Structural and Stereochemical Aspects of the Group 4 Metal Chemistry of Constrained-Geometry 2-(Indenyl)phenoxide Ligation

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The reactivity of 2-(inden-3-yl)-4,6-di-*tert*-butylphenol (**1**) and its 2-methyl (**2**), 1,2-dimethyl (**3**), 2,4,7-trimethyl (**4**), and 1,2,4,7-tetramethyl (**5**) derivatives toward group 4 metal dialkylamides has been examined. Reaction of 1 equiv of the phenols **1**−**4** with the tetrakis(dialkylamido) compounds $[M(NR_2)_4]$ (M = Ti, R = Me; M = Zr, R = Me, Et; M = Hf, R = Et) has allowed isolation of a series of bis(dialkylamido) compounds: e.g., $[Ti(OC_6H_2\{\eta^5\text{-Ind}\}\text{-}2\text{-}Bu^t_2\text{-}4,6)(NMe_2)_2]$. In these compounds the parent phenol was found to be deprotonated at both the phenolic OH and indenyl ring, leading to the elimination of 2 equiv of dialkylamine. Structural studies of eight of these derivatives allow the variation of metal and methyl substitution to be assessed. The metal coordination of the series of compounds is best described as pseudo-tetrahedral, with the indenyl ring occupying one site of a three-legged piano-stool geometry. The M−C(indenyl) distances are consistent with an essentially η^5 coordination for all bis(dialkylamido) compounds structurally characterized. The M−O−C angles for the chelates fall in the very narrow range of 126−129°. In the solution NMR spectra, nonequivalent dialkylamido ligands give rise to sharp, well-separated resonances. It was found possible to introduce two chelating indenylphenoxide ligands into the coordination sphere of titanium, zirconium, or hafnium either by treatment of the tetra(dialkylamides) with 2 equiv of the parent phenol and overall loss of 4 equiv of amine or using metathetical exchange of the dilithio salt of the indenylphenol with the corresponding metal tetrachloride. The combination of the three chiral elements (two planar chiral indenyl rings and an axially chiral metal center) within $[M(OC_6H_2\{\eta^n\text{-Ind}\}\text{-}2\text{-}Bu^t_2\text{-}4,6)_2]$ generates three distinct diastereoisomers. Two of the enantiomer pairs, (*S*,p*R*,p*R*)/(*R*,p*S*,p*S*) and (*R*,p*R*,p*R*)/(*S*,p*S*,p*S*), contain a C_2 axis leading to equivalent chelates and one set of ligand signals. In both of these diastereomers there are *rac* arrangements of indenyl ligands. The only difference between the two lies in the chelation of the aryloxide ligands to the metal center. The third enantiomer pair (*S*,p*R*,p*S*)/(*R*,p*R*,p*S*) has no symmetry element and has two equal-intensity sets of ligand resonances (*meso* indenyl rings). Spectroscopic evidence for all three enantiomer pairs has been obtained, while two forms have been structurally characterized. The compound $[Ti(OC_6H_2\{\eta^n\text{-Ind}\}\text{-}2\text{-}Bu^t_2\text{-}4,6)_2]$ was found to possess the (*S*,p*R*,p*S*)/(*R*,p*R*,p*S*) geometry in the solid state, while isomorphous crystals of $[M(OC_6H_2\{\eta^n\text{-Ind}\}\text{-}2\text{-}Bu^t_2\text{-}4,6)_2]$ (M = Zr, Hf) were isolated and identified as containing the (*R*,p*R*,p*R*)/(*S*,p*S*,p*S*) enantiomeric pair within the unit cell. The reaction of $[Ti(NMe_2)_4]$ with 2 equiv of 2-methyl substituted phenol **2**, under ambient conditions, led to the isolation of the compound $[Ti(OC_6H_2\{\eta^5\text{-IndMe-2}\}\text{-}2\text{-}Bu^t_2\text{-}4,6)(OC_6H_2\{C_9H_6Me\text{-}2\}\text{-}2\text{-}Bu^t_2\text{-}4,6)_2(NMe_2)]$, containing both chelated and simple O-bound indenylphenoxide ligation. Structural studies showed that isolated crystals contained a (*R*,a*S*,p*S*)/(*S*,a*R*,p*R*) configuration within the unit cell. Thermolysis of this compound led to formation of the bis(indenylphenoxide). The pathways leading to formation of particular bis(chelate) geometries is discussed along with the bonding of the indenyl rings to the various metal centers.

Introduction

Past research in our group has focused on the chemistry of the bis(aryloxide) compounds of the group 4 metals in which the $[(ArO)_2M]$ unit has an isolobal relationship with the $[Cp_2M]$ fragment.[1] Besides supporting novel and complimentary stoichiometric reactivity, aryloxide-supported titanacycles demonstrate a variety of catalytic processes.[2] More recently, we and others have begun to explore the chemistry and synthetic utility of "hybrid" $[Cp(ArO)TiCl_2]$ systems con-

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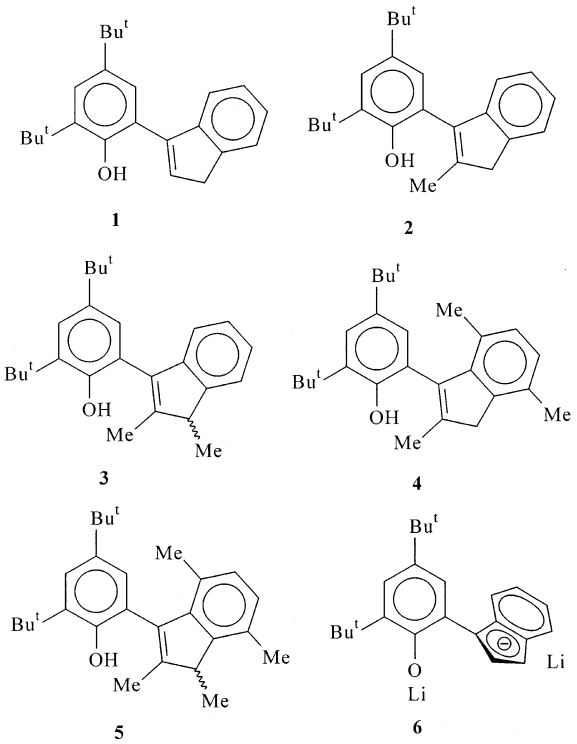
taining a variety of chiral and achiral aryloxide ligands.[3,4] Initial studies have shown that new metallacycles can be supported by the [Cp(ArO)M] fragment. However, there is evidence in the titanium system that the presence of even one cyclopentadienyl group diminishes greatly the catalytic activity present in bis(aryloxide) systems.[5] This is presumably a result of the greater electronic saturation and reduced electrophilicity caused by the cyclopentadienyl ligand. This has caused us to consider related indenyl−aryloxide ligand sets, leading to an exploration of the chemistry associated with 2-(inden-3-yl)-4,6-di-*tert*-butylphenol and various methyl-substituted derivatives.[6] The indenyl ligand has been particularly well studied recently, as it is an integral part of many chiral *ansa*-metallocenes[7] and bis(2-R-indenyl)metallocenes[8] of the group 4 metal single-site polymerization catalysts, where the ligands control the morphology (and properties) of generated polymers. The foundation of the "indenyl effect"[9] lies in the ease with which the ligand can slip from an η^5- to an η^3-bonding mode, relieving electronic saturation at the metal and spawning new reactivity patterns.[10,11]

This indenylphenoxide group is an inherently chiral, "constrained geometry" ligand system.[12] Some related alkoxo- and aryloxocyclopentadienyl ligands have been developed and studied.[13−15] Great interest in amido-linked systems, pioneered by Bercaw and Shapiro[16] with bridged amidocyclopentadienyl ligands, has been stimulated by their application in single-component olefin polymerization catalysts.[17] In this paper we report on the synthesis of group 4 metal derivatives containing one or two chelated indenylphenoxide ligands, paying particular attention to the structural ramifications of the chiral nature of the chelated form of the ligand.

Chart 1



Results and Discussion

Synthesis and Structure of Bis(dialkylamido) Compounds. The synthesis of the 2-(inden-3-yl)-4,6-di-*tert*-butylphenols **1**−**5** (Chart 1) has recently been reported.[6c] Structural studies of **2**−**4** show torsion angles (between the vinyl group and phenoxy ring) of 57, 61, and 79°, respectively. In solution restricted rotation about the indenyl−phenoxy bond occurs, with the barrier increasing upon methylation at the 2- and 4,7-positions. Simple O-bound aryloxides derived from these ligands, [Cp(ArO)$TiCl_2$], have been isolated and shown to possess even higher barriers to indenyl rotation.[6c] Although the dilithio salt **6** can be formed by reacting **1** with 2 equiv of n-BuLi, deprotonation of the indenyl ring in [Cp(ArO)$TiCl_2$] proved difficult. The lack of coplanarity of the indenyl and phenoxide rings in **1**−**5** leads to atropisomerism for the phenols and their simple O-bound metal derivatives.[6c] The two enanti-

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Chart 2

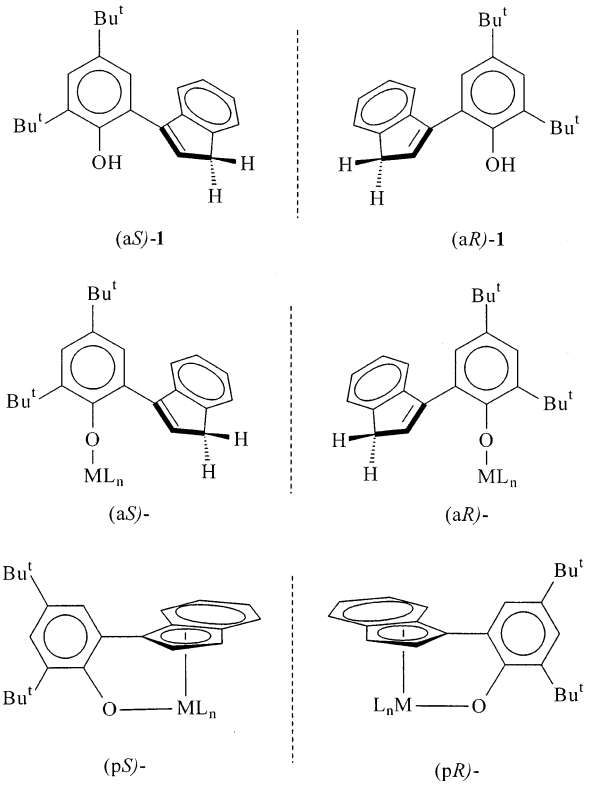
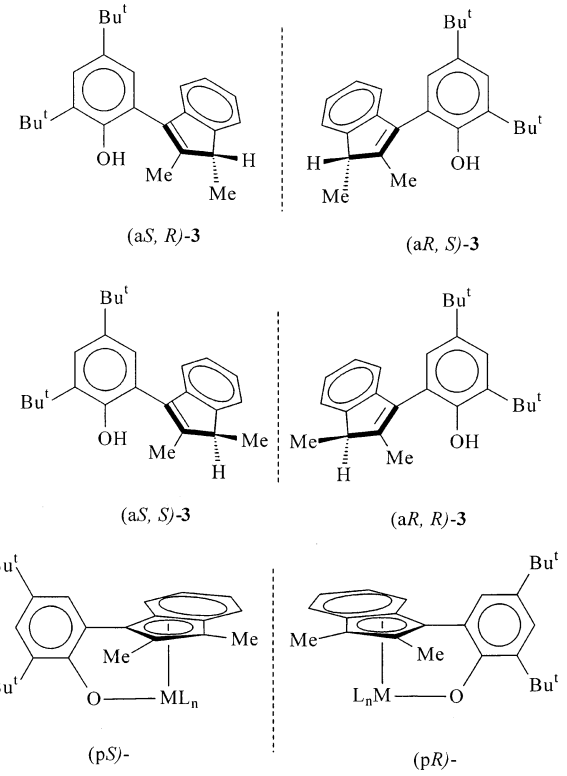


Chart 3



omers formed by restricted rotation about the indenyl−phenoxide bond (axial symmetry) are given the designations a*R* and a*S* on the basis of the Cahn−Ingold−Prelog rules applied to biaryls (Chart 2).[6c] The presence of a 3-methyl substituent in **3** and **5** introduces a second element of chirality (Chart 3).

Reaction of 1 equiv of the phenols **1**−**4** with the tetrakis(dialkylamido) compounds $[M(NR_2)_4]$ (M = Ti, R = Me; M = Zr, R = Me, Et; M = Hf, R = Et) has allowed isolation of the series of bis(dialkylamido) compounds **8**−**18** (Scheme 1). In all cases the parent phenol was found to be deprotonated at both the phenolic OH and indenyl ring, leading to the elimination of 2 equiv of dialkylamine. The indenyl ring of the ligand used in this study has enantiotopic faces. Hence, chelation (deprotonation and metalation) can also lead to two enantiomeric complexes. The nomenclature used to define the planar chirality of the chelates obtained is based upon that used for *ansa*-metallocenes. The planar chirality of the indenyl ring is assigned as p*R* or p*S* on the basis of the Cahn−Ingold−Prelog configuration of the 1-position of the metal-bound ring. In this case the 1-position is the stereogenic center bound to the ortho position of the phenoxide nucleus. It can be seen that the a*R* and a*S* forms of the O-bound ligand lead to the p*R* and p*S* forms of the chelate, respectively (Charts 2 and 3). It should also be noted that, once formed, the chiralities of p*R* and p*S* forms are not affected by the presence of chelation via the phenoxide oxygen. Interconversion (racemization) can only occur via "flipping" of the indenyl ring.

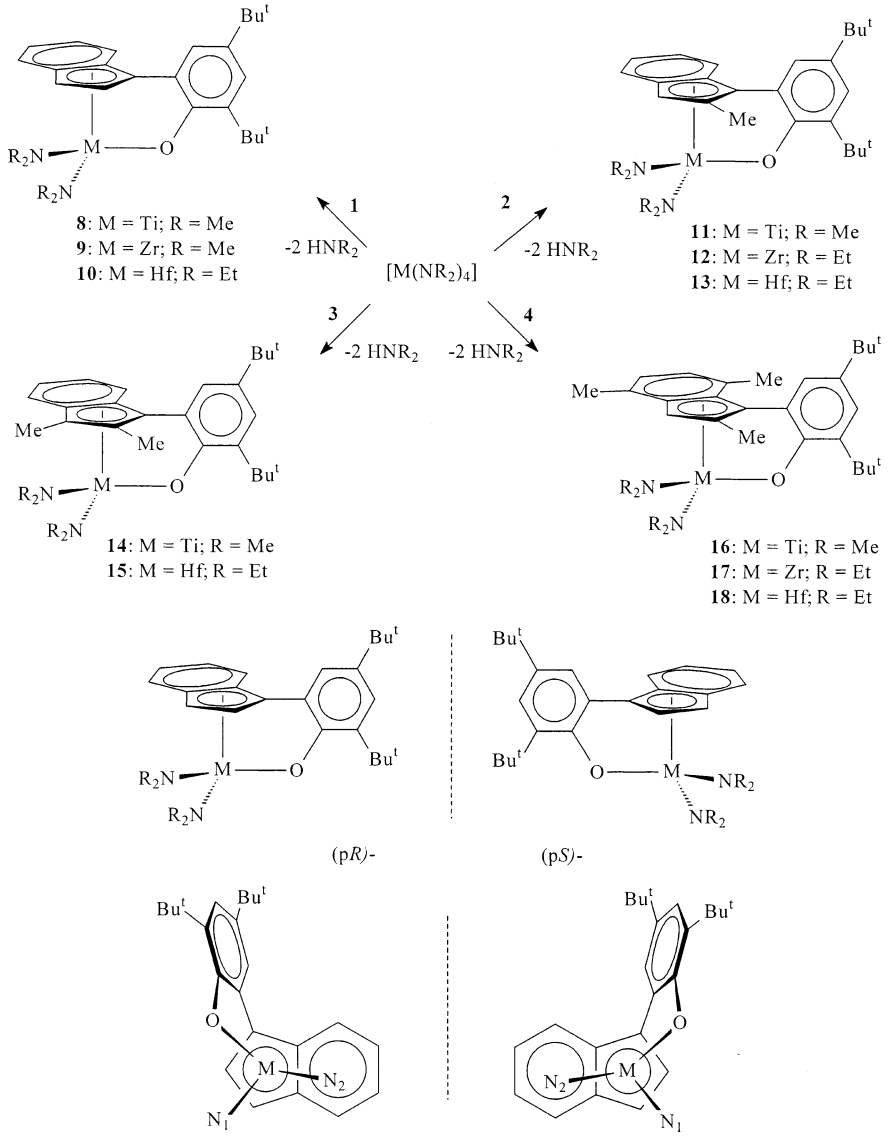
To fully parametrize the coordination properties of this ligand architecture, the solid-state structures of

Table 1. Structural Parameters (Å and deg) for the Series of Compounds $[M(OC_6H_2\{\eta^5\text{-Ind}\}\text{-2-Bu}^t_2\text{-4,6})(NR_2)_2]$[a]

	8	**9**		**10**	**11**		**12**	**13**	**14**	**16**
M	Ti	Zr		Hf	Ti		Zr	Hf	Ti	Ti
Me substn					2-Me		2-Me	2-Me	2,3-Me_2	2,4,7-Me_3
N−R	Me	Me		Et	Me		Et	Et	Me	Me
M−O	1.895(1)	2.026(2)	2.034(2)	2.026(5)	1.904(2)	1.890(2)	2.027(2)	2.006(5)	1.889(2)	1.904(1)
M−N1	1.905(2)	2.033(3)	2.041(3)	2.073(5)	1.906(3)	1.912(3)	2.037(2)	2.030(7)	1.929(2)	1.903(2)
M−N2	1.913(2)	2.038(3)	2.032(3)	2.053(5)	1.904(3)	1.903(3)	2.059(2)	2.050(7)	1.898(3)	1.917(2)
M−C1	2.366(2)	2.522(3)	2.516(3)	2.448(7)	2.361(3)	2.358(3)	2.493(3)	2.475(8)	2.365(2)	2.358(2)
M−C2	2.381(2)	2.547(3)	2.550(3)	2.498(5)	2.419(3)	2.405(3)	2.573(3)	2.549(8)	2.428(3)	2.420(2)
M−C3	2.380(2)	2.526(3)	2.545(3)	2.478(7)	2.400(3)	2.387(3)	2.555(2)	2.520(8)	2.430(3)	2.387(2)
M−C4	2.417(2)	2.544(3)	2.577(3)	2.492(7)	2.427(3)	2.415(3)	2.566(3)	2.545(8)	2.441(2)	2.415(2)
M−C5	2.405(2)	2.540(3)	2.554(3)	2.463(5)	2.393(3)	2.403(3)	2.524(3)	2.506(8)	2.411(2	2.387(2)
Ind−M−O	105.8	100.2	100.0	101.9	105.5	106.2	100.9	101.6	105.5	105.8
Δ[b]	0.038	0.008	0.033	0.005	0.020	0.028	0.012	0.014	0.030	0.012
Ind−M−N1	115.5	115.9	117.9	115.0	117.2	118.3	113.6	115.9	120.9	115.6
Ind−M−N2	124.2	121.2	120.2	125.5	124.4	124.1	123.9	123.9	122.3	125.7
N1−M−N2	102.02(6)	105.7(1)	104.4(1)	106.4(2)	99.6(1)	101.2(1)	106.5(1)	105.0(3)	100.7(1)	99.70(6)
M−O−C	126.5(1)	128.4(2)	128.8(2)	126.3(4)	127.3(2)	127.1(2)	127.1(1)	126.8(5)	127.5(2)	126.4(1)

[a] Ind parameters refer to the centroid of the η^5-indenyl ring. [b] $\Delta = d\{M-C(4,5)\}_{av} - d\{M-C(1,3)\}_{av}$.

Scheme 1



8−**14** and **16** have been determined. These allow variation of metal and methyl substitution to be compared. In all cases both the p*R* and p*S* forms were present within the unit cell. Two independent molecules were present for **9** and **11**. In Table 1 is collected key structural parameters for all eight bis(dialkylamido) compounds structurally characterized. In Figures 1−3 are shown ORTEP representations for [Ti(OC_6H_2\{η^5-Ind\}-2-Bu^t_2-4,6)(NMe_2)$_2$] (**8**), [Zr(OC_6H_2\{η^5-IndMe-2\}-2-Bu^t_2-4,6)(NEt_2)$_2$] (**12**), and [Ti(OC_6H_2\{η^5-$IndMe_3$-2,4,7\}-2-Bu^t_2-4,6)(NMe_2)$_2$] (**16**). The metal coordination of the series of compounds is best described as pseudo-tetrahedral with the indenyl ring occupying one site: a three-legged piano-stool geometry. The M−C(indenyl) distances are consistent with an essentially η^5 coordination for all bis(dialkylamido) compounds structurally characterized. This is highlighted by "Radar" plots presented in Figure 7 for the titanium compounds **8**, **11**, **14**, and **16** and in the Supporting Information for the other compounds. The "slip value" has been defined as $\Delta = d\{M-C(3a),(7a)\}_{av} - d\{M-C(1),(3)\}_{av}$.[18] This corresponds to $\Delta = d\{M-C(4),(5)\}_{av} - d\{M-C(1),(3)\}_{av}$ in the labeling used here. For a "true η^5-indenyl" this value would be close to 0 Å, whereas values of ∼0.75 Å are calculated for "true η^3-indenyl" compounds. For the

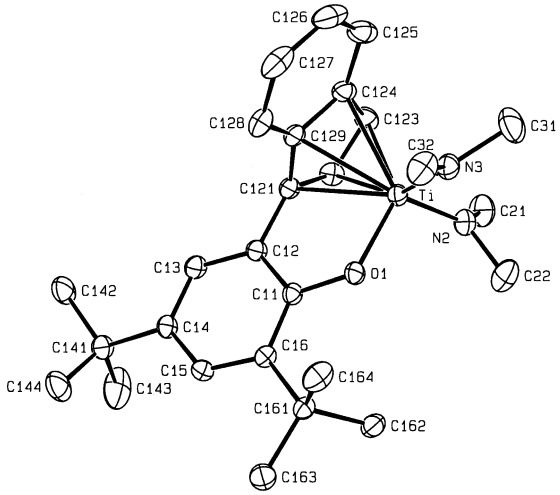


Figure 1. Molecular structure of [Ti(OC_6H_2\{η^5-Ind\}-2-Bu^t_2-4,6)(NMe_2)$_2$] (**8**). The (p*R*) form is shown.

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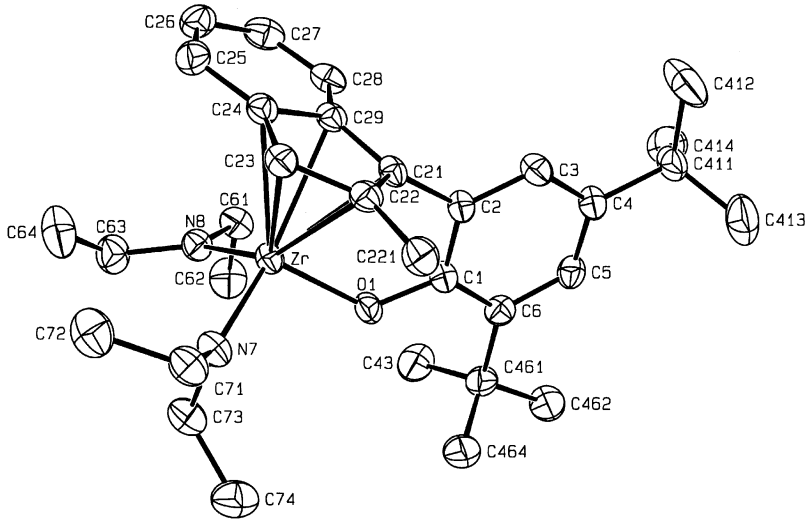


Figure 2. Molecular structure of [Zr(OC_6H_2\{η^5-IndMe-2\}-2-Bu^t_2-4,6)(NEt_2)$_2$] (**12**). The (p*R*) form is shown.

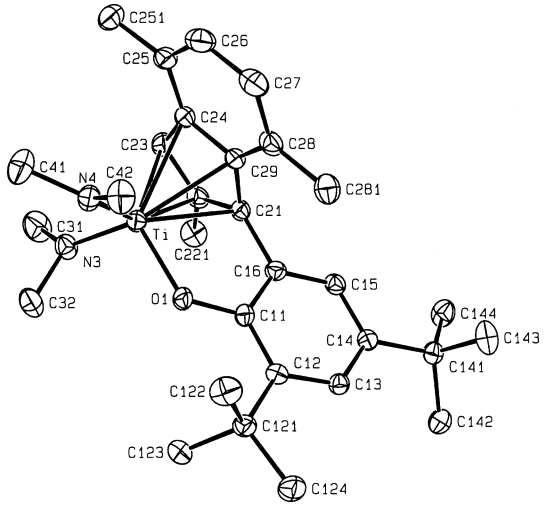


Figure 3. Molecular structure of [Ti(OC_6H_2\{η^5-$IndMe_3$-2,4,7\}-2-Bu^t_2-4,6)(NMe_2)$_2$] (**16**). The (p*S*) form is shown.

bis(amido) compounds this parameter is close to zero (Table 1). As expected, there is an increase in all M−X distances on moving from Ti to (Zr, Hf) with those for the second- and third-row d-block metals being very similar (lanthanide contraction). The M−O−C angles for the chelates fall in the very narrow range of 126−129°. There are some subtle but interesting variations in the pseudo-tetrahedral geometry. The Ind(centroid)−M−O angle varies from 0 to 102° (Zr, Hf) to 106° (Ti). The orientation of the 1-indenyl ring results in different environments for the dialkylamido ligands. One of the groups (N2, Scheme 1) is positioned below the arene ring of the indenyl ligand. It can be seen (Table 1) that the Ind−M−N2 angle is larger than the Ind−M−N1 angle in compounds **8**−**10** due to the differing steric pressures on the amido ligands. This difference is decreased as methyl groups are introduced at the 2- and 2,3-positions (Table 1). In the 2,3-dimethyl-substituted titanium compound **14** the angles are almost identical.

In the solution NMR spectra of **8**−**18** the nonequivalent dialkylamido ligands give rise to sharp, well-separated resonances. The protons on the η^5-indenyl ring can typically be readily assigned in the ^{1}H NMR spectra. These features are highlighted in Figure 4 by the ^{1}H NMR spectrum of [Zr(OC_6H_2\{η^5-Ind\}-2-Bu^t_2-4,6)(NMe_2)$_2$] (**9**). The diethylamido compounds contain diastereotopic methylene protons, leading to pairs of ABX_3 patterns within the ^{1}H NMR spectra.

The pathway leading to the bis(dialkylamido) compounds **8**−**18** presumably proceeds via tris(amido) intermediates (Scheme 2). Initial protonolysis of an amido group by the phenolic OH is followed by intramolecular metalation of the indenyl ring and elimination of a second equivalent of $HNMe_2$. However, the intimate details of this second step are interesting. Previous studies have demonstrated that dialkylamido ligands can act as leaving groups in the activation and cleavage of carbon−hydrogen bonds at high- and mid-valent early d-block as well as p-block metal centers.[19,20] In a recent study it was shown that chelation of inden-3-ylphenol **1** by reaction with [Ta(NMe_2)$_5$] led to the η^1 derivative [Ta(OC_6H_2\{η^1-Ind\}-2-Bu^t-4,6)(NMe_2)$_3$].[21] The carbon atom, C1, of the indenyl ring is bound in a purely σ fashion to tantalum, leading to a five-membered metallacycle ring. The structural parameters for the indenyl ring show that there is a localized double bond between C2 and C3. What is not clear in the formation of this compound and the bis(amido) derivatives **8**−**18** is whether activation of the CH bond occurs directly or whether a tautomerization (1,3-shift) precedes ring closure (Scheme 2). What is apparent, however, is that interconversion of p*R* and p*S* forms of the chelate via a reverse of the process and indenyl ring flipping require the proton at some stage to migrate to the 3-position (Scheme 2).

Synthesis and Structure of [Ti(OC_6H_2\{η^5-$IndMe_4$-2,3,4,7\}-2-Bu^t_2-4,6)(NMe_2)Cl] (19). It was also found possible to synthesize **8** via reaction of the dilithio compound **6** with [$(Me_2N)_2TiCl_2$]. Treatment of (1,2,4,7-tetramethylinden-3-yl)phenol (**5**) with Bu^nLi followed by [$(NMe_2)_2TiCl_2$] was found to lead to a reaction mixture from which was isolated the mixed amido chloride **19** (Scheme 3). Formation of **19** presumably occurs via a metathesis reaction of a lithium aryloxide followed by

(19) Kerschner, J. L.; Yu, J.; Fanwick. P. E.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1989**, *8*, 1414−1418.
(20) Smith, G. D.; Visciglio, V. M.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1992**, *11*, 1064−1071.
(21) Thorn, M. G.; Parker, J. R.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **2003**, *22*, 4658.

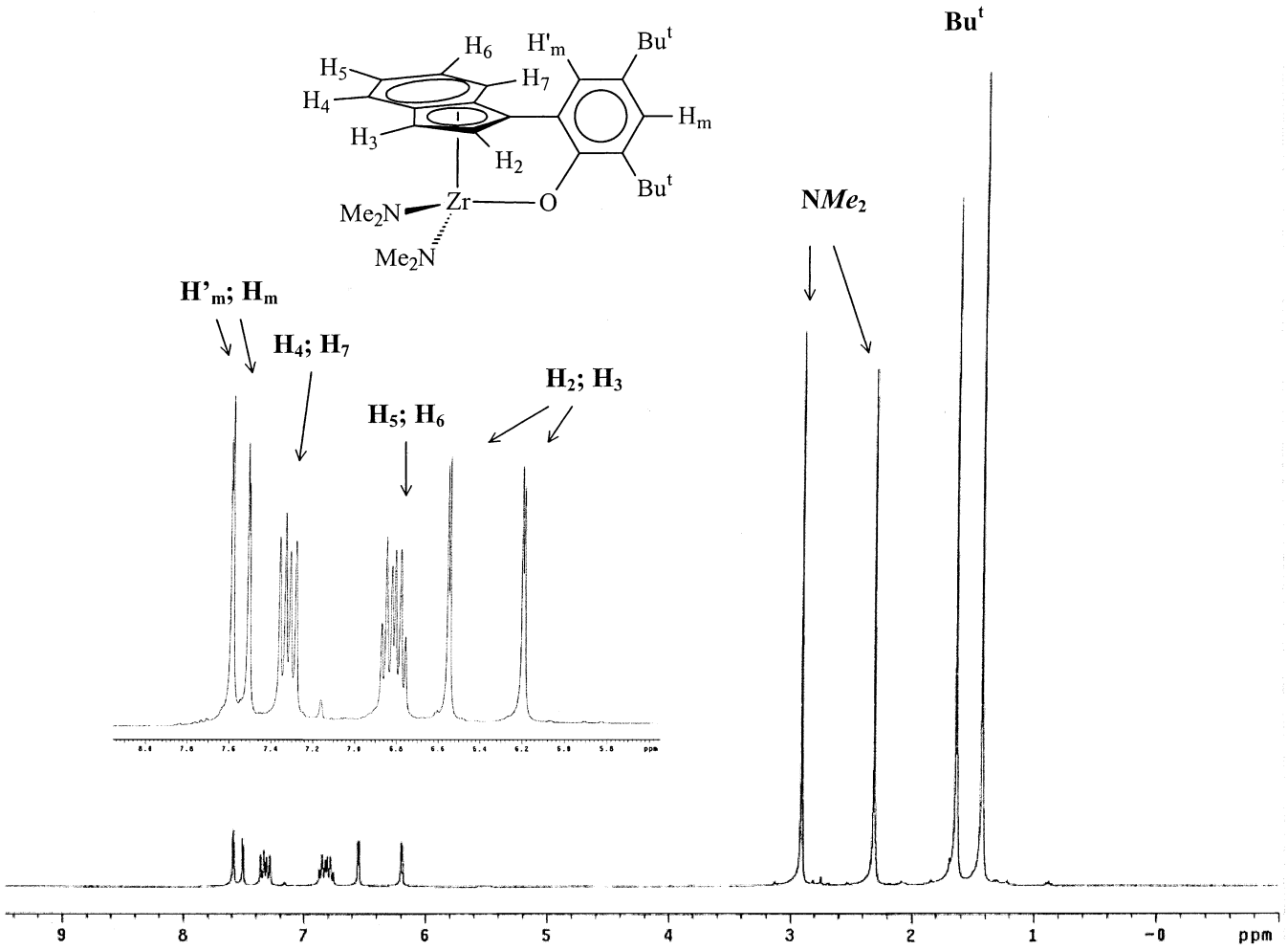


Figure 4. ^{1}H NMR (C_6D_6) spectrum of [Zr(OC$_6$H$_2${η^5-Ind}-2-Bu$^t_2$-4,6)(NMe$_2$)$_2$] (**9**).

elimination of 1 equiv of dimethylamine. The NMR spectra of crystals isolated from this reaction showed a single set of resonances. An X-ray diffraction study showed the presence of a single diastereoisomer in the solid state (Figure 5, Table 2). The presence of the chloride ligand in **19** leads to a slight shortening of the Ti−N and Ti−O distances compared to those in the corresponding bis(amido) compounds (Tables 1 and 2). The coordination sphere in **19** leads to a molecule that is chiral at titanium. The observed isomer in the solid state has the amido ligand positioned "below" the indenyl arene ring (Scheme 3). Use of the Cahn−Ingold−Prelog rules leads to the designation (*S*,p*R*)/(*R*,p*S*) for the pair of enantiomers observed in the unit cell.

Formation and Stereochemistry of Bis(indenylphenoxide) Compounds. It was found possible to introduce two chelating indenylphenoxide ligands into the coordination sphere of titanium, zirconium, or hafnium. One method entailed treatment of the tetra(dialkylamides) with 2 equiv of the parent phenol and overall loss of 4 equiv of amine. The second involved metathetical exchange of the dilithio salt of the indenylphenol with the corresponding metal tetrachloride. By these procedures the compounds **20**−**28** (Scheme 4) could be obtained.

The metalation of two identical indenyl ligands having enantiotopic faces at a single metal center will lead to *dl* (p*S*,p*S*)/(p*R*,p*R*) and *meso* (p*R*,p*S*) diastereomers. This is a common situation encountered with bis(indenyl) *ansa*-metallocenes, where synthetic strategies have been devised to isolate the preferred enantiomeric (*dl*) form.[22] In the case of the pseudo-tetrahedral molecules obtained here, the chelation via the aryloxide ligands also introduces axial chirality to the compounds. The introduction of this extra chiral element has been noted in other bis(chelates) of the group 4 metals containing a cyclopentadienyl ring.[15] The resulting chiral axis in simplified molecules [M(Cp-O)$_2$] lies perpendicular to the C_2 axis of the molecule (Chart 4). In this respect the molecules are related closely to spiranes (see also allenes and biaryls). However, for the purposes of nomenclature related spiranes are considered to have a chiral center.[23] One ring is arbitrarily given preference, and priorities 1 and 3 are given to the atoms attached to the spiro center, followed by 2 and 4 for the other ring. Using this approach to the compounds obtained in this study leads to an *R* or *S* assignment for the metal center (Chart 4). Alternatively, the sense of chirality of a molecule with a chiral axis can be specified as a*R* or a*S*, using Cahn−Ingold−Prelog rules with the added sequence rule that near groups precede far groups when viewed down the chiral axis. Molecules with a chiral axis can also have their configuration designated *P* or *M*: i.e., assigned on the basis of helical symmetry.[15] However, it has recently been stated that the use of the helical descriptors should be avoided when *R* and *S* descriptors will unambiguously define a ste-

Scheme 2

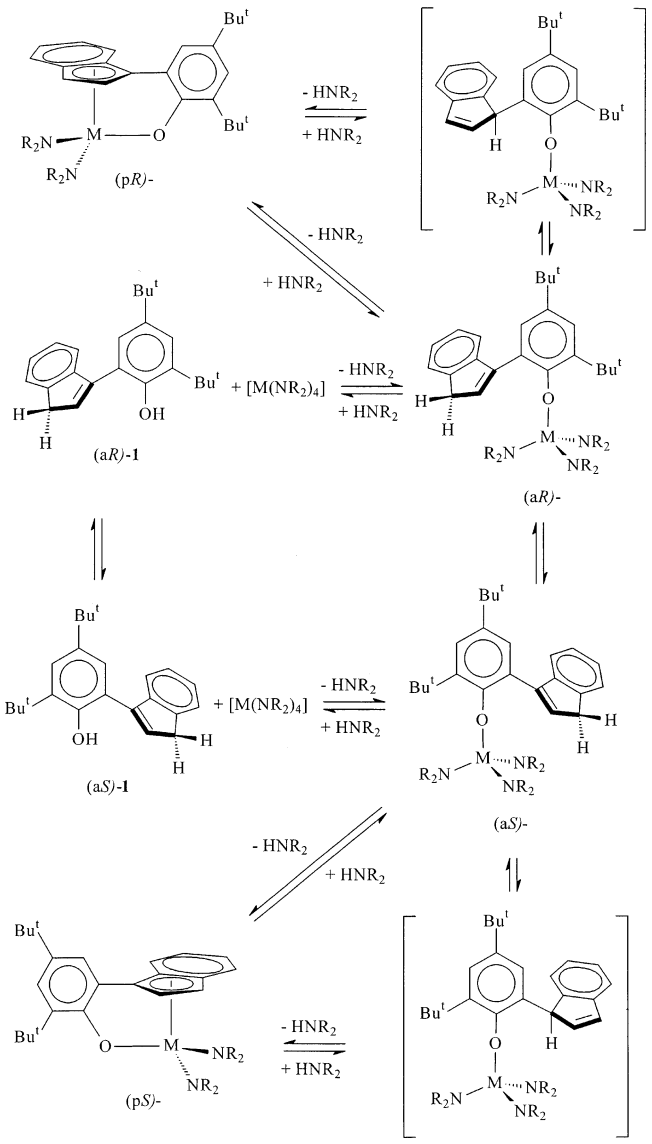


Table 2. Structural Parameters (Å and deg) for the Series of Compounds [M(OC$_6$H$_2${η^5-Ind}-2-Bu$^t_2$-4,6)(NR$_2$)(X)]^a

	19	**23**
M	Ti	Ti
Me substn	2,3,4,7-Me$_3$	2-Me
X	Cl	OAr
M−O	1.863(1)	1.866(1)
M−N	1.884(1)	1.885(2)
M−X	2.3066(5)	1.865(1)
M−C1	2.340(2)	2.384(2)
M−C2	2.402(2)	2.392(2)
M−C3	2.414(2)	2.376(2)
M−C4	2.404(2)	2.449(2)
M−C5	2.352(2)	2.454(2)
Δ^c	0.007	0.064
Ind−M−O	106.1	104.1
Ind−M−N	124.8	119.8
Ind−M−X	113.9	122.2
N−M−X	102.07(5)	107.31(5)
M−O−C	128.2(1)	128.4(1), 145.4(1)^b

^{a} Ind parameters refer to the centroid of the η^5-indenyl ring. ^{b} Nonchelated OC$_6$H$_2${C$_9$H$_6$Me-2}-2-Bu$^t_2$-4,6 aryloxide. ^{c} $\Delta = d\{M-C(4,5)\}_{av} - d\{M-C(1,3)\}_{av}$.

reogenic element.[24] Representations of the central core of the enantiomeric pair are shown (side view, and down

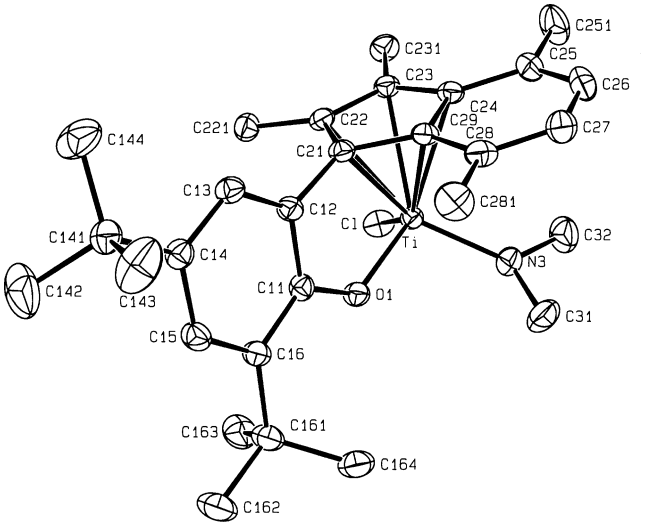


Figure 5. Molecular structure of [Ti(OC$_6$H$_2${η^5-IndMe$_4$-2,3,4,7}-2-Bu$^t_2$-4,6)(NMe$_2$)Cl] (**19**). The (*S*,p*R*) form is shown.

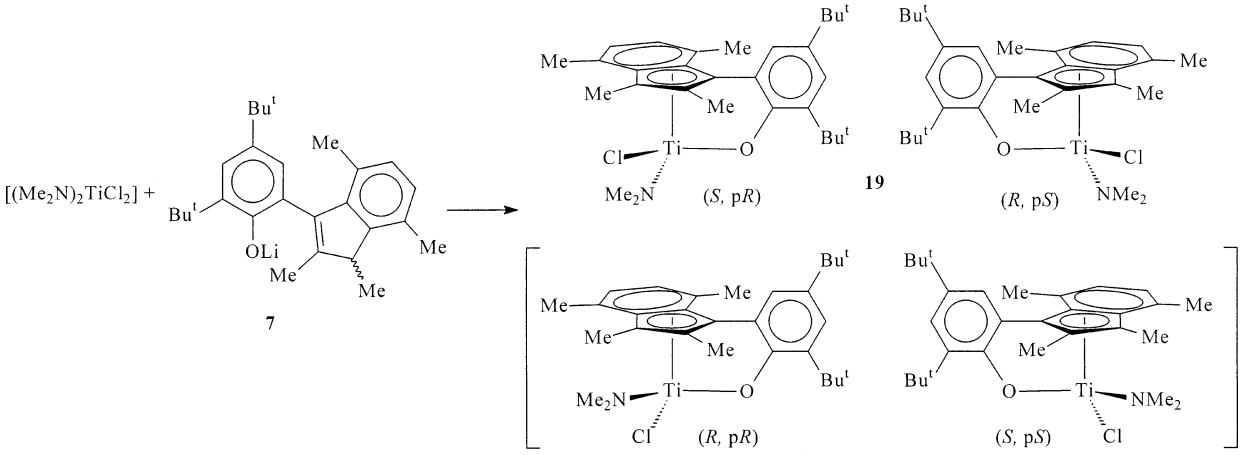
the chiral and C_2 axes, Chart 4) along with the assigned stereochemistry using either the preferred chiral center or alternative chiral axis naming.

The combination of the three chiral elements generates three distinct diastereomeric pairs for the bis(indenylphenoxide) derivatives of the group 4 metals. One enantiomer for each diastereomer is shown (Scheme 5) along with the assigned stereochemistry. Spectroscopically these three diastereoisomers would be expected to generate three distinct sets of ^{1}H and ^{13}C NMR signals. Two of the compounds, (*S*,p*R*,p*R*)/(*R*,p*S*,p*S*) and (*R*,p*R*,p*R*)/(*S*,p*S*,p*S*), contain a C_2 axis leading to equivalent chelates and one set of ligand signals. The third isomer, (*S*,p*R*,p*S*)/(*R*,p*R*,p*S*), has no symmetry element and would have two equal-intensity sets of ligand resonances.

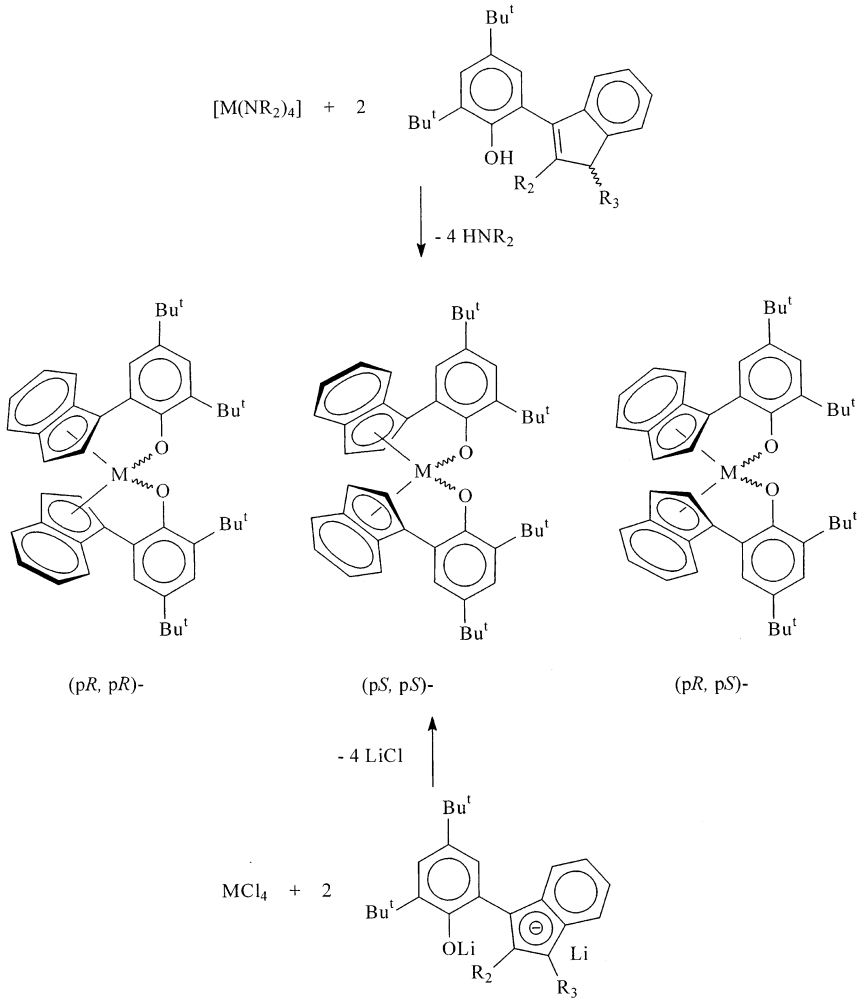
Spectroscopic evidence for all three enantiomer pairs has been obtained, while two forms have been structurally characterized. In Table 3 is collected the selected structural data for the five compounds examined by X-ray diffraction methods. The first compound isolated, [Ti(OC$_6$H$_2${η^n-Ind}-2-Bu$^t_2$-4,6)$_2$] (**20**), was found to possess the (*S*,p*R*,p*S*)/(*R*,p*R*,p*S*) geometry in the solid state (Figure 6). The solution NMR properties of this compound clearly show the presence of nonequivalent, chelated indenylphenoxide ligands. Specifically, the ^{1}H NMR spectrum (Figure 8) shows four well-resolved doublets (2.4 and 3.0 Hz coupling) for the two pairs of 2-H and 3-H protons. Another useful spectroscopic handle is the ^{13}C NMR spectrum, where two Ti−O−*C* carbon resonances are observed at δ 177.0 and 175.0 ppm and four sets of *C*(*C*H$_3$)$_3$ signals (two ortho and two para) are readily resolved. In the solid state the derived structural parameters for **20** (Table 3) indicate a slight displacement of both indenyl rings toward a η^3-bonding mode. This is highlighted in the "Radar" plot shown in Figure 9 and the slip values (Table 3). However, this parameter is not in the range consistent with "true" η^3 bonding.[18]

(22) *Metallocenes*; Togni, A., Halterman, R. L., Eds.; Wiley: New York, 1998; Vols. 1 and 2.
(23) Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; Wiley: New York, 1994.
(24) Nicolaou, K. C.; Christopher, N. C. B.; Siegel, J. S. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 701.

Scheme 3



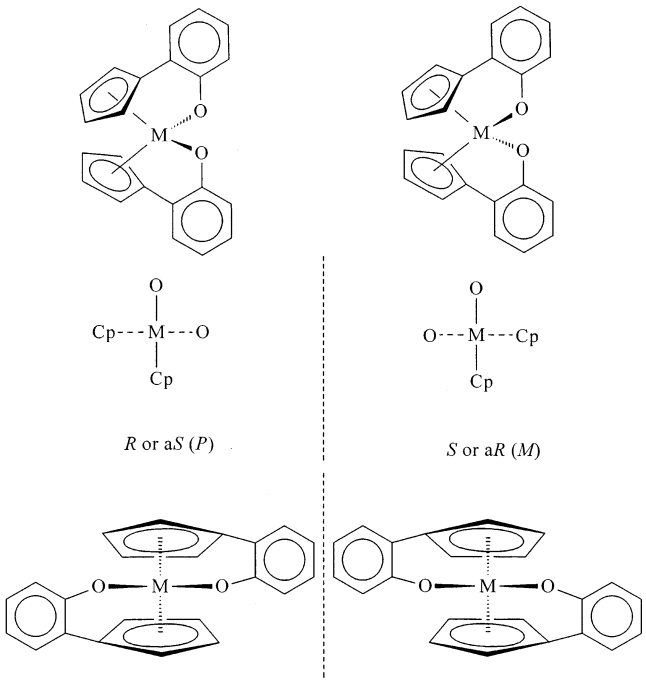
Scheme 4



20: M = Ti; R_2 = H; R_3 = H
21: M = Zr; R_2 = H; R_3 = H
22: M = Hf; R_2 = H; R_3 = H
24: M = Ti; R_2 = Me; R_3 = H
25: M = Zr; R_2 = Me; R_3 = H
26: M = Hf; R_2 = Me; R_3 = H
27: M = Zr; R_2 = Me; R_3 = Me
28: M = Hf; R_2 = Me; R_3 = Me

In contrast, the reaction of $[Zr(NMe_2)_4]$ with phenol **1** was found to produce (NMR) a reaction mixture of isomers. Crystals of the major isomer of $[Zr(OC_6H_2\{\eta^n\text{-Ind}\}\text{-2-Bu}^t_2\text{-4,6})_2]$ (**21**) were isolated and identified as containing the (*R*,p*R*,p*R*)/(*S*,p*S*,p*S*) enantiomeric pair within the unit cell; the central coordination sphere of the (*S*,p*S*,p*S*) form is highlighted in Figure 10 (see also Table 3). The molecule contains a crystallographic C_2 axis of symmetry. When these crystals were dissolved in $CDCl_3$ or C_6D_6, a single set of ligand signals were observed in the ^1H NMR spectrum. However, over the course of a few hours a second isomer was observed to form. This second isomer contained only one set of indenylphenoxide ligands and, therefore, was assigned

Chart 4



the structural configuration (*S*,p*R*,p*R*)/(*R*,p*S*,p*S*). In both of these isomers there is a *rac* arrangement of indenyl ligands. The only difference between the two lies in the chelation of the aryloxide ligands to the metal center. The mechanism of this particular isomerization is presently unknown. In the case of the reaction of [Hf(NEt$_2$)$_4$] with **1**, a similar situation was found, leading to crystals of [Hf(OC$_6$H$_2${η^n-Ind}-2-Bu$^t_2$-4,6)$_2$] (**22**) which were isomorphous with the zirconium compound **21** (Figure 11, Table 3). The interatomic distances for the isostructural zirconium and hafnium compounds (Table 3) indicate only a very slight distortion toward any η^3-bonding situation. This is again highlighted in the "Radar" plots shown in Figure 9 and the slip values (Table 3).

The reaction of [Ti(NMe$_2$)$_4$] with 2 equiv of the 2-methyl-substituted phenol **2** under ambient conditions led to the isolation of a compound containing both chelated and simple O-bound indenylphenoxide ligation. This compound was identified as [Ti(OC$_6$H$_2${η^5-IndMe-2}-2-Bu$^t_2$-4,6)(OC$_6$H$_2${C$_9$H$_6$Me-2}-2-Bu$^t_2$-4,6)$_2$(NMe$_2$)] (**23**). Structural studies showed that isolated crystals contained a (*R*,a*S*,p-*S*)/(*S*,a*R*,p-*R*) configuration within the unit cell (Table 2, Figure 12). The nonchelated aryloxide has a Ti−O−C angle of 145.4(1)°, and structural studies indicate no isomerization of the double bond between C2 and C3 in this terminal aryloxide.

The isolation and observed structure of **23** are significant. We envisage the formation of the bis(chelates) from [M(NR$_2$)$_4$] as proceeding via initial formation of bis(dialkylamides) such as **8**−**18**. During the discussion of the structures of these molecules it was noted that there is a significant difference in the nature of the remaining two amido ligands. Protonolysis of one of these by the phenolic proton can lead to two substitutional isomers (displacement of N1 or N2). The combination of three symmetry elements leads to eight possible isomeric products. Four of these are shown (Scheme 5) for those containing a p*R* configuration for the bound indenyl ring. The isomer isolated for **23** (Scheme 6) contains the (*R*,a*S*,p*S*)/(*S*,a*R*,p*R*) configurations that arise via substitution by indenylphenol of the dialkylamido ligand (N1) not positioned below the indenyl aromatic ring (Scheme 1). Direct ring closure will lead to the (*S*,a*S*,p*S*)/(*R*,a*R*,p*R*) geometry (Scheme 5), whereas indenyl rotation followed by ring metalation leads to the (*S*,p*S*,p*R*)/(*R*,p*S*,p*R*) pair. These are exactly the two configurations obtained in **20**−**22** (Table 3). Formation of the third isomer (*S*,a*R*,p*R*)/(*R*,a*S*,p*S*) can only occur via substitution on N2 by the second equivalent of indenylphenol (Scheme 5). Even then, the (*S*,p*S*,p*R*)/(*R*,p*S*,p*R*) pair can also be formed, depending upon the rotational conformer prior to metalation. Consistent with this argument, when **23** was heated the resulting bis(chelate) product **24** was found to contain either (*S*,p*S*,p*S*)/(*R*,p*R*,p*R*) or (*R*,p*S*,p*S*)/(*S*,p*R*,p*R*) isomers. A similar situation was also observed in the products [M(OC$_6$H$_2${η^5-IndMe-2}-2-Bu$^t_2$-4,6)$_2$] (M = Zr (**25**), Hf (**26**)) obtained by adding **2** to [M(NEt$_2$)$_4$].

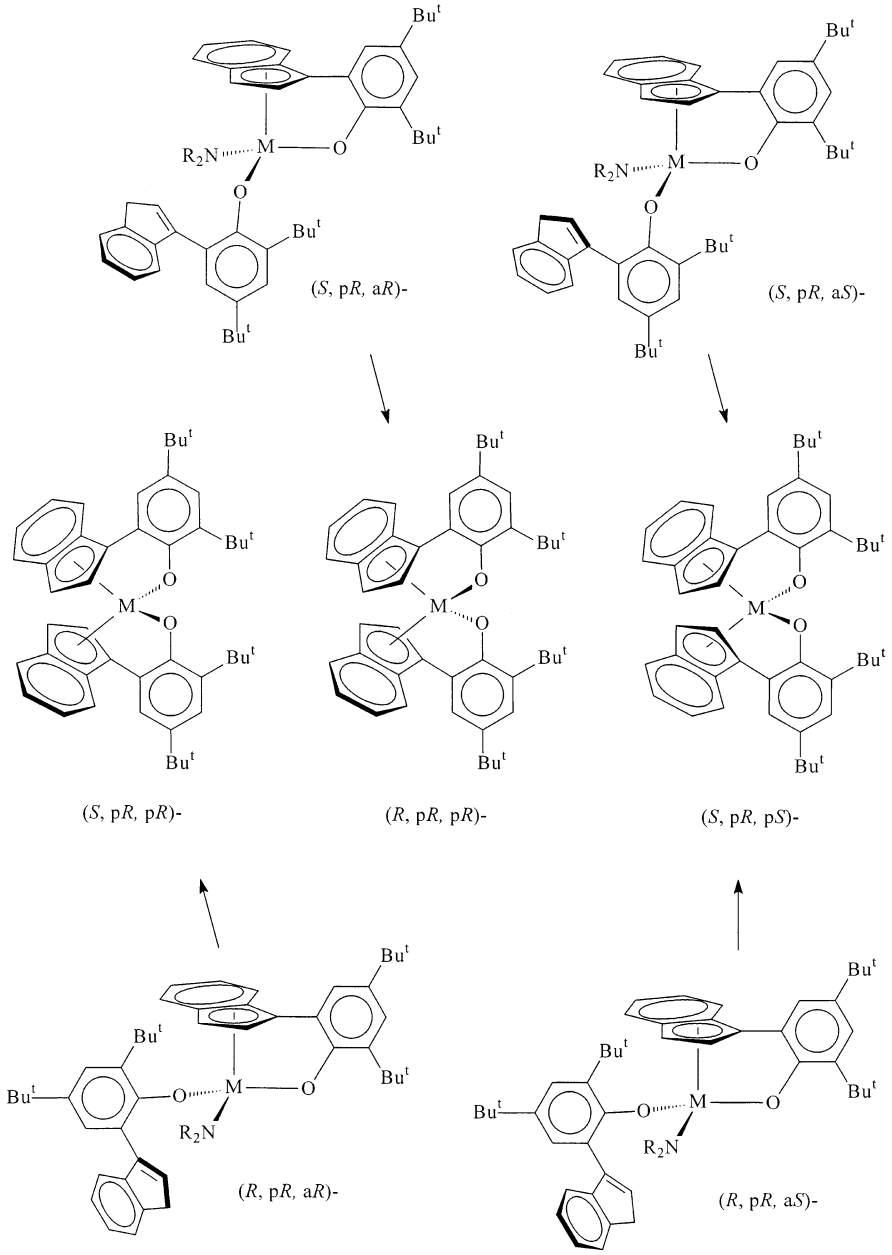
In the case of the reaction of [M(NEt$_2$)$_4$] (M = Zr, Hf) with the (1,2-dimethylinden-3-yl)phenol **3**, crystals isolated of **27** and **28** were shown to be isomorphous and isostructural. The solid-state structure was found to consist of the (*S*,p*S*,p*R*)/(*R*,p*S*,p*R*) pair of isomers (Figure 13, Table 3). The ^{1}H NMR spectrum of the hafnium crystals **28** is shown in Figure 14 and clearly shows the two nonequivalent indenylphenoxide ligands. The ^{1}H NMR of the reaction mixture and supernatant shows either (*S*,p*S*,p*S*)/(*R*,p*R*,p*R*) or (*R*,p*S*,p*S*)/(*S*,p*R*,p*R*) isomers present. The indenyl bonding in this case is interesting. Structural parameters (Table 3, Figure 15)

Table 3. Structural Parameters (Å and deg) for the Series of Compounds [M(OC$_6$H$_2${η^n-Ind}-2-Bu$^t_2$-4,6)$_2$]^a

	20		**21**	**22**	**27**		**28**	
M	Ti		Zr	Hf	Zr		Hf	
isomer	(*R*,p*R*,p*S*)/(*S*,p*R*,p*S*)		(*R*,p*R*,p*R*)/(*S*,p*S*,p*S*)	(*R*,p*R*,p*R*)/(*S*,p*S*,p*S*)	(*R*,p*R*,p*S*)/(*S*,p*R*,p*S*)		(*R*,p*R*,p*S*)/(*S*,p*R*,p*S*)	
M−O	1.913(2)	1.909(2)	2.015(2)	1.998(3)	2.034(3)	2.041(3)	2.010(6	2.016(6)
M−C1	2.368(3)	2.397(3)	2.532(3)	2.503(4)	2.443(3)	2.451(3)	2.412(7)	2.419(8)
M−C2	2.326(3)	2.334(3)	2.500(3)	2.474(3)	2.555(3)	2.519(4)	2.525(7)	2.481(7)
M−C3	2.375(3)	2.356(3)	2.487(3)	2.488(3)	2.575(4)	2.588(4)	2.536(9)	2.576(9)
M−C4	2.569(3)	2.542(3)	2.568(3)	2.572(4)	2.606(4)	2.601(4)	2.504(10)	2.579(8)
M−C5	2.525(3)	2.529(3)	2.640(3)	2.612(4)	2.495(4)	2.561(3)	2.480(9)	2.522(7)
Δ^c	0.200	0.170	0.088	0.104	0.052	0.096	0.024	0.101
Ind−M−Ind	131.2		143.7	143.1	139.6		138.7	
Ind−M−O^b	104.4	102.1	99.0	99.4	100.6	99.9	101.6	100.7
Ind−M−O	108.5	108.0	104.7	104.8	106.5	108.2	107.8	106.5
O−M−O	97.79(9)		97.6(1)	97.79(9)	92.7(1)		92.3(2)	
M−O−C	126.4(2)	129.1(2)	128.4(2)	129.1(2)	121.7(2)	121.3(2)	121.5(5)	121.9(5)

^{a} Ind parameters refer to the centroid of the η^n-indenyl ring. ^{b} Chelate. ^{c} $\Delta = d\{M-C(4,5)\}_{av} - d\{M-C(1,3)\}_{av}$.

Scheme 5



show that the 2,3-dimethyl substituents lead to a symmetrical lengthening between the metal and the C2/C5 and C3/C4 atoms compared to the M−C1 distance. This is highlighted in the "Radar" plot in Figure 15.

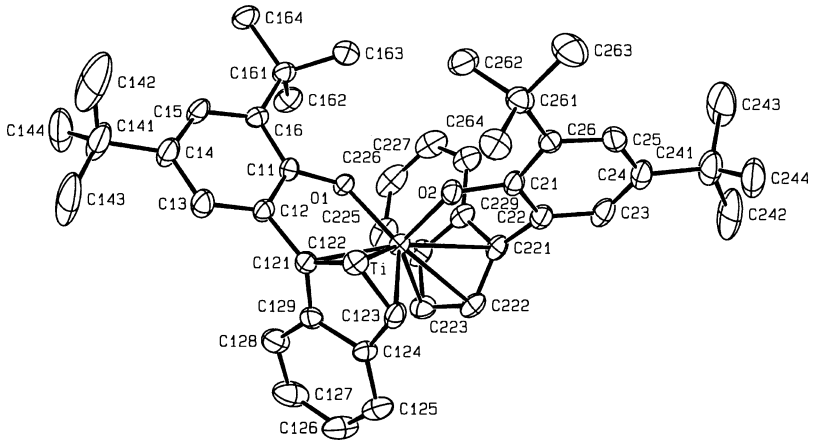


Figure 6. Molecular structure of [Ti(OC_6H_2{η^3-Ind}-2-Bu^t_2-4,6)$_2$] (**20**). The (*S*,p*R*,p*S*)/(*R*,p*R*,p*S*) forms are present within the unit cell.

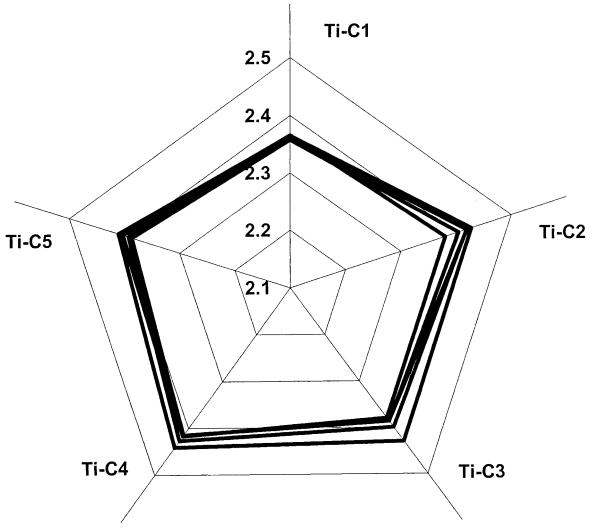


Figure 7. "Radar" plot of the Ti−C(indenyl) distances in titanium compounds **8**, **11**, **14**, and **16**. The coordination is exaggerated by using a plot scale of 2.1−2.5 Å from the metal center.

Experimental Section

General Details. All operations were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. The hydrocarbon solvents were distilled from sodium/benzophenone and stored over sodium ribbons under nitrogen until use. The phenols **1**−**5** were prepared as previously reported.[6c] The tetrakis(dialkylamido) compounds [$M(NR_2)_4$] (M = Ti, R = Me; M = Zr, R = Me, Et; M = Hf, R = Et) were obtained commercially and used as received. The ^1H and ^{13}C NMR spectra were recorded on a Varian Associates Gemini-200, Inova-300, or General Electric QE−300 spectrometer and referenced to protio impurities of commercial benzene-d_6 as internal standard. Elemental analyses and molecular structures were obtained through Purdue in-house facilities. In a number of cases low carbon analyses were obtained, presumably due to metal carbide formation.[25]

Synthesis of [Ti(OC$_6$H$_2${η^5-Ind}-2-Bu$^t_2$-4,6)(NMe$_2$)$_2$] (8). Method A. A flask was charged with [$Ti(NMe_2)_4$] (500 mg, 2.2 mmol) and benzene (~10 mL). As this mixture was stirred, **1** (710 mg, 2.2 mmol) dissolved in benzene was slowly added. The reaction mixture was stirred for 30 min and evacuated. Pentane was added to this initial crude material, and upon standing orange crystals of **7** formed (700 mg, 70%). Anal. Calcd for $C_{27}H_{38}N_2OTi$: C, 71.35; H, 8.43; N, 6.16. Found: C, 70.81; H, 8.64; N, 6.03. ^1H NMR (C_6D_6, 25 °C): δ 6.75−7.61 (m, aromatics); 6.43 (d), 6.33 [d, $^3J(^1H-^1H) = 3.3$ Hz, η^5-CH_2]; 3.27 (s), 2.49 (s, NMe_2); 1.68 (s), 1.44 (s, CMe_3). ^{13}C NMR (C_6D_6, 25 °C): δ 172.5 (Ti−O−*C*); 152.0, 144.8, 142.8, 141.5, 134.9, 129.9, 125.4, 124.8, 124.7, 124.0, 123.2, 122.5, 121.7, 120.2 (unsaturated *C*); 101.3 (η^5-*C*H$_2$); 48.5, 46.5 (NMe_2); 35.3, 34.6 (*C*Me$_3$); 32.1, 30.1 (CMe_3).

Method B. To a stirred solution of [$(NMe_2)_2TiCl_2$] (420 mg, 2.0 mmol) in benzene was added 670 mg (2.0 mmol) of **6** suspended in benzene. The reaction mixture immediately

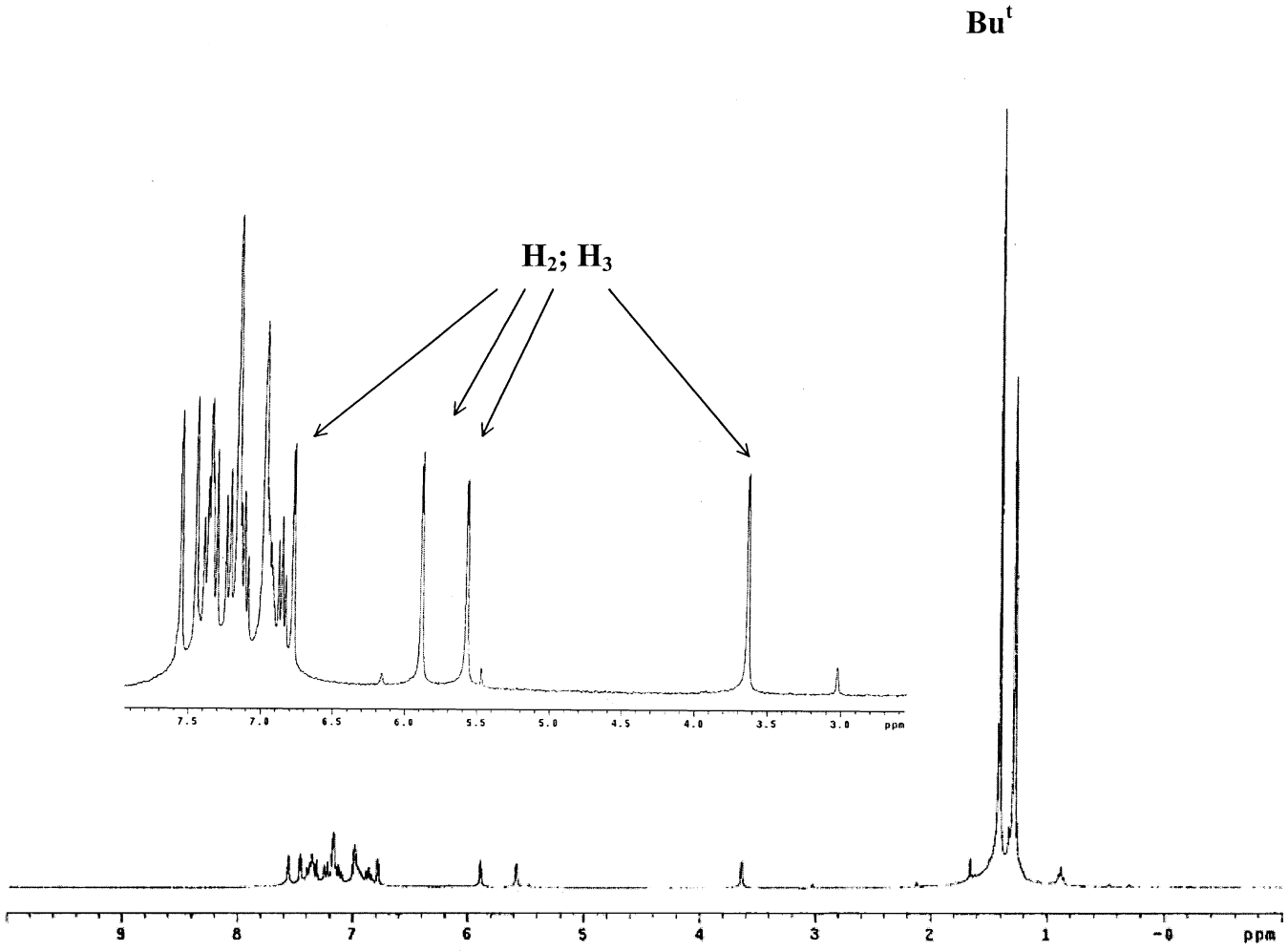


Figure 8. ^1H NMR (C_6D_6) spectrum of [Ti(OC$_6$H$_2${η^3-Ind}-2-Bu$^t_2$-4,6)$_2$] (**20**). The (*S*,p*R*,p*S*)/(*R*,p*S*,p*R*) forms generate two distinct sets of ligand signals.

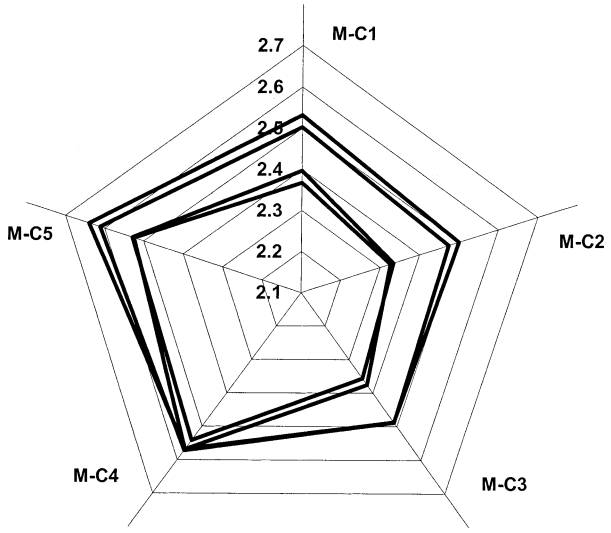


Figure 9. "Radar" plot of the M−C(indenyl) distances in compounds [M($OC_6H_2\{\eta^n$-Ind$\}$-2-Bu^t_2-4,6)$_2$] (M = Ti (**20**), Zr (**21**), Hf (**22**)). The coordination is exaggerated by using a plot scale of 2.1−2.7 Å from the metal center.

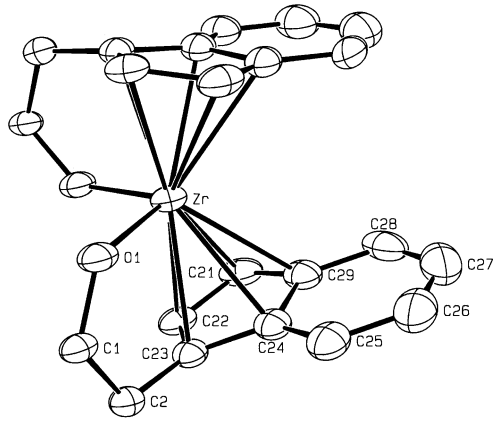


Figure 10. ORTEP plot showing the inner coordination sphere of [Zr($OC_6H_2\{\eta^n$-Ind$\}$-2-Bu^t_2-4,6)$_2$] (**21**). The (*S*,p*S*,p*S*) form of the (*R*,p*R*,p*R*)/(*S*,p*S*,p*S*) enantiomeric pair within the unit cell is shown.

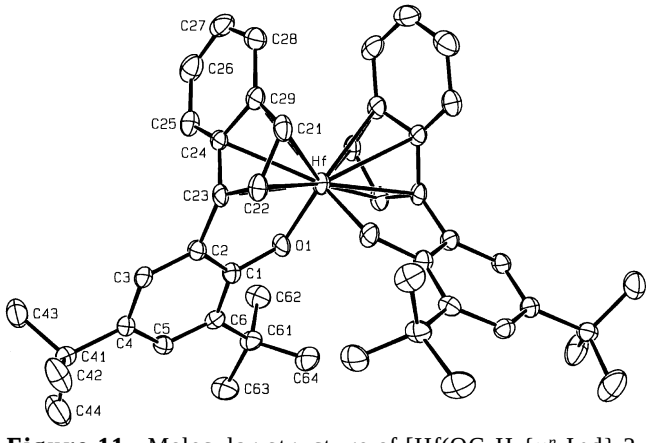


Figure 11. Molecular structure of [Hf($OC_6H_2\{\eta^n$-Ind$\}$-2-Bu^t_2-4,6)$_2$] (**22**). The (*S*,p*S*,p*S*) form of the (*R*,p*R*,p*R*)/(*S*,p*S*,p*S*) enantiomeric pair within the unit cell is shown.

turned dark red, and stirring was continued for 45 min. The crimson solution was filtered over Celite and the solvent removed under vacuum. The red solid was found to be pure by ^{1}H NMR spectroscopy (550 mg, 60%).

Synthesis of [Zr($OC_6H_2\{\eta^5$-Ind$\}$-2-Bu^t_2-4,6)(NMe_2)$_2$] (9). A sample of Zr(NMe_2)$_4$ (520 mg, 1.9 mmol) was dissolved in toluene. This solution was stirred vigorously as **1** (620 mg, 1.9 mmol) dissolved in toluene was slowly added. The mixture was stirred for 8 h and the solution evacuated to dryness, affording a light brown solid. Dissolution in pentane produced clear needlelike crystals on standing overnight (430 mg, 44%). Anal. Calcd for $C_{27}H_{38}N_2OZr$: C, 65.14; H, 7.69; N, 5.63. Found: C, 64.89; H, 7.54; N, 5.54. ^{1}H NMR (C_6D_6, 25 °C): δ 7.59 (d), 7.51 (d), 7.28−7.36 (m), 6.78−6.85 (m, aromatics); 6.55 (d), 6.19 [d, $^3J(^1H-^1H)$ = 3.3 Hz, η^5-CH_2]; 2.91 (s), 2.31 (s, NMe_2); 1.64 (s), 1.44 (s, CMe_3). ^{13}C NMR (C_6D_6, 25 °C): δ 171.0 (Zr−O−*C*); 141.3, 136.1, 129.4, 128.3, 126.3, 125.1, 124.7, 124.3, 123.8, 123.4, 122.6, 121.8 (unsaturated *C*); 95.5 (η^5-C_5H_2); 43.8, 41.8 (NMe_2); 35.4, 34.6 (*C*Me$_3$); 32.1, 30.0 (CMe_3).

Synthesis of [Hf($OC_6H_2\{\eta^5$-Ind$\}$-2-Bu^t_2-4,6)(NEt_2)$_2$] (10). Using a procedure identical with that for **9**, 1.20 g (2.6 mmol) of Hf(NEt)$_4$ was reacted with 0.82 g (2.6 mmol) of **1** to produce a tan solid. Dissolution of the crude material in pentane produced clear needles on standing for days (710 mg, 43%). Anal. Calcd for $C_{31}H_{46}N_2OHf$: C, 58.07; H, 7.23; N, 4.37. Found: C, 57.18; H, 7.15; N, 4.06. ^{1}H NMR (C_6D_6, 25 °C): δ 7.63 (d), 7.53 (d), 7.43 (d), 7.31 (d), 6.89 (t), 6.79 (t, aromatics); 6.59 (d), 6.14 [d, $^3J(^1H-^1H)$ = 3.0 Hz, η^5-CH_2]; 3.34 [d of sept, $^2J(^1H-^1H)$ = 42.0 Hz; $^3J(^1H-^1H)$ = 6.9 Hz, N−CH_2Me], 2.69 [d of sept, $^2J(^1H-^1H)$ = 40.0 Hz; $^3J(^1H-^1H)$ = 6.9 Hz, N−CH_2-Me]; 1.64 (s), 1.42 (s, CMe_3); 1.02 (t), 0.88 [t, $^3J(^1H-^1H)$ = 6.9 Hz, N−CH$_2$*Me*]. ^{13}C NMR (C_6D_6, 25 °C): δ 170.3 (Hf−O−*C*); 141.4, 137.1, 129.6, 128.3, 127.8, 126.2, 124.9, 124.8, 124.7, 124.2, 123.6, 123.2, 122.5, 122.3 (unsaturated *C*); 93.7 (η^5-*C*H$_2$); 43.8, 43.6 (N-*C*H$_2$Me); 35.5, 34.5 (*C*Me$_3$); 32.1, 30.2 (C*Me*$_3$); 16.2, (N−CH$_2$*Me*).

Synthesis of [Ti($OC_6H_2\{\eta^5$-IndMe-2$\}$-2-Bu^t_2-4,6)(NMe_2)$_2$] (11). Using a procedure identical with that for **9**, 0.76 g (3.4 mmol) of Ti(NMe_2)$_4$ was reacted with 1.13 g (3.4 mmol) of **2** to produce a red glassy solid. Slow evaporation of a hexane solution for weeks produced blocks of crimson crystals (580 mg, 37%). Suitable microanalysis was not obtained for this compound. ^{1}H NMR (C_6D_6, 25 °C): δ 7.55 (s), 7.23−7.34 (m), 6.83, (t), 6.74 (t, aromatics); 6.17 (s, η^5-C*H*); 3.28 (s), 2.50 (s, NMe_2); 2.00 (s, η^5-C-*Me*); 1.64 (s), 1.42 (s, CMe_3). ^{13}C NMR (C_6D_6, 25 °C): δ 172.0 (Ti−O−*C*); 141.7, 135.0, 133.6, 130.3, 127.0, 126.1, 124.9, 124.5, 124.3, 124.2, 123.1, 121.8 (unsaturated *C*); 101.7 (η^5-*C*H); 49.2, 47.3 (NMe_2); 35.3, 34.6 (*C*Me$_3$); 32.2, 30.2 (C*Me*$_3$); 13.0 (η^5-C-*Me*).

Synthesis of [Zr($OC_6H_2\{\eta^5$-IndMe-2$\}$-2-Bu^t_2-4,6)(NEt_2)$_2$] (12). Using a procedure identical with that for **9**, 950 mg (2.5 mmol) of Zr(NEt_2)$_4$ was reacted with 830 mg (2.5 mmol) of **2**. Evaporation of the solvent under vacuum afforded an off-white solid. Dissolution of the crude material in toluene followed by slow cooling to −20 °C produced clear platelets (450 mg, 32%). Anal. Calcd for $C_{32}H_{48}N_2OZr$: C, 67.67; H, 8.52; N, 4.93. Found: C, 67.33; H, 8.60; N, 4.75. ^{1}H NMR (C_6D_6, 25 °C): δ 7.60 (s), 7.24−7.43 (m), 6.72−6.90 (m, aromatics); 6.04 (s, η^5-C*H*); 3.34 [d of sext, $^2J(^1H-^1H)$ = 65.9 Hz; $^3J(^1H-^1H)$ = 6.9 Hz, N−CH_2CH$_3$], 2.64 [d of sext, $^2J(^1H-^1H)$ = 54.3 Hz; $^3J(^1H-^1H)$ = 6.9 Hz, N−CH_2CH$_3$]; 2.10 (s, η^5-C−*Me*); 1.63 (s), 1.42 (s, CMe_3); 0.99 (t), 0.87 [t, $^3J(^1H-^1H)$ = 6.9 Hz, N−CH$_2$*Me*]. ^{13}C NMR (C_6D_6, 25 °C): δ 170.2 (Zr−O−*C*); 141.4, 136.1, 135.4, 128.8, 128.3, 127.8, 127.3, 125.5, 125.0, 124.2, 124.0, 123.8, 123.7, 123.4, 122.8, 121.9 (unsaturated *C*); 95.8 (η^5-*C*H); 44.7, 43.4 (N−*C*H$_2$Me); 35.3, 34.5 (*C*Me$_3$); 32.1, 30.2 (C*Me*$_3$); 16.3, 15.3 (N−CH$_2$*Me*); 13.0 (η^5-C−*Me*).

Synthesis of [Hf($OC_6H_2\{\eta^5$-IndMe-2$\}$-2-Bu^t_2-4,6)(NEt_2)$_2$] (13). Using a procedure identical with that for **9**, 1.10 g (2.4 mmol) of Hf(NEt_2)$_4$ was reacted with 790 mg (2.4 mmol) of **2**. Evaporation of the solvent under vacuum afforded a tan solid. Dissolution of the crude material in toluene followed by slow

(25) Chesnut, R. W.; Durfee, L. D.; Fanwick, P. E.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *Polyhedron* **1987**, *6*, 2019.

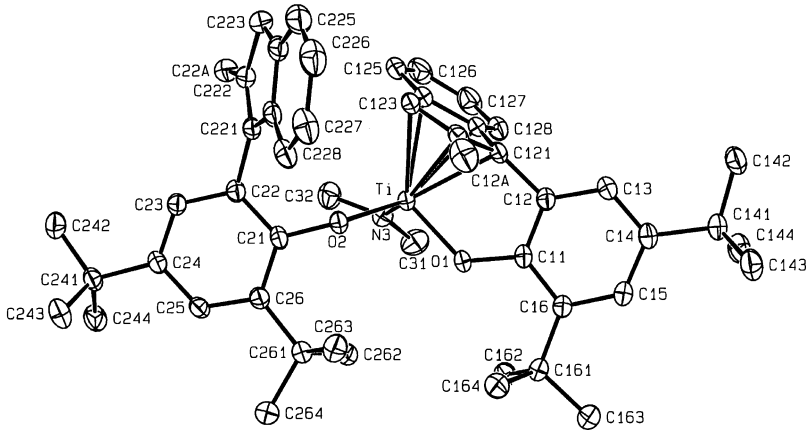
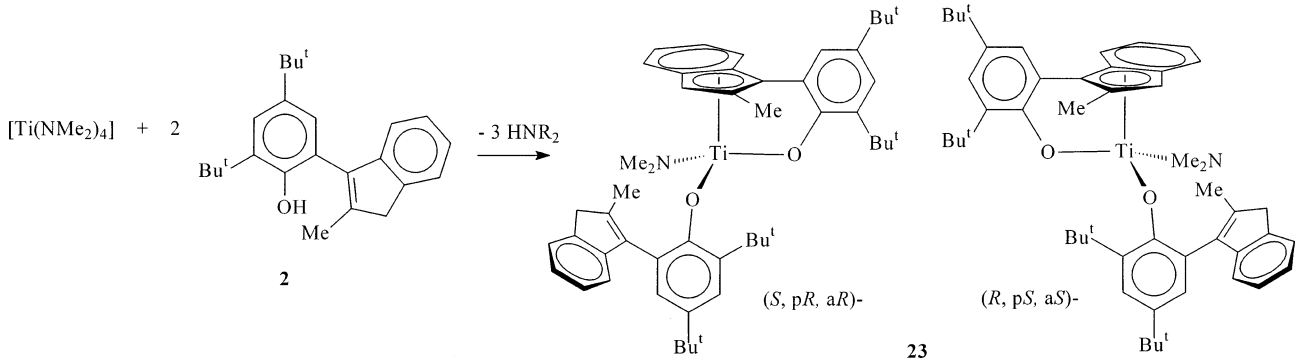


Figure 12. Molecular structure of [Ti(OC_6H_2\{η^5-IndMe-2\}-2-Bu$^t_2$-4,6)(OC_6H_2\{C_9H_6Me-2\}-2-Bu$^t_2$-4,6)$_2$(NMe_2)] (**23**). The (*S*,a*R*,p*R*) form of the (*R*,a*S*,p*S*)/(*S*,a*R*,p*R*) enantiomeric pair within the unit cell is shown.

Scheme 6



cooling to −20 °C produced clear platelets (820 mg, 53%). Anal. Calcd for $C_{32}H_{48}N_2OHf$: C, 58.66; H, 7.38; N, 4.28. Found: C, 58.59; H, 7.38; N, 4.12. ^{1}H NMR (C_6D_6, 25 °C): δ 7.62 (d), 7.38−7.44 (m), 7.23 (s), 7.19 (s), 6.72−6.91 (m, aromatics); 5.95 (s, η^5-C*H*); 3.36 [d of sext, $^2J(^1H-^1H) = 54.7$ Hz; $^3J(^1H-^1H) = 7.0$ Hz, N−CH_2CH$_3$], 2.60 [d of sext, $^2J(^1H-^1H) = 40.4$ Hz; $^3J(^1H-^1H) = 7.0$ Hz, N−CH_2CH$_3$]; 2.16 (s, η^5-C−*Me*); 1.62 (s), 1.41 (s, C*Me*$_3$); 1.00 (t), 0.87 [t, $^3J(^1H-^1H) = 7.0$ Hz, N−CH$_2$*Me*]. ^{13}C NMR (C_6D_6, 25 °C): δ 169.5 (Hf−O−*C*); 141.5, 137.0, 135.3, 130.0, 125.2, 124.4, 123.9, 123.7, 122.7, 122.1, 121.3 (unsaturated *C*); 94.9 (η^5-*C*H); 44.8, 44.0 (N−*C*H$_2$Me); 36.0, 35.4 (*C*Me$_3$); 33.0, 31.1 (C*Me*$_3$); 17.5, 16.6 (N−CH$_2$*Me*); 14.3 (η^5-C−*Me*).

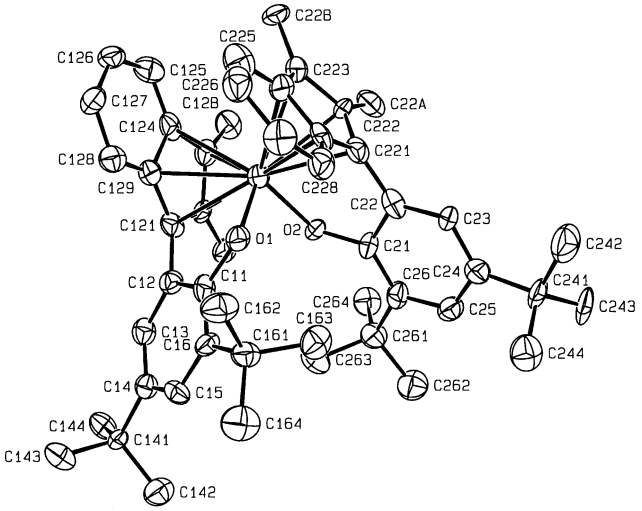


Figure 13. Molecular structure of [Zr(OC_6H_2\{η^5-IndMe$_2$-2,3\}-2-Bu$^t_2$-4,6)$_2$] (**27**). The (*S*,p*R*,p*S*)/(*R*,p*R*,p*S*) forms are present within the unit cell.

Synthesis of [Ti(OC_6H_2\{η^5-IndMe$_2$-2,3\}-2-Bu$^t_2$-4,6)(NMe_2)$_2$] (14). A flask was charged with [Ti(NMe_2)$_4$] (1.03 g, 4.60 mmol) and xylenes (50 mL). As this mixture was stirred, **3** (1.60 g, 4.60 mmol) dissolved in xylenes was slowly added at room temperature. The reaction mixture was stirred for 30 min, sealed under nitrogen, and transferred to an oil bath. The deep red reaction mixture was slowly heated to 150 °C with occasional nitrogen flushing to remove $HNMe_2$. After 8 h the deep red solution was evacuated to produce a glassy red solid that was pure by ^{1}H NMR. Dissolution of the solid in minimal hexane yielded red blocky crystals on standing overnight. A second and third crop were collected following slow evaporation of the solvent (1.45 g, 65.3%). Anal. Calcd for $C_{29}H_{42}N_2OTi$: C, 72.18; H, 8.77; N, 5.81. Found: C, 71.80; H, 8.87; N, 5.75. ^{1}H NMR (C_6D_6, 25 °C): δ 7.60 (d), 7.28−7.36 (m), 6.92, (t), 6.81 (t, aromatics); 3.11 (s), 2.59 (s, N*Me*$_2$); 2.22 (s), 1.99 (s, η^5-C−*Me*); 1.65 (s), 1.44 (s, C*Me*$_3$). ^{13}C NMR (C_6D_6, 25 °C): δ 172.2 (Ti−O−*C*); 141.8, 135.0, 133.2, 128.5, 126.9, 125.6, 124.6, 124.5, 124.1, 123.5, 123.2, 122.9, 122.0 (unsaturated *C*); 108.1 (η^5-*C*H); 48.1, 46.9 (N*Me*$_2$); 35.3, 34.6 (*C*Me$_3$); 32.2, 30.2 (C*Me*$_3$); 11.6, 10.5 (η^5-C−*Me*).

Synthesis of [Hf(OC_6H_2\{η^5-IndMe$_2$-2,3\}-2-Bu$^t_2$-4,6)(NEt_2)$_2$] (15). Using a procedure identical with that for **14**, 980 mg (2.1 mmol) of Hf(NEt_2)$_4$ was reacted with 730 mg (2.1 mmol) of **3**. Evaporation of the solvent under vacuum afforded a tan solid. Dissolution of the crude material in toluene followed by slow cooling to −20 °C afforded a white crystalline solid (680 mg, 48%). Anal. Calcd for $C_{33}H_{50}N_2OHf$: C, 59.22; H, 7.53; N, 4.19. Found: C, 57.13; H, 7.16; N, 3.68. ^{1}H NMR (C_6D_6, 25 °C): δ 7.63 (d), 7.40−7.44 (m), 7.29 (s), 7.25 (s), 6.95 (t), 6.81 (t, aromatics); 3.15−3.41 (m), 2.58−2.91 (m, N−CH_2-CH$_3$); 2.28 (s), 2.13 (s, η^5-C−*Me*); 1.63 (s), 1.42 (s, C*Me*$_3$); 0.99 (t), 0.87 [t, $^3J(^1H-^1H) = 6.9$ Hz, N−CH$_2$*Me*]. ^{13}C NMR (C_6D_6, 25 °C): δ 168.8 (Hf−O−*C*); 141.7, 137.0, 134.1, 128.8, 128.3, 127.8, 125.9, 125.4, 124.0, 123.8, 123.5, 123.1, 121.7 (unsatur-

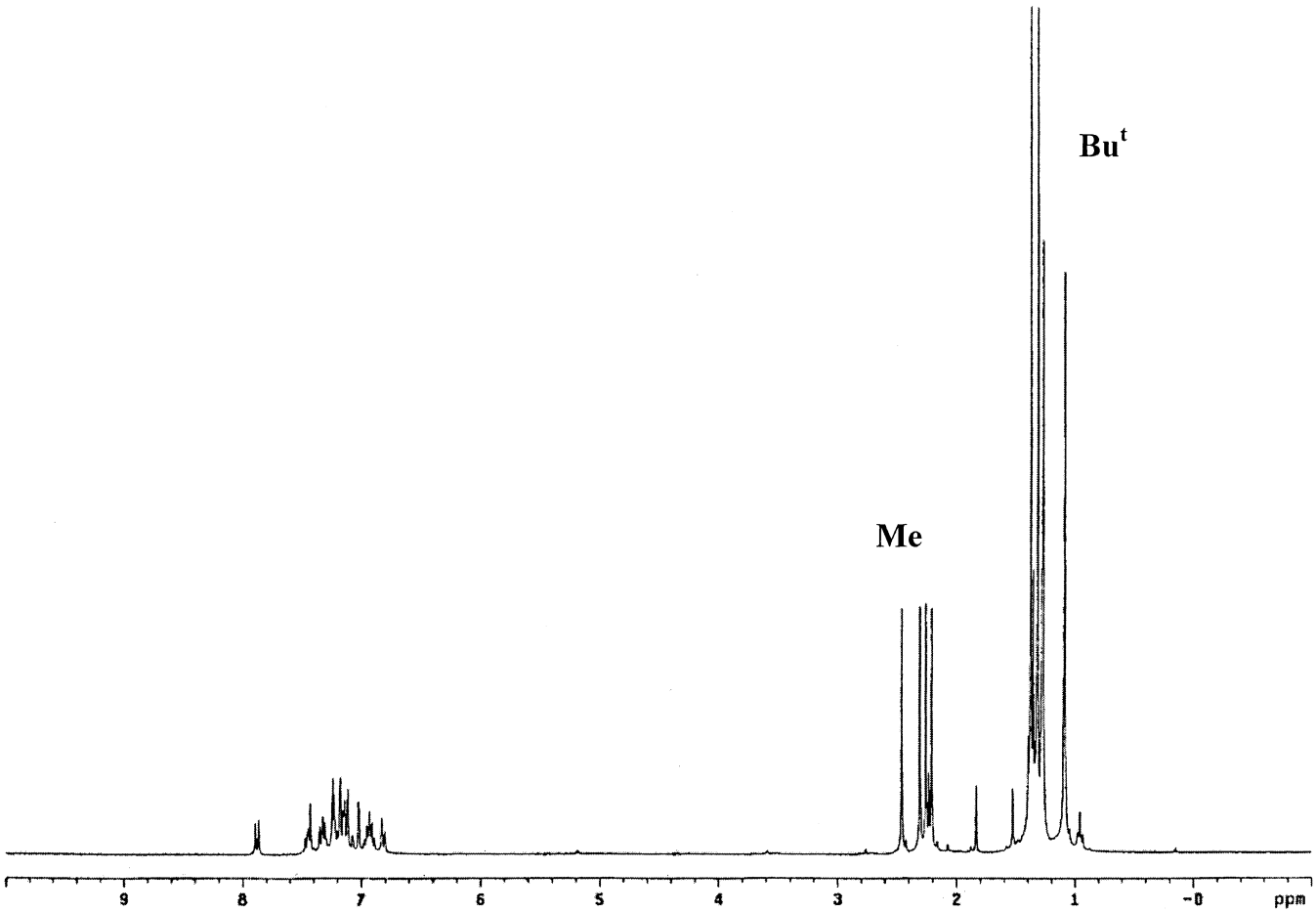


Figure 14. ^{1}H NMR (C_6D_6) spectrum of [Hf(OC_6H_2\{η^5-$IndMe_2$-2,3\}-2-Bu^t_2-4,6)$_2$] (**28**). The (*S*,p*R*,p*S*)/(*R*,p*R*,p*S*) forms generate two distinct sets of ligand signals.

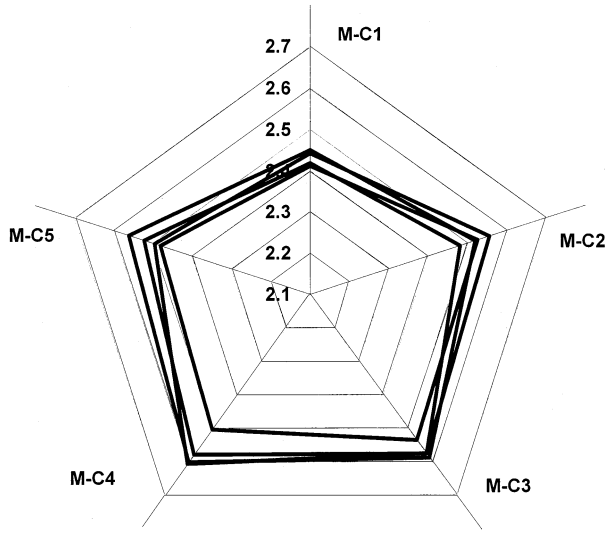


Figure 15. "Radar" plot of the M−C(indenyl) distances in compounds [M(OC_6H_2\{η^5-$IndMe_2$-2,3\}-2-Bu^t_2-4,6)$_2$] (M = Zr (**27**), Hf (**28**)). The coordination is exaggerated by using a plot scale of 2.1−2.7 Å from the metal center. The (*S*,p*R*,p*S*)/(*R*,p*R*,p*S*) forms generate two distinct sets of metal−ligand parameters.

ated *C*); 102.4 (η^5-*C*H); 43.3, 42.6 (N−*C*H_2Me); 35.2, 34.5 (*C*Me_3); 32.1, 30.2 (C*Me*$_3$); 16.3, 15.6 (N−CH_2*Me*); 11.5, 10.3 (η^5-C−*Me*).

Synthesis of [Ti(OC_6H_2\{η^5-$IndMe_3$-2,4,7\}-2-Bu^t_2-4,6)-(NMe_2)$_2$] (16). Using a procedure identical with that for **9**, 650 mg (2.1 mmol) of Ti(NMe_2)$_4$ was reacted with 730 mg (2.1 mmol) of **4** to produce an orange solid. Dissolution of the crude material in minimal pentane produced red crystals on standing for weeks (530 mg, 59%). Satisfactory microanalysis was not obtained for this compound. ^{1}H NMR (C_6D_6, 25 °C): δ 7.53 (d), 7.31 (d), 6.58 (q, aromatics); 6.25 (s, η^5-C*H*); 3.34 (s), 2.53 (s, N*Me*$_2$); 2.28 (s), 2.15 (s), 2.06 (s, η^5-C-*Me*); 1.67 (s), 1.43 (s, C*Me*$_3$). ^{13}C NMR (C_6D_6, 25 °C): δ 168.8 (Ti−O−*C*); 141.3, 134.1, 133.3, 132.1, 131.6, 125.4, 124.6, 123.5, 122.5, 122.0 (unsaturated *C*); 101.5 (η^5-*C*H); 50.2, 47.2 (N*Me*$_2$); 36.0, 35.4 (*C*Me_3); 33.0, 31.0 (C*Me*$_3$); 20.8, 20.0, 13.9 (η^5-C−*Me*).

Synthesis of [Zr(OC_6H_2\{η^5-$IndMe_3$-2,4,7\}-2-Bu^t_2-4,6)-(NEt_2)$_2$] (17). Using a procedure identical with that for **9**, 540 mg (1.4 mmol) of Hf(NEt_2)$_4$ was reacted with 520 mg (1.4 mmol) of **4**. Evaporation of the solvent under vacuum afforded a tan solid. Dissolution of the crude material in minimal pentane afforded a white crystalline solid on standing for days (440 mg, 45%). Anal. Calcd for $C_{34}H_{52}N_2OZr$: C, 68.52; H, 8.79; N, 4.70. Found: C, 67.00; H, 8.63; N, 4.54. ^{1}H NMR (C_6D_6, 25 °C): δ 7.58 (d), 7.40 (d), 6.68 (q, aromatics); 6.17 (s, η^5-C*H*); 3.41 [d of sext., ^2J(^{1}H−^{1}H) = 87.6 Hz; ^3J(^{1}H−^{1}H) = 6.9 Hz, N−CH_2CH$_3$], 30.5 [d of sext, ^2J(^{1}H−^{1}H) = 48.9 Hz; ^3J(^{1}H−^{1}H) = 6.9 Hz, N−CH_2CH$_3$]; 2.42 (s), 2.18 (s), 2.17 (s, η^5-C−*Me*); 1.67 (s), 1.44 (s, C*Me*$_3$); 1.04 (t), 0.90 [t, ^3J(^{1}H−^{1}H) = 6.9 Hz, N−CH_2*Me*]. ^{13}C NMR (C_6D_6, 25 °C): δ 171.1 (Zr−O−*C*); 141.0, 135.4, 135.2, 130.9, 130.4, 128.3, 127.7, 125.4, 124.9, 124.2, 123.6, 123.4, 122.8 (unsaturated *C*); 95.3 (η^5-*C*H); 43.9, 43.7 (N−*C*H_2Me); 35.2, 34.5 (*C*Me_3); 32.1, 30.1 (C*Me*$_3$); 19.9, 19.5, 13.2 (η^5-C−*Me*); 16.0, 15.6 (N−CH_2*Me*).

Synthesis of [Hf(OC_6H_2\{η^5-$IndMe_3$-2,4,7\}-2-Bu^t_2-4,6)-(NEt_2)$_2$] (18). Using a procedure identical with that for **9**, 1.00 g (2.1 mmol) of Hf(NEt_2)$_4$ was reacted with 0.77 g (2.1 mmol)

of **4**. Evaporation of the solvent under vacuum afforded a tan solid. On standing for days in minimal pentane, an off-white solid was formed (900 mg, 62%). Anal. Calcd for $C_{33}H_{50}N_2OHf$: C, 59.77; H, 7.67; N, 4.10. Found: C, 59.47; H, 7.73; N, 4.00. ^{1}H NMR (C_6D_6, 25 °C): δ 7.56 (d), 7.37 (d), 7.65 (q aromatics); 6.05 (s, η^5-C*H*); 3.50−3.67 (m), 3.14−3.42 (m), 2.64−2.95 (m, N−CH_2CH$_3$); 2.38 (s), 2.19 (s), 2.12 (s, η^5-C−*Me*); 1.63 (s), 1.41 (s, C*Me*$_3$); 1.03 (t), 0.87 [t, $^3J(^1H-^1H) = 6.9$ Hz, N−CH$_2$*Me*]. ^{13}C NMR (C_6D_6, 25 °C): δ 170.4 (Hf−O−*C*); 141.2, 136.4, 135.1, 131.0, 130.5, 128.9, 128.8, 128.3, 127.3, 125.6, 125.0, 123.8, 123.2, 122.9 (unsaturated *C*); 94.2 (η^5-*C*H); 43.6, 43.1 (N−*C*H$_2$Me); 35.1, 34.5 (*C*Me$_3$); 32.1, 30.1 (C*Me*$_3$); 19.8, 19.5, 13.1 (η^5-C−*Me*); 16.0, 15.9 (N−CH$_2$*Me*).

Synthesis of [Ti(OC$_6$H$_2${η^5-IndMe$_4$-2,3,4,7}-2-Bu$^t_2$-4,6)-(NMe$_2$)Cl] (19). A flask was charged with 270 mg (1.3 mmol) of [(NMe$_2$)$_2$TiCl$_2$] and 50 mL of benzene. To this stirred mixture was added **7** in 20 mL of benzene. The reaction mixture immediately turned crimson red, and stirring was continued overnight. The red mixture was filtered over Celite and the solvent removed under vacuum to produce an orange-red solid. Upon standing in pentane, red crystals of diastereopure **19** were deposited on the sides of the flask (220 mg, 33%). X-ray diffraction analysis confirmed the configuration as the (*R*,p*R*)/(*S*,p*S*) isomers. Anal. Calcd for $C_{29}H_{40}ClNOTi$: C, 69.39; H, 8.03; N, 2.79. Found: C, 68.08; H, 8.16; N, 2.80. ^{1}H NMR (C_6D_6, 25 °C): δ 7.52 (d), 7.29 (d), 6.42 (q, aromatics); 2.59 (s, N*Me*$_2$); 2.62 (s), 2.33 (s), 2.05 (s), 2.02 (s, η^5-C−*Me*); 1.53 (s), 1.37 (s, C*Me*$_3$). ^{13}C NMR (C_6D_6, 25 °C): δ 173.5 (Ti−O−*C*); 144.5, 138.4, 134.2, 134.0, 133.3, 130.2, 130.1, 126.1, 124.8, 124.5, 122.7, 117.9 (unsaturated *C*); 46.8 (N*Me*$_2$); 35.2, 34.7 (*C*Me$_3$); 32.0, 30.0 (C*Me*$_3$); 21.7, 20.0, 14.5, 11.5 (η^5-C−*Me*).

Synthesis of [Ti(OC$_6$H$_2${η^5-Ind}-2-Bu$^t_2$-4,6)$_2$] (20). Method A. A sample of [Ti(NMe$_2$)$_4$] (110 g, 0.49 mmol) was dissolved in benzene. This mixture was stirred as **1** (320 mg, 1.0 mmol) dissolved in benzene was slowly added. The mixture was stirred for 3 h and then heated to 100 °C in an oil bath. After 2 days the black-red reaction mixture was evacuated to dryness, affording a glassy red solid. Addition of minimal pentane and standing undisturbed for days resulted in the formation of red crystals (50 mg, 22%). The solid-state structure of the isolated diastereomer established the epimeric (*R*,p*R*,p*S*)/(*S*,p*R*,p*S*) configuration. Anal. Calcd for $C_{46}H_{52}O_2Ti$: C, 80.68; H, 7.65. Found: C, 76.68; H, 7.69. ^{1}H NMR (C_6D_6, 25 °C): δ 6.83−7.56 (m, aromatics); 6.78 [d, $^3J(^1H-^1H) = 3.0$ Hz], 5.89 [d, $^3J(^1H-^1H) = 2.4$ Hz], 5.58 [d, $^3J(^1H-^1H) = 3.0$ Hz], 3.64 [d, $^3J(^1H-^1H) = 2.4$ Hz, η^5-CH_2]; 1.41 (s), 1.29 (s), 1.28 (s, C*Me*$_3$). ^{13}C NMR (C_6D_6, 25 °C): δ 177.0, 175.0 (Ti−O−*C*); 150.0, 144.7, 142.6, 142.1, 141.7, 139.0, 135.7, 135.4, 132.7, 130.8, 130.5, 130.0, 129.9, 129.3, 129.1, 128.6, 128.5, 127.7, 126.9, 126.5, 125.9, 125.8, 125.7, 125.3, 124.5, 124.4, 124.2, 123.9, 123.6, 123.5, 123.2, 122.8, 122.7, 122.4, 122.0, 121.4, 121.1, 118.9 (unsaturated *C*); 105.0, 98.2 (η^5-*C*H$_2$); 35.1, 34.6, 34.5 (*C*Me$_3$); 32.1, 32.0, 30.9, 30.0 (C*Me*$_3$).

Method B. To a stirred solution of TiCl$_4$ (0.50 g, 2.6 mmol) in 50 mL of benzene was added solid **6** (1.76 g, 5.3 mmol). The solution immediately turned deep red, and stirring was continued for 3 h. The crimson mixture was filtered over Celite and the solvent removed under vacuum. Dissolution of the glassy red solid in minimal pentane produced deep red crystals on standing for days (110 mg, 6.1%). ^{1}H NMR analysis revealed a product composition identical with that observed for method A.

Synthesis of [Zr(OC$_6$H$_2${η^5-Ind}-2-Bu$^t_2$-4,6)$_2$] (21). A sample of [Zr(NMe$_2$)$_4$] (0.5 g, 1.87 mmol) was dissolved in benzene. This solution was stirred vigorously as **1** (1.2 g, 3.75 mmol) dissolved in benzene was slowly added. This mixture was stirred for an additional 30 min and the solution evacuated to dryness, affording a glassy solid. Minimal pentane was added, and upon standing colorless crystals formed (0.5 g, 36%). The solid-state structure confirmed the configuration of the isolated diastereomer as the (*R*,p*R*,p*R*)/(*S*,p*S*,p*S*) enantiomers within the unit cell. Upon dissolution in $CDCl_3$ or C_6D_6, the formation of the (*S*,p*R*,p*R*)/(*R*,p*S*,p*S*) enantiomers was observed. Anal. Calcd for $C_{46}H_{52}O_2Zr$: C, 75.88; H, 7.20. Found: C, 75.80; H, 7.58. ^{1}H NMR [(*R*,p*R*,p*R*)/(*S*,p*S*,p*S*) enantiomers; $CDCl_3$, 30 °C]: δ 7.13−7.49 (m, aromatics); 6.76 [d, $^3J(^1H-^1H) = 3.2$ Hz], 5.43 [d, $^3J(^1H-^1H) = 3.4$ Hz, η^5-C$_5H_2$]; 1.31 (s), 1.20 (s, C*Me*$_3$). (C_6D_6, 30 °C): δ 6.79−7.40 (aromatics); 6.18 [d, $^3J(^1H-^1H) = 2.9$ Hz], 6.12 [d, $^3J(^1H-^1H) = 2.9$ Hz], 5.19 [d, $^3J(^1H-^1H) = 3.1$ Hz, η^5−C$_5H_2$]; 1.36 (s), 1.29 (s), 1.29 (s), 1.24 (s, C*Me*$_3$). ^{1}H NMR [(*S*,p*R*,p*R*)/(*R*,p*S*,p*S*) isomers; $CDCl_3$, 30 °C]: δ 6.99−7.48 (m, aromatics); 6.89 [d, $^3J(^1H-^1H) = 2.9$ Hz], 6.75 [d, $^3J(^1H-^1H) = 3.2$ Hz, η^5-C$_5H_2$]; 1.31 (s), 1.05 (s, C*Me*$_3$). ^{13}C NMR [(*R*,p*R*,p*R*)/(*S*,p*S*,p*S*)/(*S*,p*R*,p*R*)/(*R*,p*S*,p*S*) isomers; $CDCl_3$, 30 °C]: δ 171.5, 170.9 (Zr−O−*C*); 141.1, 141.0, 136.3, 135.2, 131.9, 130.0, 129.9, 128.3, 127.2, 127.1, 127.0, 126.3, 124.9, 124.8, 124.5, 124.2, 123.9, 123.8, 123.2, 122.9, 122.8, 121.8, 121.4, 115.2 (unsaturated *C*); 99.9, 96.6, 96.4 (η^5-*C*$_5$H$_2$); 34.7, 34.3, 34.2, 34.1 (*C*Me$_3$); 31.8, 31.8, 30.2, 29.2 (C*Me*$_3$). ^{13}C NMR (C_6D_6, 30 °C): δ 172.2, 171.5 (Zr−O−*C*); 141.8, 141.6, 136.7, 135.8, 132.5, 130.3, 130.2, 128.5, 127.3, 125.6, 125.4, 125.1, 125.0, 124.6, 124.2, 124.0, 123.6, 123.5, 123.3, 123.1, 122.0, 121.9, 115.5 (unsaturated *C*); 97.0, 96.9 (η^5-*C*$_5$H$_2$); 35.1, 34.5, 34.4 (*C*Me$_3$); 31.9, 29.6 (C*Me*$_3$).

Synthesis of [Hf(OC$_6$H$_2${η^5-Ind}-2-Bu$^t_2$-4,6)$_2$] (22). Method A. A flask was charged with HfCl$_4$ (1.6 g, 5.0 mmol) and 25 mL of benzene. This mixture was stirred as solid **6** (2.0 g, 6.0 mmol) was added. The mixture was stirred for 3 h and then evacuated to dryness. The crude material was extracted into pentane, the extract filtered over Celite, and the solvent removed to afford a yellow solid. Addition of minimal pentane and standing undisturbed for days resulted in the formation of colorless crystals (380 mg, 9.3%). X-ray diffraction analysis confirmed the stereochemistry of the enantiomers to have the (*R*,p*R*,p*R*)/(*S*,p*S*,p*S*) configurations. ^{1}H NMR analysis of the crude material also revealed the presence of the (*R*,p-*S*,p*S*)/(*S*,p-*R*,p*R*) isomer. Anal. Calcd for $C_{52}H_{58}O_2Hf$: C, 69.90; H, 6.54. Found: C, 69.79; H, 6.93. ^{1}H NMR [(*S*,p*S*,p*S*)/(*R*,p*R*,p*R*) isomers; C_6D_6, 25 °C]: δ 6.84−7.44 (m, aromatics); 5.03 [d, $^3J(^1H-^1H) = 3.3$ Hz, η^5-CH_2]; 1.38(s), 1.34 (s, C*Me*$_3$). ^{1}H NMR [(*S*,p*S*,p*S*)/(*R*,p*R*,p*R*) isomers; $CDCl_3$, 25 °C]: δ 7.25−7.56 (m, aromatics); 6.74 [d, $^3J(^1H-^1H) = 3.0$ Hz], 5.22 [d, $^3J(^1H-^1H) = 3.3$ Hz, η^5-CH_2]; 1.42 (s), 1.26 (s, C*Me*$_3$). ^{13}C NMR (C_6D_6, 25 °C): δ 169.6 (Hf−O−*C*); 141.7, 136.5, 129.0, 128.9, 128.5, 127.5, 126.7, 125.9, 124.9, 124.6, 124.5, 124.2, 124.1, 123.4, 123.3 (unsaturated *C*); 94.5 (η^5-*C*H$_2$); 35.0, 34.5 (*C*Me$_3$); 32.0, 29.6 (C*Me*$_3$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 169.1 (Hf−O−*C*); 141.0, 125.9, 128.3, 127.3, 126.4, 125.6, 124.8, 123.9, 123.8, 123.1, 122.9, 122.8 (unsaturated *C*); 94.5 (η^5-*C*H$_2$); 34.8, 34.5 (*C*Me$_3$); 32.0, 29.4 (C*Me*$_3$); ^{1}H NMR [(*R*,p*R*,p*S*)/(*S*,p*R*,p*S*) isomers; $CDCl_3$, 25 °C]: δ 7.15−8.07 (m, aromatics); 6.84 [d, $^3J(^1H-^1H) = 3.0$ Hz], 6.48 [d, $^3J(^1H-^1H) = 2.7$ Hz], 6.24 [d, $^3J(^1H-^1H) = 2.8$ Hz], 4.03 [d, $^3J(^1H-^1H) = 2.6$ Hz, η^5-CH_2)]; 1.49 (s), 1.47 (s), 1.45 (s), 1.19 (s, C*Me*$_3$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 172.1, 170.6 (Hf−O−*C*); 143.1, 141.2, 136.1, 128.6, 127.6, 126.9, 126.6, 125.8, 125.1, 124.6, 124.4, 124.1, 123.8, 123.4, 123.2, 123.1, 123.0, 122.4, 119.4, 118.1, 114.0, 113.3, 112.8, 112.7, 112.6, 112.1, 111.5, 111.2, 111.1, 110.9, 110.8, 110.7, 110.5, 110.3, 110.2, 110.0, 109.6, 106.6 (unsaturated *C*); 96.5, 91.9 (η^5-*C*H$_2$); 35.0, 34.7, 34.6 (*C*Me$_3$); 32.1, 30.4, 29.8 (C*Me*$_3$).

Method B. To a stirred solution of Hf(NEt$_2$)$_4$ (250 mg, 0.55 mmol) in toluene (50 mL) was added **1** (350 mg, 1.1 mmol) in 20 mL of toluene. The yellow solution was stirred overnight, followed by removal of the solvent under vacuum to produce a tan solid (330 mg, 74%). ^{1}H NMR analysis revealed a product composition identical with that observed from method A.

Synthesis of [Ti(OC$_6$H$_2${η^5-IndMe-2}-2-Bu$^t_2$-4,6)(OC$_6$H$_2$-{C$_9$H$_6$Me-2}-2-Bu$^t_2$-4,6)$_2$(NMe$_2$)] (23). To a stirred solution of [Ti(NMe$_2$)$_4$] (250 mg, 1.1 mmol) in toluene (50 mL) was slowly added a toluene solution of **2** (750 mg, 2.2 mmol). The solution was stirred overnight and then dried under vacuum

to give an orange-red solid. Dissolution in minimal pentane afforded red blocky crystals suitable for X-ray analysis on standing for days (150 mg, 17%). The solid-state structure confirmed the (*R*,a*S*,p*S*)/(*S*,a*R*,p*R*) configuration of the isolated isomer. Satisfactory microanalysis was not obtained. ^{1}H NMR (C_6D_6, 25 °C): δ 7.08−7.64 (m), 6.54−6.81 (m, aromatics); 5.78 (s), 5.61 (s, η^5-C*H*); 3.16−3.48 (m, CH_2); 2.97 (s), 2.45 (s, N*Me*$_2$); 2.27 (s), 2.01 (s), 2.00 (s, η^5-C−*Me*); 1.70 (s), 1.68 (s), 1.66 (s), 1.65 (s), 1.38 (s), 1.33 (s, C*Me*$_3$). ^{13}C NMR (C_6D_6, 25 °C): δ 172.9, 172.5, 163.4 (Ti−O−*C*); 148.4, 143.0, 141.9, 140.6, 129.2, 138.8, 135.2, 130.9, 127.3, 126.0, 125.6, 124.6, 124.2, 123.9, 123.7, 123.6, 123.3, 121.1 (unsaturated *C*); 102.7, 98.0 (η^5-*C*H); 47.3, 47.1 (N*Me*$_2$); 36.0, 35.5, 35.4, 34.6, 34.5 (*C*Me$_3$); 32.1, 32.0, 31.9, 31.3, 30.9, 30.8 (C*Me*$_3$); 23.7, 22.7, 15.8, 15.7, 14.2, 12.9 (η^5-C−*Me*).

Synthesis of [Ti(OC$_6$H$_2${η^5-IndMe-2}-2-Bu$^t_2$-4,6)$_2$] (24). In a Solv-Seal flask, a sample of **23** (300 mg, mmol) was dissolved in toluene. The solution was heated to 100 °C in an oil bath for 3 days. The black-green solution was dried under vacuum to produce a dark green solid. On standing in minimal pentane for days, dark green crystals were deposited (120 mg, 43%). ^{1}H NMR analysis of the crystals indicated a single diastereomer of either the (*S*,p*S*,p*S*)/(*R*,p*R*,p*R*) or (*R*,p*S*,p*S*)/(*S*,p*R*,p*R*) isomers. The configuration of the isolated diastereomer could not be established using X-ray diffraction. Satisfactory microanalysis was not obtained. ^{1}H NMR (C_6D_6, 25 °C): δ 7.71 (d), 7.39 (d), 7.29 (d), 7.03−7.07 (m), 6.89 (t, aromatics); 4.24 (s, η^5-C*H*); 2.18 (s, η^5-C−*Me*); 1.35 (s), 1.26 (s, C*Me*$_3$). ^{13}C NMR (C_6D_6, 25 °C): δ 172.8 (Ti−O−*C*); 142.6, 141.2, 133.2, 128.9, 127.4, 125.8, 125.0, 124.7, 123.9, 122.9, 122.7 (unsaturated *C*); 106.8 (η^5-*C*H); 34.8, 34.4 (*C*Me$_3$); 31.9, 29.6 (C*Me*$_3$); 16.6 (η^5-C−*Me*).

Synthesis of [Zr(OC$_6$H$_2${η^5-IndMe-2}-2-Bu$^t_2$-4,6)$_2$] (25). To a stirred solution of [Zr(NEt$_2$)$_4$] (320 mg, 0.84 mmol) in toluene (50 mL), was added a toluene solution of **2** (570 mg, 1.7 mmol). The yellow solution was stirred for 1 h at room temperature, followed by heating to 100 °C in an oil bath. Heating was continued overnight, producing an orange-yellow solution. Removal of the solvent under vacuum afforded a brown solid that was recrystallized from minimal pentane at room temperature (80 mg, 13%). The clear crystalline material was found to be a single diastereomer of either the (*S*,p*S*,p*S*)/(*R*,p*R*,p*R*) or (*R*,p*S*,p*S*)/(*S*,p*R*,p*R*) configurations, as indicated by ^{1}H NMR analysis. The ^{1}H NMR spectrum of the pentane filtrate revealed the presence of the two other diastereomers. Anal. Calcd for $C_{48}H_{56}O_2Zr$: C, 76.24; H, 7.46. Found: C, 75.91; H, 7.41. ^{1}H NMR (isolated diastereomer; $CDCl_3$, 25 °C): δ 7.03−7.57 (aromatics); 4.93 (s, η^5-C*H*); 2.24 (s, η^5-C−*Me*); 1.31 (s), 1.15 (s, C*Me*$_3$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 169.4 (Zr−O−*C*); 141.7, 140.7, 139.2, 135.0, 128.3, 127.2, 126.5, 125.6, 124.8, 124.6, 124.4, 124.3, 124.1, 123.5, 123.3, 122.9, 122.6, 119.9 (unsaturated *C*); 99.1 (η^5-*C*H); 34.5, 34.2 (*C*Me$_3$); 31.7, 29.3 (C*Me*$_3$); 15.0 (η^5-C-*Me*). ^{1}H NMR (other isomers; $CDCl_3$, 25 °C): δ 8.07 (d), 7.00−7.65 (m, aromatics); 5.90 (s), 4.17 (s, η^5-C*H*); 2.33, 2.32, 2.18 (η^5-C−*Me*); 1.47 (s), 1.45 (s), 1.40 (s), 1.39 (s, C*Me*$_3$). ^{13}C NMR (C_6D_6, 25 °C): δ 172.4, 171.1, 171.3 (Zr−O−*C*); 149.3, 145.9, 143.8, 142.7, 141.7, 141.4, 141.2, 141.1, 140.7, 139.2, 136.8, 136.3, 136.1, 135.9, 135.0, 134.8, 131.7, 130.6, 130.4, 130.2, 129.3, 128.1, 127.5, 127.2, 126.7, 126.6, 126.5, 126.4, 126.3, 125.5, 125.3, 125.2, 124.8, 124.6, 124.4, 124.2, 124.0, 123.9, 123.8, 123.5, 123.3, 123.0, 122.9, 122.7, 122.6, 121.8, 121.5, 121.1, 120.6, 119.9 (unsaturated *C*); 101.4, 96.7, 96.6 (η^5-*C*H); 34.7, 34.8, 34.4 (*C*Me$_3$); 31.9, 31.8, 30.2, 29.7 (C*Me*$_3$); 14.2, 14.1, 12.8 (η^5-C-*Me*).

Synthesis of [Hf(OC$_6$H$_2${η^5-IndMe-2}-2-Bu$^t_2$-4,6)$_2$] (26). Using a procedure identical with that for **25**, 410 mg (0.88 mmol) of Hf(NEt$_2$)$_4$ was reacted with 590 mg (1.8 mmol) of **2**. Dissolution of the tan crude material in minimal pentane produced a white crystalline powder (60 mg, 8.1%). ^{1}H NMR analysis of the recrystallized material indicated a single diastereomer of the (*S*,p*S*,p*S*)/(*R*,p*R*,p*R*) or (*R*,p*S*,p*S*)/(*S*,p*R*,p*R*) isomers. The pentane filtrate was found to contain a mixture of the isolated diastereomer as well as the (*S*,p*R*,p*S*)/(*R*,p*R*,p*S*) isomer. Anal. Calcd for $C_{48}H_{56}O_2Hf$: C, 68.35; H, 6.69. Found: C, 68.52; H, 6.46. ^{1}H NMR (isolated diastereomer; $CDCl_3$, 25 °C): δ 7.77 (d), 7.53 (d), 7.44 (t), 7.16 (d), 7.11 (d, aromatics); 4.78 (s, η^5-C*H*); 2.37 (s, η^5-C−*Me*); 1.36 (s), 1.15 (s, C*Me*$_3$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 167.6 (Hf−O−*C*); 140.5, 138.4, 135.7, 127.4, 124.3, 123.7, 123.4, 123.3, 123.0, 122.7, 121.1 (unsaturated *C*); 96.8 (η^5-*C*H); 34.4, 34.2 (*C*Me$_3$); 31.7, 29.2 (C*Me*$_3$); 15.2 (η^5-C−*Me*). ^{1}H NMR (other isomers; $CDCl_3$, 25 °C): δ 8.06 (d), 7.78 (d), 6.97−7.59 (m, aromatics); 5.86 (s), 4.15 (s, η^5-C*H*); 2.40 (s), 2.19 (s, Ind−*Me*); 1.47 (s), 1.41 (s), 1.40 (s), 1.19 (s, C*Me*$_3$). ^{13}C NMR (C_6D_6, 25 °C): δ 171.5, 170.1 (Hf−O−*C*); 143.8, 141.7, 141.3, 141.1, 141.0, 140.5, 138.3, 137.2, 137.0, 136.9, 135.8, 135.7, 130.0, 129.3, 128.8, 128.1, 127.8, 127.4, 127.0, 126.7, 126.5, 126.3, 125.6, 124.7, 124.6, 124.4, 124.3, 123.9, 123.7, 123.6, 123.4, 123.3, 123.1, 123.0, 122.7, 122.0, 121.8, 121.8, 121.3, 121.1, 119.9 (unsaturated *C*); 98.9, 94.3 (η^5-*C*H); 34.7, 34.6, 34.3, 34.1 (*C*Me$_3$); 31.9, 31.8, 30.3, 29.7 (C*Me*$_3$); 14.2, 14.0 (η^5-C-*Me*).

Synthesis of [Zr(OC$_6$H$_2${η^5-IndMe$_2$-2,3}-2-Bu$^t_2$-4,6)$_2$] (27). To a stirred solution of Zr(NEt$_2$)$_4$ (380 mg, 1.0 mmol) in xylenes (50 mL) was added a xylene solution of **3** (700 mg, 2.0 mmol). The yellow solution was stirred for 1 h at room temperature, followed by heating to 150 °C in an oil bath overnight. The chartreuse solution was dried under vacuum to produce a yellow-green solid. Rinsing of the crude material with pentane produced a white powder (120 mg, 15%). ^{1}H NMR analysis of the powder revealed enrichment of a single diastereomer. Slow evaporation of the pentane filtrate produced clear platelets suitable for X-ray diffraction analysis. The solid-state structure of the isolated diastereomer confirmed the epimeric (*S*,p*R*,p*S*)/(*R*,p*S*,p*R*) configuration. ^{1}H NMR analysis of the isolated diastereomer revealed the presence of the (*S*,p*R*,p*S*)/(*R*,p*S*,p*R*) and (*S*,p*S*,p*S*)/(*R*,p*R*,p*R*) isomers upon dissolution in $CDCl_3$. The pentane filtrate was found to contain a mixture of the (*R*,p*S*,p*S*)/(*S*,p*R*,p*R*) and (*S*,p*S*,p*S*)/(*R*,p*R*,p*R*) diastereomers. Suitable microanalysis was not obtained. ^{1}H NMR [(*R*,p*R*,p*S*)/(*S*,p*R*,p*S*) isomers; C_6D_6, 25 °C]: δ 6.78−7.52 (m, aromatics); 2.20 (s), 2.00 (s), 1.69 (s), 1.60 (s, η^5-C−*Me*); 1.50 (s), 1.39 (s), 1.34 (s), 1.32 (s, C*Me*$_3$). ^{13}C NMR (C_6D_6, 25 °C): δ 171.8, 171.5 (Zr−O−*C*); 141.6, 141.5, 139.3, 139.1, 136.3, 136.1, 135.9, 130.3, 128.6, 127.5, 126.4, 125.7, 125.6, 125.5, 125.4, 124.9, 124.7, 124.4, 124.3, 124.2, 124.0, 123.8, 123.7, 123.6, 123.5, 123.2, 123.1, 122.7, 122.3, 122.1, 121.4, 120.3 (unsaturated *C*); 106.1, 105.8 (η^5-*C3*); 35.1, 34.5, 34.4 (*C*Me$_3$); 32.1, 30.3, 30.2 (C*Me*$_3$); 10.9, 9.6, 9.4 (η^5-C-*Me*). ^{1}H NMR [(*S*,p*S*,p*S*)/(*R*,p*R*,p*R*)/(*R*,p*S*,p*S*)/(*S*,p*R*,p*R*) isomers; $CDCl_3$, 25 °C]: δ 7.77 (d), 6.88−7.51 (m, aromatics); 2.33 (s), 2.16 (s), 1.87 (s), 1.85 (s, η^5-C-*Me*); 1.38 (s), 1.35 (s), 1.32 (s), 1.11 (s, C*Me*$_3$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 171.2, 170.9 (Zr−O−*C*); 140.9, 129,0, 134.6, 134.3, 128.3, 127.1, 126.0, 125.5, 125.0, 124.9, 124.2, 123.9, 123.7, 123.6, 123.4, 123.2, 122.9, 122.6, 122.1, 122.0, 121.7, 121.2, 120.0 (unsaturated *C*); 106.0, 104.8 (η^5-*C*H); 34.8, 34.7, 34.2 (*C*Me$_3$); 31.8, 29.9, 29.8, 29.6 (C*Me*$_3$); 12.9, 10.8, 9.8, 9.3, 8.3 (η^5-C−*Me*).

Synthesis of [Hf(OC$_6$H$_2${η^5-IndMe$_2$-2,3}-2-Bu$^t_2$-4,6)$_2$] (28). Using a procedure identical with that for **27**, 340 mg (0.73 mmol) of Hf(NEt$_2$)$_4$ was reacted with 510 mg (1.5 mmol) of **3**. Rinsing of the yellow-green solid with pentane resulted in enrichment of a single diastereomer, as determined by ^{1}H NMR spectroscopy. Slow evaporation of the pentane solution produced chartreuse blocks that were analyzed by X-ray diffraction (170 mg, 27%). The solid-state structure of the isolated diastereomer revealed an epimeric (*S*,p*R*,p*S*)/(*R*,p*R*,p*S*) configuration. Upon dissolution in $CDCl_3$, the isolated diastereomer rapidly interconverts (NMR time scale) with either the (*R*,p*S*,p*S*)/(*S*,p*R*,p*R*) or the (*S*,p*S*,p*S*)/(*R*,p*R*,p*R*) isomer. Suitable microanalysis was not obtained. ^{1}H NMR [(*R*,p*R*,p*S*)/(*S*,p*R*,p*S*) diastereomer; $CDCl_3$, 25 °C]: δ 7.88 (d), 6.78−7.52 (m, aromatics); 2.45 (s), 2.30 (s), 2.25 (s), 2.20 (s, η^5-C−*Me*);

Table 4. Crystal Data and Data Collection Parameters

	8	**9**	**10**	**11**	**12**
formula	$C_{27}H_{38}N_2OTi$	$C_{27}H_{38}N_2OZr$	$C_{31}H_{46}N_2OHf$	$C_{28}H_{40}N_2OTi$	$C_{32}H_{48}N_2OZr$
formula wt	454.52	497.84	641.22	468.54	567.97
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	Cc (No. 9)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a, Å	12.4594(3)	12.9534(3)	9.1508(2)	11.6188(3)	10.1052(2)
b, Å	11.7575(3)	14.0719(4)	24.6001(6)	14.2531(4)	13.8334(3)
c, Å	18.0226(4)	15.2631(4)	13.8974(3)	17.6305(5)	21.8681(5)
α, deg	90	96.9498(9)	90	71.2896(1)	90
β, deg	108.173(1)	109.842(1)	106.847(1)	81.265(1)	99.4331(9)
γ, deg	90	91.895(1)	90	79.759(2)	90
V, Å^3	2508.5(2)	2589.5(2)	2994.2(2)	2707.2(2)	3015.6(2)
Z	4	4	4	4	4
ρ_{calcd}, g cm^{-3}	1.203	1.277	1.422	1.150	1.251
temp, K	150	150	150	150	150
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
R	0.041	0.053	0.026	0.064	0.045
R_w	0.099	0.136	0.062	0.162	0.098

	13	**14**	**16**	**19**	**20**
formula	$C_{32}H_{48}N_2OHf$	$C_{29}H_{42}N_2OTi$	$C_{30}H_{44}N_2OTi$	$C_{29}H_{40}ClNOTi$	$C_{46}H_{52}O_2Ti$
formula wt	655.24	482.57	496.60	502.00	684.83
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$Pbca$ (No. 61)
a, Å	10.089(1)	10.0202(2)	10.6409(4)	23.9152(4)	11.9710(2)
b, Å	13.8166(2)	13.0802(3)	11.8465(4)	9.7407(2)	34.4852(3)
c, Å	21.8999(3)	22.0926(4)	12.2321(6)	11.7799(2)	18.4918(6)
α, deg	90	90	106.792(1)	90	90
β, deg	99.5791(6)	102.311(1)	95.645(1)	94.985(1)	90
γ, deg	90	90	104.847(2)	90	90
V, Å^3	3010.0(1)	2829.0(2)	1401.9(2)	2733.8(2)	7633.8(4)
Z	4	4	2	4	8
ρ_{calcd}, g cm^{-3}	1.446	1.133	1.176	1.220	1.192
temp, K	150	150	150	150	150
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
R	0.056	0.061	0.042	0.037	0.050
R_w	0.137	0.160	0.100	0.095	0.105

	21	**22**	**23**	**27**	**28**
formula	$C_{52}H_{58}O_2Zr$	$C_{52}H_{58}O_2Hf$	$C_{50}H_{63}NO_2Ti$	$C_{50}H_{60}O_2Zr$	$C_{50}H_{60}O_2Hf$
formula wt	806.26	893.53	757.97	784.25	871.52
space group	$C2/c$ (No. 15)	$C2/c$ (No. 15)	P$\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	14.3043(4)	14.2854(3)	10.0835(3)	13.0989(8)	13.010(1)
b, Å	10.7900(5)	10.8175(3)	13.4228(4)	15.6376(9)	15.570(2)
c, Å	28.522(1)	28.2331(7)	17.0315(5)	20.6633(13)	20571(3)
α, deg	90	90	78.647(1)	90	90
β, deg	97.875(3)	98.152(1)	88.126(1)	97.936(2)	97.576(5)
γ, deg	90	90	72.648(1)	90	90
V, Å^3	4360.7(5)	4318.8(3)	2156.4(2)	4192.0(8)	4137.0(2)
Z	4	4	2	4	4
ρ_{calcd}, g cm^{-3}	1.228	1.374	1.167	1.243	1.399
temp, K	203	150	150	150	150
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
R	0.055	0.040	0.046	0.058	0.053
R_w	0.132	0.071	0.107	0.137	0.104

1.36 (s), 1.31 (s), 1.26 (s), 1.08 (s, CMe_3). ^{13}C NMR ($CDCl_3$, 25 °C): δ 168.4, 167.9 (Hf−O−*C*); 103.4, 102.4 (η^5-*C3*); 140.9, 140.8, 140.6, 138.5, 138.3, 136.2, 136.1, 128.9, 128.4, 125.5, 125.1, 124.5, 124.3, 124.2, 124.0, 123.9, 123.8, 123.5, 123.2, 122.9, 122.7, 122.6, 122.4, 122.0, 121.7, 121.3, 120.7, 120.0 (unsaturated *C*); 34.6, 34.5, 34.2 (*C*Me_3); 31.8, 29.6 (C*Me*$_3$); 13.2, 10.9, 10.2, 9.7 (η^5-C-*Me*). ^{1}H NMR [(*R*,p*S*,p*S*)/(*S*,p*R*,p*R*)/(*R*,p*S*,p*S*)/(*S*,p*R*,p*R*) isomers; $CDCl_3$, 25 °C]: δ 6.80−7.47 (m, aromatics); 2.22, 1.83 (s, η^5-C−*Me*); 1.34 (s), 1.27 (s, C*Me*$_3$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 169.5 (Hf−O−*C*); 102.4 (η^5-*C3*); 140.8, 138.5, 136.1, 125.1, 124.5, 124.3, 124.2, 123.9, 123.8, 123.5, 123.2, 122.9, 122.6, 122.4, 122.0, 121.7 (unsaturated *C*); 34.5, 34.2 (*C*Me_3); 31.8, 29.6 (C*Me*$_3$); 13.0, 8.1 (η^5-C−*Me*).

X-ray Data Collection and Reduction. Crystal data and data collection parameters are contained in Table 4. A suitable crystal was mounted on a glass fiber in a random orientation under a cold stream of dry nitrogen. Preliminary examination and final data collection were performed with Mo Kα radiation (λ = 0.710 73 Å) on a Nonius Kappa CCD. Lorentz and polarization corrections were applied to the data.[26] An empirical absorption correction using SCALEPACK was applied.[27] Intensities of equivalent reflections were averaged. The structure was solved using the structure solution program PATTY in DIRDIF92.[28] The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The structure was refined in full-matrix least squares, where the function minimized was $\sum w(|F_o|^2 - |F_c|^2)^2$ and the weight w is defined as $w = 1/[\sigma^2(F_o^2) + (0.0585P)^2 + 1.4064P]$, where $P = (F_o^2 + 2F_c^2)/3$. Scattering

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factors were taken from ref 29. Refinement was performed on a AlphaServer 2100 using SHELX-97.[30] Crystallographic drawings were done using ORTEP programs.[31]

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Supporting Information Available: Tables giving X-ray crystallographic data for **8**−**14**, **16**, **19**−**23**, **27**, and **28**. This material is available free of charge via the Internet at http://pubs.acs.org.

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