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Cationic Re(V) Oxo Complexes with Poly(pyrazolyl)borates: Synthesis, Characterization, and Stability

António Paulo, Ângela Domingos, Raquel Garcia, and Isabel Santos*

Departamento de Química, ITN, Estrada Nacional 10, 2686-953 Sacavém Codex, Portugal

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Cationic Re(V) oxo compounds of the type $[ReO(OSiMe_3)\{\eta^2\text{-}B(pz)_4\}(L)_2]X$ [X = Cl, L = 4-$(NMe_2)C_5H_4N$ (**1**), 1-Meimz (1-methylimidazole; **2**), 1/2 dmpe (1,2-bis(dimethylphosphino)ethane; **3**), py (**4a**); X = I, L = py (**4b**)] can be prepared by reacting *trans*-$[ReO_2\{\eta^2\text{-}B(pz)_4\}(L)_2]$ with $XSiMe_3$. In solution, cations **1**−**4** are reactive species, and those with unidentate nitrogen donor ligands (**1**, **2**, and **4**) rearrange into the neutral derivatives $[ReO(Cl)(OSiMe_3)\{\eta^2\text{-}B(pz)_4\}(L)]$ [L = py (**5**), 4-$(NMe_2)C_5H_4N$ (**6**), 1-Meimz (**7**)], which are also reported herein. Compounds **1**−**3** and **5**−**7** have been fully characterized by the usual spectroscopic techniques, which in some cases includes X-ray crystallographic analysis (**3**, **6**, and **7**). Compound **3** crystallizes from CH_2Cl_2/*n*-hexane as yellow crystals with one molecule of CH_2Cl_2 solvent, and compounds **6** and **7** crystallize from THF/*n*-hexane as violet and red crystals, respectively, with one molecule of THF solvent in the case of **6**. Crystallographic data: **3**, orthorhombic space group $Pn2_1a$, $a = 11.311(2)$ Å, $b = 19.135(2)$ Å, $c = 15.443(2)$ Å, $V = 3342.4(8)$ Å^3, $Z = 4$; **6**, triclinic space group $P\bar{1}$, $a = 8.7179(11)$ Å, $b = 12.5724(8)$ Å, $c = 17.750(2)$ Å, $\alpha = 70.454(7)°$, $\beta = 77.935(9)°$, $\gamma = 77.129(8)°$, $V = 1768.1(3)$ Å^3, $Z = 2$; **7**, monoclinic space group $P2_1/c$, $a = 16.356(2)$ Å, $b = 20.384(3)$ Å, $c = 17.360(3)$ Å, $\beta = 106.971(12)°$, $V = 5535.8(14)$ Å^3, $Z = 8$.

Introduction

In the past few years, a relatively large variety of Re(V), Re(VI), and Re(VII) oxo complexes with $[RB(pz)_3]^-$ (R = H, pz) and with related ligands have been described, allowing the development of a diversified chemistry based, namely, in oxygen- and electronic-transfer processes.[1−26] In some of these studies, Mayer's group claimed the formation of Re(V) cations of the type $[Re(O)(HB(pz)_3)(X)(OSMe_2)]OTf$ as intermediates in a series of interesting chemical transformations, such as thermal migration of alkyl ligands from the rhenium metal center to the oxo group or oxidation of alkoxide ligands to aldehydes or ketones. However, for such cations no unequivocal structural characterization has been reported, and the formulation has been based mainly on NMR.[11,13−16]

In our laboratory, we have been studying the chemistry of Re oxo complexes with the $[B(pz)_4]^-$ ligand, and we have demonstrated that, in these systems, tetrakis(pyrazolyl)borate presents a higher coordination versatility ($\eta^3-\eta^2$) than those of hydrotris(pyrazolyl)borates.[18−25] This versatility allowed the entrance into the chemistry of rather unusual neutral Re(V) *trans*-dioxo complexes of the type *trans*-$[ReO_2\{\eta^2\text{-}B(pz)_4\}(L)_2]$, using an unprecedented synthetic approach.[23] In this work, we report on the usefulness of *trans*-$[ReO_2\{\eta^2\text{-}B(pz)_4\}(L)_2]$ for the preparation of the first fully characterized cationic Re(V) oxo complexes with poly(pyrazolyl)borates: $[ReO(OSiMe_3)\{\eta^2\text{-}B(pz)_4\}(L)_2]X$ [X = Cl, L = 4-$(NMe_2)C_5H_4N$ (**1**), 1-Meimz (1-methylimidazole; **2**), 1/2 dmpe (1,2-bis(dimethylphosphino)ethane; **3**), py (**4a**); X = I, L = py (**4b**)]. The stability of these cations, which have been obtained by reacting *trans*-$[ReO_2\{\eta^2\text{-}B(pz)_4\}(L)_2]$ with the corresponding trimethylsilyl halide, depends on the nature of the neutral ligands coordinated to the metal. The reactivity of the cations with unidentate coligands allowed the synthesis of the new neutral compounds $[ReO(Cl)(OSiMe_3)\{\eta^2\text{-}B(pz)_4\}(L)]$ [L = py (**5**), 4-$(NMe_2)C_5H_4N$ (**6**), 1-Meimz (**7**)], which are obtained in moderate (**5** and **6**) to low (**7**) yield. Herein is also reported the synthesis and characterization of complexes **5**−**7**.

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* To whom correspondence should be addressed. E-mail: isantos@itn1.itn.pt.

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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 the described procedures. Compounds *trans*-[ReO$_2${η^2-B(pz)$_4$}(L)$_2$] (L = py, 4-(NMe$_2$)C$_5$H$_4$N, 1-Meimz, 1/2 dmpe) were prepared as described previously.[23] The other chemicals were used as purchased.

^{1}H and ^{31}P 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 and the ^{31}P NMR chemical shifts with an external 85% H$_3$PO$_4$ solution. NMR spectra were run in CDCl$_3$, which was dried and distilled prior to use. The pyrazolyl protons always display J_{HH} coupling constants around 2.0 Hz, which are not included in the NMR data reported below. 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.

[ReO(OSiMe$_3$){η^2-B(pz)$_4$}{4-(NMe$_2$)C$_5$H$_4$N}$_2$]Cl (1). To a solution of *trans*-[ReO$_2${η^2-B(pz)$_4$}{4-(NMe$_2$)C$_5$H$_4$N}$_2$] (500 mg, 0.67 mmol) in dichloromethane was added ClSiMe$_3$ (850 μL, 6.7 mmol). The resulting violet solution was allowed to stir for 24 h. After this period of time, the solvent was removed under vacuum, yielding a violet and microcrystalline solid which was formulated as **1** (460 mg, 0.54 mmol, yield 80%).

Anal. Calcd for C$_{29}$H$_{41}$N$_{12}$O$_2$BClSiRe: C, 40.93; H, 4.82; N, 19.76. Found: C, 39.41; H, 4.49; N, 19.49. IR (cm^{-1}): 880 s [ν(Re═O)]. ^{1}H NMR (300 MHz, CDCl$_3$, δ): −0.32 (9H, s, SiMe$_3$), 3.26 (12H, s, NCH$_3$), 6.22 (1H, br, H(4)), 6.29 (1H, br, H(4)), 6.57 (2H, tr, H(4)), 6.59 (1H, d, H(3/5)), 6.76 (4H, d, *m*-py), 6.79 (1H, d, H(3/5)), 7.34 (2H, d, H(3/5)), 7.51 (2H, d, H(3/5)), 7.61 (1H, br, H(3/5)), 7.86 (1H, br, H(3/5)), 8.00 (4H, d, *o*-py).

[ReO(OSiMe$_3$){η^2-B(pz)$_4$}(1-Meimz)$_2$]Cl (2). To a suspension of *trans*-[ReO$_2${η^2-B(pz)$_4$}(1-Meimz)$_2$] (300 mg, 0.45 mmol) in dichloromethane was added ClSiMe$_3$ (60 μL, 0.47 mmol). The reaction mixture was stirred for 1 h, with formation of a pink precipitate. The solution was filtered, and the solid obtained was washed with 2 × 3 mL of THF and vacuum-dried, yielding a microcrystalline pink solid formulated as **2** (260 mg, 0.34 mmol, yield 75%).

Anal. Calcd for C$_{23}$H$_{33}$N$_{12}$O$_2$BClSiRe: C, 35.86; H, 4.29; N, 21.83. Found: C, 35.73; H, 4.23; N, 21.39. IR (cm^{-1}): 885 s [ν(Re═O)]. ^{1}H NMR (300 MHz, CDCl$_3$, δ): −0.30 (9H, s, SiMe$_3$), 4.17 (6H, s, CH$_3$, 1-Meimz), 6.19 (1H, tr, H(4)), 6.29 (1H, tr, H(4)), 6.53 (2H, tr, H(4)), 6.60 (1H, d, H(3/5)), 6.79 (1H, d, H(3/5)), 7.03−7.05 (2 + 2H, br, 1-Meimz), 7.33 (2H, d, H(3/5)), 7.50 (2H, d, H(3/5)), 7.60 (1H, d, H(3/5)), 7.87 (1H, d, H(3/5)), 9.18 (2H, br, 1-Meimz).

[ReO(OSiMe$_3$){η^2-B(pz)$_4$}(dmpe)]Cl (3). *trans*-[ReO$_2${η^2-B(pz)$_4$}(dmpe)] (300 mg, 0.46 mmol) reacts with ClSiMe$_3$ (60 μL, 0.47 mmol), in dichloromethane, yielding, after 1 h at room temperature, a pale-yellow solution. After removal of the solvent, the pale-yellow residue was washed with *n*-hexane, yielding an insoluble microcrystalline solid that was formulated as compound **3** (260 mg, 0.34 mmol, yield 74%).

Anal. Calcd for C$_{21}$H$_{37}$N$_8$O$_2$BClP$_2$SiRe: C, 33.35; H, 4.89; N, 14.82. Found: C, 32.63; H, 4.89; N, 14.52. IR (cm^{-1}): 880 s [ν(Re═O)]. ^{1}H NMR (300 MHz, CDCl$_3$, δ): −0.45 (9H, s, SiMe$_3$), 1.99 (6H, d, $^2J_{PH}$ = 10.8 Hz, P−C*H*$_3$), 2.24 (6H, d, $^2J_{PH}$ = 10.8 Hz, P−C*H*$_3$), 2.44 (2H, m, P−C*H*$_2$), 3.17 (2H, m, P−C*H*$_2$), 6.04 (1H, tr, H(4)), 6.29 (1H, tr, H(4)), 6.57 (1H, d, H(3/5)), 6.66 (2H, tr, H(4)), 6.72 (1H, d, H(3/5)), 7.44 (1H, d, H(3/5)), 7.50 (2H, d, H(3/5)), 7.88 (1H, d, H(3/5)), 8.02 (2H, d, H(3/5)). ^{31}P NMR (300 MHz, CDCl$_3$, δ): 10.63.

[ReO(OSiMe$_3$){η^2-B(pz)$_4$}(py)$_2$]X (X = Cl (4a), I (4b)). Compounds **4a** and **4b** are formed upon the addition of XSiMe$_3$ (X = Cl, I) to *trans*-[ReO$_2${η^2-B(pz)$_4$}(py)$_2$] solutions, in either chlorinated solvents or THF. Compound **4a** forms rapidly but disproportionates very fast into the neutral [ReO(Cl)(OSiMe$_3$){η^2-B(pz)$_4$}(py)] **(5).** For this reason, **4a** was not obtained in a preparative scale. The formulation of **4a** was based on the ^{1}H NMR spectrum, which was obtained immediately after the addition of the reagents in the CDCl$_3$ solution. Compound **4b** is more stable and was obtained in a preparative scale. By reacting 0.31 mmol of *trans*-[ReO$_2${η^2-B(pz)$_4$}(py)$_2$] with 0.34 mmol of ISiMe$_3$ in THF, we obtained 0.17 mmol of **4b** (yield 56%), after appropriate workup as described above for **3**.

Compound 4a. ^{1}H NMR (300 MHz, CDCl$_3$, δ): −0.19 (9H, s, SiMe$_3$), 6.25 (1H, tr, H(4)), 6.31 (1H, tr, H(4)), 6.61 (2H, tr, H(4)), 6.68 (1H, d, H(3/5)), 6.81 (1H, d, H(3/5)), 7.10 (2H, d, H(3/5)), 7.56 (2H, d, H(3/5)), 7.62 (1H, d, H(3/5)), 7.88 (1H, d, H(3/5)), 7.95 (4H, br, *m*-py), 8.13 (2H, tr, *p*-py), 8.90 (4H, m, *o*-py).

Compound 4b. IR (cm^{-1}): 885 s [ν(Re═O)]. ^{1}H NMR (300 MHz, CDCl$_3$, δ): −0.17 (9H, s, SiMe$_3$), 6.24 (1H, tr, H(4)), 6.30 (1H, tr, H(4)), 6.58 (2H, tr, H(4)), 6.69 (1H, d, H(3/5)), 6.79 (1H, d, H(3/5)), 7.07 (2H, d, H(3/5)), 7.54 (2H, d, H(3/5)), 7.62 (1H, d, H(3/5)), 7.87 (1H, d, H(3/5)), 7.97 (4H, br, *m*-py), 8.04 (2H, br, *p*-py), 8.94 (4H, br, *o*-py).

[ReO(Cl)(OSiMe$_3$){η^2-B(pz)$_4$}(py)] (5). *trans*-[ReO$_2${η^2-B(pz)$_4$}(py)$_2$] (500 mg, 0.76 mmol) and ClSiMe$_3$ (≈100 mg, 0.92 mmol) were allowed to react in dichloromethane for 2 h. The resulting solution was vacuum-dried and the residue extracted with toluene. After filtration, a clear red toluene solution was obtained, and by the addition of *n*-hexane, a red microcrystalline solid precipitated, which was formulated as **5** (250 mg, 0.36 mmol, yield 47%).

Anal. Calcd for C$_{20}$H$_{26}$N$_9$O$_2$BClSiRe: C, 35.03; H, 3.80; N, 18.40. Found: C, 34.97; H, 3.80; N, 17.90. IR (cm^{-1}): 885 s [ν(Re═O)]. ^{1}H NMR (300 MHz, CDCl$_3$, δ): −0.42 (9H, s, SiMe$_3$), 6.14 (1H, br, H(4)), 6.28 (1H, tr, H(4)), 6.43 (1H, tr, H(4)), 6.58 (1H, d, H(3/5)), 6.63 (1H, tr, H(4)), 6.81 (1H, d, H(3/5)), 7.02 (1H, d, H(3/5)), 7.42 (1H, d, H(3/5)), 7.59−7.64 (1 + 2H, m, H(3/5) + *m*-py), 7.86−7.91 (1 + 1H, m, H(3/5) + *p*-py), 8.72 (2H, d, *o*-py), 7.87 (1H, d, H(3/5)), 9.20 (1H, d, H(3/5)).

[ReO(Cl)(OSiMe$_3$){η^2-B(pz)$_4$}{4-(NMe$_2$)C$_5$H$_4$N}] (6). Compound **6** was prepared by dissolving compound **1** (500 mg, 0.58 mmol) in dichloromethane and by stirring the resulting solution for 4 days. The final red solution was vacuum-dried, and the resulting residue was extracted into toluene. After filtration, *n*-hexane was added to the toluene solution, precipitating on standing a red microcrystalline solid, which was formulated as **6** (230 mg, 0.32 mmol, yield 55%).

Anal. Calcd for C$_{22}$H$_{31}$N$_{10}$O$_2$BClSiRe: C, 36.29; H, 4.25; N, 19.20. Found: C, 36.19; H, 4.15; N, 19.05. IR (cm^{-1}): 900 s [ν(Re═O)]. ^{1}H NMR (300 MHz, CDCl$_3$, δ): −0.44 (9H, s, SiMe$_3$), 3.20 (6H, s, NCH$_3$), 6.11 (1H, tr, H(4)), 6.27 (1H, tr, H(4)), 6.42 (1H, tr, H(4)), 6.55 (1H, d, H(3/5)), 6.58−6.61 (2 + 1H, m, *m*-py + H(4)), 6.80 (1H, d, H(3/5)), 7.21 (1H, d, H(3/5)), 7.37 (1H, d, H(3/5)), 7.47 (1H, d, H(3/5)), 7.57 (1H, d, H(3/5)), 7.86 (1H, d, H(3/5)), 8.18 (2H, d, *o*-py), 9.16 (1H, d, H(3/5)).

[ReO(Cl)(OSiMe$_3$){η^2-B(pz)$_4$}(1-Meimz)] (7). Compound **2** (600 mg (0.78 mmol)) was left in dichloromethane for 7 days. After evaporation of the solvent, the crude product was analyzed by ^{1}H NMR. The spectrum indicated the presence of compound **2** and indicated also the presence of a small amount of **7**. Recrystallization of the crude product from THF/hexane allowed the isolation of a few red crystals, which were formulated as **7** by X-ray diffraction analysis and by ^{1}H NMR spectroscopy.

^{1}H NMR (300 MHz, CDCl$_3$, δ): −0.42 (9H, s, SiMe$_3$), 3.90 (3H, s, CH$_3$, 1-Meimz), 6.10 (1H, tr, H(4)), 6.27 (1H, tr, H(4)), 6.43 (1H, tr, H(4)), 6.52 (1H, d, H(3/5)), 6.60 (1H, tr, H(4)), 6.79 (1H, d, H(3/5)), 7.07 (1H, d, 1-Meimz), 7.21 (1H, d, H(3/5)), 7.33 (1H, d, 1-Meimz), 7.37 (1H, d, H(3/5)), 7.48 (1H, d, H(3/5)), 7.55 (1H, d, H(3/5)), 7.71 (1H, br, 1-Meimz), 7.85 (1H, d, H(3/5)), 9.20 (1H, d, H(3/5)).

X-ray Crystallographic Analysis. X-ray data were collected from yellow crystals of **3** (0.54 × 0.27 × 0.09 mm), violet crystals of **6** (0.90 × 0.25 × 0.11 mm), and red crystals of **7** (0.29 × 0.23 × 0.18 mm). The crystals were obtained by recrystallization from dichloromethane/*n*-hexane (**3**) or from THF/*n*-hexane (**6** and **7**) and mounted in thin-walled glass capillaries under a nitrogen atmosphere.

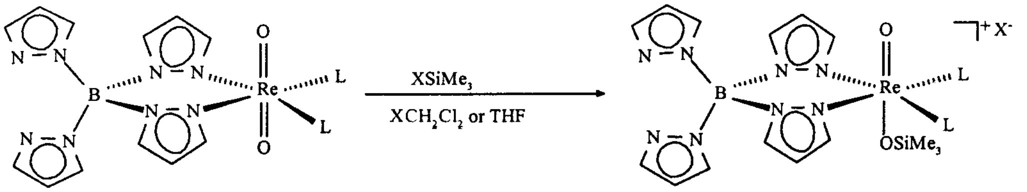
Data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å), using a $\omega-2\theta$ scan mode. Unit cell dimensions were obtained by least-squares refinement of the setting angles of 25 reflections with $15.9 < 2\theta < 29.7°$ for **3**, $16.0 < 2\theta < 29.2°$ for **6**, and $15.1 < 2\theta < 24.9°$ for **7**. The crystal data are summarized in Table 1.

Table 1. Crystallographic Data for **3**, **6**, and **7**

	3	**6**	**7**
formula	$C_{21}H_{37}BClN_8O_2P_2SiRe{\cdot}CH_2Cl_2$	$C_{22}H_{31}BClN_{10}O_2SiRe{\cdot}THF$	$C_{19}H_{27}BClN_{10}O_2SiRe$
mol wt	841.00	800.22	688.06
crystal system	orthorhombic	triclinic	monoclinic
space group	$Pn2_1a$	$P\bar{1}$	$P2_1/c$
a, Å	11.311(2)	8.7179(11)	16.356(2)
b, Å	19.135(2)	12.5724(8)	20.384(3)
c, Å	15.443(2)	17.750(2)	17.360(3)
α, deg		70.454(7)	
β, deg		77.935(9)	106.971(12)
γ, deg		77.129(8)	
V, Å^3	3342.4(8)	1768.1(3)	5535.8(14)
Z	4	2	8
ρ_{calc}, g cm^{-3}	1.671	1.503	1.651
μ, mm^{-1}	4.041	3.587	4.565
R_1[a]	0.0460	0.0425	0.0852
wR_2[a]	0.1022	0.1011	0.0972

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$, with $I > 2\sigma(I)$ only.

Scheme 1



(X = Cl, L = 4-(NMe$_2$)C$_5$H$_4$N (**1**), 1-Meimz (**2**), 1/2 dmpe (**3**), py (**4a**); X = I, L = py (**4b**))

The data were corrected[27] for Lorentz polarization effects and for absorption (Ψ scans). The heavy-atom positions were located by Patterson methods using SHELXS-86.[28] The remaining atoms were located by successive least-squares refinements on F^2 using SHELXL-93.[29] The structural analysis of **3** and **6** reveals one CH_2Cl_2 or one THF solvent molecule per asymmetric unit, respectively. The measured crystal of **7** diffracted weakly which, worsened by the packing of two independent molecules in the asymmetric unit, gave structural parameters with great standard deviations and was, therefore, less accurate than those of **3** and **6**. In one of the molecules of **7**, the nitrogen and the methyl group of imidazole are disordered. The disorder was modeled for the group of atoms C(2)−N(6)−C(4) with site occupancies of 0.53 and 0.47, respectively. Because of this disorder, a few distances between atoms within this imidazole group, as well as the planarity of the ring, had to be restrained. All of the non-hydrogen atoms were refined anisotropically. The contributions of the hydrogen atoms were included in the calculated positions and constrained to ride on their carbon atoms with group U_{iso} values assigned. The final difference Fourier syntheses revealed electron densities between +1.20 and −1.51 e Å^{-3} for **3**, +1.54 and −1.52 e Å^{-3} for **6**, and +0.766 and −0.81 e Å^{-3} for **7** near the rhenium atom. Atomic-scattering factors and anomalous-dispersion terms were the same as those in SHELXL-93.[29] The drawings were made with ORTEP,[30] and all of the calculations were performed on a 3000 Dec α computer.

Results and Discussion

Synthesis and Characterization of the Cationic Re(V) Mono-oxo Complexes. The new Re(V) cations **1**−**4** have been synthesized by reacting $XSiMe_3$ with the neutral *trans*-[ReO$_2$-{η^2-B(pz)$_4$}(L)$_2$][23] (Scheme 1).

Compounds **1**−**3** are obtained as microcrystalline solids in good isolated yields (74−80%) and have been fully characterized by the usual techniques in inorganic chemistry. The isolation of compound **4a** was not possible, because it rearranges in solution almost immediately, yielding the neutral compound **5** (see below). The formulation of **4a** was based on the ^{1}H NMR spectrum obtained immediately after the addition of trimethylsilyl chloride to a $CDCl_3$ solution of the starting dioxo complex. To evaluate the effect of the anion on the stability of cation **4**, we attempted the preparation of the iodide congener (**4b**) by a similar reaction with trimethylsilyl iodide. In fact in this case, it was possible to isolate the complex **4b** in moderate yield (56%; Scheme 1).

The infrared spectra of compounds **1**−**3** and **4b** display the characteristic bands of tetrakis(pyrazolyl)borate as well as those of the corresponding coligands. For **1**, **2**, and **4b** the ν(Re═O) stretching bands were also easily assigned at 880 cm^{-1} (**1**) and 885 cm^{-1}(**2** and **4b**). These values appear at the low end of the range usually observed for the ν(Re═O) stretching vibration (900−1200 cm^{-1}).[31] The spectrum of compound **3** shows a strong and broad band centered at 940 cm^{-1} and a medium-broad band centered at 880 cm^{-1}. The former appears in the range of frequencies where the dmpe ligand also absorbs.[32] Therefore, by comparison with the spectroscopic data obtained for **1**, **2**, and **4b**, the ν(Re═O) stretching vibration for **3** has been assigned to the band at 880 cm^{-1}.

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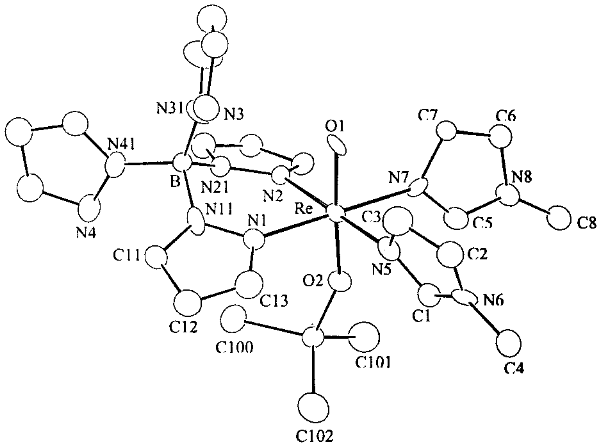

Figure 1. ORTEP view of the cation of **2**. Vibrational ellipsoids are drawn at the 20% probability level.

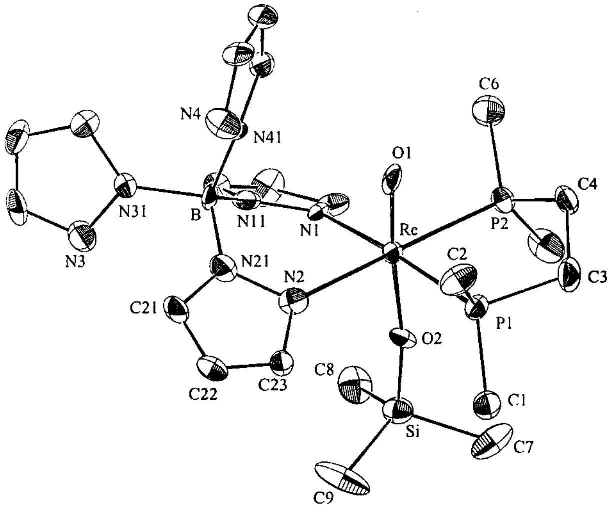

Figure 2. ORTEP view of the cation of **3**. Vibrational ellipsoids are drawn at the 35% probability level.

Table 2. Selected Bond Lengths and Angles for **3**

	Distances (Å)		
Re−O(1)	1.620(14)	Re−O(2)	1.968(13)
Re−N(1)	2.21(2)	Re−N(2)	2.172(13)
Re−P(1)	2.379(5)	Re−P(2)	2.424(4)
O(2)−Si	1.646(14)		
	Angles (deg)		
O(1)−Re−O(2)	174.3(2)	O(1)−Re−N(1)	96.3(5)
O(2)−Re−N(1)	84.8(6)	O(1)−Re−N(2)	96.9(7)
O(2)−Re−N(2)	88.8(7)	N(1)−Re−N(2)	82.8(7)
O(1)−Re−P(1)	90.0(5)	O(1)−Re−P(2)	84.7(5)
O(2)−Re−P(1)	88.7(4)	O(2)−Re−P(2)	89.7(4)
N(1)−Re−P(1)	173.5(5)	N(1)−Re−P(2)	96.3(4)
N(2)−Re−P(1)	97.9(6)	N(2)−Re−P(2)	178.3(7)
P(1)−Re−P(2)	82.8(2)	Si−O(2)−Re	171.4(9)

ORTEP diagrams for the cations of compounds **2** and **3** are shown in Figures 1 and 2, and selected bond lengths and angles for **3** are given in Table 2.

The structure of **3** consists of monomeric and discrete [ReO(OSiMe$_3$){η^2-B(pz)$_4$}(dmpe)]$^+$ cations and chloride counterions, without any intermolecular interaction between them. The X-ray crystallographic analysis performed on a poor-quality crystal of **2** did not provide an adequate data set for an accurate determination of the structure of this compound. (Compound **2** crystallizes from dichloromethane/*n*-hexane as pink crystals in the orthorhombic space group *Fdd*2 with cell parameters $a = 34.719(3)$ Å, $b = 41.969(3)$ Å, $c = 9.6484(12)$ Å, $V = 14059(2)$ Å^3, $Z = 16$, and $\rho_{\text{calc}} = 1.455$ g cm^{-3}. The refinement converged to $R_1 = 0.0726$ and w$R_2 = 0.1226$ for 1096 observed reflections ($I \geq 0$).) However, the collected data allowed us to establish unambiguously the connectivity between the atoms of the cation (Figure 1) and confirmed the presence of the chloride counterion, proving that the structure of **2** is analogous to the one found for **3**. In both cases, the coordination geometry around the Re atom is approximately octahedral, the axial positions being occupied by the oxo and siloxide ligands. The equatorial positions are defined by two pyrazolyl rings of [η^2-B(pz)$_4$]$^-$ and by two 1-Meimz coligands (**2**) or by a bidentate dmpe (**3**).

The Re═O bond distance in **3** (1.620(14) Å) is relatively short and is at the low end of the range (1.65−1.70 Å),[19−25] found for neutral mono-oxo Re(V) complexes with tetrakis(pyrazolyl)borate. All of the other metrical parameters obtained for the structure of **3** are unexceptional compared to the ones obtained for other rhenium(V) mono-oxo complexes containing [η^2-B(pz)$_4$]$^-$, other rhenium(V) oxosiloxides, or other Re(V) complexes containing diphosphine ligands.[19−25,33,34]

The ^{1}H NMR spectra of compounds **1**−**4** are consistent with the C_s symmetry expected, in solution, for this family of compounds. In fact, in these spectra, a 2:1:1 pattern is observed for the protons of the pyrazolyl rings of tetrakis(pyrazolyl)borate, and the intensity and number of resonances observed for the monodentate and neutral coligands (**1**, **2**, **4a**, and **4b**) are consistent with their magnetic equivalence. For compound **3**, only one resonance is observed for the two phosphorus atoms and appears at 10.63 ppm. However, the methylenic and the methyl protons of dmpe are diastereotopic, and this justifies the presence, in the ^{1}H NMR spectrum of **3**, of two doublets each of intensity 6 and of two multiplets of intensity 2, which are due to the methyl and methylenic protons of dmpe, respectively.

The formation of the cationic compounds **1**−**4** shows that the oxo groups in the starting dioxo complexes *trans*-[ReO$_2${η^2-B(pz)$_4$}(L)$_2$] have a significant nucleophilic character. We should remark that these cationic oxosiloxides (**1**−**4**) are formed even by using a large excess of ClSiMe$_3$, without further replacement of the siloxide by a chloride. This contrasts with the behavior that we have previously observed for the dimer [ReO(μ-O){η^3-B(pz)$_4$}]$_2$, which reacts with an excess of ClSiMe$_3$ leading exclusively to [ReO{η^3-B(pz)$_4$}Cl$_2$], without formation of oxosiloxide complexes.[20] These results clearly show that the presence of σ-donor coligands influences the reactivity of the unity "ReO$_2${B(pz)$_4$}", apparently increasing the nucleophilicity of the oxo ligands. The oxosiloxide derivatives (**1**−**4**) described in this work have been prepared by a method similar to the one that we have previously used to prepare the neutral compounds [ReO(OSiMe$_3$){H$_2$B(pz*)$_2$}$_2$] (pz* = pz, 3,5-Me$_2$pz).[33] However, the stability of the previously described compounds [ReO(OSiMe$_3$){H$_2$B(pz*)$_2$}$_2$] (pz* = pz, 3,5-Me$_2$pz) contrasts significantly with the reactivity found for the cationic complexes (**1**−**4**) described in this work.

Synthesis and Characterization of the Neutral Re(V) Mono-oxo Complexes. Complexes **1**, **2**, and **4a** rearrange in solution, leading to neutral oxosiloxides **5**−**7** (Scheme 2). Most probably, these neutral compounds result from a nucleophilic attack of the counteranion to the metallic center. The rate and efficiency of this attack are strongly dependent on the donor capability of the heterocycle coligands [py (**4a**) < 4-(NMe$_2$)-C$_5$H$_4$N (**1**) < 1-Meimz (**2**)], reflecting therefore the positive

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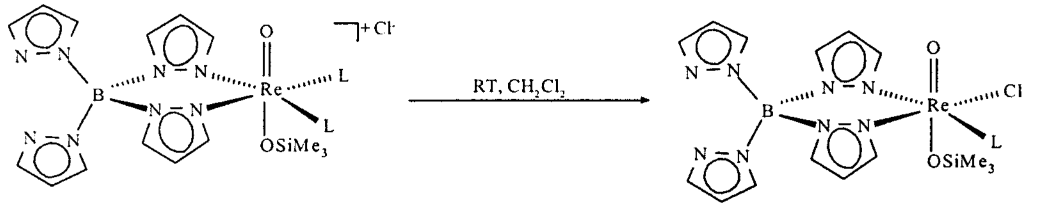
Scheme 2



(L = py (**5**), 4-(NMe$_2$)C$_5$H$_4$N (**6**), 1-Meimz (**7**))

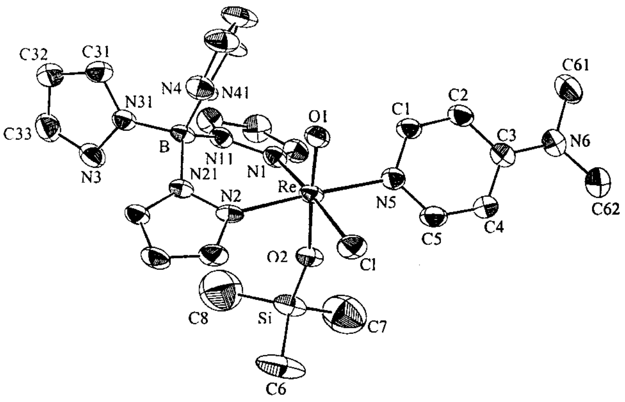


Figure 3. ORTEP view of **6**. Vibrational ellipsoids are drawn at the 35% probability level.

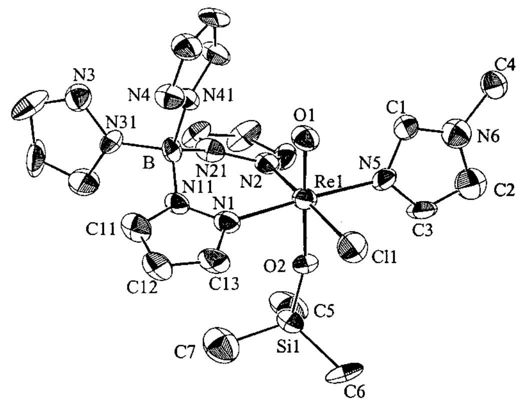


Figure 4. ORTEP view of molecule 1 of **7**. Vibrational ellipsoids are drawn at the 35% probability level.

Table 3. Selected Bond Lengths and Angles for **6**

	Distances (Å)		
Re−O(1)	1.658(4)	Re−O(2)	1.887(4)
Re−N(1)	2.109(5)	Re−N(2)	2.159(5)
Re−N(5)	2.217(5)	Re−Cl(1)	2.402(2)
O(2)−Si	1.612(5)		
	Angles (deg)		
O(1)−Re−O(2)	174.8(2)	O(1)−Re−N(1)	97.2(2)
O(1)−Re−N(2)	93.0(2)	O(2)−Re−N(1)	81.0(2)
O(2)−Re−N(2)	91.9(2)	O(1)−Re−N(5)	90.9(2)
O(2)−Re−N(5)	84.2(2)	O(1)−Re−Cl	89.8(2)
O(2)−Re−Cl	92.0(2)	N(1)−Re−N(5)	87.8(2)
N(1)−Re−Cl	172.98(14)	N(2)−Re−N(5)	176.1(2)
N(2)−Re−Cl	88.63(14)	N(5)−Re−C	91.7(2)
Si−O(2)−Re	164.2(3)		

Table 4. Selected Bond Lengths and Angles for **7**

	Molecule 1		
	Distances (Å)		
Re(1)−O(1)	1.675(10)	Re(1)−O(2)	1.885(10)
Re(1)−N(1)	2.094(13)	Re(1)−N(2)	2.06(2)
Re(1)−N(5)	2.129(13)	Re(1)−Cl(1)	2.388(5)
O(2)−Si(1)	1.639(11)		
	Angles (deg)		
O(1)−Re(1)−O(2)	175.9(5)	O(1)−Re(1)−N(1)	93.5(5)
O(2)−Re(1)−N(1)	89.4(5)	O(1)−Re(1)−N(2)	91.5(5)
O(2)−Re(1)−N(2)	85.5(5)	N(1)−Re(1)−N(2)	90.9(6)
O(1)−Re(1)−Cl(1)	94.3(4)	O(1)−Re(1)−N(5)	89.3(5)
O(2)−Re(1)−Cl(1)	88.5(3)	O(2)−Re(1)−N(5)	87.9(5)
N(1)−Re(1)−Cl(1)	91.6(4)	N(1)−Re(1)−N(5)	177.0(5)
N(2)−Re(1)−Cl(1)	173.5(4)	N(2)−Re(1)−N(5)	90.2(5)
Cl(1)−Re(1)−N(5)	87.1(3)	Si(1)−O(2)−Re(1)	166.1(7)
	Molecule 2		
	Distances (Å)		
Re(2)−O(1A)	1.687(11)	Re(2)−O(2A)	1.901(10)
Re(2)−N(1A)	2.09(2)	Re(2)−N(2A)	2.092(13)
Re(2)−N(5A)	2.14(2)	Re(2)−Cl(1A)	2.378(5)
O(2A)-Si(1A)	1.623(11)		
	Angles (deg)		
O(1A)−Re(2)−O(2A)	172.7(5)	O(1A)−Re(2)−N(1A)	98.0(6)
O(2A)−Re(2)−N(1A)	88.0(5)	O(1A)−Re(2)−N(2A)	91.5(5)
O(2A)−Re(2)−N(2A)	84.3(5)	N(1A)−Re(2)−N(2A)	89.1(6)
O(1A)−Re(2)−Cl(1A)	94.6(4)	O(1A)−Re(2)−N(5A)	88.7(6)
O(2A)−Re(2)−Cl(1A)	89.6(3)	O(2A)−Re(2)−N(5A)	85.5(5)
N(1A)−Re(2)−Cl(1A)	90.4(5)	N(1A)−Re(2)−N(5A)	173.1(6)
N(2A)−Re(2)−Cl(1A)	173.9(4)	N(2A)−Re(2)−N(5A)	92.6(6)
Cl(1A)−Re(2)−N(5A)	87.3(4)	Si(1A)−O(2A)-Re(2)	163.5(7)

charge on the metal center of cations **1**, **2**, and **4a**. Compound **4b**, the iodide congener of complex **4a**, also disproportionates in solution into the oxoiodide [ReO(I)(OSiMe$_3$){η^2-B(pz)$_4$}(py)] analogous to **5**. This disproportionation reaction was only followed by ^{1}H NMR, and the identification of the neutral oxoiodide was made by comparing its ^{1}H NMR spectrum with the NMR data obtained for isolated **5**. These NMR studies have shown that the disproportionation of **4b** is much slower than that of **4a**, and this is certainly related with the poorer donor ability of iodide compared to that of chloride.

Complexes **5** and **6** were isolated in 47% and 55% yields, after appropriate workup, in the form of microcrystalline solids and were characterized by the usual analytical techniques, which included X-ray diffraction analysis in the case of **6**. As referred to in the experimental part, the conversion of cation **2** into compound **7** is very slow and rather low. Even after 1 week, the ^{1}H NMR analysis of the reaction mixture indicated that there are still about 90% of cation **2** in solution, the amount of compound **7** being very small ($<$10%). Fortunately, from this reaction mixture we were able to obtain single crystals of **7** which were used for ^{1}H NMR and also for X-ray diffraction analysis.

The most striking feature of the IR spectra of complexes **5** and **6** is the presence of strong bands at 885 and 900 cm^{-1}, respectively, which are due to ν(Re=O). The frequencies of these stretching vibrations are very close to those of the cationic complexes discussed above. In fact, the ν(Re=O) stretching bands of the cationic (**1**, **2**, and **4b**) and neutral complexes (**5** and **6**) appear in a narrow range, between 880 and 900 cm^{-1}, and at the low end of the range where the rhenium−oxygen stretching vibration usually appears in rhenium(V) mono-oxo complexes.[31] Then, the ν(Re═O) frequency does not depend on the charge of the complexes and is also almost insensitive to the nature of the neutral coligands, being determined essentially by the competition of the siloxide group with the oxo ligand in π bonding with the metal.

The crystal structures of complexes **6** and **7** consist of discrete molecular units, with no short intermolecular contacts. In the case of **7**, there are two independent molecules per asymmetric unit which are chemically equivalent. ORTEP diagrams for complex **6** and for molecule 1 of **7** are shown in Figures 3 and 4, respectively. Selected bond lengths and angles are listed in Tables 3 and 4.

In complexes **6** and **7**, the coordination geometry around the rhenium atom is approximately octahedral, the axial positions being occupied by the oxo and siloxide ligands. Showing similarity to the structures of the cationic complexes discussed above, B(pz)$_4$ is bidentate and coordinated in the equatorial plane. The remaining two equatorial positions are occupied by the chloride and by the corresponding neutral coligand [4-(NMe$_2$)-C$_5$H$_4$N (**6**) and 1-Meimz (**7**)].

The Re═O bond distances of 1.658(4) and 1.681(11) Å in compounds **6** and **7**, respectively, are within the range normally found for mono-oxo Re(V) complexes. All of the other metrical parameters obtained for the structures of **6** and **7** are comparable with those previously described for rhenium(V) mono-oxo complexes containing η^2-B(pz)$_4$, for rhenium(V) oxosiloxides, and for Re(V) complexes containing pyridine or imidazole.[18−25,33,35−40]

The ^{1}H NMR spectra of the neutral complexes **5**−**7** show a 1:1:1:1 pattern for the protons of the pyrazolyl rings of the η^2-B(pz)$_4$ ligand that is consistent with the C_1 symmetry expected for these complexes and confirmed by X-ray structural analysis of **6** and **7**. As for the cationic complexes (**1**−**4**), the methyl protons of the OSiMe$_3$ ligand in the neutral derivatives (**5**−**7**) are shielded because of the trans effect of the oxo group. The shielding of these protons is more significant for the neutral complexes than for the precursor cations, most probably as a consequence of the higher electronic density along the axis O═Re−OSiMe$_3$ for the former.

Concluding Remarks

The first cationic Re(V) oxo complexes with poly(pyrazolyl)-borates (**1**−**3**) have been isolated and fully characterized, including by X-ray crystallographic analysis. The stability of these cations is strongly dependent on the σ-donor properties of the neutral coligands. The cations with monodentate-neutral coligands rearrange in solution, yielding neutral compounds **5**−**7** and alleviating the positive charge of the d^2 metal center. The use of chelating 1,2-bis(dimethylphosphino)ethane considerably improved the stability of the corresponding cation, preventing its rearrangement. The neutral complexes with pyridine coligands, although being obtained in moderate yield, can be seen as useful compounds for further studies on the chemistry of rhenium(V) oxo complexes with [η^2-B(pz)$_4$]$^-$.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of **3**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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