Reactivity of a Tetrakis(pyrazolyl)borate Oxorhenium Complex

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Received September 7, 1994[⊗]

The rhenium(VII) compound $[ReO_3\{B(pz)_4\}]$ (**1**) is easily reduced by triphenylphosphine in tetrahydrofuran providing, in 60% yield, a very reactive oxo complex of Re that, on the basis of its reactivity, we tentatively formulate as "$[ReO(\mu\text{-}O)\{B(pz)_4\}]_2$" (**2**). This air-stable compound is insoluble in tetrahydrofuran and water and slightly soluble in chloroform and dichloromethane and is a versatile material for the synthesis of monomeric compounds of Re(V): $[ReO\{B(pz)_4\}Cl_2]$ (**3**), $[ReO(L)\{B(pz)_4\}]$ (L = OCH_2CH_2O (**4**), $C_6H_4O_2$ (**5**)), $[ReO\{B(pz)_4\}(OR)_2]$ (R = Me (**6**), Et (**7**), Pr^i (**8**), Ph (**9**)), $[ReO\{B(pz)_4\}(SPh)_2]$ (**10**), and $[ReO(\eta^2\text{-}OCONPh)\{B(pz)_4\}]$ (**11**). Compounds **3**–**11** were characterized by elemental analyses, IR and ^1H NMR spectroscopies, and, in the case of compounds **9** and **10**, X-ray crystallography. Compound **9** crystallizes in the triclinic space group $P\bar{1}$ with cell parameters $a = 9.611(4)$ Å, $b = 11.808(3)$ Å, $c = 12.400(5)$ Å, $\alpha = 88.69(2)°$, $\beta = 69.61(3)°$, $\gamma = 74.01(3)°$, $V = 1264(1)$ Å^3, $Z = 2$, and $R = 0.031$, $R_w = 0.037$ for 5226 reflections ($F_o > 3\sigma(F_o)$); compound **10** also crystallizes in the triclinic space group $P\bar{1}$ with cell parameters $a = 10.563(3)$ Å, $b = 11.768(2)$ Å, $c = 12.149(3)$ Å, $\alpha = 94.10(2)°$, $\beta = 100.50(2)°$, $\gamma = 92.44(2)°$, $V = 1479(1)$ Å^3, $Z = 2$, and $R = 0.043$, $R_w = 0.051$ for 4721 reflections ($F_o > 3\sigma(F_o)$). For all the compounds the characterization includes laser desorption and electron impact Fourier transform ion cyclotron resonance mass spectrometry. For complex **2** variable-temperature ^1H NMR studies are also described.

Introduction

The total or partial deoxygenation of oxometal centers by Lewis bases, with the simultaneous reduction of the metal and sometimes with formation of oxo-bridged dimers, is a well-known process.[1] Typical examples of dimerization are the oxorhenium(V) compound $[ReO(\mu\text{-}O)(\eta^5\text{-}C_5Me_5)]_2$, obtained by reduction of $[ReO_3(\eta^5\text{-}C_5Me_5)]$ with triphenylphosphine, and the compound $[ReO(\mu\text{-}O)(tacn)]_2^{2+}$ (tacn = 1,4,7-triazacyclononane), obtained by reduction of $[ReO(OCH_2CH_2O)(tacn)]^+$ with zinc amalgam or by reduction of $(ReO_3(tacn))^+$ with triphenylphosphine.[2-4]

As part of our ongoing studies on the chemistry of Re(VII), Re(V), and Re(III) with the ligand $[B(pz)_4]^-$,[5,6] we have previously described the compound $[ReO\{B(pz)_4\}Cl_2]$ (**3**), and one of the synthetic methods used was the reduction of $[ReO_3\{B(pz)_4\}]$ (**1**) with triphenylphosphine in the presence of trimethylsilyl chloride.[5] For better insight regarding possible intermediates of this reaction, we studied the reduction of compound **1** in tetrahydrofuran using stoichiometric amounts of triphenylphosphine, but in the absence of trimethylsilyl chloride. This reaction leads to a very reactive compound that we tentatively formulate as "$[ReO(\mu\text{-}O)\{B(pz)_4\}]_2$" (**2**). Using this compound as starting material, we have investigated the possibility of preparing the previously described complexes $[ReO\{B(pz)_4\}Cl_2]$ (**3**)[5] and $[ReO(OCH_2CH_2O)\{B(pz)_4\}]$ (**4**),[6] as well as other new oxorhenium compounds with the ligand $[B(pz)_4]^-$. We now report the synthesis and characterization of compound **2** and of the new compounds $[ReO(C_6H_4O_2)\{B(pz)_4\}]$ (**5**), $[ReO\{B(pz)_4\}(OR)_2]$ (R = Me (**6**), Et (**7**), Pr^i (**8**), Ph (**9**)), $[ReO\{B(pz)_4\}(SPh)_2]$ (**10**), and $[ReO(\eta^2\text{-}OCONPh)\{B(pz)_4\}]$ (**11**) prepared by reacting **2** with cathecol, alcohols, thiophenol, and phenyl isocyanate, respectively.

Experimental Section

General Procedures. All reactions were carried under an argon atmosphere, using freshly distilled solvents which were dried and deoxygenated by standard methods.[7] $[ReO_3\{B(pz)_4\}]$ (**1**) was prepared as previously described.[5] PPh_3 was recrystallized from ethanol and dried under vacuum at 70 °C. Me_3SiCl was dried over P_2O_5 and deoxygenated prior to use. Phenol and catechol were sublimated prior to use. Thiophenol was dried over Na_2SO_4 and distilled under reduced pressure. All the other reactants were used as supplied.

^1H NMR spectra were recorded on a General Electric 300 MHz instrument and were referenced internally using the residual solvent resonance relative to tetramethylsilane. The FTICR mass spectra were obtained by laser desorption (LD) and electron impact (EI), with an Extrel (Waters) FTMS 2001-DT instrument, following a published technique.[5] IR spectra were recorded as KBr pellets on a Nicolet 5DXC FT-IR spectrometer. Carbon, hydrogen, and nitrogen analyses were performed on a Perkin-Elmer automatic analyzer.

Synthesis and Characterization of "$[ReO(\mu\text{-}O)\{B(pz)_4\}]_2$" (2). To a suspension of $[ReO_3\{B(pz)_4\}]$ (**1**) (1.2 g, 2.30 mmol) in THF (50 mL) was added, at room temperature, a solution of PPh_3 (640 mg, 2.40 mmol) in THF. The original white suspension turned immediatly to a dark brown solution. The reaction mixture was stirred overnight, and a significant amount of a dark green insoluble material was formed. The dark green solid was isolated, washed with THF and *n*-hexane, and dried under vacuum (680 mg, 1.36 mmol of Re, yield 60%).

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1995.

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0020-1669/95/1334-2113$09.00/0

Anal. Calcd for $C_{24}H_{24}B_2N_{16}O_4Re_2$: C, 29.0; N, 22.5; H, 2.4. Found: C, 29.9; N, 21.8; H, 2.5. IR (KBr, ν (cm^{-1})): 3132 m, 1501 m, 1440 m, 1406 s, 1379 s, 1308 s, 1259 w, 1210 s, 1183 s, 1114 m, 1091 w, 1072 s, 1064 s, 951 s (ν (Re = O)), 920 m, 853 s, 816 w, 794 s, 757 s, 646 s (ν(Re−O−Re)), 614 m, 563 m (ν(Re−O−Re)), 400 m, 355 w.

Synthesis of [ReO{B(pz)$_4$}Cl$_2$] (3). To a suspension of **2** (100 mg, 0.2 mmol of Re) in THF was added a 10:1 excess of $(CH_3)_3SiCl$. The clear blue solution obtained, after 2 h at room temperature, was evaporated to dryness, yielding a blue oil; this oil was washed with *n*-hexane and dried under vacuum, providing 90 mg (0.16 mmol) of a blue microcrystalline solid identified by infrared and ^{1}H NMR spectroscopies as the previously described complex **3** (yield 80%).[5,6]

Synthesis of [ReO(OCH$_2$CH$_2$O){B(pz)$_4$}] (4). This complex was obtained by reacting 100 mg (0.20 mmol of Re) of **2** and 15 mg (0.24 mmol) of ethylene glycol in CH_2Cl_2. A clear violet solution was obtained after 30 min at room temperature. This solution was taken to dryness, and the violet solid obtained was washed with water and dried under vacuum, yielding 85 mg (0.16 mmol, yield 80%) of a violet microcrystalline solid identified by infrared and ^{1}H NMR spectroscopies as **4**.[6]

Synthesis and Characterization of [ReO(C$_6$H$_4$O$_2$){B(pz)$_4$}] (5). To a suspension of **2** (100 mg, 0.2 mmol of Re) in CH_2Cl_2 was added 22 mg (0.2 mmol) of catechol dissolved in the minimum volume of CH_2Cl_2. The mixture turned almost immediatly to an orange brown solution. The CH_2Cl_2 was evaporated under vacuum, and the orange oil obtained was washed with *n*-hexane. After drying under vacuum, 95 mg (0.16 mmol) of **5** was obtained, as a microcrystalline orange-brown solid (yield 80%).

Anal. Calcd for $C_{18}H_{16}BN_8O_3Re$: C, 36.7; N, 19.0; H, 2.9. Found: C, 37.2; N, 18.3; H, 2.8. IR (KBr, ν (cm^{-1})): 3130 m, 3064 vw, 3010 vw, 2944 vw, 1505 s, 1470 s, 1442 m, 1408 s, 1389 m, 1381 m, 1309 s, 1236 s, 1209 s, 1183 m, 1110 s, 1075 s,1061 s, 1049 w, 1003 w, 974 s (ν(Re=O)), 921 m, 871 w, 858 s, 831 w, 802 s, 764 s, 666 s, 650 w, 615 m, 551 w, 453 w, 402 m, 371 w, 350 w, 310 m, 272 w. FTICR/MS (*m/z* referenced to the species with ^{187}Re and ^{11}B; relative abundance in parentheses): EI(+) (180 °C, 8 eV) 590 (100%) (M), 523 (5%) (M − pz), 110 (65%) (H_2cat); EI(−) (180 °C, 70 eV) 590 (100%) (M), 522 (4%) (M − pzH), 378 (10%) (M − B(pz)$_3$).

Synthesis and Characterization of [ReO{B(pz)$_4$}(OMe)$_2$] (6). At room temperature, 100 mg (0.2 mmol of Re) of **2** was added to 20 mL of methanol. After 30 min of stirring, a clear deep blue solution was obtained. The methanol was evaporated under vacuum, and the blue oil residue obtained was washed with *n*-hexane. After drying under vacuum, a microcrystalline blue solid was obtained, formulated as **6** (90 mg, 0.17 mmol, 85%).

Anal. Calcd for $C_{14}H_{18}BN_8O_3Re$: C, 30.9; N, 20.6; H, 3.3. Found: C, 30.4; N, 19.9; H, 3.5. IR (KBr, ν (cm^{-1})): 3139 m, 2894 m, 2790 m, 1500 m, 1442 w, 1430 w, 1408 s, 1388 m, 1308 s, 1263 w, 1207 m, 1184 w, 1111 m, 1068 m, 1024 s, 965 s (ν(Re=O)), 919 w, 857 s, 811 s, 796 s, 774 s, 763 s, 669 w, 616 m, 559 s, 532 s, 396 w, 300 w. FTICR/MS (*m/z* referenced to the species with ^{187}Re and ^{11}B; relative abundance in parentheses): EI(+) (180 °C, 8 eV) 544 (100%) (M), 514 (30%) (M − OCH_2), 512 (20%) (M − HOMe), 482 (17%) (M − 2OMe), 446 (6%) (M − OCH_2, pzH); EI(−) (180 °C, 70 eV) 544 (6%) (M), 514 (12%) (M − OCH_2), 482 (8%) (M − 2OMe), 279 (100%) (B(pz)$_4$).

Synthesis and Characterization of [ReO{B(pz)$_4$}(OEt)$_2$] (7). This compound was synthesized and purified according to the procedure described for **6**. The only difference was that this reaction was complete only after 12 h. Starting with 100 mg (0.2 mmol of Re) of **2**, we obtained 90 mg (0.16 mmol) of **7**, as a microcrystalline deep blue solid (yield 80%).

Anal. Calcd for $C_{16}H_{22}BN_8O_3Re$: C, 33.6; N, 19.6; H, 3.9. Found: C, 33.4; N, 19.2; H, 4.0. IR (KBr, ν (cm^{-1})): 3120 m, 2962 m, 2924 m, 2859 m, 1516 w, 1501 m, 1459 w, 1439 m, 1407 s, 1389 s, 1350 w, 1314 s, 1302 s, 1260 w, 1240 w, 1208 s, 1182 w, 1152 w, 1109 s, 1092 s, 1073 s, 1059 s, 1043 s, 995 w, 960 s (ν(Re=O)), 918 w, 907 m, 887 m, 871 w, 856 s, 833 w, 812 s, 792 s, 781 s, 762 s, 674 w, 665 w, 653 w, 619 m, 551 s, 477 w, 398 w, 366 w. FTICR/MS (*m/z* referenced to the species with ^{187}Re and ^{11}B; relative abundance in parentheses): EI(+) (180 °C, 8 eV) 572 (100%) (M), 528 (20%) (M − OC_2H_4), 526 (45%) (M − HOEt), 482 (12%) (M − 2OEt), 460 (5%) (M − OC_2H_4, pzH); EI(−) (180 °C, 70 eV) 572 (5%) (M), 528 (9%) (M − OC_2H_4), 482 (5%) (M − 2OEt), 279 (100%) (B(pz)$_4$).

Synthesis and Characterization of [ReO{B(pz)$_4$}(OPr^i)$_2$] (8). This compound was synthesized and purified using the same procedure described for **6** and **7**. However, to obtain compound **8**, we needed to reflux the mixture for 2 h. Starting with 100 mg (0.2 mmol of Re) of **2**, we obtained 90 mg (0.15 mmol) of **8**, as a green microcrystalline solid (yield 75%).

Anal. Calcd for $C_{18}H_{26}BN_8O_3Re$: C, 36.1; N, 18.7; H, 4.3. Found: C, 34.9; N, 17.5; H, 4.3. IR (KBr, ν (cm^{-1})): 3134 w, 2960 s, 2920 w, 1503 m, 1440 w, 1407 s, 1388 m, 1360 w, 1315 s, 1301 s, 1262 m, 1210 s, 1184 w, 1165 w, 1109 s, 1069 s, 952 s (ν(Re=O)), 920 w, 856 m, 842 w, 810 m, 795 s, 760 s, 648 m, 636 m, 615 m, 541 w, 466 w, 393 w. FTICR/MS (*m/z* referenced to the species with ^{187}Re and ^{11}B; relative abundance in parentheses): EI(+) (180 °C, 8 eV) 600 (85%) (M), 542 (28%) (M − OC_3H_6), 540 (100%) (M − HOPr^i), 482 (7%) (M − 2OPr^i); EI(−) (180 °C, 70 eV) 600 (20%) (M), 542 (15%) (M − OC_3H_6), 482 (4%) (M − 2OPr^i), 279 (100%) (B(pz)$_4$).

Synthesis and Characterization of [ReO{B(pz)$_4$}(OPh)$_2$] (9). To a suspension of **2** (100 mg, 0.2 mmol of Re) in CH_2Cl_2 was added 40 mg (0.43 mmol) of phenol dissolved in the minimum amount of CH_2Cl_2. After 2 h at room temperature, a clear deep green solution was obtained. Evaporation of the solvent gave a dark green oil; this oil was washed with *n*-hexane and dried under vacuum, yielding 120 mg (0.18 mmol) of a dark green microcrystalline solid formulated as **9** (yield 90%).

Anal. Calcd for $C_{24}H_{22}BN_8O_3Re$: C, 43.2; N, 16.8; H, 3.3. Found: C, 42.9; N, 16.8; H, 3.4. IR (KBr, ν (cm^{-1})): 3134 w, 3025 vw, 2957 vw, 1588 s, 1502 w, 1482 s, 1441 m, 1407 s, 1388 s, 1303 s, 1223 s, 1208 s, 1183 w, 1160 w, 1108 m, 1092 w, 1063 s, 1021 w, 998 w, 967 s (ν(Re=O)), 921 w, 892 w, 853 s, 809 w, 793 w, 759 s, 692 m, 641 w, 614 m, 549 w, 492 w, 392 w. FTICR/MS (*m/z* referenced to the species with ^{187}Re and ^{11}B; relative abundance in parentheses): EI(+) (180 °C, 8 eV) 668 (100%) (M), 575 (18%) (M − OPh), 574 (16%) (M − HOPh), 507 (6%) (M − OPh,pzH), 94 (6%) (HOPh); EI(−) (180 °C, 70 eV) 668 (66%) (M), 575 (100%) (M − OPh), 507 (5%) (M − OPh,pzH), 279 (8%) (B(pz)$_4$).

Synthesis and Characterization of [ReO{B(pz)$_4$}(SPh)$_2$] (10). This compound has been synthesized according to the procedure described above for **9**. Starting with 100 mg (0.2 mmol of Re) of **2**, we obtained 110 mg (0.16 mmol) of a yellow-brown microcrystalline solid that we formulated as **10** (yield 80%).

Anal. Calcd for $C_{24}H_{22}BN_8OS_2Re$: C, 41.2; N, 16.0; H, 3.2. Found: C, 39.9; N, 15.9; H, 3.1. IR (KBr, ν (cm^{-1})): 3140 w, 3053 vw, 2961 vw, 1578 m, 1511 w, 1500 m, 1469 w, 1437 m, 1406 s, 1387 s, 1299 s, 1262 w, 1206 s, 1186 w, 1172 w, 1107 m, 1091 w, 1065 s, 1044 w, 1025 w, 999 w, 954 s, (ν(Re=O)), 922 w, 872 w, 855 s, 821 w, 799 s, 779 m, 764 s, 743 s, 695 m, 614 m, 486 w, 382 w, 354 w. FTICR/MS (*m/z* referenced to the species with ^{187}Re and ^{11}B; relative abundance in parentheses): EI(+) (180 °C, 8 eV) 700 (50%) (M), 523 (10%) (M − SPh,pzH), 514 (100%) (M − SPh,C_6H_5), 218 (60%) ((SPh)$_2$); EI(−) (180 °C, 70 eV) 700 (10%) (M), 591 (15%) (M − SPh), 279 (100%) (B(pz)$_4$).

Synthesis and Characterization of [ReO(η^2-OCONPh){B(pz)$_4$}] (11). To a suspension of **2** (100 mg, 0.2 mmol of Re) in CH_2Cl_2 was added 30 mg (0.25 mmol) of phenyl isocyanate dissolved in the minimum volume of CH_2Cl_2. After 2 h of stirring at room temperature, a clear dark red solution was obtained. This dark red solution was evaporated to dryness, yielding a red oil. This oil was redissolved in the minimum volume of toluene and a dark red solid precipitated by adding *n*-hexane. The solid was dried under vacuum, yielding 90 mg (0.15 mmol) of **11** (yield 73%).

Anal. Calcd for $C_{19}H_{17}BN_9O_3Re$: C, 37.0; N, 20.5; H, 2.8. Found: C, 38.8; N, 19.0; H, 3.2. IR (KBr, ν (cm^{-1})): 3124 m, 2959 w, 1724 vs (ν(C=O)), 1596 m, 1505 s, 1488 s, 1442 m, 1409 s, 1388 vs, 1308 s, 1264 w, 1213 s, 1136 m, 1112 s, 1068 s, 1002 w, 985 s (ν(Re=O), 943 m, 923 m, 853 s, 815 w, 798 s, 762 s, 720 s, 688 m, 614 m, 545 w, 512 w, 437 m, 398 w, 379 m, 293 m. FTICR/MS (*m/z* referenced to the species with ^{187}Re and ^{11}B; relative abundance in

Table 1. Crystallographic Data for $[ReO\{B(pz)_4\}(OPh)_2]$ (**9**) and $[ReO\{B(pz)_4\}(SPh)_2]$ (**10**)

	9	**10**
formula	$C_{24}H_{22}BN_8O_3Re$	$C_{24}H_{22}BN_8OS_2Re$
mol wt	667.51	699.64
cryst system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.611(4)	10.563(3)
b (Å)	11.808(3)	11.768(2)
c (Å)	12.400(5)	12.149(3)
α (deg)	88.69(2)	94.10(2)
β (deg)	69.61(3)	100.50(2)
γ (deg)	74.01(3)	92.44(2)
V (Å^3)	1264(1)	1479(1)
Z	2	2
D_{calc} (g cm^{-3})	1.754	1.571
linear abs coeff (cm^{-1}) (Mo Kα)	46.27	40.82
2θ range (deg)	3.0−56.0	3.0−52.0
no. of reflns ($F_o > 3\sigma(F_o)$)	5226	4721
range in decay corr factors	1.000 00, 1.001 21	1.000 03, 1.069 76
range in abs corr factors	0.9175, 1.0000	0.8191, 0.9991
no. of params refined	336	348
weighting scheme used, $w = (\sigma^2(F_o) + gF_o^2)^{-1}$, g	0.0005	0.001
final R, R_w	0.031, 0.037	0.043, 0.051

parentheses): EI(+) (180 °C, 10 eV): 573 (80%) (M − CO_2), 498 (100%) (M − PhNCO); EI(−) (180 °C, 10 eV): 573 (100%) (M − CO_2).

Reaction of "$[ReO(\mu\text{-}O)\{B(pz)_4\}]_2$" (2) with DMSO. Dimethyl sulfoxide (10 mL) was added to 50 mg (0.1 mmol of Re) of **2**. After 12 h at room temperature, a white precipitate formed, as well as a yellow-green supernatant. The white solid was isolated and identified by infrared and ^{1}H NMR spectroscopies as $(ReO_3\{B(pz)_4\})$ (**1**). The DMSO solution was taken to dryness, and the solid obtained was washed with THF. The THF removed impurities, leaving a white solid that was dried under vacuum and also identified as $(ReO_3\{B(pz)_4\})$ (**1**). We obtained 30 mg (0.06 mmol) of **1** (yield 60%).

Reaction of $[ReO\{B(pz)_4\}(OMe)_2]$ (6) with H_2O. A 20 μL portion of H_2O was added to a solution of **6** (50 mg, 0.09 mmol) in THF (20 mL). The blue solution yielded after 12 h an insoluble dark green solid and a red-brown supernatant. The precipitate was isolated, washed with THF and *n*-hexane, and dried under vacuum. The green solid obtained was identified by IR and ^{1}H NMR spectroscopies as **2** (25 mg, 0.05 mmol of Re, yield 55%).

X-ray Crystallographic Analysis. X-ray data were collected from a green crystal of **9**, obtained from a saturated solution of the compound in *n*-hexane, and from a yellow-brown crystal of **10**, obtained by slow diffusion of *n*-hexane into a saturated solution of the compound in toluene. 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 an $\omega-2\theta$ scan mode. Unit cell dimensions were obtained by least-squares refinement of the setting angles of 25 reflections with $16 < 2\theta < 32°$ for **9** and $15 < 2\theta < 28°$ for **10**. Crystal data and details of the data collection and refinement are given in Table 1. Data were corrected for Lorentz−polarization effects, for linear decay, 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.[8] 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. The structural analysis of **10** revealed a solvent molecule in the lattice, completely disordered, whose chemical identity was not possible to identify. The three strongest peaks in the residual electron density map were introduced in the refinement as full-occupancy carbon atoms. The lattice solvent was then excluded from the formula, from the molecular weight, and from the calculation of the density in Table 1. In the final difference Fourier map, the highest peaks were 1.2 and 1.6 e Å^{-3} for compounds **9** and **10**, respectively, and were near the Re atom. Atomic scattering factors and anomalous dispersion terms were taken from ref 9.

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Results and Discussion

As indicated in Scheme 1, the white complex $[ReO_3\{B(pz)_4\}]$ (**1**) is easily reduced by a stoichiometric amount of triphenylphosphine in tetrahydrofuran, providing, in 60% yield, a very reactive dark green oxo compound of Re that we tentatively formulate as **2**. This compound is insoluble in tetrahydrofuran, in water, and in aromatic and aliphatic hydrocarbon solvents and slightly soluble in CH_2Cl_2 and $CHCl_3$. Until now, no single crystals suitable for X-ray crystallographic analysis have been obtained for **2**, but the analytical data and specially its reactivity toward different substrates (Scheme 1) suggest the formation of an oxo-bridged diamagnetic dimer "$[ReO(\mu\text{-}O)\{B(pz)_4\}]_2$" (**2**).

Analogous dinuclear rhenium compounds, such as $[ReO(\mu\text{-}O)(C_5Me_5)]_2$ and $[ReO(\mu\text{-}O)(tacn)]_2^{2+}$, have been previously described as products of the reduction of $[ReO_3(\eta^5\text{-}C_5Me_5)]$ with triphenylphosphine and of $[ReO(OCH_2CH_2O)(tacn)]^+$ with zinc amalgam.[2,3] However, we observed that **2** is air stable and can be obtained with similar yields even under aerobic conditions, which is different from what has been described for the analogous compound with the ligand (C_5Me_5): in this case, the reduction of $[ReO_3(\eta^5\text{-}C_5Me_5)]$ with triphenylphosphine in the presence of oxygen leads to $[Re_3(\mu\text{-}O)_6(\eta^5\text{-}C_5Me_5)_3][ReO_4]_2$.[2]

As can be seen in Scheme 1, compound **2** is quantitatively converted to the dichloro derivative **3** when treated with hydrochloric acid or with trimethylsilyl chloride, and this result indicates that **2** might be intermediate in the synthetic method previously described for compound **3**.[5] The high reactivity of **2** was also demonstrated by the reactions with diols, alcohols, thiophenol, and phenyl isocyanate, which allowed the synthesis of compounds **4**−**11** spectroscopically pure in high yields (73−90%). All the reactions were studied in dichloromethane, except the ones with aliphatic alcohols which were run in the respective alcohols. In this case, we observed rates of alcoholysis increasing in the order HOMe > HOEt > HOPr^i (see Experimental Section).

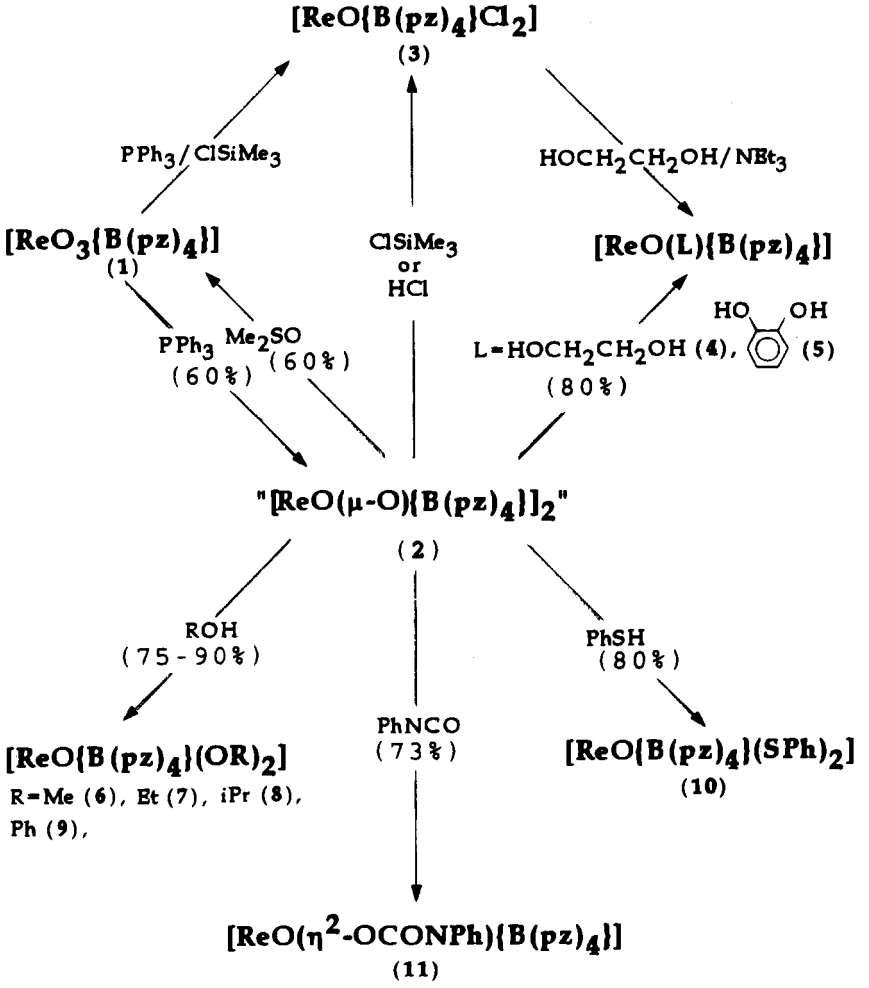
Some reactions of **2** presented in Scheme 1, namely with hydrochloric acid and phenyl isocyanate, have also been described for $[ReO(\mu\text{-}O)(C_5Me_5)]_2$, and the results are comparable.[10,11] Recently, reactions of $[ReO(\mu\text{-}O)(C_5Me_5)]_2$ with diols were also described, and the products obtained compare with ours;[12] however, the preparation of the ethylene glycolate oxo complex is apparently slower than in our case and needs excess diol and the presence of TsOH.[12]

Compounds **4**−**11** present different stabilities in solution. During recrystallization processes, we observed that compounds **4**, **5**, and **9**−**11** were quite stable while the alkoxide compounds **6**−**8** slowly decomposed when the solvent was not the respective alcohol, regenerating compound **2**. In THF, compound **6** reacts with H_2O, providing **2** in 60% isolated yield.

The Re(VII) complex **1** can also be easily regenerated by reacting **2** with Me_2SO, and this compares with other results

(9) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.
(10) Herrmann, W. A.; Kusthardt, U.; Floel, M.; Kulpe, J.; Herdtweck, E.; Voss, E. *J. Organomet.Chem.* **1986**, *314*, 151.
(11) Kusthardt, U.; Hermann, W. A.; Ziegler, M. L.; Zahn, T.; Nuber, B. *J. Organomet. Chem.* **1986**, *311*, 163.
(12) Gable, K. P. *Organometallics* **1994**, *13*, 2486.

Scheme 1. Reactivity of the Oxo Complex "$[ReO(\mu\text{-}O)\{B(pz)_4\}]_2$" (**2**)



previously described which indicate that Me_2SO is a suitable substrate for the oxidation of Re(V) to Re(VII).[4]

Previously, attempts to reduce the compound $[ReO_3\{HB(pz)_3\}]$ have been described, but the reduced species have not been identified.[13] We observed that $[ReO_3\{HB(pz)_3\}]$[14] can also be reduced by a stoichiometric amount of triphenylphosphine, providing a dark green compound (70% yield), insoluble in THF, with spectroscopic properties analogous to those of **2**.[15] This complex with $[HB(pz)_3]^-$ reacts also with HOMe, yielding the compound $[ReO\{HB(pz)_3\}(OMe)_2]$ (85% yield), which has also been characterized by spectroscopic techniques.[15] We must report that the rate of alcoholysis is slower in this case than with **2**.

Infrared Spectra. The infrared spectra of compounds **2** and **5**–**11** present the bands characteristic of the $(B(pz)_4)^-$ ligand, as well as strong bands corresponding to ν(Re=O) in the range 951–985 cm^{-1} (see Table 2). These ν(Re=O) stretching bands are within the range normally found for other six-coordinate oxorhenium complexes previously isolated with the stabilizing ligand $[B(pz)_4]^-$.[5,6] However, for **2** we also observed two relatively strong bands at 646 and 563 cm^{-1}, which are in the range normally assigned to ν(Re–O–Re) (500–700 cm^{-1}).[2] We must also report that in the IR spectrum of **2** no band attributable to the perrhenate anion is present, even when the reaction takes place under aerobic conditions (cf. $\nu(ReO_4^-)$ = 913 cm^{-1} for $KReO_4$,[16] $\nu(ReO_4^-)$ = 905 cm^{-1} for $[Re_2(O)_2(\mu\text{-}O)(\mu\text{-pz})\{HB(pz)_3\}_2]ReO_4$,[17] $\nu(ReO_4^-)$ = 911 cm^{-1} for $[Re_3(\mu\text{-}O)_6(\eta^5\text{-}C_5Me_5)_3][ReO_4]_2$,[2] and $\nu(ReO_4^-)$ = 900 cm^{-1} for $[Re(tacn)(O)(\mu\text{-}O)_2ReO(ReO_4)_2]$[3]).

In the IR spectrum of **11**, we also observed a very strong band at 1724 cm^{-1} that we assigned to ν(C=O); this value compares with the value found for the analogous compound $[ReO(\eta^2\text{-}OCONPh)(C_5Me_5)]$ (ν(C=O) = 1728 cm^{-1}).[11]

Table 2. Infrared Data (cm^{-1}) for Compounds **2**–**11**

compd	ν(Re=O)	other bands	ref
2	951 s	646 s, 563 s (ν(O–Re–O))	this work
3	985 s	360 m, 330 m (ν(Re–Cl))	5, 6
4	968 s		6
5	974 s		this work
6	965 s	559 m, 532 m (ν(Re–O))	this work
7	960 s	551 m (ν(Re–O))	this work
8	952 s		this work
9	967 s		this work
10	954 s		this work
11	985 s	1724 vs (ν(C=O))	this work

(13) Degnan, I. A.; Behm, J.; Cook, M. R.; Hermann, W. A. *Inorg. Chem.* **1991**, *30*, 2165.

(14) Degnan, I. A.; Herrmann, W. A.; Herdtweck, E. *Chem. Ber.* **1990**, *123*, 1347.

(15) The dark green compound with $[HB(pz)_3]^-$ analogous to **2** has the following spectroscopic properties: IR (KBr, ν (cm^{-1})) 2497 m (ν(B–H)), 952 s (ν(Re=O)), 636 s and 564 m (ν(O–Re–O)); ^1H NMR ($CDCl_3$, δ (ppm)) (300 MHz) (298 K) 6.30 (3H, H(4), br s), 7.74 (3H, br s), 8.20 (3H, br s); (253 K) 6.13 (1H, H(4), br s), 6.39 (2H, H(4), br s), 7.45 (1H, br s), 7.91 (2H, br s), 7.94 (2H, br s), 8.85 (1H, br s). This $(HB(pz)_3)^-$ complex also reacts with methanol, yielding $[ReO\{HB(pz)_3\}(OMe)_2]$ (85% yield): IR (KBr, ν (cm^{-1})) 2514 (ν(B–H)), 960 (ν(Re=O)); ^1H NMR ($CDCl_3$, δ (ppm)) 4.64 (6H, s, CH_3), 6.04 (1H, H(4), br s), 6.38 (2H, H(4), br s), 7.40 (1H, br s), 7.58 (1H, br s), 7.72 (2H, br s), 7.87 (2H, br s).

(16) Jesowska-Trzebiatowska, B.; Hanuza, J.; Baluka, M. *Spectrochim. Acta* **1971**, *27A*, 1753.

Table 3. ^{1}H NMR Data for Re(V) Complexes[a]

	$[B(pz)_4]^-$					
	H(4)			H(3)/H(5)		
complex	trans to O	trans to L	free	trans to O/free	trans to L	other ligands
2[b]	6.23 (1H, s, br)	6.43 (2H, s, br)	6.67 (1H, s, br)	7.77 (1 + 1H) 7.92 (1H, s, br) 8.93 (1H, s, br)	7.99 (2H, s, br) 8.02 (2H, s, br)	
5	5.92 (1H, t, ^3J = 2.4)	6.45 (2H, t, ^3J = 2.1)	6.65 (1H, s, br)	7.25−7.29[c] (1H) 7.94 (1H, s, br) 7.99 (1H, d, ^3J = 2.1) 8.17 (1H, d, ^3J = 2.1)	7.60 (2H, d, ^3J = 2.4) 8.14 (2H, d, ^3J = 1.5)	6.84 (2H, m, Ph) 7.25−7.29[c] (2H)
6	6.09 (1H, s, br)	6.41 (2H, t, ^3J = 2.1)	6.62 (1H, s, br))	7.59 (1 + 1H) 7.64 (1H, d, ^3J = 1.5) 7.93 (1H, s, br)	7.94−7.97 (2 + 2H)	4.64 (6H, s, CH_3)
7	6.06 (1H, s, br)	6.38 (2H, s, br)	6.61 (1H, s, br)	7.58 (1 + 1H) 7.63 (1H, s, br) 7.87 (1H, d, ^3J = 0.9)	7.91−7.94 (2 + 2H, br)	1.38 (6H, tr, ^3J = 7.1, CH_3) 4.92 (4H, m, CH_2)
8	6.03 (1H, s, br)	6.38 (2H, s, br)	6.61 (1H, s, br)	7.62 (1 + 1H) 7.91 (1H, br) 7.96 (1H, d, ^3J = 2.1)	7.71 (2H, d, ^3J = 2.1) 7.91 (2H, br)	1.21 (6H, d, ^3J = 6.0) 1.40 (6H, d, ^3J = 6.0) 5.73 (2H, d, ^3J = 6.0)
9	6.19 (1H, t, ^3J = 2.3)	6.26 (2H, t, ^3J = 2.4)	6.65 (1H, t, ^3J = 2.1)	7.90 (1H, d, ^3J = 1.5) 7.95 (1H, d, ^3J = 1.5) 8.03 (1H, d, ^3J = 2.4) 8.24 (1H, d, ^3J = 2.4)	7.46 (2H, d, ^3J = 2.1) 7.48 (2H, d, ^3J = 2.4)	6.60 (4H, dd, ^3J = 8.25, ^4J = 1.0, Ph) 6.75 (2H, m, *p*-Ph) 7.17 (4H, m, Ph)
10	6.08 (1H, t, ^3J = 2.1)	6.20 (2H, s, br)	6.63 (1H, t, ^3J = 1.8)	7.07−7.21 (1 + 1H) 7.76 (1H, d, ^3J = 2.4) 8.03 (1H, d, ^3J = 2.4)	7.74 (2H, d, ^3J = 1.8) 7.94 (2H, d, ^3J = 2.1)	7.07−7.21 (10H, m, br, Ph)
11[d]	5.99 (1H, t, ^3J = 2.4)	6.42 (1H, t, ^3J = 2.1) 6.52 (1H, t, ^3J = 2.4)	6.68 (1H, t, ^3J = 2.4)	7.38 (1H, d, ^3J = 2.4) 7.43 (1H, d, ^3J = 2.1) 7.98 (1 + 1H, s, br) 8.03 (1 + 1H, s, br) 8.22 (1H, d, ^3J = 2.7) 8.29 (1H, d, ^3J = 2.1)		7.00−7.08 (2H, m, Ph) 7.18−7.30 (3H, m, Ph)

[a] For compounds **5**−**11** the spectra were obtained at 298 K. For compound **2** the spectrum was obtained at 208 K. 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; m, multiplet; br, broad. [b] For **2** the spectrum at T = 298 K presented only three signals at 6.41 ppm (4H, H(4), s, br), 7.89 ppm (4H, s, br), and 8.24 ppm (4H, s, br). [c] Occasionnally one proton of the $[B(pz)_4]^-$ ligand overlaps two protons of the catecholate. [d] For complex **11** we did not assign any of the H(3) and H(5).

FTICR/MS Analysis. Laser desorption (LD) and electron impact (EI) Fourier transform ion cyclotron resonance (FTICR) mass spectrometry was undertaken for compound **2**, as well as for all the new derivatives described in this work.

For compound **2**, EI/FTICR mass spectra could not be obtained due to the nonvolatility of the compound. In the negative-ion LD mass spectra, the heaviest fragment appears at m/z = 498, which corresponds to $(ReO_2\{B(pz)_4\})^-$ ($(M/2)^-$, 50%), and other fragments resulting from losses of pyrazolyl groups were also observed at m/z = 430 ($(M/2 - pzH)^-$, 50%) and at m/z = 364 ($(M/2 - 2pz)^-$, 100%). The positive-ion LD mass spectra were not reproducible, and while in some spectra peaks corresponding to the molecular ion of **2** ($(M)^+$, m/z = 996) and to a fragment resulting from loss of pyrazole ($(M - pzH)^+$, m/z = 928) appeared, in other spectra peaks at m/z = 1047 and m/z = 1141 assigned to $(M + pz - O)^+$ and $(M + B(pz)_2)^+$, respectively, were observed. Whether these species are due to the high reactivity of compound **2** and are formed in the laser desorption process or are due to the presence of any impurity formed during the reduction of **1** by PPh_3 is not clear.

As detailed in the Experimental Section, positive- and negative-ion EI mass spectra showed, for the new derivatives of compound **2**, the molecular ion peaks, with isotopic patterns in agreement with the elemental compositions of the complexes. Compound **11** was an exception, as the peak at highest mass (m/z = 573) corresponded to $(M - CO_2)^{+/-}$ in both positive- and negative-ion spectra, with the base peak in the positive-ion mode being $(M - PhNCO)^+$; this can be compared with the positive EI mass spectrum of the analogue $[ReO(\eta^2\text{-}OCONPh)(C_5Me_5)]$[11]: $(M)^+$ (11%), $(M - CO_2)^+$ (27%), $(M - PhNCO)^+$ (100%), $(M - PhNOCO)^+$ (20%).

The fragmentation patterns of the derivatives of **2**, including the previously reported complex **3**,[5,6] showed preferential losses from the coligands, with the exception of complex **5**, where the catecholato ligand resisted fragmentation and the preferential losses involved the pyrazolyl groups.

Negative-ion LD mass spectra were also obtained for all the derivatives of **2** and were similar to the negative EI spectra, with less intense fragmentation.

NMR Spectra. The ^{1}H NMR data obtained at 298 K for compounds **5**−**11** are presented in Table 3, as well as the ^{1}H NMR data obtained for complex **2** at 298 K and at 208 K.

For compounds **5**−**10**, we observed three sets of resonances of relative intensities 2:1:1 for the protons of the pyrazolyl rings of the $[B(pz)_4]^-$ ligand. As we have previously reported,[6] this pattern is consistent with a Re(V) center six-coordinated by the tridentate $[B(pz)_4]^-$, by the oxygen, and by two identical monoanionic ligands or a dianionic ligand, like cathecolate, and indicates a static behavior for these compounds on the NMR time scale, as the pattern agrees with the solid state structures determined for this family of complexes (see X-ray structural analysis below). For compound **11**, we observed four sets of resonances of relative intensities 1:1:1:1 for the protons of the pyrazolyl rings of the $[B(pz)_4]^-$ ligand. This pattern agrees with

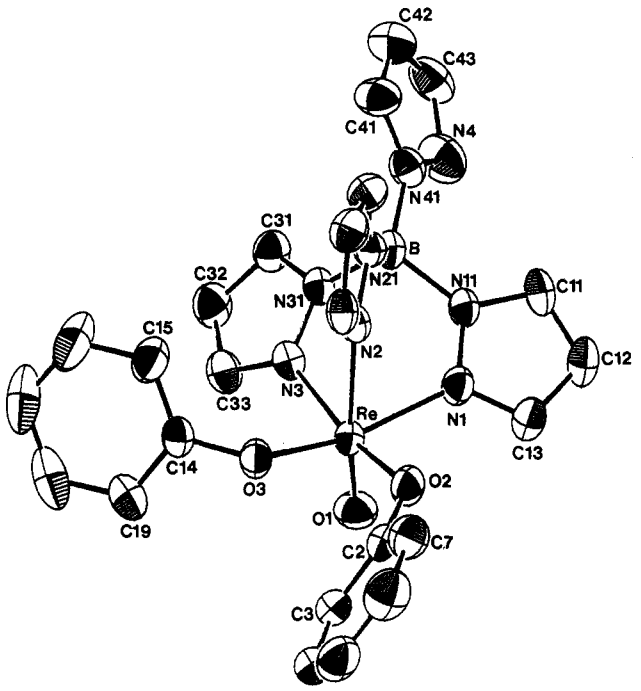
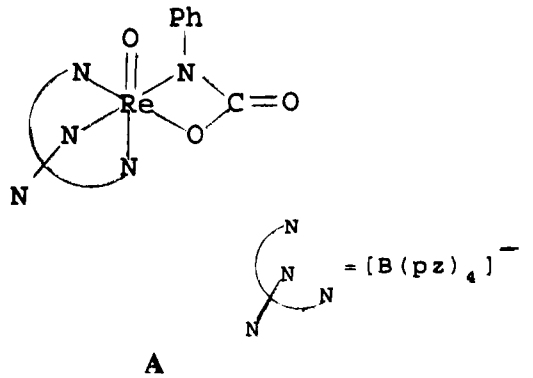


Figure 1. ORTEP drawing of $[ReO\{B(pz)_4\}(OPh)_2]$.

the infrared data and is consistent with the formation of a cyclic derivative containing an O, N-coordinate ligand as shown in **A**.

For complex **2**, the ^1H NMR spectrum at 298 K presents only one set of three broad resonances of equal intensity, indicating that a dynamic process in solution must be responsible for the equilibration of the four pyrazolyl rings. In fact, when the temperature is lowered, all the resonances broaden and collapse and, in the limiting static spectrum obtained at 208 K, eight signals of relative intensities 1:2:1:2:1:2:2:1 are observed, due to the occasional overlapping of two resonances of intensity 1 (Table 3). The resonances due to the H(4) protons of the pyrazolyl rings are easily assigned at 6.23 (1H), 6.43 (2H), and 6.67 (1H) ppm, as they appear in the same region of the spectrum for all the rhenium diamagnetic compounds isolated and characterized with $[B(pz)_4]^-$ (Table 3 and refs 5 and 6) and indicates a splitting of the type 2:1:1 for the pyrazolyl rings of the ligand.



A

The fluxional behavior observed for **2** is in contrast with the static behavior that has been observed for all the monomeric Re(V) compounds isolated with the ligands $[B(pz)_4]^-$ [5,6] and $[HB(pz)_3]^-$,[13,14,17] as well as for the compound $[Re_2(O)_2(\mu\text{-}O)(\mu\text{-}pz)\{HB(pz)_3\}_2]ReO_4$.[17]

(17) Brown, S. N.; Mayer, J. M. *Inorg. Chem.* **1992**, *31*, 4091.

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

Re−O(1)	1.682(5)	Re−N(1)	2.115(6)
Re−O(2)	1.963(5)	Re−N(2)	2.238(6)
Re−O(3)	1.946(5)	Re−N(3)	2.101(6)
O(2)−C(2)	1.355(6)	O(3)−C(14)	1.379(6)
B−N[a]	1.54(2)	C−C[a]	1.37(2)
N−N[a]	1.368(6)	C−C[b]	1.379(6)
N−C[a]	1.341(8)		
O(1)−Re−O(2)	103.0(3)	O(2)−Re−N(1)	87.2(2)
O(1)−Re−O(3)	109.2(3)	O(2)−Re−N(2)	85.2(2)
O(2)−Re−O(3)	84.9(2)	O(2)−Re−N(3)	165.1(1)
N(1)−Re−N(2)	76.4(2)	O(3)−Re−N(1)	159.1(1)
N(1)−Re−N(3)	88.9(2)	O(3)−Re−N(2)	83.6(2)
N(2)−Re−N(3)	79.9(2)	O(3)−Re−N(3)	93.8(2)
O(1)−Re−N(1)	91.5(3)	Re−O(2)−C(2)	127.5(4)
O(1)−Re−N(2)	165.2(1)	Re−O(3)−C(14)	125.9(4)
O(1)−Re−N(3)	91.5(3)	N−B−N[a]	110(3)
C−C−C[b]	120(1)		

[a] Mean value for the pyrazolyl rings. [b] Mean value for the phenyl rings.

Table 5. Positional ($\times 10^4$) and Thermal Parameters for $[ReO\{B(pz)_4\}(OPh)_2]$

atom	*x*	*y*	*z*	B_{eq} (Å^2)
Re	1719.1(2)	1591.5(2)	3910.2(1)	2.68(1)
O(1)	1668(4)	185(3)	4079(3)	4.13(11)
O(2)	2315(4)	1965(3)	5191(3)	3.49(9)
O(3)	−306(3)	2650(3)	4796(3)	3.22(9)
N(1)	4109(4)	1035(3)	2903(3)	3.2(1)
N(2)	2230(4)	3264(3)	3237(3)	2.9(1)
N(3)	1228(4)	1594(3)	2387(3)	3.0(1)
N(4)	5376(6)	1437(5)	−734(4)	5.2(2)
N(11)	4705(4)	1335(3)	1805(3)	2.9(1)
N(21)	3003(4)	3385(3)	2096(3)	2.9(1)
N(31)	2229(4)	1802(3)	1363(3)	2.8(1)
N(41)	4483(4)	2393(3)	48(3)	3.3(1)
C(11)	6255(5)	858(4)	1406(4)	3.7(1)
C(12)	6665(6)	220(5)	2243(5)	4.1(1)
C(13)	5277(5)	357(4)	3175(4)	3.8(1)
C(21)	3089(6)	4505(4)	1993(4)	3.6(1)
C(22)	2349(6)	5124(4)	3057(4)	3.8(1)
C(23)	1842(5)	4316(4)	3803(4)	3.3(1)
C(31)	1703(5)	1664(4)	514(4)	3.5(1)
C(32)	382(6)	1302(5)	984(5)	4.1(1)
C(33)	112(5)	1286(4)	2153(4)	3.5(1)
C(41)	4234(7)	3364(4)	−501(5)	4.3(2)
C(42)	4939(7)	3058(6)	−1627(5)	5.3(2)
C(43)	5646(6)	1857(6)	−1788(4)	4.7(2)
C(2)	1393(5)	2260(4)	6313(4)	3.2(1)
C(3)	213(6)	1751(5)	6882(4)	3.8(2)
C(4)	−635(6)	2066(6)	8058(5)	4.9(2)
C(5)	−340(7)	2892(6)	8648(5)	5.5(2)
C(6)	839(8)	3392(6)	8083(5)	5.3(2)
C(7)	1703(6)	3069(5)	6924(5)	4.1(2)
C(14)	−1565(5)	2985(4)	4447(4)	3.1(1)
C(15)	−1695(6)	3838(5)	3686(5)	4.3(2)
C(16)	−2979(8)	4126(6)	3361(7)	6.3(3)
C(17)	−4132(8)	3584(7)	3792(8)	6.9(3)
C(18)	−4014(7)	2736(6)	4571(7)	5.9(2)
C(19)	−2733(6)	2436(5)	4903(5)	4.3(2)
B	3637(5)	2246(4)	1296(4)	2.8(1)

The complex with $[HB(pz)_3]^-$ analogous to **2**,[15] obtained by reducing $[ReO_3(HBpz)_3]$ with triphenylphosphine, is also fluxional in solution, and the activation energy of the dynamic process allowed us to obtain a static spectrum at 253 K, with a pattern which indicates a splitting of the type 2:1 for the protons of the pyrazolyl rings.[15] This pattern is consistent with the one observed for **2** and by comparison allowed us to assign the protons due to the coordinated and uncoordinated pyrazolyl rings in **2** (see Table 3 and ref 15).

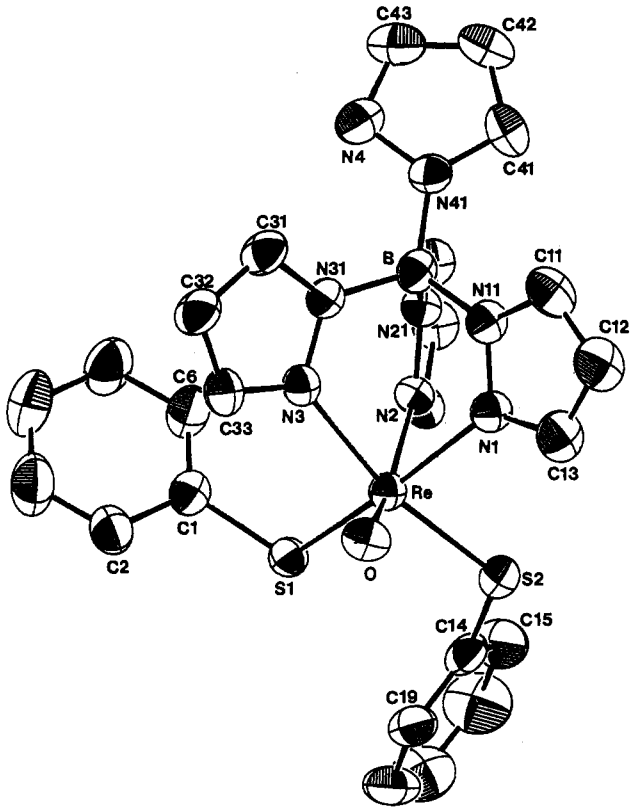


Figure 2. ORTEP drawing of $[ReO\{B(pz)_4\}(SPh)_2]$.

Crystal Structure of $[ReO\{B(pz)_4\}(OPh)_2]$ (9). An ORTEP diagram of the structure of **9** is shown in Figure 1. The compound is monomeric with an approximately octahedral coordination geometry. The tridentate tetrakis(pyrazol-1-yl)-borate ligand occupies one triangular face while the oxo oxygen and the two oxygen atoms of the phenoxide groups form the other staggered triangular face.

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

The Re=O bond length, 1.682(5) Å, is comparable to the values found in other similar oxo Re(V) complexes with the ligands $[HB(pz)_3]^-$ and $[B(pz)_4]^-$.[6,13] The Re−N bond lengths are not equivalent, and as observed for other compounds of Re(V) and Tc(V) isolated with $[HB(pz)_3]^-$ or $[B(pz)_4]^-$,[6,13,18] the Re−N bond trans to the oxo ligand is the longest, 2.238(6) Å, due to the trans effect. The other two Re−N bonds are shorter, with values of 2.115(6) and 2.101(6) Å, and are in the range observed in the previously reported Re(V) complexes.[6] The large steric demand of the oxo group is manifested by the bending of the pyrazolyl rings away from the oxo ligand and toward the trans pyrazolyl ring and explains the large N(3)−Re−N(1) angle of 88.9(2)° (compared with the angles N(3)−Re−N(2) and N(2)−Re−N(1) of 79.9(2) and 76.4(2)°, respectively), as already observed in other Re(V) and Tc(V) complexes.[6,13,18] The Re−O bond lengths in the phenoxide ligands are 1.963(5) and 1.946(5) Å, with a mean value of 1.955(5) Å, which is comparable with the mean Re−O bond distance of 1.93(2) Å in $[ReO(OCH_2CH_2O)\{B(pz)_4\}]$.[6] The bond lengths and angles within the $[B(pz)_4]^-$ ligand show no unusual features and compare well to the values found in $[ReO_3\{B(pz)_4\}]$ and $[ReO(OCH_2CH_2O)\{B(pz)_4\}]$.[5,6] There are a few short intramolecular contacts, mainly O(2)···O(3) 2.64 Å, O(2)···N(1) 2.81 Å, O(2)···N(2) 2.85 Å, and O(3)···N(2) 2.80 Å.

(18) Thomas, R. W.; Estes, G. W.; Elder, R. C.; Deutsch, E. *J. Am. Chem. Soc.* **1979**, *101*, 4581.

Table 6. Selected Bond Lengths (Å) and Bond Angles (deg) for $[ReO\{B(pz)_4\}(SPh)_2]$

Re−O	1.693(7)	Re−N(1)	2.130(8)
Re−S(1)	2.316(4)	Re−N(2)	2.243(7)
Re−S(2)	2.311(4)	Re−N(3)	2.155(8)
S(1)−C(1)	1.79(1)	S(2)−C(14)	1.77(1)
B−N[a]	1.53(2)	C−C[a]	1.38(1)
N−N[a]	1.373(1)	C−C[b]	1.39(1)
N−C[a]	1.34(1)		
S(1)−Re−S(2)	90.0(2)	S(1)−Re−N(1)	162.1(2)
O−Re−S(1)	104.1(3)	S(1)−Re−N(2)	86.3(3)
O−Re−S(2)	103.9(3)	S(1)−Re−N(3)	94.6(3)
N(1)−Re−N(2)	76.3(2)	S(2)−Re−N(1)	85.2(3)
N(1)−Re−N(3)	86.1(3)	S(2)−Re−N(2)	87.3(3)
N(2)−Re−N(3)	78.7(2)	S(2)−Re−N(3)	164.9(2)
O−Re−N(1)	93.7(3)	Re−S(1)−C(1)	111.3(4)
O−Re−N(2)	164.5(2)	Re−S(2)−C(14)	115.4(4)
O−Re−N(3)	88.9(3)	N−B−N[a]	110(3)
C−C−C[b]	120(1)		

[a] Mean value for the pyrazolyl rings. [b] Mean value for the phenyl rings.

Table 7. Positional ($\times 10^4$) and Thermal Parameters for $[ReO\{B(pz)_4\}(SPh)_2]$

atom	*x*	*y*	*z*	B_{eq} (Å^2)
Re	2338.1(1)	1015.0(3)	1953.5(2)	2.66(1)
S(1)	4565(2)	1045(2)	2184(2)	3.07(5)
S(2)	2234(2)	−948(2)	1627(2)	3.79(9)
O(1)	1865(5)	1480(5)	663(4)	3.5(1)
N(1)	418(6)	789(5)	2244(5)	3.2(1)
N(2)	2604(5)	752(5)	3790(5)	2.7(1)
N(3)	2299(6)	2739(5)	2671(5)	3.1(2)
N(4)	874(7)	3517(6)	5622(6)	4.3(2)
N(11)	−69(6)	1439(5)	3037(5)	3.3(2)
N(21)	1906(6)	1344(5)	4467(5)	2.9(2)
N(31)	1555(6)	3084(5)	3436(5)	3.0(2)
N(41)	262(6)	2602(5)	4938(5)	3.5(2)
C(11)	−1374(7)	1309(8)	2823(7)	4.2(2)
C(12)	−1746(8)	547(9)	1892(7)	4.8(3)
C(13)	−603(8)	239(8)	1564(7)	4.4(2)
C(21)	2303(7)	1071(7)	5542(6)	3.6(2)
C(22)	3234(8)	280(7)	5541(6)	3.7(2)
C(23)	3388(7)	117(7)	4429(6)	3.4(2)
C(31)	1509(9)	4219(6)	3494(7)	3.9(2)
C(32)	2239(9)	4638(7)	2748(7)	4.2(2)
C(33)	2704(8)	3693(7)	2265(7)	3.8(2)
C(41)	−561(8)	2035(8)	5473(8)	4.8(3)
C(42)	−493(9)	2591(9)	6527(8)	5.0(3)
C(43)	371(10)	3493(8)	6560(8)	4.9(3)
C(1)	5291(7)	2367(6)	2886(6)	3.3(2)
C(2)	5972(9)	3071(7)	2300(7)	4.3(3)
C(3)	6605(11)	4065(9)	2829(9)	6.0(3)
C(4)	6598(11)	4373(9)	3952(10)	6.1(3)
C(5)	5914(10)	3680(9)	4531(8)	5.5(3)
C(6)	5281(9)	2665(7)	4010(7)	4.5(3)
C(14)	3727(8)	−1563(6)	1595(6)	3.6(2)
C(15)	4153(10)	−2318(8)	2427(8)	5.0(3)
C(16)	5308(13)	−2838(10)	2433(11)	7.0(4)
C(17)	6033(11)	−2636(10)	1614(10)	6.3(3)
C(18)	5603(10)	−1924(9)	783(8)	5.1(3)
C(19)	4459(9)	−1393(7)	776(7)	4.1(3)
B	870(8)	2146(7)	3982(7)	3.2(2)

Crystal Structure of $[ReO\{B(pz)_4\}(SPh)_2]$ (10). Compound **10** is monomeric with an approximately octahedral coordination geometry. An ORTEP diagram of the structure is shown in Figure 2. Selected bond distances and angles are listed in Table 6, and the final positional parameters are given in Table 7.

The Re=O bond length of 1.693(7) Å is similar to the values found for **9** and close to the value for the analogous $[ReO\{HB(pz)_3\}(SPh)_2]$ (1.668(5) Å).[13] It is also comparable to the values

found in other related Re(V) complexes: 1.689(5) Å in [ReOCl{HB(pz)$_3$}(SPh)],[13] 1.694(9) Å in [ReO(SCH$_2$CH$_2$S){HB(pz)$_3$}],[19] and 1.69(2) Å in [ReO(OCH$_2$CH$_2$O){B(pz)$_4$}].[6] The Re−N bond lengths are also not equivalent, and the longest is, as usually, trans to the oxo ligand, 2.243(7) Å.

The Re−S bond lengths are 2.316(4) and 2.311(4) Å, with a mean value of 2.314(4) Å, which is comparable to the values of 2.301(2) Å in [ReOCl{HB(pz)$_3$}(SPh)] and 2.311(2) Å in [ReO{HB(pz)$_3$}(SPh)$_2$].[13] As expected, and due to the large steric requirement of the oxo group, there is bending of the equatorial pyrazolyl rings away from the oxo ligand and toward the trans pyrazolyl ring, which is reflected in the large N(3)−Re−N(1) angle of 86.1(3)°.

There are a few short intramolecular contacts, mainly S(1)···S(2) 3.27 Å, S(1)···O(1) 3.19 Å, S(2)···O(1) 3.18 Å, S(1)···N(3) 3.29 Å, S(1)···N(2) 3.12 Å, S(2)···N(1) 3.01 Å, and S(2)···N(2) 3.14 Å. There are no short intermolecular contacts.

The bond lengths and angles within [B(pz)$_4$]$^-$ are comparable to the values found in other Re compounds with the ligand [B(pz)$_4$]$^-$.

(19) Tisato, F.; Bolzati, C.; Duatti, A.; Bandoli, G.; Refosco, F. *Inorg. Chem.* **1993**, *32*, 2042.

Concluding Remarks

In summary, the oxorhenium compound obtained by reduction of [ReO$_3${B(pz)$_4$}] (**1**) with PPh$_3$, that we tentatively formulated as [ReO(μ-O){B(pz)$_4$}]$_2$ (**2**), is most probably an intermediate in the synthesis of the previously described complex [ReO{B(pz)$_4$}Cl$_2$] (**3**).[5] The oxorhenium compound **2** proved to be a versatile key compound for the synthesis of several monomeric Re(V) compounds, including the first structurally characterized mononuclear oxorhenium containing a poly(pyrazolyl)borate and unidentate aryloxide ligands (**9**). The broad scope of the reactivity of **2** and its unusual fluxional behavior in solution continue to be studied in our laboratory, and we are gaining clear evidence of the advantage of using **2**, as an alternative to [ReO{B(pz)$_4$}Cl$_2$],[5,6] to enter into the chemistry of monomeric or dimeric oxo complexes of Re(V).

Acknowledgment. The authors thank Prof. C. Maycock (FCL-University of Lisbon) and Ana Isabel Rodrigues (INETI) for NMR facilities.

Supplementary Material Available: Tables of positional and thermal parameters, calculated hydrogen atom positions, and complete bond distances and angles (5 pages). Ordering information is given on any current masthead page.

IC941044+