Scandium and Yttrium Complexes Supported by NNCp Heteroscorpionate Ligands: Synthesis, Structure, and Polymerization of ϵ-Caprolactone

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Mixtures of two scorpionate/cyclopentadiene regioisomers—bpzcpH (1-[2,2-bis(3,5-dimethylpyrazol-1-yl)-1,1-diphenylethyl]-1,3-cyclopentadiene (**1a**) and 2-[2,2-bis(3,5-dimethylpyrazol-1-yl)-1,1-diphenylethyl]-1,3-cyclopentadiene (**1b**)) and bpztcpH (1-[2,2-bis(3,5-dimethylpyrazol-1-yl)-1-*tert*-butylethyl]-1,3-cyclopentadiene (**2a**) and 2-[2,2-bis(3,5-dimethylpyrazol-1-yl)-1-*tert*-butylethyl]-1,3-cyclopentadiene (**2b**))—were prepared by deprotonation of bis(3,5-dimethylpyrazol-1-yl)methane with Bu^{n}Li followed by reaction with 6,6-diphenylfulvene or 6-*tert*-butylfulvene and subsequent treatment with saturated aqueous ammonium chloride. Reactions of hybrid scorpionate/cyclopentadiene compounds with $[M(CH_2SiMe_3)_3(THF)_3]$ (M = Sc, Y) afford the dialkyl complexes $[M(CH_2SiMe_3)_2(bpzcp)]$ (M = Sc (**3**), Y (**4**)) and $[M(CH_2SiMe_3)_2(bpztcp)]$ (M = Sc (**5**), Y (**6**)). The cationic alkyl complexes $[M(CH_2SiMe_3)(bpzcp)]^+$ (M = Sc (**7**), Y (**8**)) were also prepared by the reaction of complexes **3** and **4** with $[CPh_3][B(C_6F_5)_4]$ in THF. The structures of these compounds were determined by spectroscopic methods, and the X-ray crystal structures of **2** and **3** were also established. The bis(alkyl) complexes **3** and **4** were found to be active initiators for the ring-opening polymerization of ϵ-caprolactone (up to 75% conversion of 200 equiv in 10 min) and yielded polymers with narrow molecular weight distributions.

Introduction

Poly(pyrazolyl)-based ("scorpionate") ligands have been widely exploited over a broad range of transition-metal applications, including organometallic, catalytic, bioinorganic, and supramolecular contexts.[1] Recently, anionic "heteroscorpionate" ligands in which a neutral pyrazole ring has been formally substituted by an arm (see Figure 1) bearing an anionic donor "E", such as carboxylate, dithiocarboxylate, aryloxide, alkoxide, amide, cyclopentadienyl, and, more recently, acetamidate, thioacetamidate, and amidinate functional groups have led to considerable interest in the "post-metallocene" chemistry of the transition metals.[2] Although there is extensive literature concerning transition metals and heteroscorpionate ligands, the chemistry of group 3 and lanthanide metals with scorpionate ligands has focused mainly on the very widely exploited tris(pyrazolyl)hydroborate ligands.[3] Only two (very recent) reports on the use of NNO, NNS, and NNN heteroscorpionates in group 3 coordination or organometallic chemistry have been published.[4]

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(1) See for example: (a) Trofimenko, S., *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1998. (b) Marques, N.; Sella, A.; Takats, J. *Chem. Rev.* **2002**, *102*, 2137. (c) Otero, A.; Fernández-Baeza, J.; Antiñolo, A.; Tejeda, J.; Lara-Sánchez, A. *Dalton Trans.* **2004**, 1499. (d) Parkin, G. *Chem. Rev.* **2004**, *104*, 699. (e) Pettinari, C.; Pettinari, R. *Coord. Chem. Rev.* **2005**, *249*, 525. (f) Pettinari, C.; Pettinari, R. *Coord. Chem. Rev.* **2005**, *249*, 663. (g) Bigmore, H. R.; Lawrence, S. C.; Mountford, P.; Tredget, C. S. *Dalton Trans.* **2005**, 635.

(2) See for example: (a) Otero, A.; Fernández-Baeza, J.; Antiñolo, A.; Tejeda, J.; Carrillo-Hermosilla, F.; Diez-Barra, E.; Lara-Sánchez, A.; Fernández-López, M.; Lanfranchi, M.; Pellinghelli, M. A. *J. Chem. Soc., Dalton Trans.* **1999**, 3537. (b) Otero, A.; Fernández-Baeza, J.; Antiñolo, A.; Tejeda, J.; Carrillo-Hermosilla, F.; Lara-Sánchez, A.; Sánchez-Barba, L.; Fernández-López, M.; Rodríguez, A. M.; López-Solera, I. *Inorg. Chem.* **2002**, *41*, 5193. (c) 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. (d) Ghosh, P.; Parkin, G. J. *Chem. Commun.* **1998**, 37. (e) Adhikari, D.; Zhao, G.; Basuli, F.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. *Inorg. Chem.* **2006**, *45*, 1604. (f) Hammes, B. S.; Chohan, B. S.; Hoffman, J. T.; Einwächter, S.; Carrano, C. J. *Inorg. Chem.* **2004**, *43*, 7800. (g) Smith, J. N.; Shirin, Z.; Carrano, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 868. (h) Kopf, H.; Pietraszuk, C.; Hübner, E.; Burzlaff, N. *Organometallics* **2006**, *25*, 2533. (i) Otero, A.; Fernández-Baeza, J.; Antiñolo, A.; Tejeda, J.; Lara-Sánchez, A.; Sánchez-Barba, L.; Sánchez-Molina, M.; Franco, S.; López-Solera, I.; Rodríguez, A. M. *Eur. J. Inorg. Chem.* **2006**, 707. (j) Otero, A.; Fernández-Baeza, J.; Antiñolo, A.; Tejeda, J.; Lara-Sánchez, A.; Sánchez-Barba, L.; Sánchez-Molina, M.; Franco, S.; López-Solera, I., Rodríguez, A. M. *Dalton Trans.* **2006**, 4359. (k) Otero, A.; Fernández-Baeza, J.; Antiñolo, A.; Tejeda, J.; Lara-Sánchez, A.; Sánchez-Barba, L.; López-Solera, I.; Rodríguez, A. M. *Inorg. Chem.* **2007**, *46*, 1760–1770. (l) Milione, S.; Montefusco, S.; Cuenca, T.; Grassi, A. *Chem. Commun.* **2003**, 1176. (m) Milione, S.; Bertolasi, V.; Cuenca, T.; Grassi, A. *Organometallics* **2005**, *24*, 4915.

(3) See for example: (a) Marques, N.; Sella, A.; Takats, J. *Chem. Rev.* **2002**, *102*, 2137. (b) Stainer, M. V. R.; Takats, J. *J. Am. Chem. Soc.* **1983**, *105*, 410. (c) Long, D. P.; Bianconi, P. A. *J. Am. Chem. Soc.* **1996**, *118*, 12453. (d) Roitershtein, D.; Domingos, A.; Pereira, L. C. J.; Ascenso, J. R.; Marques, N. *Inorg. Chem.* **2003**, *42*, 7666. (e) Blackwell, J.; Lehr, C.; Sun, Y.; Piers, W. E.; Zaworotko, M. J.; Pearce-Batchilder, S. D.; Young, G. *Can. J. Chem.* **1997**, *75*, 702.

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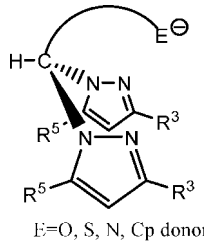


Figure 1. Overall view of anionic heteroscorpionate ligands.

Furthermore, cyclopentadienyl systems with an additional donor function are attracting increased interest in the chemistry of early transition metals because of their potential applications as catalysts in polymerization processes.[5] Ligands that possess both a cyclopentadienyl ring and heteroatoms connected by an appropriate spacer are receiving considerable attention in synthesis and catalysis, as they lead to significant changes in both steric and electronic effects on the metal centers.[6] Bearing in mind the development of donor-functionalized cyclopentadienyl ligands and the emerging importance of the heteroscorpionate systems, it would be interesting to prepare hybrid scorpionate/cyclopentadienyl compounds as precursors for the introduction of these ligands into transition-metal complexes. This type of ligand was unknown until we recently reported the first hybrid scorpionate/cyclopentadienyl ligands.[2c,7] The preparation of this new class of tridentate ligand by a simple and efficient synthetic route led us to develop and fully explore the potential offered by this type of ligand in the organometallic or coordination chemistry of group 3 metals, especially to prepare scandium and yttrium derivatives that could have potential interest as initiators in the ring-opening polymerization (ROP) of cyclic esters such as lactones. These types of catalytic processes are currently generating a great deal of interest because of the biodegradability and biocompatibility of the resulting polyesters.[8,9]

In this paper we describe the preparation, in a simple one-pot procedure, of new scorpionate/cyclopentadiene compounds. These compounds were subsequently employed in a series of protonolysis processes to prepare scorpionate/cyclopentadienyl alkyl derivatives of scandium and yttrium. In addition, several electron-deficient cationic alkyl complexes were also prepared. Finally, the reactivity toward ring-opening polymerization of ϵ-caprolactone is reported for some of these complexes.

Results And Discussion

Ligand Syntheses. First, we prepared a series of new hybrid scorpionate/cyclopentadiene compounds. The one-pot reaction of bis(3,5-dimethylpyrazol-1-yl)methane (bdmpzm)[10] with Bu^n-Li, followed by treatment with 6,6-diphenylfulvene or 6-*tert*-butylfulvene[11] and then with a saturated aqueous solution of ammonium chloride, afforded the desired compounds as a mixture of two regioisomers in a 3:1 ratio: bpzcpH (1-[2,2-bis(3,5-dimethylpyrazol-1-yl)-1,1-diphenylethyl]-1,3-cyclopentadiene (**1a**), 2-[2,2-bis(3,5-dimethylpyrazol-1-yl)-1,1-diphenylethyl]-1,3-cyclopentadiene (**1b**)) and bpztcpH (1-[2,2-bis(3,5-dimethylpyrazol-1-yl)-1-*tert*-butylethyl]-1,3-cyclopentadiene (**2a**), 2-[2,2-bis(3,5-dimethylpyrazol-1-yl)-1-*tert*-butylethyl]-1,3-cyclopentadiene (**2b**)), which were isolated as white solids in good yield (ca. 90%) after the appropriate workup. These compounds can be stored indefinitely under an air atmosphere (see Scheme 1).

For compounds **1** and **2** there are three possible tautomers (see Figure 2), isomers **a**−**c**, in which the cyclopentadiene group is bonded by C^1, C^2, or C^5 to the bis(pyrazol-1-yl)methane moiety, respectively. Two sets of ^{1}H NMR signals are observed for these mixtures, and this is consistent with the presence of only two tautomers. Additionally, for both **1** and **2** the H^5 signal in the ^{1}H NMR spectra is integrated for two protons, meaning that the presence in the mixtures of tautomer **c** (in which the cyclopentadiene group is bonded by C^5 to the bis(pyrazol-1-yl)methane unit) can be ruled out. Furthermore, the ^{1}H and ^{13}C{H} NMR spectra of both tautomers of **1** show only one set of resonances for the pyrazole rings, indicating that the pyrazoles are equivalent. However, the tautomers of **2**, each of which contains a stereogenic carbon center that makes the pyrazole rings diastereotopic, show different signals for Me^3, Me^5, and H^4 in both rings in the ^{1}H NMR spectra. ^{1}H NOESY-1D experiments were carried out in order to assign the signals of the two tautomers. The absence of a response in the ^{1}H NOESY-1D experiment from the methine proton on irradiating the H^5 protons of the major tautomer leads us to propose that tautomer **b** is the major component. In addition, X-ray diffraction studies were carried out on **2**. Selected bond lengths and angles are collected in Table 1. Only one tautomer was isolated in the solid state (see Figure 3). The shorter distances for C(16)−C(17) (1.396 (6) Å), C(16)−C(20) (1.396 (6) Å), and C(20)−C(19) (1.405 (8) Å) are indicative of conjugated systems, whereas the distances C(17)−C(18) (1.411 (7) Å) and C(18)−C(19) (1.451 (8) Å) are longer than those typically found for the classic cyclopentadiene,[12] which indicates single bonds between these atoms. These results are consistent with the structural disposition described for tautomer **2b**. The pyrazole rings of this compound are oriented in a quasi-antiparallel disposition with respect to each other, presumably to minimize the intramolecular steric interactions between the N(2) and N(4) atoms of the two rings.

(4) See for example: (a) Otero, A.; Fernández-Baeza, J.; Antiñolo, A.; Tejeda, J.; Lara-Sánchez, A.; Sánchez-Barba, L.; Martínez-Caballero, E.; Rodriguez, A. M.; López-Solera, I. *Inorg. Chem.* **2005**, *44*, 5336. (b) Howe, R. G.; Tredget, C. S.; Lawrence, S. C.; Subongkoj, S.; Cowley, A. R.; Mountford, P. *Chem. Commun.* **2006**, 223.

(5) See for example: (a) Deng, D.; Qian, C.; Wu, G.; Zheng, P. *J. Chem. Soc., Chem. Commun.* **1990**, 880. (b) Qian, C.; Wang, B.; Wu, G.; Zheng, P. J. *J. Organomet. Chem.* **1992**, *427*, C29. (c) Anwander, R.; Hermann, W. A.; Scherer, W.; Munck, F. C. *J. Organomet. Chem.* **1993**, *462*, 163. (d) Molander, G.; Schumann, H.; Rosenthal, E. C. E.; Demtschuk, J. *Organometallics* **1996**, *15*, 3817. (e) Schumann, H.; Rosenthal, E. C. E.; Demtschuk, J. *Organometallics* **1998**, *17*, 5324. (f) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428. (g) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283.

(6) See for example: (a) McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587. (b) Siemeling, U. *Chem. Rev.* **2000**, *100*, 1495. (c) Butenschön, H. *Chem. Rev.* **2000**, *100*, 1527. (d) Qian, Y.; Huang, J.; Bala, M. D.; Lian, B.; Zhang, H.; Zhang, H. *Chem. Rev.* **2003**, *103*, 2633.

(7) (a) Otero, A.; Fernández-Baeza, J.; Antiñolo, A.; Tejeda, J.; Lara-Sánchez, A.; Sánchez-Barba, L.; Sanchez-Molina, M.; Rodríguez, A. M.; Bo, C.; Urbano-Cuadrado, M. *Organometallics* **2007**, *26*, 4310. (b) Recently the preparation of a new type of boron-containing cyclopentadienyl/scorpionate hybrid ligand has been described: Kunz, K.; Vitze, H.; Botte, M.; Lerner, H.-W.; Wagner, M. *Organometallics* **2007**, *26*, 4663.

(8) Selected reviews on aspects of biodegradable polymers: (a) Okada, M. *Prog. Polym. Sci.* **2002**, *27*, 87. (b) Drumright, R. R.; Gruber, P. R.; Henton, D. E. *Adv. Mater.* **2000**, *12*, 1841.

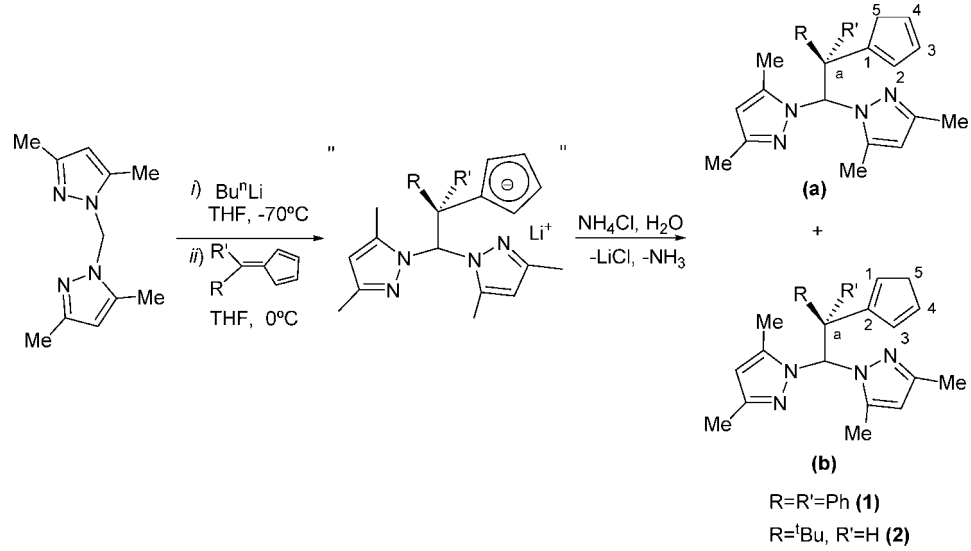
(9) Reviews addressing the polymerization of cyclic esters: (a) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. *Chem. Rev.* **2004**, *104*, 6147. (b) Coates, G. W. *Dalton Trans.* **2002**, 467. (c) Hou, A.; Wakatsuki, Y. *Coord. Chem. Rev.* **2002**, *231*, 1.

(10) (a) Sebastian, J.; Sala, P.; del Mazo, J.; Sancho, M.; Ochoa, C.; Elguero, J.; Fayet, J.; Vertut, M. C. *J. Heterocyclic Chem.* **1982**, *19*, 1141. (b) Diez-Barra, E.; de la Hoz, A.; Sanchez-Mingallon, A.; Tejeda, J. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1079.

(11) Stone, K. J.; Little, R. D. *J. Org. Chem.* **1984**, *49*, 1849.

(12) (a) Haumann, T.; Benet-Buchholz, J.; Boese, R. *J. Mol. Struct.* **1996**, *374*, 299. (b) Liebling, G.; Marsh, R. E. *Acta Crystallogr.* **1965**, *19*, 202.

Scheme 1. Summary of Reactions Leading to Compounds 1 and 2



This conformation is similar to that found in the (2-hydroxyphenyl)bis(pyrazolyl)methane derivative.[13]

Group 3 Alkyl Compounds. Having prepared this new class of hybrid scorpionate/cyclopentadiene compound, we explored their potential utility as ligands in the preparation of new group 3 metal complexes. It is well-known that the alkane elimination reaction is frequently the route of choice to prepare early-transition-metal organometallics, as the precursors are readily available and "ate" complex formation is avoided. The deprotonation of the cyclopentadiene moiety is a well-known procedure, and it normally proceeds by either acid–base or protonolysis processes; for example, the reaction of scandium or yttrium tris(alkyl) complexes and cyclopentadiene gives the corresponding mono(cyclopentadienyl)metal−bis(alkyl) complexes with elimination of alkane.[14] In this way, the reaction of the protio compounds **1** and **2** with $[M(CH_2SiMe_3)_3(THF)_3]$[15] (M = Sc, Y) in a 1:1 molar ratio in hexane at 0 °C yielded the THF-free scandium and yttrium dialkyl complexes $[M(CH_2SiMe_3)_2(bpzcp)]$ (M = Sc (**3**), Y (**4**)) and $[M(CH_2SiMe_3)_2(bpztcp)]$ (M = Sc (**5**), Y (**6**)), after the appropriate workup procedure, as pale yellow solids in good yield (Scheme 2). These complexes are solvent-free and thermally stable. Complexes **3**–**6** constitute the first examples of group 3 metal complexes bearing a hybrid scorpionate/cyclopentadienyl ligand.

The molecular structure of **3** was determined by X-ray diffraction (Figure 4). Selected bond lengths and angles are collected in Table 2. In this case, the heteroscorpionate ligand is κ^1NN-η^5-Cp coordinated to the Sc atom, forming a pseudo-four-coordinate tetrahedral complex with C_1 symmetry. This kind of coordination has never been observed before for these hybrid scorpionate/cyclopentadienyl ligands. Recently, we described the synthesis and reactivity of lithium and group 4 metal complexes containing these ligands, which in these cases are in a facial, tripodal, κ^2NN-η^5-Cp coordination mode.[2c,7a] The distance between N(3) and Sc(1) of 3.44(4) Å is too long to consider bonding or interaction between N(3) and the scandium atom, probably due to the steric hindrance caused by the two bulky alkyl groups. The dihedral angle between the N(1)−Sc(1)−Cp(cent) and C(13)−Sc(1)−C(17) planes (94.6°) indicates a slightly distorted tetrahedral geometry. Furthermore, the angles around the scandium atom show considerable deviation from ideal values (range 99.7(2)−123.8°). The most acute angle of 99.7(2)° is observed for C13−Sc1−C17, which is constrained by the bite of the heteroscorpionate ligand. The C_5H_4 ring is symmetrically bonded to the Sc atom with Sc−C bond distances in the range 2.466(6)−2.491(6) Å. The Sc(1)−N(1) bond distance of 2.279(4) Å is slightly shorter than one would expect for a Sc/pyrazolyl complex.[4,16] The Sc-(1)−C(13) and Sc(1)−C(17) bond distances of 2.213(5) and 2.232(5) Å, respectively, and Sc−C−Si bond angles of 129.5(3) and 131.0(3)°, respectively, are in good agreement with literature data.[16,17]

It is worth noting that, given the coordination mode of the heteroscorpionate ligand, complex **3** is a chiral compound. This complex crystallizes as a racemic mixture with both enantiomers included in the unit cells belonging to a noncentrosymmetric space group.

Solution NMR Characterization. In the present study, effort has been focused on determining whether the κ^1NN-η^5-Cp bpzcp ligand coordination mode observed in the solid-state structure of **3** persists in solution and if complexes **3**–**6** exhibit flexible structures in solution. The dynamic behavior of these complexes was studied by VT NMR spectroscopy. The ^{1}H NMR spectra of the dialkyl complexes **3** and **4** at room temperature show a singlet for each of the H^4, Me^3, and Me^5 pyrazole protons, indicating that the pyrazoles are equivalent, along with two multiplets for the cyclopentadienyl protons and one methyl resonance for the two equivalent CH_2SiMe_3 ligands. Furthermore, the room-temperature ^{1}H NMR spectra of complexes **5** and **6**, both of which have a stereogenic carbon, show two singlets for each of the H^4, Me^3, and Me^5 pyrazole protons, four multiplets for the H^2, H^3, H^4, and H^5 cyclopentadienyl

(13) Higgs, T. C.; Carrano, C. J. *Inorg. Chem.* **1997**, *36*, 291.

(14) See for example: (a) Hultzsch, K. C.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 227. (b) Li, X.; Baldamus, J.; Hou, Z. *Angew. Chem., Int. Ed.* **2005**, *44*, 962. (c) Luo, Y.; Baldamus, J.; Hou, Z. *J. Am. Chem. Soc.* **2004**, *126*, 13910.

(15) (a) Lappert, M. F.; Pearce, R. *J. Chem. Soc., Chem. Commun.* **1973**, 126. (b) Hultzsch, K. C.; Volh, P.; Beckerle, K.; Spaniol, T. P.; Okuda, J. *Organometallics* **2000**, *19*, 228. (c) Ewans, J. W.; Brady, J. C.; Ziller, J. W. *J. Am. Chem. Soc.* **2001**, *123*, 7711.

(16) (a) Lawrence, S. C.; Ward, B. D.; Dubberley, S. R.; Kozak, C. M.; Mountford, P. *Chem. Commun.* **2003**, 2880. (b) Tredgdet, C. S.; Lawrence, S. C.; Ward, B. D.; Howe, G. R.; Cowley, A. R.; Mountford, P. *Organometallics* **2005**, *24*, 3136.

(17) (a) Allen, F. H.; Kennard, O. *Chem. Des. Automation News* **1993**, *8* (1), 31. (b) Fletcher, D. A.; McMeeking, R. F.; Parkin, D. J. *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 746.

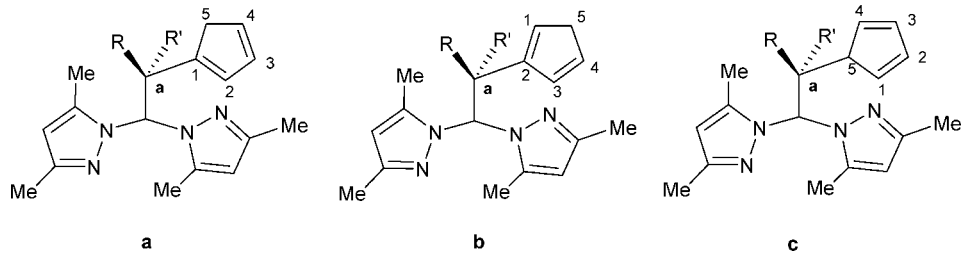


Figure 2. Proposed structures for the three isomers of compounds **1** and **2**.

Table 1. Bond Lengths (Å) and Angles (deg) for 2b

Bond Lengths			
C(2)−C(3)	1.361(6)	C(16)−C(20)	1.396(6)
C(3)−C(4)	1.399(6)	C(17)−C(18)	1.411(7)
C(7)−C(8)	1.356(6)	C(18)−C(19)	1.451(8)
C(8)−C(9)	1.394(6)	C(19)−C(20)	1.405(8)
C(16)−C(17)	1.396(6)		
Bond Angles			
N(1)−C(1)−N(3)	110.4(3)	C(16)−C(17)−C(18)	109.5(5)
N(1)−C(1)−C(21)	112.8(3)	C(17)−C(18)−C(19)	106.6(5)
N(3)−C(1)−C(21)	115.3(3)	C(18)−C(19)−C(20)	106.4(5)
C(17)−C(16)−C(20)	107.5(4)	C(16)−C(20)−C(19)	109.9(5)
C(20)−C(16)−C(21)	124.6(4)		

protons, and two methyl resonances for the two inequivalent CH_2SiMe_3 ligands. Additionally, the methylene protons of complex **6**, YCH_2SiMe_3, are diastereotopic, giving rise to a pair of doublet of doublets at −0.45 and −0.19 ppm ($^2J_{YH}$ = 2.9 Hz, $^2J_{HH}$ = 11.2 Hz) due to coupling with the Y atom. On lowering the temperature in the VT NMR study of **3** and **4**, the resonances of the alkyl groups bound to the metal center and those due to the methyl groups and H^4 of the pyrazole rings broadened but did not resolve into two separate peaks. Even at −90 °C the resonances did not become sharp and well resolved and the NMR spectrum did not become consistent with the observed solid-state structure for **3**. These observations indicate highly fluxional behavior (Scheme 3), thought to be due to an exchange process between the coordinated and the noncoordinated pyrazole rings, and this results in the interconversion from one stereoisomer to the other (Scheme 3, **a** and **c**). At room temperature the exchange is too fast to be detected on the NMR time scale and, thus, the two pyrazole rings appear equivalent.

The same fluxional behavior was observed for complexes **5** and **6** in the corresponding VT NMR studies. Two different mechanisms for the racemization of **3**–**6** can be envisaged. The first involves an intramolecular associative displacement (S_N2) in which the pyrazole ring that is outside the coordination sphere of the metal center displaces the coordinated pyrazole ring through a pentacoordinate transition state. The approach of the free pyrazole ring is necessarily from the opposite side of the coordinated pyrazole ring; therefore, inversion of configuration at the metal center occurs (see Scheme 3). In the second possible dissociative mechanism (S_N1), the first step would involve the pyrazole ring coordinated to the metal center leaving the coordination sphere of the metal atom to produce a "three-coordinate" transition state; in the second step, one of the two free pyrazole rings would coordinate to the metal center to give the final four-coordinate complex. In this step both stereoisomers could be formed. It was not possible to distinguish between these two mechanisms, as the exchange was too fast on the NMR time scale. However, it is worth noting that a similar exchange of coordinated and uncoordinated pyrazole groups has already been observed in other complexes containing tridentate scorpionate or heteroscorpionate ligands, with the conclusion that the dynamic exchange process involves an intramolecular associative displacement of one pyrazole group for the other.[18]

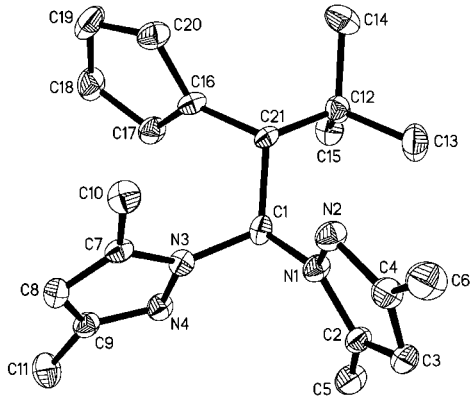


Figure 3. ORTEP view of 1-[2,2-bis(3,5-dimethylpyrazol-1-yl)-1-*tert*-butylethyl]-1,3-cyclopentadiene (**2b**). Ellipsoids are given at the 30% probability level.

Cationic Group 3 Alkyl Compounds. Recently, rare-earth alkyl cations have attracted considerable attention because of their increased Lewis acidity/electrophilicity, and they should have a great deal of potential as homogeneous catalysts in olefin polymerization and organic transformations.[19] The generation of cationic derivatives of the heteroscorpionate scandium and yttrium alkyl complexes was explored by reacting the neutral complexes **3** and **4** with an alkyl-abstracting agent. Thus, treatment of **3** and **4** with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ afforded the expected cationic mono(alkyl) species $[Sc(CH_2SiMe_3)(bpzcp)]^+$ (**7**) and $[Y(CH_2SiMe_3)(bpzcp)]^+$ (**8**) as borate salts (Scheme 4) in good yield (70%).

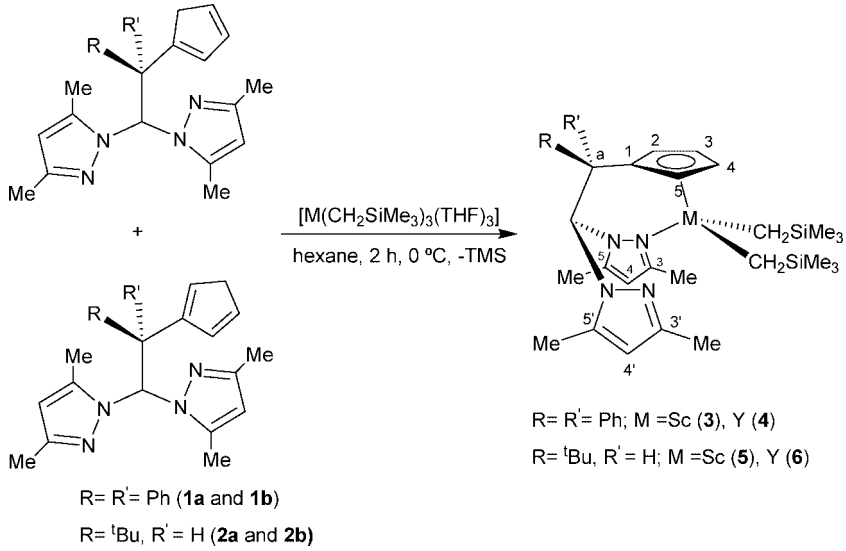
The reaction was monitored by ^1H NMR spectroscopy. It was found that the reaction is fast (a few minutes) and quantitative. The cationic complexes **7** and **8** are more stable in solvents with coordinative capacity such as THF ($t_{1/2}$(25 °C) = 4 days for **7**; $t_{1/2}$(25 °C) = 7 days for **8**), and they slowly decompose to unknown species, thus hampering the crystallization.

The molecular structures of **7** and **8** were studied in solution by NMR spectroscopy. The ^1H NMR spectra of **7** and **8** in THF-d_8 show a high-field shift of the signal due to the methylene protons to −0.22 and −0.76 ppm, respectively. In the $^{13}C\{^1H\}$ NMR spectra the MCH_2 resonances for the cations are found downfield from those in the neutral dialkyl precursors, while the J_{YC} coupling constant increases by about 13.7 Hz, as observed for other cationic alkyl complexes of Sc and Y.[20] The two pyrazole rings appear to be equivalent, and this fact suggests

(18) (a) Milione, S.; Grisi, F.; Centore, R.; Tuzi, A. *Organometallics* **2006**, *25*, 266. (b) Looney, A.; Parkin, G. *Polyhedron* **1990**, *9*, 265. (c) Chisholm, M. H.; Eilerts, N. W.; Huffman, J. C. *Inorg. Chem.* **1996**, *35*, 445. (d) Jones, W. D.; Hessell, E. T. *Inorg. Chem.* **1991**, *30*, 778. (e) Eaves, R.; Parkin, S.; Ladipo, F. T. *Inorg. Chem.* **2007**, *46*, 9495.

(19) Arndt, S.; Okuda, J. *Adv. Synth. Catal.* **2005**, *347*, 339.

Scheme 2. Summary of Reactions Leading to Compounds 3–6



a symmetrical disposition for both coordinated pyrazole rings, as depicted in Scheme 4, in a pseudotetrahedral disposition in which the ligand is in an "s-cis" conformation and κ^2NN-η^5-Cp coordinated. A similar stabilizing effect by a pendant arm was previously observed by Gibson et al.,[21] who found that a weakly bonding or nonbonding donor arm in the neutral precursor becomes a strong ligand occupying the fourth coordination position in the cation that stabilizes the electropositive metal center. The noncoordinating nature of the $[B(C_6F_5)_4]^-$ anion is further confirmed by the small chemical shift difference (about $\Delta\delta$ = 3.9 ppm) between the *m*- and *p*-fluorines in the ^{19}F NMR spectra of **7** and **8**.[22]

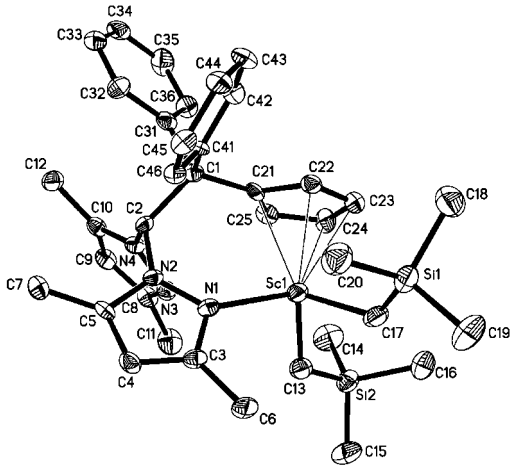
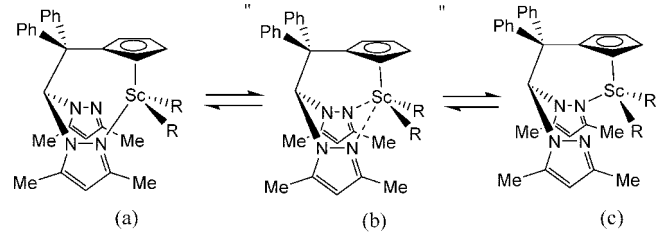


Figure 4. ORTEP view of **3**. Ellipsoids are given at the 30% probability level, and hydrogen atoms have been omitted for clarity.

Table 2. Bond Lengths (Å) and Angles (deg) for 3

Bond Lengths			
Sc(1)−N(1)	2.279(4)	Sc(1)−C(22)	2.466(6)
Sc(1)−C(13)	2.213(5)	Sc(1)−C(23)	2.471(6)
Sc(1)−C(17)	2.232(5)	Sc(1)−C(24)	2.491(6)
Sc(1)−C(21)	2.482(5)	Sc(1)−C(25)	2.490(6)
Bond Angles			
N(1)−Sc(1)−C(13)	103.1(2)	C(1)−C(2)−N(4)	115.4(4)
N(1)−Sc(1)−C(17)	106.4(2)	N(2)−C(2)−N(4)	107.5(4)
C(13)−Sc(1)−C(17)	99.7(2)	Sc(1)−C(13)−Si(2)	129.5(3)
C(2)−C(1)−C(21)	114.0(4)	Sc(1)−C(17)−Si(1)	131.0(3)
C(1)−C(2)−N(2)	115.7(4)		

Scheme 3. Mechanism Proposed for the Dynamic Behavior of Complex 3 in Solution



It is worth noting that proton resonances for both cationic derivatives **7** and **8** are sharp and well-resolved even at low temperatures (ca. −90 °C) in THF-d_8, indicating the elevated coordination energy of the ligand to the metal center and the absence of any fluxional equilibrium involving the neutral moiety of the ligand.

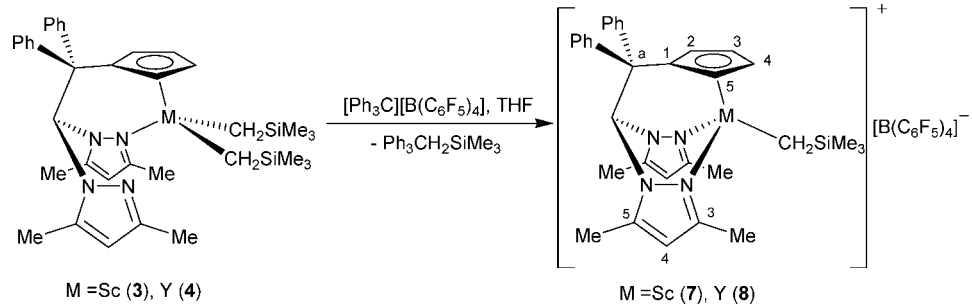
Preliminary Studies on Ring-Opening Polymerization of ϵ-Caprolactone Promoted by 3 and 4. Ring-opening polymerization (ROP) of ϵ-caprolactone (ϵ-CL) has been well established for a large number of lanthanide compounds and so serves as an appropriate benchmark for the new compounds described above. In general, the catalytic activities of the new dialkyl complexes **3** and **4** toward ROP of ϵ-CL (200 equiv per metal center) were assessed in toluene solution at room temperature. A rapid increase in the viscosity of the solution was immediately observed and, after quenching with wet toluene, the mixture was poured into ethanol or methanol/hexane to precipitate poly(ϵ-CL). The preliminary results are summarized in Table 3. Complexes **3** and **4** exhibited remarkably different behavior under rigorously identical polymerization conditions. First, complex **3** yielded only traces of polymer after 1 min, while complex **4** was much more active and gave a

(20) (a) Bambirra, S.; Meetsma, A.; Hessen, B.; Bruñís, A. P. *Organometallics* **2006**, *25*, 3486. (b) Bambirra, S.; Bouwkamp, M. W.; Meetsma, A.; Hessen, B. *J. Am. Chem. Soc.* **2004**, *126*, 9182. (c) Elvidge, B. R.; Arndt, S.; Zeimentz, P. M.; Spaniol, T. P.; Okuda, J. *Inorg. Chem.* **2005**, *44*, 6777.

(21) Cameron, P.; Gibson, V. C.; Redshaw, C.; Segal, J. A.; Bruce, M. D.; White, A. J. P.; Williams, D. J. *Dalton Trans.* **2002**, 415.

(22) Blackwell, J. M.; Morrison, D. J.; Piers, W. E. *Tetrahedron* **2002**, *58*, 8247.

Scheme 4. Preparation of Compounds 7 and 8



M =Sc (**3**), Y (**4**) M =Sc (**7**), Y (**8**)

Table 3. Ring-Opening Polymerization of ϵ-Caprolactone initiated by [Sc{CH_2SiMe_3}$_2$(bpzcp)] (3) and [Y{CH_2SiMe_3}$_2$(bpzcp)] (4)[a]

entry	initiator	time (min)	yield[b] (g)	conversn (%)	M_n[c]	M_w[c]	PDI[c]
1	3	5	0.338	65	20237	24134	1.19
2	3	10	0.389	75	25511	33291	1.30
3	3	30	0.352	68	22546	28977	1.28
4	3	60	0.212	40	7915	10014	1.26
5	4	1	0.175	33	5918	7301	1.23
6	4	5	0.251	47	8068	9980	1.23
7	4	10	0.312	59	9867	13077	1.32
8	4	30	0.281	53	8989	11456	1.27
9	4	60	0.116	22	3379	4269	1.26

[a] Polymerization conditions: 2.0×10^{-5} mol of complex **3** or **4**, T = 25 °C; solvent toluene (4 mL); [ϵ-CL]/[M] = 200. [b] Isolated yield. [c] Measured by GPC at 40 °C in THF relative to polystyrene standards.

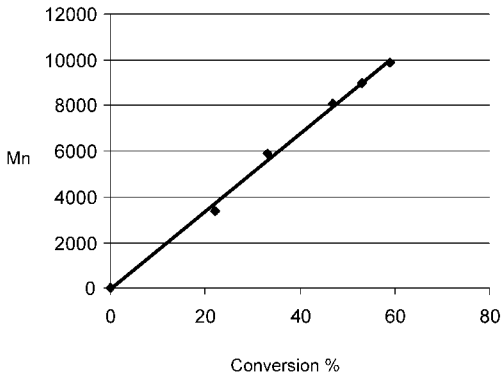


Figure 5. Relationship between Mn and monomer conversion for the polymerization of ϵ-CL promoted by complex **4**.

conversion of 33% after 1 min (entry 5). However, complex **3** showed a higher activity than complex **4** for longer reaction times, with a conversion of 65% after 5 min and the highest conversion of 75% after 10 min. Both complexes showed a decrease in conversion with prolonged reaction times, and this behavior may presumably be due to their high sensitivity toward side reactions. Although the ϵ-caprolactone used was exhaustively dried (see Experimental Section), some deactivation of the initiator could not be avoided.

The polydispersity indexes (PDIs, evaluated by gel permeation chromatography, GPC) of the polyesters formed with these heteroscorpionate complexes (entry 1–9) range from 1.19 to 1.32 and the molecular weights (Mn) increase linearly in proportion to the conversion (Figure 5), suggesting that the scandium (**3**) and yttrium (**4**) dialkyl complex-initiated polymerization can be considered to proceed in a living fashion.

As expected, an end-group NMR study of various poly(ϵ-caprolactone) samples indicated that, in principle, polymerization can be envisaged to occur by the transfer of the nucleophilic alkyl ligands to the monomer with the formation of a metal alkoxide propagating species.[23] Thus, in addition to the main polymer chain peaks, a [C(O)$CH_2Si\mathit{Me}_3$] resonance was clearly identified at δ 0.49 and 4.5 ppm in the ^{1}H NMR and $^{13}C\{^1H\}$ NMR spectra, respectively; additionally, the other end-group (CH_2OH) resonance was observed at δ 3.66 and 62.6 ppm in the ^{1}H NMR and $^{13}C\{^1H\}$ NMR spectra, respectively. This suggests that both ends, P−CH_2SiMe_3 and P−CH_2OH, of the polymer chain result from a possible alkyl transfer in the initiation stage and upon hydrolysis of the products, respectively.

Conclusion

An easy one-pot synthetic procedure based on the reaction of bis(3,5-dimethylpyrazol-1-yl)methane with Bu^nLi and fulvenes and final hydrolysis with an aqueous solution of an ammonium salt yielded the sterically encumbered scorpionate/cyclopentadiene hybrid species **1** and **2**. These compounds were both isolated as a mixture of two tautomers. The potential utility of these ligands as valuable scaffolds in organometallic chemistry has been verified through the preparation of new group 3 metal complexes. Thus, the series of neutral and cationic scandium and yttrium complexes **3**–**8** were synthesized and characterized by X-ray diffraction analysis and NMR spectroscopy.

Reaction of the neutral scandium and yttrium complexes **3** and **4** with the alkyl abstracting agent $[Ph_3C][B(C_6F_5)_4]$ produced the expected cationic derivatives **7** and **8** as borate salts in which the bpzcp fragment was proposed to be coordinated κ^2NN-η^5-Cp to the metal center.

Furthermore, the dialkyl complexes **3** and **4** proved to be efficient initiators for the ring-opening polymerization (ROP) of ϵ-caprolactone, with the highest productivity being found for the scandium complex **3**. The polymerization takes place with narrow molecular weight distributions and with a linear increase of the peak molecular weight with conversion, which corresponds to a living-polymerization. Work is currently under way to increase the scope of this field.

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. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Varian Inova FT-

(23) (a) Yamashita, M.; Takemoto, Y.; Ihara, E.; Yasuda, H. *Macromolecules* **1996**, *29*, 1798. (b) Guillaume, S. M.; Schappacher, M.; Soum, A. *Macromolecules* **2003**, *36*, 54. (c) Sarazin, Y.; Schormann, M.; Bochmann, M. *Organometallics* **2004**, *23*, 3296. (d) Liu, X.; Shang, X.; Tang, T.; Hu, N.; Pei, F.; Cui, D.; Chen, X.; Ping, X. *Organometallics* **2007**, *26*, 2747.

500 (^{1}H NMR 500 MHz, ^{13}C NMR 125 MHz, and ^{19}F NMR 470 MHz) spectrometer and referenced to the residual deuterated solvent. The NOESY-1D spectra were recorded with the following acquisition parameters: irradiation time 2 s and number of scans 256, using standard VARIAN-FT software. Two-dimensional NMR spectra were acquired using standard VARIAN-FT software and processed using an IPC-Sun computer. Gel permeation chromatography (GPC) measurements were performed on a Polymer Laboratories PL-GPC-220 instrument equipped with a PLgel 5 Å Mixed-C column, a refractive index detector, and a PD2040 light-scattering detector. The GPC column was eluted with THF at 40 °C at 1 mL/min and was calibrated using eight monodisperse polystyrene standards in the range 580–483 000 Da.

The compounds 6,6-diphenylfulvene and $[Ph_3C][B(C_6F_5)_4]$ were purchased from Aldrich. ϵ-Caprolactone was purchased from Aldrich, degassed and dried over CaH_2 and over calcinated $CaCl_2$, and then freshly vacuum-distilled before use. The compounds bdmpzm (bdmpzm = bis(3,5-dimethylpyrazol-1-yl)methane),[10] 6-*tert*-butylfulvene,[11] and $[M(CH_2SiMe_3)_3(THF)_3]$[15] (M = Sc, Y) were prepared as reported previously.

Synthesis of a Mixture of Isomers 1a and 1b (bpzcpH). In a 250 mL Schlenk tube, bdmpzm (1.00 g, 4.89 mmol) was dissolved in dry THF (70 mL) and cooled to −70 °C. A 1.6 M solution of Bu^{n}Li (3.06 mL, 4.89 mmol) in hexane was added, and the suspension was stirred for 1 h. The reaction mixture was warmed to 0 °C, and the resulting yellow suspension was treated with 6,6-diphenylfulvene (0.75 g, 4.89 mmol). The solution was stirred for 40 min, and the product was hydrolyzed with 15 mL of saturated aqueous NH_4Cl (which was added dropwise). The organic layer was extracted, dried over $MgSO_4$ overnight, and filtered, and the solvent was removed under vacuum to give the product as a yellow oil. The oil was broken with a mixture of THF/hexane to give **1** as a white solid. Yield: 92%. Anal. Calcd for $C_{29}H_{30}N_4$: C, 80.15; H, 6.95; N, 12.89. Found: C, 80.31; H, 7.01; N, 12.75. ^{1}H NMR (C_6D_6, 297 K): tautomer **1a**, δ 7.92 (s, 1 H, CH), 5.57 (s, 2 H, H^4), 2.07 (s, 6 H, Me^3), 1.36 (s, 6 H, Me^5), 7.53 (d, J_{HH} = 7.8 Hz, 4 H, H^o-Ph), 7.25–7.04 (m, 6 H, H^m-Ph, H^p-Ph), 6.23 (m, 1 H, H^2-Cp), 6.61 (m, 1 H, H^3-Cp), 6.19 (m, 1 H, H^4-Cp), 3.53 (*br*s, 2 H, H^5-Cp); tautomer **1b**, δ 8.17 (s, 1 H, CH), 5.58 (s, 2 H, H^4), 2.08 (s, 6 H, Me^3), 1.46 (s, 6 H, Me^5), 7.71 (d, J_{HH} = 7.5 Hz, 4 H, H^o-Ph), 7.25–7.04 (m, 6 H, H^m-Ph, H^p-Ph), 6.12 (m, 1 H, H^1-Cp), 6.52 (m, 1 H, H^3-Cp), 6.83 (m, 1 H, H^4-Cp), 2.82 (*br*s, 2 H, H^5-Cp). ^{13}C{^{1}H} NMR (C_6D_6, 297 K): tautomer **1a**, δ 77.2 (CH), 149.9, 142.9 (C$^{3\text{ or }5}$), 106.1 (C^4), 13.4 (Me^3), 10.1 (Me^5), 145.7, 131.7, 126.3, 125.7 (Ph), 60.9 (C^a), 141.5 (C^1-Cp), 132.7 (C^2-Cp), 131.1 (C^3-Cp), 129.8 (C^4-Cp), 42.6 (C^5-Cp); tautomer **1b**, δ 77.3 (CH), 153.9, 142.2 (C$^{3\text{ or }5}$), 106.1 (C^4), 13.4 (Me^3), 10.3 (Me^5), 145.8, 131.4, 126.5, 125.9 (Ph), 62.1 (C^a), 135.3 (C^1-Cp), 141.6 (C^2-Cp), 131.2 (C^3-Cp), 127.9 (C^4-Cp), 40.8 (C^5-Cp).

Synthesis of a Mixture of Isomers 2a and 2b (bpztcpH). The synthetic procedure was the same as for compound **1**, using bdmpzm (2.00 g, 9.79 mmol), a 1.6 M solution of Bu^{n}Li (6.12 mL, 9.79 mmol) and 6-*tert*-butylfulvene (1.32 g, 9.79 mmol), to give **2** as a white solid. Yield: 90%. Anal. Calcd for $C_{21}H_{30}N_4$: C, 74.51; H, 8.93; N, 16.55. Found: C, 74.62; H, 9.03; N, 16.43. ^{1}H NMR (C_6D_6, 297 K): tautomer **2a**, δ 6.86 (d, J_{HH} = 11.2 Hz, 1 H, CH), 5.57, 5.41 (s, 1 H, 1H, H$^{4,4'}$), 2.19, 2.08 (s, 3 H, 3 H, Me$^{3,3'}$), 2.40, 2.28 (s, 3 H, 3 H, Me$^{5,5'}$), 4.44 (m, 1 H, CH^a), 0.87 (s, 9 H, C(CH$_3$)$_3$), 6.18 (m, 1 H, H^2-Cp), 6.12 (m, 1 H, H^3-Cp), 6.27 (m, 1 H, H^4-Cp), 2.38 (br, 2 H, H^5−Cp); tautomer **2b**, δ 6.99 (d, J_{HH} = 10.2 Hz, 1 H, CH), 5.62, 5.45 (s, 1 H, 1 H, H$^{4,4'}$), 2.21, 2.14 (s, 3 H, 3 H, Me$^{3,3'}$), 2.40, (s, 6 H, Me$^{5,5'}$), 4.64 (m, 1 H, CH^a), 0.92 (s, 9 H, C(CH$_3$)$_3$), 5.96 (m, 1 H, H^1-Cp), 6.50 (m, 1 H, H^3-Cp), 6.05 (m, 1 H, H^4-Cp), 5.56 (br, 2 H, H^5-Cp). ^{13}C{^{1}H} NMR (C_6D_6, 297 K): tautomer **2a**, δ 74.9 (CH), 146.7, 145.2, 140.0, 139.8 (C$^{3,3\text{ or }5,5'}$), 107.0, 106.1 (C$^{4,4'}$), 13.8, 13.6 (Me$^{3,3'}$), 12.0, 11.5 (Me$^{5,5'}$), 51.3 (C^a), 34.7 (*C*(CH$_3$)$_3$), 28.6 (C(*C*H$_3$)$_3$), 130.5 (C^1-Cp), 131.8 (C^2-Cp), 133.4 (C^3-Cp), 131.6 (C^4-Cp), 40.9 (C^5-Cp), tautomer **2b**, δ 74.1 (CH), 148.0, 146.3, 146.0, 139.6 (C$^{3,3'\text{ or }5,5'}$), 107.0, 106.1 (C$^{4,4'}$), 14.3, 13.7 (Me$^{3,3'}$), 11.5 (Me$^{5,5'}$), 50.9 (C^a), 34.3 (*C*(CH$_3$)$_3$), 28.5 (C(*C*H$_3$)$_3$), 130.8 (C^1-Cp), 128.3 (C^2-Cp), 133.2 (C^3-Cp), 131.4 (C^4-Cp), 54.3 (C^5-Cp).

Synthesis of [Sc(CH$_2$SiMe$_3$)$_2$(bpzcp)] (3). A solution of bpzcpH (**1**; 0.33 g, 0.76 mmol) in hexane (20 mL) was added dropwise to a cooled (0 °C) solution of $[Sc(CH_2SiMe_3)_3(THF)_3]$ (0.40 g, 0.76 mmol) in hexane (25 mL). The reaction mixture was stirred for 2 h at 0 °C, after which time a pale yellow precipitate had formed. The solid was filtered off and dried under reduced pressure. This material was recrystallized from toluene/hexane (10:1, 20 mL at −20 °C) to give colorless crystals of the title compound. Yield: 72%. Anal. Calcd for $C_{37}H_{51}N_4ScSi_2$: C, 68.06; H, 7.87; N, 8.58. Found: C, 68.45; H, 8.03; N, 8.21. ^{1}H NMR (C_6D_6, 297 K): δ 6.45 (s, 1 H, CH), 5.24 (s, 2 H, H^4), 2.55 (s, 6 H, Me^3), 1.33 (s, 6 H, Me^5), 7.35–6.99 (m, 10 H, Ph), 5.86 (m, 2 H, H^{2,5}-Cp), 6.96 (m, 2 H, H^{3,4}-Cp), 0.52 (br s, 4 H, ScC*H*$_2$SiMe$_3$), 0.57 (s, 18 H, ScCH$_2$Si*Me*$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 297 K): δ 74.1 (CH), 144.2, 141.7 (C$^{3\text{ or }5}$), 108.0 (C^4), 16.4 (Me^3), 11.4 (Me^5), 152.2–129.6 (Ph), 67.8 (C^a), 117.9 (C^1-Cp), 120.1 (C^{2,5}-Cp), 113.1 (C^{3,4}-Cp), 41.8 (Sc*C*H$_2$SiMe$_3$), 4.1 (ScCH$_2$Si*Me*$_3$).

Synthesis of [Y(CH$_2$SiMe$_3$)$_2$(bpzcp)] (4). The synthetic procedure was the same as for complex **3**, using $[Y(CH_2SiMe_3)_3(THF)_3]$ (0.40 g, 0.70 mmol) and bpzcpH (**1**; 0.30 g, 0.70 mmol), to give **4** as a white solid. Yield: 75%. Anal. Calcd for $C_{37}H_{51}N_4Si_2Y$: C, 63.76; H, 7.37; N, 8.03. Found: C, 63.99; H, 7.62; N, 7.81. ^{1}H NMR (C_6D_6, 297 K): δ 6.90 (s, 1 H, CH), 5.19 (s, 2 H, H^4), 2.40 (s, 6 H, Me^3), 1.32 (s, 6 H, Me^5), 7.10–6.95 (m, 10 H, Ph), 5.76 (m, 2 H, H^{2,5}-Cp), 6.80 (m, 2 H, H^{3,4}-Cp), −0.20 (d, J_{YH} = 2.9 Hz, 4 H, YC*H*$_2$SiMe$_3$), 0.48 (s, 18 H, YCH$_2$Si*Me*$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 297 K): δ 74.8 (CH), 145.2, 142.3 (C$^{3\text{ or }5}$), 108.0 (C^4), 15.5 (Me^3), 11.3 (Me^5), 150.3–127.2 (Ph), 61.3 (C^a), 115.4 (C^1-Cp), 118.3 (C^{2,5}-Cp), 110.4 (C^{3,4}-Cp), 30.5 (d, J_{YC} = 36.2 Hz, Y*C*H$_2$SiMe$_3$), 4.9 (YCH$_2$Si*Me*$_3$).

Synthesis of [Sc(CH$_2$SiMe$_3$)$_2$(bpztcp)] (5). The synthetic procedure was the same as for complex **3**, using $[Sc(CH_2SiMe_3)_3(THF)_3]$ (0.40 g, 0.76 mmol) and bpztcpH (**2**; 0.25 g, 0.76 mmol), to give **5** as a white solid. Yield: 68%. Anal. Calcd for $C_{29}H_{51}N_4ScSi_2$: C, 62.54; H, 9.23; N, 10.06. Found: C, 62.84; H, 9.41; N, 9.79. ^{1}H NMR (C_6D_6, 297 K): δ 6.33 (d, J_{HH} = 3.6 Hz, 1 H, CH), 5.27 (s, 2 H, H$^{4,4'}$), 2.40, 2.30 (s, 3 H, 3 H, Me$^{3,3'}$), 1.75 (s, 3 H, Me$^{5'}$), 1.61 (s, 3 H, Me^5), 2.91 (d, J_{HH} = 3.6 Hz, 1 H, CH^a), 0.96 (s, 9 H, C(CH$_3$)$_3$), 6.08 (m, 1 H, H^2-Cp), 6.28 (m, 1 H, H^5-Cp), 6.95, 6.90 (m, 1 H, 1 H, H^{3,4}-Cp), 0.30, 0.28 (br s, 2 H, 2 H, ScC*H*$_2$SiMe$_3$), 0.39 (s, 18 H, ScCH$_2$Si*Me*$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 297 K): δ 66.3 (CH), 151.5, 150.2, 140.6, 139.4 (C$^{3,3'\text{ or }5,5'}$), 107.4, 107.2 (C$^{4,4'}$), 15.1, 15.0 (Me$^{3,3'}$), 12.2 (Me$^{5'}$), 11.2 (Me^5), 58.2 (C^a), 35.2 (*C*(CH$_3$)$_3$), 28.8 (C(*C*H$_3$)$_3$), 112.4 (C^1-Cp), 112.9 (C^2-Cp), 115.8 (C^3-Cp), 112.8, 110.3 (C^{4,5}-Cp), 33.0, 30.6 (Sc*C*H$_2$SiMe$_3$), 5.4 (ScCH$_2$Si*Me*$_3$).

Synthesis of [Y(CH$_2$SiMe$_3$)$_2$(bpztcp)] (6). The synthetic procedure was the same as for complex **3**, using $[Y(CH_2SiMe_3)_3(THF)_3]$ (0.40 g, 0.70 mmol) and bpztcpH (**2**; 0.23 g, 0.70 mmol), to give **6** as a white solid. Yield: 70%. Anal. Calcd for $C_{29}H_{51}N_4Si_2Y$: C, 57.97; H, 8.55; N, 9.32. Found: C, 58.31; H, 8.92; N, 9.10. ^{1}H NMR (C_6D_6, 297 K): δ 6.27 (s, 1 H, CH), 5.33 (s, 2 H, H$^{4,4'}$), 2.40, 2.26 (s, 3 H, 3 H, Me$^{3,3'}$), 1.78 (s, 3 H, Me$^{5'}$), 1.64 (s, 3 H, Me^5), 2.59 (s, 1 H, CH^a), 0.80 (s, 9 H, C(CH$_3$)$_3$), 5.67 (m, 1 H, H^2-Cp), 6.16 (m, 1 H, H^5-Cp), 6.95, 6.88 (m, 1 H, 1 H, H^{3,4}-Cp), −0.19 (dd, J_{HH} = 11.2 Hz, J_{YH} = 2.9 Hz, 2 H, YC*H*$_2$SiMe$_3$), −0.45 (dd, J_{HH} = 10.7 Hz, J_{YH} = 2.9 Hz, 2 H, YC*H*$_2$SiMe$_3$), 0.55 (s, 18 H, YCH$_2$Si*Me*$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 297 K): δ 66.4 (CH), 151.9, 150.8, 140.5, 139.0 (C$^{3,3'\text{ or }5,5'}$), 107.9, 107.0 (C$^{4,4'}$), 15.6, 15.3 (Me$^{3,3'}$), 12.1 (Me$^{5'}$), 11.1 (Me^5), 57.9 (C^a), 34.9 (*C*(CH$_3$)$_3$), 28.5 (C(*C*H$_3$)$_3$), 112.2 (C^1-Cp), 112.9 (C^2-Cp), 116.0 (C^5-Cp), 112,9, 110.1 (C^{3,4}-Cp), 33.1, (d, J_{YC} = 37.4 Hz,

YCH_2SiMe_3), 28.6 (d, J_{YC} = 35.3 Hz, YCH_2SiMe_3), 5.2 ($YCH_2Si\mathit{Me}_3$).

Synthesis of [Sc(CH$_2$SiMe$_3$)(bpzcp)][B(C$_6$F$_5$)$_4$] (7). In a 100 mL Schlenk tube, [Sc(CH$_2$SiMe$_3$)$_2$(bpzcp)] (**3**; 40.0 mg, 0.06 mmol) and [PPh$_3$][B(C$_6$F$_5$)$_4$] (50.0 mg, 0.06 mmol) were dissolved in THF (8.0 mL). The resulting bright yellow solution was stirred for 30 min at room temperature and then evaporated to dryness to yield a yellow solid. The residue was washed with hexane (5.0 mL). The solvent was filtered off by a short cannula and the resulting solid dried under vacuum to afford complex **7** as a yellow solid. Yield: 65%. Anal. Calcd for $C_{57}H_{40}BF_{20}N_4ScSi$: C, 54.99; H, 3.24; N, 4.50. Found: C, 55.51; H, 3.57; N, 4.05. ^{1}H NMR (THF-d_8, 297 K): δ 6.91 (s, 1 H, CH), 6.09 (s, 2 H, H^4), 2.20 (s, 6 H, Me^3), 2.15 (s, 6 H, Me^5), 7.37–7.11 (m, 10 H, Ph), 5.69 (m, 2 H, H^{2,5}-Cp), 6.96 (m, 2 H, H^{3,4}-Cp), −0.22 (br, 2 H, ScCH_2SiMe$_3$), 0.07 (s, 9 H, ScCH$_2$SiMe_3). ^{13}C{^{1}H} NMR (THF-d_8, 297 K): δ 75.2 (CH), 145.7, 144.9 (C$^{3\text{ or }5}$), 109.2 (C^4), 14.6 (Me^3), 11.5 (Me^5), 150.3–128.3 (Ph), 62.0 (C^a), 116.8 (C^1-Cp), 118.0 (C^{2,5}-Cp), 111.5 (C^{3,4}-Cp), 43.5 (ScCH_2SiMe$_3$), 4.8 (ScCH$_2$SiMe_3). ^{19}F NMR (THF-d_8, 297 K): δ −133.4 (s, 2 F, *o*-C$_6$F$_5$), −163.9 (t, $^3J_{FF}$ = 21.4, 2 F, *m*-C$_6$F$_5$), −167.8 (s, 1 F, *p*-C$_6$F$_5$).

Synthesis of [Y(CH$_2$SiMe$_3$)(bpzcp)][B(C$_6$F$_5$)$_4$] (8). The synthetic procedure was the same as for complex **7**, using [Y(CH$_2$SiMe$_3$)$_2$(bpzcp)] (**4**; 40.0 mg, 0.05 mmol) and [PPh$_3$][B(C$_6$F$_5$)$_4$](45.0 mg, 0.05 mmol), to give **8** as a bright yellow solid. Yield: 70%. Anal. Calcd for $C_{57}H_{40}BF_{20}N_4SiY$: C, 53.12; H, 3.12; N, 4.34. Found: C, 53.69; H, 3.42; N, 4.09. ^{1}H NMR (THF-d_8, 297 K): δ 7.35 (s, 1 H, CH), 6.17 (s, 2 H, H^4), 2.25 (s, 6 H, Me^3), 2.17 (s, 6 H, Me^5), 7.30–7.09 (m, 10 H, Ph), 5.71 (m, 2 H, H^{2,5}-Cp), 6.98 (m, 2 H, H^{3,4}-Cp), −0.76 (d, J_{YH} = 2.9 Hz, 2 H, YCH_2SiMe$_3$), 0.06 (s, 9 H, YCH$_2$SiMe_3). ^{13}C{^{1}H} NMR (THF-d_8, 297 K): δ 74.4 (CH), 146.4, 145.0 (C$^{3\text{ or }5}$), 109.5 (C^4), 14.4 (Me^3), 11.8 (Me^5), 150.1–128.2 (Ph), 61.2 (C^a), 117.1 (C^1-Cp), 118.2 (C^{2,5}-Cp), 111.2 (C^{3,4}-Cp), 42.1 (d, J_{YC} = 59.9 Hz, YCH_2SiMe$_3$), 4.6 (YCH$_2$SiMe_3). ^{19}F NMR (THF-d_8, 297 K): δ −133.4 (s, 2 F, *o*-C$_6$F$_5$), −163.9 (t, $^3J_{FF}$ = 21.4, 2 F, *m*-C$_6$F$_5$), −167.8 (s, 1 F, *p*-C$_6$F$_5$).

Typical Living Polymerization of ϵ-Caprolactone by [Sc(CH$_2$SiMe$_3$)$_2$(bpzcp)] (3) and [Y(CH$_2$SiMe$_3$)$_2$(bpzcp)] (4). To a stirred toluene solution (4–5 mL) of **3** or **4** (0.02 mmol) was added ϵ-caprolactone (4.0 mmol) by syringe. The mixture was magnetically stirred at room temperature for different times. The viscous mixture was quenched with wet toluene and poured into ethanol or methanol/hexane. The white polymer was filtered off and dried under vacuum to a constant weight.

X-ray Crystallography. Data for compounds **2b** and **3** were collected on a Bruker X8 APPEX II CCD-based 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 are summarized in Table 4. Data were integrated using SAINT,[24] and an absorption correction was performed with the program SADABS.[25] The structure was solved by direct methods using SHELXTL[26] and refined by full-matrix least-squares methods based on F^2. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed using a "riding model" and included in the refinement at calculated positions. Complex **3** crystallizes with a hexane molecule, which shows C55 in a disordered position (0.63 population).

Table 4. Crystal Data and Structure Refinement Details for 2b and 3

	2b	**3**
empirical formula	$C_{21}H_{30}N_4$	$C_{37}H_{51}N_4ScSi_2\cdot C_6H_{14}$
formula wt	338.49	739.13
temp (K)	180(2)	200(2)
wavelength (Å)	0.710 73	0.710 73
crystal syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	8.817(5)	12.093(2)
b (Å)	10.720(5)	12.191(2)
c (Å)	10.796(5)	17.037(3)
α (deg)	90.095(9)	83.874(3)
β (deg)	103.026(9)	70.672(3)
γ (deg)	99.885(8)	67.402(2)
V (Å^3)	978.6(9)	2187.4(7)
Z, calcd density (g/cm^3)	2, 1.149	2, 1.122
abs coeff (mm^{-1})	0.069	0.255
F(000)	368	800
cryst size (mm)	0.35 × 0.15 × 0.20	0.51 × 0.27 × 0.12
limiting indices	$-7 \le h \le 8$	$-11 \le h \le 11$
	$-10 \le k \le 9$	$-11 \le k \le 11$
	$-10 \le l \le 9$	$-15 \le l \le 13$
no. of collected/unique rflns	3409/1568	6581/3211
R(int)	0.0628	0.0411
no. of data/restraints/params	1568/0/257	3211/0/474
goodness of fit on F^2	0.947	1.023
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0615	R1 = 0.0475
	wR2 = 0.1564	wR2 = 0.1166
R indices (all data)	R1 = 0.0811	R1 = 0.0697
	wR2 = 0.1802	wR2 = 0.1334
largest diff peak, hole (e Å^{-3})	0.207, −0.261	0.248, −0.262

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Supporting Information Available: CIF files giving details of data collection, refinement, atom coordinates, anisotropic displacement parameters, and bond lengths and angles for complexes **2b** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM701033R

(24) SAINT+v7.12a: Area-Detector Integration Program; Bruker-Nonius AXS, Madison, WI, 2004.

(25) Sheldrick, G. M. SADABS version 2004/1. A Program for Empirical Absorption Correction; University of Göttingen, Göttingen, Germany, 2004.

(26) SHELXTL-NT version 6.12. Structure Determination Package; Bruker-Nonius AXS, Madison, WI, 2001.