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Article

New Complexes of Zirconium(IV) and Hafnium(IV) with Heteroscorpionate Ligands and the Hydrolysis of Such Complexes To Give a Zirconium Cluster[#]

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A series of zirconium and hafnium heteroscorpionate complexes have been prepared by the reaction of MCl_4 (M = Zr, Hf) with the compounds [{Li(bdmpza)(H_2O)}$_4$] [bdmpza = bis(3,5-dimethylpyrazol-1-yl)acetate], [{Li(bdmpzdta)(H_2O)}$_4$] [bdmpzdta = bis(3,5-dimethylpyrazol-1-yl)dithioacetate], and (Hbdmpze) [bdmpze = 2,2-bis(3,5-dimethylpyrazol-1-yl)ethoxide] (the latter with the prior addition of Bu^{n}Li). Under the appropriate experimental conditions, mononuclear complexes, namely, [MCl_3(κ^3-bdmpzx)] [x = a, M = Zr (**1**), Hf (**2**); x = dta, M = Zr (**3**), Hf (**4**); x = e, M = Zr (**5**), Hf (**6**)], and dinuclear complexes, namely, [{MCl_2(μ-OH)(κ^3-bdmpzx)}$_2$] [x = a, M = Zr (**7**), Hf (**8**); x = dta, M = Zr (**9**); x = e, M = Zr (**10**)], were isolated. A family of alkoxide-containing complexes of the general formula [$ZrCl_2$(κ^3-bdmpzx)(OR)] [x = a, R = Me (**11**), Et (**12**), ^{i}Pr (**13**), ^{t}Bu (**14**); x = dta, R = Me (**15**), Et (**16**), ^{i}Pr (**17**), ^{t}Bu (**18**); x = e, R = Me (**19**), Et (**20**), ^{i}Pr (**21**), ^{t}Bu (**22**)] was also prepared. Complexes **11**–**14** underwent an interesting hydrolysis process to give the cluster complex [Zr_6(μ_3-OH)$_8$(OH)$_8$(κ^2-bdmpza)$_8$] (**23**). The structures of these complexes have been determined by spectroscopic methods, and the X-ray crystal structures of **7**, **8**, and **23** were also established.

Introduction

Since the initial development of tris(pyrazol-1-yl)borate or “scorpionate” ligands by Trofimenko in the late 1960s, a significant number of complexes using most metals of the periodic table has been prepared with these ligands.[1] As a result of our research in the field of niobium complexes with Tp or Tp* ligands [Tp = hydridotris(pyrazol-1-yl)borate, Tp* = hydridotris(3,5-dimethylpyrazol-1-yl)borate], some of us reported the preparation of several complexes of the type $TpNb(Cl)_2(RC{\equiv}CR')$ or $Tp^*Nb(O)(Cl)(OR)$.[2] We subsequently carried out research on the synthesis of new “heteroscopionate” ligands[3] with pyrazole rings. The target compounds are related to the tris(pyrazol-1-yl)methane system,[4] but one of the pyrazole groups has been replaced by a carboxylate, dithiocarboxylate, or ethoxide group, namely, bis(3,5-dimethylpyrazol-1-yl)acetate (bdmpza), bis(3,5-dimethylpyrazol-1-yl)dithioacetate (bdmpzdta), and 2,2-bis(3,5-dimethylpyrazol-1-yl)ethoxide (bdmpze). These ligands

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[#] Dedicated to Professor José Vicente on the occasion of his 60th birthday.

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were prepared in order to provide a small degree of steric hindrance and considerable coordinative flexibility. The compounds were found to be excellent reagents for the introduction of scorpionate ligands into niobium complexes, and a series of alkyne-containing niobium complexes were isolated and charaterized.[5] These complexes were found to have an interesting dynamic behavior in solution, and this was studied by variable-temperature NMR techniques. More recently, we reported the preparation of heteroscorpionate-containing titanium complexes that through an interesting nucleophilic THF ring-opening process give rise to alkoxide species. We also described a preliminary study of the ethylene polymerization activities for some of these complexes.[6] We are now interested in extending the scope of the chemistry to include the preparation of new heteroscorpionate complexes of the rest of the group 4 metals. We describe here the synthesis and characterization of three new classes of zirconium and hafnium complexes containing halide, hydroxide, and alkoxide ancillary ligands. These target complexes constitute the first examples of this class of compounds with a heteroscorpionate ligand. In addition, the complexes $[ZrCl_2(\kappa^3\text{-bdmpza})(OR)]$ (**11**−**14**) undergo an interesting hydrolysis process to give the cluster complex $[Zr_6(\mu_3\text{-OH})_8(OH)_8(\kappa^2\text{-bdmpza})_8]$ (**23**). Although a number of the oxo/hydroxo clusters of zirconium are known,[7] this complex constitutes the first example of such a compound with a scorpionate ligand.

Experimental Section

All of the reactions were performed using standard Schlenk-tube techniques under an atmosphere of dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before use. Microanalyses were carried out with a Perkin-Elmer 2400 CHN analyzer. Mass spectra were recorded on a VG Autospec instrument using the FAB technique and nitrobenzyl alcohol as the matrix. Infrared spectra were obtained in the region 4000−200 cm^{-1} using a Perkin-Elmer 883 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity FT-300 spectrometer and referenced to the residual deuterated solvent. The NOE difference spectra were recorded with the following acquisition parameters: spectrum width 5000 Hz, acquisition time 3.27 s, pulse width 90°, relaxation delay 4 s, irradiation power 5−10 dB, number of scans 120. Two-dimensional NMR spectra were acquired using standard VARIAN−FT software and processed using an IPC−Sun computer.

The complexes $ZrCl_4$ and $HfCl_4$ were purchased from Aldrich. The compounds $[\{Li\,(bdmpza)(H_2O)\}_4]$, $[\{Li(bdmpzdta)(H_2O)\}_4]$, and (Hbdmpze) were prepared as reported previously.[3a,5,6b]

Synthesis of $[ZrCl_3(\kappa^3\text{-bdmpza})]$ (1). To a THF (50 mL) solution of $ZrCl_4$ (0.50 g, 2.14 mmol) was added an equimolar quantity of $[\{Li(bdmpza)(H_2O)\}_4]$ (0.58 g, 0.53 mmol). The solution was stirred for 12 h at room temperature. The solvent was removed under vacuum, and the solid was extracted with CH_2Cl_2. A white solid was obtained after removal of the CH_2Cl_2. Yield: 92%. Anal. Calcd for $C_{12}H_{15}Cl_3N_4O_2Zr$: C, 32.4; H, 3.3; N, 12.6. Found: C, 32.5; H, 3.5; N, 12.8. ^{1}H NMR ($CDCl_3$, 293 K) δ: 6.61 (s, 1 H, CH), 6.11 (s, 2 H, H^4), 2.65 (s, 6 H, Me^3), 2.51 (s, 6 H, Me^5). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 67.1 (CH), 155.9, 143.0 (C$^{3\text{ or }5}$), 109.0 (C^4), 15.4 (Me^3), 11.3 (Me^5), 162.8 (CO_2^-). IR (Nujol mull, cm^{-1}): 1691 [$\nu_{asym}(CO_2^-)$], 1452 [$\nu_{sym}(CO_2^-)$], 418, 295 [ν(Zr−Cl)]. MS [FAB (m/z assignment, % intensity)]: 409 [M − Cl], 100.

Synthesis of $[HfCl_3(\kappa^3\text{-bdmpza})]$ (2). The synthetic procedure was the same as that for complex **1**, using $HfCl_4$ (0.50 g, 1.56 mmol) and $[\{Li(bdmpza)(H_2O)\}_4]$ (0.42 g, 0.39 mmol) to give **2** as a white solid. Yield: 93%. Anal. Calcd for $C_{12}H_{15}Cl_3Hf\,N_4O_2$: C, 27.0; H, 2.8; N, 10.5. Found: C, 27.2; H, 2.9; N, 10.6. ^{1}H NMR ($CDCl_3$, 293 K) δ: 6.62 (s, 1 H, CH), 6.14 (s, 2 H, H^4), 2.67 (s, 6 H, Me^3), 2.51 (s, 6 H, Me^5). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 68.7 (CH), 154.2, 141.3 (C$^{3\text{ or }5}$), 107.9 (C^4), 15.8 (Me^3), 11.3 (Me^5), 161.8 (CO_2^-). IR (Nujol mull, cm^{-1}): 1683 [$\nu_{asym}(CO_2^-)$], 1441 [$\nu_{sym}(CO_2^-)$], 402, 289 [ν(Hf−Cl)]. MS [FAB (m/z assignment, % intensity)]: 496 [M − Cl], 100.

Synthesis of $[ZrCl_3(\kappa^3\text{-bdmpzdta})]$ (3). To a THF (50 mL) solution of $ZrCl_4$ (0.50 g, 2.14 mmol) was added an equimolar quantity of $[\{Li(bdmpzdta)(H_2O)\}_4]$ (0.64 g, 0.53 mmol). The solution was stirred for 12 h at room temperature. The solvent was removed under vacuum, and the solid was extracted with CH_2Cl_2. A red solid was obtained after removal of the solvent. Yield: 87%. Anal. Calcd for $C_{12}H_{15}Cl_3N_4S_2Zr$: C, 30.2; H, 3.2; N, 11.7. Found: C, 30.3; H, 3.3; N, 11.9. ^{1}H NMR ($CDCl_3$, 293 K) δ: 7.52 (s, 1 H, CH), 6.17 (s, 2 H, H^4), 2.74 (s, 6 H, Me^3), 2.54 (s, 6 H, Me^5). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 77.5 (CH), 155.4, 143.8 (C$^{3\text{ or }5}$), 108.3 (C^4), 15.9 (Me^3), 11.2 (Me^5), 233.4 (CS_2^-). IR (Nujol mull, cm^{-1}): 1061 [$\nu_{asym}(CS_2^-)$], 811 [$\nu_{sym}(CS_2^-)$], 415, 293 [ν(Zr−Cl)]. MS [FAB (m/z assignment, % intensity)]: 441 [M − Cl], 100.

Synthesis of $[HfCl_3(\kappa^3\text{-bdmpzdta})]$ (4). The synthetic procedure was the same as that for complex **3**, using $HfCl_4$ (0.50 g, 1.56 mmol) and $[\{Li(bdmpzdta)(H_2O)\}_4]$ (0.47 g, 0.39 mmol) to give **4** as a red solid. Yield: 94%. Anal. Calcd for $C_{12}H_{15}Cl_3Hf\,N_4S_2$: C, 25.5; H, 2.6; N, 9.9. Found: C, 25.6; H, 2.8; N, 10.2. ^{1}H NMR ($CDCl_3$, 293 K) δ: 7.50 (s, 1 H, CH), 6.15 (s, 2 H, H^4), 2.73 (s, 6 H, Me^3), 2.52 (s, 6 H, Me^5). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 78.5 (CH), 155.5, 143.6 (C$^{3\text{ or }5}$), 108.4 (C^4), 15.8 (Me^3), 11.3 (Me^5), 232.9 (CS_2^-). IR (Nujol mull, cm^{-1}): 1053 [$\nu_{asym}(CS_2^-)$], 804 [$\nu_{sym}(CS_2^-)$], 399, 287 [ν(Hf−Cl)]. MS [FAB (m/z assignment, % intensity)]: 528 [M − Cl], 100.

Synthesis of $[ZrCl_3(\kappa^3\text{-bdmpze})]$ (5). To a cooled (−70 °C) solution of Hbdmpze (0.50 g, 2.12 mmol) in dry THF (100 mL) was added a 1.6 M solution of Bu^{n}Li in hexane (1.33 mL, 2.12 mmol). After 30 min, a solution of $ZrCl_4$ (0.49 g, 2.12 mmol) in THF (50 mL) was added, and the reaction mixture was stirred for 12 h at room temperature. The solvent was removed under vacuum, and the solid was extracted with CH_2Cl_2. A white solid was obtained after removal of the solvent. Yield: 85%. Anal. Calcd for $C_{12}H_{17}Cl_3N_4OZr$: C, 33.4; H, 3.9; N, 13.0. Found: C, 33.6; H, 4.1; N, 13.1. ^{1}H NMR ($CDCl_3$, 293 K) δ: 6.45 (br s, 1 H, CH), 6.04 (s, 2 H, H^4), 4.59 (br s, 2 H, CH_2O), 2.64 (s, 6 H, Me^3), 2.45 (s, 6 H, Me^5). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 70.5 (CH), 154.2, 142.8 (C$^{3\text{ or }5}$),

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108.2 (C^4), 15.3 (Me^3), 11.3 (Me^5), 66.2 (CH_2O). IR (Nujol mull, cm^{-1}): 411, 291 [ν(Zr−Cl)]. MS [FAB (m/z assignment, % intensity)]: 395 [M − Cl], 100.

Synthesis of [$HfCl_3$(κ^3-bdmpze)] (6). The synthetic procedure was the same as that for complex **5**, using Hbdmpze (0.36 g, 1.56 mmol), Bu^nLi (1.00 mL, 1.56 mmol), and $HfCl_4$ (0.50 g, 1.56 mmol) to give **6** as a white solid. Yield: 89%. Anal. Calcd for $C_{12}H_{17}Cl_3HfN_4O$: C, 27.8; H, 3.2; N, 10.8. Found: C, 28.1; H, 3.4; N, 10.9. ^1H NMR ($CDCl_3$, 293 K) δ: 6.77 (br s, 1 H, CH), 6.06 (s, 2 H, H^4), 4.75 (br s, 2 H, CH_2O), 2.61 (s, 6 H, Me^3), 2.52 (s, 6 H, Me^5). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 70.6 (CH), 154.3, 141.9 ($C^{3\text{ or }5}$), 108.4 (C^4), 15.4 (Me^3), 11.2 (Me^5), 66.8 (CH_2O). IR (Nujol mull, cm^{-1}): 405, 282 [ν(Hf−Cl)]. MS [FAB (m/z assignment, % intensity)]: 482 [M − Cl], 100.

Synthesis of [{$ZrCl_2$(μ-OH)(κ^3-bdmpza)}$_2$] (7). To a CH_2Cl_2 (100 mL) suspension of $ZrCl_4$ (2.00 g, 8.58 mmol) was added an equimolar quantity of [{Li(bdmpza)(H_2O)}$_4$] (2.34 g, 2.14 mmol). After 12 h at room temperature, the mixture was filtered. The solvent from the filtrate was evaporated to dryness to yield complex **7** as a white solid. Yield: 75%. Anal. Calcd for $C_{24}H_{32}Cl_4N_8O_6Zr_2$: C, 33.8; H, 3.7; N, 13.3. Found: C, 33.5; H, 3.7; N, 13.5. ^1H NMR ($CDCl_3$, 293 K) δ: 7.09 (s, 2 H, CH), 5.85 (s, 4 H, H^4), 2.51 (s, 12 H, Me^3), 2.06 (s, 12 H, Me^5). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 72.9 (CH), 146.7, 140.2 ($C^{3\text{ or }5}$), 106.4 (C^4), 10.8 (Me^3), 13.3 (Me^5), 165.9 (CO_2^-). IR (Nujol mull, cm^{-1}): 1680 [ν_{asym}(CO_2^-)], 1470 [ν_{sym}(CO_2^-)], 328, 295 [ν(Zr−Cl)], 3533 [ν(OH)]. MS [FAB (m/z assignment, % intensity)]: 836 [M − OH], 100.

Synthesis of [{$HfCl_2$(μ-OH)(κ^3-bdmpza)}$_2$] (8). The synthetic procedure was the same as that for complex **7**, using $HfCl_4$ (1.00 g, 3.12 mmol) and [{Li(bdmpza)(H_2O)}$_4$] (0.85 g, 0.78 mmol) to give **8** as a white solid. Yield: 85%. Anal. Calcd for $C_{24}H_{32}Cl_4Hf_2N_8O_6$: C, 28.0; H, 3.1; N, 10.9. Found: C, 28.3; H, 3.2; N, 10.7. ^1H NMR ($CDCl_3$, 293 K) δ: 7.09 (s, 2 H, CH), 6.04 (s, 4 H, H^4), 2.51 (s, 12 H, Me^3), 2.06 (s, 12 H, Me^5). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 72.5 (CH), 146.7, 141.2 ($C^{3\text{ or }5}$), 105.4 (C^4), 15.3 (Me^3), 11.8 (Me^5), 165.2 (CO_2^-). IR (Nujol mull, cm^{-1}): 1672 [ν_{asym}(CO_2^-)], 1451 [ν_{sym}(CO_2^-)], 395, 328 [ν(Hf−Cl)], 3430 [ν(OH)]. MS [FAB (m/z assignment, % intensity)]: 1010 [M − OH], 100.

Synthesis of [{$ZrCl_2$(μ-OH)(κ^3-bdmpzdta)}$_2$] (9). The synthetic procedure was the same as that for complex **7**, using $ZrCl_4$ (2.00 g, 8.58 mmol) and [{Li(bdmpzdta)(H_2O)}$_4$] (2.46 g, 2.14 mmol) to give **9** as an orange solid. Yield: 65%. Anal. Calcd for $C_{24}H_{32}Cl_4N_8O_2S_4Zr_2$: C, 31.4; H, 3.5; N, 12.2. Found: C, 31.3; H, 3.6; N, 12.3. ^1H NMR ($CDCl_3$, 293 K) δ: 7.53 (s, 2 H, CH), 6.18 (s, 4 H, H^4), 2.75 (s, 12 H, Me^3), 2.54 (s, 12 H, Me^5). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 65.4 (CH), 155.1, 141.2 ($C^{3\text{ or }5}$), 109.1 (C^4), 14.5 (Me^3), 12.7 (Me^5), 235.4 (CS_2^-). IR (Nujol mull, cm^{-1}): 1049 [ν_{asym}(CS_2^-)], 808 [ν_{sym}(CS_2^-)], 317, 279 [ν(Zr−Cl)], 3330 [ν(OH)]. MS [FAB (m/z assignment, % intensity)]: 900 [M − OH], 100.

Synthesis of [{$ZrCl_2$(μ-OH)(κ^3-bdmpze)}$_2$] (10). To a cooled (−70 °C) solution of Hbdmpze (0.50 g, 2.12 mmol) in dry THF (100 mL) was added a 1.6 M solution of Bu^nLi in hexane (1.33 mL, 2.12 mmol). After 30 min, a suspension of $ZrCl_4$ (0.49 g, 2.12 mmol) in CH_2Cl_2 (50 mL) was added, and the reaction mixture was stirred for 12 h at room temperature. The mixture was filtered to give a solution, which was evaporated to dryness to yield complex **10** as a white solid. Yield: 75%. Anal. Calcd for $C_{24}H_{36}Cl_4N_8O_4Zr_2$: C, 34.9; H, 4.4; N, 13.5. Found: C, 35.1; H, 4.3; N, 13.7. ^1H NMR ($CDCl_3$, 293 K) δ: 6.61 (br s, 2 H, CH), 6.02 (s, 4 H, H^4), 4.61 (br s, 4 H, CH_2O), 2.62 (s, 12 H, Me^3), 2.49 (s, 12 H, Me^5). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 66.3 (CH), 154.1, 140.3 ($C^{3\text{ or }5}$), 108.1 (C^4), 15.3 (Me^3), 11.4 (Me^5), 70.7 (CH_2O). IR (Nujol mull, cm^{-1}): 357, 299 [ν(Zr−Cl)], 3480 [ν(OH)]. MS [FAB (m/z assignment, % intensity)]: 808 [M − OH], 100.

Synthesis of [$ZrCl_2$(κ^3-bdmpza)(OMe)] (11). A solution of **1** (0.50 g, 1.12 mmol) in MeOH (75 mL) was stirred for 12 h at 30 °C. The solvent was removed under vacuum, and the solid was extracted with toluene. A yellow solid was obtained after removal of the solvent. Yield: 82%. Anal. Calcd for $C_{13}H_{18}Cl_2N_4O_3Zr$: C, 35.4; H, 4.0; N, 12.7. Found: C, 35.5; H, 4.1; N, 12.8. ^1H NMR ($CDCl_3$, 293 K) δ: 7.82 (s, 1 H, CH), 6.05 (s, 2 H, H^4), 2.35 (s, 6 H, Me^3), 2.47 (s, 6 H, Me^5), 3.98 (s, 3 H, OMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 71.3 (CH), 149.1, 145.3 ($C^{3\text{ or }5}$), 108.4 (C^4), 13.6 (Me^3), 11.9 (Me^5), 162.6 (CO_2^-), 55.5 (OMe). IR (Nujol mull, cm^{-1}): 1730 [ν_{asym}(CO_2^-)], 1513 [ν_{sym}(CO_2^-)], 653 [ν(Zr−OMe)], 418, 314 [ν(Zr−Cl)]. MS [FAB (m/z assignment, % intensity)]: 406 [M − Cl], 100.

Synthesis of [$ZrCl_2$(κ^3-bdmpza)(OEt)] (12). A solution of **1** (0.50 g, 1.12 mmol) in EtOH (75 mL) was stirred for 12 h at 30 °C. The solvent was removed under vacuum, and the solid was extracted with toluene. A yellow solid was obtained after removal of the solvent. Yield: 87%. Anal. Calcd for $C_{14}H_{20}Cl_2N_4O_3Zr$: C, 36.9; H, 4.4; N, 12.3. Found: C, 37.0; H, 4.4; N, 12.3. ^1H NMR ($CDCl_3$, 293 K) δ: 7.85 (s, 1 H, CH), 5.98 (s, 2 H, H^4), 2.31 (s, 6 H, Me^3), 2.41 (s, 6 H, Me^5), 4.35 (q, 2 H, $^3J_{HH}$ = 6.2 Hz, $OC\mathit{H}_2CH_3$), 1.30 (t, 3 H, $^3J_{HH}$ = 6.2 Hz, $OCH_2C\mathit{H}_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 70.3 (CH), 148.9, 145.1 ($C^{3\text{ or }5}$), 108.2 (C^4), 13.8 (Me^3), 12.5 (Me^5), 162.7 (CO_2^-), 63.5 ($O\mathit{C}H_2CH_3$), 11.9 ($OCH_2\mathit{C}H_3$). IR (Nujol mull, cm^{-1}): 1705 [ν_{asym}(CO_2^-)], 1483 [ν_{sym}(CO_2^-)], 681 [ν(Zr−OEt)], 415, 320 [ν(Zr−Cl)]. MS [FAB (m/z assignment, % intensity)]: 420 [M − Cl], 100.

Synthesis of [$ZrCl_2$(κ^3-bdmpza)(O^iPr)] (13). A solution of **1** (0.50 g, 1.12 mmol) in ^iPrOH (75 mL) was stirred for 12 h at 30 °C. The solvent was removed under vacuum, and the solid was extracted with toluene. A yellow solid was obtained after removal of the solvent. Yield: 68%. Anal. Calcd for $C_{15}H_{22}Cl_2N_4O_3Zr$: C, 38.4; H, 4.6; N, 12.9. Found: C, 38.4; H, 4.7; N, 12.9. ^1H NMR ($CDCl_3$, 293 K) δ: 6.58 (s, 1 H, CH), 6.11 (s, 1 H, H^4), 6.05 (s, 1 H, $H^{4'}$), 2.65 (s, 3 H, Me^3), 2.55 (s, 3 H, $Me^{3'}$), 2.47 (s, 3 H, Me^5), 2.46 (s, 3 H, $Me^{5'}$), 4.59 [m, 1 H, $^3J_{HH}$ = 7.0 Hz, $OC\mathit{H}(CH_3)_2$], 1.37 [d, 6 H, $^3J_{HH}$ = 7.0 Hz, $OCH(C\mathit{H}_3)_2$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 67.4 (CH), 155.2, 154.1, 142.1, 141.3 ($C^{3\text{ or }3'}$ and $C^{5\text{ or }5'}$), 108.2 (C^4), 108.7 ($C^{4'}$), 14.7 (Me^3), 15.0 ($Me^{3'}$), 11.1 (Me^5), 11.2 ($Me^{5'}$), 162.4 (CO_2^-), 77.8 [$O\mathit{C}H(CH_3)_2$], 25.1 [$OCH(\mathit{C}H_3)_2$]. IR (Nujol mull, cm^{-1}): 1678 [ν_{asym}(CO_2^-)], 1461 [ν_{sym}(CO_2^-)], 689 [ν(Zr−O^iPr)], 411, 307 [ν(Zr−Cl)]. MS [FAB (m/z assignment, % intensity)]: 434 [M − Cl], 100.

Synthesis of [$ZrCl_2$(κ^3-bdmpza)(O^tBu)] (14). A solution of **1** (0.50 g, 1.12 mmol) in ^tBuOH (75 mL) was stirred for 12 h at 30 °C. The solvent was removed under vacuum, and the solid was extracted with toluene. A yellow solid was obtained after removal of the solvent. Yield: 91%. Anal. Calcd for $C_{16}H_{24}Cl_2N_4O_3Zr$: C, 39.9; H, 4.9; N, 11.6. Found: C, 39.9; H, 5.1; N, 11.6. ^1H NMR ($CDCl_3$, 293 K) δ: 6.57 (s, 1 H, CH), 6.05, (s, 1 H, H^4), 6.03 (s, 1 H, $H^{4'}$), 2.66 (s, 3 H, Me^3), 2.60 (s, 3 H, $Me^{3'}$), 2.48 (s, 3 H, Me^5), 2.46 (s, 3 H, $Me^{5'}$), 1.48 [s, 9 H, $OC(CH_3)_3$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 67.4 (CH), 155.1, 154.0, 144.8, 142.2 ($C^{3\text{ or }3'}$ and $C^{5\text{ or }5'}$), 108.1 (C^4), 108.4 ($C^{4'}$), 14.9 (Me^3), 15.1 ($Me^{3'}$), 10.9 (Me^5), 11.1 ($Me^{5'}$), 162.5 (CO_2^-), 30.9 [$O\mathit{C}(CH_3)_3$], 25.1 [$OC(\mathit{C}H_3)_3$]. IR (Nujol mull, cm^{-1}): 1653 [ν_{asym}(CO_2^-)], 1442 [ν_{sym}(CO_2^-)], 683 [ν(Zr−O^tBu)], 418, 327 [ν(Zr−Cl)]. MS [FAB (m/z assignment, % intensity)]: 448 [M − Cl], 100.

Synthesis of [$ZrCl_2$(κ^3-bdmpzdta)(OMe)] (15). A solution of **3** (0.50 g, 1.04 mmol) in MeOH (75 mL) was stirred for 12 h at 30 °C. The solvent was removed under vacuum, and the solid was extracted with toluene. An orange solid was obtained after removal of the solvent. Yield: 78%. Anal. Calcd for $C_{13}H_{18}Cl_2N_4OS_2Zr$: C, 33.0; H, 3.8; N, 11.8. Found: C, 33.1; H, 3.8; N, 11.9. ^{1}H NMR ($CDCl_3$, 293 K) δ: 7.52 (s, 1 H, CH), 6.08 (s, 2 H, H^4), 2.71 (s, 6 H, Me^3), 2.48 (s, 6 H, Me^5), 4.52 (s, 3 H, OMe). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 81.1 (CH), 155.1, 144.8 (C$^{3\text{ or }5}$), 108.4 (C^4), 15.5 (Me^3), 11.5 (Me^5), 242.8 (CS_2^-), 56.8 (OMe). IR (Nujol mull, cm^{-1}): 1112 [$\nu_{asym}(CS_2^-)$], 833 [$\nu_{sym}(CS_2^-)$], 635 [ν(Zr−OMe)], 412, 326 [ν(Zr−Cl)]. MS [FAB (*m*/*z* assignment, % intensity)]: 438 [M − Cl], 100.

Synthesis of [ZrCl$_2$(κ^3-bdmpzdta)(OEt)] (16). A solution of **3** (0.50 g, 1.04 mmol) in EtOH (75 mL) was stirred for 12 h at 30 °C. The solvent was removed under vacuum, and the solid was extracted with toluene. An orange solid was obtained after removal of the solvent. Yield: 82%. Anal. Calcd for $C_{14}H_{20}Cl_2N_4OS_2Zr$: C, 34.5; H, 4.1; N, 11.5. Found: C, 34.6; H, 4.1; N, 11.5. ^{1}H NMR ($CDCl_3$, 293 K) δ: 7.48 (s, 1 H, CH), 6.11 (s, 2 H, H^4), 2.70 (s, 6 H, Me^3), 2.49 (s, 6 H, Me^5), 4.99 (q, 2 H, $^3J_{HH}$ = 6.2 Hz, OC*H*$_2$CH$_3$), 1.54 (t, 3 H, $^3J_{HH}$ = 6.2 Hz, OCH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 80.7 (CH), 155.4, 144.9 (C$^{3\text{ or }5}$), 108.6 (C^4), 15.6 (Me^3), 11.4 (Me^5), 244.0 (CS_2^-), 67.3 (O*C*H$_2$CH$_3$), 15.8 (OCH$_2$*C*H$_3$). IR (Nujol mull, cm^{-1}): 1083 [$\nu_{asym}(CS_2^-)$], 813 [$\nu_{sym}(CS_2^-)$], 623 [ν(Zr−OEt)], 415, 335 [ν(Zr−Cl)]. MS [FAB (*m*/*z* assignment, % intensity)]: 452 [M − Cl], 100.

Synthesis of [ZrCl$_2$(κ^3-bdmpzdta)(O^{i}Pr)] (17). A solution of **3** (0.50 g, 1.04 mmol) in ^{i}PrOH (75 mL) was stirred for 12 h at 30 °C. The solvent was removed under vacuum, and the solid was extracted with toluene. An orange solid was obtained after removal of the solvent. Yield: 75%. Anal. Calcd for $C_{15}H_{22}Cl_2N_4OS_2Zr$: C, 35.9; H, 4.3; N, 11.1. Found: C, 35.9; H, 4.4; N, 11.2. ^{1}H NMR ($CDCl_3$, 293 K) δ: 7.50 (s, 1 H, CH), 6.10, (s, 1 H, H^4), 6.08 (s, 1 H, H$^{4'}$), 2.76 (s, 3 H, Me^3), 2.62 (s, 3 H, Me$^{3'}$), 2.50 (s, 3 H, Me^5), 2.49 (s, 3 H, Me$^{5'}$), 4.65 [m, 1 H, $^3J_{HH}$ = 7.0 Hz, OC*H*(CH$_3$)$_2$], 1.34 [d, 6 H, $^3J_{HH}$ = 7.0 Hz, OCH(C*H*$_3$)$_2$]. ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 80.3 (CH), 155.1, 154.8, 144.1, 142.1 (C$^{3\text{ or }3'}$ and C$^{5\text{ or }5'}$), 108.5 (C^4), 108.9 (C$^{4'}$), 15.3 (Me^3), 15.5 (Me$^{3'}$), 11.3 (Me^5), 11.6 (Me$^{5'}$), 242.8 (CS_2^-), 81.3 [O*C*H(CH$_3$)$_2$], 21.8 [OCH(*C*H$_3$)$_2$]. IR (Nujol mull, cm^{-1}): 1081 [$\nu_{asym}(CS_2^-)$], 803 [$\nu_{sym}(CS_2^-)$], 604 [ν(Zr−O^{i}Pr)], 402, 338 [ν(Zr−Cl)]. MS [FAB (*m*/*z* assignment, % intensity)]: 466 [M − Cl], 100.

Synthesis of [ZrCl$_2$(κ^3-bdmpzdta)(O^{t}Bu)] (18). A solution of **3** (0.50 g, 1.04 mmol) in ^{t}BuOH (75 mL) was stirred for 12 h at 30 °C. The solvent was removed under vacuum, and the solid was extracted with toluene. An orange solid was obtained after removal of the solvent. Yield: 89%. Anal. Calcd for $C_{16}H_{24}Cl_2N_4OS_2Zr$: C, 37.3; H, 4.6; N, 10.8. Found: C, 37.3; H, 4.6; N, 10.9. ^{1}H NMR ($CDCl_3$, 293 K) δ: 7.50 (s, 1 H, CH), 6.10, (s, 1 H, H^4), 6.08 (s, 1 H, H$^{4'}$), 2.77 (s, 3 H, Me^3), 2.66 (s, 3 H, Me$^{3'}$), 2.50 (s, 3 H, Me^5), 2.49 (s, 3 H, Me$^{5'}$), 1.48 [s, 9 H, OC(CH$_3$)$_3$]. ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 80.6 (CH), 155.4, 153.9, 143.5, 142.4 (C$^{3\text{ or }3'}$ and C$^{5\text{ or }5'}$), 108.4 (C^4), 108.9 (C$^{4'}$), 15.4 (Me^3), 15.6 (Me$^{3'}$), 11.4 (Me^5), 11.5 (Me$^{5'}$), 243.1 (CS_2^-), 30.9 [O*C*(CH$_3$)$_3$], 28.9 [OC(*C*H$_3$)$_3$]. IR (Nujol mull, cm^{-1}): 1073 [$\nu_{asym}(CS_2^-)$], 805 [$\nu_{sym}(CS_2^-)$], 601 [ν(Zr−O^{t}Bu)], 399, 329 [ν(Zr−Cl)]. MS [FAB (*m*/*z* assignment, % intensity)]: 480 [M − Cl], 100.

Synthesis of [ZrCl$_2$(κ^3-bdmpze)(OMe)] (19). A solution of **5** (0.50 g, 1.16 mmol) in MeOH (75 mL) was stirred for 12 h at 30 °C. The solvent was removed under vacuum, and the solid was extracted with toluene. A yellow solid was obtained after removal of the solvent. Yield: 81%. Anal. Calcd for $C_{13}H_{20}Cl_2N_4O_2Zr$: C, 36.6; H, 4.6; N, 13.2. Found: C, 36.7; H, 4.7; N, 13.2. ^{1}H NMR ($CDCl_3$, 293 K) δ: 7.20 (br s, 1 H, CH), 6.03 (s, 2 H, H^4), 4.55 (d, 2 H, $^3J_{HH}$ = 7.0 Hz, CH$_2$O), 2.39 (s, 6 H, Me^3), 2.15 (s, 6 H, Me^5), 3.48 (s, 3 H, OMe). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 66.3 (CH), 147.3, 144.9 (C$^{3\text{ or }5}$), 108.2 (C^4), 12.5 (Me^3), 11.3 (Me^5), 73.9 (CH$_2$O), 50.8 (OMe). IR (Nujol mull, cm^{-1}): 636 [ν(Zr−OMe)], 405, 325 [ν(Zr−Cl)]. MS [FAB (*m*/*z* assignment, % intensity)]: 392 [M − Cl], 100.

Synthesis of [ZrCl$_2$(κ^3-bdmpze)(OEt)] (20). A solution of **5** (0.50 g, 1.16 mmol) in EtOH (75 mL) was stirred for 12 h at 30 °C. The solvent was removed under vacuum, and the solid was extracted with toluene. A yellow solid was obtained after removal of the solvent. Yield: 91%. Anal. Calcd for $C_{14}H_{22}Cl_2N_4O_2Zr$: C, 38.1; H, 4.9; N, 12.7. Found: C, 38.2; H, 5.0; N, 12.8. ^{1}H NMR ($CDCl_3$, 293 K) δ: 7.18 (br s, 1 H, CH), 6.00 (s, 2 H, H^4), 4.57 (d, 2 H, $^3J_{HH}$ = 7.0 Hz, CH$_2$O), 2.38 (s, 6 H, Me^3), 2.13 (s, 6 H, Me^5), 3.95 (q, 2 H, $^3J_{HH}$ = 6.2 Hz, OC*H*$_2$CH$_3$), 1.30 (t, 3 H, $^3J_{HH}$ = 6.2 Hz, OCH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 63.3 (CH), 147.6, 144.1 (C$^{3\text{ or }5}$), 108.1 (C^4), 12.4 (Me^3), 11.1 (Me^5), 71.7 (CH$_2$O), 81.3 (O*C*H$_2$CH$_3$), 15.3 (OCH$_2$*C*H$_3$). IR (Nujol mull, cm^{-1}): 624 [ν(Zr−OEt)], 399, 336 [ν(Zr−Cl)]. MS [FAB (*m*/*z* assignment, % intensity)]: 406 [M − Cl], 100.

Synthesis of [ZrCl$_2$(κ^3-bdmpze)(O^{i}Pr)] (21). A solution of **5** (0.50 g, 1.16 mmol) in ^{i}PrOH (75 mL) was stirred for 12 h at 30 °C. The solvent was removed under vacuum, and and the solid was extracted with toluene. A yellow solid was obtained after removal of the solvent. Yield: 90%. Anal. Calcd for $C_{15}H_{24}Cl_2N_4O_2Zr$: C, 39.6; H, 5.2; N, 12.4. Found: C, 39.6; H, 5.3; N, 12.4. ^{1}H NMR ($CDCl_3$, 293 K) δ: 7.23 (br s, 1 H, CH), 6.01, (s, 1 H, H^4), 5.99 (s, 1 H, H$^{4'}$), 4.52 (d, 2 H, $^3J_{HH}$ = 7.0 Hz, CH$_2$O), 2.48 (s, 3 H, Me^3), 2.36 (s, 3 H, Me$^{3'}$), 2.13 (s, 3 H, Me^5), 2.36 (s, 3 H, Me$^{5'}$), 4.02 [m, 1 H, $^3J_{HH}$ = 7.0 Hz, OC*H*(CH$_3$)$_2$], 1.22 [d, 6 H, $^3J_{HH}$ = 7.0 Hz, OCH(C*H*$_3$)$_2$]. ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 65.1 (CH), 147.3, 145.4, 144.1, 142.3 (C$^{3\text{ or }3'}$ and C$^{5\text{ or }5'}$), 108.1 (C^4), 108.3 (C$^{4'}$), 12.3 (Me^3), 12.5 (Me$^{3'}$), 11.1 (Me^5), 11.3 (Me$^{5'}$), 72.3 (CH$_2$O), 89.8 [O*C*H(CH$_3$)$_2$], 21.3 [OCH(*C*H$_3$)$_2$]. IR (Nujol mull, cm^{-1}): 614 [ν(Zr−O^{i}Pr)], 402, 338 [ν(Zr−Cl)]. MS [FAB (*m*/*z* assignment, % intensity)]: 420 [M − Cl], 100.

Synthesis of [ZrCl$_2$(κ^3-bdmpze)(O^{t}Bu)] (22). A solution of **5** (0.50 g, 1.16 mmol) in ^{t}BuOH (75 mL) was stirred for 12 h at 30 °C. The solvent was removed under vacuum, and the solid was extracted with toluene. A yellow solid was obtained after removal of the solvent. Yield: 93%. Anal. Calcd for $C_{16}H_{26}Cl_2N_4O_2Zr$: C, 41.0; H, 5.5; N, 11.9. Found: C, 41.0; H, 5.5; N, 11.9. ^{1}H NMR ($CDCl_3$, 293 K) δ: 7.17 (br s, 1 H, CH), 6.03, (s, 1 H, H^4), 6.01 (s, 1 H, H$^{4'}$), 4.48 (d, 2 H, $^3J_{HH}$ = 7.0 Hz, CH$_2$O), 2.65 (s, 3 H, Me^3), 2.59 (s, 3 H, Me$^{3'}$), 2.43 (s, 3 H, Me^5), 2.41 (s, 3 H, Me$^{5'}$), 1.42 [s, 9 H, OC(CH$_3$)$_3$]. ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 66.4 (CH), 147.8, 145.3, 144.6, 142.1 (C$^{3\text{ or }3'}$ and C$^{5\text{ or }5'}$), 107.8 (C^4), 107.6 (C$^{4'}$), 12.0 (Me^3), 12.6 (Me$^{3'}$), 11.2 (Me^5), 11.4 (Me$^{5'}$), 69.8 (CH$_2$O), 30.3 [O*C*(CH$_3$)$_3$], 26.3 [OC(*C*H$_3$)$_3$]. IR (Nujol mull, cm^{-1}): 603 [ν(Zr−O^{t}Bu)], 395, 329 [ν(Zr−Cl)]. MS [FAB (*m*/*z* assignment, % intensity)]: 434 [M − Cl], 100.

Synthesis of [Zr$_6$(μ_3-OH)$_8$(OH)$_8$(κ^2-bdmpza)$_8$] (23). A solution of **11**−**14** (4.14 mmol) in THF (40 mL) was added to water (0.15 mL, 8,28 mmol). The solution was stirred for 12 h at room temperature. The solvent was removed under vacuum, and the solid was extracted with CH_2Cl_2. A yellow solid was obtained after removal of CH_2Cl_2. Yield: 70−75%. Anal. Calcd for $C_{96}H_{136}N_{32}O_{32}Zr_6$: C, 41.0; H, 4.8; N, 15.9. Found: C, 41.2; H, 4.9; N, 15.7. ^{1}H NMR ($CDCl_3$, 293 K) δ: 6.08 (s, 8 H, CH), 5.79 (s, 16 H, H^4), 2.18 (s, 48 H, Me^3), 2.42 (s, 48 H, Me^5). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 60.2 (CH), 146.1, 142.3 (C$^{3\text{ or }5}$), 106.3 (C^4), 13.9 (Me^3), 10.7 (Me^5), 173.8 (CO_2^-). IR (Nujol mull, cm^{-1}): 1670 [$\nu_{asym}(CO_2^-)$], 1510 [$\nu_{sym}(CO_2^-)$], 3550 [ν(OH)], 3433 [ν(μ-OH)].

Table 1. Crystal Data and Structure Refinement for **7**, **8**, and **23**

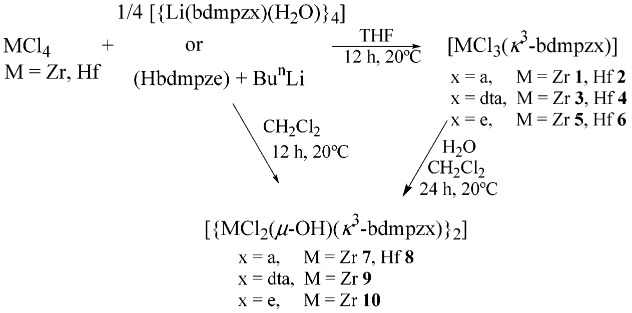
	7	**8**	**23**
formula	$C_{24}H_{32}Cl_4N_8O_6Zr_2$·8THF	$C_{24}H_{32}Cl_4Hf_2N_8O_6$·8THF	$C_{96}H_{136}N_{32}O_{32}Zr_6$·8HCl·$4H_2O$
fw	1429.65	1604.19	3153.35
T (K)	153(2)	153(2)	293(2)
cryst syst	triclinic	triclinic	orthorombic
space group	$P\bar{1}$	$P\bar{1}$	$Fddd$
a (Å)	12.048(1)	11.986(1)	21.947(1)
b (Å)	12.491(1)	12.478(1)	28.636(1)
c (Å)	13.052(1)	12.970(1)	56.476(2)
α (deg)	104.26(1)	104.24(1)	
β (deg)	104.24(1)	104.05(1)	
γ (deg)	107.20(1)	107.16(1)	
V (Å^3)	1707.3(2)	1689.2(2)	35 494(2)
Z	1	1	8
D_{calcd} (gr cm^{-3})	1.390	1.577	1.180
μ (mm^{-1})	0.525	3.293	0.524
F (000)	748	812	12 864
cryst dimens (mm)	0.2 × 0.3 × 0.3	0.3 × 0.2 × 0.1	0.4 × 0.3 × 0.3
θ range (deg)	2.02−27.97	2.03−27.99	2.15−28.04
hkl ranges	$-15 \le h \le 15, -16 \le k \le 15, 0 \le l \le 17$	$-15 \le h \le 15, -16 \le k \le 15, 0 \le l \le 13$	$-23 \le h \le 23, -23 \le k \le 23, 0 \le l \le 37$
no. of rflns measd	8552	7894	9918
no. of obsd rflns	3454	6501	2427
GOF	1.115	1.080	1.398
final R indices $[I > 2\sigma I)]^a$	$R_1 = 0.0999$, $wR_2 = 0.2282$	$R_1 = 0.0325$, $wR_2 = 0.0785$	$R_1 = 0.1242$, $wR_2 = 0.2109$
largest diff. peak (eÅ^{-3})	0.702/−0.898	1.014/−1.277	2.195/−0.714

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$.

X-ray Structure Determinations for Complexes 7, 8, and 23. We mounted several crystals of **23** but were unable to obtain good data. However, considering the importance of the structure, it was solved despite the aforementioned problems. Crystals of **7** and **8** were mounted at low temperatures in inert oil on a glass fiber. However, whereas crystals of **7** were stable under the aforementioned experimental conditions, crystals of **8** decomposed under these conditions during the data collection. We attempted to repeat the data collection with several crystals but were unable to obtain better data.

Intensity data were collected on a NONIUS-MACH3 diffractometer equipped with a graphite monochromator (Mo $K\alpha$ radiation, $\lambda = 0.710\ 73$ Å) using an $\omega/2\theta$ scan. The final unit-cell parameters were determined from 25 well-centered reflections and refined by the least-squares method. Two reflections were measured every 98 reflections as the orientation and intensity controls, and no significant intensity decay was observed for compounds **7** and **23**; however, an intensity decay of 36% was observed for compound **8**. The structures of **7** and **23** were solved by direct methods, and the structure of compound **8** was solved by the Patterson method using the SHELXS computer program.[8] In all cases, the structures were refined on F^2 by full-matrix least-squares (SHELXL-97).[9] All non-hydrogen atoms were refined with anisotropic thermal parameters for complexes **8** and **23**. The hydrogen atoms were included in the calculated positions and were refined with an overall isotropic temperature factor using a riding model, except the bridging HO hydrogens in **7** and **8**, which were located in a difference Fourier map and refined freely. Weights were optimized in the final cycles. Crystallographic data are given in Table 1. Complexes **7** and **8** crystallize with several THF molecules as the solvent. Complex **23** crystallizes with HCl and H_2O molecules as the solvents.

Scheme 1. Synthesis of Complexes [$MCl_3(\kappa^3$-bdmpzx)] (**1**−**6**) and [{$MCl_2(\mu$-OH)(κ^3-bdmpzx)}$_2$] (**7**−**10**)



Results and Discussion

Compounds [{Li(bdmpza)(H_2O)}$_4$],[3a] [{Li(bdmpzdta)(H_2O)}$_4$],[6b] and (Hbdmpze)[5] were used in the complexation of a number of zirconium and hafnium fragments. These compounds (the latter with the prior addition of Bu^{n}Li) reacted with a solution of MCl_4 (M = Zr, Hf) (Scheme 1) in THF to give, after stirring for 12 h at 20 °C, a solution from which the complexes [$MCl_3(\kappa^3$-bdmpzx)] [x = a, M = Zr (**1**), Hf (**2**); x = dta, M = Zr (**3**), Hf (**4**); x = e, M = Zr (**5**), Hf (**6**)] were isolated as white and red (**3** and **4**) solids after the appropriate workup procedure. When these reactions were performed under the same conditions but with CH_2Cl_2 as the solvent, the hydroxo complexes [{$MCl_2(\mu$-OH)(κ^3-bdmpzx)}$_2$] [x = a, M = Zr (**7**), Hf (**8**); x = dta, M = Zr (**9**); x = e, M = Zr (**10**)] were isolated as white and orange (**9**) solids after the appropriate workup procedure. The complexes **7**−**10** could also be obtained by the hydrolysis of compounds **1**−**3** and **5** in CH_2Cl_2 as the solvent (Scheme 1).

We think that, probably, the more coordinative capacity of THF versus CH_2Cl_2 impedes the hydrolysis process in the synthesis of complexes **1**−**6**. Examples of this type of

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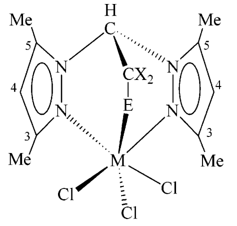
(8) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.
(9) Sheldrick, G. M. *Program for the Refinement of Crystal Structures from Diffraction Data*, University of Göttingen, Göttingen, Germany, 1997.



X_2 = O, E = O, M = Zr **1**, Hf **2**
X_2 = S, E = S, M = Zr **3**, Hf **4**
X_2 = H_2, E = O, M = Zr **5**, Hf **6**

Figure 1. Proposed structure for complexes **1**−**6**.

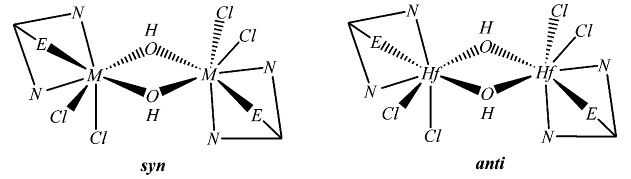


Figure 2. Proposed structures for the two isomers of complexes [{MCl_2-(μ-OH)(κ^3-bdmpzx)}$_2$] (**7**−**10**).

reactivity between the [Cp^*ZrCl_3] species and water have been described previously.[10] The different zirconium and hafnium complexes discussed above were characterized by spectroscopic methods. The ^{1}H NMR spectra of **1**−**10** show a set of resonances for H4, Me3, and Me5, indicating that both of the pyrazole rings are equivalent. The ^{13}C{^{1}H} NMR spectra exhibit the corresponding signals for C3, C4, C5, Me3, and Me5. These results agree with an octahedral structure for complexes **1**−**6**, as depicted in Figure 1, where a κ^3-N,N,E (E = O or S) coordination for the bdmpza, bdmpzdta, and bdmpze is proposed. Although several tris(pyrazol-1-yl)borate group 4 metal complexes have been described previously,[11] as far as we know, these complexes constitute the first examples of this class of compounds with a heteroscorpionate ligand. A different structural disposition was found for complexes **7**−**10**. The mass spectra of these complexes indicate a dinuclear formulation (see the Experimental Section). A strong band is observed in the IR spectra at ca. 3400 cm^{-1}, and this has been assigned to ν(OH) of the hydroxo-bridging group. This observation, along with the NMR data, indicates the presence of a seven-coordinate model, as depicted in Figure 2, with κ^3-N,N,E (E = O or S) coordination for the heteroscorpionate ligands. This disposition gives rise to two possible isomers, syn and anti, with respect to the M−E bond of κ^3-N,N,E (see Figure 2).

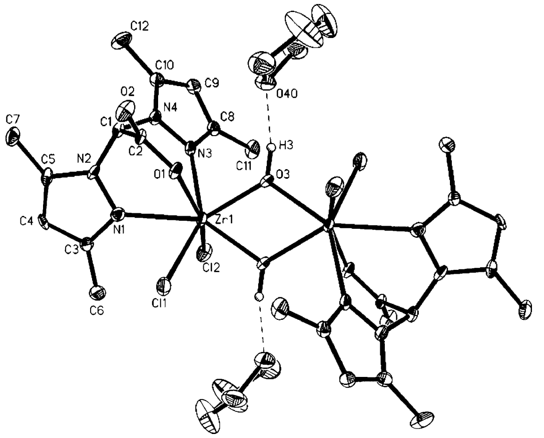


Figure 3. Molecular structure and atom-labeling scheme for **7**, with thermal ellipsoids at 20% probability. Hydrogen bond distances and angle: d(O3−H3) = 0.94 Å, d(H3···O40) = 1.80 Å, d(O3···O40) = 2.72(1) Å, ∠O3−H3···O40 = 167.6°.

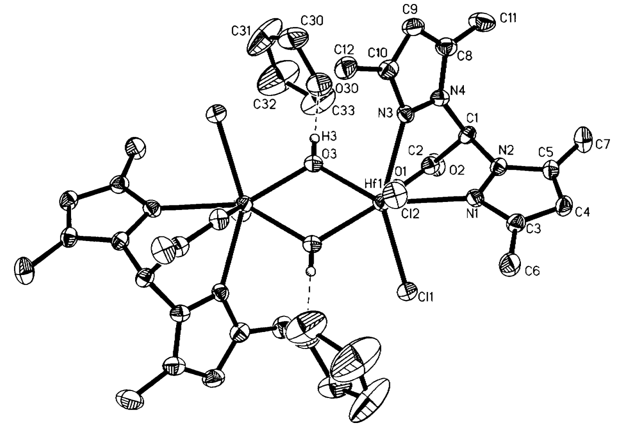


Figure 4. Molecular structure and atom-labeling scheme for **8**, with thermal ellipsoids at 20% probability. Hydrogen bond distances and angle: d(O3−H3) = 0.79 Å, d(H3···O30) = 1.92 Å, d(O3···O30) = 2.70(1) Å, ∠O3−H3···O30 = 173.6°.

The molecular structures of complexes **7** and **8** were determined by X-ray diffraction (XRD) studies, and only the anti isomer was observed in the solid state. This is not unexpected given the lower degree of steric hindrance inherent in this isomer. The molecular structures and atomic numbering schemes are shown in Figures 3 and 4. Significant bond distances and angles are listed in Tables 2 and 3. Both of the structures exhibit a heteroscorpionate ligand bonded to the zirconium or hafnium atom, respectively, through the two nitrogen atoms and the oxygen from the acetate group. In addition, the metal center is coordinated to two chlorine atoms and two bridging hydroxyl groups.

The two bridging hydroxyl groups are involved in hydrogen bonds with the oxygens of THF molecules in the both compounds (Figures 3 and 4).

To extend the range of alkoxide-containing zirconium species, we prepared a new class of heteroscorpionate−metal complexes that contain an alkoxide ancillary ligand. Direct reaction of complexes [$ZrCl_3$(κ^3-bdmpzx)] [x = a (**1**), x = dta (**3**), and x = e (**5**)] with several alcohols (see Scheme 2) gave, after the appropriate workup procedure, the complexes [$ZrCl_2$(κ^3-bdmpzx)(OR)] [x = a, R = Me (**11**), Et (**12**), ^{i}Pr (**13**), ^{t}Bu (**14**); x = dta, R = Me (**15**), Et (**16**), ^{i}Pr (**17**), ^{t}Bu

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[11] (a) Kouba, J. K.; Wreford, S. S. *Inorg. Chem.* **1976**, *15*, 2313. (b) Reger, D. L.; Tarquini, M. E. *Inorg. Chem.* **1982**, *21*, 840. (c) Reger, D. L.; Tarquini, M. E. *Inorg. Chem.* **1983**, *22*, 1064. (d) Reger, D. L.; Tarquini, M. E.; Lebioda, L. *Organometallics* **1983**, *12*, 1763. (e) Kresinski, R. A.; Isam, L.; Hamor, T. A.; Jones, C. J.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **1991**, 1835. (f) Antiñolo, A.; Carrillo-Hermosilla, F.; Corrochano, A. E.; Fernandez-Baeza, J.; Lanfranchi, M.; Otero, A.; Pellinghelli, M. A. *J. Organomet. Chem.* **1999**, *577*, 174. (g) Murtuza, S.; Casagrande, O. L.; Jordan, R. F. *Organometallics* **2002**, *21*, 1882. (h) Lawrence, S. C.; Skinner, M. E. G.; Green, J. C.; Mountford, P. *Chem. Commun.* **2001**, 705.

Table 2. Bond Lengths (Å) and Angles (deg) for **7**

bond distances (Å)		bond angles (deg)	
Zr1−Cl1	2.476(3)	Cl1−Zr1−Cl2	103.3(1)
Zr1−Cl2	2.449(3)	Cl1−Zr1−N1	76.8(2)
Zr1−O1	2.085(7)	Cl1−Zr1−N3	147.1(2)
Zr1−O3	2.094(7)	Cl2−Zr1−N1	81.0(2)
Zr1−O3[a]	2.121(6)	Cl2−Zr1−N3	83.9(2)
Zr1−N1	2.421(8)	N1−Zr1−N3	72.8(3)
Zr1−N3	2.386(8)	N1−Zr1−O3	145.8(3)
		N3−Zr1−O3	75.1(3)
		O3−Zr1−O3[a]	65.8(3)

[a] Symmetry transformations used to generate equivalent atoms: $-x + 1, -y + 1, -z + 1$.

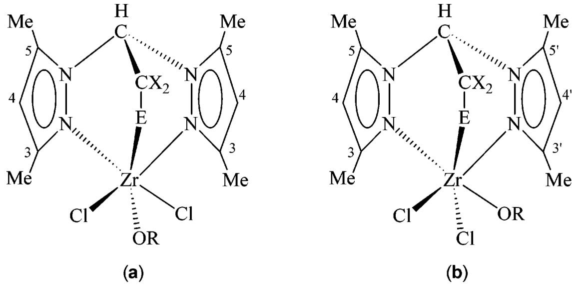
Table 3. Bond Lengths (Å) and Angles (deg) for **8**

bond distances (Å)		bond angles (deg)	
Hf1−Cl1	2.468(1)	Cl1−Hf1−Cl2	103.6(1)
Hf1−Cl2	2.416(1)	Cl1−Hf1−O3	130.4(1)
Hf1−O1	2.074(3)	Cl1−Hf1−O3[a]	78.2(1)
Hf1−O3	2.084(3)	Cl1−Hf1−N1	77.1(1)
Hf1−O3[a]	2.106(3)	Cl1−Hf1−N3	147.1(1)
Hf1−N1	2.387(4)	Cl2−Hf1−O3	106.2(1)
Hf1−N3	2.364(3)	Cl2−Hf1−O3[a]	85.8(1)
Hf1−Hf1[a]	3.523(1)	Cl2−Hf1−N1	81.4(1)
		Cl2−Hf1−N3	83.8(1)
		N1−Hf1−O3	145.8(1)
		N1−Hf1−O3[a]	148.6(1)
		N1−Hf1−N3	72.4(1)
		N3−Hf1−O3	75.3(1)
		N3−Hf1−O3[a]	134.6(1)
		O3−Hf1−O3[a]	65.6(1)

[a] Symmetry transformations used to generate equivalent atoms: $-x + 1, -y + 1, -z + 1$.

(**18**); x = e, R = Me (**19**), Et (**20**), ^{i}Pr (**21**), ^{t}Bu (**22**)], which were isolated as yellow or orange solids. In all cases of our experimental condition, only one alkoxide ligand was incorporated on the metal center. The mass spectra of complexes **11**−**22** indicate a mononuclear formulation (see the Experimental Section). Three strong bands are observed in the IR spectra at ca. 650, 400, and 300 cm^{-1}. The first of these bands was assigned to ν(M−OR) and the latter two to ν(M−Cl).

The ^{1}H NMR spectra of complexes bearing a nonbulky alkoxide group, i.e., R = Me, Et (**11**, **12**, **15**, **16**, **19**, and **20**), show a single set of resonances for H4, Me3, and Me5, indicating that both of the pyrazole rings are equivalent. These results are consistent with the proposed octahedral disposition in which the alkoxide ligand bisects the plane of the scorpionate ligand (see Figure 5a). NOE experiments were carried out in order to confirm this situation. In addition, the ^{13}C{^{1}H} NMR spectra exhibit signals for C3, C4, C5, Me3, Me5, and the different carbon atoms of the corresponding alkoxide ligand. Complexes bearing a bulky alkoxide group, i.e., R = ^{i}Pr, ^{t}Bu (**13**, **14**, **17**, **18**, **21**, and **22**) give ^{1}H NMR spectra that contain two resonances for each of the H4, Me3, and Me5 pyrazole protons, indicating that in this case the two pyrazole rings are not equivalent. These results agree with the proposed octahedral disposition in which two pyrazole rings are located in cis and trans positions with respect to the alkoxide ligand, i.e., an asymmetric structural disposition (see Figure 5b). NOE experiments confirmed these findings.



X_2 = O, E = O, R = Me **11**, Et **12**
X_2 = S, E = S, R = Me **15**, Et **16**
X_2 = H_2, E = O, R = Me **19**, Et **20**

X_2 = O, E = O, R = ^{i}Pr **13**, ^{t}Bu **14**
X_2 = S, E = S, R = ^{i}Pr **17**, ^{t}Bu **18**
X_2 = H_2, E = O, R = ^{i}Pr **21**, ^{t}Bu **22**

Figure 5. Proposed structure for complexes **11**−**22**.

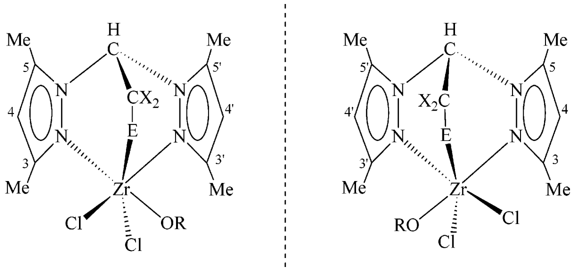


Figure 6. Proposed structures for the two enantiomers of a complex with a bulky alkoxide ligand.

In addition, the ^{13}C{^{1}H} NMR spectra exhibit two resonances for the different pyrazole carbon atoms C3, C4, C5, Me3, and Me5, and their assignments were made on the basis of HETCOR correlation experiments (see the Experimental Section). In these asymmetric complexes, the zirconium atom is a chiral center, and we confirmed the presence of the corresponding two enantiomers in solution by the addition of a chiral shift reagent, namely, (*R*)-(−)-(9-anthryl)-2,2,2-trifluoroethanol. This addition gave rise to the appearance of two signals for each proton in the ^{1}H NMR spectra, resulting from the two diastereoisomers of the corresponding two enantiomers (see Figure 6).

Finally, an interesting hydrolysis process was observed when we attempted to obtain by different procedures single crystals suitable for XRD from the solutions of complexes **11**−**14**. For example, when a THF solution of **14** was slowly evaporated at room temperature in an air atmosphere, after 48 h, yellow crystals were deposited from the solution, which were identified as the cluster complex **23**. This complex results from a partial hydrolysis of the alkoxide-containing complex. We have subsequently rationalized the synthesis of **23**; in fact, the addition of the appropriate amount of water to a THF solution of complexes **11**−**14** gives rise to the isolation of **23** after the appropriate workup (see Scheme 3). This compound was spectroscopically characterized. The IR spectrum shows two strong bands at 1670 and 1510 cm^{-1}, which were assigned to $\nu_{asym}(CO_2^-)$ and $\nu_{sym}(CO_2^-)$ of a carboxylate moiety, respectively. The value of $\Delta\nu_{asym-sym}$ (160 cm^{-1}) is consistent with a bonding mode through the two oxygen atoms (bridge mode).[12] These data suggest that in the cluster the bdmpza ligand acts as a bidentate-bridge carboxylate with the two pyrazole rings behaving as spectators. A similar bonding situation was previously found for

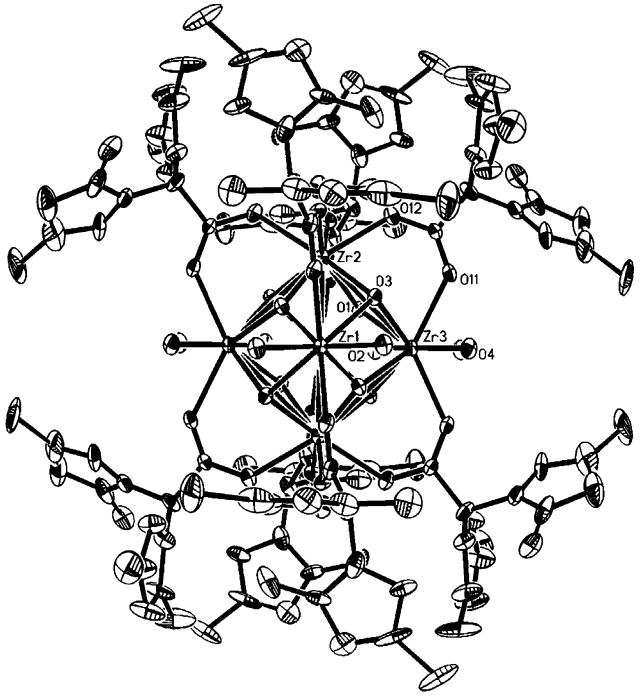


Figure 7. Molecular structure and atom-labeling scheme for **23**, with thermal ellipsoids at 20% probability.

Scheme 2. Synthesis of Complexes [ZrCl$_2$(κ^3-bdmpzx)(OR)] (**11**−**22**)

$$[\mathrm{ZrCl_3}(\kappa^3\text{-bdmpzx})] \xrightarrow[12\ \mathrm{h},\ 30\,^{\circ}\mathrm{C}]{+\mathrm{HOR},\ -\mathrm{HCl}} [\mathrm{ZrCl_2}(\kappa^3\text{-bdmpzx})(\mathrm{OR})]$$

x = a **1**, dta **3**, e **5**

x = a, R = Me **11**, Et **12**, ^{i}Pr **13**, ^{t}Bu **14**
x = dta, R = Me **15**, Et **16**, ^{i}Pr **17**, ^{t}Bu **18**
x = e , R = Me **19**, Et **20**, ^{i}Pr **21**, ^{t}Bu **22**

Scheme 3. Synthesis of Cluster Complex [Zr$_6$(μ_3-OH)$_8$(OH)$_8$(κ^2-bdmpza)$_8$] (**23**)

$$\underset{\mathbf{11\text{-}14}}{8\,[\mathrm{ZrCl_2}(\kappa^3\text{-bdmpza})(\mathrm{OR})]} + 16\,\mathrm{H_2O} \xrightarrow{-8\,\mathrm{HOR},\ -8\,\mathrm{HCl}} \underset{\mathbf{23}}{[\mathrm{Zr_6}(\mu_3\text{-OH})_8(\mathrm{OH})_8(\kappa^2\text{-bdmpza})_8]} + 2\,[\mathrm{ZrCl_4}]$$

Table 4. Bond Lengths (Å) and Angles (deg) for **23**

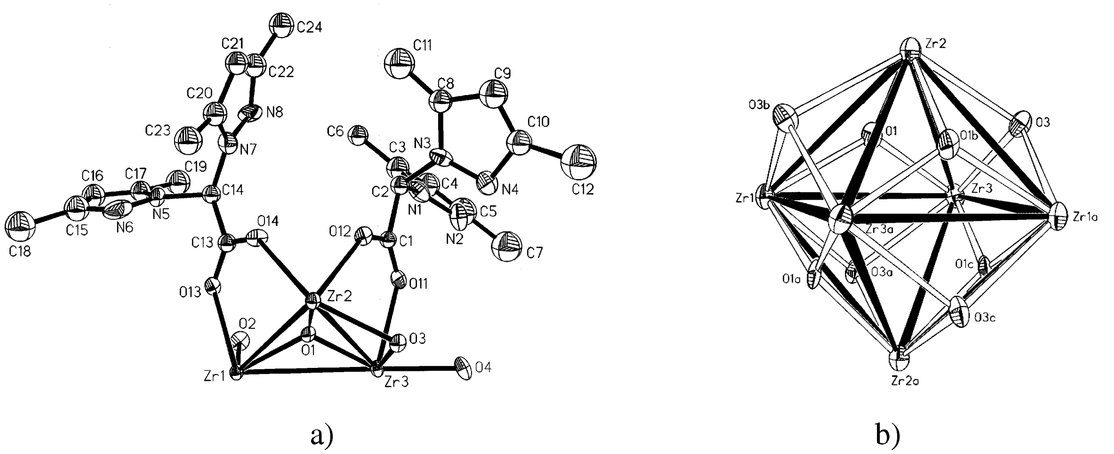
bond distances (Å)		bond angle (deg)	
Zr1−Zr2	3.497(2)	Zr2−Zr1−Zr3	59.82(3)
Zr2−Zr3	3.503(2)	Zr2−Zr1−Zr2^a	89.18(7)
Zr1−Zr3	3.528(2)	Zr3−Zr1−Zr3^b	90.19(7)
Zr1−O1	2.08(1)	Zr1−Zr2−Zr1^a	90.82(7)
Zr1−O2	2.19(1)	Zr1−Zr2−Zr3	60.53(3)
Zr1−O13	2.22(1)	Zr3−Zr2−Zr3^b	91.01(7)
Zr1−O3^a	2.23(1)	Zr2−Zr3−Zr2^a	88.99(7)
Zr2−O1	2.05(1)	Zr2−Zr3−Zr1	59.65(3)
Zr2−O12	2.20(1)	Zr1−Zr3−Zr1^a	89.81(7)
Zr2−O14	2.23(1)	Zr1−O1−Zr2	115.5(5)
Zr2−O3	2.28(1)	Zr2−O1−Zr3	116.5(5)
Zr3−O1	2.06(1)	Zr1−O1−Zr3	116.7(4)
Zr3−O3	2.25(1)	Zr1−O3−Zr2^a	101.4(4)
Zr3−O4	2.17(1)	Zr1−O3−Zr3^a	103.6(4)
Zr3−O11	2.30(1)	Zr2−O3−Zr3	101.0(5)

[a] Symmetry transformations used to generate equivalent atoms: $-x + {}^1/_4, y + {}^5/_4, z$. [b] Symmetry transformations used to generate equivalent atoms: $-x + {}^1/_4, y, -z + {}^1/_4$.

the tetrameric lithium compound [{Li(bdmpza)(H$_2$O)}$_4$],[3a] where the $\Delta\nu_{\mathrm{asym-sym}}$ was 180 cm^{-1}, revealing the versatility of the bdmpza and related ligands in their ability to coordinate to the metal centers. In addition, other bands of interest at 3550 and 3433 cm^{-1}, which were assigned to ν(OH) of the terminal and bridging groups, respectively, were observed. This structural disposition was corroborated by means of an XRD study (see below).

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **23** show single sets of resonances for the pyrazole rings, indicating that both pyrazoles from each ligand, at least in solution, are equivalent. The molecular structure of this complex was determined by XRD, and the structure is shown in Figure 7. Significant bond distances and angles are listed in Table 4. The cluster consists of six zirconium atoms in an octahedral disposition with eight μ_3-OH groups, one per face, and eight OH terminal groups, two per equatorial zirconium atom. Finally, all of the edges of the Zr$_6$ octahedron are bridged by bdmpza ligands in a κ^2-O,O bridged mode (see Figure 8a). This compound contains the Zr$_6$(μ_3-OH)$_8$ cluster core with the μ_3-OH groups capping the triangular faces of a Zr$_6$ octahedron (see Figure 8b).

The angles between the adjacent zirconium atoms are either 60° or 90°. The O−Zr−O angles range from 69.8(4) to 122.4(6)°, and the Zr−O−Zr angles range from 101.0(5) to 116.6(4)° in the Zr$_6$(μ_3-OH) cluster core, which are normal.



a) b)

Figure 8. (a) Asymmetric unit of compound **23**. (b) Cluster core of compound **23**.

Table 5. Hydrogen Bonds for Compound **23**

D−H	d(D−H)	d(H···A)	<DHA	d(D···A)	symmetry[a]
O1−H1···Cl2	0.98	2.943	154.2	3.849	$0.25 - x, 1.25 - y, z$
O2−H2···O100	0.82	2.031	149.4	2.768	$0.25 - x, 1.25 - y, z$
O3−H3···O100	0.98	1.784	158.4	2.719	x, y, z
O4−H4···Cl1	0.82	2.524	116.0	2.977	x, y, z
O100−H10A···N6	0.85	2.145	138.8	2.841	$x, 1.25 - y, 0.25 - z$
O100−H10B···Cl1	0.85	2.459	161.0	3.275	x, y, z

[a] Symmetry operation for A.

The Zr−Zr distances range from 3.497(2) to 3.528(2) Å, which are normal for this type of cluster.[7a] The crystal is stabilized by an extensive hydrogen-bonding network, and the geometrical features of this system are shown in Table 5. The bridging and terminal hydroxyl groups are involved in hydrogen bonds with the water and HCl molecules (Figure 9).

In conclusion, we have prepared new mononuclear and binuclear zirconium and hafnium species that incorporate heteroscorpionate ligands and contain halide, hydroxide, and alkoxide ancillary ligands. These complexes constitute the first examples of this class of compounds. In addition, the hydrolysis of the alkoxide-containing complexes gives a zirconium cluster with a $Zr_6(\mu_3\text{-OH})_8$ cluster core and μ_3-OH groups capping the triangular faces of a Zr_6 octahedron.

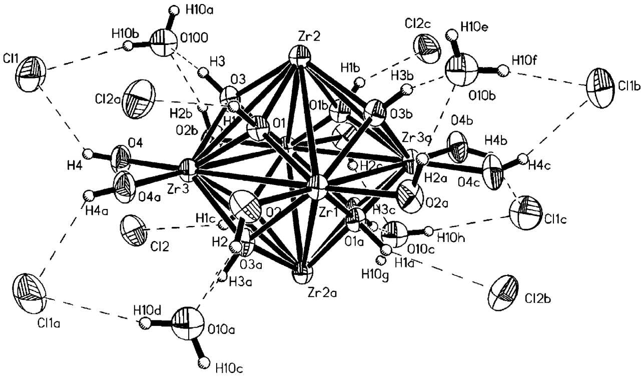


Figure 9. Hydrogen bonds (dashed lines) for compound **23**. The bdmpza molecules are omitted for clarity.

Acknowledgment. We gratefully acknowledge the financial support from the Dirección General de Enseñanza Superior e Investigación Científica, Spain (Grant no. BQU2002-04638-CO2-02) and the Junta de Comunidades de Castilla−La Mancha (Grant no. PAC-02-003, GC-02-010, and PAI-02-016).

Supporting Information Available: Details of data collection, refinement, atom coordinates, anisotropic displacement parameters, and bond lengths and angles for complexes **7**, **8**, and **23**. This material is available free of charge via the Internet at http://pubs.acs.org.

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