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Article

Versatile Scorpionates and New Developments in the Denticity Changes of NNCp Hybrid Scorpionate/Cyclopentadienyl Ligands in Sc and Y Compounds: From κ^1-Nη^5-Cp to κ^2-NNη^5-Cp

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Reaction of hybrid scorpionate/cyclopentadienyl ligands in the form of the lithium derivatives [Li(bpzcp)(THF)] [bpzcp = 2,2-bis(3,5-dimethylpyrazol-1-yl)-1,1-diphenylethylcyclopentadienyl], [Li(bpztcp)(THF)] [bpztcp = 2,2-bis(3,5-dimethylpyrazol-1-yl)-1-*tert*-butylethylcyclopentadienyl], and the in situ-generated “Li(bpzpcp)” [bpzpcp = 2,2-bis(3,5-dimethylpyrazol-1-yl)-1-phenylethylcyclopentadienyl] with $MCl_3(THF)_3$ afforded the group 3 halide compounds [MCl_2(bpzcp)(THF)] (M = Sc, **1**; Y, **2**), [MCl_2(bpztcp)(THF)] (M = Sc, **3**; Y, **4**), and [MCl_2(bpzpcp)(THF)] (M = Sc, **5**; Y, **6**). The H_2O adduct of **4**, [YCl_2(bpztcp)(H_2O)] (**7**), was formed when a solution of **4** was allowed to stand at room temperature in the presence of moisture. Complexes **1**−**7** adopt a pseudo-octahedral structure with heteroscorpionate ligands κ^2-NNη^5-Cp coordinated to the metal through the cyclopentadienyl group and two imino nitrogens of pyrazole rings. The alkyl heteroscorpionate scandium and yttrium complexes recently reported by our group, [$M(CH_2SiMe_3)_2$(bpzcp)], react with 2,6-dimethylphenol and 3,5-dimethylphenol to give the bis(aryloxide) derivatives [$M(OAr)_2$(bpzcp)] (M = Sc, OAr = 2,6-dimethylphenoxide, **8**; M = Y, OAr = 2,6-dimethylphenoxide, **9**; M = Y, OAr = 3,5-dimethylphenoxide, **10**). Complex **9** underwent an interesting hydrolysis process to give the tetranuclear complex [{Y(bpzcp)}(μ-OH)$_2$(μ_3-OH){$Y(OAr)_2$}]$_2$ (**11**). Variable-temperature ^{1}H NMR experiments on **9** and **10** revealed a rapid fluxional exchange between coordinated and noncoordinated pyrazolyl rings, producing interconversion between the two enantiomers in which the scorpionate ligand can be coordinated in a κ^1-Nη^5-Cp form. The structures of the complexes were determined by spectroscopic methods and the X-ray crystal structures of **2**, **7**, and **11** were also established. Complexes **1** and **2** are active olefin polymerization catalysts after activation with methylaluminoxane. These compounds gave atactic polystyrenes with narrow molecular weight distribution (M_n/M_w 1.26−1.91) and with low molecular weights.

Introduction

Group 3 and lanthanide complexes have been extensively employed as catalysts for the polymerization of olefins.[1] While the chemistry of cyclopentadienyl-based complexes is well established,[2] there has been increasing interest in recent years in the respective chemistry employing noncyclopentadienyl ligands.[3] In this context, scorpionate ligands such as poly(pyrazolyl)borates are also attractive ancillary ligands for the synthesis of complexes of these metals.[4] Related with the tris(pyrazolyl)borates, in this important field of ligand design we and others have reported the synthesis

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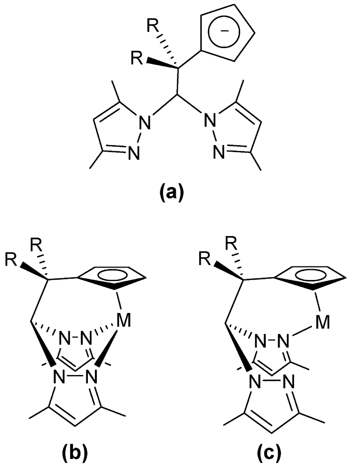
of new "heteroscorpionate" ligands based on bis(pyrazol-1-yl)methane that contain two pyrazole rings and different anionic "arms".[5]

Bearing in mind the development of donor-functionalized cyclopentadienyl ligands[6] and the emerging importance of the heteroscorpionate ligands, a new class of heteroscorpionate, namely, a family of hybrid scorpionate/cyclopentadienyl, ligands have been reported (Chart 1a) by us.[7] Mixed pyrazole/cyclopentadienyl ligands have also been described by other authors.[8] The easy preparation of heteroscorpionate ligands bearing a cyclopentadienyl anionic arm led us to develop and fully explore the potential offered by this type of ligand. Thus, it was found that the hybrid scorpionate/cyclopentadienyl ligands 2,2-bis(3,5-dimethylpyrazol-1-yl)-1,1-diphenylethylcyclopentadienyl (bpzcp), 2,2-bis(3,5-dimethylpyrazol-1-yl)-1-*tert*-butylethylcyclopentadienyl (bpztcp), and 2,2-bis(3,5-dimethylpyrazol-1-yl)-1-phenylethylcyclopentadienyl (bpzpcp) bind in a facial, tripodal fashion that is κ^2-NNη^5-Cp in lithium complexes (for the two first ligands) and in group 4 transition-metal complexes (see Chart 1b).[7]

Chart 1. Hybrid Scorpionate/Cyclopentadienyl Ligands and Their Possible Coordination Modes



However, we recently reported new dialkylscandium and -yttrium complexes that display an unprecedented κ^1-Nη^5-Cp bonding mode (see Chart 1c) with these ligands,[9] although these complexes show dynamic behavior in solution with an exchange process between the coordinated and noncoordinated pyrazole rings.

As a continuation of our research into the coordination chemistry of these hybrid scorpionate/cyclopentadienyl ligands (Chart 1a) and subsequent catalytic applications of their complexes, we describe here the application of these ligands in the synthesis of neutral scandium and yttrium halide and alkoxide complexes. In addition, an interesting hydrolysis process to give an air- and moisture-stable hydroxo multinuclear derivative of yttrium (complex **11**) has been studied. Finally, complexes **1** and **2** were tested as catalysts in the polymerization of styrene.

Results and Discussion

Synthesis and Structure of Halide Complexes. Compounds [Li(bpzcp)(THF)][7] and [Li(bpztcp)(THF)][7b] (THF = tetrahydrofuran) and the mixture of the two scorpionate/cyclopentadiene regioisomers 1-[2,2-bis(3,5-dimethylpyrazol-1-yl)-1-phenylethyl]-1,3-cyclopentadiene and 2-[2,2-bis(3,5-dimethylpyrazol-1-yl)-1-phenylethyl]-1,3-cyclopentadiene (bpzpcpH)[7b] were used to prepare scandium and yttrium complexes. These compounds (the latter with prior addition of $\mathrm{Bu^nLi}$) reacted with a solution of $\mathrm{MCl_3(THF)_3}$ (M = Sc, Y; Scheme 1) in THF to give, after stirring for 12 h at room temperature, a solution from which the THF adduct complexes $\mathrm{[MCl_2(bpzcp)(THF)]}$ (M = Sc, **1**; Y, **2**), $\mathrm{[MCl_2(bpztcp)(THF)]}$ (M = Sc, **3**; Y, **4**), and $\mathrm{[MCl_2(bpzpcp)(THF)]}$ (M = Sc, **5**; Y, **6**) were isolated as white (**1**, **3**, and **5**) and pale-yellow (**2**, **4**, and **6**) solids after the appropriate workup procedure. Complexes **1**−**6** are slightly air-sensitive and slowly decompose in air. In one attempt to obtain crystals of **4** in $\mathrm{CH_2Cl_2}$, we obtained its water adduct $\mathrm{[YCl_2(bpztcp)(H_2O)]}$ (**7**). The formation of this compound is probably due

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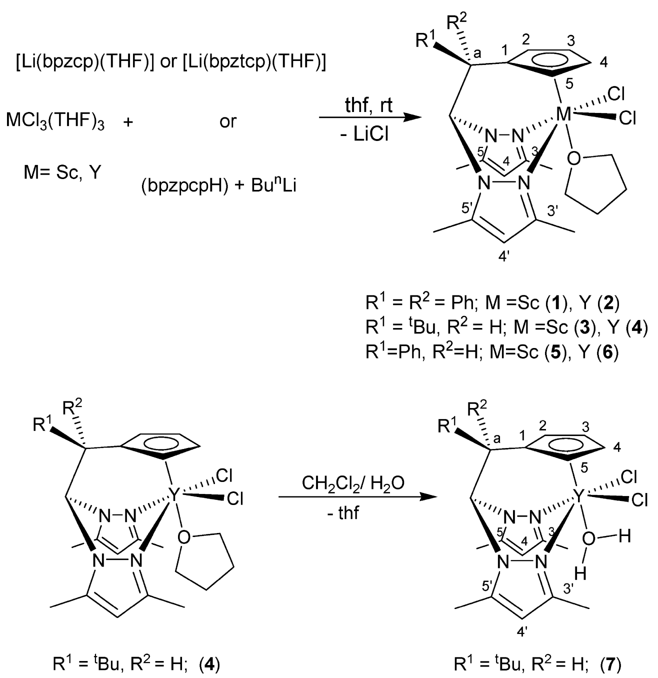
Scheme 1. Synthesis of Complexes **1**−**7**



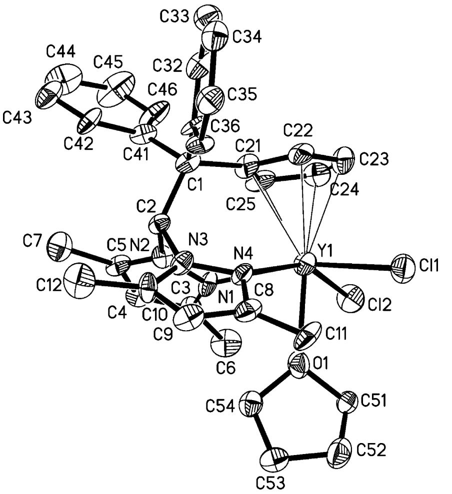


Figure 1. ORTEP view of **2**. Ellipsoids are at the 30% probability level, and hydrogen atoms have been omitted for clarity.

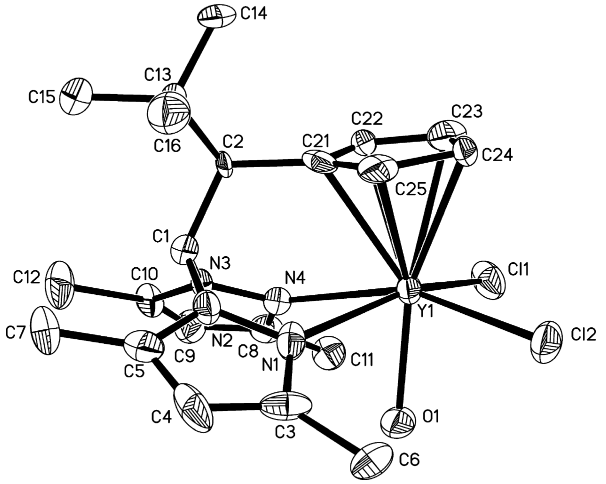


Figure 2. ORTEP view of **7**. Ellipsoids are at the 30% probability level, and hydrogen atoms have been omitted for clarity.

to the presence of trace amounts of water in the solvent. We believe that the lower coordinative capacity of CH_2Cl_2 in comparison to THF probably enables the formation of the water adduct **7**. We rationalized the synthesis of **7**; in fact, the addition of an appropriate amount of water to a CH_2Cl_2 solution of complex **4** gives rise to the isolation of **7** after the appropriate workup. Complexes **1**−**7** constitute the first examples of group 3 metal halide complexes bearing a hybrid scorpionate/cyclopentadienyl ligand.

The different group 3 metal halide complexes were characterized spectroscopically. The mass spectra of these complexes indicate a mononuclear formulation (see the Experimental Section). The ^1H and $^{13}C\{^1H\}$ NMR spectra of **1** and **2** (nonchiral compounds) exhibit 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 two multiplets for the THF protons. These results are consistent with an octahedral disposition, where the THF donor lies trans to the cyclopentadienyl ring, for which a symmetric plane exists (see Scheme 1). However, the ^1H NMR spectra of complexes **3**−**7** (chiral compounds) show two singlets for each of the H^4, Me^3, and Me^5 pyrazole protons and four multiplets for the H^2, H^3, H^4, and H^5 cyclopentadienyl protons, along with two multiplets for the THF protons in complexes **3**−**6** or a broad singlet at 3.50 ppm for the H_2O protons in complex **7**. These results are also consistent with an octahedral structural disposition where a κ^2-NNη^5-Cp coordination for the scorpionate ligand is proposed. The phase-sensitive ^1H NOESY-1D NMR 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. The assignment of the $^{13}C\{^1H\}$ NMR signals was made on the basis of $^1H-^{13}C$ heteronuclear correlation (g-HSQC) experiments. In these asymmetric complexes, the carbon atom (C^a) 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 ^1H NMR spectrum, resulting from the two diastereoisomers of the corresponding two enantiomers.

In order to confirm the proposed structure for these complexes, X-ray diffraction studies on **2** and **7** were carried out (see Figures 1 and 2). It is worth noting that complex **7** crystallized enantiopure. Crystallographic data and selected interatomic distances and angles are given in Tables 1 and 2, respectively. The molecular structures determined by X-ray diffraction are in good agreement with the solution structures deduced from the NMR experiments. The structures of both complexes are similar and consist of the heteroscorpionate ligand bonded to the yttrium atom through the two nitrogen atoms and the cyclopentadienyl ring in a κ^2-NNη^5-Cp coordination in the expected *fac* coordination mode. In addition, the yttrium center is coordinated to two chloride atoms and one THF or H_2O molecule, trans to the cyclopentadienyl ring, in **2** and **7**, respectively. The overall

Table 1. Experimental Data for the Crystal Structure Determination of **2**, **7**, and $[\{Y(bpzcp)\}(\mu\text{-}OH)_2(\mu_3\text{-}OH)\{Y(O\text{-}2,6\text{-}C_6H_3Me_2)_2\}]_2$ (**11**)

	2	**7**	**11**
empirical formula	$C_{33}H_{37}Cl_2N_4OY \cdot THF$	$C_{21}H_{31}Cl_2N_4OY \cdot 3THF$	$C_{90}H_{100}N_8O_{10}Y_4 \cdot 8CH_2Cl_2$
fw	737.58	731.62	2484.83
temperature (K)	200(2)	200(2)	180(2)
wavelength (Å)	0.710 73	0.710 73	0.710 73
cryst syst, space group	monoclinic, $P2_1/c$	orthorhombic, $Pna2_1$	triclinic, $P\bar{1}$
a (Å)	21.111(6)	24.480(4)	12.473(3)
b (Å)	8.692(3)	14.790(2)	13.904(3)
c (Å)	20.747(6)	10.266(2)	16.673(4)
α (deg)	90	90	102.857(4)
β (deg)	113.315(4)	90	90.188(4)
γ (deg)	90	90	106.033(4)
volume (Å^3)	3496(2)	3717(1)	2703(1)
Z, D_{calcd} (g/cm^3)	4, 1.401	4, 1.307	1, 1.529
abs coeff (cm^{-1})	1.857	1.752	2.58
F (000)	1536	1544	1268
cryst size (mm)	0.45 × 0.22 × 0.17	0.46 × 0.10 × 0.31	0.52 × 0.31 × 0.25
limiting indices	$-20 \leq h \leq 20$	$-21 \leq h \leq 20$	$-12 \leq h \leq 12$
	$-8 \leq k \leq 8$	$-13 \leq k \leq 13$	$-12 \leq k \leq 14$
	$-19 \leq l \leq 16$	$-9 \leq l \leq 9$	$-17 \leq l \leq 17$
reflns collected/unique	13 201/3139 [R(int) = 0.3139]	11 551/2684 [R(int) = 0.0800]	12 735/5954 [R(int) = 0.1168]
data/restraints/param	3139/0/464	2684/1/414	5954/0/621
GOF on F^2	0.728	1.093	1.013
final R indices [$I > 2\sigma(I)$]	R1 = 0.0674, wR2 = 0.1586	R1 = 0.0590, wR2 = 0.1522	R1 = 0.0876, wR2 = 0.1862
R indices (all data)	R1 = 0.1234, wR2 = 0.1911	R1 = 0.0747, wR2 = 0.1656	R1 = 0.1832, wR2 = 0.2403
largest diff peak and hole (e/Å^3)	+0.607 and −0.727	+0.383 and −0.259	+0.997 and −0.774

Table 2. Bond Lengths [Å] and Angles [deg] for **2** and **7**

2		**7**	
	Bond Lengths		
Y1−Cl1	2.609(3)	Y1−Cl1	2.606(5)
Y1−Cl2	2.618(3)	Y1−Cl2	2.620(4)
Y1−O1	2.399(8)	Y1−O1	2.34(1)
Y1−N1	2.497(9)	Y1−N1	2.53(1)
Y1−N4	2.538(9)	Y1−N4	2.52(1)
Y1−C21	2.69(1)	Y1−C21	2.65(1)
Y1−C22	2.67(1)	Y1−C22	2.67(1)
Y1−C23	2.62(1)	Y1−C23	2.69(2)
Y1−C24	2.62(1)	Y1−C24	2.67(2)
Y1−C25	2.62(1)	Y1−C25	2.66(1)
	Angles		
Cl1−Y1−Cl2	93.6(1)	Cl1−Y1−Cl2	92.3(2)
Cl1−Y1−O1	85.5(2)	Cl1−Y1−O1	85.8(3)
N1−Y1− Cl1	159.8(2)	Cl1−Y1−N1	158.7(3)
Cl1−Y1−N4	91.4(2)	Cl1−Y1−N4	92.7(4)
Cl2−Y1−O1	81.1(2)	Cl2−Y1−O1	80.7(3)
Cl2−Y1−N1	95.7(2)	Cl2−Y1−N1	96.6(3)
N4−Y1−Cl2	154.7(2)	Cl2−Y1−N4	156.0(3)
O1−Y1−N1	78.3(3)	O1−Y1−N1	76.6(4)
O1−Y1−N4	74.5(3)	O1−Y1−N4	76.4(4)
N1−Y1−N4	72.9(3)	N1−Y1−N4	71.6(4)
C2−C1−C21	112.8(9)	C1−C2−C21	115.8(13)

geometries at the yttrium centers show a distorted octahedral environment with major distortions in the N1−Y1−Cl1 and N4−Y1−Cl2 angles of 159.8(2) and 154.7(2)° for complex **2** and 158.7(3) and 156.0(3)° for complex **7**, respectively. The Y−Cl and Y−N bond distances of around 2.60 and 2.50 Å, respectively, in the two complexes are as one would expect for yttrium pyrazolyl complexes.[3d–f,10] In these complexes, the C_5H_4 ring is symmetrically bonded to the metal center with Y−C bond distances of 2.62(1)−2.69 (1) Å. The Y1−O1 bond distance of 2.399(8) Å in complex **2** is longer than the Y1−O1 bond distance of 2.34(1) Å in complex **7**, a situation that is attributed to the higher steric demands of the THF ring.

Finally, it is worth noting that in complexes **1**−**7** (both in solution and in the solid state) a κ^2-NNη^5-Cp coordination mode was found for the ligand; however, with ligands that are bulkier than chloride, such as in alkyl-containing complexes $[M(CH_2SiMe_3)_2(bpzcp)]$ or $[M(CH_2SiMe_3)_2(bpztcp)]$ (M = Sc, Y), the ligand adopts a κ^1-Nη^5-Cp mode in the solid state (see Figure 3)[9] and, furthermore, dynamic behavior in solution κ^1-Nη^5-Cp—κ^2-NNη^5-Cp—κ^1-Nη^5-Cp was observed.

Synthesis and Structure of Aryloxide Derivatives. First, complexes **1**−**7** were employed as starting materials to prepare alkyl-containing complexes analogous to previously prepared $[M(CH_2SiMe_3)_2(bpzcp)]$[9] by means of reactions with either Grignard or lithium alkyl reagents, but unfortunately in all cases under different experimental conditions, mixtures of untractable products were isolated. Afterward, we proceeded to explore the synthesis of aryloxide derivatives starting from the dichloride scorpionate/cyclopentadienyl group 3 metal complexes described above. Alkoxide or aryloxide derivatives of scorpionate-containing group 3 metal complexes are relatively rare,[3d–f] although several examples of alkoxide- or aryloxide-containing noncyclopentadienyl and cyclopentadienyl group 3 metal complexes have been documented.[3f,11] However, the reaction of $[MCl_2(bpzcp)(THF)]$ (**1** and **2**) with sodium or potassium salts of different phenol derivatives, such as MOAr (M = Na, K; OAr = 2,6-

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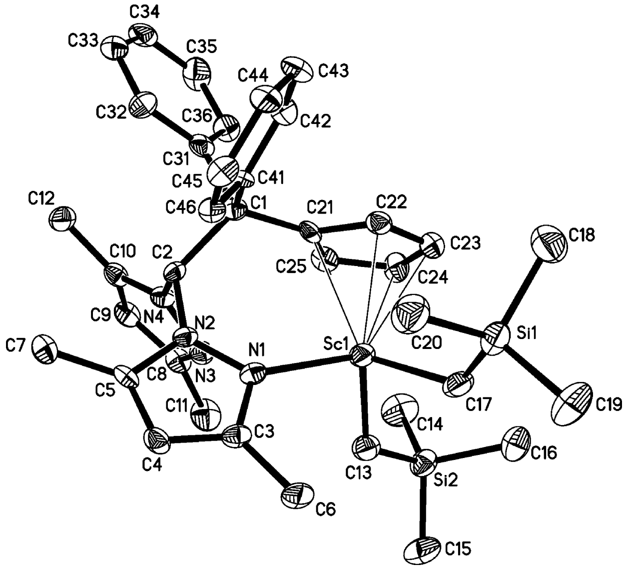
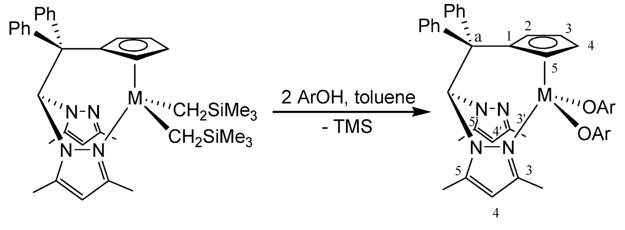


Figure 3. ORTEP drawing of the complex [Sc(CH_2SiMe_3)$_2$(bpzcp)].[9]

Scheme 2. Synthesis of Bis(aryloxide) Complexes **8**−**10**

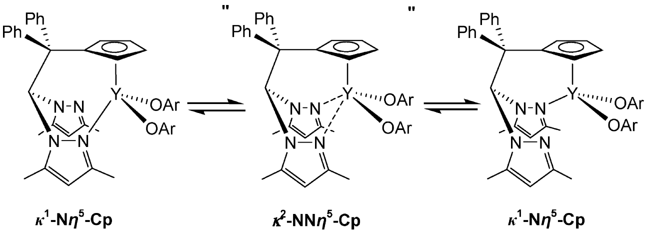


M=Sc, Ar= 2,6-$C_6H_3Me_2$, (**8**)
M=Y, Ar= 2,6-$C_6H_3Me_2$, (**9**)
M=Y, Ar= 3,5-$C_6H_3Me_2$, (**10**)

dimethylphenoxide, OAr = 3,5-dimethylphenoxide), in different molar ratios and under different conditions proved unsuccessful. Thus, we attempted to prepare aryloxide derivatives of scorpionate-containing compounds using the dialkyl complexes [M(CH_2SiMe_3)$_2$(bpzcp)][9] through an alcoholysis reaction with ArOH (2 equiv; Ar = 2,6-$C_6H_3Me_2$, 3,5-$C_6H_3Me_2$) to yield analytically pure [M(OAr)$_2$(bpzcp)] (M = Sc, Ar = 2,6-$C_6H_3Me_2$, **8**; M = Y, Ar = 2,6-$C_6H_3Me_2$, **9**; M = Y, Ar = 3,5-$C_6H_3Me_2$, **10**) in ca. 80% isolated yield (Scheme 2). The corresponding reaction of 3,5-$C_6H_3Me_2OH$ with [Sc(CH_2SiMe_3)$_2$(bpzcp)] did not give a clean product on either the preparative or NMR-tube scale (toluene-d_8).

The room-temperature ^1H and $^{13}C\{^1H\}$ NMR spectra of complex **8** show two sharp resonances for each of the H^4, Me^3, and Me^5 pyrazole groups and broad resonances for ortho groups of the Ar substituents. The sharpness of the ^1H NMR signals of the heteroscorpionate ligand suggests a high coordination energy of the ligand to the metal center and the absence of any fluxional equilibrium involving the two N,N donors at room temperature. The signals indicate that in this case the two pyrazole rings are not equivalent and that in solution a fluxional process does not exist between the coordinated and noncoordinated pyrazole rings, unlike the bis(alkyl) complex precursor, which shows dynamic behavior in solution between the two pyrazole rings.[9] The stereorigid environment is stable at least up to 340 K, up to which fluxional behavior involving the ligand was not detected by ^1H NMR spectroscopy. These results are consistent with a tetrahedral structural disposition with a κ^1-Nη^5-Cp scorpionate coordination mode with two aryloxide ligands occupying the other two coordination positions (see Scheme 2). The room-temperature ^1H and $^{13}C\{^1H\}$ NMR spectra of complexes **9** and **10** show one set of resonances for each of the H^4, Me^3, and Me^5 pyrazole groups and for ortho and meta groups on the Ar substituents due to the presence of a very fast interconversion of two tetrahedral complexes with a κ^1-Nη^5-Cp scorpionate coordination (see below). Moreover, the signals of the ortho and meta methyl groups of the Ar substituents appear as single broad resonances at 2.00 ppm for complex **9** and at 2.20 ppm for complex **10**. The variable-temperature (VT) NMR analysis shows that at subambient temperature the resonances of the methyl group on the aryloxide ligands, along with those of the pyrazole rings and the resonance of the H^4 of the same rings, broaden and resolve into two separate peaks. At −100 °C, the resonances become well-resolved and the NMR spectrum becomes consistent with a tetrahedral structural disposition with κ^1-Nη^5-Cp scorpionate coordination and two aryloxide ligands occupying the other two coordination positions (see Scheme 2). This picture indicates the presence of an exchange process between the coordinated and noncoordinated pyrazole rings, resulting in interconversion from one stereoisomer to the other (Scheme 3). This dynamic behavior has been observed previously in other scorpionate-containing metal complexes.[9,12]

Scheme 3. Mechanism Proposed for the Dynamic Behavior in Solution of Complexes **9** and **10**



Free-energy values, $\Delta G^{\ddagger}$, for complexes **9** and **10** were calculated[13] from VT NMR studies. Complex **9** has higher activation barriers, with a coalescence temperature of −80 °C and $\Delta G^{\ddagger} = 11.3 \pm 0.1$ kcal/mol, whereas **10** has a coalescence point of −90 °C with $\Delta G^{\ddagger} = 10.5 \pm 0.1$ kcal/mol. The different behavior of **8** in comparison to **9** and **10** can probably be explained on the basis of the larger size of the yttrium atom in comparison to scandium.

Finally, an interesting hydrolysis process was observed when we attempted to use different procedures to obtain single crystals suitable for X-ray diffraction studies from the solution of complex **9** in CH_2Cl_2. For example, when a CH_2Cl_2 solution of **9** was slowly evaporated at room temperature in air for 48 h, white crystals were deposited from the solution, and these were identified as the poly-

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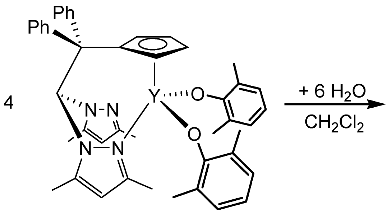
Scheme 4. Synthesis of Polynuclear Yttrium Complex **11**



[{Y(bpzcp)}(μ-OH)$_2$(μ_3-OH){Y(O-2,6-C$_6$H$_3$Me$_2$)$_2$}]$_2$ **(11)**
+
2 bpzcpH
+
4 2,6-C$_6$H$_3$Me$_2$-OH

nuclear complex **11**. This complex results from partial hydrolysis of the scorpionate/aryloxide-containing complex. We subsequently rationalized the synthesis of **11**; in fact, the addition of an appropriate amount of water to a CH$_2$Cl$_2$ solution of complex **9** gives rise to the isolation of **11** after the appropriate workup (see Scheme 4).

When the process was followed in an NMR tube (CD$_2$Cl$_2$), the reaction was quantitative after 12 h and the only side products were bpzcpH, 2-[2,2-bis(3,5-dimethylpyrazol-1-yl)-1,1-diphenylethyl]-1,3-cyclopentadiene,[9] and free phenol 2,6-C$_6$H$_3$Me$_2$OH. Compound **11** was characterized spectroscopically. The IR spectrum shows a broad strong band at 3150 cm^{-1}, and this is assigned to ν(OH) of the bridging groups. The ^{1}H and ^{13}C{^{1}H} NMR spectra show single sets of resonances for the pyrazole rings and for the aryloxide substituents, indicating that the pyrazoles from scorpionate and aryloxide ligands, at least in solution, are equivalent. This finding is consistent with a structural disposition with a κ^2-NNη^5-Cp scorpionate coordination mode. The molecular structure of this complex was determined by X-ray diffraction, and the structure is shown in Figure 4. Crystallographic data and significant bond distances and angles are listed in Tables 1 and 3, respectively. The centrosymmetric tetranuclear yttrium hydroxo complex consists of four yttrium atoms in the same plane in a rhombic disposition, with bridging by two μ_3-OH groups and four μ_2-OH groups (see Figure 5). Each yttrium atom has a pseudo-octahedral coordination.

The complex exhibits two different yttrium environments: Y1 is bonded to three hydroxo groups and a hybrid scorpionate/cyclopentadienyl ligand with a κ^2-NNη^5-Cp coordination mode, whereas Y2 is bonded to two aryloxide ligands with an octahedral disposition and to four hydroxo groups, which complete its coordination sphere. Furthermore, Y1 shows a distorted octahedral environment, with O2 out of the plane defined by N1, N3, O1, and Y1 by 0.89(1) Å, whereas Y2 is practically in the plane defined by O1, O2, O5, and O3A, probably because of constraints imposed by the scorpionate ligand. The Y−O core bond lengths are in the range 2.208(8)−2.403(8) Å and follow the order Y−OAr < Y−μ_2-OH < μ_3-OH. The Y−OH bond distances are consistent with the values reported for other polynuclear yttrium hydroxo complexes.[14] The Y−O(aryloxide) bond distances [Y2−O4, 2.12 (1) Å; Y2−O5, 2.12(1) Å] are slightly longer than the range reported for five- and six-coordinated yttrium aryloxides [2.046(6)−2.103(10) Å].[15] The angle around the aryloxide oxygen is 171−175°.[15d] However, the angle around the aryloxide oxygen O5 [Y2−O5−C61] is 165.4(9)°,[15d] which is probably due to the steric hindrance caused by the methyl group, Me^3, of the pyrazolyl ring closest to this aryloxide ligand. The Y−Cp carbon distances of 2.66(1)−2.74(1) Å indicate that the C$_5$H$_4$ rings are symmetrically bonded to the metal centers.

Although a number of the oxo/hydroxo clusters or polynuclear complexes of yttrium are known,[14] the compound reported here represents the first example of this type of complex containing a scorpionate ligand.

Styrene Polymerization Catalyzed by 1 and 2. Preliminary styrene polymerization experiments catalyzed by **1** and **2** were carried out in toluene at room temperature using methylaluminoxane (MAO) as the cocatalyst. The results of these experiments are summarized in Table 4.

The chloride derivatives **1** and **2**, activated with MAO, showed moderate but significant activity in styrene polymerization. GPC analyses of the polystyrenes obtained indicate that they have narrow molecular weight distributions (M_w/M_n = 1.26−1.91), with the polystyrene produced showing low molecular weights and reproducibly exhibiting molecular weight distributions of less than 2, as expected for single-site catalysts. The molecular weight of the resulting polymers increased as the monomer-to-catalyst ratio was increased, while the molecular weight distribution remained very narrow (Table 4; M_n/M_w = 1.67−1.91, runs 1−3; M_n/M_w = 1.26−1.87, runs 4−6). The low molecular weights of the resulting polymers are most likely caused by chain-transfer reactions.[16]

It is worth noting that there are some reports of group 3 and 4 metals combined with scorpionate and heteroscorpionate ligands that exhibit moderate and high activity—mainly in ethylene but also in propene polymerization[3f,g,13,17] —but in styrene polymerization, complexes containing scorpionate

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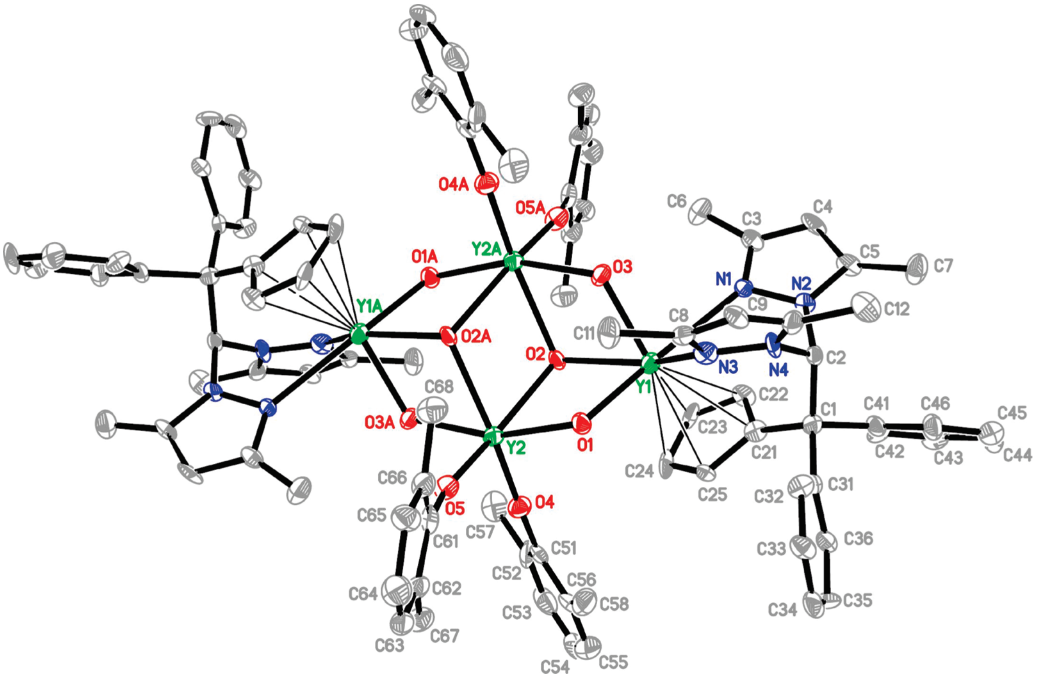

Figure 4. ORTEP view of **11**. Ellipsoids are at the 30% probability level, and hydrogen atoms have been omitted for clarity.

Table 3. Bond Lengths [Å] and Angles [deg] for **11**[a]

bond lengths		angles	
Y1−O1	2.21(1)	O1−Y1−O2	72.7(3)
Y1−O2	2.38(1)	O1−Y1−O3	92.6(3)
Y1−O3	2.20(1)	O2−Y1−O3	71.6(3)
Y1−N1	2.57(1)	O1−Y1−N1	153.3(4)
Y1−N3	2.48(1)	O2−Y1−N1	128.5(3)
Y1−C21	2.73(1)	O3−Y1−N1	81.6(3)
Y1−C22	2.74(1)	O1−Y1−N3	84.6(4)
Y1−C23	2.70(1)	O2−Y1−N3	147.0(4)
Y1−C24	2.66(1)	O3−Y1−N3	86.2(3)
Y1−C25	2.67(1)	N1−Y1−N3	69.1(4)
Y2−O1	2.27(1)	O1−Y2−O2	71.3(3)
Y2−O2	2.40(1)	O1−Y2−O3A	162.7(3)
Y2−O2A	2.40(1)	O1−Y2−O4	102.9(3)
Y2−O3A	2.27(1)	O1−Y2−O5	91.2(4)
Y2−O4	2.12(1)	O2−Y2−O4	95.7(3)
Y2−O5	2.12(1)	O2−Y2−O5	157.6(3)
		O3A−Y2−O4	90.6(3)
		O3A−Y2−O5	96.5(4)
		O4−Y2−O5	102.0(4)
		Y1−O1−Y2	112.4(4)
		Y1−O2−Y2	102.3(3)
		Y1−O2−Y2A	103.5(3)
		Y2−O2−Y2A	106.4(3)
		Y1−O3−Y2A	114.6(4)

[a] Symmetry transformations used to generate equivalent atoms: 2 − *x*, 1 − *y*, 1 − *z*.

ligands have not been reported to date. The polymers obtained were examined by $^{13}C\{^1H\}$ NMR spectroscopy to obtain detailed information on the microstructure of polystyrenes isolated.[18] The crude polymers were substantially stereoirregular in the ^{13}C NMR analysis, showing five main peaks in the range 145.2−146.7 ppm due to phenyl C1 carbons, which correspond to the various configurational sequences of atactic polystyrene and are in agreement with the symmetry of the catalyst precursors.

Conclusions

The hybrid scorpionate/cyclopentadienyl ligands bpzcp, bpztcp, and bpzpcp were used to prepare a series of halide and aryloxide complexes of scandium and yttrium. Halide complexes **1**−**6** exhibit in the solid state a pseudo-octahedral geometry in which the scorpionate ligand is κ^2-NNη^5-Cp-coordinated to the metals along with one THF ligand. The solid-state structure is retained in solution. The H_2O adduct of **4**, [YCl_2(bpztcp)(H_2O)] (**7**), is formed when a solution of **4** is allowed to stand at room temperature in the presence of moisture.

The aryloxide complexes **8**−**10** consist of a racemic mixture in which each stereoisomer adopts a pseudotetrahedral structure. The more sterically demanding of aryloxide ligands induces a κ^1-Nη^5-Cp coordination mode of the bpzcp ligand in complex **8**. However, a fluxional coordinative behavior of the bpzcp ligand was monitored in solution, and an exchange between coordinated and noncoordinated pyrazole rings is observed in yttrium complexes **9** and **10**. In addition, the hydrolysis of complex **9** gives a tetranuclear yttrium complex with a $Y_4(\mu\text{-}OH)_4(\mu_3\text{-}OH)_2$ core that has two different yttrium environments; two yttrium atoms are

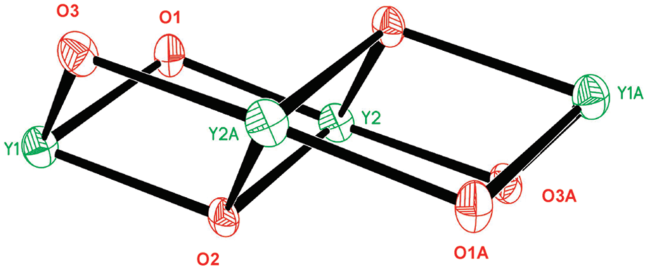

Figure 5. Tetranuclear core of complex **11**.

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Table 4. Polymerization of Styrene with Scorpionate Scandium and Yttrium Complexes **1** and **2**[a]

run no.	complex	Al/M	[M$_o$]/[cat]	*t* (min)	yield[b] (%)	activity[c]	M_n[d]	M_w[d]	M_w/M_n[d]
1	**1**	2000	500	15	90	186	5107	9036	1.77
2	**1**	2000	1000	15	68	278	5271	10060	1.91
3	**1**	2000	1500	15	78	464	6202	10341	1.67
4	**2**	2000	500	15	75	154	5671	10634	1.87
5	**2**	2000	1000	15	68	280	6584	9986	1.52
6	**2**	2000	1500	15	80	494	8869	11214	1.26
7	**1**	500	500	15	34	17	4760	8449	1.77
8	**1**	1000	500	15	63	130	4808	8824	1.83
9	**2**	500	500	15	31	16	4693	8553	1.82
10	**2**	1000	500	15	65	134	5289	10107	1.91

[a] Conditions: M, 6.0 μmol. M$_o$ = styrene. T = 25 °C. Solvent = toluene. [b] Weight of the polymer obtained/weight of the monomer used. [c] Given in kg of PS/(mol of M·h). [d] Measured by GPC at 40 °C in THF with antioxidant, using a Polymer Laboratories GPC-220 instrument equipped with PL Gel mixed-B columns relative to a polystyrene standard.

supported by a scorpionate ligand with a κ^2-NNη^5-Cp coordination mode and bridged by two yttrium atoms bonded to two aryloxide ligands with an octahedral disposition.

Finally, complexes **1** and **2** were active styrene polymerization catalysts after activation with excess MAO, producing atactic polystyrenes with low molecular weights but characterized by narrow molecular weight distributions.

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 fast atom bombardment (FAB) technique and nitrobenzyl alcohol as the matrix. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova FT-500 spectrometer (^{1}H NMR 500 MHz and ^{13}C NMR 125 MHz) and referenced to the residual deuterated solvent. The NOESY-1D NMR spectra were recorded with the following acquisition parameters using standard VARIAN-FT software: irradiation time 2 s and number of scans 256. Two-dimensional NMR spectra were acquired using standard VARIAN-FT software and processed using an IPC-Sun computer. GPC measurements were performed on a Polymer Laboratories PL-GPC-220 instrument equipped with a PL Gel 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 [Li(bpzcp)(THF)],[7] [Li(bpztcp)(THF)],[7] (bpzpcpH),[7] and [M(CH_2SiMe_3)$_2$ (bpzcp)] (M = Sc, Y),[9] were prepared according to literature procedures. Anhydrous trichlorides of scandium and yttrium (Aldrich and Strem) were used as received, and all other chemicals were commercially available and used after appropriate purification. Styrene was purchased from Aldrich and was dried by stirring with CaH_2 for 48 h followed by distillation under reduced pressure.

Synthesis of [ScCl$_2$(bpzcp)(THF)] (1). A solution of [Li(bpzcp)(THF)] (0.48 g, 0.95 mmol) in THF (25 mL) was added to a solution of [ScCl$_3$(THF)$_3$] (0.35 g, 0.95 mmol) in THF (25 mL). The reaction mixture was stirred for 12 h at room temperature, after which a pale-yellow suspension was formed. The solvent was removed under vacuum and the solid extracted with CH_2Cl_2. A white solid was obtained after removal of the solvents. This material was recrystallized from THF/hexane, yielding white crystals of the title compound. Yield: 86%. Anal. Calcd for $C_{33}H_{37}Cl_2N_4OSc$: C, 63.77; H, 5.99; N, 9.01. Found: C, 63.85; H, 6.11; N, 8.94. ^{1}H NMR ($CDCl_3$, 297 K): δ 7.19 (s, 1 H, CH), 5.88 (s, 2 H, H^4), 2.59 (s, 6 H, Me^3), 2.02 (s, 6 H, Me^5), 7.26−6.99 (m, 10 H, Ph), 6.78 (m, 2 H, H^{3,4}-Cp), 5.80 (m, 2 H, H^{2,5}-Cp), 3.75 (m, 4 H, THF), 1.85 (m, 4 H, THF). ^{13}C{^{1}H} NMR ($CDCl_3$, 297 K): δ 74.2 (CH), 143.8, 143.1 (C$^{3\text{ or }5}$), 109.3 (C^4), 16.6 (Me^3), 12.1 (Me^5), 153.6−127.9 (Ph), 59.9 (C^a), 121.7 (C^{2,5}-Cp), 115.7 (C^{3,4}-Cp), 106.3 (C^1-Cp), 68.1 (THF), 25.8 (THF). MS [FAB (*m*/*z* [assignment], % intensity)]: 513 [M − THF − Cl], 100.

Synthesis of [YCl$_2$(bpzcp)(THF)] (2). The synthetic procedure was the same as that for complex **1**, using [YCl$_3$(THF)$_3$] (0.50 g, 1.21 mmol) and [Li(bpzcp)(THF)] (0.62 g, 1.21 mmol), to give **2** as a pale-yellow solid. Yield: 90%. Anal. Calcd for $C_{33}H_{37}Cl_2N_4OY$: C, 59.56; H, 5.60; N, 8.42. Found: C, 59.74; H, 5.62; N, 8.23. ^{1}H NMR ($CDCl_3$, 297 K): δ 7.29 (s, 1 H, CH), 5.97 (s, 2 H, H^4), 2.47 (s, 6 H, Me^3), 2.06 (s, 6 H, Me^5), 7.17−6.92 (m, 10 H, Ph), 6.55 (m, 2 H, H^{3,4}-Cp), 5.64 (m, 2 H, H^{2,5}-Cp), 3.66 (m, 4 H, THF), 1.80 (m, 4 H, THF). ^{13}C{^{1}H} NMR ($CDCl_3$, 297 K): δ 73.8 (CH), 146.3, 143.5 (C$^{3\text{ or }5}$), 108.8 (C^4), 15.5 (Me^3), 12.1 (Me^5), 153.3−126.9 (Ph), 60.5 (C^a), 116.3 (C^1-Cp), 114.9 (C^{3,4}-Cp), 106.2 (C^{2,5}-Cp), 68.9 (THF), 25.6 (THF). MS [FAB (*m*/*z* [assignment], % intensity)]: 557 [M − THF − Cl], 100.

Synthesis of [ScCl$_2$(bpztcp)(THF)] (3). The synthetic procedure was the same as that for complex **1**, using [ScCl$_3$(THF)$_3$] (0.35 g, 0.95 mmol) and [Li(bpztcp)(THF)] (0.39 g, 0.95 mmol), to give **3** as a white solid. Yield: 85%. Anal. Calcd for $C_{25}H_{37}Cl_2N_4OSc$: C, 57.10; H, 7.09; N, 10.65. Found: C, 57.24; H, 7.18; N, 10.45. ^{1}H NMR ($CDCl_3$, 297 K): δ 6.80 (s, 1 H, CH), 5.92 (s, 1 H, H$^{4'}$), 5.86 (s, 1 H, H^4), 2.53 (s, 6 H, Me$^{3,3'}$), 2.53 (s, 3 H, Me$^{5'}$), 2.44 (s, 3 H, Me^5), 3.02 (s, 1 H, CH^a), 1.09 [s, 9 H, C(CH$_3$)$_3$], 5.60 (m, 1 H, H^5-Cp), 5.51 (m, 1 H, H^2-Cp), 6.42 (m, 1 H, H^3-Cp), 6.20 (m, 1 H, H^4-Cp), 3.75 (m, 4 H, THF), 1.86 (m, 4 H, THF). ^{13}C{^{1}H} NMR ($CDCl_3$, 297 K): δ 68.1 (CH), 143.7, 143.5, 141.1, 140.8 (C$^{3,3'\text{ or }5,5'}$), 109.2 (C^4), 107.8 (C$^{4'}$), 15.4 (Me$^{3,3'}$), 12.9 (Me$^{5'}$), 11.9 (Me^5), 35.6 [*C*(CH$_3$)$_3$], 28.6 [C(*CH*$_3$)$_3$], 57.4 (C^a), 111.0 (C^2-Cp), 117.5 (C^3-Cp), 113.8 (C^4-Cp), 116.1 (C^5-Cp), 107.6 (C^1-Cp), 68.2 (THF), 21.3 (THF). MS [FAB (*m*/*z* [assignment], % intensity)]: 418 [M − THF − Cl], 100.

Synthesis of [YCl$_2$(bpztcp)(THF)] (4). The synthetic procedure was the same as that for complex **1**, using [YCl$_3$(THF)$_3$] (0.50 g, 1.21 mmol) and [Li(bpztcp)(THF)] (0.51 g, 1.21 mmol), to give **4** as a pale-yellow solid. Yield: 80%. Anal. Calcd for $C_{25}H_{37}Cl_2N_4OY$: C, 52.69; H, 6.54; N, 9.83. Found: C, 52.75; H, 6.66; N, 9.58. ^{1}H NMR ($CDCl_3$, 297 K): δ 6.81 (s, 1 H, CH), 6.06 (s, 1 H, H$^{4'}$), 5.98 (s, 1 H, H^4), 2.53 (s, 6 H, Me$^{3,3'}$), 2.56 (s, 3 H, Me$^{5'}$), 2.45 (s, 3 H, Me^5), 3.00 (s, 1 H, CH^a), 0.99 [s, 9 H, C(CH$_3$)$_3$], 6.46 (m, 1 H, H^3-Cp), 6.26 (m, 1 H, H^4-Cp), 5.64 (m, 1 H, H^5-Cp), 5.55 (m, 1 H, H^2-Cp), 3.61 (m, 4 H, THF), 1.82 (m, 4 H, THF). ^{13}C{^{1}H} NMR ($CDCl_3$, 297 K): δ 67.0 (CH), 143.5, 143.2, 141.7, 141.0 (C$^{3,3'\text{ or }5,5'}$), 109.0 (C^4), 107.9 (C$^{4'}$), 15.5 (Me$^{3,3'}$), 12.1 (Me$^{5'}$), 11.8 (Me^5), 35.7 [*C*(CH$_3$)$_3$], 28.7 [C(*CH*$_3$)$_3$], 57.4 (C^a), 118.0 (C^3-Cp), 116.2 (C^5-Cp), 113.8 (C^4-Cp), 111.0 (C^2-Cp), 107.9 (C^1-Cp), 68.2 (THF), 21.3 (THF). MS [FAB (*m/z* [assignment], % intensity)]: 462 [M − THF − Cl], 100.

Synthesis of [ScCl$_2$(bpzpcp)(THF)] (5). To a cooled (−70 °C) solution of bpzpcpH (0.34 g, 0.95 mmol) in dry THF (50 mL) was added a 1.6 M solution of Bu^{n}Li (0.60 mL, 0.95 mmol) in hexane, and the mixture was stirred for 30 min. A suspension of [ScCl$_3$(THF)] (0.35 g, 0.95 mmol) in THF (50 mL) was added, and the reaction mixture was stirred for 12 h at room temperature. The solvent was removed under vacuum and the solid extracted with CH$_2$Cl$_2$. A white solid was obtained after removal of the solvents. Yield: 78%. Anal. Calcd for C$_{27}$H$_{33}$Cl$_2$N$_4$OSc: C, 59.45; H, 6.10; N, 10.27. Found: C, 59.68; H, 6.51; N, 10.03. ^{1}H NMR (CDCl$_3$, 297 K): δ 6.50 (br s, 1 H, CH), 5.85, (s, 1 H, H^4), 5.58 (s, 1 H, H$^{4'}$), 2.36, (s, 3 H, Me^3), 2.13 (s, 3 H, Me$^{3'}$), 2.35 (s, 3 H, Me$^{5'}$), 2.08 (s, 3 H, Me^5), 7.35−7.20 (m, 5 H, Ph), 5.28 (s, 1 H, H^a), 6.35 (m, 1 H, H^5-Cp), 6.31 (m, 1 H, H^2-Cp), 6.21 (m, 1 H, H^3-Cp), 6.13 (m, 1 H, H^4-Cp), 3.71 (m, 4 H, THF), 1.82 (m, 4 H, THF). ^{13}C{^{1}H} NMR (CDCl$_3$, 297 K): δ 68.1 (CH), 145.8, 143.5, 141.8, 140.3 (C$^{3,3'\text{ or }5,5'}$), 106.0 (C^4), 105.4 (C$^{4'}$), 12.8 (Me^3), 10.4 (Me$^{3'}$), 12.9 (Me$^{5'}$), 10.7 (Me^5), 152.2−128.5 (Ph), 52.2 (C^a), 107.6 (C^1-Cp), 117.5 (C^5-Cp), 116.1 (C^2-Cp), 113.8 (C^4-Cp), 111.0 (C^3-Cp), 68.0 (THF), 25.4 (THF). MS [FAB (*m/z* [assignment], % intensity)]: 438 [M − THF − Cl], 100.

Synthesis of [YCl$_2$(bpzpcp)(THF)] (6). The synthetic procedure was the same as that for complex **5**, using bpzpcpH (0.43 g, 1.21 mmol), Bu^{n}Li (0.75 mL, 1.21 mmol) and [YCl$_3$(THF)$_3$] (0.50 g, 1.21 mmol), to give **6** as a pale-yellow solid. Yield: 82%. Anal. Calcd for C$_{27}$H$_{33}$Cl$_2$N$_4$OY: C, 55.02; H, 5.64; N, 9.50. Found: C, 55.36; H, 5.84; N, 9.21. ^{1}H NMR (CDCl$_3$, 297 K): δ 6.49 (s, 1 H, CH), 6.09 (s, 1 H, H$^{4'}$), 6.05 (s, 1 H, H^4), 2.67 (s, 3 H, Me$^{3'}$), 2.64 (s, 3 H, Me^3), 2.46 (s, 3 H, Me^5), 1.81 (s, 3 H, Me$^{5'}$), 7.32−7.00 (m, 5 H, Ph), 4.73 (br s, 1 H, H^a), 5.78 (m, 1 H, H^2-Cp), 5.54 (m, 1 H, H^5-Cp), 6.36 (m, 1 H, H^3-Cp), 6.33 (m, 1 H, H^5-Cp), 3.66 (m, 4 H, THF), 1.81 (m, 4 H, THF). ^{13}C{^{1}H} NMR (CDCl$_3$, 297 K): δ 70.8 (CH), 146.4, 144.4, 141.5, 141.0 (C$^{3,3'\text{ or }5,5'}$), 106.1 (C^4), 105.5 (C$^{4'}$), 14.6 (Me$^{3'}$), 14.5 (Me^3), 11.0 (Me^5), 10.8 (Me$^{5'}$), 149.7−128.7 (Ph), 51.7 (C^a), 106.1 (C^{1}Cp), 115.6 (C^{4}Cp), 116.0 (C^{3}Cp), 114.2 (C^{2}Cp), 106.2 (C^{5}Cp), 67.8 (THF), 25.3 (THF). MS [FAB (*m/z* [assignment], % intensity)]: 482 [M − THF − Cl], 100.

Synthesis of [YCl$_2$(bpztcp)(H$_2$O)] (7). To a solution of [YCl$_2$(bpztcp)(THF)] (**6**; 0.20 g, 0.35 mmol) in CH$_2$Cl$_2$ (50 mL) was added H$_2$O (6.3 μL, 0.35 mmol). The mixture was stirred for 1 h at room temperature and then concentrated to 15 mL and cooled at −10 °C, affording a white microcrystalline powder. Yield: 95%. Anal. Calcd for C$_{21}$H$_{31}$Cl$_2$N$_4$OY: C, 48.94; H, 6.06; N, 10.87. Found: C, 49.08; H, 6.21; N, 10.68. ^{1}H NMR (CDCl$_3$, 297 K): δ 6.79 (s, 1 H, CH), 5.95 (s, 1 H, H^4), 6.00 (s, 1 H, H$^{4'}$), 2.55, 2.53 (s, 3 H, 3 H, Me$^{3,3'}$), 2.42 (s, 3 H, Me^5), 2.54 (s, 3 H, Me$^{5'}$), 0.97 [s, 9 H, C(CH$_3$)$_3$], 2.97 (br s, 1 H, CH^a), 6.42 (m, 1 H, H^3-Cp), 6.23 (m, 1 H, H^5-Cp), 5.60 (m, 1 H, H^5-Cp), 5.51 (m, 1 H, H^2-Cp), 3.50 (br s, 2 H, H$_2$O). ^{13}C{^{1}H} NMR (CDCl$_3$, 297 K): δ 67.1 (CH), 144.4, 143.4, 141.1, 140.9 (C$^{3,3'\text{ or }5,5'}$), 109.1 (C^4), 107.5 (C$^{4'}$), 15.4, 14.9 (Me$^{3,3'}$), 11.8 (Me^5), 12.8 (Me$^{5'}$), 35.7 [*C*(CH$_3$)$_3$], 28.5 [C(*CH*$_3$)$_3$], 58.2 (C^a), 108.0 (C^1-Cp), 118.2 (C^3-Cp), 116.4 (C^5-Cp), 113.5 (C^4-Cp), 111.0 (C^2-Cp). MS [FAB (*m/z* [assignment], % intensity)]: 462 [M − H$_2$O − Cl], 100.

Synthesis of [Sc(O-2,6-C$_6$H$_3$Me$_2$)$_2$ (bpzcp)] (8). To a stirred solution of [Sc(CH$_2$SiMe$_3$)$_2$(bpzcp)] (0.15 g 0.23 mmol) in cold (0 °C) toluene (20 mL) was added dropwise a solution of 2,6-dimethylphenol (55 mg, 0.46 mmol) in cold toluene (20 mL). The reaction mixture was warmed to room temperature and stirred for 1 h before removal of the volatiles under reduced pressure to afford **8** as a yellow solid. This material was recrystallized from THF/hexane, yielding pale-yellow crystals of the title compound. Yield: 62%. Anal. Calcd for C$_{45}$H$_{47}$N$_4$O$_2$Sc: C, 74.98; H, 6.57; N, 7.77. Found: C, 75.10; H, 6.83; N, 7.55. ^{1}H NMR (CDCl$_3$, 297 K): δ 7.19 (s, 1 H, CH), 5.89, 5.88 (s, 1 H, 1 H, H$^{4,4'}$), 2.60, 2.19 (s, 3 H, 3 H, Me$^{3,3'}$), 2.04, 2.02 (s, 3 H, 3 H, Me$^{5,5'}$), 7.25−6.69 (m, 10 H, Ph), 6.67, 6.54 (m, 1 H, 1 H, H^{2,5}-Cp), 5.82, 5.73 (m, 1 H, 1 H, H^{3,4}-Cp), 2.18 (br s, 12 H, −O-2,6-Ph*Me*$_2$), 6.89 (d, $^3J_{HH}$ = 7.3 Hz, 4 H^m, −O-2,6-*Ph*Me$_2$), 6.53 (t, $^3J_{HH}$ = 7.3 Hz, 2 H^p, −O-2,6-*Ph*Me$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$, 297 K): δ 72.7 (CH), 145.3, 144.8, 142.1, 140.4 (C$^{3,3'\text{ or }5,5'}$), 108.3, 107.1 (C$^{4,4'}$), 13.8, 13.4 (Me$^{3,3'}$), 11.9 (Me$^{5,5'}$), 151.0−128.2 (Ph), 68.2 (C^a), 114.7 (C^1-Cp), 107.4 (C^{2,5}-Cp), 120.2 (C^{3,4}-Cp), 15.9, 14.2 (−O-2,6-Ph*Me*$_2$), 160.2−116.5 (−O-2,6-*Ph*Me$_2$). MS [FAB (*m/z* [assignment], % intensity)]: 600 [M − OAr], 100.

Synthesis of [Y(O-2,6-C$_6$H$_3$Me$_2$)$_2$(bpzcp)] (9). The synthetic procedure was the same as that for complex **8**, using [Y(CH$_2$SiMe$_3$)$_2$(bpzcp)] (0.15 g, 0.20 mmol) and 2,6-dimethylphenol (49 mg, 0.40 mmol), to give **9** as a white solid. Yield: 60%. Anal. Calcd for C$_{45}$H$_{47}$N$_4$O$_2$Y: C, 70.67; H, 6.57; N, 7.77. Found: C, 70.84; H, 6.71; N, 7.35. ^{1}H NMR (CDCl$_3$, 297 K): δ 7.37 (s, 1 H, CH), 5.96 (s, 2 H, H^4), 2.28 (s, 6 H, Me^3), 2.04 (s, 6 H, Me^5), 7.31−7.05 (m, 10 H, Ph), 6.39 (m, 2 H, H^{2,5}-Cp), 5.59 (m, 2 H, H^{3,4}-Cp), 2.09 (br s, 12 H, −O-2,6-Ph*Me*$_2$), 6.93 (d, $^3J_{HH}$ = 7.3 Hz, 4 H, H^m, −O-2,6-*Ph*Me$_2$), 6.52 (m, 2 H, H^p, −O-2,6-*Ph*Me$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$, 297 K): δ 74.8 (CH), 145.4, 142.5 (C$^{3\text{ or }5}$), 108.2 (C^4), 13.9 (Me^3), 11.7 (Me^5), 152.6−128.2 (Ph), 61.3 (C^a), 117.7 (C^1-Cp), 109.5 (C^{2,5}-Cp), 118.2 (C^{3,4}-Cp), 17.6 (−O-2,6-Ph*Me*$_2$), 161.9 (*C*^{ipso}-O-2,6-*Ph*Me$_2$), 125.6 (*C*^{o}-O-2,6-*Ph*Me$_2$), 127.5 (*C*^{m}-O-2,6-*Ph*Me$_2$), 115.0 (*C*^{p}-O-2,6-*Ph*Me$_2$). MS [FAB (*m/z* [assignment], % intensity)]: 644 [M − OAr], 100.

Synthesis of [Y(O-3,5-C$_6$H$_3$Me$_2$)$_2$(bpzcp)] (10). The synthetic procedure was the same as that for complex **8**, using [Y(CH$_2$SiMe$_3$)$_2$(bpzcp)] (0.15 g, 0.20 mmol) and 3,5-dimethylphenol (49 mg, 0.40 mmol), to give **10** as a white solid. Yield: 58%. Anal. Calcd for C$_{45}$H$_{47}$N$_4$O$_2$Y: C, 70.67; H, 6.57; N, 7.77. Found: C, 70.89; H, 6.81; N, 7.82. ^{1}H NMR (CDCl$_3$, 297 K): δ 7.38 (s, 1 H, CH), 5.82 (s, 2 H, H^4), 2.40 (s, 6 H, Me^3), 2.05 (s, 6 H, Me^5), 7.60−6.96 (m, 10 H, Ph), 6.27 (m, 2 H, H^{2,5}-Cp), 5.61 (m, 2 H, H^{3,4}-Cp), 2.20 (br s, 12 H, −O-3,5-Ph*Me*$_2$), 6.41 (s, 4 H, H^o, −O-3,5-*Ph*Me$_2$), 6.96 (br s, 2 H, H^p, −O-3,5-*Ph*Me$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$, 297 K): δ 73.9 (CH), 144.5, 142.9 (C$^{3\text{ or }5}$), 107.8 (C^4), 14.1 (Me^3), 11.6 (Me^5), 153.5−138.0 (Ph), 60.4 (C^a), 117.1 (C^1-Cp), 110.0 (C^{2,5}-Cp), 118.2 (C^{3,4}-Cp), 18.4 (−O-3,5-Ph*Me*$_2$), 162.0 (*C*^{ipso}-O-3,5-*Ph*Me$_2$), 126.3 (*C*^{o}-O-3,5-*Ph*Me$_2$), 128.8 (*C*^{m}-O-3,5-*Ph*Me$_2$), 130.8 (*C*^{p}-O-3,5-*Ph*Me$_2$). MS [FAB (*m/z* [assignment], % intensity)]: 644 [M − OAr], 100.

Synthesis of [{Y(bpzcp)}(μ-OH)$_2$(μ_3-OH){Y(O-2,6-C$_6$H$_3$Me$_2$)$_2$}]$_2$ (11). To a solution of **9** (0.200 g, 0.26 mmol) in CH$_2$Cl$_2$ (30 mL) was added dropwise H$_2$O (9 μL, 0.50 mmol). The reaction mixture was stirred for 12 h at room temperature, during which time a white precipitate appeared. The solid was filtered off and dried under reduced pressure to give **11** as a white solid. Yield: 81%. Anal. Calcd for C$_{90}$H$_{100}$N$_8$O$_{10}$Y$_4$: C, 59.74; H, 5.57; N, 6.19. Found: C, 60.20; H, 5.85; N, 6.07. ^{1}H NMR (DMSO, 297 K): δ 7.74 (s, 2 H, CH), 5.76 (s, 4 H, H^4), 2.36 (s, 12 H, Me^3), 2.01 (s, 12 H, Me^5), 7.32−6.86 (m, 20 H, Ph), 6.27 (m, 4 H, H^{2,5}-Cp), 5.77 (m, 4 H, H^{3,4}-Cp), 2.18 (br s, 24 H, −O-2,6-Ph*Me*$_2$), 6.92 (m, 8 H, H^m, −O-2,6-*Ph*Me$_2$), 6.42 (m, 4 H, H^p, −O-2,6-*Ph*Me$_2$). ^{13}C{^{1}H} NMR (DMSO, 297 K): δ 75.2 (CH), 145.8, 142.0 (C$^{3\text{ or }5}$), 106.8 (C^4), 13.5 (Me^3), 10.6 (Me^5), 152.8−128.5 (Ph), 62.3 (C^a), 116.3 (C^1-Cp), 108.8 (C^{2,5}-Cp), 117.9 (C^{3,4}-Cp), 16.6 (−O-2,6-Ph*Me*$_2$), 160.3−116.4 (−O-2,6-*Ph*Me_2). IR (Nujol mull, cm^{-1}): 3150 [$\nu(\mu$-OH) and $\nu(\mu_3$-OH)].

Polymerization of Styrene. A typical polymerization reaction is described (run 3, Table 4). A toluene solution of MAO (Witco, 10 wt %, solution in toluene; 6.96 mL) was added to a toluene solution (5 mL) of **2** (4 mg, 6.0 μmol) in a 100 mL Schlenk tube. The mixture was stirred at room temperature for a few minutes, and styrene (0.936 g, 9 mmol) was added with vigorous stirring. After ca. 15 min, methanol (5 mL) was added to terminate the polymerization. The mixture was poured into methanol (200 mL) to precipitate the polymeric product. The white polymer powder was collected by filtration and dried under vacuum at 60 °C to a constant weight (0.730 g, 78%).

X-ray Crystallography. A summary of crystal data collection and refinement parameters for all compounds is given in Tables 1–3. Data for compounds **2**, **7**, and **11** were collected on a Bruker X8 APPEX II CCD-based diffractometer, equipped with a graphite-monochromated Mo Kα radiation source ($\lambda = 0.710\,73$ Å). The crystal data, data collection, structural solution, and refinement parameters are summarized in Table 1. Data were integrated using *SAINT*,[19] and an absorption correction was performed with the program *SADABS*.[20] The structure of **2** was solved by the Patterson method, whereas the structures of **7** and **11** were solved by direct methods using *SHELXTL*[21] 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, except some hydrogen atoms from OH groups in complex **11**, which are not clear of its direction. Complexes **2** and **7** crystallize with THF molecules as the solvent, which show several atoms in a disordered position (approximately 0.50 population). Because of the poor quality of the crystals for **2** and **11**, the calculated values of *R*(int) and wR2 are high.

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Supporting Information Available: CIF file giving details of data collection, refinement, atom coordinates, anisotropic displacement parameters, and bond lengths and angles for complexes **2**, **7**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) *SAINT+, Area-Detector Integration Program*, version 7.12a; Bruker-Nonius AXS: Madison, WI, 2004.

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

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