity fritted glass disc. After adding 20 ml n-heptane to the filtrate, the solution was concentrated by rotary evaporation until precipitation commenced. Further precipitation was effected by chilling to -20°C. The green microcrystalline precipitate was isolated on a medium porosity fritted glass funnel

and rinsed with n-heptane and n-hexane, then dried in vacuo overnight. Yield: 72.01 mg, 72%.

Anal. Calcd. for $C_{20}H_{24}ClN_2O_3Tc$: C, 50.60%; H, 5.10; Cl, 7.47; N, 5.90. Found: C, 50.01%; H, 5.06; Cl, 7.43; N, 5.88.

IR (KBr): 3052 cm^{-1}(w), 2957(w), 2929(w), 2902(w), 2870(w), 1518(w), 1464(w), 1457(w), 1425(m), 1413(w), 1223(w), 1069(w), 990(w), 944(s), 911(w), 873(w), 856(m), 779(w), 739(w), 725(s), 693(w), 680(w), 662(w), 649(w). ^1H NMR ($CDCl_3$): δ 10.39 (dd, integral = 8), 10.17 (dd, 5), 9.01 (m, 12), 8.42 (dd, 12), 8.33 (m, 11), 7.94 (m, 13), 7.90 (s, 20), 7.63 (m, 12), 5.77 (m, 7), 5.02 (q, 4), 4.78 (q, 4), 4.19 (m, 7), 2.6-0.7 (^{n}Pr multiplets, 165). UV-vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ 270 nm(29,700 $l \cdot mol^{-1} \cdot cm^{-1}$), 320(shoulder), 440(3,000), 640(46), 820(41). FABMS(+): m/z [ion, abundance] = 913 [$(2M-Cl)^+$, 3.4%], 894 [$(2M+O-2Cl)^+$, 9.4%], 474 [M^+, 5.6%], 439 [$(M-Cl)^+$, 100%], 330 [(M-octanediolate)$^+$, 60%], 327 [(M-Cl-octene)$^+$, 52%].

Preparation of TcOCl(*meso*-4,5,-octanediolate)(phen):

Using the procedure above but reacting 78.68 mg TcO_3Cl(phen) (0.217 mmol) and 0.42 g *cis*-4-octene. Yield: 64.0 mg, 70%.

IR (KBr): νTc=O 951 cm^{-1}. ^1H NMR ($CDCl_3$): δ 10.33 (dd, integral = 18), 10.24 (d, 10), 8.99 (dd, 32), 8.42 (dd, 33), 8.33 (dd, 34), 7.95 (m, 30), 7.89 (s, 64), 7.7-7.5 (overlapping multiplets, 29), 5.98 (m, 19), 5.36 (m, 32), 4.82 (m, 11), 2.4-0.6 (^{n}Pr multiplets, ~640). FABMS(+): m/z 439 $(M-Cl)^+$.

Preparation of TcOCl(*dl*-4,5-octanediolate)(5-NO_2-phen):

Using the procedure above but reacting 23.78 mg TcO_3Cl(5-NO_2-phen) (0.058 mmol) and 0.25 g *cis*-4-octene. Yield: 18.6 mg, 61%.

Anal. Calcd. for $C_{20}H_{23}ClN_3O_5Tc$: C, 46.22%; H, 4.46; Cl, 6.82; N, 8.08. Found: C, 46.26%; H, 4.48; Cl, 6.75; N, 8.15.

IR (KBr): νTc=O 956 cm^{-1}. ^1H NMR ($CDCl_3$): δ 10.60 (m, integral = 6), 10.37 (m, 4), 9.2 (overlapping multiplets, 21), 8.86 (m, 9), 8.63 (d, 6), 8.54 (m, 4), 8.1 (m, 11), 7.8 (m, 11), 5.76 (m, 8), 4.96 (m, 4), 4.72 (m, 4), 4.18 (m, 8), 2.6-0.6 (^nPr multiplets, ~136). UV-vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ 234 nm(27,000 $l \cdot mol^{-1} \cdot cm^{-1}$), 276(32,000), 305(sh), 315(sh), 330(sh), 474(3,300). FABMS(+): m/z 484 $(M-Cl)^+$.

Preparation of TcOCl(*meso*-dibutyltartrate)(phen):

Using the procedure above but reacting 61.34 mg TcO_3Cl(phen) (0.169 mmol) and 0.26 g dibutyl maleate (*cis*-$C_4H_9OC(O)CH{:}CHC(O)OC_4H_9$) (Aldrich, 90%). Yield: 61.18 mg, 61%.

IR (KBr): νTc=O 953 cm-1. ^1H NMR ($CDCl_3$): δ 10.28 (m, integral = 5), 10.08 (dd, 8), 9.48 (m, 8), 8.95 (td, 5), 8.51 (dd, 13), 8.37 (m, 13), 7.97 (overlapping multiplets, 38), 7.64 (m, 14), 6.7 (methine, 5), 6.0-5.5 (methine, 21), 4.5-3.8 (α methylene, 56), 1.9-1.1 (methylene, 110), 1.1-0.7 (methyl, 60). FABMS(+): m/z [ion, abundance] 555 $[(M-Cl)^+$, 100%], 460 $[(M-(C_4H_9)_2O)^+$, 8%], 425 $[(M-Cl-(C_4H_9)_2O)^+$, 36%], 327 $[(M-Cl-C_{12}H_{20}O_4)^+$, 5%].

Preparation of TcOCl(*dl*-dibutyltartrate)(phen):

Using the procedure above but reacting 32.64 mg TcO_3Cl(phen) (0.090 mmol) and 0.23 g dibutyl fumarate. Yield: 21.94 mg, 41%.

IR (KBr): νTc=O 960 cm^{-1}. ^1H NMR ($CDCl_3$): δ 10.15 (dd, integral = 10), 10.04 (dd, 15), 9.47 (dd, 15), 8.91 (dd, 10), 8.47 (dd, 24), 8.34 (m, 24), 7.94 (m, 25), 7.90 (s, 46), 7.63 (m, 28), 6.61 (d, 11), 5.49 (d, 11), (AB quartet: δA = 5.63, δB =

5.53, J_{AB} = 7.7 Hz, integral = 24), 4.5-3.8 (α methylene, 97), 2.0-1.1 (methylene, 217), 1.1-0.5 (methyl, 126).

Preparation of TcOCl(*threo*-5,6-decanediolate)(3,4,7,8-Me_4-phen):

Using the procedure above but reacting 13.75 mg TcO_3Cl(3,4,7,8-Me_4-phen) (0.033 mmol) and *trans*-5-decene. Yield: 11.5 mg, 63%.

IR(KBr): νTc=O 939 cm^{-1}. ^1H NMR ($CDCl_3$): δ 10.07 (s, integral = 9), 9.88 (s, 6), 8.98 (s, 3), 8.74 (s, 3), 8.70 (s, 9), 8.14 (s, 3), 7.98 (s, 23), 5.74 (m, 8), 5.02 (m, 3), 4.79 (m, 3), 4.20 (m, 7), 2.9-2.3 (7 singlets, 150), 2.3-0.7 (^{n}Bu multiplets, 200). FABMS(+): m/z [ion, abundance] 559 $[(MH)^+$, 8%], 523 $[(M-Cl)^+$, 100%], 387 [(MH-decanediolate)$^+$, 53%], 584 [(MH-Cl-decene)$^+$, 27%], 368 [(MH-Cl-decene-O)$^+$, 57%], 352 [(MH-Cl-decene-2O)$^+$, 63%].

Reaction of TcO_3Cl(AA) with alkenes in acetone:

Preparation of TcOCl(phenyl-1,2-ethanediolate)(phen):

To 1 ml styrene combined with 1 ml acetone was added 50.66 mg chlorotrioxo(1,10-phenanthroline)technetium(V) (0.140 mmol). After 20 minutes, 15 ml CH_2Cl_2 was added to the resulting yellow-green slurry to dissolve the product. The solution was filtered through paper then concentrated by evaporation. To the filtrate was added hexane until precipitation was incipient. After chilling to -20 °C, a precipitate formed which was filtered in a fritted glass funnel and washed with hexane. The product was dried in vacuo overnight yielding 48.05 mg (74%) of the green microcrystalline product.

Anal. Calcd. for $C_{20}H_{16}ClN_2O_3Tc$: C, 51.47; H, 3.46; Cl, 7.60; N, 6.00. Found: C, 51.14; H, 3.48; Cl, 7.67; N, 6.00.

IR (KBr): 3056 cm^{-1}(w), 2903(w), 2845(w), 1629(w), 1605(w), 1579(w), 1520(m), 1490(w), 1452(w), 1429(s), 1305(w), 1226(w), 1142(w), 1110(w), 1082(w), 1025(w), 1013(m), 999(m), 948(s), 916(m), 873(w), 856(m), 847(s),

806(w), 761(w), 740(w), 724(s), 703(m), 685(m), 649(m), 631(w), 595(w), 586(w), 575(w), 508(w), 445(w). ^{1}H NMR ($CDCl_3$): δ 10.42, 10.40 (2 overlapping dd, area = 11), 10.14 (d, 4), 9.13 (m, 11), 9.06 (dd, 4), 8.86 (d, 3), 9.0-8.3 (m, 30), 8.1-7.8 (m, 49), 7.8-7.6 (m, 13), 7.55-7.3 (m, 28), 7.20 (s, 36), 6.9 (dd, 5), 6.42 (dd, 3), 6.21 (dd, 7), 6.0 (2 overlapping dd, 4), 5.85 (dd, 5), 5.74 (dd, 4), 5.48 (2 overlapping dd, 8), 5.09 (dd, 3), 4.86 (dd, 3), 4.31 (t, 4). FABMS(+): m/z [ion, abundance] 467 [$(M+H)^+$, 3%], 431 [$(M-Cl)^+$, 100%], 330 [$(M+H\text{-styrenediolate})^+$, 41%], 327 [$(M+H\text{-Cl-styrene})^+$, 16%].

Preparation of TcOCl(1,2-cyclohexanediolate)(bpy):

Using the procedure above but reacting 13.29 mg TcO_3Cl(bpy) (0.039 mmol) and cyclohexene (MC/B). Yield: 5.0 mg, 30%.

IR (KBr): νTc=O 949 cm^{-1}. FABMS(+): m/z [ion, abundance] 420 [M^+, 3%], 385 [$(M-Cl)^+$, 100%].

Preparation of TcOCl(phenyl-1,2-ethanediolate)(bpy):

Using procedure above but reacting 9.14 mg TcO_3Cl(bpy) (0.027 mmol) and distilled styrene. Yield: 5.07 mg, 42%.

IR (KBr): νTc=O 952 cm^{-1}. FABMS(+): m/z [ion, abundance] 849 [$(2M-Cl)^+$, 3%], 830 [$(2M-2Cl+O)^+$, 0.4%], 443 [$(M+H)^+$, 4%], 407 [$(M-Cl)^+$, 100%], 306 [$(M\text{-styrenediolate})^+$, 45%], 303 [$(M\text{-Cl-styrene})^+$, 26%], 287 [$(M\text{-Cl-styrene-O})^+$, 39%].

Preparation of TcOCl(*dl*-diphenyl-1,2-ethanediolate)(phen):

Using procedure above but reacting 24.66 mg TcO_3Cl(phen) (0.068 mmol) and *trans*-stilbene (Aldrich, 96%). Yield: 18.19 mg, 49%.

IR (KBr): νTc=O 947 cm^{-1}. ^1H NMR ($CDCl_3$): δ 10.5 (d), 9.3 (d), 8.5 (d), 7.9 (m), 7.6-6.6 (overlapping multiplets), 6.7 (d), 5.2 (d).

Preparation of TcOCl(*meso*-diphenyl-1,2-ethanediolate)(phen):

Using procedure above but reacting 28.54 mg TcO_3Cl(phen) (0.079 mmol) and *cis*-stilbene (Aldrich, 97%). Yield: 16.65 mg, 39%.

Anal. Calcd. for $C_{26}H_{20}ClN_2O_3Tc$: C, 57.53%; H, 3.71; Cl, 6.53. Found: C, 56.49%; H, 3.99; Cl, 6.49.

^1H NMR ($CDCl_3$): δ 10.24 (dd, 1H), 9.14 (dd, 1H), 8.45 (overlapping multiplets, 2H), 7.93 (overlapping multiplets, 3H), 7.70 (dd, 1H), 7.45 (d, *J*=6.1 Hz, 1H), 7.3-6.9 (overlapping multiplets, ~10H), 6.62 (d, *J*=6.2 Hz, 1H). FABMS(+): m/z [ion, abundance] 543 $[(M+H)^+$, 4%], 507 $[(M-Cl)^+$, 100%], 330 [(M-stilbenediol)$^+$, 82%], 327 [(M-Cl-stilbene)$^+$, 16%], 543 [(M-Cl-stilbene-O)$^+$, 66%].

Preparation of TcOCl(*dl*-5,6-decanediolate)(phen):

Using procedure above but reacting 46.2 mg TcO_3Cl(phen) (0.127 mmol) and 5-decene (Aldrich, 99+%). Yield: 49.1 mg (77%).

Anal. Calcd. for $C_{22}H_{28}ClN_2O_3Tc$: C, 52.55%; H, 5.67; Cl, 7.05; N, 5.57. Found: C, 52.40%; H, 5.56; Cl, 7.09; N, 5.60.

IR (KBr): νTc=O 948 cm^{-1}. ^1H NMR ($CDCl_3$): δ 10.38 (dd, integral = 6), 10.18 (dd, 3), 9.02 (dd, 10), 8.41 (dd, 10), 8.33 (dd, 10), 7.95 (m, 10), 7.89 (s, 18), 7.63 (m, 12), 5.78 (m, 6), 5.04 (q, 3), 4.78 (q, 3), 4.20 (m, 7), 2.5-0.7 (^{n}Bu multiplets, 180). UV-vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ 270 nm(32,100 $l \cdot mol^{-1} \cdot cm^{-1}$), 444(3000), 628(70), 810(60). FABMS(+): m/z [ion, abundance] 503 $[(M+H)^+$, 0.6%], 467 [(M-Cl)$^+$, 100%], 409 [(M-Cl-C_4H_{10})$^+$, 1%], 330 [(M-decanediolate)$^+$, 27%], 327[(M-Cl-decene)$^+$, 10%].

Reaction of $TcO_3Cl(AA)$ with gaseous alkenes:

Preparation of TcOCl(eg)(phen):

To 18 ml CH_2Cl_2 in a 20 ml disposable vial was added 34.59 mg chlorotrioxo(1,10-phenanthroline)technetium(VII) (0.095 mmol). Ethene (Matheson, C.P. grade) was gently bubbled through the solution for approximately 1 h, periodically adding dichloromethane to compensate for evaporative losses, until the solution became clear green. Heptane was added and the solution was concentrated under vacuum until green microcrystalline precipitate appeared. Yield: 28.33 mg, 76%.

The product is spectroscopically identical to the crystallographically characterized material[14] prepared by the reaction of $[TcOCl_4]^-$ with $HOCH_2CH_2OH$ and phen (chapter 1).

Preparation of TcOCl(1,1-dimethyl-1,2-ethanediolate)(phen):

Into a 100 ml round bottomed flask with a side-arm and stopcock was added 20 ml acetone and 29.58 mg chlorotrioxo(1,10-phenanthroline)technetium(VII) (0.082 mmol). The flask was then sealed with a latex balloon and isobutene (Matheson, C.P.) was admitted through the side-arm. The balloon was filled and deflated twice to purge the air trapped in the system. The balloon was once again filled and the solution stirred rapidly. The dissolution of isobutylene in the acetone solution was enhanced by chilling the flask in a salt/ice/water bath until the balloon had completely collapsed. The solution was stirred at ambient temperature for two additional hours, by which time the solution had become clear green. The solvent was removed at reduced pressure and the residue was recrystallized from CH_2Cl_2/hexane.

IR (KBr): νTc=O 948 cm^{-1}. ^1H NMR ($(CD_3)_2CO$): δ 10.29 (dd), 10.11 (dd), 8.95 (dd), 8.80 (dd), 8.70 (dd), 8.19(m), 7.85 (m), (AB: δ_A = 5.80, δ_B = 5.53, J = 11.0

Hz), (AB: δ_A = 4.91, δ_B = 4.78, J = 10.5 Hz), 1.53 (s), 1.29(s), 1.17 (s), 1.05 (s). FABMS(+): 383 $(M\text{-}Cl)^+$.

Preparation of TcOCl(vinyl-1,2-ethanediolate)(phen):

Using the procedure above, but substituting 1,3-butadiene (Matheson, C.P.) for the isobutylene, 8.42 mg TcO_3Cl(phen) (0.023 mmol) was converted to the corresponding diolate complex.

IR (KBr): νTc=O 951 cm^{-1}. ^1H NMR ($CDCl_3$): δ 10.5-7.5(aromatic protons, integral = 69), 6.6-4.1(olefinic and aliphatic protons, integral = 47). Ratio of aromatic to others: 8 to 5.4; calculated for TcOCl(vinyl-1,2-ethanediolate)(phen): 8 to 6. FABMS(+): m/z 381 $(M\text{-}Cl)^+$.

One pot reaction from pertechnetate:

Preparation of TcOCl(*dl*-4,5-octanediolate)(phen):

To 20 ml anhydrous EtOH in a 50 ml Erlenmeyer flask was added 0.28 g 1,10-phenanthroline monohydrate (1.41 mmol) followed by 0.5 ml 0.42 *M* $(NH_4)[TcO_4]$ (0.21 mmol). To the stirring solution was added 3 ml conc. HCl. After one minute, 0.6 g *trans*-4-octene was added followed by sufficient CH_2Cl_2 and water to form two phases. The green organic layer was separated and the aqueous layer was discarded. The organic layer was washed with two portions of dilute HCl, then dried over anhydrous Na_2SO_4. After filtration, the solvent was removed at reduced pressure leaving small green crystals suspended in a colorless oil. The product was isolated by adding Et_2O then filtering in a fritted glass funnel. The product was washed with additional Et_2O and dried in vacuo overnight. Yield: 40.16 mg, 40%.

Reactions with cholesterol:

To 20 ml alkene-free CH_2Cl_2 was added 250 mg cholesterol (MC/B, 0.65 mmol) and 28.53 mg chlorotrioxo(1,10-phenanthroline)technetium(VII) (0.079 mmol). The resulting slurry was stirred for 24 h during which the color became yellow-green. No identifiable products could be isolated. A similar reaction using chlorotrioxo(5-nitro-1,10-phenanthroline)technetium(VII) also gave no isolable products.

Hydrolysis reactions:

Preparation of 4,5-octanediols:

Into a stirred mixture of 30 ml Et_2O and 10 ml conc HCl in a 100 ml Erlenmeyer flask was added 57.41 mg chlorooxo(*dl*-4,5-octanediolato)(1,10-phenanthroline)technetium(V) (0.121 mmol). The color rapidly changed from green to bright yellow. The yellow solid was removed by filtration through paper. The precipitate was determined to be $TcOCl_3$(phen) by its IR spectrum νTc=O 978 cm^{-1} (lit.[11] 977 cm^{-1}). The two phases of the filtrate were separated saving the organic layer then drying it with $MgSO_4$. The drying agent was removed by filtration and the filtrate was evaporated to a colorless oil. Yield ~7 mg, 40%.

A similar hydrolysis reaction was performed for the *meso* isomer.

Preparation of phenyl-1,2-ethanediol:

Hydrolysis was carried out as above, but reacting HCl with 15.36 mg $TcOCl(OCHPhCH_2O)$(phen) (0.033 mmol). The product was purified by vacuum sublimation at 100 °C.

^1H NMR ($CDCl_3$): δ 7.37 (m, 5H), 4.84 (dd, 1H), 3.76 (dd, 1H), 3.68 (dd, 1H), 2.5 (broad, ~1H), 1.26 (s, ~1H). EIMS(+) 20 °C, 30eV; m/z [ion, abundance]: 138 [$(M)^+$, 39%], 120 [$(M\text{-}H_2O)^+$, 4%], 107 [$(M\text{-}CH_2OH)^+$, 100%], 91 [$(C_7H_7)^+$, 5%], 79

[$(C_6H_7)^+$, 45%].

Preparation of $TcBr_4$(phen):

Chloro(1,2-ethanediolato)oxo(1,10-phenanthroline)technetium(V) (12.63 mg, 0.032 mmol) was suspended in 15 ml acetone in a disposable vial. Concentrated aqueous HBr (2 ml) was added causing a rapid color change from bright green to pale orange. After stirring unstoppered overnight, the solution turned dark red. The dark red liquid was diluted with 10 ml of CH_2Cl_2 and $MgSO_4$ was added to remove the water. The slurry was filtered through paper and the filtrate was evaporated to a red oil.

Thin layer chromatography (Baker silica gel IB-F, CH_2Cl_2 eluant) showed a red band at the baseline and an orange band with R_f=0.48. The reaction mixture was purified by slurrying it in CH_2Cl_2 with silica gel (Fisher grade 12, 28-200 mesh) and then filtering through a fritted glass funnel. Heptane was added to the deep orange filtrate which was then evaporated under reduced pressure until small red crystals of $TcBr_4(phen)\cdot 1/2CH_2Cl_2$ formed. The solid (12.87 mg, 67% yield) was collected on a fritted glass funnel and rinsed with hexane, then dried in vacuo overnight.

Anal. Calcd. for $C_{12.5}H_9Br_4ClN_2Tc$: C, 23.41%; H, 1.41; N, 4.37. Found: C, 23.65%; H, 1.47; N, 4.48; total halogen as Br, 63.80.

IR (KBr): 3075 cm^{-1}(w), 2921(w), 2917(w), 1516(m), 1492(w), 1425(s), 1415(w), 1303(w), 1222(m), 1148(w), 1108(w), 1098(m), 844(s), 739(m), 712(s), 668(m), 653(m), 430(m). UV-vis (CH_2Cl_2): λ_{max} (ε) 232 nm (41,580 $l\cdot mol^{-1}\cdot cm^{-1}$), 272 (30,900), 426 (7,400). FABMS(+) m/z: 515 $(M-H-Br)^+$, 437 $(M-2Br)^+$. No electrical conductivity was measurable at 0.34 mM in CH_2Cl_2.

Preparation of ReOCl(eg)(phen):

To 35.05 mg $(Ph_4As)[ReOCl_4]$ (0.048 mmol) in a disposable vial was added 1.5 ml

MeOH and 0.5 ml 1,2-ethanediol (Fisher). The resulting blue solution was stirred for five minutes before adding 41 mg of crystalline 1,10-phenanthroline monohydrate (Baker, 0.207 mmol) with vigorous stirring. The solution immediately became red-brown and a precipitate gradually formed. The solid (17.29 mg, 75%) was collected on a medium porosity fritted glass funnel and rinsed with methanol and hexanes, then dried in vacuo at room temperature. The product is slightly soluble in CH_2Cl_2.

IR (KBr): 3050 cm^{-1}(w), 2914(w), 2845(m), 1631(w), 1574(w), 1516(w), 1489(w), 1454(w), 1429(m), 1414(w), 1326(w), 1250(w), 1226(w), 1210(w), 1061(w), 1021(s), 963(vs), 907(s), 875(w), 851(s), 829(w), 781(w), 740(w), 719(s), 656(m), 651(m), 617(s), 541(m), 514(w), 508(w). ^1H NMR ($CDCl_3$): δ 9.42 (dd, 1H), 8.90 (dd,1H), 8.39 (dd, 1H), 7.97 (m, 1H), (AB quartet: δA = 8.04, δB = 7.89, J_{AB} = 9.17 Hz, 2H), 7.72 (dd, 1H), 7.63 (m, 1H), 5.67 (m, 1H), 5.11 (m, 1H), 4.68 (m, 1H), 4.27 (m,1H). FABMS(+): m/z [ion, abundance] = 478 [$(M)^+$, 55%], 443 [$(M\text{-}Cl)^+$, 100%], 418 [$(M\text{-}OCH_2CH_2O)^+$, 30%], 415 [$(M\text{-}Cl\text{-}C_2H_4)^+$, 60%], 399 [$(M\text{-}Cl\text{-}C_2H_4\text{-}O)^+$, 30%].

Thermolysis of ReOCl(eg)(phen):

Preparation of ReO_3Cl(phen)

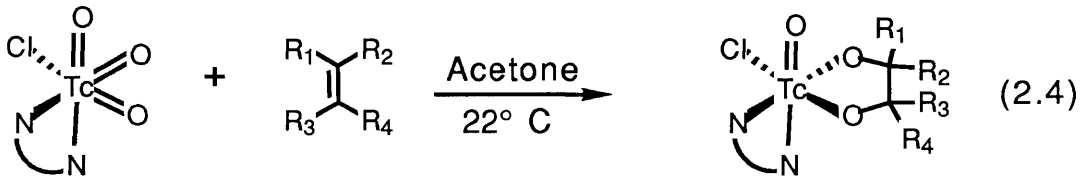
Chloro(1,2-ethanediolato)oxo(1,10-phenanthroline)rhenium(V), 26.0 mg (0.054 mmol) was placed a 25 ml round-bottom flask. The system was carefully evacuated to ~0.2 torr and then heated in an oil bath to 160 °C for 1 hr. No reaction was evident. On subsequent heating to 220 °C while maintaining vacuum, the red-brown color faded within 5 minutes. The resulting off-white powder was cooled under vacuum and reweighed (22.3 mg). Mechanical losses in transfer make accurate weight-loss determination impossible at this scale.

IR (KBr): 3058 cm^{-1}(w), 1629(w), 1583(W), 1520(m), 1494(w), 1428(m),

1412(w), 1314(w), 1224(w), 1203(w), 1144(w), 1111(w), 942(s), 922(s), 910(s), 873(m), 851(s), 776(w), 743(m), 722(s), 653(w), 509(w), 492(w), 430(w), 419(w). FABMS(+): m/z 415 $(M\text{-}Cl)^+$.

RESULTS AND DISCUSSION:

All of the transition metal species previously known[15] to effect the *cis*-dihydroxylation of alkenes (ie. OsO_4, RuO_4, and MnO_4^-) are tetrahedral tetraoxides. Although alkaline MnO_4^- is capable of oxidizing alkenes,[4,15] its second row congener, TcO_4^- has no such activity. The chlorotrioxobis(amine)technetium(VII) derivatives, on the other hand, are extremely effective dihydroxylating agents. As shown in Reaction 2.4, slurries of $TcO_3Cl(AA)$ (AA = phen, bpy, Me_4-phen, NO_2-phen) in acetone or dichloromethane react rapidly with a wide variety of alkenes (C_2R_4) to form the corresponding technetium(V) diolates, $TcOCl(OCR_2CR_2O)(AA)$.



The isolated yields of the diolate products, summarized in Table 2.I, are generally greater than 70%. Variations in the yield depend strongly on the scale of the reaction, since mechanical losses in manipulations are significant. Slight changes in the solubilities of the various products also affect the amount of product remaining in solution after the majority is isolated. The choice of alkene, however, does not seem to alter the percent conversion, except for cholesterol, which gave no isolable product. The one pot reaction involving $TcO_3Cl(phen)$ generated in situ has a comparable productivity based on pertechnetate, since the starting materials are typically isolated[11] in yields of less than 80%.

The different chelating aromatic diamine ligands 1,10-phenanthroline, 2,2'-bipyridine, 5-nitro-1,10-phenanthroline, and 2,3,7,8-tetramethyl-1,10-phenanthroline were studied in order to investigate the possibility of manipulating the

reaction with subtle inductive changes in the trioxotechnetium complexes. The inductive effect of these ligands on the reduction potential of metals is well known because the tris-chelate complexes of iron are commonly used as redox indicators. The reduction potential of these iron complexes is shown on Table 2.II. Although these potentials vary over a range of >400 mV,[16] the complexes with just one of these ligands would presumably have smaller variations. No qualitative differences in the reactivity of $TcO_3Cl(AA)$ as a function of AA are noted. The nitrophenanthroline ligand, however, does induce changes in the spectral and solubility properties of the complexes. The complex $TcO_3Cl(5\text{-}NO_2\text{-phen})$ is produced in nearly quantitative yields due to its extreme insolubility in the reaction mixture. This trioxotechnetium starting material is olive green, quite unlike all of the others which are pale yellow. Furthermore, when this species is reacted with alkenes, the resulting technetium(V) diolate complexes are red-brown rather than the usual bright yellow-green.

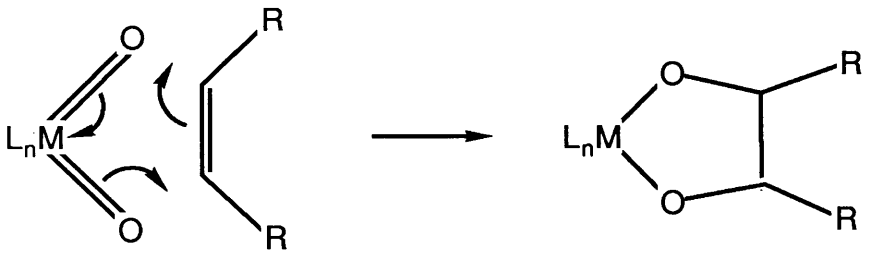
Different chelating aromatic amine ligands such as hydridotris(pyrazoyl)borate ($HB(pyz)_3$) and 2,9-dimethyl-1,10-phenanthroline (trivially named neocuproine) give different technetium(VII) complexes which are significantly less active at oxidizing alkenes than the complexes $TcO_3Cl(AA)$ described above. When pertechnetate is reacted with neocuproine in alcohol acidified with HCl, a complex with the stoichiometry TcO_4H(neocuproine) is isolated, instead of the expected chlorotrioxo(neocuproine) technetium(VII). This complex might be formulated as the ionic (neocuproineH^+)[TcO_4^-] or as the neutral complex $TcO_3(OH)$(neocuproine). The latter might be envisioned being just like the oxidation reagents, but with a hydroxyl group substituting for the usual chloride. Although the IR and NMR and mass spectral results are consistent with the latter formulation, the steric hindrance of the 2,9-disubstituted phenanthroline would argue for the uncoordinated ionic formulation. When this neocuproine product is reacted with alkenes, a pale green color gradually forms, but no products can be isolated.

The reaction of $HB(pyz)_3$ with pertechnetate in alcohol acidified with H_2SO_4 gives a

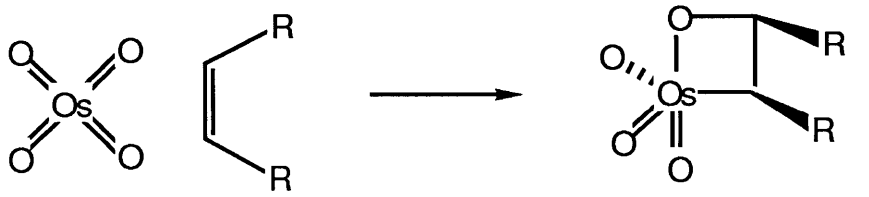
product tentatively identified as $TcO_3(HB(pyz)_3)$. The most significant spectral evidence for this formulation is the technetium-99 NMR spectrum. A solution of this compound in acetone has a ^{99}Tc shift of +196 ppm from TcO_4^- with a half-width of ~800 Hz. These values compare well with those reported[17] for the TcO_3^+ ion (δ = +161, $\Delta\nu_{1/2}$ = 670 Hz). Reaction of this complex with alkene does not proceed cleanly, however one of the products separated by thin layer chromatography has the same characteristic pale-blue color[18] of $TcO(eg)(HB(pyz)_3)$. The chloride ligand is apparently necessary, therefore, for the dihydroxylation reaction to go effectively.

Although the oxidative cleavage reaction of osmate(VI)esters of diols has long been assumed to regenerate OsO_4 as the catalytically active species[2], recent evidence[19] suggests that an osmium(VII) oxyhalide complex may also be involved in some cases. Myers and coworkers noted that the rate of O_2 oxidized Cu cocatalyzed Os catalyzed diol formation depends directly on halide:Os ratio up to values of 5:1. The absence of OsO_4 in the distillates of these reactions gives further evidence for halide coordination since the oxyhalides are expected to be significantly less volatile than the tetroxide. The technetium system validates this hypothesis, being the first example of an isolated oxyhalide which has *cis*-dihydroxylation abilities that are diminished significantly with halide-free derivatives.

The mechanism generally proposed for the metal-mediated vicinal dihydroxylation reactions involves a concerted [3+2] cycloaddition[1] (Reaction 2.5). Arguing that transition metals are more electropositive than oxygen; Sharpless[1] suggests that alkenes, being weak nucleophiles, might be bonding to the metal atom in the first step of these reactions (reaction 2.6). The fact that OsO_4 preferentially reacts with more nucleophilic alkenes further supports this hypothesis. The direct attack at the metal, however, seems unlikely for the coordinatively saturated octahedral trioxotechnetium complexes.



(2.5)



(2.6)

Scheme 2.I shows the three possible paths through which an alkene can approach two of the oxo ligands in the cycloaddition reaction. Note that the two oxo ligands *cis* to the coordinated chloride in the $TcO_3Cl(AA)$ starting material are equivalent by virtue of a mirror plane passing through the *trans* oxo and the chloride and bisecting the bidentate aromatic amine. In the case of a symmetric alkene (e.g. ethene), paths (a) and (b) are degenerate, each yielding one of the enantiomers of the asymmetric center at the technetium atom. Path (c) would yield a complex with mutually *trans* oxo and chloride ligands. Since all of the spectral evidence suggests that only *cis* complexes are formed, path (c) must therefore not contribute appreciably to the formation of products.

When substituted alkenes are used, the possibility of geometric isomers arises. Proton NMR spectroscopy therefore becomes extremely useful in analyzing the technetium(V) diolate complexes. Although oxotechnetium(V) complexes are effectively closed-shell and diamagnetic,[20] appreciable position dependent variations in chemical shifts can be induced[21] by the ring currents associated with the multiple bonding to the oxo ligand.

Circulation of electrons about the aromatic amine ligands presumably adds to this local magnetic field anisotropy. All of the spectra indicate that the substituents on the ethanediolate backbone are diastereotopic with the distinctive splitting patterns being well separated due to the combined ring currents. Furthermore, since the protons α to the nitrogen donors of the aromatic amine ligands are most shifted, often to >10 ppm, and are therefore far removed from the other signals, the number of these resonances is indicative of the number of isomers in solution.

The NMR spectrum of the product from the reaction of styrene with TcO_3Cl(phen) is shown in Figure 2.1 as an example of a monosubstituted diolate. There are at least three multiplets corresponding to one of the α protons in the range of 10.5-10.1 ppm, and what appears to be four multiplets between 9.2-8.8 ppm from the other. The intensities of these peaks are different and indicate a non-statistical mixture of four isomers. Further evidence for the existence of four isomers comes from the 12 different doublets of doublets which appear between 6.9-4.3 ppm arising from the protons on the phenylethanediolate backbone. Scheme 2.II demonstrates how the these different isomers might be envisioned: one with the phenyl group *cisoid* to the chloride and *syn* to the oxo, one *cisoid* to the chloride and *anti* to the oxo, one *transoid* to the chloride and *syn* to the oxo, and the last *transoid* to the chloride and *anti* to the oxo.

The analysis is simpler for a 1,2-disubstituted alkene, e.g. *trans*-4-octene. The proton NMR spectrum of *dl*-TcOCl(OCHPrCHPrO)(phen), shown in Figure 2.2, clearly shows two resonances for one of the α protons on the phenanthroline ligand at 10.4 and 10.2 ppm with relative intensities ~2:1 indicating a non-statistical mixture of two isomers. There is also a 2:1 ratio of intensities of the resonances for the methine protons of the octanediolate backbone. The major isomer has resonances at 5.8 and 4.2 ppm and the minor isomer has resonances at 5.0 and 4.7 ppm. Since the largest shifts from the average value for the methine protons occur in the major isomer, it might be deduced that the alkyl groups are preferentially going to the lesser shifting region of space which is presumably

also a less sterically crowded area. The two possible isomers are shown in Scheme 2.III.

When bulkier 1,2-disubstituted alkenes such as stilbene are used, only one isomer is isolated. For example, the proton NMR spectrum of *meso*-TcOCl(OCHPhCHPhO)(phen), shown in Figure 2.3, has only one sizeable resonance attributable to each α proton at 10.2 and 9.1 ppm. There are two barely resolved resonances at 10.5 and 9.2 ppm arising from traces of the other isomer. The methine protons on the diphenylethanediolate backbone resonate at 7.4 and 6.6 ppm. In the spectrum of the other stereoisomer, *dl*-TcOCl(OCHPhCHPhO)(phen), these methine resonances fall at 6.8 and 5.2 ppm.

As demonstrated in Scheme 2.IV, the 1,1-disubstituted alkene isobutylene also gives two possible isomers, even though there are no chiral centers on the ligand. The NMR spectrum (Figure 2.4) indicates that the two isomers exist in nearly equal abundance, as might be expected due to the minimal steric requirements of methyl groups. The diastereotopic methylene protons give one AB quartet for each isomer in the spectrum recorded in deuteroacetone, however when the spectrum is recorded in dueterochloroform, an AB quartet and a singlet appear in the spectrum. This can be attributed to accidental chemical shift equivalence of the methylene protons in one of the isomers. When the polarity of the solvent is changed, the shifts vary sufficiently to resolve the spin splitting.

When conjugated dienes, e.g. 1,3-butadiene, react with $TcO_3Cl(AA)$, there are two possible products corresponding to 1,2 and 1,4 additions. As shown in Scheme 2.V, the 1,2 addition forms five membered chelate rings whereas the 1,4 addition yields seven membered rings. Since the five membered Tc(V) chelates have been shown to be significantly more stable[22] than larger rings, the 1,2 addition reaction is expected. This prediction is supported by the proton NMR spectrum of the product resulting from bubbling 1,3-butadiene through a slurry of $TcO_3Cl(phen)$. The relative areas of the aromatic protons compared to the other protons indicate a 1:1 diene to technetium stoichiometry for this product. The presence of four resonances for the α protons of the phenanthroline

ligand between 10.5-10.0 ppm, indicative of four isomers as seen with styrene, implies 1,2 addition since only one isomer is expected for the 1,4 addition product.

In contrast to the technetium catalyzed epoxidations[8], the NMR spectra indicate that the diol-forming reactions are completely stereospecific since *cis* and *trans* alkenes give totally different products. In order to determine the stereochemistry of addition, the octanediolate derivatives were hydrolyzed by treating them with concentrated aqueous HCl yielding free diols and $TcOCl_3$(phen). Gas chromatographic retention times were compared to those of authentic samples of *meso*- and *dl*-4,5-octanediol which were prepared by osmium tetroxide oxidation[23] of *cis*- and *trans*-4-octene, respectively. The reaction of TcO_3Cl(phen) with *cis*-4-octene gives only the *meso* diol whereas a similar reaction with *trans*-4-octene gives 80% of the *dl* and 20% of the *meso* isomers. Some racemization may have occurred during the latter hydrolysis reaction.

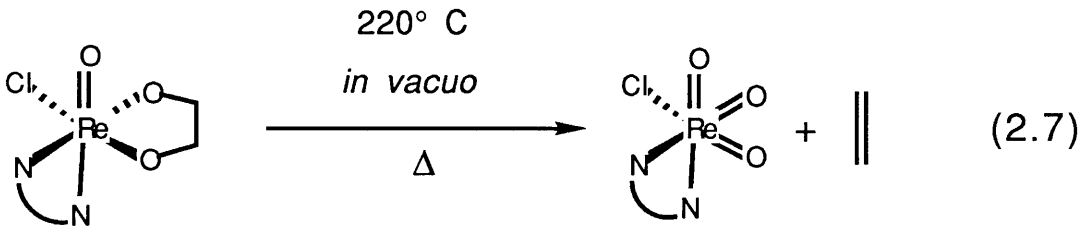
When hydrolysis is attempted with HBr instead of HCl, simple replacement of two halides for the diol no longer occurs. Bromide is apparently reducing the technetium by one electron producing the tetravalent species $TcBr_4$(AA). A similar complex, $TcCl_4$(bpy), has previously been prepared[24] by thermolysis of $[Tc(bpy)_2Cl_2]Cl$ in vacuo. The bis-bipyridyl starting material, in turn, was prepared from $TcCl_4$. There has been little further study of these technetium(IV) complexes due to the experimental difficulty[25] involved in preparing the binary technetium halides.

Crystals of tetrabromo(1,10-phenanthroline)technetium(IV) were grown by slow evaporation from a CH_2Cl_2/heptane solution. A thin red plate was selected for X-ray structure determination. The pertinent crystallographic parameters are given in Table 2.III. Data collection and reduction have been described previously.[26,27] The heavy atoms were located by direct methods[28] and the remaining non-hydrogen atoms of the molecule were found using difference Fourier maps. Hydrogen atoms in calculated positions (d_{C-H} = 0.95 Å) were used in structure factor calculations.

An ORTEP[29] diagram of [$TcBr_4$(phen)] is shown in Figure 2.5. Atomic positional parameters are given in Table 2.IV and selected bond distances and angles are given in Table 2.V. The molecule shows distorted octahedral geometry imposed primarily by the 78(1)° bite angle of the phenanthroline ligand. The mutually trans atoms Br(3) and Br(4) are displaced towards the phenanthroline ligand, presumably due to steric crowding by the other two bromine atoms.

The half methylene chloride molecule per asymmetric unit was disordered resulting in rather large residuals and a peak of 4.34 $eÅ^{-3}$ in the difference map with coordinates 0.482, 0.423, 0.579 (4.2 Å from Br(3)). This electron density was adequately modelled with one chlorine atom and a half-occupancy carbon atom per asymmetric unit. The other atoms of the solvent are generated by the inversion center at 0.5, 0.5, 0.5. As shown in Figure 2.6 the disordered methylene chloride sits between the stacked aromatic rings of adjacent molecules. The angles and distances within the solvent molecule are consistent with literature values[30] within experimental error.

Although perrhenyl chloride has been shown to oxidize alkenes,[5] no products could be isolated from the reaction of chlorotrioxo(diamine)rhenium(VII) complexes with alkenes. A slight color change was noted, however, when these species were heated in the presence of alkenes suggesting a small conversion to a Re(V) product. Conversely, as shown in Reaction 2.7, the Re(V) diolate complex ReOCl(eg)(phen) is converted to ReO_3Cl(phen) on heating in vacuo whereas the technetium(V) diolates have no such reactivity.

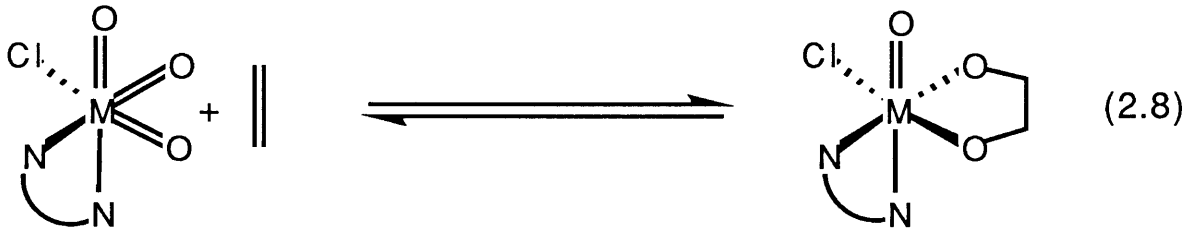


(2.7)

The differences in the direction of these reactions is dominated by the redox potentials

of the central metals in their +5 and +7 oxidation states.. A number of examples exist which demonstrate the significantly greater oxidizing powers of technetium complexes relative to the analogous rhenium complexes. For example, the oxotetrachlorometallate(V) anion is formed rapidly from pertechnetate[31] in cold concentrated HCl, but requires heating in HCl with the addition of a stronger reducing agent (Zn metal) when prepared[13] from perrhenate. Pertechnetate therefore has the ability to oxidize $2Cl^-$ ions to Cl_2, requiring a reduction potential of >1.37 V vs NHE, whereas perrhenate does not.

The technetium centered oxidation of olefins and the rhenium centered reduction of diols are conceptually the forward and reverse reactions of the equilibrium shown below in Reaction 2.8.



(2.8)

Although the stoichiometric oxidation of alkenes with technetium is not likely to be commercially feasible due to the radioactivity of this element, this reaction provides the basis for investigating catalytic oxidation of alkenes to diols using the group seven metals. Furthermore, the reactions discussed here give significant new insights into the already oft utilized reactions of osmium tetroxide and permanganate.

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Table 2.1 : Isolated yields of diolate complexes.

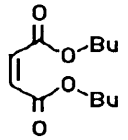
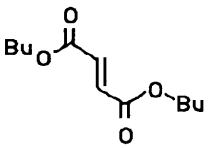
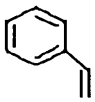
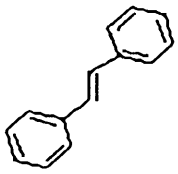
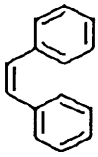
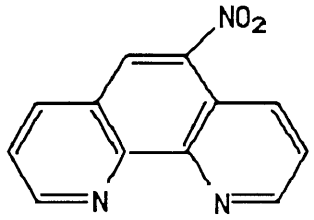
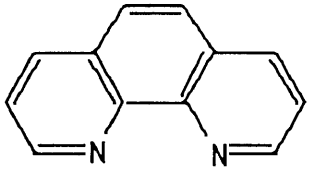
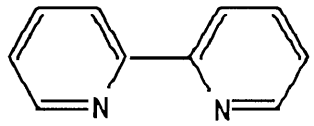
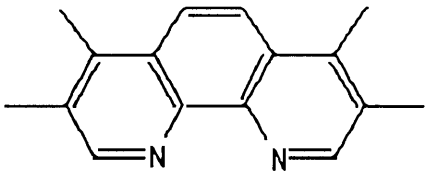
Alkene	% yield	scale (mmol)
	72	0.212
	70	0.217
	61	0.169
	41	0.090
	42 74	0.027 0.140
	30	0.039
	49	0.068
	39	0.079
	77	0.127
	76	0.095

Table 2.II

Comparison of Reduction Potentials for

$Fe(AA)_3^{3+/2+}$

AA	$E_{1/2}$ V vs N.H.E.
	1.25
	1.06
	0.97
	0.81

Adapted from GFS Chemicals catalog, 1988 edition.

Table 2.III: X-ray data for structure determination of $TcBr_4(phen)\cdot 1/2CH_2Cl_2$

Empirical formula	$C_{12.5}H_9Br_4ClN_2Tc$
Formula weight	641.2
Crystal color, habit	red plate
Crystal dimensions, mm	0.2 X 0.2 X 0.05
Crystal system	orthorhombic
a, Å	18.504(4)
b, Å	14.427(3)
c, Å	12.640(2)
Volume, $Å^3$	3374(2)
Space group	Pbca (#61)
Z	8
D(calcd), g/cm	2.52
μ, cm^{-1}	110.00
Radiation (λ, Å)	Mo K_α (0.71069) Graphite Monochromated
Temperature, °C	23
No. of reflctions measured	3630
Corrections	empirical absorption Lorentz-polarization
T_{max}, T_{min}	1.48, 0.58
Refinement	Full-Matrix Least Squares
Function minimized	$\Sigma w(\|F_o\| - \|F_c\|)^2$
Least-squares weights	$4F_o^2/\sigma^2(F_o^2)$
Anomalous dispersion	all non-H atoms
No. observations $I>3\sigma(I)$	859
No. variables	115
Goodness of fit	2.20
R, R_w	0.097, 0.109
Max shift/error in final cycle	0.02
Maximum peak in final diff. map $eÅ^{-3}$	2.63
Minimum peak in final diff. map $eÅ^{-3}$	-2.39

Table 2.IV: Atomic positional parameters for $TcBr_4(phen)\cdot 1/2CH_2Cl_2$.

Atom	x	y	z
Tc	0.3146(2)	0.3742(3)	0.2044(4)
Br(1)	0.2991(3)	0.2155(4)	0.1494(5)
Br(2)	0.2632(3)	0.3533(4)	0.3799(5)
Br(3)	0.4400(3)	0.3419(4)	0.2682(5)
Br(4)	0.1982(3)	0.4265(5)	0.1298(5)
N(1)	0.359(2)	0.416(3)	0.056(3)
N(2)	0.336(2)	0.518(2)	0.230(3)
C(1)	0.370(3)	0.369(4)	-0.028(5)
C(2)	0.400(3)	0.409(4)	-0.123(4)
C(3)	0.417(3)	0.495(4)	-0.123(5)
C(4)	0.416(2)	0.552(4)	-0.031(4)
C(5)	0.437(3)	0.645(4)	-0.026(4)
C(6)	0.426(3)	0.692(4)	0.056(5)
C(7)	0.393(2)	0.655(4)	0.160(4)
C(8)	0.378(3)	0.699(4)	0.243(4)
C(9)	0.349(3)	0.652(4)	0.326(4)
C(10)	0.330(3)	0.567(4)	0.319(4)
C(11)	0.370(2)	0.563(3)	0.149(3)
C(12)	0.378(2)	0.509(4)	0.063(4)
C†	0.462(6)	0.50(1)	0.50(1)
Cl(1)	0.483(2)	0.423(3)	0.576(2)

† Half-occupancy

Table 2.V: Selected bond distances (Å) and angles (°) for $TcBr_4(phen)\cdot CH2Cl2$.

Tc-Br(1)	2.410(8)	Tc-Br(2)	2.433(7)	Tc-Br(3)	2.501(7)
Tc-Br(4)	2.469(7)	Tc-N(1)	2.13(4)	Tc-N(2)	2.14(3)
C-Cl(1)	1.4(1)				

Br(1)-Tc-Br(2)	95.7(3)	Br(1)-Tc-Br(3)	91.5(2)
Br(1)-Tc-Br(4)	94.4(3)	Br(1)-Tc-N(1)	93(1)
Br(1)-Tc-N(2)	171(1)	Br(2)-Tc-Br(3)	92.6(2)
Br(2)-Tc-Br(4)	92.6(2)	Br(2)-Tc-N(1)	171(1)
Br(2)-Tc-N(2)	93(1)	Br(3)-Tc-Br(4)	171.7(3)
Br(3)-Tc-N(1)	89(1)	Br(3)-Tc-N(2)	87.7(8)
Br(4)-Tc-N(1)	85(1)	Br(4)-Tc-N(2)	85.6(8)

Bond lengths and angles involving symmetry-generated atoms:

C-Cl(1)'	1.8(1)	Cl(1)-C-Cl(1)'	131(8)

Figure 2.1: Proton NMR spectrum (300 MHz) of $TcOCl(OCHPhCH_2O)(phen)$.

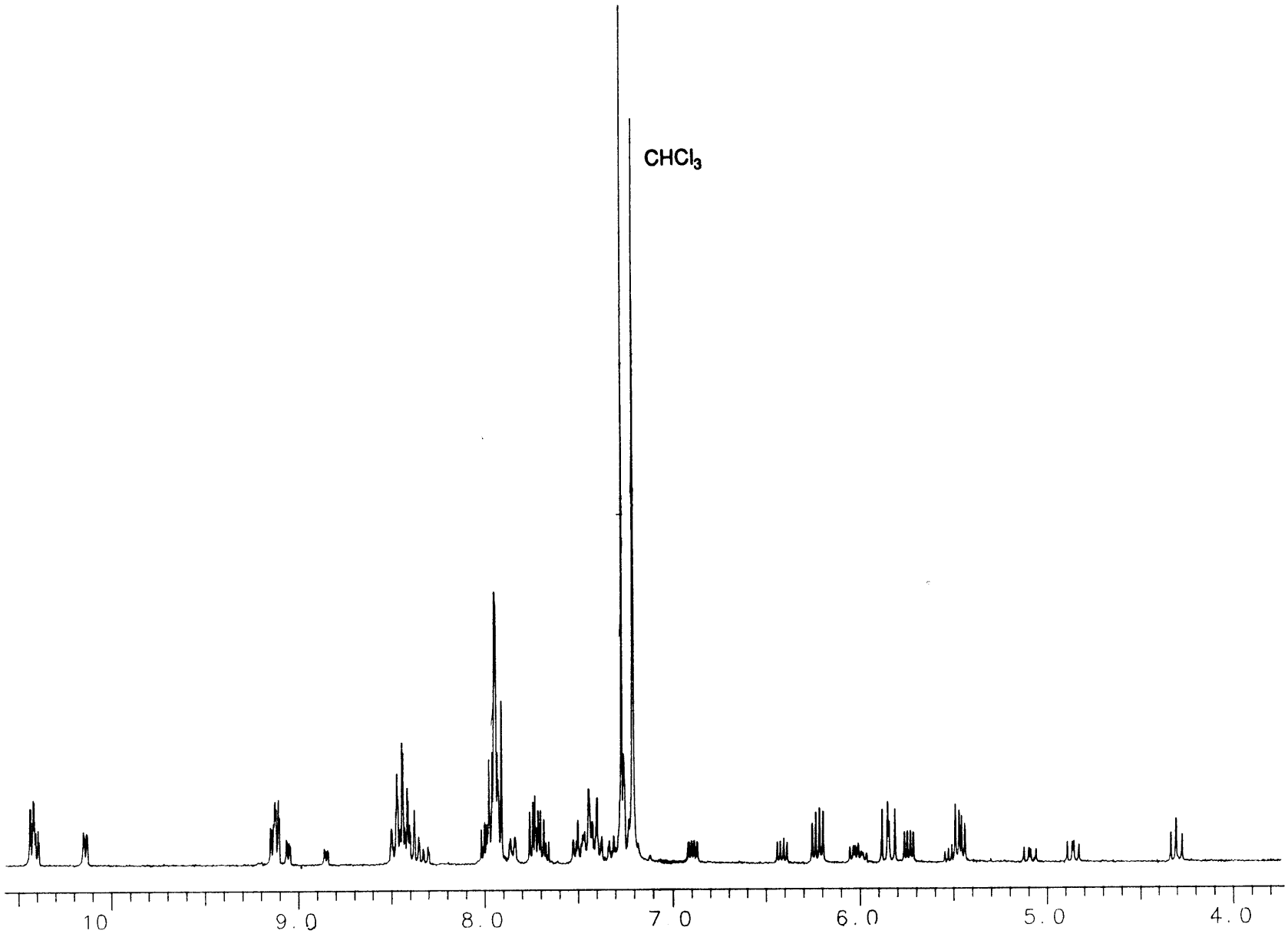

CHCl3
10
9.0
8.0
7.0
6.0
5.0
4.0

Figure 2.2: Proton NMR spectrum (300 MHz) of *dl*-TcOCl(OCHPrCHPrO)(phen).

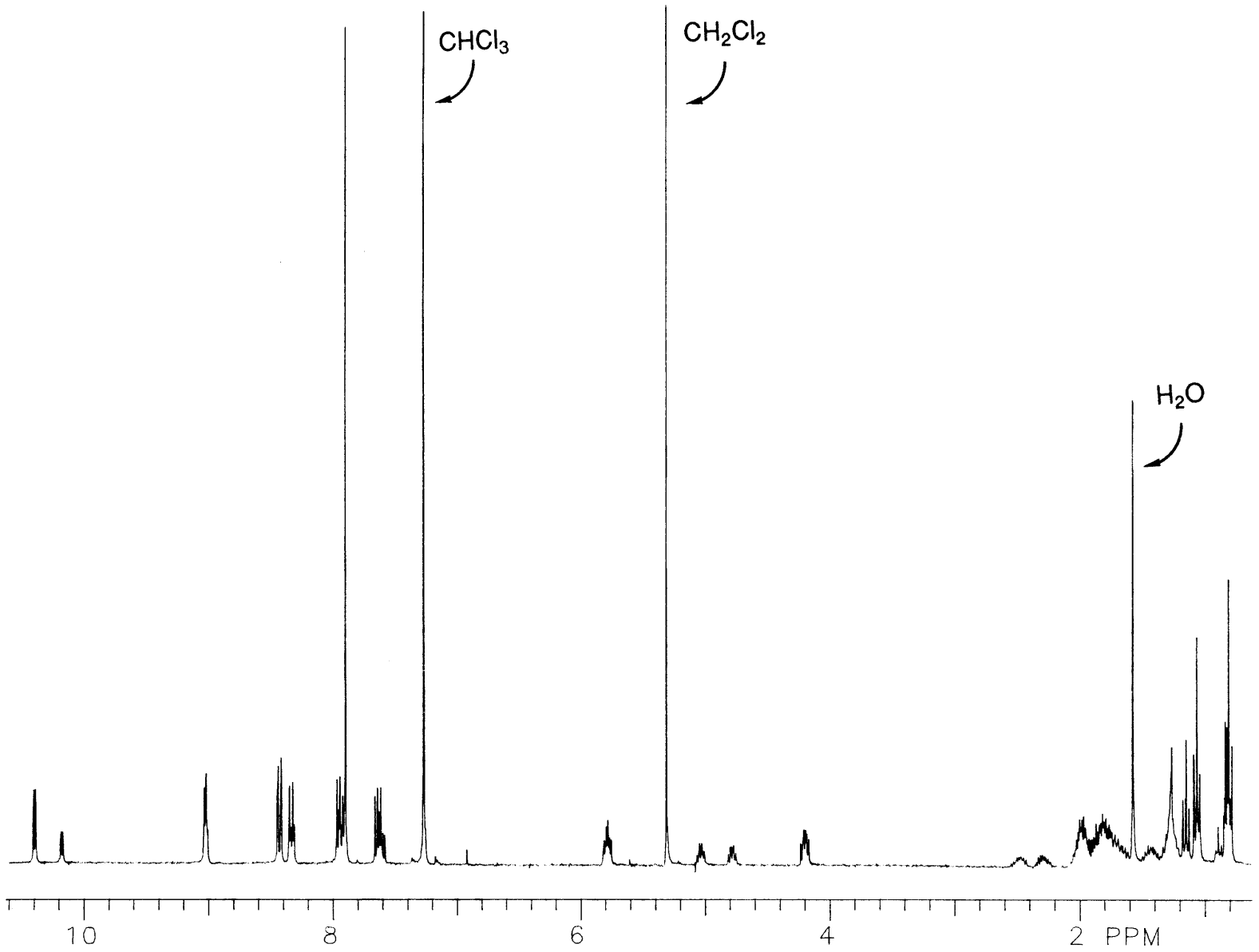

CHCl3
CH2Cl2
H2O
10
8
6
4
2 PPM

Figure 2.3: Proton NMR spectrum (250 MHz) of *meso*-TcOCl(CHPhCHPhO)(phen).

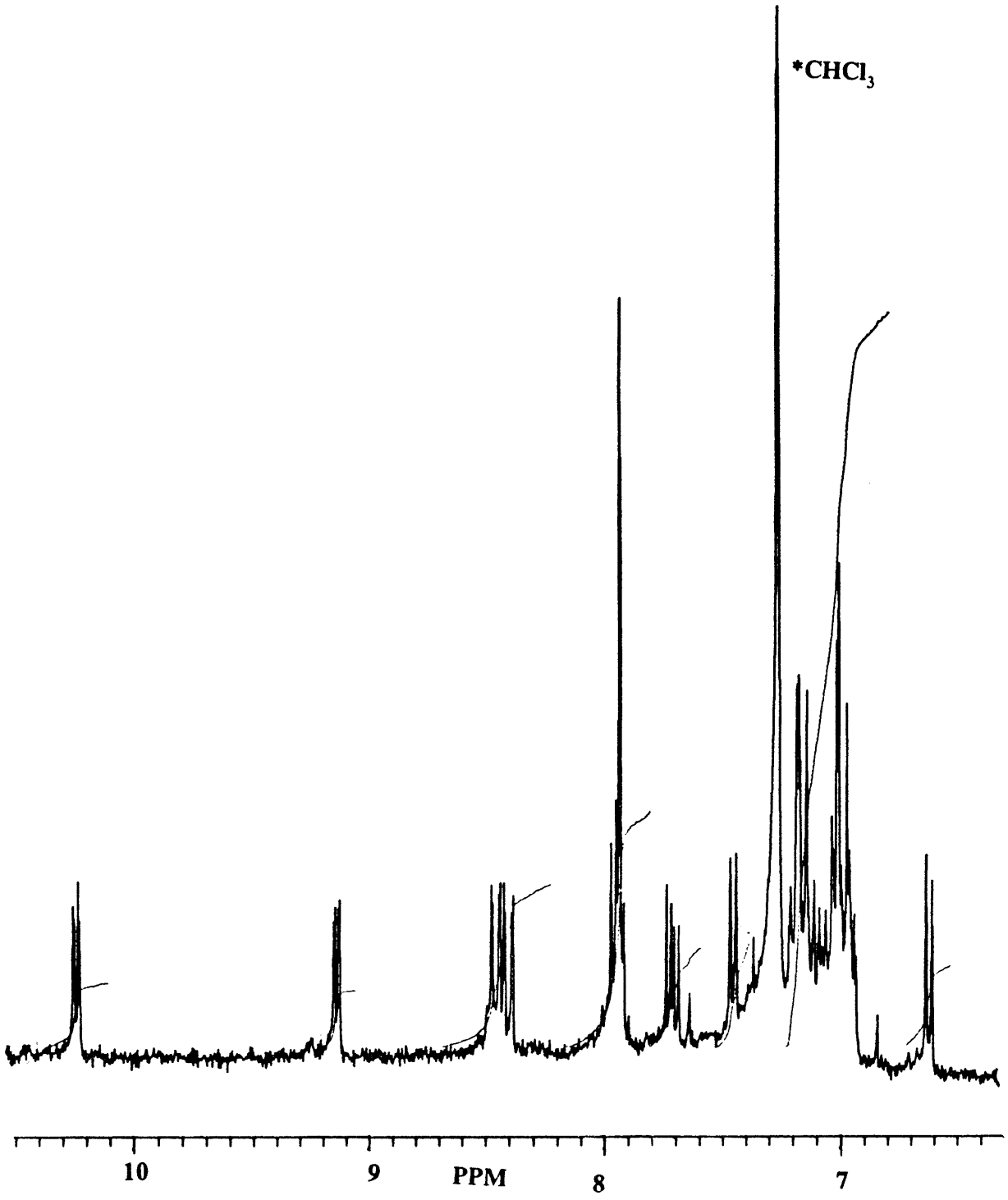

*CHCl3
10
9
PPM
8
7

Figure 2.4: A portion of the proton NMR spectrum (300 MHz) of $TcOCl(OCMe_2CH_2O)(phen)$.

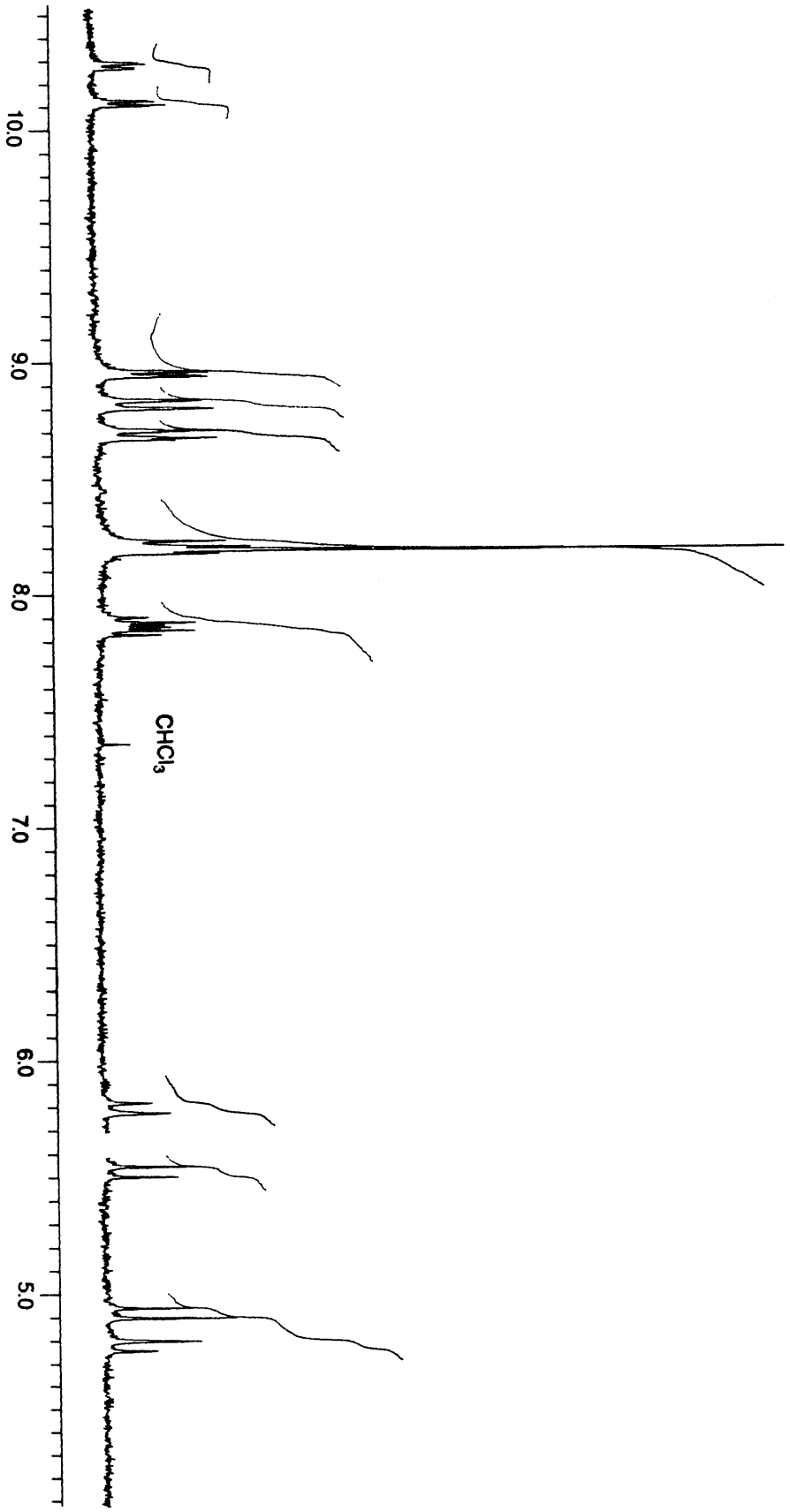

10.0
9.0
8.0
7.0
6.0
5.0
CHCl3

Figure 2.5: ORTEP drawing of $TcBr_4(phen)$ showing 50% probability ellipsoids.

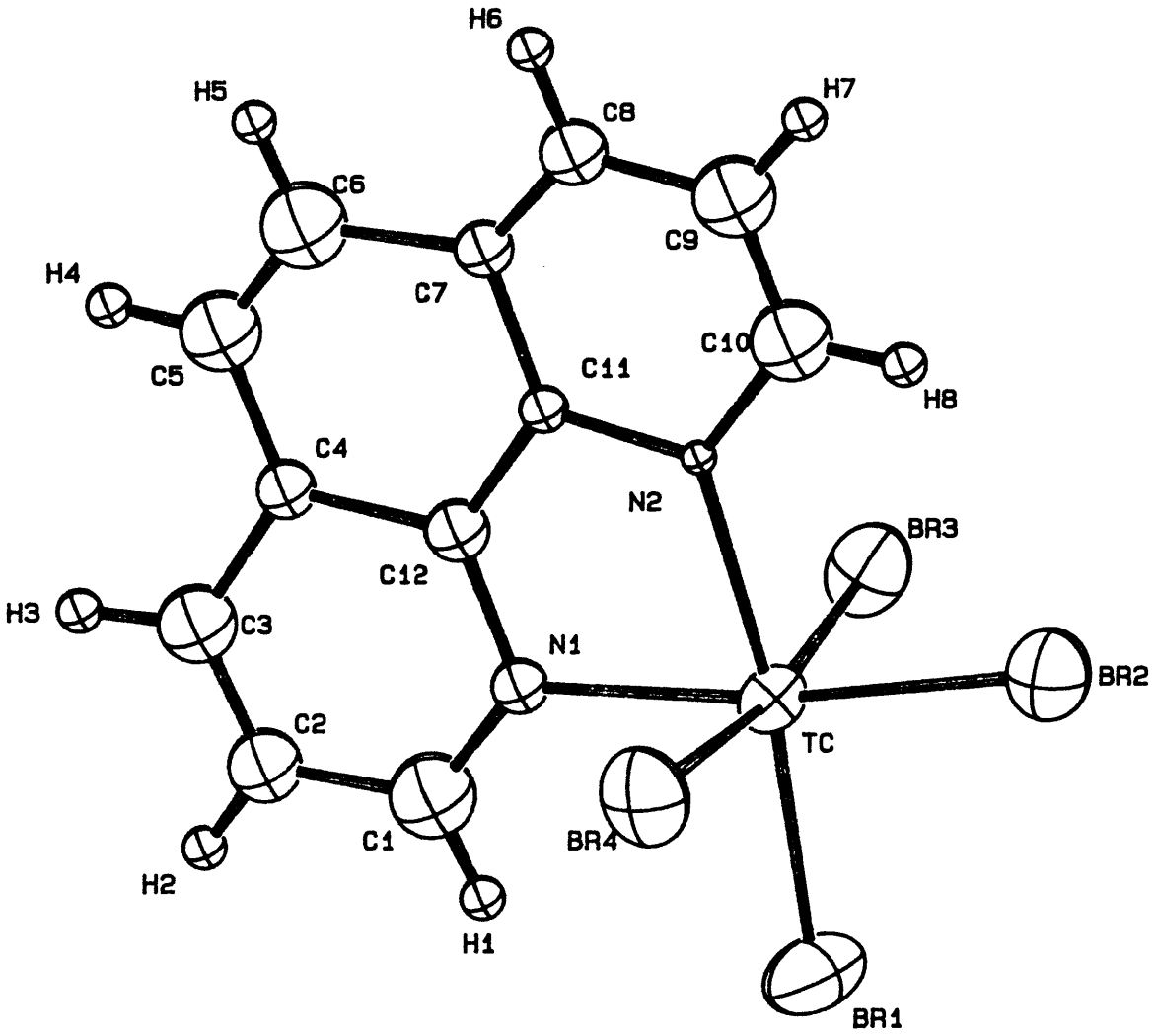
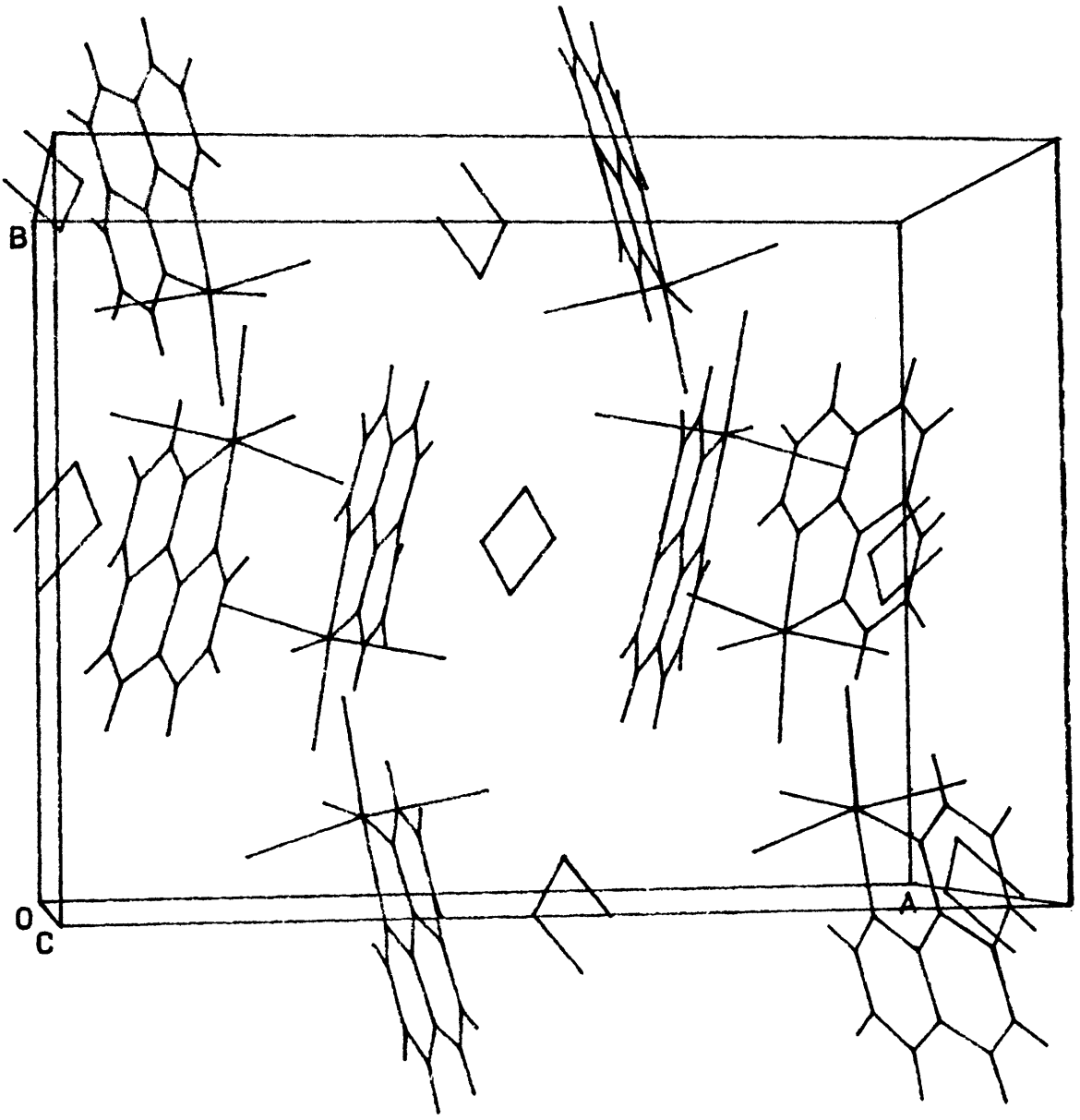
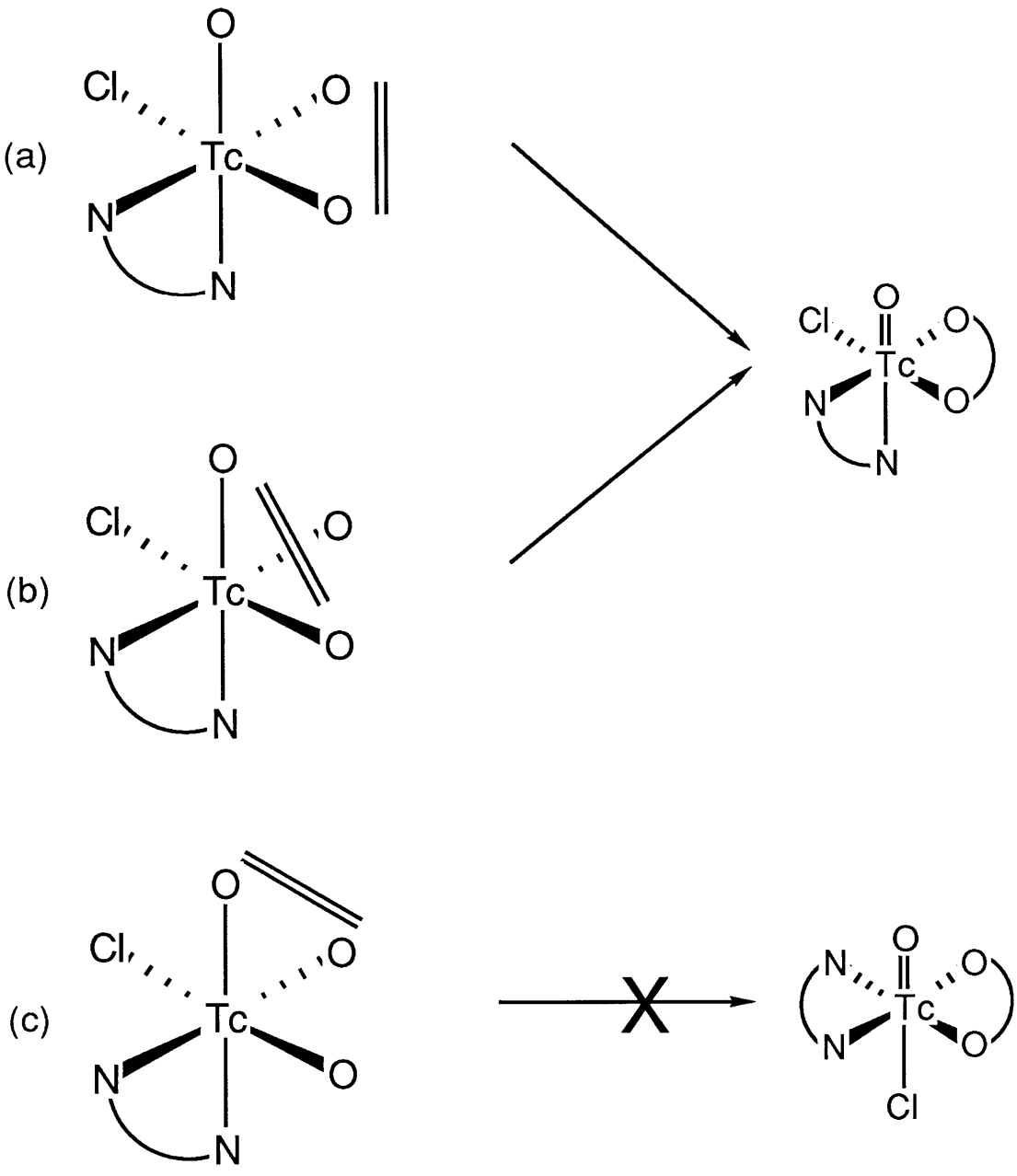

H6
H5
C8
H7
C6
C9
H4
C7
C10
C5
C11
H8
C4
N2
BR3
C12
H3
C3
N1
BR2
C2
TC
BR4
C1
H2
H1
BR1

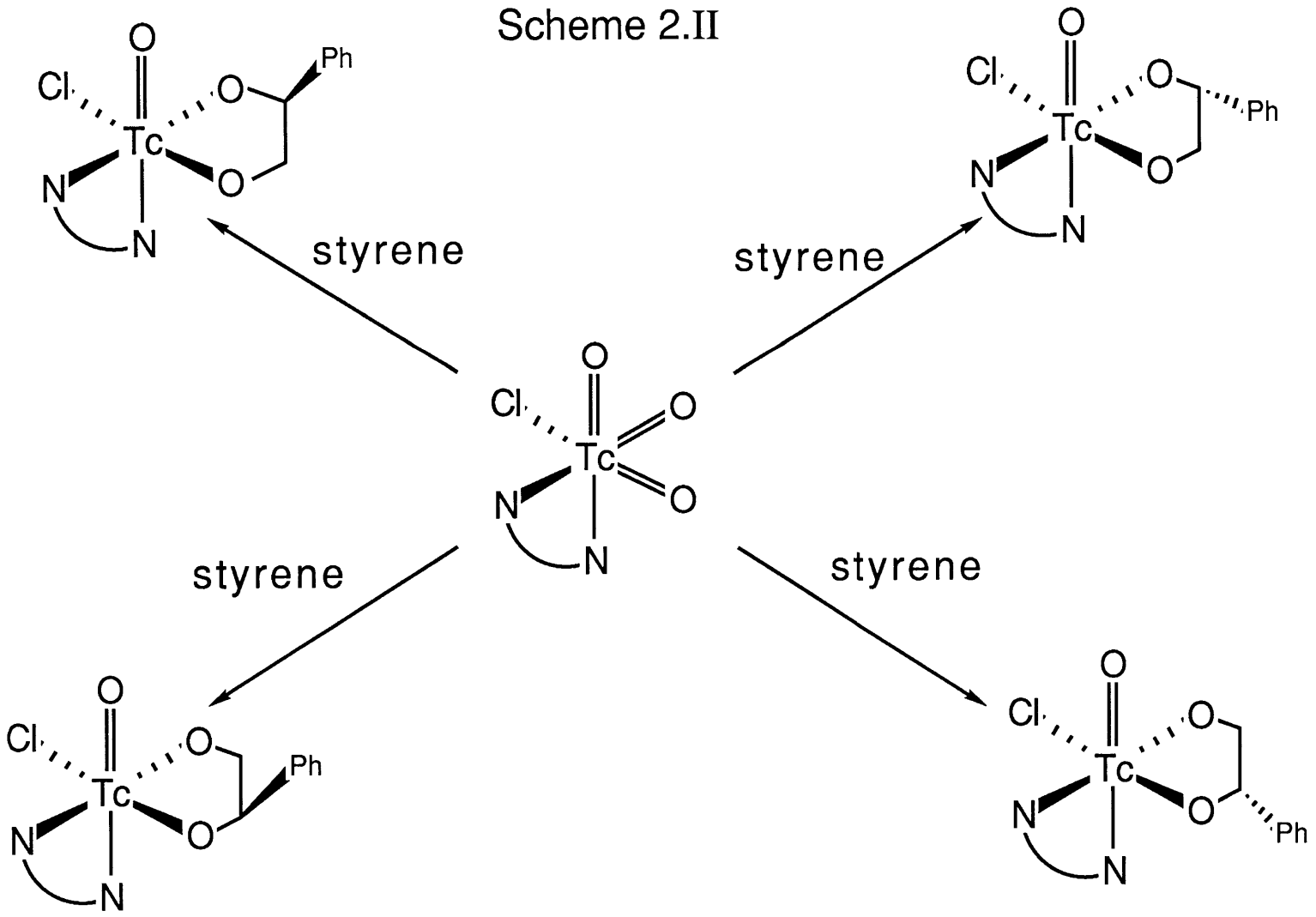
Figure 2.6: Packing diagram for $TcBr_4(phen)\cdot 1/2CH_2Cl_2$.


B
O
C
A

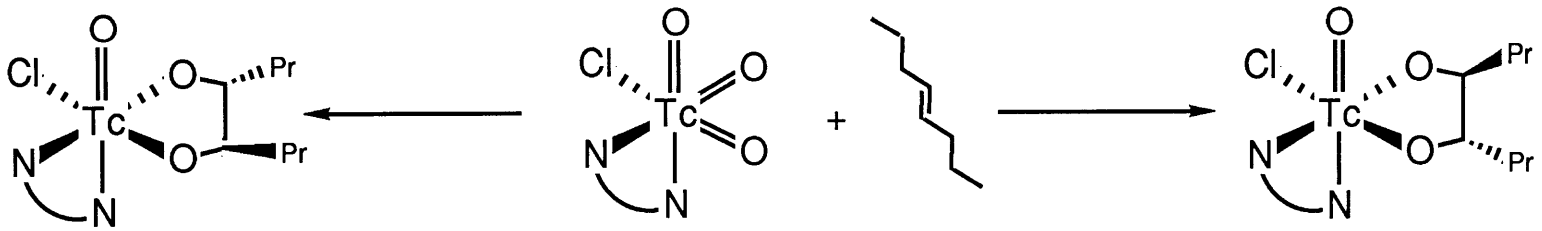
Scheme 2.I



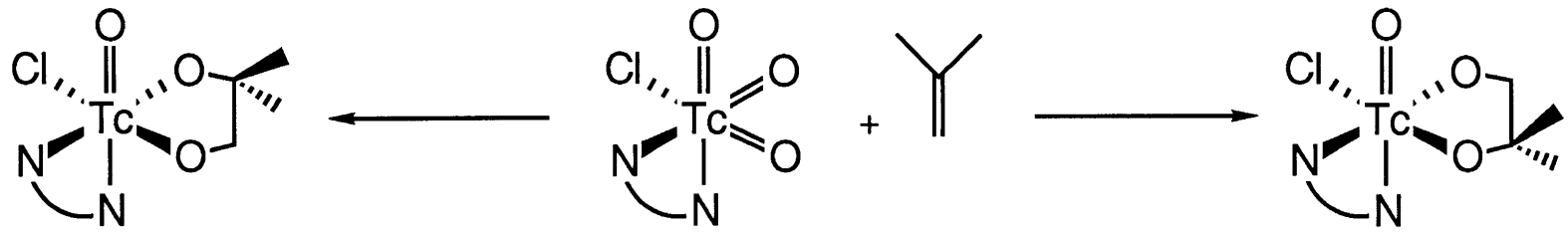
Scheme 2.II



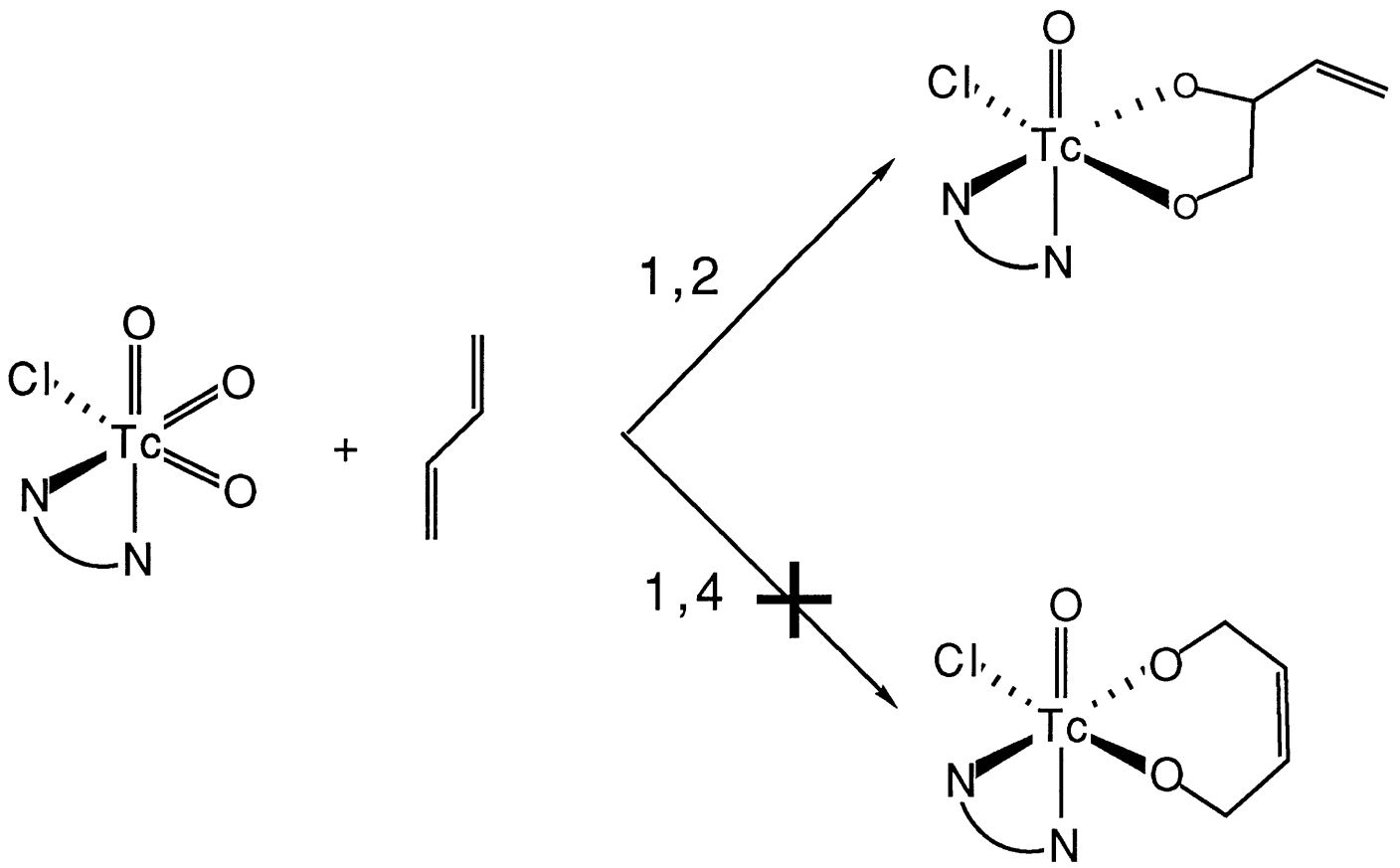
Scheme 2.III



Scheme 2.IV



Scheme 2.V



Chapter 3

Triphenylphosphine Complexes of Technetium With One Replaceable Ligand

INTRODUCTION:

There has been a great deal of study of technetium complexes with tertiary phosphine ligands which was due, in part, to the prospects[1] of a ^{99m}Tc-phosphine myocardial imaging agent. A limitation in this research was imposed by the lack of suitable technetium phosphine starting materials which could readily be prepared in good yields. The most notable starting materials,[2] $TcCl_4P_2$ (P = PPh_3, PMe_2Ph) and $TcCl_3(PMe_2Ph)_3$ have some drawbacks. The former is a complex of technetium(IV) which often undergoes unpredictable redox changes in addition to ligand substitution. The latter complex cannot be prepared with the less expensive triphenylphosphine, presumably due to the large steric requirement of this ligand which inhibits *cis*-octahedral coordination.

Trop[3] noted that the oxotetrachlorotechnetate ion reacted with triphenylphosphine in acetonitrile to give an unidentified orange material. In this chapter, a slightly improved preparation of this material and its identification as $TcCl_3(PPh_3)_2(MeCN)$ are described. Since the analogous rhenium complex[4] has been shown to be a useful synthetic reagent, some reactions of the technetium complex were performed to explore its utility.

EXPERIMENTAL:

Instrumentation:

Fourier transform IR spectra were measured from 4800 to 400 cm^{-1} on an IBM IR/30S spectrometer with DTGS detector and 2 cm^{-1} bandwidth. ^1H NMR spectra were recorded at 300 MHz on a Varian XL-300 spectrometer.

Fast atom bombardment mass spectra were measured on samples dissolved in a 3-nitrobenzyl alcohol matrix using a MAT 731 mass spectrometer operating at an accelerating voltage of 8 kV. The source was equipped with an Ion Tech B11N FAB gun producing a beam with 6-8 keV xenon neutrals.

Ultraviolet and visible absorption spectra were recorded on a Hewlett Packard 8451A photodiode array spectrophotometer. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA.

Syntheses:

Caution! ^{99}Tc is a β^- emitter ($t_{1/2} = 2.1 \cdot 10^5$ y). All manipulations of solutions and solids were performed in a laboratory approved for the handling of radioisotopes using precautions outlined elsewhere.[5]

All solvents were of at least reagent grade and used as received, except for toluene, which was distilled under N_2 from molten sodium. The complex[6] $(n\text{-}Bu_4N)[TcOCl_4]$ was prepared by literature methods.

Preparation of $TcCl_3(PPh_3)_2(MeCN)$:

To 103.97 mg $(n\text{-}Bu_4N)[TcOCl_4]$ (0.208 mmol) in a disposable vial was added with stirring 256 mg triphenylphosphine dissolved in 12 ml MeCN. The solution rapidly became very dark colored but within one minute it was bright orange. Precipitation was then

induced by adding a glass bead which was agitated by the magnetic stirbar. The solution was stirred for an additional ten minutes while the bright orange solid precipitated. The precipitate was collected on a medium porosity fritted glass funnel and rinsed with 10 ml MeCN followed by 2 ml hexane. After drying in vacuo overnight the product weighed 98.75 mg (62% yield). This material is slightly soluble with slow decomposition in MeCN, acetone, and toluene. It decomposes more rapidly in CH_2Cl_2.

Anal. Calcd. for $C_{38}H_{33}Cl_3NP_2Tc$: C, 59.21%; H, 4.31; Cl, 13.79; N, 1.82. Found: C, 58.99%; H, 4.43; Cl, 13.17; N, 1.89.

IR (KBr): 3055 cm^{-1}(w), 2928(w), 2917(w), 1481(m), 1433(s), 1400(w), 1385(w), 1367(w), 1316(w), 1189(w), 1163(w), 1120(w), 1091(m), 1072(w), 1027(w), 998(w), 753(w), 747(m), 742(m), 696(s), 521(s), 511(s), 496(m), 479(w), 454(w). FABMS(+): m/z [ion, abundance] 769 [$(M)^+$, 19%], 728 [$(M\text{-}MeCN)^+$, 91%], 693 [$(M\text{-}MeCN\text{-}Cl)^+$, 100%].

Preparation of $TcCl_3(PPh_3)_2(CO)$:

To 28.38 mg $TcCl_3(PPh_3)_2(MeCN)$ (0.037 mmol) in a nitrogen purged 100 ml round bottomed flask with a sidearm was added 20 ml toluene. Carbon monoxide (Matheson) was then bubbled through the resulting suspension while gently warming to 65 °C. The acetonitrile starting material dissolved as it reacted, forming a clear wine-red solution within ten minutes. The bubbling of CO continued for 5 additional minutes to insure complete reaction. The reaction mixture was filtered through paper and the solvent was evaporated under reduced pressure. The residue was recrystallized from CH_2Cl_2/heptane yielding 17.27 mg (62%) of small red parallelograms.

Anal. Calcd. for $C_{37}H_{30}Cl_3OP_2Tc$: C, 58.64%; H, 3.99; Cl, 14.03. Found: C, 57.58%; H, 3.98; Cl, 14.19. A separate preparation gives: C, 57.51; H, 3.94.

IR (KBr): νCO 2054 cm^{-1}(vs). ^1H NMR ($CDCl_3$): δ 9.9 (broad, 12H), 7.5 (broad

with shoulder, 18H). Visible (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ 562 nm(770 $l \cdot mol^{-1} \cdot cm^{-1}$). FABMS(+): m/z [ion, abundance] 693 [$(M\text{-}Cl\text{-}CO)^+$, 100%], 686 [$(M\text{-}2Cl)^+$, 95%].

Preparation of $TcCl_3(PPh_3)_2(NO)$:

To 35.24 mg $TcCl_3(PPh_3)_2(MeCN)$ (0.046 mmol) in a nitrogen purged 50 ml round bottomed flask with a sidearm was added 15 ml toluene. Nitric oxide (Matheson) was then bubbled through the resulting suspension while gently warming with a water bath. The acetonitrile starting material dissolved as it reacted, forming a green solution. The reaction was allowed to proceed for a total of 35 minutes. An aliquot of the reaction mixture gave an electron spin resonance spectrum consisting of a three line pattern (<g> ~ 2.0, <a> ~ 12 G) due to NO superimposed on a ten line pattern (<g> ~ 2.0, <a> ~ 130 G) due to the technetium(II) complex. The remaining green solution was filtered and the solvent was evaporated under reduced pressure. The residue was recrystallized from CH_2Cl_2/MeOH yielding a dark-green microcrystalline solid.

IR (KBr): νNO 1805 cm^{-1}(vs). FABMS(+): m/z [ion, abundance] 723 [$(M\text{-}Cl)^+$, 89%], 688 [$(M\text{-}2Cl)^+$, 100%].

RESULTS AND DISCUSSION:

The reduction of $ReOCl_3(PPh_3)_2$ with triphenylphosphine, forming $ReCl_3(PPh_3)_2(MeCN)$, was shown to require the prior coordination of acetonitrile.[4] As discussed in Chapter 2, technetium complexes are generally easier to reduce than rhenium complexes in similar environments. Furthermore, oxo transfer reactions in which oxotechnetium(V) complexes are converted to technetium(III) complexes are well established with PR_3 as the oxygen atom acceptor.[7] Nevertheless, the reduction of oxotetrachlorotechnetate anion with triphenylphosphine also only appears to go cleanly in the presence of acetonitrile. Since the product, $TcCl_3(PPh_3)_2(MeCN)$, is unstable toward aerial oxidation while in solution, its rapid precipitation from the reaction mixture is essential when the reaction is carried out in air. Induction of crystallization is conveniently provided by placing a glass bead in the stirred reaction mixture, creating nucleation sites on the walls of the reaction vessel. Solutions of this complex, however, may be manipulated under a nitrogen atmosphere.

The characterization of this product as (acetonitrile)trichlorobis(triphenylphosphine)technetium(III) is straightforward based on analogy with the rhenium complex[4] as well as the fast atom bombardment mass spectrum showing molecular ion and sequential losses of MeCN and Cl. The elemental analysis fits well for C, H, and N; but deviates by 0.62% for Cl. No infrared band attributable to νCN is observed as is also the case for the rhenium analog.

Substitution reactions of $ReCl_3(PPh_3)_2(MeCN)$ follow a predictable course depending on the nature of the incoming ligands. Addition of neutral ligands first displaces the acetonitrile and then the phosphine ligands as demonstrated in Reactions 3.1-3.3.[4,8-9] In contrast, salts of anionic ligands first substitute for the chlorides via elimination of alkali metal chlorides as shown in Reactions 3.4 and 3.5.[10-11]

$$ReCl_3(PPh_3)_2(MeCN) + MeNC \text{ ----------> } ReCl_3(PPh_3)_2(MeNC) \quad (3.1)$$

$$ReCl_3(PPh_3)_2(MeCN) + bpy \text{ ----------> } ReCl_3(PPh_3)(bpy) \quad (3.2)$$

$$ReCl_3(PPh_3)_2(MeCN) + 3\ AsPr_3 \text{ ----------> } ReCl_3(AsPr_3)_3 \quad (3.3)$$

$$ReCl_3(PPh_3)_2(MeCN) + 3\ NaSPh \text{ ----------> } Re(SPh)_3(PPh_3)(MeCN) \quad (3.4)$$

$$ReCl_3(PPh_3)_2(MeCN) + 3\ Na(Et_2NCS_2) \text{ ----------> } Re(Et_2NCS_2)_3 \quad (3.5)$$

It is expected that $TcCl_3(PPh_3)_2(MeCN)$ should have the same substitution chemistry as its rhenium analog. The reaction of $TcCl_3(PPh_3)_2(MeCN)$ with carbon monoxide gas in toluene cleanly replaces just the acetonitrile ligand with a carbonyl group yielding carbonytrichlorobis(triphenylphosphine)technetium(III). It is surprising, therefore, that this reaction has not been reported with the rhenium analog. This derivative has an intense infrared band at 2054 cm^{-1} assigned as νCO. In addition, there are five very weak bands in the range 2100 $cm^{-1} > \nu > 1800\ cm^{-1}$ which may be due to carbonyl impurities not removeable by recrystallization or which form in the KBr disk. The high frequency of νCO in this complex is suggestive of terminal carbonyl ligation with minimal π-backbonding.[12] Although *mer*-$TcCl_3(PMe_2Ph)_3$ reacts with CO to form[13] the diamagnetic C_{3v} seven-coordinate complex $TcCl_3(PMe_2Ph)_3(CO)$, there is no evidence for the formation of a seven-coordinate dicarbonyl complex in the acetonitrile substitution reaction described above. This difference in reactivity may be attributed to the greater σ-basicity of PMe_2Ph compared to PPh_3, leading to a higher affinity for π-acids (e.g. CO) in complexes of the former.

The proton NMR spectrum of $TcCl_3(PPh_3)_2(CO)$ shows two slightly broadened resonances, one clearly having a shoulder. The most reasonable interpretation is that the resonance having the shoulder and having a relative integration for three protons corresponds to the *meta* and *para* protons of the six equivalent phenyl rings. The other resonance, shifted downfield and integrating for two protons, corresponds to the *ortho* protons of the equivalent phenyl groups. Like a number of other pseudo-octahedral d^4 systems,[9] the spectra for these complexes do not display large contact shifts. The line broadening seen, in fact, could be due to unresolved coupling to the phosphorus nuclei, and thus might not be related to the paramagnetism of the complex. A phosphorus NMR signal could not, however, be detected for this complex.

The reaction of $TcCl_3(PPh_3)_2(MeCN)$ with nitric oxide is similar to the reaction with CO, except that there is now a change in the formal oxidation state of the technetium. The product, trichloronitrosylbis(triphenylphosphine)technetium(II), can be visualized as a simple substitution product. Since the neutral NO molecule carries three electrons for donation, one of which formally assigned to the metal in forming a coordinated NO^+, the oxidation state of the metal is reduced. The assignment of the unpaired electron onto the metal is verified by the presence of a ten line pattern in the electron spin resonance (ESR) spectrum of the isolated complex dissolved in CH_2Cl_2 attributed to hyperfine coupling to a ^{99}Tc nucleus which has nuclear spin I = 9/2. No superhyperfine coupling to phosphorus was noted. The NO stretching mode in the infrared spectrum at 1805 cm^{-1} is consistent with a terminal linear NO^+ linkage.[14] This complex is entirely analogous to the complex $TcCl_3(PMe_2Ph)_2(NO)$ previously prepared[15] from the trisphosphine-trichloride. Although the ESR spectra for these two analogs are identical, a slight lowering of νNO is noted for the PMe_2Ph derivative which may be understood similarly as for the carbonyl phosphines discussed above.

The reactions described in this chapter are summarized in Scheme 3.I. As demonstrated

in Figure 3.1, the technetium(III) complexes reported here form the 'early' side of the border for two classes[16,17] of trivalent triphenylphosphine complexes. The complex on the 'late' border, $IrCl_3(PPh_3)_2(CO)$, is the oxidative addition product of Cl_2 with the 16-electron species, Vaska's complex[17e] ($IrCl(PPh_3)_2(CO)$). In comparison, it might be expected that the 16-electron technetium analog, $TcCl_3(PPh_3)_2(CO)$, might undergo reductive elimination to form 18-electron technetium(I) complexes on addition of two neutral donors. Alternatively, one-electron redox chemistry might be expected considering that the ruthenium(II) analog, $[RuCl_3(PPh_3)_2(CO)]^-$ can be reversibly oxidized electrochemically to the +3 state.[17b] In addition, it has been shown that complexes of technetium(III) with similar ligands can be chemically reduced by one electron.[18] The technetium(III) species described in this chapter, therefore, should be good starting materials for rational syntheses of complexes in oxidation states +1 to +3.

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Figure 3.1: Graphical representation of the transition metals known to form complexes of the types: $MCl_3(PPh_3)_2(MeCN)$ and $MCl_3(PPh_3)_2(CO)$.

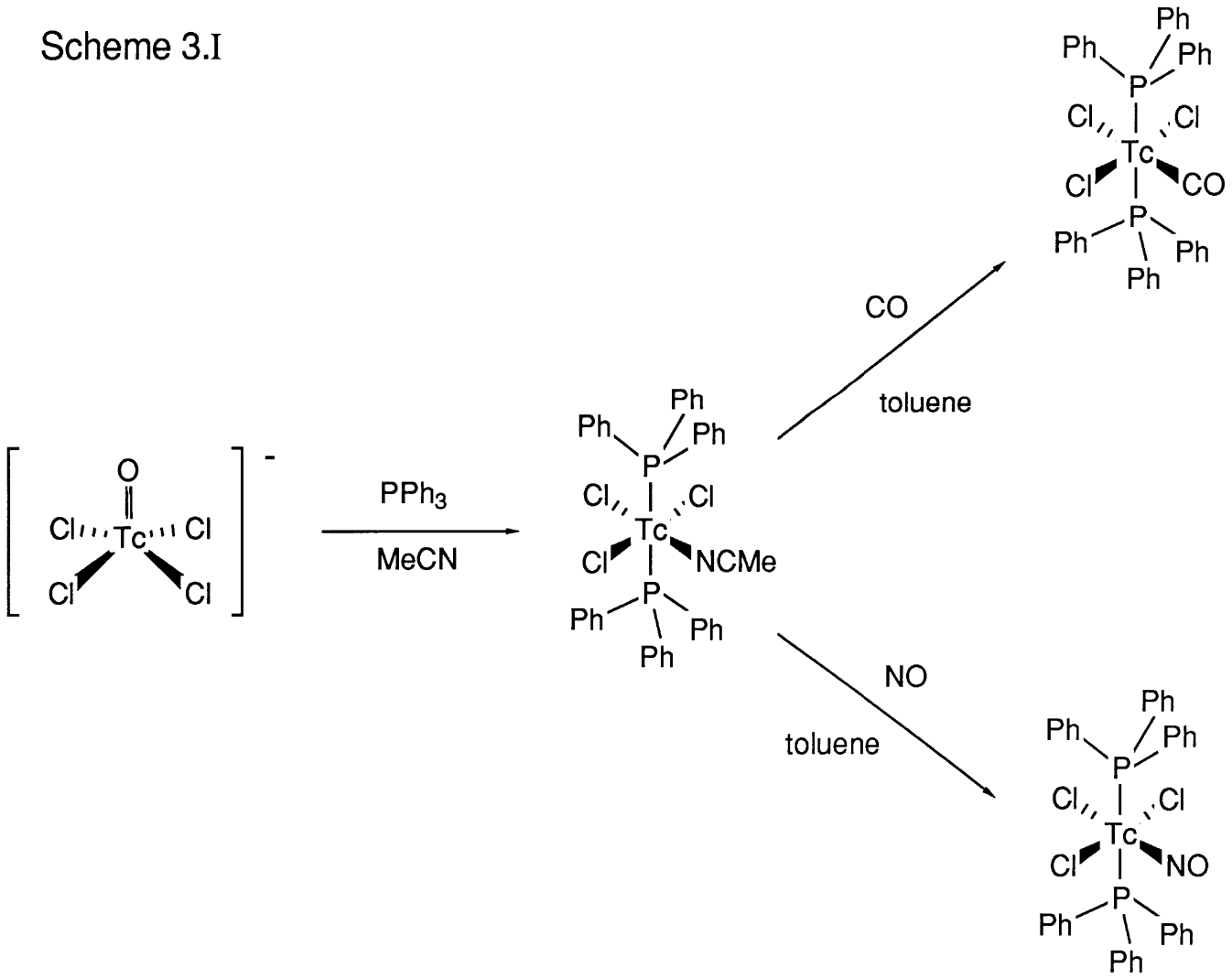
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg


$MCl_3(PPh_3)_2(MeCN)$ reported.


$MCl_3(PPh_3)_2(CO)$ reported.


Both reported

Scheme 3.I


O
Cl
Tc
Cl
Cl
Cl
-
PPh3
MeCN
Ph
Ph
P
Cl
Cl
Tc
Cl
NCMe
P
Ph
Ph
Ph
CO
toluene
Ph
Ph
P
Cl
Cl
Tc
Cl
CO
P
Ph
Ph
Ph
NO
toluene
Ph
Ph
P
Cl
Cl
Tc
Cl
NO
P
Ph
Ph
Ph

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BIOGRAPHICAL NOTE:

The author was born on July 27, 1962 in Philadelphia, PA. After 13 years of education in the Philadelphia public schools, he graduated from Northeast High School in June, 1980. He attended the University of Pennsylvania from 1980 to 1984, pursuing chemical research under the tutelage of Professor Larry Sneddon. In June 1984, he was awarded a Bachelor of Arts degree in chemistry with honors, *summa cum laude*, and a Bachelor of Science degree in Chemical Engineering, *summa cum laude*.

After graduating college, the author began graduate studies at the Massachusetts Institute of Technology under the guidance of Professor Alan Davison, and was awarded the degree of Doctor of Philosophy in June, 1988. He is the recipient of the American Institute of Chemists' medal and the annual award of the Priestly club at the University of Pennsylvania. He has been elected into membership in the ΤΒΠ engineering society and is a member of the American Chemical Society.

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