Chiral Alkoxide-Functionalized Guanidinates from Ring-Opening Rearrangement of Aminooxazolinate Complexes

Andrew L. Gott, Stuart R. Coles, Adam J. Clarke, Guy J. Clarkson, and Peter Scott*

Department of Chemistry, University of Warwick, Gibbet Hill Road, Coventry CV4 7AL, U.K.

Received August 22, 2006

Treatment of $Cp^*M(NMe_2)_3$ (M = Zr, Hf) with both achiral and optically pure chiral aminooxazoline proligands H**L** yields metastable aminooxazolinate half-sandwich diamide complexes $[Cp^*M\mathbf{L}(NMe_2)_2]$. These species undergo clean rearrangement via oxazoline ring-opening to carbodiimides followed by amide migratory insertion. The chiral-at-metal products contain tridentate alkoxide-functionalized guanidinates, as confirmed by X-ray diffraction. In some of the chiral ligand systems, single diastereomer samples can be prepared, either by direct reaction or after recrystallization. As a result of the chelate structure, no thermal conversion between diastereomers is observed. A mechanism leading to the observed diastereoselection involving an intramolecular CH-π interaction in the major product is proposed.

Introduction

Tetrasubstituted guanidine-derived compounds can bind to metals in a variety of different modes.[1] From the organometallic chemist's perspective, it is perhaps the deprotonated η^2-form (Figure 1) that has been of most interest, not least because of the similarity to the less electron-rich amidinates.[2] Guanidinate complexes of group 4 elements were first synthesized by Lappert and co-workers in 1970, via the insertion of carbodiimides into the homoleptic group 4 dialkylamides $M(NMe_2)_4$ (M = Ti/Zr/Hf).[3] Since this time, they have been used as spectator ligands in a variety of systems in which the electronic and steric properties can be subtly altered by the correct choice of substituents in the positions R^1-R^3. In addition to a series of synthetic studies into structural chemistry and the reaction of such complexes with small molecules,[4] guanidinate ligands have recently been applied to a series of group 4 complexes that catalytically mediate organic transformations including the metathesis of carbodiimides,[5] hydroamination of alkynes,[6] and guanylation of amines.[7] Guanidinate ligands have also been used to support both neutral and cationic zirconium complexes, which were subsequently employed in α-olefin polymerization[8] and have also been employed in the synthesis of dinitrogen complexes of titanium.[9] Very recently, Ti guanidinate complexes were used as precursors for titanium carbonitride via low-pressure chemical vapor deposition.[10]

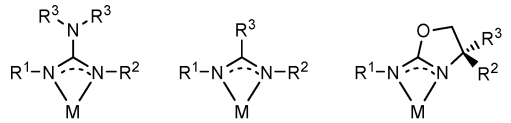


Figure 1. Relationship between guanidinate, amidinate, and aminooxazolinate.

The use of the related amidinate[2] ligand set is undoubtedly more widespread than its guanidinate counterpart, and half-sandwich complexes containing the general structural unit [(η^5-C_5R_5)M(η^2-amidinate)] (where R = H, Me and M = Ti/Zr/Hf) have been extensively studied. Following early work on silyl benzamidinates,[11] related compounds have been actively employed as polymerization catalysts by Sita[12] and others.[13] In the context of half-sandwich complexes, the amidinate ligand is also a useful ancillary in related metal-centered reactivity studies,[14] binuclear compounds,[15] and complexes containing imide[16] and phosphinimide functionalities.[17]

Given the successes of the half-sandwich group 4 amidinates in catalysis, we sought to incorporate our recently developed chiral diazaallyl ligand system aminooxazolinate[18] into similar

* To whom correspondence should be addressed. E-mail: peter.scott@warwick.ac.uk.

(1) (a) Coles, M. P. *Dalton Trans.* **2006**, 985. (b) Bailey, P. J.; Pace, S. *Coord. Chem. Rev.* **2001**, *214*, 91. (c) Schug, K. A.; Lindner, W. *Chem. Rev.* **2005**, *105*, 67. (d) Best, M. D.; Tobey, S. L.; Anslyn, E. V. *Coord. Chem. Rev.* **2003**, *240*, 3. (e) Hosseni, M. W. *Coord. Chem. Rev.* **2003**, *240*, 157.

(2) (a) Edelmann, F. T. *Coord. Chem. Rev.* **1994**, *137*, 403. (b) Barker, J.; Kilner, M. *Coord. Chem. Rev.* **1994**, *133*, 219.

(3) Chandra, G.; Jenkins, A. D.; Lappert, M. F.; Srivastava, R. C. *J. Chem. Soc. A* **1970**, 2550.

(4) (a) Ong, T. G.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2003**, *22*, 387. (b) Bazinet, P.; Wood, D.; Yap, G. P. A.; Richeson, D. S. *Inorg. Chem.* **2003**, *42*, 6225. (c) Coles, M. P.; Hitchcock, P. B. *Organometallics* **2003**, *22*, 5201. (d) Ong, T. G.; Wood, D.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2002**, *21*, 1. (e) Coles, M. P.; Hitchcock, P. B. *J. Chem. Soc., Dalton Trans.* **2001**, 1169. (f) Giesbrecht, G. R.; Whitener, G. D.; Arnold, J. *Organometallics* **2000**, *19*, 2809. (g) Wood, D.; Yap, G. P. A.; Richeson, D. S. *Inorg. Chem.* **1999**, *38*, 5788.

(5) Ong, T. G.; Yap, G. P. A.; Richeson, D. S. *Chem. Commun.* **2003**, 2612.

(6) Ong, T. G.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2002**, *21*, 2839.

(7) Ong, T. G.; Yap, G. P. A.; Richeson, D. S. *J. Am. Chem. Soc.* **2003**, *125*, 8100.

(8) Duncan, A. P.; Mullins, S. M.; Arnold, J.; Bergman, R. G. *Organometallics* **2001**, *20*, 1808.

(9) Mullins, S. M.; Duncan, A. P.; Bergman, R. G.; Arnold, J. *Inorg. Chem.* **2001**, *40*, 6952.

(10) Carmalt, C. J.; Newport, A. C.; O'Neill, S. A.; Parkin, I. P.; White, A. J. P.; Williams, D. J. *Inorg. Chem.* **2005**, *44*, 615.

(11) (a) Gomez, R.; Green, M. L. H.; Haggitt, J. L. *J. Chem. Soc., Dalton Trans.* **1996**, 939. (b) Gomez, R.; Duchateau, R.; Chernega, A. N.; Teuben, J. H.; Edelmann, F. T.; Green, M. L. H. *J. Organomet. Chem.* **1995**, *491*, 153. (c) Gomez, R.; Duchateau, R.; Chernega, A. N.; Meetsma, A.; Edelmann, F. T.; Teuben, J. H.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1995**, 217. (d) Bijpost, E. A.; Duchateau, R.; Teuben, J. H. *J. Mol. Catal. A* **1995**, *95*, 121. (e) Gomez, R.; Green, M. L. H.; Haggitt, J. L. *J. Chem. Soc., Chem. Commun.* **1994**, 2607. (f) Sotoodeh, M.; Leichtweis, I.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H. G. *Chem. Ber.* **1993**, *126*, 913. (g) Chernega, A. N.; Gomez, R.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1993**, 1415. (h) Buijink, J. K.; Noltemeyer, M.; Edelmann, F. T. *Z. Naturforsch. B* **1991**, *46*, 1328.

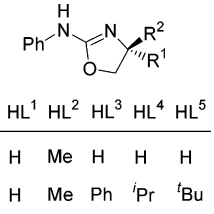
10.1021/om0607649 CCC: $37.00
Publication on Web 12/01/2006

complexes. The proligands are readily synthesized from isothiocyanates and aminoalcohols,[19] and the wide range of such starting materials allows the synthesis of many variants. We have incorporated this diazaallyl moiety into other chiral organic ligand frameworks including 2,2′-diamino-6,6′-dimethylbiphenyl[20] and 1,2-diaminocyclohexyl.[21]

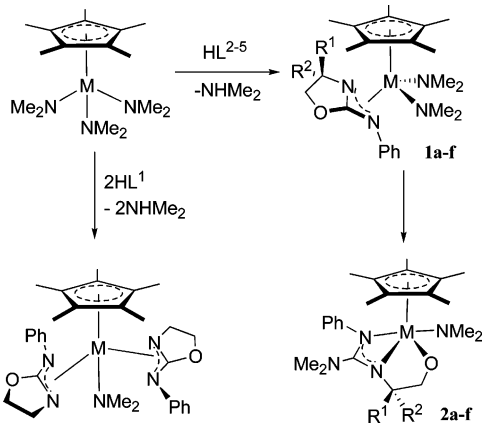
Results and Discussion

Preliminary Observations. The aminooxazoline proligands H**L**^{n} (n = 1−5, Chart 1) were synthesized by previously reported methods.[18] Deprotonation with NaH and ^{n}BuLi readily gave the compounds Na**L**^{n} and Li**L**^{n}. Subsequent reaction of these materials with Cp*MCl_3 (M = Zr, Hf) gave intractable mixtures. Reaction between Cp*MMe_3 (M = Zr, Hf) and H**L**$^{1-5}$ also failed to yield tractable products. Treatment of the readily available Cp*M$(NMe_2)_3$ (M = Zr, Hf) with H**L**$^{1-5}$ in NMR tube scale reactions however led to slow consumption of the poorly soluble proligand and the generation of 1 equiv of dimethylamine.

Chart 1. Aminooxazoline Proligands Used in This Work



Scheme 1. Synthesis of Half-Sandwich Aminooxazolinate Complexes



Synthesis of [Cp*ML^n$(NMe_2)_2$]. In the case of the reaction between Cp*$Zr(NMe_2)_3$ and the least sterically demanding proligand H**L**^{1} a ca. 1:1 mixture of unreacted metal precursor and a species assigned as the (bis)ligand complex [Cp*Zr**L**$^1{}_2$-(NMe_2)] was observed (Scheme 1); the use of this ligand was not explored further. In contrast, treatment of Cp*M$(NMe_3)_3$ with H**L**$^{2-5}$ cleanly yielded the metastable complexes [Cp*Zr**L**^{n}-$(NMe_2)_2$] (n = 2−5) and [Cp*Hf**L**$^n(NMe_2)_2$] (n = 2, 3) (**1a**−**f**). No reaction was observed with Cp*$Ti(NMe_2)_3$, even after heating to elevated temperatures for 3 days.

In the ^{1}H NMR spectrum of [Cp*Zr**L**$^2(NMe_2)_2$] (**1a**) thus synthesized in situ, the two inequivalent oxazoline methyl groups give rise to broad singlets, and a broad resonance is observed for the oxazoline OCH_2 unit at δ 3.52 ppm. Cooling the sample to 213 K resulted in sharpening of resonances and decoalescence of the latter into a pair of AB doublets at 3.37 and 3.45 ppm. This behavior is consistent with the presence of a chiral-at-metal system undergoing racemization on the NMR chemical shift time scale.[18]

For the complexes **1c**−**f**, the presence of elements of chirality centered at both the ligand and the metal gives rise to the possibility of diastereoisomerism. The ^{1}H NMR spectra of [Cp*Zr**L**$^3(NMe_2)_2$] (**1c**) are typical; at 233 K two diastereomers are observed (diastereomeric ratio (d.r.) 2.5:1), as demonstrated by two sets of two resonances for the inequivalent dimethylamido ligands (major δ 2.58 and 3.12 ppm, minor δ 3.02 and 3.04 ppm). A series of overlapping multiplets was observed in the oxazoline region. By 293 K the diastereomers are rapidly interconverting on this time scale; the mutually coupled protons of the oxazoline ring give resonances at 3.86, 4.08, and 4.72 ppm, and *two* amido NMe_2 group resonances are observed at 2.69 and 3.05 ppm. Coalescence of these two amido unit resonances was not observed up to 323 K, whereupon the rate of an irreversible isomerization reaction (vide infra) became too rapid to allow further study. These observations are consistent with epimerization either by *N*-dissociation or in-place rotation (ring flipping) of the diazaallyl unit. The latter would fail to equilibrate the two amido units, and the former would have to

(12) (a) Harney, M. B.; Zhang, Y. H.; Sita, L. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 2400. (b) Harney, M. B.; Keaton, R. J.; Fettinger, J. C.; Sita, L. R. *J. Am. Chem. Soc.* **2006**, *128*, 3420. (c) Kissounko, D. A.; Zhang, Y. H.; Harney, M. B.; Sita, L. R. *Adv. Synth. Catal.* **2005**, *347*, 426. (d) Zhang, Y. H.; Sita, L. R. *J. Am. Chem. Soc.* **2004**, *126*, 7776. (e) Zhang, Y. H.; Reeder, E. K.; Keaton, R. J.; Sita, L. R. *Organometallics* **2004**, *23*, 3512. (f) Harney, M. B.; Keaton, R. J.; Sita, L. R. *J. Am. Chem. Soc.* **2004**, *126*, 4536. (g) Zhang, Y. H.; Sita, L. R. *Chem. Commun.* **2003**, 2358. (h) Zhang, Y. H.; Keaton, R. J.; Sita, L. R. *J. Am. Chem. Soc.* **2003**, *125*, 9062. (i) Kissounko, D. A.; Fettinger, J. C.; Sita, L. R. *Inorg. Chim. Acta* **2003**, *345*, 121. (j) Keaton, R. J.; Sita, L. R. *J. Am. Chem. Soc.* **2002**, *124*, 9070. (k) Keaton, R. J.; Jayaratne, K. C.; Henningsen, D. A.; Koterwas, L. A.; Sita, L. R. *J. Am. Chem. Soc.* **2001**, *123*, 6197. (l) Jayaratne, K. C.; Sita, L. R. *J. Am. Chem. Soc.* **2001**, *123*, 10754. (m) Keaton, R. J.; Jayaratne, K. C.; Fettinger, J. C.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 12909. (n) Jayaratne, K. C.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 958. (o) Jayaratne, K. C.; Keaton, R. J.; Henningsen, D. A.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 10490.

(13) (a) van Meerendonk, W. J.; Schroder, K.; Brussee, E. A. C.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Eur. J. Inorg. Chem.* **2003**, 427. (b) Richter, J.; Edelmann, F. T.; Noltemeyer, M.; Schmidt, H. G.; Shmulinson, M.; Eisen, M. S. *J. Mol. Catal. A* **1998**, *130*, 149.

(14) (a) Kissounko, D. A.; Epshteyn, A.; Fettinger, J. C.; Sita, L. R. *Organometallics* **2006**, *25*, 1076. (b) Kissounko, D.; Epshteyn, A.; Fettinger, J. C.; Sita, L. R. *Organometallics* **2006**, *25*, 531. (c) Kissounko, D. A.; Sita, L. R. *J. Am. Chem. Soc.* **2004**, *126*, 5946. (d) Zhang, Y. H.; Keaton, R. J.; Sita, L. R. *J. Am. Chem. Soc.* **2003**, *125*, 8746. (e) Kissounko, D. A.; Fettinger, J. C.; Sita, L. R. *J. Organomet. Chem.* **2003**, *683*, 29. (f) Zhang, Y. H.; Kissounko, D. A.; Fettinger, J. C.; Sita, L. R. *Organometallics* **2003**, *22*, 21. (g) Keaton, R. J.; Sita, L. R. *Organometallics* **2002**, *21*, 4315. (h) Keaton, R. J.; Koterwas, L. A.; Fettinger, J. C.; Sita, L. R. *J. Am. Chem. Soc.* **2002**, *124*, 5932. (i) Babcock, J. R.; Incarvito, C.; Rheingold, A. L.; Fettinger, J. C.; Sita, L. R. *Organometallics* **1999**, *18*, 5729. (j) Koterwas, L. A.; Fettinger, J. C.; Sita, L. R. *Organometallics* **1999**, *18*, 4183. (k) Sita, L. R.; Babcock, J. R. *Organometallics* **1998**, *17*, 5228.

(15) (a) McNevin, M. J.; Hagadorn, J. R. *Inorg. Chem.* **2004**, *43*, 8547. (b) Hagadorn, J. R.; McNevin, M. J.; Wiedenfeld, G.; Shoemaker, R. *Organometallics* **2003**, *22*, 4818. (c) Hagadorn, J. R.; McNevin, M. J. *Organometallics* **2003**, *22*, 609.

(16) (a) Guiducci, A. E.; Boyd, C. L.; Mountford, P. *Organometallics* **2006**, *25*, 1167. (b) Boyd, C. L.; Clot, E.; Guiducci, A. E.; Mountford, P. *Organometallics* **2005**, *24*, 2347. (c) Guiducci, A. E.; Cowley, A. R.; Skinner, M. E. G.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **2001**, 1392. (d) Stewart, P. J.; Blake, A. J.; Mountford, P. *J. Organomet. Chem.* **1998**, *564*, 209. (e) Stewart, P. J.; Blake, A. J.; Mountford, P. *Organometallics* **1998**, *17*, 3271.

(17) (a) Cabrera, L.; Hollink, E.; Stewart, J. C.; Wei, P. R.; Stephan, D. W. *Organometallics* **2005**, *24*, 1091. (b) Hollink, E.; Wei, P. R.; Stephan, D. W. *Organometallics* **2004**, *23*, 1562.

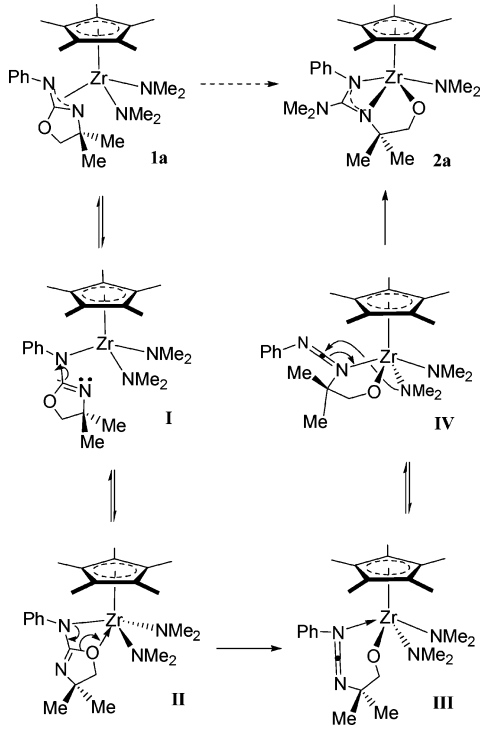
(18) Munslow, I. J.; Wade, A. R.; Deeth, R. J.; Scott, P. *Chem. Commun.* **2004**, 2596.

(19) Kim, T. H.; Lee, N.; Lee, G. J.; Kim, J. N. *Tetrahedron* **2001**, *57*, 7137.

(20) Westmoreland, I.; Munslow, I. J.; Clarke, A. J.; Clarkson, G.; Scott, P. *Organometallics* **2004**, *23*, 5066.

(21) Crust, E. J.; Munslow, I. J.; Scott, P. *J. Organomet. Chem.* **2005**, *690*, 3373.

Scheme 2. Mechanism of the Conversion 1a → 2a



be accompanied by site exchange in the three-legged piano stool intermediate.[14j] While it is thus difficult to exclude either possibility, compounds **1a**−**f** certainly undergo an *N*-dissociative exchange process (vide infra), and we thus we favor the former mechanism.

Ring-Opening Reactions of [Cp*ML^n(NMe$_2$)$_2$]. Compounds **1a**−**f** cleanly isomerized at room temperature to new chiral species **2a**−**f** (Scheme 1), as confirmed by NMR spectroscopy, the X-ray structure of one example (vide infra), and other data. Preparative-scale reactions in toluene yielded the compounds in near quantitative yield. Crystallization from pentane at −30 °C yielded analytically pure materials in the case of **2a**−**d**, albeit in low/moderate yields due to the high solubility of the complexes. Purification of the highly pentane soluble semisolids **2e** and **2f** was achieved by sublimation under high vacuum (10^{-6} mmHg).

The ^{1}H NMR spectrum of **2a** is sharp and essentially invariant with temperature between 213 and 363 K. At room temperature, inequivalent methyl groups are observed at δ 1.20 and 1.24 ppm. A pair of AB doublets at δ 3.87 and 4.37 ppm correspond to the OCH$_2$ unit. Elsewhere in the spectrum, the major feature of interest is the presence of two singlets (6H each) for Me$_2$N groups at δ 3.17 and 2.21 ppm. The former is in the expected chemical shift region for a Zr-bound amide,[22] and the latter corresponds to the uncoordinated guanidinate NMe$_2$ moiety.[8] In the ^{13}C{^{1}H} NMR spectrum the central C atom of the guanidinate appears at δ 163.5 ppm, cf. δ 171.0 ppm for [Cp-{(Me$_2$N)C(N^{i}Pr)$_2$}ZrCl$_2$].[8]

A mechanism for the formation of **2a** is shown in Scheme 2. It is evident from ^{1}H NMR spectra described above that **1a** is undergoing structural exchange with respect to the amino-oxazolinato unit, and the presence at equilibrium of intermediate **II** (Scheme 2) featuring the [N,O] coordination mode is feasible. Ring-opening of **II** as shown, promoted by coordination of the O atom to the Lewis acid forms the alkoxide unit and

(22) Irigoyen, A. M.; Martin, A.; Mena, M.; Palacios, F.; Yelamos, C. *J. Organomet. Chem.* **1995**, *494*, 255.

Table 1. Key to Complexes 2 with Associated Diastereoselectivities

2	R^1	R^2	M	d.r. of 2 [a]
a	Me	Me	Zr	n/a
b	Me	Me	Hf	n/a
c	H	Ph	Zr	6:1[b]
d	H	Ph	Hf	>20:1[c]
e	H	^{i}Pr	Zr	1.7:1
f	H	^{t}Bu	Zr	2.3:1

[a] Determined by ^{1}H NMR spectroscopy on crude products. [b]Improved to >20:1 after recrystallization. [c]Structure determined by X-ray diffraction.

coordinated carbodiimide of **III**. While the ring-opening of oxazolines in polymerization is well documented,[23] few examples of such a process occurring in transition metal complexes have been observed; it has recently been demonstrated that acetate counter-anions in Pd(II) complexes supported by pyridyl bisoxazoline ligands promote ring-opening, although the manner in which the ring-opened ligand binds to the metal is entirely different.[24] Molecular modeling suggests that the seven-membered-ring species **III** is not susceptible to migratory insertion of one of the zirconium amide ligands at the carbodiimide unit, but *N*-dissociative rearrangement to the more stable chelate **IV** would lead eventually to the guanidinate complex **2a**. The latter insertion process is analogous to the intermolecular reaction of M(NMe$_2$)$_4$ with diimides[3] (vide supra). Intramolecular migration of amide co-ligands to coordinated C═N bonds is nevertheless rare, a recent (first) example being reversible attack of dimethylamide co-ligands at the imine carbon atom of Schiff-base tin complexes.[25]

The formally tridentate, dianionic ligand formed in this process is best described as a guanidinate functionalized by an alkoxide pendent arm. Such functionalization is known for amidinate ligands bound to transition metals;[13a,16b,26] however these compounds are, to our knowledge, the first such guanidinate complexes of either the main group or transition metal elements.

Diastereoselective Syntheses of 2c−**f.** For the chiral ligand complexes there arises the possibility of formation of diastereomers with opposite configurations at the metal. The zirconium compound **2c** was formed with d.r. 6:1, on both the NMR tube and preparative scales. Crystallization from pentane yielded the major diastereomer as the single product (d.r. >100) in 21% yield, the low yield once again a reflection of the high solubility of the complex. Given these results, we were somewhat surprised to find that only one diastereomer of the Hf analogue **2d** was observed. The remaining compounds **2e** and **2f** gave lower selectivities, and their solubility precluded attempts to improve the d.r. via crystallization (Table 1).

A single-crystal X-ray diffraction study was performed on a crystal of **2d** grown from a saturated pentane solution of the pure material at room temperature. The molecular structure is

(23) (a) Kobayashi, S.; Uyama, H. *J. Polym. Sci., Part A; Polym. Chem.* **2002**, *40*, 192. (b) Culbertson, B. M. *Prog. Polym. Sci.* **2002**, *27*, 579. (c) Aoi, K.; Okada, M. *Prog. Polym. Sci.* **1996**, *21*, 151.

(24) Kazi, A. B.; Jones, G. D.; Vicic, D. A. *Organometallics* **2005**, *24*, 6051.

(25) Nimitsiriwat, N.; Marshall, E. L.; Gibson, V. C.; Elsegood, M. R. J.; Dale, S. H. *J. Am. Chem. Soc.* **2004**, *126*, 13598.

(26) (a) Boyd, C. L.; Guiducci, A. E.; Dubberley, S. R.; Tyrell, B. R.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **2002**, 4175. (b) Doyle, D.; Gun'ko, Y. K.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **2000**, 4093. (c) Bambirra, S.; Brandsma, M. J. R.; Brussee, E. A. C.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **2000**, *19*, 3197. (d) Kincaid, K.; Gerlach, C. P.; Giesbrecht, G. R.; Hagadorn, J. R.; Whitener, G. D.; Shafir, A.; Arnold, J. *Organometallics* **1999**, *18*, 5360. (e) Brandsma, M. J. R.; Brussee, E. A. C.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Eur. J. Inorg. Chem.* **1998**, 1867.

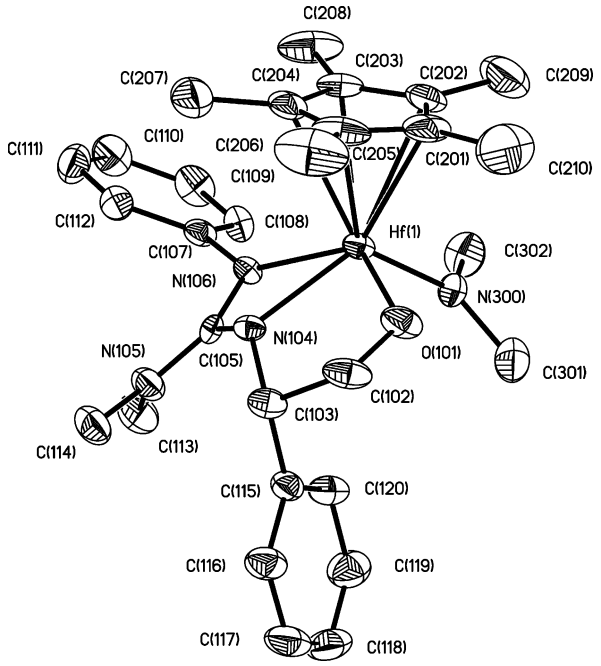


Figure 2. Molecular structure of **2d**. Displacement ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 2. Selected Data Collection and Refinement Parameters for [Cp*HfL$^{3'}$(NMe$_2$)], 2d

formula	$C_{29}H_{40}HfN_4O$
M	639.14
cryst morphology	colorless block
cryst dimens (mm)	0.20 × 0.12 × 0.10
cryst syst	orthorhombic
space group	$P2_12_12_1$
a (Å)	9.0546(11)
b (Å)	15.272(2)
c (Å)	20.203(3)
V (Å^3)	2793.8(7)
Z	4
d(calc) (g/cm^3)	1.520
μ(Mo Kα) (mm^{-1})	7.106
T (K)	180(2)
F(000)	1288
no. of reflns measd	15 518
no. of unique reflns	4885 [*R*(int) = 0.0389]
R_1 [$I > 2\sigma(I)$]	0.0261
wR_2	0.0588
no. of data/restraints/params	4885/18/325
goodness of fit	1.017
largest diff peak and hole (e·Å^{-3})	0.716 and −0.662

given in Figure 2, with crystallographic data and selected bond lengths and angles in Tables 2, 3, and 4. The complex crystallized in the orthorhombic space group $P2_12_12_1$, with one molecule in the asymmetric unit. The guanidinate is bound in an η^2-fashion through both nitrogen atoms. The two bond lengths C(105)−N(104) and C(105)−N(106) of 1.355(5) and 1.326(5) Å, respectively, are significantly different and indicate a contribution from a more localized RN(106)═C−N(104)R resonance form. This is borne out in that Hf−N(106) at 2.267(4) Å is shorter than Hf−N(104) at 2.203 Å and that N(104) is significantly pyramidalized (sum of angles = 340.0°). Although the latter is certainly not a requirement for assignment of amido character at that atom, this distortion does serve to reduce ring strain in the bicyclic chelate structure.

The angle of the mean least-squares planes between the NMe$_2$ of the guanidinate ligand and the diazaallyl moiety, defined by the planes N(106)−C(105)−N(105) and C(113)−N(105)−C(114), is 27.4°. The guanidinate amine group is distorted away from planarity with the diazaallyl unit due to steric crowding from the two adjacent phenyl groups. There appears to be some donation of the lone pair of the guanidinate nitrogen toward the metal center as the C(105)−N(105) bond distance of 1.358(6) Å demonstrates: this connectivity is shorter than the bond length observed in the typical C−N single bonds N(105)−C(114) (1.462(6) Å) and N(105)−C(113) (1.456(6) Å).

Table 3. Bond Lengths (Å) for 2d (estimated standard deviations are given in parentheses)

Hf(1)−O(101)	1.999(3)	N(104)−C(105)	1.326(5)
Hf(1)−N(300)	2.067(4)	C(105)−N(106)	1.355(5)
Hf(1)−N(104)	2.203(4)	C(105)−N(105)	1.358(6)
Hf(1)−N(106)	2.267(4)	N(105)−C(113)	1.456(6)
Hf(1)−C(201)	2.481(5)	N(105)−C(114)	1.462(6)
Hf(1)−C(205)	2.509(5)	N(106)−C(107)	1.429(6)
Hf(1)−C(202)	2.531(5)	C(201)−C(205)	1.401(9)
Hf(1)−C(204)	2.549(5)	C(201)−C(202)	1.415(8)
Hf(1)−C(203)	2.554(5)	C(202)−C(203)	1.401(7)
Hf(1)−Cp$_{cent}$*	2.225	C(103)−C(115)	1.507(7)
Hf(1)−C(105)	2.694(4)	C(203)−C(204)	1.402(7)
O(101)−C(102)	1.400(6)	C(204)−C(205)	1.405(8)
C(102)−C(103)	1.557(7)	N(300)−C(301)	1.449(7)
C(103)−N(104)	1.465(6)	N(300)−C(302)	1.460(7)

The Hf(1)−N(300) distance in the terminal dimethylamide unit at 2.067(4) Å is at the shorter end of the range of Hf amides (2.04−2.24 Å).[27] In the alkoxide the Hf(1)−O(101) bond distance of 1.999(3) Å is comparable with the only other reported hafnium alkoxide (1.969 Å) supported by a Cp* ligand,[28] and the bond angle Hf(1)−O(101)−C(102) of 123.1(3)° is indicative of sp^3 hybridization at oxygen, and thus formally a one-electron donor. The distance between the central hafnium and the centroid of the Cp* ligand is 2.223 Å. This falls within the range of values reported (2.188−2.230 Å) for related hafnium amidinate complexes supported by a Cp* ancillary.[14e] All other bond lengths and angles are unremarkable.

The ^{1}H−^{1}H NOESY and nOe difference spectra of the major isomers of **2c** and **2d** are analogous, suggesting that both compounds have the same diastereomeric structure as determined by X-ray diffraction for the latter.

Origin of Diastereoselection. Variable-temperature ^{1}H NMR spectroscopy on the diastereomeric mixtures of **2e** and **2f** revealed no exchange between isomers on this time scale. Storage of an NMR sample containing diastereomerically pure **2c** at 60 °C for weeks led to no appearance of the minor diastereomer observed earlier. Thus, the thermal interconversion between diastereomers of **2a** is severely restricted, and the diastereomeric ratios reported in Table 1 are of the kinetic products. These ratios then reflect the ratio between diastereomers of the immediate precursor to **2c**, i.e., **IVa** and **IVb** (Scheme 3).

An explanation of the observed diastereoselection in the formation of **2c** is immediately apparent from examination of molecular models of the diastereomers **IV**. (The MM2 package of Chem3D Ultra was used to compute structures based on standard bond lengths and angles taken from the molecular structure of **2d** and related compounds.) For **IVa** there is minor steric pressure between the Cp* ligand and the phenyl group attached to the stereogenic C center (Scheme 3). In **IVb** the

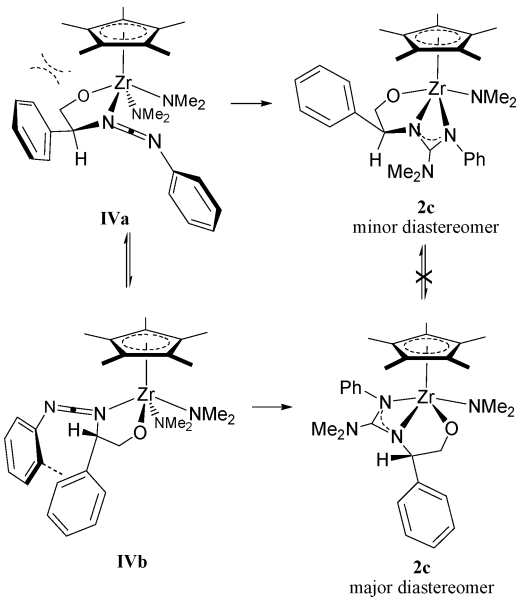
(27) (a) Yasumoto, T.; Yamagata, T.; Mashima, K. *Organometallics* **2005**, *24*, 3375. (b) Castillo, I.; Tilley, T. D. *J. Organomet. Chem.* **2002**, *431*, *643*−644. (c) Kloppenburg, L.; Petersen, J. L. *Polyhedron* **1995**, *14*, 69. (d) Chivers, T.; Gao, X.; Parvez, M. *Inorg. Chem.* **1995**, *34*, 1681. (e) Bol, J. E.; Hessen, B.; Teuben, J. H.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1992**, *11*, 1981. (f) Bai, H.; Roesky, H. W.; Noltemeyer, M.; Witt, M. *Chem. Ber.* **1992**, *125*, 825.

(28) Arnold, J.; Woo, H.-G.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1988**, *7*, 2045.

Table 4. Selected Bond Angles (deg) for 2d (estimated standard deviations are given in parentheses)

O(101)−Hf(1)−N(300)	91.69(16)	O(101)−Hf(1)−N(106)	127.95(13)
O(101)−Hf(1)−N(104)	73.53(13)	N(300)−Hf(1)−N(106)	95.12(15)
N(300)−Hf(1)−N(104)	121.39(14)	N(104)−Hf(1)−N(106)	59.08(14)
O(101)−Hf(1)−Cp_{cent}*	109.8	N(104)−Hf(1)−Cp_{cent}*	120.3
N(106)−Hf(1)−Cp_{cent}*	111.8	N(300)−Hf(1)−Cp_{cent}*	118.2
C(102)−O(101)−Hf(1)	123.1(3)	O(101)−C(102)−C(103)	110.9(4)
C(102)−C(103)−N(104)	102.3(4)	N(104)−C(105)−N(106)	110.6(4)

Scheme 3. Origin of Diastereoselection in the Formation of 2c



carbodiimide spacer orients the two phenyl groups very well for formation of a CH-π interaction, thus favoring the formation of this diastereomer and perhaps increasing its reactivity with respect to the migratory insertion reaction. An explanation for the still higher d.r. observed in the synthesis of the otherwise identical hafnium analogue **2d** would require a more detailed analysis. The mechanism of diastereoselection shown in Scheme 3 is however consistent with the observation of relatively low d.r. for **2e** and **2f**. In these alkyl-substituted compounds we would rely solely on steric effects for stereoselection, and while this distinguishes relatively poorly between isomers of **IV**, it is encouraging that the *tert*-butyl compound **2f** displays significantly higher selectivity than the isopropyl species **2e**.

Conclusions

For this half-sandwich group 4 system (and unlike our earlier examples[18,20,21]) the aminooxazolinato ligand is unstable with respect to a fascinating ring-opening/amido migratory insertion process. The product alkoxide-functionalized guanidinates are also very interesting since they provide a chiral-at-metal system which—unusually for early transition metals—is configurationally stable. Also, diastereoselection in the synthesis of certain of these compounds arises unexpectedly from an intramolecular CH-π interaction; steric effects play a minor role.

With regard to the potential uses of this type of chiral system in early metal catalysis, we might look to the readily available aminothiazolinyl analogues[21] or indeed the pyrrolyl compounds to reduce susceptibility to ring opening, but the problems of diastereoselection and epimerization are likely to be solved only through the use of multidentate chelates.[20]

Experimental Section

General Considerations. All manipulations were conducted using standard inert-atmosphere techniques using a dual-manifold argon/vacuum Schlenk line or an MBraun LabStar glovebox. All glassware and cannulae were stored in an oven at >373 K. Solvents were predried and then refluxed under nitrogen from an appropriate drying agent—toluene from sodium; pentane from NaK alloy—and were stored in glass ampules and rigorously degassed before use. C_6D_6 and $C_6D_5CD_3$ were freeze−thaw−degassed and refluxed in vacuo for 3 days over potassium metal and vacuum transferred before use. The aminooxazoline proligands H**L**$^{1-5}$,[18] Cp*Zr(NMe$_2$)$_3$,[22] and Cp*HfCl$_3$[29] were prepared according to published procedures. LiNMe$_2$ (99.9% grade) was obtained from Chemat Technology and used as received. NMR spectra were recorded on Bruker DPX300, DPX400, and DRX 500 spectrometers. ^{1}H and ^{13}C NMR spectra were referenced internally using residual protiosolvent resonances relative to tetramethylsilane (δ = 0 ppm). Elemental analyses were obtained by Warwick Analytical Services and MEDAC Ltd, Surrey, U.K. Mass spectra were obtained on a VG Autospec mass spectrometer by the Department of Chemistry Mass Spectrometry Service. Attempts to purify **2f** by sublimation led to partial decomposition, reflected in a less than satisfactory microanalysis.

Synthesis of Cp*Hf(NMe$_2$)$_3$. A Schlenk tube was charged with Cp*HfCl$_3$ (2.64 g, 6.3 mmol) and LiNMe$_2$ (1.00 g, 19.5 mmol, 3.1 equiv). The reaction vessel was cooled to −78 °C (dry ice/acetone slush bath), and cold toluene (50 mL) was added with stirring. The reaction was left to stir at −78 °C for 30 min and then allowed to slowly warm to ambient temperature overnight. The resulting pale yellow suspension was filtered through a frit packed with Celite, and the solvent was removed in vacuo to yield an oily yellow residue, which was redissolved in pentane. The volatiles were then removed to yield the title compound as a waxy, pale yellow solid (some of which could not be removed from the reaction vessel). Isolated yield: 2.24 g (5.0 mmol, 80%). While the above material was spectroscopically pure, 1.15 g (82%) of analytically pure material could be obtained by sublimation of 1.40 g of crude material at 120 °C and 10^{-3} mmHg. Anal. Calcd for $C_{16}H_{33}N_3Hf$: C 43.09; H 7.46; N 9.42. Found: C 43.26; H 7.42; N 9.25. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 1.99 ppm (s, 15H, C_5*Me*$_5$), 2.96 (s, 18H, 3 × Hf−N*Me*$_2$). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, 298 K): δ 10.9 ppm (C_5*Me*$_5$), 43.6 (Hf−N*Me*$_2$), 117.2 (*C*$_5$Me$_5$). MS (EI +ve) *m/z*: 447 (33, M$^+$), 399 (37, M$^+$ − NMe$_2$), 354 (29, M$^+$ − 2NMe$_2$).

General NMR-Scale Synthesis of Aminooxazoline Complexes. An NMR tube fitted with J. Young concentric stopcock was charged with an appropriate amount of proligand (ca. 0.05 mmol) and taken into the glovebox, whereupon it was slurried in C_6D_6. Addition of 1 equiv of Cp*M(NMe$_2$)$_3$ (M = Zr, Hf) in C_6D_6 led to slow dissolution of the proligand. The sample was then transferred to an NMR spectrometer for analysis. All ^{1}H NMR spectra were recorded at 300 MHz in C_6D_6 at 298 K. The subsequent rearrangements were monitored by running further spectra at regular intervals.

[Cp*ZrL^2(NMe$_2$)$_2$], 1a. ^{1}H NMR: δ 1.10 ppm (m, v br, 6H, 2 × NC*Me*$_2$ oxazoline), 1.95 (s, 15H, C_5*Me*$_5$), 2.95 (s, 12H, 2 × Zr−N*Me*$_2$), 3.52 (m, v br, 2H, OC*H*$_2$ oxazoline), 6.91 (t, 1H, *p*-Ar C-*H*, $^3J_{HH}$ = 8 Hz), 7.14 (d, 2H, *o*-Ar C-*H*, $^3J_{HH}$ = 7 Hz), 7.26 (t, 2H, *m*-Ar C−H, $^3J_{HH}$ = 8 Hz).

[Cp*HfL^2(NMe$_2$)$_2$], 1b. ^{1}H NMR: δ 1.03 ppm (s, br, 3H, NC*Me*$_2$ oxazoline), 1.13 (s, br, 3H, NC*Me*$_2$ oxazoline), 1.99 (s,

(29) Wolczanski, P. T.; Bercaw, J. E. *Organometallics* **1982**, *1*, 793.

15H, C_5Me_5), 3.01 (s, br, 12H, Hf−NMe_2), 3.49 (d of d, v br, 2H, OCH_2 oxazoline), 6.93 (t, 1H, *p*-Ar C−*H*, $^3J_{HH}$ = 8 Hz), 7.21 (d, 2H, *o*-Ar C−*H*, $^3J_{HH}$ = 8 Hz), 7.29 (t, 2H, *m*-Ar C−*H*, $^3J_{HH}$ = 8 Hz).

[Cp*ZrL^3(NMe$_2$)$_2$], 1c. ^{1}H NMR: δ 1.92 ppm (s, 15H, C_5Me_5), 2.69 (s, br, 6H, Zr−NMe_2), 3.05 (s, 6H, Zr−NMe_2), 3.86 (d of d, 1H, OCH_2 oxazoline, $^2J_{HH}$ = 8 Hz, $^3J_{HH}$ = 5 Hz), 4.08 (d of d, 1H OCH_2 oxazoline, $^2J_{HH}$ = 8 Hz), 4.72 (d of d, 1H, NC*H*Ph oxazoline, $^2J_{HH}$ = 8 Hz, $^3J_{HH}$ = 5 Hz), 6.94 (m, 1H, Ar C−*H*), 7.05−7.14 (m, 5H, Ar C−*H*), 7.30 (m, 4H, Ar C−*H*).

[Cp*HfL^3(NMe$_2$)$_2$], 1d. ^{1}H NMR: δ 1.96 ppm (s, 15H, C_5Me_5), 2.72 (s, br, 6H, Hf−NMe_2), 3.10 (s, 6H, Hf−NMe_2), 3.85 (d of d, 1H, OCH_2 oxazoline, $^2J_{HH}$ = 8 Hz, $^3J_{HH}$ = 4 Hz), 4.06 (d, 1H OCH_2 oxazoline, $^2J_{HH}$ = 8 Hz), 4.68 (d of d, 1H, NC*H*Ph oxazoline, $^2J_{HH}$ = 8 Hz ,$^3J_{HH}$ = 4 Hz), 6.95 (m, 1H, Ar C−*H*), 7.07−7.13 (m, 5H, Ar C−*H*), 7.33 (m, 4H, Ar C−*H*).

[Cp*ZrL^4(NMe$_2$)$_2$], 1e. ^{1}H NMR: δ 0.61 ppm (d, 3H, $(CH_3)_2$-CH, $^3J_{HH}$ = 7 Hz), 0.76 (d, br, 3H, $(CH_3)_2$CH, $^3J_{HH}$ = 8 Hz), 1.96 (s, 15H, C_5Me_5), 2.05 (m, 1H, $(CH_3)_2CH$), 2.96 (s, 6H, Zr−NMe_2), 3.03 (s, 6H, Zr−NMe_2), 3.71 (m, 2H, OCH_2 oxazoline), 3.94 (m, 1H, NC*H*^{i}Pr oxazoline), 6.90 (t, 1H, *p*-Ar C−*H*, $^3J_{HH}$ = 7 Hz), 7.21 (d, br, 2H, *o*-Ar C−*H*, $^3J_{HH}$ = 7 Hz), 7.27 (t, 2H, *m*-Ar C−*H*, $^3J_{HH}$ = 7 Hz).

[Cp*ZrL^5(NMe$_2$)$_2$], 1f. ^{1}H NMR: δ 0.80 ppm (s, 9H, NCH^t*Bu* oxazoline), 1.95 (s, br, 15H, C_5Me_5), 2.92 (s, 6H, Zr−NMe_2), 3.03 (s, 6H, Zr−NMe_2), 3.36 (m, 1H, OCH_2 oxazoline), 3.75 (m, br, 1H, OCH_2 oxazoline), 4.03 (m, 1H, br, NC*H*^{t}Bu oxazoline), 6.92 (m, 1H, *p*-Ar C−*H*), 7.26 (m, br, 4H, *o*- and *p*-Ar C−*H*).

Preparative-Scale Reactions of Ring-Opened Guanidinate Complexes. [Cp*ZrL$^{2'}$(NMe$_2$)], 2a. A Schlenk tube was charged with H**L^2** (0.159 g, 0.84 mmol) and Cp*Zr(NMe_2)$_3$ (0.300 g, 0.84 mmol). Toluene (10 mL) was added, and the reaction vessel evacuated and left to stir at room temperature for 24 h. After this time, the solvent was removed in vacuo, and the oily yellow residue was redissolved in pentane and evaporated to dryness to remove residual toluene. The resulting white solid was dissolved in the minimum amount of pentane and allowed to stand at room temperature until crystalline material was deposited. Yield: 0.172 g (0.34 mmol, 41%). Anal. Calcd for $C_{25}H_{40}N_4OZr$: C, 59.60; H, 8.00; N, 11.12. Found: C, 59.14; H, 8.07; N, 11.07. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 1.20 ppm (s, 3H, Zr−OCH$_2$CMe_2), 1.24 (s, 3H, Zr−OCH$_2$CMe_2N), 1.99 (s, 15H, C_5Me_5), 2.21 (s, 6H, NMe_2 guanidinate), 3.17 (s, 6H, Zr−NMe_2), 3.87 (d, 1H, Zr−OCH_2CMe$_2$, $^2J_{HH}$ = 10 Hz), 4.37 (d, 1H, Zr−OCH_2CMe$_2$, $^2J_{HH}$ = 10 Hz), 6.69 (d, 2H, *o*-Ar C−*H*, $^3J_{HH}$ = 8 Hz), 6.88 (t, 1H, *p*-Ar C−*H*, $^3J_{HH}$ = 8 Hz), 7.20 (t, 2H, *m*-Ar C−*H*, $^3J_{HH}$ = 8 Hz). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, 298 K): δ 9.8 ppm (C_5Me_5), 22.7, 24.4 (2 × Zr−OCH$_2$CMe_2), 38.3 (NMe_2 guanidinate), 42.5 (Zr−NMe_2), 59.7 (Zr−OCH$_2$*C*Me$_2$), 82.9 (Zr−OCH$_2$CMe$_2$), 116.9 (C_5Me$_5$), 119.9 (*p*-Ar *C*−H), 121.3 (*m*-Ar *C*−H), 127.4 (*o*-Ar *C*−H), 146.4 (Ar C_q), 163.5 (C_q guanidinate). MS (EI +ve) *m/z*: 458 (100, M$^+$ − NMe$_2$).

[Cp*HfL$^{2'}$(NMe$_2$)], 2b. A Schlenk tube was charged with H**L^2** (0.213 g, 1.12 mmol) and Cp*Hf(NMe_2)$_3$ (0.500 g, 1.12 mmol). Toluene (10 mL) was added, and the reaction vessel evacuated and left to stir at room temperature for 48 h. After this time, the solvent was removed in vacuo, and the oily yellow residue was redissolved in pentane and evaporated to dryness to remove residual toluene. The resulting white solid was dissolved in the minimum amount of pentane and cooled to −30 °C until crystalline material was deposited. Cooling of the supernatant to −30 °C yielded further crystalline material. Total yield: 0.332 g (0.56 mmol, 50%). Anal. Calcd for $C_{25}H_{40}N_4OHf$: C, 50.80; H, 6.82; N, 9.48. Found: C, 50.44; H, 6.84; N, 9.16. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 1.17 (s, 3H, Hf−OCH$_2$CMee_2), 1.21 (3H, Hf−OCH$_2$CMe_2), 2.01 (s, 15H, C_5Me_5), 2.19 (s, 6H, NMe_2 guanidinate), 3.26 (s, 6H, Hf−NMe_2), 4.03 (d, 1H, Hf−OCH_2CMe$_2$, $^2J_{HH}$ = 10 Hz), 4.21 (d, 1H, Hf−OCH_2CMe$_2$, $^2J_{HH}$ = 10 Hz), 6.75 (d, 2H, *o*-Ar C−*H*, $^3J_{HH}$ = 8 Hz), 6.91 (t, 1H, *p*-Ar C−*H*, $^3J_{HH}$ = 7 Hz), 7.20 (t, 2H, *m*-Ar C−*H*, $^3J_{HH}$ = 7 Hz). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, 298 K): δ 11.2 ppm (C_5Me_5), 24.2, 25.8 (2 × Hf−OCH$_2$CMe_2), 39.7 (NMe_2 guanidinate), 44.5 (Hf−NMe_2), 60.9 (Hf−OCH$_2$*C*Me$_2$), 83.0 (Hf−OCH$_2$CMe$_2$N), 117.4 (C_5Me$_5$), 121.6, 123.2, 128.8 (all Ar *C*−H), 147.5 (Ar C_q), 164.9 (guanidinate C_q). MS (EI +ve) *m/z*: 592 (60, M$^+$), 547 (100, M$^+$ − NMe$_2$).

[Cp*ZrL$^{3'}$(NMe$_2$)], 2c. A J. Young ampule was charged with (*S*)-H**L^3** (0.266 g, 1.12 mmol) and Cp*Zr(NMe_2)$_3$ (0.400 g, 1.12 mmol). Toluene (10 mL) was added, and the reaction vessel was evacuated and heated to 60 °C for 48 h. After this time, the solvent was removed in vacuo, and the oily yellow residue was redissolved in pentane and evaporated to dryness to remove residual toluene. The resulting white solid was dissolved in the minimum amount of pentane and allowed to stand at 4 °C until crystalline material was deposited. Yield: 0.131 g (0.24 mmol, 21%). Anal. Calcd for $C_{29}H_{40}N_4OZr$: C, 63.11; H, 7.31; N, 10.15. Found: C, 63.29; H, 7.44; N, 10.12. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 1.84 ppm (s, 6H, NMe_2 guanidinate), 2.03 (s, 15H, C_5Me_5), 3.29 (s, 6H, Zr−NMe_2), 4.27 (d, 1H, Zr−OC*H*CHPh, $^2J_{HH}$ = 10 Hz), 4.51 (d, 1H, Zr−OCH$_2$C*H*Ph, $^3J_{HH}$ = 6 Hz), 4.98 (d of d, 1H, Zr−OCH_2CHPh, $^3J_{HH}$ = 10 Hz, $^2J_{HH}$ = 6 Hz), 6.91 (t, 1H, Ar C−*H*, $^3J_{HH}$ = 8 Hz), 7.03 (m, 3H, Ar C−*H*), 7.17−7.23 (m, 4H, Ar C−*H*), 7.32 (d, 2H, Ar C−*H*, $^3J_{HH}$ = 8 Hz). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, 298 K): δ 11.5 (C_5Me_5), 38.2 (NMe_2 guanidinate), 46.8 (Zr−NMe_2), 68.3 (N−*C*HPh), 79.6 (Zr−OCH$_2$), 118.9 (C_5Me_5), 121.6, 122.1, 124.3, 127.0, 128.3, 129.3 (all Ar *C*−H), 147.5, 149.4 (both Ar C_q), 165.6 (guanidinate C_q). MS (EI +ve) *m/z*: 550 (24, M$^+$), 506 (100, M$^+$ − NMe$_2$).

[Cp*HfL$^{3'}$(NMe$_2$)], 2d. A J. Young ampule was charged with (*S*)-H**L^3** (0.300 g, 1.20 mmol) and Cp*Hf(NMe_2)$_3$ (0.535 g, 1.20 mmol). Toluene (10 mL) was added, and the reaction vessel was evacuated and heated to 60 °C for 48 h. After this time, the solvent was removed in vacuo, and the oily yellow residue was redissolved in pentane and evaporated to dryness to remove residual toluene. The resulting white solid was dissolved in the minimum amount of pentane and allowed to stand at room temperature, yielding the title compound as a colorless crystalline solid. Yield: 0.348 g (0.54 mmol, 45%). Anal. Calcd for $C_{29}H_{40}N_4OHf$: C, 54.50; H, 6.31; N, 8.77. Found: C, 54.75; H, 6.28; N, 8.61. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 1.88 ppm (s, br, 6H, NMe_2 guanidinate), 2.05 (s, 15H, C_5Me_5), 3.34 (s, 6H, Hf−NMe_2), 4.39 (d, 1H, Hf−OCH_2-CHPh, $^2J_{HH}$ = 10 Hz), 4.50 (d, 1H, Hf−OCH$_2$C*H*Ph,$^3J_{HH}$ = 6 Hz), 4.85 (d of d, 1H, Hf−OCH_2CHPh, $^2J_{HH}$ = 10 Hz, $^3J_{HH}$ = 6 Hz), 6.90 (t, 1H, Ar C−*H*, $^3J_{HH}$ = 7 Hz), 7.04 (m, 3H, Ar C−*H*), 7.12−7.19 (m, 4H, Ar C−*H*), 7.31 (d, 2H, Ar C−*H*, $^3J_{HH}$ = 7 Hz). ^{13}C-{^{1}H} NMR (75.5 MHz, C_6D_6, 298 K): δ 11.3 ppm (C_5Me_5), 37.8 (NMe_2 guanidinate), 46.6 (Hf−NMe_2), 67.8 (Hf−OCH$_2$*C*HPh), 77.8 (Hf−OCH$_2$CHPh), 117.6 (C_5Me$_5$), 122.0, 124.4, 126.6, 128.9 (Ar *C*−H), 147.2, 148.7 (Ar C_q), 165.0 (guanidinate C_q). MS (EI +ve) *m/z*: 640 (66, M$^+$), 595 (100, M$^+$ − NMe$_2$).

[Cp*ZrL$^{4'}$(NMe$_2$)], 2e. A J. Young ampule was charged with (*S*)-H**L^4** (0.756 g, 3.70 mmol) and Cp*Zr(NMe_2)$_3$ (1.32 g, 3.70 mmol). Toluene (10 mL) was added, and the reaction vessel was evacuated and heated to 60 °C for 48 h. After this time, the solvent was removed in vacuo, and the residue redissolved in pentane and evaporated to dryness to remove residual toluene. The resulting yellow oily residue was transferred to a sublimation tube via pentane solution and sublimated at 185 °C/10^{-6} mmHg to yield the title compound as a yellow semisolid. Isolated yield: 0.358 g, (0.70 mmol, 19%). Anal. Calcd for $C_{26}H_{42}N_4OZr$: C, 60.30; H, 8.17; N, 10.82. Found: C, 60.38; H, 8.20; N, 10.59. ^{1}H NMR (300 MHz, C_6D_6, 298 K) major diastereomer: δ 0.85 ppm (d, 3H, CH_3 of ^{i}Pr, $^3J_{HH}$ = 7 Hz), 1.17 (d, 3H, CH_3 of ^{i}Pr, $^3J_{HH}$ = 7 Hz), 1.77 (m, 1H, C*H* of ^{i}Pr), 1.98 (s, 15H, C_5Me_5), 2.10 (s, 6H, NMe_2 guanidinate), 3.20 (s, 6H, Zr−NMe_2), 3.45 (m, 1H, NC*H*^{i}Pr oxazoline), 4.44 (d of d, 1H, Zr−OCH_2, $^2J_{HH}$ = 11 Hz), 4.57 (m, 1H, Zr−OCH_2), 6.93

(t, 1H, *p*-Ar C−*H*, $^3J_{HH}$ = 8 Hz), 7.00 (d, 2H, *o*-Ar C−*H*, $^3J_{HH}$ = 8 Hz), 7.22 (t, 2H, *m*-Ar C−*H*, $^3J_{HH}$ = 8 Hz); minor diastereomer: δ 1.04 ppm (d, 3H, CH_3 of ^{i}Pr, $^3J_{HH}$ = 7 Hz), 1.08 (d, 3H, CH_3 of ^{i}Pr, $^3J_{HH}$ = 7 Hz), 2.04 (s, 15H, C_5Me_5), 2.18 (m, 1H, C*H* of ^{i}Pr), 2.25 (s, 6H, NMe_2 guanidinate), 3.11 (s, 6H, Zr−NMe_2), 3.26 (m, 1H, NC*H*^{i}Pr), 4.48 (m, 2H, Zr−OCH_2), 6.74 (d, 2H, *o*-Ar C−*H*, $^3J_{HH}$ = 8 Hz), 6.89 (t, 1H, *p*-Ar C−*H*, $^3J_{HH}$ = 8 Hz), 7.22 (t, 2H, *m*-Ar C−*H*, $^3J_{HH}$ = 8 Hz). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, 298 K) major diastereomer: δ 11.4 ppm (C_5Me_5), 17.2, 21.6 (both *C*H_3 of ^{i}Pr), 30.1 (*C*H of ^{i}Pr), 38.3 (NMe_2 guanidinate), 46.3 (Zr−NMe_2), 67.2 (N*C*H^{i}Pr), 71.2 (Zr−O*C*H_2), 118.4 (C_5Me$_5$), 122.7, 124.7, 129.5 (all Ar *C*−H), 149.6 (Ar C_q), 165.2 (guanidinate C_q); minor diastereomer: δ 11.7 ppm (C_5Me_5), 20.2, 21.7 (both *C*H_3 of ^{i}Pr), 31.6 (*C*H of ^{i}Pr), 40.2 (NMe_2 guanidinate), 45.0 (Zr−NMe_2), 68.0 (N*C*H^{i}Pr), 73.2 (Zr−O*C*H_2), 119.0 (C_5Me$_5$), 121.6, 122.1, 129.7 (all Ar *C*−H), 149.0 (Ar C_q), 165.2 (guanidinate C_q). MS (EI +ve) *m/z*: 472 (100, $M^+ - NMe_2$).

[Cp*ZrL$^{5'}$(NMe$_2$)], 2f. A J. Young ampule was charged with (*S*)-H**L^5** (0.200 g, 0.91 mmol) and Cp*Zr(NMe$_2$)$_3$ (0.328 g, 0.91 mmol). Toluene (10 mL) was added, and the reaction vessel evacuated and heated to 60 °C for 48 h. After this time, the solvent was removed in vacuo, and the oily yellow residue was redissolved in pentane and evaporated to dryness to remove residual toluene. The process was repeated to yield the title compound as a white semisolid. Isolated yield: 0.192 g (0.36 mmol, 40%). Anal. Calcd for $C_{27}H_{44}N_4OZr$: C, 60.97; H, 8.34; N, 10.53. Found: C, 60.05; H, 8.29; N, 9.84. ^{1}H NMR (300 MHz, C_6D_6, 298 K) major diastereomer: δ 1.13 ppm (s, 9H, ^{t}*Bu*), 2.04 (s, 15H, C_5Me_5), 2.28 (s, 6H, NMe_2 guanidinate), 3.12 (s, 6H, Zr−NMe_2), 3,34 (d, 1H, NC*H*^{t}Bu, $^3J_{HH}$ = 6 Hz), 4.52 (m, 1H, Zr−OCH_2), 4.72 (d, 1H, Zr−OCH_2, $^3J_{HH}$ = 6 Hz) 6.80 (d, 2H, *o*-Ar C−*H*, $^3J_{HH}$ = 8 Hz), 6.91 (t, 1H, *p*-Ar C−*H*, $^3J_{HH}$ = 8 Hz), 7.22 (t, 2H, *m*-Ar C−*H*); minor diastereomer: δ 1.02 ppm (s, 9H, ^{t}*Bu*), 1.94 (s, 15H, C_5Me_5), 2.12 (s, 6H, guanidinate NMe_2), 3.11 (s, 6H, Zr−NMe_2), 3.39 (d, 1H, NC*H*^{t}Bu, $^3J_{HH}$ = 6 Hz), 4.43 (m, 1H, Zr−OCH_2), 4.75 (d, 1H, Zr−OCH_2, $^3J_{HH}$ = 6 Hz), 6.95−7.03 (m, 3H, *m*- and *p*-Ar C−*H*), 7.08 (d, 2H, *o*-Ar C−*H*, $^3J_{HH}$ = 8 Hz). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, 298 K): major diastereomer: δ 11.3 ppm (C_5Me_5), 28.4 (*C*H_3 of ^{t}Bu), 36.6 (C_q of ^{t}Bu), 40.5 (NMe_2 guanidinate), 45.0 (Zr−NMe_2), 70.2 (N*C*HtBu), 74.8 (Zr−O*C*H_2), 118.2 (C_5Me$_5$), 122.7, 125.8, 129.1 (Ar *C*−H), 150.1 (Ar C_q), 164.9 (guanidinate C_q); minor diastereomer: δ 11.7 ppm (C_5Me_5), 29.3 (*C*H_3 of ^{t}Bu), 35.3 (C_q of ^{t}Bu), 39.3 (NMe_2 guanidinate), 46.3 (Zr−NMe_2), 68.6 (N*C*H^{t}Bu), 73.9 (Zr−O*C*H_2), 119.2 (C_5Me$_5$), 121.6, 122.5, 129.5 (Ar *C*−H), 149.5 (Ar C_q), 166.0 (guanidinate C_q). MS (EI +ve) *m/z*: 486 (100, $M^+ - NMe_2$).

X-ray Crystallography. Single crystals of [Cp*Hf**L$^{3'}$**(NMe$_2$)] (**2d**) were obtained from a saturated pentane solution at room temperature as colorless blocks. The crystal was coated in an inert oil prior to transfer to a 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, and intensities corrected using SADABS.[30] 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. The absolute structure of the crystal was confirmed by a Flack parameter of $x = -0.020(11)$. Programs used were Bruker AXS SMART (control), SAINT (integration),[31] and SHELXTL[32] for structure solution, refinement, and molecular graphics.

Acknowledgment. We acknowledge the EPSRC for financial support (to A.L.G.). We are extremely grateful to Dr. Benson M. Kariuki and the Department of Chemistry, University of Birmingham, U.K., for assistance in the collection of the X-ray data.

Note Added in Proof. During the processing of this manuscript a report by Gade and co-workers appeared which describes a similar ring-opening reaction of bis(aminooxazolinates), although a different mechanistic hypothesis was presented. Ward, B. D.; Risler, H.; Weitershaus, K.; Bellemin-Laponnaz, S.; Wadepohl, H.; Gade, L. H. *Inorg. Chem.* **2006**, *45*, 7777.

Supporting Information Available: CIF file for the structural determination of **2d**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0607649

(30) Sheldrick, G. M. *SADABS*, Program for Area Detector Absorption Correction; Institute for Inorganic Chemistry, University of Gottingen: Germany, 1996.

(31) *SMART and SAINT*; Bruker Analytical X-Ray Systems Inc.: Madison, WI, 1998.

(32) Sheldrick, G. M. *SHELXTL*, Version 5.1; Bruker Analytical X-ray Systems: Madison, WI, 1997.