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Synthesis, Characterization, and Study of the Redox Properties of Rhenium(V) and Rhenium(III) Compounds with Tetrakis(pyrazol-1-yl)borate

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The rhenium(V) ethylene glycolate complex $[ReO(OCH_2CH_2O)\{B(pz)_4\}]$ (**1**) has been prepared in one step synthesis by reacting $[ReOCl_3(SMe_2)(OPPh_3)]$ or $[ReOCl_3(PPh_3)_2]$ with ethylene glycol and $K[B(pz)_4]$ (50–60% isolated yield). Complex **1** reacts with 2-mercaptoethanol and with 1,2-ethanedithiol in the presence of triethylamine providing respectively $[ReO(OCH_2CH_2S)\{B(pz)_4\}]$ (**2**) and $[ReO(SCH_2CH_2S)\{B(pz)_4\}]$ (**3**) in 70–75% isolated yield. These compounds have been characterized by elemental analyses, IR and ^1H NMR spectroscopies, and, in the case of compound **1**, X-ray crystallography. Compound **1** crystallizes from toluene/hexane in the orthorhombic space group *Pbca* with cell parameters $a = 15.255(1)$ Å, $b = 22.442(3)$ Å, $c = 20.960(2)$ Å, $V = 7176$ Å^3, and $Z = 16$. The ethylene glycolate complex **1** reacts with HCl providing in almost quantitative yield $[ReO\{B(pz)_4\}Cl_2]$ (**4**). Compound **4** is reduced by several phosphines giving compounds of general formula $[Re\{B(pz)_4\}Cl_2L]$ (L = PEt_3 (**5**), PEt_2Ph (**6**), $PEtPh_2$ (**7**), and PPh_3 (**8**) in 60–70% yield. These paramagnetic compounds were characterized by elemental analyses, IR and ^1H and ^{31}P NMR spectroscopies, and, in the case of compound **6**, X-ray crystallography. Compound **6** crystallizes from tetrahydrofuran/hexane in the monoclinic space group $P2_1/a$ with cell parameters $a = 14.187(2)$ Å, $b = 11.985(1)$ Å, $c = 15.535(2)$ Å, $\beta = 91.40(1)°$, $V = 2641$ Å^3, and $Z = 4$. The redox behavior of all the complexes and of $K[B(pz)_4]$ was studied by cyclic voltammetry.

Introduction

The complex $[ReOCl_2\{HB(pz)_3\}]$ is a convenient starting material to enter into the chemistry of oxo complexes of Re(V) as well as into the chemistry of Re(III),[1–4] and the methods described for its synthesis involve the use of $M(ReO_4)$ (M = K or NH_4)[1,3,4] or Re_2O_7[2] as starting material. In the first method a large excess of poly(pyrazolyl)borate has to be used to reduce Re(VII) to Re(V), and in the second method a relatively sensitive oxide such as Re_2O_7 is required. For Re(III) compounds a useful synthetic method is the reduction of oxorhenium(V) complexes by phosphines.[1,5–13] However the oxygen atom transfer to phosphines depends on the Re coordination environment and for some compounds no reduction is observed using this method.[14,15]

As part of our ongoing studies on the coordination chemistry of Re(V) and Re(III), we have investigated the possibility of preparing oxorhenium(V) complexes with the stabilizing ligand $[B(pz)_4]^-$ using as starting materials $[ReOCl_3(SMe_2)(OPPh_3)]$[16] or $[ReOCl_3(PPh_3)_2]$,[17] as well as reducing some of these compounds by an oxygen atom transfer process, with phosphines of different reducing properties. We now report the synthesis and characterization, including X-ray crystallographic analysis, of the complex $[ReO(OCH_2CH_2O)\{B(pz)_4\}]$ (**1**), which has been obtained in one step preparation from $[ReOCl_3(SMe_2)(OPPh_3)]$ or from $[ReOCl_3(PPh_3)_2]$, as well as the synthesis of $[ReO(OCH_2CH_2S)\{B(pz)_4\}]$ (**2**) and $[ReO(SCH_2CH_2S)\{B(pz)_4\}]$ (**3**) prepared from complex **1**. An improved method for the previously described complex $[ReO\{B(pz)_4\}Cl_2]$[18] is also reported, as well as the synthesis and characterization of several Re(III) compounds of general formula $[Re\{B(pz)_4\}Cl_2L]$ (L = PEt_3 (**5**), PEt_2Ph (**6**), $PEtPh_2$ (**7**), and PPh_3 (**8**)); these complexes were obtained by reduction of $[ReO\{B(pz)_4\}Cl_2]$ with the respective phosphines. The electrochemical behavior of complexes **1**–**8** and of the ligand $K[B(pz)_4]$ was studied by cyclic voltammetry and whenever important by controlled potential electrolysis, in an aprotic medium.

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Experimental Section

General Procedures. All reactions were carried out under an argon atmosphere, using freshly distilled solvents dried and deoxygenated by standard methods.[19] $[ReCl_3(CH_3CN)(PPh_3)_2]$, $[ReOCl_3(SMe_2)(OPPh_3)]$, $[ReOCl_3(PPh_3)_2]$, and $[ReO\{B(pz)_4\}Cl_2]$ were obtained as previously described.[16–18,20] PPh_3 was recrystallized from ethanol and dried under vacuum at 70 °C. All the other phosphines ($PEtPh_2$, PEt_2Ph, and PEt_3) were used as supplied. Mercaptoethanol, 1,2-ethylene glycol, 1,2-ethanedithiol, and triethylamine were distilled from 4 Å molecular sieves under reduced pressure and kept over molecular sieves prior to use. $CDCl_3$ was dried over P_2O_5.

^1H and ^{31}P NMR spectra were recorded on a Varian Unity 300 MHz instrument. ^1H NMR spectra were referenced internally using the residual solvent resonance relative to tetramethylsilane; ^{31}P NMR chemical shifts are relative to $P(OMe)_3$. IR spectra were recorded as KBr pellets on a Cary 2350 Varian spectrometer. Absorption electronic spectra were performed on a Cary 2390 Varian spectrometer. Carbon, hydrogen, and nitrogen analyses were performed on a Perkin-Elmer automatic analyzer.

Synthesis and Characterization of $[ReO(OCH_2CH_2O)\{B(pz)_4\}]$ (1). Method A. To a suspension of $[ReOCl_3(SMe_2)(OPPh_3)]$ (500 mg, 0.77 mmol) in ethanol (50 mL) were added 100 mg (1.61 mmol) of ethylene glycol, 330 mg (3.26 mmol) of triethylamine, and 250 mg (0.79 mmol) of solid $K[B(pz)_4]$. After 3 h at room temperature, the violet mixture was centrifuged and the KCl separated. The ethanolic solution was concentrated, and after overnight at room temperature, the microcrystalline blue violet solid that precipitates was separated by centrifugation, washed with water, and recrystallized from toluene/hexane (250 mg, 0.46 mmol, yield 60%).

Method B. To a suspension of $[ReOCl_3(PPh_3)_2]$ (150 mg, 0.18 mmol) in ethanol were added 23 mg (0.37 mmol) of ethylene glycol, 75 mg (0.74 mmol) of triethylamine dissolved in ethanol, and 60 mg (0.19 mmol) of solid $K[B(pz)_4]$. The final suspension was then stirred at room temperature for 24 h. The initial yellow-green insoluble starting material was converted to a dark green insoluble material after 3 h of reaction, but after 24 h at room temperature a blue-violet solution was obtained, as well as insoluble KCl. The solvent was then evaporated under vacuum, and the blue violet residue obtained was redissolved in the minimum amount of dichloromethane. By application of this dichloromethane solution onto a silica gel column chromatography and by elution with dichloromethane, followed by THF, a violet solution of compound **1** in THF was obtained. The THF was removed under vacuum and the oil obtained washed with *n*-hexane yielding 50 mg (0.09 mmol) of microcrystalline **1** (yield 50%).

Anal. Calcd for $C_{14}H_{16}BN_8O_3Re$: C, 31.10; H, 3.0; N, 20.70. Found: C, 31.40; H, 3.0; N, 20.30. IR (KBr, ν (cm^{-1})): 3105 w, 2905 vw, 2820 w, 1500 w, 1440 w, 1405 w, 1385 m, 1305 s, 1205 m, 1192 w, 1183 w, 1172 w, 1103 m, 1067 m, 1015 m, 968 s (ν(ReO)), 891 s, 857 s, 820 m, 794 s, 767 s, 646 w, 634 w, 617 w, 556 w, 415 w. UV–vis (CH_2Cl_2) (λ_{max} (nm)): 215 (vs), 580 (m).

Synthesis and Characterization of $[ReO(OCH_2CH_2S)\{B(pz)_4\}]$ (2). A solution of compound **1** (50 mg, 0.09 mmol) with 2-mercaptoethanol (35 mg, 0.45 mmol) and with triethylamine (100 mg, 0.99 mmol) in toluene was refluxed for 2 h. The reddish solution obtained was filtered and the solvent evaporated under vacuo; the dark red residue obtained was redissolved in the minimum volume of CH_2Cl_2, and the solution was applied on a silica gel column. Elution with CH_2Cl_2, followed by elution with THF, gave a dark red solution of the compound in THF. Evaporation of the THF gave an oil that was washed with hexane providing 39 mg of **2** (0.07 mmol, yield 75%).

Anal. Calcd for $C_{14}H_{16}BN_8O_2SRe$: C, 30.1; H, 2.9; N, 20.1. Found: C, 29.1; H, 2.9; N, 19.8. IR (KBr, ν (cm^{-1})): 3109 w, 2903 vw, 2828 vw, 1944 m, 1464 m, 2001 s, 1381 m, 1298 s, 1258 vw, 1203 s, 1201 s, 1058 s, 1023 w, 992 w, 953 s (ν(ReO)), 923 m, 868 w, 853 s, 828 w, 806 m, 791 m, 760 s, 603 m, 523 w, 368 w, 321 w. UV–vis (CH_2Cl_2) (λ_{max} (nm)): 356 (vs), 520 (m).

Synthesis and Characterization of $[ReO(SCH_2CH_2S)\{B(pz)_4\}]$ (3). A solution of compound **1** (150 mg, 0.28 mmol) with 1,2-ethanedithiol (105 mg, 1.12 mmol) and with triethylamine (225 mg, 2.22 mmol) in toluene (20 mL) was refluxed for 2 h. The orange-brown solution obtained was taken to dryness in vacuo, and the orange-brown residue obtained redissolved in the minimum volume of CH_2Cl_2. This solution was chromatographed on silica gel, and elution with CH_2Cl_2 followed by THF gave an orange brown solution of **1** in THF. The THF solution was evaporated to dryness yielding an orange-brown microcrystalline solid (120 mg, 0.21 mmol, yield 75%).

Anal. Calcd for $C_{14}H_6BN_8OS_2Re$: C, 29.3; H, 2.8; N, 19.5. Found: C, 29.6; H, 2.9; N, 19.4. IR (KBr, ν (cm^{-1})): 3105 w, 2880 vw, 1495 m, 1435 w, 1400 s, 1383 s, 1298 s, 1205 w, 1200 s, 1100 s, 1057 s, 993 w, 947 s (ν(ReO)), 917 m, 865 w, 850 s, 800 s, 760 s, 607 m, 380 m, 347 m, 293 w. UV–vis (CH_2Cl_2) (λ_{max} (nm)): 243 (vvs), 314 (vs), 376 (vs).

Synthesis and Characterization of $[Re\{B(pz)_4\}Cl_2(PEt_3)]$ (5). At room temperature triethylphosphine (110 mg, 0.93 mmol), dissolved in the minimum volume of toluene, was added dropwise to a solution of $[ReO\{B(pz)_4\}Cl_2]$ (100 mg, 0.18 mmol) in toluene (20 mL). The original sky-blue solution turned almost immediately to green, and by heating of the solution at reflux temperature a pink red color appeared. After 1 h the reduction of the compound **4** was complete, as shown by TLC chromatography on silica gel plates using CH_2Cl_2 as eluent (R_f(**4**) = 0.8 and R_f(**5**) = 0.0). The pink red solution was concentrated and *n*-hexane added. A microcrystalline pink red solid precipitated and after separation by centrifugation was washed with *n*-hexane and dried under vacuum (80 mg, 0.12 mmol, yield 70%).

Anal. Calcd for $C_{18}H_{27}BCl_2N_8PRe$: C, 33.0; H, 4.1; N, 17.1. Found: C, 33.1; H, 4.0; N, 16.6. IR (KBr, ν (cm^{-1})): 3100 w, 2910 w, 2860 w, 1495 w, 1399 w, 1381 m, 1305 s, 1293 s, 1255 w, 1242 w, 1205 s, 1127 m, 992 w, 903 w, 855 s, 808 m, 794 s, 777 s, 757 m, 715 m, 665 w, 606 w, 314 m, 285 m. UV–vis (CH_2Cl_2) (λ_{max} (nm)): 295 (vs), 340 (vs), 550 (vw). ^{31}P NMR ($CDCl_3$): −98.7 ppm.

Synthesis and Characterization of $[Re\{B(pz)_4\}Cl_2(PEt_2Ph)]$ (6). This compound has been synthesized and purified according to the procedure above described for **5**. Starting with 100 mg (0.18 mmol) of **4** and using a 10:1 excess of PEt_2Ph, we obtained 80 mg (0.11 mmol) of a red microcrystalline solid that we formulated as **6** (yield 60%).

Anal. Calcd for $C_{22}H_{27}BCl_2N_8PRe$: C, 37.6; H, 3.8; N, 15.9. Found: C, 38.2; H, 3.5; N, 15.6. IR (KBr, ν (cm^{-1})): 3100 w, 2900 w, br, 1495 w, 1430 w, 1400 m, 1380 m, 1290 s, 1258 w, 1198 s, 1100 s, 1058 s, 915 w, 850 m, 805 s, 885 m, 755 s, 725 m, 700 w, 610 w, 502 w, 450 w, 315 m, 287 m. UV–vis (CH_2Cl_2) (λ_{max} (nm)): 270 (vs), 336 (sh). ^{31}P NMR ($CDCl_3$): −100.2 ppm.

Synthesis and Characterization of $[Re\{B(pz)_4\}Cl_2(PEtPh_2)]$ (7). A 100 mg amount (0.18 mmol) of **4** reacts with 1.8 mmol of $PEtPh_2$ as described for **5** and **6**. However, due to the low solubility of compound **7** in most common solvents, its purification, from the excess of $PEtPh_2$ and $O{=}PEtPh_2$ formed during the reaction, was made by washing of the crude product with toluene. After drying under vacuo, 100 mg (0.13 mmol) of **7** was obtained (yield 72%).

Anal. Calcd for $C_{22}H_{27}BCl_2N_8PRe$: C, 41.6; H, 3.6; N, 14.9. Found: C, 40.2; H, 3.0; N, 14.7. IR (KBr, ν (cm^{-1})): 3200 w, 2900 vw, br, 1495 w, 1430 m, 1400 s, 1383 s, 1293 s, 1205 s, 1105 s, 1057 s, 1008 w, 982 w, 917 w, 853 m, 825 w, 805 s, 792 s, 775 s, 747 s, 695 m, 667 w, 607 m, 523 m, 483 w, 473 w, 420 vw, 310 m, 283 m. UV–vis (CH_2Cl_2) (λ_{max} (nm)): 272 (vs), 342 (sh).

Synthesis and Characterization of $[Re\{B(pz)_4\}Cl_2(PPh_3)]$ (8). The procedure used was the same as described for **5**–**7**, using again a 10:1 molar excess of triphenylphosphine. After the mixture was refluxed for 1 h, a clear orange solution was obtained with a very small amount of a yellow-green insoluble solid. After filtration under argon to remove this insoluble species the solvent was evaporated under vacuum and the orange residue obtained was redissolved in CH_2Cl_2, *n*-hexane added to the solution. An orange microcrystalline solid precipitated and after separation from the supernatant was dried under vacuum (100 mg, 0.13 mmol, yield 70%).

Anal. Calcd for $C_{30}H_{27}BCl_2N_8PRe$: C, 45.1; H, 3.4; N, 14.0 Found: C, 45.5; H, 3.2; N, 12.8. IR (KBr, ν (cm^{-1})): 3115 w, 1495 w, 1480 w, 1433 w, 1403 w, 1385 m, 1311 m, 1300 s, 1286 m, 1261 w, 1208 m, 1127 w, 1163 w, 1108 m, 1091 w, 1068 w, 1053 s, 921 w, 851 m, 805 m, 783 m, 768 s, 741 w, 693 m, 613 w, 540 s, 516 w, 496 w, 466 w, 310 m, 285 m. UV–vis (CH_2Cl_2) (λ_{max} (nm)): 280 (vs), 360 (sh).

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Table 1. Crystallographic Data for Compounds **1** and **6**

compd	[ReO(OCH_2CH_2O)-{B(pz)$_4$}] (**1**)	[Re{B(pz)$_4$}Cl_2-(PEt_2Ph)] (**6**)
formula	$C_{14}H_{16}BN_8O_3Re$	$C_{22}H_{27}BCl_2N_8PRe$
mol wt	541.35	702.41
cryst size, mm	0.50 × 0.07 × 0.04	0.40 × 0.25 × 0.20
cryst system	orthorhombic	monoclinic
space group	*Pbca*	$P2_1/a$
a (Å)	15.255(1)	14.187(2)
b (Å)	22.442(3)	11.985(1)
c (Å)	20.960(2)	15.535(2)
β (deg)		91.40(1)
V (Å^3)	7176	2641
Z	16	4
D_{calc} (g cm^{-3})	2.004	1.767
linear abs coeff (cm^{-1}) (Mo Kα)	65.1	46.6
2θ range (deg)	3.0−46.0	3.0−56.0
no. of reflns	3237 ($F_o > 2\sigma(F_o)$)	4590 ($F_o > 3\sigma(F_o)$)
decay corrs: min, max		1.00001, 1.01842
range in abs corr factors	0.9648−1.0000	0.6854−0.9997
no. of params refined	349	319
weighting scheme used: $w = (\sigma^2(F_o) + gF_o^2)^{-1}$, g	0.001	0.0008
final R, R_w	0.064, 0.061	0.044, 0.060

Electrochemical Studies. Electrochemical experiments were performed on a EG&G PARC 173 potentiostat/galvanostat and a EG&G PARC 175 universal programmer. As a general procedure, a 0.2 mol^{-1} [NBu_4][BF_4]−acetonitrile solution was used, and the experiments were performed either at a platinum electrode for cyclic voltammetry or at a platinum gauze for controlled potential electrolysis. The values of the oxidation or reduction potentials are quoted relative to SCE and were measured using as internal reference the redox couple [Fe(η^5-C_5H_5)$_2$]$^{0/+}$ ($E_{1/2}^{ox} = 0.40$ V vs SCE).

X-ray Crystallographic Analysis. X-ray data were collected from a blue violet crystal of **1**, obtained by diffusion of *n*-hexane into a saturated solution of the compound in toluene, and from a red crystal of **6**, obtained by slow diffusion of *n*-hexane into a saturated solution of the compound in tetrahydrofuran. The crystals 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 $\omega-2\theta$ scan mode. Unit cell dimensions were obtained by least-squares refinement of the setting angles of 25 reflections with $14 < 2\theta < 28°$ for **1** and $24 < 2\theta < 32°$ for **6**. Details of the crystal data and data collection and refinement are given in Table 1. Data were corrected for Lorentz−polarization effects, for linear decay (no decay was observed for **1**), and for absorption by empirical corrections based on ψ scans, using the Enraf-Nonius program. The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures.[21] For **1** all but the carbon atoms and for **6** all the non-hydrogen atoms were refined anisotropically. The contributions of the hydrogen atoms were included in calculated positions, constrained to ride on their carbon atoms with group U_{iso} values assigned. In the final difference Fourier map, the highest peaks were 1.3 and 1.4 e Å^{-3} for compounds **1** and **6**, respectively, and were near the Re atom. Atomic scattering factors and anomalous dispersion terms were taken from ref 22.

Results and Discussion

Re(V) Compounds. As is shown in Scheme 1, [ReOCl_3-(SMe_2)($OPPh_3$)] reacts, in a one step experiment, with ethylene glycol (present in a 2-fold molar ratio) and 1 equiv of K[B(pz)$_4$] in ethanol in the presence of triethylamine to yield, after 3 h, the ethylene glycolate complex [ReO(OCH_2CH_2O){B(pz)$_4$}] (**1**) in 60% isolated yield. When the same reaction is run using as starting material [ReOCl_3(PPh_3)$_2$], the complex **1** can also be obtained but after 24 h (50%). This blue violet microcrystalline compound is air and water stable, is soluble in dichloromethane and aromatic solvents, and almost insoluble in *n*-hexane and water. In ethanolic solution **1** reacts with concentrated hydrochloric acid providing in almost quantitative yield the previously reported [ReO{B(pz)$_4$}Cl_2].[18] In toluene and in the presence of triethylamine, after 2 h in reflux, the ethylene glycolate in compound **1** can be replaced by 2-mercaptoethanolate or by 1,2-ethylenedithiolate providing, after purification by column chromatography, the compounds [ReO(OCH_2CH_2S){B(pz)$_4$}] (**2**) and [ReO(SCH_2CH_2S){B(pz)$_4$}] (**3**) in 70−75% isolated yield. These two compounds present a behavior analogous to **1** in what concerns stability toward air and also solubility.

We think that the oxo−ethylene glycolate complex **1** is a useful precursor for compounds containing the ligand [B(pz)$_4$]$^-$ and other ligands whose conjugate acids are more acidic than ethylene glycol. Our results agree with others previously described by Mayer *et al.*,[3] who also used the compound [ReO-(OCH_2CH_2O){HB(pz)$_3$}] to synthesize [ReO(C_2O_4){HB(pz)$_3$}] and [ReO(9,10-phenanthrenediolate){HB(pz)$_3$}]. However, in this case, as in others, the ethylene glycolate complex has been obtained from [ReOCl_2{HB(pz)$_3$}], by replacing the two chlorides by the dianionic ligand, and the latter complex was isolated either by reacting [ReO_4]$^-$ with excess of the potassium salt of the hydrotris(pyrazolyl)borate[3] or by reducing [ReO_3-{HB(pz)$_3$}] with PPh_3 in the presence of trimethylsilyl chloride.[2] We have used the compounds [ReOCl_3(SMe_2)($OPPh_3$)][16] and [ReOCl_3(PPh_3)$_2$][17] which are easily synthesized and manipulated, and thus their application to prepare Re(V) oxo compounds with the ligand [B(pz)$_4$]$^-$ shows some advantages. Moreover, the process is faster, avoids the use of a very sensitive material such as Re_2O_7,[23] and allows the preparation of compounds **1**−**3** with a final yield higher than the methods previously described for some analogous compounds with [HB(pz)$_3$]$^-$.[2−4] The faster reaction of [ReOCl_3(SMe_2)($OPPh_3$)] with ethylene glycol and with K[B(pz)$_4$], compared to [ReOCl_3-(PPh_3)$_2$], can probably be explained because the ligands SMe_2 and $OPPh_3$ are better leaving groups than PPh_3. The ethylene glycolate cation [ReO($O_2C_2H_4$)L]$^+$ (L = 1,4,7-triazacyclononane) has also been isolated by reacting [ReOCl_3(PPh_3)$_2$] wth triazacyclononane in the presence of ethylene glycol.[24]

Infrared Spectra. The infrared spectra of compounds **1**−**3** present the bands characteristic of the [B(pz)$_4$]$^-$ ligand, as well as the bands due to the bidentate dianionic ligands. However for these it is difficult to do any assignment due to the complexity of the IR of the [B(pz)$_4$]$^-$ ligand. All the compounds show strong IR bands corresponding to ν(Re=O) in the range 947−968 cm^{-1}. These are within the accepted range for six-coordinate oxorhenium(V) compounds[25] and are shifted to lower energy than that for the corresponding dichloride [ReO{B(pz)$_4$}-Cl_2], which is found at 985 cm^{-1}.[18] The decrease observed in ν(Re=O) for compounds **1**−**3** compared to [ReO{B(pz)$_4$}Cl_2] is possibly due to the competition between the oxo ligand and the sulfur and oxygen donor atoms of the bidentate chelating ligands for bonding to the metal (see Experimental Section).

NMR Spectra. The ^{1}H NMR data for compounds **1**−**3** as well for the previously reported [ReO{B(pz)$_4$}Cl_2] (**4**) are presented in Table 2.

For **1** and **3** we observed three sets of resonances of relative

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Scheme 1. Synthesis of Re(V) Complexes with $[B(pz)_4]^-$

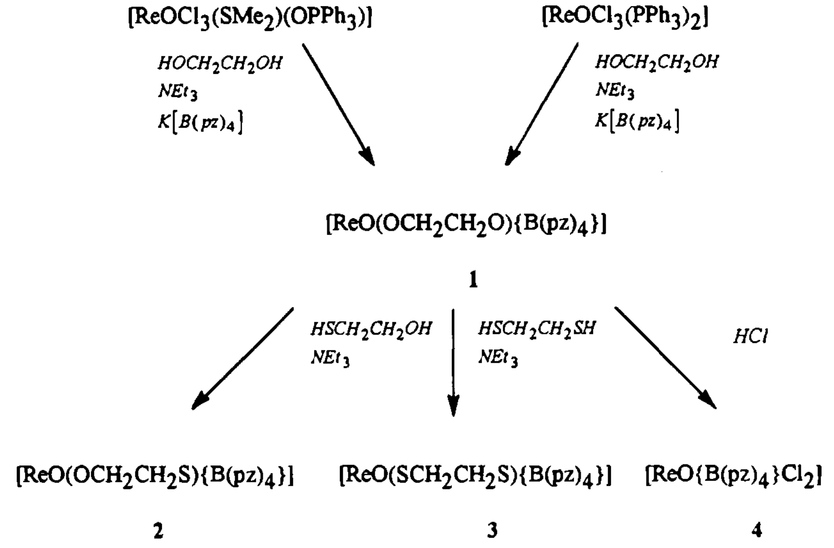

Table 2. ^{1}H NMR Data for Re(V) Complexes[a]

	B(pz)$_4$					
	H(4)			H(3)/H(5)		other ligands
complex	trans to O	trans to L[b]	free	trans to O/free	trans to L[b]	
1	5.99 (1H, s, br)	6.40 (2H, s, br)	6.63 (1H, s, br)	7.63 (1H, s, br)	7.57 (2H, s, br)	4.95 (2H, m)
				7.93 (1H, s, br)	8.05 (2H, s, br)	5.20 (2H, m)
				7.99 (1H, d, $^3J = 2.14$)		
				8.10 (1H, s, br)		
2[c]	5.92 (1H, s, br)	6.39 (1H, tr, $^3J = 2.1$)	6.63 (1H, s, br)	7.41 (1H, d, $^3J = 2.7$)		3.10 (1H, m)
		6.45 (1H, tr, $^3J = 2.1$)		7.64 (1H, s, br)		3.62 (1H, m)
				7.94 (2H, s, br)		5.24 (1H, m)
				7.95 (1H, s, br)		6.00 (1H, m)
				7.97 (1H, d, $^3J = 2.7$)		
				8.25 (1H, d, $^3J = 2.1$)		
				8.27 (1H, d, $^3J = 2.1$)		
3	5.82 (1H, s, br)	6.46 (2H, s, br)	6.63 (1H, s, br)	7.33 (1H, s, br)	7.82 (2H, d, $^3J = 2.4$)	3.98 (2H, m)
				7.68 (1H, d, $^3J = 2.4$)	8.55 (2H, s, br)	3.64 (2H, m)
				7.94 (1H, s, br)		
				7.97 (1H, d, $^3J = 2.1$)		
4[d]	6.00 (1H, t, $^3J = 2.4$)	6.56 (2H, t, $^3J = 2.4$)	6.67 (1H, dd, $^3J = 1.7$, $^4J = 2.4$)	7.53 (1H, dd, $^3J = 2.1$, $^4J = 0.6$)	8.32 (2H, dd, $^3J = 2.6$, $^4J = 0.8$)	
				7.96 (1H, d, $^3J = 1.5$)	7.70 (2H, dd, $^3J = 2.6$, $^4J = 0.8$)	
				7.98 (1 + 1H, m)		

[a] All the spectra were run in CDCl$_3$; data are given as chemical shifts δ (relative integral, multiplicity, coupling constant J in Hz). Abbreviations: s, singlet; d, doublet; t, triplet; dd, doublet of doublets; m, multiplet; br, broad. [b] L = OCH$_2$CH$_2$O (1), OCH$_2$CH$_2$S (2), SCH$_2$CH$_2$S (3), Cl$_2$ (4). [c] For this complex we did not assign any of the H(3) and H(5) resonances. [d] See ref 18.

intensities 2:1:1 for the protons of the pyrazolyl rings of the $[B(pz)_4]^-$ ligand, as previously observed for complex **4**.[18] For complex **2** due to the nature of the dianionic ligand all the pyrazolyl rings are magnetically different and we observed four sets of resonances of relative intensities 1:1:1:1 (two protons occasionally overlapped at 7.94 ppm). Although the X-ray structural analysis has only been undertaken for **1** (see below), it is reasonable to assume that in all the compounds the Re(V) is six-coordinate by the tridentate $[B(pz)_4]^-$, by the oxygen, and by the dianionic ligands, displaying approximately octahedral geometry. The pattern observed for the protons of the pyrazolyl rings is consistent with this coordination geometry and indicates a static behavior for these oxo compounds in solution. For **1** and **3** two multiplets of equal intensity were observed for the methylenic protons of the ethylene glycolate or of the ethylenedithiolate, respectively. This is consistent with the fact that the methylenic protons of the bidentate ligands are diastereotopic and that there is a mirror plane bisecting the glycolate ligand in **1** and the ethylenedithiolate ligand in **3**. This plane bisects also the two equatorial pyrazolyl rings and contains the boron and the rhenium atoms. For complex **2** the ^{1}H NMR spectrum presents four multiplets of equal intensity at 3.10, 3.62, 5.24, and 6.00 ppm and they are due to the four protons of the 2-mercaptoethanolate; this pattern is interpreted by considering that the methylenic protons of this ligand are diastereotopic and there is no mirror plane bisecting the 2-mercaptoethanolate, in contrast with compounds **1** and **3**.

As can be seen in Table 2 for compounds **1**–**3** most of the resonances due to the protons of the $[B(pz)_4]^-$ ligand lost their multiplicity, compared to [ReO{B(pz)$_4$}Cl$_2$], and this makes difficult their unambiguous assignment. However the resonances due to the H(4) protons are easily assigned as they appear in the same region of the spectrum for all the compounds and, in this family of complexes, their chemical shifts are relatively different from those observed for the H(3) and H(5) protons. The assignment is also possible by comparing with [ReO{B(pz)$_4$}Cl$_2$], and for this compound the multiplicity of the resonances facilitates the identification of the different protons; the assignment presented in Table 2 for the H(4) protons was also based on their relative intensities, on the fact that the protons of the free pyrazolyl ring are less affected by the nature of the dianionic ligands, and on the *trans* effect of the oxo oxygen. For compounds **1** and **3** the assignment for the protons H(3)/H(5) was based on the intensity of the resonances, but for

Table 3. Electrochemical Data[a] for Complexes [ReO(L){B(pz)$_4$}] (**1**–**4**) and [Re{B(pz)$_4$}Cl$_2$L] (**5**–**8**)

ligand	$E_{1/2}^{ox}$	$E_{1/2}^{red}$	ligand	$E_{1/2}^{ox}$	$E_{1/2}^{red}$
1 (OCH$_2$CH$_2$O)	1.08	−1.98[b]	**5** (PEt$_3$)	0.50	−1.02
2 (OCH$_2$CH$_2$S)	1.22[b,c]	−1.62	**6** (PEt$_2$Ph)	0.52	−1.04
3 (SCH$_2$CH$_2$S)	1.54[b]	−1.42	**7** (PEtPh$_2$)	0.54	−0.96
4 (Cl$_2$)	1.84	−0.70	**8** (PPh$_3$)	0.62	−0.86

[a] Values in V ± 20 mV *vs* SCE, measured (at 200 mV s^{-1}) at a Pt electrode in CH$_3$CN/0.2 M [NBu$_4$][BF$_4$], using as internal standard [Fe(η^5-C$_5$H$_5$)$_2$]$^{0/+}$ ($E_{1/2}^{ox}$ = 0.40 V *vs* SCE). [b] Irreversible (E_p^{ox}). [c] A second irreversible anodic wave is observed at a higher potential (E_p^{ox} = 2.02 V).

compound **2** no assignment was possible, due to the nature of the dianionic ligand (see above).

Electrochemical Studies. In acetonitrile, complexes [ReO(L){B(pz)$_4$}] (**1**–**4**) display by cyclic voltammetry one anodic process at values of potential which extend over a considerable range (1.08–1.84 V *vs* SCE; Table 3), as a consequence of the substantial variation of the electronic (and, possibly, stereochemical) characteristics of the ligand L. The higher oxidation potential measured for [ReO{B(pz)$_4$}Cl$_2$] (**4**), compared to the other Re(V) complexes, can result from the stronger net electron donor character of the ethanolate or thiolate ligands (in **1**–**3**) relative to chloride (in **4**) or to their chelating effect.

Within the chelating ligands, ethylene glycolate and ethylenedithiolate present the strongest and the weakest net electron donor ability (their complexes, **1** and **3**, exhibit the lowest and the highest oxidation potentials, 1.08 and 1.54 V, respectively), whereas the mixed 2-mercaptoethanolate ligand, as expected, shows an intermediate electron donor character (its complex, **2**, is oxidized at an intermediate potential, 1.22 V).

This trend points to a higher net electron donor ability of the oxygen over the corresponding sulfur ligands at these Re(V) complexes.

In contrast to compounds **1** and **4**, with anodic waves presenting a considerable degree of reversibility, compounds **2** and **3** display irreversible oxidation waves indicating that the oxidized forms are less stabilized by the thiolate than by the ethanolate ligands which are stronger net electron donors than the former ones (see below).

In all complexes but **4**, the first anodic wave occurs at a considerably lower potential than that measured for the free [B(pz)$_4$]$^-$ ligand, which exhibits two irreversible anodic waves at 1.86 V and 2.02 V, by cyclic voltammetry run in conditions similar to those used for the complexes, suggesting that such oxidation is mainly localized at the metal rather than at the ligand.

Controlled potential electrolysis performed at the first anodic wave of compounds **1**–**4** indicates that chemical reactivity is induced by electron transfer. For complex **4**, and to a minor extent for **3**, upon the first electron transfer, a multi-electron process is activated, as shown by the plot of the current intensity *versus* charge for the electrolysis; see insert in Figure 1.

Complexes **1**–**4** display cathodic waves within the range of potentials available, following the order of potentials reported above for the corresponding anodic processes (Table 3). All complexes, but **1**, display a single electron reversible reduction process, confirmed by controlled potential electrolysis on **3** and **4**. However, for these two compounds, chemical reactivity is induced by electron transfer and new species are detected by cyclic voltammetry at the electrolyzed solutions. Upon cathodic controlled potential electrolysis on **4**, a new reduction wave is detected at $E_{1/2}^{red}$ = −1.38 V, and in this reduction process, one electron per molecule is also involved. Chemical reduction of **4** with sodium naphthalenide was essayed, but no full characterization of the product was achieved.

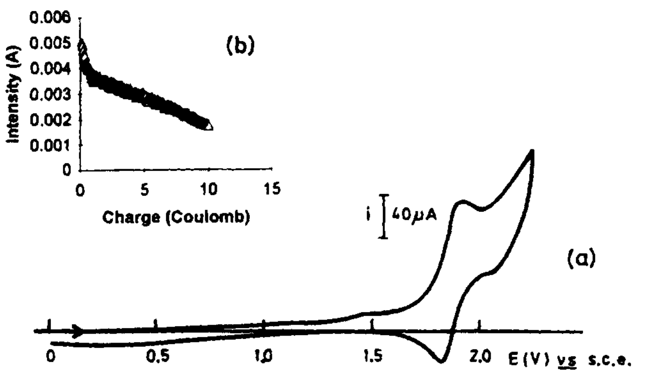

Figure 1. (a) Cyclic voltammogram of [ReO{B(pz)$_4$}Cl$_2$] (**4**) at 200 mV s^{-1}. (b) Plot of the variation of intensity of current *versus* charge, during electrolysis of **4** at its anodic wave.

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for [ReO(OCH$_2$CH$_2$O){B(pz)$_4$}]

molecule 1		molecule 2	
Re(1)–O(1)	1.677(15)	Re(2)–O(1a)	1.710(13)
Re(1)–O(2)	1.932(15)	Re(2)–O(2a)	1.913(14)
Re(1)–O(3)	1.913(15)	Re(2)–O(3a)	1.955(15)
Re(1)–N(1)	2.083(16)	Re(2)–N(1a)	2.227(18)
Re(1)–N(2)	2.098(17)	Re(2)–N(2a)	2.108(17)
Re(1)–N(3)	2.287(17)	Re(2)–N(3a)	2.101(17)
O(2)–C(2)	1.44(3)	O(2a)–C(2a)	1.49(2)
O(3)–C(3)	1.42(3)	O(3a)–C(3a)	1.44(2)
C(2)–C(3)	1.39(3)	C(2a)–C(3a)	1.49(3)
B–N	1.54(4)	B–N	1.53(3)
N–N	1.39(3)	N–N	1.38(3)
N–C	1.34(2)	N–C	1.35(3)
C–C	1.37(4)	C–C	1.38(3)
N–B–N	109(4)	N–B–N	109(3)
O(1)–Re(1)–O(2)	106.4(7)	O(1a)–Re(2)–O(2a)	107.5(6)
O(1)–Re(1)–O(3)	106.9(8)	O(1a)–Re(2)–O(3a)	104.9(7)
O(2)–Re(1)–O(3)	82.1(7)	O(2a)–Re(2)–O(3a)	83.2(6)
O(1)–Re(1)–N(1)	92.1(8)	O(1a)–Re(2)–N(1a)	163.3(6)
O(1)–Re(1)–N(2)	92.7(8)	O(1a)–Re(2)–N(2a)	88.1(7)
O(1)–Re(1)–N(3)	164.4(6)	O(1a)–Re(2)–N(3a)	93.3(7)
O(2)–Re(1)–N(1)	91.0(7)	O(2a)–Re(2)–N(1a)	87.5(6)
O(2)–Re(1)–N(2)	160.9(7)	O(2a)–Re(2)–N(2a)	164.3(6)
O(2)–Re(1)–N(3)	84.9(7)	O(2a)–Re(2)–N(3a)	88.2(7)
O(3)–Re(1)–N(1)	160.9(6)	O(3a)–Re(2)–N(1a)	83.5(7)
O(3)–Re(1)–N(2)	91.2(7)	O(3a)–Re(2)–N(2a)	94.0(6)
O(3)–Re(1)–N(3)	85.0(7)	O(3a)–Re(2)–N(3a)	161.5(6)
N(1)–Re(1)–N(2)	89.7(7)	N(1a)–Re(2)–N(2a)	76.8(7)
N(1)–Re(1)–N(3)	76.7(6)	N(1a)–Re(2)–N(3a)	79.7(7)
N(2)–Re(1)–N(3)	76.6(7)	N(2a)–Re(2)–N(3a)	89.8(7)

The redox behavior detected for these Re(V) oxo complexes is consistent with the formation of reactive Re(IV) and Re(VI) species by reduction or oxidation, respectively, but their instability precluded their identification.

Crystal Structure of [ReO(OCH$_2$CH$_2$O){B(pz)$_4$}] (1). The crystal structure of **1** consists of discrete molecular units; there are two independent molecules in the asymmetric unit. In both molecules the rhenium atom is six-coordinate and displays approximately octahedral geometry. Distortions from the regular octahedral geometry are observed in both molecules: the Re(1) and the Re(2) atoms are respectively 0.26 and 0.23 Å out of the mean equatorial plane toward the axial O(1) and O(1a) atoms; the bent axial O(1)–Re(1)–N(3) and O(1a)–Re(2)–N(1a) angles are 164.4(6) and 163.3(6)° for molecule 1 and 2, respectively. The above referred distortion can also be seen in the values of the other angles around Re (Table 4).

An ORTEP view of molecule 1 is shown in Figure 2, along with the numbering scheme for the atoms around Re(1). For molecule 2, the atoms around Re(2) are distinguished by the postscript A after the numbers of the atoms.

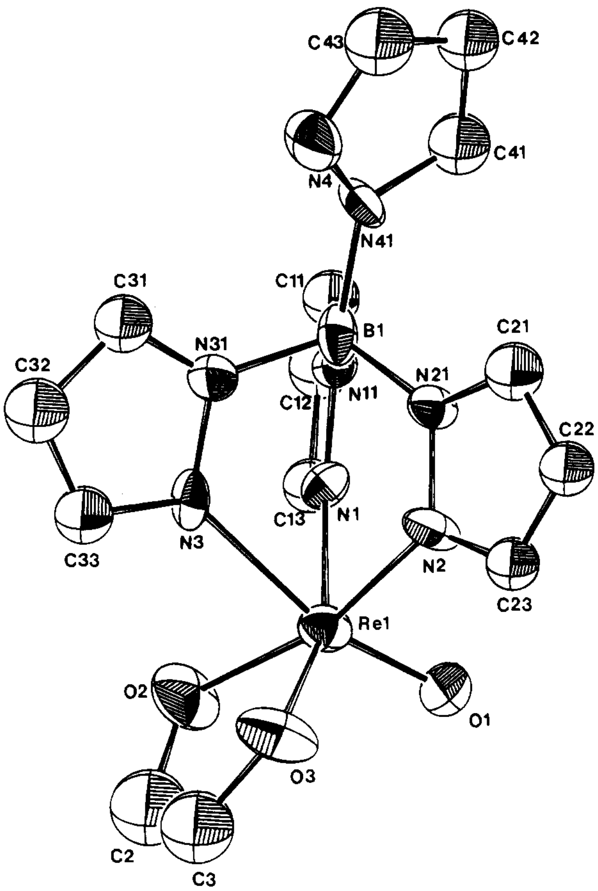

Figure 2. ORTEP drawing of molecule 1 of [ReO(OCH$_2$CH$_2$O)-{B(pz)$_4$}].

Selected bond distances and bond angles are listed in Table 4, and the final positional parameters are given in Table 5.

Table 5. Positional and Thermal Parameters for [ReO(OCH$_2$CH$_2$O){B(pz)$_4$}]

atom	*x*	*y*	*z*	U_{eq}/U_{iso} ($\times 10^3$ Å^2)
Re(1)	0.02713(5)	0.02614(4)	0.14723(4)	32.9(3)
Re(2)	0.23458(5)	0.24275(3)	0.59817(4)	27.8(2)
O(1)	−0.0022(10)	0.0845(6)	0.1021(6)	52(5)
O(2)	0.0127(10)	−0.0438(7)	0.0946(7)	58(6)
O(3)	0.1484(9)	0.0112(7)	0.1305(6)	56(6)
O(1a)	0.2556(8)	0.3075(5)	0.6385(5)	37(5)
O(2a)	0.2634(8)	0.1780(6)	0.6538(6)	40(5)
O(3a)	0.1143(8)	0.2218(6)	0.6213(6)	41(5)
N(1)	−0.0995(10)	0.0167(7)	0.1830(7)	29(5)
N(2)	0.0590(10)	0.0806(8)	0.2252(7)	38(6)
N(3)	0.0444(9)	−0.0402(6)	0.2290(8)	31(6)
N(4)	−0.0445(13)	0.0124(8)	0.4170(9)	58(8)
N(1a)	0.2146(11)	0.1755(7)	0.5214(7)	33(6)
N(2a)	0.1966(9)	0.2950(7)	0.5193(7)	34(6)
N(3a)	0.3623(9)	0.2374(7)	0.5611(7)	35(6)
N(4a)	0.2868(11)	0.2529(8)	0.3324(7)	46(6)
N(11)	−0.1223(9)	0.0191(7)	0.2469(7)	29(6)
N(21)	0.0134(10)	0.0774(7)	0.2811(7)	30(6)
N(31)	0.0103(10)	−0.0321(7)	0.2902(8)	35(5)
N(41)	−0.0843(10)	0.0342(7)	0.3641(7)	34(6)
N(11a)	0.2586(12)	0.1837(6)	0.4652(8)	45(7)
N(21a)	0.2397(10)	0.2940(7)	0.4596(7)	35(6)
N(31a)	0.3808(9)	0.2491(6)	0.4980(6)	25(5)
N(41a)	0.3391(10)	0.2398(7)	0.3819(7)	30(5)
C(2)[b]	0.0896(17)	−0.0559(12)	0.0568(14)	78(8)
C(3)[b]	0.1650(16)	−0.0266(12)	0.0775(12)	69(7)
C(2a)[b]	0.1890(14)	0.1538(10)	0.6919(11)	53(6)
C(3a)[b]	0.1178(14)	0.1988(10)	0.6853(10)	45(6)
C(11)[b]	−0.2080(13)	0.0111(9)	0.2531(10)	42(5)
C(12)[b]	−0.2438(15)	0.0034(9)	0.1947(10)	49(5)
C(13)[b]	−0.1739(12)	0.0042(9)	0.1516(10)	38(5)
C(21)[b]	0.0470(13)	0.1201(9)	0.3198(10)	44(6)
C(22)[b]	0.1111(13)	0.1514(9)	0.2890(9)	39(5)
C(23)[b]	0.1187(13)	0.1255(9)	0.2314(9)	37(5)
C(31)[b]	0.0318(13)	−0.0756(9)	0.3294(10)	44(6)
C(32)[b]	0.0869(15)	−0.1145(10)	0.2955(11)	54(6)
C(33)[b]	0.0896(14)	−0.0902(10)	0.2344(10)	44(6)
C(41)[b]	−0.1433(14)	0.0784(10)	0.3792(11)	50(6)
C(42)[b]	−0.1436(14)	0.0821(10)	0.4430(11)	49(6)
C(43)[b]	−0.0822(16)	0.0419(10)	0.4645(12)	62(7)
C(11a)[b]	0.2399(12)	0.1362(8)	0.4274(9)	32(5)
C(12a)[b]	0.1861(13)	0.0983(9)	0.4595(10)	44(6)
C(13a)[b]	0.1672(13)	0.1248(9)	0.5189(10)	42(5)
C(21a)[b]	0.2055(13)	0.3357(9)	0.4226(11)	47(6)
C(22a)[b]	0.1426(13)	0.3675(9)	0.4573(10)	42(5)
C(23a)[b]	0.1413(14)	0.3421(9)	0.5147(11)	47(6)
C(31a)[b]	0.4653(13)	0.2637(9)	0.4943(10)	44(5)
C(32a)[b]	0.5047(13)	0.2622(9)	0.5550(9)	43(5)
C(33a)[b]	0.4378(12)	0.2468(9)	0.5930(10)	38(5)
C(41a)[b]	0.4118(15)	0.2091(10)	0.3602(11)	58(6)
C(42a)[b]	0.4040(15)	0.2051(10)	0.2941(11)	53(6)
C(43a)[b]	0.3246(12)	0.2346(9)	0.2806(10)	35(5)
B(1)	−0.0506(15)	0.0252(10)	0.2957(11)	35(8)
B(1a)	0.3065(12)	0.2435(9)	0.4491(10)	22(7)

[a] U_{eq} = $^1/_3$ of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Isotropic temperature factors were used.

The mean Re═O bond length of 1.69(2) Å is comparable to the values found in other similar Re(V) complexes: 1.689(5) Å in [ReOCl(SC$_6$H$_5$){HB(pz)$_3$}],[2] 1.668(5) Å in [ReO(SC$_6$H$_5$)$_2${HB(pz)$_3$}],[2] 1.694(9) Å in [ReO(SCH$_2$CH$_2$S){HB(pz)$_3$}],[4] and at the short end range 1.654(7) Å in [ReO(C$_2$O$_4$){HB(pz)$_3$}]·0.5C$_6$H$_6$.[3] In complex **1** the Re—N bond *trans* to the oxo ligand is the longest Re—N bond, mean value 2.26(4) Å compared with the mean value of 2.10(1) Å for the other two Re—N bond distances *trans* to the ethylene glycolate ligand, and this is what has been observed for the above referred Re(V) complexes with the tripodal [HB(pz)$_3$]$^-$, as well as for [TcOCl$_2${HB(pz)$_3$}],[26] and is due to the *trans* effect of the oxo ligand. The bond lengths and angles within the [B(pz)$_4$]$^-$ ligand show no unusual features and compare well to the values found in the previously reported complex [ReO$_3${B(pz)$_4$}].[18] The mean Re—O bond distance in the glycolate ligand is 1.93(2) Å (ranges: molecule 1, 1.93(2)−1.91(2) Å; molecule 2, 1.91(1)−1.96(2) Å), and the mean O—Re—O angle is 83(1)°. These values compare with the corresponding values found in [ReO(OCH$_2$CH$_2$O)(η^5-C$_5$Me$_5$)] (1.965(2) Å; 80.2(1)°).[27] The [B(pz)$_4$]$^-$ ligand is more sterically demanding than η^5-C$_5$Me$_5$,[29] but the differences observed, which are within three standard deviations, may not be significant because of the quite large estimated standard deviations associated with the bond lengths and the bond angles in [ReO(OCH$_2$CH$_2$O){B(pz)$_4$}]. The ethylene glycolate is bound forming a five-membered ReO$_2$C$_2$ ring, twisted such that both carbon atoms lie on the same side of the Re—O(2)—O(3) plane toward the axial oxygen atom: in molecule 1, C(2) and C(3) lie by 0.43 and 0.40 Å, while, in molecule 2, C(2a) and C(3a) lie by 0.23 and 0.71 Å, respectively. These distortions can be caused by intramolecular repulsions since there are a few short intraligand contacts between the three nitrogens of the pyrazolyl rings and the oxygen atoms of the glycolate ligand (there are no short intermolecular contacts in the packing of the molecules in the unit cell). These short intraligand contacts come certainly because the oxo group has a large steric requirement, and this is manifested by the equatorial pyrazolyl rings bending away from the oxo ligand and toward the trans pyrazolyl ring and explains the large N(1)—Re(1)—N(2) and N(2a)—Re(2)—N(3a) angles of 89.7(7) and 89.8(7)° observed in molecules, 1 and 2, respectively (compared with the angles of N(1)—Re(1)—N(3)

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and N(2)—Re(1)—N(3) of 76.7(6) and 76.6(7)° for molecule 1 and the corresponding angles for molecule 2 of 76.8(7) and 79.7(7)°).

Re(III) Compounds. The complex $[ReO\{B(pz)_4\}Cl_2]$ is easily reduced by tertiary phosphines in refluxing toluene affording Re(III) phosphine adducts of the type $[Re\{B(pz)_4\}Cl_2L]$ in 60−70% yield (eq 1).

$$[ReO\{B(pz)_4\}Cl_2] + L \xrightarrow{\text{toluene}} [Re\{B(pz)_4\}Cl_2L] + O{=}L \qquad (1)$$

(L= PEt_3 (**5**), PEt_2Ph (**6**), $PEtPh_2$ (**7**), PPh_3 (**8**))

Reaction with PEt_3 is fast, and even at room temperature the sky-blue solution of compound **1** immediately changes its color upon addition of that phosphine. With all the other phosphines, only after refluxing the reaction mixture could we observe a significant change of the color. This behavior agrees with the nucleophilicity of the phosphines that increases in the order $PPh_3 < PEtPh_2 < PEt_2Ph < PEt_3$. When we tried the same reaction using an excess of $AsPh_3$, we did not observe any reduction and the unreacted materials were recovered.

We also tried to synthesize complex **8** by reacting $[ReCl_3(CH_3CN)(PPh_3)_2]$[20] with $K[B(pz)_4]$ in refluxing toluene, but the unreacted materials were also recovered, even after several hours of reflux. The strong interaction between the soft acid Re(III) and the soft PPh_3 is consistent with the low reactivity of $[ReCl_3(CH_3CN)(PPh_3)_2]$ with the tridentate nitrogen donor $K[B(pz)_4]$.

In polar organic solvents, such as CH_2Cl_2, THF, or CH_3CN, compounds **5** and **6** are very soluble, compound **8** is moderately soluble, and compound **7** is only slightly soluble. In aromatic solvents all the complexes are moderately soluble, except $[Re\{B(pz)_4\}Cl_2(PEtPh_2)]$ which is almost insoluble.

Several attempts have been made to reduce compounds **1**−**3** with excess of PEt_3 in refluxing toluene. However, even after several hours of reflux, compounds **1** and **2** were recovered, as indicated by ^1H NMR and IR spectroscopies, and compound **3** was reduced, as indicated by the absence of any band in the $\nu(Re{=}O)$ region, but we were not able to fully characterize the species formed. These results agree with the electrochemical studies, which have shown that $E_{1/2}^{red}$ increases in the order **1** < **2** < **3** < **4** (Table 3), *i.e.*, **4** is the easiest one to be reduced, followed by **3**.

The chemistry of Re(III) with tridentate monoanionic nitrogen donors is limited, and to the best of our knowledge only Davison *et al.*[1] has described the synthesis of the compound $[ReCl_2\{HB(pz)_3\}(PPh_3)]$. With the neutral nitrogen tridentate ligand 1,4,7-Me_3-1,4,7-triazacyclononane (Me_3-tacn), Mayer *et al.*[9] stabilized the cationic Re(V) compound $[ReOCl_2(Me_3\text{-tacn})]^+$, and by reduction with PPh_3 or PMe_3 he characterized the Re(III) phosphine oxide adduct $[ReCl_2(Me_3\text{-tacn})(OPR_3)]$ (R = Me or Ph). The impossibility of preparing the phosphine adduct of the complex presenting the ligand Me_3-tacn, compared to $[HB(pz)_3]^-$ or $[B(pz)_4]^-$, arises probably from the different electronic proprieties of these ligands. With pentamethylcyclopentadienyl (that has been several times compared to poly(pyrazolyl)borates of the type $[RB(pz)_3]^-$ (R = H or pz), as they are both six electron donors, monoanionic species, and occupy formally three coordination sites), the complex $[ReOCl_2(\eta^5\text{-}C_5Me_5)]$, which has been isolated by Hermman *et al.*,[8] can be reduced by PMe_3 yielding $[ReCl_2(\eta^5\text{-}C_5Me_5)(PMe_3)_2]$. However, the ligands $(C_5Me_5)^-$ and $[RB(pz)_3]^-$ led to complexes of Re(III) with different coordination numbers. Even taking into account that the steric demands of PMe_3 and the phosphines used in this work are different,[28] this result must probably be related to the different sizes and shapes of the ligands $[RB(pz)_3]^-$ and $(C_5Me_5)^-$. On the basis of a cone angle packing model, the evaluation of the steric crowding about the metal center in many structurally characterized compounds led to a new definition of steric coordination number, and according to this model, the ligands $[HBpz_3]^-$ and $(C_5Me_5)^-$ present steric coordination numbers 2.90 and 2.49, respectively.[29]

Infrared Spectra. The most significant feature of the IR spectra of compounds **5**−**8** is the presence of two medium intensity bands close to 300 cm^{-1} that we attribute to $\nu(Re{-}Cl)$. The nature of the coordinated phosphine does not affect significantly the energy associated with this vibration. In the IR spectra of complexes **5**−**8** were also found P—C active bands in the region *ca.* 700 cm^{-1}, characteristic of coordinated phosphines, as well as the characteristic bands of the $[B(pz)_4]^-$ ligand in the regions 1500−1000 and 850−750 cm^{-1}.

NMR Spectra. All the Re(III) complexes are paramagnetic as would be expected for a metal center with a d^4 configuration in an octahedral environment. However, the relaxation time of the rhenium is sufficiently short to permit observation of the ^1H NMR spectra with relatively narrow line widths. Table 6 presents the chemical shifts as well as the spin−spin splitting patterns for all the Re(III) compounds (**5**−**8**).

The patterns of the ^1H NMR spectra are quite similar, and we did not observe any significant influence of the nature of the phosphine in the chemical shifts of the protons of the pyrazolyl rings, the most notable difference being the loss of multiplicity of those resonances as we replace aliphatic by aromatic groups in the phosphine. The pattern observed for the protons of the pyrazolyl rings of the $[B(pz)_4]^-$ ligand is of the type 2:1:1, which is consistent with the octahedral symmetry found in the solid for compound **6**.

In the ^1H NMR spectrum of **5** all the protons of the pyrazolyl rings present a multiplicity which makes it possible to assign H(4) and H(3)/H(5). On the basis of this multiplicity and on the relative intensities, we can say that the H(3)/H(5) protons of the pyrazolyl rings *trans* to chloride resonate at −18.92 and −13.19 ppm and are the furthest upfield signals; H(4) of the same pyrazolyl rings resonates near the diamagnetic position at 5.86 ppm. On the basis of the intensities and multiplicities, we attributed the resonances at 4.96 and at 12.90 ppm to H(4) and the other resonances to H(3)/H(5). However, it is not possible to say if they are due to the free pyrazolyl ring or to the ring *trans* to phosphine. For compounds **6**−**8** the resonances due to the pyrazolyl rings lose partially or totally their multiplicities, but due to the similarity of the NMR spectra of these compounds and the spectrum of compound **5**, in terms of chemical shifts and relative intensities, the types of assignments previously made for **5** are also made for **6**−**8** (Table 6).

The assignment of the protons due to the phosphine ligands was based on their multiplicities and on their intensities. The protons due to the phenyl groups always appear at low field, compared with the resonances due to the ethyl groups, which in all compounds appear at high field. Relatively to the ethyl groups the most interesting feature is that for compound **6** we observed two resonances of equal intensity for the methylenic protons and only one resonance for the methyl protons of the same ligand; this pattern indicates that the methylenic protons are diastereotopic as the complex does not have any symmetry plane passing through the prochiral carbon.

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Table 6. ^{1}H NMR Data for [Re{B(pz)$_4$}Cl$_2$(L)]^a

complex	B(pz)$_4$ trans to Cl	B(pz)$_4$ trans to L^b or free	other ligands
5	−18.92 (2H, d, ^3J = 2.4)	−5.35 (1H, d, ^3J = 2.4)	3.06 (6H, br, C*H2*)
	−13.19 (2H, d, ^3J = 1.8)	4.96 (1H, t, ^3J = 2.1)	5.63 (9H, t, ^3J = 5.4, C*H3*)
	5.86 (2H, t, ^3J = 2.4)	5.16 (1H, d, ^3J = 2.4)	
		6.02 (1H, d, ^3J = 1.8)	
		11.06 (1H, d, ^3J = 1.8)	
		12.90 (1H, t, ^3J = 1.8)	
6	−18.83 (2H, d, ^3J = 2.4)	−5.07 (1H, d, ^3J = 3.0)	−0.52 (2H, m, C*H2*)
	−13.07 (2H, s, br)	4.96 (1H, s, br)	3.66 (2H, m, C*H2*)
	5.49 (2H, d, ^3J = 1.8)	5.19 (1H, t, ^3J = 3.9)	4.76 (6H, m, br, C*H3*)
		6.02 (1H, d, ^3J = 1.8)	8.64 (1H, t, ^3J = 6.6, *p-H*)
		10.26 (1H, s, br)	8.93 (2H, t, ^3J = 6.0, *m-H*)
		12.71 (1H, s, br)	14.85 (2H, s, br, *o-H*)
7	−18.59 (2H, s, br)	−4.10 (1H, s, br)	−3.77 (2H, m, C*H2*)
	−14.49 (2H, s, br)	5.09 (1H, s, br)	3.94 (3H, m C*H3*)
	5.02 (2H, s, br)	5.46 (1H, s, br)	8.75 (2H, t, ^3J = 6.9, *p-H*)
		6.15 (1H, s, br)	9.55 (4H, t, ^3J = 7.5, *m-H*)
		12.00 (1H, s, br)	14.04 (4H, s, br, *o-H*)
		12.94 (1H, s, br)	
8	−18.44 (2H, s, br)	−4.21 (1H, s, br)	8.09 (3H, t, ^3J = 7.5, *p-H*)
	−14.16 (2H, s, br)	5.06 (1H, s, br)	8.59 (6H, t, ^3J = 7.5, *m-H*)
	5.52 (2H, s, br)	5.33 (1H, s, br)	10.91 (6H, s, br, *o-H*)
		6.18 (1H, s, br)	
		9.69 (1H, s, br)	
		12.71 (1H, s, br)	

^{a} All the spectra were run in CDCl$_3$; data are given as chemical shifts δ (relative integral, multiplicity, coupling constant J in Hz). Abbreviations: s, singlet; d, doublet; t, triplet; dd, doublet of doublets; m, multiplet; br, broad. ^{b} L = PEt$_3$ (**5**), PEt$_2$Ph (**6**), PEtPh$_2$ (**7**), and PPh$_3$ (**8**).

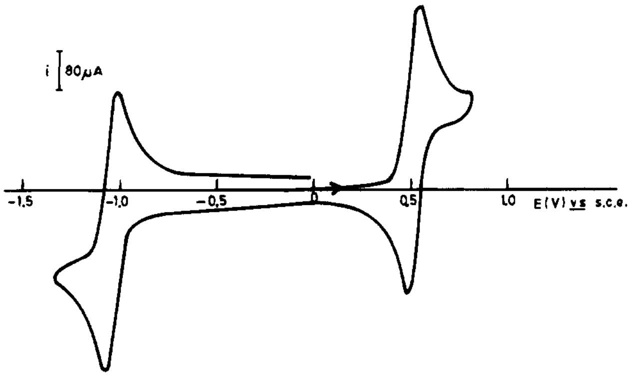

Figure 3. Cyclic voltammogram obtained for [Re{B(pz)$_4$}Cl$_2$(PEt$_2$Ph)] at 200 mV s^{-1}.

^{31}P NMR spectra were recorded for compounds **5**−**8**, but only for **5** and **6** could we observe broad resonances at −98.7 and −100.2 ppm, respectively. For **7** and **8** no resonances were observed; this result probably indicates that these two compounds have a higher magnetic moment than **5** and **6**, and this probably also explains the line broadening observed in their ^{1}H NMR spectra (Table 6).

Electrochemical Studies. The electrochemical behavior of compounds **5**−**8** was studied using conditions similar to those used for Re(V) complexes. They display, by cyclic voltammetry, one electron reversible diffusion-controlled oxidation and reduction processes, as indicated by Figure 3 for [Re{B(pz)$_4$}Cl$_2$(PEt$_2$Ph)] (**6**).

The oxidation potential (0.50−0.62 V range) of these Re(III) complexes is, as expected, substantially lower than that observed for the Re(V) compounds (see above) and follows the order of the electron donor character of the phosphine ligand: i.e., $E_{1/2}^{\mathrm{ox}}$ increases with a decrease of the net electron donor ability of that ligand. Moreover, for sterically hindered compounds there is often an influence of the steric characteristics of the ligands on the redox behavior and we observed for this family of Re(III) compounds that the oxidation potential also appears to correlate with the Tolman's cone angle of the respective phosphine (θ).[28]

The reduction potential values do not show such a good correlation when plotted versus (θ), in what concerns L = PEt$_2$Ph, but they show a good correlation with the electronic parameter (E_r),[28] thus suggesting that the electronic characteristics of the phosphines have a predominant influence on the reduction potentials of the complexes.

However we are aware that these conclusions should be taken cautiously since the redox potentials of the compounds **5**−**8** fall in a narrow range of values (Table 3).

From the electrochemical behavior observed for Re(III) complexes we can also say that on the cyclic voltammetry time scale electron transfer to or from the complexes is conveniently accommodated by the metal center and no chemical reaction is induced.

$$\mathrm{Re(II)} \underset{-1e-}{\overset{+1e-}{\rightleftharpoons}} \mathrm{Re(III)} \underset{+1e-}{\overset{-1e-}{\rightleftharpoons}} \mathrm{Re(IV)}$$

Crystal Structure of [Re{B(pz)$_4$}Cl$_2$(PEt$_2$Ph)] (6). An ORTEP diagram of the structure is shown in Figure 4. Selected bond distances and angles are listed in Table 7, and the final positional parameters are given in Table 8.

The crystal structure consists of monomeric molecules in which the rhenium atom is six-coordinate and displays a slightly distorted octahedral geometry. The rhenium, the two chlorides, and the two equatorial nitrogen atoms are approximately in a plane, with a maximum deviation of the Re atom of 0.10 Å toward the P atom. The slight distortion from the regular octahedral geometry can also be seen in the values of the angles around the rhenium atom presented in Table 7.

Bond length comparison with other related Re(III) complexes is difficult since no structures are known involving poly(pyrazolyl)borates or other monoanionic tridentate nitrogen donors and phosphines. However, the Re−P bond distance of 2.422(4) Å is in the usual range for low-valent complexes of technetium and rhenium[31,32] and can be compared with the value

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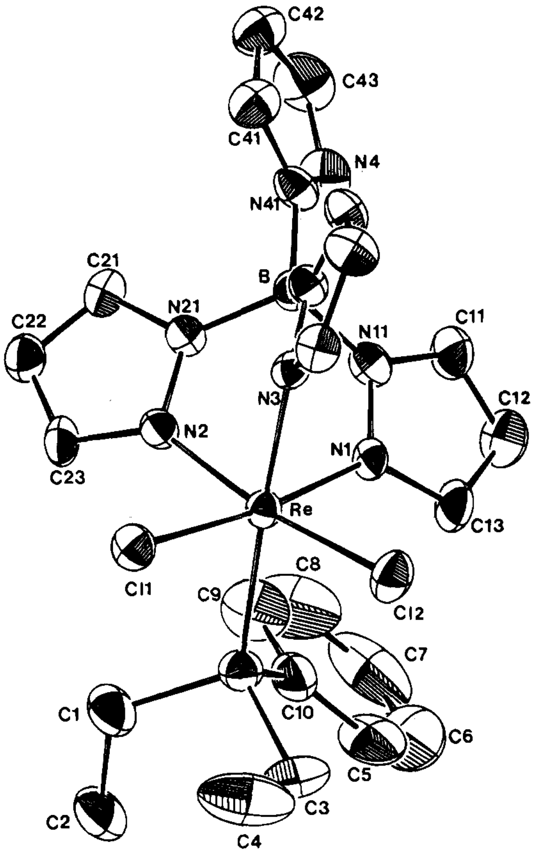

Figure 4. ORTEP drawing of $[Re\{B(pz)_4\}Cl_2(PEt_2Ph)]$.

Table 7. Selected Bond Lengths (Å) and Bond Angles (deg) for $[Re\{B(pz)_4\}Cl_2(PEt_2Ph)]$

Re—Cl(1)	2.373(4)	Re—N(1)	2.095(8)
Re—Cl(2)	2.365(4)	Re—N(2)	2.090(8)
Re—P	2.422(4)	Re—N(3)	2.112(8)

B—N(11)	1.54(1)	B—N(21)	1.56(1)	B—N(31)	1.55(1)
N(1)—N(11)	1.36(1)	N(2)—N(21)	1.38(1)	N(3)—N(31)	1.38(1)
N(1)—C(13)	1.39(1)	N(2)—C(23)	1.34(1)	N(3)—C(33)	1.34(1)
N(11)—C(11)	1.38(1)	N(21)—C(21)	1.36(1)	N(31)—C(31)	1.37(1)
C(11)—C(12)	1.34(2)	C(21)—C(22)	1.38(1)	C(31)—C(32)	1.36(1)
C(12)—C(13)	1.38(1)	C(22)—C(23)	1.38(1)	C(32)—C(33)	1.38(1)
B—N(41)	1.51(1)	P—C(1)	1.82(1)	C(5)—C(6)	1.44(2)
N(4)—N(41)	1.36(1)	P—C(3)	1.83(1)	C(5)—C(10)	1.38(2)
N(4)—C(43)	1.33(1)	P—C(10)	1.82(1)	C(6)—C(7)	1.40(2)
N(41)—C(41)	1.36(1)	C(1)—C(2)	1.53(2)	C(7)—C(8)	1.37(2)
C(41)—C(42)	1.38(1)	C(3)—C(4)	1.51(2)	C(8)—C(9)	1.38(2)
C(42)—C(43)	1.41(2)	C(5)—C(6)	1.44(2)	C(9)—C(10)	1.40(2)

Cl(1)—Re—Cl(2)	94.0(2)	Cl(2)—Re—N(3)	87.9(3)
Cl(1)—Re—P	89.8(2)	P—Re—N(1)	95.3(3)
Cl(2)—Re—P	89.7(2)	P—Re—N(2)	98.4(3)
Cl(1)—Re—N(1)	173.1(2)	P—Re—N(3)	177.3(2)
Cl(1)—Re—N(2)	89.0(2)	N(1)—Re—N(2)	85.7(2)
Cl(1)—Re—N(3)	91.7(3)	N(1)—Re—N(3)	83.5(3)
Cl(2)—Re—N(1)	90.7(3)	N(2)—Re—N(3)	83.9(3)
Cl(2)—Re—N(2)	171.4(2)	Re—P—C(1)	117.0(4)
N(11)—B—N(21)	107.9(7)	Re—P—C(3)	116.4(4)
N(11)—B—N(31)	106.5(7)	Re—P—C(10)	113.0(4)
N(21)—B—N(31)	107.7(7)	C(10)—P—C(1)	101.2(5)
N(41)—B—N(11)	114.4(8)	C(10)—P—C(3)	104.0(6)
N(41)—B—N(21)	108.5(7)	P—C(1)—C(2)	115.5(8)
N(41)—B—N(31)	111.6(8)	P—C(3)—C(4)	113.0(10)

Table 8. Positional and Thermal Parameters for $[Re\{B(pz)_4\}Cl_2(PEt_2Ph)]$

atom	x	y	z	$U_{eq}{}^{a}$ ($\times 10^3$ Å^2)
Re	0.23992(2)	0.06760(2)	0.20157(2)	26.4(1)
Cl(1)	0.1294(1)	0.0461(2)	0.0856(1)	37.8(6)
Cl(2)	0.1793(2)	0.2424(2)	0.2441(1)	43.3(6)
P	0.1319(2)	−0.0249(2)	0.2966(1)	36.0(6)
N(1)	0.3499(4)	0.0810(5)	0.2934(4)	29(2)
N(2)	0.3111(4)	−0.0734(5)	0.1580(4)	30(2)
N(3)	0.3341(4)	0.1548(5)	0.1227(4)	28(2)
N(4)	0.6240(5)	−0.0367(6)	0.2293(5)	47(3)
N(11)	0.4420(5)	0.0601(5)	0.2757(4)	34(2)
N(21)	0.4082(4)	−0.0699(5)	0.1528(4)	29(2)
N(31)	0.4299(4)	0.1348(5)	0.1277(4)	29(2)
N(41)	0.5689(4)	0.0120(5)	0.1674(5)	35(2)
C(1)	0.0740(7)	−0.1507(9)	0.2560(6)	56(3)
C(2)	0.0053(9)	−0.2059(11)	0.3175(8)	80(5)
C(3)	0.0338(8)	0.0593(9)	0.3353(7)	59(4)
C(4)	−0.0358(8)	0.0917(12)	0.2643(11)	96(6)
C(5)	0.1689(9)	−0.0386(12)	0.4760(7)	74(5)
C(6)	0.2191(12)	−0.0827(14)	0.5500(8)	92(6)
C(7)	0.2903(11)	−0.1614(14)	0.5359(9)	100(6)
C(8)	0.3114(9)	−0.1969(14)	0.4546(9)	99(6)
C(9)	0.2612(8)	−0.1555(10)	0.3843(8)	70(4)
C(10)	0.1891(7)	−0.0768(8)	0.3946(6)	47(3)
C(11)	0.4969(7)	0.0805(8)	0.3482(6)	49(3)
C(12)	0.4407(7)	0.1157(9)	0.4107(5)	54(3)
C(13)	0.3490(7)	0.1143(8)	0.3792(5)	44(3)
C(21)	0.4393(6)	−0.1657(6)	0.1167(5)	36(2)
C(22)	0.3623(6)	−0.2313(7)	0.0965(6)	41(3)
C(23)	0.2852(6)	−0.1719(7)	0.1238(6)	42(3)
C(31)	0.4757(6)	0.2181(6)	0.0858(5)	37(2)
C(32)	0.4097(6)	0.2902(7)	0.0542(6)	43(3)
C(33)	0.3229(6)	0.2498(7)	0.0785(5)	35(2)
C(41)	0.6137(7)	0.0139(7)	0.0914(6)	45(3)
C(42)	0.7021(7)	−0.0313(8)	0.1039(7)	49(3)
C(43)	0.7045(7)	−0.0615(8)	0.1919(8)	64(4)
B	0.4658(6)	0.0346(7)	0.1818(6)	30(3)

[a] U_{eq} = $^1/_3$ of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

of 2.401(6) Å for Re—P (trans to Cl) in the octahedral *mer*-$[ReCl_3(PMe_2Ph)_3]$[33] but it is shorter than the values for Re—P (*trans* to P) in the same compound (2.458(6) Å). The Re—P bond distance in **6** is also shorter than the corresponding distances in the octahedral compounds $[ReCl_3(PPh_3)_2(MeCN)]$ (2.47 and 2.48 Å)[34] and $[ReCl_2(p\text{-}MeC_6H_4N\text{-}N\text{-}N\text{-}C_6H_4Me\text{-}p)(PPh_3)_2]$ (2.51(1) and 2.50(1) Å).[7]

The Re—N bond distance *trans* to the phosphine ligand is not significantly longer than the two equatorial Re—N bond distances, and so the three Re—N bond distances can be considered equivalent, with a mean value of 2.10(1) Å. This value can be compared with the mean value of the equatorial Re—N bond distances in the Re(V) glycolate complex **1** (mean value, 2.10(1) Å).

The two Re—Cl distances are similar, mean value of 2.37(1) Å, and are in the range expected for the equatorial Re—Cl distances in Re(III) complexes.[33]

There are a few short intraligand contacts (Cl(1)···Cl(2) = 3.47 Å, P···Cl(1) = 3.39 Å, P···Cl(2) = 3.38 Å, Cl(1)···N(2) = 3.13 Å, Cl(1)···N(3) = 3.22 Å, Cl(2)···N(1) = 3.18 Å, Cl(2)···N(3) = 3.11 Å) which corroborate the steric crowding about the metal center, showing how the $[B(pz)_4]^-$, the PEt_2Ph, and the two chloride ligands can pack efficiently around the Re atom.

Acknowledgment. A.P. and I.S. thank Prof. J. Ascenso, from CQE, IST, for use of the ^1H NMR facilities and for his help with running the spectra.

Supplementary Material Available: Tables of anisotropic thermal parameters, calculated hydrogen atom positions, complete bond distances and angles, and equations of mean-least-squares planes and an ORTEP drawing of molecule 2 of **1** (7 pages). Ordering information is given on any current masthead page.

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