ALKENE–GLYCOL INTERCONVERSION WITH TECHNETIUM AND RHENIUM OXO COMPLEXES

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Abstract—The trioxotechnetium(VI) complexes TcO₂Cl(AA) (AA = phen, bpy, 5-NO₂-phen, 3,4,7,8-Me₄-phen) cleanly oxidize olefins (C₂R₄) in solution at 22°C, forming in high yields the corresponding oxotechnetium(V) diolate complexes, TcOCl(OOCR₂CR₂O)(AA). The complexes have been characterized by 'H 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(OCH₂CH₂O)(phen) undergoes the reverse reaction when thermalized, releasing ethylene and producing ReO₂Cl(phen).

All of the transition metal species known to effect the cis-dihydroxylation of olefins (i.e. OsO₄, RuO₄ and MnO₄⁻) are tetrahedral tetraoxides. Although alkaline permanganate is capable of oxidizing alkenes to cis-1,2-diols, the reaction conditions must be carefully controlled to prevent over-oxidation. No such activity has been demonstrated with the heavier group seven species pertechnetate (TcO₄²⁻) and perrhenate (ReO₄⁻). A few examples of the reverse reaction, the conversion of a coordinated vicinal diolate into an olefin, have been reported with the third row elements tungsten and rhenium. This paper describes the oxidation of olefins to the corresponding diolates with the trioxotechnetium(VI) complexes TcO₂Cl(AA) (AA = phen, bpy, Me₄-phen, NO₂-phen) and the thermal decomposition of the oxorhenium(V) diolate ReOCl(phen)(eg) (eg = 1,2-ethanediolate) into ReO₂Cl(phen) and ethylene.

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. '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. UV 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 μm film of DB-5 (5% phenylmethyl silicone). The temperature programmer held the column at 50°C for 4 min then ramped at 8° min⁻¹ to a maximum temperature of 250°C.

Syntheses

Caution! ⁹⁹Tc is a β⁻ emitter (t½ = 2.1 × 10⁵ y). All manipulations of solutions and solids were performed in a laboratory approved for the handling of radioisotopes using precautions outlined elsewhere. All solvents were of at least reagent grade and were used as received unless otherwise noted. Dichloromethane, preserved with 70 ppm of iso-pentene, was stirred overnight with concentrated H₂SO₄, washed with saturated aqueous Na₂CO₃,
and predried over anhydrous CaCl₂. It was then distilled under N₂ from P₂O₁₀ and stored in the dark under N₂. Water was passed through a Barnstead Ultrapure ion-exchange column and distilled using a Corning AG-1 glass still. TcO₂Cl (phen) and TcO₂Cl(bpy) were prepared by the method of Davison et al.⁶ (Ph₃As)[ReOCl₃] was prepared by the method of Cotton and Lippard.⁷

Preparation of TcO₂Cl(5-NO₂-phen)

To 0.109 g 5-nitro-1,10-phenanthroline (G. F. Smith) was added 10 cm³ MeOH. The ligand was dissolved by gentle heating and the resulting solution cooled to ambient temperature before adding 0.5 cm³ of 0.385 M (NH₄)[TcO₂] (0.193 mmol). The solution was stirred and 1.5 cm³ concentrated HCl. A white precipitate (presumably HCl) formed immediately and became yellow after stirring overnight. The mixture was filtered on a fritted glass funnel and rinsed with n-heptane, then dried in vacuo overnight. Yield: 72.01 mg, 72%. Found: C, 50.0; H, 5.1; Cl, 5.9. IR (KBr): vTc=O 892 cm⁻¹(s), 874(m).

Preparation of TcOCl(DL-4,5-octenediohete) (phen)

Using the procedure above but reacting 78.68 mg of TcO₂Cl(phen) (0.217 mmol) and 0.42 g of cis-4-octene. Yield: 64.0 mg, 70%. IR (KBr): vTc=O 951 cm⁻¹, 1H NMR (CDCl₃): δ 10.33 (dd, integral = 18), 10.24(d, lo), 8.99(dd, 32), 8.43(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("Pr multiplets, ~640). FABMS(+) m/z 373 (M+Cl⁺), 357 (M+H-Cl-O⁺), 340 (M-Cl-2O)⁺.

Preparation of TcOCl(meso-4,5-octenediolate) (phen)

Using the procedure above but reacting 23.78 mg of TcO₂Cl(phen) (0.058 mmol) and 0.25 g of cis-4-octene. Yield: 18.6 mg, 61%. Found: C, 46.3; H, 4.5; Cl, 6.7; N, 8.1. Calc. for C₂₂H₂₆Cl₂N₃0₃Tc: C, 46.2; H, 4.5; Cl, 6.8; N, 8.1%. IR (KBr): vTc=O 956 cm⁻¹, 1H NMR (CDCl₃): δ 10.60(m, integral = 6), 10.37(m, 4), 9.2(overlapping multiplets, 21), 8.86(m, 9), 8.63(d, 23.8); 7.7-7.5 (overlapping multiplets, 26), 7.3-7.1 (overlapping multiplets, 19), 6.9-6.7 (overlapping multiplets, 12), 6.2-5.8 (overlapping multiplets, 12), 1.2-0.6("Pr multiplets, ~640). FABMS(+) m/z 439 (M-Cl⁻).
Preparation of TcOCl(meso-dibutyltartrate) (phen). Using the procedure above but reacting 61.34 mg of TcOCl(phen) (0.169 mmol) and 0.26 g of dibutyl maleate (Aldrich, 90%). Yield: 61.18 mg, 61%. IR (KBr): \(\nu_{\text{Tc}=\text{O}}\) 951 cm\(^{-1}\). 

Preparation of TcOCl(1,2-cyclohexanediolate)(phen). Using the procedure above but reacting 9.14 mg of TcOCl(bpy) (0.027 mmol) and trans-stilbene (Aldrich, 96%). Yield: 5.07 mg, 42%. IR (KBr): \(\nu_{\text{Tc}=\text{O}}\) 952 cm\(^{-1}\). 

Reaction of TcOCl(AA) with alkene in acetone

Preparation of TcOCl(phenyl-1,2-ethanediolate) (phen). To 1 cm\(^3\) styrene combined with 1 cm\(^3\) acetonitrile(1,10-phenanthroline)technetium(V) (0.140 mmol). After 20 min, 15 cm\(^3\) CH\(_2\)Cl\(_2\) was added to the resulting yellow-green slurry to dissolve C\(_2\)H\(_5\)ClN\(_2\)O\(_3\)Tc: C, 57.5; H, 3.7; Cl, 6.5%.

Preparation of TcOCl(1,2-cyclohexanediolate)(phen). Using the procedure above but by reacting 13.29 mg of TcOCl(bpy) (0.039 mmol) and cyclohexene (MC/B). Yield: 5.0 mg, 30%. IR (KBr): \(\nu_{\text{Tc}=\text{O}}\) 949 cm\(^{-1}\). FABMS(+) : \(m/z\) 484 [(M+Cl)+, 100%].

Preparation of TcOCl(1,2-decanediolate)(phen). Using the procedure above but reacting 24.66 mg of TcOCl(phen) (0.068 mmol) and trans-stilbene (Aldrich, 96%). Yield: 18.19 mg, 49%. IR (KBr): \(\nu_{\text{Tc}=\text{O}}\) 947 cm\(^{-1}\). 

Preparation of TcOCl(3,4,7,8-Me\(_4\)-phen). Using the procedure above but reacting 13.75 mg of TcOCl(bpy) (0.039 mmol) and 0.23 g dibutyl maleate (Aldrich, 90%). Yield: 21.94 mg, 41%. TR (KBr): \(\nu_{\text{Tc}=\text{O}}\) 960 cm\(^{-1}\). 

Preparation of TcOCl(1,2-cyclohexanediolate) (bpy). Using the procedure above but by reacting 13.29 mg of TcOCl(bpy) (0.039 mmol) and cyclohexene (MC/B). Yield: 5.0 mg, 30%. IR (KBr): \(\nu_{\text{Tc}=\text{O}}\) 949 cm\(^{-1}\). FABMS(+) : \(m/z\) [ion, abundance]: 467 [(M+H)+, 3%], 431 [(M+Cl)+, 100%].

Preparation of TcOCl(phenyl-1,2-ethanediolate) (bpy). Using the procedure above but reacting 9.14 mg of TcOCl(bpy) (0.027 mmol) and distilled styrene. Yield: 5.07 mg, 42%. IR (KBr): \(\nu_{\text{Tc}=\text{O}}\) 952 cm\(^{-1}\). FABMS(+) : \(m/z\) [ion, abundance]: 849 [(2M+Cl)+, 3%], 830 [(2M+Cl+O)+, 0.4%], 443 [(M+H)+, 4%], 407 [(M+Cl)+, 100%], 306 [(M-styrenediolate)+, 45%], 303 [(M+Cl-styrene)+, 26%], 287 [(M+Cl-styrene)+, 39%].

Preparation of TcOCl(1,2-diphenyl-1,2-ethanediolate)(phen). Using the procedure above but by reacting 24.66 mg of TcOCl(phen) (0.068 mmol) and trans-stilbene (Aldrich, 96%). Yield: 18.19 mg, 49%. IR (KBr): \(\nu_{\text{Tc}=\text{O}}\) 947 cm\(^{-1}\). 

Preparation of TcOCl(3,4,7,8-Me\(_4\)-phen)(phen). Using the procedure above but by reacting 28.54 mg of TcOCl(phen) (0.079 mmol) and cis-stilbene (Aldrich 97%). Yield: 16.65 mg, 39%. Found: C, 56.5; H, 4.0; Cl, 6.5. Calc. for C\(_{44}H\_32ClN\_2O\_3Tc: C, 57.5; H, 3.7; Cl, 6.5%.

Preparation of TcOCl(meso-diphenyl-1,2-ethanediolate)(phen). Using the procedure above but by reacting 28.54 mg of TcOCl(phen) (0.079 mmol) and cis-stilbene (Aldrich 97%). Yield: 16.65 mg, 39%. Found: C, 56.5; H, 4.0; Cl, 6.5. Calc. for C\(_{44}H\_32ClN\_2O\_3Tc: C, 57.5; H, 3.7; Cl, 6.5%.

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Preparation of $\text{TcOCl(DL-5,6-decanediolate)}$(phen). Using the procedure above but by reacting 46.2 mg of $\text{TcO}_2\text{Cl(phen)}$ (0.127 mmol) and 5-decene (Aldrich, 99 %). Yield: 49.1 mg, 77%. Found: C, 52.4; H, 5.7; Cl, 7.0; N, 5.6. Calc. for $\text{C}_{22}\text{H}_{28}\text{ClN}_2\text{Tc}$: C, 52.5; Cl, 7.1; N, 5.6. Calc. for $\text{C}_{22}\text{H}_{28}\text{ClN}_2\text{Tc}$: C, 52.5; Cl, 7.1; N, 5.6.

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Preparation of $\text{TcOCl(eg)(phen)}$. To 18 cm$^3$ of anhydrous EtOH in a 50 cm$^3$ Erlenmeyer flask was dissolved 0.28 g of chlorotrioxo(1,10-phenanthroline)technetium(VII) (0.095 mmol). Ethylene (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 a green microcrystalline precipitate appeared. Yield: 28.33 mg, 76%.

The product is spectroscopically identical to the crystallographically characterized material prepared by the reaction of $[\text{TcOCl}_4]^{-}$ with HOCH$_2$CH$_2$OH and phen.$^*$

Preparation of $\text{TcOCl(1,1-dimethyl-1,2-ethanediolate)(phen)}$. Into a 100 cm$^3$ round bottomed flask with a side-arm and stopcock was added 20 cm$^3$ of acetone and 29.58 mg of chlorotrioxo(1,10-phenanthroline)technetium(VII) (0.082 mmol). The flask was then sealed with a latex balloon and isobutylene (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 acetic 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 solution was then transferred to a separatory funnel and the organic layer separated, saving the organic layer then drying it with MgSO$_4$. The precipitate was determined to be preferable.

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Preparation of $\text{TcOCl(DL-5,6-decanediolate)}$ (phen). Using the procedure above but by reacting 46.2 mg of $\text{TcO}_2\text{Cl(phen)}$ (0.127 mmol) and 5-decene (Aldrich, 99 %). Yield: 49.1 mg, 77%. Found: C, 52.4; H, 5.7; Cl, 7.0; N, 5.6. Calc. for $\text{C}_{22}\text{H}_{28}\text{ClN}_2\text{Tc}$: C, 52.5; Cl, 7.1; N, 5.6.

IR (KBr): $\nu_{\text{Tc}=\text{O}}$ 948 cm$^{-1}$. $^1$H NMR for $\text{C}_{22}\text{H}_{28}\text{ClN}_2\text{Tc}$: C, 52.5; Cl, 7.0; N, 5.6.

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IR (KBr): $\nu_{\text{Tc}=\text{O}}$ 948 cm$^{-1}$. $^1$H NMR for $\text{C}_{22}\text{H}_{28}\text{ClN}_2\text{Tc}$: C, 52.5; Cl, 7.0; N, 5.6. Calc. for $\text{C}_{22}\text{H}_{28}\text{ClN}_2\text{Tc}$: C, 52.5; Cl, 7.1; N, 5.6. **Other drying agents, such as Na$_2$SO$_4$ or K$_2$CO$_3$, were subsequently determined to be preferable.**
hydrolysis reaction was performed for the meso isomer.

Preparation of phenyl-1,2-ethanediol. Hydrolysis was carried out as above, but reacting 15.36 mg of TcOCl(OCHPhCH$_2$O)(phen) (0.033 mmol). The product was purified by vacuum sublimation at 100°C. 1H NMR (CDCl$_3$): $\delta$ 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, 30 eV; $m/z$ [ion, abundance]: 138 [(M$^+$), 39%], 120 [(M$-$H$_2$O$^+$), 4%], 107 [(M$-$CH$_2$OH$^+$), 100%], 91 [(C$_7$H$_7^+$), 5%], 79 [(C$_6$H$_5^+$), 45%].

Preparation of ReOCl(eg)(phen). To 35.05 mg of (Ph$_4$As)[ReOCl$_2$] (0.048 mmol) in a disposable vial was added 1.5 cm$^3$ of MeOH and 0.5 cm$^3$ of 1,2-ethanediol (Fisher). The resulting blue solution was stirred for 5 min before adding 41 mg of crystalline 1,10-phenanthroline monohydrate (Baker, 0.207 mmol) with vigorous stirring. The solution immediately under vacuum, the red-brown colour faded within 5 min. 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), 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 (s), 851 (s), 829 (w), 781 (w), 740 (w), 722 (w), 653 (w), 609 (w), 492 (w), 430 (w). FABMS (+): $m/z$ 415 (M$-$Cl$^+$).

RESULTS AND DISCUSSION

Slurries of TcO$_3$Cl(AA) (AA = phen, bpy, Me$_2$phen, NO$_2$-phen) in acetone or dichloromethane react with a wide variety of olefins (C$_2$H$_4$R$_2$) to form the corresponding trioxotechnetium(V) diolates, TcOCl(OOCR$_2$OC$_2$O)(AA) [eq. (1)].

\[
\text{Acetone} \quad 22^\circ\text{C} \quad \text{NO}_2 \quad \text{Bpy} \quad \text{Me}_2 \quad \text{Phen} \quad \text{NO}_2 \quad \text{Phen}
\]

The isolated yields of the diolate products, summarized in Table 1, are generally greater than 70%. Variations in the yield depend strongly on the scale of the reaction, since mechanical losses in manipulations are significant. The choice of olefin, however, does not seem to alter the per cent conversion. The one pot reaction involving TcO$_3$Cl(phen) generated in situ has a comparable productivity based on pertechnetate, since the starting material is generally isolated 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. No qualitative differences in the reactivity of TcO$_3$Cl(AA) as a function of AA were noted. The nitrophenanthroline ligand, however, does induce changes in the spectral and solubility properties of the complexes. The complex TcO$_3$Cl(NO$_2$-phen) is produced in nearly quantitative yields due to its extreme insolubility in the reaction mixture. This trioxotechnetium starting material is olive-green.
Table 1. Isolated yields of diolates from Tc mediated oxidation of olefins

<table>
<thead>
<tr>
<th>Olefin</th>
<th>Yield (%)</th>
<th>Scale (mmol)</th>
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<tr>
<td></td>
<td>72</td>
<td>0.212</td>
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<tr>
<td></td>
<td>70</td>
<td>0.217</td>
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<tr>
<td></td>
<td>61</td>
<td>0.169</td>
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<tr>
<td></td>
<td>41</td>
<td>0.090</td>
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<td></td>
<td>42</td>
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<tr>
<td></td>
<td>74</td>
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<td></td>
<td>30</td>
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<tr>
<td></td>
<td>49</td>
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<tr>
<td></td>
<td>39</td>
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<tr>
<td></td>
<td>77</td>
<td>0.127</td>
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<tr>
<td></td>
<td>76</td>
<td>0.095</td>
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</table>

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.

Although perrhenyl chloride has been shown to oxidize olefins with the major product being the corresponding chlorohydrin, no significant conversion was detected from the reaction of chlorotrioxo(1,10-phenanthroline)rhenium(VII) with olefins, even after prolonged refluxing. Conversely, the Re\textsuperscript{V} diolate complex ReOCl(eg)(phen) is converted to ReO\textsubscript{2}Cl(phen) on heating \textit{in vacuo}, whereas the technetium(V) diolates have no such reactivity.

The oxidative cleavage reaction of the osmate (VI) esters of diols has long been assumed to regenerate OsO\textsubscript{4} as the catalytically active species. However, recent evidence suggests that an osmium(VIII) oxyhalide complex may also be involved in some cases. Myers \textit{et al.} noted that the rate of O\textsubscript{2} oxidized, Cu cocatalysed, Os catalysed, diol formation depends directly on the halide:Os ratio up to values of 5:1. The absence of OsO\textsubscript{4} in the distillates of these reactions gives further evidence for halide coordination since the oxyhalides are expected to be significantly less volatile. The technetium system validates this hypothesis being the first example of an isolated oxyhalide with which \textit{cis}-dihydroxylation of olefins has been demonstrated.

The mechanism generally proposed for the metal mediated vicinal dihydroxylation reactions involves a concerted [3+2] cycloaddition [eq. (2)]. Arguing that transition metals are more electropositive than oxygen; Sharpless \textit{et al.} suggest that alkenes, being weak nucleophiles, might be bonded to the metal atom in the first step of these reactions [eq. (3)]. The fact that OsO\textsubscript{4} preferentially reacts with more nucleophilic alkenes further supports this hypothesis. The direct attack at the metal, however, seems unlikely for the trioxotechnetium complexes, which are coordinatively saturated octahedral complexes.

Scheme 1 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 TcOCl₂Cl(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. ethylene), paths (a) and (b) are degenerate, each yielding one of the enantiomers of the asymmetric centre at the technetium atom. Path (c) would yield a complex with mutually cis 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 analysing the technetium(V) diolate complexes. Although oxotechnetium(V) complexes are effectively closed-shell and diamagnetic,13 appreciable position dependent variations in chemical shifts can be induced14 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 analysis is straightforward for a 1,2-disubstituted alkene, e.g. trans-4-octene. The proton NMR spectrum of DL-TcOCl(OC(Pr)CHPrO)Cl(phen) (Fig. 1) clearly shows two resonances for one of the α protons on the phenanthroline ligand at 10.4 and 10.2 ppm with relative intensities of ~ 2:1 indicating a non-statistical mixture of the 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.

The NMR spectra indicate that the oxidation reaction is completely stereospecific since cis and trans alkenes give totally different products. In order to determine the stereochemistry of addition, the octanediolate derivatives were hydrolysed by treating them with concentrated aqueous HCl yielding free diols and TcOCl₃(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 of cis- and trans-4-octene, respectively. The reaction of TcOCl₃(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.

The technetium centred oxidation of olefins and the rhenium centred reduction of diols are conceptually the forward and reverse reactions of the equilibrium shown below in eq. (4).
The direction of the reaction is governed primarily by the oxidation/reduction potentials of the central metals in their +5 and +7 oxidation states. These results are therefore consistent with the usual periodic trends for second and third row transition metals having similar environments in which the third row elements are more easily oxidized and the second row elements are more easily reduced.

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 7 metals. Furthermore, the reactions discussed here give significant new insights into the already well utilized reactions of osmium tetroxide and permanganate.

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