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Rhenium(V) Dioxo Complexes with Dihydrobis(pyrazolyl)borates: Synthesis and Reactivity toward Electrophilic Substrates

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The compounds *trans*,*trans*-$[ReO_2(py)_4][ReO_2\{H_2B(pz^*)_2\}_2]$ (pz* = pz (**1**), 3,5-Me_2pz (**2**)) have been prepared by reacting *trans*-$[ReO_2(py)_4]Cl$ with the corresponding dihydrobis(pyrazolyl)borate. Compounds **1** and **2** react with electrophilic substrates, such as $ClXMe_3$ (X = Si, Sn), leading to the neutral monoxo derivatives $[ReO(OSiMe_3)\{H_2B(pz^*)_2\}_2]$ (pz* = pz (**3**), 3,5-Me_2pz (**4**)) and $[ReO(OSnMe_3)\{H_2B(pz)_2\}_2]$ (**5**) and regenerating *trans*-$[ReO_2(py)_4]Cl$. Compounds **1** and **3** crystallize from dichloromethane/*n*-hexane as yellow crystals, with one molecule of solvated CH_2Cl_2 in the case of **1**. Crystallographic data: **1**, triclinic space group $P\bar{1}$, $a = 9.419(1)$ Å, $b = 9.584(1)$ Å, $c = 12.652(1)$ Å, $\alpha = 89.03(1)°$, $\beta = 82.41(1)°$, $\gamma = 72.75(1)°$, $V = 1080.9(2)$ Å^3, $Z = 2$; **3**, monoclinic space group $P2_1/n$, $a = 10.785(2)$ Å, $b = 17.680(2)$ Å, $c = 11.971(2)$ Å, $\beta = 98.67(1)°$, $V = 2256.5(6)$ Å^3, $Z = 4$.

Introduction

With hydrotris- and tetrakis(pyrazolyl)borates a rich and versatile chemistry has been developed for Re(V), Re(VI), and Re(VII).[1−27] Some recent examples are the Re(V) and Re(VI) dioxo complexes *trans*-$[ReO_2\{\eta^2\text{-}RB(pz)_3\}(py)_2]$ (R = H, pz)[24] and *cis*-$[ReO_2X\{\eta^3\text{-}HB(pz)_3\}]$ (X = Cl, Br, I).[16] In contrast, with dihydrobis(pyrazolyl)borates ($[H_2B(pz^*)_2]^-$, pz* = pz or substituted pz) the chemistry of rhenium remains rather unexplored. To the best of our knowledge, $[Re\{H_2B(pz)_2\}(CO)_3(L)]$ (L = pzH, $MeC(CH_2O)_3P$) are the only examples of complexes with this type of ligand.[26] One of the reasons for the lack of results is the relative fragility of dihydrobis(pyrazolyl)borates when they react with different oxorhenium starting materials, such as $ReOCl_4^-$, Re_2O_7, or $ReOCl_3(PPh_3)_2$. In our hands, reactions of these starting materials with dihydrobis(pyrazolyl)borates did not allow the preparation of oxo complexes and total or partial modification of the ligands occurred.[25,27] As part of our ongoing studies, we decided to evaluate the possibility of entering into Re(V) oxo complexes with dihydrobis(pyrazolyl)borates through dioxo complexes, namely using *trans*-$[ReO_2(py)_4]Cl$ as starting material.

Reported here are the synthesis and characterization of the novel complexes *trans*,*trans*-$[ReO_2(py)_4][ReO_2\{H_2B(pz^*)_2\}_2]$ (pz* = pz (**1**), 3,5-Me_2pz (**2**)), obtained by reacting *trans*-$[ReO_2(py)_4]Cl$ with $K[H_2B(pz^*)_2]$. Also reported is the reactivity of **1** and **2** toward $ClSiMe_3$ or $ClSnMe_3$, which allowed the preparation and characterization of the first oxo−siloxy and oxo−stannoxy derivatives stabilized by dihydrobis(pyrazolyl)borates: $[ReO(OSiMe_3)\{H_2B(pz^*)_2\}_2]$ (pz* = pz (**3**), 3,5-Me_2pz (**4**)) and $[ReO(OSnMe_3)\{H_2B(pz)_2\}_2]$ (**5**).

Experimental Section

General Procedures. The reactions were carried 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 compound $[ReO_2(py)_4]Cl$ and the ligands $K[H_2B(pz^*)_2]$ (pz* = pz, 3,5-Me_2pz) were prepared as described previously.[28−30] The other chemicals were used as purchased.

^{1}H NMR spectra were recorded on a Varian Unity 300 MHz spectrometer; ^{1}H chemical shifts were referenced with the residual solvent resonances relative to tetramethylsilane. NMR spectra were run in $CDCl_3$, CD_2Cl_2, and toluene-d_8 which were dried and distilled prior

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to use. IR spectra were recorded as KBr pellets on a Perkin-Elmer 577 spectrometer. Carbon, hydrogen, and nitrogen analyses were performed on a Perkin-Elmer automatic analyzer.

Synthesis of *trans,trans*-$[ReO_2(py)_4][ReO_2\{H_2B(pz)_2\}_2]$ (1). To an ethanolic solution of $[ReO_2(py)_4]Cl$ (303 mg, 0.50 mmol) was added $K[H_2B(pz)_2]$ (98 mg, 0.52 mmol) dissolved in ethanol. After 64 h of stirring, a light yellow solid precipitate formed, which was separated from the supernate by centrifugation. This solid was washed with ethanol and *n*-hexane and extracted with CH_2Cl_2. Removal of the solvent yielded 120 mg (0.23 mmol of Re) of **1** ($\eta = 45\%$).

Anal. Calcd for $C_{32}H_{36}N_{12}O_4B_2Re_2$: C, 36.7; H, 3.5; N, 16.1. Found: C, 36.9; H, 3.4; N, 15.9. IR (cm^{-1}): 3108 m, 3037 w, 2964 w, 2416 s (ν(B−H)), 2289 m (ν(B−H)), 1605 m, 1500 m, 1476 s, 1450 s, 1411 s, 1346 w, 1304 s, 1261 w, 1211 s, 1183 m, 1157 s, 1096 w, 1060 s, 1017 m, 880 m, 819 s (ν(Re−O_2)), 799 s (ν(Re−O_2)), 771 m, 752 m, 699 s, 640 m, 615 w, 467 w. ^{1}H NMR (300 MHz, CD_2Cl_2, δ (ppm)): 3.90 (4H, BH_2), 6.19 (4H, tr, H(4), $J = 1.8$ Hz), 7.34 (8H, m, *m*-py), 7.61 (4+4H, m, *p*-py and H(3/5)), 7.73 (4H, d, H(3/5), $J = 1.8$ Hz), 8.98 (8H, d, *o*-py).

Synthesis of *trans,trans*-$[ReO_2(py)_4][ReO_2\{H_2B(3,5\text{-}Me_2pz)_2\}_2]$ (2). To an ethanolic solution of $[ReO_2(py)_4]Cl$ (303 mg, 0.5 mmol) was added $K[H_2B(3,5Me_2pz)_2]$ (120 mg, 0.52 mmol). After overnight reaction (18 h), the yellow complex **2** was isolated as described above for **1**. Yield: 60 mg (0.10 mmol of Re, $\eta = 20\%$).

Anal. Calcd for $C_{40}H_{52}N_{12}O_4B_2Re_2$: C, 41.5; H, 4.5; N: 14.5. Found: C, 41.5; H, 4.7; N, 14.3. IR (cm^{-1}): 2962 m, 2922 m, 2451 m (ν(B−H)), 2356 w (ν(B−H)), 1606 w, 1541 s, 1479 m, 1448 s, 1420 m, 1379 s, 1261 m, 1210 m, 1183 s, 1151 w, 1101 s, 1067 m, 1018 m, 889 w, 821 s ($\nu(ReO_2)$), 802 s ($\nu(ReO_2)$), 767 s, 698 s, 468 w. ^{1}H NMR (300 MHz, CD_2Cl_2, δ (ppm)): 2.14 (12H, s, CH_3, pz*), 2.26 (12H, s, CH_3, pz*), 3.84 (4H, BH_2), 5.70 (4H, s, H(4)), 7.40 (8H, m, *m*-py), 7.63 (4H, m, *p*-py), 9.00 (8H, d, *o*-py).

Synthesis of $[ReO(OSiMe_3)\{H_2B(pz)_2\}_2]$ (3). A solution of compound **1** (100 mg, 0.2 mmol of Re) in CH_2Cl_2 reacted immediately and quantitatively with 0.02 mL (0.16 mmol) of Me_3SiCl. After removal of the solvent, the solid was extracted with *n*-hexane, the extract was filtered to remove $[ReO_2(py)_4]Cl$, and the supernatant solution was dried under vacuum, yielding the yellow complex **3**.

Anal. Calcd for $C_{15}H_{25}N_8O_2B_2SiRe$: C, 30.8; H, 4.3; N, 19.1. Found: C, 31.2; H, 4.1; N, 18.7. IR (cm^{-1}): 3135 w, 3120 w, 2950 w, 2420 s (ν(B−H)), 2350 w (ν(B−H)), 2280 m (ν(B−H)), 1502 m, 1410 s, 1310 s, 1260 m, 1250 s, 1215 s, 1195 s, 1168 s, 1152 s, 1102 m, 1060 s, 1000 s, 992 s, 900 br s (ν(Re−O)), 835 br, 775 s, 759 s, 712 m, 632 s, 610 m, 420 w, 390 w, 360 w, 350 m, 320 m. ^{1}H NMR (300 MHz, toluene-d_8, δ (ppm)): $T = 298$ K, −0.54 (9H, s, $SiMe_3$), 4.40 (4H, br, BH_2), 5.94 (4H, tr, H(4), $J = 2.4$ Hz), 7.57 (4H, d, H(3/5), $J = 2.4$ Hz), 7.58 (4H, d, H(3/5), $J = 2.1$ Hz); $T = 223$ K, −0.53 (9H, s, $SiMe_3$), 4.26 (1H, br, BH_2), 4.38 (1H, br, BH_2), 4.46 (1H, br, BH_2), 5.17 (1H, br, BH_2), 5.76 (2H, s, H(4)), 5.83 (2H, s, H(4)), 7.30 (2H, s, H(3/5)), 7.45 (2H, s, H(3/5)), 7.52 (2H, s, H(3/5)), 7.58 (2H, s, H(3/5)).

Synthesis of $[ReO(OSiMe_3)\{H_2B((3,5\text{-}Me_2pz)_2\}_2]$ (4). Complex **4**, a pink microcrystalline solid, was prepared and recovered quantitatively by starting from compound **2** as described above for **3**.

Anal. Calcd for $C_{23}H_{41}N_8O_2B_2SiRe$: C, 39.6; H, 5.9; N, 16.1. Found: C, 40.7; H, 6.4; N, 16.0. ^{1}H NMR (300 MHz, $CDCl_3$, δ (ppm)): −0.39 (9H, s, $SiMe_3$), 1.96 (6H, s, CH_3, pz*), 2.26 (6H, s, CH_3, pz*), 2.48 (6H, s, CH_3, pz), 2.49 (6H, s, CH_3, pz), 5.89 (2H, s, H(4), pz*), 5.95 (2H, s, H(4), pz*).

Synthesis of $[ReO(OSnMe_3)\{H_2B(pz)_2\}_2]$ (5). Compound **1** (100 mg, 0.2 mmol of Re) in CH_2Cl_2 reacted immediately and quantitatively with 20 mg (0.1 mmol) of Me_3SnCl. Complex **5** precipitated as a yellow solid, which was isolated by centrifugation, washed with dichloromethane, and vacuum-dried.

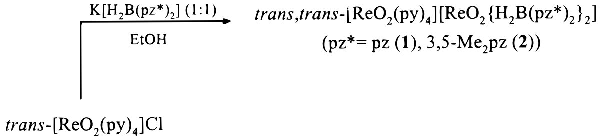
Anal. Calcd for $C_{15}H_{25}N_8O_3B_2SnRe$: C, 26.1; H, 3.6; N, 16.2. Found: C, 25.5; H, 3.4; N, 16.2. IR (cm^{-1}): 2900−3100 w, 2420 s (ν(B−H)), 2336 w (ν(B−H)), 2290 w (ν(B−H)), 1498 m, 1433 w, 1408 s, 1305 s, 1221 m, 1185 s, 1163 m, 1150 s, 1100 w, 1061 s, 989 w, 895 w, 890 m (ν(Re−O)), 845 br, 771 m, 754 s, 712 m, 632 s, 690 m, 610 m, 645 w, 619 w, 609 w, 551 m, 275 m. ^{1}H NMR (300 MHz, CD_2Cl_2, δ (ppm)): −0.12 (9H, s, $SnMe_3$), 3.9 (4H, br, BH_2), 6.37 (4H, tr, H(4), $J = 2.2$ Hz), 7.72 (4H, d, H(3/5), $J = 2.4$ Hz), 7.78 (4H, d, H(3/5), $J = 1.8$ Hz).

Table 1. Crystallographic Data for 1 and 3

	1	3
formula	$C_{32}H_{36}B_2N_{12}O_4Re_2 \cdot CH_2Cl_2$	$C_{15}H_{25}B_2N_8O_2SiRe$
mol wt	1131.68	585.34
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a, Å	9.419(1)	10.785(2)
b, Å	9.584(1)	17.680(2)
c, Å	12.652(1)	11.971(2)
α, deg	89.03(1)	90
β, deg	82.41(1)	98.67(1)
γ, deg	72.75(1)	90
V, Å^3	1080.9(2)	2256.5(6)
Z	2	4
ρ_{calc}, g cm^{-3}	1.869	1.723
$R_1{}^{a,c}$	0.0476 (0.0313)	0.0366 (0.0257)
$wR_2{}^{b,c}$	0.0798 (0.0674)	0.0679 (0.0577)

[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.

Scheme 1



X-ray Crystallographic Analysis. X-ray data were collected from yellow crystals of **1** (0.45 × 0.34 × 0.14 mm) and **3** (0.56 × 0.45 × 0.36 mm). The crystals were obtained by recrystallization from dichloromethane/*n*-hexane and mounted in thin-walled glass capillaries under nitrogen atmosphere.

Data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated 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 $17.5 < 2\theta < 31.7°$ for **1** and $20.4 < 2\theta < 29.8°$ for **3**. The crystal data are summarized in Table 1.

The data were corrected[31] for Lorentz−polarization effects and for absorption (Ψ scans). The heavy-atom positions were located by Patterson methods using SHELXS-86.[32] The remaining atoms were located by sucessive least-squares refinements on F^2 using SHELXL-93.[33] The structural analysis of **1** reveals one CH_2Cl_2 solvent molecule per asymmetric unit. All 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 +1.06 and −0.87 e Å^{-3} for **1** and between 0.40 and −0.73 e Å^{-3} for **4**, near the rhenium atom. Atomic scattering factors and anomalous dispersion terms were as in SHELXL-93.[33] The drawings were made with ORTEP,[34] and all calculations were performed on a 3000 DEC α computer.

Results and Discussion

Syntheses. As shown in Scheme 1, reaction of *trans*-$[ReO_2(py)_4]Cl$ with 1 equiv of $K[H_2B(pz)_2]$ or $K[H_2B(3,5\text{-}Me_3pz)_2]$ in EtOH yields *trans,trans*-$[ReO_2(py)_4][ReO_2\{H_2B(pz)_2\}_2]$ (**1**) or *trans,trans*-$[ReO_2(py)_4][ReO_2\{H_2B(3,5\text{-}Me_2pz)_2\}_2]$ (**2**), respectively. Even when excess of these ligands are used,

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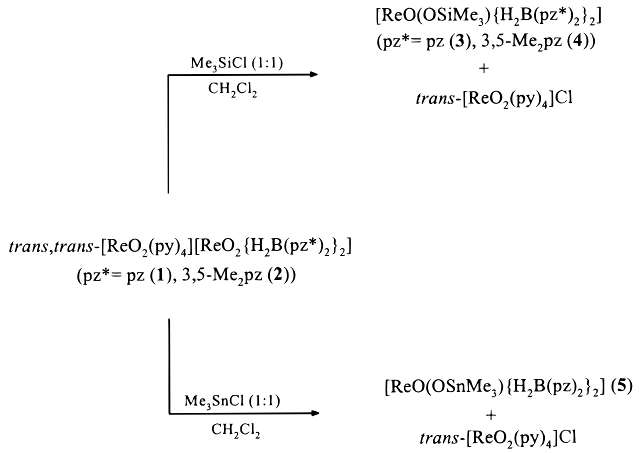
Scheme 2



compounds **1** and **2** are the only species formed. The reaction with K[$H_2B(3,5\text{-}Me_3pz)_2$] is faster, most probably because the inductive effect of the methyl substituents makes the replacement of pyridines easier. However, **1** and **2** are very reactive compounds, and specially compound **2** decomposes very quickly when in solution, leading to unidentified species. This instability of **2** is certainly one of the reasons that this compound is synthesized in low yield and with poor reproducibility. One possible explanation for the high reactivity of **2** is the presence of a congested and electron-rich metallic center in the anion $[ReO_2\{H_2B(3,5\text{-}Me_2pz)_2\}_2]^-$ ($\mathbf{2}^-$). In fact, the presence of two ligands with methyl substituents in the 3- and 5-positions of the pyrazolyl rings must be responsible for such properties.

The stabilization of the dioxo compounds **1** and **2** contrasts with other results previously described.[25,27] In fact, we have found that $[ReOCl_3(PPh_3)_2]$ reacts with K[$H_2B(pz^*)_2$] (pz* = pz, 3,5-Me_2pz), in alcohols, leading to the polyhydrides $[ReH_4\{(H(\mu\text{-}OR)B(3,5\text{-}Me_2pz)_2\}(PPh_3)]$ and $[ReH_2\{(OR)(\mu\text{-}OR)B(pz)_2\}(PPh_3)_2]$ (R = Me, Et).[25,27] The formation of these polyhydrides compared to the results described in this work attests to the importance of the oxorhenium complex used as starting material in the reactions with dihydrobis(pyrazolyl)borates. Apparently, the electronic properties of the metallic center are important for the modification or complete degradation of the dihydrobis(pyrazolyl)borates and for the abstraction of the oxo ligand.

As indicated in Scheme 2, **1** and **2** are good starting materials to enter into the chemistry of complexes with the moiety $[ReO]^{3+}$. At room temperature, the anions *trans*-$[ReO_2\{H_2B(pz^*)_2\}_2]^-$ (pz* = pz, 3,5-Me_2pz) react immediately with Me_3XCl (X = Si, Sn), yielding the neutral oxo−siloxy and oxo−stannoxy derivatives **3**−**5**. Following the reactions indicated in Scheme 2 by ^1H NMR showed that anions $\mathbf{1}^-$ and $\mathbf{2}^-$ are quantitatively converted to complexes **3**−**5**, with *trans*-$[ReO_2(py)_4]^+$ remaining intact, even when an excess of Me_3XCl (X = Si, Sn) is used. These results can be explained by the stronger nucleophilic character of the oxo groups in $\mathbf{1}^-$ and $\mathbf{2}^-$ than in *trans*-$[ReO_2(py)_4]^+$, and this is certainly due to the presence of dihydrobis(pyrazolyl)borates.

The reactivity of rhenium(V) *trans*-dioxo complexes toward electrophilic substrates (e.g., H^+ and methyl trifluoromethanesulfonate)[35−37] is well-known, but to the best of our knowledge, the transformation of the core *trans*-$[Re^VO_2]^+$ into $[Re^VO(OSiMe_3)]^{2+}$ or $[Re^VO(OSnMe_3)]^{2+}$ is unprecedented. However, conversion of an oxo group into siloxide or stannoxide ligands is a well-documented process for Re(VII) oxides.[38]

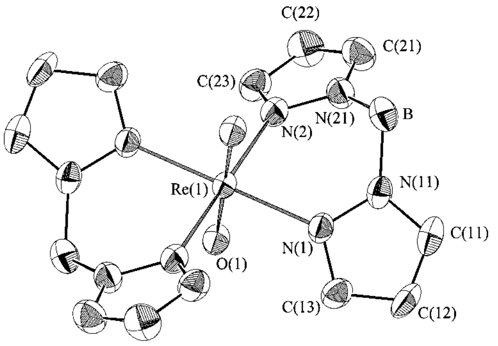


Figure 1. ORTEP view of the anion *trans*-$[ReO_2\{H_2B(pz)_2\}_2]^-$ ($\mathbf{1}^-$). Vibrational ellipsoids are drawn at the 40% probability level.

The behavior observed for $\mathbf{1}^-$ and $\mathbf{2}^-$ in reactions with $ClSiMe_3$ contrasts with that observed for $[ReO(\mu\text{-}O)\{\kappa^3\text{-}B(pz)_4\}]_2$ or $[ReO(RC{\equiv}CR)_2]^-$.[21,39] In the first case, the complex formed is $[ReO\{\kappa^3\text{-}B(pz)_4\}Cl_2]$[2c], and in the second case, depending on the stoichiometry, the species formed are $[Re(OSiMe_3)(RC{\equiv}CR)_2]$ or $[Re(Cl)(RC{\equiv}CR)_2]$.[39] The trans arrangement of the oxo and $OXMe_3$ (X = Si, Sn) ligands in **3**−**5** (see X-ray data) certainly justifies the inertness of these complexes toward excess of Me_3XCl.

Characterization of the Dioxo Complexes. Complexes **1** and **2** are microcrystalline solids, almost insoluble in most common organic solvents and quite soluble in dichloromethane. Compounds **1** and **2** have rhenium−oxo stretches for the cation at 819 and 821 cm^{-1} and for the anion at 799 and 802 cm^{-1}, respectively. For all these complexes ν_{as}(O=Re=O) appears in the range expected for complexes containing the core *trans*-$[ReO_2]^+$.[40] Compared to pyridines, dihydrobis(pyrazolyl)borates are expected to be stronger electron donors, and this explains the displacement of the ν(O=Re=O) antisymmetric stretching vibration to lower energies for $\mathbf{1}^-$ and $\mathbf{2}^-$. In addition, in the IR spectra of **1** and **2** are also observed other bands typical of the coordinated ligands, namely ν(B−H) at 2416 and 2289 cm^{-1} for **1** and at 2451 cm^{-1} for **2**.

^1H NMR spectra of **1** and **2** show three resonances due to the ortho, meta, and para protons of the pyridines, one set of three resonances for the protons of the pyrazolyl rings, and one broad resonance for the BH_2 protons of the dihydrobis(pyrazolyl)borates. These data are consistent with the centrosymmetric nature of the cations and anions of compounds **1** and **2**, as shown by X-ray analysis of **1**.

The ORTEP diagram for compound **1** is shown in Figure 1, and selected bond lengths and angles are presented in Table 2.

The structure of **1** consists of *trans*-$[ReO_2(py)_4]^+$ cations and *trans*-$[ReO_2\{H_2B(pz)_2\}_2]^-$ anions, which are both discrete, monomeric, and octahedral units. Both rhenium atoms lie on a center of symmetry. The structural parameters of the cation compare with those previously described for $[ReO_2(py)_4]Cl$.[41] In the anion *trans*-$[ReO_2\{H_2B(pz)_2\}_2]^-$, the oxo ligands are axially coordinated in a strictly linear arrangement imposed by the symmetry. The Re−O bond distance of 1.763(5) Å is typical

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Table 2. Selected Bond Lengths and Angles for 1

Distances (Å)			
Re(1)−O(1)	1.763(5)	Re(1)−N(1)	2.137(5)
Re(1)−N(2)	2.153(5)	Re(2)−O(2)	1.763(5)
Re(2)−N(3)	2.144(5)	Re(2)−N(4)	2.148(7)
Angles (deg)			
O(1)−Re(1)−N(1)	89.0(2)	O(1)−Re(1)−N(1)*	91.0(2)[a]
O(1)−Re(1)−N(2)	89.3(2)	O(1)−Re(1)−N(2)*	90.7(2)[a]
N(1)−Re(1)−N(2)	87.6(2)	N(1)−Re(1)−N(2)*	92.4(2)[a]
O(2)−Re(2)−N(3)	90.5(2)	O(2)−Re(2)−N(3)*	89.5(2)[b]
O(2)−Re(2)−N(4)	89.3(3)	O(2)−Re(2)−N(4)*	90.7(3)[b]
N(3)−Re(2)−N(4)	88.8(2)	N(3)−Re(2)−N(4)*	91.2(2)[b]

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

of a rhenium−oxygen double bond and is in the range usually observed for *trans*-dioxo Re(V) compounds.[42−53] In particular, this distance compares with the mean values found for Re═O bond lengths in *trans*-[ReO$_2${κ^2-B(pz)$_4$}(4-NMe$_2$py)$_2$] (1.759(3) Å) and *trans*-[ReO$_2${κ^2-HB(pz)$_3$}(dmpe)] (1.763(5) Å).[24] The two bidentate [H$_2$B(pz)$_2$]$^-$ ligands are coordinated equatorially, each defining a ReN$_4$B six-membered chelating ring in the typical boat conformation and pointing alternatively toward O(1) and O(1)*. In **1**$^-$, the mean Re−N bond distance of 2.145(5) Å compares with the mean values of 2.111(4) and 2.191(4) Å found for the equatorial Re−N bond distances in *trans*-[ReO$_2${κ^2-B(pz)$_4$}(4-NMe$_2$py)$_2$] and *trans*-[ReO$_2${κ^2-HB(pz)$_3$}(dmpe)], respectively.[24] The other bond distances and angles involving the [H$_2$B(pz)$_2$] ligands are typical.

Characterization of the Monoxo Complexes. Complexes **3**−**5** are microcrystalline solids, stable in solid and in solution. Complexes **3** and **4** are soluble in most common organic solvents, including aliphatic hydrocarbons. Complex **5** presents a low solubility except in dichloromethane, where it is moderately soluble.

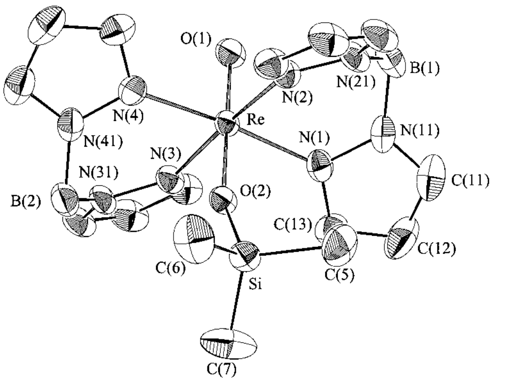

Figure 2. ORTEP view of [ReO(OSiMe$_3$){H$_2$B(pz)$_2$}$_2$] (**3**). Vibrational ellipsoids are drawn at the 40% probability level.

Table 3. Selected Bond Lengths and Angles for 3

Distances (Å)			
Re−O(1)	1.688(4)	Re−O(2)	1.886(3)
Re−N(1)	2.105(5)	Re−N(4)	2.113(5)
Re−N(3)	2.110(4)	Re−N(2)	2.124(4)
O(2)−Si	1.641(4)		
Angles (deg)			
O(1)−Re−O(2)	178.8(2)	O(1)−Re−N(1)	94.5(2)
O(2)−Re−N(1)	86.1(2)	O(1)−Re−N(4)	91.9(2)
O(2)−Re−N(4)	87.5(2)	N(1)−Re−N(4)	173.6(2)
O(1)−Re−N(3)	91.3(2)	O(2)−Re−N(3)	89.7(2)
N(1)−Re−N(3)	90.5(2)	N(4)−Re−N(3)	88.9(2)
O(1)−Re−N(2)	92.9(2)	O(2)−Re−N(2)	86.2(2)
N(1)−Re−N(2)	87.9(2)	N(4)−Re−N(2)	92.2(2)
N(3)−Re−N(2)	175.7(2)	Si−O(2)−Re	160.7(2)

The molecular structure of complex **3** is shown in Figure 2, and selected bond lengths and angles are presented in Table 3. The rhenium atom is six-coordinated and displays an approximately octahedral coordination geometry. The oxo and siloxide ligands are coordinated at the axial positions, and the pair of nitrogens of each dihydrobis(pyrazolyl)borate are coordinated equatorially. The O(1)−Re−O(2) bond angle (178.8(2)°) indicates that the oxygen from the siloxide is almost trans to the oxo group. The Re−O(1) bond distance (1.688(4) Å) is comparable to the values found in other rhenium(V) complexes with poly(pyrazolyl)borates and is in the usual range for rhenium(V) monooxo complexes.[1−25,54] The coordination of the siloxide ligand is characterized by a Re−O(2) distance of 1.886(3) Å, which is comparable to and shorter than the values described for [ReOCl$_2$(OSiMe$_3$)(py)$_2$] (1.889(4) Å) and [(η^5-C$_5$Me$_5$)ReCl(OSiMe$_3$)(NCH$_2$-2-C$_5$H$_4$N)] (2.020(6) Å), respectively.[55,56] These data are consistent with some competition of the siloxide for π bonding with the metal, the Re−OSiMe$_3$ having bond some multiple character. Each dihydrobis(pyrazolyl)borate defines a six-membered ReN$_4$B chelating ring in a typical boat conformation, with the apexes of each boat conformation pointing alternatively toward the oxo and siloxide ligands. The average Re−N bond length of 2.113(5) Å is comparable to the values found in other rhenium monooxo complexes with poly(pyrazolyl)borate ligands.[1−25] The siloxide ligand bends (Re−O(2)−Si angle of 160.7(2)°) toward the bidentate ligand which has the boat conformation directed toward the oxo group, certainly to minimize repulsive interactions.

The X-ray crystallographic analysis performed on a poor-quality crystal of **4** did not provide an adequate data set for an accurate determination of the structure of this complex. However, it was possible to define unambiguously the connectivities of the atoms (Figure 3) and to confirm that the molecular structure of complex **4** is analogous to that of **3**. Compound **4** crystallizes from a saturated dichloromethane solution as pink crystals in the triclinic space group P$\bar{1}$ with cell parameters a = 9.477(2) Å, b = 10.772(2) Å, c = 17.965 (2) Å, α = 96.28 (1)°, β = 99.63 (1)°, γ = 114.6(1)°, V = 1610.9(5) Å^3, Z = 2, and ρ_{calc} = 1.438 g cm^{-3}.

The IR spectra of complexes **3** and **5** show the presence of strong bands close to 900 cm^{-1} which are certainly due to ν-

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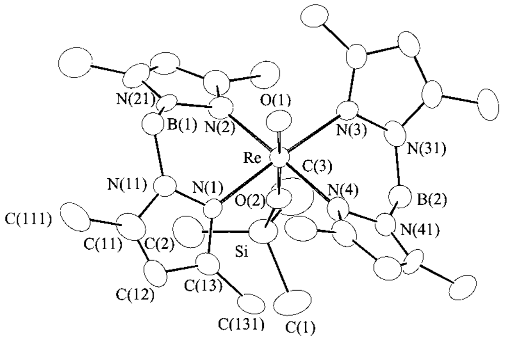

Figure 3. ORTEP view of [ReO(OSiMe$_3$){H$_2$B(3,5-Me$_2$pz)$_2$}$_2$] (**4**). Vibrational ellipsoids are drawn at the 30% probability level.

(Re−O). These value are in the low end of the range where the rhenium−oxygen stretching vibration usually appears for rhenium(V) monooxo complexes.[40] This can be accounted for by the competition of the siloxide and stannoxide ligands in π-bonding interactions with the metal. Another significant feature of the IR spectra of complexes **3** and **5** is the presence of bands due to ν(B−H), between 2280 and 2420 cm^{-1}, which are consistent with the coordination of the dihydrobis(pyrazolyl)borates.

At room temperature, the ^{1}H NMR spectra of complexes **3** and **5** show only three resonances for the protons of the pyrazolyl rings (H(3), H(4), H(5)) and a broad resonance for BH$_2$. The methyl protons of the Me$_3$Si (**3**) and Me$_3$Sn (**5**) groups are shielded, as a consequence of the trans effect of the oxo group, and appear as singlets at −0.54 and at −0.12 ppm, respectively. This pattern does not agree with the solid-state structure of **3** and indicates a fluxional behavior for the complexes.

Variable-temperaure ^{1}H NMR studies were then performed for compounds **3** and **5**. At −80 °C, for complex **5** all the resonances broadened but no splitting was observed. For **3**, upon lowering the temperature, we observed the coalescence of the three resonances due to the H(3), H(4), and H(5) protons of the pyrazolyl rings, and each one split into two resonances of equal intensity. The original BH$_2$ resonance also split into four broad resonances, although three of them present very close chemical shifts (see the Experimental Section). The pattern of the static spectrum obtained at −50 °C is consistent with two magnetically different dihydrobis(pyrazolyl)borates, and this agrees with the solid-state structure of **3** (Figures 2 and 4). The fluxionality of this molecule can certainly be explained by a dynamic process which involves a rapid boat−boat flip with an associated arrangement of the atoms of the six-membered ring, as proposed for other complexes with dihydrobis(pyrazolyl)borates.[57−59]

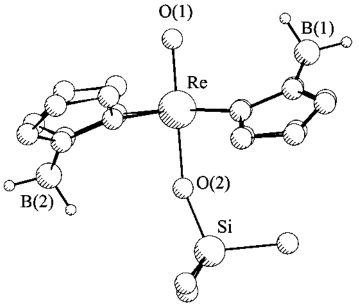

Figure 4. View of [ReO(OSiMe$_3$){H$_2$B(pz)$_2$}$_2$] (**3**) emphasizing the boat conformation of the ReN$_4$B chelate rings.

At room temperature, the ^{1}H NMR spectrum of complex **4** displays only one resonance at −0.39 ppm for the methyl protons of the siloxide group which is trans to the Re−O bond. However, four resonances of relative intensities 6:6:6:6 were observed at 1.96, 2.26, 2.48, and 2.49 ppm for the methyl protons of the pyrazolyl rings, as well as two resonances at 5.89 and at 5.95 ppm for the H(4) protons. A very broad BH$_2$ resonance spans between 4 and 5 ppm due, probably, to quadrupolar coupling and relaxation effects from the boron atoms. The pattern of this spectrum is consistent with the symmetry found in the solid state for **4** and indicates a static behavior for the complex in solution. The presence of the methyl substituents in the ligand [H$_2$B(3,5-Me$_2$pz)$_2$]$^-$ certainly increases the energy barrier for the boat−boat flip and explains the rigidity found for complex **4** at room temperature.

Concluding Remarks

The first Re(V) dioxo complexes with dihydrobis(pyrazolyl)borates have been isolated, characterized, and shown to react with electrophilic substrates, such as ClXMe$_3$ (X = Si, Sn). This reactivity allowed an easy entrance into the chemistry of monoxo Re(V) complexes stabilized with [H$_2$B(pz)$_2$]$^-$ or [H$_2$B(3,5-Me$_2$pz)$_2$]$^-$ ligands, which is an unprecedented process. The presence of methyl substituents in the 3,5-positions of the pyrazolyl rings seems to affect the stability of the Re(V) dioxo compound **2**, probably due to electronic and stereochemical influences.

Acknowledgment. K.R.R. thanks the Fundação Oriente for a postdoctoral grant.

Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of **1** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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