Inorg. Chem. **2005**, *44*, 5336–5344

First Complexes of Scandium and Yttrium with NNO and NNS Heteroscorpionate Ligands

Antonio Otero,* Juan Fernández-Baeza,* Antonio Antiñolo, Juan Tejeda, Agustín Lara-Sánchez, Luis Sánchez-Barba, Emilia Martínez-Caballero, Ana M. Rodríguez, and Isabel López-Solera

Departamento de Química Inorgánica, Orgánica y Bioquímica, Universidad de Castilla-La Mancha, 13071-Ciudad Real, Spain

Received April 6, 2005

The reaction of $ScCl_3(THF)_3$ or YCl_3 in a 1:1 molar ratio under reflux for 8 h with $[\{Li(bdmpza)(H_2O)\}_4]$ [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] affords the corresponding complexes $[MCl_2(\kappa^3\text{-bdmpzx})(THF)]$ (x = a, M = Sc (**1**), Y (**2**); x = dta, M = Sc (**3**), Y (**4**); x = e, M = Sc (**5**), Y (**6**)). However, when the reaction was carried out for 1 h under reflux between $ScCl_3(THF)_3$ and $[\{Li(bdmpzdta)(H_2O)\}_4]$, a new anionic complex $[Li(THF)_4][ScCl_3(\kappa^3\text{-bdmpzdta})]$ (**7**) was obtained. Reaction of $[\{Li(bdmpza)(H_2O)\}_4]$ with YCl_3 in a 2:1 molar ratio under reflux for 8 h gave the complex $[YCl(\kappa^3\text{-bdmpza})_2]$ (**8**). The same reaction, but with the lithium compound $[\{Li(bdmpzdta)(H_2O)\}_4]$, led to the formation of an anionic complex $[Li(THF)_4][YCl_3(\kappa^3\text{-bdmpzdta})]$ (**9**). The X-ray crystal structures of **7** and **9** were established. Finally, the addition of 1 equiv of $[\{Li(bdmpza)(H_2O)\}_4]$ or $[\{Li(bdmpzdta)(H_2O)\}_4]$ to a solution of YCl_3 in THF under reflux, followed by the addition of 1 equiv of 1,10-phenanthroline, resulted in the formation of the corresponding complexes $[YCl_2(\kappa^3\text{-bdmpzx})(phen)]$ (x = a (**10**), x = dta (**11**)). These complexes are the first examples of group 3 metals stabilized by heteroscorpionate ligands. In addition, we have explored the reactivity of some of these complexes with alcohols and amides. For example, the direct reaction of $[YCl_2(\kappa^3\text{-bdmpza})(THF)]$ (**2**) with several alcohols gave the alkoxide complexes $[YCl(\kappa^3\text{-bdmpza})(OR)]$ (R = Et (**12**), *i*Pr (**13**)). Finally, the reaction between $[ScCl_2(\kappa^3\text{-bdmpzdta})(THF)]$ (**3**) or $[Li(THF)_4][ScCl_3(\kappa^3\text{-bdmpzdta})]$ (**7**) and $LiN(SiMe_3)_2\cdot Et_2O$ in 1:1 and 1:2 molar ratios gave rise to the complexes $[ScCl(\kappa^3\text{-bdmpzdta})\{N(SiMe_3)_2\}]$ (**14**) and $[Sc(\kappa^3\text{-bdmpzdta})\{N(SiMe_3)_2\}_2]$ (**15**), respectively.

Introduction

Scorpionates such as poly(pyrazolyl)borates are attractive ancillary ligands for the stabilization of the group 3 metals and lanthanide complexes.[1] These ligands have several characteristics that are similar to those of cyclopentadienyl systems,[2] and their unique properties provide advantages that make them especially attractive for the synthesis of lanthanide or group 3 metal complexes.[3] The first examples of hydrotris(pyrazolyl)borate derivatives for these elements were homoleptic compounds of the type Tp_3M (M = Sc, Y, La, Ce−Lu).[4] A large number of heteroleptic Tp complexes have also been reported, most of which are eight-coordinate and are of the type $Tp_2M(L)$ (L = bidentate ligand)[5] or $(Tp)_2MX(solv)$ (X = halide, solv = neutral coordinating solvent).[6] Dihalide hydrotris(pyrazolyl)borate complexes, $TpMX_2(solv)$[7] or $TpMX_2(L)$,[5c] have also been described. Further-

* Authors to whom correspondence should be addressed. E-mail: antonio.otero@uclm.es (A.O.); juan.fbaeza@uclm.es (J.F.-B.). Fax: +34926295318 (A.O., J.F.-B.). Tel: +34926295300 (A.O., J.F.-B.).

(1) Trofimenko, S. *Scorpionates. The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999.
(2) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943.
(3) (a) Marques, N.; Sella, A.; Takats, J. *Chem. Rev.* **2002**, *102*, 2137. (b) Piers, W. E.; Emslie, D. J. H. *Coord. Chem. Rev.* **2002**, *233*, 131. (c) Mountford, P.; Ward, B. D. *Chem. Commun*. **2003**, 1797 (feature article).
(4) (a) Bagnall, K. W.; Tempest, A. C.; Takats, J.; Masino, A. P. *Inorg. Nucl. Chem. Lett*. **1976**, *12*, 555. (b) Stainer, M. V. R.; Takats, J. *Inorg. Chem*. **1982**, *21*, 4050.
(5) (a) Moss, M. A.; Jones, C. J.; Edwards, A. J. *Polyhedron* **1988**, *7*, 79. (b) Moss, M. A.; Jones, C. J.; Edwards, A. J. *J. Chem. Soc., Dalton Trans.* **1989**, 1393. (c) Roitershtein, D.; Domingos, A.; Pereira, L. C. J.; Ascenso, J. R.; Marques, N. *Inorg. Chem*. **2003**, *42*, 7666.
(6) Reger, D. L.; Lindeman, J. A.; Lebioda, I. *Inorg. Chim. Acta* **1987**, *139*, 71.
(7) (a) Apostolidis, C.; Carvalho, A.; Domingos, A.; Kanellakopoulos, B.; Maier, R.; Marques, N.; Pires de Matos, A.; Rebizant, J. *Polyhedron* **1999**, *18*, 263. (b) Long, D. P.; Chandrasekaran, A.; Day, R. O.; Bianconi, P. A.; Rheingold, A. L. *Inorg. Chem*. **2000**, *39*, 4476.

10.1021/ic050525y CCC: $30.25
Published on Web 06/24/2005

more, the alkyl derivatives $TpMR_2$ (R = Ph, CH_2SiMe_3) are known and were found to be active ethylene polymerization catalysts.[8]

We have previously reported the synthesis of new "heteroscorpionate" ligands based on bis(pyrazol-1-yl)methane[9] that contain two pyrazole rings and a carboxylate, dithiocarboxylate, or methoxide 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). More recently we developed the synthesis of the first hybrid scorpionate/cyclopentadienyl ligand.[10] These tridentante ligands can coordinate to a wide variety of elements, e.g. from early to late transition metals. Thus, we have reported heteroscorpionate complexes containing group 4 and 5 metals.[11] However, heteroscorpionate−lanthanide complexes have not been reported to date in the literature. For this reason we became interested in extending the scope of this chemistry to include the preparation of new heteroscorpionate complexes of the group 3 metals. We describe here the synthesis and characterization of new classes of neutral and anionic scandium and yttrium complexes containing heteroscorpionate ligands along with halide and phenanthroline as ancillary ligands. These *target* complexes constitute the first examples of this class of compound with a heteroscorpionate ligand. We also explored the reactivity of some of these complexes with alcohols and amides to give new alkoxide and amide complexes.

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 and ^{13}C NMR spectra were recorded on Varian Unity FT-300 and Varian Inova FT-500 spectrometers 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. The NOESY-1D spectra were recorded with the acquisition parameters irradiation time 2 s and number of scans 256, using standard VARIANT-FT software. Two-dimensional NMR spectra were acquired using standard VARIAN-FT software and processed using an IPC-Sun computer.

The anhydrous scandium and yttrium trichlorides were used as received. The complexes [{Li(bdmpza)(H_2O)}$_4$], [bdmpza = bis(3,5-dimethylpyrazol-1-yl)acetate], [{Li(bdmpzdta)(H_2O)}$_4$], and [bdmpzdta = bis(3,5-dimethylpyrazol-1-yl)dithioacetate] and the compound (Hbdmpze) [bdmpze = 2,2-bis(3,5-dimethylpyrazol-1-yl)ethoxide] were prepared as reported previously.[11a,12a,b]

Preparations. Synthesis of [$ScCl_2(\kappa^3$-bdmpza)(THF)] (1). To a THF (100 mL) solution of [$ScCl_3(THF)_3$] (0.50 g, 1.36 mmol) was added an equimolar quantity of [{Li(bdmpza)(H_2O)}$_4$] (0.37 g, 0.34 mmol). The reaction mixture was stirred for 8 h under reflux. The solvent was removed under vacuum and the solid extracted with CH_2Cl_2. A white solid was obtained after removal of the solvent, and this was crystallized from a mixture of THF−hexane. Yield: 70%. Anal. Calcd for $C_{16}H_{23}Cl_2N_4O_3Sc$: C, 44.1; H, 5.3; N, 12.8. Found: C, 44.2; H, 5.5; N, 12.5. ^1H NMR (300 MHz, $CDCl_3$, 297 K): δ 6.73 (s, 1 H, CH), 5.81 (s, 2 H, H^4), 2.06 (s, 6 H, Me^3), 2.20 (s, 6 H, Me^5), 3.85 (m, 4 H, THF), 1.95 (m, 4 H, THF). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 73.3 (CH), 146.3, 140.6 (C^{3or5}), 106.2 (C^4), 13.4 (Me^3), 11.3 (Me^5), 69.4 (THF), 26.4 (THF), 177.6 (CO_2^-). IR (Nujol): 1575 ν(C═N), 1638 $\nu_{as}(CO_2^-)$, 1377 $\nu_s(CO_2^-)$, 343 ν(Sc−Cl) cm^{-1}. MS [FAB (*m*/*z* [assignment], % intensity)]: 328 [M − THF − Cl], 100.

Synthesis of [$YCl_2(\kappa^3$-bdmpza)(THF)] (2). The synthetic procedure was the same as for complex **1**, using YCl_3 (0.50 g, 2.56 mmol) and [{Li(bdmpza)(H_2O)}$_4$] (0.71 g, 0.64 mmol) to give **2** as a white solid. Yield: 95%. Anal. Calcd for $C_{16}H_{23}Cl_2N_4O_3Y$: C, 40.1; H, 4.8; N, 11.7. Found: C, 40.5; H, 4.9; N, 11.4. ^1H NMR (300 MHz, $CDCl_3$, 297 K): δ 6.75 (s, 1 H, CH), 5.84 (s, 2 H, H^4), 2.01 (s, 6 H, Me^3), 2.19 (s, 6 H, Me^5), 3.45 (m, 4 H, THF), 1.87 (m, 4 H, THF). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 73.8 (CH), 146.8, 141.2 (C^{3or5}), 106.7 (C^4), 13.9 (Me^3), 11.9 (Me^5), 71.4 (THF), 25.4 (THF), 173.1 (CO_2^-). IR (Nujol): 1545 ν(C═N), 1668 $\nu_{as}(CO_2^-)$, 1403 $\nu_s(CO_2^-)$, 275 ν(Y−Cl) cm^{-1}. MS [FAB (*m*/*z* [assignment], % intensity)]: 372 [M − THF − Cl], 100.

Synthesis of [$ScCl_2(\kappa^3$-bdmpzdta)(THF)] (3). The synthetic procedure was the same as for complex **1**, using [$ScCl_3(THF)_3$] (0.50 g, 1.36 mmol) and [{Li(bdmpzdta)(H_2O)}$_4$] (0.41 g, 0.34 mmol) to give **3** as a red solid. Yield: 85%. Anal. Calcd for $C_{16}H_{23}Cl_2N_4OS_2Sc$: C, 41.1; H, 4.9; N, 11.9. Found: C, 41.5; H, 5.1; N, 11.7. ^1H NMR (300 MHz, $CDCl_3$, 297 K): δ 7.53 (s, 1 H, CH), 6.02 (s, 2 H, H^4), 2.74 (s, 6 H, Me^3), 2.38 (s, 6 H, Me^5), 3.91 (m, 4 H, THF), 1.95 (m, 4 H, THF). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 80.5 (CH), 153.7, 141.7 (C^{3or5}), 108.0 (C^4), 15.4 (Me^3), 11.4 (Me^5), 71.0 (THF), 25.6 (THF), 234.2 (CS_2^-). IR (Nujol): 1585 (C═N), 1078 $\nu_{as}(CS_2^-)$, 812 $\nu_s(CS_2^-)$, 346 ν(Sc−Cl) cm^{-1}. MS [FAB (*m*/*z* [assignment], % intensity)]: 359 [M − THF − Cl], 100.

Synthesis of [$YCl_2(\kappa^3$-bdmpzdta)(THF)] (4). The synthetic procedure was the same as for complex **1**, using YCl_3 (0.50 g, 2.56 mmol) and [{Li(bdmpzdta)(H_2O)}$_4$] (0.78 g, 0.64 mmol) to give **4** as a red solid. Yield: 85%. Anal. Calcd for $C_{16}H_{23}Cl_2N_4OS_2Y$: C, 37.6; H, 4.5; N, 10.9. Found: C, 37.8; H, 4.7; N, 10.6. ^1H NMR (300 MHz, $CDCl_3$, 297 K): δ 7.56 (s, 1 H, CH), 5.94 (s, 2 H, H^4), 2.57 (s, 6 H, Me^3), 2.41 (s, 6 H, Me^5), 3.81 (m, 4 H, THF), 1.95 (m, 4 H, THF). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 67.9 (CH), 145.4, 141.8

(8) Long, D. P.; Bianconi, P. A. *J. Am. Chem. Soc*. **1996**, *118*, 12453.
(9) Otero, A.; Fernández-Baeza, J.; Antiñolo, A.; Tejeda, J.; Lara-Sánchez, A. *Dalton Trans*. **2004**, 1499 (perspective article).
(10) Otero, A.; Fernández-Baeza, J.; Antiñolo, A.; Tejeda, J.; Lara-Sánchez, A.; Sánchez-Barba, L.; Rodríguez, A. M.; Maestro, M. A. *J. Am. Chem. Soc.* **2004**, *126*, 1330.
(11) For group 5 metal complexes see for example: (a) Otero, A.; Fernández-Baeza, J.; Tejeda, J.; Antiñolo, A.; Carrillo-Hermosilla, F.; Diez-Barra, E.; Lara-Sánchez, A.; Fernández-Lopez, M.; Lanfranchi, M.; Pellinghelli, M. A. *J. Chem. Soc., Dalton Trans.* **1999**, 3537. (b) Otero, A.; Fernández-Baeza, J.; Antiñolo, A.; Tejeda, J.; Lara-Sánchez, A.; Sánchez-Barba, L.; Rodríguez, A. M. *Eur. J. Inorg. Chem.* **2004**, 260. For group 4 metal complexes, see for example: (c) Otero, A.; Fernández-Baeza, J.; Antiñolo, A.; Carrillo-Hermosilla, F.; Tejeda, J.; Díez-Barra, E.; Lara-Sánchez, A.; Sánchez-Barba, L.; López-Solera, I.; Ribeiro, M. R.; Campos, J. M. *Organometallics* **2001**, *20*, 2428. (d) Otero, A.; Fernández-Baeza, J.; Antiñolo, A.; Tejeda, J.; Lara-Sánchez, A.; Sánchez-Barba, L.; Fernández-López, M.; López-Solera, I. *Inorg. Chem.* **2004**, *43*, 1350.
(12) (a) Otero, A.; Fernández-Baeza, J.; Antiñolo, A.; Carrillo-Hermosilla, F.; Tejeda, J.; Lara-Sánchez, A.; Sánchez-Barba, L.; Fernández-López, M.; Rodríguez, A. M.; López-Solera, I. *Inorg. Chem.* **2002**, *41*, 5193. (b) Otero, A.; Fernández-Baeza, J.; Tejeda, J.; Antiñolo, A.; Carrillo-Hermosilla, F.; Diez-Barra, E.; Lara-Sánchez, A.; Fernández-Lopez, M. *J. Chem. Soc., Dalton Trans.* **2000**, 2367.

(C^{3or5}), 108.1 (C^4), 15.4 (Me^3), 11.4 (Me^5), 71.4 (THF), 25.3 (THF), 233.8 (CS_2^-). IR (Nujol): 1531 (C═N), 1058 $\nu_{as}(CS_2^-)$, 886 $\nu_s(CS_2^-)$, 272 ν(Y−Cl) cm^{-1}. MS [FAB (*m*/*z* [assignment], % intensity)]: 404 [M − THF − Cl], 100.

Synthesis of [$ScCl_2(\kappa^3$-bdmpze)(THF)] (5). To a cooled (−70 °C) solution of Hbdmpze (0.63 g, 2.72 mmol) in dry THF (100 mL) was added a 1.6 M solution of Bu^nLi in hexane (1.70 mL, 2.72 mmol). After 30 min, a solution of [$ScCl_3(THF)_3$] (1.50 g, 2.72 mmol) in THF (100 mL) was added and the reaction mixture stirred for 8 h under reflux. 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, and this was crystallized from a mixture of THF−hexane. Yield: 65%. Anal. Calcd for $C_{16}H_{25}Cl_2N_4O_2Sc$: C, 45.6; H, 5.9; N, 13.3. Found: C, 45.8; H, 6.0; N, 13.3. ^{1}H NMR (300 MHz, $CDCl_3$, 297 K): δ 6.27 (t, 1 H, $^3J_{HH}$ = 6.6 Hz, CH), 5.79 (s, 2 H, H^4), 4.23 (d, 2 H, $^3J_{HH}$ = 6.6 Hz, CH_2O), 2.06 (s, 6 H, Me^3), 2.22 (s, 6 H, Me^5), 3.84 (m, 4 H, THF), 1.87 (m, 4 H, THF). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 71.0 (CH), 148.1, 141.3 (C^{3or5}), 106.4 (C^4), 61.9 (CH_2O), 14.2 (Me^3), 11.4 (Me^5), 69.5 (THF), 25.7 (THF). IR (Nujol): 1545 ν(C═N), 575 ν(Sc−O), 331 ν(Sc−Cl) cm^{-1}. MS [FAB (*m*/*z* [assignment], % intensity)]: 313 [M − THF − Cl], 100.

Synthesis of [$YCl_2(\kappa^3$-bdmpze)(THF)] (6). The synthetic procedure was the same as for complex **5**, using Hbdmpze (1.20 g, 5.12 mmol), Bu^nLi (3.2 mL, 5.12 mmol), and YCl_3 (1.00 g, 5.12 mmol) to give **6** as a white solid. Yield: 70%. Anal. Calcd for $C_{16}H_{25}Cl_2N_4O_2Y$: C, 41.3; H, 5.4; N, 12.0. Found: C, 41.5; H, 5.4; N, 11.8. ^{1}H NMR ($CDCl_3$, 297 K): δ 6.30 (t, 1 H, $^3J_{HH}$ = 6.8 Hz, CH), 5.78 (s, 2 H, H^4), 4.21 (d, 2 H, $^3J_{HH}$ = 6.8 Hz, CH_2O), 2.05 (s, 6 H, Me^3), 2.22 (s, 6 H, Me^5), 3.94 (m, 4 H, THF), 1.95 (m, 4 H, THF). $^{13}C\{^1H\}$ NMR (300 MHz, $CDCl_3$): δ 70.9 (CH), 147.0, 140.3 (C^{3or5}), 106.2 (C^4), 62.2 (CH_2O), 14.1 (Me^3), 11.4 (Me^5), 69.4 (THF), 25.1 (THF). IR (Nujol): 1513 ν(C═N), 563 ν(Y−O), 288 ν(Y−Cl) cm^{-1}. MS [FAB (*m*/*z* [assignment], % intensity)]: 358 [M − THF − Cl], 100.

Synthesis of [$Li(THF)_4$][$ScCl_3(\kappa^3$-bdmpzdta)] (7). To a THF (100 mL) solution of [$ScCl_3(THF)_3$] (1.00 g, 2.72 mmol) was added an equimolar quantity of [{Li(bdmpzdta)(H_2O)}$_4$] (0.83 g, 0.68 mmol). The reaction mixture was stirred for 1 h under reflux. The solvent was removed under vacuum and the solid extracted with CH_2Cl_2. The solution was evaporated to dryness to yield a mixture of **3** and **7** as a red solid. Compound **7** was isolated by crystallization from cold THF. Yield: 35%. Anal. Calcd for $C_{28}H_{47}Cl_3LiN_4O_4S_2Sc$: C, 46.3; H, 6.5; N, 7.7. Found: C, 46.5; H, 6.6; N, 7.5. ^{1}H NMR (500 MHz, $CDCl_3$, 297 K): δ 7.53 (s, 1 H, CH), 6.05, 6.04 (s, 2 H, $H^{4,4'}$), 2.76, 2.47 (s, 6 H, $Me^{3,3'}$), 2.49 (s, 6 H, $Me^{5,5'}$), 4.50 (m, 16 H, THF), 2.12 (m, 16 H, THF). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 80.5 (CH), 154.0, 152.5, 142.8, 142.4 ($C^{3,3'or5,5'}$), 108.2, 108.1 ($C^{4,4'}$), 15.0, 14.3 ($Me^{3,3'}$), 11.6, 11.4 ($Me^{5,5'}$), 74.7 (THF), 25.6 (THF), 233.9 (CS_2^-). IR (Nujol): 1586 ν(C═N), 1039 $\nu_{as}(CS_2^-)$, 798 $\nu_s(CS_2^-)$, 344 ν(Sc−Cl) cm^{-1}.

Synthesis of [$YCl(\kappa^3$-bdmpza)$_2$] (8). To a THF (100 mL) suspension of [YCl_3] (0.50 g, 2.56 mmol) was added a solution of [{Li(bdmpza)(H_2O)}$_4$] (1.39 g, 1.28 mmol) in THF (50 mL). The reaction mixture was stirred for 8 h under reflux. The solvent was removed under vacuum and the solid extracted with CH_2Cl_2. A white solid was obtained after removal of the solvent, and this was crystallized from a mixture of THF−hexane. Yield: 60%. Anal. Calcd for $C_{24}H_{30}ClN_8O_4Y$: C, 46.6; H, 4.8; N, 18.1. Found: C, 46.8; H, 4.9; N, 18.0. ^{1}H NMR (500 MHz, $CDCl_3$, 297 K): δ 6.57 (s, 2 H, CH), 5.78 (s, 4 H, H^4), 2.23 (s, 12 H, Me^3), 2.05 (s, 12 H, Me^5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 74.1 (CH), 146.6, 141.1 (C^{3or5}), 106.5 (C^4), 14.2 (Me^3), 12.3 (Me^5), 170.3 (CO_2^-). IR (Nujol): 1536 ν(C═N), 1670 $\nu_{as}(CO_2^-)$, 1430 $\nu_s(CO_2^-)$, 280 ν(Y−Cl) cm^{-1}. MS [FAB (*m*/*z* [assignment], % intensity)]: 583 [M − Cl], 100.

Synthesis of [$Li(THF)_4$][$YCl_3(\kappa^3$-bdmpzdta)] (9). To a THF (100 mL) suspension of [YCl_3] (0.50 g, 2.56 mmol) was added a suspension of [{Li(bdmpzdta)(H_2O)}$_4$] (1.56 g, 1.28 mmol) in THF (50 mL). The reaction mixture was stirred for 8 h under reflux. The solvent was removed under vacuum and the solid extracted with CH_2Cl_2. The solution was evaporated to dryness to yield a mixture of **9** and starting lithium compound as an orange solid. Compound **9** was isolated by crystallization from cold THF. Yield: 58%. Anal. Calcd for $C_{28}H_{47}Cl_3LiN_4O_4S_2Y$: C, 43.6; H, 6.1; N, 7.2. Found: C, 43.8; H, 6.3; N, 7.3. ^{1}H NMR (500 MHz, $CDCl_3$, 297 K): δ 7.70 (s, 1 H, CH), 6.10, 6.04 (s, 2 H, $H^{4,4'}$), 2.85, 2.47 (s, 6 H, $Me^{3,3'}$), 2.51, 2.49 (s, 6 H, $Me^{5,5'}$), 4.59 (m, 16 H, THF), 2.20 (m, 16 H, THF). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 75.9 (CH), 154.8, 152.5, 142.3, 141.4 ($C^{3,3'or5,5'}$), 107.2, 106.1 ($C^{4,4'}$), 14.9, 14.1 ($Me^{3,3'}$), 11.5, 11.3 ($Me^{5,5'}$), 75.7 (THF), 25.4 (THF), 255.9 (CS_2^-). IR (Nujol): 1575 ν(C═N), 1025 $\nu_{as}(CS_2^-)$, 750 $\nu_s(CS_2^-)$, 275 ν(Y−Cl) cm^{-1}.

Synthesis of [$YCl_2(\kappa^3$-bdmpza)(phen)] (10). To a THF (100 mL) suspension of [YCl_3] (0.50 g, 2.56 mmol) was added a solution of [{Li(bdmpza)(H_2O)}$_4$] (0.71 g, 0.64 mmol) in THF (50 mL). The reaction mixture was stirred, and a solution of 1,10-phenanthroline (0.46 g, 2.56 mmol) in THF (10 mL) was added. The mixture was stirred for 8 h under reflux, and the resulting precipitate was separated by filtration, washed with THF, and dried under vacuum. The white solid was extracted with CH_2Cl_2 (3 × 200 mL). Removal of the solvent afforded compound **10**, and this was crystallized from THF. Yield: 55%. Anal. Calcd for $C_{24}H_{23}Cl_2N_6O_2Y$: C, 49.1; H, 3.9; N, 14.3. Found: C, 49.2; H, 4.1; N, 14.1. ^{1}H NMR (500 MHz, $CDCl_3$, 297 K): δ 6.67 (s, 1 H, CH), 5.79 (s, 2 H, H^4), 2.16 (s, 6 H, Me^3), 2.04 (s, 6 H, Me^5), 9.86 (d, 2 H, H^1-phen), 8.55 (d, 2 H, J_{HH} = 7.3 Hz, H^3-phen), 8.01 (s, 2 H, H^4-phen), 7.79 (m, 2 H, H^2-phen). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 73.2 (CH), 146.1, 140.9 (C^{3or5}), 105.9 (C^4), 13.3 (Me^3), 11.1 (Me^5), 171.4 (CO_2^-), 150.3 (C^1-phen), 145.0 (C^{quat}-phen), 138.0 (C^{quat}-phen), 128.6 (C^3-phen), 126.7 (C^4-phen), 123.7 (C^2-phen). IR (Nujol): 1575, 1495 ν(C═N), 1706 $\nu_{as}(CO_2^-)$, 1450 $\nu_s(CO_2^-)$, 280 ν(Y−Cl) cm^{-1}. MS [FAB (*m*/*z* [assignment], % intensity)]: 552 [M − Cl], 100.

Synthesis of [$YCl_2(\kappa^3$-bdmpzdta)(phen)] (11). Compound **11** was prepared as described for **10** using [YCl_3] (0.50 g, 2.56 mmol), [{Li(bdmpzdta)(H_2O)}$_4$] (0.78 g, 0.64 mmol), and 1,10-phenanthroline (0.46 g, 2.56 mmol). The final product was isolated as an orange solid. Yield: 56%. Anal. Calcd for $C_{24}H_{23}Cl_2N_6S_2Y$: C, 46.5; H, 3.7; N, 13.6. Found: C, 46.7; H, 3.9; N, 13.3. ^{1}H NMR (500 MHz, $CDCl_3$, 297 K): δ 7.56 (s, 1 H, CH), 6.19 (s, 2 H, H^4), 2.78 (s, 6 H, Me^3), 2.49 (s, 6 H, Me^5), 9.75 (d, 2 H, H^1-phen), 8.43 (d, 2 H, J_{HH} = 7.0 Hz, H^3-phen), 8.10 (s, 2 H, H^4-phen), 7.68 (m, 2 H, H^2-phen). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 75.9 (CH), 150.2, 143.9 (C^{3or5}), 107.9 (C^4), 15.3 (Me^3), 11.5 (Me^5), 245.3 (CS_2^-), 153.3 (C^1-phen), 146.0 (C^{quat}-phen), 139.0 (C^{quat}-phen), 128.4 (C^3-phen), 125.7 (C^4-phen), 122.3 (C^2-phen). IR (Nujol): 1545, 1476 ν(C═N), 1059 $\nu_{as}(CS_2^-)$, 806 $\nu_s(CS_2^-)$, 260 ν(Y−Cl) cm^{-1}. MS [FAB (*m*/*z* [assignment], % intensity)]: 584 [M − Cl], 100.

Synthesis of [$YCl(\kappa^3$-bdmpza)(OEt)] (12). A solution of [YCl_2-(κ^3-bdmpza)(THF)] (**2**) (1.00 g, 2.45 mmol) in EtOH (100 mL) was stirred for 12 h under reflux. The solvent was removed in a vacuum, and the product was extracted with toluene to give a white solid after removal of the solvent. Yield: 65%. Anal. Calcd for $C_{14}H_{20}ClN_4O_3Y$: C, 40.3; H, 4.8; N, 13.4. Found: C, 40.5; H, 4.9; N, 13.7. ^{1}H NMR (500 MHz, $CDCl_3$, 297 K): δ 6.84 (s, 1 H, CH), 5.77 (s, 2 H, H^4), 2.12 (s, 6 H, Me^3), 2.04 (s, 6 H, Me^5), 4.12 (q,

2 H, $^3J_{HH}$ = 6.8 Hz, O*CH*$_2$CH$_3$), 1.23 (t, 3 H, $^3J_{HH}$ = 6.8 Hz, OCH$_2$*CH*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 73.2 (CH), 147.6, 141.6 (C^{3or5}), 107.5 (C^4), 13.5 (Me^3), 10.9 (Me^5), 164.8 (CO_2^-), 62.7 (O*CH*$_2$CH$_3$), 14.0 (OCH$_2$*CH*$_3$). IR (Nujol): 1563 ν(C=N), 1690 $\nu_{as}(CO_2^-)$, 1435 $\nu_s(CO_2^-)$, 673 ν(Y−OEt), 265 ν(Y−Cl) cm^{-1}. MS [FAB (*m*/*z* [assignment], % intensity)]: 382 [M − Cl], 100.

Synthesis of [YCl(κ^3-bdmpza)(O^{i}Pr)] (13). A solution of [YCl$_2$(κ^3-bdmpza)(THF)] (**2**) (1.00 g, 2.45 mmol) in ^{i}PrOH (100 mL) was stirred for 12 h under reflux. The solvent was removed in a vacuum and the product extracted with toluene to give a white solid after removal of the solvent. Yield: 75%. Anal. Calcd for $C_{15}H_{22}ClN_4O_3Y$: C, 41.8; H, 5.1; N, 13.0. Found: C, 41.9; H, 5.2; N, 13.2. ^{1}H NMR (500 MHz, $CDCl_3$, 297 K): δ 6.87 (s, 1 H, CH), 5.85 (s, 2 H, H^4), 2.12 (s, 6 H, Me^3), 2.10 (s, 6 H, Me^5), 5.24 [m, 1 H, $^3J_{HH}$ = 6.3 Hz, O*CH*(CH$_3$)$_2$], 1.29 [d, 6 H, $^3J_{HH}$ = 6.3 Hz, OCH(*CH*$_3$)$_2$]. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 73.4 (CH), 148.2, 141.4 (C^{3or5}), 107.3 (C^4), 13.4 (Me^3), 10.9 (Me^5), 164.3 (CO_2^-), 70.7 [O*CH*(CH$_3$)$_2$], 21.5 [OCH(*CH*$_3$)$_2$]. IR (Nujol): 1580 ν(C=N), 1710 $\nu_{as}(CO_2^-)$, 1495 $\nu_s(CO_2^-)$, 689 ν(Y−O^{i}Pr), 250 ν(Y−Cl) cm^{-1}. MS [FAB (*m*/*z* [assignment], % intensity)]: 396 [M − Cl], 100.

Synthesis of [ScCl(κ^3-bdmpzdta){N(SiMe$_3$)$_2$}] (14). To a cooled (−70 °C) solution of [ScCl$_2$(κ^3-bdmpzdta)(THF)] (**3**) (0.50 g, 1.06 mmol) or [Li(THF)$_4$][ScCl$_3$(κ^3-bdmpzdta)] (**7**) (0.76 g, 1.06 mmol) in THF (50 mL) was added a 1.0 M solution of [LiN(SiMe$_3$)$_2$] in Et$_2$O (1.06 mL, 1.06 mmol). The reaction mixture was stirred for 6 h at room temperature. The solvent was removed in a vacuum and the product extracted with hexane to give a yellow solid after removal of the solvent. Yield: 60%. Anal. Calcd for $C_{18}H_{33}ClN_5S_2ScSi_2$: C, 41.5; H, 6.4; N, 13.5. Found: C, 41.7; H, 6.5; N, 13.2. ^{1}H NMR (500 MHz, $CDCl_3$, 297 K): δ 7.57 (s, 1 H, CH), 6.03 (s, 1 H, $H^{4'}$), 5.92 (s, 1 H, H^4), 2.66 (s, 3 H, $Me^{3'}$), 2.52, 2.50 (s, 6 H, $Me^{5,5'}$), 1.95 (s, 3 H, Me^3), −0.10 [s, 18 H, N(SiMe$_3$)$_2$]. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 80.2 (CH), 153.1, 152.8, 141.8, 141.4 ($C^{3,3'or5,5'}$), 107.9 (C^4), 107.6 ($C^{4'}$), 14.5 ($Me^{3'}$), 13.2 (Me^3), 11.6, 11.5 ($Me^{5or5'}$), 237.1 (CS_2^-), 2.5 [N(SiMe$_3$)$_2$]. IR (Nujol): 1580 ν(C=N), 1050 $\nu_{as}(CS_2^-)$, 815 $\nu_s(CS_2^-)$, 350 ν(Sc−Cl) cm^{-1}. MS [FAB (*m*/*z* [assignment], % intensity)]: 360 [M − N(SiMe$_3$)$_2$], 100.

Synthesis of [Sc(κ^3-bdmpzdta){N(SiMe$_3$)$_2$}$_2$] (15). To a cooled (−70 °C) solution of [ScCl$_2$(κ^3-bdmpzdta)(THF)] (**3**) (0.50 g, 1.06 mmol) or [Li(THF)$_4$][ScCl$_3$(κ^3-bdmpzdta)] (**7**) (0.76 g, 1.06 mmol) in THF (50 mL) was added a 1.0 M solution of [LiN(SiMe$_3$)$_2$] in Et$_2$O (2.12 mL, 2.12 mmol). The reaction mixture was stirred for 6 h at room temperature. The solvent was removed in a vacuum and the product extracted with hexane to give an orange solid after removal of the solvent. Yield: 55%. Anal. Calcd for $C_{24}H_{51}N_6S_2ScSi_4$: C, 44.6; H, 7.9; N, 13.1. Found: C, 44.8; H, 8.1; N, 13.0. ^{1}H NMR (500 MHz, $CDCl_3$, 297 K): δ 7.50 (s, 1 H, CH), 5.87 (s, 2 H, H^4), 2.50 (s, 6 H, Me^3), 2.27 (s, 6 H, Me^5), 0.17 [s, 36 H, N(SiMe$_3$)$_2$]. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 79.5 (CH), 152.5, 141.4 (C^{3or5}), 106.1 (C^4), 14.4 (Me^3), 11.0 (Me^5), 240.1 (CS_2^-), 1.3 [N(SiMe$_3$)$_2$]. IR (Nujol): 1535 ν(C=N), 1045 $\nu_{as}(CS_2^-)$, 798 $\nu_s(CS_2^-)$ cm^{-1}. MS [FAB (*m*/*z* [assignment], % intensity)]: 486 [M − N(SiMe$_3$)$_2$], 100.

X-ray Crystallographic Structure Determination. Single crystals of a red block of **7** and orange prism of **9** were placed in a cooled nitrogen gas stream at 230 and 200 K, respectively, in a NONIUS-MACH3 diffractometer equipped with a graphite-monochromated Mo Kα radiation source (λ = 0.710 73 Å). The crystal data, data collection, structural solution, and refinement parameters for both compounds are summarized in Table 1. Intensity data were collected using an $\omega/2\theta$ scan technique. Examination of two standard reflections, monitored after 60 min, showed no sign of crystal deterioration. Data were corrected for Lorentz and polarization effects, and a semiempirical absorption correction (ψ-scans) was made.[13] The structures were solved by direct methods using the SHELXS computer program,[14] completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures (SHELXL97)[15] on F^2. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed using a "riding model" and included in the refinement at calculated positions. The crystal of **7** diffracted particularly poorly. The THF groups of the Li(THF)$_4$ cation, comprising atoms C30−C33 and C50−C53, were disordered over two sites, and due to the low data-to-parameter ratio "rigid bond" restraints were applied to these molecules.

Table 1. Crystallographic Data, Collection, and Refinement Parameters for **7** and **9**

param	**7**	**9**
empirical formula	$C_{12}H_{15}Cl_3N_4S_2Sc$, $C_{16}H_{32}LiO_4$	$C_{12}H_{15}Cl_3N_4S_2Y$, $C_{16}H_{32}LiO_4$
fw	726.07	770.02
temp (K)	230(2)	200(2)
wavelength (Å)	0.710 73	0.710 73
cryst system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.614(4)	9.707(2)
b (Å)	13.016(5)	12.937(3)
c (Å)	15.496(7)	15.528(3)
α (deg)	71.65(4)	71.92(3)
β (deg)	86.50(4)	86.56(3)
γ (deg)	80.98(3)	81.40(3)
V (Å^3)	1818(1)	1832.7(7)
Z	2	2
d(calcd) (g/cm^3)	1.327	1.395
abs coeff (cm^{-1})	5.74	19.60
F(000)	764	800
cryst size (cm^3)	0.3 × 0.2 × 0.2	0.4 × 0.3 × 0.2
θ range for data collcn (deg)	2.15−27.97	2.12−27.96
index ranges	$-12 \le h \le 12$ $-16 \le k \le 17$ $0 \le l \le 20$	$-12 \le h \le 12$ $-16 \le k \le 17$ $0 \le l \le 20$
reflcns collcd	9060	9120
indpndnt reflcns	8740 [R(int) = 0.0901]	8799 [R(int) = 0.0600]
max and min transmn	0.7971 and 0.4036	0.8505 and 0.5233
data/restraints/params	8740/15/381	8799/0/385
goodness-of-fit on F^2	0.946	1.182
final R indices [$I > 2\sigma(I)$]	R1 = 0.0841, wR2 = 0.1764	R1 = 0.0735, wR2 = 0.1737
largest diff peak and hole (e·Å^{-3})	0.534 and −0.368	0.513 and −0.547

Results and Discussion

The reagents [{Li(bdmpza)(H$_2$O)}$_4$][11a] [bdmpza = bis(3,5-dimethylpyrazol-1-yl)acetate], [{Li(bdmpzdta)(H$_2$O)}$_4$][12a] [bdmpzdta = bis(3,5-dimethylpyrazol-1-yl)dithioacetate], and (Hbdmpze)[12b] [bdmpze = 2,2-bis(3,5-dimethylpyrazol-1- yl)-ethoxide] (see Figure 1) were used in the complexation of a number of scandium and yttrium precursors. These compounds (the latter with the prior addition of ^{n}BuLi) reacted with solutions of ScCl$_3$(THF)$_3$ or YCl$_3$ (Scheme 1) on stirring for 8 h under reflux in a 1:1 molar ratio in THF to give a solution from which the complexes [MCl$_2$(κ^3-bdmpzx)(THF)] (x = a, M = Sc (**1**), Y (**2**); x = dta, M = Sc (**3**), Y (**4**); x = e, M = Sc (**5**), Y (**6**)) were isolated as white (**1**, **2**, **5**, **6**)

(13) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *24*, 351.
(14) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.
(15) Sheldrick, G. M. *Program for the Refinement of Crystal Structures from Diffraction Data*; University of Göttingen: Göttingen, Germany, 1997.

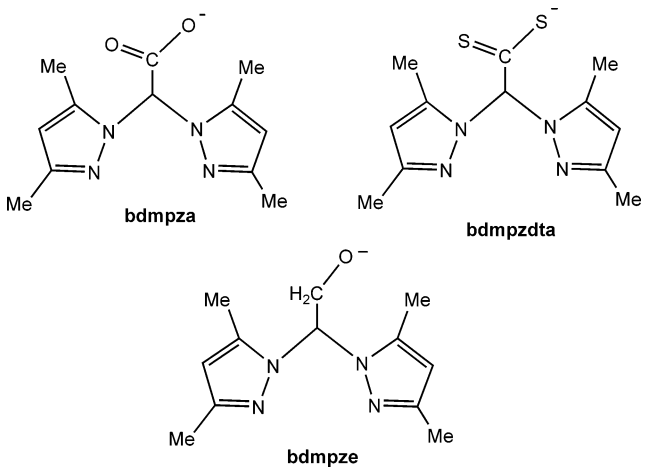
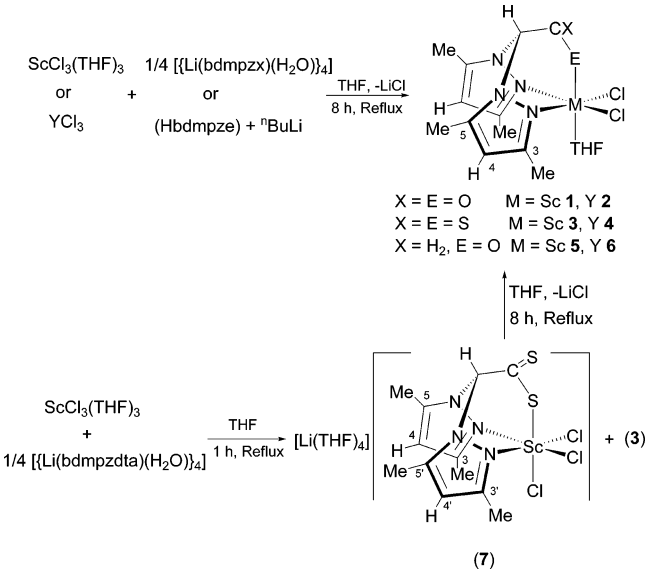


Figure 1. Heteroscorpionate ligands used in the synthesis of scandium and yttrium complexes.

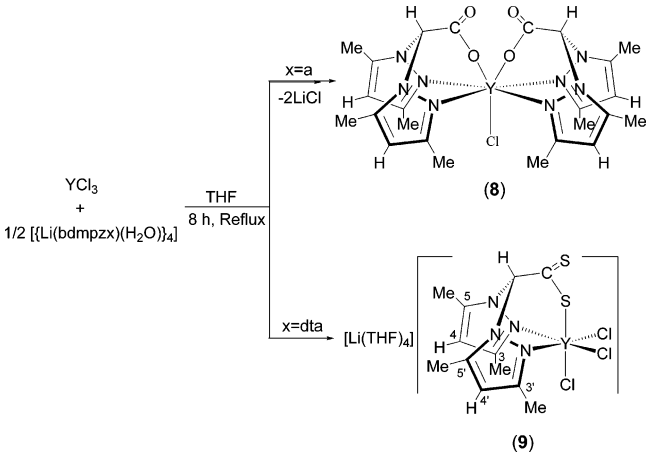
Scheme 1. Synthesis of $[MCl_2(\kappa^3\text{-bdmpzx})(THF)]$ (**1**−**6**) and $[Li(THF)_4][ScCl_3(\kappa^3\text{-bdmpzdta})]$ (**7**)



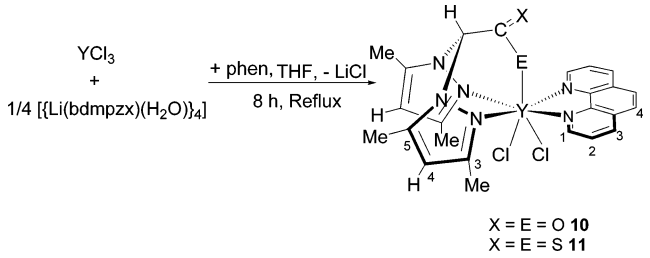
or red (**3**, **4**) solids after the appropriate workup. However, when the reactions were carried out for 1 h under reflux, the same complexes were isolated together with starting material—except for the reaction between $ScCl_3(THF)_3$ and $[\{Li(bdmpzdta)(H_2O)\}_4]$, where a mixture of the complex $[ScCl_2(\kappa^3\text{-bdmpzdta})(THF)]$ (**3**) and a new anionic complex $[Li(THF)_4][ScCl_3(\kappa^3\text{-bdmpzdta})]$ (**7**) was obtained in a 3:2 molar ratio. These complexes were separated by their different solubility in cold THF, and **7** could be isolated as a red solid in up to 35% yield from the reaction mixture. Finally, when the THF solution of this mixture of complexes **3** and **7** was heated under reflux for 8 h, only complex **3** was obtained after the appropriate workup procedure, indicating that a transformation of complex **7** to complex **3** takes place.

When the reactions between the lithium compounds $[\{Li(bdmpzx)(H_2O)\}_4]$ or the alcohol (Hbdmpze) and the complex $ScCl_3(THF)_3$ were carried out for 8 h under reflux but in a 2:1 molar ratio, the same complexes $[ScCl_2(\kappa^3\text{-bdmpzx})(THF)]$ **1**, **3**, and **5** were obtained (as when the reactions were carried out in a 1:1 molar ratio) together with starting

Scheme 2. Synthesis of $[YCl(\kappa^3\text{-bdmpza})_2]$ (**8**) and $[Li(THF)_4][YCl_3(\kappa^3\text{-bdmpzdta})]$ (**9**)



Scheme 3. Synthesis of $[YCl_2(\kappa^3\text{-bdmpzx})(phen)]$ (**10**, **11**)



ligand. However, new complexes were obtained when the same reactions with $[\{Li(bdmpzx)(H_2O)\}_4]$ were performed with YCl_3. Thus, reaction of $[\{Li(bdmpza)(H_2O)\}_4]$ with YCl_3 (Scheme 2) in a 2:1 molar ratio for 8 h under reflux gave the complex $[YCl(\kappa^3\text{-bdmpza})_2]$ (**8**) as a white solid. On the other hand, the same reaction but with $[\{Li(bdmpzdta)(H_2O)\}_4]$ resulted in the formation of a new anionic complex $[Li(THF)_4][YCl_3(\kappa^3\text{-bdmpzdta})]$ (**9**) (similar to the scandium complex **7**) together with the starting lithium compound. Compound **9** was isolated by crystallization from cold THF (Scheme 2). The transformation of complex **9** to complex **4** takes place when on heating under reflux for 24 h. The stabilization of the anionic species **7** and **9**, where the chloride ligand is not displaced by the dithioacetate unit of the heteroscorpionate ligand, may be apparently related with the presence of a soft sulfur donor. The increase in the coordination number for Y in **8** with respect to the behavior observed for the Sc complexes can be explained in terms of the larger atomic size of the Y atom.

To confirm this ability of yttrium complexes to expand their coordination number beyond six, 1 equiv of $[\{Li(bdmpza)(H_2O)\}_4]$ or $[\{Li(bdmpzdta)(H_2O)\}_4]$ was added to a solution of YCl_3 in THF under reflux followed by the addition of 1 equiv of 1,10-phenanthroline. This resulted in the formation of the corresponding $[YCl_2(\kappa^3\text{-bdmpzx})(phen)]$ (x = a (**10**), x = dta (**11**)) complexes, which precipitated from THF as white and orange solids, respectively (Scheme 3). The same reactions with scandium trichloride led to complexes **1**, **3**, and **5**, but the coordination of 1,10-phenanthroline does not take place.

The different complexes were characterized spectroscopically. The mass spectra of these complexes indicate a

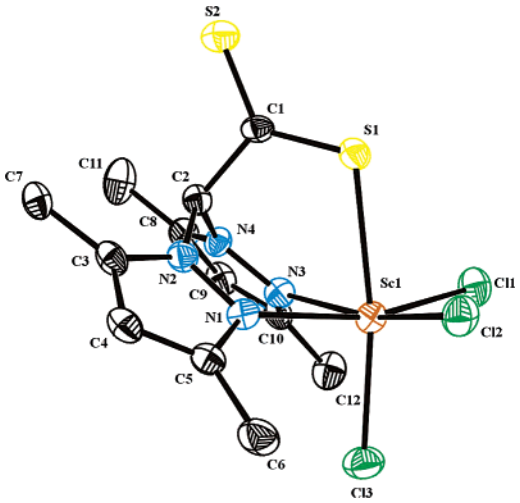


Figure 2. ORTEP view of $[ScCl_3(\kappa^3\text{-bdmpzdta})]^-$ (**7**). Ellipsoids are at the 30% probability level, and hydrogen atoms have been omitted for clarity.

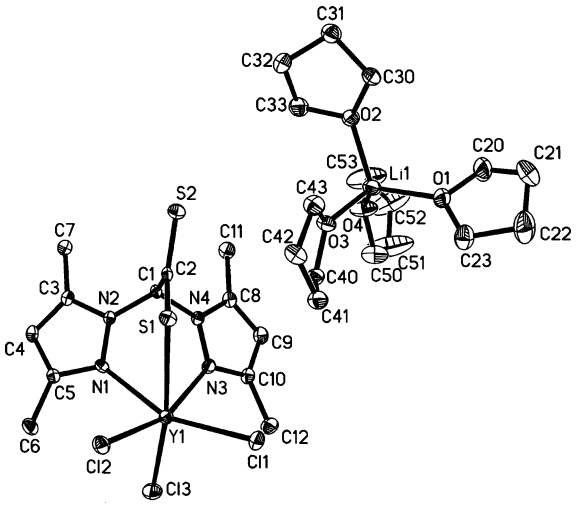


Figure 3. ORTEP view of complex (**9**). Ellipsoids are at the 30% probability level, and hydrogen atoms have been omitted for clarity.

mononuclear formulation (see Experimental Section). The IR spectra of **1**, **2**, **8**, and **10** show two strong bands at ca. 1690 and 1430 cm^{-1}, which are assigned to $\nu_{as}(CO_2^-)$ and $\nu_s(CO_2^-)$, respectively. The value of $\Delta\nu_{as-s}$ (ca. 260 cm^{-1}) for these compounds is consistent with an O-coordination (monodentate) mode.[16] The IR spectra of **3**, **4**, **7**, **9**, and **11** contain two strong bands at ca. 1050 and 800 cm^{-1}, which are assigned to $\nu_{as}(CS_2^-)$ and $\nu_s(CS_2^-)$, respectively. IR spectra of complexes **5** and **6** show a strong band at ca. 570 cm^{-1} that is assigned to ν(M−O). All complexes **1**−**11** show in their IR spectra another band of interest at ca. 300 cm^{-1}. This band was assigned to ν(M-Cl) of the terminal group. The ^{1}H and ^{13}C{H} NMR spectra of **1**−**6** show a single set of resonances for the pyrazole rings, indicating that the pyrazoles are equivalent. These data confirm an octahedral disposition with κ^3-NNE coordination (E = O or S) for the heteroscorpionate ligand with a THF ligand trans with respect to the oxygen or sulfur atom of the bdmpzx ligands (see Scheme 1). However, the ^{1}H and ^{13}C{H} NMR spectra of the anionic complexes **7** and **9** exhibit two resonances for each H^4, Me^3, and Me^5 pyrazole protons, indicating that the two pyrazole rings are nonequivalent. These results are consistent with a proposed octahedral disposition in which protons of a methyl group of a pyrazole ring would interact with chloride atoms from a neighboring molecule, a situation leading to the nonequivalent pyrazole rings as depicted in Figure 4 (see below) for complex **7**.

This above arrangement in the solid state was corroborated by X-ray diffraction studies on **7** and **9**. The crystal structures are shown in Figures 2 and 3 along with the atom-numbering scheme. The most important bond lengths and angles are presented in Table 2. Both complexes show an ionic complex structure. Monomeric anion complexes contain one tridentate heteroscorpionate ligand bonded to the metal atom through the two nitrogen atoms and the sulfur atom from the κ^3-bdmpzdta ligand. In addition, the metal center is coordinated to three chloride ligands in a distorted octahedral geometry, probably due to the constraints imposed by the chelating ligand. This substantial distortion is manifested in the bent axis defined by N1−metal−Cl1, with values for this angle of 162.4(2) and 158.5(1)° for complexes **7** and **9**, respectively. The metal atoms are displaced from the equatorial plane defined by the N1−N3−Cl1−Cl2 atoms by 0.254(4) and 0.319(2) Å for complexes **7** and **9**, respectively. The distance of the axial and equatorial chlorine and the distance of the metal−N of pyrazole ring fall within the expected range.[17] The C1−S1 and C2−S2 bond distances indicate the existence of a delocalized S−C−S bond in both complexes. Both crystals are stabilized by an extensive hydrogen-bonding network, the geometrical features of which are shown in Tables 3 and 4. In both complexes the chloride ligand Cl1 is involved in an intermolecular hydrogen bond to the CH_3 methyl group of one pyrazole ring, which is supported by the NMR data (vide supra). In complex **7** the chlorine atom Cl3 is involved in an asymmetrically bifurcated hydrogen bond with H33c and H51c, corresponding to two different THF molecules (Figure 4a). In complex **9** the chlorine atom Cl3 is not hydrogen bonded, but Cl2 is involved in three interactions (Figure 4b). Both complexes show infinite chains of $[MCl_3(\kappa^3\text{-bdmpzdta})]-$ running along the *a*-axis, and these are linked by the $Li(THF)_4$ counterion (Figure 5). Anionic complexes of this stoichiometry constitute the first examples of scandium and yttrium derivatives with scorpionate or cyclopentadienyl ancillary ligands.

The ^{1}H and ^{13}C{H} NMR spectra of **8**, **10**, and **11** also show a single set of resonances for the pyrazole rings, indicating that the pyrazoles are equivalent. These results are consistent with the proposed seven-coordinate disposition in which a symmetric plane exists containing the carboxylate groups of the heteroscorpionate ligands and the chloride ligand in complex **8** (Scheme 2). In complexes **10** and **11**

(16) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley-VCH: New York, 1997.

(17) (a) Hajela, S.; Schaefer, W. P.; Bercaw, J. E. *J.Organomet. Chem.* **1997**, *532*, 45. (b) Blackwell, J.; Lehr, C.; Sun, Y.; Piers, W. E.; Pearce-Batchilder, S. D.; Zaworotko, M. J.; Young, V. G. *Can. J. Chem.* **1997**, *75*, 702. (c) Boyd, C. L.; Toupance, T.; Tyrrell, B. R.; Ward, B. D.; Wilson, C. R.; Cowley, A. R.; Mountford, P. *Organometallics* **2005**, *24*, 309.

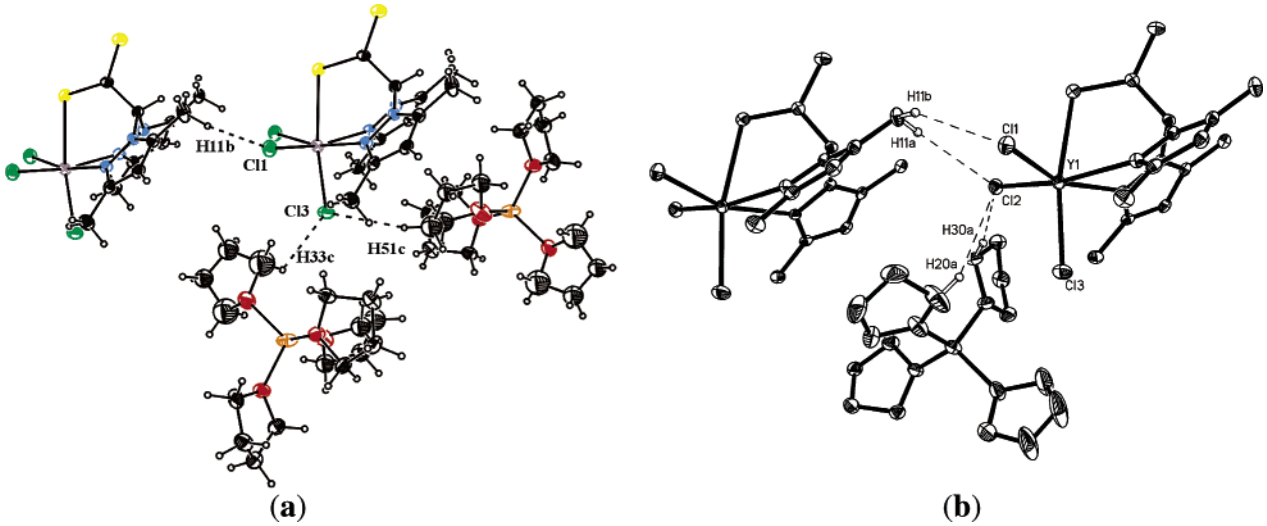


Figure 4. Hydrogen-bonding network: (a) complex **7**; (b) complex **9**.

Table 2. Bond Lengths (Å) and Angles (deg) for **7** and **9**

7		**9**	
	Bond Lengths		
Sc(1)−Cl(1)	2.414(3)	Y(1)−Cl(1)	2.563(2)
Sc(1)−Cl(2)	2.412(3)	Y(1)−Cl(2)	2.560(2)
Sc(1)−Cl(3)	2.396(3)	Y(1)−Cl(3)	2.550(2)
Sc(1)−N(1)	2.310(8)	Y(1)−N(1)	2.445(5)
Sc(1)−N(3)	2.276(8)	Y(1)−N(3)	2.445(5)
Sc(1)−S(1)	2.674(3)	Y(1)−S(1)	2.809(2)
S(1)−C(1)	1.669(9)	S(1)−C(2)	1.663(7)
S(2)−C(1)	1.647(8)	S(2)−C(2)	1.663(7)
N(2)−C(2)	1.45(1)	N(2)−C(1)	1.448(8)
N(4)−C(2)	1.44(1)	N(4)−C(1)	1.461(7)
C(1)−C(2)	1.54(1)	C(1)−C(2)	1.544(9)
	Angles		
N(3)−Sc(1)−N(1)	76.4(3)	N(3)−Y(1)−N(1)	72.5(2)
N(3)−Sc(1)−Cl(3)	93.4(2)	N(3)−Y(1)−Cl(3)	94.6(1)
N(1)−Sc(1)−Cl(3)	92.0(2)	N(1)−Y(1)−Cl(3)	92.1(1)
N(3)−Sc(1)−Cl(2)	164.6(2)	N(3)−Y(1)−Cl(2)	160.8(1)
N(1)−Sc(1)−Cl(2)	93.0(2)	N(1)−Y(1)−Cl(2)	93.6(1)
Cl(3)−Sc(1)−Cl(2)	98.1(1)	Cl(3)−Y(1)−Cl(2)	99.15(7)
N(3)−Sc(1)−Cl(1)	90.0(2)	N(3)−Y(1)−Cl(1)	89.8(1)
N(1)−Sc(1)−Cl(1)	162.4(2)	N(1)−Y(1)−Cl(1)	158.5(1)
Cl(3)−Sc(1)−Cl(1)	100.0(1)	Cl(3)−Y(1)−Cl(1)	101.73(7)
Cl(2)−Sc(1)−Cl(1)	97.9(1)	Cl(2)−Y(1)−Cl(1)	100.30(7)
N(3)−Sc(1)−S(1)	82.6(2)	N(3)−Y(1)−S(1)	79.9(1)
N(1)−Sc(1)−S(1)	79.1(2)	N(1)−Y(1)−S(1)	75.6(1)
Cl(3)−Sc(1)−S(1)	170.9(1)	Cl(3)−Y(1)−S(1)	167.49(7)
Cl(2)−Sc(1)−S(1)	84.5(1)	Cl(2)−Y(1)−S(1)	83.83(7)
Cl(1)−Sc(1)−S(1)	88.2(1)	Cl(1)−Y(1)−S(1)	89.59(7)
C(1)−S(1)−Sc(1)	108.6(3)	C(2)−S(1)−Y(1)	108.8(3)
C(2)−C(1)−S(2)	115.7(7)	C(1)−C(2)−S(2)	115.0(5)
C(2)−C(1)−S(1)	117.2(6)	C(1)−C(2)−S(1)	119.9(5)
S(2)−C(1)−S(1)	127.1(6)	S(2)−C(2)−S(1)	125.1(4)

Table 3. Hydrogen Bonds for Compound **7** (Å, deg)

D−H···A	*d*(D−H)	*d*(H···A)	<DHA	*d*(D···A)	symmetry[a]
C11−H11B···Cl1	0.96	2.773	149.21	3.631	$x-1, +y, +z$
C33A−H33C···Cl 3	0.97	2.767	119.10	3.348	$-x+1, -y+1, -z$
C51A−H51C···Cl 3	0.97	2.805	166.26	3.755	x, y, z

[a] Symmetry operation for A.

this plane contains the carboxylate or dithiocarboxylate fragments as well as the chloride ligands, and the plane bisects the 1,10-phenanthroline ligand (Scheme 3). Another possible symmetric geometry for **10** and **11** could be one in which the phenanthroline ligand is in a cis position with respect to the pyrazole rings, but the absence of a response in the ^{1}H NOESY-1D experiment from phenanthroline

Table 4. Hydrogen Bonds for Compound **9** (Å, deg)

D−H···A	*d*(D−H)	*d*(H···A)	<DHA	D(D···A)	symmetry[a]
C11−H11b···Cl1	0.96	2.889	141.8	3.691(6)	$x-1, y, z$
C11−H11a···Cl2	0.96	2.901	155.2	3.794(6)	$x-1, y, z$
C20−H20a···Cl2	0.97	2.859	144.7	3.69(1)	$x-1, 1+y, z$
C30−H30a···Cl2	0.97	2.927	170.8	3.888(9)	$x-1, 1+y, z$

[a] Symmetry operation for A.

protons on irradiating the methyl groups of the pyrazole rings confirms the trans disposition represented in Scheme 3. The disposition of the phenanthroline ligand is consistent with the ^{1}H NMR spectra. The NMR spectra of complexes **10** and **11** contain four resonances assigned to this ligand, whereas in other possible geometrical dispositions eight resonances would be observed.[5c]

Furthermore, we have prepared a new class of heteroscorpionate−metal complex which contains an alkoxide ancillary ligand. Direct reaction of [YCl$_2$(κ^3-bdmpza)(THF)] (**2**) with several alcohols (Scheme 4) gave, after the appropriate workup, the complexes [YCl(κ^3-bdmpza)(OR)] (R = Et (**12**), *i*Pr (**13**)), which were isolated as white solids (the analogous scandium complexes do not react with alcohols). The mass spectra of these complexes indicate a mononuclear formulation. In the IR spectra the $\Delta\nu_{as-s}$ values for the $\nu(CO_2^-)$ vibrations are 255 and 215 cm^{-1}, respectively, which are in agreement with monodentate coordination of the acetate moiety. Two strong bands are also observed at ca. 680 and 280 cm^{-1}; the first of these was assigned to ν(Y−OR), and the latter, to ν(Y−Cl). The ^{1}H NMR spectra of these complexes exhibit a single set of resonances for H^4, Me^3, and Me^5, indicating that the pyrazole rings are equivalent. These results are consistent with the proposed five-coordinate disposition in which a symmetric plane exists that contains the carboxylate group of heteroscorpionate, the alkoxide, and the chloride ligands to give a trigonal bipiramidal geometry (Scheme 4). In addition, the ^{13}C{H} NMR spectra show 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).

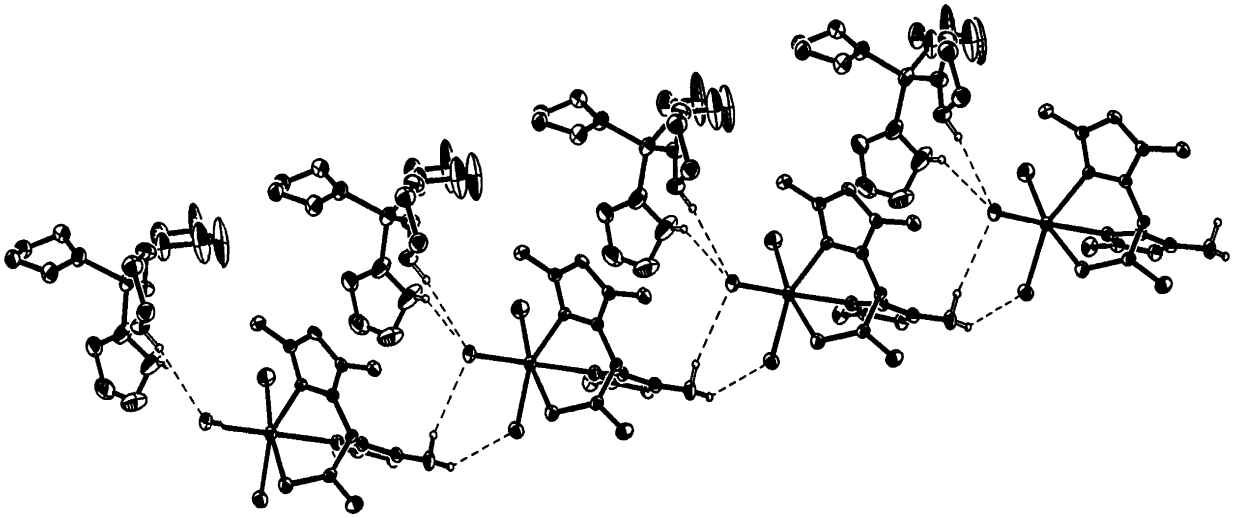
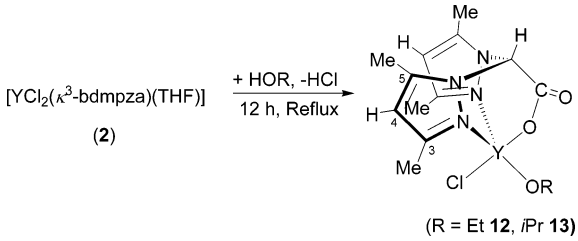
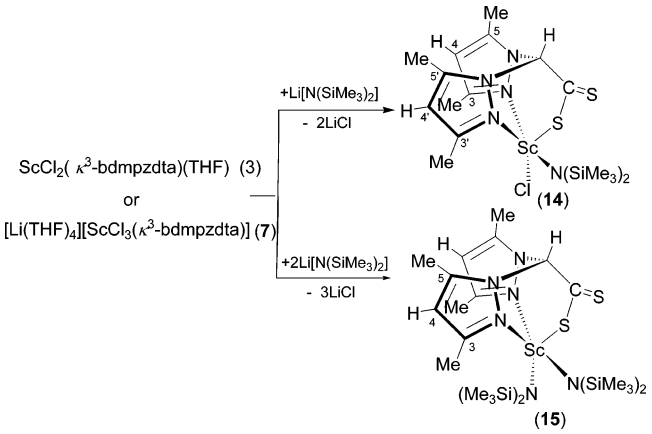


Figure 5. Portion of the infinite one-dimensional chain of **9** showing the hydrogen bonding.

Scheme 4. Synthesis of [YCl(κ^3-bdmpza)(OR)] (**12**, **13**)



Scheme 5. Synthesis of Complexes [ScCl(κ^3-bdmpzdta){N(SiMe$_3$)$_2$}] (**14**) and [Sc(κ^3-bdmpzdta){N(SiMe$_3$)$_2$}$_2$] (**15**)



Finally, we explored the reactivity of [ScCl$_2$(κ^3-bdmpzdta)(THF)] (**3**) and [Li(THF)$_4$][ScCl$_3$(κ^3-bdmpzdta)] (**7**) toward LiN(SiMe$_3$)$_2$·Et$_2$O in 1:1 and 1:2 molar ratios. These reactions gave the complexes [ScCl(κ^3-bdmpzdta){N(SiMe$_3$)$_2$}] (**14**) and [Sc(κ^3-bdmpzdta){N(SiMe$_3$)$_2$}$_2$] (**15**), respectively (Scheme 5) (the analogous yttrium complexes react with the lithium amide to produce a complex mixture of products which could not be isolated). The ^{1}H and ^{13}C{^{1}H} NMR spectra of **14** exhibit two distinct sets of pyrazol-1-yl resonances, indicating the existence of two types of pyrazol-1-yl ring. A five-coordinate environment for this complex can be proposed in which the two pyrazole rings are located in cis and trans positions with respect to the chloride ligand or to the amide ligand, i.e. a square planar pyramidal geometry (see Scheme 5). The phase-sensitive ^{1}H NOESY-

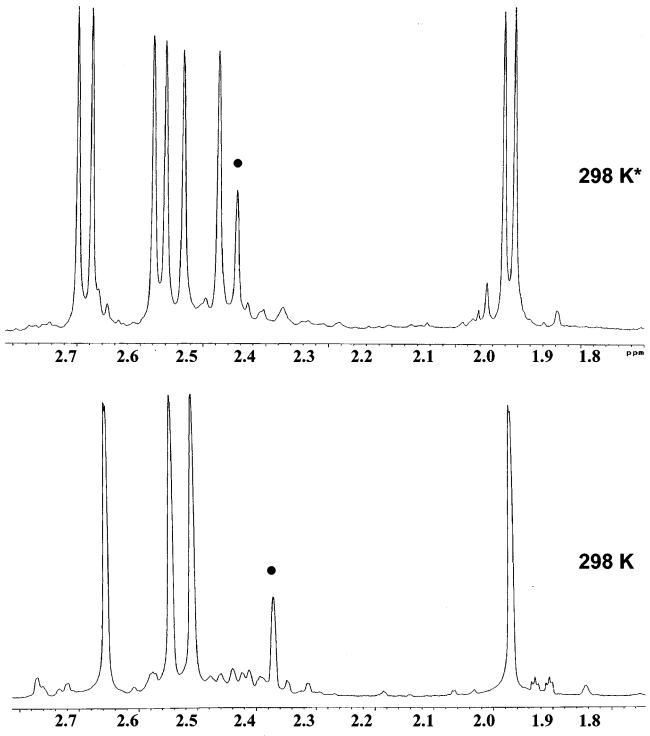


Figure 6. ^{1}H NMR spectra in the region of the Me group of the complex [ScCl(κ^3-bdmpzdta){N(SiMe$_3$)$_2$}] (**14**). Key: (∗) with chiral shift reagent; (●) impurity of 3,5-dimethylpyrazole.

1D spectra were also obtained in order to confirm the assignments of the signals for the Me^3, Me^5, and H^4 groups of each pyrazole ring. In this complex the metal atom is a chiral center, and we confirmed the presence in solution of the corresponding two enantiomers by adding a chiral shift reagent, namely (*R*)-(−)-(9-anthryl)-2,2,2-trifluoroethanol. This process gave rise to two signals for each proton in the ^{1}H NMR spectra, resulting from the two diastereoisomers of the corresponding two enantiomers (Figure 6). However, the ^{1}H and ^{13}C{H} NMR spectra of **15** show a single set of resonances for the pyrazole rings, indicating that the pyrazoles are equivalent. These results are consistent with the proposed five-coordinate disposition in which two isomers are possible—one with a square planar pyramidal geometry

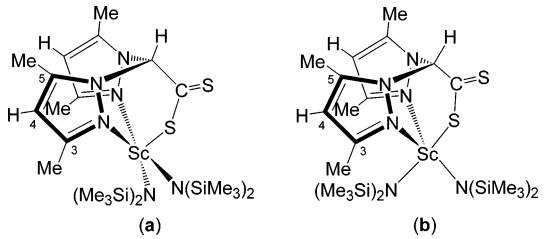


Figure 7. Proposed structures for the two isomers of complex **15**.

(Figure 7a) and another with a trigonal bipyramidal geometry (Figure 7b). In both isomers the pyrazole rings are equivalent. However, in the first isomer the amide ligands are equivalent whereas in the second they are different. A VT-NMR study (297−193 K in CD_2Cl_2) was carried out, and only one set of NMR signals was observed for the amide ligands in this complex, which is consistent with a square planar pyramidal geometry (Figure 7a).

In conclusion, we have synthesized and characterized the first scandium and yttrium complexes containing heteroscopionate ligands. We have reported here a large number of neutral and anionic complexes of group 3 metals stabilized by NNO and NNS tripod ligands of different types: [(κ^3-NNE)MX_2(solv)]; [(κ^3-NNE)MX_3]$^-$; [(κ^3-NNE)$_2$MX]; [(κ^3-NNE)MX_2(LL)]; [(κ^3-NNE)MX(OR)]; [(κ^3-NNE)MX(NR_2)]; [(κ^3-NNE)M(NR_2)$_2$]. In addition, the X-ray crystal structures of **7** and **9** were established and anionic complexes of this stoichiometry constitute the first examples of scandium and yttrium derivatives with scorpionate or cyclopentadienyl ancillary ligands.

Acknowledgment. We gratefully acknowledge financial support from the Dirección General de Enseñanza Superior e Investigación Científica of Spain (Grant. No. BQU2002-04638-CO2-02) and the Junta de Comunidades de Castilla-La Mancha (Grant. N*o*s. 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**, and **9** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC050525Y