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High oxidation state technetium and rhenium complexes of hydrotris(1-pyrazolyl)borate

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Abstract

The known complex, [(ReO$_3$(HB(pz)$_3$)], where [HB(pz)$_3$]$^-$ is hydrotris(1-pyrazolyl)borate, has been prepared by three new methods: (i) the nitric acid oxidation of [ReOCl$_2$(HB(pz)$_3$)]; (ii) the thermolysis of [ReO(eg)(HB(pz)$_3$)], where eg is ethylene glycolate; (iii) the reaction of [NH$_4$(ReO$_4$)] and [HB(pz)$_3$]$^-$ in acidified methanol. The technetium analogue, [TcO$_3$(HB(pz)$_3$)], has also been synthesized here by two methods; (i) the nitric acid oxidation of [TcOCl$_2$(HB(pz)$_3$)]; (ii) the reaction of [TcO$_4$]$^-$ and [HB(pz)$_3$]$^-$ in acidified ethanol. Both complexes have been characterized by elemental analyses, mass spectrometry, and IR and NMR spectroscopies. The reaction of [TcO$_3$(HB(pz)$_3$)] with ethylene to form [TcO(eg)(HB(pz)$_3$)] is also discussed.

Introduction

Several complexes which incorporate the Re^{VII}O$_3$$^+$ moiety and contain a tridentate ligand (1,4,7-triazacyclononane (TACN) [1,2], 1,4,7-trimethyltriazacyclononane (Me$_3$TACN) [2], ((η^5-C$_5$H$_5$)Co{P(OR)$_2$(=O)}$_3$) [3], 1,4,7-trithiacyclononane [4] and hydrotris(1-pyrazolyl)borate [HB(pz)$_3$]$^-$ [5]) have recently been reported. Herrmann and coworkers have reported the X-ray crystal structure of [ReO$_3$(HB(pz)$_3$)] [5]. Three new preparations of the latter complex are reported here. The new complex, [TcO$_3$(HB(pz)$_3$)], has also been synthesized and is of interest because trioxotechnetium(VII) complexes are known to oxidize olefins to diolates [6a,b]. Indeed, [TcO$_3$(HB(pz)$_3$)] reacts with ethylene to form [TcO(eg)(HB(pz)$_3$)].

Experimental

Caution: technetium-99 is a weak β^--emitter ($E = 292$ keV, $t_{1/2} = 2.12 \times 10^5$ years). All experiments have been done in laboratories approved for a low-level radioactive materials following precautions detailed elsewhere [7].

Ammonium pertechnetate was obtained as a gift from Du Pont/Biomedical Products. Ammonium perrhenate was obtained from Johnson Matthey Alfa Products. Solvents and reagents were used as received unless otherwise indicated. Ethylene glycol was obtained from Fisher Chemical Company. Methylene chloride was distilled over calcium hydride. Tetrahydrofuran was distilled over sodium metal and benzophenone. Pentane was washed with sulfuric acid/nitric acid and water and was distilled over calcium chloride. Sodium hydrotris(1-pyrazolyl)borate was prepared by the method of Trofimenko [8]. [ReOCl$_2$(HB(pz)$_3$)] and [TcOCl$_2$(HB(pz)$_3$)] were synthesized according to published procedures [9]. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA. Fast atom bombardment mass spectra (FAB-MS) were recorded with a MAT 731 mass spectrometer equipped with an Ion Tech B11N FAB gun that produced a beam of 6–8 keV xenon neutrals. The samples were dissolved in a *p*-nitrobenzyl alcohol matrix. IR spectra were recorded on a Mattson Cygnus 100 FT spectrophotometer. UV–Vis spectra were measured on a Hewlett Packard 8451A photodiode array spectrophotometer. NMR spectra were run on either a Varian XL-300 MHz instrument or a Gemini 300 MHz instrument.

Preparation of hydrotris(1-pyrazolyl)borato(ethylene glycolate)oxorhenium(V)

To [ReOCl$_2$(HB(pz)$_3$)] (45 mg, 0.093 mmol) was added a solution of NaOC$_2$H$_5$ (17 mg, 0.25 mmol) dissolved in 4.5 ml of methanol and 0.4 ml of ethylene glycol. The sky blue solution was refluxed for 2 h during which time it became deeper blue. The solution

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was concentrated to about 1 ml under reduced pressure and the blue complex was extracted into CH_2Cl_2. The CH_2Cl_2 layer was evaporated to dryness under reduced pressure and the resulting blue residue was dried *in vacuo*. Yield of [ReO(eg)(HB(pz)$_3$)], 34 mg (77%). The compound was recrystallized from acetone/water, m.p. 215 °C (dec.).

Anal. Calc. for $C_{11}H_{14}BN_6O_3Re$: C, 27.79; H, 2.95; N, 17.68. Found: C, 27.77; H, 2.94; N, 17.59%. FAB-MS(+): *m/z* (% relative abundance): 476/474 (43.9/26.3) [^{187}ReO(eg)(HB(pz)$_3$)]$^+$/[^{185}ReO(eg)(HB(pz)$_3$)]$^+$; 432/430 (3.9/2.3) [^{187}ReO$_2$(HB(pz)$_3$)]$^+$/^{185}ReO$_2$(HB(pz)$_3$)]$^+$; 416/414 (6.3/3.8) [^{187}ReO(HB(pz)$_3$]$^+$/[^{185}ReO(HB(pz)$_3$)]$^+$; 409/407(18.3/11) [^{187}ReO(eg)(HB(pz)$_2$)]$^+$/[^{185}ReO(eg)(HB)(pz)$_2$)]$^+$; 381/379 (3.9/2.3) [^{187}ReO$_3$(HB(pz)$_2$)]$^+$/[^{185}ReO$_3$(HB(pz)$_2$)]$^+$; 365/363 (3.2/1.9) [^{187}ReO$_2$(HB(pz)$_2$)]$^+$/[^{185}ReO$_2$(HB(pz)$_2$)]$^+$. IR (KBr): $\nu = 3127$w, 3082w, 2927w, 2832w, 2508w, 2484w, 1504m, 1394vs, 1387m, 1312s, 1207s, 1113m, 1050vs, 1020s, 991w, 964vs, 903m, 758s, 713s, 651s, 620s, 543m cm^{-1}. UV–Vis (CH$_3$OH) (λ_{max} (nm) (ϵ, 1 M^{-1} cm^{-1})): 214 (14 300); 232 (12 260); 580 (75); 710 (sh). ^{1}H NMR ((CD$_3$)$_2$CO): $\delta = 8.15$ (d, 2H); 7.92 (d, 2H); 7.63 (d, 1H); 7.55 (d, 1H); 6.52 (t, 2H); 6.00 (t, 1H); 5.08 (m, 2H); 4.75 (m, 2H).

Preparation of hydrotris(1-pyrazolyl)borato-trioxorhenium(VII)

Method 1

To [ReOCl$_2$(HB(pz)$_3$)] (76 mg, 0.16 mmol) were added 10 ml of dichloromethane and 0.25 ml of concentrated nitric acid. The resulting blue solution was refluxed for 4 h during which time it became colorless. Subsequently, the solution was evaporated to dryness under vacuum and the residue was dissolved in tetrahydrofuran; a small amount of white solid, which did not dissolve, was shown to be [ReO$_4$]$^-$, by IR and UV–Vis spectroscopies. Vapor diffusion of n-pentane into the tetrahydrofuran solution at room temperature yielded clear, colorless crystals within 24 h. The crystals were filtered onto a fritted glass funnel and dried *in vacuo*. Yield of [ReO$_3$(HB(pz)$_3$)], 24 mg (34%), m.p. > 260 °C.

Anal. Calc. for $C_9H_{10}BN_6O_3Re$: C, 24.17; H, 2.25; N, 18.8. Found: C, 24.50; H, 2.18; N, 18.40%. FAB-MS(+): *m/z* (% relative abundance): 449/447 (14/8.4) [^{187}ReO$_3$(HB(pz)$_3$) + H]$^+$/[^{185}ReO$_3$(HB(pz)$_3$) + H]$^+$; 380/378 (4.4/2.6) [^{187}ReO$_3$(HB(pz)$_2$) − H]$^+$/[^{185}ReO$_3$(HB(pz)$_2$) − H]$^+$; 365/363 (3.9/2.3) [^{187}ReO$_2$(HB(pz)$_2$)]$^+$/[^{185}ReO$_2$(HB(pz)$_2$)]$^+$. IR (KBr): $\nu = 3127$w, 3114w, 2529(ν BH)w, 1500m, 1405m, 1389m, 1313m, 1212s, 1120m, 1050s, 992w, 943(ν ReO)m, 924(ν ReO)s, 909(ν ReO)s, 892(ν ReO)m, 879m, 857w, 795m, 761m, 757m, 710m, 657m, 611m cm^{-1}. UV–vis (CH$_2$Cl$_2$) (λ_{max} (nm) (ϵ, 1 M^{-1} cm^{-1})): 234 (6400); 270(sh). ^{1}H NMR (CD$_2$Cl$_2$): $\delta = 8.26$ (d, 3H); 7.77 (d, 3H); 6.39 (t, 3H).

Method 2

To a 5 ml round bottom flask was added [ReO(eg)(HB(pz)$_3$)] (12 mg, 0.03 mmol). The flask was heated in an oil bath to 160 °C *in vacuo* (0.5 mm Hg) for 3 h during which time the blue solid became grey. The grey powder (3.5 mg) was collected; m.p. > 260 °C.

FAB-MS(+): *m/z* (% relative abundance): 449/447 (12.4/7.4) [^{187}ReO$_3$(HB(pz)$_3$) + H]$^+$/[^{185}ReO$_3$(HB(pz)$_3$) + H]$^+$; 409/407 (8.9/5.3) [^{187}ReO(eg)(HB(pz)$_2$)]$^+$/[^{185}ReO(eg)(HB(pz)$_3$)]$^+$; 381/379 (7.5/4.5) [^{187}ReO$_3$(HB(pz)$_2$)]$^+$/[^{185}ReO$_3$(HB(pz)$_2$)]$^+$; 365/363 (5/2.9) [^{187}ReO$_2$(HB(pz)$_2$)]$^+$/[^{185}ReO$_2$(HB(pz)$_2$)]$^+$. IR (KBr): $\nu = 3126$w, 2963w, 2527w, 1501m, 1405m, 1388m, 1313m, 1262m, 1222s, 1120s, 1055vs, 969w, 943s, 923s, 909vs, 893m, 857w, 795s, 780s, 762s, 710m, 657w, 611w cm^{-1}.

Method 3

Ammonium perrhenate (40 mg, 0.15 mmol) was dissolved in 2 ml of methanol, 0.25 ml of acetonitrile and 0.25 ml of water with gentle heating. The solution of [NH$_4$(ReO$_4$)] was added to Na(HB(pz)$_3$) (66 mg, 0.28 mmol), which was dissolved in 0.5 ml of methanol. The resulting clear, faint blue solution became cloudy and yellow upon the addition of concentrated sulfuric acid (0.10 ml). The solution was filtered and a white solid was collected. The yellow filtrate was stored at −20 °C for 14 days and was subsequently evaporated to dryness under reduced pressure. The resulting yellow–brown residue was dissolved in tetrahydrofuran. Vapor diffusion at room temperature of n-pentane into the solution yielded colorless crystals within 24 h. The crystals were filtered onto a fritted glass funnel, washed with 5 ml of acetone and air dried. Yield of [ReO$_3$(HB(pz)$_3$)], 5 mg (7.6%).

The IR spectrum of the crystals was identical to that obtained for the solid prepared by method 1 ([ReO$_3$(HB(pz)$_3$)]).

Preparation of hydrotris(1-pyrazolyl)borato-trioxotechnetium(VII)

Method 1

To [TcOCl$_2$(HB(pz)$_3$)] (48 mg, 0.12 mmol) were added 4 ml of dichloromethane and 0.20 ml of concentrated nitric acid. The green solution was refluxed for 2 h, during which time it became pale yellow. Subsequently, the reaction mixture was evaporated to dryness under vacuum, and the resulting residue was dissolved in tetrahydrofuran. Vapor diffusion of n-pentane into the tetrahydrofuran solution at room temperature yielded pale yellow crystals within 24 h. The yellow solid was filtered onto a fritted glass funnel and dried *in vacuo*. Yield of the yellow crystals $[TcO_3(HB(pz)_3)]$, 9.5 mg (22%), m.p. > 260 °C (at 140 °C, sample turns brown).

Anal. Calc. for $C_9H_{10}BN_6O_3Tc$: C, 30.03; H, 2.80; N, 23.34. Found: C, 29.87: H, 2.85; N, 23.27%. FAB-MS(+): *m/z* (% relative abundance): 227 (19) $[TcO_2(HB(pz)_2)]^+$; 361 (6) $[TcO_3(HB(pz)_3)+H]^+$; 344 (11) $[TcO_2(HB(pz)_3)]^+$; 328 (24) $[TcO(HB(pz)_3)]^+$; 672 (3.5) $[Tc_2O_3(HB(pz)_3)_2]^+$. IR (KBr): ν = 3116w, 2518(ν BH)w, 1498m, 1402m, 1387s, 1313s, 1222s, 1118m, 1072w, 1053s, 989w, 922(ν TcO)w, 898(ν TcO)vs, 885(ν TcO)vs, 852m, 794m, 777m, 759m, 711m, 658m, 612m cm^{-1}. UV–Vis (CH_2Cl_2) (λ_{max} (nm) (ϵ, l M^{-1} cm^{-1})): 232 (4 400); 256 (5 300); 348 (sh). ^1H NMR (CD_2Cl_2): δ = 8.197 (d, 3H); 7.706 (d, 3H); 6.348 (t, 3H). ^{99}Tc NMR (CD_2Cl_2): δ = 196 ppm versus TcO_4^-.

Method 2 [10]

To $Na(HB(pz)_3)$ (67 mg, 0.28 mmol) and $[NH_4TcO_4]$ (0.1 mmol) were added 5 ml of ethanol. On addition of 0.1 ml of concentrated sulfuric acid, a white solid precipitated and was filtered. The yellow filtrate was stored at −20 °C for two days during which time a yellow solid precipitated. The solid filtered onto a fritted glass funnel, washed with 3 ml of cold water and dried *in vacuo*. Yield 16 mg (44%).

The IR, NMR and mass spectra of the solid are identical to those of the product obtained from method 1.

Preparation of hydrotris(1-pyrazolyl)borato(ethylene glycolate)oxotechnetium(V)

To $[TcO_3(HB(pz)_3)]$ (6.25 mg, 0.017 mmol) were added 2 ml of methylene chloride to form a yellow solution. Ethylene was bubbled through the solution which became blue within 1 min. After 1 h, the solvent had evaporated and a bluish residue was collected, 3.46 mg (51%), m.p. 207 °C (dec.).

FAB-MS(+): *m/z* (% relative abundance): 261 (30) $[TcO(HB(pz)_2)]^+$; 277 (63) $[TcO_2(HB(pz)_2)]^+$; 328 (100) $[TcO(HB(pz)_3)]^+$; 344 (23) $[TcO_2(HB(pz)_3)]^+$; 361 (23) $[TcO_3(HB(pz)_3)+H]^+$; 389 (27) $[TcO(eg)(HB(pz)_3)+H]^+$. IR (KBr): ν = 3114m, 2917s, 2849s, 2518(ν BH)m, 1506s, 1385vs, 1336s, 1314s, 1240m, 1216s, 1121vs, 1054vs, 1021s, 969m, 959m, 899s, 767m, 714m, 653m, 614s cm^{-1}. UV–Vis (CH_3OH) (λ_{max} (nm) (ϵ, l, M^{-1} cm^{-1})]: 212 (6060); 252 (5060); 282 (sh); 590 (sh); 674 (24). ^1H NMR (CD_3OD): δ = 8.07 (s, 2H); 7.98 (s, 2H); 7.69 (s, 1H); 7.43 (s, 1H); 6.55 (s, 2H); 5.99 (s, 1H); 5.75 (m, 2H); 5.03 (m, 2H).

Results and discussion

$M^{VII}O_3^+$ (M = Re or Tc) complexes of tridentate, facially coordinating ligands have been reported [1–5]. In particular, several rhenium and technetium compounds of the monoanionic, tridentate ligand, hydrotris(1-pyrazolyl)borate, $[HB(pz)_3]^-$ have been characterized. The metal is in the 5+ oxidation state in many of these complexes, as in $[ReOCl_2(HB(pz)_3)]$ and $(TcOCl_2(HB(pz)_3)]$, but Herrmann and co-workers [5] have recently prepared a rhenium(VII) complex. $[ReO_3(HB(pz)_3)]$, by the reaction of $Na(HB(pz)_3)$ and $[Re_2O_7]$ in frozen tetrahydrofuran. The yield of $[ReO_3(HB(pz)_3)]$ is 78% based on $[Re_2O_7]$ (but 39% based on rhenium) by this method.

The same rhenium(VII) complex has been synthesized here by the nitric acid oxidation of $[ReOCl_2(HB(pz)_3)]$; Fig. 1 summarizes the reactions performed to prepare $[ReO_3(HB(pz)_3)]$. This method has previously been used to oxidized $[ReOCl_2(TACN)]$ and $[ReOCl_2(Me_3TACN)]$ to $[ReO_3(TACN)]$ and $[ReO_3(Me_3TACN)]$, respectively [2]. The method is facile and satisfactory yields (34% overall yield and 34% yield based on rhenium) of $[ReO_3(HB(pz)_3)]$ have been obtained. The yield loss is due partly to the formation of $[ReO_4]^-$, but this method produces $[ReO_3(HB(pz)_3)]$ in comparable yield (based on rhenium) to the one described above [5]. The mass spectrum of the product shows a peak that corresponds to $([ReO_3(HB(pz)_3)]+H)^+$. The ^1H NMR spectrum of the product shows that the three pyrazolyl rings of the ligand are equivalent in solution. The IR spectrum of $[ReO_3(HB(pz)_3)]$ is identical to the reported one [5]. It is interesting to note that Herrmann and co-workers [11] have recently performed the opposite reaction, and have synthesized $[ReOCl_2(HB(pz)_3)]$ from $[ReO_3(HB(pz)_3)]$ in the presence of triphenylphosphine and excess $(CH_3)_3SiCl$.

The complex, $[ReO_3Cl(phen)]$, when phen is 1,10-phenanthroline, can be synthesized by the thermolysis

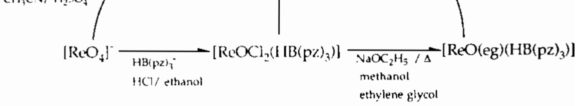


Fig. 1. Schematic representation of the reactions performed to produce $[ReO_3(HB(pz)_3)]$.

of [ReOCl(phen)(eg)] from which ethylene is lost [6a]. [ReO(eg)(HB(pz)$_3$)] has been synthesized here in order to attempt a similar thermolysis reaction. The blue complex is made in high yield from [ReOCl$_2$(HB(pz)$_3$)] and ethylene glycol, which is deprotonated by sodium ethoxide. The ^{1}H NMR spectrum shows the equivalence of two pyrazolyl rings and the uniqueness of the third, whose coordinated nitrogen is *trans* to the oxo functionality. The ethylene glycolate protons give rise to two multiplets; each integrates to two protons. The mass spectrum shows high intensity parent peaks and a readily assignable fragmentation pattern.

The thermolysis of [ReO(eg)(HB(pz)$_3$)] at 160 °C *in vacuo* for 3 h also yields [ReO$_3$(HB(pz)$_3$)]. The thermolysis is not complete; the peak in the mass spectrum at 409 *m/z* represents [^{187}ReO(eg)-(HB(pz)$_2$)]$^+$. Unreacted [ReO(eg)(HB(pz)$_3$)] is also detected by weak peaks in the IR spectrum at 2963 and 964 cm^{-1}, which correspond to the aliphatic C$-$H absorption of the coordinated ethylene glycolate and the Re$-$O stretch, respectively. However, the strong, characteristic νReO bands in the IR spectrum at 943, 923, 909 and 893 cm^{-1} and the strong peak at 449 *m/z* in the mass spectrum, which represents ([ReO$_3$(HB(pz)$_3$)]+H) and is not observed in the spectrum of pure [ReO(eg)(HB(pz)$_3$)], indicate the presence of [ReO$_3$(HB(pz)$_3$)] in the product mixture. The incomplete thermolysis is most likely due to the non-uniformity of heat transfer to a solid. The loss of ethylene and the oxidation of rhenium(V) to rhenium(VII) is thermodynamically favorable and is a manifestation of the third row transition metals' propensity to be good reducing agents as compared to the first and second row transition metals.

The reaction of [NH$_4$(ReO$_4$)] and [Na(HB(pz)$_3$)] in methanol/water/acetonitrile/sulfuric acid produces [ReO$_3$(HB(pz)$_3$)] in low yield. However, the reaction of [MO$_4$]$^-$, where M is Tc or Re, and a tridentate, anionic ligand (L) in acidified solutions seems to be a general method to produce [LM$^{\mathrm{VII}}$O$_3$] complexes. The compounds, [((η^5-C$_5$H$_5$)Co{P(OCH$_3$)$_2$-(=O)}$_3$)MO$_3$], have been prepared in acidified solutions of perrhenate or pertechnetate [3]. Pearlstein [10] first synthesized [TcO$_3$(HB(pz)$_3$)], in good yield, from [TcO$_4$]$^-$ and [Na(HB(pz)$_3$)] in ethanol/sulfuric acid (0.1 ml H$_2$SO$_4$ in 5 ml of ethanol).

The new compound, [TcO$_3$(HB(pz)$_3$)], has also been synthesized by the nitric acid oxidation of [TcOCl$_2$(HB(pz)$_3$)]. Figure 2 summarizes the reactions performed to generate [TcO$_3$(HB(pz)$_3$)]. The pale yellow complex gives an IR spectrum similar to that of its rhenium analogue, but the characteristic νTc–O bands appear at 922, 898 and 885 cm^{-1} as compared to νRe–O at 943, 924, 909 and 892 cm^{-1}; [TcO$_3$(HB(pz)$_3$)] has weaker metal–oxygen bonds than [ReO$_3$(HB(pz)$_3$)]. The mass spectrum shows peaks at 361 *m/z* ([TcO$_3$(HB(pz)$_3$)]+H)$^+$, 344 ([TcO$_2$(HB(pz)$_3$])$^+$, 328 ([TcO(HB(pz)$_3$)])$^+$, and a low intensity peak at 672 ([Tc$_2$O$_3$(HB(pz)$_3$)$_2$])$^+$. The ^{1}H NMR spectrum shows that the C_{3v} molecule has three equivalent pyrazolyl rings. The ^{99}Tc NMR shows a resonance at +196 ppm versus [TcO$_4$]$^-$, which indicates that [TcO$_3$(HB(pz)$_3$)] falls within the established 'Tc(VII) window', based on oxidation state versus ^{99}Tc chemical shift correlations [12]. Confirming that the oxidation state of technetium is VII in [TcO$_3$(HB(pz)$_3$)] shows that the three coordinated oxygen ligands must be doubly bonded oxo ligands, rather than hydroxo or aquo ligands.

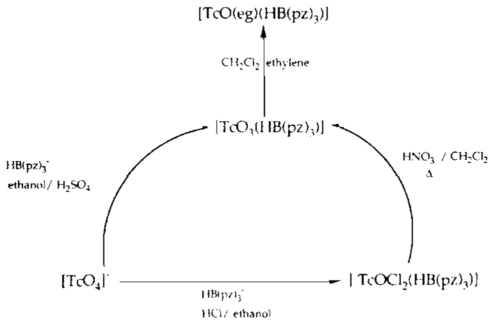
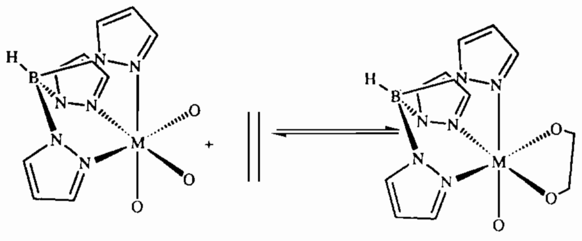


Fig. 2. Schematic representation of the reactions performed to produce [TcO$_3$(HB(pz)$_3$)].

Technetium(VII) trioxo compounds, [TcO$_3$Cl(AA)] [6a] (where AA is phen, bpy or a substituted derivate of phen) and [CH$_3$TcO$_3$] [6b], add olefins to form oxotechnetium(V) diolate complexes. The reaction of [TcO$_3$(HB(pz)$_3$)] with ethylene yields [TcO(eg)(HB(pz)$_3$)]. The mechanism of this reaction is not known, but it is improbable that the ethylene binds to the technetium, because [TcO$_3$(HB(pz)$_3$)] is a coordinatively saturated molecule. The mechanism for the formation of [TcO(eg)(HB(pz)$_3$)] most likely involves direct attack of ethylene to the oxo moieties of [TcO$_3$(HB(pz)$_3$)]. The complex, [TcO(eg)(HB(pz)$_3$)], has been synthesized previously from [TcO(eg)$_2$]$^-$ and [HB(pz)$_3$]$^-$ in acidified solutions of methanol and ethylene glycol [13]. The characterization of [TcO(eg)(HB(pz)$_3$)] is very similar to that of [ReO(eg)(HB(pz)$_3$)]. The ^{1}H NMR spectrum of [TcO(eg)(HB(pz)$_3$)] indicates that two pyrazolyl rings of the [HB(pz)$_3$]$^-$ ligand are equivalent in solution and the third ring is unique; the nitrogen of the unique ring is coordinated *trans* to the oxo functionality. The ethylene glycolate protons show two multiplets and each corresponds to two protons. The mass spectrum shows a parent peak plus one proton at 398 *m/z*, and the fragmentation pattern is readily assignable.

The reaction of $[TcO_3(HB(pz)_3)]$ (but not $[ReO_3(HB(pz)_3)]$ with ethylene is a consequence of the ease of reducing technetium as compared to rhenium. This situation is illustrated in eqn. (1).



(1)

When M is Tc, the forward equation is favored. When M is Re, the reverse equation is favored.

When M is Re, the left hand side of the equation is favored, as shown by the thermolysis of $[ReO(eg)(HB(pz)_3)]$ to produce $[ReO_3(HB(pz)_3)]$ and ethylene. When M is Tc, the right hand side of the equation is favored, producing $[TcO(eg)(HB(pz)_3)]$. The new compound, $[TcO_3(HB(pz)_3)]$, is a member of the series of technetium trioxo complexes which perform the dihydroxylation of olefins. Conceivable, a new series of Tc(V) complexes of $[HB(pz)_3]^-$, based on $[TcO(OAO)HB(pz)_3)]$, where A is an alkene and OAO is its corresponding diolate, could be synthesized from $[TcO_3(HB(pz)_3)]$.

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