# Chiral Complexes of a New Diazaallyl Ligand: Group 4 Aminooxazolinates

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A new biaryl-bridged bis(iminooxazolidine) proligand $H_2$**L** is prepared in good yield from 2,2-diamino-6,6′-dimethylbiphenyl. The direct reaction of $H_2$**L** with [Ti($CH_2Ph$)$_4$] leads via deprotonation of the ligand to the $C_2$-symmetric dibenzyl complex [**L**Ti($CH_2Ph$)$_2$] (85%) containing diazaallyl ligation. The analogous group 4 complexes [**L**Zr($CH_2Ph$)$_2$] (79%) and [**L**Hf($CH_2Ph$)$_2$] (91%) are similarly obtained. Molecular structures of these three compounds indicate $C_2$-symmetry in all cases and that the chirality of the backbone is well expressed in the coordination sphere. Reaction of $H_2$**L** with Ti($NMe_2$)$_4$ gives the amide [**L**Ti($NMe_2$)$_2$] (90%), which on reaction with $SiMe_3Cl$ gives the chloride [**L**Ti$Cl_2$] (78%). The dichloride [**L**Zr($NMe_2H$)$Cl_2$] is prepared via treatment of $H_2$**L** with Zr($NMe_2$)$_2Cl_2$(THF)$_2$ (86%). The direct reaction of $H_2$**L** with Ti$Cl_4$(THF)$_2$ gives the adduct [($H_2$**L**)Ti$Cl_4$] (83%), which is shown by X-ray crystallography to contain intramolecular NH···Cl hydrogen bond contacts. The complexes were tested as precatalysts for the polymerization of ethene and 1-hexene using a range of cocatalysts and were found to display low activity. Correspondingly, NMR studies on a presumed active species [**L**Zr($CH_2Ph$)][B($C_6F_5$)$_3$($CH_2Ph$)] were consistent with tight ion pairing on the NMR chemical shift time scale.



## Introduction

The exceptional ability of chiral *ansa*-metallocenes of the group 4 metals, e.g., [(ebthi)Zr$Cl_2$], **I**,[1] to mediate both stereoselective polymerizations and the enantioselective transformation of small molecules has been well documented.[2,3] However the drawbacks associated with the resolution of these compounds may ultimately preclude their commercial use in nonracemic form for asymmetric catalysis.[4] One approach to this problem has been via the development of chiral cyclopentadienyl (Cp) ligands,[5,6] but apart from some notable exceptions[5c,7] this has led to limited success. We are engaged in another approach whereby chiral non-Cp ligands are used to generate stereogenic architectures directly.[8] The potential drawback here is that, as with many "alterna-

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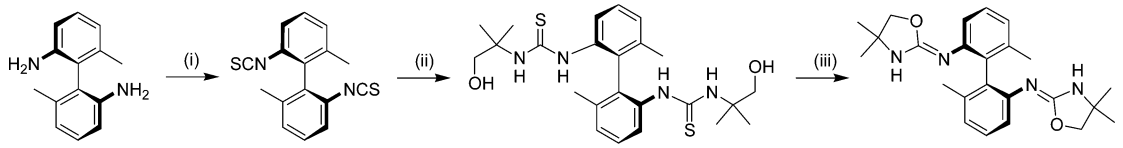
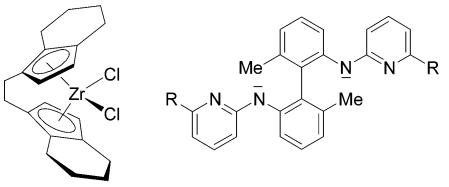
**Scheme 1. Synthesis of the $C_2$-Symmetric Oxazoline Ligand $H_2L$[a]**




[a] Reagents and conditions: (i) 1,1′-thiocarbonyldi-2(1*H*)-pyridone, DCM (97%); (ii) 2-amino-2-methylpropanol, THF (94%); (iii) *p*-toluenesulfonyl chloride, NaOH, THF (85%).

tives" to the metallocenes,[9] the complexes may simply not operate with usefully high turnover rate or number in the target catalyses. For example, while the expression of chirality in early transition metal complexes of **II** appears to be very good, little catalytic activity was observed.[10] In contrast, our related biaryl-bridged com-




I II

plexes with amide and alkoxide ligation have been rather more successful in, for example, enantioselective hydroamination.[11] Encouraged by the success of amidinate complexes in the arena of olefin polymerization,[12,13] we have recently developed a new class of $C_2$-symmetric diazaallyl complexes $H_2$**L** (Scheme 1), and this work is reported here. As with the guanidinate anions,[14] we envisioned that the delocalization of charge would be extensive in $\mathbf{L}^{2-}$, thus improving the stability of the spectator ligand sphere of its complexes in comparison to aminopyridinates based on **II**. We also note that other classes of oxazoline complexes of the early transition metals and lanthanides have been used successfully in catalysis.[15,16]

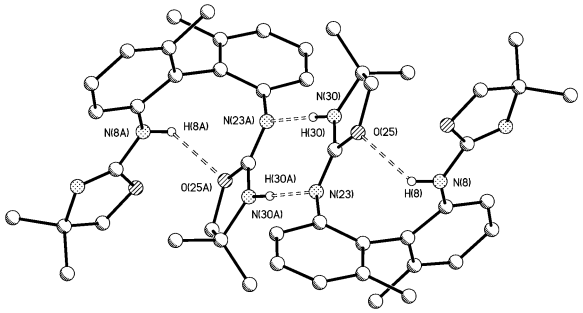



**Figure 1.** Molecular structure of $H_2$**L** dimer showing the inter- and intramolecular hydrogen bonds.

## Results and Discussion

The $C_2$-symmetric iminooxazolidine proligand $H_2$**L** was synthesized in high yield from **1**[17] via a three-step procedure. The reaction of **1** with 1,1′-thiocarbonyldi-2(1*H*)-pyridone gives the di(isothiocyanate) **2** in 97% yield after passing a solution of the crude product through silica to remove the 2-hydoxypyridine byproduct.[18] Using Kim's synthesis of 2-phenylamino-2-oxazolines[19] we prepared the thiourea **3** via reaction of **2** with 2-amino-2-methylpropanol in 94% yield. Subsequent ring closure of **3** by treatment with TsCl and NaOH is straightforward, and the proligand $H_2$**L** was obtained in 85% yield. Crystals of racemic $H_2$**L** suitable for X-ray structural determination were grown from a concentrated solution in dichloromethane, and the molecular structure is shown in Figure 1. The crystallographically centrosymmetric dimer is assembled via two hydrogen bonds [H(30)−N(23) 1.96(7) Å] in a manner reminiscent



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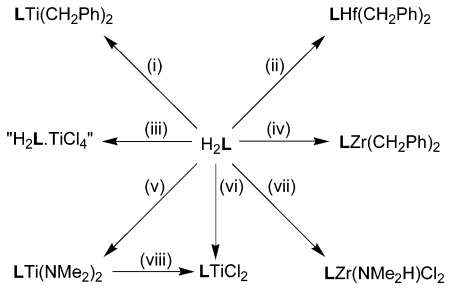
**Scheme 2. Synthesis and Reactions of [LMX$_2$] (M = Ti, Zr, Hf; X = chloride, amide, alkyl)[a]**




[a] Reagents and conditions: (i) $Ti(CH_2Ph)_4$, toluene (85%); (ii) $Hf(CH_2Ph)_4$, toluene (91%); (iii) $TiCl_4(THF)_2$, DCM (83%); (iv) $Zr(CH_2Ph)_4$, toluene (79%); (v) $Ti(NMe_2)_4$, $Et_2O$ (90%); (vi) $Ti(NMe_2)_4$, $Et_2O$, then TMSCl, toluene (89%); (vii) $Zr(NMe_2)_2Cl_2(THF)_2$, toluene (86%); (viii) TMSCl, toluene (78%).

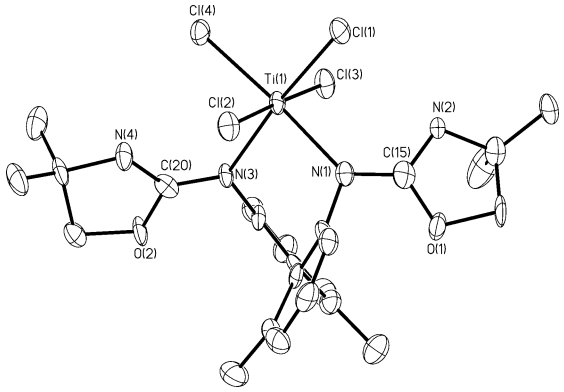



**Figure 2.** Molecular structure of [(H$_2$**L**)TiCl$_4$].

of carboxylic acids. A second pair of intra-monomer hydrogen bonds is also present [H(8)−O(25) 2.54(6) Å].

The dibenzyl compound [**L**Ti(CH$_2$Ph)$_2$] (Scheme 2) was readily obtained as fine black crystals following direct reaction of H$_2$**L** with tetrabenzyltitanium(IV) in toluene (85% yield). The $^1$H and $^{13}$C NMR spectra of this compound are indicative of a $C_2$-symmetric environment in solution. The *cis* dialkyl structure of [**L**Ti(CH$_2$Ph)$_2$] was confirmed via X-ray diffraction studies, but the data were unfortunately not of suitable quality for publication.

The reaction of H$_2$**L** with TiCl$_4$(THF)$_2$ gave the adduct [(H$_2$**L**)TiCl$_4$], rather than the desired dichloride product [**L**TiCl$_2$]. The $^1$H NMR spectrum of this compound in $d_6$-benzene solution contains a singlet resonance at 7.24 ppm, for which there is no corresponding cross-peak in the $^1$H−$^{13}$C correlation spectrum, and which we assign to the oxazolidine N-H protons. Single crystals of [(H$_2$**L**)TiCl$_4$] were grown from a concentrated solution in dichloromethane, and the molecular structure, determined by X-ray crystallography, shows that the coordination sphere is essentially octahedral (Figure 2). The two imino N atoms occupy mutually *cis* coordination sites with N(1)−Ti(1) and N(3)−Ti(1) bond lengths of 2.137(6) and 2.153(5) Å, respectively. These distances are almost identical to those observed in a previously reported α-*cis* Schiff-base complex of titanium.[8c] The complex [(H$_2$**L**)TiCl$_4$] exhibits a bond angle N(1)−Ti(1)−N(3) of 85.3°, slightly greater than the 76.7° observed in the biaryldiimine Schiff-base compound.

The N−C−N bond angles in [(H$_2$**L**)TiCl$_4$], observed at 127.4(7)° and 128.7(6)°, are very similar to the values of 125.3(6)° and 129.8(7)° in the solid state structure of the free ligand (Figure 1). The N−C bond lengths are 1.301(9) and 1.321(9) Å, compared to 1.253(7) and 1.364(8) Å in the proligand.

A range of methods were employed in an attempt to convert [(H$_2$**L**)TiCl$_4$] to the corresponding dichloride; treatments with KH, BuLi, TEA, and DBU under various conditions were all unsuccessful. We have, however, developed a convenient method for the synthesis of [**L**TiCl$_2$] via the corresponding amide (vide infra).

The proligand H$_2$**L** reacts very cleanly with Ti(NMe$_2$)$_4$ in diethyl ether at ambient temperature to give the titanium amido complex [**L**Ti(NMe$_2$)$_2$] as a bright orange solid. The $^1$H and $^{13}$C NMR spectra of [**L**Ti(NMe$_2$)$_2$] are as expected for a $C_2$-symmetric complex in solution.

Reaction of [**L**Ti(NMe$_2$)$_2$] with an excess of chlorotrimethylsilane in toluene at −78 °C gave the dichloride [**L**TiCl$_2$] as a brown microcrystalline solid (78%). It is also possible, and somewhat more convenient, to prepare the dichloride via reaction of chlorotrimethylsilane with [**L**Ti(NMe$_2$)$_2$] formed in-situ (see Experimental Section).

As observed with the analogous titanium compound (vide supra), the direct reaction of the proligand H$_2$**L** with tetrabenzylzirconium(IV) gave the complex [**L**Zr(CH$_2$Ph)$_2$] as fine yellow microcrystals (Scheme 2). The $^1$H and $^{13}$C NMR spectra of this compound are consistent with a $C_2$-symmetric environment in solution. The hafnium analogue [**L**Hf(CH$_2$Ph)$_2$] was similarly accessed. Crystals of [**L**Hf(CH$_2$Ph)$_2$] suitable for X-ray structural determination were obtained from a concentrated solution in heptane, and the molecular structure is shown in Figure 3.

The six-coordinate complex is $C_2$-symmetric, and the auxiliary benzyl groups occupy mutually *cis* positions, at a C−Hf−C bond angle of 99.0(3)°. The Hf−N$_{biaryl}$ and Hf−N$_{oxazoline}$ bond lengths, measured at 2.27 and 2.22 Å, respectively, are similar to those observed in two half-sandwich Cp-amidinate complexes of hafnium[20,21] and Polomo's aminopyridinato complex,[22] all falling within the range 2.18−2.28 Å. Zirconium amidinates have similar bond lengths, but the M−N$_{pyridyl}$ bonds tend to be slightly longer at 2.34−2.36 Å.[12a,g,h,23,24] The N−Hf−N bond angle of 60.24(18)° observed in [**L**Hf(CH$_2$Ph)$_2$] is typical of those measured for the amidinate compounds of both Hf and Zr detailed above, which lie in the range 58.94(6)−64.17(9)°. The aminopyridinato compounds have slightly smaller N−M−N angles; an aminopyridinato N−Hf−N angle of 58.4° was found in tetrakis{2-(phenylamido)pyridine}hafnium(IV).[22] Deprotonation and coordination have significantly reduced the N−C−N bond angle from 129.8(7)° observed in the free ligand to 116.5(6)° in [**L**Hf(CH$_2$Ph)$_2$]. This angle is, however,



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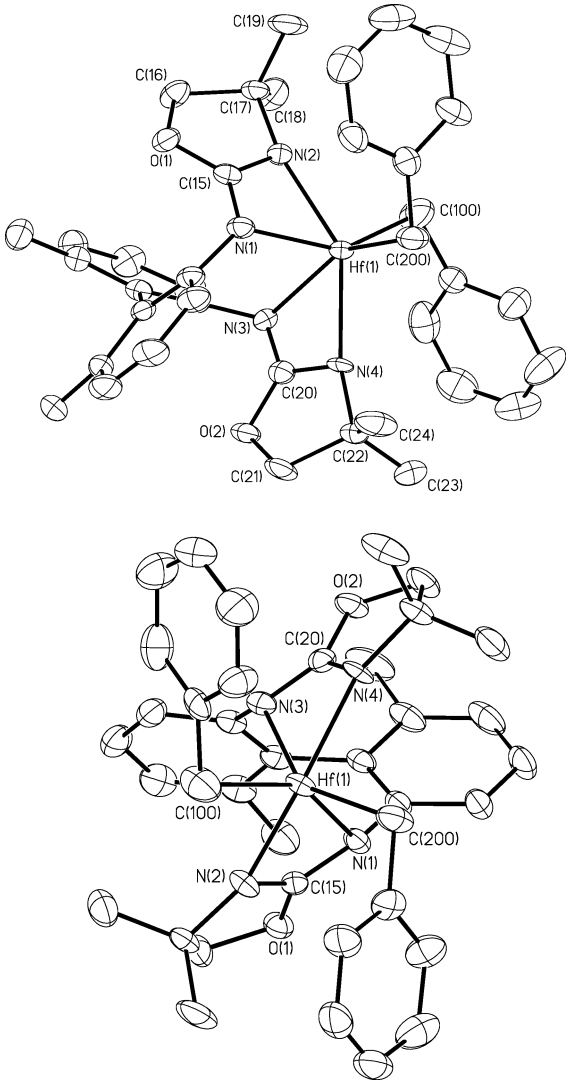


**Figure 3.** Views of the molecular structure of [**L**Hf($CH_2$-Ph)$_2$].

slightly larger than those measured in comparable group 4 compounds, which fall within the range 111.8(2)−115.0(5)°. The aminopyridinato compounds have slightly smaller N−C−N bond angles of 108.4(3)° and 110.1(5)°.

The proligand $H_2$**L** reacts cleanly with sodium hydride in THF to give the doubly deprotonated species $Na_2$**L**·*n*(THF). The amount of THF present in the complex was established by integration of the THF resonances observed in the $^1$H NMR spectrum obtained in deuterated pyridine. The potassium salt $K_2$**L**·*n*(THF) was similarly obtained and characterized. However, rather surprisingly, we were unable to access [**L**$MCl_2$] (M = Zr, Hf) via reaction of either of these salts with $MCl_4$ or $MCl_4$(THF)$_2$.

The reaction of $H_2$**L** with $ZrCl_4$ or $ZrCl_4$(THF)$_2$ in the presence of TEA or DBU did not yield [**L**$ZrCl_2$]. When $H_2$**L** was treated with Zr($NMe_2$)$_4$, a poorly defined and possibly polymeric material was obtained. We have experienced problems of this type with an aminopyridine ligand related to **L**.[10b] Attempts to convert the dibenzyl compound [**L**Zr($CH_2Ph$)$_2$] to [**L**$ZrCl_2$] via reaction with TEA·HCl failed.

The compound [**L**Zr($NMe_2H$)$Cl_2$] was obtained via the reaction of $H_2$**L** with Zr($NMe_2$)$_2Cl_2$(THF)$_2$.[25] The coordination of a dimethylamine ligand is unusual. Gibson[26] and Passarelli[27] have both reported zirconium compounds containing this moiety, and Kempe has described a related aminopyridinate titanium complex.[28] The molecule [**L**Zr($NMe_2H$)$Cl_2$] is not $C_2$-symmetric, and at room temperature the $^1$H NMR spectrum is broad. Cooling to 243 K gave a sharp spectrum corresponding to a $C_1$-symmetric structure, which contained four 6H singlets for the oxazolinyl ring methyls between 1.16 and 1.79 ppm and a further two 6H singlets for the backbone aromatic methyls at 1.96 and 2.14 ppm. Two pairs of AB doublets (4H in total) centered at 3.56 and 3.36 ppm were observed for the ring methylene protons. As the temperature was increased to 313 K, the peaks began to coalesce, consistent with reversible loss of the dimethylamine ligand. By 363 K the system is in rapid exchange on the NMR chemical shift time scale, and a spectrum corresponding to a $C_2$-symmetric structure is obtained.

Perhaps, given the structure of this compound, it is unsurprising that we were unable to access [**L**$ZrCl_2$] via the methods discussed above. It is also worth noting that we were unable to synthesize the hafnium analogue via reaction of either the sodium or potassium salt of $H_2$**L** with $HfCl_4$.

Given the ability of amidinate[12f,g,29] and half-sandwich Cp-acetamidinate complexes[13,20,23b] to act as precatalysts for alkene polymerization, we were interested to study how the aminooxazolinyl complexes would fare. The results of attempts to polymerize ethylene and 1-hexene using a variety of catalyst activators are summarized in Table 1.

First it is evident that none of the compounds are efficient initiators for polymerization of these olefins. (MAO is unsuccessful as a cocatalyst in this system. This may be due to reaction of the activator at the oxazoline O atom.) Nevertheless, some useful observations can be made. The protic borate activator [$PhNMe_2H$]-[$B(C_6F_5)_4$] in the presence of the intended alkylating agent and scavenger $Al^iBu_3$ gave at least a trace of poly(ethylene) in most cases, but the presence of dimethylaniline coproduct may be the cause of deactivation via coordination to the metal center. Correspondingly, the borane $B(C_6F_5)_3$ in the presence of $Al^iBu_3$ gives some activity with the metal halides, even giving a small amount of poly(hexene) with the zirconium compound. The trityl borate activator [$Ph_3C$][$B(C_6F_5)_4$] in conjunction with $Al^iBu_3$ gave significant amounts of poly(ethylene) with the titanium compounds but not the zirconium or hafnium species, and a seemingly random selection of "hits" with 1-hexene.

We note that Sita's half-sandwich acetamidinate catalysts for 1-hexene polymerization were found to operate most successfully in chlorobenzene solution.[13] However, in our system this solvent gave results similar to those obtained with toluene.

To probe the formation of cationic species, we studied the reactions between the group 4 dibenzyl compounds

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(27) Passarelli, V.; Benetollo, F.; Zanella, P.; Carta, G.; Rossetto, G. *J. Chem. Soc., Dalton Trans.* **2003**, 1411.
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**Table 1. Results of Polymerization Experiments: Productivity of Polymer/g$^{-1}$ mmol h bar[a]**

| | precatalyst | | | | |
|---|---|---|---|---|---|
| cocatalyst | [**L**TiBn$_2$] | [**L**TiCl$_2$] | [**L**ZrBn$_2$] | [**L**Zr(NMe$_2$H)Cl$_2$] | [**L**HfBn$_2$] |
| ethylene | | | | | |
| [Me$_2$NHPh][B(C$_6$F$_5$)$_4$]/Al$^i$Bu$_3$ | trace | trace | trace | 6 | 0 |
| B(C$_6$F$_5$)$_3$/Al$^i$Bu$_3$ | trace | 14 | trace | 9 | 0 |
| [B(C$_6$F$_5$)$_4$][Ph$_3$C]/Al$^i$Bu$_3$ | 14 | 14 | trace | trace | 0 |
| hexene | | | | | |
| [Me$_2$NHPh][B(C$_6$F$_5$)$_4$]/Al$^i$Bu$_3$ | 0 | 7 | 0 | 0 | 0 |
| B(C$_6$F$_5$)$_3$/Al$^i$Bu$_3$ | 0 | 0 | 0 | 8 | 0 |
| [B(C$_6$F$_5$)$_4$][Ph$_3$C]/Al$^i$Bu$_3$ | 0 | 6 | 0 | 9 | 10 |
| [B(C$_6$F$_5$)$_4$][Ph$_3$C]/Al$^i$Bu$_3$[b] | | 7 | | 0 | |

[a] 45 min runs, see Experimental Section for conditions. [b]Employing chlorobenzene as solvent.

**Table 2. Crystallographic Data, Collection Parameters, and Refinement Parameters for H$_2$L, [(H$_2$L)TiCl$_4$], and [LHf(CH$_2$Ph)$_2$]**

| | H$_2$**L** | [(H$_2$**L**)TiCl$_4$] | [**L**Hf(CH$_2$Ph)$_2$] |
|---|---|---|---|
| empirical formula | C$_{24}$H$_{30}$N$_4$O$_2$ | C$_{25}$H$_{32}$Cl$_6$N$_4$O$_2$Ti | C$_{38}$H$_{42}$HfN$_4$O$_2$C$_{1.5}$ |
| fw | 406.52 | 681.15 | 765.25 |
| cryst size (mm$^3$) | 0.32 × 0.12 × 0.08 | 0.20 × 0.20 × 0.18 | 0.21 × 0.18 × 0.17 |
| cryst syst | monoclinic | monoclinic | monoclinic |
| space group | *P*2$_1$/*c* | *P*2(1)/*n* | *P*2(1)/*n* |
| *a* (Å) | 9.127(2) | 10.8613(2) | 16.8011 |
| *b* (Å) | 12.697(3) | 20.8319(3) | 13.0020 |
| *c* (Å) | 19.664(5) | 13.3001(3) | 17.0017 |
| *β* (deg) | 92.187(4) | 94.44 | 90.9210(10) |
| *V* (Å$^3$) | 2277.2(9) | 3000.29(10) | 3713.5(2) |
| $D_{calcd}$ (Mg/m$^3$) | 1.186 | 1.508 | 1.401 |
| *μ* (mm$^{-1}$) | 0.077 | 0.850 | 2.846 |
| $F_{000}$ | 872 | 1400 | 1580 |
| total no. of reflns | 11 009 | 15 744 | 23 017 |
| no. of indep reflns | 3990 | 5266 | 8964 |
| $R_{int}$ | 0.1998 | 0.1099 | 0.0670 |
| no. of data/restraints/ params | 3990/0/284 | 5277/0/350 | 8964/0/424 |
| R1, [$I > 2\sigma(I)$] | 0.0823 | 0.0879 | 0.0498 |
| wR2 | 0.1400 | 0.1704 | 0.1081 |
| GoF on $F^2$ | 0.924 | 1.212 | 0.928 |

**Table 3. Selected Bond Lengths and Angles for H$_2$L, [(H$_2$L)TiCl$_4$], and [LHf(CH$_2$Ph)$_2$]**

| H$_2$**L** | [(H$_2$**L**)TiCl$_4$] | [**L**Hf(CH$_2$Ph)$_2$] |
|---|---|---|
| O(1)−C(2) = 1.350(7) | Ti(1)−N(1) = 2.137(6) | Hf(1)−N(4) = 2.216(5) |
| O(1)−C(7) = 1.429(6) | Ti(1)−N(3) = 2.153(5) | Hf(1)−N(2) = 2.218(5) |
| C(2)−N(3) = 1.253(7) | Ti(1)−Cl(2) = 2.262(2) | Hf(1)−C(100) = 2.248(7) |
| C(2)−N(8) = 1.364(8) | Ti(1)−Cl(1) = 2.288(2) | Hf(1)−N(1) = 2.263(5) |
| N(3)−C(4) = 1.476(7) | Ti(1)−Cl(4) = 2.315(2) | Hf(1)−C(200) = 2.274(7) |
| C(4)−C(7) = 1.542(8) | Ti(1)−Cl(3) = 2.328(2) | Hf(1)−N(3) = 2.279(5) |
| N(8)−C(9) = 1.408(7) | N(3)−C(20) = 1.301(9) | Hf(1)−C(20) = 2.613(6) |
| C(9)−C(10) = 1.400(8) | N(4)−C(20) = 1.323(9) | Hf(1)−C(15) = 2.617(6) |
| C(22)−N(23) = 1.426(7) | N(1)−C(15) = 1.320(9) | N(1)−C(15) = 1.330(8) |
| N(23)−C(24) = 1.279(7) | N(2)−C(15) = 1.321(9) | N(1)−C(6) = 1.414(7) |
| C(24)−N(30) = 1.356(7) | | N(2)−C(15) = 1.315(8) |
| O(25)−C(26) = 1.430(6) | | N(2)−C(17) = 1.487(8) |
| C(27)−N(30) = 1.475(7) | | N(3)−C(20) = 1.317(8) |
| | | N(3)−C(9) = 1.412(8) |
| | | N(4)−C(20) = 1.332(8) |
| | N(1)−Ti(1)−N(3) = 85.3(2) | N(4)−C(22) = 1.484(8) |
| | N(1)−Ti(1)−Cl(2) = 90.29(17) | N(4)−Hf(1)−N(2) = 147.14(19) |
| C(2)−O(1)−C(7) = 105.8(5) | N(3)−Ti(1)−Cl(2) = 89.78(16) | N(4)−Hf(1)−C(100) = 114.6(2) |
| N(3)−C(2)−O(1) = 119.4(6) | N(1)−Ti(1)−Cl(1) = 90.03(16) | N(2)−Hf(1)−C(100) = 86.5(2) |
| N(3)−C(2)−N(8) = 129.8(7) | N(3)−Ti(1)−Cl(1) = 174.72(16) | N(4)−Hf(1)−N(1) = 95.77(18) |
| O(1)−C(2)−N(8) = 110.9(7) | Cl(2)−Ti(1)−Cl(1) = 92.62(8) | N(2)−Hf(1)−N(1) = 60.24(18) |
| C(2)−N(8)−C(9) = 128.4(6) | N(1)−Ti(1)−Cl(4) = 174.90(17) | C(100)−Hf(1)−N(1) = 146.7(2) |
| C(10)−C(9)−N(8) = 121.0(6) | N(3)−Ti(1)−Cl(4) = 89.79(16) | N(4)−Hf(1)−C(200) = 88.9(2) |
| C(15)−C(9)−N(8) = 117.4(6) | Cl(2)−Ti(1)−Cl(4) = 90.86(8) | N(2)−Hf(1)−C(200) = 113.5(2) |
| C(16)−C(22)−N(23) = 124.3(6) | Cl(1)−Ti(1)−Cl(4) = 94.88(8) | C(100)−Hf(1)−C(200) = 99.0(3) |
| C(21)−C(22)−N(23) = 116.3(6) | N(1)−Ti(1)−Cl(3) = 89.16(16) | N(1)−Hf(1)−C(200) = 94.7(2) |
| C(24)−N(23)−C(22) = 117.6(5) | N(3)−Ti(1)−Cl(3) = 87.08(16) | N(4)−Hf(1)−N(3) = 60.13(19) |
| N(23)−C(24)−O(25) = 124.4(6) | Cl(2)−Ti(1)−Cl(3) = 176.84(9) | N(2)−Hf(1)−N(3) = 91.89(18) |
| N(23)−C(24)−N(30) = 125.3(6) | Cl(1)−Ti(1)−Cl(3) = 90.50(8) | C(100)−Hf(1)−N(3) = 102.6(3) |
| O(25)−C(24)−N(30) = 110.3(6) | Cl(4)−Ti(1)−Cl(3) = 89.39(8) | N(1)−Hf(1)−N(3) = 80.25(18) |
| C(24)−O(25)−C(26) = 109.3(5) | N(1)−C(15)−N(2) = 127.4(7) | C(200)−Hf(1)−N(3) = 147.6(2) |
| C(24)−N(30)−C(27) = 111.3(6) | N(4)−C(20)−N(3) = 128.7(6) | N(1)−C(15)−N(2) = 116.5(6) |

and various boron-based activators. The results were varied, usually giving complex mixtures. However, the reaction between [**L**Zr(CH$_2$Ph)$_2$] and B(C$_6$F$_5$)$_3$ was more interesting, and the $^1$H NMR spectrum recorded at 253 K is shown in Figure 4. Four AB doublet resonances for the chemically inequivalent methylene protons H$^{a-d}$

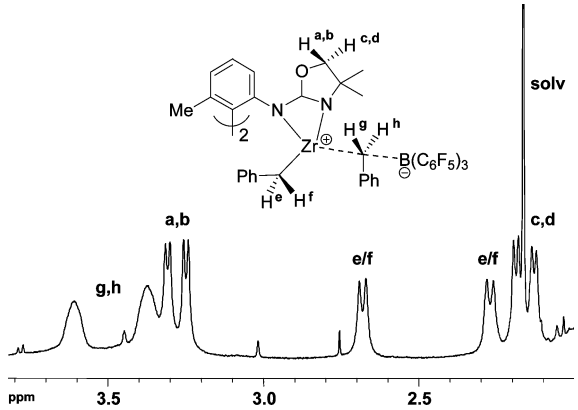


**Figure 4.** $^1$H NMR spectrum obtained from the reaction between [**L**Zr($CH_2Ph$)$_2$] and B($C_6F_5$)$_3$ recorded in $C_6D_5Br$ at 253 K.

were detected. This indicates $C_1$-symmetry for the compound, and all other resonances are consistent with this. One Zr-bound benzyl group $H^{e,f}$ gives rise to a pair of AB doublets. Two broad peaks, each of integral 1H, appear also, and we attribute these to $H^{g,h}$ of the boron-bound benzyl group in the anionic component [B($C_6F_5$)$_3$($CH_2Ph$)]$^-$. The inequivalence of these resonances is evidence that the ion pair is tightly bound to the metal center and is thus rendered diastereotopic. This is perhaps the reason for the low activity of these systems in olefin polymerization.

## Concluding Remarks

The atropisomerism of $H_2$**L** strongly directs the helicity of the resulting complexes [**L**M$X_2$], such that only a single diastereomer (with respect to the chiral metal center) is formed on reaction with homoleptic alkyls of group 4 metals. These systems are potentially well suited for application to enantioselective catalysis and/or stereoselective polymerization, because they contain two mutually *cis* coordination sites at which reactions can be mediated under the potent influence of the well-expressed chiral architecture.

The complexes display low activity for the polymerization of olefins, and this is perhaps a result of close association between the presumed active species cation and the counteranion, as indicated by NMR studies.

## Experimental Details

**General Comments.** Where necessary, procedures were carried out under an inert atmosphere of argon by using a dual-manifold vacuum/argon line and standard Schlenk techniques, or in an MBraun drybox. Solvents were dried by refluxing for 3 days under dinitrogen over the appropriate drying agents (sodium for toluene; potassium for THF, benzene, and heptane; sodium−potassium alloy for diethyl ether, petroleum ether, and pentane; calcium hydride for dichloromethane, chlorobenzene, and 1-hexene) and were degassed before use. Solvents were stored in glass ampules under argon. All glassware and cannulae were stored in an oven (>373 K) and flame dried immediately prior to use. Most chemicals and reagents were purchased from either Aldrich Chemical Co. or Acros Chemical Co. and used without further purification. Deuterated solvents were freeze−thaw degassed and dried by refluxing over potassium (or calcium hydride for $d_2$-dichloromethane) for 3 days before being vacuum distilled (trap-to-trap) to a clean, dry Young's tap ampule and being stored in the drybox. Deuterated chloroform was dried in the bottle over molecular sieves (4 Å).

NMR spectra were recorded on Bruker ACF-250,DPX-300, DPX-400, AV-400, and DPX-500 spectrometers. $^1$H and $^{13}$C spectra were referenced internally using residual protio solvent resonances relative to tetramethylsilane ($\delta = 0$ ppm); EI and CI mass spectra were obtained on a VG Autospec mass spectrometer. Infrared spectra were obtained either as Nujol mulls using a Perkin-Elmer Paragon 1000 FTIR spectrometer or directly using an Avatar 320 FTIR instrument. Elemental analyses were performed by Warwick Analytical Services. The low carbon values obtained in the elemental analysis of two of the titanium complexes, [**L**Ti($Ch_2Ph$)$_2$] and [**L**Ti($NMe_2$)$_2$], are attributed to the partial formation of metal carbides in the combustion process, as often observed with organometallic complexes of this type.[30] Flash chromatography was performed either in standard glassware or with a FlashMaster Personal chromatography system and a selection of prepacked disposable columns. Thin-layer chromatography was performed using Merck 0.25 mm silica layer foil-backed plates.

**2,2′-Diisothiocyanato-6,6′-dimethylbiphenyl (2).** Dichloromethane (100 mL) was added to a round-bottom flask charged with **1**[17] (500 mg, 2.36 mmol), and the mixture was stirred to dissolve the solids. 1,1′-Thiocarbonyldi-2(1*H*)-pyridone (1.16 g, 5.00 mmol) was added via powder funnel, and the resulting orange solution was stirred at ambient temperature. The progress of the reaction was monitored by TLC. After 15 h the solution was washed with water (2 × 30 mL), and the aqueous washings were back-extracted with dichloromethane. The combined organic phases were washed with brine (1 × 30 mL) and dried over $MgSO_4$. Concentration of the solution under reduced pressure gave an orange residue. The crude material was purified by flash chromatography on silica gel with a hexane/ethyl acetate (2:1) mobile phase (essentially a filtration through a column of silica). The product was obtained as a fine white microcrystalline solid. Yield: 680 mg, 97%. Anal. Calcd for $C_{16}H_{12}N_2S_2$: C, 64.83; H, 4.08; N, 9.34. Found: C, 64.86; H, 4.08; N, 9.34. $^1$H NMR (400 MHz, 298 K, $CDCl_3$): $\delta$ 7.25 (2H, t, $^3J_{HH} = 8$ Hz, Ar-*H*), 7.18 (2H, d, $^3J_{HH} = 2$ Hz, Ar-*H*), 7.08 (2H, d, $^3J_{HH} = 8$ Hz, Ar-*H*), 1.97 (6H, s, *Me*). $^{13}$C{$^1$H} NMR (100.6 MHz, 298 K, $CDCl_3$): $\delta$ 139.0, 137.4, 134.8, 131.6, 129.7, 129.6, 123.5, (Ar), 20.2 (*Me*). MS (EI): *m*/*z* 296 [$M^+$], 281 [40%, $M^+ - CH_3$]. IR (Golden Gate $\nu$ $cm^{-1}$): 2034, 1588, 1568, 1458, 1377, 1259, 1164, 1102, 1029, 970, 894, 828, 738, 673.

***N′,N′*-Bis(1-hydroxy-2-methylprop-2-yl)-2,2′-bis(thiourea)-6,6′-dimethylbiphenyl (3).** A solution of **2** (480 mg, 1.62 mmol) in THF (30 mL) was added dropwise over 5 min to a solution of 2-amino-2-methylpropanol (302 mg, 3.40 mmol) in THF (30 mL). The resulting colorless solution was stirred for 15 h at ambient temperature. After this time the solvent was removed in vacuo. The crude material was suspended in diethyl ether and heated to 40 °C. After 1 h at this temperature the mixture was filtered under suction and the solid was dried under reduced pressure. The product was thus obtained as a fine white microcrystalline solid. Yield: 720 mg, 94%. Anal. Calcd for $C_{24}H_{34}N_4O_2S_2$: C, 60.73; H, 7.22; N, 11.80. Found: C, 60.58; H, 7.31; N, 11.50. $^1$H NMR (400 MHz, 298 K, $CDCl_3$): $\delta$ 9.53 (2H, s, N*H*), 7.84 (2H, d, $^3J_{HH} = 8$ Hz, Ar-*H*), 7.29 (2H, m, Ar-*H*), 7.15 (2H, d, $^3J_{HH} = 7$ Hz, Ar-*H*) 6.47 (2H, s, N*H*) 4.18 (2H, s, O*H*), 3.51 (2H, d, $^3J_{HH} = 6$ Hz, $CH_2$) 3.09 (2H, d, $^3J_{HH} = 6$ Hz, $CH_2$) 1.95 (6H, s, *Me*), 1.35 (6H, s, *Me*), 1.12 (6H, s, *Me*). $^{13}$C{$^1$H} NMR (100.6 MHz, 298 K, $CDCl_3$): $\delta$ 181.8 (sulfonic $C_q$), 138.5, 138.3, 129.9, 127.8, 127.3, 124.9, (Ar), 70.4 ($CH_2$), 58.8 (aliphatic $C_q$), 27.63, 22.1, 20.1 (*Me*). MS

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

(EI): *m/z* 474 [$M^+$], 459 [$M^+ - CH_3$]. IR (Golden Gate $\nu$ $cm^{-1}$): 1573, 1533, 1459, 1395, 1289, 1240, 1163, 1049, 969, 827, 780, 750.

**$H_2$L.** THF (30 mL) was added to a Schlenk vessel charged with **3** (520 mg, 1.10 mmol), and the mixture was stirred to dissolve the solid. A solution of sodium hydroxide (220 mg, 5.50 mmol) in water (5 mL) was added to a solution of *p*-toluenesulfonyl chloride (460 mg, 2.41 mmol) in THF (5 mL). This mixture was added dropwise via syringe to the solution of **3**. The resulting pale yellow solution was stirred for 15 h in the absence of light. After this time the solution was washed with water (2 × 20 mL) and the organic layer taken. The aqueous washings were back-extracted with diethyl ether (2 × 20 mL). The combined organic phases were washed with brine (1 × 30 mL) and dried over $MgSO_4$. Concentration under reduced pressure gave an off-white residue. The crude material was heated to 120 °C for 2 h under vacuum. After this time the product was obtained as a microcrystalline white solid. Yield: 379 mg, 85%. Anal. Calcd for $C_{24}H_{30}N_4O_2$: C, 70.91; H, 7.44; N, 13.78. Found: C, 70.81; H, 7.48; N, 13.65. $^1$H NMR (400 MHz, 298 K, $CDCl_3$): $\delta$ 8.02 (2H, s, Ar-*H*), 7.21 (2H, t, $^3J_{HH}$ = 8 Hz, Ar-*H*), 6.87 (2H, d, $^3J_{HH}$ = 8 Hz, Ar-*H*) 5.54 (2H, s, N*H*) 3.76 (4H, s, C$H_2$), 1.85 (6H, s, *Me*) 1.20 (12H, s, *Me*). $^{13}$C{$^1$H} NMR (100.6 MHz, 298 K, $CDCl_3$): $\delta$ 153.6, 137.8, 136.3, 127.8, 123.0, 115.6, (Ar), 83.2, ($C_q$), 76.8, (C$H_2$) 66.9, ($C_q$), 27.5, 18.8 (*Me*). MS (EI): *m/z* 406 [$M^+$], 391 [$M^+ - CH_3$]. IR (Golden Gate $\nu$ $cm^{-1}$): 3412, 2657, 2354, 2046, 1517, 1443, 1330, 1287, 746.

**[$Na_2$L·(THF)$_{0.45}$].** To a Schlenk vessel charged with $H_2$**L** (200 mg, 0.49 mmol) and sodium hydride (60 mg, 2.46 mmol) was added THF (20 mL). The resulting white suspension was stirred for 15 h under reduced pressure. After this time the stirring was ceased and unreacted NaH was allowed to settle. The solution was filtered, and the colorless filtrate was evaporated in vacuo to yield a microcrystalline off-white solid. Analysis by $^1$H NMR spectroscopy in $d_5$-pyridine showed the composition of the product to be $Na_2$**L**·(THF)$_{0.45}$. Yield: 222 mg, 94%. $^1$H NMR (400 MHz, 298 K, $d_5$-pyridine): $\delta$ 8.77 (2H, d, $^3J_{HH}$ = 8 Hz, Ar-*H*), 7.18 (2H, t, $^3J_{HH}$ = 8 Hz, Ar-*H*), 6.54 (2H, d, $^3J_{HH}$ = 7 Hz, Ar-*H*), 3.63 (m, THF), 3.60 (2H, d, *J* = 8 Hz, C$H_2$), 3.34 (2H, d, *J* = 8 Hz, C$H_2$), 1.93 (6H, s, *Me*), 1.58 (m, THF), 1.31 (6H, s, *Me*), 1.22 (6H, s, *Me*). $^{13}$C{$^1$H} NMR (100.6 MHz, 298 K, $d_5$-pyridine): $\delta$ 177.6 (oxazoline $C_q$), 138.2, 138.0, 137.24, 128.8, 122.0, 120.6 (Ar), 77.6 ($CH_2$), 70.2 ($C_q$), 67.3 (THF), 32.8, 32.7 (Me), 28.2 (THF), 23.1 (Me).

**[$K_2$L·(THF)$_{0.33}$].** THF (20 mL) was added to a Schlenk vessel charged with $H_2$**L** (200 mg, 0.49 mmol) and potassium hydride (100 mg, 2.46 mmol). The pale yellow suspension obtained was stirred for 15 h under reduced pressure. After this time the stirring was ceased and unreacted KH was allowed to settle before filtering the solution. The filtrate was evaporated in vacuo to yield a microcrystalline white solid. Analysis by $^1$H NMR spectroscopy in $d_5$-pyridine showed the composition of the product to be $K_2$**L**·(THF)$_{0.33}$. Yield: 218 mg, 88%. $^1$H NMR (400 MHz, 298 K, $d_5$-pyridine): $\delta$ 8.67 (2H, d, $^3J_{HH}$ = 8 Hz, Ar-*H*), 7.09 (2H, t, $^3J_{HH}$ = 8 Hz, Ar-*H*), 6.53 (2H, d, $^3J_{HH}$ = 7 Hz, Ar-*H*), 3.67 (m, THF), 3.65 (2H, d, *J* = 7 Hz, C$H_2$), 3.47 (2H, d, *J* = 7 Hz, C$H_2$), 2.03 (6H, s, *Me*), 1.63 (m, THF), 1.40 (6H, s, *Me*), 1.26 (6H, s, *Me*). $^{13}$C{$^1$H} NMR (100.6 MHz, 298 K, $d_5$-pyridine): $\delta$ 167.1 (oxazoline $C_q$), 156.2, 138.1, 137.9, 128.1, 122.2, 119.4 (Ar), 77.1 ($CH_2$), 69.8 (THF), 66.4 ($C_q$), 32.6, 32.2 (Me), 27.8 (THF), 22.8 (Me).

**[LTi($CH_2$Ph)$_2$].** To a Schlenk vessel charged with $H_2$**L** (330 mg, 0.81 mmol) and titanium tetrabenzyl[31] (334 mg, 0.81 mmol) was added toluene (20 mL). The dark purple solution obtained was stirred for 15 h in the absence of light. After this time the solvent was removed under reduced pressure to give a dark red solid. This material was redissolved in heptane (30 mL) and filtered via cannula. Cooling of the concentrated filtrate to −30 °C afforded the product as fine black prisms. The material was collected by filtration and dried in vacuo. Yield: 436 mg, 85%. Anal. Calcd for $C_{38}H_{42}N_4O_2Ti$: C, 71.92; H, 6.67; N, 8.83. Found: C, 70.51; H, 6.70; N, 8.63. $^1$H NMR (400 MHz, 298 K, $CD_2Cl_2$): $\delta$ 7.15 (4H, d, $^3J_{HH}$ = 7 Hz, Ar-*H*), 7.06 (6H, m, Ar-*H*), 6.89 (2H, d, $^3J_{HH}$ = 7 Hz, Ar-*H*), 6.85 (2H, d, $^3J_{HH}$ = 7 Hz, Ar-*H*), 6.79 (2H, t, $^3J_{HH}$ = 7 Hz, Ar-*H*), 3.68 (2H, d, *J* = 8 Hz, C$H_2$), 2.95 (4H, s, C$H_2$), 2.50 (2H, d, *J* = 8 Hz, C$H_2$), 1.86 (6H, s, *Me*), 0.97 (6H, s, *Me*), 0.67 (6H, s, *Me*). $^{13}$C{$^1$H} NMR (100.6 MHz, 298 K, $CD_2Cl_2$): $\delta$ 167.6 (oxazoline $C_q$), 148.3, 145.6, 140.4, 131.8, 129.3, 128.7, 128.4, 126.4, 125.2, 122.7 (Ar), 99.35, 82.1 ($CH_2$), 65.8 ($C_q$), 28.6, 27.4, 20.5 (Me). MS (EI): *m/z* 465 [$M^+ - CH_2Ph$, − Ph], 406 [$H_2$**L**]. IR (Nujol $\nu$ $cm^{-1}$): 1556, 1260, 1204, 1064, 802.

**[($H_2$L)TiCl$_4$].** Dichloromethane (25 mL) was added at −78 °C to a Schlenk vessel charged with $H_2$**L** (200 mg, 0.49 mmol) and $TiCl_4$·2THF (129 mg, 0.49 mmol). The mixture was stirred to dissolve the solids, and a dark red solution was obtained. The cold bath was then removed, and the solution was allowed to warm to ambient temperature. Stirring was continued for 15 h with the exclusion of light. After this time the solution was concentrated to dryness and was washed with pentane. The orange residue obtained was redissolved in dichloromethane (10 mL), and pentane (5 mL) was added. Cooling of the solution to −30 °C afforded the product as fine orange prisms. The solid material was isolated by filtration and dried in vacuo. Yield: 242 mg, 83%. Anal. Calcd for $C_{24}H_{30}Cl_4N_4O_2Ti$: C, 48.75; H, 5.07; N, 9.30. Found: C, 48.79; H, 5.06; N, 9.02. $^1$H NMR (400 MHz, 298 K, $CD_2Cl_2$): $\delta$ 7.24 (2H, s, N*H*), 7.13 (2H, t, $^3J_{HH}$ = 8 Hz, Ar-*H*), 7.05 (2H, d, $^3J_{HH}$ = 8 Hz, Ar-*H*), 6.92 (2H, d, $^3J_{HH}$ = 8 Hz, Ar-*H*), 3.98 (2H, d, *J* = 9 Hz, C$H_2$), 3.84 (2H, d, *J* = 9 Hz, C$H_2$), 1.95 (6H, s, *Me*), 1.34 (6H, s, *Me*), 1.00 (6H, s, *Me*). $^{13}$C{$^1$H} NMR (100.6 MHz, 298 K, $CD_2Cl_2$): $\delta$ 162.1 (oxazoline $C_q$), 148.1, 137.0, 133.8, 128.7, 128.1, 125.4 (Ar), 80.1, ($CH_2$), 60.8 ($C_q$), 27.3, 26.4, 19.6 (Me). MS (EI): *m/z* 594 [$M^+$]. IR (Nujol $\nu$ $cm^{-1}$): 1611, 1202, 1052, 723.

**[LTi($NMe_2$)$_2$].** A Schlenk vessel was charged with tetrakis(dimethylamido)titanium (0.83 mL, 0.45 M in pentane, 0.37 mmol), and the bright yellow solution was stirred and cooled to −78 °C. A solution of $H_2$**L** (150 mg, 0.37 mmol) in diethyl ether (15 mL) was added dropwise to the titanium amide solution over 10 min. The addition was accompanied by a color change to deep red. Light was excluded from the vessel, and stirring was continued for 60 min at this temperature. After this time the cold bath was removed and the reaction vessel was allowed to warm to ambient temperature. Stirring was continued for a further 15 h in the dark. The solvent was then removed in vacuo to afford dark orange residue. Recrystallization from DCM/pentane at −30 °C gave the product as a microcrystalline orange solid. The solid material was isolated by filtration and dried under reduced pressure. Yield: 180 mg, 90%. Anal. Calcd for $C_{28}H_{40}N_6O_2Ti$: C, 62.22; H, 7.46; N, 15.55. Found: C, 61.78; H, 7.19; N, 15.31. $^1$H NMR (400 MHz, 298 K, $CD_2Cl_2$): $\delta$ 7.30 (2H, t, $^3J_{HH}$ = 8 Hz, Ar-*H*), 6.84 (2H, d, $^3J_{HH}$ = 8 Hz, Ar-*H*), 6.79 (2H, d, $^3J_{HH}$ = 7 Hz, Ar-*H*), 3.55 (2H, d, *J* = 8 Hz, C$H_2$), 3.36 (12H, s, N$Me_2$), 2.41 (2H, d, *J* = 8 Hz, C$H_2$), 1.88 (6H, s, *Me*), 1.05 (6H, s, *Me*), 0.99 (6H, s, *Me*). $^{13}$C{$^1$H} NMR (100.6 MHz, 298 K, $CD_2Cl_2$): $\delta$ 164.9 (oxazoline $C_q$), 146.2, 139.8, 133.7, 127.6, 124.6, 124.5 (Ar), 80.3, ($CH_2$), 64.2 ($C_q$), 48.4 ($NMe_2$), 29.7, 28.0, 20.7 (Me) ppm. MS (CI): *m/z* 540 [$M^+$], 510 [$M^+ - 2 \times CH_3$]. IR (Nujol $\nu$ $cm^{-1}$): 1601, 1579, 1067, 722.

**[LTiCl$_2$]. Method A.** Toluene (15 mL) was added to a Schlenk vessel charged with **L**Ti($NMe_2$)$_2$ (85 mg, 0.16 mmol). The resulting orange solution was stirred and cooled to −78 °C. Chlorotrimethylsilane (0.1 mL, 88 mg, 0.80 mmol) was added to the solution via cannula, and the mixture was stirred for 15 min at this temperature in the absence of light. After this time the cold bath was removed and the reaction vessel was allowed to warm to ambient temperature. Stirring was

(31) Zucchini, Z.; Aibizatti, E.; Gianni, U. *J. Organomet. Chem.* **1971**, *26*, 357.

continued for a further 15 h in the dark. All volatiles were then removed under reduced pressure to give a dark red residue. This material was extracted with warm heptane (2 × 10 mL). Cooling of the combined extracts to 0 °C afforded the product as fine brown prisms. The solid material was isolated by filtration and dried under reduced pressure (yield = 65 mg, 78%).

**Method B.** A Schlenk vessel was charged with tetrakis(dimethylamido)titanium (138 mL, 0.45 M in pentane, 0.62 mmol), and the bright yellow solution was cooled to −78 °C with stirring. A solution of $H_2$**L** (250 mg, 0.62 mmol) in diethyl ether (20 mL) was added dropwise to the titanium amide solution over 10 min. The resulting deep red solution was stirred for 2 h at this temperature in the absence of light. After this time the cold bath was removed and the mixture was allowed to warm to room temperature. Stirring was continued for a further 15 h. All volatiles were then removed in vacuo to yield a bright orange residue. The residue was redissolved in toluene (20 mL) and cooled to 0 °C. Chlorotrimethylsilane (0.2 mL, 167 mg, 1.54 mmol) was added to the solution via cannula, and a color change to dark brown was observed. The mixture was stirred for 30 min following the addition and was then allowed to warm to ambient temperature. Stirring in the absence of light was continued for 15 h. All remaining volatiles were then removed under reduced pressure to leave a dark brown residue. This material was extracted with hot heptane (3 × 15 mL), and the combined extracts were cooled to 0 °C. The product was subsequently obtained as fine brown prisms. Yield: 286 mg, 89%. Anal. Calcd for $C_{24}H_{28}Cl_2N_4O_2Ti$: C, 55.09; H, 5.39; N, 10.71. Found: C, 55.14; H, 5.68; N, 10.88. $^1$H NMR (400 MHz, 298 K, $CD_2Cl_2$): $\delta$ 7.16 (2H, t, $^3J_{HH}$ = 8 Hz, Ar-*H*), 7.05 (2H, d, $^3J_{HH}$ = 8 Hz, Ar-*H*), 7.02 (2H, d, $^3J_{HH}$ = 8 Hz, Ar-*H*), 3.87 (2H, d, $J$ = 8 Hz, C*H*$_2$), 2.67 (2H, d, $J$ = 8 Hz, C*H*$_2$), 1.93 (6H, s, *Me*), 1.31 (6H, s, *Me*), 1.29 (6H, s, *Me*). $^{13}$C{$^1$H} NMR (100.6 MHz, 298 K, $CD_2Cl_2$): $\delta$ 170.1 (oxazoline $C_q$), 144.4, 140.4, 131.7, 129.0, 128.4, 125.8 (Ar), 83.3, ($CH_2$), 68.0 ($C_q$), 29.3, 27.2, 20.5 (Me). MS (EI): *m*/*z* 522 [$M^+$], 487 [$M^+$ − Cl]. IR (Nujol $\nu$ cm$^{-1}$): 1560, 1262, 1078, 944, 802, 722.

**[LZr(CH$_2$Ph)$_2$].** A Schlenk vessel charged with $H_2$**L** (315 mg, 0.77 mmol) and tetrabenzyl zirconium[31] (353 mg, 0.77 mmol) was cooled to −78 °C. Toluene (30 mL) was added, and the yellow mixture was stirred in the absence of light for 1 h. After this time the cold bath was removed and the reaction vessel was allowed to warm to ambient temperature. Stirring was continued for a further 12 h in the dark. After this time the solution was filtered. The bright yellow filtrate was concentrated to dryness, and the residue obtained was washed with pentane. The residue was redissolved in heptane (15 mL). Cooling of the solution to 0 °C gave the product as bright yellow needles. The solid material was collected by filtration and dried in vacuo. Yield: 412 mg, 79%. Anal. Calcd for $C_{38}H_{42}N_4O_2Zr$: C, 67.32; H, 6.24; N, 8.26. Found: C, 67.57; H, 6.48; N, 8.07. $^1$H NMR (400 MHz, 298 K, $CD_2Cl_2$): $\delta$ 7.08 (4H, t, $^3J_{HH}$ = 8 Hz, Ar-*H*), 7.01 (6H, m, Ar-*H*), 6.88 (2H d, $^3J_{HH}$ = 8 Hz, Ar-*H*), 6.80 (4H, m, Ar-*H*), 3.60 (2H, d, $J$ = 8 Hz, C*H*$_2$), 2.53 (2H, d, $J$ = 8 Hz, C*H*$_2$), 2.38 (2H, d, $J$ = 8 Hz, C*H*$_2$), 2.10 (2H, d, $J$ = 8 Hz, C*H*$_2$), 1.85 (6H, s, *Me*), 0.87 (6H, s, *Me*), 0.77 (6H, s, *Me*). $^{13}$C{$^1$H} NMR (100.6 MHz, 298 K, $CD_2Cl_2$): $\delta$ 166.8 (oxazoline $C_q$), 144.8, 143.1, 140.4, 132.6, 130.0, 129.1, 128.3, 126.2, 124.8, 122.9 (Ar), 81.2, 71.0 ($CH_2$), 64.3 ($C_q$), 29.3, 27.9, 20.5 (Me). MS (EI): *m*/*z* 585 [$M^+$ − $CH_2Ph$], 494 [$M^+$ − 2 × $CH_2Ph$]. IR (Nujol $\nu$ cm$^{-1}$): 1560, 1262, 1202, 1066, 802, 722.

**[LZr(NMe$_2$H)Cl$_2$].** A solution of $Zr(NMe_2)_2Cl_2(THF)_2$[25] (257 mg, 0.65 mmol) in toluene (15 mL) was cooled to −78 °C with stirring. To this was added a solution of $H_2$**L** in toluene (10 mL). The resulting colorless mixture was stirred for 20 min at this temperature. The cold bath was then removed, and the solution was allowed to warm to ambient temperature. Stirring was continued for a further 15 h. After this time the volatiles were removed under reduced pressure and a white residue was obtained. The solid was washed with pentane and dried in vacuo to leave a white microcrystalline solid. Yield: 343 mg, 86%. Anal. Calcd for $C_{26}H_{35}Cl_2N_5O_2Zr$: C, 51.05; H, 5.77; N, 11.45. Found: C, 50.89; H, 5.83; N, 11.61. $^1$H NMR (500 MHz, 243 K, $d_8$-toluene): $\delta$ 7.65 (1H, d, $^3J_{HH}$ = 8 Hz, Ar-*H*), 7.27 (1H, t, $^3J_{HH}$ = 8 Hz, Ar-*H*), 7.11 (1H, t, $^3J_{HH}$ = 8 Hz, Ar-*H*), 6.95 (1H, d, $^3J_{HH}$ = 8 Hz, Ar-*H*), 6.91 (1H, d, $^3J_{HH}$ = 8 Hz, Ar-*H*), 6.88 (1H, d, $^3J_{HH}$ = 8 Hz, Ar-*H*), 3.68 (1H, d, $^2J_{HH}$ = 8 Hz, C*H*$_2$), 3.43 (1H, d, $^2J_{HH}$ = 8 Hz, C*H*$_2$), 3.41 (1H, d, $^2J_{HH}$ = 8 Hz, C*H*$_2$), 3.31 (1H, d, $^2J_{HH}$ = 8 Hz, C*H*$_2$), 2.16 (1H, septet, *H*NMe$_2$), 2.14 (3H, s, Ar-*Me*), 1.96 (3H, s, Ar-*Me*), 1.81 (3H, d, $^3J_{HH}$ = 6 Hz, HN*Me*$_2$), 1.79 (3H, s, Ox-*Me*), 1.53 (3H, d, $^3J_{HH}$ = 6 Hz, HN*Me*$_2$), 1.41 (3H, s, Ox-*Me*), 1.18 (3H, s, Ox-*Me*), 1.16 (3H, s, Ox-*Me*). $^1$H NMR (500 MHz, 363 K, $d_8$-toluene): $\delta$ 7.06 (2H, t, $^3J_{HH}$ = 8 Hz, Ar-*H*), 7.00 (2H, d, $^3J_{HH}$ = 7 Hz, Ar-*H*), 6.85 (2H, d, $^3J_{HH}$ = 7 Hz, Ar-*H*), 3.78 (2H, d, $^2J_{HH}$ = 8 Hz, C*H*$_2$), 3.65 (2H, d, $^2J_{HH}$ = 8 Hz, C*H*$_2$), 2.16 (1H, septet, *H*NMe$_2$), 2.05 (6H, s, Ar-*Me*), 1.95 (6H, s, HN*Me*$_2$), 1.59 (6H, s, Ox-*Me*), 1.24 (6H, s, Ox-*Me*). $^{13}$C{$^1$H} NMR (100.6 MHz, 298 K, $d_8$-toluene): $\delta$ 169.3, 168.6 (oxazoline $C_q$), (144.5, 142.4, 138.2, 136.1, 133.7, 133.1, 127.8, 125.4, 124.6, 123.4, 119.0, 116.8 (Ar), 80.5, 80.2 ($CH_2$), 63.1, 62.9 ($C_q$), 38.6, 38.0 ($HNMe_2$), 27.0, 26.8, 26.6, 26.5, 19.0, 18.8 (Me). MS (EI): *m*/*z* 610 [$M^+$], 566 [$M^+$ − $HNMe_2$], 551 [$M^+$ − Me, − $HNMe_2$]. IR (Nujol $\nu$ cm$^{-1}$): 2360, 1639, 1556, 1532, 1462, 1413, 1377, 1284, 1261, 1199.

**[LHf(CH$_2$Ph)$_2$].** Toluene (30 mL) was added at −78 °C to a Schlenk vessel charged with $H_2$**L** (240 mg, 0.59 mmol) and tetrabenzyl hafnium[32] (320 mg, 0.59 mmol). The mixture was stirred to dissolve the solids, and a pale yellow solution was obtained. The cold bath was removed after stirring for 10 min at this temperature, and the reaction vessel was allowed to warm to ambient temperature. Stirring was continued for a further 15 h in the absence of light. The solution was then concentrated in vacuo, and an off-white residue was obtained. Recrystallization of this material from toluene/pentane at −30 °C gave the product as fine colorless prisms, which were isolated by filtration, washed with pentane, and dried under reduced pressure. Yield: 410 mg, 91%. Anal. Calcd for $C_{38}H_{42}N_4O_2Hf$: C, 59.64; H, 5.53; N, 7.32. Found: C, 59.84; H, 5.79; N, 7.04. $^1$H NMR (400 MHz, 298 K, $CD_2Cl_2$): $\delta$ 7.05 (10H, m, Ar-*H*), 6.89 (4H, m, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, Ar-*H*), 6.71 (2H, m, Ar-*H*), 3.62 (2H, d, $J$ = 8 Hz, C*H*$_2$), 2.55 (2H, d, $J$ = 8 Hz, C*H*$_2$), 1.90 (4H, s, C*H*$_2$), 1.86 (6H, s, *Me*), 0.87 (6H, s, *Me*), 0.63 (6H, s, *Me*). $^{13}$C{$^1$H} NMR (100.6 MHz, 298 K, $CD_2Cl_2$): $\delta$ 167.4 (oxazoline $C_q$), 145.3, 143.5, 140.5, 132.8, 128.9, 128.4, 128.3, 126.5, 125.1 121.9 (Ar), 82.5, 76.0 ($CH_2$), 64.0 ($C_q$), 28.8, 27.8, 20.5 (Me). MS (EI): *m*/*z* 675 [$M^+$ − $CH_2Ph$] 584 [$M^+$ − 2 × $CH_2Ph$]. IR (Nujol $\nu$ cm$^{-1}$): 1562, 1284, 1200, 1072, 959, 790, 723, 694.

**Ethylene Polymerizations.** Polymerizations were performed at ca. 1 atm in a 500 mL round-bottom Schlenk flask. The vessel was evacuated and filled with argon. Toluene (150 mL) and either triisobutylaluminum (2.0 mL, 0.086 M in toluene, 0.17 mmol) or methylaluminoxane (10 wt % solution in toluene, 1000 equiv relative to precatalyst) were added to the flask, and the mixture was stirred. Approximately 20 mL of this solution was transferred to a Schlenk vessel charged with precatalyst (10 mg, ca. 15 $\mu$mol, 1 equiv) and, when triisobutylaluminum was employed, catalyst activator (1 equiv). A colored solution was obtained, which was then transferred to the polymerization flask. The system was evacuated and then reopened to a continuous supply of ethylene gas. The mixture was stirred for 45 min before the gas flow was closed, and the polymerization was stopped by the addition of methanol (50 mL). Hydrochloric acid (50 mL, 2.0 M in methanol) was then added, and the resulting mixture was stirred for 10 min. After this time the flask was allowed to stand for 30 min and the resulting polymer was separated by filtration and dried at 90 °C to constant mass.

(32) Felten, J. J.; Anderson, W. P. *J. Organomet. Chem.* **1972**, *36*, 87.

**1-Hexene Polymerizations.** Polymerizations were performed in a standard Schlenk vessel. Toluene (15 mL) and either triisobutylaluminum (2.0 mL, 0.086 M in toluene, 0.17 mmol) or methylaluminoxane (10 wt % solution in toluene, 500 equiv relative to precatalyst) were added to the vessel, and the mixture was stirred. The solution was added to a Schlenk vessel charged with precatalyst (10 mg, ca. 15 $\mu$mol, 1 equiv) and, when triisobutylaluminum was employed, catalyst activator (1 equiv). To the colored solution thus obtained was added 1-hexene (40 mL), and the resulting mixture was stirred for 45 min. After this time the polymerization was stopped by the addition of methanol (50 mL). Hydrochloric acid (50 mL, 2.0 M in methanol) was then added, and the resulting mixture was stirred for 10 min. After this time the vessel was allowed to stand for 30 min. All volatiles were removed in vacuo to leave an off-white residue. This material was extracted with toluene, and the combined extracts were precipitated into acidic methanol. Polymer obtained in this way was dried under reduced pressure.

**Crystallography.** Crystals of $H_2$**L** were obtained as fine colorless prisms from a concentrated solution in dichloromethane, via slow evaporation of the solvent at ambient temperature. Crystals of [($H_2$**L**)$TiCl_4$] were obtained as fine orange prisms by cooling a concentrated solution in dichloromethane to −30 °C. Crystals of [**L**Hf($CH_2Ph)_2$] were similarly obtained from a concentrated solution in heptane. 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 system equipped with Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å). Data were collected using narrow (0.3° in $\omega$) frame exposures. Intensities were corrected semiempirically for absorption, based on symmetry-equivalent and repeated reflections (SADABS). The structures were solved by direct methods (SHELXS) with additional light atoms found by Fourier methods. For $H_2$**L** hydrogen atoms attached to N(30) and N(8) were located from a difference map. They were given isotropic displacement parameters equal to 1.5 times the equivalent isotropic displacement parameter of the nitrogen atom to which they are attached, and their positions were allowed to refine. The crystal structure of [($H_2$**L**)$TiCl_4$] contains one molecule of the crystallization solvent, dichloromethane, within the asymmetric unit of the unit cell. For [**L**Hf($CH_2Ph)_2$] a region of diffuse electron density, probably due to the presence of disordered solvent, was located. This was modeled as three half-occupancy carbon atoms. All non-hydrogen atoms were refined anisotropically. All H atoms were constrained with a riding model; $U$(H) was set at 1.2 (1.5 for methyl and amido hydrogen atoms as applicable) times $U_{eq}$ for parent atom. Programs used were Bruker AXS SMART (control), SAINT (integration), and SHELXTL for structure solution, refinement, and molecular graphics.

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**Supporting Information Available:** Tables of crystal data, atomic coordinates, distances and angles, and hydrogen coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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