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Novel Rhenium(V) Oxo Complexes Containing Bis(pyrazol-1-yl)acetate and Bis(pyrazol-1-yl) Sulfonate as Tripodal N,N,O-heteroscorpionate Ligands

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Reactions of $[NBu_4][Re(O)Cl_4]$ with bis(pyrazol-1-yl)methane (bpzm) and bis(pyrazol-1-yl)acetate (Hbpza) and with the lithium salts lithium [bis(3,5-dimethylpyrazol-1-yl)acetate] (Libdmpza) and lithium [bis(3,5-dimethylpyrazol-1-yl)-methanesulfonate] (Libdmpzs) produce a series of new compounds containing either a κ^2-N,N bidentate pyrazolyl ligand $[Re(O)(bpzm)Cl_3$ (**1**), $Re(O)(bpzm)(OMe)Cl_2$ (**2**), $Re(O)(bpzaOMe)(OMe)Cl_2$ (**4**)] or a κ^3-N,N,O heteroscorpionate $[Re(O)(bpza)Cl_2$ (**3**), $Re(O)(bdmpza)Cl_2$ isomers **5** and **6**, Re(O)(bdmpza)(OMe)Cl (**7**), Re(O)(bdmpza)(OEt)Cl (**8**), Re(O)(bdmpzs)(OMe)Cl (**9**), Re(O)(bdmpzs)(OEt)Cl (**10**)]. X-ray analyses of **1** and **3** show in both cases a distorted octahedral environment around the rhenium atom. The nature and the geometry of the products are strongly determined by the reaction solvent and by the heteroscorpionate ligand itself. When scorpionates bear methylated pyrazolyl rings mixed heterocomplexes Re(O)(bdmpza)(glycol) (**11**) and Re(O)(bdmpzs)(glycol) (**12**) are obtained (H_2glycol = ethylene glycol). Also **11** shows an octahedral geometry as assessed by X-ray study.

Introduction

Potentially useful therapeutic radionuclides include two isotopes of rhenium: ^{186}Re and ^{188}Re. They are both β-emitters (^{186}Re: $\beta^-_{max} = 1.07$ MeV, $t_{1/2} = 90$ h; ^{188}Re: $\beta^-_{max} = 2.10$ MeV, $t_{1/2} = 17$ h) with associated energies that give a suitable range in tissues and half-lives within an appropriate range for human use, while not presenting a long-term environmental radiation hazard.[1−3] For research purposes, ^{188}W/^{188}Re generators, based on the same approach utilized for the widespread clinically used ^{99}Mo/^{99m} Tc generator, have become recently available.[4] Because of the chemical similarity of the group 7 elements Re and Tc, most investigations on technetium-based imaging agents currently employed in the clinical practice for diagnosis[5] provide an important scientific background for the development of therapeutic rhenium analogues.

In the past few years part of the research on the design and synthesis on technetium and rhenium radiopharmaceuticals has been focused on the so-called "metal-fragment" strategy. An example of this approach is represented by stable $[M(N)(PXP)]^{2+}$ or $[M(NPh)(PXP)]^{3+}$ moieties (M = Tc, Re) including a terminal nitride or phenylimido group and PXP heterodiphosphines.[6,7] To these entities various bidentate ligands (BID) can be attached to produce mixed ligand compounds of the type M(N)(BID)(PXP) and $[M(NPh)(BID)(PXP)]^+$.[7,8] This strategy can be successfully employed to obtain simple coordination compounds, potential metal-

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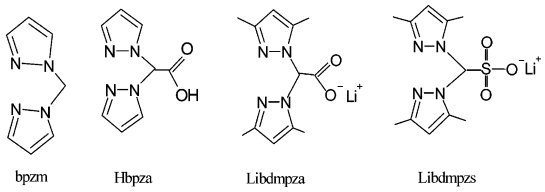
essential radiopharmaceuticals, or more sophisticated metal-tagged species by conjugation of BID to a proper biomolecule or pharmacophore.[9]

Following this strategy we looked for chelate ligands able to stabilize the monooxo rhenium core. Poly(pyrazolyl)-borates[10] and related scorpionates[11] are potentially tridentate ligands extensively employed as anionic σ-donor chelates in a variety of metal complexes. They have found wide application in coordination, organometallic, and bioinorganic chemistry.[12] These ligands have a general structure $[RR'B(pz)_2]^-$, where pz is either an unsubstituted or C-substituted pyrazolyl group that can coordinate metals to give complexes $[RR'B(\mu\text{-}pz)_2ML_n]$. If neither R nor R′ is pz the ligand is called heteroscorpionate, a description that also includes ligands where R′ is a pyrazolyl group different from the other two bridging pyrazolyl units. Modifications of poly(pyrazolyl)borates can be made by replacement of the boron bridging atom by other elements such as carbon,[13] silicon[14] or phosphorus.[15] Recent contributions are related to the heteroscorpionate ligands derived from bis(pyrazol-1-yl)methane, with $[RR'C(pz)_2]$ as general structure and bearing a coordinating moiety (R′) such as acetate,[16] dithioacetate,[17] sulfonate,[18] ethoxide,[19] phenolate,[20] thiolate,[21] or other class of moieties.[22]

On this basis, we have focused our attention on the study of the coordinative ability of the aforementioned monoanionic heteroscorpionate ligands based on bis(pyrazol-1-yl)methanes containing acetate or sulfonate groups ("NNO") as the third coordinating moiety toward rhenium. This paper describes the synthesis and the spectroscopic characterization of new monooxo rhenium(V) compounds containing NNO ligands (NNO = bdmpza, bdmpzs, or bpza) (see Chart 1),

Chart 1



as well as the synthesis and characterization of mixed complexes comprising the new stable metal fragment $[Re(O)(NNO)]^{2+}$ and a representative bidentate ligand (H_2glycol).

Experimental Section

Materials. All solvents and commercially available substances were of reagent grade and used without further purification. Tetrahydrofuran was distilled under dinitrogen from the potassium ketyl of benzophenone. The complex $[NBu_4][Re(O)Cl_4]$ was prepared according to literature methods.[23]

Instrumentation. Elemental analyses were performed on a Carlo Erba 1106 elemental analyzer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX-300 instrument, using $SiMe_4$ as internal reference (^{1}H, ^{13}C). FT IR spectra were recorded on a Mattson 3030 Fourier transform spectrometer in the range 400−4000 cm^{-1} in Nujol or in KBr pellets. ESI experiments were performed on an LCQ (ThermoFinnigan, San Jose, CA) ion trap instrument. The ca. 5×10^{-6} M solutions of the different compounds dissolved in acetonitrile were directly infused into the ion source pump at a flow rate of 8 μL/min by a syringe pump. The spray capillary voltage was set at 4 kV, and the entrance capillary temperature was set at 270 °C. The nebulizing gas was N_2. MS^n experiments were obtained by resonance activation of preselected species and by varying the resonant excitation voltage in the range 0−2 V.

Synthesis of the Ligands. The ligands bis(pyrazol-1-yl)methane (bpzm), bis(pyrazol-1-yl)acetate (Hbpza), and the lithium salt of bis(3,5-dimethylpyrazol-1-yl)acetate (Libdmpza) were synthesized in accordance with the literature methods.[13,16a,b,f]

Lithium [Bis(3,5-dimethylpyrazol-1-yl)methanesulfonate] (Libdmpzs). *n*-Butyllithium (16.0 mL, 1.6 M solution) was slowly added to a solution of bis(pyrazol-1-yl)methane (5.1 g, 25.0 mmol) in

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dry tetrahydrofuran (35 mL) at −78 °C. The solution immediately turned yellow and turbid. After 2 h a sulfurtrioxide−trimethylamine complex (3.7 g, 27.0 mmol) was added at −60 °C. The resulting mixture was allowed to warm to 0 °C and kept under constant stirring for 4 h. The solvent was then evaporated under vacuum, and a yellowish solid was obtained. Recrystallization from diethyl ether yielded colorless crystals of Li(bdmpzs). Yield 72%. M.p. 136 °C (dec). Anal. Calcd for $C_{11}H_{15}LiN_4O_3S$: C, 45.5; H, 5.2; N, 19.3; S, 11.1. Found: C, 45.4; H, 5.3; N, 19.3; S, 11.0. ^{1}H NMR (D_2O; ppm): δ 2.10 (s, 6H, CH_3), 2.19 (s, 6H, CH_3), 6.00 (s, 2H, H^4), 7.06 (s, 1H, C*H*). ^{1}H NMR ($CDCl_3$, ppm): δ 1.91 (s, 6H, CH_3), 2.45 (s, 6H, CH_3), 5.83 (s, 2H, H^4), 6.70 (s, 1H, C*H*). ^{13}C{^{1}H}NMR (D_2O; ppm): δ 11.5 (*C*H_3), 13.8 (*C*H_3), 72.8 (*C*H), 105.6 (*C*^{4}), 141.2 (C_{pz}), 146.3 (C_{pz}). IR (Nujol, cm^{-1}): 3135w (CH), 1612s, 1563s (C═C + C═N), 1112s, 1070s, 594m, 543m (SO_3). IR (KBr, cm^{-1}): 1560s (C−N), 1256s (SO_3), 1204s (SO_3). ESI-MS (*m*/*z* assignment, % intens): (+) 591 [Na{O_3SCH(3,5-Me_2Pz)$_2$}$_2$ + H]$^+$, 25; 97 [(3,5-Me_2Pz) + H]$^+$, 100. ESI-MS (*m*/*z* assignment, % intens): (−) 589 [Na{O_3SCH(3,5-Me_2Pz)$_2$}$_2$]$^-$, 45; 153 [Na(OH)(3,5-Me_2Pz)(H_2O)]$^-$, 100.

Syntheses of the Complexes. (a) Re(O)(bpzm)Cl$_3$ (1). [NBu_4][Re(O)Cl_4] (0.050 g, 0.085 mmol) was dissolved in acetonitrile, and bpzm (0.013 g, 0.087 mmol) was added at room temperature. The reaction mixture immediately turned to blue and was stirred at room-temperature overnight. A turquoise powder precipitated from the reaction mixture. It was recovered by filtration and washed with diethyl ether. Crystallization from acetone of the light blue residue gave **1** in 55% yield. Crystals suitable for X-ray analysis were obtained from slow evaporation of the solvent from acetonitrile solution of **1**. M.p. 278−280 °C (dec). Anal. Calcd for $C_7H_8Cl_3N_4ORe$: C, 18.4; H, 1.8; N 12.3. Found: C, 18.7; H, 1.7; N, 12.0. ^{1}H NMR (CD_3COCD_3; ppm): δ 6.98 (t, 2H, H^4), 7.18 (d, 1H, H^I, CH_2), 7.42(d, 1H, H^{II},CH_2), 8.69 (dd, 2H, H_{pz}), 8.76 (dd, 2H, H_{pz}). IR (Nujol, cm^{-1}): 3118w (CH), 1519m (C═C + C═N), 977s (Re═O), 620 (μ-oxo). ESI-MS (*m*/*z* assignment, % intens): 935 [2{Re(O)Cl_3(bpzm)} + Na$^+$]$^+$, 49; 881 [{Re(O)Cl_2(bpzm)$_2$O} + Na$^+$]$^+$, 56; 479 [{Re(O)Cl_3(bpzm)}+ Na$^+$]$^+$, 100; 421 [{Re(O)Cl_3(bpzm)} + Na$^+$ − NaCl]$^+$, 42.

(b) Re(O)(bpzm)(OMe)Cl$_2$ (2). [NBu_4][Re(O)Cl_4] (0.05 g, 0.085 mmol) was dissolved in methanol, and bpzm (0.013 g, 0.087 mmol) was added at room temperature. The reaction mixture immediately turned to violet and was stirred at room temperature overnight. A violet powder precipitated from the reaction mixture. It was recovered by filtration, washed with diethyl ether, and characterized as **2**. Yield 85%. M.p. 232−233 °C (dec). Anal. Calcd for $C_8H_{11}Cl_2N_4O_2Re$: C, 21.2; H, 2.4; N, 12.4. Found: C, 21.2; H, 2.1; N, 11.8. ^{1}H NMR (CD_3COCD_3, ppm): δ 2.58 (s, 3H, CH_3), 6.86 (t, 2H, H^4), 7.20 (s, 2H, CH_2), 8.51 (d, 2H, H_{pz}), 8.52 (d, 2H, H_{pz}). IR (Nujol, cm^{-1}): 3130w (CH), 1519m (C═C + C═N), 940s (Re═O), 503s. ESI-MS (*m*/*z* assignment, % intens): 927 [2{Re(O)(OMe)(bpzm)Cl_2} + Na]$^+$, 100; 475 [{Re(O)(OMe)-(bpzm)Cl_2} + Na]$^+$, 82; 417 [{Re(O)(OMe)(bpzm)Cl_2} − Cl]$^+$, 73.

(c) Re(O)(bpza)Cl$_2$ (3). [NBu_4][Re(O)Cl_4] (0.12 g, 0.2 mmol) was dissolved in acetonitrile, and Hbpza (0.039 g, 0.2 mmol) was added at room temperature. Triethylamine (50 μL, 0.38 mmol) was added to the reaction mixture that immediately turned from emerald green to dark green. After 18 h at room temperature the solution was blue-green. The solvent was removed and the sticky residue washed with a few drops of methanol and with diethyl ether. The blue product was identified as **3**. Yield 55%. M.p. 181−184 °C (dec). Anal. Calcd for $C_8H_7Cl_2N_4O_3Re$: C, 20.7; H, 1.5; N, 12.0. Found: C, 20.3; H, 1.3; N, 11.8. ^{1}H NMR (CD_3CN, ppm): δ 6.89 (t, 2H, H^4), 7.28 (s,1H, C*H*), 8.28 (dd, 2H, H_{pz}), 8.35 (dd, 2H, H_{pz}). IR (Nujol, cm^{-1}): 3118w (CH), 1722s (C═O), 1555m (C═C + C═N), 935s (Re═O). ESI-MS (*m*/*z* assignment, % intens): 950 [2{Re(O)(bpza)Cl_2} + Na$^+$]$^+$, 90; 487 [{Re(O)(bpza)-Cl_2} + Na$^+$]$^+$, 100; 443 [{Re(O)(bpza)Cl_2} + Na$^+$ − CO_2]$^+$, 10.

(d) Re(O)(bpzaOMe)(OMe)Cl$_2$ (4). [NBu_4][Re(O)Cl_4] (0.15 g, 0.25 mmol) was dissolved in methanol, and Hbpza (0.05 g, 0.25 mmol) was added at room temperature. Triethylamine (50 μL, 0.38 mmol) was added to the reaction mixture that immediately turned from emerald green to violet, and the solution was stirred at room temperature overnight. A violet powder precipitated from the reaction mixture, which was recovered by filtration, washed with diethyl ether, and characterized as **4**. Yield 80%. M.p. 227 °C (dec). Anal. Calcd for $C_{10}H_{13}Cl_2N_4O_4Re$: C, 23.5; H, 2.6; N, 11.0. Found: C, 23.2; H, 2.4; N, 11.0. ^{1}H NMR (CD_3CN, ppm): δ 2.50 (s, 3H, CH_3), 3.50 (s, 3H, CH_3), 6.91 (t, 2H, H^4), 7.74 (s, 1H, C*H*), 8.34 (dd, 2H, H_{pz}), 8.77 (dd, 2H, H_{pz}). IR (Nujol, cm^{-1}): 3118w (CH), 1772s (C═O), 1555m (C═C + C═N), 945s (Re═O), 620 (μ-oxo). ESI-MS (*m*/*z* assignment, % intens): 1043 [2{Re(O)-(OMe)(bpzaOMe)Cl_2} + Na$^+$]$^+$, 100; 533 [{Re(O)(OMe)(bpza-OMe)Cl_2} + Na$^+$]$^+$, 57; 475 [{Re(O)(OMe)(bpzaOMe)Cl_2} + Na$^+$ - NaCl]$^+$, 75; 445 [{Re(O)(OMe)(bpzaOMe)Cl_2} + Na$^+$- NaCl − OCH_3]$^+$, 46.

(e) (*OC*-6-44)Re(O)(bdmpza)Cl$_2$ (5) and (*OC*-6-42)Re(O)-(bdmpza)Cl$_2$ (6).[24] [NBu_4][Re(O)Cl_4] (57 mg, 0.1 mmol) was dissolved in acetonitrile, and Li(bdmpza) (26 mg, 0.1 mmol) was added to the yellow solution at room temperature. Immediately the reaction mixture turned to green. The reaction mixture was refluxed for 2 h and then stirred at room temperature overnight. After 18 h at room temperature the solution was emerald green. The solvent was removed and the sticky residue washed with few drops of methanol and with diethyl ether. The blue-green product, identified as **5**, was insoluble in methanol and ethanol, slightly soluble in dichloromethane and chloroform, and soluble in acetonitrile. If the reaction between [NBu_4][Re(O)Cl_4] and Li(bdmpza) was carried out in chloroform at room temperature for 20 h, the ^{1}H NMR analysis of the reaction mixture showed the presence of two different species. The solvent was removed, the blue-green residue washed with diethyl ether, and the mixture was separated by a silica chromatographic column using as mobile phase chloroform/ethanol 7:3. A green product was eluted with the solvent and was characterized as **6** (yield, 40%). Product **5** was recovered later (R_f 0.7) as a blue compound (yield, 25%). Several reactions carried out at different temperature and with different reaction time gave rise to a mixture of the two isomers in a variable ratio. Compound **5**: Anal. Calcd for $C_{12}H_{15}Cl_2N_4ReO_3$: C, 27.7; H, 2.9; N, 10.8. Found: C, 28.0; H, 3.0; N, 10.4. ^{1}H NMR ($CDCl_3$; ppm): δ 2.74 (s, 6H, CH_3), 3.03 (s, 6H, CH_3), 6.38 (bm, 3H, C*H* and H$^{4,4'}$). IR (KBr, cm^{-1}): 1719s (CO_2), 1555m (C═N), 1461s (CO_2), 941m (Re═O). ESI-MS (*m*/*z* assignment, % intens): 559 [MK$^+$], 30; 543 [MNa$^+$], 100; 499 [MNa$^+$ − CO_2], 7.

Compound **6**: Anal. Calcd for $C_{12}H_{15}Cl_2N_4ReO_3$: C, 27.7; H, 2.9; N, 10.8. Found: C, 27.2; H, 3.2; N, 10.3. ^{1}H NMR ($CDCl_3$; ppm): δ 2.36 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 2.81 (s, 3H, CH_3), 3.10 (s, 3H, CH_3), 6.47 (s, 1H, H^4), 6.42 (s,1H, H$^{4'}$), 5.96 (s,1H, C*H*). ^{13}C{^{1}H} NMR ($CDCl_3$; ppm): δ 10.7 (*C*H_3), 10.9 (*C*H_3), 14.4 (*C*H_3), 14.7 (*C*H_3), 109.0 (C_{pz}), 110.6 (C_{pz}). IR (KBr, cm^{-1}): 1707s (CO_2), 1557m (C═N), 1458s (CO_2). ESI-MS (*m*/*z* assignment, % intens): 559 [MK$^+$], 53; 543 [MNa$^+$], 100.

(24) The two isomers **5** and **6** are named in accordance with *IUPAC Provisional Recommendations, Nomenclature of Inorganic Chemistry*, Draft March 2004, available in www. IUPAC.org.

(f) Re(O)(bdmpza)(OMe)Cl (7). To a pale-green solution of $[NBu_4][Re(O)Cl_4]$ (65 mg, 0.11 mmol) in methanol Li(bdmpza) (36 mg, 0.14 mmol) was added, and immediately the solution turned blue. The reaction mixture was left at room temperature and stirred overnight. A light blue powder precipitated from the reaction mixture. It was recovered by filtration and washed with diethyl ether (yield 65−70%). In some cases a variable amount of **5** (5−10%) was formed. Anal. Calcd for $C_{13}H_{18}ClN_4ReO_4$: C, 30.3; H, 3.5; N, 10.9. Found: C, 31.3; H, 3.4; N, 10.7. ^{1}H NMR ($CDCl_3$; ppm): δ 2.66 (s, 3H, C*H*$_3$), 2.69 (s, 3H, C*H*$_3$), 2.87 (s, 3H, C*H*$_3$), 2.97 (s, 3H,C*H*$_3$), 5.30 (s, 3H, OC*H*$_3$), 6.26 (s, 1H, C*H*), 6.32 (s, 2H, H^4). ^{13}C{^{1}H} NMR (300 MHz, $CDCl_3$; ppm): δ 10.7 (*C*H$_3$), 10.8 (*C*H$_3$), 13.3 (*C*H$_3$), 14.0 (*C*H$_3$), 67.1 (O*C*H$_3$), 75.8 (*C*H), 109.8-(C_{pz}), 109.3 (C_{pz}). ESI-MS (*m*/*z* assignment, % intens): 555 [MK^+], 60; 539 [MNa^+], 90; 495 [$MNa^+ - CO_2$], 65.

(g) Re(O)(bdmpza)(OEt)Cl (8). $[NBu_4][Re(O)Cl_4]$ (51 mg, 0.09 mmol) was dissolved in ethanol, and Li(bdmpza) (26 mg, 0.1 mmol) was added to the greenish solution at room temperature. Immediately the reaction mixture turned green-blue. After 18 h at room temperature a light blue solid precipitated which was filtered from the reaction mixture and washed with diethyl ether. ^{1}H NMR analysis of the reaction mixture showed the presence of **5**, **6**, and traces together with a new product identified as **8**. Soxlet extraction with ethanol of the residue afforded pure **8** as a blue microcrystalline powder. Yield: 60−65%. Anal. Calcd for $C_{14}H_{20}ClN_4ReO_4$: C, 31.7; H, 3.8; N, 10.6. Found: C, 32.1; H, 4.0; N, 10.4. ^{1}H NMR ($CDCl_3$; ppm): δ 1.25 (t, 3H, OCH$_2$C*H*$_3$), 2.66 (s, 3H, C*H*$_3$), 2.69 (s, 3H, C*H*$_3$), 2.90 (s, 3H, C*H*$_3$), 2.96 (s, 3H, C*H*$_3$), 5.67 (m, 1H, OC*H*$_2$CH$_3$), 5.96 (m, 1H, OC*H*$_2$CH$_3$), 6.25(s, 1H, C*H*), 6.32 (s, 2H, C*H*^{4}). ^{13}C{^{1}H} NMR ($CDCl_3$; ppm): δ 10.7 (*C*H$_3$), 10.9 (*C*H$_3$), 13.2(*C*H$_3$), 13.9 (*C*H$_3$), 18.3 (OCH$_2$*C*H$_3$), 67.0 (O*C*H$_2$CH$_3$), 81.5 (CH), 109.1(C_{pz}), 109.9 (C_{pz}). IR (KBr; ν, cm^{-1}): 1706s (CO_2), 1554m (C−N), 1462m (CO_2), 937m (Re═O). ESI-MS (*m*/*z* assignment, % intens): 569 [MK^+], 50; 553 [MNa^+], 100; 531 [MH^+], 20.

(h) Re(O)(bdmpzs)(OMe)Cl (9). To a pale green solution of $[NBu_4][Re(O)Cl_4]$ in methanol (50 mg, 0.068 mmol), Li (bdmpzs) (22 mg, 0.068 mmol) dissolved in methanol was added at room temperature. The solution immediately darkened and was stirred 2 h at room temperature. A blue precipitated formed, which was filtrated, washed with diethyl ether, and dried under vacuum. The compound, identified as **9** (yield, 42%), is almost insoluble in all the common organic solvents except for acetonitrile. Anal. Calcd for $C_{12}H_{18}ClN_4ReO_5S$: C, 26.1; H, 3.3; N, 10.2. Found: C, 26.2; H, 3.4; N, 10.3. ^{1}H NMR ($CDCl_3$; ppm): δ 2.70 (s, 3H, C*H*$_3$), 2.73 (s, 3H, C*H*$_3$), 2.89 (s, 3H, C*H*$_3$), 3.11 (s, 3H,C*H*$_3$), 5.50 (s, 3H, OC*H*$_3$), 6.38 (s, 1H, H^4), 6.44 (s, 1H, H$^{4'}$), 6.58 (s, 1H, C*H*). IR (KBr, cm^{-1}): 1560m (C−N), 1227s (SO_3), 1181s (SO_3), 978m (Re═O). ESI-MS (*m*/*z* assignment, % intens): 575 [MNa^+], 87; 552 [M^+], 100; 539 [$M^+ - Cl$], 80.

(i) Re(O)(bdmpzs)(OEt)Cl (10). $[NBu_4][Re(O)Cl_4]$ (50 mg, 0.068 mmol) was dissolved in ethanol, and Li(bdmpzs) (22 mg, 0.068 mmol) was added at room temperature. The pale green solution immediately became dark green. After 2 h of stirring at room temperature, a light blue solid was recovered by filtration and, after washing with diethyl ether and drying, was identified as **10** (yield, 52%). Compound **10** is soluble in acetonitrile and almost insoluble in other common organic solvents. Anal. Calcd for $C_{13}H_{20}ClN_4ReO_5S$: C, 27.5; H, 3.5; N, 9.8; S, 5.6. Found: C, 27.8; H, 3.3; N, 9.6; S, 5.3. ^{1}H NMR ($CDCl_3$; ppm): δ 1.08 (t, 3H, OCH$_2$C*H*$_3$), 2.70 (s, 3H, C*H*$_3$), 2.73 (s, 3H, C*H*$_3$), 2.92 (s, 3H, C*H*$_3$), 3.01 (s, 3H,C*H*$_3$), 5.90 (m, 1H, OC*H*$_2$CH$_3$), 6.16 (m, 1H, OC*H*$_2$CH$_3$), 6.37 (s, 1H, H^4), 6.44 (s, 1H, H$^{4'}$), 6.57 (s, 1H, C*H*). IR (KBr,cm^{-1}): 1559m (C−N), 1226s (SO_3), 1181s (SO_3), 977m (Re═O).

(j) Re(O)(bdmpza)(glycol) (11). (1) Method A. To a yellow solution of $[NBu_4][Re(O)Cl_4]$ in dichloromethane (35 mg, 0.06 mmol), an excess both of ethylene glycol (H_2glycol; 10 μL, 0.18 mmol) and of triethylamine (20 μL, 0.15 mmol) was added at room temperature. Almost immediately the reaction mixture turned to violet, and, after 5 min, Li(bdmpza) (20 mg, 0.079 mg) was added. The solution became blue in a short while and was stirred at room temperature overnight. The solvent was removed under vacuum, and the sticky blue residue was washed with diethyl ether and with a small amount of water in order to eliminate the excess of ethylene glycol and triethylamine. The bright blue product was further purified by dissolution in chloroform and precipitation by addition of diethyl ether. Yield, 90%. Anal. Calcd for $C_{14}H_{19}N_4ReO_5$: C, 33.0; H, 3.8; N, 11.0. Found: C, 33.4; H, 4.0; N, 10.8. ^{1}H NMR ($CDCl_3$; ppm): δ 2.64 (s, 6H, C*H*$_3$), 2.82 (s, 6H, C*H*$_3$), 4.78−4.86 (m, 2H, OC*H*$_2$), 4.89−4.95 (m, 2H, OC*H*$_2$), 6.27 (s, 2H, H^4), 6.33 (s, 1H, C*H*). ^{13}C{^{1}H} NMR ($CDCl_3$; ppm): 10.9 (*C*H$_3$), 14.4 (*C*H$_3$), 28.9 (O*C*H$_2$), 85.2 (CH), 108.7 (C_{pz}), 158.0 (C_{pz}). IR (KBr, cm^{-1}): 1668vs (CO_2), 1550m (C−N), 976s (Re═O). ESI-MS (*m*/*z* assignment, % intens): 1060 [M_2K^+], 10; 1043 [M_2Na^+], 30; 549 [MK^+], 50; 533 [MNa^+], 55; 511 [MH^+], 100; 483 [$MH^+ - CO$], 15.

(2) Method B. A mixture of **5**−**8** was dissolved in dichloromethane, and an excess both of ethylene glycol and triethylamine was added at room temperature. The solution was stirred overnight, and its color changed from blue to bright deep blue. The solvent was removed under vacuum, and the residue, washed with diethyl ether and water, was identified as **11**. The yield was almost quantitative. Crystals suitable for X-ray analysis were obtained from slow evaporation of a dichloromethane solution of the crude product.

(k) Re(O)(bdmpzs)(glycol) (12). (1) Method A. To a green methanolic solution of $[NBu_4][Re(O)Cl_4]$ (50 mg, 0.068 mmol), ethylene glycol (20 μL, 0.36 mmol) and of triethylamine (50 μL, 0.38 mmol) were added at room temperature. The reaction mixture in a few minutes turned dark violet, and Li(bdmpzs) (27 mg, 0.094 mmol) was added. The solution was stirred overnight at room temperature; after then the volume was reduced under a dinitrogen stream, and the formed precipitated was filtered and washed with ethanol, diethyl ether, and water. The bright blue product was identified as **12**. Yield, 83%.

(2) Method B. To a light blue suspension of **9** in methanol, an excess of ethylene glycol and triethylamine were added at room temperature, and the reaction mixture was stirred for 2 h at room temperature, and then the same workup procedure of method A was followed. Yield, 78%.

Anal. Calcd for $C_{13}H_{19}N_4ReO_6S$: C, 28.5; H, 3.5; N, 10.2; S, 5.9. Found: C, 28.7; H, 3.6; N, 10.4; S, 5.5. ^{1}H NMR ($CDCl_3$; ppm): δ 2.68 (s, 6H, C*H*$_3$), 2.86 (s, 6H, C*H*$_3$), 4.81−4.85 (m, 2H, OC*H*$_2$), 4.91−4.94 (m, 2H, OC*H*$_2$), 6.39 (s, 2H, H^4), 6.58 (s, 1H, C*H*). IR (KBr, cm^{-1}): 1557m (C−N), 1225s (SO_3), 1186s (SO_3), 981m (Re═O). ESI-MS (*m*/*z* assignment, % intens): 547 [MH^+], 100; 503 [$M^+ - CH_2CH_2$], 15.

X-ray Crystallographic Analysis. Suitable crystals of the complexes **1**, **3**, and **11** were mounted on the top of a glass fiber, coated with epoxy resin, and immediately transferred to a STADI4 CCD diffractometer. Data were collected at room temperature, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å), and corrected for Lorentz and polarization effects as well as for absorption.

All the structures were solved by means of the heavy-atom method, using the SHELXTL-NT package,[25] and were refined by

Table 1. Summary of X-ray Crystallographic Data

	1	**11**
formula	$C_7H_8Cl_3N_4ORe$	$C_{14}H_{19}N_4O_5Re$
molecular mass	456.72	509.53
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	6.897(1)	7.274(2)
b, Å	7.479(1)	8.618(2)
c, Å	12.358(3)	12.822(3)
α, deg	103.67(3)	89.91(3)
β, deg	98.45(3)	80.86(3)
γ, deg	102.00(3)	84.40(3)
V, Å^3	592.8(2)	789.7(3)
Z	2	2
abs coeff (μ), cm^{-1}	10.91	7.73
ρ_{calcd}, g cm^{-3}	2.559	2.142
obsd unique reflcns[a]	2366	3142
R1[a,b]	0.0617	0.0406
wR2[a,c]	0.1516	0.0997
S[a,d]	1.046	1.143

[a] Observation criterion: $I \geq 2\sigma(I)$. [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [d] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$: $n =$ no. of reflections; $p =$ no. of parameters.

Table 2. Selected Bond Distances (Å) and Angles (deg) of Complexes **1**, **3**, and **11**

	1	**3**	**11**
Re−Cl(1)	2.362(3)	2.334(3); 2.351(3)	
Re−Cl(2)	2.359(3)	2.343(3); 2.336(3)	
Re−Cl(3)	2.445(2)		
Re−O(1)	1.659(8)	1.684(9); 1.667(9)	1.673(5)
Re−O(2)		2.094(8); 2.081(8)	2.168(5)
Re−N(1)	2.108(8)	2.102(9); 2.085(9)	2.140(6)
Re−N(3)	2.094(9)	2.098(9); 2.08(1)	2.128(6)
Re−O(4)			1.943(5)
Re−O(5)			1.933(5)
Cl(1)−Re−Cl(2)	90.2(1)	89.5(1); 89.0(1)	
Cl(3)−Re−O(1)	175.3(3)		
O(1)−Re−O(2)		166.5(4); 167.1(4)	163.6(2)
N(1)−Re−N(3)	87.7(3)	86.9(4); 87.8(4)	87.6(2)
Cl(1)−Re−N(3)	169.1(2)	167.1(3); 168.5(3)	
Cl(2)−Re−N(1)	171.7(2)	165.6(3); 165.7(3)	
O(1)−Re−N(1)	91.9(4)	93.3(5); 93.3(4)	90.2(3)
O(1)−Re−N(3)	94.0(4)	90.3(4); 90.6(4)	90.8(3)
N(1)−Re−O(4)			161.9(2)
N(3)−Re−O(5)			162.3(2)
O(4)−Re−O(5)			83.1(2)

full matrix least-squares methods on F^2 with the SHELXL-98.[26] All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in calculated positions and refined as riding model.

The crystal data and refinement parameters are summarized in Table 1; none of the structures revealed any anomalous feature. Selected interatomic distances and angles are shown in Table 2.

Results and Discussion

Syntheses. The ligands have been synthesized according to literature methods,[13,16a,b,f] except for Li(bdmpzsa) whose workup procedure was slightly modified. In particular, recrystallization of the raw material from diethyl ether allowed us to recover an anhydrous, though very hygroscopic, product, different from the reported procedure, which gave a hydrated species,[27] impossible to be used with $[NBu_4][Re(O)Cl_4]$.

Scheme 1 summarizes the results obtained by reacting the rhenium precursor $[NBu_4][Re(O)Cl_4]$ with the nonsubstituted pyrazolyl derivatives, bpzm and Hbpza.

Despite the different hapticity (bidentate bpzm vs tridentate bpza) their reactivity was very similar and strongly dependent on the reaction solvent. In acetonitrile solutions blue compounds $Re(O)(bpzm)Cl_3$ (**1**) and $Re(O)(bpza)Cl_2$ (**3**) were formed by substitution of one or two chlorides, respectively. Raw **1** was contaminated by an additional species and then identified as the μ-oxo dimer $\{Re(O)(bpzm)Cl_2\}_2O$ on the basis of spectroscopic analysis (vide infra). Several μ-oxo-bridged rhenium species have been previously reported, mainly as side products formed adventitiously, probably by hydrolysis of monooxo− or dioxo−Re(V) complexes.[28] Anyway, pure **1** could be collected by recrystallization from acetone. In the reactions with tridentate Hbpza identical reactivity was observed by addition of a base such as triethylamine (Et_3N) or potassium *tert*-butoxide.

Reactions of labile $[NBu_4][Re(O)Cl_4]$ with bpzm and Hbpza in methanol did not produce the chlorinated species **1** and **3**, but $Re(O)(bpzm)(OMe)Cl_2$ (**2**) and $Re(O)(bpza-OMe)(OMe)Cl_2$ (**4**) were isolated, respectively. The latter displayed a bright violet color characteristic of a linear MeO−Re═O moiety.[29] The ligand esterification process did not occur when free Hbpza was dissolved in methanol, indicating that the presence of rhenium in the alcoholic solvent induced both bpza esterification and, at the same time, favored methoxide trans-coordination in **4**. As depicted in Scheme 2, such a process is reversible and can be monitored by proton NMR spectroscopy (vide infra).

The exact mechanism of such a process has not been clarified yet. However, analogous ligand esterification was observed in the reaction of $[NBu_4][Re(O)Cl_4]$ in methanol with the new scorpionate $CH_2(Pz^{COOH,Me})(Pz^{Me,COOH})$,[30] supporting the view of involvement of the metal in the reaction mechanism.

The chemistry of 3,5-dimethylpyrazolyl derivatives Li(bdmpza) and Li(bdmpzs) toward $[NBu_4][Re(O)Cl_4]$ is summarized in Scheme 3.

Both ligands had quite a similar behavior notwithstanding the different carboxylate or sulfonate "tail". As it comes out from Scheme 3, the solvent played once more a crucial role determining the formation of mixed species such as Re(O)-(bdmpza)(OMe)Cl (**7**), Re(O)(bdmpza)(OEt)Cl (**8**), Re(O)-(bdmpzs)(OMe)Cl (**9**), and Re(O)(bdmpzs)(OEt)Cl (**10**) in alcohols. In these cases, the reactions were straightforward by mixing equimolar amounts of the reagents at room temperature and giving good yields especially with Li(bdmpza).

The reactivity in aprotic solvents was considerably different. In particular, in acetonitrile Li(bdmpza) gave the symmetric $Re(O)(bdmpza)Cl_2$ complex **5**, analogous to **3**, and a trace amount of dissymmetric **6**, whereas from reactions conducted in chloroform symmetric **5** and dissymmetric

(25) *SHELXTL/NT*, Version 5.10; Bruker AXS Inc.: Madison, WI, 1999. Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473.
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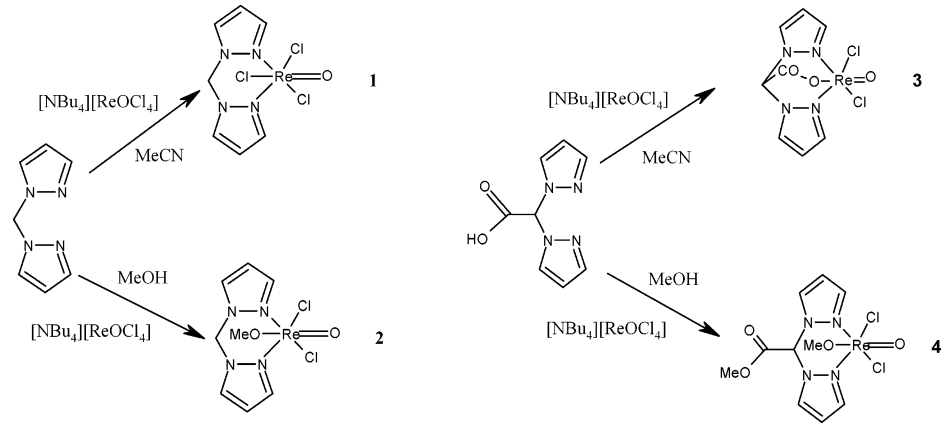
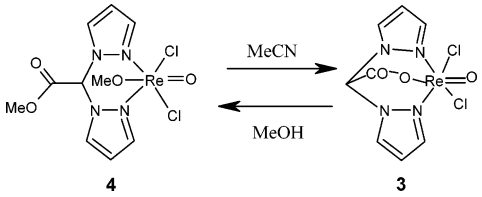
(27) Ortiz, M.; Dìaz, A.; Cao, R.; Otero, A.; Fernandez-Baeza, J. *Inorg. Chim. Acta* **2004**, *357*, 19−24.
(28) Paulo, A.; Domingos, A.; Santos, I. *Inorg. Chem.* **1996**, *35*, 1798−1807.
(29) Tisato, F.; Refosco, F.; Bolzati, C.; Cagnolini, A.; Gatto, S.; Bandoli, G. *J. Chem. Soc., Dalton Trans.* **1997**, 1421−1427.
(30) (a) Santini, C. Unpublished results. (b) Santini, C. *Inorg. Chem. Commun.* **2004**, *7*, 834−837.

Scheme 1



Scheme 2



6 were formed in comparable amounts and separated by means of silica gel chromatography (Figure 1). A similar dissymmetric isomer has been recently reported by Otero et al. in a series of niobium complexes containing the κ^3-*N*,*N*,*O*-2,2-bis(3,5-dimethylpyrazol-1-yl)ethoxide ligand.[19b]

Negligible amounts of **5** and **6** were detected also in the reactions carried out in alcohols. Traces of water in acetonitrile or alcohols induced the formation of a further species formulated as Re(O)(bdmpza)(OH)Cl [31] on the basis of NMR and ESI analyses.

As reported above, reactions of Li(bdmpzs) in methanol and ethanol yielded **9** and **10** as main products, respectively, along with low amounts of the symmetric Re(O)(bdmpzs)-Cl_2,[32] analogous to **5.** Conversely, reactions in chloroform and acetonitrile gave rise to mixtures of insoluble products difficult to separate and characterize.

All the intermediate species containing a heteroscorpionate bearing 3,5-dimethylpyrazolyl rings underwent substitution of monodentate groups (Cl, OMe, OEt, OH) with bidentate H_2glycol in the presence of triethylamine, giving rise to mixed complexes Re(O)(bdmpza)(glycol) (**11**) and Re(O)(bdmpzs)(glycol) (**12**) (Scheme 4). On the contrary, compounds **1**−**4** containing heteroscorpionates bearing nonsubstituted pyrazolyl rings showed no reactivity toward glycolate.

It's worth noting that the reactivity was not affected by the different tails of the scorpionate ligand, i.e., CO_2^- vs SO_3^-. Moreover, mixed ligand compounds could be prepared using a one-pot procedure starting from $[NBu_4]$-$[Re(O)Cl_4]$ in the presence of the relevant scorpionate and ethylene glycol in basic media. This behavior indicated that the combination of a mixed coordination sphere comprising a heteroscorpionate and a glycolate is strongly preferred compared to potentially accessible bis-glycolate complexes.

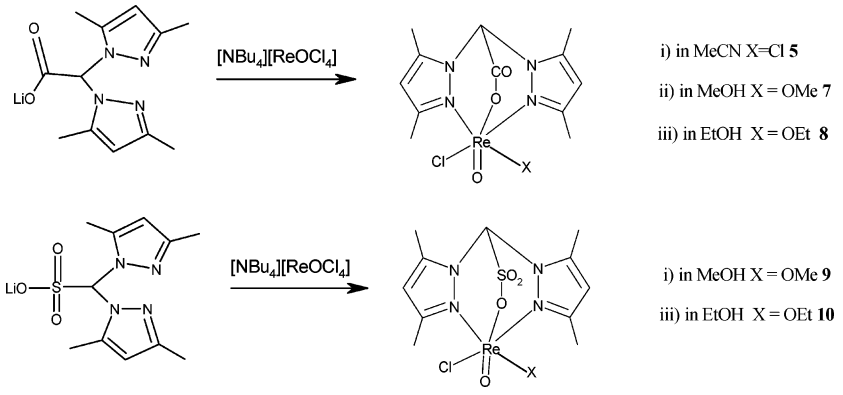
The aim of using more hydrophilic carboxylate and sulfonate containing scorpionates instead of poly(pyrazolyl)borates was, in principle, to make this oxo−rhenium chemistry accessible in hydro alcoholic media for a potential application with ^{188}Re. The different reactivity exhibited by scorpionates bearing substituted versus nonsubstituted pyrazolyl rings illustrated that steric and electronic effects produced by the ligands set onto the oxo core had to be considered in addition to solubility properties. As previously observed with other metals,[11] scorpionates bearing 3,5-methylpyrazolyl rings are better donors than those incorporating unsubstituted pyrazole. In our case, the increasing donor ability of the 3,5-dimethylpyrazolyl nitrogens provided the right electronic balance to enhance the overall stability of the facially arranged $[Re(O)(NNO)]^{2+}$ moiety and, at the same time, labilized equatorially positioned chloride or alcoholate groups, which were readily replaced by bidentate glycolate. Such facial moiety was much less stabilized in the case of less donating nonsubstituted bpza nitrogens, and formation of the linear RO−Re═O moiety became predominant in alcohols. In this case, equatorially coordinated halides were not labilized and formation of the mixed scorpionate/glycolate compound was unfavored.

The nature of the scorpionate tail had a negligible effect on the reactivity and on the stereochemistry of the substitution processes analyzed in this study. However, as a general behavior, carboxylate containing scorpionates gave "cleaner" reactions and more soluble products and recrystallization procedures provided better crystals for X-ray investigation.

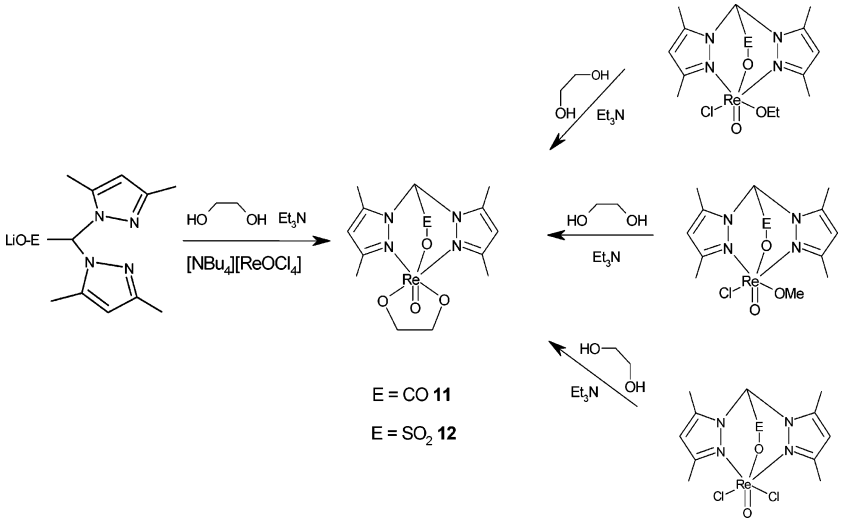
Mixed oxo−Re(V) scorpionate/glycolate compounds synthesized in this work resembled analogous rhenium complexes containing facially arranged poly(pyrazolyl)borate and diolate ligands (vide infra Table 3).[33] In addition, $[Re^{I}(CO)_3]^+$ and $[Re^{VII}O_3]^+$ species containing facially arranged bpza and bdmpza ligands have been recently reported by other authors.[16f,34]

Characterization. Elemental analyses, as shown in the Experimental Section, were in good agreement with the proposed formulation. All the compounds were bright blue or blue-green colored materials (except violet **2** and **4**), stable in solid and in solution. Their solubility was not easily predictable from the nature of the scorpionate employed. In

Scheme 3

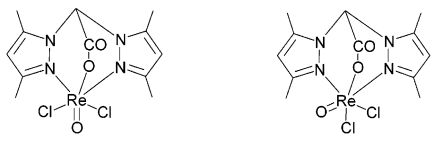


Scheme 4



particular the presence of a sulfonate group in the ligand was expected to confer a better solubility in alcohols and water. On the contrary bdmpzs complexes **9** and **10** were fairly soluble only in acetonitrile, but sparingly soluble or insoluble in chlorinated solvents, alcohols and water, whereas both bdmpza and dmpza containing derivatives were quite soluble in chlorinated solvents and acetonitrile and slightly soluble in alcohols.

The infrared spectra of bpza and bdmpza derivatives exhibited absorptions in the ranges 1668−1772 and 1461−1464 cm^{-1}, which could be ascribed to ν_{as} and ν_{sym} of the carboxylate group, respectively. The highest value of the asymmetric stretch (1772 cm^{-1}) occurred in complex **4**, confirming the noncoordination of the tail of the ligand, while the value of the corresponding tris-coordinated carboxylate ligand in **3** was bathochromically shifted at 1722 cm^{-1}. Bands ascribed to the sulfonate stretching modes were present in the KBr spectra of compounds **9**, **10**, and **12** in the ranges 1227−1224 and 1181−1186 cm^{-1}. The observed bathochromic shift of ca. 25 cm^{-1} compared to the values observed in uncoordinated Libdmpzs indicate coordination through the sulfonate group, as previously reported by Ortiz et al.[27]



(*OC*-6-44) **Re(O)(bdmpza)Cl$_2$** (*OC*-6-42) **Re(O)(bdmpza)Cl$_2$**

Figure 1. Two isomeric forms of Re(O)(bdmpza)Cl_2, **5** and **6**.

The ν(Re═O) stretching vibrations fell at 935−997 cm^{-1}, a range usually observed for six-coordinated monooxo Re(V) compounds, but in most cases they were not very strong. An additional oxo rhenium vibration at 620 cm^{-1} corresponding to a μ-oxo stretching mode was present in complex **1** (raw material), indicating the contamination of monomeric **1** with the μ-oxo dimer [{Re(O)(bpzm)Cl_2}$_2$O] (see also ESI mass data).

^{1}H NMR spectroscopy was the technique of choice for characterizing these rhenium species in the solution state. For instance, the number of singlets arising from the 3,5-methyl substituents of the pyrazolyl rings was used to distinguish between symmetric and dissymmetric derivatives. In detail, coordination spheres comprising two chloride atoms or the symmetric glycolate in the equatorial plane yielded simplified patterns (two singlets for 3,3′ and 5,5′ methyl groups in **5**, **11**, and **12**) because of the magnetic equivalence of the pyrazolyl rings. Coordination of different monodentate ligands on the equatorial plane (Cl/OMe, Cl/OEt, and Cl/OH couples) removed such magnetic equivalence, and more complicated patterns were observed (four singlets for 3,3′,5,5′ methyl groups in **6**−**10**). In this way isomeric

Table 3. Selected Structural Data of Octahedral Rhenium Complexes Containing scorpionate or poly(pyrazolyl)Borate Ligands

compound	Re=O (Å)	Re−O/N[a] (Å)	Re−N_{pz} (Å) in the equatorial plane	Re−X (Å) in the equatorial plane	ref
Re(O)(bpza)Cl_2	1.684(9)	2.094(8)	2.102(9)/2.085(9)	Re−Cl: 2.334(3)/2.351(3)	this work
	1.667(9)	2.081(8)	2.098(9)/2.08(1)	Re−Cl: 2.343(2)/2.336(3)	
Re(O)(bdmpza)(glycol)	1.673(5)	2.168(5)	2.140(6)	Re−O: 1.943(5)	this work
			2.128(6)	Re−O: 1.933(5)	
Re(O)($HBpz_3$)(SPh)Cl	1.689(5)	2.256(6)	2.123(6)	Re−Cl: 2.339(2)	38
			2.104(5)	Re−S: 2.301(2)	
Re(O)($HBpz_3$)$(SPh)_2$	1.661(5)	2.237(7)	2.161(8)/2.152(7)	Re−S: 2.312(2)/2.309(2)	38
	1.674(5)	2.267(6)	2.129(8)/2.1489(7)	Re−S: 2.310(2)/2.309(2)	
Re(O)($HBpz_3$)(edt)[b]	1.694(9)	2.31(1)	2.17(1)	Re−S: 2.280(4)	39
			2.14(1)	Re−S: 2.299(4)	
Re(O)($HBpz_3$)(C_2O_4)	1.654(7)	2.258(7)	2.066(7)	Re−O: 2.007(6)	40
			2.062(7)	Re−O: 2.000(6)	
Re(O)(Tp^{Me2})(edt)[c]	1.668(5)	2.275(5)	2.189(5)	Re−S: 2.276(2)	41
			2.193(5)	Re−S: 2.286(2)	
Re(O)(Bpz_4)$(SPh)_2$	1.693(7)	2.243(7)	2.130(8)	Re−S: 2.316(4)	42
			2.155(8)	Re−S: 2.311(4)	
Re(O)(Bpz_4)(glycol)	1.68(1)	2.29(2)	2.08(2)/2.11(2)	Re−O: 1.93(1)/1.91(1)	43
	1.71(1)	2.23(2)	2.10(2)/2.10(2)	Re−O: 1.91(1)/1.95(1)	
Re(O)(Bpz_4)$(OPh)_2$	1.682(5)	2.238(6)	2.115(6)	Re−O: 1.963(5)	42
			2.101(6)	Re−O: 1.946(5)	
Re(bpza)$(CO)_3$		2.184(5)	2.216(6)	Re−C: 1.952(9)	16f
			2.211(6)	Re−C: 1.947(8)	
Re(bdmpza)$(CO)_3$		2.164(8)	2.21(1)	Re−C: 1.96(1)	16f
			2.20(1)	Re−C: 1.97(1)	
Re(bpa^{4menth})$(CO)_3$[d]		2.164(5)	2.160(5)	Re−C: 1.910(7)	44
			2.190(5)	Re−C: 1.922(7)	
Re$(O)_3$(bdmpza)		2.12(1)	2.32(1)	Re−O: 1.72(1)	34
			2.28(1)	Re−O: 1.721(9)	

[a] Distance between rhenium and the third donor atom of the chelating ligand: oxygen for heteroscorpionates and nitrogen for poly(pyrazolyl)borates. [b] edt = ethaneditiolate. [c] Tp^{Me2} = tris(3,5-dimethylpyrazolyl)hydridoborate. [d] $Hbpa^{4menth}$ = bis(menthylpyrazo-1-yl)acetate.

symmetric and dissymmetric complexes **5** and **6**, showing identical elemental analysis and ESI mass spectra, were identified on the basis of different chromatographic properties and of nonequivalent proton NMR profiles of the methyl substituents. Also Re(O)(bdmpza)(OH)Cl [31] and Re(O)-(bdmpzs)Cl_2 [32] were identified in solution by ^{1}H NMR analysis of the reaction mixtures. Comparison of the ^{1}H NMR spectra of analogous bdmpza or bdmpzs containing compounds (i.e. **7** vs **9**, **8** vs **10**, and **11** vs **12**) showed evidence of a small downfield shift of the pyrazolyl signals of the sulfonate derivatives. This behavior indicated that in this series of rhenium carboxylate interactions were stronger than rhenium sulfonate ones.

In the ^{1}H spectrum of **1** the bridging methylene signals of equatorially coordinated bpzm occurred as a doublet of doublets (AB system) centered at 7.18 and 7.42 ppm, respectively. As sketched in Figure 2, the diastereotopic character of the vicinal protons was likely determined by an intramolecular interaction with the chloride atom trans to the oxo−rhenium core.

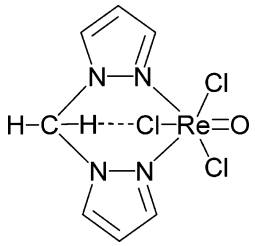


Figure 2. Intramolecular contact in complex **1**.

Such interaction was absent in complex **2**, where a methoxide group (singlet at 2.50 ppm) replaced the chloride atom positioning trans to the Re−oxo moiety, in accordance with the physical features of the compound (violet color) and with the magnetic equivalence of the two pyrazolyl rings protons.

The reversible, solvent-mediated interconversion of **3** and **4** (see Scheme 2) could be conveniently monitored by proton NMR spectroscopy. Acetonitrile or acetone solutions of **4** exhibited two distinct singlets at 2.50 and 3.50 ppm, which were assigned to the methoxide methyl protons coordinated trans to the oxo group and to the uncoordinated methyl ester, respectively. With time, free methanol was released (new singlet at 3.30 ppm) and the other methyl-related signals disappeared, giving a profile corresponding to **3**. On the other hand, the interconversion of pure **3** into **4** is almost instantaneous in methanol solutions.

ESI mass spectrometry in the positive ion mode gave additional data which supported the products formulation and was fundamental for the identification of complexes **4** and **6**. All of the investigated compounds formed cationized $[M + Na]^+$ and $[M + K]^+$ molecular ions. $[M_2 + Na]^+$ dimers were detectable in the spectra of intermediate compounds

(31) [Re(O)(bdmpza)(OH)Cl]: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 2.67 (s, 3H, CH_3), 2.72 (s, 3H, CH_3), 2.92 (s, 3H, CH_3), 2.98 (s, 3H, CH_3), 6.27 (s, 2H, H^4), 6.33(s, 1H, C*H*). ^{13}C{^{1}H}NMR (300 MHz, $CDCl_3$): δ 10.7 (*C*H_3), 10.9 (*C*H_3), 13.8 (*C*H_3), 14.4 (*C*H_3), 73.9 (*C*H), 109.2-(C_{pz}), 109.7 (C_{pz}). The signal due to coordinated OH was not detected. The formulation was based on the strict similarity of NMR proton and carbon profiles with those arising from the methoxide and ethoxide analogues **7** and **8**, respectively. In addition, ESI^+ mass spectra of crude **7** and **8** contain a peak at *m*/*z* 503 corresponding to the protonated [Re(O)(bdmpza)(OH)Cl] species, along with fragment ions at *m*/*z* 485 (loss of water) and 459 (loss of CO_2).

(32) [Re(O)(bdmpzs)Cl_2]: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 2.78 (s, 6H, CH_3), 3.11(s, 6H, CH_3), 6.50 (s, 2H, H^4), 6.74 (s, 1H, C*H*).

(33) Paulo, A.; Correia, J. D. G.; Campello, M. P. C.; Santos, I. *Polyhedron* **2004**, *23*, 331−360.

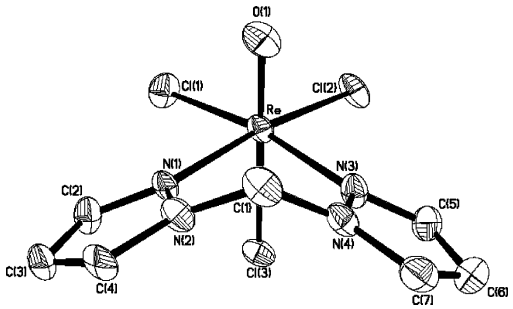


Figure 3. ORTEP view of Re(O)(bpzm)Cl_3 (**1**) with 40% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

1−**4**, being the most abundant species for **2** and **4**, but they were not detectable for compounds **5**−**8**, evidencing again a different behavior associated with the presence of 3,5-methylated or nonsubstituted pyrazolyl rings. In the spectrum of raw **1** an additional ion at *m*/*z* 881 (50%), due to the cationized μ-oxo-bridged dimer $[\{Re(O)(bpzm)Cl_2\}_2O + Na]^+$, was detected. The formulation of the methyl-esterificated complex **4** was confirmed by the presence of abundant $[M + Na]^+$ and $[M_2 + Na]^+$ molecular ions at *m*/*z* 533 and 1043 and less abundant $[M + K]^+$ and $[M_2 + K]^+$ ions at *m*/*z* 549 and 1058. Glycolate containing mixed compounds **11** and **12** showed the most abundant peaks associated with $[M + H]^+$ ions at *m*/*z* 511 and 547, respectively.

MS^n collision experiments provided further information on the activation of low critical energy decomposition channels. The main fragmentation pattern for carboxylate containing scorpionates (compounds **3** and **5**−**8**) corresponded to the loss of CO_2 followed by release of Cl (or NaCl) and OR groups. No evidence of CO_2 loss but elimination of the OMe group was instead observed in the collisional-induced fragmentation pathway of complex **4**. Sulfonate containing derivatives **9** and **12** did not show loss of SO_3. Generally, no fragmentation of the pyrazolyl rings or loss of methyl substituents was detected, as the rings were released in toto. The decomposition pathway of glycolate mixed compounds **11** and **12** gave primarily the loss of the *m*/*z* 28 fragment, producing the ions at *m*/*z* 483 and 519, respectively. This decomposition corresponded to the loss of ethylene from the glycolate backbone, favoring the formation of the known oxidized $Re(O)_3$(bdmpza) and $Re(O)_3$(bpza) species.[34]

X-ray Crystallography. The ORTEP[35] drawings of complexes **1**, **3**, and **11** are depicted in Figures 3−5, respectively. In **3** the asymmetric unit comprised two molecules of the complex. In all cases, the environment around the metal center was distorted octahedral. The deviation from a regular octahedron was measured by looking at the dihedral angle formed by the face O(1), Cl(1), Cl(2) (in **1** and **3**) or by the face O(1), O(4), O(5) (in **11**) with the triangle opposed to it. The dihedrals were 11.1°, 8.7° (9.6°), and 6.4° in **1**, **3**, and **11**, respectively.

As expected in the structures showing the Re^V═O moiety, the metal core was displaced toward the apical oxygen O(1) by 0.18, 0.26 (0.25), and 0.31 Å in **1**, **3**, and **11**, respectively. In the chelating bis-pyrazolyl ligand, the mean planes of the two five-membered rings defined a dihedral angle of 49.6° and 49.6° (51.7°) in **1** and **3**, respectively. In **11**, the replacement of the two equatorial chloride ions with a bidentate ligand widened the angle until 58.4°.

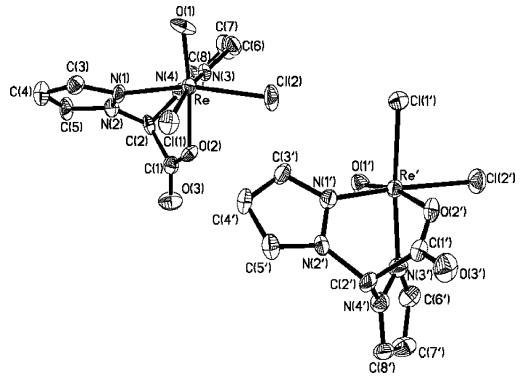


Figure 4. ORTEP view of Re(O)(bpza)Cl_2 (**3**) with 40% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

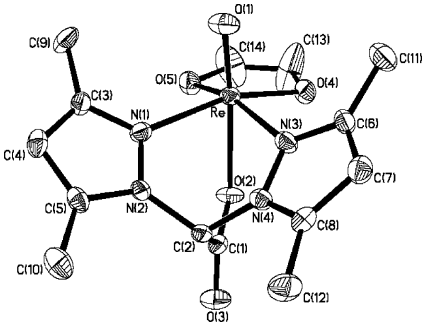


Figure 5. ORTEP view of Re(O)(bdmpza)(glycol) (**11**) with 40% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

Besides, the mean plane of the bidentate ligand in **11** defined itself a dihedral angle of 39.0° with both the five-membered rings. Upon coordination, the bis-pyrazolyl synthon also formed another ring, made by the four nitrogen atoms, the rhenium atom, and the carbon atom joining the two penta-atomic rings. This six-membered ring showed a *boat* arrangement, with the rhenium and the carbon atoms off the plane defined by the four nitrogen atoms. In **1**, **3**, and **11**, respectively, the rhenium atom deviated by 0.56, 0.68 (0.64), and 0.58 Å, whereas the carbon atom was off by 0.63, 0.65 (0.70), and 0.70 Å.

Table 2 shows that the Re−Cl(3) bond distance trans to the oxo group in **1** (2.445(2) Å) was lengthened by ca. 0.10 Å compared with cis positioned Re−Cl distances in **1** and **3**, a feature frequently observed in neutral six-coordinated oxo−Re(V) complexes and ascribed to the trans labilizing influence of the oxo group.[36]

Complex **11** showed $Re-O_{glycol}$ distances of 1.943(5) and 1.933(5) Å, which were in close agreement with the average value of 1.933 Å found in the Cambridge Crystallographic

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Database (CCD)[37] for covalent Re−O bonds in octahedral oxo−Re(V) complexes. However, the metal scorpionate bond distances were 0.03−0.07 Å longer than the corresponding distances in **3**. This lengthening could arise from the steric influence of the methyl substituents of the pyrazolyl rings and/or from the increased donor ability of glycolate compared to halides.

None of the three complexes showed intermolecular interactions which deserved any comment.

For comparison purposes, Table 3 collects structural data of monooxo Re(V) complexes containing poly(pyrazolyl)-borate and the scorpionate compounds described in this study. All of these complexes have a distorted octahedral geometry comprising two pyrazolyl nitrogens and two monodentate or a bidentate ligand in the equatorial plane. The replacement of poly(pyrazolyl)borate for bpzm or bdmpza ligands does not significantly modify the structural features of the resulting compounds, as illustrated by the Re═O distance, which ranges between 1.654(7) and 1.694(9) Å in accordance with the occurrence of a multiple bond. In both cases the $Re-N_{pz}$ distances on the equatorial plane are mainly affected by the nature of the other ligand(s), rather than by the type of tridentate chelate, and are generally longer (up to 2.193-(5) Å in $Re(O)(Tp^{Me2})$(edt)) when thiolate ligands are employed. Interestingly, analogous compounds **11** and $Re(O)(Bpz_4)$(glycol) display almost identical multiple and single metal−oxygen distances, but the presence of 3,5-methyl-substituted pyrazols in **11** lengthens the $Re-N_{pz}$ distances by 0.03−0.06 Å compared to those exhibited in $Re(O)(Bpz_4)$(glycol). This behavior exactly parallels the difference already noticed above between complexes **11** and **3**, containing bulky and nonsubstituted scorpionates, respectively.

The second part of Table 3 summarizes selected structural data of additional octahedral rhenium complexes bearing carboxylate containing κ^3-N,N,O-heteroscorpionate reported so far in the literature. The three tricarbonyl Re(I) complexes show slightly longer $Re-N_{pz}$ bond lengths (trans labilizing influence of CO) compared to those exhibited by monooxo Re(V) species **3** and **11**. The high-valent trioxo Re(VII) complex $Re(O)_3$(bdmpza) shows the longest $Re-N_{pz}$ distances of the series, which are balanced by a relatively short metal carboxylate bond.

Conclusions

The monooxo Re(V) core is conveniently stabilized by tripodal scorpionate ligands comprising carboxylate or sulfonate tails, giving a series of intermediate complexes of the type Re(O)(NNO)Cl(X) (X = Cl, OR), whose structure depends on the type of NNO ligand and solvent utilized. The presence of 3,5-substituted pz in the NNO framework is crucial for further replacement of monodentate groups giving stable "3 + 2" mixed ligand complexes.

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Supporting Information Available: X-ray crystallographic data for **1**, **3**, and **11** and ^{1}H NMR spectra of selected rhenium complexes (**2**, **3**, and **7**) (CIF, PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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