Single Diastereomer Half-Sandwich Salicyloxazoline Complexes of Titanium and Zirconium

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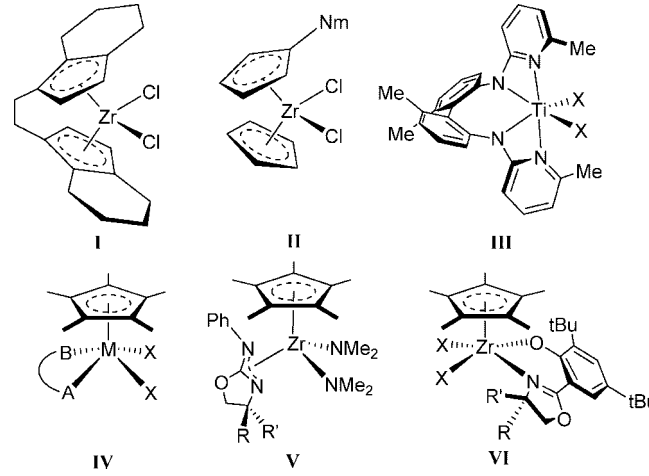
A series of half-sandwich complexes [Cp*MLX$_2$] (L = four optically pure κ^2-salicyloxazolines, M = Ti, Zr; X = Cl, Me) have been prepared via salt elimination and protonolysis routes. X-ray crystallographic analyses demonstrate that the complexes contain stereogenic metal centers as a result of diastereoselective coordination of the N−O ligand. This chirality persists in solution; NMR spectroscopic investigations revealed that for most members of both the Ti and Zr series a single diastereomeric species is present at all accessible temperatures. Systems with incomplete diastereoselection are also accessible by notionally moving the *C*-stereogenic center on the oxazoline ring to a position where its chirality is less well expressed in the structure of the complex. In one such case (for M = Zr) a lower limit barrier to epimerization of 80 kJ mol^{-1} is estimated at high temperature, while for an analogous Ti complex no exchange between epimers could be observed on the NMR chemical shift time scale. In contrast, unsubstituted cyclopentadienyl series CpTiLX$_2$ gives diastereomeric mixtures in most cases and undergoes thermally accessible exchange between epimers.

Introduction

Chiral *ansa*-metallocenes of the group 4 elements, such as [(EBTHI)ZrCl$_2$] (**I**),[1] Chart 1, have found widespread application in the mediation of both stereoselective α-olefin polymerization[2] and enantioselective transformation of organic substrates.[3] Nevertheless, the resolution[4] or diastereoselective synthesis[5] protocols needed to produce optically pure samples represent a barrier to widespread application in the latter area.[6] Cyclopentadienyl ligands with chiral nonracemic substituents have been widely investigated, but apart from notable exceptions such as **II**[7] this approach has met with limited success.[8] We have taken an alternative approach: the use of multidentate chiral noncyclopentadienyl ligands to generate single diastereomer complexes directly by stereoselective synthesis. For example, we have reported a number of group 4 metal biaryl complexes, such as **III**,[9–12] and some successes in enantioselective catalysis have followed.[9,13] We have also been engaged with a further strategy in which more readily accessible chiral bidentate ligands A−B are used in diastereoselective syntheses of chiral-at-metal octahedral M(A−B)$_2$X$_2$ or half-sandwich CpM(A−B)X$_2$ (**IV**) complexes. We recently reported the synthesis of chiral aminooxazoline complexes such as **V**, but these were unstable with respect to a highly selective ring-opening rearrangement resulting in their configurational instability[14] and susceptibility to Lewis acids.[15] The related salicyloxazolines **L** (Scheme 1),

Chart 1



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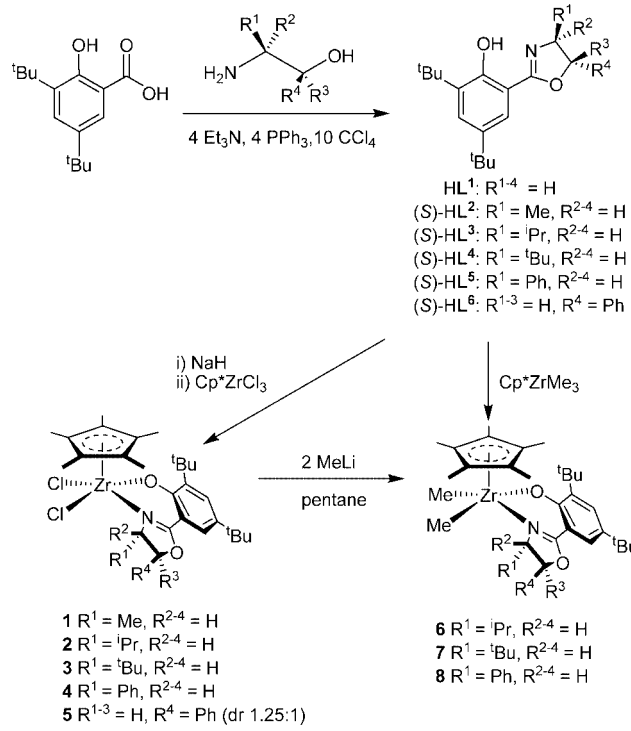
readily synthesized from amino alcohols and salicylic acids,[16,17] are more stable. We have shown that group 4 complexes of the general type $[L_2MX_2]$ are very highly active catalysts for ethylene polymerization.[18] Complexes [Cp*MLX_2] **VI** bearing achiral ligands (R = R′) provide very well defined polymerization catalysts.[19] In this contribution we describe synthetic routes, structural studies, and diastereoselection in complexes **VI** bearing optically pure salicyloxazolinates, our objective being to develop early transition metal analogues of the extensively studied (and configurationally stable) later metal complexes.[20] Applications of complexes of type **VI** in enantioselective catalysis are beginning to emerge.[21]

Scheme 1. Synthesis of Proligands and Zr Derivatives



Results and Discussion

Cp*Zr Complex Synthesis. The new proligands (*S*)-HL^2, (*S*)-HL^6, and the previously reported HL^1 and (*S*)-HL^{3-5} were prepared as described in the literature, or with slight modifications, from the appropriate salicylic acids and amino alcohols (Scheme 1). Treatment of the proligands with excess NaH in THF yielded the sodium salts $NaL^n(THF)_x$ in essentially quantitative yields; however it was more convenient to form the sodium salts *in situ* as ligand transfer agents before filtration directly onto Cp^*ZrCl_3. This reaction and subsequent workup furnished the complexes [Cp*ZrL^nCl_2] **1**−**5** ($n = 2-6$) as air- and water-sensitive, off-white solids in high yield (we have previously reported the Zr complex of L^1).[19] The syntheses were generally very clean, but further purification could be accomplished where necessary by recrystallization from diethyl ether or toluene or sublimation under high vacuum (typically ca. 250 °C and 10^{-6} mmHg).

Samples of **1**−**4** showed a single species in the ^1H and $^{13}C\{^1H\}$ NMR spectra; no minor isomers were observed. The spectrum of **4** is typical (Figure 1a), with three multiplets corresponding to the oxazoline ring in the region 4−5.5 ppm. The spectra were essentially invariant with temperature. The oxazoline region of the room-temperature ^1H NMR spectrum of complex **5**, shown in Figure 1b, is very different. Here, two epimers in the ratio 1.25:1 are apparent (Scheme 2). A sample of **5** in toluene-d_8 began to show line broadening at 348 K, and by 368 K (the highest accessible temperature) signals for the two epimers had almost collapsed into a single series. From these data we estimate a lower-limiting value of $\Delta H^{\ddagger}$ ca. 80 kJ mol^{-1} for the energy barrier for epimerization. Earlier studies of racemic systems give barriers to racemization of a similar order.[19]

The dimethyl complexes [Cp*ZrL^nMe_2] **6**−**8** ($n = 3-5$) were prepared by reaction of (*S*)-HL^n and Cp^*ZrMe_3, the latter

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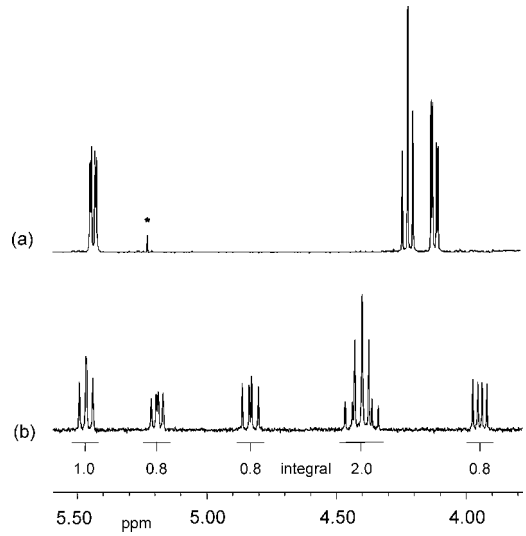
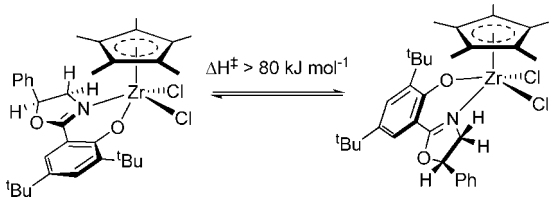
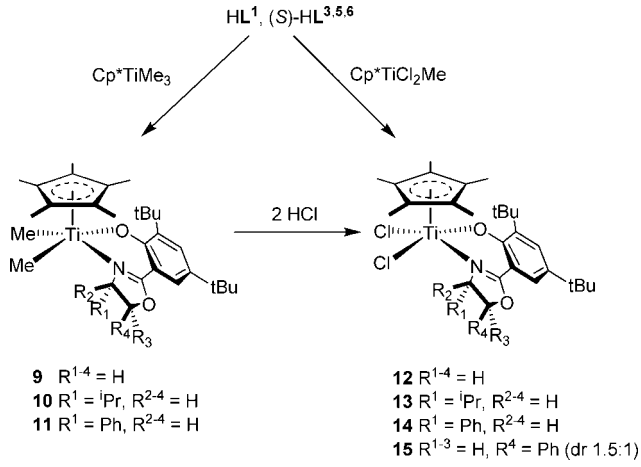


Figure 1. ^{1}H NMR spectra of the oxazoline regions of (a) single diastereomer **4** and (b) 1.25:1 diastereomeric mixture **5**. Residual protio resonance of deuterated dichloromethane solvent is shown (*).

Scheme 2. Interconversion of Diastereomers of 5



Scheme 3. Synthesis of Cp*Ti Compounds



9 R^{1-4} = H
10 R^1 = ^{i}Pr, R^{2-4} = H
11 R^1 = Ph, R^{2-4} = H

12 R^{1-4} = H
13 R^1 = ^{i}Pr, R^{2-4} = H
14 R^1 = Ph, R^{2-4} = H
15 R^{1-3} = H, R^4 = Ph (dr 1.5:1)

prepared *in situ* from Cp*$ZrCl_3$[22] or by methylation of the dichloride complexes **2**−**4** with 2 equiv of methyllithium. These complexes were isolated in lower yield than the chloride complexes due to their much higher solubility, but NMR spectra indicated complete conversion in all cases.[23] The spectroscopic data of **6** and **8** are broadly similar to their dichloride analogues, with the exception of two resonances indicative of inequivalent methyl groups at low chemical shift, for example at −0.21 and +0.55 ppm for **8**. In contrast, **7** is contaminated with a small amount of a second compound, the composition varying according to the method of preparation described above (5−10%). This implies that the complexes are not diastereomers in equilibrium, and indeed variable-temperature NMR experiments confirmed that there was no coalescence/exchange behavior; we tentatively suggest that the minor species present is a monomethyl complex caused by C−H activation/deprotonation of the *tert*-butyl oxazoline substituent by methyl lithium during the preparation of **7**. Such chemistry is not uncommon.[21,24]

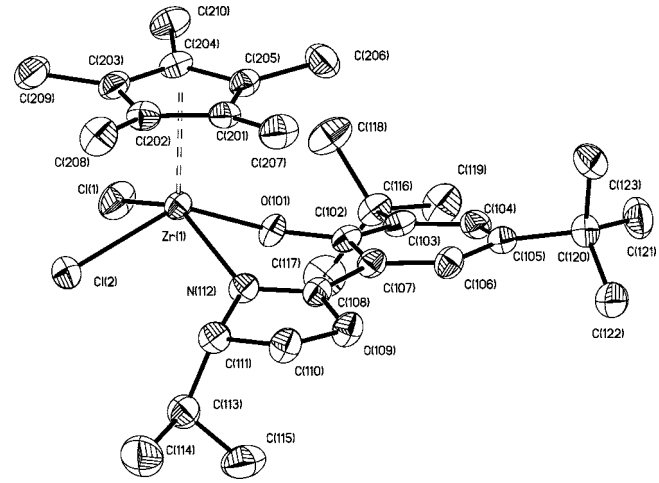


Figure 2. Molecular structure of **2**. Solvent of crystallization is omitted for clarity. Displacement ellipsoids are at the 50% probability level.

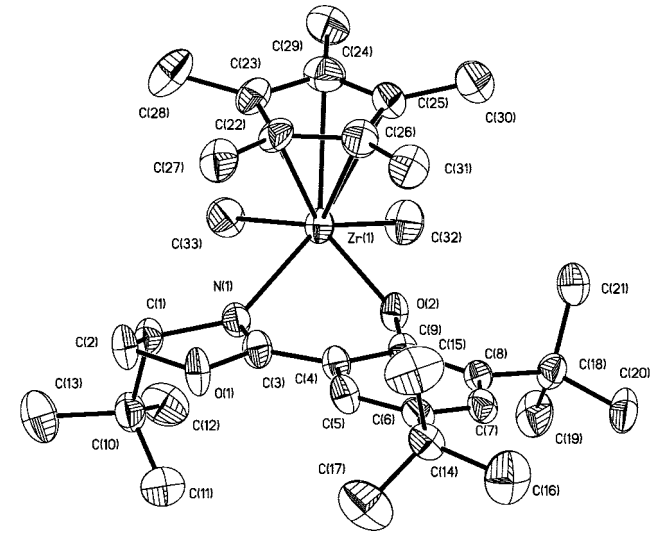


Figure 3. Molecular structure of **7**. Displacement ellipsoids are at the 50% probability level.

Structural Characterization of Cp*Zr Complexes. Single crystals of **2** and **7** suitable for X-ray diffraction were obtained from saturated toluene and pentane solutions respectively at −30 °C. The molecular structures can be seen in Figures 2 and 3. Data collection and refinement parameters can be found in Table 1, with relevant bond lengths and angles in Tables 2 and 3. The structures are both best described as adopting a four-legged "piano stool" coordination geometry and are broadly similar to those of previously reported complexes.[19] The metal−oxygen bond length Zr(1)−O(101) of **2** [2.012(3) Å] is somewhat

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Table 1. Crystallographic Data and Collection/Refinement Parameters for 2 and 7

	$[Cp^*ZrL^3Cl_2]\cdot C_7H_8$, **2**	$[Cp^*ZrL^4Me_2]$, **7**
formula	$C_{37}H_{53}NO_2Cl_2$	$C_{33}H_{53}NO_2Zr$
fw	705.92	586.98
cryst morphology	colorless block	colorless block
cryst dimens/mm	0.60 × 0.18 × 0.14	0.21 × 0.18 × 0.15
cryst syst	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_1$
a/Å	9.861(3)	9.9231(6)
b/Å	16.787(5)	17.3758(11)
c/Å	22.046(6)	9.9311(6)
α/deg	90	90
β/deg	90	105.1710(10)
δ/deg	90	90
V/Å^3	3649.3(18)	1652.66(18)
Z	4	2
d(calc)/mg·m^3	1.285	1.180
μ(Mo Kα)/mm^{-1}	0.479	0.359
T/K	180(2)	180(2)
F(000)	1488	628
no. of reflns measd	23 794	10 368
no. of unique reflns	9072 [*R*(int) = 0.0608]	7138 [*R*(int) = 0.0453]
R_1 [$I > 2\sigma(I)$]	0.0557	0.0502
wR_2	0.1425	0.0820
no. of data/restraints/params	9072/24/390	7138/1/350
goodness of fit on F^2	1.047	0.916
largest peak and hole/e·Å^{-3}	1.221 and −0.848	0.580 and −0.373

shorter than the corresponding distance in **7** [2.072(3) Å] on the basis of electrostatics; chloride is more electronegative than methyl. The Zr−O−C bond angles in the phenoxide groups [138.9(3)° in **2**, 136.5(2)° in **7**] are consistent with sp^2 hybridization at oxygen, and thus the alkoxide is formally acting as a three-electron donor.[25] The Zr(1)−N(112) bond length for **2** of 2.307(5) Å is shorter than those observed for analogous imino-phenolate systems[10,26] at ca. 2.35 Å and may be due to a stronger interaction due to the presence of the conjugated O atom in the oxazoline ring. An unfavorable steric compression between the isopropyl oxazoline substituent and Cl(2) in **2** causes a fold (the angle between the mean least-squares planes defined by the oxazoline ring and O(101)−Zr(1)−N(112)) of 29.93°, as compared to 8.64° for $[Cp^*ZrL^1Cl_2]$ (where the oxazoline is unsubstituted).[19] In **7**, the distortion is even more marked (42.23°) due to the more sterically demanding *tert*-butyl and methyl groups. Both oxazoline rings are distorted for the same reason; the fold angle in the oxazoline ring [the angle between the least-squares planes defined by N(112)−C(108)−O(109)−C(110) and N(112)−C(111)−C(110) in **2**] is 21.99° for **2** and 25.85° for **7**. The centroid of the cyclopentadienyl ring of **2** is held somewhat more closely to the metal than in **7** (again as a result of the greater electronegativity of Cl than Me), at 2.209 Å for the former and 2.240 Å for the latter.

Synthesis of Cp*Ti Complexes. In comparison with their zirconium analogues, the syntheses of the titanium complexes of L^n ($n = 1-5$) required more forcing conditions. Attempted salt metathesis reactions of NaL^n with Cp^*TiCl_3 were entirely unsuccessful, presumably due to the greater steric protection of the smaller Ti center by the Cp* moiety. However, while proligands HL^n did not react with Cp^*TiMe_3 at room temperature, NMR tube scale experiments showed that complete conversion was possible in some instances at higher temperatures. In this manner, $[Cp^*TiL^1Me_2]$ (**9**), $[Cp^*TiL^3Me_2]$ (**10**), and $[Cp^*TiL^5Me_2]$ (**11**) were synthesized as air- and thermally sensitive orange solids in low to moderate yields, which darkened on exposure to light (Scheme 2). It was not possible to access the complex of (*S*)-HL^4 by this method, presumably due to the greater steric demand of the *tert*-butyl substituent. The chirality of the system is once again demonstrated in the ^{1}H NMR spectra of the complexes at ambient temperature. For example, in **9** all four oxazoline protons are inequivalent, resulting in a pair of mutually coupled multiplets at 2.92 and 3.57 ppm and two overlapping multiplets centered at 3.37 ppm. Two inequivalent methyl groups are also observed at 0.52 and 1.11 ppm. In the complexes of the chiral nonracemic ligands L^3 and L^5, three separate resonances are observed for the oxazoline protons, and only one diastereomer is present at accessible temperatures.

Given the lack of success of direct syntheses of the dichloride complexes, we chose to investigate the conversion of the methyls with appropriate sources of chloride. To this end, **9** was treated with 2 equiv of anhydrous hydrogen chloride, resulting in methane elimination and rapid, clean conversion to $[Cp^*TiL^1Cl_2]$ (**12**) as a red-orange solid. However, similar reactions with **10** and **11** yielded intractable mixtures. Treatment of **10** and **11** with weaker Brønsted acids[27] such as $Et_3N.HCl$ was also unsuccessful, as was treatment with chlorinated solvents[28] and trimethylchlorosilane.[29]

An alternative synthetic protocol was developed, utilizing the known compound Cp^*TiCl_2Me.[30] Reaction with (*S*)-HL^3 in toluene at 75 °C overnight resulted in the elimination of methane and clean formation of red-orange $[Cp^*TiL^3Cl_2]$ (**13**) upon cooling to ambient temperature; $[Cp^*TiL^5Cl_2]$ (**14**) and $[Cp^*TiL^6Cl_2]$ (**15**) were formed similarly.[31] These complexes were much less soluble than the methylated analogues and could be recrystallized from pentane at low temperature. The complexes of the chiral nonracemic L^3 and L^5, i.e., **13** and **14** showed very high diastereopurity, with no minor resonances present in the oxazoline region at all accessible temperatures. In contrast, and as expected, **15** was formed as a diastereomeric mixture (1.5:1). In this case however, no evidence of epimerization of the stereogenic Ti center could be seen, save a slight broadening of some peaks at 368 K (toluene-d_8).

CpM Complexes. To gauge the effect of the pentamethylcyclopentadienyl group on the diastereoselection of the complexes described above, we investigated nonmethylated Cp analogues. Despite strenuous efforts, we were unable to access CpZr complexes. However, reaction of the *in situ* generated $CpTiMe_3$[32] with (*S*)-HL^3 at low temperature, followed by a further reaction period at room temperature, yielded the desired complex $[CpTiL^3Me_2]$ (**16**) as an orange solid after recrystallization from pentane. In contrast to the reactions with Cp^*TiCl_3, reaction of $NaL^5(THF)_x$ with the less sterically protected

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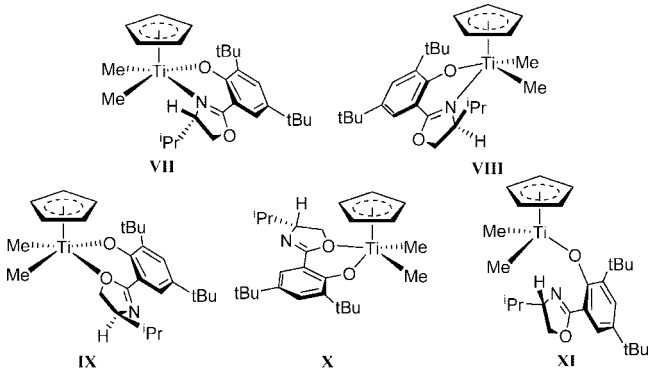
Table 2. Selected Bond Lengths (Å) and Angles (deg) for 2

Zr(1)−Cl(1)	2.4613(13)	Zr(1)−Cl(2)	2.4441(13)
Zr(1)−O(101)	2.012(3)	Zr(1)−N(112)	2.307(4)
N(112)−C(108)	1.298(6)	C(108)−O(109)	1.346(5)
N(112)−C(111)	1.493(5)	C(111)−C(110)	1.536(6)
O(109)−C(110)	1.453(5)	O(101)−C(102)	1.335(5)
Zr(1)−C(201)	2.530(4)	Zr(1)−C(202)	2.530(5)
Zr(1)−C(203)	2.509(4)	Zr(1)−C(204)	2.504(4)
Zr(1)−C(205)	2.523(4)	Zr(1)−Cp*(centroid)	2.209
Cl(1)−Zr(1)−Cl(2)	88.04(4)	Cl(1)−Zr(1)−O(101)	84.45(9)
Cl(2)−Zr(1)−N(112)	84.33(10)	Zr(1)−O(101)−C(102)	138.9(3)
C(108)−N(112)−Zr(1)	123.1(3)	N(112)−C(108)−O(109)	115.9(4)
C(108)−O(109)−C(110)	106.4(3)	O(109)−C(110)−C(111)	103.6(3)
C(110)−C(111)−N(112)	101.2(3)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 7

Zr(1)−N(1)	2.371(3)	Zr(1)−O(2)	2.072(3)
Zr(1)−C(32)	2.273(4)	Zr(1)−C(33)	2.294(5)
O(2)−C(9)	1.323(4)	N(1)−C(3)	1.302(6)
C(3)−O(1)	1.356(4)	O(1)−C(2)	1.446(5)
C(2)−C(1)	1.532(6)	C(1)−N(1)	1.513(5)
Zr(1)−C(22)	2.532(4)	Zr(1)−C(23)	2.557(4)
Zr(1)−C(24)	2.570(4)	Zr(1)−C(25)	2.540(4)
Zr(1)−C(26)	2.523(5)	Zr(1)−Cp*(centroid)	2.240
C(32)−Zr(1)−C(33)	83.08(17)	C(33)−Zr(1)−N(1)	86.90(18)
C(32)−Zr(1)−O(2)	137.17(15)	O(2)−Zr(1)−N(1)	74.38(11)
Zr(1)−O(2)−C(9)	136.5(2)	N(1)−C(3)−O(1)	115.9(4)
C(3)−O(1)−C(2)	106.6(3)	C(2)−C(1)−N(1)	101.2(4)
C(1)−N(1)−C(3)	105.8(3)		

Chart 2. Possible Diastereoisomers of 16



$CpTiCl_3$ readily yielded an orange crystalline solid, whose analytical data were consistent with the formulation $[CpTiL^5Cl_2]$ (**17**).

Diastereoselectvity in these CpTi complexes is rather poorer than in the Cp* systems. At 368 K, the spectrum of a toluene-d_8 solution of **16** gave a single set of sharp resonances, but at room temperature the spectrum was extremely broad, and by 213 K a number of complexes were apparent: two major isomers (ca. 35% and 45%) and three minor ones in roughly equal proportions. Some suggested isomeric species are shown in Chart 2. The N-bonded oxazoline complexes in "down" **VII** and "up" **VIII** orientations are, on the basis of molecular structure determinations, probably the major isomers observed. We have very recently observed an O-bonded mode like **IX** and **X** in a related system.[33] A six-coordinate three-legged piano stool complex **XI** is also very feasible in this system. Similarly, the ^{1}H NMR spectrum of **17** at 368 K is sharp and exhibits one set of ligand resonances. At room temperature, a major isomer (90%) and perhaps four minor isomers could be observed.

(33) Gott, A. L.; Clarkson, G. J.; Scott, P., unpublished results.

Conclusions

A convenient route of entry is provided into a new class of chiral and configurationally well-defined group 4 transition metal complexes, $Cp^*ML^nX_2$. The modular nature of the ligand synthesis allows the further modification of electronic and to some extent steric properties of the system. With suitable oxazoline substitution (i.e., one alkyl or aryl group at the stereogenic center adjacent to the nitrogen atom) the thermodynamic diastereoselection is essentially perfect and the system also has an unusually high barrier to N-decoordination (as evidenced by exchange behavior, or lack of it, in deliberately poorly diastereoselective examples for both metals). With the unsubstituted Cp ring complexes of titanium, minor isomers are observed and epimerization processes were more readily accessible.

Given the promising performance of this ligand class in olefin polymerization[18,19] and our recent discovery that the amido compounds are selective and unusually fast catalysts for cyclohydroamination of aminoalkenes,[21] we are encouraged to investigate other potential catalytic applications.[3]

Experimental Details

General Considerations. All manipulations were conducted using standard inert-atmosphere techniques using a dual-manifold argon/vacuum Schlenk line or a glovebox (MBraun) operating at <1 ppm O_2/H_2O. All glassware and cannulae were stored in an oven at >373 K. The following solvents were predried over sodium wire, refluxed for 3 days under dinitrogen with an appropriate drying agent, and distilled: pentane and diethyl ether from Na/K alloy; heptane and THF from potassium; toluene from sodium. Dichloromethane and acetonitrile were similarly distilled from CaH_2. Solvents were stored in glass ampules and were rigorously degassed before use. Benzene-d_6 and toluene-d_8 were freeze−thaw degassed and then refluxed *in vacuo* over potassium for 3 days before vacuum transfer. Dichloromethane-d_2 and pyridine-d_5 were dried similarly from CaH_2. Chloroform-*d* was stored over 4 Å molecular sieves.

Cp^*ZrCl_3,[34] Cp^*ZrMe_3,[34] Cp^*TiCl_3,[35] Cp^*TiMe_3,[36] Cp^*TiCl_2Me,[30] $CpTiCl_3$,[35] and salicyloxazoline proligands HL^n (n = 1, 3−5)[16–18] were prepared according to published procedures. Anhydrous HCl (as a 1 M solution in diethyl ether) and methyllithium (as a 1.6 M solution in diethyl ether) were purchased from Acros Organics and used as received. (*S*)-(+)-2-Amino-1-propanol and (*S*)-(+)-2-amino-1-phenylethanol were purchased from Aldrich and used as received. 3,5-Di-*tert*-butylsalicylic acid hydrate was purchased from TCI Europe and dried overnight (as a diethyl ether solution) over Na_2SO_4 prior to use. Triphenylphosphine (Aldrich) was recrystallized from hot hexane. Triethylamine and carbon tetrachloride were distilled from CaH_2 under

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nitrogen and stored in graduated glass ampules. Sodium hydride (Aldrich, 60% dispersion in mineral oil) was repeatedly washed on a frit with dry diethyl ether under an inert atmosphere, before drying and storage in a glovebox. Flash chromatography was performed with a FlashMaster Personal Chromatography system and a series of prepacked, disposable columns (Anachem). Thin-layer chromatography was performed using Merck 0.25 mm silica layer foil-backed plates.

NMR spectra were recorded on Bruker DPX300 and DPX400 spectrometers. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced internally using residual protio-solvent resonances relative to tetramethylsilane (δ = 0 ppm). Routine NMR assignments were confirmed by ^{1}H−^{1}H (COSY) and ^{13}C−^{1}H (HMQC) correlation experiments where necessary. Elemental analyses were obtained by Warwick Analytical Services, Coventry, UK, and MEDAC Ltd., Surrey, UK. Some of the carbon analyses of the metal methyl compounds are low, despite repeated crystallization attempts and the use of combustion aids. We attribute this to metal carbide formation, as has been reported in the literature.[37] Mass spectra were obtained using a VG Autospec mass spectrometer by the Department of Chemistry Mass Spectrometry Service, University of Warwick.

Synthesis of (*S*)-HL^2. To a Schlenk tube containing 3,5-di-*tert*-butylsalicylic acid (2.50 g, 10.0 mmol), (*S*)-(+)-2-amino-1-propanol (0.731 g, 10.0 mmol), and triphenylphosphine (7.87 g, 30.0 mmol) was added acetonitrile (50 mL). To the resulting white suspension was added triethylamine (6.0 mL, 40.0 mmol) with stirring, and a clear colorless solution was obtained. Carbon tetrachloride (9.9 mL, 100.0 mmol) was added dropwise to the reaction mixture over 4 h, via syringe pump. During the course of the addition of the CCl_4, a precipitate formed and the reaction mixture changed color to dark red. The reaction was stirred for a further 48 h, resulting in a dark red suspension. The solution was then filtered, and the colorless residue was washed with diethyl ether (2 × 30 mL). The filtrate and washings were combined, the resulting precipitate was removed by filtration, and the process was repeated until no more solids precipitated. The filtrate was evaporated under reduced pressure to leave a sticky, dark red-brown residue, which was extracted with hexane (200 mL) overnight. The solvent was removed *in vacuo* to give a viscous, pale yellow residue. The product was purified via flash chromatography on silica using hexane/ethyl acetate (50:1) as the mobile phase. Collection of product-containing fractions and drying *in vacuo* gave the product as a yellow oil. Dissolution in pentane and drying *in vacuo* yielded the title compound as an extremely viscous yellow gum which retained solvent. Yield = 2.08 g (7.2 mmol, 72%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.30 ppm (s, 9H, C*Me*$_3$), 1.36 (d, 3H, C*H*$_3$ of oxazoline, $^3J_{HH}$ = 7 Hz), 1.44 (s, 9H, C*Me*$_3$), 3.93 (t, 1H, OC*H*$_2$ oxazoline, $^2J_{HH}$ = 7 Hz), 4.41−4.51 (m, 2H, OC*H*$_2$ and NC*H*Me oxazoline, overlapping), 7.43 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 3 Hz), 7.53 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 3 Hz), 12.59 (s, br, 1H, O*H*). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 298 K): δ 21.5 ppm (*Me* of oxazoline), 29.4, 31.5 (both C*Me*$_3$), 34.2, 35.1 (both *C*Me$_3$), 60.9 (N*C*HMe oxazoline), 73.0 (O*C*H$_2$ oxazoline), 109.8 (Ar C_q), 122.1, 127.8 (both Ar *C*-H), 136.4, 140.0, 156.8 (all Ar C_q), 165.8 (oxazoline C_q). Anal. Calcd for $C_{18}H_{27}NO_2 \cdot (C_5H_{12})_{0.5}$: C, 75.65; H, 10.22; N, 4.30. Found: C, 75.74; H, 9.75 N, 3.95. MS (EI +ve): *m*/*z* 289 [M$^+$].

Synthesis of (*S*)-HL^6. The procedure for (*S*)-HL^2 above was used, with 3,5-di-*tert*-butylsalicylic acid (2.00 g, 8.00 mmol) and (*S*)-(+)-2-amino-1-phenylethanol (1.10 g, 8.00 mmol), yielding the title compound as a crystalline yellow solid. Yield = 1.97 g (5.6 mmol, 70%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 1.20 ppm (s, 9H, C*Me*$_3$), 1.36 (s, 9H, C*Me*$_3$), 3.91 (d of d, 1H, NC*H*$_2$ oxazoline, $^2J_{HH}$ = 14 Hz, $^3J_{HH}$ = 8 Hz), 4.39 (d of d, 1H, NC*H*$_2$ oxazoline, $^2J_{HH}$ = 14 Hz, $^3J_{HH}$ = 10 Hz), 5.55 (d of d, 1H, OC*H*Ph oxazoline, $^3J_{HH}$ = 10 Hz, 8 Hz), 7.36 (m, 5H, Ar C-*H* of Ph), 7.45 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz), 7.60 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz), 12.53 (s, br, 1H, O*H*). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 298 K): δ 29.3, 31.4 ppm (both C*Me*$_3$), 34.2, 35.1 (both *C*Me$_3$), 61.5 (N*C*H$_2$ oxazoline), 79.9 (O*C*HPh oxazoline), 109.6 (Ar C_q), 122.1, 125.8 (both Ar *C*-H), 128.0, 128.4, 128.7, 136.4, 140.0, 140.3, 156.9 (all Ar C_q), 166.5 (C_q oxazoline). Anal. Calcd for $C_{23}H_{29}NO_2$: C, 78.59; H, 8.32; N, 3.99. Found: C, 78.64; H, 8.40; N, 3.96. MS (EI +ve): *m*/*z* 351 [M$^+$], 336 [M$^+$ − CH$_3$], 294 [M$^+$ − CMe$_3$].

General Procedure for NaL^n(THF)$_x$ (n = 2−5). A Schlenk tube was charged with HL^n (ca. 1.00 g) and sodium hydride (4−5 equiv). The vessel was cooled to −78 °C (dry ice/acetone slush bath), and cold THF was added (ca. 30 mL), with concomitant effervescence. The reaction was stirred for 15 min at low temperature before being allowed to warm slowly to ambient temperature. The vessel was evacuated and allowed to stir at room temperature under static vacuum overnight; the excess sodium hydride was then allowed to settle and removed by filtration. All volatiles were removed *in vacuo* to yield the title compounds as bright yellow, air-sensitive solids in effectively quantitative yields. The amount of THF (x) in the material was deduced by careful integration of ^{1}H NMR spectra in pyridine-d_5.

NaL^2(THF)$_x$. According to the above procedure, (*S*)-HL^2 (0.900 g, 3.1 mmol) and NaH (0.298 g, 12.4 mmol) gave the title compound as a bright yellow solid. ^{1}H NMR (300 MHz, pyridine-d_5, 298 K): δ 0.97 ppm (d, 3H, C*H*$_3$ of oxazoline, $^3J_{HH}$ = 8 Hz), 1.43 (s, 9H, C*Me*$_3$), 1.60 (m, 4H, THF), 1.76 (s, 9H, C*Me*$_3$), 3.61 (m, 1H, NC*H*Me oxazoline), 4.11 (m, 2H, OC*H*$_2$ oxazoline), 7.64 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz), 8.15 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz).

NaL^3(THF)$_x$. According to the above procedure, (*S*)-HL^3 (0.980 g, 3.1 mmol) and NaH (0.298 g, 12.4 mmol) gave the title compound as a bright yellow solid. ^{1}H NMR (300 MHz, pyridine-d_5, 298 K): δ 0.73 ppm (d, 3H, C*H*$_3$ of ^{i}Pr, $^3J_{HH}$ = 7 Hz), 0.83 (d, 3H, C*H*$_3$ of ^{i}Pr, $^3J_{HH}$ = 7 Hz), 1.43 (s, 9H, C*Me*$_3$), 1.60 (m, 4H, THF), 1.74 (s, 9H C*Me*$_3$), 1.85 (hept., 1H, C*H* of ^{i}Pr, $^3J_{HH}$ = 7 Hz), 3.60 (m, 4H, THF), 3.95 (m, 2H, OC*H*$_2$ oxazoline), 4.15 (m, 1H, NC*H*^{i}Pr oxazoline), 7.60 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz), 8.07 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz).

NaL^4(THF)$_x$. According to the above procedure, (*S*)-HL^4 (1.15 g, 3.47 mmol) and NaH (0.417 g, 17.4 mmol) gave the title compound as a bright yellow solid. ^{1}H NMR (300 MHz, pyridine-d_5, 298 K): δ 0.82 ppm (s, 9H C*Me*$_3$ oxazoline), 1.45 (s, 9H, C*Me*$_3$), 1.63 (m, 4H, THF), 1.78 (s, 9H, C*Me*$_3$), 3.68 (m, 4H, THF), 3.89 (m, 1H, NC*H*^{t}Bu), 4.08 (m, 2H, OC*H*$_2$ oxazoline), 7.68 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz), 8.17 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz).

NaL^5(THF)$_x$. According to the above procedure, (*S*)-HL^5 (1.26 g, 3.59 mmol) and NaH (0.431 g, 17.9 mmol) gave the title compound as a bright yellow solid. ^{1}H NMR (300 MHz, pyridine-d_5, 298 K): δ 1.42 ppm (s, 9H, C*Me*$_3$), 1.62 (m, 4H, THF), 1.80 (s, 9H, C*Me*$_3$), 3.66 (m, 4H, THF), 3.73 (d of d, 1H, OC*H*$_2$ oxazoline, $^2J_{HH}$ = 14 Hz, $^3J_{HH}$ = 7 Hz), 4.24 (d of d, 1H, OC*H*$_2$ oxazoline, $^2J_{HH}$ = 14 Hz, $^3J_{HH}$ = 10 Hz), 5.42 (d of d, 1H, NC*H*Ph oxazoline, $^3J_{HH}$ = 10 Hz, 7 Hz), 7.22 (m, 3H, Ar C-*H* of Ph), 7.33 (m, 2H, Ar C-*H* of Ph), 7.68 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz), 8.24 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz).

General Procedure for [Cp*ZrL^{n}Cl$_2$]. A Schlenk tube was charged with NaL^n(THF)$_x$ (ca. 0.250 g) and Cp*ZrCl$_3$ (1 equiv). The reaction vessel was cooled to −78 °C (dry ice/acetone slush bath), and THF (ca. 10 mL) was added. The yellow suspension was allowed to stir at low temperature for 15 min before being allowed to warm to ambient temperature overnight. All volatiles were removed *in vacuo*, and the yellow residue was extracted with toluene (30 mL) and filtered. The solvent was removed to yield [Cp*ZrL^{n}Cl$_2$] as a yellow solid, which was recrystallized (where necessary) from diethyl ether or toluene at −30 °C. Purification was also possible by sublimation (typically 250 °C, 10^{-6} mmHg).

[Cp*ZrL^{2}Cl$_2$] (1). Using the general procedure described above, NaL^2(THF)$_x$ (0.323 g, 0.90 mmol) and Cp*ZrCl$_3$ (0.300

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g, 0.90 mmol) yielded the title compound as a yellow crystalline solid as the toluene extract was concentrated. Yield: 0.430 g (0.73 mmol, 81%). ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.95 ppm (d, 3H, CH_3 of oxazoline, $^3J_{HH}$ = 6 Hz), 1.28 (s, 9H, CMe_3), 1.64 (s, 9H, CMe_3), 1.90 (s, 15H, C_5Me_5), 3.45 (d of d, 1H, OCH_2 oxazoline, $^2J_{HH}$ = 8 Hz, $^3J_{HH}$ = 2 Hz), 3.60 (t, 1H, OCH_2 oxazoline, $^2J_{HH}$ = 8 Hz), 4.01 (m, 1H, NC*H*Me oxazoline), 7.75 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 3 Hz), 8.00 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 3 Hz). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, 298 K): δ 12.2 ppm (C_5Me_5), 21.3 (*C*H$_3$ of oxazoline), 30.1, 31.5 (both CMe_3), 34.6, 35.6 (both *C*Me$_3$), 63.2 (N*C*HMe oxazoline), 74.1 (O*C*H$_2$ oxazoline), 112.2 (Ar C_q), 123.1 (Ar *C*-H), 125.5 (C_5Me_5), 131.1 (Ar *C*-H), 140.6, 141.6, 163.0 (all Ar C_q), 169.4 (oxazoline C_q). Anal. Calcd for $C_{28}H_{41}NO_2ZrCl_2 \cdot (C_7H_8)_{0.33}$: C, 58.94; H, 7.13; N, 2.28. Found: C, 58.83; H, 7.50; N, 2.28. MS (EI +ve): *m*/*z* 583 [M$^+$], 449 [M$^+$ − C_5Me_5].

[Cp*ZrL^{3}Cl$_2$] (2). Using the general procedure described above, NaL^3(THF)$_x$ (0.209 g, 0.56 mmol) and Cp*ZrCl$_3$ (0.185 g, 0.56 mmol) yielded the title compound as a pale yellow solid following sublimation or crystallization from toluene. Data below are from sublimated material. Yield: 0.277 g (0.46 mmol, 81%). ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.20 ppm (d, 3H, CH_3 of ^{i}Pr, $^3J_{HH}$ = 7 Hz), 0.56 (d, 3H, CH_3 of ^{i}Pr, $^3J_{HH}$ = 7 Hz), 1.24 (s, 9H, CMe_3), 1.65 (s, 9H, CMe_3), 1.90 (s, 15H, C_5Me_5), 2.81 (hept., 1H, C*H* of ^{i}Pr, $^3J_{HH}$ = 7 Hz), 3.64 (t, 1H, OCH_2 oxazoline, $^2J_{HH}$ = 9 Hz, $^3J_{HH}$ = 1 Hz), 3.96 (d of d, 1H, OCH_2 oxazoline, $^2J_{HH}$ = 9 Hz, $^3J_{HH}$ = 7 Hz), 4.10 (d of d, 1H, NC*H*^{i}Pr oxazoline, $^3J_{HH}$ = 7 Hz, 1 Hz), 7.73 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 1 Hz), 7.97 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 1 Hz) ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): δ 12.2 ppm (C_5Me_5), 13.5, 18.9 (both *C*H$_3$ of ^{i}Pr), 30.9 (*C*H of ^{i}Pr), 31.5, 32.4 (both CMe_3), 34.5, 35.8 (both *C*Me$_3$), 67.8 (N*C*H^{i}Pr oxazoline), 72.0 (O*C*H$_2$ oxazoline), 111.8 (Ar C_q), 122.9 (Ar *C*-H), 125.6 (C_5Me_5), 131.2 (Ar *C*-H), 140.5, 141.6, 163.0 (all Ar C_q), 169.9 (oxazoline C_q). Anal. Calcd for $C_{30}H_{45}NO_2ZrCl_2$: C, 58.70; H, 7.39; N, 2.28. Found: C, 58.10; H, 7.28; N, 1.94. MS (EI +ve): *m*/*z* 613 [M$^+$], 478 [M$^+$ − C_5Me_5].

[Cp*ZrL^{4}Cl$_2$] (3). Using the general procedure described above, NaL^4(THF)$_x$ (0.234 g, 0.60 mmol) and Cp*ZrCl$_3$ (0.200 g, 0.60 mmol) yielded the title compound as a pale yellow solid. Yield: 0.287 g (0.46 mmol, 76%). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 0.71 ppm (s, 9H, CMe_3 oxazoline), 1.30 (s, 9H, CMe_3), 1.69 (s, 9H, CMe_3), 1.95 (s, 15H, C_5Me_5), 3.71 (d of d, 1H, OCH_2 oxazoline, $^2J_{HH}$ = 9 Hz, $^3J_{HH}$ = 7 Hz,), 4.07 (d of d, 1H, OCH_2 oxazoline, $^2J_{HH}$ = 9 Hz, $^3J_{HH}$ = 1 Hz), 4.52 (d of d, 1H, NC*H*^{t}Bu oxazoline, $^3J_{HH}$ = 7 Hz, 1 Hz), 7.76 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 3 Hz), 7.94 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 3 Hz). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, 298 K): δ 12.2 ppm (C_5Me_5), 26.4 (CMe_3 of oxazoline), 30.0, 31.5 (both CMe_3), 34.5, 35.8, 36.3 (all *C*Me$_3$), 69.7 (N*C*H^{t}Bu oxazoline), 74.8 (O*C*H$_2$ oxazoline), 112.4 (Ar C_q), 122.2 (Ar *C*-H), 125.8 (C_5Me_5), 131.2 (Ar *C*-H), 140.8, 141.3, 164.3 (all Ar C_q), 171.4 (oxazoline C_q). Anal. Calcd for $C_{31}H_{47}NO_2ZrCl_2$: C, 59.30; H, 7.55; N, 2.23. Found: C, 59.22; H, 7.57; N, 2.20. MS (EI +ve): *m*/*z* 625 [M$^+$], 490 [M$^+$ − C_5Me_5].

[Cp*ZrL^{5}Cl$_2$] (4). Using the general procedure described above, NaL^5(THF)$_x$ (0.192 g, 0.47 mmol) and Cp*ZrCl$_3$ (0.156 g, 0.47 mmol) yielded the title compound as a pale yellow solid. Yield: 0.258 g (0.40 mmol, 85%). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 1.33 ppm (s, 9H, CMe_3), 1.72 (s, 9H, CMe_3), 1.98 (s, 15H, C_5Me_5), 3.89 (d of d, 1H, OCH_2 oxazoline, $^2J_{HH}$ = 9 Hz, $^3J_{HH}$ = 2 Hz), 4.00 (t, 1H, OCH_2 oxazoline, $^2J_{HH}$ = 8 Hz), 5.25 (d of d, 1H, NC*H*Ph oxazoline, $^2J_{HH}$ = 8 Hz, $^3J_{HH}$ = 2 Hz), 6.90 (m, 5H, Ar C-*H* of oxazoline Ph), 7.85 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 3 Hz), 8.15 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 3 Hz) ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, 298 K): δ 12.2 ppm (C_5Me_5), 25.8, 30.1 (both CMe_3), 31.5, 35.8 (both *C*Me$_3$), 70.9 (N*C*HPh oxazoline), 75.6 (O*C*H$_2$ oxazoline), 111.5 (Ar C_q), 123.3 (Ar *C*-H), 125.4 (C_5Me_5), 125.7, 128.5, 129.3 (all Ar *C*-H of Ph), 131.7 (Ar *C*-H), 140.9, 141.5, 141.7, 163.4 (all Ar C_q), 171.1 (oxazoline C_q). Anal. Calcd for $C_{33}H_{43}NO_2ZrCl_2$: C, 61.18; H, 6.69; N, 2.16. Found: C, 61.26; H, 6.67; N, 2.09. MS (EI +ve): *m*/*z* 647 [M$^+$], 612 [M$^+$ − Cl], 512 [M$^+$ − C_5Me_5].

[Cp*ZrL^{6}Cl$_2$] (5). Using the general procedure described above, NaL^6(THF)$_x$ (0.210 g, 0.51 mmol) and Cp*ZrCl$_3$ (0.169 g, 0.51 mmol) yielded the title compound as a pale yellow solid, which crystallized from the toluene extract under vacuum. Yield: 0.214 g (0.33 mmol, 65%). ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K), major diastereomer: δ 1.19 ppm (s, 9H, CMe_3), 1.69 (s, 9H, CMe_3), 1.97 (s, 15H, C_5Me_5), 4.12 (d of d, 1H, NCH_2 oxazoline, $^2J_{HH}$ = 15 Hz, $^3J_{HH}$ = 10 Hz), 4.25 (d of d, 1H, NCH_2 oxazoline, $^2J_{HH}$ = 15 Hz, $^3J_{HH}$ = 11 Hz), 5.21 (d of d, 1H, OC*H*Ph oxazoline, $^3J_{HH}$ = 11 Hz, 10 Hz), 7.00 - 7.12 (m, 5H, Ar C-*H* of oxazoline Ph), 7.77 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 3 Hz), 7.95 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 3 Hz). Minor diastereomer: δ 1.27 ppm (s, 9H, CMe_3), 1.37 (s, 9H, CMe_3), 1.81 (s, 15H, C_5Me_5), 3.88 (d of d, 1H, NCH_2 oxazoline, $^2J_{HH}$ = 14 Hz, $^3J_{HH}$ = 8 Hz), 4.88 (d of d, 1H, NCH_2 oxazoline, $^2J_{HH}$ = 14 Hz, $^3J_{HH}$ = 10 Hz), 5.78 (d of d, 1H, OC*H*Ph oxazoline, $^3J_{HH}$ = 10 Hz, 8 Hz), 7.32−7.41 (m, 5H, Ar C-*H* of Ph), 7.57 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 3 Hz), 7.80 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 3 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, 298 K), major diastereomer: δ 12.0 ppm (C_5Me_5), 29.9, 31.2 (both CMe_3), 34.5, 35.4 (both *C*Me$_3$), 64.4 (N*C*H$_2$ oxazoline), 82.4 (O*C*HPh oxazoline), 111.3 (Ar C_q), 123.6 (Ar *C*-H), 125.7 (C_5Me_5), 128.3, 129.2 (Ar *C*-H of Ph), 129.4 (Ar *C*-H), 131.2 (Ar *C*-H of Ph), 137.7, 139.5, 141.8, 161.7 (all Ar C_q), 169.0 (oxazoline C_q). Minor diastereomer: δ 12.0 ppm (C_5Me_5), 30.0, 31.3 (both CMe_3), 34.5, 35.5 (both *C*Me$_3$), 64.6 (N*C*H$_2$ oxazoline), 80.1 (O*C*HPh oxazoline), 111.5 (Ar C_q), 123.5 (Ar *C*-H), 125.2 (C_5Me_5), 128.3 (Ar *C*-H of Ph), 128.8 (Ar *C*-H), 129.1, 131.3 (Ar *C*-H of Ph), 139.2, 139.5, 141.9, 162.0 (all Ar C_q), 169.2 (oxazoline C_q). Anal. Calcd for $C_{30}H_{45}Cl_2NO_2Zr \cdot (C_7H_8)_{0.33}$: C, 62.53; H, 6.78; N, 2.07. Found: C, 62.71; H, 6.95; N, 1.96. MS (EI +ve): *m*/*z* 647 [M$^+$], 512 [M$^+$ − C_5Me_5].

General Procedure for [Cp*ZrL$''$Me$_2$] (*n* = 3−5). In a Schlenk tube [Cp*ZrL$''$Cl$_2$] (0.250 g, ca. 0.40 mmol) was slurried in pentane (10 mL) and the reaction vessel cooled to 0 °C. Added dropwise, via syringe, was methyllithium (2 mL of a 1.6 M solution in diethyl ether, >4 equiv). The suspension changed color from yellow to white, before stirring at room temperature for 2 h in the absence of light. Chlorotrimethylsilane (0.5 mL) was added via syringe and the reaction stirred for a further 30 min. The reaction was filtered, and all volatiles were removed *in vacuo* to yield the title compound as an off-white residue. Crystallization from pentane (ca. 2 mL) at −30 °C yielded the title compounds [Cp*ZrL$''$Me$_2$] as colorless crystalline solids.

[Cp*ZrL^{3}Me$_2$] (6). Using the procedure described above, [Cp*ZrL^{3}Cl$_2$] and MeLi yielded the title compound as a colorless solid. Yield: 0.071 g (0.12 mmol, 30%). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 0.29 ppm (s, 3H, Zr-CH_3), 0.36 (d, 3H, CH_3 of ^{i}Pr, $^3J_{HH}$ = 7 Hz), 0.52 (d, 3H, CH_3 of ^{i}Pr, $^3J_{HH}$ = 7 Hz), 0.68 (s, 3H, Zr-CH_3), 1.29 (s, 9H, CMe_3), 1.63 (s, 9H, CMe_3), 1.83 (s, 15H, C_5Me_5), 2.28 (m, 1H, C*H* of ^{i}Pr), 3.54 (m, 1H, oxazoline), 3.70 (m, 1H, oxazoline), 3.90 (m, 1H, oxazoline), 7.76 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz), 8.08 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, 298 K): δ 11.4 ppm (C_5Me_5), 14.4, 19.1 (both *C*H$_3$ of ^{i}Pr), 28.8 (*C*H of ^{i}Pr), 30.0, 31.5 (both CMe_3), 34.4, 35.6 (both *C*Me$_3$), 39.9, 41.5 (both Zr-*C*H$_3$), 111.1 (Ar C_q), 118.9 (C_5Me_5), 123.2, 130.3 (both Ar *C*-H), 139.9, 140.4, 163.6 (all Ar C_q), 169.2 (oxazoline C_q) Anal. Calcd for $C_{32}H_{51}NO_2Zr$: C, 67.08; H, 8.97; N, 2.44. Found: C, 66.69; H, 8.80; N, 2.41. MS (EI +ve): *m*/*z* 556 [M$^+$ − CH_3], 541 [M$^+$ − 2CH_3].

[Cp*ZrL^{4}Me$_2$] (7). Using the procedure described above, [Cp*ZrL^{4}Cl$_2$] and MeLi yielded the title compound as a colorless solid. Yield: 0.056 g (0.10 mmol, 24%). ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.15 ppm (s, 3H, Zr-CH_3), 0.63 (s, 9H, CMe_3 oxazoline), 0.70 (s, 3H, Zr-CH_3), 1.29 (s, 9H, CMe_3), 1.38 (s, 9H, CMe_3), 1.81 (s, 15H, C_5Me_5), 3.54−3.62 (m, 2H, OCH_2 and NC*H*^{t}Bu oxazoline,

overlapping), 3.88 (d of d, 1H, OCH_2 oxazoline, $^2J_{HH}$ = 14 Hz, $^3J_{HH}$ = 7 Hz), 7.71 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz), 8.13 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 298 K): δ 11.3 ppm (C_5Me_5), 26.2 (CMe_3 oxazoline), 30.0, 31.6 (both CMe_3), 34.2, 35.6, 36.3 (all *C*Me$_3$), 43.3, 43.6 (both Zr-*C*H$_3$), 68.8 (N*C*HCMe$_3$ oxazoline), 73.5 (O*C*H$_2$ oxazoline), 113.3 (Ar C_q), 119.7 (C_5Me$_5$), 122.7, 130.5 (both Ar *C*-H), 134.7, 138.8, 139.0, 164.5 (all Ar C_q), 171.2 (oxazoline C_q). Anal. Calcd for $C_{33}H_{53}NO_2Zr$: C, 67.52; H, 9.10; N, 2.39. Found: C, 66.18; H, 9.16; N, 2.35. MS (EI +ve): *m*/*z* 587 [M^+], 571 [$M^+ - CH_3$].

[Cp*ZrL^{5}Me$_2$] (8). Using the procedure described above, [Cp*ZrL^{5}Cl$_2$] and MeLi yielded the title compound as a pale yellow solid. Yield: 0.050 g (0.08 mmol, 21%). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ −0.21 ppm (s, 3H, Zr-C*H*$_3$), 0.55 (s, 3H, Zr-C*H*$_3$), 1.32 (s, 9H, CMe_3), 1.66 (s, 9H, CMe_3), 1.86 (s, 15H, C_5Me_5), 3.78 (d of d, 1H, OCH_2 oxazoline, $^2J_{HH}$ = 8 Hz, $^3J_{HH}$ = 3 Hz), 3.87 (t, 1H, OCH_2 oxazoline, $^2J_{HH}$ = 8 Hz), 4.81 (d of d, 1H, NC*H*Ph oxazoline, $^3J_{HH}$ = 8 Hz, 3 Hz), 6.82−6.93 (m, 5H, Ar C-*H* of Ph), 7.83 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 3 Hz), 8.20 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 3 Hz). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 298 K): δ 11.5 ppm (C_5Me_5), 30.1, 30.7 (both CMe_3), 34.5, 35.8 (both *C*Me$_3$), 41.2, 42.4 (both Zr-*C*H$_3$), 69.8 (N*C*HPh oxazoline), 74.8 (O*C*H$_2$ oxazoline), 110.9 (Ar C_q), 119.3 (C_5Me$_5$), 123.6, 125.7, 127.8, 129.0, 130.8 (all Ar *C*-H), 139.6, 140.2, 141.7, 164.3 (all Ar C_q), 170.8 (oxazoline C_q). Anal. Calcd for $C_{35}H_{49}NO_2Zr$: C, 69.26; H, 8.14; N, 2.31. Found: C, 68.49; H, 8.25; N, 1.90. MS (EI +ve): *m*/*z* 590 [$M^+ - CH_3$], 575 [$M^+ - 2CH_3$].

[Cp*TiL^{1}Me$_2$] (9). A J. Young ampule was charged with a magnetic stirrer bar, Cp*TiMe$_3$ (0.300 g, 1.31 mmol), and HL^1 (0.362 g, 1.31 mmol). Toluene (10 mL) was added, and the vessel evacuated and heated to 100 °C for 2 days in the absence of light. After this time, the reaction vessel was allowed to cool to ambient temperature and the volatiles were removed *in vacuo* to yield an oily, dark residue. Addition of cold pentane (5 mL) saw the precipitation of a microcrystalline orange solid (0.169 g) of analytical purity, which was isolated by filtration and dried *in vacuo*. The filtrate was stored at −30 °C overnight, resulting in the deposition of a further amount of orange, crystalline solid (0.177 g), which was isolated similarly. Total yield: 0.346 g (0.71 mmol, 54%). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 0.52 ppm (s, 3H, Ti-C*H*$_3$), 1.11 (s, 3H, Ti-C*H*$_3$), 1.36 (s, 9H, CMe_3), 1.64 (s, 9H, CMe_3), 1.75 (s, 15H, C_5Me_5), 2.93 (m, 1H, NCH_2 oxazoline), 3.37 (m, 2H, OCH_2 oxazoline), 3.57 (m, 1H, NCH_2 oxazoline), 7.79 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 3 Hz), 8.09 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 3 Hz). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 298 K): δ 11.9 ppm (C_5Me_5), 30.4, 31.7 (both CMe_3), 34.5, 35.8 (both *C*Me$_3$), 55.8 (N*C*H$_2$ oxazoline), 56.0, 61.9 (both Ti-*C*H$_3$), 66.2 (O*C*H$_2$ oxazoline), 110.6 (Ar C_q), 122.1 (C_5Me$_5$), 123.1, 129.5 (both Ar *C*-H), 139.0, 139.1, 162.5 (all Ar C_q), 167.2 (oxazoline C_q). Anal. Calcd for $C_{29}H_{45}NO_2Ti$: C, 71.44; H, 9.30; N, 2.87. Found: C, 71.03; H, 9.37; N, 2.82. MS (EI +ve): *m*/*z* 472 [$M^+ - CH_3$], 457 [$M^+ - 2CH_3$].

[Cp*TiL^{3}Me$_2$] (10). As for **9** above, using Cp*TiMe$_3$ (0.250 g, 1.10 mmol) and (*S*)-HL^3 (0.348 g, 1.10 mmol) at 60 °C for 2 days in the absence of light. Yield: 0.105 g (0.20 mmol, 18%). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 0.49 (d, 3H, CH_3 of ^{i}Pr, $^3J_{HH}$ = 7 Hz), 0.51 (d, 3H, CH_3 of ^{i}Pr, $^3J_{HH}$ = 7 Hz), 0.68 (s, 3H, Ti-CH_3), 1.16 (s, 3H, Ti-CH_3), 1.32 (s, 9H, CMe_3), 1.63 (s, 9H, CMe_3), 1.74 (s, 15H, C_5Me_5), 2.38 (hept, 1H, C*H* of ^{i}Pr, $^3J_{HH}$ = 7 Hz), 3.52 (m, 2H, OCH_2 and NC*H*^{i}Pr oxazoline, overlapping), 3.93 (d, 1H, OCH_2 oxazoline, $^3J_{HH}$ = 8 Hz), 7.77 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 3 Hz), 8.08 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 3 Hz). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 298 K): δ 11.9 ppm (C_5Me_5), 14.0, 19.1 (both *C*H$_3$ of ^{i}Pr), 29.5 (*C*H of ^{i}Pr), 30.2, 31.7 (both CMe_3), 34.5, 35.7 (both *C*Me$_3$), 57.5, 63.1 (both Ti-*C*H$_3$), 66.5 (N*C*H^{i}Pr oxazoline), 71.5 (OCH$_2$ oxazoline), 122.4 (C_5Me$_5$), 122.8, 129.9 (2 × Ar *C*-H), 139.0, 139.2, 164.6, 165.9 (all Ar C_q), 168.3 (oxazoline C_q). Anal. Calcd for $C_{32}H_{51}NO_2Ti$: C, 72.57; H, 9.71; N, 2.64. Found: C, 72.31; H, 9.70; N, 2.70. MS (EI +ve): *m*/*z* 514 [$M^+ - CH_3$], 499 [$M^+ - 2CH_3$].

[Cp*TiL^{5}Me$_2$] (11). As for **10** above, using Cp*TiMe$_3$ (0.250 g, 1.10 mmol) and (*S*)-HL^5 (0.385 g, 1.10 mmol). Yield: 0.328 g (0.57 mmol, 52%). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 0.24 ppm (s, 3H, Ti-C*H*$_3$), 1.03 (s, 3H, Ti-C*H*$_3$), 1.36 (s, 9H, CMe_3), 1.66 (s, 9H, CMe_3), 1.76 (s, 15H, C_5Me_5), 3.77 (d of d, 1H, OCH_2 oxazoline, $^2J_{HH}$ = 8 Hz, $^3J_{HH}$ = 2 Hz), 3.87 (t, 1H, OCH_2 oxazoline, $^2J_{HH}$ = 8 Hz), 4.59 (d of d, 1H, NC*H*Ph oxazoline, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 2 Hz), 6.91 (m, 5H, Ar C-*H*, oxazoline), 7.84 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 3 Hz), 8.23 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 3 Hz). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 298 K): δ 11.9 ppm (C_5Me_5), 30.3, 31.7 (both CMe_3), 34.5, 35.8 (both *C*Me$_3$), 61.1, 62.8 (both Ti-*C*H$_3$), 70.4 (N*C*HPh oxazoline), 74.6 (O*C*H$_2$ oxazoline), 109.8 (Ar C_q), 122.3 (C_5Me$_5$), 123.0, 125.8, 127.6, 129.0, 130.6 (all Ar *C*-H), 139.2, 139.6, 142.0, 166.1 (all Ar C_q), 169.6 (oxazoline C_q). Anal. Calcd for $C_{35}H_{49}NO_2Ti$: C, 74.58; H, 8.76; N, 2.49. Found: C, 73.78; H, 8.72; N, 1.97. MS (EI +ve): *m*/*z* 548 [$M^+ - CH_3$], 533 [$M^+ - 2CH_3$].

[Cp*TiL^{1}Cl$_2$] (12). Method A. A Schlenk tube was charged with a dark yellow solution of [Cp*TiL^{1}Me$_2$] (**9**) (0.200 g, 0.41 mmol) in diethyl ether (10 mL). Anhydrous hydrogen chloride (0.82 mL of a 1 M solution in diethyl ether, 2 equiv) was added dropwise via syringe at ambient temperature, with concomitant effervescence and a color change to dark red. The reaction was left to stir at room temperature for 30 min. All volatiles were removed *in vacuo* to yield the title compound as a microcrystalline red-orange solid.

Method B. A J. Young ampule was charged with HL^1 (0.409 g, 1.5 mmol) and Cp*TiCl$_2$Me (0.400 g, 1.5 mmol). Heptane (ca. 10 mL) was added, and the vessel evacuated and heated to 75 °C for 36 h. After this time, a crystalline orange solid had precipitated. The suspension was allowed to cool, and the solid isolated by filtration and dried *in vacuo* to yield the title compound in analytical purity. Yield: 0.757 g (1.43 mmol, 96%). ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 1.28 ppm (s, 9H, CMe_3), 1.68 (s, 9H, CMe_3), 1.92 (s, 15H, C_5Me_5), 3.52 (m, 2H, NCH_2 oxazoline), 3.62 (m, 1H, OCH_2 oxazoline), 4.01 (m, 1H, OCH_2 oxazoline), 7.75 (d, 1H Ar C-*H*, $^4J_{HH}$ = 2 Hz), 7.86 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz). $^{13}C\{^1H\}$ NMR (100.7 MHz, C_6D_6, 298 K): δ 13.3 ppm (C_5Me_5), 30.5, 31.5 (both CMe_3), 34.6, 35.9 (both *C*Me$_3$), 58.9 (N*C*H$_2$ oxazoline), 67.3 (O*C*H$_2$ oxazoline), 111.3 (Ar C_q), 122.8, 130.2 (both Ar *C*-H), 132.7 (C_5Me$_5$), 139.7, 142.0, 165.0 (all Ar C_q), 166.9 (oxazoline C_q). Anal. Calcd for $C_{27}H_{39}NO_2TiCl_2.C_7H_{16}$: C, 64.97; H, 8.82; N, 2.23. Found: C, 64.73; H, 8.61; N, 1.98. MS (EI +ve): *m*/*z* 492 [$M^+ - Cl$].

[Cp*TiL^{3}Cl$_2$] (13). Using method B above, heating Cp*TiCl$_2$Me (0.250 g, 0.93 mmol) and (*S*)-HL^3 (0.295 g, 0.93 mmol) in toluene at 75 °C for 48 h yielded the title compound as a crystalline orange solid, which was isolated by filtration and dried *in vacuo*. Yield: 0.349 g (0.60 mmol, 65%). ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 0.35 ppm (d, 3H, CH_3 of ^{i}Pr, $^3J_{HH}$ = 7 Hz), 0.76 (d, 3H, CH_3 of ^{i}Pr, $^3J_{HH}$ = 7 Hz), 1.27 (s, 9H, CMe_3), 1.38 (s, 9H, CMe_3), 1.93 (s, 15H, C_5Me_5), 2.66 (d of hept, 1H, C*H* of ^{i}Pr, $^3J_{HH}$ = 7 Hz, 3 Hz), 4.25 (d of t, 1H, N-C*H*^{i}Pr oxazoline, $^3J_{HH}$ = 7 Hz, 2 Hz), 4.30 (t, 1H, OCH_2 oxazoline, $^2J_{HH}$ = 7 Hz), 4.50 (d of d, 1H, OCH_2 oxazoline, $^2J_{HH}$ = 9 Hz, $^3J_{HH}$ = 2 Hz), 7.55 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz), 7.63 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, 298 K): δ 12.5 ppm (C_5Me_5), 14.0, 19.1 (both *C*H$_3$ of ^{i}Pr), 29.6 (*C*H of ^{i}Pr), 30.0, 31.5 (both CMe_3), 34.8, 35.6 (both *C*Me$_3$), 68.4 (N*C*H^{i}Pr oxazoline), 73.3 (O*C*H$_2$ oxazoline), 110.9 (Ar C_q), 122.5, 129.4 (both Ar *C*-H), 134.1 (C_5Me$_5$), 139.1, 142.9, 165.8 (all Ar C_q), 168.2 (oxazoline C_q). Anal. Calcd for $C_{30}H_{45}NO_2TiCl_2 \cdot (C_7H_8)_{0.5}$: C, 65.26; H, 8.01; N, 2.46. Found: C, 65.18; H, 7.94; N, 2.18. MS (EI +ve): *m*/*z* 534 [$M^+ - Cl$].

[Cp*TiL^{5}Cl$_2$] (14). Using method B above, heating Cp*TiCl$_2$Me (0.400 g, 1.5 mmol) and (*S*)-HL^5 (0.522 g, 1.5 mmol) at 85 °C for 48 h. After removal of all volatiles *in vacuo*, the resulting orange solid was dissolved in hot toluene (ca. 5 mL), and an equal amount

of heptane added. Standing at −30 °C for 48 h yielded the title compound as a crystalline red-orange solid, which was isolated by filtration and dried *in vacuo*. Material of analytical purity could also be obtained by layering a methylene chloride solution with pentane. Yield: 0.368 g (0.61 mmol, 41%). ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 1.28 ppm (s, 9H, C*Me*$_3$), 1.42 (s, 9H, C*Me*$_3$), 1.98 (s, 15H, C$_5$*Me*$_5$), 4.37 (d of d, 1H, OC*H*$_2$ oxazoline, $^2J_{HH}$ = 9 Hz, $^3J_{HH}$ = 2 Hz), 4.72 (t, 1H, OC*H*$_2$ oxazoline, $^2J_{HH}$ = 9 Hz), 5.40 (d of d, 1H, NC*H*Ph oxazoline,$^2J_{HH}$ = 9 Hz, $^3J_{HH}$ = 2 Hz), 6.75 (d, 2H, *o*-Ar C-*H* of Ph, $^3J_{HH}$ = 7 Hz), 7.13 (m, 3H, *m*- and *p*-Ar C-*H* of Ph), 7.62 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz), 7.72 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, 298 K): δ 13.6 ppm (C$_5$*Me*$_5$), 30.1, 31.5 (both C*Me*$_3$), 34.9, 35.7 (both *C*Me$_3$), 72.1 (N*C*HPh oxazoline), 76.4 (O*C*H$_2$ oxazoline), 110.4 (Ar *C*$_q$), 122.8 (Ar *C*-H), 125.7, 127.6, 128.8 (Ar *C*-H of oxazoline Ph), 131.4 (Ar *C*-H), 133.9 (*C*$_5$Me$_5$), 134.7, 139.5, 142.6, 143.0, 166.0 (all Ar *C*$_q$), 169.4 (oxazoline *C*$_q$). Anal. Calcd. for $C_{33}H_{43}NO_2TiCl_2\cdot(CH_2Cl_2)_{0.4}$: C, 62.83; H, 6.91; N, 2.19. Found: C, 62.66 H, 7.36; N, 1.75. MS (EI +ve): *m*/*z* 568 [M$^+$ − Cl].

[Cp*TiL^{6}Cl$_2$] (15). A J. Young ampule was charged with Cp*TiCl$_2$Me (0.200 g, 0.74 mmol) and (*S*)-HL^6 (0.250 g, 0.74 mmol). Toluene (10 mL) was added, and the reaction vessel evacuated and heated at 85 °C for 3 days. The reaction was then allowed to cool to ambient temperature, and all volatiles were removed *in vacuo*. The dark red residue was recrystallized from the minimum volume of hot heptane, yielding an orange microcrystalline solid. Yield: 0.242 g (0.40 mmol, 54%). ^{1}H NMR (400 MHz, C_6D_6, 298 K), major diastereomer: δ 1.21 ppm (s, 9H, C*Me*$_3$), 1.71 (s, 9H, C*Me*$_3$), 2.00 (s, 15H, C$_5$*Me*$_5$), 4.17 (d of d, 1H, NC*H*$_2$ oxazoline, $^2J_{HH}$ = 15 Hz, $^3J_{HH}$ = 10 Hz), 4.36 (d of d, 1H, NC*H*$_2$ oxazoline, $^2J_{HH}$ = 15 Hz, $^3J_{HH}$ = 12 Hz), 5.31 (d of d, OC*H*Ph oxazoline, $^3J_{HH}$ = 12 Hz, 10 Hz), 6.87 (m, 2H, Ar C-*H* of Ph), 7.00 (m, 3H, Ar C-*H* of Ph), 7.78 (d, 1H Ar C-*H*, $^4J_{HH}$ = 2 Hz), 7.97 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz). Minor diastereomer: δ 1.30 (s, 9H, C*Me*$_3$), 1.71 (s, 9H, C*Me*$_3$), 1.86 (s, 15H, C$_5$*Me*$_5$), 3.75 (d of d, 1H, NC*H*$_2$ oxazoline, $^2J_{HH}$ = 14 Hz, $^3J_{HH}$ = 8 Hz), 4.90 (d of d, 1H, NC*H*$_2$ oxazoline, $^2J_{HH}$ = 14 Hz, $^3J_{HH}$ = 11 Hz), 5.01 (d of d, OC*H*Ph oxazoline, $^3J_{HH}$ = 11 Hz, 8 Hz), 7.03−7.14 (m, 5H, Ar C-*H* of Ph), 7.80 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz), 8.04 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 2 Hz). ^{13}C{^{1}H} NMR (100.7 MHz, C_6D_6, 298 K), major diastereomer: δ 13.4 ppm (C$_5$*Me*$_5$), 30.5, 31.4 (both C*Me*$_3$), 34.6, 35.9 (both *C*Me$_3$), 66.5 (N*C*H$_2$ oxazoline), 82.5 (O*C*HPh oxazoline), 111.1, 122.8 (both *C*$_q$ of Ar), 125.0 (Ar *C*-H), 127.3, 129.1 (both Ar *C*-H of Ph), 129.2 (Ar *C*-H), 129.3 (Ar *C*-H of Ph), 130.6 (Ar *C*$_q$), 132.9 (*C*$_5$Me$_5$), 142.3, 165.5 (both Ar *C*$_q$), 166.5 (oxazoline *C*$_q$). Minor diastereomer: δ 13.4 ppm (C$_5$*Me*$_5$), 30.6, 31.5 (both C*Me*$_3$), 34.6, 36.0 (both *C*Me$_3$), 66.6 (N*C*H$_2$ oxazoline), 79.5 (O*C*HPh oxazoline), 111.3, 122.7 (both Ar *C*$_q$), 125.0 (Ar *C*-H), 128.3, 128.9, 129.0 (all Ar *C*-H of Ph), 130.4 (Ar *C*$_q$), 132.9 (*C*$_5$Me$_5$), 142.3, 165.4 (both Ar *C*$_q$), 166.6 (oxazoline *C*$_q$). Anal. Calcd for $C_{33}H_{43}NO_2TiCl_2$: C, 65.57; H, 7.17; N, 2.32. Found: C, 65.33 H, 7.18; N, 1.80. MS (EI +ve): *m*/*z* 568 [M$^+$ − Cl], 468 [M$^+$ − C$_5$Me$_5$].

[CpTiL^{3}Me$_2$] (16). A Schlenk tube was charged with an orange slurry of CpTiCl$_3$ (0.200 g, 0.91 mmol) in diethyl ether (20 mL). The reaction vessel was cooled to −40 °C (dry ice/acetonitrile slush bath), and methyllithium (2 mL of a 1.6 M solution in diethyl ether, excess) was added, with a gradual change to a yellow suspension. The reaction was left to stir for 2 h at −40 °C, whereupon chlorotrimethylsilane (1 mL) was added via syringe. The reaction was allowed to stir for a further 30 min, before being allowed to warm to ambient temperature. A solution of (*S*)-HL^3 (1 equiv) in diethyl ether (5 mL) was then added via cannula. Effervescence was observed. The resulting orange-brown suspension was allowed to stir for a further 2 h (in the absence of light) at room temperature before filtration. All volatiles were removed *in vacuo* to yield an orange solid, which was crystallized from pentane at −30 °C overnight. Yield: 0.267 g (0.58 mmol, 64%). ^{1}H NMR (400 MHz, $C_6D_5CD_3$, 368 K, fast exchange): δ 0.51 ppm (d, 1H, C*H*$_3$ of ^{i}Pr, $^2J_{HH}$ = 7 Hz), 0.60 (d, 1H, C*H*$_3$ of ^{i}Pr, $^2J_{HH}$ = 7 Hz), 0.99 (s, br, 6H, 2 × Ti−C*H*$_3$), 1.38 (s, 9H, C*Me*$_3$), 1.56 (s, 9H, C*Me*$_3$), 2.38 (mult., 1H, C*H* of ^{i}Pr), 3.66 (t, 1H, OC*H*$_2$ oxazoline, $^2J_{HH}$ = 10 Hz), 3.85 (d of d, 1H, OC*H*$_2$ oxazoline, $^2J_{HH}$ = 10 Hz, $^3J_{HH}$ = 7 Hz) 3.99 (d, 1H, NC*H*^{i}Pr oxazoline, $^3J_{HH}$ = 7 Hz), 6.09 (s, 5H, C$_5$*H*$_5$), 7.76 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 7 Hz), 7.99 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 7 Hz). Anal. Calcd for $C_{27}H_{41}NO_2Ti$: C, 70.58; H, 8.99; N, 3.05. Found: C, 69.70; H, 8.99; N 2.75. MS (EI +ve) *m*/*z*: 444 [M$^+$ − CH$_3$], 429 [M$^+$ − 2CH$_3$].

[CpTiL^{5}Cl$_2$] (17). A Schlenk tube was charged with (*S*)-HL^5 (0.320 g, 0.91 mmol) and NaH (0.118 g, 4.55 mmol, 5 equiv). The reaction vessel was cooled to −78 °C, and THF (20 mL) was added. The reaction was allowed to warm to room temperature, with effervescence, before being evacuated and stirred overnight at ambient temperature. The excess NaH was allowed to settle before filtration into a second Schlenk, charged with a slurry of CpTiCl$_3$ (0.200 g, 0.91 mmol) in THF (10 mL). The resulting dark red solution was stirred overnight at ambient temperature before all volatiles were removed *in vacuo*. The red residue was extracted with toluene, the solvent removed under reduced pressure, and the orange solid recrystallized from hot heptane to yield a crystalline orange solid. Yield: 0.279 g (0.52 mmol, 57%). ^{1}H NMR (400 MHz, C_6D_6, 298 K), major diastereomer: δ 1.27 ppm (s, 9H, C*Me*$_3$), 1.59 (s, 9H, C*Me*$_3$), 3.67 (d of d, 1H, OC*H*$_2$ oxazoline, $^2J_{HH}$ = 10 Hz, $^3J_{HH}$ = 8 Hz), 3.81 (d of d, 1H, NC*H*Ph oxazoline, $^3J_{HH}$ = 8 Hz, 4 Hz), 5.85 (d of d, 1H, OC*H*$_2$ oxazoline,$^2J_{HH}$ = 10 Hz, $^3J_{HH}$ = 4 Hz), 5.93 (s, 5H, C$_5$*H*$_5$), 6.94 (m, 3H, Ar C-*H* of Ph), 7.17 (m, 2H, Ar C-*H* of Ph), 7.76 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 3 Hz), 7.92 (d, 1H, Ar C-*H*, $^4J_{HH}$ = 3 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, 298 K), major diastereomer: δ 30.0, 31.5 ppm (both C*Me*$_3$), 35.0, 35.6 (both *C*Me$_3$), 73.6 (N*C*HPh oxazoline), 76.4 (O*C*H$_2$ oxazoline), 112.8 (Ar *C*$_q$), 122.7 (*C*$_5$H$_5$), 123.4 (Ar *C*-H), 126.0, 128.9, 129.6 (all Ar *C*-H of Ph), 131.0 (Ar *C*-H), 131.8, 137.7, 141.3, 144.3, 165.1 (all Ar *C*$_q$), 168.1 (oxazoline *C*$_q$). Anal. Calcd for $C_{28}H_{33}NO_2TiCl_2$: C, 62.94; H, 6.22; N, 2.62. Found: C, 62.62; H, 6.42; N, 1.99. MS (EI +ve): *m*/*z* 434 [M$^+$ − Cl − C$_5$H$_5$].

X-ray Crystallography. Single crystals of [Cp*ZrL^{3}Cl$_2$]·C$_7$H$_8$ (**2**) and [Cp*ZrL^{4}Me$_2$] (**7**) were grown from saturated toluene and pentane solutions, respectively, at −30 °C. Crystals were immersed in an inert oil prior to transfer to the cold nitrogen gas stream on a Bruker AXS-SMART three-circle CCD area detector diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å). Data were collected using narrow (0.3° in ω) frame exposures. Intensities were corrected semiempirically for absorption, on the basis of symmetry-equivalent and repeated reflections using SADABS.[38] The structure was solved using direct methods via SHELXS and refined using SHELXL. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms placed in calculated positions using a riding model (with free rotation for methyl groups). All H atoms were assigned isotropic thermal parameters 1.2 × (1.5 × for methyl groups) the equivalent isotropic displacement parameter of the parent atom. Programs used were Bruker AXS SMART and SAINT[39] (control and integration) and SHELXTL[40] for structure solution, refinement, and molecular graphics.

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Supporting Information Available: CIF files for the structural determinations of **2** and **7**. This can be obtained free of charge via the Internet at http://pubs.acs.org.

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