Coordination of Tetrakis(pyrazolyl)borate in Rhenium Complexes Containing the $[Re^{V}{=}O]^{3+}$ Core

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The complex $[ReO\{\eta^3\text{-}B(pz)_4\}(OMe)_2]$ (**1**) reacts with potentially bidentate protic substrates yielding several monomeric and dimeric oxorhenium compounds in which the tetrakis(pyrazolyl)borate presents different coordination modes: $[ReO(acac)\{\eta^2\text{-}B(pz)_4\}(OMe)]$ (**3**), $[ReO(acac)\{\eta^2\text{-}B(pz)_4\}]_2(\mu\text{-}O)$ (**4**), $[ReO\{\eta^2\text{-}B(pz)_4\}\text{-}(quinolin\text{-}8\text{-}olate)(OMe)]$ (**5**), $[ReO\{\eta^2\text{-}B(pz)_4\}(OMe)(pz^*)(pz^*H)]$ (pz* = pz (**6**) or 3,5-Me$_2$pz (**7**)), $[ReO\{\eta^2\text{-}B(pz)_4\}(\mu\text{-}pz^*)]_2(\mu\text{-}O)$ (pz* = pz (**9**) or 3,5-Me$_2$pz (**10**)), $[ReO(HNCH_2CH_2NH)\{\eta^3\text{-}B(pz)_4\}]$ (**14**), and $[ReO(m\text{-}nitrophenyl\text{-}o\text{-}diaminate)\{\eta^3\text{-}B(pz)_4\}]$ (**15**). Using the analogous alkoxide $[ReO\{\eta^3\text{-}B(pz)_4\}(OEt)_2]$ (**2**), the compound $[ReO\{\eta^2\text{-}B(pz)_4\}(OEt)(pz)(pzH)]$ (**8**) has also been obtained. Compounds **3** and **5** react with trimethylsilyl chloride providing the monochlorides $[ReO(acac)\{\eta^2\text{-}B(pz)_4\}Cl]$ (**12**) and $[ReO\{\eta^2\text{-}B(pz)_4\}(quinolin\text{-}8\text{-}olate)Cl]$ (**13**), respectively. Compounds **9**, **10**, and **14** were also prepared by reacting $[ReO(\mu\text{-}O)\{B(pz)_4\}]_2$ (**11**) with the respective substrates. The new compounds **3**−**10** and **12**−**15** were characterized by elemental analysis and IR and ^{1}H NMR spectroscopies. Compounds **3**, **4**, and **9** have also been characterized by X-ray crystallography. Compounds **3** and **4** both crystallize in the monoclinic space group $P2_1/c$, with $a = 7.862(1)$ Å, $b = 14.152(2)$ Å, $c = 19.975(3)$ Å, $\beta = 91.79(1)°$, $V = 2221(1)$ Å^3, and Z = 4 (**3**) and $a = 13.547(2)$ Å, $b = 9.959(1)$ Å, $c = 15.878(2)$ Å, $\beta = 102.00(1)°$, $V = 2095(1)$ Å^3 and $Z = 2$ (**4**). Compound **9** crystallizes in the monoclinic space group $P2_1$, with cell parameters $a = 11.086(2)$ Å, $b = 15.269(1)$ Å, $c = 12.133(1)$ Å, $\beta = 93.51(1)°$, V = 2050(1) Å^3 and Z = 2.

Introduction

The tetrakis(pyrazolyl)borate ligand usually coordinates to transition metals in a tridentate way, although some examples are known where it acts as bidentate or bis-bidentate.[1,2]

We have recently initiated an investigation into the synthesis and characterization of tetrakis(pyrazolyl)borate rhenium compounds, and we found for the complexes previously described, either by X-ray crystallographic analysis and/or by ^{1}H NMR spectroscopy, a tridentate coordination mode for the poly(pyrazolyl)borate ligand.[3−5] Some of the complexes previously synthesized were of the type $[ReO\{\eta^3\text{-}B(pz)_4\}(OR)_2]$ and two of these alkoxides, $[ReO\{\eta^3\text{-}B(pz)_4\}(OMe)_2]$ (**1**) and $[ReO\{\eta^3\text{-}B(pz)_4\}(OEt)_2]$ (**2**), are unstable in solution giving the dimer $[ReO(\mu\text{-}O)\{B(pz)_4\}]_2$ (**11**).[5] The high reactivity of these alkoxides can be used for the synthesis of several oxorhenium compounds. In this work we report reactions of $[ReO\{\eta^3\text{-}B(pz)_4\}(OMe)_2]$ (**1**) with potentially monoanionic and dianionic bidentate substrates which allowed the synthesis and characterization of monomeric and dimeric rhenium(V) complexes, in which the tetrakis(pyrazolyl)borate ligand presents different coordination modes: $[ReO(acac)\{\eta^2\text{-}B(pz)_4\}(OMe)]$ (**3**), $[ReO(acac)\{\eta^2\text{-}B(pz)_4\}]_2(\mu\text{-}O)$ (**4**) $[ReO\{\eta^2\text{-}B(pz)_4\}(quinolin\text{-}8\text{-}olate)(OMe)]$ (**5**), $[ReO\{\eta^2\text{-}B(pz)_4\}(OMe)(pz^*)(pz^*H)]$ (pz* = pz (**6**) or 3,5-Me$_2$pz (**7**)), $[ReO\{\eta^2\text{-}B(pz)_4\}(\mu\text{-}pz^*)]_2(\mu\text{-}O)$ (pz* = pz (**9**) or 3,5-Me$_2$pz (**10**)), $[ReO(HNCH_2CH_2NH)\{\eta^3\text{-}B(pz)_4\}]$ (**14**), and $[ReO(m\text{-}nitrophenyl\text{-}o\text{-}diaminate)\{\eta^3\text{-}B(pz)_4\}]$ (**15**). The analogous $[ReO\{\eta^3\text{-}B(pz)_4\}(OEt)_2]$ (**2**), which is also very reactive, was only evaluated in reactions with pzH leading to $[ReO\{\eta^2\text{-}B(pz)_4\}(OEt)(pz)(pzH)]$ (**8**). We will also report the synthesis of the monochlorides $[ReO(acac)\{\eta^2\text{-}B(pz)_4\}Cl]$ (**12**) and $[ReO(quinolin\text{-}8\text{-}olate)\{\eta^2\text{-}B(pz)_4\}Cl]$ (**13**), prepared by reacting trimethylsilyl chloride with **3** and **5**, respectively. The use of the ^{1}H NMR spectroscopy to evaluate the denticity of the tetrakis(pyrazolyl)borate will be also discussed.

Experimental Part

General Procedures. The reactions were carried under an argon atmosphere; the solvents were dried, degassed, and distilled prior to use. $[ReO\{B(pz)_4\}(OMe)_2]$ (**1**), $[ReO\{B(pz)_4\}(OEt)_2]$ (**2**), and $[ReO(\mu\text{-}O)\{B(pz)_4\}]_2$ (**11**) were prepared as previously described.[5] Pyrazole and 3,5-dimethylpyrazole were sublimed prior to use. 8-hydroxyquinoline and *m*-nitrophenyl-*o*-diamine were dried under vacuo. Trimethylsilyl chloride was dried over P_2O_5 and deoxygenated prior to use. Acetylacetone (acacH) was washed with NaOH 2N and with H_2O, dried over Na_2SO_4 and distilled under vacuo. Ethylenediamine was dried over 5 Å molecular sieves and distilled prior to use.

^{1}H NMR spectra were recorded on a Varian Unity 300 MHz instrument and were referenced internally using the residual solvent resonance relative to tetramethylsilane. IR spectra were recorded as KBr pellets on a Perkin-Elmer 577 spectrophotometer. Carbon, hydrogen, and nitrogen analyses were performed on a Perkin-Elmer automatic analyzer.

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Synthesis and Characterization of [ReO(acac){η^2-B(pz)$_4$}(OMe)] (3) and [ReO(acac){η^2-B(pz)$_4$}]$_2$(μ-O) (4). Acetylacetone (40 mg, 0.40 mmol) was added to a blue solution of **1** (200 mg, 0.36 mmol) in toluene, and the mixture heated under reflux for 2 h. The dark red solution obtained was taken to dryness in vacuo, and the red oil was chromatographed on silica gel using as solvent THF/*n*-hexane (2:1). It has been possible to collect a pink-red solid formulated as **3** and a violet solid formulated as **4** (**3**, 120mg, 0.20 mmol, 55% yield; **4**, 22 mg, 0.04 mmol, 10% yield). Data for **3** follow. Anal. Calcd for $C_{18}H_{22}BN_8O_4Re$: C, 35.3; H, 3.6; N, 18.8. Found: C, 35.6; H, 3.7; N, 18.4. IR (KBr, ν (cm^{-1})): 1560 s, 1520 s (ν(C═O)+ ν(C═C)), 955s (ν(Re═O)). Data for **4** follow. Anal. Calcd for $C_{34}H_{38}B_2N_{16}O_7Re_2$: C, 34.7; H, 3.2; N, 19.0. Found: C, 35.8; H, 3.0; N, 17.9. IR (KBr, ν (cm^{-1})): 1550 s, 1520 s (ν(C═O) + ν(C═C)), 970 w (ν(Re═O)), 720 s (ν (Re−O−Re)).

Synthesis and Characterization of [ReO{η^2-B(pz)$_4$}(quinolin-8-olate)(OMe)] (5). At room temperature, 8-hydroxyquinoline (47 mg, 0.19mmol), dissolved in the minimum volume of CH_2Cl_2, was added slowly to a solution of **1** (100 mg, 0.18 mmol) in CH_2Cl_2. After this mixture was stirred for 2 h, a brown solution was obtained. This solution was taken to dryness in vacuo and the resulting green-brown oil obtained was washed several times with *n*-hexane. After drying, the green-brown microcrystalline solid obtained was formulated as **5** (90 mg, 0.14 mmol, yield ≈75%). Anal. Calcd for $C_{22}H_{21}BN_9O_3Re$: C, 40.2; H, 3.1; N, 19.2. Found: C, 40.8; H, 3.0; N, 19.1. IR (KBr, ν (cm^{-1})): 967s (ν(Re═O)).

Synthesis and Characterization of [ReO{η^2-B(pz)$_4$}(OR)(pz)(pzH)] (R = Me (6), R = Et (8)). To a blue solution of [ReO{B(pz)$_4$}(OR)$_2$] (R═Me (**1**) or Et (**2**)) (100 mg, 0.18 mmol) in CH_2Cl_2 was added pyrazole (25 mg, 0.37 mmol). The reaction mixtures reacted for 1 h, at room temperature, and after workup, as referred to for **5,** reddish microcrystalline solids were isolated and formulated as **6** (100 mg, 0.15 mmol, 85% yield) and **8** (95 mg, 0.14 mmol, 80% yield), respectively. Data for **6** follow. Anal. Calcd for $C_{19}H_{22}BN_{12}O_2Re$: C, 35.2; H, 3.4; N, 26.0. Found: C, 34.0; H, 3.6; N, 25.6. IR (KBr, ν (cm^{-1})): 960 s (ν(Re═O)). UV−vis (CH_2Cl_2) (λ_{max}(nm)): 485 (m). Data for **8** follow. Anal. Calcd for $C_{20}H_{24}BN_{12}O_2Re$: C, 36.3; H, 3.6; N, 25.4. Found: C, 36.2; H, 3.2; N, 25.4. IR (KBr, ν (cm^{-1})): 963s (ν(Re═O)). UV−vis (CH_2Cl_2) (λ_{max}(nm)): 478 (m).

Synthesis of [ReO{η^2-B(pz)$_4$}(OMe)(3,5-Me$_2$pz)(3,5-Me$_2$pzH)] (7). This compound has been synthesized according to the procedure above described for **6**. Starting with 100 mg (0.18 mmol) of [ReO{B(pz)$_4$}(OMe)$_2$] (**1**) and using 35 mg (0.36 mmol) of 3,5-Me$_2$pzH, we obtained, after workup, a reddish microcrystalline solid that, on the basis of ^{1}H NMR (see Table 2), IR, and absorption electronic spectroscopies, we formulated as **7.** This compound is very unstable, and it was not possible to obtain accurate elemental analysis (see discussion). IR (KBr, ν (cm^{-1})): 968 s (ν(Re═O)). UV−vis (CH_2Cl_2) (λ_{max}(nm)): 505 (m).

Synthesis and Characterization of [ReO{η^2-B(pz)$_4$}(μ-pz*)]$_2$(μ-O) (pz* = pz (9), pz* = 3,5-Me$_2$pz (10)). Method 1. Compounds **6** (50 mg, 0.077 mmol) or **7** (50 mg, 0.070 mmol) slowly decompose in dichloromethane/*n*-hexane yielding compounds **9** and **10**, respectively. Compound **9** is recovered from the dichloromethane/*n*-hexane solution by chromatography on silica gel, using as eluent THF/*n*-hexane (2:1) (15 mg, 0.027 mmol, 35% yield) and compound **10** precipitates as a blue microcrystalline solid from the dichloromethane/*n*-hexane solution, being separated by centrifugation (20 mg, 0.034 mmol, 50% yield).

Method 2. To a suspension of **11** (200 mg, 0.40 mmol of Re) in CH_2Cl_2 was added pyrazole or 3,5-dimethylpyrazole in the 1:1 molar ratio. After this was allowed to react for 2 h, dark green mixtures were obtained. Compound **9** is isolated from the mixture by the chromatographic process described in method 1 (70 mg, 0.13 mmol of Re, 30% yield). The separation of **10** from the reaction mixture was done by washing the solid obtained, after evaporation of CH_2Cl_2, with CH_3CN, where **10** is almost insoluble (80 mg, 0.14 mmol of Re, 30% yield). Data for **9** follow. Anal. Calcd for $C_{30}H_{30}B_2N_{20}O_3Re_2$: C, 32.4; H, 2.7; N, 25.2%. Found C, 33.6; H, 2.6; N, 24.6%. IR (KBr, ν (cm^{-1})): 967 m (ν(Re═O)), 637 s (ν(Re−O−Re)). UV−vis (CH_2Cl_2) (λ_{max}(nm)): 583 (m). Data for **10** follow. Anal. Calcd for: $C_{34}H_{38}B_2N_{20}O_3Re_2$: C, 34.9; H, 3.3; N, 24.0%. Found: C, 33.4; H, 3.2; N, 22.6%. IR (KBr, ν (cm^{-1})): 968m (ν(Re═O)), 639s (ν(Re-O-Re)). UV−vis (CH_2Cl_2) (λ_{max}(nm)): 617 (m).

Table 1. Crystallographic Data for [ReO(acac){η^2-B(pz)$_4$}(OMe)] (**3**), [ReO(acac){η^2-B(pz)$_4$}]$_2$(μ-O) (**4**), and [ReO{η^2-B(pz)$_4$}(μ-pz)]$_2$(μ-O) (**9**)

	(**3**)	(**4**)	(**9**)
formula	$C_{18}H_{22}BN_8O_4Re$	$C_{34}H_{38}B_2N_{16}O_7Re_2$	$C_{30}H_{30}B_2N_{20}O_3Re_2\cdot CH_2C_{l2}$
mol wt	611.45	1176.82	1197.67
space group	$P2_1/c$	$P2_1/c$	$P2_1$
a, Å	7.862(1)	13.547(2)	11.086(2)
b, Å	14.152(2)	9.959(1)	15.269(1)
c, Å	19.975(3)	15.878(2)	12.133(1)
β, deg	91.79(1)	102.00(1)	93.51(1)
V, Å^3	2221(1)	2095(1)	2050(1)
Z	4	2	2
ρ_{calc}, gcm^{-3}	1.828	1.865	1.940
μ, cm^{-1}	55.1	58.4	60.9
decay cor factors	1.00001, 1.00861	1.00001, 1.01991	
transm coeff	0.8532−0.9992	0.7701−0.9987	0.7258−0.9997
R_1[a]	0.0357	0.0565	0.0299
wR$_2$[b]	0.0782	0.1103	0.0741

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$. The values of $R_1$and wR$_2$ are those with $I > 2\sigma(I)$ only.

Synthesis and Characterization of [ReO(acac){η^2-B(pz)$_4$}Cl] (12) and [ReO{η^2-B(pz)$_4$}(quinolin-8-olate)Cl] (13). Trimethylsilyl chloride was added, in 50% excess, to THF solutions of **3** or **5.** The resulting mixtures were stirred at room temperature for 24 h. Removal of the solvent and stirring of the solids obtained with *n*-hexane yielded the blue microcrystalline compound **12** and the dark green compound **13,** respectively. These compounds are obtained in almost quantitative yields. Data for **12** follow. Anal. Calcd for $C_{17}H_{19}BN_8O_3ClRe$: C, 33.1; H, 3.1; N, 18.2. Found: C, 33.3; H, 2.6; N, 17.9. IR (KBr, cm^{-1}): 1550−1500 br.s (ν(C═O) + ν(C═C)), 990s (ν(Re═O)), 320 (ν(Re−Cl)). Data for **13** follow. Anal. Calcd for $C_{21}H_{18}BN_9O_2ClRe$: C, 38.1; H, 2.7; N, 18.1. Found: C, 38.9; H, 2.7; N, 18.2. IR (KBr, ν (cm^{-1})): 976 s (ν(Re═O)), 314 m (ν(Re−Cl)).

Synthesis and Characterization of [ReO(HNCH$_2$CH$_2$NH){η^3-B(pz)$_4$}] (14) and [Re(O)(*m*-nitrophenyl-*o*-diaminate){η^3-B(pz)$_4$}] (15). To a blue solution of [ReO{B(pz)$_4$}(OMe)$_2$] (**1**) (100 mg, 0.18 mmol) in CH_2Cl_2 was added ethylenediamine (≈15 mg, 0.25 mmol) or *m*-nitrophenyl-*o*-diamine (30 mg, 0.2 mmol) and the mixtures stirred for 60 min, at room temperature. Compound **14** precipitates and is separated by centrifugation as a pale yellow-brown solid (70 mg, 0.13 mmol, yield 72%). Compound **15** is obtained as a dark red brown microcrystalline solid, by recrystallization from toluene/*n*-hexane (90 mg, 0.14 mmol, 80% yield). Data for **14** follow. Anal. Calcd for $C_{14}H_{18}BN_{10}ORe$: C, 31.2; H, 3.8; N, 24.7. Found: C, 29.6; H, 3.8; N, 24.0. IR (KBr, cm^{-1}): 3500−2800 s (br) (ν(N−H)), 920 m (ν(Re═O)). Data for **15** follow. Anal. Calcd for $C_{18}H_{17}BN_{11}O_3Re$: C, 34.2; H, 2.7; N, 24.4. Found: C, 36.0; H, 3.8; N, 24.4. IR (KBr, ν (cm^{-1})): 3335 m (ν(N−H)), 942 s (ν(Re═O)).

X-ray Crystallographic Analysis. X-ray data were collected from a pink-red crystal of **3**, obtained by recrystallization from toluene/*n*-hexane, from a blue-violet crystal of **4**, obtained by diffusion of *n*-hexane into a saturated solution of the compound in toluene, and from a blue crystal of **9**, obtained by slow diffusion of *n*-hexane into a saturated solution of the compound in dichloromethane. The crystals were mounted in thin-walled glass capillaries in an argon filled glovebox.

Data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.710 69 Å), using an $\omega-2\theta$ scan mode. Unit cell dimensions were obtained by least-squares refinement of the setting angles of 25 reflections with $24 < 2\theta < 32°$ for **3**, $15 < 2\theta < 28°$ for **4**, and $21 < 2\theta < 34°$ for **9**. Details of the crystal data and data collection and refinement are given in Table 1. Data were corrected[6] for Lorentz−polarization effects, for linear decay (no decay was observed for **9**), and for absorption by empirical corrections based on ψ scans. The

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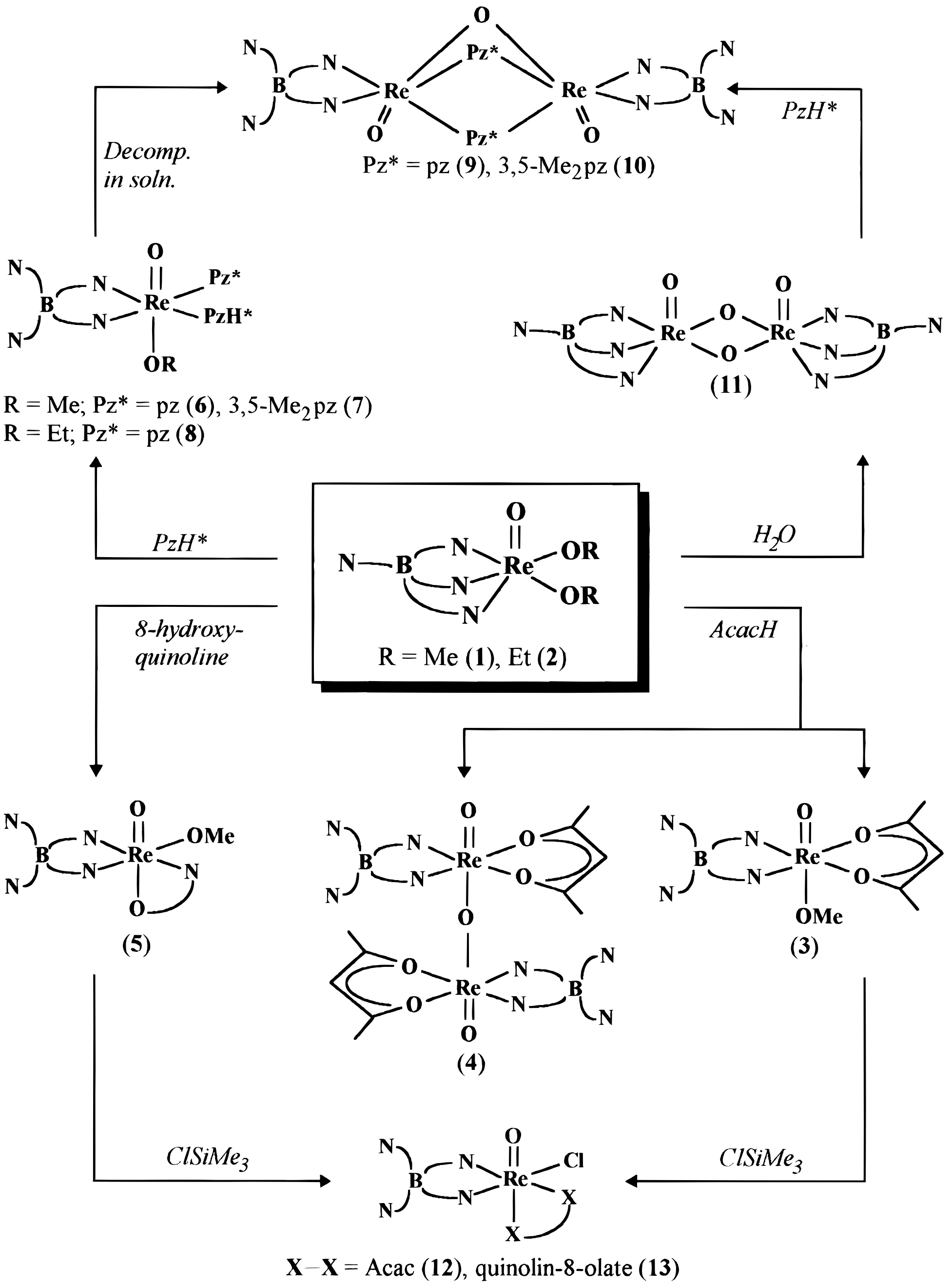
(6) Fair, C. K. MOLEN. Enraf-Nonius, Delft, The Netherlands, 1990.

Scheme 1



structures were solved by Patterson methods[7] and subsequent Fourier difference techniques.[8] The structures were refined by full-matrix least-squares methods based on F^2.[8] All non-hydrogen atoms were refined anisotropically and the contributions of the hydrogen atoms were included in calculated positions, constrained to ride on their carbon atoms with group U_{iso} values assigned. The structural analysis of **9** revealed a solvent molecule in the lattice, CH_2Cl_2, disordered. The solvent atoms were refined isotropically, and the contribution of the hydrogen atoms associated with it was ignored. Refinement of the other enantiomer indicated that this final choice was the correct one, as was also confirmed by the Flack parameter. Atomic scattering factors and anomalous dispersion terms were as in SHELXL-93.[8]

Results and Discussion

Syntheses of Complexes. We have previously shown [ReO(μ-O){B(pz)$_4$}]$_2$ (**11**) to be an excellent starting material for Re(V) complexes, where the [B(pz)$_4$]$^-$ is coordinated in a tridentate way.[5] In particular, **11** reacts almost quantitatively with alcohols, yielding compounds of the type [ReO{η^3-B(pz)$_4$}(OR)$_2$] (R=Me, Et, ^{i}Pr, Ph). We also noted that when R = Me (**1**) or Et (**2**) the alkoxides are unstable in solvents other than the respective alcohols and quite reactive.

As can be seen in Scheme 1, [ReO{B(pz)$_4$}(OMe)$_2$] (**1**) reacts with potentially bidentate monoanionic protic substrates (acetylacetone, 8-hydroxyquinoline, pyrazole, and 3,5-dimethylpyrazole) yielding, in moderate to high yield (55−85%), the compounds **3** and **5**−**7,** where the [B(pz)$_4$]$^-$ acts as a bidentate ligand. Compound **8** can also be easily obtained by reacting **2** with pyrazole.

The formation of compounds **3** and **5**−**8** takes place with release of alcohol and with the breaking of the Re−N bond *trans* to the oxo-oxygen in compounds [ReO{η^3-B(pz)$_4$}(OMe)$_2$] (**1**) and [ReO{η^3-B(pz)$_4$}(OEt)$_2$] (**2**). In fact, the X-ray structural analysis that has been undertaken for complexes of Re(V) with

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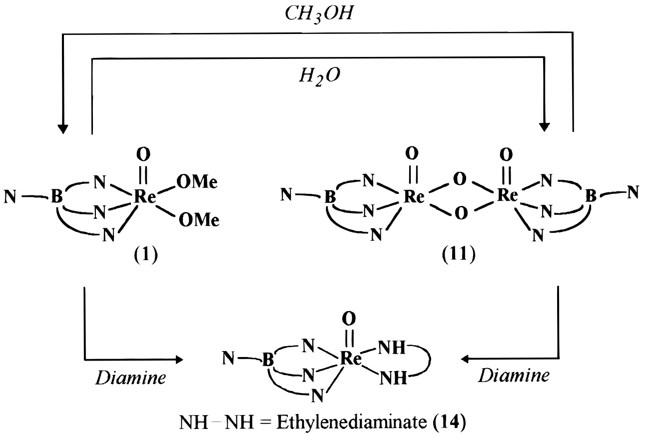
(7) Sheldrick, G. M. SHELXS-86: Program for the Solution of Crystal Structure. University of Göttingen, Germany, 1986

(8) Sheldrick, G. M. SHELXL-93: Program for Crystal Structure Refinement. University of Göttingen, Germany, 1993.

Scheme 2



NH NH = Ethylenediaminate (**14**)
m-nitrophenyl-o-diaminate (**15**)

tridentate poly(pyrazolyl)borates has shown that the three Re−N bond lengths are not equivalent and, due to the *trans* effect, the Re−N bond *trans* to the oxo ligand is the longest.[4,5,9−11] The labilization effect on the Re−N bond *trans* to the oxygen oxo, the strong donor character of the $(OMe)^-$ group, and the use of potentially monoanionic bidentate protic substrates justifies certainly the stabilization of the neutral six-coordinated compounds **3, 5**−**8**.

When **3** or **5** react with an excess of trimethylsilyl chloride, the alkoxide group in these compounds is easily replaced by the chloride, the $[B(pz)_4]^-$ remains bidentate, and compounds **12** and **13** are obtained in almost quantitative yield.

Compound **3** is obtained in a relatively low yield (55%), and one of the reasons can be the formation of the dimer **4** during the reflux. Several oxo-bridged binuclear rhenium compounds containing the linear backbone O═Re—O—Re═O have been described, and their formation has been explained considering the hydrolysis of Re(V) oxocomplexes.[12] In our synthetic work all the reagents and solvents were dried before use and the reflux was done under argon. However, the presence of some residual humidity during the reflux can possibly justify the formation of the side product **4** (10% yield). The formation of **4** during the chromatographic process is excluded, as the ^1H NMR spectrum of the reaction mixture before chromatographic purification indicated already the presence of compounds **3** and **4** in about the same ratio.

Compound **6** is stable in the solid state but slowly decomposes in CH_2Cl_2/*n*-hexane solution, providing the dimer **9**. This dimer **9** can also be synthesized by reacting **11** with pyrazole in dichloromethane. In both cases, compound **9** is obtained in a relatively low yield, approximately 30−35%, as other species are formed. By chromatography on silica gel, **9** can be easily separated from the other products that we were not able to characterize. The blue compound **9** is eluted with THF/hexane (2:1) and the other species are eluted with THF. On the basis of the IR as well as on the very complicated ^1H NMR we only can say that these green species contain pz and $[B(pz)_4]^-$ and that they must be oxocomplexes of Re, as shown by the presence of strong stretching bands at 991 and 957 cm^{-1}, which can be easily assigned to $\nu(Re{=}O)$.[4,5] Compound **7**, probably due to stereochemical reasons, is much more unstable then **6** either in the solid state or in solution, and satisfactory analytical data were never obtained. ^1H NMR studies showed that **7** decomposes in $CDCl_3$ yielding the blue microcrystalline dimer **10**, with release of 3,5-Me_2pzH and MeOH. To prevent this decompositon **7** has to be maintained in the presence of excess of 3,5-Me_2pzH. When this is not the case **10** precipitates as a blue microcrystalline solid from a reddish solution of **7** in CH_2Cl_2/*n*-hexane, and is separated by centrifugation (50% isolated yield). Another synthetic method to prepare **10** is by reacting the dimer **11** with stoichiometric amounts of 3,5-Me_2pzH, but in this case the compound is isolated in 30% yield. We have evidence that **10** is not the main product of this reaction, but an extraction with acetonitrile allows its separation from the reaction mixture.

As far as we have observed, **9** and **10** are the only compounds with $\{\eta^2\text{-}B(pz)_4\}$ which can be obtained from **11**. Reactions of **11** with some of the other potentially monoanionic protic substrates have also been studied but the species formed are different from the ones obtained using **1**.[13]

The formation of compounds **9** and **10** is difficult to explain, as we did not identify all the species formed in these reactions. However, in spite of other side reactions, the formation of **9** and **10** will be understandable assuming the following processes:

$$\begin{tikzcd}
2[ReO\{\eta^2\text{-}B(pz)_4\}(OMe)(pz^*)(pz^*H)] \\
(\mathbf{6}\ \text{or}\ \mathbf{7}) \arrow[d, "+H_2O"', "\begin{matrix}-2pz^*H\\ -2\ MeOH\end{matrix}"] \\
[ReO\{\eta^2\text{-}B(pz)_4\}(\mu\text{-}pz^*)]_2(\mu\text{-}O) \\
(\mathbf{9}\ \text{or}\ \mathbf{10}) \\
[ReO(\mu\text{-}O)\{\eta^3\text{-}B(pz)_4\}]_2 \arrow[u, "+2pz^*H", "-H_2O"'] \\
(\mathbf{11})
\end{tikzcd}$$

As can be seen in Scheme 2, when **1** reacts with potentially dianionic protic substrates, as ethylenediamine and *m*-nitrophenyl-*o*-diamine, the two methoxide groups are replaced by the dianionic ligands and the tetrakis(pyrazolyl)borate remains tridentate, leading to compounds **14** and **15**. So far, in reactions with these type of substrates compound **1** is not an alternative to **11**.[5]

Characterization of the Complexes. All the compounds, except **14,** are soluble in chloroform, dichloromethane, aromatic hydrocarbon solvents and slightly soluble in aliphatic ones. Compound **14** is only slightly soluble in polar solvents.

Compounds **3**−**10** and **12**−**15** present in the infrared spectra the bands characteristic of the tetrakis(pyrazolyl)borate,[3−5] the bands due to the co-ligands[14] and stretching bands in the ranges 920−990 and 637−720 cm^{-1} which can be assigned to $\nu(Re{=}O)$ and $\nu(Re{-}O{-}Re)$, respectively.[3−5,9−12,15,16]

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Table 2. ^{1}H NMR Data for Complexes Containing the Unit "[ReO{η^2-B(pz)}$_4$]"[a]

	$[B(pz)_4]^-$				
	H(4)		H(3)/H(5)		
complex	coordinated	free	free	coordinated	other ligands
3	6.60 (2H, t, $^3J = 2.4$)	6.23 (1H, dd, $^3J = 1.7$, $^3J = 2.4$) 6.14 (1H, dd, $^3J = 1.5$, $^3J = 2.4$)	7.63 (1H, d, $^3J = 1.2$) 7.59 (1H, d, $^3J = 0.9$) 6.76 (1H, d, $^3J = 1.8$) 6.55 (1H, d, $^3J = 1.8$)	8.43 (2H, dd, $^3J = 2.4$, $^4J = 0.9$) 7.48 (2H, dd, $^3J = 2.7$, $^4J = 0.9$)	5.69 (1H, s, CH) 2.96 (3H, s, OCH_3) 2.31 (6H, s, CH_3)
4	6.65 (2H, t, $^3J = 2.4$)	6.27 (1H, t, $^3J = 2.0$) 5.99 (1H, t, $^3J = 2.0$)	7.85 (1H, d, $^3J = 1.5$) 7.45 (1H, br, m) 6.77 (1H, d, $^3J = 2.1$) 6.23 (1H, d, $^3J = 2.4$)	7.89 (2H, dd, $^3J = 2.4$, $^4J = 0.8$) 7.45 (2H, br, m)	5.51 (1H, s, CH) 2.13 (6H, s, CH_3)
5[c−e]	6.76 (1H, br, m) 6.27 (1H, br, t) 6.17 (1+1H, br, m)		9.27 (1H, br, s) 7.81 (1H, br, s) 7.59−7.63 (1H, br, m) 7.58 (1H, br, d) 7.41 (1H, d, $^3J = 2.7$) 6.76 (1H, br, m) 6.56 (1H, d, $^3J = 2.1$) 6.38 (1H, d, $^3J = 2.4$)		8.57 (1H, d, $^3J = 5.4$, arom) 8.12 (1H, d, $^3J = 9.0$, arom) 7.59−7.63 (1H, br, m, arom) 7.50 (1H, t, $^3J = 8.1$, arom) 7.22 (1H, d, $^3J = 8.1$, arom) 6.66 (1H, d, $^3J = 8.1$, arom) 3.96 (3H, s, OCH_3)
6[b,c]	6.41 (2H, tr, $^3J = 2.1$)	6.28 (1H, t, $^3J = 1.5$) 6.18 (1H, t, $^3J = 1.5$)	7.77 (2 + 2 + 1H, br) 7.65 (2 + 1H, br) 7.39 (2H, br) 6.84 (1H, br) 6.82 (1H, br)		15.47 (1H, s, NH) 6.52 (2H, t, $^3J = 2.4$, H(4)-pz) 2.97 (3H, s, OCH_3)
7	6.44 (2H, br)	6.29 (1H, br) 6.16 (1H, br)	7.85 (1H, br) 7.57 (1H, br) 6.89 (1H, br) 6.84 (1H, br)	7.53 (2H, br) 7.39 (2H, br)	11.7 (1H, s, NH) 5.92 (2H, s, H(4)-3, 5-Me_2pz) 3.14 (3H, s, OCH_3) 2.45 (6H, s, CH_3) 2.17 (6H, s, CH_3)
8[b]	6.40 (2H, br)	6.28 (1H, br) 6.16 (1H, br)	7.81 (1H, br) 7.76 (2 + 1H, br) 7.69 (2H, br) 7.39 (2H, d, $^3J = 2.4$) 6.84 (2H, br)		14.77 (1H, s, NH) 6.50 (2H, br, H(4)-pz) 3.30 (2H, s, OCH_2) 0.54 (3H, CH_3)
9[b,c]	6.41 (2H, br)	6.21 (1H, br) 6.17 (1H, br)	7.64 (2H, br) 7.51 (2H, br) 7.44 (2H, br) 7.41 (2H, br) 6.68 (1H, br) 6.55 (1H, br)		6.41 (1H, br, H(4)-pz)
10	6.38 (2H, t, $^3J = 2.0$)	6.24 (1H, t, $^3J = 1.7$) 6.18 (1H, br)	7.75 (1H, br) 7.56 (1H, d, $^3J = 1.1$) 6.85 (1H, d, $^3J = 2.2$) 6.58 (1H, d, $^3J = 2.0$)	7.42 (2H, d, $^3J = 2.5$) 7.23 (2H, d, $^3J = 2.6$)	6.05 (1H, s, H(4)-3, 5-Me_2pz) 2.29 (6H, s, CH_3)
12[c]	6.76 (1H, br) 6.57 (1H, br)	6.28 (1H, br) 6.18 (1H, br)	9.26 (1H, $^3J = 0.9$) 7.82 (1H, br) 7.62 (1 + 1H, br) 7.53 (1H, d, $^3J = 1.2$) 7.41 (1H, br) 6.79 (1H, br) 6.57 (1H, br, m)		5.92 (1H, s, CH) 3.03 (3H, s, CH_3) 2.00 (3H, s, CH_3)
13[c,e]		6.79 (1H, br) 6.31 (1H, br) 6.29 (1H, tr, $^3J = 2.4$) 6.24 (1H, br)	9.48 (1H, d, $^3J = 2.1$) 7.84 (1H, br) 7.67 (1H, br) 7.65 (1H, d, $^3J = 1.8$) 7.51 (1H, d, $^3J = 1.8$) 6.82 (1H, br) 6.63 (1H, br d) 6.54 (1H, d, $^3J = 1.8$)		8.75 (1H, d, $^3J = 4.2$, arom) 8.32 (1H, d, $^3J = 7.8$, arom) 7.73−7.69 (1H, m, arom) 7.55 (2H, tr, $^3J = 8.0$, arom) 7.41 (1H, d, $^3J = 8.1$, arom) 6.79 (1H, br, arom)

[a] For all compounds the spectra were obtained at 298 K; All the spectra were run in $CDCl_3$; Data are given as chemical shifts δ (relative integral, multiplicity, coupling constant J in Hz); Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad; arom, aromatic. [b] H(3) and H(5) of pyrazole occasionnally overlap with those of$[B(pz)_4]^-$ and are not possible to assign. [c] For these complexes we did not assign any of the H(3) and H(5) resonances. [d] For these complexes we did not assign any of the H(4) resonances. [e] Occasionnally one proton of the $[B(pz)_4]^-$ ligand overlaps two protons of the quinolin-8-olate ligand.

The ν(Re═O) stretching bands are within the accepted range for six-coordinated oxorhenium(V), and the results described in this work, as well as others previously described,[4,5] indicate that the values found do not seem to be significantly affected by the denticity of the $[B(pz)_4]^-$, as long as the co-ligands compensate the electron density at the metal atom (compare: 965 cm^{-1}, **1**; 967 cm^{-1}, **5**; 960 cm^{-1}, **2**; 955 cm^{-1}, **3**). However, independently of the denticity of the $[B(pz)_4]^-$, there are some

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Table 3. ^{1}H NMR Data for Complexes Containing the Unit "[ReO{η^3-B(pz)$_4$}]"[a]

	$[B(pz)_4]^-$					
	H(4)			H(3)/H(5)		
complex	trans to O	trans to L	free	trans to O/free	trans to L	other ligands
14	5.91 (1H, t, $^3J = 2.1$)	6.39 (2H, t, $^3J = 2.1$)	6.63 (1H, t, $^3J = 1.8$)	8.03 (1H, d, $^3J = 2.4$) 7.93 (1H, d, $^3J = 1.2$) 7.54 (1H, d, $^3J = 2.4$) 7.32 (1H, d, $^3J = 1.8$)	8.22 (2H, d, $^3J = 2.1$) 7.54 (2H, $^3J = 2.4$)	10.5 (2H, br, NH) 4.36 (2H, m, CH_2) 4.17 (2H, m, CH_2)
15[b,c]	5.93 (1H, t, $^3J = 2.4$)	6.45−6.43 (1+1H, m)	6.66 (1H, t, $^3J = 2.4$)	8.13 (1H, dd, $^3J = 2.4$, $^4J = 0.6$) 8.09 (1H, d, $^3J = 2.1$) 8.07 (1H, dd, $^3J = 2.4$, $^4J = 0.6$) 8.02 (1H, d, $^3J = 2.7$) 7.95 (1H, d, $^3J = 1.8$) 7.65−7.62 (1H, m) 7.57 (1H, dd, $^3J = 1.8$, $^4J = 0.6$) 7.13 (1H, dd, $^3J = 2.3$, $^4J = 0.6$)		10.61 (1H, s, NH) 10.49 (1H, s, NH) 7.73 (1H, dd, $^3J =$ 8.7, $^4J = 2.4$, arom) 7.65−7.62 (1H, m, arom) 6.70 (1H, d, $^3J = 8.4$)

[a] All the spectra were run in $CDCl_3$; Data are given as chemical shifts δ (relative integral, multiplicity, coupling constant J in Hz); Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad; arom, aromatic. [b] Occasionnally one proton of the $[B(pz)_4]^-$ ligand overlaps one proton of the diaminate. [c] For complex **15** we did not assign any of the H(3) and H(5) resonances.

compounds which present ν(Re═O) stretching frequencies significantly shifted to lower ($\Delta\nu$(Re═O) = 45 cm^{-1}, **14**; 23 cm^{-1}, **15)** or to higher ($\Delta\nu$(Re═O) = 25 cm^{-1}, **12**; 10 cm^{-1}, **13**) energies than that for the corresponding compound **1**, which is found at 965 cm^{-1}.[5] These differences, which indicate different rhenium−oxygen bond orders, are certainly due to the replacement of (OMe) groups by strong electron-donating or electron-attracting ligands, such as ethylenediaminate and chloride, respectively.

We do not have solid state structures for compounds **12**−**15**, to see whether the differences in the ν(Re═O) frequencies have some correspondence in the rhenium−oxygen bond distances. However, X-ray structural analysis that has been done for Re(V) compounds with poly(pyrazolyl)borates,[4,5,9−11] or even with the analogous pentamethylcyclopentadienyl,[15] indicate that all the Re−oxo distances compare well, and all of them are in the typical range for rhenium oxygen triple bonds.[17] Nevertheless, for some of these complexes significative differences have been found in the ν(Re═O) stretching frequencies, indicating different rhenium oxygen bond orders.[4,5,9−11,15]

As referred by a recent study,[18] the geometrical factors do not seem adequate to explain the bond order of the rhenium oxygen bonds, which are better explained by electronic factors. The infrared spectroscopy, as well as ^{17}O NMR, seem to be good probes to evaluate the electron density at the metal atom and consequently the rhenium−oxygen bond order.[18]

For the monomeric compounds the ν(Re═O) stretching bands are very strong, but in the dimeric **4**, **9**, and **10** they present weak or medium intensities. The frequency of the ν(Re−O−Re) stretching band decreases when we go from complex **4** (720 cm^{-1}) to complex **9** (636 cm^{-1}) and this agrees with the X-ray crystallographic analysis, which has shown that **4** is a dinuclear complex with an almost linear O═Re─O─Re═O backbone (O═Re─O, 175.6°; Re─O─Re, 180°) and **9** is a triple bridged dinuclear compound with a bent O═Re─O─Re═O backbone (O═Re─O, 165.3°; Re─O─Re, 125.4°). The infrared spectrum of **10** ressembles that of **9** which, together with the ^{1}H NMR data, suggests analogous structures for these two compounds.

For **14** and **15** a strong ν(N−H) band in the 3500−2800 cm^{-1} region[14] was observed, but for **6**, **7**, and **8** no stretching band appears in this range, as would be expected from the ^{1}H NMR spectra obtained for these complexes (see Table 2).

Table 2 presents the ^{1}H NMR data for the monomeric and dimeric complexes, in which the $[B(pz)_4]^-$ is acting as bidentate.

As can be seen, for **3**−**10**, **12**, and **13** one set of resonances of relative intensities 2:1:1 (**3**, **4**, **6**−**10**) or 1:1:1:1 (**5**, **12**, **13**) was found for the H(4) protons of the $[B(pz)_4]^-$, and they appear in the range 5.99−6.79 ppm, as normally observed for other oxocompounds of Re(V) previously reported.[4,5] For **3**, **4**, **7**, and **10** the H(3) and H(5) protons of the two coordinated pyrazolyl rings, which are magnetically equivalent, are assigned due to their intensities and multiplicities and they appear in the range 7.23−8.43 ppm. For **5**, **12** and **13** the H(3) and H(5) protons are easily identified but, due to the symmetry of the complexes, we can not assign the protons of the coordinated and uncoordinated pyrazolyl rings. The area of the H(3) and /or H(5) protons, in **6**, **8**, and **9**, is not easily assigned due to the occasional overlapping with some resonances of the co-ligands (pz and pzH) (Table 2).

One interesting feature of all these spectra is that two of the resonances of intensity one, which are due to H(3) and/or H(5) protons, are anormally shifted to high field, appearing between 6.23 and 6.89 ppm, and this is quite different from what we observed for other compounds of this family where the $[B(pz)_4]^-$ coordinates in a tridentate way (Table 3 and refs 4 and 5). These resonances are from the noncoordinated pyrazolyl rings and are not from the same ring, as indicated the irradiation of the two H(4) protons which appear at 6.23 and at 6.14 ppm for **3** and at 6.27 and 5.99 ppm for **4** (Table 2).

As an example, Figure 1 presents the ^{1}H NMR spectra of two compounds structurally characterized where the ligand tetrakis(pyrazolyl)borate acts either as tridentate or as bidentate. As can be seen, the pattern for the $[B(pz)_4]^-$ is of the type 2:1:1 in both complexes, but the range where the H(3)/H(5) protons appear is quite different. The spectrum presented in Figure 1 b) compares quite well with the spectra described for compounds **14** and **15** in Table 3.

The solid state structures of **3**, **4**, and **9** can be used to explain the abnormal shielding observed for the H(3)/H(5) protons of the noncoordinated rings in the compounds where the ligand is bidentate. In fact, X-ray structural analysis indicated that these rings are almost perpendicular, and if we assume that this relative position is roughly maintained in solution, it is possible

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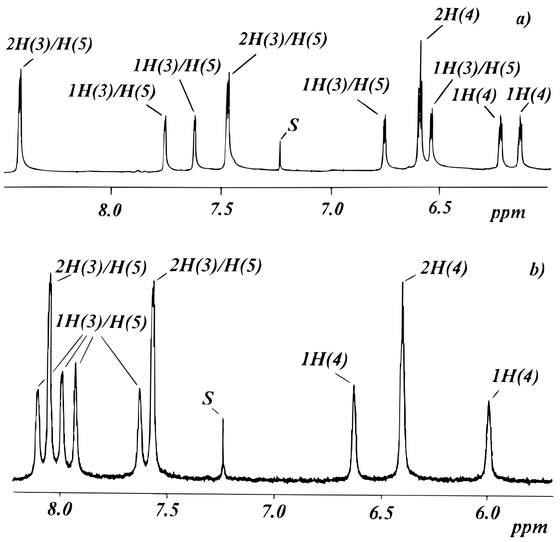
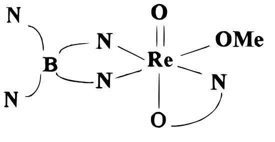


Figure 1. ^{1}H NMR spectra of oxorhenium (V) compounds (expanded [B(pz)$_4$]$^-$ area): (a) [ReO(acac){η^2-B(pz)$_4$}(OMe)]; (b) [ReO(OCH$_2$CH$_2$O){η^3-B(pz)$_4$}].[4]

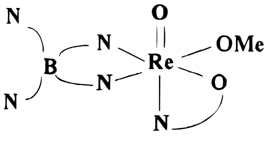
that the aromatic rings currents cause the protons to be shielded when compared to similar groups in complexes where the ligand is tridentate. Analogous effects, in compounds with the ligands [B(pz)$_4$]$^-$ and [HB(3,5-Me$_2$pz)$_3$]$^-$, have also been recently referred by Reger *et al.*[19,20]

As can be seen in Table 2, typical resonances arising from the alkyl chain of the alcoholate group coordinated to the metal center can be easily identified in the ^{1}H NMR spectra of compounds **3**, **5**, **6**, **7**, and **8**; for the acac ligand two resonances of relative intensities 1:6 are observed in the ^{1}H NMR spectra of **3** and **4**, but in the spectrum of **12** there are three resonances one integrating for one proton and other two integrating for three protons each, due to the methin and to the methyl protons of the acac ligand. The pattern obtained for **3** and **4** agrees with the structures found in the solid state, and the pattern observed for **12** clearly indicates that in this complex the acac ligand is twisted with one of the oxygen atoms coordinated *trans* to the Re═O (Scheme 1).

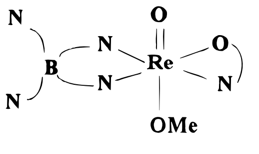
For **5** and **13** six resonances of equal intensity appear for the protons of the quinolin-8-olate; these resonances, although appearing in the area of the H(3) and H(5) protons of the [B(pz)$_4$]$^-$, are clearly differentiate due to their multiplicities and coupling constants (see Table 2). The nature of the quinolin-8-olate ligand does not allow the use of the ^{1}H NMR of the [B(pz)$_4$]$^-$ to conclude if the bidentate O, N donor ligand occupies two equatorial positions or if it occupies one equatorial and one axial. For **5**, three types of structures can be assumed:



(I)



(II)

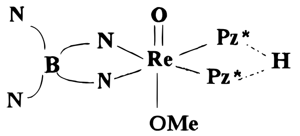


(III)

However, the chemical shift of the resonance due to the protons of the methoxide group, which for **5** appears at low field (3.96 ppm) compared with 2.96 ppm in compound **3**, the frequency of the stretching band ν(Re═O), which is higher in **5** than in **3**, and the solid state structures known for oxocomplexes of rhenium and technetium which indicate that the oxygen of the quinolin-8-olate normally coordinates to the metal *trans* to the oxo-oxygen lead us to assume structure I for **5**.[21,22] In **13**, we expect to have the quinolin-8-olate coordinated as in **5** and the chloride ligand in the equatorial position.

In the ^{1}H NMR spectra of **6**, **7**, and **8** only one resonance which integrates for two protons is observed for the H(4) protons of the co-ligands pz and pzH, in **6** and **8**, and of the 3,5-Me$_2$pz and 3,5-Me$_2$pzH in **7**. In these spectra is also clear the presence of one resonance integrating for one proton due to the N-H of the pzH, in **6** and **8,** and of the 3,5-Me$_2$pzH in **7**. The splitting of the H(3)/H(5) protons of the co-ligands pz and pzH is not clear due to the overlapping of these resonances with other of the [B(pz)$_4$]$^-$, but in the spectrum of **7** two resonances, which integrate six protons each, appear at 2.17 and at 2.45 ppm clearly indicating the magnetic equivalence of 3,5-Me$_2$pz and 3,5-Me$_2$-pzH.

The magnetic equivalence of the coligands pz and pzH, in **6** and **8** and 3,5-Me$_2$pz and 3,5-Me$_2$pzH in **7,** as well as the downfield shift of the N-H protons, lead us to consider that there is an interaction between this proton and the two nitrogen atoms of the equatorial pyrazol ligands, which are not coordinated to the metal center:



As we referred to earlier, in the IR spectra of compounds **6, 7,** and **8** no stretching band clearly assignable to ν(N−H) was observed, and this can be explained assuming that the interaction above referred would decrease the frequency of the ν(N−H) stretching band and this could be masked by the weak to medium bands of the [B(pz)$_4$]$^-$, which normally appear between 3100 and 3132 cm^{-1}. Although the magnetic equivalence in solution of the two pyrazolyl ligands could be explained by a dynamic process, this would not explain the non observation of the stretching band ν(N-H) in the IR, which has been done in KBr. In iridium complexes with pyrazole ligands a strong hydrogen bond between two N atoms has been previously observed by ^{1}H NMR and confirmed by X-ray structural analysis.[23,24]

These results indicate that when **1** and **2** react with pzH or 3,5-Me$_2$pzH these potentially monoanionic bidentate protic substrates do not coordinate to the Re center as the acac and quinolin-8-olate ligands; instead, they coordinate as neutral monodentate and anionic monodentate ligands and this is probably due to geometrical reasons, in particular the bite of the pyrazole ligands which is not adequate to promote the octahedral geometry normally adopted by these neutral oxo complexes containing the fragment RO-Re═O.

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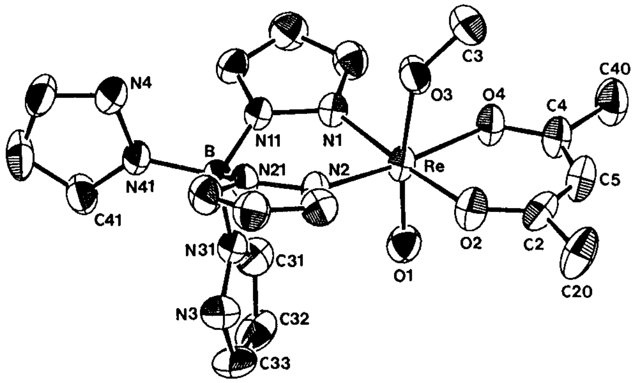

Figure 2. ORTEP drawing of [ReO(acac){η^2-B(pz)$_4$}(OMe)].

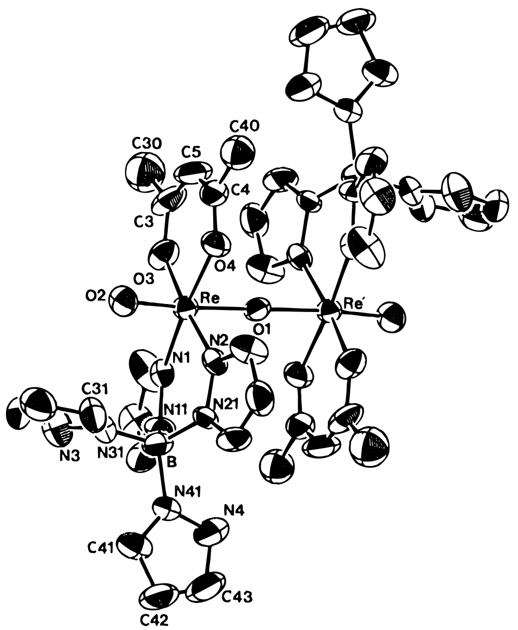

Figure 3. ORTEP drawing of [ReO(acac){η^2-B(pz)$_4$}]$_2$(μ-O).

For **10** we do not have a solid state structure, but the ^{1}H NMR compares with the one obtained for **9,** indicating analogous solid state structures.

Solid State Structures of [ReO(acac){η^2-B(pz)$_4$}(OMe)] (3) and [ReO(acac){η^2-B(pz)$_4$}]$_2$(μ-O) (4). Ortep views of the molecular structures are shown in Figures 2 and 3 and selected bond distances and bond angles are listed in Tables 4 and 5.

The crystal structure of **3** consists of discrete molecular units, with no short intermolecular contacts. The structure of **4** is dimeric and consists of two "[ReO(acac){η^2-B(pz)$_4$}]" moieties bridged by an oxygen atom lying on a centre of symmetry and imposing a strictly linear Re–O–Re bridge. In both compounds the coordination geometries around the rhenium atom are approximately octahedral with the oxygen atoms occupying the axial sites, the bidentate [B(pz)$_4$]$^-$ and acac ligands lying in the equatorial plane, with the metal atoms lying 0.11 Å and 0.10 Å out of the mean equatorial plane toward the axial oxo-oxygen group.

The Re=O bond lengths, 1.681(5) Å in **3** and 1.663(10) Å in **4** are in the range of M=O bond lengths in monomeric Re(V) and Tc(V) complexes and in dimeric with O=M–O–M=O units[9–11,15,25–29] and are comparable to the values found in previously structural determinations of similar monomeric oxo Re(V) complexes: 1.682(5), 1.693(7), and 1.69(2) Å in [ReO{η^3-B(pz)$_4$}(OPh)$_2$], [ReO{η^3-B(pz)$_4$}(SPh)$_2$], and [ReO(OCH$_2$CH$_2$O){η^3-B(pz)$_4$}], respectively.[4,5]

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for [ReO(acac){η^2-B(pz)$_4$}(OMe)] (**3**)

Re–O(1)	1.681(5)	O(2)–C(2)	1.291(8)
Re–O(2)	2.082(5)	O(4)–C(4)	1.280(8)
Re–O(3)	1.896(5)	C(2)–C(20)	1.501(9)
Re–O(4)	2.094(5)	C(2)–C(5)	1.363(11)
Re–N(1)	2.072(5)	C(4)–C(40)	1.497(10)
Re–N(2)	2.064(5)	C(4)–C(5)	1.399(10)
O(3)–C(3)	1.396(8)		
B–N[a]	1.53(1)	C–C[a]	1.37(1)
N–N[a]	1.37(2)	N–C[a]	1.33(1)
O(1)–Re–O(3)	171.1(2)	O(3)–Re–N(2)	89.3(2)
O(1)–Re–O(2)	89.1(2)	O(2)–Re–O(4)	90.9(2)
O(1)–Re–O(4)	90.5(2)	O(2)–Re–N(1)	175.0(2)
O(1)–Re–N(1)	95.9(2)	O(2)–Re–N(2)	87.8(2)
O(1)–Re–N(2)	96.8(2)	O(4)–Re–N(1)	88.6(2)
O(3)–Re–O(2)	84.6(2)	O(4)–Re–N(2)	172.5(2)
O(3)–Re–O(4)	83.3(2)	N(1)–Re–N(2)	92.0(2)
O(3)–Re–N(1)	90.4(2)	Re–O(3)–C(3)	143.1(5)
N–B–N[a]	110(1)		

[a] Mean value for the pyrazolyl rings.

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) for [ReO(acac){η^2-B(pz)$_4$}]$_2$(μ-O) (**4**)

Re–O(1)	1.910(1)	O(3)–C(3)	1.32(2)
Re–O(2)	1.663(10)	O(4)–C(4)	1.28(2)
Re–O(3)	2.053(10)	C(3)–C(30)	1.45(2)
Re–O(4)	2.057(10)	C(3)–C(5)	1.38(3)
Re–N(1)	2.080(11)	C(4)–C(40)	1.49(2)
Re–N(2)	2.049(12)	C(4)–C(5)	1.36(3)
B–N[a]	1.53(3)	C–C[a]	1.35(3)
N–N[a]	1.36(1)	N–C[a]	1.34(2)
O(1)–Re–O(2)	175.6(4)	O(2)–Re–N(2)	94.8(5)
O(1)–Re–O(3)	86.1(3)	O(3)–Re–O(4)	92.1(4)
O(1)–Re–O(4)	85.6(3)	O(3)–Re–N(1)	88.1(4)
O(1)–Re–N(1)	88.9(3)	O(3)–Re–N(2)	174.1(4)
O(1)–Re–N(2)	88.1(3)	O(4)–Re–N(1)	174.4(4)
O(2)–Re–O(3)	91.1(5)	O(4)–Re–N(2)	87.9(4)
O(2)–Re–O(4)	91.2(4)	N(1)–Re–N(2)	91.3(4)
O(2)–Re–N(1)	94.3(5)	Re–O(1)–Re′	180
N–B–N[a]	110(1)		

[a] Mean value for the pyrazolyl rings.

In **3** the Re–O(3) bond distance and the Re–O(3)–C(3) bond angle of the methoxide group are 1.896(5) Å and 143.1(5)°, respectively. The structure of **3** is similar in terms of the [O=M^V–OR]$^{2+}$ core to the structures of the compounds [ReOL$_2$(OEt)] and [TcOL$_2$(OMe)] (L = (*o*-aminophenyl)diphenylphosphine),[30] though with the axial angles O=Re–O(Et) and O=Tc–O(Me) (160.8(3)° and 158.3(3)°) significantly different from the angle 171.1(2)° found in **3**, probably due to the less distorted octahedral geometry observed here. The Re–O(3) bond distance is significantly shorter than 2.004(7) and 1.999(8) Å observed for the Re–O(Et) and Tc–O(Me) bond distances, indicating a stronger Re–O(Me) bond**,** but is comparable to the corresponding value of 1.890(2) Å in [ReOCl$_2$-

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$(O^iPr)(PPh_3)_2]$.[31] In this compound the Re═O bond length of 1.698(2) Å, and the nearly linear O═Re—O unit (174.25(9)°) are in the range of the values found in **3**.

The dimeric structure of **4** has a quasi linear O═Re—O—Re═O group (O═Re—O angle, 175.6(4)°), which is comparable to the structure of $Re_2O_3Cl_4(Me_2pzH)_4{\cdot}Me_2CO$ (O═Re—O angles of 172.5(3), 173.5(3)°; Re—O—Re angle, 177.7(4)°).[32] The terminal and the bridging Re−O bond lengths, 1.663(10) and 1.910(1) Å respectively, compare well with the corresponding mean values of 1.690 and 1.93 Å in $Re_2O_3Cl_4(Me_2pzH)_4{\cdot}Me_2CO$.[32] These values are also in good agreement with those found for other dimeric Re(V) and Tc(V) complexes containing the O═M—O—M═O unit (1.67−1.72 Å for terminal M═O and 1.90−1.94 Å for bridging M—O bond lengths).[12,26−29,32−34]

In both compounds the $[B(pz)_4]^-$ ligand acts in a bidentate manner, with similar Re−N bond lengths and N−Re−N bond angles (average values of 2.07(1) Å and 91.6(4)°). These values are respectively, shorter and greater than the corresponding values found in the three previously reported Re(V) complexes in which the $[B(pz)_4]^-$ ligand is tridentate (2.10−2.29 Å and 76−90°).[4−5] The bond distances and angles of the coordinated pyrazolyls do not present any significant difference from those of the noncoordinated, and compare well to the values found in previously reported Re(V) complexes.[4,5]

In the acac ligand, the mean Re−O bond distances are 2.09(1) and 2.06(1) Å, and the O−Re−O angles are 90.9(2) and 92.1(4)° for compounds **3** and **4**, respectively. In both compounds the dimensions of the acac ligand are normal. The ligand is not rigorously planar but slightly distorted, as shown by the angles of 4.2° and 3.3° made by the O−Re−O planes with the acac plane in **3** and **4**, respectively, probably to minimize the nonbonded contacts within the molecule. There is steric crowding on the coordination sphere of the two compounds, which manifests in short ligand⋯ligand contacts (less than the respective sums of Van de Waals radii). There are no short intermolecular contacts in **4**.

Solid State Structure of $[ReO\{B(pz)_4\}(\mu\text{-}pz)]_2(\mu\text{-}O)$ (9). The crystal structure consists of two independent "ReO{B(pz)$_4$}" units triple bridged by an oxygen atom and two pyrazolyl rings. The characteristic feature of this structure is the presence of an O═Re—O—Re═O group, with a quite bent Re(1)−O(3)−Re(2) bridging unit (angle of 125.4(3)°), certainly due to the steric requirements of the two bridging pyrazolyl rings. The angles O(1)−Re(1)−O(3) and O(2)−Re(2)−O(3) are 164.6(2) and 166.1(3)°, respectively. The coordination geometries at the Re atoms are distorted octahedral, as can be seen in the values of the angles around the rhenium atoms. The Re atoms are 0.19 and 0.18 Å out the mean equatorial planes toward the axial oxo-oxygen atoms.

An ORTEP view of the structure is shown in Figure 4, and selected bond distances and angles are presented in Table 6.

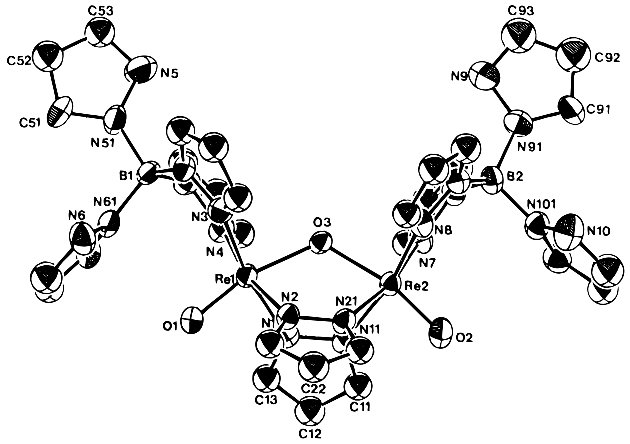

Figure 4. ORTEP drawing of $[ReO\{\eta^2\text{-}B(pz)_4\}(\mu\text{-}pz)]_2(\mu\text{-}O)$.

Table 6. Selected Bond Lengths (Å) and Bond Angles (deg) for $[ReO\{\eta^2\text{-}B(pz)_4\}(\mu\text{-}pz)]_2(\mu\text{-}O)$ (**9**)

Re(1)−O(1)	1.680(6)	Re(2)−O(2)	1.693(6)
Re(1)−O(3)	1.930(5)	Re(2)−O(3)	1.923(5)
Re(1)−N(1)	2.125(6)	Re(2)−N(11)	2.138(6)
Re(1)−N(2)	2.128(7)	Re(2)−N(21)	2.113(7)
Re(1)−N(3)	2.077(6)	Re(2)−N(7)	2.095(6)
Re(1)−N(4)	2.085(7)	Re(2)−N(8)	2.073(6)
B−N[a]	1.53(2)	C−C[a]	1.37(2)
N−N[a]	1.36(1)	N−C[a]	1.34(2)
O(1)−Re(1)−O(3)	164.6(2)	O(2)−Re(2)−O(3)	166.1(3)
O(1)−Re(1)−N(1)	88.7(3)	O(2)−Re(2)−N(11)	89.3(3)
O(1)−Re(1)−N(2)	90.6(3)	O(2)−Re(2)−N(21)	90.7(3)
O(1)−Re(1)−N(3)	100.4(3)	O(2)−Re(2)−N(7)	99.4(3)
O(1)−Re(1)−N(4)	100.9(3)	O(2)−Re(2)−N(8)	100.0(3)
O(3)−Re(1)−N(1)	79.6(2)	O(3)−Re(2)−N(11)	79.9(2)
O(3)−Re(1)−N(2)	78.9(2)	O(3)−Re(2)−N(21)	79.9(2)
O(3)−Re(1)−N(3)	91.0(2)	O(3)−Re(2)−N(7)	89.7(2)
O(3)−Re(1)−N(4)	89.4(2)	O(3)−Re(2)−N(8)	90.2(2)
N(1)−Re(1)−N(2)	86.5(3)	N(11)−Re(2)−N(21)	85.1(3)
N(1)−Re(1)−N(3)	170.6(2)	N(11)−Re(2)−N(7)	92.2(3)
N(1)−Re(1)−N(4)	91.4(3)	N(11)−Re(2)−N(8)	169.6(2)
N(2)−Re(1)−N(3)	91.0(3)	N(21)−Re(2)−N(7)	169.5(2)
N(2)−Re(1)−N(4)	168.3(3)	N(21)−Re(2)−N(8)	90.0(3)
N(3)−Re(1)−N(4)	89.2(3)	N(7)−Re(2)−N(8)	90.9(3)
Re(1)−O(3)−Re(2)	125.4(3)		
N−B−N[a]	109(2)		

[a] Mean value for the pyrazolyl rings.

The structure shows roughly two planes of symmetry, perpendicular to each other: one containing the O(3), C(12), C(22) atoms; the other passing through the Re(1), Re(2), O(1), O(2), O(3), B(1), and B(2) atoms and the two pyrazolyl rings N(5) and N(9). The Re═O bond lengths average 1.686 (6) Å and the bridging Re—O bond lengths, 1.930(5) and 1.923(5) Å, average 1.926 (5) Å. These are comparable to the values observed in **3** and **4**, and are in the range of the values found in the dimeric oxo-bridged structures of Re(V) and Tc(V) complexes.[12,26−29,32−34] The $[B(pz)_4]^-$ ligand acts in a bidentate manner, as also observed in **3** and **4** and in other poly(pyrazolyl)borate complexes.[2,19,20] The Re−N bond lengths of the coordinated pyrazolyls of the $[B(pz)_4]^-$ ligands are quite similar (average 2.08(1) Å), and are identical to the average Re−N bond lengths in **3** and **4**. These are shorter than the average Re−N bond lengths of the two bridging pyrazolyl rings (average 2.13(1) Å). The N−Re−N bond angles in $[B(pz)_4]^-$ ligands (average 90.1(3)°) are similar to the corresponding angles in **3** and **4**. In a geometric arrangement similar to that found in **3** and **4**, the noncoordinated pyrazolyl ring farthest from the metal, on each ligand, bisects the planes of the two coordinated rings, and is almost perpendicular to the other noncoordinated ring (dihedral angles of 85.8 and 88.7° in **9**; 83.2° in **3**; 89.2° in **4**).

Several dinuclear Re(V) compounds containing the $[Re_2(\mu\text{-}O)_2]^{6+}$ unit, either planar or puckered, have been crystallographically characterized.[15,16,35] The short Re−Re distances (range: 2.4−2.7 Å), the acute Re−O−Re angles and the obtuse O−Re−O angles have been interpreted as indicative of metal−metal bonding.[16,35] Apparently $[(Cp^*)_2Re_2O_2(\mu\text{-}O)_2]{\cdot}2H_2O$ is the only Re(V) compound containing this type of unit, where

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no Re−Re bond was found (Re−Re distance, 3.142(1) Å; Re−O−Re angle, 106.6(1)°, O=Re−O angle, 73.4(1)).[14d] The Re(1)···Re(2) distance of 3.425 Å found in **9** is a clear indication of no interaction. This larger distance, when compared to $[(Cp^*)_2Re_2O_2(\mu\text{-}O)_2]\cdot 2H_2O$, is certainly due to the two pyrazolate groups in the triple bridged complex **9**. This is also the reason why larger Re−O−Re and O−Re−N angles were found. So far, **9** is the first triple-bridged Re(V) complex structurally characterized, and the nature of the $[B(pz)_4]^-$ ligand, especially its coordination versatility, seems to be crucial in its stabilization.

Concluding Remarks

The poly(pyrazolyl)borates, namely $[HB(pz)_3]^-$ and $[B(pz)_4]^-$, are compared to cyclopentadienyl and substituted cyclopentadienyl ligands and have been largely used in coordination chemistry. One interesting feature of both type of ligands is that they may undergo hapticity changes. However, as far as we know, in all the Re(V) oxo complexes with these ligands they present their maximum hapticity: η^5 for cyclopentadienyls[15] and η^3 for poly(pyrazolyl)borates.[3−5,9−11]

We have shown that $[ReO\{\eta^3\text{-}B(pz)_4\}(OMe)_2]$ (**1**) is a versatile compound for the synthesis of monomeric and dimeric complexes of Re(V), including the first structurally characterized mononuclear and dinuclear Re compounds where the tetrakis(pyrazolyl)borate ligand coordinates in a bidentate way. By using **1** and choosing properly the protic substrate the denticity of the $[B(pz)_4]^-$ can be modulated: reactions with potentially monoanionic protic substrates lead to complexes where the $[B(pz)_4]^-$ is bidentate and reactions with potentially dianionic protic substrates lead to complexes where the $[B(pz)_4]^-$ is tridentate. As in previous reported work, the ^1H NMR spectroscopy proved again to be a powerful technique to evaluate the coordination geometry around the metal center as well as the denticity of the poly(pyrazolyl)borate ligand, and this is due to the nature of these ligands.

Acknowledgment. The authors thank Prof. José Ascenso and Prof. Alberto Romão Dias (CQE, IST) for NMR facilities.

Supporting Information Available: Tables of complete crystallographic data, final coordinates, equivalent thermal parameters, calculated hydrogen atom positions, anisotropic thermal parameters, complete bond distances and angles, and equations of mean-least-squares planes (29 pages). Ordering information is given on any current masthead page.

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