Neutral *trans*-Dioxorhenium(V) Complexes with the Anionic Tetrakis(pyrazolyl)borate Ligand

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Reduction of $[ReO_3\{\eta^3\text{-}B(pz)_4\}]$ (**1**) with PPh_3 in the presence of mono- or bidentate σ-donor ligands (pyridines, imidazoles, or diphosphines) is a very convenient method for the synthesis of the neutral dioxorhenium(V) complexes: *trans*-$[ReO_2\{\eta^2\text{-}B(pz)_4\}(L)_2]$ (L = py (**3**), 4-Mepy (**4**), 4-NMe_2py (**5**), 1-MeImz (**6**)) and *trans*-$[ReO_2\{\eta^2\text{-}B(pz)_4\}(P\frown P)]$ ($P\frown P$ = dmpe (**7**), dppe (**8**)). In the presence of pyridine or dimethylphosphinoethane, the analogous $[ReO_3\{\eta^3\text{-}HB(pz)_3\}]$ is also reduced by PPh_3 to *trans*-$[ReO_2\{\eta^2\text{-}HB(pz)_3\}(py)_2]$ (**9**) and *trans*-$[ReO_2\{\eta^2\text{-}HB(pz)_3\}(dmpe)]$ (**10**), respectively. In contrast, the reaction of $[ReO_2(py)_4]Cl$ with $K[B(pz)_4]$ leads to a mixture of species from which were identified the neutral mono-oxo complexes $[ReO(\eta^2\text{-}N,O)(\mu\text{-}O)B(pz)_3\}\text{-}(pz)(pzH)_2]$ (**11**) and $[ReO\{(\eta^2\text{-}N,O)(\mu\text{-}O)B(pz)_3\}Cl(py)_2]$ (**12**). Complexes **3**−**12** were characterized by different techniques, namely, IR, $^1H/^{31}P\{^1H\}$ NMR spectroscopies and X-ray crystallographic analysis (**5**, **10**, and **11**). Compound **5** crystallizes from dichloromethane/*n*-hexane as orange crystals containing 3 molecules of solvated CH_2Cl_2 (crystal data: triclinic space group $P\bar{1}$, with cell parameters a = 10.907(2) Å, b = 11.113(1) Å, c = 16.922(2) Å, α = 97.91(1)°, β = 102.37(1)°, γ = 94.21(1)°, V = 1973(1) Å^3, Z = 2). Compound **10** crystallizes from dichloromethane/*n*-hexane as yellowish crystals containing one molecule of pzH (crystal data: orthorhombic space group *Pnma*, with cell parameters a = 18.422(2) Å, b = 11.850(1) Å, c = 11.434(1) Å, $\alpha = \beta = \gamma$ = 90°, V = 2496.1(4) Å^3, Z = 4). Compound **11** crystallizes from dichloromethane/*n*-hexane in the monoclinic space group $P2_1/n$, with cell parameters a = 10.890(1) Å, b = 15.162(1) Å, c = 14.137(2) Å, β = 102.07(1)°, V = 2282.6(4) Å^3, Z = 4.

Introduction

There has been a renewed interest in the nature and chemical behavior of organorhenium oxides because of their potential relevance to many catalytic oxidation processes and to oxygen atom transfer between substrates.[1,2] The chemistry developed for $(Me_5C_5)ReO_3$ and $(Me)ReO_3$ is clearly an example of this interest, and some of the results found for these organometallic oxides are clearly an indication of the importance of the electronic and coordinative saturation of the metal center.[1−7]

In previous work[8] we have described several rhenium oxo complexes stabilized by tetrakis(pyrazolyl)borate, particularly the trioxide $[ReO_3\{\eta^3\text{-}B(pz)_4\}]$ (**1**) which can be considered an inorganic congener of the organometallic oxides mentioned above. We have shown[9] that reduction of **1** with PPh_3 leads to the dimer $[ReO(\mu\text{-}O)\{\eta^3\text{-}B(pz)_4\}]_2$ (**2**). To get a better insight of the chemical behavior of **1**, we decided to study its reduction with PPh_3 in the presence of neutral σ-donor substrates (pyridines, imidazoles, and diphosphines).

In this work, we describe the synthesis and characterization of the neutral *trans*-$[ReO_2\{\eta^2\text{-}B(pz)_4\}(L)_2]$ (L = pyridine (**3**), 4-methylpyridine (**4**), 4-(dimethylamino)pyridine (**5**), 1-methylimidazole (**6**)) and *trans*-$[ReO_2\{\eta^2\text{-}B(pz)_4\}(P\frown P)]$ ($P\frown P$ = dimethylphosphinoethane (**7**), diphenylphosphinoethane (**8**)), which have been obtained by reduction of $[ReO_3\{\eta^3\text{-}B(pz)_4\}]$ with PPh_3 in the presence of the respective neutral substrates. To compare the behavior of the ligands $[B(pz)_4]^-$ and $[HB(pz)_3]^-$, we also studied the reduction of $[ReO_3\{\eta^3\text{-}HB(pz)_3\}]$[10] with PPh_3 in the presence of py or dmpe and the complexes isolated, *trans*-$[ReO_2\{\eta^2\text{-}HB(pz)_3\}(py)_2]$ (**9**) and *trans*-$[ReO_2\{\eta^2\text{-}HB(pz)_3\}(dmpe)]$ (**10**), are also described in this report. The synthesis and characterization of $[ReO(\eta^2\text{-}N,O)(\mu\text{-}O)B(pz)_3\}\text{-}(pz)(pzH)_2]$ (**11**) and $[ReO\{(\eta^2\text{-}N,O)(\mu\text{-}O)B(pz)_3\}Cl(py)_2]$ (**12**), which were obtained when we tried to prepare dioxo complexes by reacting $[ReO_2(py)_4]Cl$ with the potassium salt of the tetrakis(pyrazolyl)borate, are also presented.

Compounds **3**−**10** are rare examples of neutral *trans*-dioxorhenium(V) complexes and have been obtained by a quite unusual synthetic process. For Re(V), as well as for other transition metals with d^2 electronic configuration, the trans arrangement of the O═Re═O unit is by far the most common and stable.[11,12] However, even being the most common, most of the described *trans*-dioxo Re(V) complexes are charged,[13] and to the best of our knowledge, *trans*-$[ReO_2(CH_2CMe_3)(py)_3]$ and *trans*-$[ReO_2I(PMe_2Ph)_3]$ are the only known examples of neutral *trans*-dioxo complexes.[14]

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Experimental Section

General Procedures. The reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques or dry gloveboxes. Solvents were dried, degassed, and distilled prior to use according to described procedures. The compounds $[ReO_3\{\eta^3\text{-}B(pz)_4\}]$ (**1**),[8] $[ReO(\mu\text{-}O)\{\eta^3\text{-}B(pz)_4\}]_2$ (**2**),[9] $[ReO_3\{\eta^3\text{-}HB(pz)_3\}]$,[10] and $[ReO_2(py)_4]Cl$[15] were prepared as described previously. Pyridine and 4-methylpyridine were distilled and kept over 4 Å molecular sieves several days prior to use. Triphenylphosphine was recrystallized from ethanol before use. The other chemicals were used as purchased.

^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Unity 300 MHz spectrometer; ^1H chemical shifts were referenced with the residual solvent resonance relative to tetramethylsilane, and the ^{31}P chemical shifts were measured with external 85% H_3PO_4 solution as reference. $CDCl_3$ was dried and distilled prior to use. IR spectra were recorded as KBr pellets on a Perkin-Elmer 577 spectrometer. The IR spectra of all the compounds show bands for the tetrakis(pyrazolyl)borate (**3**−**8**)[9] and for the hydrotris(pyrazolyl)borate (**9** and **10**),[25] which are relatively constant. In these spectra were also observed the bands due to the respective coligands (**3**−**10**). Absorption electronic spectra were performed on a Cary 2390 Varian spectrophotometer. Carbon, hydrogen, and nitrogen analyses were performed on a Perkin-Elmer automatic analyzer. The FTICR mass spectra were obtained with an Extrel FTMS 2001-DT as previously described.[8] FAB mass spectra were performed on a Carlo Erba Instruments Auto/HRGC/Trio 2000 MS spectrometer.

Synthesis of *trans*-$[ReO_2\{\eta^2\text{-}B(pz)_4\}(py)_2]$ (3). To a suspension of **1** (100 mg, 0.19 mmol) in 15 mL of THF was added an excess of pyridine (≈80 mg, ≈1 mmol), followed by dropwise addition of 50 mg (0.19 mmol) of PPh_3 dissolved in 10 mL of THF. Immediatly, a yellow-orange solution appeared. After the addition was completed, the mixture was stirred for 1 h at room temperature, and the solution was evaporated to dryness, yielding a yellow-orange solid. This solid was washed with diethyl ether, to remove $O{=}PPh_3$, and vacuum-dried, giving a yellow-orange microcrystalline product formulated as **3** (95 mg, 0.74 mmol, yield = 74%).

Anal. Calcd for $C_{22}H_{22}BN_{10}O_2Re$: C, 40.3; H, 3.4; N, 21.4. Found: C, 40.4; H, 3.4; N, 21.6. UV−vis (CH_2Cl_2), λ_{max}(nm) (ϵ, L mol^{-1} cm^{-1}): 416 (0.9×10^3), 301 (3.0×10^3), 246 (1.1×10^4). ^1H NMR (300 MHz, $CDCl_3$, 25 °C, δ (ppm)): 6.23 (2H, tr, ^3J = 1.5 Hz, H(4), *pz*), 6.28 (2H, tr, ^3J = 2.3 Hz, H(4), *pz*), 6.76 (2H, d, H(3/5), ^3J = 1.8 Hz, *pz*), 7.10 (2H, br, H(3/5), *pz*), 7.25 (2H, br, H(3/5), *pz*), 7.35 (4H, m, ^3J = 6.4 Hz, *m*-py), 7.66 (2H, m, ^3J = 7.6 Hz, *p*-py), 7.73 (2H, br, H(3/5), *pz*), 9.28 (4H, d, ^3J = 5.7 Hz, *o*-py).

Synthesis of *trans*-$[ReO_2\{\eta^2\text{-}B(pz)_4\}(4\text{-}Mepy)_2]$ (4). 4 was prepared and purified as described above for **3**. Starting with 100 mg (0.19 mmol) of **1**, 90 mg (0.14 mmol, yield = 70%) of **4** was obtained as a yellow-orange microcrystalline solid.

Anal. Calcd for $C_{24}H_{26}BN_{10}O_2Re$: C, 42.2; H, 3.8; N, 20.5. Found: C, 41.8; H, 3.7; N, 20.1. UV−vis (CH_2Cl_2), λ_{max}(nm) (ϵ, L mol^{-1} cm^{-1}): 409 (1.3×10^3), 340 (9.4×10^3), 257 (1.6×10^4). ^1H NMR (300 MHz, $CDCl_3$, 25 °C, δ (ppm)): 2.53 (6H, s, CH_3), 6.23 (2H, tr, ^3J = 1.7 Hz, H(4), *pz*), 6.27 (2H, tr, ^3J = 2.4 Hz, H(4), *pz*), 6.75 (2H, d, H(3/5), ^3J = 2.4 Hz, *pz*), 7.12−7.17 (2 + 4H, m, H(3/5)-*pz*, *m*-py), 7.21 (2H, br, H(3/5), *pz*), 7.73 (2H, d, ^3J = 1.5 Hz, H(3/5), *pz*), 9.09 (4H, d, ^3J = 6.3 Hz, *o*-py).

Synthesis of *trans*-$[ReO_2\{\eta^2\text{-}B(pz)_4\}(4\text{-}NMe_2py)_2]$ (5). To a suspension of **1** (100 mg, 0.19 mmol) in 15 mL of THF was added 4-NMe_2-py (≈0.38 mmol), followed by dropwise addition of 50 mg (0.19 mmol) of PPh_3 dissolved in 10 mL of THF. After the addition was completed, the mixture was stirred for 1 h. The crude product obtained after evaporation of the solvent was purified by recrystallization from dichloromethane/*n*-hexane, yielding an orange crystalline solid formulated as **5** (90 mg, 0.12 mmol, yield = 62%).

Anal. Calcd for $C_{26}H_{32}BN_{12}O_2Re$: C, 42.1; H, 4.3; N, 22.7. Found: C, 41.1; H, 4.2; N, 22.0. UV−vis (CH_2Cl_2), λ_{max}(nm) (ϵ, L mol^{-1} cm^{-1}): 418 (0.7×10^3), 320 (1.3×10^4), 260 (2.4×10^4).^1H NMR (300 MHz, $CDCl_3$, 25 °C, δ (ppm)): 3.03 (12H, s, N−CH_3), 6.20 (2H, tr, ^3J = 1.8 Hz, H(4), *pz*), 6.25 (2H, tr, ^3J = 2.1 Hz, H(4), *pz*), 6.44 (4H, d, ^3J = 7.5 Hz, *m*-py), 6.74 (2H, d, H(3/5), ^3J = 2.1 Hz, *pz*), 7.20 (2H, d, ^3J = 2.4 Hz, H(3/5), *pz*), 7.23 (2H, br, H(3/5), *pz*), 7.71 (2H, d, ^3J = 1.5 Hz, H(3/5), *pz*), 8.70 (4H, d, ^3J = 7.2 Hz, *o*-py).

Synthesis of *trans*-$[ReO_2\{\eta^2\text{-}B(pz)_4\}(1\text{-}MeImz)_2]$ (6). Compound **6** was prepared and purified as described above for **3** and **4**. Starting with 100 mg of **1**, an orange microcrystalline solid formulated as **6** (90 mg, 0.14 mmol, yield = 70%) was obtained.

Anal. Calcd for $C_{20}H_{24}BN_{12}O_2Re$: C, 36.3; H, 3.7; N, 25.4. Found: C, 36.3; H, 3.5; N, 24.7. UV−vis (CH_2Cl_2), λ_{max}(nm) (ϵ, L mol^{-1} cm^{-1}): 415 (1.4×10^3), 250 (2.4×10^4), 224 (3.1×10^4). ^1H NMR (300 MHz, $CDCl_3$, 25 °C, δ (ppm)): 3.68 (6H, s, N−CH_3), 6.18 (2H, tr, ^3J = 1.8 Hz, H(4), *pz*), 6.25 (2H, tr, ^3J = 2.1 Hz, H(4), *pz*), 6.73 (2H, d, H(3/5), ^3J = 2.4 Hz, *pz*), 6.87 (2H, tr,^3J = 1.2 Hz, H(4/5), 1-MeImz), 7.20 (2H, d, ^3J = 2.1 Hz, H(3/5), *pz*), 7.30 (2H, d, ^3J = 1.8 Hz, H(3/5), *pz*), 7.55 (2H, tr,^3J = 1.2 Hz, H(4/5), 1-MeImz), 7.69 (2H, d, ^3J = 1.2 Hz, H(3/5), *pz*), 7.94 (2H, br, H(3), 1-MeImz).

Synthesis of *trans*-$[ReO_2\{\eta^2\text{-}B(pz)_4\}(dmpe)]$ (7). To a suspension of **1** (0.19 mmol) in THF was added dropwise a solution of dmpe (30 mg, 0.2 mmol) and PPh_3 (50 mg, 0.19 mmol) in THF. The reaction, which occurred almost immediately, gave, after stirring for 1 h, a pale yellow solution. The removal of the solvent under vacuum, followed by washing with diethyl ether of the residue, gave compound **7** (95 mg, 0.15 mmol), as a pale yellow microcrystalline solid in approximately 75% yield.

Anal. Calcd for $C_{18}H_{28}BN_8O_2P_2Re$: C, 33.4; H, 4.3; N, 17.3. Found: C, 33.6; H, 4.3; N, 17.0. UV−vis (CH_2Cl_2), λ_{max}(nm) (ϵ, L mol^{-1} cm^{-1}): 352 (0.3×10^3), 274 (4.8×10^3), 226 (2.1×10^4). ^1H NMR (300 MHz, $CDCl_3$, 25 °C, δ (ppm)): 1.73 (12H, d, $^2J_{P-H}$ = 9.6 Hz, P−CH_3), 1.96 (4H, d, $^2J_{P-H}$ = 12.3 Hz, P−CH_2), 6.13 (2H, tr, ^3J = 1.5 Hz, H(4), *pz*), 6.39 (2H, tr, ^3J = 2.4 Hz, H(4), *pz*), 6.67 (2H, d, H(3/5), ^3J = 2.4 Hz, *pz*), 7.16 (2H, d, ^3J = 2.4 Hz, H(3/5), *pz*), 7.65 (2H, br, H(3/5), *pz*), 7.97 (2H, br, H(3/5), *pz*). ^{31}P NMR ($CDCl_3$, 25 °C, δ (ppm)): 7.99.

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Synthesis of *trans*-[$ReO_2\{\eta^2$-B(pz)$_4\}$(dppe)] (8). This compound was prepared as described above for **7.** Analytically pure **8** can be isolated as a pale yellow microcrystalline solid. Yield: 120 mg (0.16 mmol, 83%).

Anal. Calcd for $C_{38}H_{36}BN_8O_2P_2Re$: C, 50.9; H, 4.0; N, 12.5. Found: C, 50.7; H, 3.7; N, 12.9. UV−vis (CH_2Cl_2), λ_{max}(nm) (ϵ, L mol^{-1} cm^{-1}): 366 (1.0×10^3), 308 (3.7×10^3), 225 (2.7×10^4).^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, δ (ppm)): 2.67 (4H, d, $^2J_{P-H} = 13.5$ Hz, P−C*H*$_2$), 6.08 (2H, tr, $^3J = 1.8$ Hz, H(4), *pz*), 6.16 (2H, tr, $^3J = 1.5$ Hz, H(4), *pz*), 6.74 (2H, d, H(3/5), $^3J = 2.1$ Hz, *pz*), 7.16 (2H, d, $^3J = 2.4$ Hz, H(3/5), *pz*), 7.34−7.43 (12H, m, *m*+*p*-Ph), 7.60 (2H, d, $^3J = 1.8$ Hz, H(3/5), *pz*), 7.65−7.75 (2+8H, H(3/5)-pz, *m* + *o*-Ph). ^{31}P NMR ($CDCl_3$, 25 °C, δ (ppm)):13.67.

Synthesis of *trans*-[$ReO_2\{\eta^2$-HB(pz)$_3\}$(py)$_2$] (9). To a suspension of [$ReO_3\{\eta^3$-HB(pz)$_3\}$] in CH_2Cl_2 (50 mg, 0.11 mmol) was added an excess of pyridine (≈80 mg, ≈1 mmol) and 38 mg (0.12 mmol of PPh_3) of a polymer-supported triphenylphosphine (200−400 mesh, 3 mmol of PPh_3/g). The resulting suspension was stirred at room temperature for 2 days. After this time, the polymeric material was separated from the clear yellow-orange supernatant by filtration through a G3 frit. Removal of dichloromethane under vacuum, followed by washing with *n*-hexane, gives compound **9** as a yellow-orange microcrystalline solid. Good elemental analysis could not be obtained because of the instability of **9** when pyridine is not present. Its characterization has been made by IR and ^{1}H NMR spectroscopies.

IR (cm^{-1}): 2455 w (ν(B−H)), 805 vs, br (ν(O═Re═O)). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, δ (ppm)): 6.31 (1H, tr, $^3J = 1.5$ Hz, H(4), *pz*), 6.15 (2H, tr, $^3J = 2.4$ Hz, H(4), *pz*), 7.83 (1H, d, $^3J = 1.8$ Hz, *pz*), 7.80 (1H, d, $^3J = 1.5$ Hz, *pz*), 7.21 (2H, d, $^3J = 2.1$ Hz, *pz*), 7.11 (2H, d, $^3J = 1.8$ Hz, *pz*), 9.42 (4H, d, $^3J = 7.5$ Hz, *o*-py), 7.64 (2H, m, *p*-py), 7.40 (4H, m, $^3J = 6.9$ Hz, *m*-py).

Synthesis of *trans*-[$ReO_2\{\eta^2$-HB(pz)$_3\}$(dmpe)] (10). To a suspension of [$ReO_3\{\eta^3$-HB(pz)$_3\}$] (86 mg, 0.19 mmol) in THF was added dropwise a solution of dmpe (30 mg, 0.2 mmol) and PPh_3 (50 mg, 0.19 mmol) in THF. The reaction, which occurred almost immediately, gave after stirring for 1 h, an orange-yellow solution from which was recovered a microcrystalline orange solid (80 mg, 0.14 mmol, yield = 71%).

IR (cm^{-1}): 2426 m (ν(B−H)), 793 s (ν(O═Re═O)). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, δ (ppm)): 6.31 (1H, tr, $^3J = 1.8$ Hz, H(4), *pz*), 6.25 (2H, tr, $^3J = 2.1$ Hz, H(4), *pz*), 7.88 (1H, d, $^3J = 2.1$ Hz, *pz*), 7.86 (2H, br, *pz*), 7.83 (1H, br, *pz*), 7.17 (2H, br, *pz*), 1.99−2.06 (2 + 2H, m, P−*CH*$_2$), 1.86 (6H, d, $J_{P-H} = 9.0$ Hz, P−*CH*$_3$), 1.75 (6H, d, $J_{P-H} = 9.9$ Hz, P−*CH*$_3$). ^{31}P NMR (300 MHz, $CDCl_3$, 25 °C, δ (ppm)): 6.06.

Syntheses of [ReO{(η^2-*N,O*)(μ-O)B(pz)$_3$}(pz)(pzH)$_2$] (11) and [ReO{(η^2-*N,O*)(μ-O)B(pz)$_3$}Cl(py)$_2$] (12). To a solution of [ReO_2(py)$_4$]Cl (420 mg, 0.8 mmol) in CH_2Cl_2 was added K[B(pz)$_4$] (250 mg, 0.8 mmol) suspended in the same solvent. After overnight reaction, a yellow green solution was obtained as well as a small amount of an insoluble white solid. After centrifugation, the solution was concentrated and transferred to a chromatography column charged with silica gel. Elution with THF/CH_2Cl_2 (10:90) gave a violet fraction, which was evaporated to dryness, yielding a solid formulated as **11**. Another fraction (blue) was recovered using as eluent THF/CH_2Cl_2 (30:70). After workup of this fraction, a blue microcrystalline solid was obtained and formulated as **12**. Compounds **11** and **12** were obtained with approximately 10 and 5% yield, respectively.

Compound 11. Anal. Calcd for $C_{18}H_{20}BN_{12}O_2Re$: C, 34.1; H, 3.2; N, 26.5. Found: C, 33.8; H, 3.3; N, 25.9. IR (cm^{-1}): 3406 m, br, 3119 m, 2960 w, 2920 w, 2848 w, 2510 m, br (ν(N−H)), 1500 s, 1408 s, 1387 s, 1345 m, 1290 s, 1262 s, 1214 s, 1184 w, 1152 s, 1095 s, 1067 s, 1028 s, 934 s (ν(Re═O)), 813 s, 757 s, 669 w, 622 m, 498 m; UV−vis (CH_2Cl_2), λ_{max}(nm): 520, 250, 225. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, δ (ppm)): 5.94 (2H, tr, $^3J = 2.4$ Hz, H(4), *uncoord pz*), 6.27 (2H, br, H(4), *pzH*), 6.37 (1H, tr, $^3J = 2.1$ Hz, *pz*), 6.46 (1H, tr, $^3J = 2.1$ Hz, *pz*), 6.92 (2H, d, $^3J = 2.2$ Hz, *uncoord pz*), 7.10 (2H, br, *pzH*), 7.15 (1H, dd,$^3J = 2.1$, 0.6 Hz), 7.54 (2H, dd, $^3J = 0.6$, 1.5 Hz, *uncoord pz*), 7.59 (1H, dd, $^3J = 2.1$, 0.6 Hz), 7.68 (1H, dd, $^3J = 2.1$, 0.6 Hz), 7.75 (2H, dd, $^3J = 2.4$, 0.6 Hz, *pzH*), 7.98 (1H, dd, $^3J = 2.1$, 0.6 Hz), 18.61 (2H, br, pz*H*). FTICR mass spectrum (*m*/*z* referenced to the species with ^{187}Re and ^{11}B; relative abundance in parentheses): EI (+): 634 (28) (M), 566 (50) (M − pzH), 498 (100) (M − 2pzH), 431 (50) (M − 2pzH − pz).

Table 1. Crystallographic Data for **5**, **10**, and **11**

	5	**10**	**11**
formula	$C_{26}H_{32}BN_{12}O_2Re\cdot 3CH_2Cl_2$	$C_{15}H_{26}BN_6O_2P_2Re\cdot pzH$	$C_{18}H_{20}BN_{12}O_2Re$
mol wt	996.42	649.45	633.47
cryst syst	triclinic	orthorhombic	monoclinic
space group	*P*1	*Pnma*	$P2_1/n$
a, Å	10.907(2)	18.422(2)	10.890(1)
b, Å	11.113(1)	11.850(1)	15.162(1)
c, Å	16.922(2)	11.434(1)	14.137(2)
α, deg	97.91(1)	90	90
β, deg	102.37(1)	90	102.07(1)
γ, deg	94.21(1)	90	90
V, Å^3	1973(1)	2496.1(4)	2282.6(4)
Z	2	4	4
ρ_{calc}, g cm^{-3}	1.677	1.728	1.843
R_1[a,c]	0.0388 (0.0311)	0.0405 (0.0290)	0.0728 (0.0505)
wR_2[b,c]	0.0787 (0.0721)	0.0673 (0.0594)	0.1802 (0.1274)

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o)^2)^2)]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. [c] The values in parentheses were calculated for data with $I > 2\sigma(I)$ only.

Compound 12. Anal. Calcd for $C_{19}H_{19}BClN_8O_2Re$: C, 36.6; H, 3.1; N, 18.0. Found: C, 36.9; H, 3.3; N, 18.4. IR (cm^{-1}): 3104 w, 2956 m, 1609 m, 1500 m, 1452 s, 1404 m, 1384 s, 1289 s, 1215 s, 1088 s, 1063 m, 1028 s, 927 s (ν(Re═O)), 914 s, 831 s, 809 s, 762 s, 757 s, 692 s, 622 m, 503 m, 341 m (ν(Re−Cl)). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, δ (ppm)): 5.98 (2H, tr, $^3J = 1.8$ Hz, H(4), *uncoord pz*), 6.50 (1H, tr, $^3J = 2.4$ Hz, H(4), *coord pz*), 7.13 (2H, d, $^3J = 2.4$ Hz, *uncoord pz*), 7.31 (2H, *uncoord pz*), 7.32 (4H, m, *m-py*), 7.34 (1H, br, *coord pz*), 7.61 (2H, m, *p-py*), 7.71 (1H, d, $^3J = 2.1$ Hz, *coord pz*), 8.47 (4H, m, *o-py*). FAB mass spectrum (*m*/*z* referenced to the species with ^{187}Re, ^{35}Cl, and ^{11}B; relative abundance in parentheses): 624 (100) (M), 557 (50) (M − pz), 478 (100) (M − pz − py), 399 (50) (M − pz − 2py).

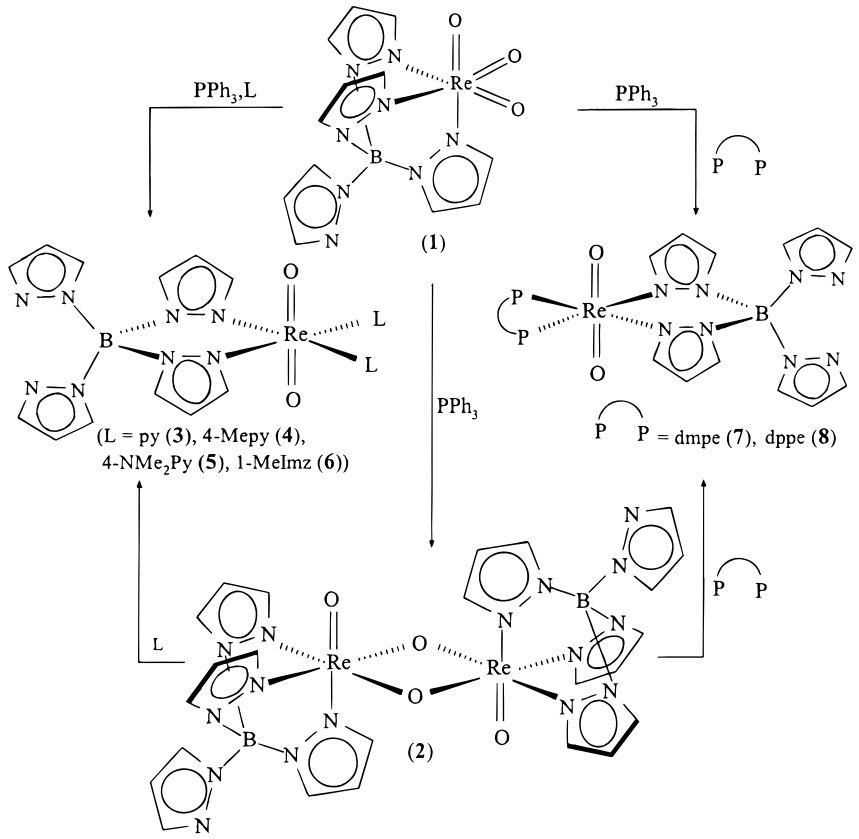
X-ray Crystallographic Analysis. X-ray data were collected from orange crystals of **5** ($0.50 \times 0.42 \times 0.36$ mm) and **10** ($0.40 \times 0.32 \times 0.22$ mm) and from a violet crystal of **11** ($0.40 \times 0.27 \times 0.08$ mm). All these crystals were obtained by recrystallization from dichloromethane/*n*-hexane and mounted in thin-walled glass capillaries within a nitrogen-filled glovebox. A crystal of **5** was mounted in the presence of the mother liquor to avoid crystal decomposition, probably due to loss of solvent trapped in the lattice.

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 $17.5 < 2\theta < 29.9°$ for **5**, $16.6 < 2\theta < 29.7°$ for **10**, and $16.2 < 2\theta < 31.9°$ for **11**. The crystal data are summarized in Table 1. The data were corrected[16] for Lorentz-polarization effects, for linear decay, and also for absorption (Ψ scans). The heavy atom positions were located by Patterson methods using SHELXS-86.[17] The remaining atoms were located by successive least-squares refinements on F^2 using SHELXL-93.[18] The structural analysis of **5** reveals three CH_2Cl_2 solvent molecules per asymmetric unit and, for **10**, one pyrazole crystallization molecule per asymmetric unit. 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. The final difference Fourier syntheses revealed electron densities between +0.96 and −0.71 e Å^{-3} for **5**, +0.58 and −1.19 e Å^{-3} for **10**, and 2.47 and −2.79 e Å^{-3} for **11**, near the rhenium atom. Atomic scattering factors and anomalous dispersion terms were as in SHELXL-93.[18] The drawings were made with ORTEPII,[19] and all of the calculations were performed on a 3000 Dec α computer (Table 1).

Results and Discussion

Syntheses of the Complexes. As can be seen in Scheme 1, the reduction of [$ReO_3\{\eta^3$-B(pz)$_4\}$] (**1**) by PPh_3 in the presence of different *σ*-donor ligands allows the preparation of *trans*-

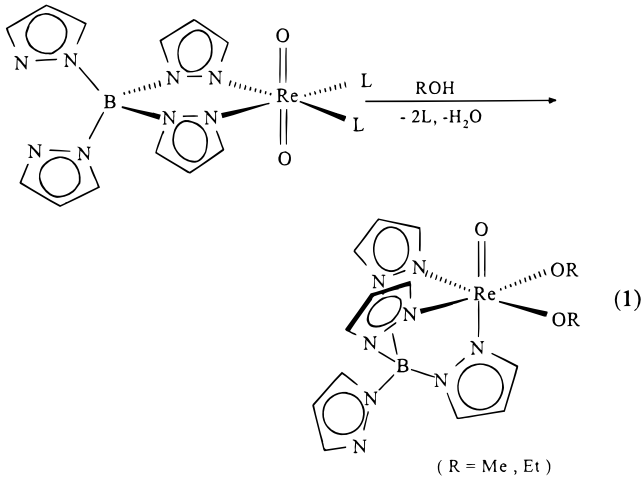
Scheme 1



$[ReO_2\{\eta^2\text{-}B(pz)_4\}(L)_2]$ (L = py (**3**), 4-Mepy (**4**), 4-NMe_2Py (**5**), 1-MeImz (**6**)) or *trans*-$[ReO_2\{\eta^2\text{-}B(pz)_4\}(\overset{\frown}{P}\ \overset{\frown}{P})]$ ($\overset{\frown}{P}\ \overset{\frown}{P}$ = dmpe (**7**), dppe (**8**)) in very high yield.

As we described previously,[9] **1** is reduced by PPh_3 yielding $[ReO(\mu\text{-}O)\{\eta^3\text{-}B(pz)_4\}]_2$ (**2**) in 60% yield (Scheme 1). The possibility of reacting the dimer **2** with the neutral substrates mentioned above, in order to prepare **3**−**8**, was also evaluated. $[ReO(\mu\text{-}O)\{\eta^3\text{-}B(pz)_4\}]_2$ reacts with 4-(dimethylamino)pyridine almost immediatly under stoichiometric conditions, but the reaction with pyridine needs an excess of the substrate and is complete only after 2 h. While **2** reacts fast with dmpe giving **7** almost quantitatively, for dppe, the dimer conversion is not total, even after 4 days at room temperature. So, the use of dimer **2** is not an alternative to prepare these *trans*-dioxo complexes because the kinetics of the cleavage of **2** is strongly dependent on the nucleophilicity of the substrates and the overall yield in complexes **3**−**8** is lower, compared to the method based in the direct reduction of **1**.

Compounds **3**−**8** are yellow or yellow-orange solids that are very soluble in halogenated hydrocarbon solvents, low to moderately soluble in THF and toluene, and almost insoluble in *n*-hexane. Compounds **7** and **8** are thermally stable in solution, but **3**−**6** slowly decompose if the corresponding nitrogen-donor ligands are not present. This thermal instability makes it possible to prepare **7** and **8** by refluxing **3** in toluene in the presence of equimolar amounts of dmpe or dppe, respectively. Another interesting point is that **7** and **8** can be kept in alcoholic solutions for several days, without any detectable decomposition. Compounds **3**−**6** react readily with methanol or ethanol, yielding, almost quantitatively, the alkoxides $[ReO\{\eta^3\text{-}B(pz)_4\}(OR)_2]$ (R = Me, Et) (eq 1).[9]

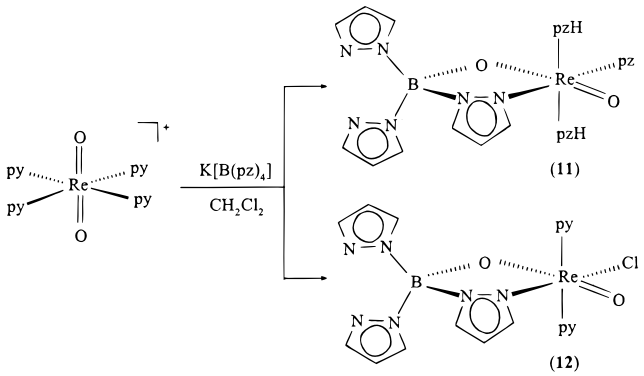


(1)

These results and others previously described[8,9,20,21] are clearly determined by the coordination versatility of the $[B(pz)_4]^-$ ($\eta^3 \Leftrightarrow \eta^2$) ligand. So far, this versatility had not been observed for Re complexes with the analogous $[HB(pz)_3]^-$.[22−25] We tried to see whether it was possible to stabilize dioxo complexes with $\{\eta^2\text{-}HB(pz)_3\}$, and we found that *trans*-$[ReO_2\{\eta^2\text{-}HB(pz)_3\}(py)_2]$ (**9**) and *trans*-$[ReO_2\{\eta^2\text{-}HB(pz)_3\}(dmpe)]$ (**10**) are formed by reducing $[ReO_3\{\eta^3\text{-}HB(pz)_3\}]$ with PPh_3 in the presence of py or dmpe. However, **9** and **10** are more unstable than the analogues with the tetrakis(pyrazolyl)borate. Compound **9** decomposes readily, even at room temperature, yielding $[ReO(\mu\text{-}O)\{\eta^3\text{-}HB(pz)_3\}]_2$[9] (see Experimental Section). Compound **10** decomposes partially in solution with liberation of pzH, as shown by the X-ray structural analysis (vide infra).

Compounds **3**−**10** represent rare examples of neutral *trans*-dioxo Re(V) complexes, and to the best of our knowledge, *trans*-$[ReO_2(CH_2CMe_3)(py)_3]$ and *trans*-$[ReO_2I(PMe_2Ph)_3]$ are the only examples previously described.[14] All of the other known *trans*-dioxo Re(V) complexes are charged, either anionically as $[ReO_2(CN)_4]^{3-}$ and $[ReO_2(PO)_2]^-$ (PO = (*o*-hydroxophenyl)-

Scheme 2



diphenylphosphine) or cationically as $[ReO_2(L)_4]^+$ (L = pyridine, substituted pyridines, imidazole, substituted imidazoles, 7-azaindole, (hydroxymethyl)phosphines, and cyclam) and $[ReO_2(L\text{-}L)_2]^+$ (L-L = ethylenodiamine).[13]

Attempts to prepare *trans*-$[ReO_2\{\eta^2\text{-}B(pz)_4\}(py)_2]$ from *trans*-$[ReO_2(py)_4]Cl$ and $K[B(pz)_4]$ were made, but without success. $[ReO_2(py)_4]Cl$ reacts rather slowly with $K[B(pz)_4]$, yielding a yellow-green mixture, after overnight reaction. From this reaction mixture only the compounds $[ReO\{(\eta^2\text{-}N,O)(\mu\text{-}O)B(pz)_3\}(pz)(pzH)_2]$ (**11**) and $[ReO\{(\eta^2\text{-}N,O)(\mu\text{-}O)B(pz)_3\}Cl(py)_2]$ (**12**) (Scheme 2) could be recovered, after purification by chromatography, although in a very low yield. Compounds **11** and **12** are air stable, at least for short periods, but in solution, **12** decomposes more easily. Both compounds are soluble in polar solvents and moderately soluble in toluene. The modification of the poly(pyrazolyl)borate arises from a nucleophilic attack to the boron atom, but it is not clear if this attack has been done by one of the oxo ligands or by some residual water coming from the starting material *trans*-$[ReO_2(py)_4]Cl$.[15]

Spectroscopic Data. IR spectra of **3**−**8** show the bands characteristic of tetrakis(pyrazolyl)borate, but the antisymmetric stretching bands, ν_{as}(O═Re═O), which would be expected in the range 750−850 cm^{-1},[13,14] were not clearly assigned because of the complexity of the $[B(pz)_4]^-$ ligand. For compounds **9** and **10**, the bands ν_{as}(O═Re═O) are easily assigned at 805 and 793 cm^{-1}, respectively. These values compare with the frequencies reported for *trans*-$[ReO_2(CH_2CMe_3)(py)_3]$ (ν_{as}(O═Re═O): 800 cm^{-1}) and *trans*-$[ReO_2I(PMe_2Ph)_3]$ (ν_{as}(O═Re═O): 785 cm^{-1})[14] and are in the range where ν_{as}(O═Re═O) normally appears in the cationic *trans*-dioxo complexes previously described.[13] In the IR spectra of **9** and **10**, the ν(B−H) stretching bands appear at 2455 and 2426 cm^{-1}, respectively. These frequencies are red shifted compared with the values described in the literature for other rhenium compounds with $[\eta^3\text{-}HB(pz)_3]^-$ (2482−2532 cm^{-1}).[10,22−25] Only a small number of Re complexes with $[\eta^2\text{-}HB(pz)_3]^-$ are described in this work, but the red shift of the ν(B−H) seems to agree with previous results which pointed out the utility of these values as indicators of the hapticity of hydrotris(pyrazolyl)borates.[26] In the IR spectra of **11** and **12**, the presence of strong ν(Re═O) absorption bands is the most significative feature (at 934 cm^{-1} for **11** and at 927 cm^{-1} for **12**). A medium and very broad ν(N−H) stretching band appears in the IR spectrum of **11** centered at 2500 cm^{-1}. This value is very low and can be explained by the N−H···N interaction found in the solid state and apparently maintained in solution (see X-ray and ^{1}H NMR). Similar effects have been observed in other complexes with pyrazole and pyrazolide ligands.[27]

The ^{1}H NMR spectra of the *trans*-dioxo complexes present a 2:2 (**3**−**8**) or a 2:1 (**9** and **10**) pattern for the protons of the pyrazolyl rings, which is indicative of the magnetic equivalence of the two coordinated rings. In **3**−**6** and **9**, the resonances due to the coligands appear in the usual range, and the pattern obtained indicates that in these compounds the two neutral nitrogen-donor ligands are magnetically equivalent. For **7**, **8**, and **10**, only one resonance was observed in the ^{31}P NMR spectra, which is consistent with the magnetic equivalence of the phosphorus atoms in each complex and with the equatorial coordination of the diphosphine ligands. An interesting feature of the ^{1}H NMR spectra of complexes **3**−**8** is the presence of two doublets of equal intensity which are abnormally highfield shifted and which are due to H(3/5) protons of the uncoordinated pyrazolyl rings. As we mentioned previously,[21] this is clearly an indication that in **3**−**8** the tetrakis(pyrazolyl)borate presents a η^2-coordination mode.

The ^{1}H NMR spectrum of **11** presents two sets of resonances of intensity 2:1 for the protons of the $[\eta^2\text{-}OB(pz)_3]$ ligand and only one set of resonances of intensity 2 for the protons of the pzH ligands. This pattern indicates magnetic equivalence of the noncoordinated pyrazolyl rings of the $[\eta^2\text{-}OB(pz)_3]$ and also magnetic equivalence of the two coordinated pzH ligands. This equivalence does not agree with the structure found in the solid state (vide infra), but can be explained assuming that in solution there is free rotation of the noncoordinated pyrazolyl rings around the B−N bond and also free rotation of the pzH and pz^- ligands around the Re−N bond. These processes are fast on the ^{1}H NMR time scale and account for the magnetic equivalence mentioned above and also for the presence of only one broad resonance of intensity 2 due to the pz*H* proton, which appears at a very low field (18.6 ppm). For **12** there is no X-ray structural analysis, but the spectroscopic data (IR, MS spectra, and ^{1}H NMR) suggest for this complex a structure analogous to **11** and also an identical solution behavior (a 2:1 pattern for the protons of $[\eta^2\text{-}OB(pz)_3]$ and magnetic equivalence of the pyridine ligands).

X-ray Crystallographic Studies. The complexes *trans*-$[ReO_2\{\eta^2\text{-}B(pz)_4\}(4\text{-}NMe_2py)_2]\cdot 3CH_2Cl_2$ (**5**) and *trans*-$[ReO_2\{\eta^2\text{-}HB(pz)_3\}(dmpe)]\cdot$pzH (**10**) are monomeric with approximately octahedral coordination geometries. ORTEP views of the structures are shown in Figures 1 and 2, and selected bond distances and angles are listed in Tables 2 and 3, respectively.

The Re−O(1) and the Re−O(2) bond distances (1.761(3), 1.756(3) Å in **5**; 1.752(5), 1.773(5) Å in **10**) are comparable to those found in neutral and cationic *trans*-dioxo complexes.[13,14] The O−Re−O bond angles (173.1(2)° and 176.3(2)° for **5** and **10**, respectively) are comparable to the O−Re−O bond angle of 174.5° found in *trans*-$[ReO_2(py)_4]Cl$ but are smaller and larger than the values of 177−180° and 165.9° found in the cationic complexes and *trans*-$[ReO_2(CH_2CMe_3)(py)_3]$, respectively.[13,14] There is a slight difference between the two axial Re═O bond distances in **10**, probably because of the presence of an interaction between the N−H of the solvated pzH and the O(2) oxo group. The presence of this interaction is indicated by the short distance N(pzH)···O(2) (2.846 Å).

The poly(pyrazolyl)borate ligands are bidentate with average Re−N bond lengths of 2.111(4) and 2.191(3) Å and N−Re−N

(26) Akita, M.; Ohta, K.; Takahashi, Y.; Hikichi, S.; Moro-oka, Y. *Organometallics* **1997**, *16*, 4121.

(27) (a) Sullivan, B. P.; Slamon, D. J.; Meyer, T. J.; Peedin, J. *Inorg. Chem.* **1979**, *16*, 3369. (b) Carmona, D.; Oro, L. A.; Lamata M. P.; Elguero, J.; Apreda, M. C.; Foces-Foces, C.; Cano, F. H. *Angew Chem., Int. Ed. Engl.* **1986**, *25*, 1114. (c) Khan, M. M. T.; Roy, P. S.; Venkatasubramanian K.; Khan, N. H. *Inorg. Chim. Acta* **1990**, *176*, 49.

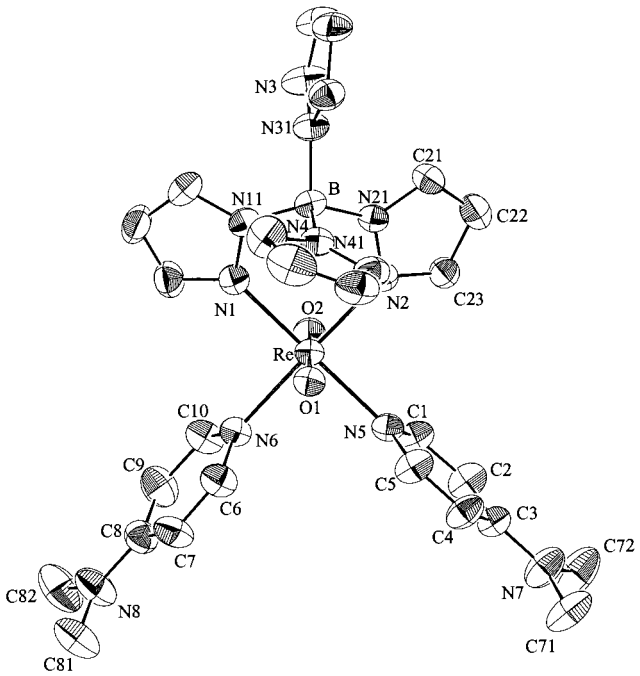


Figure 1. ORTEP view of *trans*-[$ReO_2\{\eta^2$-$B(pz)_4\}$(4-$NMe_2py)_2$] (**5**). Vibrational ellipsoids are drawn at the 50% probability level.

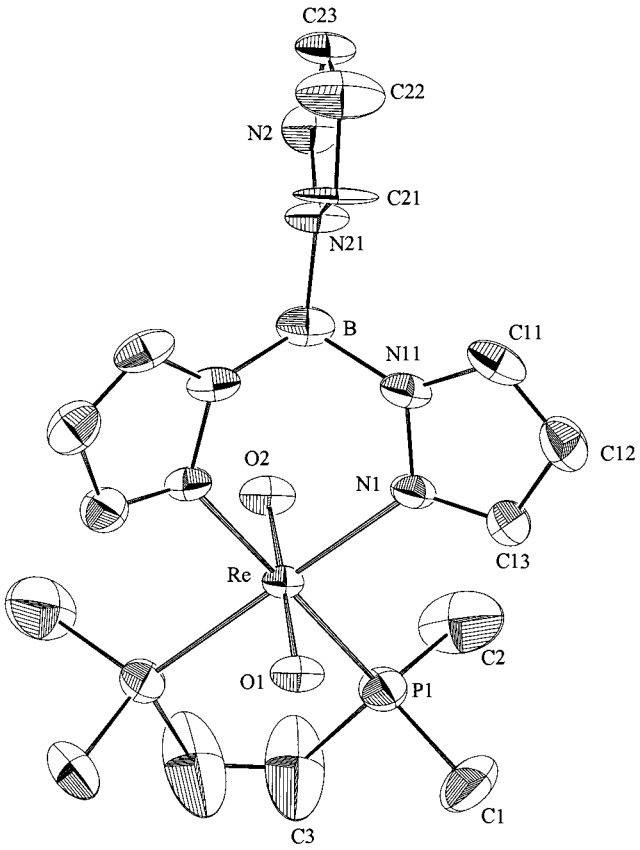


Figure 2. ORTEP view of *trans*-[$ReO_2\{\eta^2$-$HB(pz)_3\}$(dmpe)] (**10**). Vibrational ellipsoids are drawn at the 50% probability level.

bond angles of 88.5(2)° and 84.6(2)° for **5** and **10**, respectively. The longer Re−N bond lengths and the smaller N−Re−N bond angles observed in **10**, compared with those in **5**, are certainly due to a larger steric crowding around the Re center imposed by the bidentate phosphine. For complex **5**, these values are respectively longer and smaller than the corresponding values in previously reported Re(V) monoxo complexes in which the

Table 2. Selected Bond Lengths and Angles for **5**

	Distances (Å)		
Re−O(1)	1.761(3)	Re−O(2)	1.756(3)
Re−N(1)	2.118(4)	Re−N(2)	2.104(4)
Re−N(5)	2.173(4)	Re−N(6)	2.174(4)
	Angles (deg)		
O(1)−Re−O(2)	173.1(2)	O(1)−Re−N(1)	91.1(2)
O(2)−Re−N(1)	93.7(2)	O(1)−Re−N(2)	94.0(2)
O(2)−Re−N(2)	91.1(2)	N(1)−Re−N(2)	88.5(2)
O(1)−Re−N(5)	87.3(2)	O(2)−Re−N(5)	87.9(2)
N(1)−Re−N(5)	178.2(2)	N(2)−Re−N(5)	90.9(2)
O(1)−Re−N(6)	87.8(2)	O(2)−Re−N(6)	87.0(2)
N(2)−Re−N(6)	177.6(2)	N(1)−Re−N(6)	93.2(2)
N(5)−Re−N(6)	87.5(2)		

Table 3. Selected Bond Lengths and Angles for **10**

	Distances (Å)		
Re−O(1)	1.752(5)	Re−O(2)	1.773(5)
Re−N(1)	2.191(4)	Re−P(1)	2.401(1)
B−N(11)	1.563(7)	B−N(21)	1.511(11)
	Angles (deg)		
O(1)−Re−O(2)	176.3(2)	O(1)−Re−N(1)	90.8(2)
O(2)−Re−N(1)	92.0(2)	N(1)−Re−N(1)*	84.6(2)[a]
O(1)−Re−P(1)	90.4(1)	O(2)−Re−P(1)	86.8(1)
N(1)−Re−P(1)	96.7(1)	N(1)*−Re−P(1)	178.3(1)
P(1)−Re−P(1)*	81.91(7)		

[a] The equivalent atoms were generated by the symmetry transformation $x, -y + 1/2, z$.

[$B(pz)_4$] ligand is bidentate.[21] The steric effect of the two oxo ligands certainly accounts for this increase in the Re−N nitrogen bond lengths with the consequent decrease of the N−Re−N bond angle. For **5**, the dihedral angle between the planes of the two coordinated pyrazolyl groups is 36.8(3)°, while for the two noncoordinated groups the dihedral angle is 79.3(2)°.

X-ray structures of several complexes with the moiety "Re(O)$\{\eta^3$-$[HB(pz)_3]\}$" have been described, but to the best of our knowledge, **10** is the first example of a rhenium complex with [η^2-$HB(pz)_3$] structurally characterized. The mean Re−N bond distance in **10** (2.191(4) Å) is slightly longer than the values found for the equatorial Re−N bond distances in oxo complexes with [η^3-$HB(pz)_3$] (2.06−2.17 Å).[22−25]

In **5**, the Re−N bond distances in the pyridine ligands are equal (2.173(4) and 2.174(4) Å) and are comparable to those observed in $[ReO_2(py)_4]Cl$ (average 2.147(12) Å) and in $[ReO_2$-$(4\text{-}Mepy)_4]ReO_4$ (average 2.14(2) Å).[13] These values are smaller than the Re−N distance for the py trans to the neopentyl group in the complex *trans*-$[ReO_2(CH_2CMe_3)(py)_3]$, which was found to be 2.348(11) Å.[14a] So, apparently the trans influence of the alkyl group is much greater than that of the bidentate poly(pyrazolyl) borate ligand.

For **10**, there is a crystallographic plane containing the Re, O(1), O(2), and B(1) atoms and the noncoordinated pyrazolyl ring (N2). The phosphine ligand is chelated to the Re atom forming a five-membered ReP_2C_2 planar ring. In this complex, the Re−P distance and the P−Re−P bond angle are 2.401(1) Å and 81.91(7)°, respectively. These values are shorter and larger than the corresponding values found in *trans*-$[ReO_2$-$\{(HOH_2C)_2PC_6H_4P(CH_2OH)_2\}_2]^+$ (average Re−P 2.459(1) Å; 80.2(1)°) and in *trans*-$[ReO_2\{(HOH_2C)_2PCH_2CH_2P(CH_2OH)_2\}_2]^+$ (average Re−P 2.477(2) Å; 80.5(1)°), probably because of the less steric crowding around the Re atom in **10**, in comparison with these two Re (V) complexes in which two phosphine units are coordinated to the metal center.[13]

X-ray crystals of *trans*-$[ReO_2\{\eta^2$-$B(pz)_4\}(dmpe)]\cdot CH_2Cl_2$ (**7**) were obtained, but of low quality. The best crystal measured did not provide a good quality data set for accurate bond

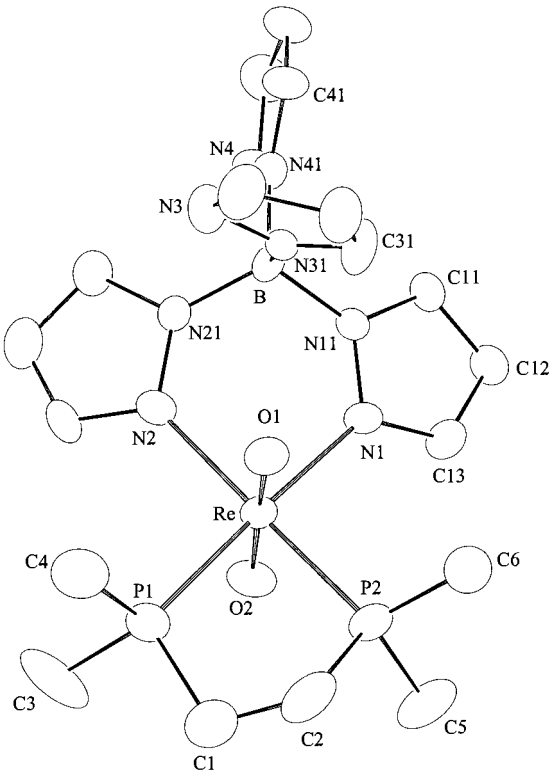


Figure 3. ORTEP view of *trans*-[$ReO_2\{\eta^2$-$B(pz)_4\}$(dmpe)] (**7**). Vibrational ellipsoids are drawn at the 30% probability level.

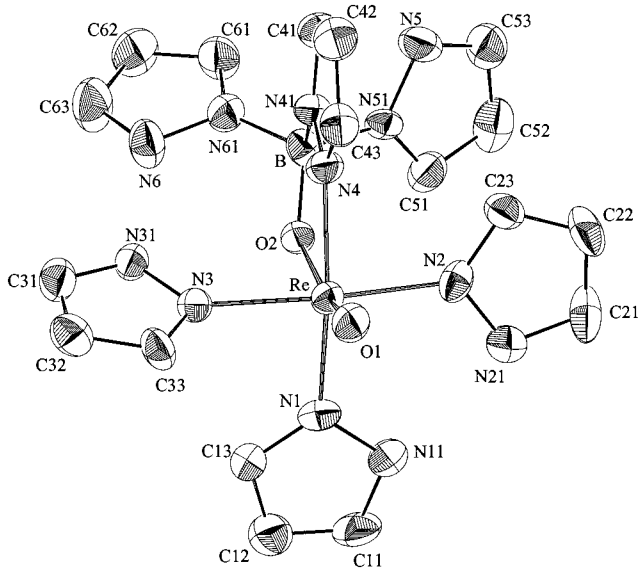


Figure 4. ORTEP view of [$ReO\{(\eta^2$-*N*,*O*)(μ-O)$B(pz)_3\}(pz)(pzH)_2$] (**11**). Vibrational ellipsoids are drawn at the 50% probability level.

distances and angles, but the connectivity of the atoms was determined unambiguously (Figure 3).[28]

Compound **11** (Figure 4; Table 4) is monomeric with an approximately octahedral coordination geometry. The Re atom, the oxygen and the nitrogen atoms of the modified poly-(pyrazoly)borate, the oxo ligand, and the pyrazolate nitrogen atom lie in the equatorial plane, the N(2) and N(3) atoms of the two pyrazole ligands being in the axial positions. The Re−O(1) bond distance of 1.691(8) Å is in the range normally found for mono-oxo Re(V) complexes.[9,21]

Table 4. Selected Bond Lengths and Angles for **11**

	Distances (Å)		
Re−O(1)	1.691(8)	Re−O(2)	1.907(7)
Re−N(1)	2.060(9)	Re−N(2)	2.106(8)
Re−N(3)	2.144(8)	Re−N(4)	2.146(9)
O(2)−B	1.419(14)	N(41)−B	1.58(2)
N(51)−B	1.534(13)	N(61)−B	1.538(13)
	Angles (deg)		
O(1)−Re−O(2)	163.3(3)	O(1)−Re−N(1)	102.6(4)
O(2)−Re−N(1)	94.0(3)	O(1)−Re−N(2)	92.5(3)
O(2)−Re−N(2)	88.8(3)	N(1)−Re−N(2)	93.5(3)
O(1)−Re−N(3)	89.8(3)	O(2)−Re−N(3)	88.0(3)
N(1)−Re−N(3)	89.3(3)	N(2)−Re−N(3)	175.8(3)
O(1)−Re−N(4)	87.1(3)	O(2)−Re−N(4)	76.3(3)
N(1)−Re−N(4)	170.0(3)	N(2)−Re−N(4)	88.5(3)
N(3)−Re−N(4)	88.1(3)	B−O(2)−Re	126.6(6)
O(2)−B−N(51)	112.3(9)	O(2)−B−N(61)	111.5(8)
N(51)−B−N(61)	109.0(8)	O(2)−B−N(41)	104.4(8)
N(51)−B−N(41)	109.2(8)	N(61)−B−N(41)	110.4(9)

In the modified poly(pyrazolyl)borate, the Re−N bond distance is 2.146(9) Å. This value is larger than the corresponding values found in other Re(V) complexes in which the $[B(pz)_4]^-$ ligand is bidentate (average values of 2.09 Å),[21] but is comparable to the values found in other complexes where this ligand is tridentate (average values of 2.10−2.29 Å).[9] The bond distances and angles of the coordinated pyrazolyl ring do not present any significant difference from those of the noncoordinated, but the B−N bond distance for the coordinated pyrazolyl ring is slightly longer (1.58(2) Å) than the corresponding distances for the noncoordinated pyrazolyl rings (1.53(1) Å and 1.54(1) Å). The dihedral angle between the planes of the two noncoordinated pyrazolyl groups is 80.2(4)°, while the coordinated ring makes dihedral angles of 64.8(4) and 76.7(4)° with the planes of the other two. The two pyrazole ligands make a dihedral angle of 61.6(4)°. The pyrazolate ligand makes dihedral angles of 17.1(4) and 77.9(4)° with the N(2) and N(3) pyrazole rings, respectively. Within the molecule there are two short N···N distances (N(21)···N(11), 2.626 Å, and N(31)···N(6), 2.786 Å), which proves the existence of two hydrogen bonds: one between a pyrazole and the pyrazolate and the other one between the pyrazole ligand and a noncoordinated pyrazolyl ring of the modified poly(pyrazolyl)borate.

Concluding Remarks. The reduction of [$ReO_3\{\eta^3$-$B(pz)_4\}$] (**1**) with PPh_3 in the presence of neutral mono or bidentate substrates gives *trans*-[$ReO_2\{\eta^2$-$B(pz)_4\}(L)_2$] or *trans*-[ReO_2-$\{\eta^2$-$B(pz)_4\}(L{-}L)_2$] in high yield. This is a new and convenient synthetic method to enter into the chemistry of neutral *trans*-dioxo complexes. The X-ray structural analysis of *trans*-[ReO_2-$\{\eta^2$-$B(pz)_4\}$(4-$NMe_2py)_2$] confirmed an octahedral geometry for this family of compounds, with η^2-$B(pz)_4$ and the neutral substrates in the equatorial position. As in previous reported work, because of the nature of this ligand, the ^1H NMR spectroscopy proved to be a powerful technique to evaluate the coordination mode of the tetrakis(pyrazolyl)borate.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structures of **5**, **7**, **10**, and **11** are available on the Internet only. Access information is given on any current masthead page.

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(28) Compound **7** crystallizes from dichloromethane/*n*-hexane as yellowish crystals containing one molecule of solvated CH_2Cl_2 in the tetragonal space group I_1/a, with cell parameters $a = b = 19.413(1)$ Å, $c = 32.193(5)$ Å, $V = 12\,133(2)$ Å^3, $Z = 16$, $\rho_{calc} = 1.599$ g cm^{-3}. The refinement of the structure by full-matrix least-squares methods on F^2 was based on 5317 unique reflections ($2\theta_{max} = 50°$). The refinement of 304 parameters and 4532 observed reflections with $F_0 > 4\sigma(F_0)$, converged to $R_1 = 0.0756$ and $wR_2 = 0.1896$.