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Preparation of New Monoanionic "Scorpionate" Ligands: Synthesis and Structural Characterization of Titanium(IV) Complexes Bearing This Class of Ligand

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The preparation of new "scorpionate" ligands in the form of the lithium derivatives [{Li(bdmpzdta)(H_2O)}$_4$] (**1**) [bdmpzdta = bis(3,5-dimethylpyrazol-1-yl)dithioacetate], [Li(bdphpza)(H_2O)(THF)] (**2**) [bdphpza = bis(3,5-diphenylpyrazol-1-yl)acetate], and [Li(bdphpzdta)(H_2O)(THF)] (**3**) [bdphpzdta = bis(3,5-diphenylpyrazol-1-yl)dithioacetate] has been carried out. Furthermore, a series of titanium complexes has been prepared by reaction of $TiCl_4(THF)_2$ with the lithium reagents [{Li(bdmpza)(H_2O)}$_4$] (**4**) [bdmpza = bis(3,5-dimethylpyrazol-1-yl)acetate] and **1**. Under the appropriate experimental conditions neutral complexes, namely [$TiCl_3$(κ^3-bdmpza)] (**5**), [$TiCl_3$(κ^3-bdmpzdta)] (**6**), and [$TiCl_2$(κ^2-bdmpzdta)$_2$] (**7**), and cationic complexes, namely [$TiCl_2$(THF)(κ^3-bdmpza)]Cl (**8**) and [$TiCl_2$(THF)(κ^3-bdmpzdta)]Cl (**9**), were isolated. Complexes **8** and **9** undergo an interesting nucleophilic THF ring-opening reaction to give the corresponding alkoxide-containing species [$TiCl_2$(κ^3-bdmpza){$O(CH_2)_4Cl$}] (**10**) and [$TiCl_2$(κ^3-bdmpzdta){$O(CH_2)_4Cl$}] (**11**). A family of alkoxide-containing complexes of general formulas [$TiCl_2$(κ^3-bdmpza)(OR)] [R = Me (**12**); R = Et (**14**); R = ^{i}Pr (**16**); R = ^{t}Bu (**18**)] and [$TiCl_2$(κ^3-bdmpzdta)(OR)] [R = Me (**13**); R = Et (**15**); R = ^{i}Pr (**17**)] was also prepared. The structures of these complexes have been determined by spectroscopic methods, and in addition, the X-ray crystal structures of **3**, **7**, **10**, and **11** were also established.

Introduction

Since Trofimenko's report of the firs tris(pyrazolyl)borate complexes in the late 1960s, scorpionate complexes of most metals in the periodic table have been prepared.[1] Our first studies in this field concerned the preparation of Tp- or Tp*-containing niobium complexes of stoichiometry TpNb(Cl)$_2$(RC≡CR′) or Tp*Nb(O)(Cl)(OR) [Tp = hydridotris(pyrazol-1-yl)borate, Tp* = hydridotris(3,5-dimethylpyrazol-1-yl)borate].[2] We have subsequently been interested in the synthesis of new "heteroscopionate" ligands[3] with pyrazole rings related to the tris(pyrazol-1-yl)methane system,[4a,b] where one of the pyrazole groups has been replaced by a carboxylate or ethoxide group, namely bis(3,5-dimethylpyrazol-1-yl)acetate (bdmpza) and 2,2-bis(3,5-dimethylpyrazol-1-yl)ethoxide (bdmpze), to provide a small degree of steric hindrance and considerable coordinative flexibility. These compounds were found to be excellent reagents for the introduction of

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scorpionate ligands into niobium complexes, and a series of alkyne-containing niobium complexes was isolated and charaterized.[5] These compounds have an interesting dynamic behavior in solution, and this was studied by variable-temperature NMR techniques. More recently, we extended the range of complexes to include group 4 metals[6] and, moreover, an interesting nucleophilic THF ring-opening process was discovered that gave an alkoxide species. A preliminary study of the ethylene polymerization activities of several of the titanium complexes was also carried out. With this aim still in mind we are now interested in extending the preparation of new, related heteroscorpionate ligands. We describe here the synthesis and characterization of three new species in the form of the lithium derivatives with both acetate and dithioacetate groups. In addition, the reactivity of both $[\{Li(bdmpza)(H_2O)\}_4]$ and $[\{Li(bdmpzdta)(H_2O)\}_4]$ toward $TiCl_4(THF)_2$ was also studied. Preliminary results of this work have been published previously.[6]

Experimental Section

All 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 matrix. Infrared spectra were obtained in the region 4000−200 cm^{-1}, using a Perkin-Elmer 883 spectrophotometer. ^1H, ^{13}C, and ^7Li 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 complex $TiCl_4(THF)_2$ was purchased from Aldrich. The compounds bis(3,5-dimethylpyrazol-1-yl)methane (bdmpzm) and bis(3,5-diphenylpyrazol-1-yl)methane (bdphpzm) and the complex $[\{Li(bdmpza)(H_2O)\}_4]$ (**4**) were prepared as reported previously.[3a,5,7]

Synthesis of $[\{Li(bdmpzdta)(H_2O)\}_4]$ (1). In a 250 mL Schlenk tube, bdmpzm (5 g, 24.5 mmol) was dissolved in dry THF (150 mL) and the solution cooled to −70 °C. A 1.6 M solution of Bu^nLi (15.3 mL, 24.5 mmol) in hexane was added, and the reaction solution was stirred for 45 min. CS_2 (1.5 mL, 24.5 mmol) was added to the reaction mixture, and the temperature was slowly allowed to reach 0 °C. After 1 h the solvent was removed under vacuum and an orange solid was obtained. This solid was crystallized from a mixture of THF/hexane. Yield: 95%. (Anal. Found: C, 47.2; H, 5.3; N, 18.0. Calcd for $C_{12}H_{17}LiN_4OS_2$: C, 47.3; H, 5.6; N, 18.4.) ^1H NMR (DMSO, 293 K): $\delta = 6.78$ (s, 1 H, CH), 5.71 (s, 2 H, H^4), 2.02 (s, 6 H, Me^3), 2.18 (s, 6 H, Me^5), 3.36 (s, 2 H, H_2O). $^{13}C\{^1H\}$ NMR (DMSO): $\delta = 86.6$ (CH), 144.9, 140.4 (C^{5or3}), 105.2 (C^4), 11.9 (Me^3), 13.6 (Me^5), 273.9 (CS_2^-). ^7Li NMR (DMSO): $\delta = 1.24$ (s). IR (Nujol mull, cm^{-1}): 1562 ν(C=N), 1081 $\nu_{asym}(CS_2^-)$, 879 $\nu_{sym}(CS_2^-)$. Mass spectrum [FAB (*m/z* assignment, % intensity)]: 865 $[Li_4(bdmpzdta)_3]$, 15; 579 $[Li_3(bdmpzdta)_2]$, 25; 293 $[Li_2(bdmpzdta)]$, 100.

Synthesis of $[Li(bdphpza)(H_2O)(THF)]$ (2). In a 250 mL Schlenk tube, bdphpzm (5 g, 11 mmol) was dissolved in dry THF (150 mL) and the solution cooled to −70 °C. A 1.6 M solution of Bu^nLi (7 mL, 11 mmol) in hexane was added, and the reaction solution was stirred for 45 min. CO_2 was added to the reaction mixture, and the temperature was slowly allowed to reach 0 °C. After 1 h the solvent was removed under vacuum and a white solid was obtained. This solid was crystallized from a mixture of THF/hexane. Yield: 93%. (Anal. Found: C, 72.9; H, 5.5; N, 9.4. Calcd for $C_{36}H_{33}LiN_4O_4$: C, 73.0; H, 5.6; N, 9.4.) ^1H NMR (DMSO, 293 K): $\delta = 7.80-7.20$ (m, 20 H, Ph), 6.50 (s, 1 H, CH), 6.79 (s, 2 H, H^4), 3.58 (m, 4 H, THF), 1.73 (m, 4 H, THF), 3.38 (s, 2 H, H_2O). $^{13}C\{^1H\}$ NMR (DMSO): $\delta = 74.1$ (CH), 147.7, 145.0 (C^{3or5}), 104.1 (C^4), 136.1−124.9 (Ph), 166.4 (CO_2^-), 67.7, 25.8 (THF). ^7Li NMR (DMSO): $\delta = 1.26$ (s). IR (Nujol mull, cm^{-1}): 1569 ν(C=N), 1632 $\nu_{asym}(CO_2^-)$, 1450 $\nu_{sym}(CO_2^-)$. Mass spectrum [FAB (*m/z* assignment, % intensity)]: 503 $[M - H_2O - THF]$, 25; 453 $[M - H_2O - THF - LiCO_2]$, 15.

Synthesis of $[Li(bdphpzdta)(H_2O)(THF)]$ (3). In a 250 mL Schlenk tube, bdphpzm (5 g, 11 mmol) was dissolved in dry THF (150 mL) and the solution cooled to −70 °C. A 1.6 M solution of Bu^nLi (7 mL, 11 mmol) in hexane was added, and the solution was stirred for 45 min. CS_2 (0.7 mL, 11 mmol) was added to the reaction mixture, and the temperature was slowly allowed to reach 0 °C. After 1 h the solvent was removed under vacuum and a brown solid was obtained. This solid was crystallized from a mixture of THF/hexane. Yield: 90%. (Anal. Found: C, 69.4; H, 5.4; N, 9.1. Calcd for $C_{36}H_{33}LiN_4O_2S_2$: C, 69.2; H, 5.3; N, 9.0.) ^1H NMR (DMSO, 293 K): $\delta = 7.80-7.20$ (m, 20 H, Ph), 7.05 (s, 1 H, CH), 6.76 (s, 2 H, H^4), 3.63 (m, 4 H, THF), 1.73 (m, 4 H, THF), 3.38 (s, 2 H, H_2O). $^{13}C\{^1H\}$ NMR (DMSO): $\delta = 76.1$ (CH), 149.7, 146.0 (C^{3or5}), 104.1 (C^4), 134.1−125.9 (Ph), 275.3 (CS_2^-), 67.7, 25.8 (THF). ^7Li NMR (DMSO): $\delta = 1.26$ (s). IR (Nujol mull, cm^{-1}): 1552 ν(C=N), 1078 $\nu_{asym}(CS_2^-)$, 831 $\nu_{sym}(CS_2^-)$. Mass spectrum [FAB (*m/z* assignment, % intensity)]: 534 $[M - H_2O - THF]$, 20; 453 $[M - H_2O - THF - LiCS_2]$, 10.

Synthesis of $[TiCl_3(\kappa^3\text{-bdmpza})]$ (5). A solution of $TiCl_4(THF)_2$ (0.800 g, 2.40 mmol) in CH_2Cl_2 (50 mL) was cooled to −30 °C, and **4** (0.608 g, 0.60 mmol) was added with vigorous stirring. The solution turned from yellow to red, and a white precipitate was formed. After 12 h at −30 °C the mixture was filtered to give a red solution, which was evaporated to dryness to yield complex **5** as a red solid. Yield: 91%. (Anal. Found: C, 36.1; H, 3.9; N, 14.1. Calcd for $C_{12}H_{15}Cl_3N_4O_2Ti$: C, 35.9; H, 3.7; N, 13.9.) ^1H NMR ($CDCl_3$, 293 K): $\delta = 6.71$ (s, 1 H, CH), 6.07 (s, 2 H, H^4), 2.69 (s, 6 H, Me^3), 2.51 (s, 6 H, Me^5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 66.6$ (CH), 155.3, 141.1 (C^{3or5}), 108.7 (C^4), 15.9 (Me^3), 11.1 (Me^5), 162.0 (CO_2^-). IR (Nujol mull, cm^{-1}): 1705 $\nu_{asym}(CO_2^-)$, 1464 $\nu_{sym}(CO_2^-)$, 360 ν(Ti−Cl). Mass spectrum [FAB (*m/z* assignment, % intensity)]: 364 $[M - Cl]$, 25; 313 $[M - 2Cl - O]$, 100.

Synthesis of $[TiCl_3(\kappa^3\text{-bdmpzdta})]$ (6). To a solution of $TiCl_4(THF)_2$ (0.800 g, 2.40 mmol) in CH_2Cl_2 (50 mL) was added **1** (0.730 g, 0.60 mmol). The solution turned from yellow to red, and a white precipitate was formed. After 12 h at room temperature the mixture was filtered to give a red solution, which was evaporated to dryness

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to yield complex **6** as a red solid. Yield: 91%. (Anal. Found: C, 33.5; H, 3.9; N, 13.1. Calcd for $C_{12}H_{15}Cl_3N_4S_2Ti$: C, 33.2; H, 3.5; N, 12.9.) ^{1}H NMR ($CDCl_3$, 293 K): $\delta = 7.39$ (s, 1 H, CH), 6.14 (s, 2 H, H^4), 2.78 (s, 6 H, Me^3), 2.53 (s, 6 H, Me^5). ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 78.6$ (CH), 155.6, 143.1 (C^{3or5}), 108.5 (C^4), 15.8 (Me^3), 11.1 (Me^5), 232.0 (CS_2^-). IR (Nujol mull, cm^{-1}): 1070 $\nu_{asym}(CS_2^-)$, 820 $\nu_{sym}(CS_2^-)$, 360 ν(Ti−Cl).

Synthesis of [$TiCl_2$(κ^2-bdmpzdta)$_2$] (7). A solution of $TiCl_4(THF)_2$ (0.800 g, 2.40 mmol) in CH_2Cl_2 (50 mL) was cooled to −30 °C, and **1** (0.730 g, 0.60 mmol) was added with vigorous stirring. The solution turned from yellow to red, and a white precipitate was formed. After 12 h at −30 °C the mixture was filtered to give a red solution, which was evaporated to dryness to yield a mixture of **6** and **7** as a red solid. Compound **7** was isolated by crystallization from CH_2Cl_2. Yield: 25%. (Anal. Found: C, 42.7; H, 4.1; N, 16.3. Calcd for $C_{24}H_{30}Cl_2N_8S_4Ti$: C, 42.5; H, 4.4; N, 16.5.) ^{1}H NMR ($CDCl_3$, 293 K): $\delta = 7.38$ (s, 1 H, CH), 6.10 (s, 1 H, H^4), 6.07 (s, 1 H, H$^{4'}$), 2.92 (s, 3 H, Me^3), 2.78 (s, 3 H, Me$^{3'}$), 2.51 (s, 3 H, Me^5), 2.50 (s, 3 H, Me$^{5'}$). ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 80.1$ (CH), 155.2, 154.4, 141.8, 141.2 (C$^{3or3'or5or5'}$), 108.9, 108.4 (C$^{4or4'}$), 17.0, 16.5 (Me$^{3,3'}$), 11.5, 11.3 (Me$^{5,5'}$), 230.5 (CS_2^-). IR (Nujol mull, cm^{-1}): 1043 $\nu_{asym}(CS_2^-)$, 885 $\nu_{sym}(CS_2^-)$, 318 ν(Ti−Cl).

Synthesis of [$TiCl_2$(THF)(κ^3-bdmpza)]Cl (8). A solution of [$TiCl_3$(bdmpza)] (**5**) (0.500 g, 1.24 mmol) in THF (50 mL) was stirred at 35 °C for 24 h. The solution was concentrated under vacuum, and after extraction with dichloromethane (40 mL) and evaporation of the solvent, an orange solid was isolated. Yield: 89%. (Anal. Found: C, 40.2; H, 4.5; N, 12.1. Calcd for $C_{16}H_{23}Cl_3N_4O_3Ti$: C, 40.6; H, 4.9; N, 11.8.) ^{1}H NMR ($CDCl_3$, 293 K): $\delta = 7.36$ (s, 1 H, CH), 6.45 (s, 1 H, H^4), 6.41 (s, 1 H, H$^{4'}$), 2.97 (s, 3 H, Me^3), 2.87 (s, 3 H, Me$^{3'}$), 2.87 (s, 3 H, Me^5), 2.86 (s, 3 H, Me$^{5'}$), 3.95 (m, 4 H, THF), 2.10 (m, 4 H, THF). ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 67.6$ (CH), 154.9, 153.7, 143.0, 142.9 (C$^{3or3'or5or5'}$), 108.6, 108.3 (C$^{4or4'}$), 15.4, 14.9 (Me$^{3,3'}$), 10.8, 10.7 (Me$^{5,5'}$), 163.2 (CO_2^-), 68.1, 26.2 (THF). IR (Nujol mull, cm^{-1}): 1650 $\nu_{asym}(CO_2^-)$, 1459 $\nu_{sym}(CO_2^-)$, 376 ν(Ti−Cl). Mass spectrum [FAB (*m*/*z* assignment, % intensity)]: 437 [M], 100; 364 [M − THF], 40.

Synthesis of [$TiCl_2$(THF)(κ^3-bdmpzdta)]Cl (9). A solution of [$TiCl_3$(bdmpzdta)] (**6**) (0.500 g, 1.15 mmol) in THF (50 mL) was stirred at 35 °C for 24 h. The solution was concentrated under vacuum, and after extraction with dichloromethane (40 mL) and evaporation of the solvent, a red solid was isolated. Yield: 92%. (Anal. Found: C, 38.3; H, 4.7; N, 11.4. Calcd for $C_{16}H_{23}Cl_3N_4OS_2Ti$: C, 38.0; H, 4.6; N, 11.1.) ^{1}H NMR ($CDCl_3$, 293 K): $\delta = 7.34$ (s, 1 H, CH), 6.12 (s, 1 H, H^4), 6.07 (s, 1 H, H$^{4'}$), 2.83 (s, 3 H, Me^3), 2.62 (s, 3 H, Me$^{3'}$), 2.57 (s, 3 H, Me^5), 2.50 (s, 3 H, Me$^{5'}$), 3.73 (m, 4 H, THF), 1.85 (m, 4 H, THF). ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 79.9$ (CH), 155.6, 153.7, 144.8, 142.2 (C$^{3or3'or5or5'}$), 108.1, 108.5 (C$^{4or4'}$), 16.2, 15.3 (Me$^{3,3'}$), 11.4, 11.3 (Me$^{5,5'}$), 234.0 (CS_2^-), 68.0, 25.6 (THF). IR (Nujol mull, cm^{-1}): 1052 $\nu_{asym}(CS_2^-)$, 889 $\nu_{sym}(CS_2^-)$, 320 ν(Ti−Cl).

Synthesis of [$TiCl_2$(κ^3-bdmpza){$O(CH_2)_4Cl$}] (10). A solution of [$TiCl_3$(bdmpza)] (**5**) (0.500 g, 1.24 mmol) in THF (50 mL) was refluxed for 8 h. The solution was concentrated under vacuum, and after extraction with dichloromethane (40 mL) and evaporation of the solvent, a yellow solid was isolated. Yield: 93%. This solid was crystallized from a mixture of THF/hexane. (Anal. Found: C, 40.8; H, 4.7; N, 11.6. Calcd for $C_{16}H_{23}Cl_3N_4O_3Ti$: C, 40.6; H, 4.9; N, 11.8.) ^{1}H NMR ($CDCl_3$, 293 K): $\delta = 6.59$ (s, 1 H, CH), 6.07 (s, 2 H, H^4), 2.72 (s, 3 H, Me^3), 2.57 (s, 3 H, Me$^{3'}$), 2.45 (s, 6 H, Me$^{5,5'}$), 4.92 (m, 2 H, H^a), 2.07 (m, 4 H, H^{b,c}), 3.67 (t, 2 H, H^d). ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 66.5$ (CH), 154.7, 153.3, 141.4, 140.5 (C$^{3or3'or5or5'}$), 108.6, 108.0 (C$^{4or4'}$), 15.2, 14.8 (Me$^{3,3'}$), 11.1, 10.1 (Me$^{5,5'}$), 163.4 (CO_2^-), 86.2 (C^a), 28.8 (C^b), 28.9(C^c), 44.6 (C^d). IR (Nujol mull, cm^{-1}): 1699 $\nu_{asym}(CO_2^-)$, 1459 $\nu_{sym}(CO_2^-)$, 314 ν(Ti−Cl).

Synthesis of [$TiCl_2$(κ^3-bdmpzdta){$O(CH_2)_4Cl$}] (11). A solution of [$TiCl_3$(bdmpzdta)] (**6**) (2.000 g, 5.98 mmol) in THF (75 mL) was refluxed for 8 h. The solution was concentrated under vacuum, and after extraction with dichloromethane (40 mL) and evaporation of the solvent, a dark red solid was isolated. This solid was crystallized from a mixture of CH_2Cl_2/hexane. Yield: 90%. (Anal. Found: C, 37.8; H, 4.9; N, 10.9. Calcd for $C_{16}H_{23}Cl_3N_4OS_2Ti$: C, 38.0; H, 4.6; N, 11.1.) ^{1}H NMR ($CDCl_3$, 293 K): $\delta = 7.35$ (s, 1 H, CH), 6.12 (s, 1 H, H^4), 6.08 (s, 1 H, H$^{4'}$), 2.83 (s, 3 H, Me^3), 2.63 (s, 3 H, Me$^{3'}$), 2.49 (s, 3 H, Me^5), 2.51 (s, 3 H, Me$^{5'}$), 4.99 (m, 2 H, H^a), 2.15 (m, 4 H, H^{b,c}), 3.70 (t, 2 H, H^d). ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 79.9$ (CH), 155.5, 153.7, 144.7, 142.2 (C$^{3or3'or5or5'}$), 109.1, 108.5 (C$^{4or4'}$), 16.2, 15.3 (Me$^{3,3'}$), 11.4, 11.3 (Me$^{5,5'}$), 228.9 (CS_2^-), 86.1 (C^a), 29.0 (C^b), 29.1(C^c), 44.6 (C^d). IR (Nujol mull, cm^{-1}): 1065 $\nu_{asym}(CS_2^-)$, 814 $\nu_{sym}(CS_2^-)$, 316 ν(Ti−Cl). Mass spectrum [FAB (*m*/*z* assignment, % intensity)]: 470 [M − Cl], 20.

Synthesis of [$TiCl_2$(κ^3-bdmpza)(OMe)] (12a). A solution of [$TiCl_2$(κ^3-bdmpza){$O(CH_2)_4Cl$}] (**10**) (0.200 g, 0.42 mmol) in MeOH (50 mL) was stirred for 12 h at room temperature. The solvent was removed in vacuo, and by extraction with toluene, a yellow solid was obtained. Yield: 67%. (Anal. Found: C, 39.6; H, 4.2; N, 14.3. Calcd for $C_{13}H_{18}Cl_2N_4O_3Ti$: C, 39.3; H, 4.6; N, 14.1.) ^{1}H NMR ($CDCl_3$, 293 K): $\delta = 6.94$ (s, 1 H, CH), 5.84 (s, 2 H, H^4), 2.18 (s, 6 H, Me^3), 2.07 (s, 6 H, Me^5), 3.87 (s, 3 H, OMe). ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 73.1$ (CH), 148.5, 141.2 (C^{3or5}), 107.5 (C^4), 10.9 (Me^3), 13.5 (Me^5), 163.3 (CO_2^-), 67.9 (OMe). IR (Nujol mull, cm^{-1}): 1761 $\nu_{asym}(CO_2^-)$, 1525 $\nu_{sym}(CO_2^-)$, 658 ν(Ti−O), 304 ν(Ti−Cl).

Synthesis of [$TiCl_2$(κ^3-bdmpza)(OMe)] (12b). A solution of [$TiCl_3$(κ^3-bdmpza)] (**5**) (0.500 g, 1.24 mmol) in MeOH (75 mL) was stirred for 12 h at room temperature. The solvent was removed in vacuo, and by extraction with toluene, a yellow solid was obtained. Yield: 82%. (Anal. Found: C, 39.3; H, 4.2; N, 14.3. Calcd for $C_{13}H_{18}Cl_2N_4O_3Ti$: C, 39.3; H, 4.6; N, 14.1.) ^{1}H NMR ($CDCl_3$, 293 K): $\delta = 6.62$ (s, 1 H, CH), 6.03 (s, 1 H, H^4), 6.02 (s, 1 H, H$^{4'}$), 2.71 (s, 3 H, Me^3), 2.55 (s, 3 H, Me$^{3'}$), 2.47 (s, 3 H, Me^5), 2.48 (s, 3 H, Me$^{5'}$), 4.69 (s, 3 H, OMe). ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 68.5$ (CH), 154.9, 153.5, 129.0, 128.1 (C$^{3or3'or5or5'}$), 108.7, 108.1 (C$^{4or4'}$), 14.7, 15.3 (Me$^{3,3'}$), 11.1, 11.2 (Me$^{5,5'}$), 163.6 (CO_2^-), 74.3 (OMe). IR (Nujol mull, cm^{-1}): 1761 $\nu_{asym}(CO_2^-)$, 1525 $\nu_{sym}(CO_2^-)$, 658 ν(Ti−O), 304 ν(Ti−Cl).

Synthesis of [$TiCl_2$(κ^3-bdmpzdta)(OMe)] (13a). A solution of [$TiCl_2$(κ^3-bdmpzdta){$O(CH_2)_4Cl$}] (**11**) (0.200 g, 0.40 mmol) in MeOH (50 mL) was stirred for 12 h at room temperature. The solvent was removed in vacuo, and by extraction with toluene, a dark red solid was obtained. Yield: 85%. (Anal. Found: C, 36.6; H, 4.4; N, 13.3. Calcd for $C_{13}H_{18}Cl_2N_4OS_2Ti$: C, 36.4; H, 4.2; N, 14.0.) ^{1}H NMR ($CDCl_3$, 293 K): $\delta = 7.32$ (s, 1 H, CH), 6.04 (s, 2 H, H^4), 2.66 (s, 6 H, Me^3), 2.47 (s, 6 H, Me^5), 4.41 (s, 3 H, OMe). ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 79.5$ (CH), 153.5, 141.8 (C^{3or5}), 108.3 (C^4), 14.7 (Me^3), 11.2 (Me^5), 233.2 (CS_2^-), 68.5 (OMe). IR (Nujol mull, cm^{-1}): 1117 $\nu_{asym}(CS_2^-)$, 835 $\nu_{sym}(CS_2^-)$, 635 ν(Ti−O), 326 ν(Ti−Cl).

Synthesis of [$TiCl_2$(κ^3-bdmpza)(OEt)] (14a). The synthetic procedure was the same as for complex **12a** using EtOH. **14a** was isolated as a yellow solid. Yield: 65%. (Anal. Found: C, 41.0; H, 4.9; N, 13.5. Calcd for $C_{14}H_{20}Cl_2N_4O_3Ti$: C, 40.9; H, 4.9; N, 13.6.) ^{1}H NMR ($CDCl_3$, 293 K): $\delta = 7.01$ (s, 1 H, CH), 5.89 (s, 2 H, H^4), 2.51 (s, 6 H, Me^3), 2.25 (s, 6 H, Me^5), 4.34 (q, 2 H, $^3J_{HH}$ = 7.0 Hz, O*CH*$_2$CH$_3$), 1.28 (t, 3 H, $^3J_{HH}$ = 7.0 Hz, OCH$_2$*CH*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 71.9 (CH), 148.1, 142.7 (C^{3or5}), 107.2 (C^4), 11.3 (Me^3), 13.0 (Me^5), 163.8 (CO$_2^-$), 63.1 (O*CH*$_2$CH$_3$), 14.18 (OCH$_2$*CH*$_3$). IR (Nujol mull, cm^{-1}): 1712 ν_{asym}(CO$_2^-$), 1498 ν_{sym}(CO$_2^-$), 682 ν(Ti−O), 325 ν(Ti−Cl).

Synthesis of [TiCl$_2$(κ^3-bdmpza)(OEt)] (14b). The synthetic procedure was the same as for complex **12b** using EtOH. **14b** was isolated as a yellow solid. Yield: 85%. (Anal. Found: C, 41.0; H, 5.0; N, 13.8. Calcd for $C_{14}H_{20}Cl_2N_4O_3Ti$: C, 40.9; H, 4.9; N, 13.6.) ^{1}H NMR (CDCl$_3$, 293 K): δ = 6.61 (s, 1 H, CH), 6.01 (s, 1 H, H^4), 6.00 (s, 1 H, H$^{4'}$), 2.70 (s, 3 H, Me^3), 2.55 (s, 3 H, Me$^{3'}$), 2.43 (s, 3 H, Me^5), 2.45 (s, 3 H, Me$^{5'}$), 4.94 (q, 2 H, $^3J_{HH}$ = 7.0 Hz, O*CH*$_2$CH$_3$), 1.50 (t, 3 H, $^3J_{HH}$ = 7.0 Hz, OCH$_2$*CH*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 66.4 (CH), 154.8, 153.5, 129.0, 128.1 (C$^{3or3'or5or5'}$), 108.6, 108.0 (C$^{4or4'}$), 15.3, 16.8 (Me$^{3,3'}$), 10.9, 11.1 (Me$^{5,5'}$), 163.6 (CO$_2^-$), 83.5 (O*CH*$_2$CH$_3$), 16.8 (OCH$_2$*CH*$_3$). IR (Nujol mull, cm^{-1}): 1712 ν_{asym}(CO$_2^-$), 1498 ν_{sym}(CO$_2^-$), 682 ν(Ti−O), 325 ν(Ti−Cl).

Synthesis of [TiCl$_2$(κ^3-bdmpzdta)(OEt)] (15a). The synthetic procedure was the same as for complex **13a** using EtOH. **15a** was isolated as a dark red solid. Yield: 90%. (Anal. Found: C, 37.8; H, 4.3; N, 12.5. Calcd for $C_{14}H_{20}Cl_2N_4OS_2Ti$: C, 37.9; H, 4.5; N, 12.6.) ^{1}H NMR (CDCl$_3$, 293 K): δ = 7.27 (s, 1 H, CH), 5.98 (s, 2 H, H^4), 2.62 (s, 6 H, Me^3), 2.41 (s, 6 H, Me^5), A = 4.65, B = 4.55, X = 1.33 [ABX$_3$, J_{AB} = 12.6 Hz, $J_{AX} = J_{BX}$ = 7.0 Hz, OEt]. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 79.4 (CH), 153.3, 140.8 (C^{3or5}), 108.2 (C^4), 18.4 (Me^3), 14.8 (Me^5), 232.5 (CS$_2^-$), 83.1 (O*CH*$_2$CH$_3$), 25.1 (OCH$_2$*CH*$_3$). IR (Nujol mull, cm^{-1}): 1090 ν_{asym}(CS$_2^-$), 843 ν_{sym}(CS$_2^-$), 643 ν(Ti−O), 355 ν(Ti−Cl).

Synthesis of [TiCl$_2$(κ^3-bdmpza)(O^{i}Pr)] (16b). The synthetic procedure was the same as for complex **12b** using ^{i}PrOH. **16b** was isolated as a yellow solid. Yield: 75%. (Anal. Found: C, 42.6; H, 5.0; N, 13.9. Calcd for $C_{15}H_{22}Cl_2N_4O_3Ti$: C, 42.4; H, 5.2; N, 13.2.) ^{1}H NMR (CDCl$_3$, 293 K): δ = 6.49 (s, 1 H, CH), 6.02 (s, 1 H, H^4), 6.01 (s, 1 H, H$^{4'}$), 2.73 (s, 3 H, Me^3), 2.60 (s, 3 H, Me$^{3'}$), 2.44 (s, 3 H, Me^5), 2.45 (s, 3 H, Me$^{5'}$), 5.30 [m, 1 H, O*CH*(CH$_3$)$_2$], 1.52 [d, 6 H, $^3J_{HH}$ = 7.0 Hz, OCH(*CH*$_3$)$_2$]. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 66.8 (CH), 154.8, 153.3, 140.9, 139.8 (C$^{3or3'or5or5'}$), 108.6, 108.0 (C$^{4or4'}$), 15.0, 15.2 (Me$^{3,3'}$), 10.9, 11.1 (Me$^{5,5'}$), 163.6 (CO$_2^-$), 91.2 [O*CH*(CH$_3$)$_2$], 23.5 [OCH(*CH*$_3$)$_2$]. IR (Nujol mull, cm^{-1}): 1683 ν_{asym}(CO$_2^-$), 1474 ν_{sym}(CO$_2^-$), 698 ν(Ti−O), 314 ν(Ti−Cl).

Synthesis of [TiCl$_2$(κ^3-bdmpzdta)(O^{i}Pr)] (17a). The synthetic procedure was the same as for complex **13a** using ^{i}PrOH. **17a** was isolated as a dark red solid. Yield: 85%. (Anal. Found: C, 39.6; H, 4.7; N, 12.4. Calcd for $C_{15}H_{22}Cl_2N_4OS_2Ti$: C, 39.4; H, 4.8; N, 12.2.) ^{1}H NMR (CDCl$_3$, 293 K): δ = 7.32 (s, 1 H, CH), 6.00 (s, 2 H, H^4), 2.69 (s, 6 H, Me^3), 2.45 (s, 6 H, Me^5), 5.08 [m, 1 H, O*CH*(CH$_3$)$_2$], 1.40 [d, 6 H, $^3J_{HH}$ = 6.1 Hz, OCH(*CH*$_3$)$_2$]. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 79.3 (CH), 153.2, 140.6 (C^{3or5}), 108.1 (C^4), 15.2 (Me^3), 11.3 (Me^5), 232.4 (CS$_2^-$), 84.2 [O*CH*(CH$_3$)$_2$], 25.1 [OCH(*CH*$_3$)$_2$]. IR (Nujol mull, cm^{-1}): 1106 ν_{asym}(CS$_2^-$), 814 ν_{sym}(CS$_2^-$), 614 ν(Ti−O), 368 ν(Ti−Cl).

Synthesis of [TiCl$_2$(κ^3-bdmpza)(O^{t}Bu)] (18b). The synthetic procedure was the same as for complex **12b** using ^{t}BuOH. **18b** was isolated as a yellow solid. Yield: 90%. (Anal. Found: C, 44.1; H, 5.3; N, 13.0. Calcd for $C_{16}H_{24}Cl_2N_4O_3Ti$: C, 43.7; H, 5.5; N, 12.8.) ^{1}H NMR (CDCl$_3$, 293 K): δ = 6.53 (s, 1 H, CH), 6.02 (s, 1 H, H^4), 6.01 (s, 1 H, H$^{4'}$), 2.72 (s, 3 H, Me^3), 2.64 (s, 3 H, Me$^{3'}$), 2.44 (s, 3 H, Me^5), 2.45 (s, 3 H, Me$^{5'}$), 1.63 (s, 9 H, O^{t}Bu). ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 66.8 (CH), 154.7, 153.3, 140.7, 139.5 (C$^{3or3'or5or5'}$), 108.7, 107.9 (C$^{4or4'}$), 15.3, 15.5 (Me$^{3,3'}$), 10.9, 11.1 (Me$^{5,5'}$), 163.6 (CO$_2^-$), 29.9 [O*C* (CH$_3$)$_3$], 26.8 [OC(*CH*$_3$)$_3$]. IR (Nujol mull, cm^{-1}): 1662 ν_{asym}(CO$_2^-$), 1452 ν_{sym}(CO$_2^-$), 687 ν(Ti−O), 337 ν(Ti−Cl).

X-ray Structure Determinations for Complexes 3, 7, 10, and 11. Crystals of **10** were mounted at room temperature, but crystals of **3**, **7**, and **11** were mounted at low temperature in inert oil on a glass fiber. Intensity data were collected on a NONIUS-MACH3 diffractometer equipped with a graphite monochromator (Mo Kα radiation, λ = 0.710 73 Å) using an $\omega/2\theta$ scan. The final unit cell parameters were determined from 25 well-centered and refined by least-squares methods. Analysis of systematic absences in the data was consistent with the monoclinic space group $P2_1/c$ for compounds **3**, **10,** and **11** and $C2/c$ for **7**. The structures were solved by direct methods using the SHELXS computer program[8a] and refined on F^2 by full-matrix least squares (SHELXL-97).[8b] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in calculated positions and were refined with an overall isotropic temperature factor using a riding model, except the H$_2$O hydrogen for **7** which was located in a difference map and refined freely. Weights were optimized in the final cycles. Crystallographic data are given in Table 1. For complex **7**, the external CH$_2$Cl$_2$ molecules were disordered over two positions. Occupancies of chlorine atoms were refined initially and then fixed. Cl3 in complex **10** is in a disordered position (0.65 population). Complex **11** crystallizes with a dichloromethane molecule as solvent. Chlorine atoms in the CH$_2$Cl$_2$ molecule and THF-opened chain, except for Cl5, are in disordered positions.

Results and Discussion

First, we prepared a series of new heteroscorpionate ligands by following the method previously described[3a,5] for [{Li(bdmpza)(H$_2$O)}$_4$] (**4**) [bdmpza = bis(3,5-dimethylpyrazol-1-yl)acetate], which consisted of the reaction between a solution of the appropriate bis(pyrazol-1-yl)methane[7] in THF and 1 equiv of Bu^{n}Li followed by treatment with CO$_2$ or CS$_2$. These reactions gave rise to the lithium carboxylate or dithiocarboxylate compounds [{Li(bdmpzdta)(H$_2$O)}$_4$] (**1**) [bdmpzdta = bis(3,5-dimethylpyrazol-1-yl)dithioacetate], [Li(bdphpza)(H$_2$O)(THF)] (**2**) [bdphpza = bis(3,5-diphenylpyrazol-1-yl)acetate], and [Li(bdphpzdta)(H$_2$O)(THF)] (**3**)-[bdphpzdta = bis(3,5-diphenylpyrazol-1-yl)dithioacetate] as air-stable solids in good yields (ca. 93%) after the appropriate workup (see Scheme 1).

Compounds **1**−**3** were characterized by spectroscopic methods. The mass spectrum (FAB) of **1** indicates a tetranuclear formulation (see Experimental Section), and in accordance with the structure found for **4**,[3a,5] we propose an analogous arrangement consisting of tetrameric units with a cubanelike array, a tetrahedral disposition for the lithium atoms, and one coordinated position of this system occupied by an H$_2$O molecule (see Figure 1).

Although the reactions were carried out under rigorously anhydrous experimental conditions, the presence of adventitious moisture in the reaction mixture during the workup

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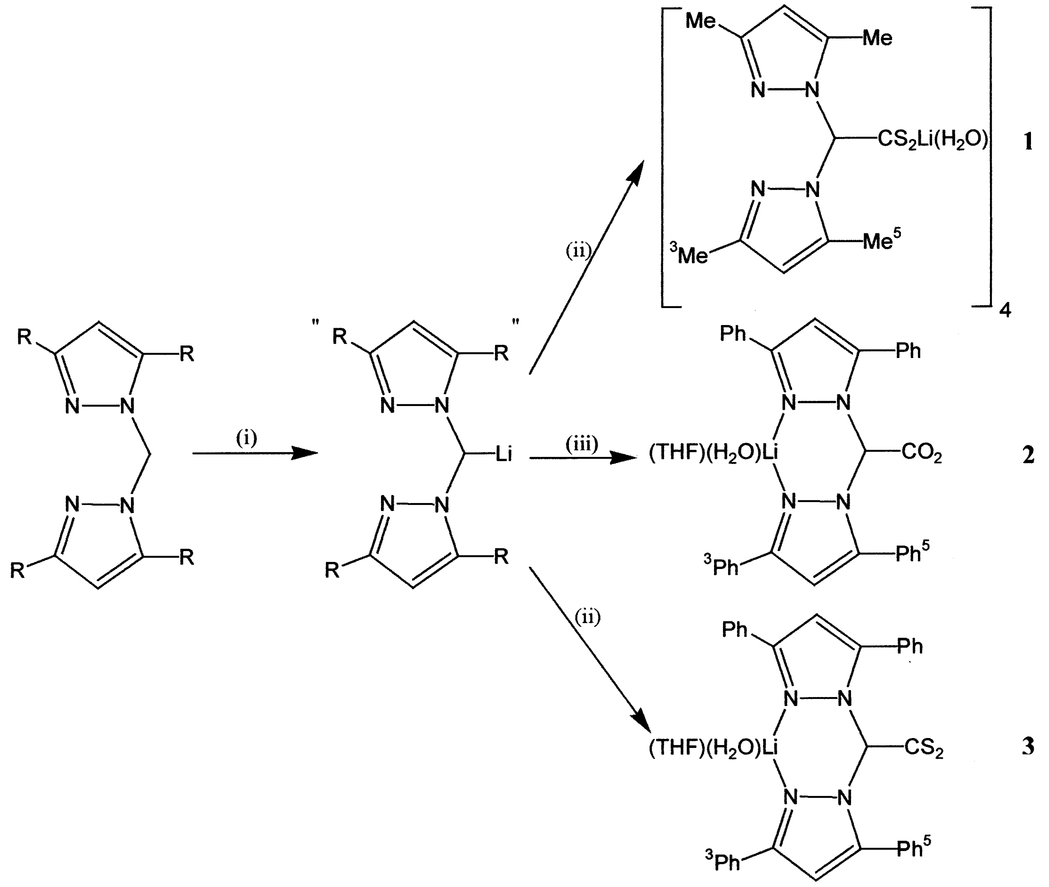
(8) (a) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467. (b) Sheldrick, G. M. *Program for the Refinement of Crystal Structures from Diffraction Data*; University of Göttingen: Göttingen, Germany, 1997.

Table 1. Crystal Data and Structure Refinement for **3**, **7**, **10**, and **11**

param	**3**	**7**	**10**	**11**
formula	$C_{36}H_{33}LiN_4O_{23}S_2$·THF	$C_{24}H_{30}Cl_2N_8S_4Ti$·$2SH_2$·$6CH_2Cl_2$	$C_{16}H_{23}Cl_3N_4O_3Ti$	$C_{16}H_{23}Cl_3N_4OS_2Ti$·$CH_2Cl_2$
fw	696.83	1257.3	473.63	590.68
T (K)	220(2)	210(2)	293(2)	200(2)
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$	$P2_1/c$	$P2_1/c$
a (Å)	11.084(3)	22.380(4)	7.987(1)	12.172(1)
b (Å)	23.701(9)	13.837(9)	16.209(1)	15.640(1)
c (Å)	14.659(4)	18.574(4)	16.996(1)	14.332(1)
β (deg)	104.47(3)	91.670(3)	100.47	112.62(1)
V (Å^3)	3717(2)	5749(3)	2163.7(3)	2519.3(3)
Z	4	4	4	4
D_c (g cm^{-3})	1.245	1.448	1.454	1.557
μ (mm^{-1})	1.86	1.049	0.789	1.054
F(000)	1472	2544	976	1208
cryst dimens (mm)	0.3 × 0.3 × 0.1	0.4 × 0.2 × 0.1	0.2 × 0.3 × 0.3	0.3 × 0.3 × 0.2
θ range (deg)	2.09−27.99	2.03−25.00	2.44−28.03	1.81−24.98
hkl ranges	$-14 \le h \le 14$	$-26 \le h \le 26$	$-10 \le h \le 10$	$-14 \le h \le 13$
	$0 \le k \le 31$	$0 \le k \le 16$	$0 \le k \le 21$	$0 \le k \le 18$
	$0 \le l \le 19$	$0 \le l \le 22$	$0 \le l \le 22$	$0 \le l \le 17$
no. of rflcns measd	9733	5206	5376	4628
no. of indep rflcns	9269	5037	5208	4435
no. of obsd rflcns	2418	2042	1761	2588
goodness-of-fit on F^2	1.025	0.967	0.961	0.999
final R indices [$I > 2\sigma(I)$][a]	R1 = 0.0796	R1 = 0.0843	R1 = 0.0861	R1 = 0.0569
	wR2 = 0.1287	wR2 = 0.2043	wR2 = 0.1600	wR2 = 0.1107
largest diff peak (e Å^{-3})	0.283/−0.307	0.704/−0.419	0.372/−0.376	0.356/−0.355

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

Scheme 1. Summary of the Reactions Leading to Compounds **1**−**3**[a]



procedure was probably responsible for the presence of the proposed coordinated water molecule. The ^1H NMR spectrum shows five singlets, which are assigned to CH, H^4, Me^3, and Me^5 of the pyrazole rings and H_2O. Homonuclear NOE (nuclear Overhauser enhancement) difference spectroscopy was also performed to confirm the assignment of the signals for the Me^3 and Me^5 groups. The $^{13}C\{^1H\}$ NMR spectrum exhibits only one set of resonances, as one would expect for the presence of two equivalent pyrazole rings in the molecule in solution. A $^1H-^{13}C$ heteronuclear correlation

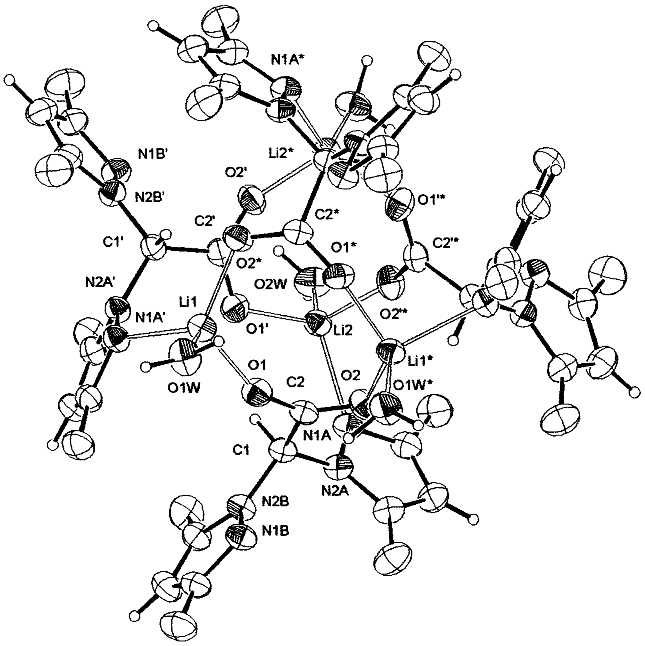


Figure 1. ORTEP drawing of the complex [{Li(bdmpza)(H$_2$O)}$_4$] (**4**).[3a,5]

(HETCOR) experiment was carried out and allowed us to assign the resonances corresponding to C^4, Me^3, and Me^5 of the pyrazole ring (see Experimental Section). Finally, the ^{7}Li NMR spectrum exhibits a singlet at δ 1.24 for the lithium atom. It is clear that in solution a structural disposition different from that in the solid state is present, a conclusion based on the equivalence of the two pyrazole rings established by NMR spectroscopy. The mass spectra (FAB) of **2** and **3** indicate a mononuclear formulation (see Experimental Section), which was corroborated by means of a crystal structure determination for **3**. An ORTEP view of the molecule with the atom labeling scheme is shown in Figure 2.

The geometry around the Li atom can be described as a distorted tetrahedron with two coordinated pyrazole rings, one molecule of THF, and one molecule of water. Both Li−N distances are in good agreement with others determined for lithium scorpionate or poly(pyrazolyl)methane complexes.[3a,4c]

The crystal is stabilized by interactions between two molecules involving a hydrogen bridge, as shown in Figure 3. This bridge results from the formation of intermolecular hydrogen bonds between the O1−HA and S1 atoms of the adjacent molecules [O1···S1′ = 3.170 Å and HA···S1′ = 1.987 Å; O1−HA···S1′ = 172.70° (the apex refers to the transformation $-x$, $-y$, $-z + 1$)]. The CS$_2$ group of the scorpionate ligand points toward the water molecule, and this suggests an intramolecular hydrogen bond between O1−HB···S2 [O1···S2 = 3.389 Å and HB···S2 = 2.815 Å; O1−HB···S2 = 135.01°].

It is worth noting the different solid structure found for complex **3** in comparison with that described for complex **4**.[3a,5] The scorpionate ligand acts in different manners in these two cases. In complex **3** a bidentate coordination through two nitrogen atoms of both pyrazole rings is observed and the CS$_2$ acts as a spectator group. In contrast, in the structure of **4** the scorpionate ligand behaves in a tridentate fashion, bridging three Li atoms through the two oxygen atoms of the carboxylate and a nitrogen atom of a pyrazole ring. Steric and/or electronic factors (the presence of phenyl groups instead of methyl groups on the pyrazole ring) are most likely responsible for the different behavior. The ^{1}H NMR spectra of **2** and **3** both exhibit three singlets, which are assigned to CH, H^4, and H$_2$O, and several multiplets, corresponding to Ph and THF groups. The ^{13}C{^{1}H} NMR spectra exhibit only

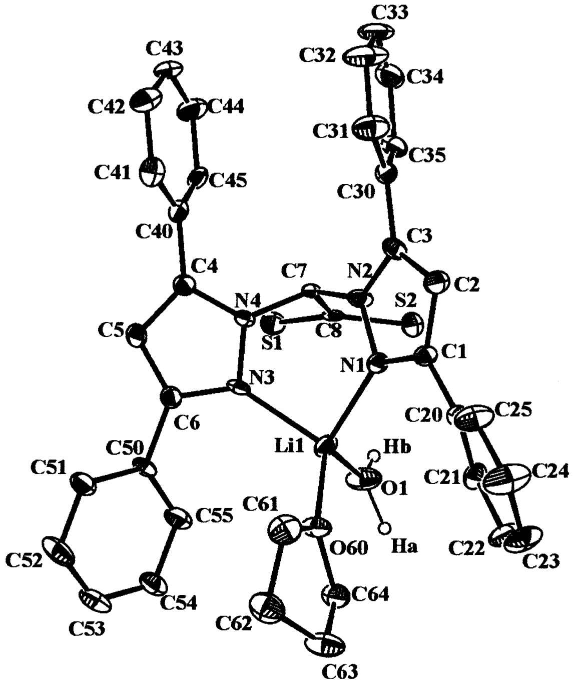


Figure 2. View of complex **3** (30% probability ellipsoids) with the atomic numbering scheme. Selected bond distances (Å) and angles (deg): S(1)−C(8), 1.663(7); S(2)−C(8), 1.655(7); O(1)−Li(1), 1.85(1); Li(1)−O(60), 1.94(1); Li(1)−N(1), 2.06(1); Li(1)−N(3), 2.07(1); C(7)−C(8), 1.556(9); O(1)−Li(1)−O(60), 103.7(6); O(1)−Li(1)−N(1), 114.7(7); O(60)−Li(1)−N(1), 115.8(7); O(1)−Li(1)−N(3), 118.9(7); O(60)−Li(1)−N(3), 114.6(7); N(1)−Li(1)−N(3), 89.5(5).

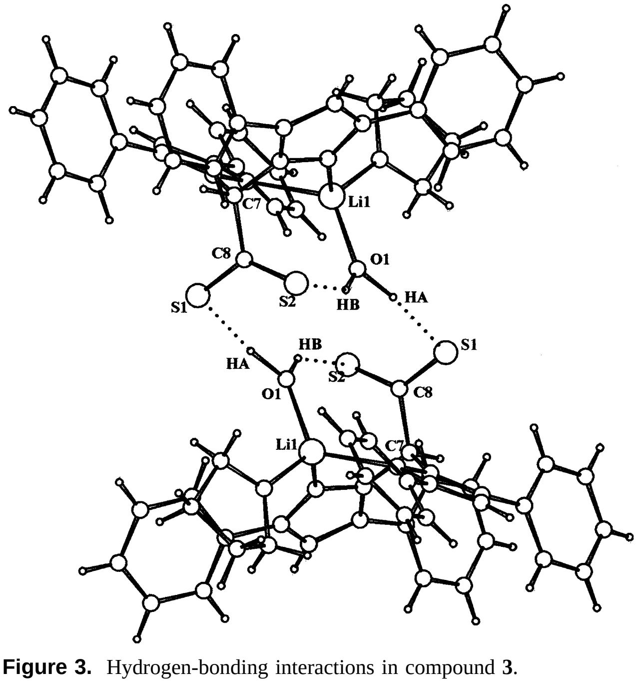
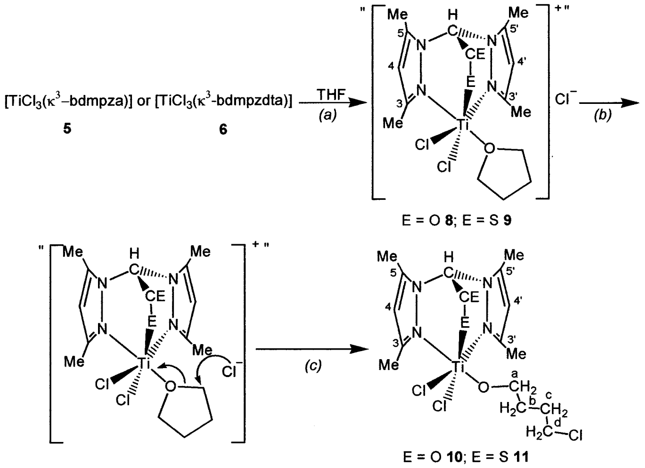


Figure 3. Hydrogen-bonding interactions in compound **3**.

Scheme 2. Proposed Reaction Pathway for the Formation of Complexes **10** and **11**



one set of resonances, which corresponds to two equivalent pyrazole rings (see Experimental Section).

In the second part of this work we focused our attention on the reactivity of the scorpionate-containing lithium derivates **1** and **4** toward $TiCl_4(THF)_2$. The aim of this study was to open new ways for the preparation of a new generation of non-cyclopentadienyl-based complexes of group 4 metals with nitrogen- and/or oxygen−sulfur-containing ligands. A number of chelating diamide[9] and dialkoxide[10] complexes have been described previously, and many of these systems are excellent catalyst precursors for the polymerization of α-olefins.

A set of different complexes was obtained by the treatment of solutions of $TiCl_4(THF)_2$ in CH_2Cl_2 with the appropriate lithium compound (**1** or **4**). It was found that when the reaction of $TiCl_4(THF)_2$ with **4** was carried out at −30 °C, the complex [$TiCl_3(\kappa^3$-bdmpza)] (**5**) was isolated after the appropriate workup procedure. A similar reaction with **1** gave rise to a mixture of the complexes [$TiCl_3(\kappa^3$-bdmpzdta)] (**6**) and [$TiCl_2(\kappa^2$-bdmpzdta$)_2$] (**7**) in 35% and 30% yields, respectively. However, complex **6** was isolated in higher yield (91%) as the only product from the solution when the temperature was raised to ca. 20 °C indicating that a transformation of complex **7** to complex **6** takes place. When solutions of **5** and **6** in THF were stirred at ca. 35 °C for 24 h, the cationic THF-containing complexes [$TiCl_2$(THF)(κ^3-bdmpza)]Cl (**8**) and [$TiCl_2$(THF)(κ^3-bdmpzdta)]Cl (**9**) were isolated after the appropriate workup procedure (see Scheme 2).

These cationic complexes result from coordination of a THF molecule and subsequent loss of a Cl^- ligand. This process appears reasonable given that several cationic d^0 titanium cyclopentadienyl species that contain THF or related coordinating solvents, namely $[Cp_2Ti(R)(L)]^+$, have previously been described.[11] Finally, an interesting reactivity was observed when solutions of **5** and **6** were refluxed. Under these experimental conditions the alkoxide-containing complexes [$TiCl_2(\kappa^3$-bdmpza){$O(CH_2)_4Cl$}] (**10**) and [$TiCl_2(\kappa^3$-bdmpzdta){$O(CH_2)_4Cl$}] (**11**) were obtained after the appropriate workup procedure (see Scheme 2). The formation of these complexes can be envisaged as being the result of a nucleophilic THF ring-opening reaction on the aforementioned cationic complexes **8** and **9**, respectively, through nucleophilic attack by the free Cl^- (step c in Scheme 2) on the activated C−O bond of the coordinated THF. This process would give rise to complexes **10** and **11**. Previous examples of this type of reactivity between the $[Cp_2Zr(R)(THF)]^+$ species and certain nucleophilic reagents, namely NR_3 and PMe_2Ph, have previously been described by Jordan et al.[12] Furthermore, nucleophilic attack of a chloride anion on a coordinated THF molecule has been previously observed in other instances where THF is bound to an electrophilic center, namely boron and uranium.[13] The different titanium complexes discussed above were characterized by spectroscopic methods. The ^1H NMR spectra of **5** and **6** each show a set of resonances for H^4, Me^3, and Me^5, indicating that both pyrazole rings are equivalent. The $^{13}C\{^1H\}$ NMR spectra exhibit the corresponding signals for C^3, C^4, C,^{5} Me^3, and Me^5 (see Experimental Section). These results agree with an octahedral structure, as depicted in Figure 4, where a κ^3-N,N,E (E = O or S) coordination for the bdmpza or

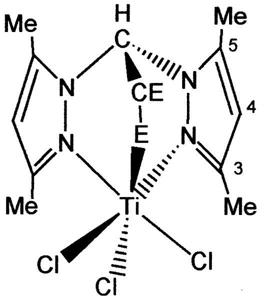


Figure 4. Proposed structure of complexes **5** (E = O) and **6** (E = S).

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[9] See for example: (a) Scollard, J. D.; McConville, D. H.; Payne, N. C.; Vittal, J. J. *Macromolecules* **1996**, *29*, 5241. (b) Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 10008. (c) Tinkler, S.; Deeth, R. J.; Duncalf, D. J.; McCamley, A. *Chem. Commun.* **1996**, 2623. (d) Scollard, J. D.; McConville, D. H.; Vittal, J. J. *Organometallics* **1997**, *16*, 4415. (e) Gibson, V. C.; Kimberly, B. S.; White, A. J. R.; Williams, D. J. *Chem. Commun.* **1998**, 313. (f) Schrock, R. R.; Schattenmann, F.; Aizenberg, M.; Davis, W. M. *Chem. Commun.* **1998**, 199. (g) Warren, T. H.; Schrock, R. R.; Davis, W. M. *Organometallics* **1998**, *17*, 308.

[10] See for example: (a) Sarsfiled, M. J.; Ewart, S. W.; Tremblay, T. L.; Roszak, A. W.; Baird, M. C. *J. Chem. Soc., Dalton Trans.* **1997**, 3097. (b) Fokken, S.; Spaniol, T. P.; Okuda, J.; Serentza, F. G.; Mullhaupt, R. *Organometallics* **1997**, *16*, 4240.

[11] See for example: (a) Bochmann, M.; Wilson, L. M.; Hursthouse, M. B.; Short, R. L. *Organometallics* **1987**, *6*, 2556. (b) Bochmann, M.; Wilson, L. M.; Hursthouse, M. B.; Motevalli, M. *Organometallics* **1988**, *7*, 1148. (c) Taube, R.; Krukowka, L. *J. Organomet. Chem.* **1988**, *347*, C9. (d) Bochmann, M.; Jagger, A. J.; Wilson, L. M.; Hursthouse, M. B.; Motevalli, M. *Polyhedron* **1989**, *8*, 1838. (e) Bochmann, M.; Jagger, A. J.; Nicholls, J. C. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 780.

[12] (a) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111. (b) Borkowsky, S. L.; Jordan, R. F.; Hinch, G. D. *Organometallics* **1991**, *10*, 1268.

[13] (a) Mair, F. S.; Morris, J. H.; Gainer, D. F.; Powell, D. *J. Chem. Soc., Dalton Trans.* **1993**, 135. (b) Campello, M. P. C.; Domingos, A.; Santos, I. *J. Organomet. Chem.* **1994**, *484*, 37. (c) Mullica, D. F.; Sappenfield, E. L.; Stone, F. G. A.; Woollam, S. F. *Organometallics* **1994**, *13*, 157. (d) Avens, L. R.; Barnhart, D. M.; Burns, C. J.; Mckee, S. D. *Inorg. Chem.* **1996**, *35*, 537. (e) Peymann, T.; Kück, K.; Gabel, D. *Inorg. Chem.* **1997**, *36*, 5138. (f) Batten, S. A.; Jeffery, J. C.; Rees, L. H.; Rudd, M. D.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1998**, 2839.

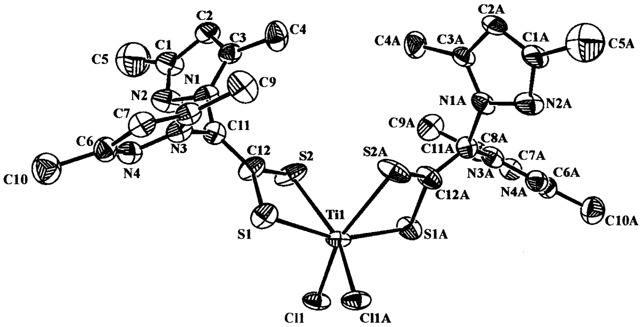

Figure 5. View of complex **7** (30% probability ellipsoids) with the atomic numbering scheme. Selected bond distances (Å) and angles (deg): Ti(1)−Cl(1), 2.315(2); Ti(1)−Cl(1), 2.315(2); Ti(1)−S(1), 2.399(3); Ti(1)−S(1), 2.399(3); Ti(1)−S(2), 2.468(3); Ti(1)−S(2), 2.468(3); S(1)−C(12), 1.742(9); S(2)−C(12), 1.73(1); C(11)−C(12), 1.34(1); Cl(1)−Ti(1)−Cl(1), 92.5(1); Cl(1)−Ti(1)−S(1), 111.1(1); S(1)−Ti(1)−S(1), 158.3(2); Cl(1)−Ti(1)−S(2), 93.55(9); S(1)−Ti(1)−S(2), 72.53(9); C(12)−C(11)−N(1), 122.6(8); C(12)−C(11)−N(3), 120.9(7); N(1)−C(11)−N(3), 116.4(8); C(11)−C(12)−S(2), 125.2(7); C(11)−C(12)−S(1), 122.9(7); S(2)−C(12)−S(1), 111.9(6).

bdmpzdta is proposed. Although several tris(pyrazol-1-yl)borate group 4 metal complexes have been described previously,[14] as far as we are aware, these complexes constitute the first examples of this class of compound with a heteroscorpionate ligand (see for example refs 3b−e). A different structural disposition was found for complex **7**. The ^{1}H and ^{13}C{^{1}H} NMR spectra exhibit two sets of resonances for the pyrazole rings, indicating that the two pyrazole rings of each of the two bdmpzdta moieties present in the molecule are not equivalent in this case (see Experimental Section). An X-ray crystal molecular structure determination for complex **7** was carried out. The molecular structure and atomic numbering scheme are shown in Figure 5.

Complex **7** crystallizes in the monoclinic space group *C*2/*c* with one independent half-molecule/asymmetric unit. The crystal structure consists of a monomeric titanium complex and appears with six molecules of CH_2Cl_2 and two molecules of H_2S. The geometry of the metal center is distorted octahedral with the two chlorine atoms coordinated in cis positions, and two equivalent bdmpzdta ligands, related by a 2-fold axis of the molecule, are coordinated to titanium atom through a κ^2-S,S coordination for each bdmpzdta ligand. The dihedral angle between the two planes defined by SCS atoms (S1, C12, S2 and S1A, C12A, S2A atoms) of the two bdmpzdta ligands is 106.3(4)°, and the dihedral angles between the two planes mentioned above and the plane defined by the Cl1, Ti1, Cl1A atoms are 60.66(5) and 119.3(3)°, respectively. The C11−S bond distances (1.739 and 1.728 Å) and the C11−C12 distance of 1.346 Å indicate the existence of a delocalized C12−C11−S bond.

The ^{1}H NMR spectra of complexes **8**−**11** exhibit two resonances for each of the H^4, Me^3, and Me^5 pyrazole protons, indicating that the two pyrazole rings are located in cis and trans positions with respect to the THF (**8** and **9**) or alkoxide (**10** and **11**) ligand (see figures in Scheme 2). NOE experiments were carried out to confirm these structures. In addition, the ^{13}C{^{1}H}NMR spectra exhibit two resonances for the different pyrazole carbon atoms C^3, C^4, C^5 Me^3, and Me^5 and their assignments were made on the basis of HETCOR correlation experiments (see Experimental Section). In the structural disposition discussed for **8**−**11**, the titanium atom is a chiral center, and we have confirmed the presence in solution of the corresponding two enantiomers by addition of a chiral shift reagent, namely (*R*)-(−)-(9-anthryl)-2,2,2-trifluoroethanol, to a solution of complex **10**. This process gives rise to the appearance in the ^{1}H NMR spectrum of two signals for each proton as a result of the presence of the two diastereoisomers from the corresponding two enantiomers. The X-ray crystal structure determinations for **10** and **11** were also carried out. These structures are represented in Figure 6.

Both structures consist of a heteroscorpionate ligand bonded to the titanium atom through the two nitrogen atoms and the oxygen or sulfur from the acetate or dithioacetate groups, respectively. In addition, the titanium center is coordinated to two chlorine atoms and an oxygen from the opened THF ring; this disposition makes the titanium atom a chiral center. In the solid state, due to the centrosymmetric space group, both enantiomers are present and one of them, namely *OC*-6−32(A) and *OC*-6−42(A), respectively, are depicted in Figure 6.

Both complexes have a pseudooctahedral geometry with Ti at a distance of 0.105(3) Å out of the plane defined by the N1, N3, O3, and Cl2 atoms for **10** and 0.170(2) Å out of the plane defined by the N1, N4, O1, and Cl1 atoms for **11**. The Ti−O(THF) bond distances [1.731(5) Å for **10** and 1.742(4) Å for **11**] indicate the existence of partial Ti−O double-bond character.

Both crystals are stabilized by a weak and extensive hydrogen-bonding network. The geometrical features of the hydrogen bond network are shown in Table 2. In complex **10**, in which both chlorine atoms are joined directly to the Ti1 atom, Cl1 and Cl2 take part in an intramolecular hydrogen bond with C11−H11c and C6−H6c, respectively (Figure 7). The Cl1 atom is also implicated in two other intermolecular hydrogen bonds with C12−H12c and C11−H11c, respectively. The O2 atom is also implicated in two intermolecular hydrogen bonds with C1−H1 and C12−H12c.

In complex **11** there are intramolecular hydrogen bonds with Cl1 and Cl2, in a similar way to complex **10**, and C7−H7c forms an intramolecular hydrogen bond with the O1 atom from the THF molecule. Chlorine atoms Cl3, Cl4, and Cl5 in complex **11** show disordered positions (namely Cl3a, Cl4a, and Cl5a, respectively), which implies that the hydrogen bonds are duplicated. All of these atoms participate in two hydrogen bonds. C16a−H16c connects two molecules in a bifurcated hydrogen bond, through Cl4a, Cl5, and Cl5a.

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(14) (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.* **1985**, *22*, 1064. (d) Reger, D. L.; Tarquini, M. E.; Lebioda, L. *Organometallics* **1983**, *12*, 1763. (e) Kresinski, R. A.; Isam, L.; Amor, J. 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.

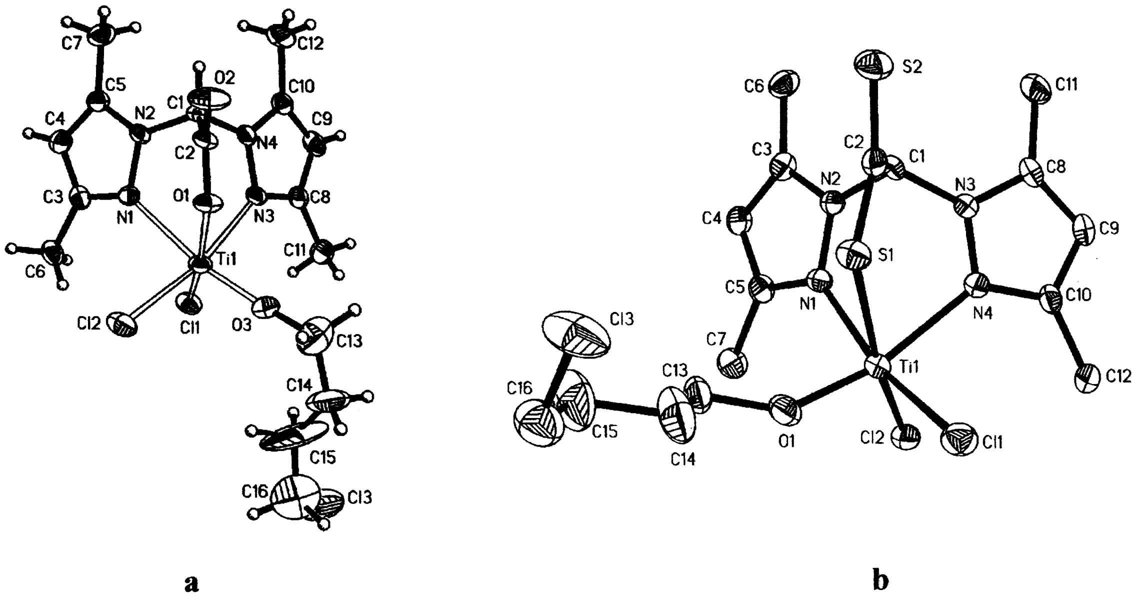


Figure 6. View of complexes **10** and **11** (25% probability ellipsoids) with the atomic numbering scheme. Selected bond distances (Å) and angles (deg) are as follows. Complex **10** (part a):[6] Ti1−Cl1, 2.296(2); Ti1−Cl2, 2.294(2); Ti1−O1, 1.984(4); Ti1−O3, 1.731(5); Ti1−N1, 2.276(6); Ti1−N3, 2.204(6); O1−Ti1−Cl1, 165.5(1); O1−Ti1−Cl2, 92.3(1); O1−Ti1−N1, 80.4(2); O1−Ti1−N3, 81.6(2); O1−Ti1−O3, 92.3(2); N1−Ti1−N3, 79.8(2); N3−Ti1−O3, 92.5(2); O3−Ti1−Cl2, 97.8(2). Complex **11** (part b): Ti1−Cl1, 2.290(2); Ti1−Cl2, 2.296(2); Ti1−S1, 2.509(2); Ti1−O1, 1.742(4); Ti1−N1, 2.188(4); Ti1−N4, 2.237(4); S1−Ti1−Cl1, 87.15(6); S1−Ti1−Cl2, 168.97(6); S1−Ti1−N1, 82.8(1); S1−Ti1−N4, 82.3(1); S1−Ti1−O1, 88.4(1); N1−Ti1−N4, 79.6(2); N4−Ti1−O1, 166.7(2); O1−Ti1−Cl2, 100.0(1).

Table 2. Hydrogen Bonds for Compounds **10 and 11**

D−H	*d*(D−H)	*d*(H···A)	<DHA	*d*(D···A)	symmetry[a]
		Compound **10**			
C1−H1···O2	0.98	2.368	161.1	3.310	$1 - x, -y, 1 - z$
C12−H12c···O2	0.96	2.549	133.7	3.287	$1 - x, -y, 1 - z$
C11−H11c···Cl1	0.96	2.723	128.2	3.401	x, y, z
C12−H12b···Cl1	0.96	2.952	140.8	3.746	$1 + x, y - 0.5, 0.5 - z$
C14−H14b···Cl1	0.97	2.878	156.9	3.789	$x - 1, y, z$
C6−H6c···Cl2	0.96	2.771	145.8	3.605	x, y, z
		Compound **11**			
C7−H7C···O1	0.96	2.445	138.1	3.224	x, y, z
C12−H12a···Cl1	0.96	2.620	138.1	3.396	x, y, z
C12−H12C···Cl2	0.96	2.842	122.8	3.457	x, y, z
C16−H16a···S2	0.97	2.917	174.3	3.883	$x, 0.5 - y, 0.5 + z$
C6−H6C···Cl3	0.96	3.008	131.2	3.711	$-x, -y, 1 - z$
C6−H6C···Cl3a	0.96	2.904	129.9	3.595	$-x, -y, 1 - z$
C12−H12c···Cl3	0.96	3.002	153.5	3.908	$x + 1, y, z$
C12−H12c···Cl3a	0.96	2.877	150.6	3.744	$x + 1, y, z$
C15−H15b···C14	0.97	3.123	133.8	3.859	$x, y, 1 + z$
C15−H15b···C14a	0.97	2.803	122.9	3.428	$x, y, 1 + z$
C16−H16b···C14	0.97	3.281	131.2	3.988	$x, y, 1 + z$
C16−H16b···C14a	0.97	2.705	134.2	3.452	$x, y, 1 + z$
C16−H16c[b]···C14a	0.97	2.809	127.8	3.489	$x, y, 1 + z$
C16a−H16c[b]···C15	0.97	2.886	153.2	3.777	$x, y, 1 + z$
C16a−H16c[b]···C15a	0.97	3.030	146.2	3.874	$x, y, 1 + z$
C7−H7a···C15	0.96	3.024	142.2	3.828	$1 + x, y, 1 + z$
C7−H7a···C15a	0.96	3.119	149.7	3.977	$1 + x, y, 1 + z$

[a] Symmetry operation for A. [b] Asymmetrically bifurcated.

To extend the range of alkoxide-containing titanium species, we considered the preparation of complexes related to **10** and **11** by using two different experimental methods. The first method involves the reactions of **10** and **11** with a range of alcohols, thus giving rise to the isolation of the corresponding alkoxide complexes (see Scheme 3) together with 4-chloro-1-butanol resulting from a displacement reaction. The complexes [TiCl$_2$(κ^3-bdmpza)(OMe)] (**12a**), [TiCl$_2$(κ^3-bdmpzdta)(OMe)] (**13a**), [TiCl$_2$(κ^3-bdmpza)(OEt)] (**14a**), [TiCl$_2$(κ^3-bdmpzdta)(OEt)] (**15a**), and [TiCl$_2$(κ^3-bdmpzdta)(O^{i}Pr)] (**17a**) were isolated after the appropriate workup procedure (see Experimental Section). The second method for the preparation of this class of complex consisted of the direct reaction of complex **5** with several alcohols (see Scheme 3). This reaction gave rise to the isolation of the alkoxide-containing complexes [TiCl$_2$(κ^3-bdmpza)(OMe)] (**12b**), [TiCl$_2$(κ^3-bdmpza)(OEt)] (**14b**), [TiCl$_2$(κ^3-bdmpza)(O^{i}Pr)] (**16b**), and [TiCl$_2$(κ^3-bdmpza)(O^{t}Bu)] (**18b**) as HCl was evolved. The notations **a** and **b** refer to the symmetric and asymmetric isomers repectively (see below for a discussion regarding the structures of these complexes). The different alkoxide-containing complexes were characterized

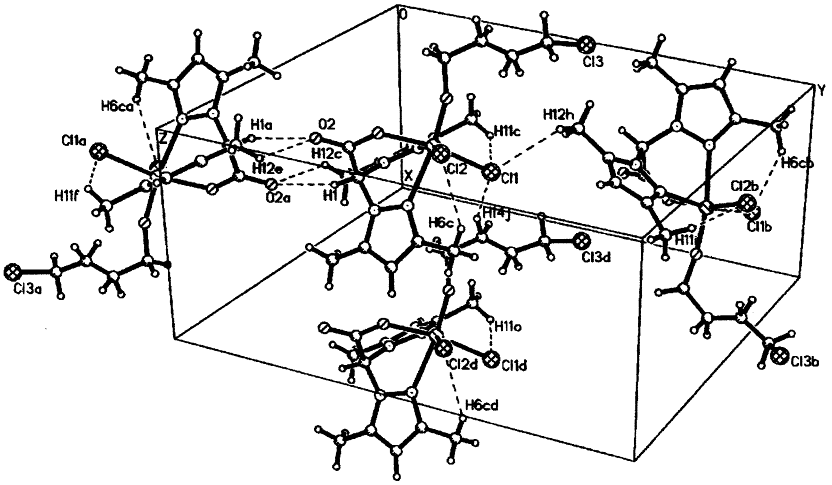
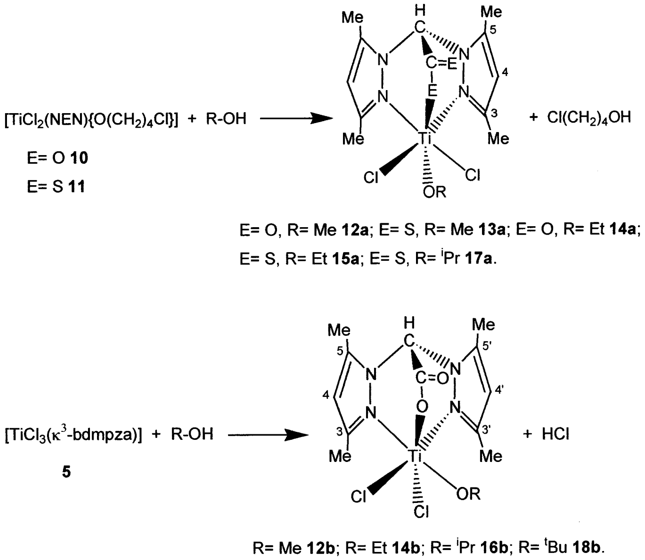


Figure 7. Packing plot of **10**. Dashed lines represent hydrogen bonds.

Scheme 3. Summary of Reactions Leading to Complexes **12**−**18**



by spectroscopic methods. The complexes prepared by the first method, i.e. from **10** and **11**, have been denoted as **a** and exhibit in their ^{1}H NMR spectra of a single set of resonances for H^{4}, Me^{3}, and Me^{5}, indicating that both pyrazole rings are equivalent. These results agree with a proposed octahedral disposition in which the alkoxide ligand bisects the plane of the scorpionate ligand (see Figure in Scheme 3). NOE experiments were carried out to confirm this situation. In addition, the ^{13}C{^{1}H} NMR spectra exhibit the corresponding signals for C^{3}, C^{4}, C^{5}, Me^{3}, and Me^{5} and the different carbon atoms of the corresponding alkoxide ligand (see Experimental Section). It is noteworthy that these processes, which start from asymmetric structures for **10** and **11**, give rise to symmetric complexes in all cases. Complexes obtained by the second method, which have been denoted as **b**, show two resonances for each of the H^{4}, Me^{3}, and Me^{5} pyrazole protons in the ^{1}H NMR spectra, indicating that in this case the two pyrazole rings are not equivalent. These results agree with a proposed octahedral disposition in which two pyrazole rings are located cis and trans positions with respect to the alkoxide ligand, i.e. an asymmetric structural disposition (see figure in Scheme 3). NOE experiments confirmed these findings. In addition, the ^{13}C{^{1}H} NMR spectra exhibit two resonances for the different pyrazole carbon atoms C^{3}, C^{4}, C^{5}, Me^{3}, and Me^{5} and their assignments were made on the basis of HETCOR correlation experiments (see Experimental Section). In these complexes the titanium atom is a chiral center and we confirmed the presence in solution of the corresponding two enantiomers by addition of a chiral shift reagent, namely (*R*)-(−)-(9-anthryl)-2,2,2-trifluoroethanol. This process gave rise to the apperance in the ^{1}H NMR spectra of two signals for each proton, resulting from the two diastereoisomers of the corresponding two enantiomers.

In conclusion, we have prepared a new series of heteroscorpionate ligands (**1**−**3**) related to the tris(pyrazol-1-yl)methane system, in which one of the pyrazole rings has been replaced by a carboxylate or dithiocarboxylate group to give a small degree of steric hindrance and considerable coordinative flexibility. These scorpionate-containing lithium derivatives, by reaction with $TiCl_4$(THF), have led to a new generation of non-cyclopentadienyl-based complexes of group 4 metals with nitrogen- and/or oxygen−sulfur-containing ligands (**5**−**11**). These complexes have the potential to be excellent catalyst precursors for the polymerization of α-olefins, as demonstrated in a preliminary study on complexes **5** and **10**.[6] In the synthesis of the titanium complexes it is worth emphasizing the interesting nucleophilic THF ring-opening reaction observed when solutions of **5** and **6** were refluxed in THF. Finally, we have extend the range of alkoxide-containing titanium species (**12**−**18**) by using two different experimental methods.

Acknowledgment. We gratefully acknowledge financial support from the Dirección General de Enseñanza Superior e Investigación Científica of Spain (Grant Nos. PB98-0159-C02-01 and PB97-0425).

Supporting Information Available: Details of data collection, refinement, atom coordinates, anisotropic displacement parameters, and bond lengths and angles in CIF format for complexes **3**, **7**, **10**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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