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On the Search for NNO-Donor Enantiopure Scorpionate Ligands and Their Coordination to Group 4 Metals

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The preparation of new chiral bis(pyrazol-1-yl)methane-based NNO-donor scorpionate ligands in the form of the lithium derivatives [Li(bpzb)(THF)] [**1**; bpzb = 1,1-bis(3,5-dimethylpyrazol-1-yl)-3,3-dimethyl-2-butoxide] and [Li(bpzte)(THF)] [**2**; bpzte = 2,2-bis(3,5-dimethylpyrazol-1-yl)-1-*p*-tolylethoxide] or the alcohol ligands (bpzbH) (**3**) and (bpzteH) (**4**) has been carried out by 1,2-addition reactions with trimethylacetaldehyde or *p*-tolualdehyde. The separation of a racemic mixture of the alcohol ligand **3** has been achieved and gave an enantiopure NNO alcohol−scorpionate ligand in three synthetic steps: (i) 1,2-addition of the appropriate lithium derivative to trimethylacetaldehyde, (ii) esterification and separation of diastereoisomers **5**, (iii) saponification. Subsequently, the enantiopure scorpionate ligand (*R*,*R*)-bpzmmH {**6**; *R*,*R*-bpzmmH = (1*R*)-1-[(1*R*)-6,6-dimethylbicyclo[3.1.1]2-hepten-2-yl]-2,2-bis(3,5-dimethylpyrazol-1-yl)-ethanol} was obtained with an excellent diastereomeric excess (>99% de) in a one-pot process utilizing the aldehyde (1*R*)-(−)-myrtenal as a chiral substrate to control the stereochemistry of the newly created asymmetric center. These new chiral heteroscorpionate ligands reacted with [MX_4] (M = Ti, Zr; X = NMe_2, O^iPr, OEt, O^tBu) in a 1:1 molar ratio in toluene to give, after the appropriate workup, the complexes [$MX_3(\kappa^3$-NNO)] (**7**−**18**). The reaction of Me_3SiCl with [$Ti(NMe_2)_3$(bpzb)] (**7**) or [$Ti(NMe_2)_3$(*R*,*R*-bpzmm)] (**11**) in different molar ratios gave the halide−amide-containing complexes [$TiCl(NMe_2)_2(\kappa^3$-NNO)] (**19** and **20**) and [$TiCl_2(NMe_2)(\kappa^3$-NNO)] (**21** and **22**) and the halide complex [$TiCl_3(\kappa^3$-NNO)] (**23** and **24**). The latter complexes can also be obtained by reaction of the lithium compound **1** with $TiCl_4(THF)_2$ and deprotonation of the alcohol group of **6** with NaH, followed by reaction with $TiCl_4(THF)_2$ in a 1:1 molar ratio, respectively. Isolation of only one of the three possible diastereoisomers of the complexes **19** and **22** revealed that chiral induction from the ligand to the titanium center took place. The structures of these complexes were elucidated by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, and the X-ray crystal structures of **3**−**7**, **12**, and **24** were also established. Finally, we evaluated the influence that the chiral center of the new heteroscorpionate complexes has on the enantioselectivity of the asymmetric epoxidation of allylic alcohols.

Introduction

In the important field of ligand design, we have previously reported the synthesis of new "heteroscorpionate" ligands based on bis(pyrazol-1-yl)methane[1] that contain two pyrazole rings and a carboxylate, dithiocarboxylate, or methoxide group. These classes of tridentate ligands can coordinate to a wide variety of elements, e.g., from early to late transition metals. More recently, we and others have been interested in the introduction of chirality into these systems in an effort to obtain new enantiopure scorpionate ligands.[1c] This chirality has been introduced by three different methods: (a) the first method employs two different pyrazolyl donor groups bound to the carbon bridge atom [this approach leads to a racemic mixture of a bis(pyrazol-1-yl)acetate tripod ligands],[2]

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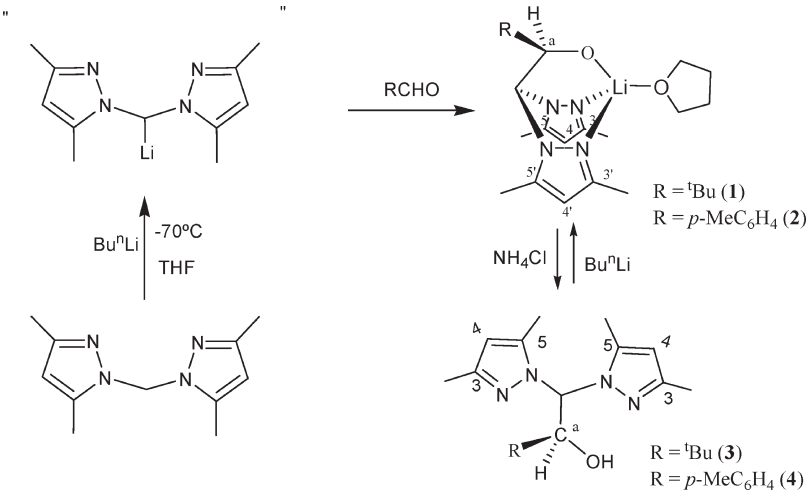
Scheme 1. Synthesis of **1**−**4**



(b) the second method uses an enantiopure heterocycle (e.g., camphorpyrazole or menthylpyrazole) to obtain a bis(pyrazol-1-yl)methane[3a] or a carbonyl or sulfinylbis(pyrazole)[3b,3c] and involves the subsequent introduction of the third coordinating moiety at the methylene bridge, (c) the third method, which was designed by our research group, involves the introduction of chirality in the substituent inserted into the methylene bridge. We recently communicated a simple and efficient synthetic route for the preparation of enantiopure scorpionate ligands in one step by an insertion reaction between a commercially available enantiopure isocyanate and an isothiocyanate in a conventional bis(pyrazol-1-yl)methane.[4] We also described a simple one-pot procedure for the synthesis of several hybrid scorpionate−cyclopentadienyl ligands that contained a chiral center in the backbone of the ligand.[5] More recently, we reported an efficient and highly diastereoselective one-pot preparation of an enantiopure scorpionate ligand by means of a 1,2-addition between a lithium bis(pyrazol-1-yl)methane derivative and (1*R*)-(−)-myrtenal.[6] The work described in the paper was stimulated by the discovery of an efficient synthetic route that led us to develop and fully explore the potential offered by a new type of chiral NNO-donor scorpionate ligand. We report here a more detailed description of the background and initial development of this synthetic approach.

This work describes the preparation of new chiral bis(pyrazol-1-yl)methane-based NNO-donor scorpionate ligands in one high-yielding step by the 1,2-addition of organometallics to aldehydes to afford chiral secondary alcohols.[7] Although these reactions are not stereoselective, an enantiopure scorpionate ligand was obtained by separation of the racemic mixture in two steps: (i) esterification of the alcohol−scorpionate ligand with a chiral acid and separation of the resulting diastereoisomers; (ii) saponification of the ester to obtain the enantiopure alcohol−scorpionate ligand. However, when this type of reaction was carried out with an enantiopure aldehyde [(1*R*)-(−)-myrtenal] as a possible chiral substrate to control the stereochemistry of a newly created asymmetric center,[8] we obtained an enantiopure scorpionate ligand in one step with a high stereoselectivity. Furthermore, the alcohol compounds were found to be excellent reagents for the introduction of scorpionate ligands into group 4 metal complexes, and a series of neutral amide and alkoxide complexes were prepared by the treatment of $M(NMe_2)_4$ or $M(OR)_4$ with these alcohol ligands. In addition, we corroborated the chiral induction from these scorpionate ligands to the metal center in the amide−halide exchange process of ligands in the coordination sphere, and we also evaluated some titanium complexes as catalysts in the asymmetric epoxidation of allylic alcohols.

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Results and Discussion

Synthesis of the Ligands. Deprotonation at the methylene group of bis(3,5-dimethylpyrazol-1-yl)methane (bdmpzm)[9] with Bu^nLi, followed by a 1,2-addition reaction with 2,2-dimethylpropionaldehyde or *p*-tolualdehyde, yielded the lithium compounds [Li(bpzb)(THF)] [**1**; bpzb = 1,1-bis-(3,5-dimethylpyrazol-1-yl)-3,3-dimethyl-2-butoxide] and [Li-(bpzte)(THF)] [**2**; bpzte = 2,2-bis(3,5-dimethylpyrazol-1-yl)-1-*p*-tolylethoxide] as colorless solids in good yield (ca. 85%) after the appropriate workup (see Scheme 1). The treatment of tetrahydrofuran (THF) solutions of **1** and **2** with NH_4Cl (saturated solution) afforded the alcohol ligands (bpzbH) (**3**) and (bpzteH) (**4**) as a white solids in good yield (ca. 90%) (see Scheme 1).

The ^1H and $^{13}C\{^1H\}$ NMR spectra of **1**−**4** exhibit two distinct sets of pyrazole resonances, indicating the existence of two types of pyrazole rings. Furthermore, the ^1H NMR spectra show the signals due to the moiety bound at the methylene bridge and the OH group in compounds **3** and **4**. A tetrahedral environment for the lithium atom in complexes **1** and **2** can be proposed in which the two pyrazole rings are located in cis and trans positions with respect to the *tert*-butyl or *p*-tolyl group (see Scheme 1). 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. In compounds **1**−**4**, the carbon atom (C^a) is a stereogenic center and the presence in solution of the two corresponding enantiomers was confirmed by the addition of 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 spectra, resulting from the two diastereoisomers of the two corresponding enantiomers. In addition, X-ray diffraction studies on **3** and **4** were carried out (see Figures 1 and 2). The X-ray diffraction study confirmed that the presence in solution of the two corresponding enantiomers for these compounds (*R* + *S*) is maintained in the solid state. The most representative bond lengths and angles are presented in Table 1. Both compounds have a monomeric structure. The methyl groups of the pyrazole rings of these compounds are oriented in an anti manner with respect to each other, presumably to minimize the electronic repulsion within the nitrogen lone pair. This conformation is similar to that found in the (2-hydroxyphenyl)bis(pyrazolyl)methane[10] and 1,1′-[2-(1,3-cyclopentadien-2-yl)-2-phenylethylidene]bis(3,5-dimethylpyrazole)[5] derivatives.

Having prepared these new chiral heteroscorpionate ligands in the form of the lithium or alcohol compounds as racemic mixtures, we proceeded to attempt their separation to obtain an enantiopure ligand. It is known that the separation of diastereoisomers is possible.[11] Reaction of the racemic alcohol ligand **3** with (*R*)-(−)-acetylmandelic acid chloride[12] and pyridine in dichloromethane gave the (*R*,*R* + *S*,*R*) ester (**5**) as a diastereoisomeric mixture in a 3:1 molar ratio and in 60% yield after the appropriate workup[13] (see Scheme 2). We propose that one of the enantiomers reacts kinetically faster than the other with the enantiopure reagent. Two sets of ^1H NMR signals were observed for this mixture in a 3:1 ratio, an observation that is consistent with the presence of two diastereoisomers (see Figure 3). The major diastereoisomer was obtained with a good diastereomeric excess (98% de) by solid−liquid chromatography and crystallization from *n*-hexane (see Figure 3). When the aforementioned esterification reaction was carried out with Et_3N as the base, racemization of (*R*)-(−)-acetylmandelic acid chloride was observed[13] and four stereoisomers were obtained: (*R*,*R* + *S*,*S*) and (*S*,*R* + *R*,*S*). Crystals suitable for X-ray diffraction of the (*R*,*R* + S,*S*) ester (**5**) were obtained after separation by chromatography and crystallization from *n*-hexane. The ORTEP diagram for compound **5** is shown in Figure 4. Significant bond distances and bond angles are listed in Table 1. The unit cell contains one diastereoisomer in enantiomeric pair (*R*,*R*/*S*,*S*). Saponification of the major diastereoisomer (*R*,*R*) (98% de; synthesis performed in pyridine) with potassium hydroxide in methanol gave the enantiopure alcohol ligand **3** in 70% yield (see Scheme 2).[11]

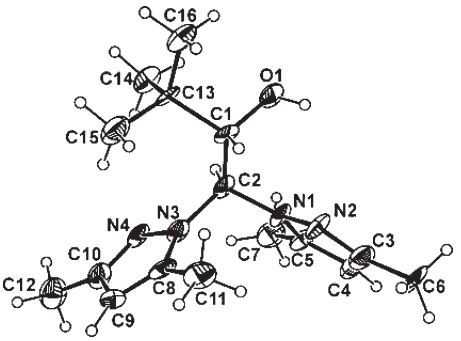

Figure 1. ORTEP view of the *S* enantiomer of **3**. Ellipsoids are at the 30% probability level.

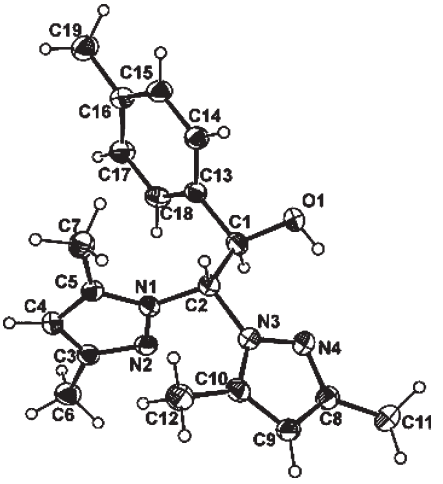

Figure 2. ORTEP view of the *R* enantiomer of **4**. Ellipsoids are at the 30% probability level.

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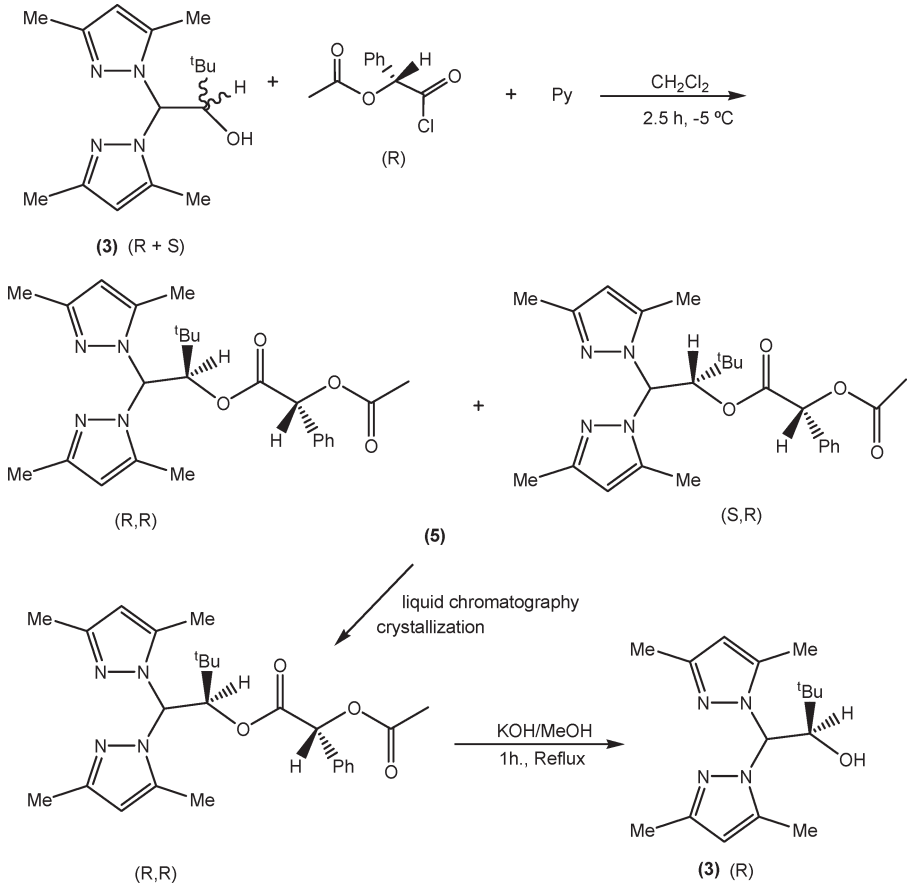
Table 1. Selected Geometrical Parameters from the X-ray Studies of Compounds **3**−**6**

3		**4**		**5**		**6**	
			Bond Lengths (Å)				
C1−O1	1.405(6)	O1−C1	1.429(3)	O1−C17	1.349(4)	N1−C11	1.457(8)
N1−N2	1.373(7)	N1−N2	1.362(3)	O1−C12	1.459(3)	N3−C11	1.468(8)
N1−C2	1.428(8)	N1−C2	1.448(3)	O2−C17	1.202(4)	O1−C12	1.460(8)
N1−C5	1.351(8)	N1−C5	1.359(3)	O3−C19	1.342(5)	C11−C12	1.555(8)
N2−C3	1.298(8)	N2−C3	1.323(3)	O3−C18	1.439(4)	C12−C13	1.49(1)
N3−N4	1.369(7)	N3−N4	1.365(3)	O4−C19	1.224(5)	N5−C32	1.469(8)
N3−C2	1.442(7)	N3−C2	1.459(3)	N1−C1	1.456(4)	N7−C32	1.470(8)
N3−C8	1.357(8)	N3−C10	1.358(3)	N3−C1	1.469(4)	O2−C33	1.434(8)
N4−C10	1.315(7)	N4−C8	1.334(3)	C1−C12	1.546(4)	C32−C33	1.553(8)
C2−C1	1.508(8)	C1−C2	1.533(3)			C33−C34	1.52(1)
C1−C13	1.534(9)	C1−C13	1.505(3)				
			Bond Angles (deg)				
C5−N1−N2	110.5(5)	C5−N1−N2	112.8(2)	C17−O1−C12	118.8(2)	N1−C11−N3	110.0(6)
C5−N1−C2	129.2(7)	C5−N1−C2	128.0(2)	C19−O3−C18	116.9(3)	N1−C11−C12	111.2(6)
N2−N1−C2	119.8(6)	N2−N1−C2	119.2(2)	N1−C1−N3	111.0(2)	N3−C11−C12	110.9(6)
C3−N2−N1	104.4(5)	C3−N2−N1	104.3(2)	N1−C1−C12	116.4(2)	O1−C12−C13	105.9(7)
C8−N3−N4	110.1(5)	C10−N3−N4	112.1(2)	N3−C1−C12	110.3(2)	O1−C12−C11	104.9(6)
C8−N3−C2	133.6(6)	C10−N3−C2	127.8(2)			C13−C12−C11	110.5(6)
N4−N3−C2	116.2(5)	N4−N3−C2	120.0(2)			C18−C13−C14	117.8(8)
C10−N4−N3	105.8(5)	C8−N4−N3	104.7(2)			C18−C13−C12	119(1)
O1−C1−C2	106.0(5)	O1−C1−C2	109.3(2)			C14−C13−C12	122.6(9)
O1−C1−C13	107.1(5)	O1−C1−C13	109.2(2)			N5−C32−N7	110.9(6)
C2−C1−C13	115.5(5)	C13−C1−C2	110.6(2)			N5−C32−C33	109.7(6)
N1−C2−N3	110.0(5)	N1−C2−N3	109.8(2)			N7−C32−C33	113.4(6)
N1−C2−C1	112.4(5)	N1−C2−C1	111.1(2)			O2−C33−C34	106.3(7)
N3−C2−C1	116.7(5)	N3−C2−C1	111.1(2)			O2−C33−C32	106.6(6)
						C34−C33−C32	110.0(6)
						C35−C34−C39	120.2(8)
						C35−C34−C33	119(1)
						C39−C34−C33	120.7(8)

Scheme 2. Process for Separation of the Racemic Mixture of **3**



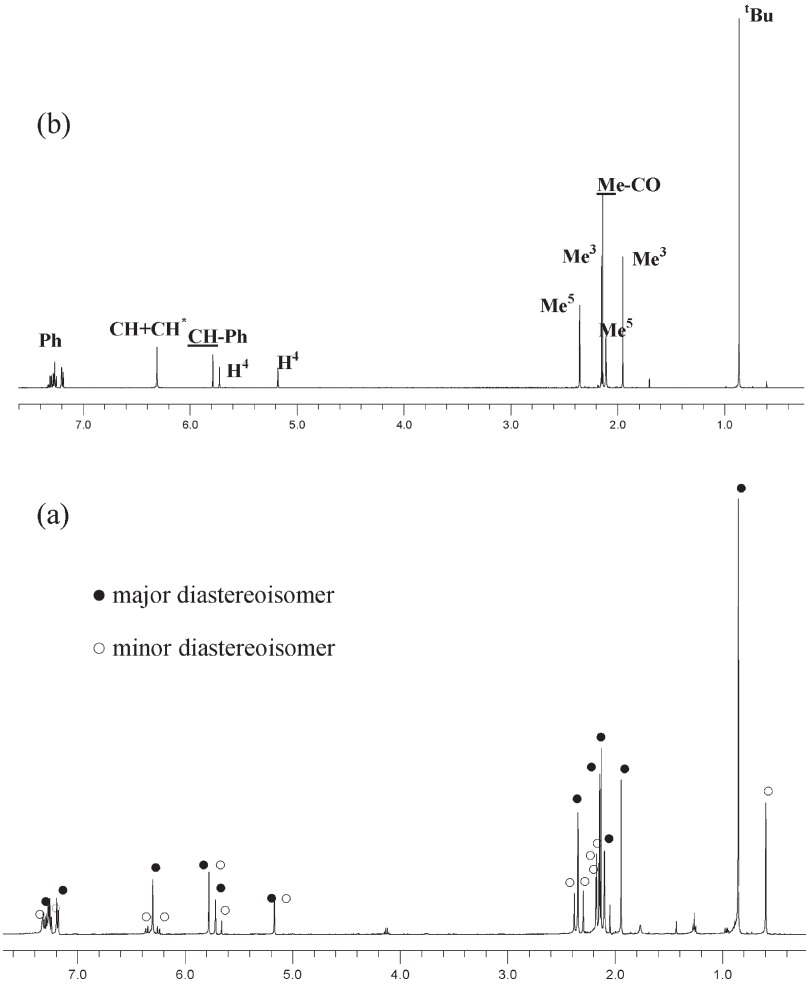


Figure 3. 500 MHz ^{1}H NMR spectra of compound **5** in $CDCl_3$ at 297 K: (a) mixture (3:1) of two diastereoisomers (*R*,*R* + *S*,*R*); (b) after separation, diastereoisomer (*R*,*R*) of compound **5**.

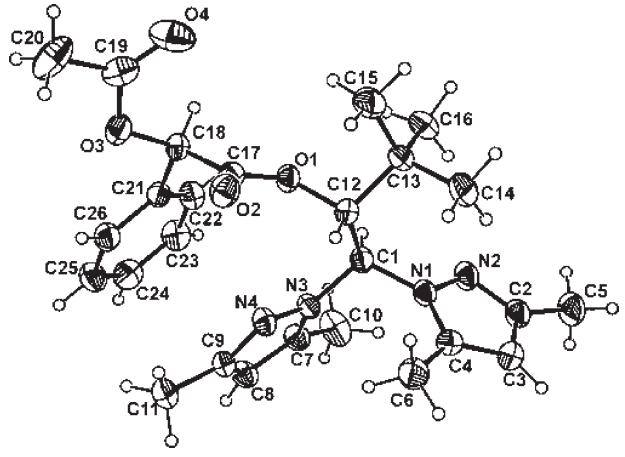


Figure 4. ORTEP view of the (*R*,*R*) diastereoisomer of compound **5**. Ellipsoids are at the 30% probability level.

The presence in solution of only one enantiomer was confirmed by the addition of a chiral shift reagent, namely, (*R*)-(−)-(9-anthryl)-2,2,2-trifluoroethanol. The addition of this shift reagent did not modify the ^{1}H NMR spectrum of this compound. In addition, the specific rotation of this compound was examined by optical polarimetry (see the Experimental Section).

The synthesis described above was used to prepare an enantiopure NNO alcohol−scorpionate ligand, and this process involved three synthetic steps: (i) 1,2-addition of organometallics to aldehydes, (ii) esterification and separation of diastereoisomers, and (iii) saponification. The main question, at this point of our research, was to ascertain whether we could obtain an enantiopure ligand through this process in one step. This idea led us to focus our attention on (1*R*)-(−)-myrtenal as a possible chiral substrate to control the stereochemistry of a newly created asymmetric center. A cold (−10 °C) THF solution of lithium bis(3,5-dimethylpyrazol-1-yl)methide, prepared in situ from Bu^{n}Li and bis(3,5-dimethylpyrazol-1-yl)methane at −70 °C, was added dropwise to a THF solution containing 1 equiv of the commercially available (1*R*)-(−)-myrtenal. After the appropriate workup, the enantiopure heteroscorpionate compound (*R*,*R*)-bpzmmH {**6**; *R*,*R*-bpzmmH = (1*R*)-1-[(1*R*)-6,6-dimethylbicyclo[3.1.1]-2-hepten-2-yl]-2,2-bis(3,5-dimethylpyrazol-1-yl)ethanol} was obtained as a white solid in good yield (83%) and with an excellent diastereomeric excess (>99% de) (Scheme 3). This procedure constitutes an efficient and highly diastereoselective method to prepare enantiopure scorpionate ligands in a one-pot process. Initial evidence for the stereochemical route was obtained from the X-ray molecular structure of **6** (Figure 5), which shows the *R* configuration for the newly formed chiral center (see below). This finding indicates that the

diastereofacial attack of the nucleophile had proceeded through the *Si* face of the carbonyl group in an *S*-trans conformation. The steric effects from the methyl groups of the bicycle moiety are probably the main driving force for the observed diastereoselectivity in the process (Scheme 3). This diastereoselectivity was assessed by considering the ^{1}H NMR spectrum and integrating the CH^a or Me signals of the bicycle in the crude reaction mixture because the chemical shifts of these protons appear systematically at higher field for the *S* epimer. A diastereomeric ratio denoted as >99:1 signifies that only the major diastereoisomer was detected. The ^{1}H NMR spectrum of **6** exhibits two singlets for each of the H^4, Me^3, and Me^5 pyrazole protons, indicating that the two pyrazole rings are inequivalent. Furthermore, the ^{1}H NMR spectrum shows the signals for the bicyclic moiety bound at the methylene bridge and also those for the OH group. As mentioned above, the absolute configuration of **6** was verified by single-crystal X-ray diffraction analysis (Figure 5) to have the *R* configuration at C^a (C12 and C33). A symmetry expansion of the asymmetric unit reveals that each molecule is intermolecularly hydrogen-bonded to one adjacent molecule in the crystal lattice through the alcohol O−H (O1 or O2) groups of one molecule and the N6 or N2 pyrazoles of the other, respectively. This arrangement gives rise to dimeric species through hydrogen bonding [O1···N6 and O2···N2 separation: 2.896(9) and 2.883(7) Å]. The methyl groups of the bicyclic system within each molecule are oriented approximately perpendicular to the middle plane of this bicyclic moiety and point outward to the *cis*-pyrazole ring, probably to minimize steric interactions between these two units.

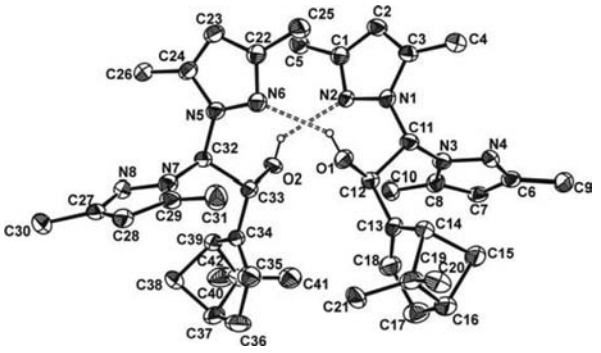
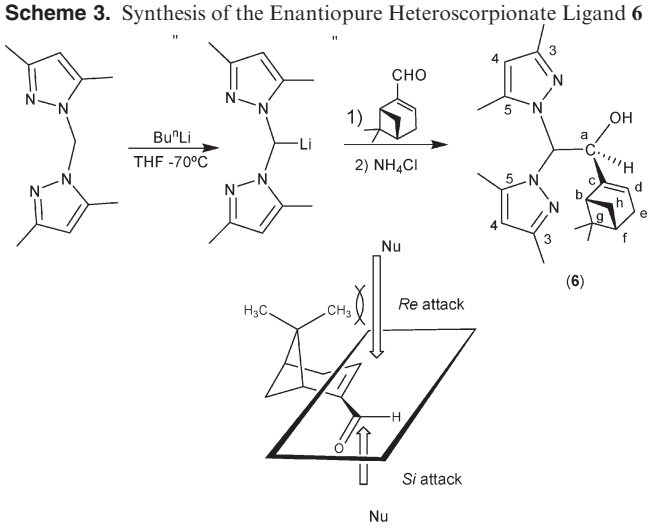


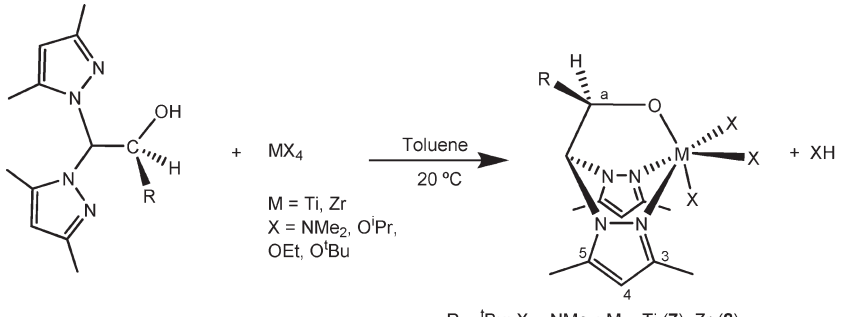
Figure 5. ORTEP view of **6**. Ellipsoids are at the 30% probability level, and hydrogen atoms have been omitted for clarity.

Scheme 3. Synthesis of the Enantiopure Heteroscorpionate Ligand **6**



Group 4 Complexes. Having prepared these new chiral and enantiopure heteroscorpionate ligands in the form of the alcohol or lithium compounds, we explored their potential utility as tridentate ligands in the preparation of chiral group 4 metal complexes. The alcohol compounds **3**, **4** (racemic mixture), and **6** (enantiopure) were reacted at room temperature with [MX$_4$] (M = Ti, Zr; X = NMe$_2$, O^{i}Pr, OEt, O^{t}Bu) in a 1:1 molar ratio in toluene to give, after the appropriate workup, the complexes [MX$_3$(κ^3-NNO)] (**7**−**18**), which were isolated as white, orange, or yellow solids in good yield (ca. 80%) (Scheme 4). The ^{1}H NMR spectra of these complexes show two singlets for each of the H^4, Me^3, and Me^5 pyrazole protons, one singlet for each of the methine groups (CH bridge of pyrazole rings and CH^a), and signals corresponding to the R moieties of the scorpionate ligands and the NMe$_2$ or OR ligands. The ^{1}H NOESY-1D NMR experiments permitted the unequivocal assignment of all ^{1}H NMR resonances. In addition, the presence in a solution of only one

Scheme 4. Synthesis of the Complexes **7**−**18**



R = ^{t}Bu (**3**)
R = *p*-MeC$_6$H$_4$ (**4**)
R = (Myr) (**6**)

R = ^{t}Bu; X = NMe$_2$; M = Ti (**7**), Zr (**8**)
R = *p*-MeC$_6$H$_4$; X = NMe$_2$; M = Ti (**9**), Zr (**10**)
R = Myr; X = NMe$_2$; M = Ti (**11**)
R = ^{t}Bu; M =Ti; X = OEt (**12**), O^{i}Pr (**13**), O^{t}Bu (**14**)
R = *p*-MeC$_6$H$_4$; M = Ti; X = O^{i}Pr (**15**)
R = Myr; M = Ti; X = OEt (**16**), O^{i}Pr (**17**)
R = Myr; M = Zr; X = O^{i}Pr (**18**)

enantiomer for complexes **11** and **16**−**18** was confirmed by the addition of a chiral shift reagent because this addition did not modify the ^{1}H NMR spectra of these compounds. However, in the rest of the complexes, which are racemic mixtures, the addition of the shift reagent gave rise to the appearance in the ^{1}H NMR spectra of two signals for each proton, resulting from the two diastereoisomers of the two corresponding enantiomers. In addition, the specific rotations of **11** and **16**−**18** were measured by polarimetry (see the Experimental Section). These results are consistent with an octahedral structure resulting from the κ^3-NNO coordination of the ligand to the metal center (Scheme 4). This disposition geometry in solution was also suggested by the solid state by X-ray structural analysis of complexes **7** and **12**·THF. The molecular views are shown in Figures 6 and 7. Selected bond parameters are listed in Table 2. The structures consist of a heteroscorpionate ligand bonded to the titanium atom through the two nitrogen atoms and the oxygen atom of the alkoxide group in a κ^3-NNO coordination mode. In addition, the titanium center is coordinated to three amide or alkoxide ligands, respectively. These centers have a distorted octahedral environment

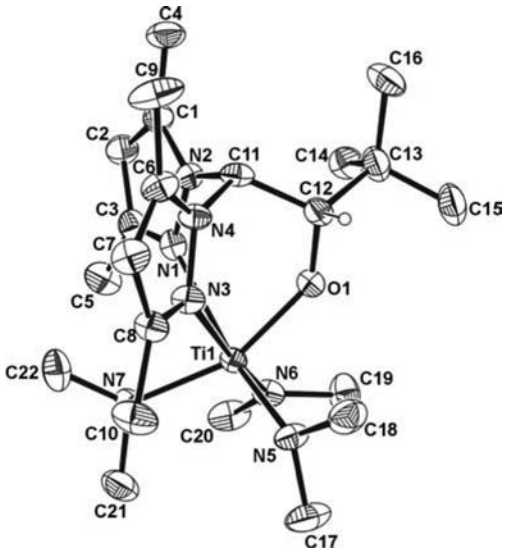


Figure 6. ORTEP view of the *S* enantiomer of complex **7**. Ellipsoids are at the 30% probability level, and hydrogen atoms have been omitted for clarity.

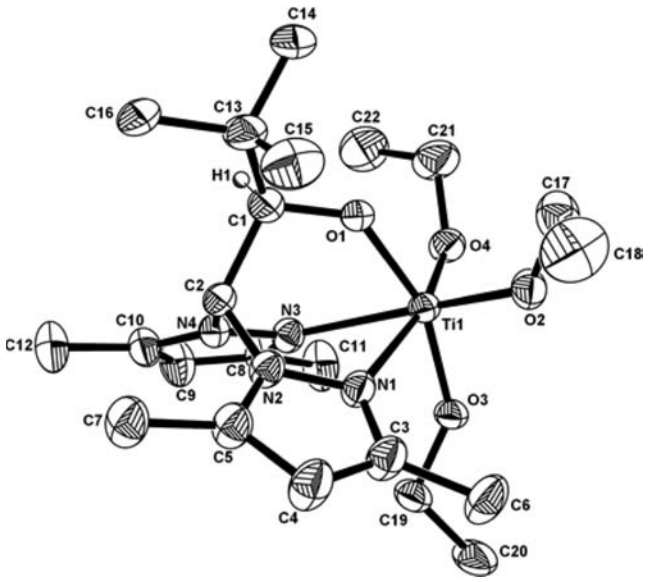


Figure 7. ORTEP view of the *R* enantiomer of complex **12**. Ellipsoids are at the 30% probability level, and hydrogen atoms have been omitted for clarity.

Table 2. Selected Geometrical Parameters from the X-ray Studies on Complexes **7**, **12**·THF, and **24**

7		**12**·THF		**24**	
		Bond Lengths (Å)			
Ti1−O1	1.908(5)	Ti1−O4	1.834(3)	Ti1−O1	1.801(4)
Ti1−N5	1.915(6)	Ti1−O3	1.843(3)	Ti1−N1	2.206(6)
Ti1−N6	1.931(5)	Ti1−O2	1.844(3)	Ti1−N3	2.210(5)
Ti1−N7	1.967(6)	Ti1−O1	1.898(3)	Ti1−Cl2	2.255(2)
Ti1−N3	2.346(5)	Ti1−N1	2.294(3)	Ti1−Cl1	2.289(2)
Ti1−N1	2.424(6)	Ti1−N3	2.311(3)	Ti1−Cl3	2.323(2)
N2−C11	1.434(8)	O1−C1	1.389(5)	O1−C12	1.412(7)
N4−C11	1.455(8)	O2−C17	1.424(6)	N2−C11	1.455(8)
N7−C21	1.48(1)	O3−C19	1.413(5)	N4−C11	1.441(8)
O1−C12	1.343(8)	O4−C21	1.418(6)	C11−C12	1.523(8)
C11−C12	1.542(9)	C1−C13	1.461(6)	C12−C13	1.515(8)
C12−C13	1.54(1)	C1−C2	1.548(6)		
		Angles (deg)			
O1−Ti1−N7	157.8(2)	O3−Ti1−O1	159.5(1)	N1−Ti1−Cl2	171.9(2)
N5−Ti1−N7	103.9(3)	O4−Ti1−N1	167.1(1)	N3−Ti1−Cl1	170.5(1)
N6−Ti1−N3	173.1(2)	O2−Ti1−N3	167.3(1)	O1−Ti1−Cl3	164.0(2)
N5−Ti1−N1	163.1(2)	C1−O1−Ti1	135.0(2)	C12−O1−Ti1	136.5(4)
C12−O1−Ti1	137.8(4)	C17−O2−Ti1	131.6(3)	N4−C11−N2	109.1(5)
N2−C11−N4	108.8(6)	C19−O3−Ti1	138.4(2)	N4−C11−C12	112.6(5)
N2−C11−C12	113.2(6)	C21−O4−Ti1	130.3(3)	N2−C11−C12	109.2(5)
N4−C11−C12	110.0(5)	O1−C1−C13	115.5(4)	O1−C12−C13	111.7(5)
O1−C12−C13	111.1(7)	O1−C1−C2	109.7(3)	O1−C12−C11	107.9(5)
O1−C12−C11	111.0(6)	C13−C1−C2	119.5(4)	C13−C12−C11	114.1(5)
C13−C12−C11	117.6(6)	N4−C2−N2	109.6(3)		
		N4−C2−C1	108.2(3)		
		N2−C2−C1	114.4(4)		

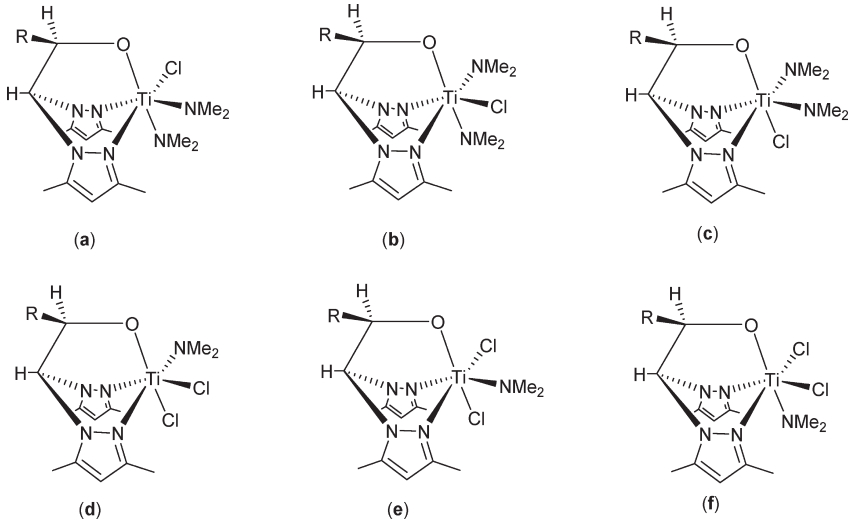
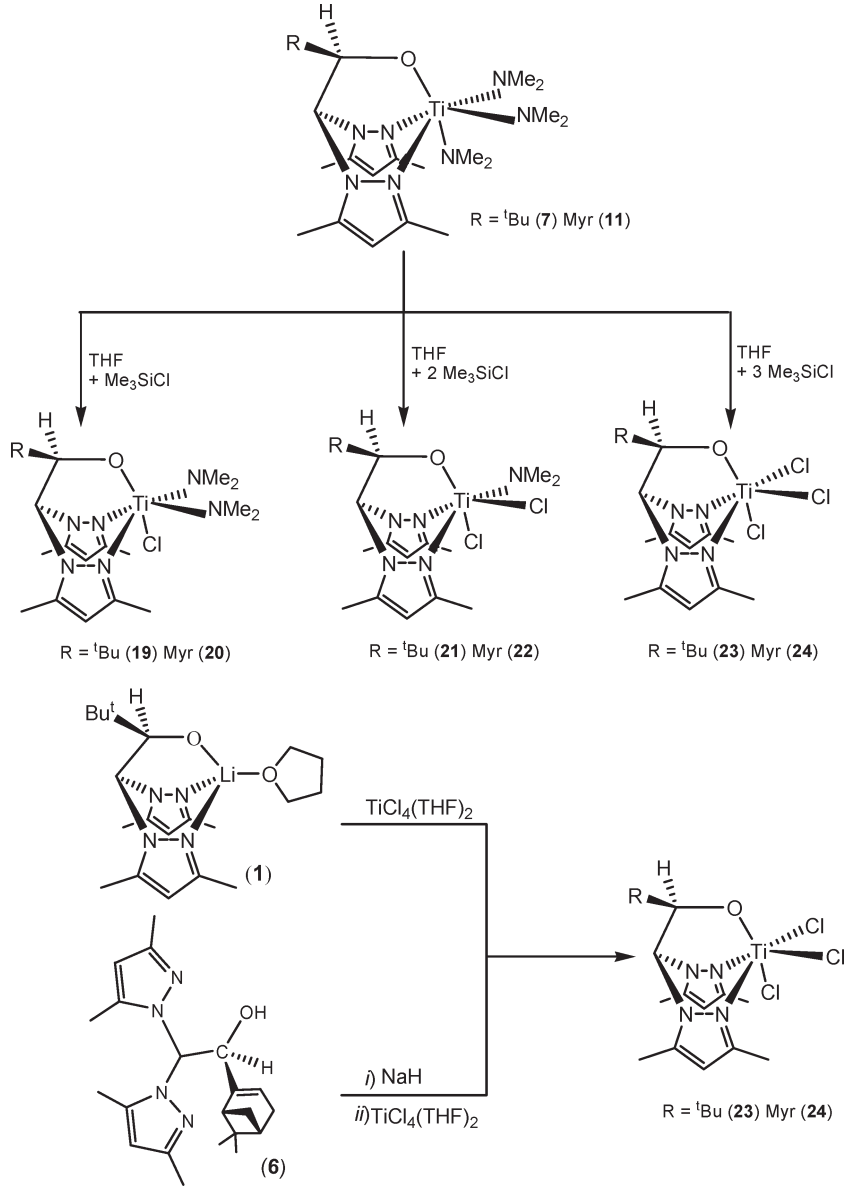


Figure 8. Proposed structures for the three possible diastereoisomers of complexes **19**−**22**.

Scheme 5. Diastereoselective Amide−Halide Exchange Process: Synthesis of Complexes **19**−**24**



with a major distortion in the O1−Ti1−N7 and N3−Ti1−O2 angles, which have values of 157.8(2)° and 167.3 (1)°, respectively. In complex **7**, the elongated Ti1−N1 and Ti1−N3 bond distances of 2.424(6) and 2.346(5) Å, respectively, as compared to similar heteroscorpionate complexes,[15] indicate that the amide ligands exert a trans influence.[16] However, in complex **12**·THF, the Ti1−N1, Ti1−N3, and Ti1−O1 bond distances of 2.294(3), 2.311(3), and 1.898(3) Å, respectively, are consistent with those in other similar complexes.[1,15] The X-ray diffraction studies confirm the presence in the solid state of two enantiomers for each complex.

Once it had been corroborated that these alcohol compounds were excellent reagents for the introduction of scorpionte ligands into group 4 metal complexes, and in view of the close proximity of the stereogenic carbon C[a] to the metal (an arrangement that is able to create an effective chiral pocket around the metal center), we thought it opportune to study the chiral induction from the scorpionate ligand to the metal center in the ligand exchange process in the coordination sphere. The amide−halide exchange reaction is well documented in group 4 metal amide complexes.[4b,15b,17] Thus, the reaction of Me_3SiCl with [Ti(NMe$_2$)$_3$(bpzb)] (**7**) or [Ti(NMe$_2$)$_3$(*R*,*R*-bpzmm)] (**11**) in different molar ratios and under different experimental conditions (see the Experimental Section) led to the preparation of the halide−amide-containing complexes [TiCl(NMe$_2$)$_2$(κ^3-NNO)] (**19** and **20**) and [TiCl$_2$(NMe$_2$)(κ^3-NNO)] (**21** and **22**) and the halide complexes [TiCl$_3$(κ^3-NNO)] (**23** and **24**). Complexes **23** and **24** can also be obtained by reaction of the lithium compound **1** with $TiCl_4(THF)_2$ and deprotonation of the alcohol group of **6** with NaH, followed by reaction with $TiCl_4(THF)_2$, respectively (Scheme 5). The ^{1}H and ^{13}C{^{1}H} NMR spectra of **19**−**22** exhibit two distinct sets of pyrazole resonances. The ^{1}H NMR spectra contain two singlets for the NMe_2 moieties in complexes **19** and **20** and single broad signals for the NMe_2 moieties in complexes **21** and **22**. These results are consistent with the presence of only one diastereoisomer and also with the proposed octahedral arrangement depicted in Scheme 5. Three isomers are possible for these complexes: two with the chloride (**19** and **20**) or amide (**21** and **22**) ligand trans to the nitrogen atoms of the pyrazolyl rings (parts a and b or parts d and e of Figure 8) and another with the chloride (**19** and **20**) or amide (**21** and **22**) ligand trans to the oxygen of the alkoxide (Figure 8c−f). In complexes **19** and **20**, the absence of a response in the ^{1}H NOESY-1D NMR experiment from both sets of Me^3 protons of the pyrazolyl rings on irradiating the methyl groups of each NMe_2 group suggests that the isomers in which the chloride ligand is trans to the oxygen atom (isomers c) had been isolated. In complexes **21** and **22**, however, the response in the ^{1}H NOESY-1D NMR experiment from the proton of the chiral carbon on irradiating the methyl groups of each NMe_2 group suggests that isomers d had been isolated. The configurations of **21** and **22** are consistent with chiral induction from these scorpionate ligands to the metal center in the amide−halide ligand exchange process in the coordination sphere. However, the configuration of monochlorinated complexes (**19** and **20**) could result from the difference of alkoxide versus pyrazole trans to the substituted ligand.[15b] Crystals of **24** were grown from a dichloromethane solution. The molecular structure determined by X-ray diffraction (Figure 9) is in good agreement with the solution structure proposed on the basis of NMR experiments. The titanium has a distorted octahedral geometry in which the heteroscorpionate ligand is coordinated by the two nitrogen atoms of the pyrazole rings and the oxygen atom of the alkoxide group. The other three sites of the octahedron are occupied by three chlorine atoms. The scorpionate ligand maintains the *R* configuration for the C[a] (C12) atom.

Finally, given the interest of the pharmaceutical and chemical industries in the development of chiral intermediates to generate enantiomerically pure products[18]

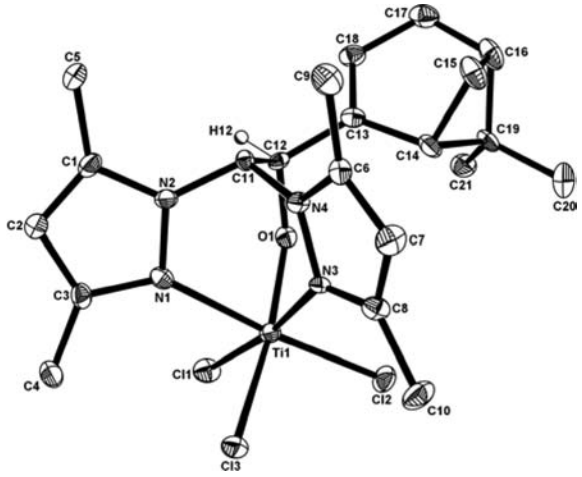


Figure 9. ORTEP view of complex **24**. Ellipsoids are at the 30% probability level, and hydrogen atoms have been omitted for clarity.

Table 3. ee Values and Yields Obtained for the Asymmetric Epoxidation of Cinnamyl Alcohol with Chiral Titanium Complexes **15** and **17**[a]

	catalyst−substrate−oxidant ratio			
	1:2:4		1:25:50	
catalyst	ee (%)[b]	yield (%)[b]	ee (%)[b]	yield (%)[b]
15		30		44
17	62	10	60	12

[a] Epoxidation conditions: Results are the averages of two different experiments with 0.7 mmol of catalyst and 18 h reaction time. [b] Determined by HPLC analysis relative to standard solutions in ethanol.

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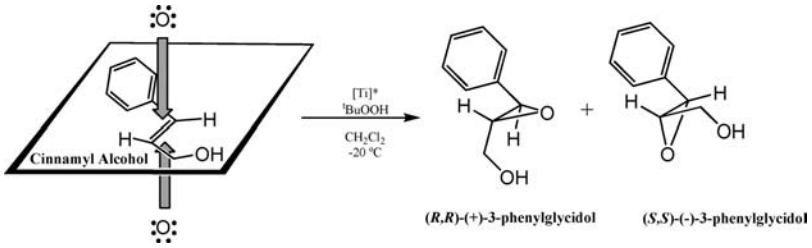
Scheme 6. Asymmetric Epoxidation of Cinnamyl Alcohol with Chiral Titanium Complexes **15** and **17** as Catalysts



and on the basis of the activity previously shown from alkoxotitanium complexes supported by chiral ligands in our group,[18c] we decided to evaluate preliminarily the influence of the chiral center of the new heteroscorpionate complexes on the enantioselectivity of the asymmetric epoxidation of allylic alcohols because this matter is a subject of current intensive research in organic synthesis.[19] The titanium complexes $[Ti(O^iPr)_3(bpzte)]$ (**15**) (racemic mixture) and $[Ti(O^iPr)_3(R,R\text{-bpzmm})]$ (**17**) (enantiomerically pure) were assessed in the asymmetric epoxidation of allylic alcohols; the preliminary results are collected in Table 3. (*E*)-3-Phenyl-2-propenol (cinnamyl alcohol) was chosen as a convenient substrate in order to study the enantioselectivity of this reaction (Scheme 6). Cinnamyl alcohol was epoxidized at −20 °C in CH_2Cl_2 in the presence of molecular sieves using experimental conditions similar to those of Sharpless' method,[20] with the exception of the reaction time, which was increased to 18 h. Generally, the substrate concentration used in the asymmetric epoxidation is a determining parameter because competing side reactions may increase with the reagent concentration. As a result, we decided to explore the asymmetric epoxidation under both catalytic and stoichiometric conditions (catalyst−substrate ratio 1:25 and 1:2, respectively). As expected, catalytic conditions (Table 3) reduced competing side reactions and led to higher reaction yields, as was clearly evidenced for complex **15** (30−44%). Interestingly, compound **17** achieved moderate and similar enantiomeric excess (ee) values under both stoichiometric and catalytic conditions (62−60%, respectively), although low yields were observed in both cases. The enantiopure complex **17** exerts a significant level of asymmetric induction in the enantioselective control of oxygen transfer (Scheme 6), in comparison with alkoxotitanium derivatives supported by chiral ligands,[18c] but lower in comparison with Sharpless' catalyst.[20] In all cases, cinnamyl alcohol led to the (2*S*,3*S*)-epoxide as the main enantiomer. Similar behavior has previously been observed in the asymmetric epoxidation of cinnamyl alcohol with optically active titanium complexes based on natural chiral sugar ligands and titanium alkoxo complexes with N,O- and O,O-chelating ligands.[18c,21] To the best of our knowledge, no examples of epoxidation processes have been previously described by using heteroscorpionate titanium complexes.

Conclusions

In conclusion, we present here our initial results in the search for enantiopure NNO-donor scorpionate ligands. In this respect, an enantiopure NNO alcohol−scorpionate ligand was prepared in three synthetic steps: (i) 1,2-addition of organometallics to aldehydes, (ii) esterification and separation of diastereoisomers, and (iii) saponification. We subsequently obtained an enantiopure scorpionate ligand with an excellent diastereomeric excess (>99% de) in a one-pot process that involved the use of the aldehyde (1*R*)-(−)-myrtenal as a chiral substrate to control the stereochemistry of a newly created asymmetric center. In the second part of this study, we verified the potential utility of these ligands as valuable scaffolds in organometallic/coordination chemistry through the preparation of new group 4 metal complexes in which the ligands behave as tridentate systems with a κ^3-NNO coordination mode. In addition, the close proximity of the stereogenic carbon to the metal, an arrangement that is able to create an effective chiral pocket around the metal center, enabled us to corroborate chiral induction from these scorpionate ligands to the metal center in the amide−halide ligand exchange process in the coordination sphere. Finally, we evaluated the influence of the chiral center of the new heteroscorpionate titanium complexes on the enantioselectivity of the asymmetric epoxidation of allylic alcohols and confirmed that the enantiopure complex exerts a significant level of asymmetric induction in the enantioselective control of oxygen transfer.

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. IR spectra were obtained in the region 4000−200 cm^{-1} using a Perkin-Elmer 883 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Varian Inova FT-500 spectrometer and referenced to the residual deuterated solvent. The NOESY-1D NMR spectra were recorded with the following acquisition parameters: irradiation time 2 s and number of scans 256, using standard VARIAN-FT software. 2D NMR spectra were acquired using standard VARIAN-FT software and processed using an IPC-Sun computer. Optical rotations were determined on a Jasco P-2000 polarimeter at the sodium D line using a quartz cell of 1.00-dm path length. The ee and yield values of

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the epoxy alcohols obtained were determined by HPLC analyses on a Varian ProStar chromatographic system equipped with a DAD 335 ProStar UV−vis detector and a Chiralpak AD-H column (250 × 4.6 mm, 10 μm size particle).[22] For HPLC analyses, the yellow oil isolated in the asymmetric epoxidation residue was reconstituted in 50 mL of ethanol, diluted, and filtered through a 0.45-μm-pore-size nylon filter membrane. Chromatographic separations were performed with a mobile phase consisting of a mixture of 85:15 (v/v) *n*-hexane−ethanol at a flow rate of 1.2 mL/min, at room temperature, and the detection wavelength was set at 254 nm.

The precursor compounds of titanium or zirconium, trimethylacetaldehyde, *p*-tolualdehyde, (1*R*)-(−)-myrtenal, (*R*)-(−)-(α)-acetylmandelic acid, *tert*-butyl hydroperoxide (TBHP; 5.0−6.0 M solution in nonane), and cinnamyl alcohol were purchased from Aldrich. The compound bdmpzm [bdmpzm = bis(3,5-dimethylpyrazol-1-yl)methane][9] was prepared as reported previously. TBHP was stored under an argon atmosphere in a Schlenk ampule with powdered 4 Å molecular sieves prior to use. Cinnamyl alcohol was distilled under vacuum and dissolved in CH_2Cl_2 (4.27 M).

Synthesis of [Li(bpzb)(THF)] (1). In a 250-cm^3 Schlenk tube, bdmpzm (1.00 g, 4.89 mmol) was dissolved in dry THF (70 cm^3) and cooled to −70 °C. A 1.6 M solution of Bu^{n}Li (3.06 cm^3, 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 2,2-dimethylpropionaldehyde (0.42 g, 4.89 mmol), after which the solution was stirred for 5 min. The solvent was removed to give a volume of 10 cm^3, and the addition of hexane (70 cm^3) gave a white solid. This solid was crystallized from a mixture of THF−hexane. Yield: 85% (1.53 g, 4.16 mmol). Anal. Calcd for $C_{20}H_{33}LiN_4O_2$: C, 65.22; H, 8.95; N, 15.22. Found: C, 65.02; H, 8.60; N, 15.42. ^{1}H NMR (DMSO, 297 K): δ 6.15 (s, 1 H, CH), 4.46 (s, 1 H, CH^a), 5.83 (s, 1 H, H^4), 5.78 (s, 1 H, H^4), 2.27 (s, 6 H, Me^3), 2.08 (s, 6 H, Me^5), 0.74 [s, 9 H, C(CH$_3$)$_3$], 3.66 (m, 4 H, THF), 1.86 (m, 4 H, THF). ^{13}C{^{1}H} NMR (DMSO, 297 K): δ 70.1 (CH), 90.2 (CH^a), 144.6, 143.8, 130.5, 130.1 (C$^{3\text{ or }5}$), 107.2, 106.8 (C^4), 13.7, 13.5 (Me^3), 11.1 (Me^5), 25.2 [*C*(CH$_3$)$_3$], 26.3 [C(*CH*$_3$)$_3$], 68.2, 26.2 (THF). IR (Nujol mull, cm^{-1}): 1567 ν(C=N).

Synthesis of [Li(bpzte)(THF)] (2). The synthetic procedure was the same as that for complex **1**, using bdmpzm (1.00 g, 4.89 mmol), a 1.6 M solution of Bu^{n}Li (3.06 cm^3, 4.89 mmol), and *p*-tolualdehyde (0.59 g, 4.89 mmol), to give **2** as a white solid. Yield: 85% (1.67 g, 4.16 mmol). Anal. Calcd for $C_{23}H_{31}LiN_4O_2$: C, 68.66; H, 7.71; N, 13.95. Found: C, 68.38; H, 7.67; N, 13.73. ^{1}H NMR (DMSO, 297 K): δ 6.08 (s, 1 H, CH), 4.60 (s, 1 H, CH^a), 5.50 (s, 1 H, H^4), 5.45 (s, 1 H, H^4), 2.34 (s, 3 H, Me^3), 2.21 (s, 3 H, Me^3), 2.12 (s, 6 H, Me^5), 7.07−6.95 (m, 4 H, *Ph*−Me), 2.34 (s, 3 H, Ph−*Me*), 3.68 (m, 4 H, THF), 1.84 (m, 4 H, THF). ^{13}C{^{1}H} NMR (DMSO, 297 K): δ 73.4 (CH), 93.5 (CH^a), 146.1, 145.8, 138.3, 137.4 (C$^{3,3'\text{ or }5,5'}$), 105.7 (C^4), 105.4 (C$^{4'}$), 14.1, 13.6 (Me^3), 12.2, 11.9 (Me^5), 147.1−127.5 (*Ph*−Me), 22.3 (Ph−*Me*), 68.2, 26.1 (THF). IR (Nujol mull, cm^{-1}): 1563 ν(C=N).

Synthesis of (bpzbH) (3). In a 250-cm^3 Schlenk tube, bdmpzm (1.00 g, 4.89 mmol) was dissolved in dry THF (70 cm^3) and cooled to −70 °C. A 1.6 M solution of Bu^{n}Li (3.06 cm^3, 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 2,2-dimethylpropionaldehyde (0.42 g, 4.89 mmol). After 5 min, the reaction mixture was treated with saturated aqueous ammonium chloride (20 cm^3). The product was extracted with Et_2O, dried over $MgSO_4$, and filtered, and the solvent was removed to give a white solid. This solid was crystallized from *n*-hexane. Yield: 90% (1.28 g, 4.40 mmol). Anal. Calcd for $C_{16}H_{26}N_4O$: C, 66.21; H, 8.97; N, 19.31. Found: C, 66.54; H, 8.72; N, 19.02. ^{1}H NMR ($CDCl_3$, 297 K): δ 6.61 (s, 1 H, CH), 4.38 (s, 1 H, CH^a), 5.78 (s, 1 H, H^4), 5.77 (s, 1 H, H^4), 2.19 (s, 6 H, Me^3), 2.10 (s, 6 H, Me^5), 0.88 [s, 9 H, C(CH$_3$)$_3$], 5.20 (s, 1 H, OH). ^{13}C{^{1}H} NMR ($CDCl_3$, 297 K): δ 72.3 (CH), 78.9 (CH^a), 147.9, 147.6, 141.5, 140.3 (C$^{3\text{ or }5}$), 107.3, 107.1 (C^4), 13.7 (Me^3), 11.5 (Me^5), 25.9 [*C*(CH$_3$)$_3$], 26.3 [C(*CH*$_3$)$_3$]. IR (Nujol mull, cm^{-1}): 3194 ν(OH), 1554 ν(C=N).

Synthesis of (bpzteH) (4). The synthetic procedure was the same as that for complex **3**, using bdmpzm (1.00 g, 4.89 mmol), a 1.6 M solution of Bu^{n}Li (3.06 cm^3, 4.89 mmol), and *p*-tolualdehyde (0.59 g, 4.89 mmol), to give **4** as a white solid. Yield: 87% (1.38 g, 4.26 mmol). Anal. Calcd for $C_{19}H_{24}N_4O$: C, 70.37; H, 7.41; N, 17.28. Found: C, 70.09; H, 7.12; N, 17.10. ^{1}H NMR ($CDCl_3$, 297 K): δ 5.87 (s, 1 H, CH), 5.87 (s, 1 H, CH^a), 5.84 (s, 1 H, H^4), 5.62 (s, 1 H, H^4), 2.27 (s, 3 H, Me^3), 2.17 (s, 3 H, Me^3), 1.93 (s, 3 H, Me^5), 1.69 (s, 3 H, Me^5), 7.05−7.00 (m, 4 H, *Ph*−Me), 2.31 (s, 3 H, Ph−*Me*), 5.05 (s, 1 H, OH). ^{13}C{^{1}H} NMR ($CDCl_3$, 297 K): δ 74.4 (CH), 74.5 (CH^a), 140.9, 139.9, 138.0, 135.6 (C$^{3,3'\text{ or }5,5'}$), 106.9, 105.9 (C$^{4,4'}$), 13.9 (Me^3), 10.9, 10.6 (Me^5), 148.8−126.8 (*Ph*−Me), 21.4 (Ph−*Me*). IR (Nujol mull, cm^{-1}): 3190 ν(OH), 1553 ν(C=N).

Process for the Separation of the Racemic Mixture of 3. Esterification. Synthesis of (*R*,*R* + *S*,*R*) Ester (5). To a cooled (−5 °C) solution of **3** (0.50 g, 1.72 mmol) in dry pyridine (7 mL) was added a solution of (*R*)-(−)-acetylmandeloyl chloride (1.10 g, 5.17 mmol) in dichloromethane (15 mL). The mixture was stirred for 2.5 h at −5 °C under a nitrogen atmosphere, and the reaction was quenched by the addition of water. The mixture was stirred for 30 min, and the solvent was evaporated. The residue was dissolved in ethyl acetate, and the solution was washed successively with water, HCl, $NaHCO_3$, and brine. The solution was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to give the ester **5** as a mixture of diastereoisomers in a 3:1 molar ratio and in 60% yield (0.48 g, 1.03 mmol). Purification by solid−liquid chromatography silica gel 60 (0.040−0.63 mm), 230−400 mesh ASTM using a mixture of AcOEt and *n*-hexane (1:4) as the eluent and crystallization from a saturated solution of *n*-hexane at −30 °C gave the major diastereoisomer with a good diastereomeric excess (98% de). Anal. Calcd for $C_{26}H_{34}N_4O_4$: C, 66.95; H, 7.30; N, 12.02. Found: C, 67.12; H, 7.18; N, 11.94. $[\alpha]_D^{25}$ −40 (*c* 1.00, THF). Major isomer. ^{1}H NMR ($CDCl_3$, 297 K) δ 6.30 (s, 1 H, CH), 6.30 (s, 1 H, CH^a), 5.78 (s, 1 H, *CH*−Ph), 5.72 (s, 1 H, H^4), 5.17 (s, 1 H, H^4), 2.14 (s, 3 H, Me^3), 1.94 (s, 3 H, Me^3), 2.34 (s, 3 H, Me^5), 2.10 (s, 3 H, Me^5), 2.13 (s, 1 H, *Me*−CO), 0.85 [s, 9 H, C(CH$_3$)], 7.18−7.31 (m, 5 H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, 297 K): δ 71.1 (CH), 77.4 (CH^a), 74.6 (*CH*−Ph), 147.8, 147.2, 140.0, 139.3 (C$^{3,3'\text{ or }5,5'}$), 106.9, 107.7 (C^4), 13.8, 13.6 (Me^3), 12.0, 11.4 (Me^5), 20.9 (*Me*−CO), 35.9 [*C*(CH$_3$)$_3$], 26.3 [C(*CH*$_3$)$_3$], 133.5−127.8 (Ph), 170.2, 167.1 (Me−*C*=O, O−*C*=O). Minor isomer. ^{1}H NMR ($CDCl_3$, 297 K): δ_A 6.36, δ_B 6.25 (system AB, J_{AB} = 10 Hz, 2 H, CH, CH^a), 5.78 (s, 1 H, *CH*−Ph), 5.66 (s, 1 H, H^4), 5.17 (s, 1 H, H^4), 2.17 (s, 3 H, Me^3), 2.13 (s, 3 H, Me^3), 2.38 (s, 3 H, Me^5), 2.29 (s, 3 H, Me^5), 2.15 (s, 1 H, *Me*−CO), 0.60 [s, 9 H, C(CH$_3$)], 7.18−7.33 (m, 5 H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, 297 K): δ 70.8 (CH), 77.1 (CH^a), 73.4 (*CH*−Ph), 148.3, 147.9, 140.2, 140.1 (C$^{3,3'\text{ or }5,5'}$), 107.1, 107.6 (C^4), 14.4, 14.3 (Me^3), 11.8, 11.7 (Me^5), 20.0 (*Me*−CO), 35.5 [*C*(CH$_3$)$_3$], 25.9 [C(*CH*$_3$)$_3$], 140.2−128.1 (Ph), 169.5, 167.0 (Me−*C*=O, O−*C*=O).

Saponification Procedure. To a solution of the major diastereoisomer **5** (0.50 g, 1.07 mmol) in methanol (30 mL) was added KOH (0.36 g, 6.04 mmol). The mixture was heated under reflux for 1 h. The mixture was washed with water and

(22) (a) Morante-Zarcero, S.; Pérez, Y.; del Hierro, I.; Fajardo, M.; Sierra, I. *J. Chromatogr. A* **2004**, *1046*, 61–66. (b) Morante-Zarcero, S.; del Hierro, I.; Fajardo, M.; Sierra, I. *Anal. Chim. Acta* **2006**, *566*, 185–192.

extracted with Et_2O (2 × 15 mL), and the combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to give **3** as a white solid. This solid was crystallized from *n*-hexane. Yield: 70% (0.22 g, 0.75 mmol). $[\alpha]_D^{25}$: +31.2 (*c* 1.00, THF).

Synthesis of (*R*,*R*)-bpzmmH (6). bdmpzm (1.00 g, 4.89 mmol) was dissolved in dry THF (70 cm^3) in a 250-cm^3 Schlenk tube, and the solution was cooled to −70 °C. A 1.6 M solution of Bu^nLi (3.06 cm^3, 4.89 mmol) in hexane was added, and the solution was stirred for 1 h. The reaction mixture was warmed to −10 °C, and the resulting yellow solution was added dropwise to a THF solution containing 1 equiv of the commercially available (1*R*)-(−)-myrtenal (0.73 g, 4.89 mmol). A rapid color change from yellow to colorless was observed. After 5 min, the reaction mixture was treated with saturated aqueous ammonium chloride (20 cm^3). The product was extracted with *n*-hexane, dried over $MgSO_4$, filtered, and cooled to give the enantiopure heteroscorpionate ligand **6** as a white solid. The product was obtained in good yield 83% (1.44 g, 4.06 mmol) and in excellent diastereomeric excess (>99% de). $[\alpha]_D^{25}$: +20.5 (*c* 1.00, THF). Anal. Calcd for $C_{21}H_{30}N_4O$: C, 71.19; H, 8.47; N, 15.82. Found: C, 70.81; H, 8.05; N, 15.42. ^{1}H NMR ($CDCl_3$, 297 K), δ 6.13 (d, 1 H, J_{HH} = 7.8 Hz, CH), 5.81 (s, 1 H, H^4), 5.75 (s, 1 H, H^4), 5.47 (bs, 1 H, H^d), 5.26 (d, 1 H, J_{HH} = 7.8 Hz, CH^a), 4.36 (d, 1 H, J_{HH} = 4.0 Hz, OH), 2.39 (m, 2 H, H^e), 2.37 (m, 1 H, H^f), 2.22 (s, 3 H, Me^3), 2.17 (s, 3 H, Me^3), 2.16, 0.95 (d, 2 H, J_{HH} = 7.8 Hz, *geminal*-H^h), 2.06 (s, 6 H, Me^5), 2.02 (m, 1 H, H^b), 1.29 (s, 3 H, Me^g), 0.78 (s, 3 H, Me^g). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 297 K): δ 148.2, 147.7, 141.7, 139.5 ($C^{3\text{ or }5}$), 123.3 (C^d), 121.2 (C^e), 107.3, 106.8 (C^4), 75.1 (CH^a), 74.0 (CH), 41.9 (C^f), 40.9 (C^b), 38.0 (C^g), 32.0 (C^e), 31.7 (C^h), 26.4, 21.3 (Me^g), 13.8, 13.6 (Me^3), 11.3, 11.2 (Me^5). The diastereoselectivity was assessed by integration of the signals of the CH^a or Me groups of the bicycle (Me^g) in the crude reaction mixture, taking into consideration that the chemical shifts of these protons appear at δ 5.10 (d, CH^a) and 1.21, 0.68 (s, Me^g) for the minor *S* epimer. IR (Nujol mull, cm^{-1}): 3199 ν(OH), 1550 ν(C=N).

Synthesis of [Ti(NMe$_2$)$_3$(bpzb)] (7). In a 250-cm^3 Schlenk tube, $Ti(NMe_2)_4$ (0.50 g, 2.24 mmol) and **3** (0.65 g, 2.24 mmol) were suspended in toluene (80 mL). The resulting orange solution was stirred overnight at room temperature. The solvent was removed under vacuum, and the resulting solid was extracted with hexane. The solvent was removed to give a yellow solid. Yield: 80% (0.84 g, 1.79 mmol). Anal. Calcd for $C_{22}H_{43}N_7OTi$: C, 56.30; H, 9.17; N, 20.90. Found: C, 55.42; H, 9.01; N, 20.63. ^{1}H NMR ($CDCl_3$, 297 K): δ 5.95 (s, 1 H, CH), 4.08 (s, 1 H, CH^a), 5.47 (s, 1 H, H^4), 5.46 (s, 1 H, $H^{4'}$), 3.48 (s, 18 H, NMe_2), 2.19 (s, 3 H, Me^3), 2.30 (s, 3 H, $Me^{3'}$), 1.67 (s, 3 H, Me^5), 1.73 (s, 3 H, $Me^{5'}$), 0.81 [s, 9 H, $C(CH_3)_3$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 297 K): δ 65.0 (CH), 87.4 (CH^a), 150.0, 149.9, 137.2, 136.1 ($C^{3,3'\text{ or }5,5'}$), 106.4, 105.8 ($C^{4,4'}$), 13.7 (Me^3), 12.7 ($Me^{3'}$), 10.8 (Me^5), 10.6 ($Me^{5'}$), 26.2 [$C(CH_3)_3$], 26.1 [$C(CH_3)_3$], 49.0 (NMe_2). IR (Nujol mull, cm^{-1}): 1572 ν(C=N).

Synthesis of [Zr(NMe$_2$)$_3$(bpzb)] (8). The synthetic procedure was the same as that for complex **7**, using $Zr(NMe_2)_4$ (0.50 g, 1.87 mmol) and **3** (0.54 g, 1.87 mmol), to give **8** as a yellow solid. Yield: 84% (0.80 g, 1.56 mmol). Anal. Calcd for $C_{22}H_{43}N_7OZr$: C, 51.54; H, 8.39; N, 19.13. Found: C, 51.20; H, 8.03; N, 18.75. ^{1}H NMR ($CDCl_3$, 297 K): δ 5.88 (s, 1 H, CH), 3.83 (s, 1 H, CH^a), 5.45 (s, 1 H, H^4), 5.43 (s, 1 H, $H^{4'}$), 3.54 (s, 6 H, NMe_2), 3.41 (s, 6 H, NMe_2), 2.98 (s, 6 H, NMe_2), 2.31 (s, 3 H, Me^3), 2.34 (s, 3 H, $Me^{3'}$), 1.59 (s, 3 H, Me^5), 1.63 (s, 3 H, $Me^{5'}$), 0.76 [s, 9 H, $C(CH_3)_3$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 297 K): δ 65.2 (CH), 85.6 (CH^a), 151.0, 150.9, 138.1, 136.8 ($C^{3,3'\text{ or }5,5'}$), 105.9 (C^4), 106.5 ($C^{4'}$), 13.0 (Me^3), 12.4 ($Me^{3'}$), 10.6 (Me^5), 10.8 ($Me^{5'}$), 25.8 [$C(CH_3)_3$], 25.9 [$C(CH_3)_3$], 45.6, 45.7, 44.5 (NMe_2). IR (Nujol mull, cm^{-1}): 1570 ν(C=N).

Synthesis of [Ti(NMe$_2$)$_3$(bpzte)] (9). The synthetic procedure was the same as that for complex **7**, using $Ti(NMe_2)_4$ (0.50 g, 2.24 mmol) and **4** (0.72 g, 2.24 mmol), to give **9** as a yellow solid. Yield: 93% (1.04 g, 2.07 mmol). Anal. Calcd for $C_{25}H_{41}N_7OTi$: C, 59.55; H, 8.40; N, 19.63. Found: C, 59.66; H, 8.15; N, 19.49. ^{1}H NMR ($CDCl_3$, 297 K): δ 5.88 (s, 1 H, CH), 5.95 (s, 1 H, CH^a), 5.51 (s, 1 H, H^4), 5.40 (s, 1 H, H^4), 3.48 (s, 18 H, NMe_2), 2.35 (s, 3 H, Me^3), 2.22 (s, 3 H, Me^3), 1.66 (s, 3 H, Me^5), 1.44 (s, 3 H, Me^5), 7.13−6.90 (m, 4 H, *Ph*−Me), 2.04 (s, 3 H, Ph−*Me*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 297 K): δ 71.7 (CH), 81.7 (CH^a), 150.1, 149.2, 137.7, 136.6 ($C^{3,3'\text{ or }5,5'}$), 106.0 (C^4), 105.5 (C^4), 13.8 (Me^3), 12.9 (Me^3), 10.6 (Me^5), 10.2 (Me^5), 141.9−126.5 (*Ph*−Me), 21.0 (Ph−*Me*), 48.5 (NMe_2). IR (Nujol mull, cm^{-1}): 1575 ν(C=N).

Synthesis of [Zr(NMe$_2$)$_3$(bpzte)] (10). The synthetic procedure was the same as that for complex **7**, using $Zr(NMe_2)_4$ (0.50 g, 1.87 mmol) and **4** (0.61 g, 1.87 mmol), to give **10** as a yellow solid. Yield: 90% (0.92 g, 1.69 mmol). Anal. Calcd for $C_{25}H_{41}N_7OZr$: C, 54.92; H, 7.51; N, 17.94. Found: C, 55.12; H, 7.70; N, 18.14. ^{1}H NMR ($CDCl_3$, 297 K): δ 5.71 (s, 1 H, CH), 5.51 (s, 1 H, CH^a), 5.52 (s, 1 H, H^4), 5.30 (s, 1 H, $H^{4'}$), 3.61 (s, 6 H, NMe_2), 3.48 (s, 6 H, NMe_2), 3.07 (s, 6 H, NMe_2), 2.37 (s, 3 H, Me^3), 2.40 (s, 3 H, $Me^{3'}$), 1.56 (s, 3 H, Me^5), 1.16 (s, 3 H, $Me^{5'}$), 7.07−6.87 (m, 4 H, *Ph*−Me), 2.03 (s, 3 H, Ph−*Me*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 297 K): δ 70.8 (CH), 79.9 (CH^a), 151.4, 150.9, 138.1, 135.7 ($C^{3,3'\text{ or }5,5'}$), 106.2 (C^4), 105.4 ($C^{4'}$), 12.4 (Me^3), 13.1 ($Me^{3'}$), 10.6 (Me^5), 9.9 ($Me^{5'}$), 141.0−125.5 (*Ph*−Me), 21.0 (Ph−*Me*), 45.7, 45.7, 44.6 (NMe_2). IR (Nujol mull, cm^{-1}): 1572 ν(C=N).

Synthesis of [Ti(NMe$_2$)$_3$(*R*,*R*-bpzmm)] (11). The synthetic procedure was the same as that for complex **7**, using $Ti(NMe_2)_4$ (1.00 g, 2.82 mmol) and **6** (0.72 g, 2.82 mmol), to give **11** as an orange solid. Yield: 82% (1.23 g, 2.31 mmol). $[\alpha]_D^{25}$: +32.3 (*c* 1.00, CH_2Cl_2) Anal. Calcd for $C_{27}H_{47}N_7OTi$: C, 60.80; H, 8.82; N, 18.39. Found: C, 61.02; H, 8.95; N, 18.71. ^{1}H NMR ($CDCl_3$, 297 K): δ 6.14 (bs, 1 H, CH), 5.81 (s, 1 H, H^4), 5.80 (s, 1 H, H^4), 5.57 (m, 1 H, H^d), 5.12 (d, 1 H, CH^a), 3.49 (s, 6 H, NMe_2), 3.33 (s, 6 H, NMe_2), 2.60 (s, 6 H, NMe_2), 2.37 (s, 3 H, Me^3), 2.32 (s, 3 H, Me^3), 2.28 (s, 3 H, Me^5), 2.22 (s, 3 H, Me^5), 2.24 (m, 2 H, H^e), 2.14, 1.00 (m, 2 H, *geminal*-H^h), 2.00 (m, 1 H, H^f), 1.60 (m, 1 H, H^b), 1.12 (s, 3 H, Me^g), 0.79 (s, 3 H, Me^g). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 297 K): δ 151.7, 148.6, 138.6, 137.3 ($C^{3\text{ or }5}$), 151.5 (C^e), 125.5 (C^d), 107.3, 107.1 (C^4), 84.9 (CH^a), 69.1 (CH), 50.7, 49.5, 43.4 (NMe_2), 41.3 (C^f), 41.2 (C^b), 37.9 (C^g), 32.3 (C^e), 31.6 (C^h), 26.1, 21.5 (Me^g), 14.2, 14.1 (Me^3), 11.5 (Me^5). IR (Nujol mull, cm^{-1}): 1569 ν(C=N).

Synthesis of [Ti(OEt)$_3$(bpzb)] (12). In a 250-cm^3 Schlenk tube, $Ti(OEt)_4$ (0.50 mL, 1.71 mmol) was dissolved in dry toluene (50 cm^3). A solution of **3** (0.49 g, 1.71 mmol) in toluene was added, and the resulting colorless solution was stirred for 4 h at room temperature. The solvent was removed under vacuum, and the resulting solid was extracted with hexane. The solvent was removed to give a white solid. Yield: 86% (0.68 g, 1.45 mmol). Anal. Calcd for $C_{22}H_{40}N_4O_4Ti$: C, 55.94; H, 8.48; N, 11.87. Found: C, 55.90; H, 8.30; N, 11.70. ^{1}H NMR ($CDCl_3$, 297 K): δ 6.27 (s, 1 H, CH), 3.96 (s, 1 H, CH^a), 5.85 (s, 1 H, H^4), 5.89 (s, 1 H, $H^{4'}$), 2.42 (s, 3 H, Me^3), 2.50 (s, 3 H, $Me^{3'}$), 2.36 (s, 3 H, Me^5), 2.41 (s, 3 H, $Me^{5'}$), 0.75 [s, 9 H, $C(CH_3)_3$], 4.38 [m, 6 H, OCH_2CH_3], 1.18 [m, 9 H, OCH_2CH_3]. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 297 K): δ 64.7 (CH), 87.7 (CH^a), 150.3, 150.0, 137.4, 136.4 ($C^{3,3'\text{ or }5,5'}$), 106.2 (C^4), 106.7 ($C^{4'}$), 13.7 (Me^3), 13.8 ($Me^{3'}$), 11.2 (Me^5), 11.5 ($Me^{5'}$), 35.6 [$C(CH_3)_3$], 26.0 [$C(CH_3)_3$], 69.0 (OCH_2CH_3), 19.5 (OCH_2CH_3). IR (Nujol mull, cm^{-1}): 1573 ν(C=N), 682 ν(Ti−O).

Synthesis of [Ti(O^{i}Pr)$_3$(bpzb)] (13). The synthetic procedure was the same as that for complex **12**, using $Ti(O^iPr)_4$ (0.50 mL, 1.71 mmol) and **3** (0.49 g, 1.71 mmol), to give **13** as a white solid. Yield: 75% (0.65 g, 1.27 mmol). Anal. Calcd for $C_{25}H_{46}N_4O_4Ti$: C, 58.38; H, 8.95; N, 10.90. Found: C, 58.02; H, 8.75; N, 10.59. ^{1}H NMR ($CDCl_3$, 297 K): δ 6.23 (s, 1 H, CH), 4.08 (s, 1 H, CH^a), 5.80 (s, 1 H, H^4), 5.83 (s, 1 H, $H^{4'}$), 2.52 (s, 6 H,

$Me^{3,3'}$), 2.32 (s, 3 H, Me^{5}), 2.36 (s, 3 H, $Me^{5'}$), 0.77 [s, 9 H, $C(CH_3)_3$], 4.91 [m, J_{HH} = 6.3 Hz, 3 H, $OCH(CH_3)_2$], 1.17 [d, J_{HH} = 6.3 Hz, 18 H, $OCH(CH_3)_2$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 297 K): δ 64.6 (CH), 88.3 (CH^a), 150.3, 150.0, 137.4, 136.0 ($C^{3,3'\ or\ 5,5'}$), 106.1 (C^4), 106.6 ($C^{4'}$), 14.5, 14.6 ($Me^{3,3'}$), 11.2 (Me^5), 11.5 ($Me^{5'}$), 35.7 [$C(CH_3)_3$], 26.0 [$C(CH_3)_3$], 74.9 [$OCH(CH_3)_2$], 26.2 [$OCH(CH_3)_2$]. IR (Nujol mull, cm^{-1}): 1576 ν(C=N), 687 ν(Ti−O).

Synthesis of [Ti(O^{t}Bu)$_3$(bpzb)] (14). The synthetic procedure was the same as that for complex **12**, using $Ti(O^tBu)_4$ (0.50 g, 1.47 mmol) and **3** (0.43 g, 1.47 mmol), to give **14** as a white solid. Yield: 74% (0.61 g, 1.10 mmol). Anal. Calcd for $C_{28}H_{52}N_4O_4Ti$: C, 60.44; H, 9.35; N, 10.07. Found: C, 60.12; H, 9.01; N, 9.76. ^1H NMR ($CDCl_3$, 297 K): δ 6.22 (s, 1 H, CH), 3.88 (s, 1 H, CH^a), 5.77 (s, 1 H, H^4), 5.78 (s, 1 H, $H^{4'}$), 2.37 (s, 3 H, Me^3), 2.54 (s, 3 H, $Me^{3'}$), 2.20 (s, 3 H, Me^5), 2.37 (s, 3 H, $Me^{5'}$), 0.85 [s, 9 H, $C(CH_3)_3$], 1.30 [s, 27 H, $OC(CH_3)_3$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 297 K): δ 64.7 (CH), 88.1 (CH^a), 150.4, 149.8, 137.4, 136.4 ($C^{3,3'\ or\ 5,5'}$), 106.3 (C^4), 105.4 ($C^{4'}$), 14.5 (Me^3), 14.8 ($Me^{3'}$), 10.3 (Me^5), 11.3 ($Me^{5'}$), 35.2 [$C(CH_3)_3$], 25.8 [$C(CH_3)_3$], 34.1 [$OC(CH_3)_3$], 27.3 [$OC(CH_3)_3$]. IR (Nujol mull, cm^{-1}): 1573 ν(C=N), 685 ν(Ti−O).

Synthesis of [Ti(O^{i}Pr)$_3$(bpzte)] (15). The synthetic procedure was the same as that for complex **12**, using $Ti(O^iPr)_4$ (0.50 g, 1.71 mmol) and **4** (0.55 g, 1.71 mmol), to give **15** as a white solid. Yield: 78% (0.72 g, 1.32 mmol). Anal. Calcd for $C_{28}H_{44}N_4O_4Ti$: C, 61.32; H, 8.03; N, 10.22. Found: C, 61.25; H, 7.69; N, 9.87. ^1H NMR ($CDCl_3$, 297 K): δ 5.94 (s, 1 H, CH), 5.44 (s, 1 H, CH^a), 5.65 (s, 1 H, H^4), 5.89 (s, 1 H, $H^{4'}$), 2.58 (s, 3 H, Me^3), 2.59 (s, 3 H, $Me^{3'}$), 2.29 (s, 3 H, Me^5), 2.35 (s, 3 H, $Me^{5'}$), 7.01−6.95 (m, 4 H, *Ph*−Me), 1.59 (s, 3 H, Ph−*Me*), 5.01 [m, J_{HH} = 6.3 Hz, 3 H, $OCH(CH_3)_2$], 1.22 [d, J_{HH} = 6.3 Hz, 18 H, $OCH(CH_3)_2$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 297 K): δ 70.2 (CH), 82.4 (CH^a), 150.6, 150.2, 137.2, 137.1 ($C^{3,3'\ or\ 5,5'}$), 105.5 (C^4), 106.6 ($C^{4'}$), 14.2 (Me^3), 14.7, ($Me^{3'}$), 11.2 (Me^5), 11.4 ($Me^{5'}$), 140.9−126.1 (*Ph*−Me), 21.3 (Ph−*Me*), 75.3 [$OCH(CH_3)_2$], 26.2 [$OCH(CH_3)_2$]. IR (Nujol mull, cm^{-1}): 1571 ν(C=N), 685 ν(Ti−O).

Synthesis of [Ti(OEt)$_3$(*R*,*R*-bpzmm)] (16). The synthetic procedure was the same as that for complex **12**, using $Ti(OEt)_4$ (0.12 mL, 0.57 mmol) and **6** (0.20 g, 0.57 mmol), to give **16** as a white solid. Yield: 85% (0.26 g, 0.48 mmol). $[\alpha]_D^{25}$: +28.64 (*c* 1.00, CH_2Cl_2). Anal. Calcd for $C_{27}H_{44}N_4O_4Ti$: C, 60.46; H, 8.21; N, 10.45. Found: C, 60.67; H, 8.34; N, 10.76. ^1H NMR ($CDCl_3$, 297 K): δ 6.11 (s, 1 H, CH), 5.25 (s, 1 H, CH^a), 5.80 (s, 1 H, H^4), 5.73 (s, 1 H, $H^{4'}$), 2.19 (s, 3 H, Me^3), 2.15 (s, 3 H, Me $^{3'}$), 2.05 (s, 6 H, $Me^{5,5'}$), 5.46 (s, 1 H, H^d), 2.14 (m, 2 H, H^e), 2.37, 0.95 (m, 2 H, *geminal*-H^h), 2.38 (m, 1 H, H^f), 2.01 (m, 1 H, H^b), 1.27 (s, 3 H, Me^g), 0.77 (s, 3 H, Me^g), 4.40 [br s, 6 H, OCH_2CH_3], 1.30 [br s, 9 H, OCH_2CH_3]. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 297 K): δ 74.0 (CH), 75.1 (CH^a), 148.1, 147.6, 144.5, 141.6 ($C^{3,3'\ or\ 5,5'}$), 106.8 (C^4), 107.3 ($C^{4'}$), 13.7, 13.6 ($Me^{3,3'}$), 11.3, 11.2 ($Me^{5,5'}$), 123.3 (C^d), 31.9 (C^e), 38.0 (C^g), 41.9 (C^f), 40.9 (C^b), 119.8 (C^c), 31.7 (C^h), 26.3 (Me^g), 21.3 (Me^g), 69.7 [OCH_2CH_3], 18.9 [OCH_2CH_3]. IR (Nujol mull, cm^{-1}): 1569 ν(C=N), 687 ν(Ti−O).

Synthesis of [Ti(O^{i}Pr)$_3$(*R*,*R*-bpzmm)] (17). The synthetic procedure was the same as that for complex **12**, using $Ti(O^iPr)_4$ (0.50 mL, 1.71 mmol) and **6** (0.60 g, 1.71 mmol), to give **17** as a white solid. Yield: 80% (0.79 g, 1.37 mmol). $[\alpha]_D^{25}$: +21.4 (*c* 1.00, CH_2Cl_2). Anal. Calcd for $C_{30}H_{50}N_4O_4Ti$: C, 62.29; H, 8.65; N, 9.69. Found: C, 62.07; H, 8.44; N, 9.50. ^1H NMR ($CDCl_3$, 297 K): δ 5.99 (s, 1 H, CH), 4.86 (s, 1 H, CH^a), 5.86 (s, 1 H, H^4), 5.84 (s, 1 H, $H^{4'}$), 2.55 (s, 6 H, $Me^{3,3'}$), 2.37 (s, 3 H, Me^5), 2.31 (s, 3 H, $Me^{5'}$), 5.47 (s, 1 H, H^d), 2.26 (m, 2 H, H^e), 2.16, 0.90 (m, 2 H, *geminal*-H^h), 2.01 (m, 1 H, H^f), 1.72 (m, 1 H, H^b), 1.20 (s, 3 H, Me^g), 0.83 (s, 3 H, Me^g), 4.90 [m, J_{HH} = 6.3 Hz, 3 H, $OCH(CH_3)_2$], 1.20 [d, J_{HH} = 6.3 Hz, 9 H, $OCH(CH_3)_2$], 1.24 [d, J_{HH} = 6.3 Hz, 9 H, $OCH(CH_3)_2$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 297 K): δ 69.9 (CH), 83.7 (CH^a), 151.4, 149.8, 138.7, 136.6 ($C^{3,3'\ or\ 5,5'}$), 106.2 (C^4), 106.4 ($C^{4'}$), 14.7, 14.6 ($Me^{3,3'}$), 11.3 (Me^5), 11.4 ($Me^{5'}$), 119.0 (C^d), 32.2 (C^e), 38.1 (C^g), 41.9 (C^f), 40.4 (C^b), 123.2 (C^c), 31.7 (C^h), 21.3 (Me^g), 26.8 (Me^g), 74.8 [$OCH(CH_3)_2$], 25.3 [$OCH(CH_3)_2$], 26.0 [$OCH(CH_3)_2$]. IR (Nujol mull, cm^{-1}): 1573 ν(C=N), 682 ν(Ti−O).

Synthesis of [Zr(O^{i}Pr)$_3$(*R*,*R*-bpzmm)] (18). The synthetic procedure was the same as that for complex **12**, using $Zr(O^iPr)_4$ (0.22 g, 0.56 mmol) and **6** (0.20 g, 0.56 mmol), to give **18** as a white solid. Yield: 70% (0.24 g, 0.39 mmol). $[\alpha]_D^{25}$: +18.67 (*c* 1.00, CH_2Cl_2). Anal. Calcd for $C_{30}H_{50}N_4O_4Zr$: C, 57.95; H, 8.05; N, 9.01. Found: C, 58.07; H, 8.44; N, 9.20. ^1H NMR ($CDCl_3$, 297 K): δ 5.96 (s, 1 H, CH), 4.75 (s, 1 H, CH^a), 5.86 (s, 1 H, H^4), 5.83 (s, 1 H, $H^{4'}$), 2.51 (s, 3 H, Me^3), 2.31 (s, 3 H, $Me^{3'}$), 2.37 (s, 3 H, Me^5), 2.28 (s, 3 H, $Me^{5'}$), 5.49 (s, 1 H, H^d), 2.20 (m, 2 H, H^e), 2.08, 0.76 (m, 2 H, *geminal*-H^h), 1.96 (m, 1 H, H^f), 1.87 (m, 1 H, H^b), 1.19 (s, 3 H, Me^g), 0.73 (s, 3 H, Me^g), 4.43 [m, J_{HH} = 6.3 Hz, 3 H, $OCH(CH_3)_2$], 1.21 [d, J_{HH} = 6.86 Hz, 9 H, $OCH(CH_3)_2$], 1.24 [d, J_{HH} = 5.37 Hz, 9 H, $OCH(CH_3)_2$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 297 K): δ 70.2 (CH), 80.9 (CH^a), 150.9, 150.6, 138.9, 137.9 ($C^{3,3'\ or\ 5,5'}$), 106.2 ($C^{4,4'}$), 14.4, 14.3 ($Me^{3,3'}$), 11.7 (Me^5), 11.5 ($Me^{5'}$), 118.9 (C^d), 32.0 (C^e), 38.1 (C^g), 41.6 (C^b), 40.4 (C^f), 123.2 (C^c), 31.6 (C^h), 21.3 (Me^g), 26.3 (Me^g), 74.2 [$OCH(CH_3)_2$], 27.69, 27.48, 27.46, 27.40, 27.24, 27.21 [$OCH(CH_3)_2$]. IR (Nujol mull, cm^{-1}): 1571 ν(C=N), 661 ν(Zr−O).

Synthesis of [TiCl(NMe$_2$)$_2$(bpzb)] (19). To an orange solution of **7** (0.50 g, 1.07 mmol) in dry THF (70 mL) was added a solution of Me_3SiCl in THF (0.13 mL, 1.07 mmol). The reaction mixture was stirred for 1 h. The solvent was removed under vacuum, and the resulting solid was extracted with hexane. The solvent was removed to give a red solid. Yield: 65% (0.32 g, 0.69 mmol). Anal. Calcd for $C_{20}H_{37}ClN_6OTi$: C, 52.13; H, 8.04; N, 18.24. Found: C, 51.93; H, 8.15; N, 18.06. ^1H NMR ($CDCl_3$, 297 K): δ 5.98 (s, 1 H, CH), 4.12 (s, 1 H, CH^a), 5.29 (s, 1 H, H^4), 5.33 (s, 1 H, $H^{4'}$), 3.67 (s, 6 H, NMe_2), 3.85 (s, 6 H, NMe_2), 2.45 (s, 3 H, Me^3), 2.44 (s, 3 H, $Me^{3'}$), 1.69 (s, 3 H, Me^5), 1.62 (s, 3 H, $Me^{5'}$), 0.75 [s, 9 H, $C(CH_3)_3$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 297 K): δ 64.3 (CH), 89.1 (CH^a), 151.8, 149.9, 137.1, 135.8 ($C^{3,3'\ or\ 5,5'}$), 106.4, 105.8 ($C^{4,4'}$), 14.1 (Me^3), 14.2 ($Me^{3'}$), 10.7 (Me^5), 10.4 ($Me^{5'}$), 25.6 [$C(CH_3)_3$], 30.0 [$C(CH_3)_3$], 50.8, 49.6 (NMe_2). IR (Nujol mull, cm^{-1}): 1575 ν(C=N), 325 ν(Ti−Cl).

Synthesis of [TiCl(NMe$_2$)$_2$(*R*,*R*-bpzmm)] (20). The synthetic procedure was the same as that for complex **19**, using **11** (1.02 g, 1.91 mmol) and Me_3SiCl in THF (0.24 mL, 1.91 mmol), to give **20** as a white solid. Yield: 70% (0.70 g, 1.34 mmol). $[\alpha]_D^{25}$: +23.74 (*c* 1.00, CH_2Cl_2). Anal. Calcd for $C_{25}H_{41}ClN_6OTi$: C, 57.22; H, 7.82; N, 16.02. Found: C, 57.07; H, 7.64; N, 16.24. ^1H NMR ($CDCl_3$, 297 K): δ 6.08 (s, 1 H, CH), 5.07 (s, 1 H, CH^a), 5.76 (s, 2 H, H^4), 2.57 (s, 3 H, Me^3), 2.17 (s, 3 H, Me ^{3}), 2.30 (s, 3 H, Me^5), 2.23 (s, 3 H, Me^5), 5.51 (s, 1 H, H^d), 2.19 (m, 2 H, H^e), 2.10, 0.90 (m, 2 H, *geminal*-H^h), 1.98 (m, 1 H, H^f), 1.56 (m, 1 H, H^b), 1.08 (s, 3 H, Me^g), 0.75 (s, 3 H, Me^g), 3.44 (s, 6 H, NMe_2), 3.28 (s, 6 H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 297 K): δ 68.8 (CH), 86.3 (CH^a), 152.1, 145.6, 139.7, 138.6 ($C^{3,3'\ or\ 5,5'}$), 108.1, 107.6 (C^4), 15.1, 14.5 (Me^3), 11.6, 11.4 (Me^5), 123.4 (C^d), 32.4 (C^e), 38.1 (C^g), 41.2 (C^f), 40.9 (C^b), 137.6 (C^c), 31.7 (C^h), 26.2, 21.5 (Me^g), 50.7 (NMe_2), 49.51 (NMe_2). IR (Nujol mull, cm^{-1}): 1569 ν(C=N), 315 ν(Ti−Cl).

Synthesis of [TiCl$_2$(NMe$_2$)(bpzb)] (21). The synthetic procedure was the same as that for complex **19**, using **7** (0.50 g, 1.07 mmol) and Me_3SiCl (0.27 mL, 2.14 mmol), to give **21** as a red solid. Yield: 73% (0.35 g, 0.78 mmol). Anal. Calcd for $C_{18}H_{31}Cl_2N_5OTi$: C, 47.80; H, 6.86; N, 15.49. Found: C, 47.31; H, 6.70; N, 15.35. ^1H NMR ($CDCl_3$, 297 K): δ 5.91 (s, 1 H, CH), 3.91 (s, 1 H, CH^a), 5.30 (s, 1 H, H^4), 5.34 (s, 1 H, $H^{4'}$), 3.98 (s, 6 H, NMe_2), 2.90 (s, 3 H, Me^3), 2.20 (s, 3 H, $Me^{3'}$), 1.63 (s, 3 H, Me^5), 1.64 (s, 3 H, $Me^{5'}$), 0.67 [s, 9 H, $C(CH_3)_3$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 297 K): δ 65.1 (CH), 85.6 (CH^a), 153.4, 151.5, 137.2, 137.1 ($C^{3,3'\ or\ 5,5'}$), 108.0 (C^4), 106.8 ($C^{4'}$), 14.3 (Me^3),

Table 4. Crystal Data and Structure Refinement for **3**−**7**, **12**·THF, and **24**

	3	**4**	**5**	**6**	**7**	**12**·THF	**24**
empirical formula	$C_{32}H_{52}N_8O_2$	$C_{19}H_{24}N_4O$	$C_{26}H_{34}N_4O_4$	$C_{21}H_{30}N_4O$	$C_{22}H_{43}N_7OTi$	$C_{26}H_{48}N_4O_5Ti$	$C_{21}H_{29}Cl_3N_4OTi$
fw	580.82	324.42	466.57	354.49	469.17	544.58	507.73
temp (K)	180(2)	200(2)	250(2)	180(2)	200(2)	200(2)	180(2)
wavelength (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
cryst syst	triclinic	triclinic	triclinic	monoclinic	orthorhombic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1$	$C2/c$	$P2_1/n$	$P2_12_12_1$
a (Å)	8.619(16)	7.3634(10)	6.928(6)	11.516(2)	41.66(1)	8.732(2)	10.667(2)
b (Å)	13.93(3)	11.025(1)	10.73(9)	13.671(3)	16.856(4)	18.087(3)	13.303(2)
c (Å)	14.29(3)	12.636(2)	18.516(1)	13.296(3)	11.276(3)	19.500(4)	17.080(3)
α (deg)	94.87(3)	65.704(2)	75.47(1)				
β (deg)	91.59(3)	81.085(2)	82.45(1)	99.851(9)		101.621(3)	
γ (deg)	102.00(3)	70.782(2)	77.83(1)				
vol (Å^3)	1670(5)	882.7(2)	1298(2)	2062.3(7)	7918(3)	3016.8(9)	2423.8(6)
Z	2	2	2	4	12	4	4
density (calcd) (g/cm^3)	1.155	1.221	1.194	1.142	1.181	1.199	1.391
abs coeff (mm^{-1})	0.075	0.078	0.081	0.072	0.350	0.322	0.704
F(000)	632	348	500	768	3044	1176	1056
cryst size (mm^3)	0.53 × 0.25 × 0.18	0.55 × 0.26 × 0.22	0.59 × 0.19 × 0.18	0.44 × 0.39 × 0.06	0.31 × 0.26 × 0.11	0.67 × 0.50 × 0.44	0.18 × 0.16 × 0.07
index ranges	$-8 \le h \le 7$	$-9 \le h \le 9$	$-7 \le h \le 6$	$-12 \le h \le 13$	$-52 \le h \le 49$	$-9 \le h \le 9$	$-11 \le h \le 10$
reflns collected	6003	5850	4902	18 402	28 330	16 490	9910
indep reflns	2823	3473	2555	7223	8089	4312	2870
data/restraints/param	2823/0/396	3473/0/222	2555/0/316	7223/1/483	8089/12/537	4312/0/362	2870/0/277
GOF on F^2	0.975	1.054	1.062	0.646	0.922	0.919	1.005
final R indices [$I > 2\sigma(I)$]	R1 = 0.0871	R1 = 0.0602	R1 = 0.0485	R1 = 0.0634	R1 = 0.0762	R1 = 0.0644	R1 = 0.0475
absolute structure param				0.13(3)			0.04(7)
extinction coeff	0.013(4)		0.013(3)				
largest diff peak and hole	0.296 and −0.320	0.218 and −0.252	0.166 and −0.152	0.159 and −0.193	0.365 and −0.431	0.846 and −0.332	0.311 and −0.346

15.2 ($Me^{3'}$), 10.5 (Me^5), 10.6 ($Me^{5'}$), 25.6 [$C(CH_3)_3$], 30.0 [C-(CH_3)$_3$], 53.0 (NMe_2). IR (Nujol mull, cm^{-1}): 1575 ν(C=N), 325 ν(Ti−Cl).

Synthesis of [TiCl$_2$(NMe$_2$)(*R*,*R*-bpzmm)] (22). The synthetic procedure was the same as that for complex **19**, using **11** (1.43 g, 2.68 mmol) and Me_3SiCl (0.68 mL, 5.36 mmol), to give **22** as a red solid. Yield: 62% (0.86 g, 1.66 mmol). $[\alpha]_D^{25}$: +22.5 (c 1.00, CH_2Cl_2). Anal. Calcd for $C_{23}H_{35}Cl_2N_5OTi$: C, 53.51; H, 6.78; N, 13.57. Found: C, 53.23; H, 6.55; N, 13.81. ^{1}H NMR ($CDCl_3$, 297 K): δ 6.32 (bs, 1 H, CH), 5.95 (s, 1 H, H^4), 5.91 (s, 1 H, H^4), 5.67 (m, 1 H, H^d), 5.26 (bs, 1 H, CH^a), 4.05 (bs, 6 H, NMe_2), 2.47 (s, 3 H, Me^3), 2.43 (s, 3 H, Me^3), 2.28 (s, 3 H, Me^5), 2.26 (s, 3 H, Me^5), 2.24 (m, 2 H, H^e), 2.21, 0.86 (m, 2 H, *geminal*-H^h), 2.07 (m, 1 H, H^f), 1.02 (m, 1 H, H^b), 0.93 (s, 3 H, Me^g), 0.77 (s, 3 H, Me^g). ^{13}C{^{1}H} NMR ($CDCl_3$, 297 K), δ 152.1, 145.6, 139.8, 138.4 ($C^{3\text{ or }5}$), 137.8 (C^c), 123.1 (C^d), 107.7, 107.3 (C^4), 88.3 (CH^a), 68.8 (CH), 53.5 (NMe_2), 41.2 (C^f), 40.9 (C^b), 38.1 (C^g), 31.8 (C^e), 31.7 (C^h), 26.2, 21.3 (Me^g), 14.7, 14.6 (Me^3), 11.5, 11.4 (Me^5). IR (Nujol mull, cm^{-1}): 1569 ν(C=N), 315 ν(Ti−Cl).

Synthesis of [TiCl$_3$(bpzb)] (23). Method a. The synthetic procedure was the same as that for complex **19**, using **7** (0.50 g, 1.07 mmol) and Me_3SiCl in THF (0.41 mL, 3.21 mmol), to give **23** as a yellow solid. Yield: 78% (0.46 g, 0.83 mmol).

Method b. In a 250-cm^3 Schlenk tube, $TiCl_4(THF)_2$ (0.5 g, 1.49 mmol) and **1** (0.55 g, 1.49 mmol) were suspended in cooled THF. The resulting suspension was stirred for 12 h at −70 °C. The solvent was removed under vacuum, and the solid was extracted with CH_2Cl_2. The solvent was removed, and the resulting solid was crystallized from a mixture of THF−hexane to give **23** as a yellow solid. Yield: 70% (0.46 g, 1.05 mmol). Anal. Calcd for $C_{16}H_{25}Cl_3N_4OTi$: C, 43.30; H, 5.64; N, 12.63. Found: C, 42.95; H, 5.39; N, 12.83. ^{1}H NMR ($CDCl_3$, 297 K): δ 6.48 (s, 1 H, CH), 4.37 (s, 1 H, CH^a), 5.90 (s, 1 H, H^4), 5.96 (s, 1 H, $H^{4'}$), 2.45 (s, 3 H, Me^3), 2.66 (s, 3 H, $Me^{3'}$), 2.23 (s, 3 H, Me^5), 2.43 (s, 3 H, $Me^{5'}$), 0.82 [s, 9 H, $C(CH_3)_3$]. ^{13}C{^{1}H} NMR ($CDCl_3$, 297 K): δ 65.5 (CH), 84.7 (CH^a), 153.1, 152.8, 137.4, 134.7 ($C^{3,3'\text{ or }5,5'}$), 109.1 (C^4), 106.9 ($C^{4'}$), 14.6 (Me^3), 15.2 ($Me^{3'}$), 10.4 (Me^5), 10.7 ($Me^{5'}$), 25.0 [$C(CH_3)_3$], 26.9 [$C(CH_3)_3$]. IR (Nujol mull, cm^{-1}): 1575 ν(C=N), 340 ν(Ti−Cl).

Synthesis of [TiCl$_3$(*R*,*R*-bpzmm)] (24). Method a. The synthetic procedure was the same as that for complex **19**, using **11** (0.87 g, 1.63 mmol) and Me_3SiCl in toluene (0.62 mL, 4.90 mmol), to give **24** as a yellow solid. Yield: 72% (0.59 g, 1.17 mmol).

Method b. 1 (0.37 g, 1.04 mmol) was deprotonated by treatment with NaH (0.025 g, 1.04 mmol) in toluene at room temperature. After 30 min, this solution was slowly added to a solution of $TiCl_4(THF)_2$ (0.35 g, 1.04 mmol) in toluene (20 cm^3) at room temperature. The resulting yellow suspension was stirred overnight at room temperature. The solvent was removed under vacuum, and the solid was extracted with CH_2Cl_2. A yellow solid was obtained after removal of CH_2Cl_2, and this was crystallized from a mixture of CH_2Cl_2−hexane. Yield: 75% (0.39 g, 0.78 mmol). $[\alpha]_D^{25}$: +43.9 (c 1.00, CH_2Cl_2). Anal. Calcd for $C_{21}H_{29}Cl_3N_4OTi$: C, 49.68; H, 5.72; N, 11.04. Found: C, 49.42; H, 5.50; N, 10.91. ^{1}H NMR ($CDCl_3$, 297 K): δ 6.32 (bs, 1 H, CH), 6.01 (bs, 2 H, H^4), 5.75 (m, 1 H, H^d), 5.26 (d, 1 H, CH^a), 2.72 (s, 3 H, Me^3), 2.68 (s, 3 H, Me^3), 2.47 (s, 3 H, Me^5), 2.38 (s, 3 H, Me^5), 2.29 (m, 2 H, H^e), 2.19, 0.87 (m, 2 H, *geminal*-H^h), 2.05 (m, 1 H, H^f), 1.02 (m, 1 H, H^b), 1.22 (s, 3 H, Me^g), 0.82 (s, 3 H, Me^g). ^{13}C{^{1}H} NMR ($CDCl_3$, 297 K), δ 154.1, 143.9, 139.2, 138.4 ($C^{3\text{ or }5}$), 136.8 (C^c), 125.3 (C^d), 108.4, 108.3 (C^4), 88.5 (CH^a), 69.2 (CH), 41.0 (C^f), 40.9 (C^b), 38.4 (C^g), 31.8 (C^e), 31.7 (C^h), 26.1, 21.3 (Me^g), 16.1, 15.9 (Me^3), 11.4 (Me^5). IR (Nujol mull, cm^{-1}): 1570 ν(C=N), 345 ν(Ti−Cl).

Epoxidation Procedures. Asymmetric epoxidations were carried out on a Schlenk line in a 250-mL flame-dried, round-bottomed, two-necked flask equipped with a dropping funnel and a magnetic stirrer. In a typical procedure, the flask was charged with 2 g of activated, powdered 4 Å molecular sieves and 100 mL of dry CH_2Cl_2. The catalyst was dissolved in the

minimum amount of solvent, the resulting mixture was transferred to the flask, and temperature equilibration of the mixture was ensured at −20 °C by stirring the solution for 15 min on a temperature bath. After that time, a 5.5 M TBHP solution in nonane, as the oxidizing agent, was added, and the mixture was stirred at −20 °C for 1 h and then treated with a 4.27 M CH_2Cl_2 solution of freshly distilled (*E*)-3-phenyl-2-propenol (cinnamyl alcohol, 98%), which was added dropwise over 1 h. The resulting heterogeneous suspension was stirred for 18 h at −20 °C. Reactions were stopped by injecting 0.4 mL of a 10% aqueous solution of sodium hydroxide saturated with sodium chloride. The cooling bath was removed, and the mixture was stirred for 10 min. Finally, the mixture was treated with $MgSO_4$ and Celite, filtered, and washed with Et_2O, and the volatiles were removed under vacuum to give a yellow oil. Yields and ee values were determined by the HPLC method.[22a] Catalysts **15**: yield 30% (*R*,*R* enantiomer = 2.1×10^{-4} mol, 31.5 mg; *S*,*S* enantiomer = 2.1×10^{-4} mol, 31.5 mg); yield 44% (*R*,*R* enantiomer = 38.5×10^{-4} mol, 577.5 mg; *S*,*S* enantiomer = 38.5×10^{-4} mol, 577.5 mg). Catalysts **17**: yield 10% (*R*,*R* enantiomer = 5.34×10^{-5} mol, 8.01 mg; *S*,*S* enantiomer = 8.65×10^{-5} mol, 12.9 mg); yield 12% (*R*,*R* enantiomer = 8.07×10^{-4} mol, 121.1 mg; *S*,*S* enantiomer = 12.9×10^{-4} mol, 193.8 mg).

X-ray Crystallography. A summary of the crystal data collection and refinement parameters for all compounds is given in Table 4.

The single crystals for **3**−**7**, **12**·THF, and **24** were mounted on a glass fiber and transferred to a Bruker X8 APEX II CCD-based diffractometer equipped with a graphite-monochromated Mo Kα radiation source (λ = 0.710 73 Å). Data were integrated using *SAINT*,[23] and an absorption correction was performed with the program *SADABS*.[24] The software package *SHELXTL*, version 6.12,[25] was used for space-group determination, structure solution, and refinement 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. For **6**, the asymmetric unit contains two molecules of ligand and the crystal diffracted weakly. For **7**, the asymmetric unit comprises 1.5 molecules of the complex. The half-molecule is highly disordered about the 2-fold rotation axis with the titanium atom into this axis. These limitations of the structural model and the weak diffraction due to disorder and quality are reflected in the relatively high crystallographic parameters. For **12**, the asymmetric unit contains one molecule of the THF solvent and O5, C18, and C22 are disordered over two positions.

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Supporting Information Available: Details of data collection, refinement, atomic coordinates, anisotropic displacement parameters, and bond lengths and angles (in CIF format) for complexes **3**−**7**, **12**·THF, and **24**. This material is available free of charge via the Internet at http://pubs.acs.org.

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