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The Synthesis and Characterization of Hydrotris(1-pyrazolyl)borate Complexes of Technetium(III) and Rhenium(V) and (III)

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The new Re(V) oxo species, $ReOCl_2HB(pyz)_3$ (where $HB(pyz)^{-1}$ = hydrotris(1-pyrazolyl)borate) has been prepared and characterized by elemental analysis, optical, IR, and ^1H NMR spectroscopy and conductivity measurements. The reactions of this complex and its Tc(V) analog with triphenylphosphine and the synthesis and characterization of the new Re(III) and Tc(III) complexes. $MCl_2LHb(pyz)_3$ (M = Re, L = Ph_3P; M = Tc, L = Ph_3P, Ph_3PO, and Py), are described.

Introduction

One common way of preparing monomeric complexes of Re(III) is to react a Re(V) oxo species with a reducing ligand capable of forming an oxide (*e.g.* triphenylphosphine) [1]. Although a large number of Tc(III) complexes have been prepared in recent years [2], none have been prepared *via* the oxygen abstraction/reduction reaction of an isolated Tc(V) oxo species. We now report the synthesis and characterization of several new Tc(III) complexes of the type $TcCl_2LHB(pyz)_3$ (L = Ph_3PO, Ph_3P, Py). The first two of these complexes were prepared *via* the known Tc(V) oxo species, $TcOCl_2HB(pyz)_3$ [3, 4] while the pyridine complex was prepared starting from $TcCl_2(Ph_3PO)HB(pyz)_3$. Also, the new Re(V) species, $ReOCl_2Hb(pyz)_3$ has been prepared and its chemistry compared to its Tc analog.

Experimental

Technetium as $NH_4{}^{99}TcO_4$ was obtained as a gift from New England Nuclear (NEN), Billerica, MA. All manipulations were carried out in laboratories approved for low level radioactivity (^{99}Tc is a weak β-emitter with a half life of 2.12×10^5 years and particle energy of 0.292 MeV). All precautions followed have been detailed elsewhere [5, 6]. Rhenium, as $NaReO_4$, was obtained from Cleveland Refractory Metals, Solon, OH.

Infrared spectra were recorded in the range 4000–300 cm^{-1} on a Perkin-Elmer PE180 grating infrared spectrophotometer as KBr pellets. Optical spectra, in solution, were measured with a Cary 17 spectrophotometer. Conductivity measurements were performed in acetonitrile using a Yellow Springs model 3403 conductivity cell and a Beckman RC-16C conductivity bridge. Magnetic susceptibility measurements were made on methylene chloride solutions *via* the Evans NMR method [7] using a Varian T-60 spectrometer. ^1H NMR measurements were also obtained with the T-60 using acetone-d_6 as solvent and TMS as internal calibrant. Melting points were obtained with a Mel-Temp apparatus and are uncorrected. Field desorption mass spectra were measured with a Varian Mat 731 instrument described elsewhere [8]. Prior to use, distilled water was passed through a Barnstead Ultrapure D8902 cartridge, followed by redistillation in a Corning AG-1 water still. Potassium hydrotris(1-pyrazolyl)borate ($KHB(pyz)_3$) was prepared using a literature method [9] and all other chemicals were used without further purification. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA, Schwarzkopf Microanalytical Laboratory, Woodside, N.Y., and Galbraith Laboratories, Inc., Knoxville, TN.

Preparation of Oxodichloro[hydrotris(1-pyrazolyl)borato] technetium(V) ($TcOCl_2Hb(pyz)_3$)

To a slurry of 0.50 g of $KHB(pyz)_3$ (2.0 mmol), ethanol (0.15 ml) and 12 *N* HCl (2.0 ml), 1.0 ml of 0.399 *M* NH_4TcO_4 (0.40 mmol) was added. The mixture was refluxed for 30 min. The deep pea green

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reaction mixture was cooled with an ice bath for 20 min and the green product collected. This material was washed with water (5.0 ml) and ethanol (5.0 ml) and recrystallized by slow evaporation of a methylene chloride/toluene solution (1:1 v/v) yielding green crystals of $TcOCl_2HB(pyz)_3$, 0.10 g, 0.25 mmol, 63% based on Tc; m.p. ~220 °C dec. *Anal.* Calcd for $C_9H_{10}BCl_2N_6OTc$: C, 27.29; H, 2.53; N, 21.07; Cl, 17.77. Found: C, 27.04; H, 2.55; N, 21.03; Cl, 17.70. The optical, IR and ^1H NMR spectra of this material are in good agreement with literature values [3,4].

Preparation of Oxodichloro[hydrotris(1-pyrazolyl)-borato]rhenium(V) ($ReOCl_2HB(pyz)_3$)

This blue, crystalline compound was prepared from $NaReO_4$ in 40% yield similarly to $TcOCl_2HB(pyz)_3$ by refluxing the reaction mixture for 2 h, m.p. ~250 °C dec. *Anal.* Calcd for $C_9H_{10}BCl_2N_6ORe$: C, 22.23; H, 2.08; N, 17.29; Cl, 14.58. Found: C, 22.43; H, 2.08; N, 17.42; Cl, 14.79. Optical Spectrum (acetonitrile): 685 nm (ϵ = 1.3 × 10^2 l mol^{-1} cm^{-1}), 259 (1.3 × 10^4). IR (KBr): 3125(m), 2515(m), 1500(s), 1440(w), 1405(vs), 1385(s), 1305(vs), 1210(vs), 1185(s), 1175(s), 1115(vs), 1070(s), 1045(vs), 990(sh), 975(vs), 925(w), 915(w), 890(w), 860(w), 815(w), 785(s), 765(vs), 715(m), 705(s), 660(w), 640(s), 605(s), 335(s), 315(s).

Conductivity (acetonitrile, 10^{-3} *M*): Λ_M = 2.4 ohm^{-1} cm^2 mol^{-1}.

^1H NMR: 8.3(d), 7.7(d), 7.4(d), 6.7(t), 6.1(t) (integration ratio 4:1:1:2:1).

Preparation of Dichlorotriphenylphosphine [hydrotris(1-pyrazolyl)borato] technetium(III) ($TcCl_2(Ph_3P)HB(pyz)_3$)

A slurry of $TcOCl_2HB(pyz)_3$ (0.19 g, 0.45 mmol) and triphenylphosphine (0.61 g, 2.3 mmol) in toluene (30 ml) was refluxed for 30 min. The resulting dark orange solution was cooled to room temperature and filtered. Ether (250 ml) and hexane (100 ml) were added to the filtrate which was then chilled (−15 °C) for several days. The resulting dark yellow solid was recrystallized from an acetone/hexane/ether (1:1:5 v/v) mixture at −15 °C yielding dark yellow crystals which were washed with isopropanol (3 × 5 ml) and dried *in vacuo*. Yield of $TcCl_2(Ph_3P)Hb(pyz)$, 0.21 g, 0.33 mmol, 73% based on Tc; m.p. ~150 °C dec. *Anal.* Calcd for $C_{27}H_{25}BCl_2N_6PTc$: C, 50.25; H, 3.91; N, 13.03; Cl, 10.99; P, 4.80. Found: C, 50.29; H, 4.05; N, 12.93; Cl, 11.18; P, 4.82. Optical spectrum (acetonitrile): 425 (1.5 × 10^3), 360(sh), 315(sh), 275(1.1 × 10^4). IR (KBr): 3120(w), 3050(w), 2505(sh), 2490(m), 1495(s), 1480(s), 1430(vs), 1400(vs), 1385(s), 1315(s), 1295(s), 1205(vs), 1185(s), 1155(w), 1115(vs), 1090(s), 1070(s), 1045(vs), 995(m), 980(s), 915(w), 875(m), 845(w), 810(m), 785(s), 760(vs), 745(vs), 735(s), 720(m), 705(vs), 690(vs), 650(m), 610(s), 525(vs), 505(s), 490(s), 450(m), 425(m), 415(m), 325(s), 310(s).

Conductivity (acetonitrile, 10^{-3} M): Λ_M = 3.2 ohm^{-1} cm^2 mol^{-1}.

Magnetic moment: μ_{eff} (308 K) = 2.9 B.M. (+) FDMS m/z 644 (calcd for $C_{27}H_{25}BCl_2N_6PTc$ = 644).

Preparation of Dichlorotriphenylphosphine[hydrotris-(1-pyrazolyl)borato]Rhenium(III) ($ReCl_2(Ph_3P)HB-(pyz)_3$)

Pale coral red crystals of this complex were prepared in 67% yield similarly to $TcCl_2(Ph_3P)HB(pyz)_3$ by refluxing a mixture of $ReOCl_2HB(pyz)_3$ (0.16 g, 0.33 mol) and triphenylphosphine (1.01 g, 3.9 mmol) in toluene. The analytical sample was dried for 12 h at 65 °C *in vacuo*, m.p. ~215 °C. *Anal.* Calcd for $C_{27}H_{25}BCl_2N_6PRe$: C, 44.27; H, 3.45; N, 11.48; Cl, 9.68; P, 4.23. Found: C, 44.40; H, 3.54; N, 11.37; Cl, 9.85; P, 4.39. Optical spectrum (acetonitrile): 360(sh), 272(1.6 × 10^4). IR (KBr): similar to $TcCl_2(Ph_3P)HB(pyz)_3$. Conductivity (acetonitrile, 10^{-3} *M*): Λ_M = 1.7 ohm^{-1} cm^2 mol^{-1}. Magnetic moment: μ_{eff} (308 K) = 2.1 B.M.

Preparation of Dichlorotriphenylphosphineoxide-[hydrotris(1-pyrazolyl)borato] technetium(III) ($TcCl_2(Ph_3PO)HB(pyz)_3$)

To a solution of $TcOCl_2HB(pyz)_3$ (0.15 g, 0.38 mmol) in methylene chloride (10 ml), triphenylphosphine (0.14 g, 0.54 mmol) in methylene chloride (5.0 ml) was added dropwise. The yellow solution was stirred for 5 min and its volume halved *in vacuo*. Ether (150 ml) was added precipitating a pale orange-yellow crystalline solid. This material was collected, washed with ether (15 ml) and dried *in vacuo*. Yield of $TcCl_2Ph_3POHB(pyz)_3$, 0.22 g, 0.33 mmol, 87% based on Tc; m.p. ~180 °C dec. *Anal.* calcd for $C_{27}H_{25}BCl_2N_6OPTc$: C, 49.04; H, 3.82; N, 12.71; Cl, 10.72; P, 4.68. Found: C, 49.13; H, 3.85; N, 12.61; Cl, 10.61; P, 4.64. Optical spectrum (acetonitrile): 350(sh), 315(sh), 272(sh), 265(1.7 × 10^4). IR (KBr): 3110(w), 3050(w), 2505(sh), 2490(m), 1585(w), 1495(s), 1485(m), 1435(s), 1395(vs), 1385(s), 1305(s), 1205(vs), 1185(m), 1160(m), 1140(vs), 1115(vs), 1080(s), 1070(s), 1045(vs), 1025(m), 990(m), 980(s), 850(w), 810(w), 785(s), 770(s), 745(s), 720(vs), 705(s), 690(s), 660(m), 645(m), 610(m), 535(vs), 515(sh), 455(w), 440(w), 410(w), 365(w), 330(m), 310(m). Conductivity (acetonitrile, 10^{-3} *M*): Λ_M = 1.9 ohm^{-1} cm^2 mol^{-1}. Magnetic moment: μ_{eff} (308 K) = 3.0 B.M. (+)FDMS m/z 661 (calcd for $C_{27}H_{25}BCl_2N_6OPTc$ = 661).

Preparation of Dichloropyridine[hydrotris(1-pyrazolyl)borato] technetium(III) ($TcCl_2(Py)HB(pyz)_3$)

A solution of $TcCl_2(Ph_3PO)HB(pyz)_3$ (0.18 g, 0.27 mmol) in acetone (20 ml) and pyridine (5.0 ml) was refluxed for 2 h. Solvent was removed *in vacuo* until the volume of the reaction mixture was ~10 ml. Ether (40 ml) was added and the yellow solution was chilled for 12 h at –15 °C. The resulting red-brown crystals were collected, washed with ethanol (15 ml) and dried *in vacuo*. Yield of $TcCl_2(Py)HB(pyz)_3$ 0.11 g, 0.24 mmol, 89% based on Tc; m.p. ~255 °C dec. *Anal.* Calcd for $C_{14}H_{15}BCl_2N_7Tc$: C, 36.39; H, 3.28; N, 21.22; Cl, 15.34. Found: C, 36.40; H, 3.30; N, 21.15; Cl, 15.31. Optical spectrum (acetonitrile): 365(sh), 315(sh), 275(1.7×10^4). IR (KBr): 3120(m), 3105(m), 2510(m), 1605(s), 1495(s), 1485(m), 1445(s), 1425(m), 1395(vs), 1385(s), 1305(vs), 1205(vs), 1185(s), 1155(m), 1115(vs), 1095(m), 1070(s), 1040(vs), 1015(m), 985(s), 895(m), 810(m), 795(s), 775(vs), 760(vs), 710(s), 695(s), 665(s), 655(s), 645(sh), 615(sh), 610(s), 440(m), 370(s), 340(s), 310(s). Conductivity (acetonitrile, 10^{-3} *M*): $\Lambda_M = 1.9$ ohm^{-1} cm^2 mol^{-1}. Magnetic moment: μ_{eff} (308 K) = 2.8 B.M.

Results and Discussion

The new Re(V) oxo species, $ReOCl_2HB(pyz)_3$ has been prepared by refluxing an ethanolic HCl solution of $NaReO_4$ with an excess of the $HB(pyz)_3^{-1}$ ligand, which acts as a reducing agent. The known Tc(V) analog of this species can also be conveniently prepared by this procedure. The optical, IR, and ^1H NMR spectral characteristics of the Re(V) species are very similar to those of its Tc analog [3]. The optical spectrum of $ReOCl_2HB(pyz)_3$ is blue shifted with respect to $TcOCl_2HB(pyz)_3$ (bands at 685 and 259 nm for Re *vs.* 784 and 311 for Tc) resulting in the blue color of the Re complex.

The two complexes exhibit different reactivity with respect to triphenylphosphine. Unlike its Re analog, $TcOCl_2HB(pyz)_3$ reacts with Ph_3P at room temperature in methylene chloride solution to form a Ph_3PO complex of Tc(III), $TcCl_2(Ph_3PO)HB(pyz)_3$. In refluxing toluene solution, in the presence of excess Ph_3P, both the Tc and Re oxo species form the analogous Ph_3P complexes. No reaction was observed when an acetone solution of $TcCl_2(Ph_3PO)HB(pyz)_3$ and excess Ph_3P was stirred for 4 h at room temperature but $TcCl_2(Ph_3P)HB(pyz)_3$ was readily formed by refluxing the reaction mixture for 30 min. By refluxing $TcCl_2(Ph_3PO)HB(pyz)_3$ in an acetone/pyridine solution $TcCl_2(Py)HB(pyz)_3$ can be prepared. All of the Tc(III) and Re(III) complexes have been characterized by elemental analysis, optical and IR spectroscopy, conductivity and magnetic susceptibility. In addition, the Tc(III) Ph_3P and Ph_3PO complexes have been characterized by positive ion field desorption mass spectrometry. In both of these complexes the signals associated with the M^+ species are the only features found in the +FD mass spectra. All of the Tc(III) and Re(III) compounds described here are non-electrolytes in acetonitrile solution and exhibit magnetic moments (2.1 B.M. for $ReCl_2(Ph_3P)HB(pyz)_3$ and between 2.8 and 3.0 B.M. for the Tc(III) complexes) consistent with their formulation as trivalent, six-coordinate Re and Tc complexes [1, 10].

In their infrared spectra both the Tc and Re oxo species have a single peak at ~2500 cm^{-1} due to the B–H stretch. In the $MCl_2LHB(pyz)_3$ (M = Re, L = Ph_3P; M = Tc, L = Ph_3P, Ph_3PO) complexes there is a shoulder on the high energy side of this band. This feature persists in the solution (methylene chloride) spectra of the compounds and can be attributed to the B_{10}/B_{11} isotope effect [9]. The 1140 cm^{-1} band in the IR spectrum of $TcCl_2(Ph_3PO)HB(pyz)_3$ is assigned to the P=O stretch. The ν(P=O) in uncomplexed Ph_3PO occurs at 1193 cm^{-1} and the shift to lower energy upon complex formation is consistent with the ligand bonding through its oxygen atom [11].

The oxidation of phosphines by metal oxo complexes is well established in the literature [12–14]. Meyer *et al.* have shown that the reaction of Ph_3P with the Ru(IV) cation, $[(bpy)_2PyRuO]^{2+}$ (where bpy is 2,2′-bipyridine) in acetonitrile to form the Ru(II) species, $[(bpy)_2PyRu(CH_3CN)]^{2+}$ proceeds *via* an intermediate Ph_3PO complex of Ru(II) [14]. Due to the lability of the Ph_3PO ligand the intermediate complex was not isolated. In the Tc(V)/Tc(III) system discussed here the Tc(III) Ph_3PO complex can be isolated and characterized, but the Ph_3PO ligand can be readily replaced (by Ph_3P or Py). The fact that $ReOCl_2HB(pyz)_3$ reacts with Ph_3P only under more forcing conditions is in keeping with the observation that Re complexes are more difficult to reduce than their Tc analogs [15, 16].

Lastly, it must be noted that not all Tc(V) oxo complexes react with Ph_3P to form Ph_3PO and a reduced Tc species. While $[TcOCl_4]^-$ reacts with Ph_3P in acetonitrile to form an orange crystalline material thought to be $Tc_2Cl_5(Ph_3P)_3$ [17], the bis(ethanedithiolato) complex, $[TcO(edt)_2]^{-1}$ does not react with Ph_3P, even in refluxing acetonitrile [5]. Therefore, the stability of the Tc(V) oxo core with respect to oxygen abstraction is very much a function of the other ligands in the coordination sphere.

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