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Direct Synthesis of NNN-Donor Enantiopure Scorpionate Ligands by an Efficient Diastereoselective Nucleophilic Addition to Imines

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New enantiopure imines (**1**−**9**) with a chiral substrate to control the stereochemistry of a newly created stereogenic center have been synthesized by reaction of the commercially available (1*R*)-(−)-myrtenal and different primary amines. The diastereomerically enriched lithium-scorpionate compounds [Li(κ^3-mbpza)(THF)] (**10**) (mbpza = *N*-*p*-methylphenyl-(1*R* and 1*S*)-1-[(1*R*)-6,6-dimethylbicyclo[3.1.1]-2-hepten-2-yl]-2,2-bis(3,5-dimethylpyrazol-1-yl)ethylamide), [Li(κ^3-mobpza)(THF)] (**11**) (mobpza = *N*-*p*-methoxyphenyl-(1*R* and 1*S*)-1-[(1*R*)-6,6-dimethylbicyclo[3.1.1]-2-hepten-2-yl]-2,2-bis(3,5-dimethylpyrazol-1-yl)ethylamide), [Li(κ^3-fbpza)(THF)] (**12**) (fbpza = *N*-*p*-fluorophenyl-(1*R* and 1*S*)-1-[(1*R*)-6,6-dimethylbicyclo[3.1.1]-2-hepten-2-yl]-2,2-bis(3,5-dimethylpyrazol-1-yl)ethylamide), and [Li(κ^3-clbpza)(THF)] (**13**) (clbpza = *N*-*p*-chlorophenyl-(1*R* and 1*S*)-1-[(1*R*)-6,6-dimethylbicyclo[3.1.1]-2-hepten-2-yl]-2,2-bis(3,5-dimethylpyrazol-1-yl)ethylamide) were obtained by a diastereoselective 1,2-addition of an organolithium reagent to imines in good yield and with good diastereomeric excess (*ca.* 80%). The complexes [LiCl(κ^2-*R*,*R*-fbpzaH)(THF)] (**14**) and [LiCl(κ^2-*R*,*R*-clbpzaH)(THF)] (**15**) were obtained in enantiomerically pure form by the treatment of THF solutions of **12** or **13** with NH_4Cl. The enantiomerically pure amines (*R*,*R*-mbpzaH) (**16**), (*R*,*R*-mobpzaH) (**17**), (*R*,*R*-fbpzaH) (**18**), and (*R*,*R*-clbpzaH) (**19**) were obtained by hydrolysis of the lithium-scorpionate compounds **10**−**13** with H_2O. The lithium compound **12** was reacted with [$TiCl_4(THF)_2$] or [$ZrCl_4$] to give the enantiopure complexes [MCl_3(κ^3-*R*,*R*-fbpza)] [M = Ti (**20**), Zr (**21**)]. The amine compound **18** reacted with [MX_4] (M = Ti, X = O^{i}Pr, OEt; M = Zr; X = NMe_2) to give the complexes [MX_3(κ^3-*R*,*R*-fbpza)] (**22**−**24**). The reaction of Me_3SiCl with [$Zr(NMe_2)_3$(κ^3-*R*,*R*-fbpza)] (**24**) in different molar ratios led to the halide-amide-containing complexes [$ZrCl(NMe_2)_2$(κ^3-*R*,*R*-fbpza)] (**25**) and [$ZrCl_2(NMe_2)$(κ^3-*R*,*R*-fbpza)] (**26**) and the halide complex **21**. The isolation of only one of the three possible diastereoisomers of complexes **25** and **26** revealed that chiral induction from the ligand to the zirconium center took place. The structures of these compounds were elucidated by ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy, and the X-ray crystal structures of **5**, **12**, **14**, **15**, and **24** were also established.

Introduction

In recent years, our research group has been interested in the synthesis of enantiopure "heteroscorpionate" ligands[1] with pyrazole rings.[2] The synthesis of chiral ligands of high enantiopurity is an important goal in organometallic chemistry in order to prepare metal-based reagents in efficient asymmetric processes.[3] Recently, we reported[4] the preparation

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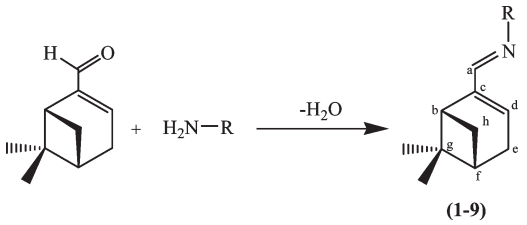
of new chiral bis(pyrazol-1-yl)methane-based NNO-donor scorpionate ligands in a single high-yielding step by the 1,2-addition of organometallics to aldehydes to afford chiral secondary alcohols.[3] When this type of reaction was carried out with an enantiopure aldehyde [(1*R*)-(−)-myrtenal] as a possible chiral substrate to control the stereochemistry of a newly created asymmetric center,[5] we obtained an enantiopure scorpionate ligand in one step with high stereoselectivity. The limited availability of commercial enantiopure aldehydes—together with the interest in extending this simple and efficient synthetic route for the preparation of other types of enantiopure scorpionate ligands in one step—led us to focus our attention on enantiopure imine compounds[6] as possible chiral substrates to control the stereochemistry of a newly created asymmetric center. The development of a new methodology for asymmetric reactions of organolithium reagents constitutes a remarkable and fundamental area of progress in recent synthetic organic chemistry; thus, asymmetric nucleophilic 1,2-addition of organolithium reagents to C=N double bonds provides a versatile method for the preparation of chiral amines.[4] Optically active amines are abundantly present in biologically active compounds and are also important chiral building blocks. Diastereoselective addition of organolithium reagents to imines has been achieved with the use of chiral auxiliaries or chiral ligands; this strategy involves a diastereoselective reaction and separation of the diastereomers. Takahashi and co-workers[7] reported pioneering work on this strategy. Organolithium reagents undergo addition to imines derived from aryl aldehydes and valinol or phenylglycinol to give amines in good yields and with high diastereoselectivity. The other strategy involves the use of chiral ligands for the direct introduction of chirality to an imine and/or an organolithium reagent. For example, the addition of the lithium carbanion of (*R*)-methyl *p*-tolyl sulfoxide to an imine afforded *β*-sulfinylamine with high diastereoselectivity.[8] Furthermore, when the imine is α,*β*-unsaturated, the enantioselective conjugate addition (or Michael reaction, 1,4-addition) and 1,2-addition to C=N double bonds are powerful methods for forming a carbon−carbon bond. The first prominent catalytic asymmetric conjugate addition reaction of an organolithium reagent was that between 1-naphthyllithium and a naphthaldehyde imine under the control of a chiral diether,

Scheme 1. Synthesis of Enantiopure Imines **1**−**9**



(1-9)

R = ^{i}Pr (**1**), *p*-MeC$_6$H$_4$ (**2**), *p*-OMeC$_6$H$_4$ (**3**), *p*-FC$_6$H$_4$ (**4**), *o*-FC$_6$H$_4$(**5**), *m*-FC$_6$H$_4$(**6**), *p*-ClC$_6$H$_4$ (**7**), *o*-ClC$_6$H$_4$ (**8**), *o*-BrC$_6$H$_4$ (**9**)

with only a catalytic amount of this chiral ether (5 mol %) required to give binaphthyl in 82% ee.[9] Tomioka and co-workers[10] also reported the stoichiometric and catalytic asymmetric 1,2-addition of organolithium reagents to N-arylimines mediated by an external chiral ligand. In this work, we have developed and fully explored the potential offered by an efficient synthetic route (enantioselective 1,2-addition to C=N double bonds by an organolithium reagent controlled by a chiral auxiliary) to obtain a new type of enantiopure NNN-donor scorpionate ligand. In order to achieve this type of reaction, we synthesized new enantiopure imines with a chiral substrate to control the stereochemistry of a newly created asymmetric center, and subsequently we obtained an enantiopure scorpionate ligand in one step with high stereoselectivity. Furthermore, the lithium amide−scorpionate or amine−scorpionate compounds were found to be excellent reagents for the introduction of scorpionate ligands into group 4 metal complexes, and a series of neutral chloride, amide, and alkoxide complexes were prepared by the treatment of MCl_4, $M(NMe_2)_4$, or $M(OR)_4$ with these lithium− or amine−scorpionate compounds. 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.

Results and Discussion

The strategy employed in the initial phase of this work led us to synthesize new enantiopure imines with a chiral substrate to control the stereochemistry of a newly created asymmetric center. Thus, the reaction of the commercially available (1*R*)-(−)-myrtenal and different primary amines, such as isopropylamine, *p*-methylaniline, *p*-methoxyaniline, *p*-fluoroaniline, *o*-fluoroaniline, *m*-fluoroaniline, *p*-chloroaniline, *o*-chloroaniline, and *o*-bromoaniline, gave new enantiopure imines **1**−**9**, which were all α,*β*-unsaturated. These imines were obtained as red solids in good yields (*ca.* 90%; Scheme 1).

The ^{1}H NMR spectra of **1**−**9** exhibit five sets of resonances for H^b, H^d, H^e, H^f, and *geminal*-H^h and three singlets for H^a and the methyl groups of the bicyclic moiety. In addition, the spectra show the corresponding signals for the alkyl or aryl substituent on the nitrogen atom. ^{1}H−^{13}C heteronuclear

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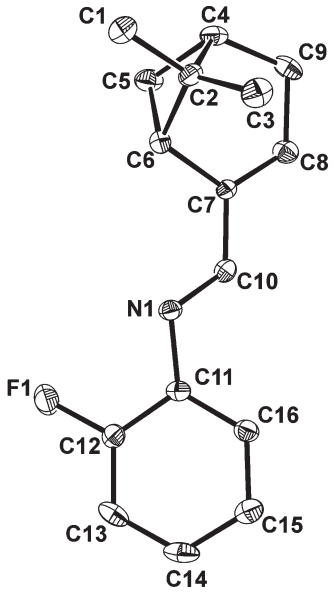


Figure 1. ORTEP view of imine **5**. Ellipsoids are at the 30% probability level.

correlation (g-HSQC) experiments were carried out and allowed us to assign the resonances corresponding to the $^{13}C\{^1H\}$ NMR spectra of these compounds. The molecular structure of **5** was determined by X-ray diffraction (Figure 1). Significant bond lengths and angles are presented in Table 2. The C(10)−N(1) distance in this compound [1.282(5) Å] is typical of C=N double bonds found in Schiff bases (*ca.* 1.26 Å) or the amidine−scorpionate derivative [1.275(3) Å].[11] The C(7)−C(8) distance of 1.331(5) Å corresponds to the C=C double bond of the bicyclic moiety bound to the nitrogen atom to form an α,β-unsaturated imine. The essentially sp^2 and planar nature of the α,β-unsaturated imine was further confirmed by the angles C(8)−C(7)−C(10) of 121.3(4)°, N(1)−C(10)−C(7) of 122.6(4)°, and C(10)−N(1)−C(11) of 118.0(3)°.

Once the new enantiopure imines had been synthesized, we focused our attention on the preparation of enantiopure scorpionate ligands by asymmetric nucleophilic 1,2-addition of organolithium reagents to C=N double bonds. Thus, a cold (−10 °C) THF solution of lithium bis(3,5-dimethylpyrazol-1-yl)methide, prepared *in situ* from Bu^nLi and bis(3,5-dimethylpyrazol-1-yl)methane at −70 °C, was added to a THF solution containing 1 equiv of the corresponding imines **1**−**9** (Table 1). After the appropriate workup, the diastereomerically enriched lithium-scorpionate compounds [Li(κ^3-mbpza)(THF)] (**10**) (mbpza = *N*-*p*-methylphenyl-(1*R* and 1*S*)-1-[(1*R*)-6,6-dimethylbicyclo[3.1.1]-2-hepten-2-yl]-2,2-bis(3,5-dimethylpyrazol-1-yl)ethylamide), [Li(κ^3-mobpza)(THF)] (**11**) (mobpza = *N*-*p*-methoxyphenyl-(1*R* and 1*S*)-1-[(1*R*)-6,6-dimethylbicyclo[3.1.1]-2-hepten-2-yl]-2,2-bis(3,5-dimethylpyrazol-1-yl)ethylamide), [Li(κ^3-fbpza)(THF)] (**12**) (fbpza = *N*-*p*-fluorophenyl-(1*R* and 1*S*)-1-[(1*R*)-6,6-dimethylbicyclo-[3.1.1]-2-hepten-2-yl]-2,2-bis(3,5-dimethylpyrazol-1-yl)ethylamide), and [Li(κ^3-clbpza)(THF)] (**13**) (clbpza = *N*-*p*-chlorophenyl-(1*R* and 1*S*)-1-[(1*R*)-6,6-dimethylbicyclo[3.1.1]-2-hepten-2-yl]-2,2-bis(3,5-dimethylpyrazol-1-yl)ethylamide) were obtained as brown or red solids in good yield and with good to moderate diastereomeric excess (Scheme 2).

(11) Otero, A.; Fernández-Baeza, J.; Antiñolo, A.; Tejeda, J.; Lara-Sánchez, A.; Sánchez-Barba, L.; Lopez-Solera, M. I.; Rodríguez, A. M. *Inorg. Chem.* **2007**, *46*, 1760–1770.

Table 1. Results of Selective Nucleophilic 1,2-Addition of "Lithium Bis(3,5-dimethylpyrazol-1-yl)methide" to α,β-Unsaturated Imines (**1**−**9**)

imine	R	complex	yield %	%R,R	de%[a]
1	^{i}Pr				
2	*p*-MeC_6H_4	**10**	70	81	62
3	*p*-$OMeC_6H_4$	**11**	75	75	50
4	*p*-FC_6H_4	**12**	90	89	78
5	*o*-FC_6H_4				
6	*m*-FC_6H_4				
7	*p*-ClC_6H_4	**13**	90	93	86
8	*o*-ClC_6H_4				
9	*o*-BrC_6H_4				

[a] Diastereomeric excess (de%) has been calculated as the diference between %RR and %RS.

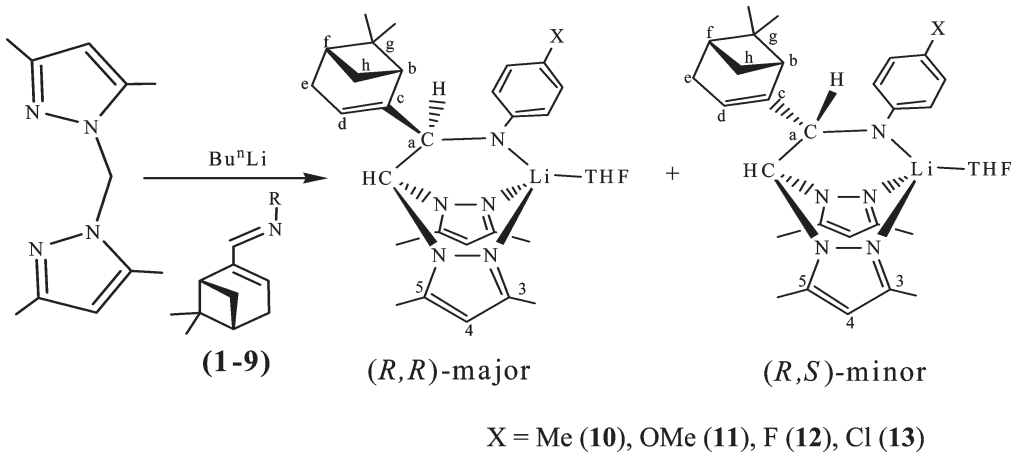
Reaction of the α,β-unsaturated imines bearing an aryl group on the imine nitrogen atom (**2**−**9**) results in selective 1,2-addition and not Michael-type conjugate addition. The *N*-aryl substituent in the starting imines has a profound effect on diastereoselectivities. This effect is particularly marked in the addition to the imines bearing *p*-fluorophenyl or *p*-chlorophenyl groups (**4** and **7**), where good diastereoselectivities were obtained. However, *N*-alkyl (**1**), *o*-aryl (**5**, **8**, and **9**), or *m*-aryl (**6**) substituents in the imines have a detrimental effect because the nucleophilic 1,2-addition of organolithium reagents to C=N double bonds does not take place (the starting materials were recovered). This situation is probably due to steric factors in the case of the *N*-*o*-aryl substitution in the imines and the lack of stabilization of the anionic amide species in the *N*-alkylimine (**1**). The result obtained with the meta substituted imine **6** is not yet understood.

Initial evidence for the stereochemical route was obtained from the X-ray molecular structures of a diverse range of synthesized compounds. These structures had the *R* configuration for the newly formed chiral center in the major diastereoisomer (see below). This finding indicates that the diastereofacial attack of the nucleophile had proceeded at the *Si* face of the imine group in an *S-trans* conformation. The steric effect of one of the methyl groups of the bicyclic moiety is probably the main driving force for the diastereoselectivity observed in the process (Figure 2). The diastereoselectivity was assessed by considering the ^1H NMR spectrum and integrating the CH^a or Me signals of the bicycle in the crude reaction mixture, since the signals for these protons appear at a higher field for the *S* epimer.

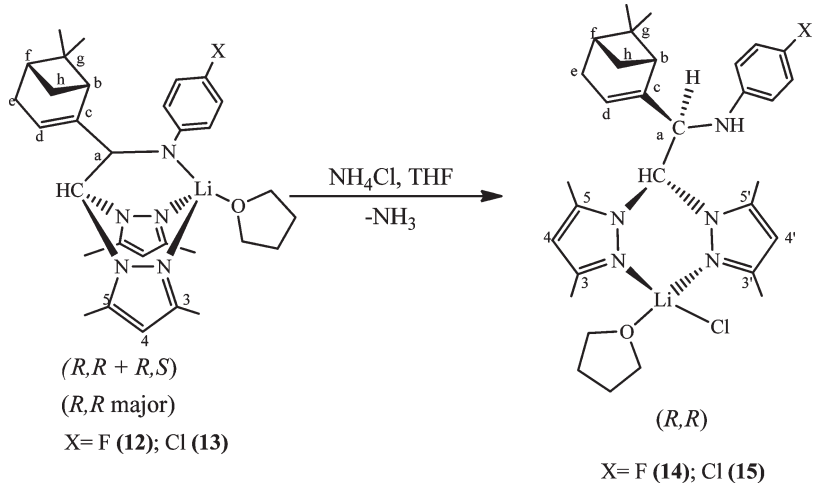
Having obtained these new chiral heteroscorpionate ligands in the form of the lithium compounds, we attempted the protonolysis of the Li−N bond to obtain the corresponding amines. Treatment of the THF solutions of **12** or **13** with NH_4Cl (saturated solution) afforded the amines, but these were coordinated to "LiCl" by the nitrogen atoms of pyrazole rings. The complexes [LiCl(κ^2-*R*,*R*-fbpzaH)(THF)] (**14**) and [LiCl(κ^2-*R*,*R*-clbpzaH)(THF)] (**15**) were obtained in enantiomerically pure form by crystallization from CH_2Cl_2/*n*-hexane as red solids in good yield (*ca.* 70%) (see Scheme 3).

In view of the difficulty in obtaining the free amines by reaction with ammonium chloride, we attempted the hydrolysis by treatment of THF solutions of lithium−scorpionate compounds (**10**−**13**) with H_2O. Thus, the amine compounds (*R*,*R*-mbpzaH) (**16**), (*R*,*R*-mobpzaH) (**17**), (*R*,*R*-fbpzaH) (**18**), and (*R*,*R*-clbpzaH) (**19**) were obtained in enantiomerically pure form by crystallization from CH_2Cl_2/*n*-hexane as red or orange solids in good yield (*ca.* 70%; see Scheme 4).

Scheme 2. Synthesis of Lithium−Scorpionate Compounds **10**−**13**



Scheme 3. Synthesis of Lithium−Amine Complexes **14** and **15**



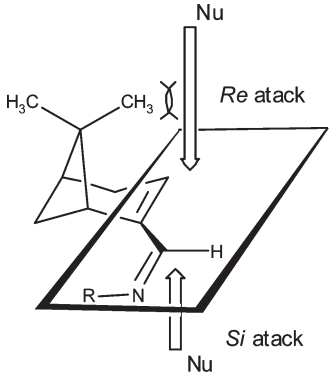
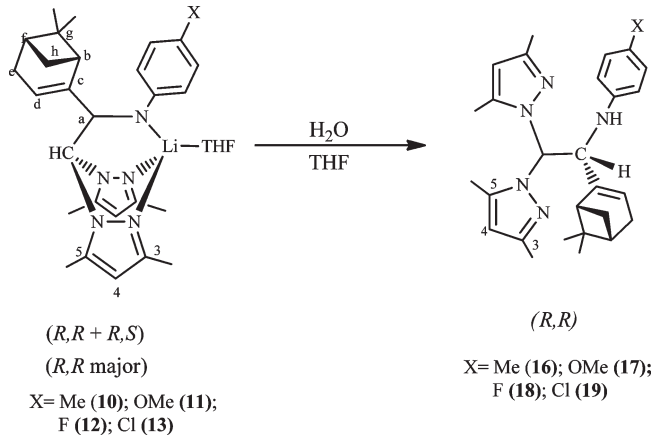


Figure 2. Diastereofacial attack of the nucleophile.

Scheme 4. Synthesis of Amine−Scorpionate Compounds **16**−**19**



Two sets of ^{1}H and ^{13}C{^{1}H} NMR signals were observed in the spectra of lithium complexes **10**−**13**, a finding that is consistent with the presence of two diastereoisomers (major and minor; see Figure 3). These spectra contain two singlets for each of the H^4, Me^3, and Me^5 pyrazole protons in both diastereoisomers, indicating that the two pyrazole rings are inequivalent. Furthermore, the ^{1}H NMR spectra show the signals for the bicyclic moiety bound at the methylene bridge and also those for the aryl substituent on the nitrogen atom. Crystals suitable for X-ray diffraction of the (*RR* + *RS*) lithium−scorpionate **12** were obtained by crystallization from CH_2Cl_2/*n*-hexane. The ORTEP diagram for compound **12** is shown in Figure 4. Significant bond distances and bond angles are listed in Table 2. The geometry around the Li atom can be described as a distorted tetrahedron. This distortion is due to the heteroscorpionate ligand, which acts in a κ^3-*NNN*-coordination mode with N(5)−Li(1)−N(1), N(5)−Li(1)−N-(3), and N(1)−Li(1)−N(3) angles of 91.6(8)°, 95.1(7)°, and 95.8(9)°, respectively, and O(1)−Li(1)−N(5), O(1)−Li(1)−N(1), and O(1)−Li(1)−N(3) angles of 141.1(1)°, 115(1)°, and

Table 2. Bond Lengths [Å] and Angles [deg] for **5** and **12**

5		**12**			
		RR		*RS*	
C(11)−N(1)	1.413(5)	Li(1)−O(1)	1.95(2)	Li(2)−O(2)	1.96(2)
C(7)−C(10)	1.434(5)	N(1)−Li(1)	2.05(2)	N(6)−Li(2)	2.05(2)
C(7)−C(6)	1.504(5)	N(3)−Li(1)	2.04(2)	N(8)−Li(2)	2.10(2)
C(10)−N(1)	1.282(5)	N(5)−Li(1)	1.99(2)	N(10)−Li(2)	1.96(2)
C(7)−C(8)	1.331(5)	N(2)−C(11)	1.43(1)	N(9)−C(42)	1.48(1)
C(12)−F(1)	1.362(4)	N(4)−C(11)	1.42(1)	N(7)−C(42)	1.47(1)
N(1)−C(10)−C(7)	122.6(4)	N(5)−C(12)	1.47(1)	N(10)−C(43)	1.43(1)
C(10)−N(1)−C(11)	118.0(3)	C(11)−C(12)	1.59(1)	C(42)−C(43)	1.53(1)
C(8)−C(7)−C(10)	121.3(4)	C(12)−C(13)	1.51(1)	C(43)−C(44)	1.55(1)
N(1)−C(10)−C(7)	122.6(4)	C(13)−C(14)	1.31(1)	C(44)−C(45)	1.31(1)
C(10)−N(1)−C(11)	118.0(3)	C(13)−C(18)	1.49(1)	C(44)−C(49)	1.49(1)
		O(1)−Li(1)−N(5)	141(1)	N(10)−Li(2)−O(2)	137(1)
		O(1)−Li(1)−N(3)	109(1)	O(2)−Li(2)−N(6)	111.7(9)
		O(1)−Li(1)−N(1)	115(1)	O(2)−Li(2)−N(8)	116.4(8)
		N(5)−Li(1)−N(3)	95.1(7)	N(10)−Li(2)−N(6)	96.6(7)
		N(5)−Li(1)−N(1)	91.6(8)	N(10)−Li(2)−N(8)	92.5(8)
		N(3)−Li(1)−N(1)	95.8(9)	N(6)−Li(2)−N(8)	93.4(8)
		C(22)−N(5)−C(12)	114.6(8)	C(53)−N(10)−C(43)	115.9(8)
		C(22)−N(5)−Li(1)	131.2(8)	C(53)−N(10)−Li(2)	129.4(8)
		C(12)−N(5)−Li(1)	113.4(9)	C(43)−N(10)−Li(2)	113.5(8)
		N(4)−C(11)−N(2)	113.1(9)	N(7)−C(42)−N(9)	108.5(8)
		N(4)−C(11)−C(12)	115.3(8)	N(7)−C(42)−C(43)	113.6(8)
		N(2)−C(11)−C(12)	110.5(9)	N(9)−C(42)−C(43)	112.7(8)
		N(5)−C(12)−C(13)	115.8(8)	N(10)−C(43)−C(44)	117.4(8)
		N(5)−C(12)−C(11)	108.5(8)	N(10)−C(43)−C(42)	113.1(8)
		C(13)−C(12)−C(11)	110.0(9)	C(42)−C(43)−C(44)	108.3(7)

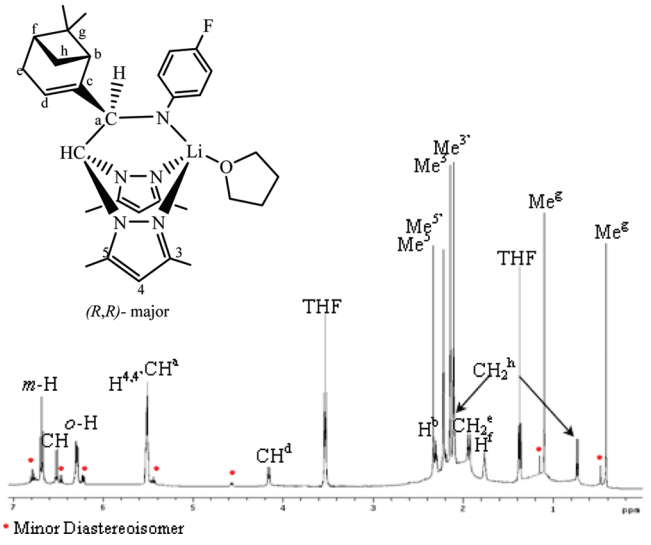


Figure 3. ^{1}H NMR spectrum of complex **12**.

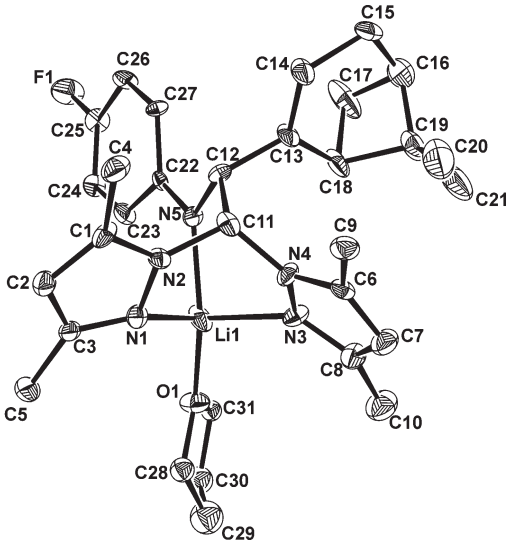


Figure 4. ORTEP view of the (*R*,*R*) diastereoisomer of complex **12**. Ellipsoids are at the 30% probability level.

109(1)°, respectively. The Li−N distances 2.05(2) and 2.04(2) Å in the bis(pyrazol-1-yl)methane moiety are in good agreement with others determined for lithium scorpionate or bis(pyrazol-1-yl)methane complexes.[12] The solid-state structure of this compound confirms that the amide is coordinated to the Li atom. The N−Li bond length [1.99(2) Å] is consistent with that reported for the only previously known amide[13] or monodentate amidinate lithium compounds.[11,14]

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **14**−**19** each exhibit one set of signals, a finding consistent with the presence of one diastereoisomer (see Figure 5). In addition, in the ^{1}H NMR spectra, the signal for the NH group of the amine is present between 8.50 and 11.70 ppm. As mentioned above, the absolute configuration of these entatiomerically pure compounds (**14**−**19**) and probably the one proposed for

(12) (a) Otero, A.; Fernández-Baeza, J.; Tejeda, J.; Antiñolo, A.; Carrillo-Hermosilla, F.; Díez-Barra, E.; Lara-Sánchez, A.; Fernández-López, M.; Lanfranchi, M.; Pellinghelli, M. A. *J. Chem. Soc., Dalton Trans.* **1999**, 3537–3539. (b) Otero, A.; Fernández-Baeza, J.; Antiñolo, A.; Tejeda, J.; Lara-Sánchez, A.; Sánchez-Barba, L.; Rodríguez, A. M.; Maestro, M. A. *J. Am. Chem. Soc.* **2004**, *126*, 1330–1331. (c) Otero, A.; Fernández-Baeza, J.; Antiñolo, A.; Tejeda, J.; Lara-Sánchez, A.; Sánchez-Barba, L.; Sanchez-Molina, M.; Franco, S.; Lopez-Solera, I.; Rodríguez, A. M. *Eur. J. Inorg. Chem.* **2006**, 707–710. (d) Otero, A.; Fernández-Baeza, J.; Antiñolo, A.; Tejeda, J.; Lara-Sánchez, A.; Sánchez-Barba, L.; Sanchez-Molina, M.; Franco, S.; Lopez-Solera, I.; Rodríguez, A. M. *Dalton Trans.* **2006**, 4359–4370. (e) Reger, D. L.; Collins, J. E.; Matthews, M. A.; Rheingold, A. L.; Liable-Sands, M.; Guzei, I. A. *Inorg. Chem.* **1997**, *36*, 6266–6269.

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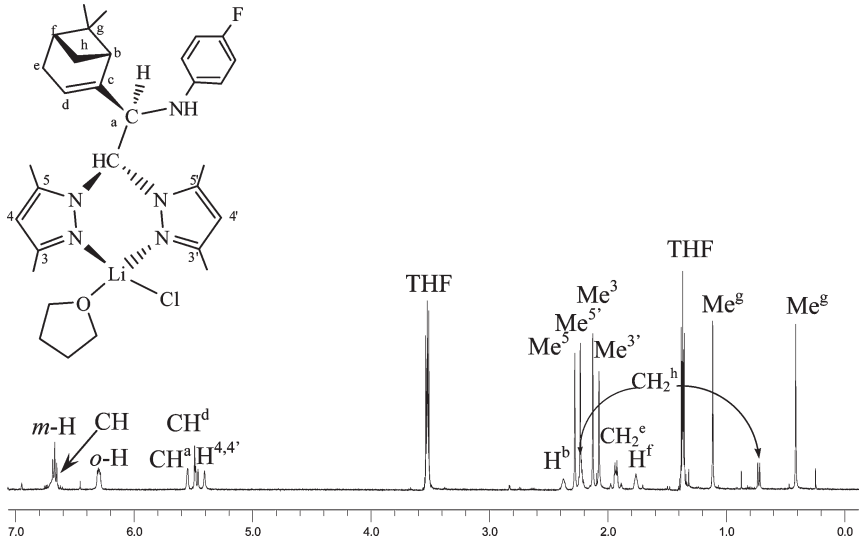


Figure 5. ^{1}H NMR spectrum of [LiCl(κ^2-*R*,*R*-fbpzaH)(THF)] (**14**).

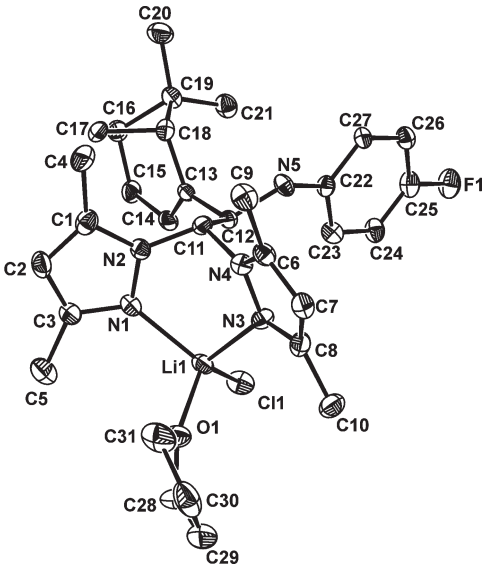


Figure 6. ORTEP view of [LiCl(κ^2-*R*,*R*-fbpzaH)(THF)] (**14**). Ellipsoids are at the 30% probability level, and hydrogen atoms have been omitted for clarity.

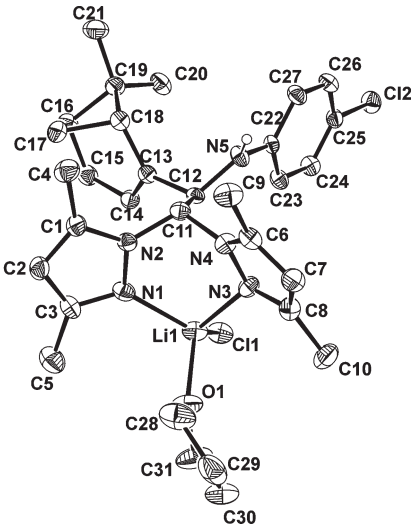


Figure 7. ORTEP view of [LiCl(κ^2-*R*,*R*-clbpzaH)(THF)] (**15**). Ellipsoids are at the 30% probability level, and hydrogen atoms have been omitted for clarity.

the major diastereoisomer of the lithium−scorpionate (**10**−**13**) was verified by single crystal X-ray diffraction analyses on compounds **14** and **15** (Figures 6 and 7) to have the *R* configuration at C^a (C12). Selected bond lengths and angles are listed in Table 3. In both complexes, the geometry around the Li atom can be described as a distorted tetrahedron with an amide−scorpionate ligand that acts in a bidentate fashion (two coordinated pyrazole rings) and one molecule of THF and chloride. Both Li−N distances [2.090(10) and 2.088(10) Å for **14** and 2.096(12) and 2.088(12) Å for **15**] are in good agreement with others determined for lithium scorpionate or poly(pyrazolyl)methane complexes.[13]

Having prepared these new heteroscorpionate ligands in the form of the lithium or amine compounds, we explored their potential utility as tridentate ligands in the preparation of group 4 metal complexes. The lithium compound **12** was reacted at −70 °C with [$TiCl_4(THF)_2$] or [$ZrCl_4$] in a 1:1 molar ratio in THF to give, after the appropriate workup, the enantiopure complexes [$MCl_3(\kappa^3$-*R*,*R*-fbpza)] [M = Ti (**20**),

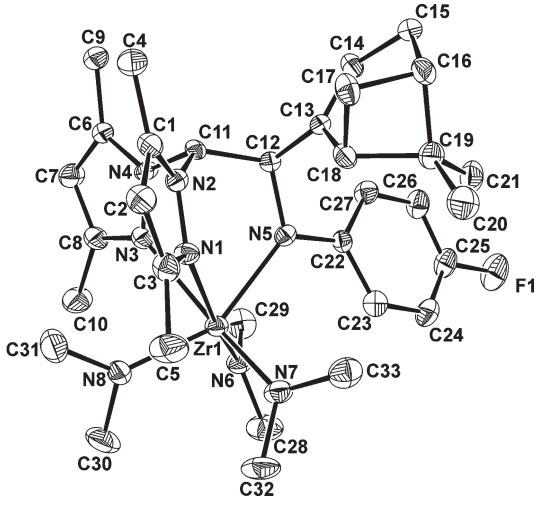
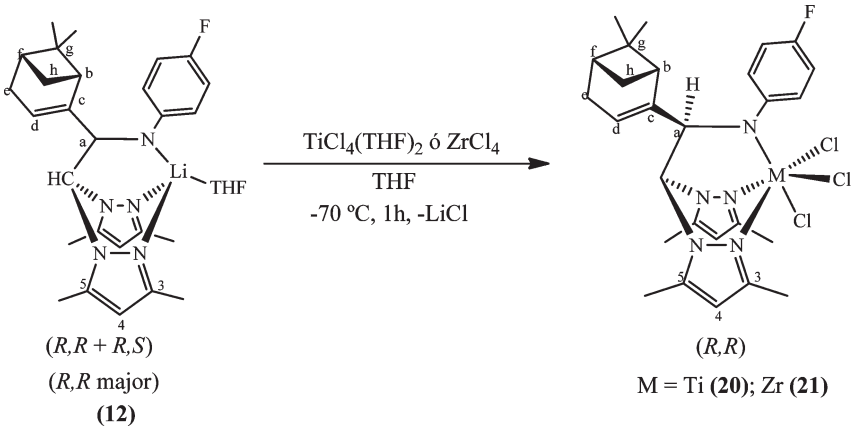


Figure 8. ORTEP view of the complex [$Zr(NMe_2)_3(\kappa^3$-*R*,*R*-fbpza)] (**24**). Ellipsoids are at the 30% probability level, and hydrogen atoms have been omitted for clarity.

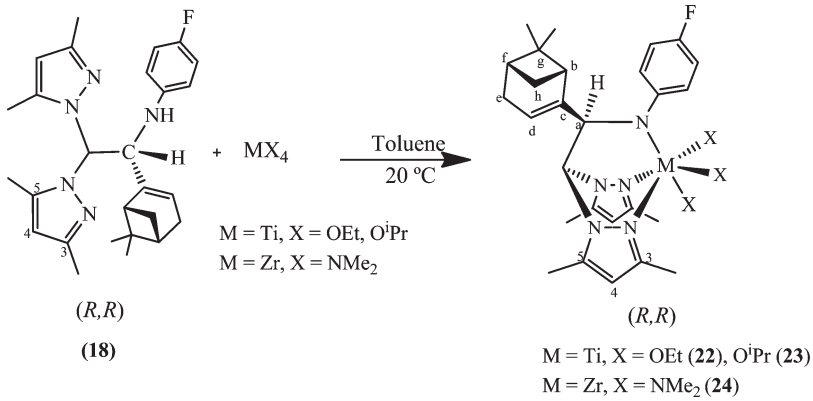
Table 3. Bond Lengths [Å] and Angles [deg] for **14**, **15**, and **24**

14		**15**		**24**	
Li(1)−O(1)	1.942(9)	N(1)−Li(1)	2.096(12)	Zr(1)−N(1)	2.423(6)
Li(1)−N(1)	2.090(10)	N(3)−Li(1)	2.088(12)	Zr(1)−N(3)	2.451(6)
Li(1)−N(3)	2.088(10)	O(1)−Li(1)	1.952(11)	Zr(1)−N(5)	2.235(6)
Li(1)−Cl(1)	2.255(9)	Cl(1)−Li(1)	2.254(11)	Zr(1)−N(6)	2.060(6)
C(12)−N(5)	1.459(6)	C(12)−N(5)	1.448(7)	Zr(1)−N(7)	2.075(6)
C(22)−N(5)	1.388(6)	C(22)−N(5)	1.395(7)	Zr(1)−N(8)	2.100(6)
C(11)−C(12)	1.539(7)	C(11)−C(12)	1.547(8)	N(5)−C(12)	1.481(8)
C(12)−C(13)	1.500(7)	C(12)−C(13)	1.514(8)	N(5)−C(22)	1.416(8)
C(25)−F(1)	1.388(6)	C(25)−Cl(2)	1.756(6)	C(11)−C(12)	1.544(9)
N(2)−C(11)−N(4)	109.8(4)	N(4)−C(11)−N(2)	110.3(4)	C(12)−C(13)	1.497(9)
N(2)−C(11)−C(12)	112.1(4)	N(4)−C(11)−C(12)	111.2(4)	C(22)−N(5)−C(12)	110.7(5)
N(4)−C(11)−C(12)	111.2(4)	N(2)−C(11)−C(12)	111.5(4)	N(2)−C(11)−N(4)	109.5(5)
N(5)−C(12)−C(13)	112.6(4)	N(5)−C(12)−C(13)	113.1(4)	N(2)−C(11)−C(12)	116.3(6)
N(5)−C(12)−C(11)	106.2(4)	N(5)−C(12)−C(11)	105.2(4)	N(4)−C(11)−C(12)	111.7(5)
C(13)−C(12)−C(11)	112.8(4)	C(13)−C(12)−C(11)	112.1(4)	N(5)−C(12)−C(13)	114.5(6)
C(22)−N(5)−C(12)	122.6(4)	C(22)−N(5)−C(12)	122.1(5)	N(5)−C(12)−C(11)	112.6(5)
O(1)−Li(1)−N(3)	103.1(4)	O(1)−Li(1)−N(3)	104.9(5)	C(13)−C(12)−C(11)	108.0(6)
N(1)−Li(1)−N(3)	92.5(4)	O(1)−Li(1)−N(1)	100.4(5)	N(6)−Zr(1)−N(5)	93.8(2)
O(1)−Li(1)−Cl(1)	115.0(4)	N(3)−Li(1)−N(1)	92.7(5)	N(7)−Zr(1)−N(5)	100.8(2)
N(1)−Li(1)−Cl(1)	127.3(4)	O(1)−Li(1)−Cl(1)	114.5(5)	N(8)−Zr(1)−N(5)	152.7(2)
N(3)−Li(1)−Cl(1)	115.0(4)	N(3)−Li(1)−Cl(1)	114.9(5)	N(6)−Zr(1)−N(1)	167.9(2)
		N(1)−Li(1)−Cl(1)	125.8(5)	N(7)−Zr(1)−N(1)	89.1(2)
				N(8)−Zr(1)−N(1)	84.0(2)
				N(5)−Zr(1)−N(1)	77.4(2)
				N(6)−Zr(1)−N(3)	93.8(2)
				N(7)−Zr(1)−N(3)	165.3(2)
				N(8)−Zr(1)−N(3)	79.9(2)
				N(5)−Zr(1)−N(3)	76.4(2)
				N(1)−Zr(1)−N(3)	76.2(2)

Scheme 5. Synthesis of Complexes [$MCl_3(\kappa^3$-*R*,*R*-fbpza)] (**20**−**21**)



Scheme 6. Synthesis of Complexes [$MX_3(\kappa^3$-*R*,*R*-fbpza)] (**22**−**24**)



Zr (**21**)], which were isolated by crystallization from CH_2Cl_2/*n*-hexane as red and yellow solids, respectively, in moderate yield (Scheme 5).

The amine compound **18** was reacted at room temperature with [MX_4] (M = Ti, X = O^{i}Pr, OEt; M = Zr; X = NMe_2,) in a 1:1 molar ratio in toluene to give, after the appropriate

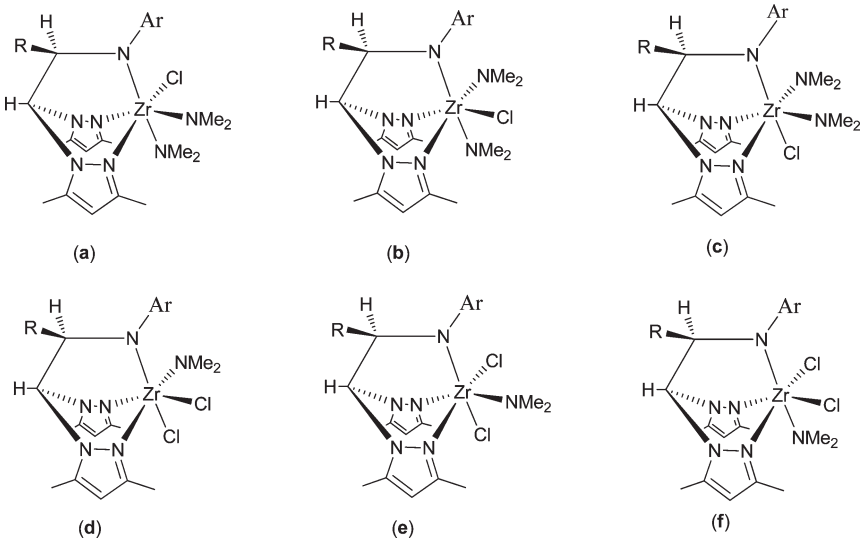
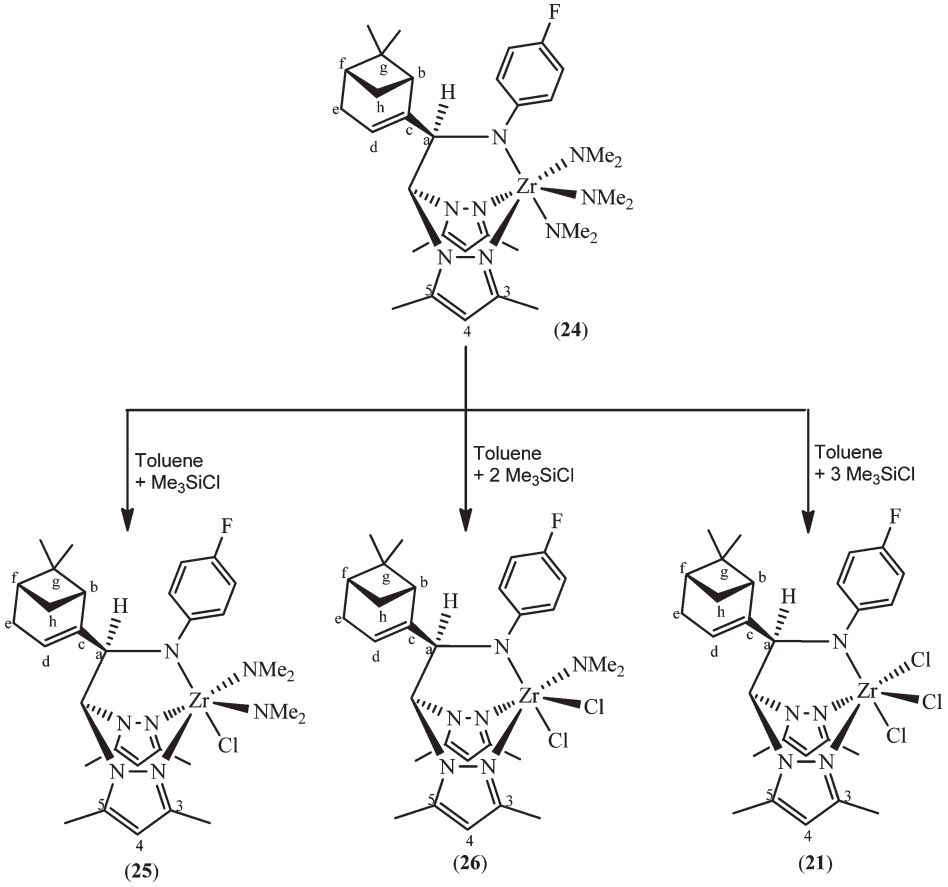


Figure 9. Proposed structures for the three possible diastereoisomers of complexes **25** and **26**.

Scheme 7. Diastereoselective Amide−Halide Exchange Process (Synthesis of Complexes **25** and **26**)



workup, the complexes $[MX_3(\kappa^3\text{-}R,R\text{-fbpza})]$ (**22**−**24**), which were isolated as yellow solids in good yield (*ca.* 75%; Scheme 6).

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **20**−**24** each exhibit one set of signals, which is consistent with the presence of one diastereoisomer. 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), the signals for the bicyclic moiety bound to the methylene bridge, and also those for the aryl substituent on the nitrogen atom. In addition, two multiplets of signals corresponding to the OR ligands and three singlets for the NMe_2 ligands were observed. The ^{1}H NOESY-1D experiments enabled the unequivocal assignment of all ^{1}H resonances. The results are consistent with an octahedral structure resulting from the κ^3-*NNN*-coordination of the ligand to the metal center (Schemes 5 and 6). The geometry found in solution was also confirmed in the solid state by an X-ray structural analysis of complex **24** (Figure 8).

The scorpionate ligand retains the *R*-configuration for the C^a (C12) atom. Selected bond lengths and angles are listed in Table 3. The structure consists of a heteroscorpionate ligand bonded to the zirconium atom through the two nitrogen atoms of pyrazole rings and the nitrogen atom of the amide group in a κ^3-*NNN*-coordination mode. In addition, the zirconium center is coordinated to three amide ligands. This center has a distorted octahedral environment with a major distortion in the N(8)−Zr(1)−N(5) angle and N(7)−Zr(1)−N(3) angle, which have values of 152.7(2)° and 165.3(2)°, respectively. The Zr(1)−N(1) and Zr(1)−N(3) bond distances of 2.423(6) Å and 2.451(6) Å, respectively, which are longer than those in similar heteroscorpionate complexes,[15] indicate that the amide ligands exert a *trans* influence.[16] The X-ray diffraction results confirm the presence in the solid state of one diastereoisomer for this complex.

Once it had been corroborated that these compounds were excellent reagents for the introduction of scorpionate 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 was 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.[3b,12d,17] The reaction of Me_3SiCl with [$Zr(NMe_2)_3(\kappa^3$-*R*,*R*-fbpza)] (**24**) in different molar ratios and under different experimental conditions (see Experimental Section) led to the preparation of the halide−amide-containing complexes [$ZrCl(NMe_2)_2(\kappa^3$-*R*,*R*-fbpza)] (**25**) and [$ZrCl_2(NMe_2)(\kappa^3$-*R*,*R*-fbpza)] (**26**) and the halide complex [$ZrCl_3(\kappa^3$-*R*,*R*-fbpza)] (**21**) (Scheme 7). The latter complex could also be obtained by the reaction of lithium compound **12** with $ZrCl_4$ (Scheme 5). The ^1H and $^{13}C\{^1H\}$ NMR spectra of **25** and **26** exhibit two distinct sets of pyrazole resonances. The ^1H NMR spectra contain two singlets for the NMe_2 moieties in complex **25** and a single broad signal for the NMe_2 moiety in complex **26**. These results are consistent with the presence of only one diastereoisomer and also with the proposed octahedral arrangement depicted in Scheme 7. Three isomers are possible for these complexes—two with the chloride (**25**) or amide (**26**) ligand *trans* to the nitrogen atoms of the pyrazolyl rings (Figure 9a−c or d,e) and another with the chloride (**25**) or amide (**26**) ligand *trans* to the nitrogen of the amide of scorpionate ligand (Figures 9c−f). In complex **25**, the absence of a response in the ^1H NOESY-1D 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 isomer in which the chloride ligand is *trans* to the nitrogen amide scorpionate ligand (isomer **c**) had been isolated. In complex **26**, however, the response in the ^1H NOESY-1D experiment from the proton of the chiral carbon on irradiating the methyl groups of NMe_2 group suggests that isomer "**d**" had been isolated. The configuration of **26** is 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 complex (**25**) could result from the difference between amide and pyrazole *trans* to the substituted ligand.[15]

Conclusions

In conclusion, we present a one-pot synthesis of new enantiopure NNN-donor scorpionate ligands by a diastereoselective nucleophilic 1,2-addition of organolithium reagents to C=N double bonds in imines, with control provided by a chiral auxiliary. The reactions studied gave good levels of diastereoselectivity. The potential offered by this efficient synthetic route has been fully developed and explored. In this respect, new enantiopure imines with a chiral substrate to control the stereochemistry of a newly created asymmetric center have been synthesized, and it was verifed that the *N*-aryl substituent in the starting imines has a profound effect on the enantioselectivity. The α,*β*-unsaturated imines and, in particular, those bearing a very electronegative (F or Cl) substituent in the *para* position, led to highly diastereoselective processes, with a preference for 1,2 addition over Michael-type conjugate addition. In the second part of this work, we verified the potential utility of these ligands as valuable scaffolds in organometallic/coordination chemistry through the preparation of new enantiomerically pure group 4 metal complexes in which the ligands behave in a tridentate manner with a κ^3-NNN coordination mode. Thus, a series of neutral chloride, amide, and alkoxide complexes was prepared by the treatment of MCl_4, $M(NMe_2)_4$, or $M(OR)_4$ with the lithium or amine−scorpionate compounds. 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 the chiral induction from these scorpionate ligands to the metal center in the amide−halide ligand exchange process in the coordination sphere.

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. ^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 spectra were recorded with the following acquisition parameters: an irradiation time of 2s and a number of scans of 256, using standard VARIAN-FT software. Two-dimensional 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 precursor compounds of titanium or zirconium, (1*R*)-(−)-myrtenal, and the different primary amines (isopropylamine, *p*-methylaniline, *p*-methoxyaniline, *p*-fluoroaniline, *o*-fluoroaniline, *m*-fluoroaniline, *p*-chloroaniline, *o*-chloroaniline and *o*-bromoaniline trime thylacetaldehyde, and *p*-tolualdehyde) were purchased

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from Aldrich. The compound bdmpzm [bdmpzm = bis-(3,5-dimethylpyrazol-1-yl)methane][18] was prepared as reported previously.

Preparation of Imines 1−9. Synthesis of Imine 1. (1*R*)-(−)-Myrtenal (1.00 g, 6.66 mmol) was added to isopropylamine (0.39 g, 6.66 mmol) in a 250 cm^3 Schlenk tube, and the reaction mixture was stirred and heated under reflux for 12 h. The reaction mixture was cooled to room temperature and dissolved in dry diethyl ether. The solution was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to give imine **1** as a red solid after crystallization from diethyl ether. Yield: 90%. $[\alpha]_D^{25}$ +21.4 (*c* 1.00, CH_2Cl_2). Anal. Calcd for $C_{14}H_{21}N$: C, 81.67; H, 11.00; N, 7.33. Found: C, 81.72; H, 11.11; N, 7.17. ^{1}H NMR (C_6D_6, 297 K): δ 7.74 (s, 1 H, CH^a), 1.26 (s, 3 H, Me^g), 0.71 (s, 3 H, Me^g), 5.86 (s, 1 H, H^d), 2.36 (m, 2 H, H^e), 2.06 (m, 1 H, H^f), 2.89 (m, 1 H, H^b), 2.34 (d, 1 H, H^h), 1.04 (d, 1 H, H^h), 3.26 (m, 1 H, *CH*Me_2), 1.08 (m, 6 H, CH*Me*$_2$). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 159.5 (C^a), 26.1 (Me^g), 21.0 (Me^g), 133.5 (C^d), 32.5 (C^e), 37.8 (C^g), 41.2 (C^f), 40.2 (C^b), 148.6 (C^c), 31.6 (C^h), 61.5 (*CH*Me_2), 24.5−24.4 (CH*Me*$_2$).

Synthesis of Imine 2. The synthetic procedure was the same as for imine **1**, using (1*R*)-(−)-myrtenal (1.00 g, 6.66 mmol) and *p*-methylaniline (0.71 g, 6.66 mmol), to give imine **2** as a red solid. Yield: 90%. $[\alpha]_D^{25}$ +25.3 (*c* 1.00, CH_2Cl_2). Anal. Calcd for $C_{17}H_{21}N$: C, 85.35; H, 8.79; N, 5.86. Found: C, 85.38; H, 8.75; N, 5.87. ^{1}H NMR (C_6D_6, 297 K): δ 8.04 (s, 1 H, CH^a), 1.41 (s, 3 H, Me^g), 0.87 (s, 3 H, Me^g), 6.24 (s, 1 H, H^d), 2.53 (m, 2 H, H^e), 2.21 (m, 1 H, H^f), 3.21 (m, 1 H, H^b), 2.54 (m, 1 H, H^h), 1.21 (d, 1 H, H^h), 2.35 (s, 3 H, *Me*Ph), 7.15 (d, 2 H, *m*-H), 7.05 (d, 2 H, *o*-H). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 160.7 (C^a), 26.2 (Me^g), 21.2 (Me^g), 137.5 (C^d), 33.0 (C^e), 37.9 (C^g), 41.1 (C^f), 40.2 (C^b), 149.2 (C^c), 31.6 (C^h), 21.3 (*Me*Ph), 129.8 (*m*-C), 121.1 (*o*-C), 135.3 (*p*-C), 150.2 (*ipso*-C).

Synthesis of Imine 3. The synthetic procedure was the same as for imine **1**, using (1*R*)-(−)-myrtenal (1.00 g, 6.66 mmol) and *p*-methoxyaniline (0.82 g, 6.66 mmol), to give imine **3** as a red solid. Yield: 89%. $[\alpha]_D^{25}$ +33.2 (*c* 1.00, CH_2Cl_2). Anal. Calcd for $C_{17}H_{21}NO$: C, 84.58; H, 9.25; N, 6.17. Found: C, 84.60; H, 9.21; N, 6.19. ^{1}H NMR (C_6D_6, 297 K): δ 7.98 (s, 1 H, CH^a), 1.24 (s, 3 H, Me^g), 0.80 (s, 3 H, Me^g), 5.81 (s, 1 H, H^d), 2.20 (m, 2 H, H^e), 1.98 (m, 1 H, H^f), 3.61 (m, 1 H, H^b), 2.39 (m, 1 H, H^h), 1.14 (d, 1 H, H^h), 3.26 (s, 3 H, Me), 6.72−7.15 (m, 4H, *m*-H or *o*-H). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 158.2 (C^a), 26.0 (Me^g), 21.1 (Me^g), 135.4 (C^d), 32.7 (C^e), 37.6 (C^g), 41.2 (C^f), 40.3 (C^b), 149.7 (C^c), 31.5 (C^h), 54.8 (O*Me*), 114.5−122.5 (*m*-C or *o*-C), 145.7 (*p*-C), 158.4 (*ipso*-C).

Synthesis of Imine 4. The synthetic procedure was the same as for imine **3**, using (1*R*)-(−)-myrtenal (1.00 g, 6.66 mmol) and *p*-fluoroaniline (0.74 g, 6.66 mmol), to give imine **4** as a red solid. Yield: 90%. $[\alpha]_D^{25}$ −51.83 (*c* 1.00, THF). Anal. Calcd for $C_{16}H_{18}FN$: C, 79.01; H, 7.41; N, 5.76. Found: C, 79.15; H, 7.43; N, 5.78. ^{1}H NMR (C_6D_6, 297 K): δ 7.73 (s, 1 H, CH^a), 1.19 (s, 3 H, Me^g), 0.74 (s, 3 H, Me^g), 5.81 (s, 1 H, H^d), 2.16 (m, 2 H, H^e), 1.91 (m, 1 H, H^f), 3.43 (m, 1 H, H^b), 2.34 (m, 1 H, H^h), 1.06 (d, 1 H, H^h), 6.85 (t, 2 H, $J_{HH} = J_{HF} = 8.3$ Hz, *m*-H), 6.73 (dd, 2 H, $J_{HH} = 8.8$ Hz, $J_{HF} = 4.9$ Hz, *o*-H). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 160.2 (C^a), 25.9 (Me^g), 21.0 (Me^g), 136.9 (C^d), 32.7 (C^e), 37.6 (C^g), 41.1 (C^f), 40.2 (C^b), 149.5 (C^c), 31.4 (C^h), 115.7 (d, $J_{CF} = 22.1$ Hz, *m*-C), 122.5 (d, $J_{CF} = 7.6$ Hz, *o*-C), 161.2 (d, $J_{CF} = 243.4$ Hz, *p*-C), 148.8 (*ipso*-C).

Synthesis of Imine 5. The synthetic procedure was the same as for imine **3**, using (1*R*)-(−)-myrtenal (1.00 g, 6.66 mmol) and *o*-fluoroaniline (0.74 g, 6.66 mmol), to give imine **5** as a red solid. Yield: 85%. $[\alpha]_D^{25}$ −37.10 (*c* 1.00, THF). Anal. Calcd for $C_{16}H_{18}FN$: C, 79.01; H, 7.41; N, 5.76. Found: C, 78.85; H, 7.46; N, 5.81. ^{1}H NMR (C_6D_6, 297 K): δ 7.68 (s, 1 H, CH^a), 1.18 (s, 3 H, Me^g), 0.72 (s, 3 H, Me^g), 5.79 (s, 1 H, H^d), 2.14 (m, 2 H, H^e), 1.52 (m, 1 H, H^f), 3.38 (m, 1 H, H^b), 2.75 (m, 1 H, H^h), 1.04 (d, 1 H, H^h), 6.62−6.85 (m, 4 H, *m*,*o*,*p*-H). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 156.5 (C^a), 25.8 (Me^g), 20.9 (Me^g), 137.8 (C^d), 32.7 (C^e), 37.6 (C^g), 41.0 (C^f), 40.0 (C^b), 151.5 (C^c), 31.3 (C^h), 116.2 (d, $J_{CF} = 19.8$ Hz, *m*-C), 124.4 (d, $J_{CF} = 3.8$ Hz, *m*-C), 155.5 (d, $J_{CF} = 248.0$ Hz, *o*-C), 122.4 (d, $J_{CF} = 2.3$ Hz, *o*-C), 126.0 (d, $J_{CF} = 7.6$ Hz, *p*-C), 149.6 (*ipso*-C).

Synthesis of Imine 6. The synthetic procedure was the same as for imine **3**, using (1*R*)-(−)-myrtenal (1.00 g, 6.66 mmol) and *m*-fluoroaniline (0.74 g, 6.66 mmol), to give imine **6** as a red solid. Yield: 90%. $[\alpha]_D^{25}$ −73.09 (*c* 1.00, THF). Anal. Calcd for $C_{16}H_{18}FN$: C, 79.01; H, 7.41; N, 5.76. Found: C, 79.20; H, 7.40; N, 5.79. ^{1}H NMR (C_6D_6, 297 K): δ 7.88 (s, 1 H, CH^a), 1.18 (s, 3 H, Me^g), 0.74 (s, 3 H, Me^g), 5.80 (s, 1 H, H^d), 2.16 (m, 2 H, H^e), 1.89 (m, 1 H, H^f), 3.48 (m, 1 H, H^b), 2.32 (m, 1 H, H^h), 1.04 (d, 1 H, H^h), 6.62−6.85 (m, 4 H, *m*,*o*,*p*-H). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 156.4 (C^a), 25.8 (Me^g), 20.9 (Me^g), 137.3 (C^d), 32.7 (C^e), 37.6 (C^g), 41.1 (C^f), 40.2 (C^b), 150.5 (C^c), 31.4 (C^h), 126.1 (d, $J_{CF} = 7.4$ Hz, *m*-C), 157.2 (d, $J_{CF} = 245.3$ Hz, *m*-C), 115.3 (d, $J_{CF} = 20.2$ Hz, *o*-C), 121.4 (d, $J_{CF} = 3.8$ Hz, *o*-C), 119.3 (d, $J_{CF} = 20.2$ Hz, *p*-C), 148.3 (*ipso*-C).

Synthesis of Imine 7. The synthetic procedure was the same as for imine **3**, using (1*R*)-(−)-myrtenal (1.00 g, 6.66 mmol) and *p*-chloroaniline (0.82 g, 6.66 mmol), to give imine **7** as a red solid. Yield: 91%. $[\alpha]_D^{25}$ −54.02 (*c* 1.00, THF). Anal. Calcd for $C_{16}H_{18}ClN$: C, 74.00; H, 6.94; N, 5.40. Found: C, 74.13; H, 6.98; N, 5.38. ^{1}H NMR (C_6D_6, 297 K): δ 7.68 (s, 1 H, CH^a), 1.19 (s, 3 H, Me^g), 0.73 (s, 3 H, Me^g), 5.80 (s, 1 H, H^d), 2.16 (m, 2 H, H^e), 1.90 (m, 1 H, H^f), 3.41 (m, 1 H, H^b), 2.33 (m, 1 H, H^h), 1.05 (d, 1 H, H^h), 7.01 (d, 2 H, *m*-H), 6.77 (d, 2 H, *o*-H). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 160.5 (C^a), 25.9 (Me^g), 21.0 (Me^g), 137.4 (C^d), 32.8 (C^e), 37.6 (C^g), 41.0 (C^f), 40.2 (C^b), 149.4 (C^c), 31.4 (C^h), 129.2 (*m*-C), 122.5 (*o*-C), 131.0 (*p*-C), 151.3 (*ipso*-C).

Synthesis of Imine 8. The synthetic procedure was the same as for imine **3**, using (1*R*)-(−)-myrtenal (1.00 g, 6.66 mmol) and *o*-chloroaniline (0.82 g, 6.66 mmol), to give imine **8** as a red solid. Yield: 83%. $[\alpha]_D^{25}$ −49.98 (*c* 1.00, THF). Anal. Calcd for $C_{16}H_{18}ClN$: C, 74.00; H, 6.94; N, 5.40. Found: C, 74.11; H, 6.86; N, 5.30. ^{1}H NMR (C_6D_6, 297 K): δ 7.63 (s, 1 H, CH^a), 1.18 (s, 3 H, Me^g), 0.76 (s, 3 H, Me^g), 5.78 (s, 1 H, H^d), 2.13 (m, 2 H, H^e), 2.87 (m, 1 H, H^f), 3.45 (m, 1 H, H^b), 2.38 (m, 1 H, H^h), 1.04 (d, 1 H, H^h), 6.62−6.82 (m, 4 H, *m*,*o*,*p*-H). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 157.5 (C^a), 25.9 (Me^g), 20.9 (Me^g), 137.3 (C^d), 32.8 (C^e), 37.6 (C^g), 41.0 (C^f), 40.1 (C^b), 149.4 (C^c), 31.3 (C^h), 122.1−126.3 (*m*,*o*,*p*-C), 162.8 (*o*-C), 149.5 (*ipso*-C).

Synthesis of Imine 9. The synthetic procedure was the same as for imine **3**, using (1*R*)-(−)-myrtenal (1.00 g, 6.66 mmol) and *o*-bromoaniline (1.15 g, 6.66 mmol), to give imine **9** as a red solid. Yield: 90%. $[\alpha]_D^{25}$ −50.23 (*c* 1.00, THF). Anal. Calcd for $C_{16}H_{18}BrN$: C, 63.18; H, 5.92; N, 4.60. Found: C, 63.21; H, 5.96; N, 4.18. ^{1}H NMR (C_6D_6, 297 K): δ 7.61 (s, 1 H, CH^a), 1.18 (s, 3 H, Me^g), 0.72 (s, 3 H, Me^g), 5.77 (s, 1 H, H^d), 2.16 (m, 2 H, H^e), 1.89 (m, 1 H, H^f), 3.36 (m, 1 H, H^b), 2.32 (m, 1 H, H^h), 1.02 (d, 1 H, H^h), 6.73−7.05 (m, 4 H, *m*,*o*,*p*-H). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 158.4 (C^a), 26.1 (Me^g), 21.2 (Me^g), 138.0 (C^d), 32.9 (C^e), 37.8 (C^g), 41.6 (C^f), 40.6 (C^b), 151.7 (C^c), 31.6 (C^h), 123.4−127.3 (*m*,*o*,*p*-C), 162.9 (*o*-C), 149.6 (*ipso*-C).

Preparation of Scorpionate Ligands 10−19. Synthesis of [Li(κ^3-mbpza)(THF)] (10). 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^nLi (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 −10 °C, and the resulting yellow suspension was treated with a solution of imine **2** (1.17 g, 4.89 mmol) in dry THF (20 cm^3), after which the solution was stirred for 30 min. The reaction mixture was warmed to room temperature and was stirred for 1 h. The solvent was removed to give a volume of 10 cm^3, and the addition of hexane (70 cm^3) gave a brown solid. The solid was filtered off (Celite) and dried under reduced pressure to give compound **10**. The yield was 70%, and the diastereomeric excess was 62% (de).

$[\alpha]_D^{25}$ −27.12 (*c* 1.00, THF). Anal. Calcd for $C_{32}H_{44}LiN_5O$: C, 74.15; H, 8.24; N, 16.02. Found: C, 74.01; H, 8.22; N, 15.84. ^{1}H NMR (C_6D_6, 297 K; major isomer): δ 6.59 (d, 1 H, CH), 5.67 (m, 1 H, CH^a), 5.53 (s, 2 H, $H^{4,4'}$), 2.16 (s, 3 H, Me^3), 2.14 (s, 3 H, $Me^{3'}$), 2.41 (s, 3 H, Me^5), 2.28 (s, 3 H, $Me^{5'}$), 1.12 (s, 3 H, Me^g), 0.50 (s, 3 H, Me^g), 4.15 (d, 1 H, H^d), 1.98 (m, 2 H, H^e), 1.80 (m, 1 H, H^f), 2.36 (m, 1 H, H^b), 2.25 (m, 1 H, $H^{h,h}$), 0.80 (m, 1 H, $H^{h,h}$), 6.86 (d, 2 H, *m*-H), 6.54 (d, 2 H, *o*-H), 2.07 (s, 3 H, Me) 3.62 (m, 4 H, THF), 1.77 (m, 4 H, THF). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 74.2 (CH), 59.7 (C^a), 107.8−106.3 ($C^{4,4'}$), 148.0−147.5 ($C^{3,3'}$), 141.2−140.0 ($C^{5,5'}$), 13.7−13.5 ($Me^{3,3'}$), 11.6−11.1 ($Me^{5,5'}$), 26.3 (Me^g), 21.2 (Me^g), 122.7 (C^d), 31.9 (C^e), 38.1 (C^g), 40.9 (C^f), 42.1 (C^b), 114.3 (C^c), 31.4 (C^h), 20.5 (*Me*Ph), 129.7 (*m*-C), 114.3 (*o*-C), 145.0 (*p*-C), 145.2 (*ipso*-C), 67.0−25.2 (THF).

^{1}H NMR (C_6D_6, 297 K; minor isomer): δ 6.53 (d, 1 H, CH), 5.67 (m, 1 H, CH^a), 5.53 (s, 2 H, $H^{4,4'}$), 2.16 (s, 3 H, Me^3), 2.14 (s, 3 H, $Me^{3'}$), 2.41 (s, 3 H, Me^5), 2.28 (s, 3 H, $Me^{5'}$), 1.17 (s, 3 H, Me^g), 0.54 (s, 3 H, Me^g), 4.54 (d, 1 H, H^d), 1.98 (m, 2 H, H^e), 1.80 (m, 1 H, H^f), 2.36 (m, 1 H, H^b), 2.25 (m, 1 H, $H^{h,h}$), 0.80 (m, 1 H, $H^{h,h}$), 6.97 (d, 2 H, *m*-H), 6.48 (d, 2 H, *o*-H), 2.07 (s, 3 H, Me), 3.62 (m, 4 H, THF), 1.77 (m, 4 H, THF). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 75.0 (CH), 59.8 (C^a), 107.6−106.7 ($C^{4,4'}$), 148.0−147.5 ($C^{3,3'}$), 140.2−140.0 ($C^{5,5'}$), 14.2−14.2 ($Me^{3,3'}$), 11.3−11.3 ($Me^{5,5'}$), 25.7 (Me^g), 20.9 (Me^g), 122.4 (C^d), 32.0 (C^e), 38.1 (C^g), 41.3 (C^f), 42.6 (C^b), 113.8 (C^c), 31.4 (C^h), 20.5 (*Me*Ph), 129.8 (*m*-C), 113.8 (*o*-C), 145.0 (*p*-C), 145.5 (*ipso*-C), 67.0−25.2 (THF).

Synthesis of [Li(κ^3-mobpza)(THF)] (11). The synthetic procedure was the same as for complex **10**, using bdmpzm (1.00 g, 4.89 mmol), 1.6 M Bu^nLi (3.06 cm^3, 4.89 mmol) in hexane, and imine **3** (1.25 g, 4.89 mmol), to give compound **11** as a red solid. The yield was 75%, and the diastereomeric excess was 50% (de). $[\alpha]_D^{25}$ −22.21 (*c* 1.00, THF). Anal. Calcd for $C_{32}H_{44}LiN_5O_2$: C, 71.53; H, 7.95; N, 15.45. Found: C, 71.55; H, 7.98; N, 15.40. ^{1}H NMR (C_6D_6, 297 K; major isomer): δ 6.56 (d, 1 H, CH), 5.58 (d, 1 H, CH^a), 5.51 (s, 2 H, $H^{4,4'}$), 2.12 (s, 3 H, Me^3), 2.08 (s, 3 H, $Me^{3'}$), 2.40 (s, 3 H, Me^5), 2.25 (s, 3 H, $Me^{5'}$), 1.11 (s, 3 H, Me^g), 0.47 (s, 3 H, Me^g), 4.29 (d, 1 H, H^d), 1.97 (m, 2 H, H^e), 1.77 (m, 1 H, H^f), 2.40 (s, 1 H, H^b), 2.20 (m, 1 H, $H^{h,h}$), 0.71 (m, 1 H, $H^{h,h}$), 6.52−6.64 (m, 4H, *m*-H or *o*-H), 3.29 (s, 3 H, Me), 3.68 (m, 4 H, THF), 1.84 (m, 4 H, THF). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 72.9 (CH), 59.1 (C^a), 106.5−105.0 ($C^{4,4'}$), 146.3−146.2 ($C^{3,3'}$), 143.8−138.8 ($C^{5,5'}$), 12.3−12.2 ($Me^{3,3'}$), 9.9−9.7 ($Me^{5,5'}$), 25.1 (Me^g), 20.0 (Me^g), 121.2 (C^d), 30.6 (C^e), 36.9 (C^g), 39.6 (C^f), 40.7 (C^b), 113.3 (C^c), 30.2 (C^h), 53.8 (*Me*OPh), 113.5−114.1 (*m*-C or *o*-C), 151.4 (*p*-C), 157.0 (*ipso*-C), 67.0−25.2 (THF).

^{1}H NMR (C_6D_6, 297 K; minor isomer): δ 6.54 (d, 1 H, CH), 5.58 (d, 1 H, CH^a), 5.51 (s, 2 H, $H^{4,4'}$), 2.12 (s, 3 H, Me^3), 2.08 (s, 3 H, $Me^{3'}$), 2.40 (s, 3 H, Me^5), 2.25 (s, 3 H, $Me^{5'}$), 0.82 (s, 3 H, Me^g), 0.21 (s, 3 H, Me^g), 4.49 (d, 1 H, H^d), 1.97 (m, 2 H, H^e), 1.77 (m, 1 H, H^f), 2.40 (s, 1 H, H^b), 2.20 (m, 1 H, $H^{h,h}$), 0.71 (m, 1 H, $H^{h,h}$), 6.50−6.72 (m, 4H, *m*-H or *o*-H), 3.26 (s, 3 H, Me), 3.62 (m, 4 H, THF), 1.77 (m, 4 H, THF). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 73.6 (CH), 59.7 (C^a), 106.3−105.4 ($C^{4,4'}$), 146.1−146.0 ($C^{3,3'}$), 144.4−139.2 ($C^{5,5'}$), 13.0−12.4 ($Me^{3,3'}$), 10.2−10.0 ($Me^{5,5'}$), 24.7 (Me^g), 19.8 (Me^g), 121.3 (C^d), 31.4 (C^e), 36.8 (C^g), 39.9 (C^f), 41.6 (C^b), 113.0 (C^c), 30.2 (C^h), 53.6 (*Me*OPh), 114.5−113.4 (*m*-C or *o*-C), 151.6 (*p*-C), 157.1 (*ipso*-C), 66.8−24.4 (THF).

Synthesis of [Li(κ^3-fbpza)(THF)] (12). The synthetic procedure was the same as for complex **10**, using bdmpzm (1.00 g, 4.89 mmol), 1.6 M Bu^nLi (3.06 cm^3, 4.89 mmol) in hexane, and imine **4** (1.19 g, 4.89 mmol), to give compound **12** as a brown solid. The yield was 90%, and the diastereomeric excess was 78% (de). $[\alpha]_D^{25}$ −4.34 (*c* 1.00, CH_2Cl_2). Anal. Calcd for $C_{31}H_{41}LiFN_5O$: C, 71.53; H, 7.28; N, 15.45. Found: C, 71.58; H, 7.32; N, 15.40. ^{1}H NMR (C_6D_6, 297 K; major isomer): δ 6.52 (d, 1 H, CH), 5.50 (m, 1 H, CH^a), 5.50 (s, 2 H, $H^{4,4'}$), 2.14 (s, 3 H, Me^3), 2.11 (s, 3 H, $Me^{3'}$), 2.33 (s, 3 H, Me^5), 2.21 (s, 3 H, $Me^{5'}$), 1.10 (s, 3 H, Me^g), 0.42 (s, 3 H, Me^g), 4.15 (d, 1 H, H^d), 1.95 (m, 2 H, H^e), 1.78 (m, 1 H, H^f), 2.31 (m, 1 H, H^b), 2.10 (m, 1 H, $H^{h,h}$), 0.74 (d, 1 H, $H^{h,h}$), 6.69 (t, 2 H, $J_{HH} = J_{HF} = 8.6$ Hz, *m*-H), 6.30 (dd, 2 H, $J_{HH} = 9.3$ Hz, $J_{HF} = 4.3$ Hz, *o*-H), 3.62 (m, 4 H, THF), 1.77 (m, 4 H, THF). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 74.1 (CH), 60.1 (C^a), 107.8−106.4 ($C^{4,4'}$), 147.6−147.5 ($C^{3,3'}$), 144.6−140.2 ($C^{5,5'}$), 13.7−13.5 ($Me^{3,3'}$), 11.5−11.1 ($Me^{5,5'}$), 26.3 (Me^g), 21.1 (Me^g), 122.9 (C^d), 31.8 (C^e), 38.1 (C^g), 40.8 (C^f), 42.0 (C^b), 113.1 (C^c), 31.4 (C^h), 115.5 (d, $J_{CF} = 22.1$ Hz, *m*-C), 114.9 (d, $J_{CF} = 7.6$ Hz, *o*-C), 156.3 (d, $J_{CF} = 234.2$ Hz, *p*-C), 157.2 (*ipso*-C), 67.0−25.1 (THF).

^{1}H NMR (C_6D_6, 297 K; minor isomer): δ 6.48 (d, 1 H, CH), 5.48 (m, 1 H, CH^a), 5.50 (s, 2 H, $H^{4,4'}$), 2.14 (s, 3 H, Me^3), 2.11 (s, 3 H, $Me^{3'}$), 2.33 (s, 3 H, Me^5), 2.21 (s, 3 H, $Me^{5'}$), 1.15 (s, 3 H, Me^g), 0.47 (s, 3 H, Me^g), 4.58 (d, 1 H, H^d), 1.95 (m, 2 H, H^e), 1.78 (m, 1 H, H^f), 2.31 (m, 1 H, H^b), 2.10 (m, 1 H, $H^{h,h}$), 0.74 (d, 1 H, $H^{h,h}$), 6.79 (t, 2 H, $J_{HH} = J_{HF} = 8.7$ Hz, *m*-H), 6.22 (dd, 2 H, $J_{HH} = 9.2$ Hz, $J_{HF} = 4.3$ Hz, *o*-H), 3.62 (m, 4 H, THF), 1.77 (m, 4 H, THF). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 74.5 (CH), 60.5 (C^a), 107.5−106.8 ($C^{4,4'}$), 147.6−147.5 ($C^{3,3'}$), 143.7−141.1 ($C^{5,5'}$), 14.1−14.0 ($Me^{3,3'}$), 11.2−10.9 ($Me^{5,5'}$), 26.2 (Me^g), 20.9 (Me^g), 122.7 (C^d), 32.0 (C^e), 38.0 (C^g), 41.3 (C^f), 42.5 (C^b), 113.0 (C^c), 31.4 (C^h), 115.1 (d, $J_{CF} = 22.2$ Hz, *m*-C), 114.3 (d, $J_{CF} = 7.3$ Hz, *o*-C), 156.8 (d, $J_{CF} = 234.8$ Hz, *p*-C), 157.3 (*ipso*-C), 67.0−25.2 (THF).

Synthesis of [Li(κ^3-clbpza)(THF)] (13). The synthetic procedure was the same as for complex **10**, using bdmpzm (1.00 g, 4.89 mmol), 1.6 M Bu^nLi (3.06 cm^3, 4.89 mmol) in hexane, and imine **7** (1.27 g, 4.89 mmol), to give compound **13** as a red solid. The yield was 90%, and the diastereomeric excess was 86% (de). $[\alpha]_D^{25}$ −6.38 (*c* 1.00, CH_2Cl_2). Anal. Calcd for $C_{31}H_{41}LiClN_5O$: C, 69.02; H, 7.03; N, 14.91. Found: C, 69.23; H, 7.16; N, 14.84. ^{1}H NMR (C_6D_6, 297 K; major isomer): δ 6.49 (d, 1 H, CH), 5.50 (m, 1 H, CH^a), 5.50 (s, 2 H, $H^{4,4'}$), 2.13 (s, 3 H, Me^3), 2.10 (s, 3 H, $Me^{3'}$), 2.28 (s, 3 H, Me^5), 2.18 (s, 3 H, $Me^{5'}$), 1.08 (s, 3 H, Me^g), 0.40 (s, 3 H, Me^g), 4.21 (d, 1 H, H^d), 1.93 (m, 2 H, H^e), 1.76 (m, 1 H, H^f), 2.26 (m, 1 H, H^b), 2.18 (m, 1 H, $H^{h,h}$), 0.75 (m, 1 H, $H^{h,h}$), 6.95 (d, 2 H, *m*-H), 6.23 (d, 2 H, *o*-H), 3.62 (m, 4 H, THF), 1.77 (m, 4 H, THF). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 74.0 (CH), 59.6 (C^a), 107.8−106.4 ($C^{4,4'}$), 147.6−145.9 ($C^{3,3'}$), 141.0−140.1 ($C^{5,5'}$), 13.7−13.5 ($Me^{3,3'}$), 11.5−11.0 ($Me^{5,5'}$), 26.2 (Me^g), 20.8 (Me^g), 123.0 (C^d), 31.8 (C^e), 38.1 (C^g), 40.8 (C^f), 42.1 (C^b), 113.6 (C^c), 31.3 (C^h), 115.2 (*m*-C), 115.1 (*o*-C), 155.2 (*p*-C), 157.0 (*ipso*-C), 66.8−25.4 (THF).

^{1}H NMR (C_6D_6, 297 K; minor isomer): δ 6.45 (d, 1 H, CH), 5.50 (m, 1 H, CH^a), 5.50 (s, 2 H, $H^{4,4'}$), 2.13 (s, 3 H, Me^3), 2.10 (s, 3 H, $Me^{3'}$), 2.28 (s, 3 H, Me^5), 2.18 (s, 3 H, $Me^{5'}$), 1.10 (s, 3 H, Me^g), 0.48 (s, 3 H, Me^g), 4.73 (d, 1 H, H^d), 1.93 (m, 2 H, H^e), 1.76 (m, 1 H, H^f), 2.26 (m, 1 H, H^b), 2.18 (m, 1 H, $H^{h,h}$), 0.75 (m, 1 H, $H^{h,h}$), 7.05 (d, 2 H, *m*-H), 6.09 (d, 2 H, *o*-H), 3.62 (m, 4 H, THF), 1.77 (m, 4 H, THF). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 74.4 (CH), 59.7 (C^a), 107.5−106.8 ($C^{4,4'}$), 148.0−147.6 ($C^{3,3'}$), 144.3−140.2 ($C^{5,5'}$), 14.2−13.6 ($Me^{3,3'}$), 12.1−11.0 ($Me^{5,5'}$), 25.6 (Me^g), 19.8 (Me^g), 122.5 (C^d), 32.8 (C^e), 38.0 (C^g), 41.0 (C^f), 43.0 (C^b), 113.9 (C^c), 31.3 (C^h), 116.0 (*m*-C), 115.2 (*o*-C), 155.3 (*p*-C), 157.2 (*ipso*-C), 67.0−25.2 (THF).

Synthesis of [LiCl(κ^2-*R*,*R*-fbpzaH)(THF)] (14). In a 250 cm^3 Schlenk tube, [Li(κ^3-fbpza)(THF)] (**12**; 1.00 g, 1.90 mmol) was dissolved in dry THF (70 cm^3). Saturated aqueous ammonium chloride (20 cm^3) was added, and the mixture was concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2. The addition of hexane gave a red solid. The solid was filtered off and dried under reduced pressure to give compound **14**. Yield: 69%. $[\alpha]_D^{25}$ −10.21 (*c* 1.00, THF). Anal. Calcd for $C_{31}H_{42}LiClFN_5O$: C, 66.26; H, 7.48; N, 12.47. Found: C, 66.31; H, 7.52; N, 12.45. ^{1}H NMR (C_6D_6, 297 K): δ 6.71 (m, 1 H, CH), 5.55 (m, 1 H, CH^a), 5.46 (s, 1 H, H^4), 5.41 (s, 1 H, $H^{4'}$), 2.13 (s, 3 H, Me^3), 2.08 (s, 3 H, $Me^{3'}$), 2.28 (s, 3 H, Me^5), 2.23 (s, 3 H, $Me^{5'}$), 0.41 (s, 3 H, Me^g), 1.11 (s, 3 H, Me^g), 5.49 (s, 1 H, H^d), 1.93 (m, 2 H, H^e), 1.76 (m, 1 H, H^f), 2.37 (s, 1 H, H^b), 2.22 (m, 1 H, $H^{h,h}$),

0.72 (d, 1 H, $H^{h,h}$), 6.71 (t, 2 H, $J_{HH} = J_{HF} = 8.7$ Hz, *m*-H), 6.30 (dd, 2 H, $J_{HH} = 9.3$ Hz, $J_{HF} = 4.3$ Hz, *o*-H), 8.95 (s, 1 H, NH), 3.57 (m, 4 H, THF), 1.39 (m, 4 H, THF). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 73.7 (CH), 60.3 (C^a), 107.9−106.5 ($C^{4,4'}$), 147.7−144.4 ($C^{3,3'}$), 147.2−143.4 ($C^{5,5'}$), 13.6−13.1 ($Me^{3,3'}$), 11.5−11.2 ($Me^{5,5'}$), 26.2 (Me^g), 21.1 (Me^g), 123.2 (C^d), 31.9 (C^e), 38.1 (C^g), 40.8 (C^f), 42.2 (C^b), 140.6 (C^c), 31.4 (C^h), 115.5 (d, J_{CF} = 22.1 Hz, *m*-C), 115.2 (d, J_{CF} = 6.9 Hz, *o*-C), 156.4 (d, J_{CF} = 235.7 Hz, *p*-C), 141.7 (*ipso*-C), 70.4−27.1 (THF).

Synthesis of [LiCl(κ^2-*R*,*R*-clbpzaH)(THF)] (15). The synthetic procedure was the same as for complex **14**, using [Li(κ^3-clbpza)(THF)] (**13**) and saturated aqueous ammonium chloride (20 cm^3), to give compound **15** as a red solid. Yield: 70%. $[\alpha]_D^{25}$ −12.46 (*c* 1.00, THF). Anal. Calcd for $C_{31}H_{42}LiCl_2N_5O$: C, 64.38; H, 7.27; N, 12.11. Found: C, 64.40; H, 7.25; N, 12.16. ^{1}H NMR (C_6D_6, 297 K): δ 6.65 (d, 1 H, CH), 5.52 (s, 1 H, CH^a), 5.48 (s, 2 H, $H^{4,4'}$), 2.15 (s, 3 H, Me^3), 2.11 (s, 3 H, $Me^{3'}$), 2.30 (s, 3 H, Me^5), 2.24 (s, 3 H, $Me^{5'}$), 0.49 (s, 3 H, Me^g), 1.10 (s, 3 H, Me^g), 5.42 (d, 1 H, H^d), 1.91 (m, 2 H, H^e), 1.74 (m, 1 H, H^f), 2.25 (s, 1 H, H^b), 2.17 (s, 1 H, $H^{h,h}$), 0.73 (m, 1 H, $H^{h,h}$), 6.97 (d, 2 H, *m*-H), 6.25 (d, 2 H, *o*-H), 8.47 (s, 1 H, NH), 3.62 (m, 4 H, THF), 1.77 (m, 4 H, THF). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 73.6 (CH), 60.0 (C^a), 108.5−106.5 ($C^{4,4'}$), 147.3−145.1 ($C^{3,3'}$), 147.6−142.9 ($C^{5,5'}$), 13.5−13.1 ($Me^{3,3'}$), 11.5−11.3 ($Me^{5,5'}$), 26.2 (Me^g), 21.1 (Me^g), 123.1 (C^d), 32.7 (C^e), 38.0 (C^g), 40.8 (C^f), 42.0 (C^b), 140.7 (C^c), 31.8 (C^h), 115.8−115.6 (*m*-C), 114.6 (*o*-C), 156.8 (*p*-C), 161.3 (*ipso*-C), 67.0−25.2 (THF).

Synthesis of (*R*,*R*-mbpzaH) (16). In a 250 cm^3 Schlenk tube, [Li(κ^3-mbpza)(THF)] (**10**; 1.00 g, 1.92 mmol) was dissolved in dry THF (70 cm^3). Distilled water (34.55 μL, 1.92 mmol) was added, and the solution was stirred for 1 h. The solvent was removed under vacuum conditions, and the resulting solid was extracted with dichloromethane. The solvent was removed to give **16** as a red solid. Yield: 63%. $[\alpha]_D^{25}$ −20.43 (*c* 1.00, THF). Anal. Calcd for $C_{28}H_{37}N_5$: C, 75.85; H, 8.35; N, 15.80. Found: C, 75.87; H, 8.37; N, 15.76. ^{1}H NMR (C_6D_6, 297 K): δ 6.51 (m, 1 H, CH), 5.60 (s, 1 H, CH^a), 5.50 (s, 2 H, $H^{4,4'}$), 1.98 (s, 3 H, Me^3), 1.96 (s, 3 H, $Me^{3'}$), 2.13 (s, 3 H, Me^5), 2.11 (s, 3 H, $Me^{5'}$), 1.10 (s, 3 H, Me^g), 0.45 (s, 3 H, Me^g), 5.48 (m, 1 H, H^d), 1.92 (m, 2 H, H^e), 1.70 (m, 1 H, H^f), 2.42 (s, 1 H, H^b), 2.10 (m, 1 H, $H^{h,h}$), 0.73 (d, 1 H, $H^{h,h}$), 6.85 (m, 2 H, *m*-H), 6.59 (m, 2 H, *o*-H), 2.07 (s, 3 H, Me), 11.64 (s, 1 H, NH). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 70.0 (CH), 59.7 (C^a), 107.7−106.1 ($C^{4,4'}$), 148.0−147.5 ($C^{3,3'}$), 145.0−141.3 ($C^{5,5'}$), 13.9−13.7 ($Me^{3,3'}$), 11.6−11.1 ($Me^{5,5'}$), 26.3 (Me^g), 21.3 (Me^g), 122.9 (C^d), 31.8 (C^e), 38.2 (C^g), 40.9 (C^f), 42.0 (C^b), 140.0 (C^c), 31.5 (C^h), 129.7 (*m*-C), 114.2 (*o*-C), 145.0 (*p*-C), 145.1 (*ipso*-C), 3.6 (Me).

Synthesis of (*R*,*R*-mobpzaH) (17). The synthetic procedure was the same as for compound **16**, using [Li(κ^3-mobpza)(THF)] (**11**; 1.00 g, 1.86 mmol) and distilled water (33.48 μL, 1.86 mmol), to give compound **17** as a red solid. Yield: 60%. $[\alpha]_D^{25}$ −23.56 (*c* 1.00, THF). Anal. Calcd for $C_{28}H_{37}N_5O$: C, 73.20; H, 8.06; N, 15.25. Found: C, 73.29; H, 8.12; N, 15.20. ^{1}H NMR (C_6D_6, 297 K): δ 6.59 (d, 1 H, CH), 5.61 (m, 1 H, CH^a), 5.51 (s, 2 H, $H^{4,4'}$), 2.14 (s, 3 H, Me^3), 2.10 (s, 3 H, $Me^{3'}$), 2.42 (s, 3 H, Me^5), 2.27 (s, 3 H, $Me^{5'}$), 1.12 (s, 3 H, Me^g), 0.49 (s, 3 H, Me^g), 4.24 (d, 1 H, H^d), 1.97 (m, 2 H, H^e), 1.78 (m, 1 H, H^f), 2.41 (m, 1 H, H^b), 2.21 (m, 1 H, $H^{h,h}$), 0.75 (d, 1 H, $H^{h,h}$), 6.54−6.67 (m, 4H, *m*-H or *o*-H), 3.28 (s, 3 H, Me), 11.70 (s, 1 H, NH). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 74.2 (CH), 60.4 (C^a), 107.8−106.1 ($C^{4,4'}$), 148.0−147.5 ($C^{3,3'}$), 145.1−141.3 ($C^{5,5'}$), 13.7−13.5 ($Me^{3,3'}$), 11.7−11.2 ($Me^{5,5'}$), 26.4 (Me^g), 21.3 (Me^g), 122.8 (C^d), 31.9 (C^e), 38.2 (C^g), 41.0 (C^f), 42.0 (C^b), 140.2 (C^c), 31.5 (C^h), 115.4 (*m*-C), 114.8 (*o*-C), 152.8 (*p*-C), 158.2 (*ipso*-C), 55.1 (O*Me*).

Synthesis of (*R*,*R*-fbpzaH) (18). The synthetic procedure was the same as for compound **16**, using [Li(κ^3-fbpza)(THF)] (**12**; 1.00 g, 1.90 mmol) and distilled water (34.29 μL, 1.90 mmol), to give compound **18** as an orange solid. Yield: 70%. $[\alpha]_D^{25}$ −26.84 (*c* 1.00, THF). Anal. Calcd for $C_{27}H_{34}FN_5$: C, 72.48; H, 7.60; N, 15.66. Found: C, 72.51; H, 7.52; N, 15.68. ^{1}H NMR (C_6D_6, 297 K): δ 6.53 (d, 1 H, CH), 5.51 (s, 1 H, CH^a), 5.51 (s, 2 H, $H^{4,4'}$), 2.12 (s, 3 H, Me^3), 2.07 (s, 3 H, $Me^{3'}$), 2.35 (s, 3 H, Me^5), 2.21 (s, 3 H, $Me^{5'}$), 1.10 (s, 3 H, Me^g), 0.41 (s, 3 H, Me^g), 4.49 (s, 1 H, H^d), 1.93 (m, 2 H, H^e), 1.77 (m, 1 H, H^f), 2.40 (s, 1 H, H^b), 2.10 (m, 1 H, $H^{h,h}$), 0.71 (m, 1 H, $H^{h,h}$), 6.68−6.35 (m, 4H, *m*-H or *o*-H), 8.72 (s, 1 H, NH). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 74.0 (CH), 60.0 (C^a), 106.3−106.1 ($C^{4,4'}$), 148.0−147.6 ($C^{3,3'}$), 143.8−141.2 ($C^{5,5'}$), 13.7−13.5 ($Me^{3,3'}$), 11.6−11.1 ($Me^{5,5'}$), 26.3 (Me^g), 21.2 (Me^g), 123.1 (C^d), 31.9 (C^e), 38.1 (C^g), 40.8 (C^f), 42.0 (C^b), 140.2 (C^c), 31.4 (C^h), 115.5 (d, J_{CF} = 22.1 Hz, *m*-C), 114.8 (d, J_{CF} = 6.9 Hz, *o*-C), 156.1 (d, J_{CF} = 235.0 Hz, *p*-C), 147.6 (*ipso*-C).

Synthesis of (*R*,*R*-clbpzaH) (19). The synthetic procedure was the same as for compound **16**, using [Li(κ^3-clbpza)(THF)] (**13**; 1.00 g, 1.85 mmol) and distilled water (33.30 μL, 1.85 mmol), to give compound **19** as an orange solid. Yield: 75%. $[\alpha]_D^{25}$ −36.01 (*c* 1.00, THF). Anal. Calcd for $C_{27}H_{34}ClN_5$: C, 69.91; H, 7.34; N, 15.10. Found: C, 70.05; H, 7.32; N, 15.54. ^{1}H NMR (C_6D_6, 297 K): δ 6.51 (d, 1 H, CH), 5.50 (s, 1 H, CH^a), 5.51 (s, 2 H, $H^{4,4'}$), 2.13 (s, 3 H, Me^3), 2.09 (s, 3 H, $Me^{3'}$), 2.31 (s, 3 H, Me^5), 2.22 (s, 3 H, $Me^{5'}$), 1.09 (s, 3 H, Me^g), 0.40 (s, 3 H, Me^g), 4.49 (d, 1 H, H^d), 1.92 (m, 2 H, H^e), 1.75 (m, 1 H, H^f), 2.28 (s, 1 H, H^b), 2.15 (s, 1 H, $H^{h,h}$), 0.74 (m, 1 H, $H^{h,h}$), 6.95 (d, 2 H, *m*-H), 6.27 (d, 2 H, *o*-H), 8.50 (s, 1 H, NH). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 73.9 (CH), 59.7 (C^a), 107.9−106.1 ($C^{4,4'}$), 148.0−147.7 ($C^{3,3'}$), 144.3−141.2 ($C^{5,5'}$), 13.7−13.6 ($Me^{3,3'}$), 11.5−11.0 ($Me^{5,5'}$), 26.3 (Me^g), 21.2 (Me^g), 123.1 (C^d), 32.7 (C^e), 38.1 (C^g), 40.8 (C^f), 42.1 (C^b), 140.2 (C^c), 31.8 (C^h), 115.7−115.5 (*m*-C), 115.1 (*o*-C), 156.0 (*p*-C), 160.0 (*ipso*-C).

Preparation of Group 4 Complexes 20−26. Synthesis of [TiCl$_3$(κ^3-*R*,*R*-fbpza)] (20). In a 250 cm^3 Schlenk tube, $TiCl_4(THF)_2$ (0.50 g, 1.50 mmol) was dissolved in dry THF (50 cm^3) and cooled to −70 °C. A cooled (−70 °C) solution of [Li(κ^3-fbpza)(THF)] (**12**; 0.79 g, 1.50 mmol) in dry THF (50 cm^3) was added, and the resulting orange solution was stirred for 12 h. The solvent was removed under vacuum conditions, and the resulting solid was extracted with dichloromethane. The solvent was removed to give complex **20** as a red solid. This solid was crystallized from dichloromethane/*n*-hexane. Yield: 65% $[\alpha]_D^{25}$ −18.26 (*c* 1.00, THF). Anal. Calcd for $C_{27}H_{33}Cl_3FN_5Ti$: C, 53.98; H, 5.50; N, 11.66. Found: C, 54.01; H, 5.51; N, 11.64. ^{1}H NMR (DMSO, 297 K): δ 6.40 (m, 1 H, CH), 5.47 (s, 1 H, CH^a), 5.60 (s, 1 H, H^4), 5.32 (s, 1 H, $H^{4'}$), 2.11 (s, 3 H, Me^3), 2.01 (s, 3 H, $Me^{3'}$), 2.27 (s, 3 H, Me^5), 2.24 (s, 3 H, $Me^{5'}$), 1.14 (s, 3 H, Me^g), 0.42 (s, 3 H, Me^g), 4.78 (s, 1 H, H^d), 1.93 (m, 2 H, H^e), 1.76 (m, 1 H, H^f), 2.50 (s, 1 H, H^b), 2.23 (d, 1 H, $H^{h,h}$), 0.71 (d, 1 H, $H^{h,h}$), 6.33 (t, 2 H, $J_{HH} = J_{HF} = 8.7$ Hz, *m*-H), 6.36 (dd, 2 H, $J_{HH} = 7.1$ Hz, $J_{HF} = 4.3$ Hz, *o*-H). ^{13}C-{^{1}H} NMR (DMSO, 297 K): δ 74.4 (CH), 60.4 (C^a), 107.9−106.5 ($C^{4,4'}$), 147.6−147.3 ($C^{3,3'}$), 141.5−140.4 ($C^{5,5'}$), 13.6−12.8 ($Me^{3,3'}$), 11.6−11.2 ($Me^{5,5'}$), 26.2 (Me^g), 21.3 (Me^g), 123.3 (C^d), 31.5 (C^e), 38.1 (C^g), 40.8 (C^f), 42.3 (C^b), 141.2 (C^c), 31.9 (C^h), 115.4 (d, J_{CF} = 22.1 Hz, *m*-C), 115.2 (d, J_{CF} = 6.9 Hz, *o*-C), 157.4 (d, J_{CF} = 235.7 Hz, *p*-C), 154.2 (*ipso*-C).

Synthesis of [ZrCl$_3$(κ^3-*R*,*R*-fbpza)] (21). Method a. The synthetic procedure was the same as for complex **20**, using $ZrCl_4$ (0.50 g, 2.14 mmol) and [Li(κ^3-fbpza)(THF)] (**12**; 1.13 g, 2.14 mmol), to give complex **21** as a light yellow solid. Yield: 67%. **Method b.** In a 250 cm^3 Schlenk tube, [Zr(NMe$_2$)$_3$(κ^3-*R*,*R*-fbpza)] (**24**; 0.50 g, 0.75 mmol) was dissolved in dry toluene (50 cm^3). Chlorotrimethylsilane (243.00 μL, 2.25 mmol) was added, and the solution was stirred for 5 h. The color of the resulting solution changed from dark yellow to light yellow. The solvent was removed under vacuum conditions and washed with *n*-hexane to give complex **21**. Yield: 75%. $[\alpha]_D^{25}$ −11.25 (*c* 1.00, THF). Anal. Calcd for $C_{27}H_{33}Cl_3FN_5Zr$: C, 50.34; H, 5.16; N, 10.87. Found: C, 50.36; H, 5.12; N, 10.84. ^{1}H NMR (DMSO, 297 K): δ 6.30 (d, 1 H, CH), 5.50 (bs, 1 H, CH^a), 5.75 (s, 1 H, H^4), 5.73 (s, 1 H, $H^{4'}$), 2.04 (s, 3 H, Me^3), 2.02 (s, 3 H, $Me^{3'}$), 2.38 (s, 3 H, Me^5), 2.37 (s, 3 H, $Me^{5'}$), 1.16 (s, 3 H, Me^g), 0.28 (s, 3 H, Me^g),

Table 4. Crystal Data and Structure Refinement for **5**, **12**, **14**, **15**, and **24**

	5	12	14	15	24
molecular formula	$C_{16}H_{18}FN$	$C_{31}H_{41}FLiN_5O$	$C_{31}H_{42}ClFLiN_5O$	$C_{31}H_{42}Cl_2LiN_5O$	$C_{33}H_{51}FN_8Zr$
fw	243.31	525.68	562.09	578.54	670.04
temp (K)	180(2)	180(2)	180(2)	180(2)	250(2)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	tetragonal	tetragonal	orthorhombic
space group	*C*2	$P2_1$	$P4_3$	$P4_3$	$P2_12_12_1$
a (Å)	10.707(4)	10.371(2)	14.336(1)	14.5316(7)	13.097(8)
b (Å)	6.833(2)	19.001(4)	14.336(1)	14.5316(7)	10.595(6)
c (Å)	18.393(6)	15.118(3)	15.199(3)	15.179(2)	25.587(5)
β (deg)	98.577(5)	96.642(7)			
vol (Å^3)	1330.5(8)	2959(1)	3123.8(7)	3205.2(4)	3551(3)
Z	4	4	4	4	4
density (calculated) (g/cm^3)	1.215	1.180	1.195	1.199	1.253
abs coeff (mm^{-1})	0.080	0.077	0.159	0.234	0.348
F(000)	520	1128	1200	1232	1416
cryst size (mm^3)	0.65 × 0.43 × 0.02	0.31 × 0.23 × 0.18	0.27 × 0.13 × 0.10	0.26 × 0.16 × 0.08	0.51 × 0.45 × 0.30
index ranges	$-11 \le h \le 11$	$-10 \le h \le 12$	$-17 \le h \le 17$	$-17 \le h \le 17$	$-15 \le h \le 11$
	$-7 \le k \le 7$	$-22 \le k \le 20$	$-17 \le k \le 17$	$-16 \le k \le 17$	$-8 \le k \le 12$
	$-19 \le l \le 19$	$-17 \le l \le 14$	$-18 \le l \le 17$	$-18 \le l \le 18$	$-30 \le l \le 27$
reflns collected	3048	15214	23769	23385	11540
independent reflns	1639	8945	5474	5560	5884
	[R(int) = 0.0578]	[R(int) = 0.1172]	R(int) = 0.0961	R(int) = 0.1152	R(int) = 0.0759
data/restraints/params	1639/1/166	8945/53/709	5474/1/368	5560/1/367	5884/0/400
goodness-of-fit on F^2	1.017	0.952	0.949	1.006	0.996
final R indices [$I > 2\sigma(I)$][a,b]	R1 = 0.0532	R1 = 0.0850	R1 = 0.0626	R1 = 0.0643	R1 = 0.0629
	wR2 = 0.1266	wR2 = 0.1588	wR2 = 0.1486	wR2 = 0.1596	wR2 = 0.1138
absolute structure param		0.12(3)	−0.20(12)	0.00(11)	−0.08(7)
largest diff. peak/hole, e.Å^{-3}	0.179 and −0.192	0.253/−0.248	0.318/−0.246	0.295/−0.261	0.480/−0.645

[a] $R = \sum\|F_o| - |F_c|/\sum|F_o|$. [b] $wR = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$. GOF = $\{\sum[w((F_o^2 - F_c^2)^2)/(n-p)\}^{1/2}$, where n = number of reflections and p = total number of parameters refined.

5.36 (t, 1 H, H^d), 1.97 (d, 2 H, H^e), 1.83 (bs, 1 H, H^f), 2.45 (m, 1 H, H^b), 2.12 (d, 1 H, H^{h,h}), 6.84 (t, 2 H, $J_{HH} = J_{HF} = 8.8$ Hz, *m*-H), 6.55 (dd, 2 H, $J_{HH} = 6.8$ Hz, $J_{HF} = 4.4$ Hz, *o*-H). ^{13}C-{^{1}H} NMR (DMSO, 297 K): *δ* 73.8 (CH), 60.6 (C^a), 106.0 (C$^{4,4'}$), 146.3−146.0 (C$^{3,3'}$), 140.1−139.0 (C$^{5,5'}$), 13.5−13.3 (Me$^{3,3'}$), 11.2−11.0 (Me$^{5,5'}$), 26.0 (Me^g), 21.0 (Me^g), 121.3 (C^d), 30.4 (C^e), 37.5 (C^g), 39.8 (C^f), 41.0 (C^b), 141.0 (C^c), 30.9 (C^h), 114.8 (d, $J_{CF} = 22.2$ Hz, *m*-C), 114.1 (d, $J_{CF} = 7.1$ Hz, *o*-C), 158.1 (d, $J_{CF} = 235.6$ Hz, *p*-C), 153.4 (*ipso*-C).

Synthesis of [Ti(OEt)$_3$(*κ*^{3}-*R*,*R*-fbpza)] (22). In a 250 cm^3 Schlenk tube, Ti(OEt)$_4$ (0.50 g, 2.19 mmol) was dissolved in dry toluene (50 cm^3). A solution of (*R*,*R*-fbpzaH) (**18**; 0.98 g, 2.19 mmol) in toluene was added, and the resulting solution was stirred for 12 h at room temperature. The solvent was removed under vacuum conditions to give complex **22** as a yellow solid. This solid was crystallized from *n*-hexane. Yield: 70%. $[\alpha]_D^{25}$ −13.85 (*c* 1.00, THF). Anal. Calcd for $C_{33}H_{48}FN_5O_3Ti$: C, 61.24; H, 8.50; N, 11.02. Found: C, 61.28; H, 8.85; N, 11.16. ^{1}H NMR (C_6D_6, 297 K): *δ* 6.29 (d, 1 H, CH), 5.48 (bs, 1 H, CH^a), 5.46 (s, 1 H, H^4), 5.46 (s, 1 H, H$^{4'}$), 2.11 (s, 3 H, Me^3), 2.06 (s, 3 H, Me$^{3'}$), 2.29 (s, 3 H, Me^5), 2.13 (s, 3 H, Me$^{5'}$), 1.20 (s, 3 H, Me^g), 0.40 (s, 3 H, Me^g), 4.01 (d, 1 H, H^d), 1.93 (m, 2 H, H^e), 1.72 (m, 1 H, H^f), 2.30 (m, 1 H, H^b), 2.20 (m, 1 H, H^{h,h}), 0.75 (d, 1 H, H^{h,h}), 6.28 (t, 2 H, $J_{HH} = J_{HF} = 8.1$ Hz, *m*-H), 6.15 (dd, 2 H, $J_{HH} = 6.8$ Hz, $J_{HF} = 4.1$ Hz, *o*-H), 1.20−1.55 (m, 9 H, OCH$_2$*CH*$_3$), 4.20−4.80 (m, 6 H, O*CH*$_2$CH$_3$). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): *δ* 73.3 (CH), 60.3 (C^a), 107.6−106.3 (C$^{4,4'}$), 148.1−148.3 (C$^{3,3'}$), 141.5−140.3 (C$^{5,5'}$), 13.5−13.5 (Me$^{3,3'}$), 11.4−11.1 (Me$^{5,5'}$), 26.3 (Me^g), 21.3 (Me^g), 123.0 (C^d), 31.4 (C^e), 38.2 (C^g), 40.8 (C^f), 42.2 (C^b), 141.3 (C^c), 31.9 (C^h), 115.8 (d, $J_{CF} = 22.2$ Hz, *m*-C), 115.1 (d, $J_{CF} = 7.1$ Hz, *o*-C), 155.4 (d, $J_{CF} = 235.1$ Hz, *p*-C), 157.3 (*ipso*-C), 70.9 (O*CH*$_2$CH$_3$), 18.3 (OCH$_2$*CH*$_3$).

Synthesis of [Ti(O^{i}Pr)$_3$(*κ*^{3}-*R*,*R*-fbpza)] (23). The synthetic procedure was the same as for complex **22**, using Ti(O^{i}Pr)$_4$ (0.50 cm^3, 1.71 mmol) and (*R*,*R*-fbpzaH) (**18**; 0.76 g, 1.71 mmol), to give **23** as a yellow solid. Yield: 72%. $[\alpha]_D^{25}$ −15.59 (*c* 1.00, THF). Anal. Calcd for $C_{36}H_{54}FN_5O_3Ti$: C, 61.24; H, 8.50; N, 11.02. Found: C, 61.28; H, 8.85; N, 11.16. ^{1}H NMR (C_6D_6, 297 K): *δ* 6.51 (d, 1 H, CH), 5.51 (bs, 1 H, CH^a), 5.55 (s, 1 H, H^4), 5.51 (s, 1 H, H$^{4'}$), 2.14 (s, 3 H, Me^3), 2.10 (s, 3 H, Me$^{3'}$), 2.32 (s, 3 H, Me^5), 2.22 (s, 3 H, Me$^{5'}$), 1.10 (s, 3 H, Me^g), 0.41 (s, 3 H, Me^g), 4.10 (d, 1 H, H^d), 1.96 (m, 2 H, H^e), 1.80 (m, 1 H, H^f), 2.34 (m, 1 H, H^b), 2.34 (m, 1 H, H^{h,h}), 0.76 (d, 1 H, H^{h,h}), 6.33 (t, 2 H, $J_{HH} = J_{HF} = 8.5$ Hz, *m*-H), 6.21 (dd, 2 H, $J_{HH} = 6.7$ Hz, $J_{HF} = 4.5$ Hz, *o*-H), 1.20−1.51 (m, 18 H, OCH(*CH*$_3$)$_2$), 4.70−4.84 (m, 3 H, OC*H*(CH$_3$)$_2$). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): *δ* 73.1 (CH), 60.1 (C^a), 107.8−106.4 (C$^{4,4'}$), 148.0−147.5 (C$^{3,3'}$), 141.1−140.2 (C$^{5,5'}$), 13.7−13.5 (Me$^{3,3'}$), 11.5−11.1 (Me$^{5,5'}$), 26.3 (Me^g), 21.2 (Me^g), 122.9 (C^d), 31.4 (C^e), 38.1 (C^g), 40.8 (C^f), 42.1 (C^b), 141.1 (C^c), 31.8 (C^h), 115.6 (d, $J_{CF} = 22.2$ Hz, *m*-C), 115.2 (d, $J_{CF} = 6.9$ Hz, *o*-C), 155.4 (d, $J_{CF} = 234.6$ Hz, *p*-C), 157.2 (*ipso*-C), 28.5−28.0 (OCH(*CH*$_3$)$_2$), 27.5−27.0 (OCH(*CH*$_3$)$_2$), 26.5−26.1 (OCH(*CH*$_3$)$_2$), 75.8 (OC*H*(CH$_3$)$_2$), 75.5 (OC*H*(CH$_3$)$_2$), 74.0 (OC*H*(CH$_3$)$_2$).

Synthesis of [Zr(NMe$_2$)$_3$(*κ*^{3}-*R*,*R*-fbpza)] (24). In a 250 cm^3 Schlenk tube, Zr(NMe$_2$)$_4$ (0.50 g, 1.87 mmol) was dissolved in dry toluene (50 cm^3). A solution of (*R*,*R*-fbpzaH) (**18**; 0.84 g, 1.87 mmol) in toluene was added, and the resulting solution was stirred overnight at room temperature. The solvent was removed under vacuum conditions and washed with *n*-hexane to give complex **24** as a yellow solid. This solid was crystallized from *n*-hexane. Yield: 75%. $[\alpha]_D^{25}$ −18.12 (*c* 1.00, THF). Anal. Calcd for $C_{33}H_{51}FN_8Zr$: C, 59.15; H, 7.67; N, 16.72. Found: C, 59.12; H, 7.65; N, 16.69. ^{1}H NMR (C_6D_6, 297 K): *δ* 5.99 (d, 1 H, CH), 4.62 (d, 1 H, CH^a), 5.46 (s, 1 H, H^4), 5.45 (s, 1 H, H$^{4'}$), 2.30 (s, 3 H, Me^3), 2.24 (s, 3 H, Me$^{3'}$), 1.70 (s, 3 H, Me^5), 1.67 (s, 3 H, Me$^{5'}$), 1.08 (s, 3 H, Me^g), 0.39 (s, 3 H, Me^g), 5.40 (bs, 1 H, H^d), 1.82 (m, 2 H, H^e), 1.87 (m, 1 H, H^f), 2.15 (m, 1 H, H^b), 2.04 (m, 1 H, H^{h,h}), 0.66 (d, 1 H, H^{h,h}), 7.02 (m, 4H, *m*,*o*-H), 3.42 (s, 6 H, N(*CH*$_3$)$_2$), 2.83 (s, 6 H, N(*CH*$_3$)$_2$), 2.82 (s, 6 H, N(*CH*$_3$)$_2$). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): *δ* 70.6 (CH), 67.8 (C^a), 107.0−106.8 (C$^{4,4'}$), 152.3−151.3 (C$^{3,3'}$), 139.4−137.5 (C$^{5,5'}$), 12.8−12.5 (Me$^{3,3'}$), 11.0−10.6 (Me$^{5,5'}$), 26.0 (Me^g), 21.2 (Me^g), 121.8 (C^d), 32.0 (C^e), 38.1 (C^g), 40.7 (C^f), 42.2 (C^b), 150.3 (C^c),

32.2 (C^h), 113.2 (d, J_{CF} = 20.6 Hz, *m*-C), 118.8 (d, J_{CF} = 6.9 Hz, *o*-C), 155.0 (d, J_{CF} = 232.7 Hz, *p*-C), 152.4 (*ipso*-C), 43.7 ($N(CH_3)_2$), 45.8 ($N(CH_3)_2$), 45.9 ($N(CH_3)_2$).

Synthesis of [ZrCl(NMe$_2$)$_2$(κ^3-*R*,*R*-fbpza)] (25). In a 250 cm^3 Schlenk tube, [Zr(NMe$_2$)$_3$(κ^3-*R*,*R*-fbpza)] (**24**; 0.50 g, 0.75 mmol) was dissolved in dry toluene (50 cm^3). Chlorotrimethylsilane (81.00 μL, 0.75 mmol) was added, and the solution was stirred for 1 h. The color of the resulting solution changed from dark yellow to light yellow. The solvent was removed under vacuum conditions and washed with *n*-hexane to give complex **25**. Yield: 75%. $[\alpha]_D^{25}$ −25.13 (*c* 1.00, THF). Anal. Calcd for $C_{31}H_{45}ClFN_7Zr$: C, 56.29; H, 6.86; N, 14.82. Found: C, 56.33; H, 6.81; N, 14.81. ^{1}H NMR (C_6D_6, 297 K): δ 6.02 (d, 1 H, CH), 4.58 (d, 1 H, CH^a), 5.36 (s, 1 H, H^4), 5.35 (s, 1 H, $H^{4'}$), 2.32 (s, 3 H, Me^3), 2.27 (s, 3 H, $Me^{3'}$), 1.72 (s, 3 H, Me^5), 1.69 (s, 3 H, $Me^{5'}$), 0.98 (s, 3 H, Me^g), 0.31 (s, 3 H, Me^g), 5.40 (bs, 1 H, H^d), 1.83 (m, 2 H, H^e), 1.88 (m, 1 H, H^f), 2.15 (m, 1 H, H^b), 2.05 (m, 1 H, $H^{h,h}$), 0.68 (d, 1 H, $H^{h,h}$), 6.89 (t, 2 H, J_{HH} = J_{HF} = 8.3 Hz, *m*-H), 7.02 (dd, 2 H, J_{HH} = 6.9 Hz, J_{HF} = 4.6 Hz, *o*-H), 3.50 (s, 6 H, $N(CH_3)_2$), 2.88 (s, 6 H, $N(CH_3)_2$). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 70.3 (CH), 67.8 (C^a), 107.0−106.8 ($C^{4,4'}$), 151.3−150.3 ($C^{3,3'}$), 139.5−137.7 ($C^{5,5'}$), 12.8−12.5 ($Me^{3,3'}$), 10.6−10.2 ($Me^{5,5'}$), 26.3 (Me^g), 21.4 (Me^g), 121.8 (C^d), 32.0 (C^e), 38.3 (C^g), 40.7 (C^f), 42.3 (C^b), 150.3 (C^c), 32.2 (C^h), 112.2 (d, J_{CF} = 21.6 Hz, *m*-C), 115.8 (d, J_{CF} = 6.9 Hz, *o*-C), 156.0 (d, J_{CF} = 234.7 Hz, *p*-C), 151.4 (*ipso*-C), 43.7 ($N(CH_3)_2$), 45.8 ($N(CH_3)_2$).

Synthesis of [ZrCl$_2$(NMe$_2$)(κ^3-*R*,*R*-fbpza)] (26). The synthetic procedure was the same as for complex **25**, but in this case the reaction mixture was stirred for 5 h, using [Zr(NMe$_2$)$_3$(κ^3-*R*,*R*-fbpza)] (**24**; 0.50 g, 0.75 mmol) and chlorotrimethylsilane (162.00 μL, 1.49 mmol), to give **26** as a light yellow solid. Yield: 65%. $[\alpha]_D^{25}$ −13.10 (*c* 1.00, THF). Anal. Calcd for $C_{29}H_{39}Cl_2FN_6Zr$: C, 53.36; H, 6.02; N, 12.87. Found: C, 53.39; H, 6.07; N, 12.90. ^{1}H NMR (C_6D_6, 297 K): δ 6.3 (d, 1 H, CH), 4.57 (d, 1 H, CH^a), 5.38 (s, 1 H, H^4), 5.35 (s, 1 H, $H^{4'}$), 2.42 (s, 3 H, Me^3), 2.37 (s, 3 H, $Me^{3'}$), 1.64 (s, 3 H, Me^5), 1.59 (s, 3 H, $Me^{5'}$), 1.03 (s, 3 H, Me^g), 0.35 (s, 3 H, Me^g), 5.30 (bs, 1 H, H^d), 1.83 (m, 2 H, H^e), 1.87 (m, 1 H, H^f), 2.15 (m, 1 H, H^b), 2.06 (m, 1 H, $H^{h,h}$), 0.69 (d, 1 H, $H^{h,h}$), 6.93 (t, 2 H, J_{HH} = J_{HF} = 7.9 Hz, *m*-H), 7.01 (dd, 2 H, J_{HH} = 7.0 Hz, J_{HF} = 4.2 Hz, *o*-H), 3.47 (s, 6 H, $N(CH_3)_2$). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 70.4 (CH), 67.8 (C^a), 107.0−106.8 ($C^{4,4'}$), 151.4−150.6 ($C^{3,3'}$), 139.6−137.8 ($C^{5,5'}$), 12.9−12.6 ($Me^{3,3'}$), 11.6−11.2 ($Me^{5,5'}$), 26.4 (Me^g), 21.4 (Me^g), 121.3 (C^d), 32.0 (C^e), 38.3 (C^g), 40.8 (C^f), 42.6 (C^b), 151.3 (C^c), 32.2 (C^h), 111.2 (d, J_{CF} = 20.6 Hz, *m*-C), 114.9 (d, J_{CF} = 6.8 Hz, *o*-C), 156.5 (d, J_{CF} = 234.7 Hz, *p*-C), 151.7 (*ipso*-C), 45.7 ($N(CH_3)_2$).

Crystal Data for 5, 12, 14, 15, and 24. A summary of crystal data collection and refinement parameters for all compounds is given in Table 4. The single crystals of these compounds 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 = 0.71073 Å). Data were integrated using SAINT,[19] and an absorption correction was performed with the program SADABS.[20] The software package SHELXTL version 6.10[21] 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. The absolute structure of **5** could not be determined, as no significant anomalous scatters were present. For **12**, the asymmetric unit contains two diatereoisomers, *RS* and *RR*. On the other hand, the crystals of **12** diffracted weakly, and X-ray data were of very low quality. The THF atoms show positional disorder, and it was necessary to apply some restrictions.

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Supporting Information Available: Details of data collection, refinement, atom coordinates, anisotropic displacement parameters, and bond lengths and angles for complexes **5**, **12**, **14**, **15**, and **24**. This material is available free of charge via the Internet at http://pubs.acs.org.

(19) *SAINT+*, v7.12a; Bruker-Nonius AXS: Madison, WI, 2004.

(20) Sheldrick, G. M. *SADABS*, version 2004/1; University of Göttingen: Göttingen, Germany, 2004.

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