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Synthesis and Characterization of Rhenium Complexes with the Stabilizing Ligand Tetrakis(pyrazol-1-yl)borate

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The Re(VII) complex $(Bpz_4)ReO_3$ (**1**) has been isolated in the reaction of Re_2O_7 with $KBpz_4$ in THF and characterized. The solid-state structure of this complex has been determined by X-ray crystallography. The complex is monomeric with an approximately octahedral arrangement of ligands around the rhenium and crystallizes in the monoclinic space group $C2/c$, with $a = 21.070(2)$ Å, $b = 14.860(1)$ Å, $c = 11.588(1)$ Å, $\beta = 121.70(1)°$, $V = 3087(4)$ Å^3, $Z = 8$, $R = 0.041$, and $R_w = 0.047$ for 227 variables and 2877 data with $F_o > 2\sigma(F_o)$. The Re(V) complex $(Bpz_4)ReOCl_2$ (**2**) with the same poly(pyrazolyl)borate ligand has also been isolated and characterized. Compound **2** has been synthesized by reacting compound **1** with Me_3SiCl and Ph_3P. For both complexes, the characterization includes laser desorption and electron impact Fourier transform ion cyclotron resonance mass spectrometry.

Introduction

Since Trofimenko synthesized the poly(pyrazolyl)borate ligands, they have been widely used in inorganic and organometallic chemistry.[1] Although a large number of ligands of the form R_nBpz_{4-n} have been prepared, where R = H, alkyl, aryl, and pz (pyrazolyl), the tripodal ligands $HB(3,5\text{-}Me_2pz)_3$ and $HBpz_3$ were the most extensively used in the chemistry of the d and f transition elements.[1–15] For rhenium, several complexes with these ligands have been isolated.[7–15] The Bpz_4 ligand, which usually coordinates in a tridentate fashion, but can also act as a bis-bidentate ligand, has been much less used. For group 7 the only described complexes with this ligand are of the type $(Bpz_4)Mn(CO)_2L$ (L = CO, $P(OMe)_3$, $P(OPh)_3$, PMe_3).[16,17] Our interest in the chemistry of rhenium comes from the potential use of ^{186}Re in nuclear medicine and from the well-known chemical similarities between Re and Tc, which is largely used for the design of ^{99m}Tc radiopharmaceuticals. In this contribution, we report on the synthesis and characterization of the rhenium complexes $(Bpz_4)ReO_3$ and $(Bpz_4)ReOCl_2$. The synthetic methods used were the same as described by Degnan et al.[11] for the analogous compounds with the $HBpz_3$ ligand. The characterization of these complexes included laser desorption (LD) and electron impact (EI) Fourier transform ion cyclotron resonance mass spectrometry (FTICR/MS).[18] This technique has been previously used, in a few instances, for the characterization of coordination and organometallic compounds,[19] in particular of poly(pyrazolyl)borate complexes of thorium and uranium.[20]

Experimental Section

General Procedures. All reactions were carried out under argon, using standard Schlenk and vacuum-line techniques or in an argon-filled glovebox. Solvents were thoroughly dried and deoxygenated by standard methods[21] and distilled immediately before use. $CDCl_3$ was dried over P_2O_5. Re_2O_7 (Aldrich commercial product) was used as supplied. Ph_3P (Sigma) was recrystallized from ethanol and dried under vacuum at 70 °C. Me_3SiCl (Aldrich) was dried over P_2O_5 and deoxygenated prior to use. $KBpz_4$ was prepared as described.[22] Column chromatography purification was carried out, under argon, using silica gel 60 (0.063–0.200 mm) as the stationary phase and CH_2Cl_2 as eluant.

^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity 300-MHz instrument, using the chemical shift of the solvent as the internal standard. IR spectra were recorded as KBr pellets on a Perkin-Elmer 577 spectrophotometer. Absorption electronic spectra were recorded as

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solutions on a Cary 2390 Varian spectrometer. Carbon, hydrogen, and nitrogen analyses were performed on a Perkin-Elmer automatic analyzer.

The FTICR mass spectra were obtained, either by laser desorption (LD) or by electron impact (EI), with an Extrel FTMS 2001-DT instrument equipped with a 3.0-T superconducting magnet and interfaced to a Spectra-Physics Quanta-Ray GCR-11 pulsed Nd:YAG laser operating at the fundamental wavelength (1064 nm) with an estimated output of 20–50 mJ/pulse. Samples were prepared under argon in a glovebox. Standard FTICR event sequences were employed, with the ions formed, trapped, excited and detected on the "source" side of the dual "source/analyzer" ion trap. The background pressure in the mass spectrometer during the experiments was 1.0×10^{-8} Torr, as measured by an uncalibrated ion gauge with a MKS 290 controller. Each positive- or negative-ion LD mass spectrum was obtained from a single laser shot, and the probe was rotated to a new position after each shot, so that a fresh spot on the sample was always struck. Positive- or negative-ion EI mass spectra were obtained with variable electron beam voltages and 10-μA emission currents. All spectra were obtained in a standard broad-band frequency-sweep excitation mode with a 500-kHz bandwidth and 2 kHz/μs sweep rate and direct-mode detection over the same bandwidth, generating 32K data-point time-domain transients (1 transient for LD spectra, 100 transients for EI spectra) to which 32K zeros were added before discrete Fourier transformation to yield magnitude-mode spectra.

Synthesis and Chacterization of $(Bpz_4)ReO_3$ (1). Under vigorous stirring, 2 g (4.13 mmol) of Re_2O_7 was dissolved in THF (20 cm^3), resulting in a pale yellow solution. At –78 °C and under continuous stirring, 1.3 g (4.13 mmol) of $KBpz_4$ was slowly added to the Re_2O_7 solution. After addition, the resulting mixture was stirred at room temperature for 2 h. The white insoluble solid obtained was separated from the supernatant by centrifugation, washed with hot water (3×20 cm^3) to remove the $KReO_4$ formed, and dried under vacuo (1.4 g, yield 65%).

Anal. Calcd for $C_{12}H_{12}BN_8O_3Re$: C, 28.1; H, 2.36; N, 21.8. Found: C, 28.7; H, 2.42; N, 21.6. IR (KBr, ν(cm^{-1})): 3110 w, 1495 w, 1435 w, 1400 m, 1380 m, 1300 m, 1220 m, 1200 w, 1180 w, 1100 w, 1075 m, 1065 m, 943 m, 923 s, 911 s, 855 m, 818 w, 790 w, 775 m, 760 m, 610 w, 390 w, 365 w. UV–vis (CH_2Cl_2) (λ_{max} (nm)): 230 (vs), 270 (sh). ^{1}H NMR ($CDCl_3$, δ (ppm)): 6.37 (3H, H(4), t, $^3J = 2.3$ Hz), 6.65 (1H, H(4), dd, $^3J = 2.5$, $^3J = 1.7$ Hz), 7.82 (3H, dd, $^3J = 2.5$, $^4J = 0.6$ Hz), 7.93 (1H, d, $^3J = 2.3$ Hz), 7.95 (1H, d, $^3J = 1.5$ Hz), 8.39 (3H, dd, $^3J = 2.2$, $^4J = 0.6$ Hz). ^{13}C NMR (CDCl3, δ (ppm)): 106.79 (3C, C(4)pz), 107.85 (1C, C(4)pz), 135.19 (1C, C(5)pz), 135.64 (3C, C(5)pz), 142.63 (1C, C(3)pz), 144.08 (3C, C(3)pz). FTICR/MS (m/z referenced to the species with ^{187}Re and ^{11}B; relative abundance in parentheses): EI(+) (150 °C, 10 eV): 514 (27%) [M]; 446 (100%) [M – pzH]. EI(–) (150 °C, 20 eV): 514 (100%) [M]; 302 (84%) [M – Bpz_3]; 235 (72%) [M – Bpz_4]. LD(–) (25 °C): 514 (100%) [M]; 302 (4%) [M – Bpz_3]; 235 (6%) [M – Bpz_4].

Synthesis and Characterization of $(Bpz_4)ReOCl_2$ (2). To a suspension of **1** (0.5 g, 0.97 mmol) in 20 cm^3 of THF was added, at –78 °C, a solution of Ph_3P (0.250 g, 0.97 mmol) and Me_3SiCl (1.2 cm^3, 9.66 mmol) in THF. The resulting mixture was allowed to react at room temperature for 2 h. After this reaction time, a clear, deep blue solution was obtained. The THF was evaporated in vacuo and the deep blue residue obtained redissolved in the minimum volume of CH_2Cl_2 and purified by column chromatography, using silica gel as the stationary phase and CH_2Cl_2 as eluent. CH_2Cl_2 eluted a blue band from which, after evaporation of the solvent in vacuo, was recovered a deep blue solid (0.390 g, yield 73%).

Anal. Calcd for $C_{12}H_{12}BCl_2N_8ORe$: C, 26.1; H, 2.17; N, 20.3. Found: C, 26.0; H, 2.12; N, 20.0. IR (KBr, ν (cm^{-1})): 3100 w, 1495 w, 1430 w, 1400 s, 1380 m, 1300 s, 1200 s, 1170 m, 1110 m, 1070 sh, 1060 s, 995 w, 980 s, 920 w, 870 w, 860 s, 810 m, 780 s, 760 sh, 610 w, 360 m, 330 m. UV–vis (CH_2Cl_2) (λ_{max} (nm)): 265 (vs), 680 (m). ^{1}H NMR ($CDCl_3$, δ (ppm)): 6.00 (1H, H(4), t, $^3J = 2.4$ Hz), 6.56 (2H, H(4), t, $^3J = 2.4$ Hz), 6.67 (1H, H(4), dd, $^3J = 1.7$, $^3J = 2.4$ Hz), 7.54 (1H, dd, $^3J = 2.1$, $^4J = 0.6$ Hz), 7.70 (2H, dd, $^3J = 2.6$, $^4J = 0.8$ Hz), 7.96 (1H, d, $^3J = 1.5$ Hz), 7.98 (1 + 1H, m), 8.33 (2H, dd, $^3J = 2.6$, $^4J = 0.8$Hz). ^{13}C NMR ($CDCl_3$, δ (ppm)): 106.34 (1C, C(4)pz), 108.17 (1C, C(4)pz), 109.08 (2C, C(4)pz), 135.03 (1C, C(5)pz), 135.26 (1C, C(5)pz), 139.11 (2C, C(5)pz), 142.79 (1C, C(3)pz), 148.38 (1C, C(3)pz), 149.00 (2C, C(3)pz). FTICR/MS (m/z referenced to the species with ^{187}Re, ^{35}Cl, and ^{11}B; relative abundance in parentheses): EI(+) (200 °C, 10 eV): 552 (100%) [M]. EI(+) 200 °C, 70 eV): 552 (100%) [M]; 517 (5%) [M – Cl]; 484 (14%) [M – pzH]; 449 (30%) [M – Cl – pzH]; 187 (10%) [Re]. EI(–) (200 °C, 70 eV): 552 (29%) [M]; 516 (100%) [M – HCl]. LD(+) (25 °C): 552 (96%) [M]; 517 (38%) [M – Cl]; 449 (51%) [M – Cl – pzH]; 187 (100%) [Re]. LD(–) (25 °C): 552 (34%) [M]; 516 (100%) [M – HCl]; 448 (7%) [M – HCl – pzH].

Table I. Crystallographic Data for $(Bpz_4)ReO_3$

formula	$C_{12}H_{12}BN_8O_3Re$
mol wt	481.30
cryst system	monoclinic
space group	$C2/c$
a (Å)	21.070(2)
b (Å)	14.860(1)
c (Å)	11.588(1)
β (deg)	121.70(1)
V (Å^3)	3087(4)
Z	8
D_{calc} (g cm^{-3})	2.071
linear abs coeff (cm^{-1}) (Mo Kα)	75.59
2θ range (deg)	3.0–54.0
no. of reflns ($F_o > 2\sigma(F_o)$)	2877
range in abs corr factors	0.6481–0.9997
no. of params refined	227
final R, R_w	0.041, 0.047

Crystallographic Analysis of 1. Regular transparent crystals of compound **1** were obtained by slow diffusion of hexane in a saturated solution of the complex in THF and were mounted in thin-walled glass capillaries in an argon-filled glovebox.

Data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Mo Kα radiation, using a ω–2θ scan mode. Unit cell dimensions were obtained by least-squares refinement of the setting angles of 25 reflections with $20 \leq 2\theta \leq 32°$. A summary of the crystal data and data collection and refinement is given in Table I. Data were corrected for Lorentz–polarization effects (no decay was observed during data collection) and for absorption by empirical corrections based on ψ scans, using the Enraf-Nonius program. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures.[23a] All non-hydrogen atoms were refined anisotropically, and the contributions of the hydrogen atoms were included in calculated positions, constrained to ride on their carbon atoms with group U_{iso} values assigned. A weighting scheme of the form $w = 1/(\sigma^2(F_o) + gF_o^2)$ with $g = 0.0008$ was used. The reflections $\bar{3}11$, 111, and 221 which were thought to be affected by extinction were removed from the data. In the final difference Fourier map, the highest peak was 1.34 e Å^{-3}, 1.06 Å from the Re atom.

Atomic scattering factors and anomalous dispersion terms were taken from ref 23b.

Results and Discussion

Re(VII) and Re(V) Compounds. Complexes of Re(VII) and Re(V) of the type $LReO_3$ and $LReXCl_2$ (X = O, S; L = $HBpz_3$, $HB(3,5\text{-}Me_2pz)_3$) have been previously described, and for these complexes different synthetic methods have been used, with different yields.[8,9,11–13]

The Re(VII) complex $(Bpz_4)ReO_3$, reported in this work, has been obtained as a white crystalline solid by reacting Re_2O_7 with $KBpz_4$ in THF. This procedure has been also successfully used for preparing other trioxo Re(VII) complexes with polypyrazolyl borates.[11,12]

The air-stable complex $(Bpz_4)ReO_3$ is quite soluble in dichloromethane and acetone, moderately soluble in tetrahydrofuran, and insoluble in water. The characterization of this complex has been made on the basis of elemental analysis, spectroscopic data, laser desorption and electron impact FTICR/MS, and X-ray analysis.

The complex $(Bpz_4)ReO_3$ can be easily reduced by triphenylphosphine in the presence of trimethylsilyl chloride to give, after purification by column chromatography, a blue crystalline solid that has been formulated as $(Bpz_4)ReOCl_2$, on the basis of elemental analysis, spectroscopic data, and FTICR/MS. So far, it has not been possible to obtain single crystals suitable for X-ray analysis. The Re(V) complex sublimes at 160 °C under reduced

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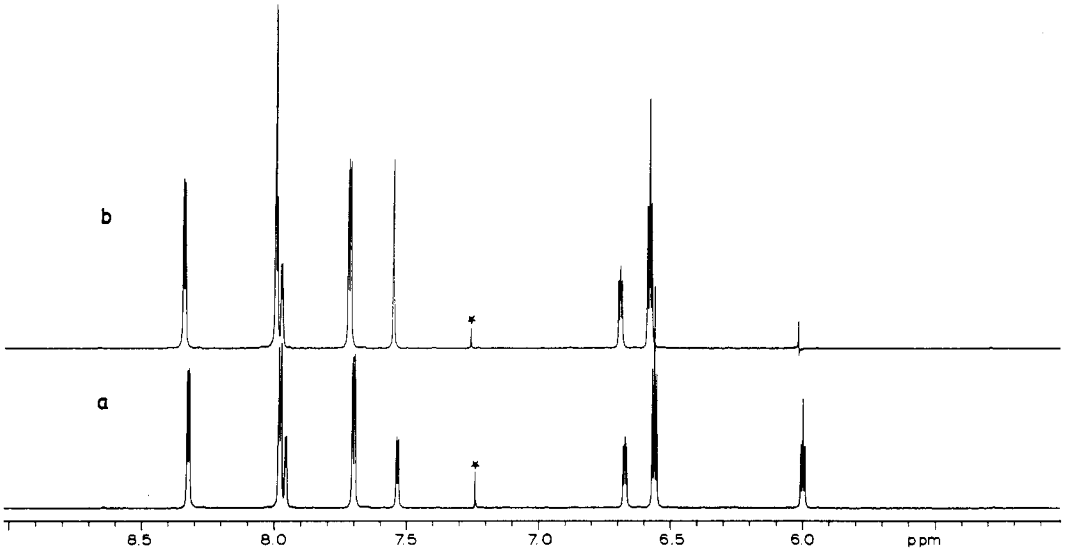

Figure 1. ^1H NMR spectra of $(Bpz_4)ReOCl_2$ in $CDCl_3$ (*): (a) before and (b) after irradiation at 6.0 ppm.

pressure and is quite soluble in tetrahydrofuran, dichloromethane, and aromatic solvents and moderately soluble in water.

Electronic and Infrared Spectra. The absorption electronic spectra obtained for complexes **1** and **2**, in the UV and UV-vis regions, respectively, present patterns consistent with d^0 and d^2 configurations. The maxima of the absorption bands (see Experimental Section) compare quite well with the values found for analogous previously isolated complexes with the ligand $HBpz_3$.[8]

For both complexes, the infrared spectra present the characteristic bands of the ligand Bpz_4 (C–H stretching vibrations at ca. 3100 cm^{-1} and ring breathing vibrations at 1495 cm^{-1}). For complex **1**, the bands assignable as $\nu(Re{=}O)$ appear at 943 s, 923 vs, 911 vs, and 871 cm^{-1} m. These values compare well with the values described for $(HBpz_3)ReO_3$, consistent with the similarities found in the solid-state structure of $(Bpz_4)ReO_3$ and $(HBpz_3)ReO_3$, as can be seen below. For complex **2**, the intense band that appears at 985 cm^{-1} can be attributed to the Re=O vibration and the bands at 360 and 330 cm^{-1} are due to the stretching vibrations Re–Cl.

NMR Spectra. The ^{13}C and ^1H NMR spectra obtained for complex **1** at room temperature present two sets of resonances of relative intensity 3:1. This pattern indicates that the ligand is acting as tridentate with the three coordinated pyrazolyl rings magnetically equivalent and the fourth noncoordinated pyrazolyl ring different. Taking into account the structure found in the solid state (see below), the NMR spectra obtained indicate a static behavior for the complex in solution at room temperature. For ^{13}C, the assignment of the resonances, presented in Experimental Section, was done on the basis of the criterion, previously referred to by Lobbia et al,[24] that the chemical shift of C(3) is larger than the one observed for C(5). In the ^1H NMR spectrum of complex **1**, the intensity of the signals as well as their multiplicity enabled us to assign the signal at 6.65 ppm to H(4) of the noncoordinated pyrazolyl ring and the signal at 6.37 ppm to H(4) of the three coordinated pyrazolyl rings. The assignment of the H(3) and H(5) resonances appears more difficult; ^1H NMR studies made by Trofimenko[16] on $MBpz_4$ salts as well as on the complex $(Bpz_4)Mo(CO)_3$ showed that the environments of the H(5) protons of noncoordinated and coordinated pyrazolyl groups were much more similar than those of H(3) protons and also showed that the chemical shifts of the H(3) protons were more sensitive to the solvents and to the cations. For Re compounds with the $HBPz_3$ ligand, some assignments have been made mainly on the basis of the values of the coupling constants $[J(H^4H^5) > J(H^3H^5)]$.[14] Any of these criteria would allow us to say that the resonances at 8.39 and 7.95 ppm are due to the H(3) protons and the resonances at 7.93 and 7.82 ppm are due to the H(5) protons.

For complex **2**, the ^{13}C NMR spectrum presents at room temperature three sets of resonances of relative intensity 2:1:1, which indicates that two of the pyrazolyl rings are equivalent and the other two magnetically different. However, as can be seen in Figure 1a, in the ^1H NMR spectrum eight signals of relative intensity 2:2:1:2:1:1:2:1 were observed, due to the occasional overlapping of two resonances. Irradiation of the triplet at 6.00 ppm indicated that it was coupled with the protons which appear at 7.54 and at 7.98 ppm (Figure 1b). On the basis of this result and the relative intensities, we can say that the signals at 6.56, 7.70, and 8.33 ppm are due to the protons of the two pyrazolyl rings which are trans to the chloride ligands. This also means that the resonances ocasionally overlapping at 7.98 ppm are due to a proton of the noncoordinated pyrazolyl ring and to a proton of the pyrazolyl which is trans to the oxygen. From the noncoordinated ring must also be the two resonances at 6.67 and at 7.96 ppm, as they have been the less affected by changing the oxidation state of the metal (see Experimental Section). For this complex, no crystallographic study has been done, but the splitting observed for the pyrazolyl rings is consistent with a tridentate coordination of the Bpz_4 ligand and with an approximately octahedral arrangement around the metal. This type of coordination geometry has been observed for the analogous complexes $(HBpz_3)TcOCl_2$, $(HBpz_3)ReOCl(SC_6H_5)$, and $(HBpz_3)ReO(SC_6H_5)_2$.[7a,11b] For complex **2**, the signals at 6.00, 7.54, and 7.98 ppm are shifted to high field relative to the resonances of the pyrazolyl rings trans to the chloride ligands; this probably means that this group of resonances are due to the ring which is trans to the oxygen, the shift being due to the trans effect.

FTICR/MS Analysis. Positive- and negative-ion EI and LD/FTICR mass spectra were obtained for compounds **1** and **2**, exhibiting prominent molecular ion peaks and different degrees of fragmentation, resulting mainly from losses of pyrazolyl groups and chloride ligands in the case of complex **2**, as described in the Experimental Section. Figure 2 shows a negative-ion LD mass spectrum for compound **1** (Figure 2a) and a positive-ion EI mass spectrum for compound **2** (Figure 2b); both spectra show negligible fragmentation and isotopic patterns in accord with the elemental compositions of the complexes. The volatility of the compounds at 150–200 °C and under the high-vacuum conditions of the spectrometer enabled us to obtain positive-ion EI and negative-

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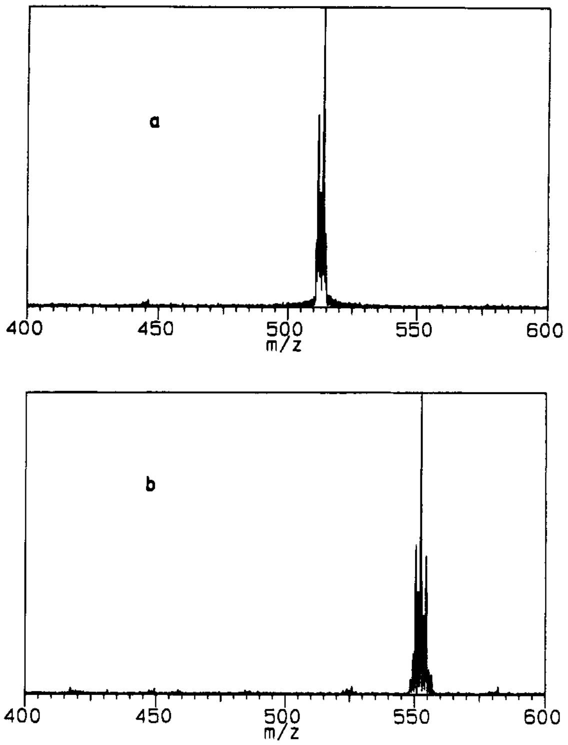

Figure 2. (a) Negative-ion LD-FTICR mass spectrum of $(Bpz_4)ReO_3$. (b) Positive-ion EI-FTICR mass spectrum of $(Bpz_4)ReOCl_2$.

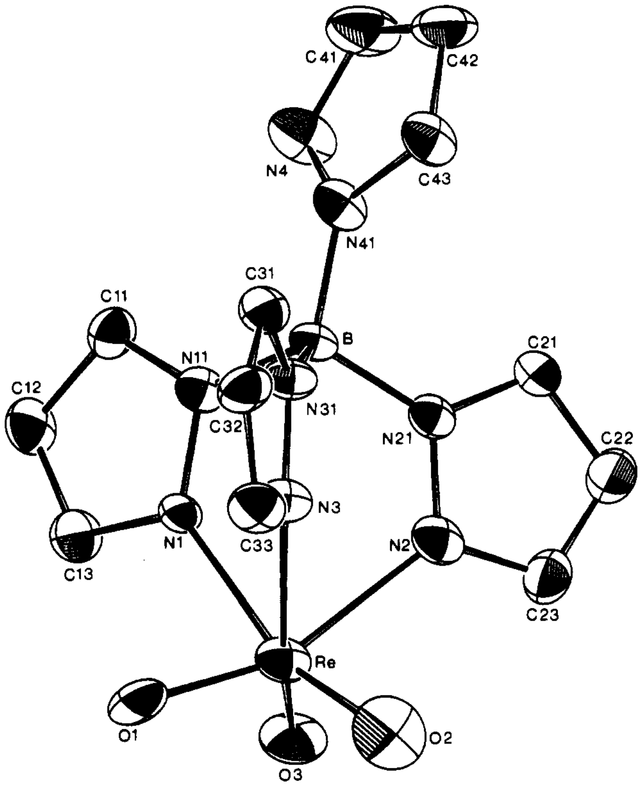

Figure 3. ORTEP drawing of $(Bpz_4)ReO_3$ with ellipsoids drawn at the 50% probability level.

ion electron capture spectra with little fragmentation. LD positive- and negative-ion spectra with fragmentation patterns similar to the ones observed with EI ionization were easily obtained, with exception of the positive-ion spectrum of $(Bpz_4)ReO_3$. In this case, the laser ionization process may be insufficient to produce the species $(Bpz_4)ReO_3^+$, which, when formed by electron impact, most probably exists as an oxygen-centered cation radical (a metal-centered ion would correspond to an improbable Re(VIII) species).

Table II. Selected Bond Lengths (Å) and Bond Angles (deg) for $(BPz_4)ReO_3$

Re–O(1)	1.713(5)	Re–N(1)	2.225(5)
Re–O(2)	1.709(5)	Re–N(2)	2.204(6)
Re–O(3)	1.721(5)	Re–N(3)	2.222(6)

B–N(11)	1.529(8)	B–N(21)	1.554(8)	B–N(31)	1.536(8)
N(1)–N(11)	1.368(7)	N(2)–N(21)	1.358(7)	N(3)–N(31)	1.363(8)
N(1)–C(13)	1.344(8)	N(2)–C(23)	1.348(8)	N(3)–C(33)	1.341(8)
N(11)–C(11)	1.338(8)	N(21)–C(21)	1.354(8)	N(31)–C(31)	1.350(8)
C(11)–C(12)	1.380(10)	C(21)–C(22)	1.368(10)	C(31)–C(32)	1.376(9)
C(12)–C(13)	1.373(10)	C(22)–C(23)	1.372(10)	C(32)–C(33)	1.378(10)
B–N(41)	1.505(8)	N(41)–C(43)	1.371(8)	C(41)–C(42)	1.397(11)
N(4)–N(41)	1.370(8)	N(4)–C(41)	1.317(9)	C(42)–C(43)	1.357(10)

O(1)–Re–O(2)	104.2(3)	O(1)–Re–N(1)	86.6(2)
O(1)–Re–O(3)	104.5(3)	O(1)–Re–N(2)	159.9(2)
O(2)–Re–O(3)	104.6(3)	O(1)–Re–N(3)	88.7(2)
N(1)–Re–N(2)	77.5(2)	O(2)–Re–N(1)	161.6(2)
N(1)–Re–N(3)	77.7(2)	O(2)–Re–N(2)	88.4(2)
N(2)–Re–N(3)	76.1(2)	O(2)–Re–N(3)	87.7(2)
N(11)–B–N(21)	107.0(6)	O(3)–Re–N(1)	86.5(2)
N(11)–B–N(31)	106.6(6)	O(3)–Re–N(2)	86.8(2)
N(21)–B–N(31)	107.7(6)	O(3)–Re–N(3)	158.8(2)
N(41)–B–N(11)	116.0(6)	N(41)–B–N(21)	108.6(6)
N(41)–B–N(31)	110.7(6)		

Table III. Positional and Thermal Parameters for $(PBz_4)ReO_3$

atom	*x*	*y*	*z*	B^a (Å^2)
Re	0.10573(2)	0.14561(2)	0.53367(3)	2.44(5)
O(1)	0.0213(3)	0.0917(3)	0.4592(6)	3.6(2)
O(2)	0.1698(3)	0.0605(4)	0.5996(6)	4.2(2)
O(3)	0.1110(3)	0.1860(4)	0.3997(5)	3.6(2)
N(1)	0.0437(3)	0.2711(4)	0.5163(5)	2.2(2)
N(2)	0.1962(3)	0.2404(4)	0.6625(5)	2.6(2)
N(3)	0.1080(3)	0.1465(3)	0.7276(6)	2.3(2)
N(4)	0.1158(4)	0.4700(4)	0.8288(7)	3.5(3)
N(11)	0.0565(3)	0.3319(3)	0.6149(5)	2.1(2)
N(21)	0.1930(3)	0.3057(3)	0.7414(5)	2.0(2)
N(31)	0.1112(3)	0.2208(3)	0.7993(5)	2.2(2)
N(41)	0.1404(3)	0.3831(4)	0.8628(5)	2.3(2)
C(11)	0.0030(4)	0.3947(4)	0.5623(7)	2.6(2)
C(12)	−0.0451(4)	0.3752(5)	0.4267(7)	2.9(3)
C(13)	−0.0182(4)	0.2982(5)	0.4018(7)	2.8(2)
C(21)	0.2547(4)	0.3581(4)	0.7944(7)	2.7(2)
C(22)	0.2979(4)	0.3262(5)	0.7475(8)	3.2(3)
C(23)	0.2611(4)	0.2531(5)	0.6677(7)	3.0(2)
C(31)	0.0971(4)	0.1958(5)	0.8956(7)	2.7(2)
C(32)	0.0867(4)	0.1041(4)	0.8881(7)	2.7(2)
C(33)	0.0931(4)	0.0758(4)	0.7814(7)	2.8(3)
C(41)	0.1524(5)	0.5142(5)	0.9444(9)	4.2(4)
C(42)	0.2009(5)	0.4596(5)	1.0540(8)	3.8(3)
C(43)	0.1925(4)	0.3767(5)	0.9988(7)	2.8(2)
B	0.1241(4)	0.3134(4)	0.7564(7)	1.8(2)

[a] Anisotropic thermal parameters are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Crystallographic Study. The crystal structure of complex **1** consists of monomeric molecules in which the rhenium atom is six-coordinate and displays approximately octahedral geometry. The tridentate ligand and the three oxygen atoms define the two staggered triangular faces, respectively, the planes of the faces being inclined by 1.5°. An ORTEP view of the structure is shown in Figure 3. Bond distances and angles are listed in Table II, and the final positional parameters are given in Table III.

A comparison of the bond lengths with the ones found in the structure of the analogue $(HBpz_3)ReO_3$[11a] shows similar values for the Re═O and Re—N bond distances (respectively 1.714(6) and 2.22(1) Å compared with 1.712(2) and 2.231(3) Å for $(HBPz_3)ReO_3$). The average Re═O bond length is also comparable with the values of 1.696(3) Å found in $(\eta^5\text{-}C_5Me_4Et)ReO_3$[25] and 1.689(5) Å observed in $(\sigma\text{-mesityl})ReO_3$.[26] The O–Re–O angles have a mean value of 104.4(2)°, which is

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(25) Okuda, J.; Herdtweck, E.; Herrmann, W. A. *Inorg. Chem.* **1988**, *27*, 1254.

comparable with the value of 104.1(1)° for $(HBpz_3)ReO_3$ and with 105.2(2)° in $(\eta^5\text{-}C_5Me_4Et)ReO_3$.

The tridentate ligand Bpz_4 retains approximately C_{3v} symmetry. The N–Re–N bond angles average 77(1)°, and the bond angles and lengths of the noncoordinated pyrazolyl ring do not present any significant differences from those of the coordinated pyrazolyls, all being in the range observed in the structures of their Na and K salts[27] and in the complexes with the Bpz_4 acting as a tridentate ligand.[28] The boron atom exhibits tetrahedral coordination with N–B–N angles in the range 107–116(1)°. Each of the four pyrazolyl rings is approximately planar.

Final Remarks. The ligands $HBpz_3$ and Bpz_4, although generally presenting similar coordinating properties, present different reducing properties, and analogous complexes with these ligands present different solubilities. Our results showed that the complexes with Bpz_4 are more soluble, especially in water, which is an advantage to prepare analogous complexes of ^{99m}Tc. Preliminary results of a comparative study of the reducing power of different poly(pyrazolyl)borates, which is being undertaken in our laboratory, have shown that $HBpz_3$ is a stronger reducing agent than Bpz_4 toward Re(V) compounds. Due to this significant difference, the complex $(Bpz_4)ReOCl_2$ can also be synthesized, with high yield, by a substitution reaction using the Re(V) complex $ReOCl_3(Me_2S)(OPPh_3)$[29] as starting material, while with $HBpz_3$ the analogous complex was isolated with a much lower yield, as other reduced species containing Re are formed. This is an interesting difference especially because Re and Tc are elements with a large variety of acessible oxidation states. Preliminary results have also shown that the complex $(Bpz_4)ReOCl_2$ can be synthesized by reducing ReO_4^- with Sn(II) in concentrated HCl aqueous solution and in the presence of $KBpz_4$. ^{99m}Tc radiopharmaceuticals are always formulated in aqueous medium and involve $^{99m}TcO_4^-$ as starting material. The tentative preparation of the analogous oxotechnetium(V) complex, as well as the possibility of using the corresponding ^{99m}Tc complex as a radiopharmaceutical, is being studied.

Supplementary Material Available: Tables of full crystal data, calculated hydrogen atom positions, anisotropic thermal parameters, complete bond distances and angles, and equations of mean least-squares planes for $(Bpz_4)ReO_3$ (4 pages). Ordering information is given on any current masthead page.

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