Structure−Activity Relationships for Group 4 Biaryl Amidate Complexes in Catalytic Hydroamination/Cyclization of Aminoalkenes

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

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

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Synthesis of bis(carboxamide) proligands derived from (*R*,*S*)-2,2′-diamino-6,6′dimethylbiphenyl was readily achieved by treatment of the amine with acid chlorides. Direct reaction with homoleptic alkyls of the group 4 metals cleanly yielded amidate complexes. These complexes were shown by single-crystal X-ray diffraction to be monomeric in the case of titanium and dimeric in the case of zirconium. The complexes formed do not yield well-defined cations upon reaction with standard borate/borane activators, and although some hydroamination catalysis was observed, it was not at a rate that is useful. *In-situ* treatment of $Zr(NMe_2)_4$ with the proligands H_2L^{1-4} yielded complexes of varying nuclearity depending on the steric bulk of the amide substituents, but in contrast to the metal alkyl series, mononuclear species are accessible; the mesityl derivative [(*S*)-$L^4Zr(NMe_2)_2$] was found to be a highly enantioselective catalyst for the hydroamination/cyclization of 1-amino-2,2-dimethylpent-4-ene, with an enantiomeric excess of 91%.

Introduction

The enantioselective, atom-efficient, cyclohydroamination of aminoalkenes to yield N-substituted heterocycles remains an area of great interest.[1] Much of the early effort in this area focused on *ansa*-metallocene complexes, which gave up to 74% ee.[2] The first non-lanthanocene catalyst for the enantioselective transformation[3] was followed by intensive studies involving several international groups,[4] leading eventually to the step-change in enantioselectivity recently reported by Hultzsch et al.[5] One remaining issue however is the high sensitivity of organolanthanides[6] to water, making them unpopular for use outside of more specialist laboratories.

We have long been interested in group 4[7,8] and other complexes[9] of biaryl-based ligands and have recently reported that one such compound, a zirconium benzyl cation, was the first non-lanthanide catalyst for the above enantioselective reaction. N-Methylated aminoalkenes were cyclized with ee up to 82%,[7c] the highest known at that time. Recent reports by

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

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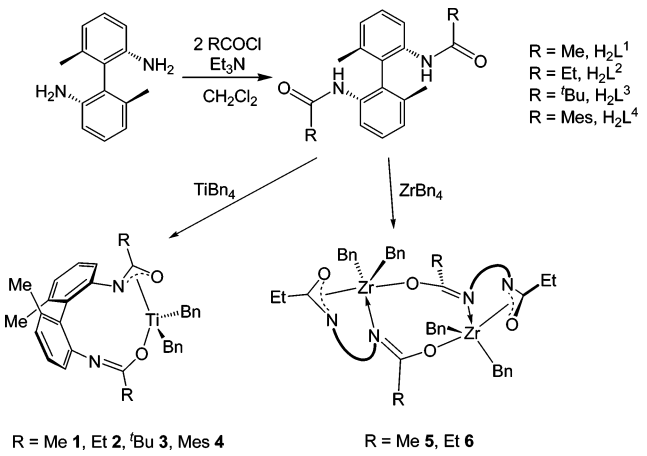
Scheme 1



Schafer and co-workers of the (racemic) catalytic intramolecular hydroamination by group 4 amidate complexes[10] and other reports of neutral group 4 amide catalysts[11] prompted us to investigate the synthesis of biaryl bis(amidate) complexes analogous to our previously reported heteroallyl systems, aminooxazolinate[7b] and aminopyridinate.[7d] Our studies reported here have involved the use of titanium and zirconium alkyls and amides, which give complexes exhibiting a variety of structural motifs and corresponding performances in catalysis. During the course of this work, Schafer and co-workers reported the successful use of very similar bis(amidate) complexes of zirconium amides of the same series in catalytic hydroamination.[12]

Results and Discussion

Proligand Synthesis. Samples of racemic 2,2′-diamino-6,6′-dimethylbiphenyl were treated with 2 equiv of a selection of carboxylic acid chlorides RCOCl (R = Me, Et, ^{t}Bu, mesityl) in the presence of excess triethylamine. The alkyl systems yielded after simple workup the proligands H_2L^n (n = 1−3) in high yield (Scheme 1). Synthesis of the mesityl derivative H_2L^4 was less straightforward. Even after extended reaction periods, crude solids were obtained that contained principally the monocarboxamide; a resonance attributable to the aromatic Ar−NH_2 was still present in the ^{1}H NMR spectrum. Treatment of the isolated solid with a further excess of 2,4,6-trimethylbenzoyl chloride in the presence of base yielded, after recrystallization, the desired proligand in moderate yield.[13]

Preliminary Reactivity Studies. Attempted deprotonation reactions of H_2L^n with a variety of reagents met with little success; NMR spectra of the products of the reaction with NaH, KH, ^{n}BuLi, and LiN($SiMe_3$)$_2$ yielded compounds that exhibited complex (or broad) NMR spectra indicative of oligomeric structures, possibly involving multiple coordination modes of the carboxamide moiety.[14] *In-situ* salt metathesis of the presumed dianions with titanium and zirconium halides led to complex mixtures. We therefore chose to employ a protonolysis approach to the amidate complex synthesis as has proved successful for Schafer[10] and Arnold.[15]

Experiments on the NMR tube scale in which H_2L^n (n = 1, 2) were treated with 1 equiv of M(CH_2Ph)$_4$ (M = Ti, Zr) were very clean. Immediate deprotonation of both amide units and concomitant elimination of 2 equiv of toluene occurred in all cases as judged by ^{1}H NMR spectroscopy. The single organometallic products produced (Scheme 1) all contained two inequivalent benzyl ligands per metal and, thus, in the chiral environment of these ligands, two (overlapping) pairs of AB doublets for the CH_2 units. These aspects of asymmetry were also reflected in the observation of two sets of signals for the amide substituents and, in the case of L^2, of complex multiplets for the diastereotopic ethyl CH_2 groups. These experiments using L^2 in particular gave the first indications that the titanium and zirconium complexes were structurally dissimilar; in the case of the titanium compound the two amidate ethyl group "triplet" resonances are almost coincident at δ ca. 0.93 ppm, whereas in the zirconium complex they appear at δ 0.71 and 1.18 ppm.

A similar reaction of H_2L^4 with 1 equiv of Ti(CH_2Ph)$_4$ gave a major product (ca. 88%) of the same type as those above plus a second component with apparent C_2 symmetry (*vide infra*). Reactions of H_2L^3 and H_2L^4 with Zr(CH_2Ph)$_4$ on the NMR tube scale gave complex mixtures of products. Neither of these reactions were pursued further. No reaction was observed between H_2L^{1-4} and Ti(CH_2CMe_3)$_4$.

Synthesis and Molecular Structure of the Titanium Alkyl Complexes. The titanium complexes [L^{1-4}Ti(CH_2Ph)$_2$] **1**−**4** were subsequently prepared by treatment of the proligands with Ti(CH_2Ph)$_4$ in diethyl ether. The high solubility of the alkylated ligand complexes **1**−**3** hampered attempts at crystallization, and these compounds were thus dried *in vacuo* and isolated as air-sensitive red-brown powders. The complex **4** was obtained as red microcrystals directly from the reaction mixture. Filtration and concentration of the supernatant followed by standing overnight at room temperature yielded a further crop of red, single crystals that were suitable for X-ray diffraction. The molecular structure is given in Figure 1 with selected bond lengths and angles in Table 1 and experimental details in Table 3.

The monomeric five-coordinate complex crystallized in the triclinic space group $P\bar{1}$. One amidate is bound κ^2 with bond lengths Ti(1)−O(8) [2.043(2) Å] and Ti(1)−N(9) [2.087(2) Å], in excellent agreement with the two other reported structures containing this unit.[10f,15] The distances C(8)−O(8) and C(8)−N(9) of 1.300(4) and 1.306(4) Å, respectively, are indicative of electron delocalization in the heteroallylic ligand group. This amidate(Ti) unit is almost planar, with a hinge angle at the O(8)−N(9) vector of ca. 176°. The second amidate unit is bound κ^1 through O(23). The C(22)−N(23) distance of 1.274(4) Å is

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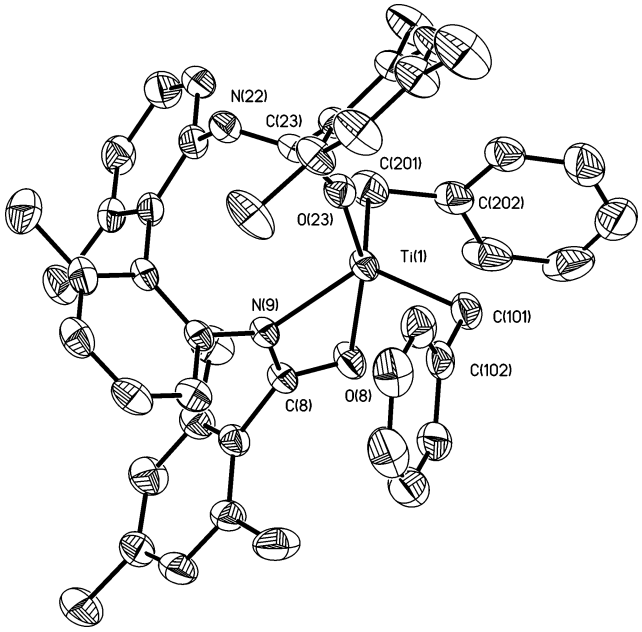

Figure 1. X-ray structure of $[L^4Ti(CH_2Ph)_2]$, **4**. Solvent of crystallization and hydrogen atoms are omitted for clarity. Displacement ellipsoids are at the 50% probability level.

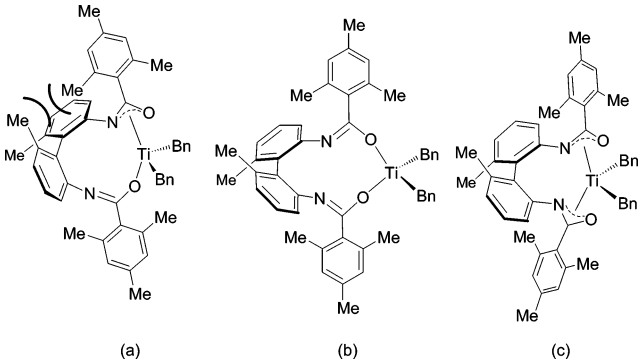

Figure 2. Structure of major isomer of **4** (a) and possible structures of minor isomer (b and c).

Table 1. Selected Bond Lengths (Å) and Angles between Interatomic Vectors (deg) for $[L^4Ti(CH_2Ph)_2]$, 4

Ti(1)−O(8)	2.043(2)	Ti(1)−O(23)	1.825(2)
Ti(1)−N(9)	2.087(2)	Ti(1)−C(101)	2.119(3)
Ti(1)−C(201)	2.111(3)	Ti(1)−C(202)	2.628(3)
O(8)−C(8)	1.300(4)	C(8)−N(9)	1.306(4)
N(22)−C(23)	1.274(4)	O(23)−C(23)	1.348(4)
C(102)−C(101)−Ti(1)	106.8(2)	C(202)−C(201)−Ti(1)	92.7(2)
C(23)−O(23)−Ti(1)	157.78(19)	C(8)−O(8)−Ti(1)	93.21(17)
C(8)−N(9)−Ti(1)	91.03(18)	O(8)−C(8)−N(9)	112.3(2)
N(22)−C(23)−O(23)	124.3(3)		

typical for a double bond and indeed rather shorter than the C−N partial double bond above. The C(23)−O(23) distance of 1.348(4) Å however lies between the usual ranges for single and double bonds, although it is longer than the C−O vector in the κ^2 unit. The most consistent picture is that of an essentially localized κ^1-*O*-iminolate ligand, as depicted in Figure 1. The Ti(1)−O(23)−C(23) bond angle of 157.78(19)° and Ti(1)−O(23) bond length of 1.825(2) Å cast this unit as a formal three-electron donor. The coordination sphere is completed by two benzyl ligands; for one of these at C(201) the C(201)−C(202)−Ti(1) angle is 92.74(2)°, implying a degree of η^2 character,[16] but it appears that this close contact is not maintained in solution since the *ipso*-^{13}C atoms appear at unremarkable chemical shifts.

Table 2. Selected Bond Lengths (Å) and Angles between Interatomic Vectors (deg) for $[\{L^2Zr(CH_2Ph)_2\}_2]$, 6

Zr(1)−O(218)	2.0727(18)	Zr(1)−O(118)	2.2352(19)
Zr(1)−N(117)	2.228(2)	Zr(1)−N(104)	2.337(2)
Zr(1)−C(401)	2.275(3)	Zr(1)−C(301)	2.279(3)
O(118)−C(118)	1.278(3)	N(117)−C(118)	1.311(4)
O(218)−C(218)	1.297(3)	N(217)−C(218)	1.294(4)
C(302)−C(301)−Zr(1)	103.59(19)	C(402)−C(401)−Zr(1)	121.3(2)
C(118)−O(118)−Zr(1)	93.67(17)	C(118)−N(117)−Zr(1)	93.05(17)
O(118)−C(118)−N(117)	114.7(3)	C(103)−N(104)−Zr(1)	131.63(19)
C(218)−O(218)−Zr(1)	160.35(19)		

Table 3. Selected X-ray Data Collection and Refinement Parameters

	$[L^4Ti(CH_2Ph)_2]$, **4**	$[\{L^2Zr(CH_2Ph)_2\}_2]$, **6**
formula	$C_{50}H_{53}N_2O_{2.5}Ti$	$C_{68}H_{72}N_4O_4Zr_2$
M	769.84	1191.74
cryst morphology	orange-red plate	yellow block
cryst dimens (mm)	0.20 × 0.16 × 0.01	0.50 × 0.50 × 0.40
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a (Å)	10.8209(10)	15.5157(12)
b (Å)	11.0568(11)	21.5593(16)
c (Å)	19.0122(18)	18.1187(14)
α (deg)	98.658(6)	90
β (deg)	97.596(6)	100.580(5)
γ (deg)	108.308(6)	90
V (Å^3)	2095.6(3)	5957.8(8)
Z	2	4
d(calc) (g·cm^{-3})	1.220	1.329
μ(Cu Kα) (mm^{-1})	2.055	3.268
T (K)	180(2)	180(2)
F(000)	818	2480
no. of reflns measd	13 721	38 664
no. of unique reflns	6396 [*R*(int) = 0.0435]	9860 [*R*(int) = 0.0491]
R_1 [$I > 2\sigma(I)$]	0.0548	0.0352
wR_2	0.1540	0.0904
no. of data/restraints/params	6396/18/498	9860/31/730
goodness of fit	1.051	1.020
largest peak and hole (e·Å^{-3})	0.645 and −0.599	0.605 and −0.409

In solution, **4** exists as a mixture of two isomers. The major component (88% at 293 K) has NMR spectra consistent with the C_1 symmetric κ^2/κ^1 molecular structure (Figure 2a) determined in the solid state. For example two pairs of AB doublets (2.53−2.85 ppm) are observed in the ^{1}H spectrum from two inequivalent benzyl ligands. The C_2 symmetry of the minor isomer is indicated by the equivalence of the two titanium benzyl moieties; a pair of mutually coupled AB doublets is clearly visible at δ 3.36 and 3.65 ppm. The possible structures (b) and (c) of the minor isomer are consistent with these observations. The molecular structure of $[L^4Ti(CH_2Ph)_2]$ reveals significant steric compression between the κ^2-amidate unit and the biaryl backbone, which would be relieved on conversion to the bis(κ^1-amidate) structure (b). Indeed, the C_2 symmetric isomer is seen only for this most sterically demanding of the ligands, and four-coordinate titanium bis(benzyl) complexes with related supporting ligature have been isolated previously.[17] Nevertheless, molecular models suggest that the bis(κ^2-amidate) (c) analogous to aminooxazolinato[7b] and aminopyridinato[7d] struc-

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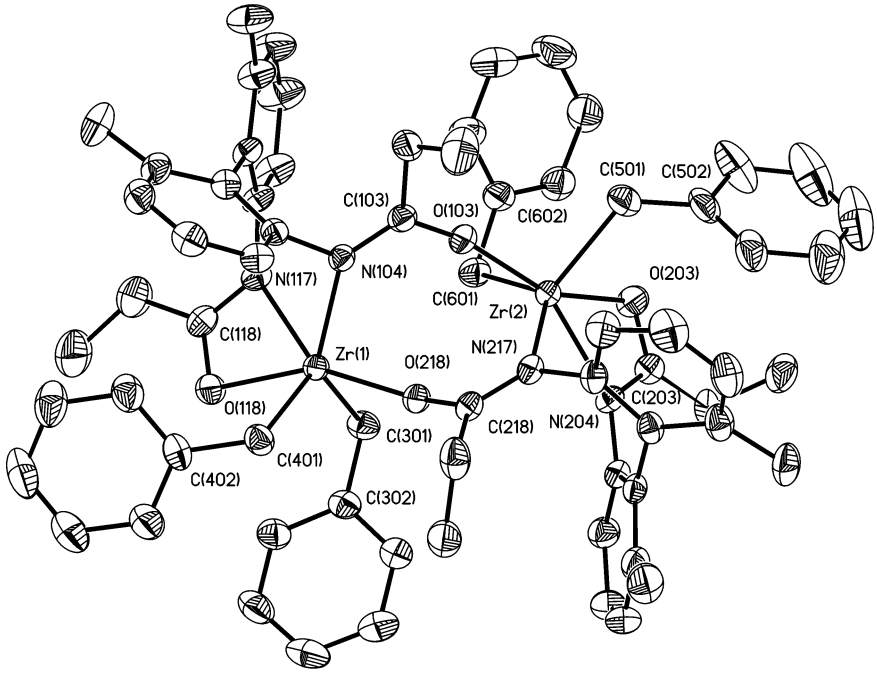


Figure 3. X-ray structure of [{$L^2Zr(CH_2Ph)_2$}$_2$], **6**. Hydrogen atoms are omitted for clarity. Displacement ellipsoids are at the 50% probability level.

tures is feasible, and we prefer the assignment of this latter structure on the basis of the $^{13}C\{^1H\}$ NMR shift for the quaternary amidate C atom of 185.2 ppm. This is in the range that we (*vide infra*) and others[12] have observed for κ^2-amidate at group 4 metals (180.1−188.5 ppm).

Heating the isomeric mixture of **4** in d_8-toluene to 363 K led to some broadening of the resonances of both isomers, but unexpectedly no coalescence was observed between signals within the major isomer or indeed between these and the minor isomer on this chemical shift time scale; the barrier to κ^1/κ^2 exchange is unexpectedly high. Nevertheless, appropriate cross-peaks were detected for exchange between major and minor isomers in the EXSY spectrum (see Supporting Information), and dissolution of a single crystal of **4**, presumably containing only the κ^2/κ^1 isomer, led to the same 88:12 equilibrium mixture of isomers.

Finally, the NMR data for the major isomer **4** closely match (where appropriate) with **1**−**3**, and we therefore assign the five-coordinate κ^2/κ^1 structure to all the titanium compounds.

Synthesis and Molecular Structure of the Zirconium Alkyl Complexes. Reactions between H_2L^n (n = 1, 2) and $Zr(CH_2Ph)_4$ were performed in diethyl ether at room temperature and yielded the dimers [{$L^1Zr(CH_2Ph)_2$}$_2$] (**5**) and [{$L^2Zr(CH_2Ph)_2$}$_2$] (**6**) as highly crystalline, air-sensitive, yellow solids. Both compounds prepared displayed identical NMR spectra to the NMR tube scale reactions. No tractable products could be isolated from the reaction between $Zr(CH_2Ph)_4$ and $H_2L^{3/4}$.

Single crystals of **6** were obtained by slow concentration of a saturated diethyl ether solution under vacuum followed by standing at room temperature. The structure determined by X-ray diffraction (shown in Figure 3 and Table 2) centers around an eight-membered bimetallic heterocycle formed by two bridging amidates. Although the dimer is not crystallographically centrosymmetric, the key bond lengths and angles in each half of the dimer are very similar, and we will focus mainly on Zr(1). Each zirconium atom is six-coordinate, with two benzyl ligands, one κ^2-amidate (as for the structure of **4** above), one intra-dimer N-dative bond, and one inter-dimer O-iminolate ligand. Nevertheless, if we take the κ^2-amidate unit as occupying a single axial coordination site, the coordination geometry is usefully described as trigonal bipyramidal; the C(118)−Zr(1)−O(218) angle is 169.84(9)° and the sum of equatorial angles about Zr(1) is 356.2°. The coordination of one amidate as a delocalized κ^2 heteroallyl is confirmed by the bond lengths N(117)−C(118) and C(118)−O(118) of 1.311(4) and 1.278(3) Å, respectively, as well as the metal ligand bond distances Zr(1)−O(118) and Zr(1)−N(117) at 2.2352(19) and 2.228(2) Å. The benzyl ligand bond distances Zr(1)−C(301) and Zr(1)−C(401) of 2.279(3) and 2.275(3) Å are at the lower end of the range commonly observed (2.3−2.35 Å).

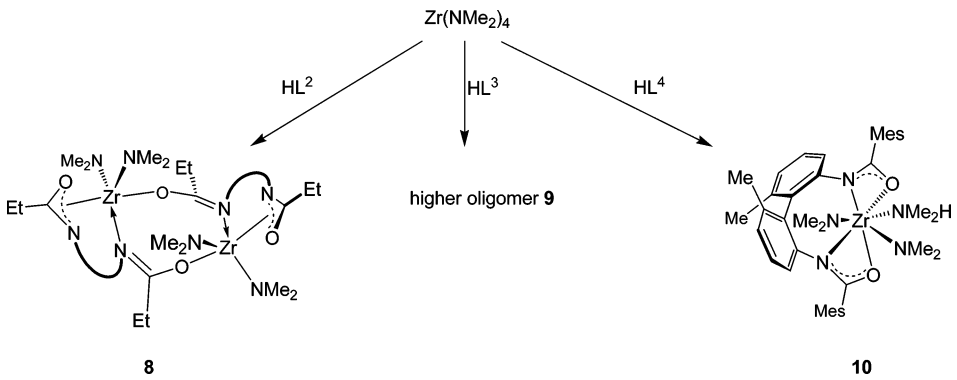
Notably, the structure determined above is homochiral, i.e., both biaryl ligands within one molecule have the same absolute configuration, and the same is true for the two chiral metal centers. This diastereoselection persists in solution, and only one enantiomer pair of the eight possible was detected.

Hydroamination Trials with Ti Alkyl Derivatives. Schafer et al. have demonstrated that unbridged bis(amidate) complexes of group 4 metals are catalysts for aminoalkyne hydroamination/cyclization at elevated temperatures.[10] The complex **4** was heated with a range of commonly used aminoalkene hydroamination substrates and found to be essentially inactive in this regard.

We,[7c] and others,[18] have previously shown that Zr alkyl cations (isoelectronic with electronically neutral group 3/lanthanide complexes) are catalysts for the intramolecular hydroamination/cyclization of N-methylated aminoalkenes, with high enantioselectivity. In an attempt to furnish such cations, the reactions of **4** with $[CPh_3][B(C_6F_5)_4]$ and $B(C_6F_5)_3$ in C_6D_5Br were studied, but they yielded ill-defined products (as judged by ^1H NMR spectroscopy). Treatment of **4** with $B(C_6F_5)_3$ in the presence of 20 equiv of *N*-methyl-3,3-dimethylaminohex-1-ene at 100 °C did yield cyclized product, but the reaction was incomplete after more than 2 weeks. Given the ill-defined nature of the catalytic species and the issue of thermal stability

(18) Gribkov, D. V.; Hultzsch, K. C. *Angew. Chem., Int. Ed.* **2004**, *43*, 5542.

Scheme 2



over such an extended reaction time, we decided not to pursue this avenue further.

The reaction of $[L^4Ti(CH_2Ph)_2]$ with $[HNMe_2Ph][B(C_6F_5)_4]$ on the NMR tube scale initially gave a product that on the basis of the ^1H NMR spectrum we formulate as $[HL^4Ti(CH_2Ph)_2][B(C_6F_5)_4]$ (**7**), in which the noncoordinated imine nitrogen of the iminolate ligand is protonated (see Supporting Information and Experimental Section). This complex subsequently decomposes at ambient temperature.

Zirconium Dimethylamide Complexes. Proligands H_2L^n ($n = 1-4$) were treated with $Zr(NMe_2)_4$ in NMR tube-scale reactions according to Scheme 2. H_2L^1 yielded a poorly defined product, possibly oligomeric, in all probability due to a lack of steric bulk in the amidate "backbone" position. In the case of H_2L^2 (R = Et), reaction with $Zr(NMe_2)_4$ led to the formation of a spectroscopically unsymmetric species, which we formulate as $[\{L^2Zr(NMe_2)_2(NHMe_2)\}_2]$, **8**. The incorporation of dimethylamine into the coordination sphere of zirconium is relatively rare,[19] but in this instance is characterized by broad resonances in the ^1H NMR spectrum (integrals 6H and 1H, respectively). The asymmetry in the complex is once again demonstrated in separate resonances for the alkyl substituents of the amidate (e.g., two resonances at δ 1.06 and 1.17 ppm for the CH_3 group of the amide ethyl substituent). Also of note are two markedly different chemical shifts corresponding to the quaternary carbon of the amide, indicative of two different (i.e., "terminal" and "bridging") coordination modes. From analysis of the crystal structure of **6** (*vide supra*) and a lack of catalytic activity (*vide infra*), we propose the structure of the corresponding dimethylamide complex is also dimeric.

The *in-situ* NMR spectra of the reaction between H_2L^3 and $Zr(NMe_2)_4$ are similar in that two separate coordination modes of the carboxamide moiety and ligation of dimethylamine are observed. From the crystal structure of **6** we can rationalize on steric grounds why the analogous Zr benzyl compound of H_2L^3 is not observed, the implication therefore being that "$[\{L^3Zr(NMe_2)_2(NHMe_2)\}_n]$" (**9**) is a higher oligomer. Attempts to crystallize these complexes were hampered by their high solubility. Attempted sublimation at high vacuum led to decomposition. Treatment of H_2L^4 with $Zr(NMe_2)_4$ yielded a mixture of products, in which the predominant species was the C_2 symmetric $[L^4Zr(NMe_2)_2(NHMe_2)]$, **10**;[20] only one tautomer of the deprotonated carboxamide was observed in the $^{13}C\{^1H\}$ NMR spectrum (δ 181.0 ppm). This is confirmed by ^1H NMR data; only a single resonance for the dimethylamide ligands and four separate aromatic methyl signals are observed.

Scheme 3

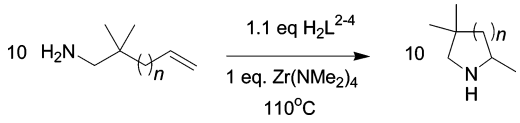
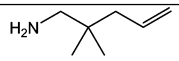
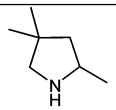
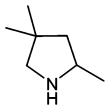
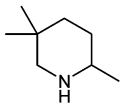
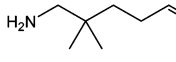
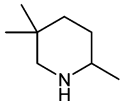


Table 4. Hydroamination Catalysis[a]

Catalyst	Substrate	Product	t/h[b]	ee (%)[c]
$[(S)\text{-}L^3Zr(NMe_2)_2]$			> 120	5
$[(S)\text{-}L^4Zr(NMe_2)_2]$			18	91
$[(S)\text{-}L^3Zr(NMe_2)_2]$			3	21
$[(S)\text{-}L^4Zr(NMe_2)_2]$			3	38

[a] Toluene-d_8 at 110 °C, 10 mol % catalyst. [b] Time taken for >95% conversion of substrate. [c] ^1H NMR analysis of (*R*)-(+)-Mosher amide at 25 °C.

Hydroamination with Zr Amide Complexes. With the *in-situ*-synthesized complexes in hand, we began to screen for hydroamination catalysis with standard substrates. None of the complexes described above were effective catalysts (toluene-d_8, 110 °C) for the cyclization of 1-aminopent-4-ene into 2-methylpyrrolidine (Scheme 3), presumably due to a lack of a Thorpe−Ingold effect[21] from the unsubstituted aminoalkene. Treatment of 1-amino-2,2-dimethylpent-4-ene yielded more interesting results. Once more, the ethyl-derived complex **8** was inactive for the cyclization to 2,4,4-trimethylpyrrolidine. However, **9** (albeit slowly) and **10** were catalysts for this process (Table 4), with the mesityl-derived complex resulting in complete conversion (by ^1H NMR) in a period of 18 h, as compared to a period of >3 days for the *tert*-butyl-substituted complex.

Repetition of the catalysis with chiral nonracemic proligands (synthesized from (*S*)-2,2′-amino-6,6′-dimethylbiphenyl[9b]) yielded

(19) (a) Dubberley, S. R.; Evans, S.; Boyd, C. L.; Mountford, P. *Dalton Trans.* **2005**, 1448. (b) Kiely, A. F.; Nelson, C. M.; Pastor, A.; Henling, L. M.; Day, M. W.; Bercaw, J. E. *Organometallics* **1998**, *17*, 1324. (c) Gibson, V. C.; Kimberley, B. S.; White, A. J. P.; Williams, D. J.; Howard, P. *Chem. Commun.* **1998**, 313.

(20) The molecular structure of this compound has been reported by Schafer. See ref 12.

(21) Beesley, R. M.; Ingold, C. K.; Thorpe, J. F. *J. Chem. Soc.* **1915**, 1080.

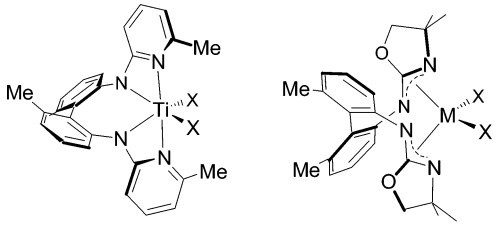


Figure 4. Related aminopyridinate (**I**) and aminooxazolinate (**II**) complexes.

2,4,4-trimethylpyrrolidine, which, when derivatized with (*R*)-(+)-Mosher chloride, was determined to have been cyclized in 5% ee (by **9**) and 91% ee (by **10**). For the cyclization of 1-amino-2,2-dimethylhex-5-ene into 3,5,5-trimethylpiperidine, similar reactivity was observed: no catalysis with **8**, slow catalysis with **9** (ee 21%), and complete conversion with **10** (ee 38%).

Conclusions

The amidate complexes reported here form the third member of a series of biaryl-bridged heterodiallyl group 4 systems, the first two being the aminopyridinates **I**[7d] and the aminooxazolinates **II** (Figure 4).[7b] For the class **I** only the titanium complexes could be isolated, and this appears now to be a result principally of the inability of the aromatic ligand to distort to accommodate the larger zirconium or hafnium ions; unbridged bis(κ^2-aminopyridinates) are well established.[22] In the case of class **II** the ligand system is more flexible, and in twisting to accommodate the larger metals the system also exhibits a more pronounced helicity than does **I**. In the present amidate system, far greater flexibility in terms of the binding mode is possible, and in order to relieve strain the titanium system adopts the κ^2-*N*,*O*/κ^1-*O* structure, made possible by the lack of steric bulk around the oxygen atom compared with the "outer" nitrogen atoms in **I** and **II**. This latter issue also leads to the possibility of bridging ligand modes, of which the observed structure of **6** is an example. Examination of space-filling models of **6** indicate that increasing the size of the amidate substituent beyond R = Et will lead to steric compression, and moreover the mesityl-substituted system based on L^4 is untenable. It is unfortunate that this does not lead however to clean production of a monomeric zirconium system analogous to **4**, but to a complex mixture of products.

In the zirconium amide series, the type of product obtained also depends strongly on the steric bulk of the ligand, the least bulky (L^1) giving poorly defined oligomers and the largest (L^4) giving principally a monomer, [$L^4Zr(NMe_2)_2(NHMe_2)$], **10**. Similarly, Schafer et al.[12] note that both reactivity and selectivity in hydroamination catalysis are maximized with this mesityl derivative (our L^4). Their less bulky adamantyl and naphthyl derivatives are suggested to be in equilibrium with other catalytically inactive coordination modes. Our findings are thus in agreement, and further it seems that the bis(κ^2-amidate) structure leads to the catalytically competent system.

The question remains as to how to fully optimize both the rate and selectivity; initial experiments suggest that substituting mesityl for 2,4,6-triisopropylphenyl greatly reduces reactivity.

(22) (a) Crust, E. J.; Munslow, I. J.; Morton, C.; Scott, P. *Dalton Trans.* **2004**, 2257. (b) Crust, E. J.; Clarke, A. J.; Deeth, R. J.; Morton, C.; Scott, P. *Dalton Trans.* **2004**, 4050. (c) Morton, C.; O'Shaughnessy, P.; Scott, P. *Chem. Commun.* **2000**, 2099.

Experimental Section

General Considerations. All manipulations were conducted using standard inert-atmosphere techniques using a dual-manifold argon/vacuum Schlenk line or an MBraun Lab Star glovebox. Solvents were refluxed under nitrogen from an appropriate drying agent; both diethyl ether and pentane were distilled from NaK alloy and were rigorously degassed before use. C_6D_6 and toluene-d_8 were refluxed *in vacuo* for 3 days over potassium metal and vacuum transferred before use. C_6D_5Br was dried in a similar manner from CaH_2. $CDCl_3$ (stored over 4 Å molecular sieves) was purchased from Aldrich and used as received. $Ti(CH_2Ph)_4$,[23] $Zr(CH_2Ph)_4$,[23] $Ti(CH_2CMe_3)_4$,[24] $Zr(NMe_2)_4$[25] and (*R*,*S*)-2,2′-diamino-6,6′-dimethylbiphenyl[9b] were prepared according to published procedures. Acetyl chloride, propionyl chloride, trimethylacetyl chloride (Aldrich), and 2,4,6-trimethylbenzoyl chloride (Alfa) were used as received. (*R*)-(+)-α-Methoxy-α-(trifluoromethyl)phenylacetyl chloride was purchased from Acros Organics and used as received. Hydroamination substrates 1-amino-2,2-dimethylpent-4-ene[26] and 1-amino-2,2-dimethylhex-5-ene[7c] were prepared according to published procedures and dried over sodium at 70 °C for 24 h before vacuum transfer and storage in the glovebox. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker DPX300, DPX400, and DRX 500 spectrometers and the spectra referenced internally using residual protio-solvent resonances relative to tetramethylsilane ($\delta = 0$ ppm). Elemental analyses were obtained by Warwick Analytical Services and MEDAC Ltd, Surrey, UK. The carbon analyses of some of the metal benzyl complexes are low; we attribute this to incomplete combustion and formation of metal carbides,[27] as has been previously observed in similar amidate alkyl complexes.[15] Mass spectra were obtained on a VG Autospec mass spectrometer by the Department of Chemistry Mass Spectrometry Service, University of Warwick.

Proligand Synthesis. General Procedure for H_2L^n ($n = 1-3$). A 250 mL round-bottomed flask was charged with a solution of (*R*,*S*)-2,2′-diamino-6,6′-dimethylbiphenyl (ca. 10 mmol) in methylene chloride (100 mL). The solution was cooled to 0 °C, and triethylamine (6 equiv) was added. To the pale yellow solution was added the appropriate acid chloride (2 equiv) in methylene chloride (50 mL), dropwise, with stirring. The resulting off-white suspension was left to stir at room temperature overnight. After this time, 2 M HCl (100 mL) was added, the layers were separated, and the organic phase was washed with water (100 mL) and saturated sodium carbonate solution (100 mL). The organic layer was dried over Na_2SO_4 and filtered, and the solvent was removed under reduced pressure to yield the appropriate proligand as a highly crystalline, off-white solid that needed no further purification.

H_2L^1. Using the general procedure described above, (*R*,*S*)-2,2′-diamino-6,6′-dimethylbiphenyl (1.00 g, 4.7 mmol) and acetyl chloride (0.74 g, 9.4 mmol) gave the title compound as an off-white solid. Yield: 0.96 g (3.3 mmol, 69%). ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ 1.89 ppm (s, 6H, 2 × Ar-C*H*$_3$), 1.94 (s, 6H, 2 × C*H*$_3$ amide), 6.78 (s, br, 2H, N*H*C(CH$_3$)=O), 7.14 (d, 2H, Ar C-*H*, $^3J_{HH} = 8$ Hz), 7.36 (t, 2H, Ar C-*H*, $^3J_{HH} = 8$ Hz), 8.04 (d, 2H, Ar C-*H*, $^3J_{HH} = 8$ Hz). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 298 K): δ 19.5 ppm (Ar-*C*H$_3$), 24.1 (NHC(*C*H$_3$)=O), 120.2 (Ar *C*-H), 126.6 (Ar *C*-H), 128.9 (Ar *C*-H), 135.5, 137.0 (2 x Ar C_q), 168.7 (NH*C*(CH$_3$)=O). Anal. Calcd for $C_{18}H_{20}N_2O_2$: C, 72.95; H, 6.80; N, 9.45. Found: C, 72.79; H, 6.73; N, 9.34. MS (EI +ve) *m*/*z*: 296 [M^+].

(23) Zucchini, U.; Albizzati, E.; Giannini, U. *J. Organomet. Chem.* **1971**, *26*, 357.

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(25) Bradley, D. C.; Thomas, I. M. *J. Chem. Soc.* **1960**, 3857.

(26) Tamaru, Y.; Hojo, M.; Higashimura, H.; Yoshida, Z.-I. *J. Am. Chem. Soc.* **1988**, *110*, 3994.

(27) Carpenetti, D. W.; Kloppenburg, L.; Kupec, J. T.; Petersen, J. L. *Organometallics* **1996**, *15*, 1572.

H_2L^2. Using the general procedure described above, (*R*,*S*)-2,2′-diamino-6,6′-dimethylbiphenyl (2.77 g, 13.0 mmol) and propionyl chloride (2.42 g, 26.1 mmol) gave the title compound as an off-white solid. Yield: 3.75 g (11.6 mmol, 89%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 0.95 ppm (t, 6H, 2 × NHC(CH_2CH_3)═O, $^3J_{HH}$ = 8 Hz), 1.95 (s, 6H, 2 × Ar-CH_3), 2.11 (q, 4H, 2 × NHC(CH_2-CH_3)═O, $^3J_{HH}$ = 8 Hz), 6.75 (s, br, 2H, N*H*C(CH_2CH_3)═O), 7.13 (d, 2H, 2 × Ar C-*H*, $^3J_{HH}$ = 8 Hz), 7.36 (t, 2H, 2 × Ar C-*H*, $^3J_{HH}$ = 8 Hz), 8.14 (d, 2H, 2 × Ar C-*H*, $^3J_{HH}$ = 8 Hz). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 298 K): δ 9.8 ppm (NHC(CH_2CH_3)═O), 20.1 (Ar-CH_3), 31.1 (NHC(CH_2CH_3)═O), 120.2, 126.8, 129.6 (3 × Ar *C*-H), 136.2, 137.6 (2 × Ar C_q) 172.8 (NH*C*(CH_2CH_3)═O). Anal. Calcd for $C_{20}H_{22}N_2O_2$: C, 74.04; H, 7.46; N, 8.64. Found: C, 74.06; H, 7.47; N, 8.60. MS (EI +ve) *m*/*z*: 324 [M^+].

H_2L^3. Using the general procedure described above, (*R*,*S*)-2,2′-diamino-6,6′-dimethylbiphenyl (2.00 g, 9.4 mmol) and trimethylacetyl chloride (2.27 g, 18.8 mmol) gave the title compound as an off-white solid. Yield: 3.54 g (9.3 mmol, 99%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 0.94 ppm (s, 18H, 2 × CMe_3), 1.99 (s, 6H, 2 × Ar-CH_3), 7.02 (s, br, 2H, N*H*(CMe_3)C═O), 7.12 (d, 2H, 2 × Ar C-*H*, $^3J_{HH}$ = 8 Hz), 7.36 (t, 2H, 2 × Ar C-*H*, $^3J_{HH}$ = 8 Hz), 8.22 (d, 2H, 2 × Ar C-*H*, $^3J_{HH}$ = 8 Hz). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 298 K): δ 20.0 ppm (Ar-CH_3), 27.5 (NHC(CMe_3)═O), 40.0 (NHC(*C*Me_3)═O), 119.4 (Ar *C*-H), 126.1 (Ar C_q), 126.4, 129.8 (2 × Ar *C*-H), 136.4, 137.4 (2 × Ar C_q), 177.1 (NH*C*(CMe_3)═O). Anal. Calcd for $C_{24}H_{32}N_2O_2$: C, 75.75; H, 8.48; N, 7.36. Found: C, 75.80; H, 8.41; N, 7.40. MS (EI +ve) *m*/*z*: 380 [M^+].

H_2L^4. The general procedure outlined above was followed, using (*R*,*S*)-2,2′-diamino-6,6′-dimethylbiphenyl (2.00 g, 9.4 mmol) and 2,4,6-trimethylbenzoyl chloride (3.44 g, 18.8 mmol); however the solid thus obtained indicated only the formation of the monocarboxamide. The solid was redissolved in methylene chloride and the solution cooled to 0 °C. Triethylamine and two further equivalents of 2,4,6-trimethylbenzoyl chloride were added. and the reaction was left to stir at room temperature for 2 further days. The workup process was repeated to yield a sticky, yellow solid. The solid was recrystallized from boiling toluene to yield H_2L^4 as a pale yellow powder. Yield: 1.9 g (3.8 mmol, 40% overall). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 1.96 (s, 6H, 2 × Ar-CH_3), 2.10 (s, 12H, 4 × mesityl CH_3), 2.22 (s, 6H, 2 × mesityl CH_3), 6.75 (s, 4H, Ar C-*H* mesityl), 7.15 (d, 2H, 2 × Ar C-*H*, $^3J_{HH}$ = 8 Hz), 7.36 (t, 2H, 2 × Ar C-*H*, $^3J_{HH}$ = 8 Hz), 8.00 (d, 2H, Ar C-*H*, $^3J_{HH}$ = 8 Hz). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 298 K): δ 18.7 ppm (2 × mesityl-CH_3), 19.8 (Ar-CH_3), 20.9 (mesityl-CH_3), 122.0 (Ar *C*-H), 127.4 (Ar *C*-H), 128.1 (mesityl *C*-H), 128.8 (aryl *C*-H), 129.5, 133.9, 134.2, 135.3, 137.1, 138.4 (C_q Ar and mesityl), 169.2 (C_q amide). Anal. Calcd for $C_{34}H_{36}N_2O_2$: C, 80.92; H, 7.19; N, 5.55. Found: C, 80.96; H, 7.19; N, 5.46. MS (EI +ve) *m*/*z*: 504 [M^+].

Synthesis of Chiral Nonracemic Proligands. The general procedure above was employed, using chiral nonracemic (*S*)-2,2′-diamino-6,6′-dimethylbiphenyl.[9b] Analytical data were identical to the racemic compounds.

General Procedure for Synthesis of [L^nTi(CH_2Ph)$_2$] (*n* = 1−4). An ampule fitted with J. Young tap and magnetic stirrer bar was charged with H_2L^n (ca. 1 mmol) and Ti(CH_2Ph)$_4$ (1 equiv). Diethyl ether was added, and the reaction was stirred overnight in the absence of light. After this time, the solvent was removed to yield a viscous red-brown residue. Pentane was added and then removed *in vacuo*, and the process repeated to yield the title compound as a red-brown solid.

[L^1Ti(CH_2Ph)$_2$], 1. Using the general procedure described above, H_2L^1 (0.215 g, 0.72 mmol) and Ti(CH_2Ph)$_4$ (0.300 g, 0.72 mmol) gave the title compound as a red-brown solid. Yield: 0.297 g (0.56 mmol, 79%). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 1.63 ppm (s, 3H, CH_3), 1.70 (s, 3H, CH_3), 1.82 (s, 3H, Ar-CH_3), 1.95 (d, 1H, Ti-CH_2Ph, $^2J_{HH}$ = 8 Hz), 2.07 (s, 3H, Ar−CH_3), 2.33 (d, 1H, Ti-CH_2Ph, $^2J_{HH}$ = 8 Hz), 2.37 (d, 1H, Ti-CH_2Ph, $^2J_{HH}$ = 8 Hz), 2.74 (d, 1H, Ti-CH_2Ph, $^2J_{HH}$ = 8 Hz), 5.89 (d, 1H, Ar C-*H*, $^3J_{HH}$ = 8 Hz), 6.77−7.12 (m, 11H, Ar C-*H*), 7.17−7.26 (m, 4H, Ar C-*H*). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, 298 K): δ 17.1 ppm (*C*H_3), 19.9, 20.2 (Ar-*C*H_3), 22.3 (*C*H_3), 84.5, 92.6 (both Ti-*C*H_2Ph), 123.0, 124.4, 125.7, 126.2, 126.9, 128.3, 128.8, 129.3, 130.4 (all Ar *C*-H), 134.0, 135.2, 135.3, 136.4, 137.9, 146.3 (all Ar C_q), 159.5 (C_q iminolate), 184.1 (C_q amidate). Anal. Calcd for $C_{32}H_{32}N_2O_2Ti$: C, 73.28; H, 6.15; N, 5.34. Found: C, 70.77; H, 6.08; N, 5.53. MS (EI +ve) *m*/*z*: 353 [M^+ − 2CH_2Ph].

[L^2Ti(CH_2Ph)$_2$], 2. Using the general procedure described above, H_2L^2 (0.236 g, 0.72 mmol) and Ti(CH_2Ph)$_4$ (0.300 g, 0.72 mmol) gave the title compound as a red-brown powder. Yield: 0.365 g (0.66 mmol, 85%). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 0.93 ppm (t, 3H, CH_2CH_3, $^3J_{HH}$ = 7 Hz), 0.95 (t, 3H, CH_2CH_3, $^3J_{HH}$ = 7 Hz), 1.73 (s, 3H, Ar-CH_3), 1.99−2.03 (m, 2H, CH_2CH$_3$), 2.08 (s, 3H, Ar-CH_3), 2.10−2.21 (m, 3H, CH_2CH$_3$ and Ti-CH_2Ph, overlapping), 2.36 (d, 1H, Ti-CH_2Ph, $^2J_{HH}$ = 8 Hz), 2.42 (d, 1H, Ti-CH_2Ph, $^2J_{HH}$ = 9 Hz), 2.42 (d, 1H, Ti-CH_2Ph, $^2J_{HH}$ = 8 Hz), 5.93 (d, 1H, Ar C-*H*, $^2J_{HH}$ = 8 Hz), 6.89 (m, 4H, Ar C-*H*), 6.93−7.13 (m, 7H, Ar C-*H*), 7.17 − 7.26 (m, 4H, Ar C-*H*). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, 298 K): δ 8.8, 11.2 ppm (both CH_2CH_3), 19.8, 20.2 (Ar-*C*H_3), 23.8, 29.3 (both *C*H_2CH$_3$), 85.0, 92.9 (both Ti-*C*H_2Ph), 120.2, 120.8, 123.0, 124.3, 126.1, 126.7, 128.2, 128.7, 129.3, 130.3, 133.7 (Ar *C*-H), 134.5, 136.0, 136.3, 140.7, 146.3, 148.9, 163.6 (Ar C_q), 165.1 (C_q iminolate), 186.8 (C_q amidate). Anal. Calcd for $C_{34}H_{36}N_2O_2Ti$: C, 73.91; H, 6.57; N, 5.07. Found: C, 72.02; H, 6.53; N, 5.09. MS (EI +ve) *m*/*z*: 462 [M^+ − CH_2Ph].

[L^3Ti(CH_2Ph)$_2$], 3. Using the general procedure described above, H_2L^3 (0.279 g, 0.72 mmol) and Ti(CH_2Ph)$_4$ (0.300 g, 0.72 mmol) gave the title compound as a slightly tacky, red-brown solid. Yield: 0.330 g (0.54 mmol, 75%). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 1.02 ppm (s, 9H, CMe_3), 1.13 (s, 9H, CMe_3), 1.96 (s, 3H, Ar-CH_3), 2.06 (s, 3H, Ar-CH_3), 2.39 (d, 1H, Ti-CH_2Ph, $^2J_{HH}$ = 8 Hz), 2.44 (d, 1H, Ti-CH_2Ph, $^2J_{HH}$ = 10 Hz), 2.73−2.79 (2 × d, overlapping, 2 × 1H, Ti-CH_2Ph, $^2J_{HH}$ = 10 and 8 Hz), 6.27 (m, 1H, Ar C-*H*), 6.86−7.18 (m, 16H, Ar C-*H*). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, 298 K): δ 20.2, 20.7 ppm (both Ar-*C*H_3), 28.2, 28.4 (both CMe_3), 38.3, 40.3 (both *C*Me_3), 87.9, 95.5 (both Ti-*C*H_2Ph), 120.6, 122.8, 123.4, 124.3, 125.7, 126.8, 127.2, 128.2, 129.6, 131.9 (all Ar *C*-H), 134.7, 136.2, 137.0, 138.8, 139.9, 141.6, 146.6, 148.5 (all Ar C_q), 167.7 (C_q iminolate), 188.5 (C_q amidate). Anal. Calcd for $C_{38}H_{44}N_2O_2Ti$: C, 74.99; H, 7.29; N, 4.60. Found: C, 74.32; H, 7.44; N, 4.93. MS (EI +ve) *m*/*z*: 518 [M^+ − CH_2Ph], 426 [M^+ − 2CH_2Ph].

[L^4Ti(CH_2Ph)$_2$], 4. Using the general procedure described above, H_2L^4 (0.303 g, 0.61 mmol) and Ti(CH_2Ph)$_4$ (0.250 g, 0.61 mmol) gave a highly crystalline red-brown solid directly from the reaction mixture, which was filtered and dried *in vacuo*. Yield: 0.251 g (0.34 mmol, 56%). ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 1.78 ppm (s, 3H, Ar-CH_3), 1.95 (s, 6H, 2 × Ar-CH_3), 2.11 (s, 9H, 3 × Ar-CH_3), 2.13 (s, 3H, Ar-CH_3), 2.15 (s, 3H, Ar-CH_3), 2.53 (d, 1H, Ti-CH_2Ph, $^2J_{HH}$ = 9 Hz), 2.58 (d, 1H, Ti-CH_2Ph, $^2J_{HH}$ = 9 Hz), 2.77 (d, 1H, Ti-CH_2Ph, $^2J_{HH}$ = 9 Hz), 2.85 (d, 1H, Ti-CH_2Ph, $^2J_{HH}$ = 9 Hz), 6.55 (m, 3H, Ar C-*H*), 6.58−6.62 (m, 2H, Ar C-*H*), 6.76−6.80 (m, 5H, Ar C-*H*), 6.86−6.91 (m, 3H, Ar C-*H*), 7.01 (t, 1H, Ar C-*H*, $^3J_{HH}$ = 7 Hz), 7.10−7.22 (m, 4H, Ar C-*H*), 7.28 (d, 2H, Ar C-*H*, $^3J_{HH}$ = 7 Hz). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 298 K): δ 20.4, 21.1, 21.3, 21.6, 22.0 ppm (all Ar-*C*H_3), 93.5, 97.6 (both Ti-*C*H_2Ph), 120.7, 121.1, 125.2, 125.8, 126.0, 127.9, 128.5, 128.7, 129.2, 129.6 (Ar *C*-H) 131.1 (Ar C_q), 132.0 (Ar *C*-H), 134.0, 134.4, 134.7, 135.2, 137.9, 138.0, 138.1, 139.1, 139.7, 139.9, 141.3, 148.8 (all Ar C_q), 159.6 (C_q iminolate), 184.1 (C_q amidate).

Anal. Calcd for $C_{48}H_{48}N_2O_2Ti.(OEt_2)_{0.5}$: C, 78.01; H, 6.94; N, 3.64. Found: C, 76.71; H, 6.47; N, 4.07. MS (EI +ve) *m/z*: 578 [M^+ − 2Ph].

[{L[1]Zr(CH$_2$Ph)$_2$}$_2$], 5. A Schlenk tube was charged with H_2L^1 (0.200 g, 0.68 mmol) and $Zr(CH_2Ph)_4$ (0.308 g, 0.68 mmol). Diethyl ether was added, and the reaction stirred overnight in the absence of light. After this time, the reaction mixture was filtered to remove a small amount of insoluble yellow material and the resulting yellow-orange solution concentrated. Standing at room temperature (in the dark) resulted in the precipitation of a crystalline, yellow solid. Yield: 0.115 g, (0.10 mmol, 30%). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 1.64 ppm (s, 6H, 2 × CH_3), 1.79 (s, 6H, 2 × Ar-CH_3), 2.07 (s, 6H, 2 × Ar-CH_3), 2.17 (s, 6H, 2 × CH_3), 2.27 (d, 2H, 2 × Zr-CH_2Ph, $^2J_{HH}$ = 11 Hz), 2.44 (d, 2H, 2 × Zr-CH_2-Ph, $^2J_{HH}$ = 11 Hz), 2.53 (d, 2H, 2 × Zr-CH_2Ph, $^2J_{HH}$ = 9 Hz), 3.13 (d, 2H, 2 × Zr-CH_2Ph, $^2J_{HH}$ = 9 Hz), 6.85 (d, 6H, Ar C-*H*, $^3J_{HH}$ = 8 Hz), 7.03 − 7.10 (m, 12H, Ar C-*H*), 7.25 (m, 4H, Ar C-*H*), 7.32−7.42 (m, 10H, Ar C-*H*). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, 298 K): δ 18.4 ppm (NCCH_3), 19.5, 19.7 (Ar-CH_3), 21.1 (NCCH_3), 73.1, 73.3 (both Zr-CH_2Ph), 120.9, 122.0, 123.0, 125.3, 127.0, 127.6, 128.7, 129.4, 129.5, 130.5 (Ar *C*-H), 131.0, 134.5, 137.1, 139.3, 140.5, 143.3, 144.3, 149.8 (Ar C_q), 176.0 (C_q bridging iminolate), 184.2 (C_q amidate). Anal. Calcd for $C_{64}H_{64}N_4O_4Zr_2$: C, 67.69; H, 5.68; N, 4.93. Found: C, 65.74; H, 5.61; N, 4.28.

[{L[2]Zr(CH$_2$Ph)$_2$}$_2$], 6. A Schlenk tube was charged with H_2L^2 (0.250 g, 0.77 mmol) and $Zr(CH_2Ph)_4$ (0.350 g, 0.77 mmol). Diethyl ether was added, and the reaction stirred overnight in the absence of light. After this time, the reaction mixture was filtered to remove insoluble yellow material and the resulting yellow-orange solution concentrated. Standing at room temperature (in the dark) resulted in the precipitation of a crystalline, yellow solid. Yield: 0.236 g (0.20 mmol, 51%). ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.71 ppm (t, 6H, CH_2CH_3, $^3J_{HH}$ = 8 Hz), 1.18 (t, 6H, CH_2CH_3, $^3J_{HH}$ = 8 Hz), 1.85 (m, 2H, CH_2CH$_3$), 2.04 (m, 2H, CH_2CH$_3$), 2.05 (s, 6H, Ar-CH_3), 2.09 (d, 2H, Zr-CH_2Ph, $^2J_{HH}$ = 11 Hz), 2.14 (m, 8H, 6 H of Ar-CH_3 and 2H of CH_2CH$_3$, overlapping), 2.18 (d, 2H, Zr-CH_2-Ph, $^2J_{HH}$ = 11 Hz), 2.29 (m, 2H, CH_2CH$_3$), 2.62 (d, 2H, Zr-CH_2-Ph, $^2J_{HH}$ = 8 Hz), 3.09 (d, 2H, Zr-CH_2Ph, $^2J_{HH}$ = 8 Hz), 6.44 (d, 4H, Ar C-*H*, $^3J_{HH}$ = 7 Hz), 6.71 (d, 2H, Ar C-*H*, $^3J_{HH}$ = 7 Hz), 6.89−6.97 (m, 8H, multiplet, Ar C-*H*), 7.06 (d, 2H, Ar C-*H*, $^3J_{HH}$ = 7 Hz), 7.14−7.21 (m, 10H, Ar C-*H*), 7.27−7.31 (m, 8H, Ar C-*H*). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): δ 8.3, 11.6 ppm (both CH_2CH_3), 19.7, 19.8 (both Ar-CH_3), 25.1, 28.3 (both CH_2-CH$_3$), 73.3, 73.6 (both Zr-CH_2Ph), 120.7, 122.3, 123.2, 125.3, 127.0, 127.2, 127.5, 127.8, 127.9 (all Ar *C*-H), 128.8, 129.3, 129.6, 131.1, 131.2, 134.7, 137.2, 139.8, 140.9, 142.7, 143.1, 149.8 (all Ar C_q), 179.0 (C_q bridging iminolate), 187.9 (C_q amidate). Anal. Calcd for $C_{66}H_{68}N_4O_4Zr_2$: C, 68.12; H, 5.89; N, 4.81. Found: C, 67.63; H, 6.05; N, 4.75.

Hydroamination Trials with Ti Cations. In the glovebox, a 2 mL sample vial was charged with **4** (5 mg). A second vial was charged with 1 equiv of $B(C_6F_5)_3$. Bromobenzene-d_5 was added to both vials, and the contents were mixed before transferring to a J. Young NMR tube. A third vial was charged with ca. 10−20 equiv of the chosen substrate and was then added to the NMR tube. The initial ^{1}H NMR spectrum was recorded, the sample was then placed in a heating block at 100 °C, and the ^{1}H NMR spectrum was recorded at regular intervals thereafter.

[HL[4]Ti(CH$_2$Ph)$_2$][B(C$_6$F$_5$)$_4$], 7. Due to the instability of the complex, characterization was carried out in situ. In the glovebox, a 2 mL sample vial was charged with **4** (7.5 mg, 9.3 μmol) and $[HNMe_2Ph][B(C_6F_5)_4]$ (8.0 mg, 10.0 μmol, 1.1 equiv). Bromobenzene-d_5 (0.4 mL) was added to the vial, and the mixture transferred to a J. Young NMR tube. The sample was immediately characterized by NMR spectroscopy. ^{1}H NMR (400 MHz, C_6D_5Br, 298 K): δ 1.56 ppm (s, 3H, *p*-Ar-CH_3 of mesityl), 1.61 (s, 3H, *p*-Ar-CH_3 of mesityl), 1.80 (s, br, 6H, 2 × *o*-Ar-CH_3 of mesityl, overlapping), 1.83 (d, 1H, Ti-CH_2Ph, $^2J_{HH}$ = 10 Hz), 2.03 (s, 3H, Ar-CH_3 of biaryl), 2.10 (d, 1H, Ti-CH_2Ph, $^2J_{HH}$ = 10 Hz), 2.13 (s, 3H, Ar-CH_3 of biaryl), 2.16 (s, 6H, 2 × *o*-Ar-CH_3 of mesityl, overlapping), 2.25 (d, 1H, Ti-CH_2Ph, $^2J_{HH}$ = 8 Hz), 2.36 (d, 1H, Ti-CH_2Ph, $^2J_{HH}$ = 8 Hz), 6.09 (d, 2H, Ar C-*H*, $^3J_{HH}$ = 8 Hz), 6.61−6.64 (m, 2H, Ar C-*H*), 6.72 (s, 2H, Ar C-*H* of mesityl, overlapping), 6.84−6.91 (m, 5H, Ar C-*H*), 7.08 (m, 3H, Ar C-*H*), 7.22 (s, 2H, Ar C-*H* of mesityl, overlapping), 7.31−7.39 (m, 3H, Ar C-*H*), 7.93 (s, br, 1H, N*H*). ^{19}F{^{1}H} NMR (282.4 MHz, C_6D_5Br, 298 K): δ −131.3 ppm (d, *o*-F), −161.5 (t, *p*-F), −165.4 (t, *m*-F). The sample is insufficiently stable for ^{13}C NMR analysis.

General Procedure for the NMR-Scale Synthesis of Zr Amide Complexes. In the glovebox, a 2 mL sample vial was charged with $Zr(NMe_2)_4$ (ca. 15 mg). A separate vial was charged with proligand (1 equiv). C_6D_6 was added to both vials, and the contents were mixed. The colorless solution was transferred to a J. Young NMR tube and immediately characterized by NMR spectroscopy. Conversion was instantaneous in all cases.

[{L[2]Zr(NMe$_2$)$_2$(NHMe$_2$)}$_2$], 8. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 1.06 ppm (t, 3H, CH_2CH_3, $^3J_{HH}$ = 8 Hz), 1.17 (t, 3H, CH_2CH_3, $^3J_{HH}$ = 8 Hz), 1.70 (s, br, 4H, Ar-CH_3 and N*H*Me$_2$, overlapping), 2.12 (s, 3H, Ar-CH_3), 2.18 (s, br, 6H, NH*Me*$_2$), 2.21−2.47 (m, 4H, CH_2CH$_3$), 3.01 (s, 6H, Zr-N*Me*$_2$), 3.04 (s, 6H, Zr-N*Me*$_2$), 6.61 (d, 1H, Ar C-*H*, $^3J_{HH}$ = 8 Hz), 6.68 (d, 1H, Ar C-*H*, $^3J_{HH}$ = 8 Hz), 6.77 (d, 1H, Ar C-*H*, $^3J_{HH}$ = 8 Hz), 6.93 (m, 2H, Ar C-*H*), 7.07 (t, 1H, Ar C-*H*, $^3J_{HH}$ = 8 Hz). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, 298 K): δ 10.3, 11.2 ppm (both CH_2CH_3), 20.0, 20.4 (both Ar-CH_3), 24.6, 31.2 (both CH_2CH$_3$), 38.9 (br, NH*Me*$_2$), 39.7, 45.7 (both Zr-N*Me*$_2$), 120.6, 122.3, 123.1, 126.3, 127.4, 127.5 (all Ar *C*-H), 132.1, 134.6, 136.7, 138.0, 142.4, 151.4 (all Ar C_q), 164.7 (C_q iminolate), 183.3 (C_q amidate).

[{L[3]Zr(NMe$_2$)$_2$(NHMe$_2$)}$_n$], 9. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 0.07 ppm (s, br, 1H, N*H*Me$_2$), 1.26 (s, 9H, C*Me*$_3$), 1.29 (s, 9H, C*Me*$_3$), 1.91 (s, 3H, Ar-CH_3 and s, br, 6H, NH*Me*$_2$, overlapping), 2.10 (s, 3H, Ar-CH_3), 2.98 (s, 6H, Zr-N*Me*$_2$), 3.01 (s, 6H, Zr-N*Me*$_2$), 6.69 (m, 2H, Ar C-*H*), 6.87−7.02 (m, 4H, Ar C-*H*). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, 298 K): δ 20.5, 20.6 ppm (both Ar-*C*H$_3$), 29.0, 29.5 (both C*Me*$_3$), 38.3 (*C*Me$_3$), 39.4 (br, NH*Me*$_2$), 39.9 (Zr-N*Me*$_2$), 40.9 (*C*Me$_3$), 42.7 (Zr-N*Me*$_2$), 120.4, 123.2, 124.4, 125.7, 126.0, 127.3 (all Ar *C*-H), 131.3, 133.9, 137.0, 138.3, 142.7, 150.9 (all Ar C_q), 168.6 (C_q iminolate), 185.3 (C_q amidate).

[L[4]Zr(NMe$_2$)$_2$(NHMe$_2$)], 10. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 0.62 ppm (s, br, 1H, N*H*Me$_2$), 1.97 (s, 6H, Ar-CH_3), 2.04 (s, 6H, Ar-CH_3), 2.10 (s, 6H, NH*Me*$_2$), 2.13 (s, 6H, Ar-CH_3), 2.74 (s, 6H, Ar-CH_3), 3.32 (s, 12H, Zr-N*Me*$_2$), 6.53 (s, 2H, Ar C-*H*), 6.57−6.82 (m, 8H, Ar C-*H*). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, 298 K): δ 20.3, 20.4, 21.1, 21.4 ppm (all Ar-*C*H$_3$), 39.1 (NH*Me*$_2$), 44.8 (Zr-N*Me*$_2$), 120.9, 125.7, 127.6, 129.2, 129.7 (all Ar *C*-H), 132.5, 133.2, 134.7, 138.1, 139.2 (2 resonances overlapping), 144.9 (all Ar C_q), 181.0 (C_q amidate).

Hydroamination with *in-situ* Zr Amide Complexes. In the glovebox, a 2 mL sample vial was charged with $Zr(NMe_2)_4$ (5.0 mg, 18.7 μmol). A second vial was charged with the appropriate chiral nonracemic proligand ((*S*)-H_2L^{2-4}, 1.1 equiv, 20.6 μmol). Toluene-d_8 (0.2 mL) was added to each vial, and the contents were mixed for 5 min. A third vial was charged with 10 equiv (187 μmol) of substrate, the Zr catalyst solution was added, and the contents of the vial were transferred to a J. Young NMR tube. The initial ^{1}H NMR spectrum was recorded, the sample was then placed in a heating block at 110 °C, and the ^{1}H NMR spectrum was recorded at regular intervals thereafter.

Determination of Enantioselectivity. Using the samples from the catalytic reactions described above, all volatiles were vacuum transferred from the NMR tube into Young's tap ampules at 10^{-3} mmHg. Methylene chloride (1 mL) was added, along with triethylamine (0.1 mL). A solution of (*R*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (1 equiv based on the amount of

catalysis substrate used) in methylene chloride (1 mL) was added, and the colorless solution left to stir at ambient temperature for 2 days. The contents of the ampule were then filtered and all volatiles removed *in vacuo* to yield an off-white residue. NMR analysis ($CDCl_3$) of well-defined resonances in the resulting diastereomeric mixture—compared to resonances from racemic products synthesized using racemic ligands—determined the enantioselectivity.

X-ray Crystallography. Single crystals of [$L^4Ti(CH_2Ph)_2$] (**4**) and [{$L^2Zr(CH_2Ph)_2$}$_2$] (**6**) were obtained from saturated diethyl ether solutions at room temperature as orange-red plates and yellow blocks, respectively. The crystals were 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 Cu Kα radiation (λ = 1.54178 Å). Both sets of crystals were fragile and weakly diffracting and gave no useful intensity above 2θ = 161°. Nevertheless, the data are sufficiently good for us to be confident in the structural assignments required for the purposes of this research (i.e., nuclearity and coordination mode).

Data were collected using narrow (0.3° in ω) frame exposures, and intensities corrected using SADABS.[28] The structures were solved using direct methods via SHELXS and refined using SHELXL. In the structure of **4**, a disordered diethyl ether molecule with the central oxygen atom occupying a special position was modeled in two orientations, each with 50% occupancy, the inversion center generating the other halves of the molecule. The atoms were refined isotropically. In the structure of **6**, one ethyl group of the nonbridging amidate is disordered over two sites, modeled with a 63:37 occupancy ratio. The minor component was refined isotropically. All other 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 (control), SAINT (integration),[29] and SHELXTL[30] for structure solution, refinement, and molecular graphics.

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Supporting Information Available: CIF files for the structure determinations of **4** and **6**, NMR spectra of relevant catalytic reactions, and determination of enantioselectivity. This material is available free of charge via the Internet at http://pubs.acs.org.

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