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Linear Trimer Analogues of Calixarene as Chiral Coordinating Ligands: X-ray Crystallographic and NMR Spectroscopic Characterization of Chiral and Achiral Trisphenolates Complexed to Titanium(IV) and Aluminum(III)

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Achiral and chiral linear trisphenol analogues of calixarene ($HOArCH_2Ar'(OH)$**C**$(R)HArOH$, Ar = 4,6-di-*tert*-butylphenyl; Ar′ = 4-*tert*-butylphenyl; R = H (achiral), Me (chiral)) were prepared in anticipation of their adoption of a chiral conformation upon coordination to Lewis acidic metal centers. The trisphenols react with 1 equiv of $Ti(OR')_4$ (R′ = *i*-Pr or *t*-Bu) to yield complexes with molecular formula $Ti_2(OArCH_2Ar'(O)$**C**$(R)HArO)_2(OR')_2$ (R = H, Me; R′ = *i*-Pr or *t*-Bu). An X-ray crystal structure of the titanium complex of the achiral trisphenol (R = H; R′ = *t*-Bu) reveals that the trisphenolate ligand adopts an unsymmetrical (and therefore chiral) conformation, with η^2-coordination to one metal center and η^1-coordination to the second metal center. The chiral trisphenol, which contains a stereogenic center (indicated as **C** in the shorthand notation used above), coordinates titanium in an analogous fashion to produce only one diastereomer (out of four possible); therefore, the configuration of the stereogenic center controls the conformation adopted by the bound ligand. The reaction of achiral trisphenol with $AlMe_3$ produces a compound with molecular formula $Al_2(OArCH_2Ar'(O)CH_2ArO)_2$. ^1H NMR spectroscopy and X-ray crystallography reveal that the trisphenolate ligand adopts an asymmetric, C_2 conformation in this complex, where the central phenolate oxygen bridges the aluminum centers and the terminal phenolate oxygens each coordinate a separate aluminum center. Because these trisphenolate ligands adopt chiral conformations when coordinated to metal centers, they may be useful for developing diastereo- or enantioselective catalysts and reagents.

One of the central challenges in chemistry is to understand and control the selectivity of organic transformations, such as carbon−carbon bond forming or polymerization reactions. Much effort has focused on developing new alkoxide and aryloxide ligands for titanium or aluminum, in order to generate more selective reagents that can be used to promote carbon−carbon bond forming reactions.[1,2] Highly enantioselective reagents have been prepared from metal complexes of tartrate,[3] binaphthol,[4] or phenolate-Schiff base[5] derivatives. Excellent chemo- and stereoselectivities using sterically hindered aluminum phenolates for a variety of carbonyl addition reactions have been demonstrated.[2] In addition,

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titanium and zirconium complexes of sterically congested bidentate aryloxides are stereoselective catalysts for α-olefin polymerization.[6] These examples demonstrate that it is important to develop new chiral ligands that are sterically congested at the metal center, so that they both increase the reactivity (by forming monomeric, unsaturated metal complexes) and increase the selectivity (by controlling substrate approach).

We have begun to investigate the synthesis and coordination properties of trisphenols (**1a**,**b**, Figure 1A), linear analogues of the macrocyclic calixarenes,[7] which we predicted would coordinate metal centers in an asymmetric fashion to yield stereoselective reagents. Calixarene complexes of metals such as titanium,[8] zirconium,[8c,9] and aluminum[10] possess cavities or pockets that are bordered by phenol substituents and are capable of binding small molecules or ligands. In particular, 4-*tert*-butylcalix[8]arene wraps around two titanium or zirconium centers to form two asymmetric cavities, and generates preferentially one diastereomeric complex when chiral alcoholate ligands are bound in the cavities (10:1 ratio of diastereomers).[8d] We envisioned that trisphenols **1a**,**b** would also bind metals in an asymmetric fashion because a steric interaction between the terminal ortho substituents would prevent the ligand from adopting a symmetrical partial-basket conformation (Figure 1B). We also anticipated that steric congestion from the *tert*-butyl groups would prevent oligomerization and subsequent coordinative saturation at the metal center. Another feature of the trisphenol that we wanted to exploit was its potential for preparation in chiral form (e.g., **1b**, Figure 1A). Chiral trisphenols are promising ligands for preparing enantio- or stereoselective Lewis acid reagents for carbonyl addition or polymerization reactions. In addition, we expect that they

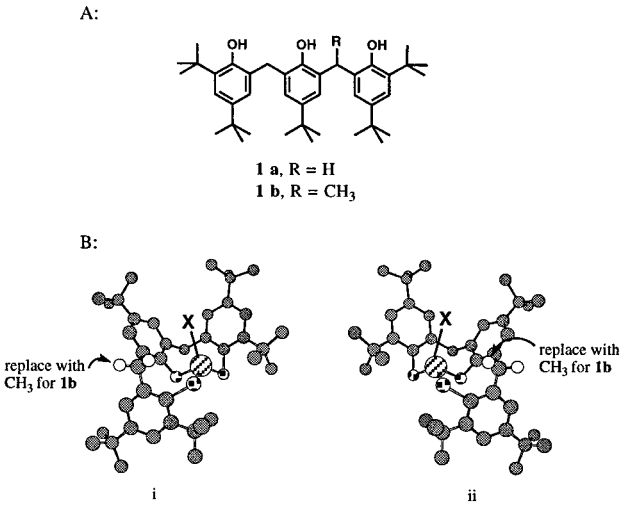

Figure 1. (A) Structures of linear trisphenols. (B) Proposed asymmetric coordination of titanium(IV) by trisphenol ligand (X = O-*t*-Bu, O-*i*-Pr). If R = H, isomers i and ii are enantiomers; if R = CH_3, i and ii are diastereomers. In this case, i would be preferred, due to the steric interaction of the methyl group with the titanium in ii.

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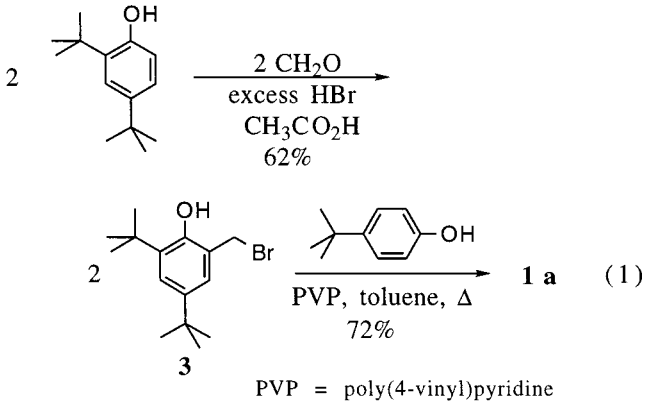
will have broader applications as coordinating ligands for a variety of other metals or chiral organic species.

Our immediate goals were to prepare linear trisphenols (**1a**,**b**) and their complexes with titanium and aluminum, and to determine the three-dimensional structure adopted by the trisphenolate ligands when coordinated to these metals. It was important to us to prepare complexes that were asymmetric and coordinatively unsaturated at the metal center, in order to exploit their reactivity in organic synthesis. Furthermore, we wanted to determine if the conformation of the *chiral* trisphenol (**1b**), upon coordinating a metal center, was controlled by the configuration at the stereogenic center. We postulated that the sterically larger methyl group introduced at the benzylic position would preferentially orient away from the metal center, thereby providing the means for achieving this control (Figure 1B). In this paper, we describe the synthesis of achiral and chiral trisphenols (**1a**,**b** (as the racemate)) and their complexes with titanium(IV) and aluminum(III). We show that the trisphenols adopt chiral conformations upon coordinating titanium or aluminum, that the titanium remains coordinatively unsaturated in complexes with trisphenol, and that the conformation adopted by the chiral trisphenol when coordinated to titanium is controlled by the configuration at the stereogenic center, according to our hypothesis.

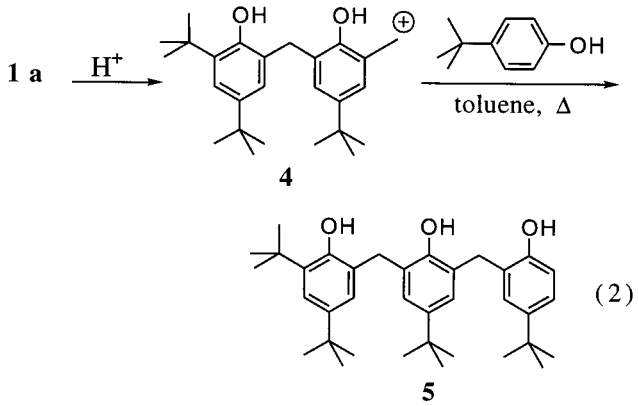
Synthesis of Achiral Trisphenol

Achiral trisphenol **1a** is easily prepared in two steps from commercially available starting materials, using a procedure modified from the literature (eq 1).[11] We found that use of



(1)

poly(4-vinylpyridine) (PVP) as a scavenger for the HBr produced in the second step prevented the formation of minor quantities of higher oligomers, thereby facilitating the purification and improving the yield of **1a**. Presumably, the higher oligomers form via an acid-catalyzed retro-Friedel−Crafts reaction that breaks apart the trisphenol in the opposite fashion to generate a resonance-stabilized benzylic carbocation on the central phenol (**4**, eq 2). This species could then couple with another 4-*tert*-butyl phenol to generate the unsymmetrical trisphenol (**5**), which could then be capped

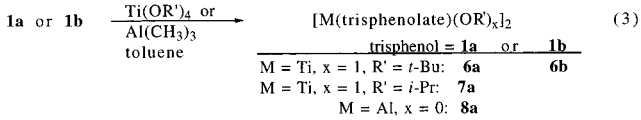


(2)

by **3** or another species such as **4** to yield the tetrakisphenol or higher polyphenols (eq 2). Alternative preparations of trisphenol **1a**[12a] and analogues of **1a**[12b] have been reported; our method is useful because it can be modified for preparing chiral versions of this ligand (e.g., **1b**, vide infra). Compound **3** has also been prepared previously via a two-step procedure.[13]

Titanium Complexes of Achiral Trisphenol

Complexes of **1a** with titanium were prepared by addition of Ti(OR′)$_4$ (R′ = *t*-Bu, *i*-Pr) to 1 equiv of trisphenol **1a**, yielding Ti$_2$(trisphenolate)$_2$(OR′)$_2$ (**6a**, **7a**, R′ = *t*-Bu, *i*-Pr, eq 3). The titanium complexes appear to have identical



(3)

structures, with the exception of the R′ group, according to ^{1}H NMR spectroscopy. Both titanium complexes form as a mixture of two predominant isomers, one of which is favored at room temperature in a solution of benzene, chloroform, THF, or pentane (the major isomer). ^{1}H NMR spectra of these compounds indicate that the trisphenolate ligand is in an unsymmetrical conformation because the benzylic hydrogens resonate as four separate doublets. Recrystallization of compound **6a** results in isomer mixtures of varying composition, with the *minor* isomer present in higher proportion than is observed in the solution equilibrium. We believe that the isomers interconvert readily in solution, and that the minor isomer crystallizes preferentially. When a pure sample of the minor isomer of **6a** (obtained after several recrystallization steps) is dissolved in benzene-d_6 and monitored over time by ^{1}H NMR spectroscopy, it eventually converts to a mixture in which the major isomer is preferred in a 10:1 ratio (see Figure 2). The major isomer of compound **7a** can be precipitated with pentane from the crude reaction product residue; however, we have been unsuccessful in

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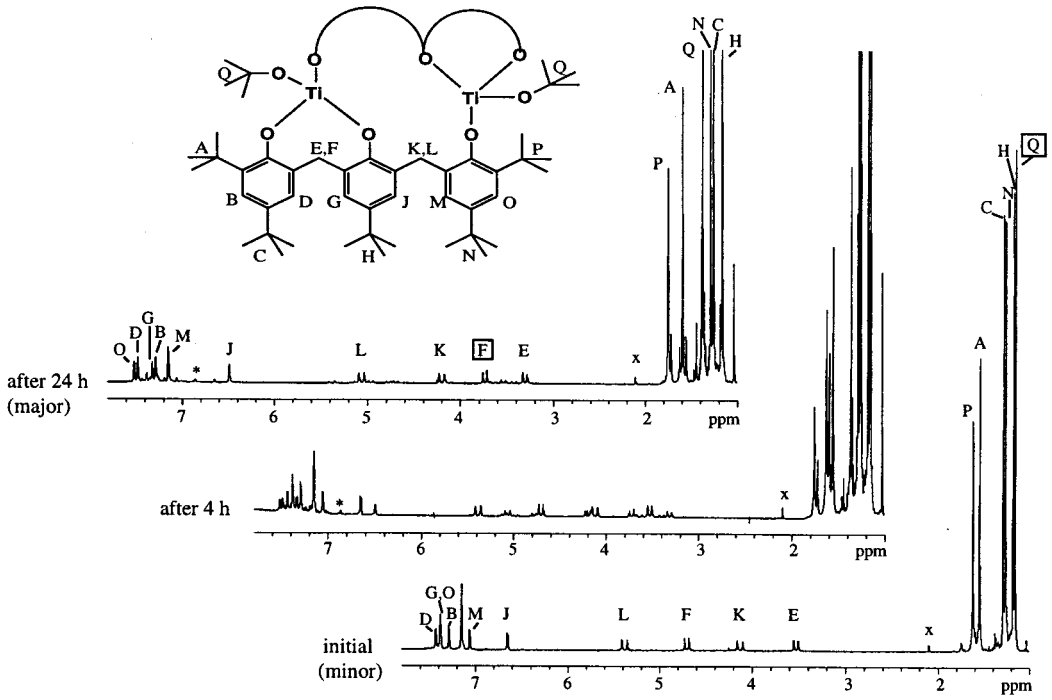

Figure 2. ^{1}H NMR spectra of **6a** (C_6D_6). Bottom: Initial sample of pure minor isomer. Middle: Sample after 4 h at room temperature. Top: Sample after 24 h at room temperature (primarily major isomer). Labels are according to diagram, determined by two-dimensional NMR spectroscopy. Signals labeled with an asterisk (∗) are due to Ti_2(trisphenoxide)$_2$O, and those labeled with x are due to toluene.

obtaining single crystals suitable for X-ray diffraction of either isomer of **7a** by recrystallization. In contrast, we were able to obtain single crystals of the minor isomer of **6a**, suitable for X-ray diffraction studies; therefore, we focused on compound **6a** for further study.

A crystal structure of the minor isomer of **6a** shows that the complex is a dimer, with inversion symmetry relating the trisphenolate ligands, the *tert*-butoxide ligands, and the titanium centers with one another, respectively (Figure 3A; crystal data and selected bond distances and angles are in Tables 1 and 2). Two phenolate oxygens of the tridentate ligand are coordinated to one titanium center, and the third phenolate oxygen coordinates the second titanium center, resulting in an overall asymmetric conformation adopted by the ligand. Surprisingly, the central phenolate oxygen does not bridge the two metal centers and the titanium center remains tetracoordinate, with O−Ti−O bond angles ranging from 107° to 112°. Thus, the electron deficient metal does not gain electron density by expanding its coordination number upon dimerization. This is unusual for titanium alkoxide or aryloxide dimer structures, which commonly have bridging oxygens that serve to increase the coordination number at titanium.[14] However, the Ti−O−C(phenolate) bond angles (143−154°) in the complex are indicative of substantial π-donation from the oxygens to the metal,[15] and this appears to prevent a single trisphenolate from simultaneously coordinating one titanium center by all three oxygens. The crystal structure makes clear why the four benzylic hydrogens are magnetically inequivalent, since the two methylene bridges are of two different types. The "straddle" methylene group links rings 2 and 3 and spans the two metal centers, and the "nonstraddle" methylene group links phenolates 1 and 2, which are coordinated to the same titanium center (Figure 3B). In addition, the two hydrogens at each methylene carbon are inequivalent, since one hydrogen points toward the metal center (the "downfield" hydrogen, vide infra), and one hydrogen points toward the aromatic hydrogens (the "upfield" hydrogen, vide infra, Figure 3B).

The solution structure of **6a** has been investigated using two-dimensional ^{1}H NMR spectroscopy. Both isomers of **6a** have very similar ^{1}H NMR spectra (C_6D_6), including features such as an upfield-shifted aromatic proton resonance at either 6.5 (major isomer) or 6.6 (minor isomer) ppm, four benzylic proton resonances from 3.3 to 5.4 ppm (vide supra), and six *tert*-butyl proton resonances from 0.9 to 1.5 ppm (Figure 2). Two-dimensional COSY and NOESY experiments were performed with the major isomer of **6a** at room temperature, enabling us to assign each of the resonances in the ^{1}H NMR spectrum. The COSY spectrum indicated which aromatic resonances were paired in the same ring (cross peaks were observed for the four-bond coupling between aromatic

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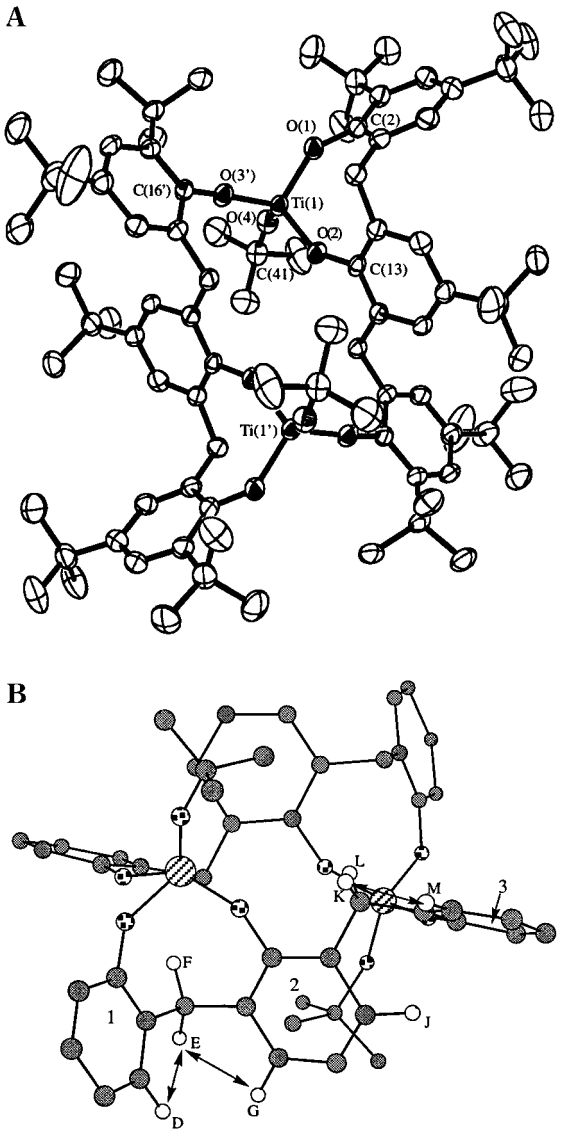


Figure 3. (A) An ORTEP representation (50% probability) of the crystal structure of the minor isomer of **6a**. Carbons are unshaded. Hydrogen and disordered *tert*-butyl carbon atoms are removed for clarity. Labeling is according to the distances and angles listed in Table 2. The inversion center is located between the two titanium centers. (B) Chem3D representation of the crystal structure of the minor isomer of **6a** with *tert*-butyl substituents on the aromatic rings removed for clarity. Benzylic and some aromatic hydrogens are shown in half of the structure. Labeling of the aromatic rings (1−3) and hydrogens (D−M) is according to the discussion in the text. See Figure 2 for NMR chemical shift assignments of these hydrogens. Double-headed arrows connect hydrogens that show NOE cross peaks in the NOESY spectrum.

hydrogens) and which benzylic resonances were due to protons attached to the same carbon. The results showed that each methylene carbon has an upfield and a downfield hydrogen associated with it. This is consistent with ^{1}H NMR data from dititanacalix[8]arenes.[8d]

The NOESY spectrum enabled us to link the *tert*-butyl resonances with the aromatic rings, by revealing cross peaks between the *tert*-butyl groups and the aromatic protons (Figure 4A). We were also able to connect the aromatic rings in order, by analyzing cross peaks between the benzylic methylene groups and the aromatic rings (Figure 4B). Only the upfield methylene resonances from each pair show cross peaks with the aromatic protons. Therefore, the upfield resonances are the ones that direct away from the metal center and toward the aromatic hydrogens. The *tert*-butyl resonance that has no NOE cross peaks with resonances from the trisphenolate ligand was assigned as that due to the *tert*-butoxide group. The combined information from both two-dimensional experiments provided a means for assigning each proton resonance relative to its neighbors in the trisphenolate

Table 1. Summary of X-ray Crystallographic Data

	[Ti(trisphenolate)(O-*t*-Bu)]$_2$ (**6a**)	[Al(trisphenolate)]$_2$ (**8a**)
formula	$C_{116}H_{184}O_{15}Ti_2$[a]	$C_{54}H_{71}AlO_3$[b]
cryst color, habit	colorless block	colorless multifaceted block
cryst size, mm^3	0.34 × 0.27 × 0.22	0.55 × 0.35 × 0.18
cryst syst	triclinic	orthorhombic
space group	$P\bar{1}$	*Pbcn*
unit cell		
a, Å	14.688(2)	23.311(2)
b, Å	15.470(2)	20.250(2)
c, Å	15.872(2)	23.093(2)
α, deg	117.321(1)	90
β, deg	108.001(2)	90
γ, deg	99.821(2)	90
V, Å^3	2831.5 (4)	10901 (2)
Z	1	8
fw	1914.43	795.09
D_{calcd}, Mg/m^3	1.123	0.969
μ, mm^{-1}	0.200	0.073
F(000)	1044	3456
diffractometer	Bruker SMART Platform CCD	Siemens SMART Platform CCD
λ(Mo Kα (graphite)), Å	0.71073	0.71073
T, K	173(2)	173(2)
θ range, deg	1.53−27.51	1.33−25.04
index ranges	$-18 \le h \le 18$ $-20 \le k \le 20$ $-20 \le l \le 19$	$0 \le h \le 27$ $0 \le k \le 24$ $0 \le l \le 27$
total no. of data	25238	53253
indep reflns	12507 (R_{int} = 0.0548)[c]	9628 (R_{int} = 0.0440)[c]
syst used	SHELXTL-V5.0	SHELXTL-V5.0
weighting scheme[d] (*a*, *b*)	*a* = 0.1204, *b* = 0	*a* = 0.1052, *b* = 2.7351
abs corrn	SADABS (Sheldrick, 1999)	SADAB (Sheldrick, 1996)
no. of obsd data ($I > 2\sigma(I)$)	6526	6828
no. of restraints	144	182
no. of params	686	634
R^e ($I > 2\sigma(I)$)	0.0705	0.0623
wR2[f] ($I > 2\sigma(I)$)	0.1785	0.1775
GOF on F^2 [g]	0.936	1.100
largest diff peak and hole, e Å^{-3}	0.671, −0.769	0.338, −0.255

[a] Includes 7 molecules of THF that crystallized with the compound. [b] Includes 2 molecules of toluene that crystallized with the compound. [c] $R_{int} = \sum|F_o - \langle F_o^2\rangle|/\sum|F_o^2|$. [d] $w = [\sigma^2(F_o^2) + (AP)^2 + (BP)]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$. [e] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [f] wR2 $= [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, where $w = q/\sigma^2(F_o^2) = (aP)^2 + bP$. [g] GOF $= S = \sum[w(F_o^2 - F_c^2)^2]/(n - p)^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for [Ti(trisphenolate)(O-*t*-Bu)]$_2$ (**6a**)

Ti(1)−O(1)	1.820(2)	Ti(1)−O(3′)	1.805(2)
Ti(1)−O(2)	1.798(2)	Ti(1)−O(4)	1.763(2)
O(1)−Ti(1)−O(2)	106.96(10)	O(3′)−Ti(1)−O(4)	111.21(10)
O(1)−Ti(1)−O(3′)	109.49(10)	C(2)−O(1)−Ti(1)	142.9(2)
O(1)−Ti(1)−O(4)	107.29(10)	C(13)−O(2)−Ti(1)	148.8(2)
O(2)−Ti(1)−O(3′)	112.16(10)	C(16′)−O(3′)−Ti(1)	169.18(19)
O(2)−Ti(1)−O(4)	109.52(10)	C(41)−O(4)−Ti(1)	154.5(2)

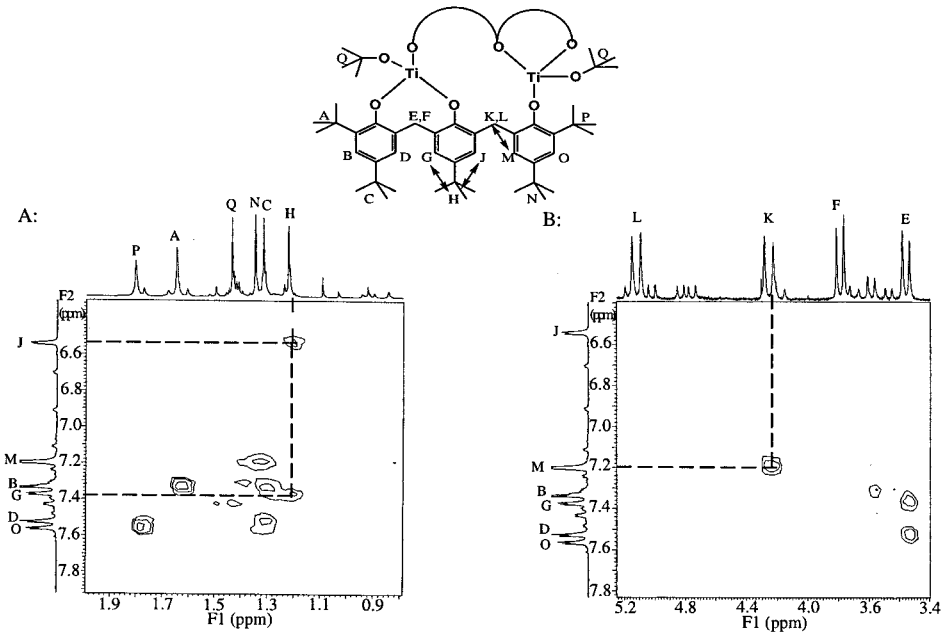


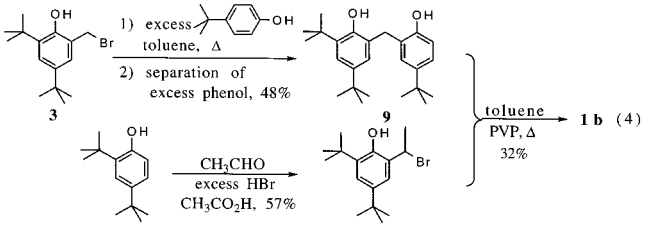
Figure 4. Expanded plots of NOESY data for **6a**. Assignments are according to the sketch above and Figure 2. (A) Expanded plot of cross peaks between *tert*-butyl (F1) and aromatic (F2) hydrogens, with representative correlations indicated for hydrogens H, J, and G. (B) Expanded plot of cross peaks between benzylic (F1) and aromatic (F2) hydrogens, with a representative correlation indicated for hydrogens K and M. Note the absence of a correlation between hydrogens K and J.

ligand. This led to the labeling scheme for the major isomer, shown at the top of Figure 2. However, we required the crystal structure of the minor isomer to correlate the NMR data with a three-dimensional understanding of the trisphenolate conformation.

Although the crystal structure is of the minor isomer and the solution structure is of the major isomer, the similarity of the NMR spectra of the two different isomers indicates that the trisphenolate ligand is in a very similar conformation in the two isomers (vide supra). Therefore, it is reasonable to compare the NMR data of the major isomer with the crystal structure, in order to evaluate whether the crystal structure conformation of the minor isomer is consistent with the NMR data from the major isomer. First, the upfield-shifted aromatic proton (observed for both isomers), located on the central phenol ring, is most likely that indicated in Figure 3B as proton J. This proton directs toward one face of the adjacent aromatic ring (distance of H_J to ring 3 is ca. 2.5 Å), the ring current from which would cause an upfield shift. Second, benzylic proton K shows an NOE cross peak with the aromatic proton of only one adjacent ring (proton M), whereas proton E shows cross peaks with the aromatic protons on both neighboring rings (protons D and G, see arrows in Figure 3B). Inspection of the crystal structure suggests why these are reasonable observations: proton J is attached to the "straddle" methylene carbon, and the resultant geometry places aromatic proton K too distant (J−K distance is ca. 3.7 Å) to observe an NOE cross peak between them. All of these assignments from the crystal structure are also consistent with the ordering of the resonances determined solely by NMR spectroscopy. Together, the NMR data and crystal structure suggest that the trisphenolate conformation in the major isomer is very similar to that in the minor isomer, at least with respect to phenolate rings 2 and 3. In further support of this conclusion, the two-dimensional NMR data acquired for the minor isomer (collected on the chiral trisphenolate complex, described below) reveal NOE cross peaks between the pairs of protons analogous to those that produce NOE cross peaks in the major isomer. The only significant differences between the NMR spectra of the isomers are chemical shift differences for several resonances (vide infra).

Synthesis of Chiral Trisphenol

We have prepared the chiral trisphenol (**1b**) as a racemate, according to the procedure outlined in eq 4. Excess 4-*tert*-butyl phenol was used to prepare the unsymmetrical bisphenol (**9**) shown in the first step. Separation of the excess phenol from the desired product according to the literature procedure for preparing an analogous compound[11] was problematic for us: it was very difficult to separate the final 2 equiv of 4-*tert*-butyl phenol from the unsymmetrical bisphenol. We have developed a simple alternative method in which we remove the remaining 4-*tert*-butyl phenol using a Kugelrohr bulb-to-bulb distillation.



Titanium Complexes of Chiral Trisphenol

The titanium complex of the chiral trisphenol (**6b**) was prepared according to eq 3. The two isomers that result

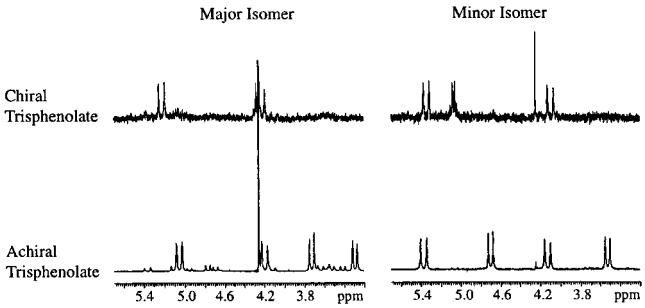


Figure 5. Benzylic region of the ^{1}H NMR (C_6D_6) spectra of **6a** (bottom) and **6b** (top), comparing major (left) and minor (right) isomers. The methyl group in **6b** replaces the benzylic hydrogen with the most upfield chemical shift in each isomer of **6a**. The singlet at 4.3 ppm is due to CH_2Cl_2 impurity in the C_6D_6 solvent.

appear to be identical to the isomers of **6a**, according to ^{1}H NMR spectroscopy. Our evidence for this is the strong similarity between the benzylic proton regions of the NMR spectra of the two isomers (Figure 5). The resonances due to one set of methylene protons are virtually identical for both isomers of **6a** and **6b**: those located at 5.1 and 4.2 ppm for the major isomer and 5.4 and 4.2 for the minor isomer. The only difference arises at the benzylic position that has become substituted with a methyl group in the chiral complex. In this case, one benzylic resonance is a quartet (because of coupling with the methyl protons) and is shifted slightly downfield relative to its achiral counterpart (3.8 shifted to 4.2 for the major isomer and 4.7 shifted to 5.2 for the minor isomer). The change in chemical shift is reasonable, since the carbon center to which this proton is attached is now tertiary, rather than secondary. The fourth benzylic resonance in the chiral complex is missing, since that proton has been replaced with a methyl group, the protons from which resonate at 1.7 ppm. *Therefore, the methyl group in the chiral complex has replaced only one hydrogen in the achiral complex: that which has the most upfield chemical shift.* We were expecting to produce two additional isomers of **6b**, which could arise from introducing the methyl group into each of the two different benzylic positions in the titanium complex. We also could have produced two additional diastereomers, if the methyl group were able to replace either hydrogen at a given benzylic position in the titanium complex. Our spectroscopic data indicate that one diastereomer is produced overwhelmingly for each of the two isomers of **6b**, and that the benzylic methyl group in these diastereomers is oriented away from the metal center (vide infra).

The minor isomer of **6b** isomerizes much more slowly than the minor isomer of **6a**; in fact, isomerization is not apparent after 24 h at room temperature. This enabled us to acquire two-dimensional ^{1}H NMR spectroscopic data from this isomer and completely assign the resonances in the ^{1}H NMR spectrum. We used a procedure analogous to that described for the major isomer of **6a** to assign all of the proton resonances relative to their neighbors in the trisphenol ring and assign the *tert*-butoxide resonance. The methyl group introduced at the benzylic position shows cross peaks that correlate with the aromatic protons (D and G) from two neighboring phenol groups, which confirm that the methyl group is oriented away from the titanium center and toward the aromatic protons of the phenol groups. In addition, these cross peaks are consistent with the methyl group being located on the "nonstraddle" methylene carbon (where proton E is indicated in Figure 3B), because only one cross peak with the aromatic region would be observed if the methyl group were on the straddle methylene carbon (vide supra). Evaluation of the crystal structure suggests that the methyl group is not introduced into the straddle group because that location is sterically more congested: the methyl group would interfere with the titanium−oxygen core if it replaced the downfield proton, or an aromatic hydrogen if it replaced the upfield proton. Therefore, the steric size of the methyl group controls both the location of this group in the nonstraddle position and the orientation (and hence, chirality) of the trisphenolate ligand when it coordinates the metal center. This explains why only two isomers are observed for **6b**, and implies that enantiomerically pure trisphenol would produce a specific enantiomer of trisphenolate conformation in the metal complex.[16]

Once we had assignments of the proton resonances for the minor isomer of **6b**, we translated those assignments to the ^{1}H NMR spectrum of the minor isomer of **6a** (Figure 2, bottom spectrum). We then compared the assigned NMR spectra of the major and minor isomers, in order to evaluate the spectroscopic differences in the isomers. There were many consistencies between the two isomers, including the upfield shift of aromatic proton J, and the fact that proton E shows NOE cross peaks with two aromatic protons (D and G), while proton K shows an NOE cross peak with only one aromatic proton (M). Altogether, there are only two significant spectroscopic differences between the isomers. The first is that the *tert*-butoxide resonance is shifted slightly upfield in the *minor* isomer, from 1.5 to 1.2 ppm (resonance Q, Figure 2). An examination of the crystal structure shows a relatively close interaction (ca. 3 Å) between the *tert*-butoxide hydrogens and the central aromatic ring of one of the trisphenolate ligands, suggesting that a ring current effect could contribute to the slight upfield shift. The second major difference is that one benzylic hydrogen resonance is shifted upfield in the *major* isomer, from 4.8 to 3.8 ppm (resonance F, Figure 2). Proton NMR spectra of dititanacalix[8]arene complexes suggest that a "normal" chemical shift for this proton is closer to 4.8 ppm.[8d] Therefore, the major isomer appears to have one benzylic hydrogen in an unusual location, either with respect to a titanium center or with respect to an aromatic ring. At this time, we have no other structural information regarding the major isomer; FAB (fast atom bombardment) mass spectra of both isomers of **6a** and **7a** produce a high-mass ion that corresponds to loss of R′OR′ from compounds **6a** and **7a**, [(Ti(trisphenoxide))$_2$O].

(16) Because the titanium complexes reported in this paper are dimers with inversion symmetry, enantiomerically pure trisphenol could not yield an enantiomerically pure chiral version of these titanium complexes. We are currently working to resolve the chiral trisphenol into enantiomerically pure form, in order to determine what titanium complexes would be produced in this case.

These spectral changes and the fact that the isomerization from the minor to the major isomer of **6b** is very slow (i.e., not apparent by ^{1}H NMR spectroscopy in 24 h at room temperature) suggest that the major isomer differs from the minor isomer by conformational "inversion" at the nonstraddle benzylic methylene group.[17] This type of inversion is proposed to occur in analogous titanium bisphenolate complexes,[18] but is slow on the NMR time scale (hence the methylene protons resonate as two separate doublets). The inversion, which occurs by rotation around the carbon−carbon bonds connecting the methylene group to the two neighboring aromatic groups, changes the orientation of the aromatic rings with respect to the other ligands on the metal center and causes the interchange of the two benzylic hydrogens; the upfield hydrogen (directed toward the aromatic rings) becomes the downfield hydrogen, and vice versa. We hypothesize that when the upfield hydrogen is replaced by a methyl group, as in the minor isomer of **6b**, the strain that would result if the methyl group oriented toward the metal center prevents the conformational inversion (and thus the isomerization) from taking place. The change in chemical shift of proton F when converting from the minor to the major isomer further supports this hypothesis, since that proton is attached to the center that would undergo inversion. Similarly, the change in chemical shift of the *tert*-butoxide group could arise from a change in its orientation with respect to the aromatic rings upon inversion. Altogether, the data support the hypothesis that the difference between the major and minor isomers is due to conformational inversion of the nonstraddle benzylic methylene group.

Reactivity of 6a and 7a

Compounds **6a** and **7a** decompose, apparently by reaction with 1 equiv of adventitious water, to yield a compound with the formula Ti_2(trisphenolate)$_2$O (**10**), as determined by FAB mass spectrometry. Both compounds are unstable with respect to **10**, since **10** is the major high-mass ion observed in the positive FAB mass spectrum of either **6a** or **7a**. The trisphenolate ligand in compound **10** also adopts an unsymmetrical conformation according to ^{1}H NMR spectroscopy. We are currently preparing this compound directly and investigating details of its structure. In addition, we are pursuing applications of all of the titanium trisphenolate compounds in promoting ring-opening polymerization of lactones.

Aluminum Complex of Achiral Trisphenol

Aluminum complexes of achiral trisphenol were prepared by addition of $Al(CH_3)_3$ to 1 equiv of trisphenol **1a**, yielding [Al(trisphenolate)]$_2$ (**8a**) (eq 3). In contrast to the titanium complexes of **1a**, the trisphenolate ligand in the aluminum complex (**8a**) is in a symmetrical conformation; the benzylic hydrogens from the two methylene groups on the ligand resonate as two doublets in the ^{1}H NMR spectrum. Mass spectrometry indicates that the complex is a dimer of Al(trisphenolate) units. The crystal structure shows that the trisphenolate ligands coordinate the two aluminum centers so that the central phenolate group bridges the two metal centers and each terminal phenolate group coordinates a different aluminum center (Figure 6). Together, the two trisphenolate ligands provide tetrahedral coordination of the aluminum atoms, expected for an Al_2O_6 core.[19] The trisphenolate in this complex adopts a C_2-symmetric S-shaped conformation, where the C_2 axis lies in the plane of the central phenolate ring, oriented along the O- to *tert*-butyl axis. Although the trisphenolate conformation in the aluminum complex is more symmetrical than in the titanium complex, on account of the bridging central phenoxide group, the ligand conformation is chiral. However, the complex is not chiral overall, due to an inversion center that interconverts the two trisphenolate ligands. We are exploring ways to

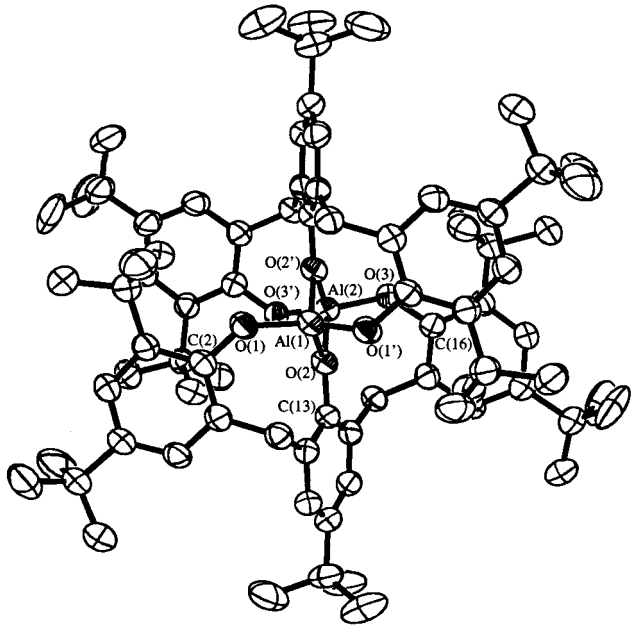


Figure 6. An ORTEP representation (50% probability) of the crystal structure of **8a**. Carbon atoms are unshaded. Hydrogen and disordered *tert*-butyl carbon atoms are removed for ease of viewing. Labeling is according to the distances and angles listed in Table 3.

Table 3. Selected Bond Distances (Å) and Angles (deg) for [Al(trisphenolate)]$_2$ (**8a**)

Al(1)−O(1)	1.6984(14)	Al(2)−O(3)	1.7023(14)
Al(1)−O(2)	1.8336(14)	Al(2)−O(2′)	1.8284(14)
Al(1)−O(1′)	1.6985(14)	Al(2)−O(3′)	1.7022(14)
Al(1)−O(2′)	1.8336(14)	Al(1)−Al(2)	2.7548(12)
Al(2)−O(2)	1.8285(14)		
O(1)−Al(1)−O(2)	116.69(6)	O(2)−Al(2)−O(2′)	82.57(9)
O(1)−Al(1)−O(2′)	108.31(7)	O(3)−Al(2)−O(3′)	119.16(10)
O(1)−Al(1)−O(1′)	119.10(11)	C(2)−O(1)−Al(1)	130.29(13)
O(2)−Al(1)−O(2′)	82.29(9)	C(13)−O(2)−Al(1)	131.98(12)
O(2)−Al(2)−O(3)	115.41(6)	C(16)−O(3)−Al(2)	130.09(12)
O(2)−Al(2)−O(3′)	109.38(6)		

(17) The authors appreciate useful suggestions provided by a reviewer.

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(19) (a) Chisholm, M. H.; Huffman, J. C.; Wesemann, J. L. *Polyhedron* **1991**, *10*, 1367−1372. (b) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. In *Advanced Inorganic Chemistry*, 6th ed.; John Wiley & Sons: New York, 1999; pp 188−189.

prepare a heterodimer of this complex, with one trisphenolate and one other multidentate, perhaps chiral ligand, in order to evaluate whether the trisphenolate ligand in these complexes would be capable of chiral recognition.

Comparison of Trisphenolate Conformation in Titanium and Aluminum Complexes

The difference in trisphenolate conformation between the titanium and aluminum structures probably results from the difference in steric congestion at the metal centers. We propose that the additional alkoxide ligand in the titanium complexes and the large terminal *tert*-butyl groups on the trisphenolate ligand combine to prevent the central phenolate oxygen from bridging the two titanium centers. This causes the Ti−O−C bond angles to open considerably (143−169°), in order to donate more electron density to the metal center. This open angle, in turn, prevents the trisphenolate ligand from coordinating to a single metal center, resulting in the observed dimeric structures. In contrast, the aluminum complexes have no additional steric bulk at the metal center, so the trisphenolate can bridge the two metal centers with the central phenolate oxygen. The Al−O−C bond angles are smaller (∼130°) because the aluminum center gains electron density via the bridging phenolate oxygen.

Conclusion

In conclusion, we have prepared linear trisphenol analogues of 4-*tert*-butylcalixarene in both a chiral (racemic) and an achiral form. We have characterized trisphenolate complexes with titanium(IV) and aluminum(III) and found that in both cases the trisphenolate ligand adopts a chiral conformation when coordinated to the metals. In addition, we have shown that the trisphenolate conformation can be controlled by incorporating a methyl group at one of the bridging methylene carbons. These results suggest that the metal−ligand complexes have potential applications in stereo- or enantioselective transformations, either directly or by amplifying the chirality of a different ligand that is coordinated to the metal center.[20] Along these lines, we are currently developing applications of the coordinatively unsaturated titanium complexes as stereoselective reagents in organic synthesis and stereoselective initiators in ring-opening polymerization reactions. We are also developing a method for resolving the chiral trisphenol into enantiomerically pure form.

Experimental Section

General. All experiments involving metal-based reagents were run under nitrogen at 25 °C in a Vacuum Atmospheres glovebox, unless specified otherwise. Solvents were purchased in anhydrous form under nitrogen in Sure/Seal bottles from Aldrich Chemical Co. and transferred into the glovebox without exposure to air. Starting materials were obtained from commercial suppliers and used as received, except as specifically noted. Titanium(IV) isopropoxide was vacuum distilled before use. Titanium(IV) *tert*-butoxide was prepared by treatment of titanium(IV) isopropoxide with 4 equiv of *tert*-butyl acetate, followed by fractional distillation.[21]

NMR spectra were recorded at room temperature on a Varian Gemini 2000 spectrometer operating at 300.1 MHz (^{1}H) and 75.5 MHz (^{13}C), equipped with Vnmr software version 5.3B. All chemical shift data are reported in parts per million downfield (+) or upfield (−) from tetramethylsilane (TMS), based on the chemical shift of $CDCl_3$(7.24 ppm, residual ^{1}H; 77.00 ppm, ^{13}C) or C_6D_6 (7.15 ppm, residual ^{1}H; 128.00 ppm, ^{13}C). Standard two-dimensional COSY experiments and two-dimensional phase-sensitive NOESY experiments using the States−Haberkorn method[22] (mixing time = 500 ms) were performed using the Vnmr software package. Mass spectra were obtained on a VG ZAB2-EQ mass spectrometer, operated by the Mass Spectrometry Laboratory in the Chemistry Department at the University of California, Berkeley, or on a VG 7070-HF or Finnegan MAT 95 mass spectrometer, operated by the Mass Spectrometry Service Laboratory in the Chemistry Department at the University of Minnesota, Minneapolis. Compounds were analyzed by positive fast atom bombardment (+FAB) using 2-nitrophenyl octyl ether (NPOE) or 3-nitrobenzyl alcohol (NBA) as a matrix solvent. Mass spectral data are reported as *m*/*e* (percent of base peak). Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA. X-ray crystallographic studies were performed by the X-Ray Crystallographic Laboratory in the Chemistry Department at the University of Minnesota, Minneapolis.

2-(Bromomethyl)-4,6-bis(1,1-dimethylethyl)phenol (3). In a 500 mL three-neck round-bottomed flask, fitted with a gas inlet tube, a thermometer, a bubbler containing water, and a magnetic stirring bar, was dissolved 2,4-di(*tert*-butyl)phenol (20.0 g, 96.9 mmol) in glacial acetic acid (35 mL). Paraformaldehyde (3.49 g, 116 mmol) was added with stirring until it completely dissolved, and hydrogen bromide gas was bubbled into the reaction mixture for 15 min, at a rate that caused the reaction temperature to increase to between 60 and 80 °C. After the paraformaldehyde had dissolved and the reaction mixture formed a two-phase system, the gas flow was turned off and the reaction mixture was stirred under ambient pressure for 0.5 h. The reaction mixture was cooled to room temperature, and the organic phase was separated, seeded with a crystal from a previous preparation of **3**, and cooled in an ice bath for 1 h. The resultant colorless crystals were collected by suction filtration, washed with water, dissolved in a minimum of warm hexane, dried ($MgSO_4$), filtered, and cooled to −30 °C. The first crop of crystals was collected by vacuum filtration, and a second crop was obtained by concentration of the mother liquors by rotary evaporation, cooling to −30 °C, and vacuum filtration. Total yield of both crops was 18.07 g (62%). ^{1}H NMR ($CDCl_3$): δ 7.33 (2H, d, J = 2.47 Hz), 7.10 (2H, d, J = 2.47 Hz), 5.28 (1H, s), 4.58 (2H, s), 1.43 (9H, s), 1.29 (9H, s). ^{13}C NMR ($CDCl_3$): δ 151.78, 143.08, 137.28, 125.72, 124.78, 123.35, 34.82, 34.23, 32.55, 31.42, 29.79.

2,6-Bis(3,5-bis(1,1-dimethylethyl)-2-hydroxyphenylmethyl)-4-(1,1-dimethylethyl)phenol (Trisphenol 1a). In a 500 mL three-necked round-bottomed flask, equipped with a thermometer, condenser, and magnetic stirring bar, was dissolved 4-*tert*-butylphenol (2.41 g, 16.1 mmol) in 20 mL of toluene. 2-(Bromomethyl)-4,6-bis(1,1-dimethylethyl)phenol (**3**, 9.65 g, 32.2 mmol) was added with stirring. Once both reagents had completely dissolved, poly(4-vinylpyridine) (PVP, 3.40 g, 32.2 mmol, based on pyridine) was added to the reaction mixture. The reaction mixture was heated to between 80 and 90 °C under dry nitrogen. After 24 h, the reaction

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mixture was cooled to room temperature and the poly(vinylpyridinium bromide) was removed by vacuum filtration. The solution was concentrated first by rotary evaporation and then under high vacuum to a red foam. The foam was transferred into the glovebox, where it was dissolved in a minimum amount of pentane at room temperature and cooled to −30 °C. Colorless crystals were isolated by vacuum filtration in the glovebox. Subsequent crops of crystals were obtained by concentrating the mother liquors and cooling them to −30 °C. Two crops of crystals were isolated, yielding a total of 6.81 g (72%). ^{1}H NMR (C_6D_6): δ 7.82 (1H, s), 7.39 (2H, d, J = 2.47 Hz), 7.34 (2H, d, J = 2.47 Hz), 7.28 (2H, s), 6.43 (2H, s), 3.89 (4H, s), 1.45 (18H, s), 1.39 (18H, s), 1.28 (9H, s). ^{13}C NMR ($CDCl_3$): δ 149.15, 147.83, 144.19, 143.2, 135.49, 127.37, 127.01, 125.95, 125.51, 122.38, 34.43, 34.14, 33.90, 31.88, 31.44, 30.09. Mass spectrum ((+)-FAB, NBA): 586.5 (43, $M^{+\bullet}$), 381.3 (41), 219.2 (90), 175.2 (55), 56.9 (100). Anal. Calcd for $C_{40}H_{58}O_3$: C, 81.86; H, 9.96. Found: C, 81.71; H, 10.66.

Ti$_2$(trisphenolate)$_2$(O-*t*-Bu)$_2$ (6a). In a 20 mL vial, **1a** (1.5 g, 2.6 mol) was dissolved in toluene (5 mL) and stirred. In another vial, titanium(IV) *tert*-butoxide (0.87 g, 2.6 mmol) was dissolved in toluene (5 mL) and the solution of titanium(IV) *tert*-butoxide was added dropwise to the solution of **1a** and stirred for 24 h. The deep orange solution was concentrated by rotary evaporation and recrystallized from a minimum amount of pentane at −30 °C. The resultant yellow crystals were isolated by vacuum filtration, and subsequent crops were obtained by successive concentration and cooling of the mother liquors. The combined yield of five crops of crystals was 9.39 g (51%). These crops varied in composition, from 100% minor isomer to a 50:50 mixture of major:minor isomers. After the last crop was isolated, the mother liquors were concentrated by rotary evaporation, and the ^{1}H NMR spectrum indicated that the residue was ca. 90% major isomer. ^{1}H NMR (major isomer, C_6D_6): δ 7.51 (2H, d, J = 2.5 Hz), 7.47 (2H, d, J = 2.5 Hz), 7.31 (2H, d, J = 2.2 Hz), 7.28 (2H, d, J = 2.5 Hz), 7.14 (2H, d, J = 2.5 Hz), 6.48 (2H, d, J = 2.2 Hz), 5.06 (2H, d, J = 16.8 Hz), 4.20 (2H, d, J = 17.3 Hz), 3.73 (2H, d, J = 14.0 Hz), 3.29 (2H, d, J = 14.3 Hz), 1.75 (18H, s), 1.59 (18H, s), 1.38 (18H, s), 1.29 (18H, s), 1.26 (18H, s), 1.17 (18H, s). ^{13}C{^{1}H} NMR (major isomer, C_6D_6): δ 162.50, 160.18, 159.29, 144.32, 144.19, 144.10, 137.25, 136.14, 134.17, 132.88, 129.82, 127.33, 126.80, 124.94, 123.59, 123.02, 122.06, 121.92, 86.76, 35.44, 35.36, 34.79, 34.48, 34.37, 34.27, 34.10, 31.95, 31.58, 31.51, 30.84, 30.56). ^{1}H NMR (minor isomer, C_6D_6): δ 7.42 (2H, d, J = 2.5 Hz), 7.38 (2H, d, J = 2.2 Hz), 7.37, (2H, d, J = 2.5 Hz), 7.28 (2H, d, J = 2.5 Hz), 7.05 (2H, d, J = 2.5 Hz), 6.64 (2H, d, J = 2.2 Hz), 5.37 (2H, d, J = 17.6 Hz), 4.69 (2H, d, J = 14.0 Hz), 4.12 (2H, d, J = 17.6 Hz), 3.53 (2H, d, J = 14.3 Hz), 1.62 (18H, s), 1.55 (18H, s), 1.29 (18H, s), 1.26 (18H, s), 1.18 (18H, s), 1.16 (18H, s). ^{13}C{^{1}H} NMR (minor isomer, C_6D_6) 162.11, 160.29, 159.52, 144.40, 144.05, 143.92, 137.81, 136.81, 135.33, 133.46, 130.23, 127.54, 124.95, 124.57, 123.91, 122.04, 121.74, 87.02, 35.36, 34.87, 34.38, 34.33, 34.18, 31.72, 31.60, 31.55, 31.45, 30.57, 30.52. Mass spectrum (major isomer, (+)-FAB, NPOE): 1353 (35, [M − $(CH_3)_2CCH_2]^{+\bullet}$), 1279 (100, [M − $(t\text{-Bu})_2O]^{+\bullet}$), 568 (23). Mass spectrum (minor isomer, (+)-FAB, NPOE): 1353 (27, [M − $(CH_3)_2CCH_2]^{+\bullet}$), 1279 (100, [M − $(t\text{-Bu})_2O]^{+\bullet}$), 568 (22). Anal. Calcd for $C_{43}H_{62}O_4Ti$ (minor isomer): C, 74.98; H, 9.15. Found: C, 74.29; H, 8.83.

Ti$_2$(trisphenolate)$_2$(O-*i*-Pr)$_2$ (7a). In a 100 mL round-bottomed flask, **1a** (1.00 g, 1.70 mmol) was dissolved in 20 mL of toluene. Titanium(IV) isopropoxide (0.484 g, 1.70 mmol), dissolved in 5 mL of toluene, was added dropwise with stirring. The resultant orange solution was stirred for 3 h at room temperature and concentrated by rotary evaporation to an orange film. The film was dissolved in pentane (10 mL) and concentrated to an orange foam, which was triturated with pentane (5 mL) to produce a yellow solid in an orange solution. The slurry was cooled to −30 °C for 48 h, and then the yellow solid was isolated by vacuum filtration, washed with cold pentane (ca. 5 mL), and dried under vacuum (0.754 g, 64%). NMR spectroscopy indicates that the product is predominantly (≥90%) the major isomer, with a small amount of contamination by the minor isomer and **10**. ^{1}H NMR (major isomer, C_6D_6): δ 7.53 (2H, d, J = 2.5 Hz), 7.51 (2H, d, J = 2.5 Hz), 7.36 (2H, d, J = 2.2 Hz), 7.31 (2H, d, J = 2.2 Hz), 7.20 (2H, d, J = 2.2 Hz), 6.57 (2H, d, J = 1.9 Hz), 5.11 (2H, d, J = 17.0 Hz), 4.57 (2H, septet, J = 6.0 Hz), 4.16 (2H, d, J = 17.0 Hz), 3.57 (2H, d, J = 14.0 Hz), 3.27 (2H, d, J = 14.0 Hz), 1.77 (18H, s), 1.59 (18H, s), 1.32 (18H, s), 1.28 (18H, s), 1.18 (12H, d, J = 6.0), 1.15 (18H, s). ^{13}C{^{1}H} NMR (major isomer, C_6D_6): δ 162.59, 160.13, 159.35, 144.50, 144.22, 137.30, 136.21, 133.66, 132.31, 130.02, 127.20, 126.91, 125.04, 123.68, 122.96, 122.07, 121.95, 81.18, 35.44, 35.38, 34.64, 34.41, 34.30, 34.12, 33.93, 31.62, 31.54, 31.47, 30.81, 30.62, 26.06, 26.03. ^{1}H NMR (minor isomer, selected resonances, C_6D_6): δ 6.75 (2H, br), 5.16 (2H, d, J = 17.4 Hz), 4.68 (2H, d, J = 15.9 Hz), 4.36 (2H, septet, J = 6.0 Hz), 4.24 (2H, d, J = 17.4 Hz), 3.49 (2H, d, J = 12.6 Hz). Mass spectrum (major isomer, (+)-FAB, NPOE): 1278.5 (100%, [M − $(i\text{-Pr})_2O]^{+\bullet}$), 486.2(74%).

2-(1-Bromoethyl)-4,6-bis(1,1-dimethylethyl)phenol (11). In a procedure similar to that for preparing the bromomethyl derivative (**3**), 2,4-bis(*tert*-butyl)phenol (16.59 g, 0.0804 mole) was dissolved in concentrated acetic acid (20 mL) in a 250 mL three-neck flask, equipped with a gas inlet, a bubbler containing water as a trap for excess HBr, a thermometer, and a magnetic stirring bar. Acetaldehyde was added (4.25 g, 0.969 mole), and then anhydrous hydrogen bromide was bubbled through the reaction mixture at a rate that caused the temperature to rise to between 60 and 80 °C. Once the solution was saturated with HBr, the addition of HBr was ceased and the reaction mixture was stirred under ambient pressure for 0.5 h. The resultant two-phase system was separated, and the organic layer was purged with dry nitrogen gas (15 min) and then concentrated by rotary evaporation at 30 °C under reduced pressure (0.1 Torr), yielding 21.54 g of viscous oil. ^{1}H NMR spectroscopy of the crude product showed that it was contaminated by ca. 33% acetic acid. The crude yield, accounting for the impurity, was approximately 57%. Attempts to further purify this product resulted in its decomposition. ^{1}H NMR ($CDCl_3$): δ 7.33 (1H, d, J = 2.2 Hz), 7.18 (1H, d, J = 2.5), 5.46 (1H, q, J = 7.1 Hz), 2.14 (3H, d, J = 7.1 Hz), 2.09 (CH_3CO_2H impurity), 1.43, (9H, s), 1.30 (9H, s). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 151.09, 142.75, 137.52, 128.15, 125.01, 120.92, 49.01, 34.88, 34.38, 31.45, 29.82, 24.83.

2-(3,5-Bis(1,1-dimethylethyl)-2-hydroxy-1-phenylethyl)- 4-(1,1-dimethylethyl)phenol (9). This procedure was adapted from an analogous literature procedure.[11b] In a 250 mL round-bottomed flask fitted with a condenser, 4-*tert*-butylphenol (17.52 g, 0.117 mol) was dissolved with stirring in 50 mL of toluene. After the phenol had dissolved, PVP (2.45 g, 0.0233 mol of pyridine) was added, followed by 2-(1-bromomethyl)-4,6-bis(1,1-dimethylethyl)phenol (6.98 g, 0.0233 mol), as a solution in 20 mL of toluene. The reaction mixture was heated at 60 °C for 18 h under dry nitrogen. The resultant dark orange reaction mixture was cooled to room temperature and filtered, and the filtrate was concentrated by rotary evaporation to an orange foam. The residue was dissolved in petroleum ether at room temperature (20 mL) and cooled to −30 °C to precipitate excess 4-*tert*-butylphenol, which was separated by filtration. The filtrate was concentrated to an orange oil by rotary evaporation, and the remaining 2 equiv of 4-*tert*-butylphenol was removed by a bulb-to-bulb Kugelrohr distillation (90 °C/6 mmHg).

The desired product (**9**) remained in the first distillation bulb as an orange, glassy solid and was used without further purification (4.2 g, 48%). ^{1}H NMR ($CDCl_3$): δ 7.29 (1H, d, $J = 2.5$ Hz), 7.15 (2H, s), 7.08 (1H, dd, $J = 8.2$ Hz, $J' = 2.5$ Hz), 6.67 (1H, d, $J = 8.2$ Hz), 6.49 (1H, s), 5.54 (1H, s), 3.89 (2H, s), 1.38 (9H, s), 1.26 (9H, s), 1.25 (9H, s).

2-(3,5-Bis(1,1-dimethylethyl)-2-hydroxy-1-phenylethyl)-6-(3,5-bis(1,1-dimethylethyl)-2-hydroxyphenylmethyl)-4-(1,1-dimethylethyl)phenol (Chiral Trisphenol, 1b). A 250 mL round-bottomed flask was equipped with a thermometer and a stir bar and charged with bisphenol **9** (0.96 g, 2.60 mmol) and toluene (20 mL). Once the bisphenol had dissolved, PVP (0.273 g, 2.60 mmol of pyridine) was added, followed by **11** (0.816 g, 2.60 mmol) as a solution in toluene (10 mL). The reaction flask was equipped with a condenser and heated to 58 °C for 72 h. After this time, ^{1}H NMR spectroscopy of an aliquot indicated that the reaction was incomplete, but that all of the 2-(1-bromoethyl)-4,6-bis(1,1-dimethylethyl)phenol had reacted. Thus, an additional 1 equiv of both 2-(1-bromoethyl)-4,6-bis(1,1-dimethylethyl)phenol and PVP (2.60 mmol of each) was added and the reaction mixture was heated to 58 °C and stirred for an additional 24 h. ^{1}H NMR spectroscopy of an aliquot still indicated that the reaction was incomplete, but the reaction mixture was filtered and the filtrate was concentrated by rotary evaporation to a glassy solid. This solid was transferred into the glovebox and dissolved in 5 mL of pentane and concentrated by rotary evaporation to a colorless foam. The foam was dissolved in 5 mL of pentane and the solution cooled to −30 °C for 48 h. A colorless powder was isolated by filtration (0.410 g), and the mother liquors were concentrated to 2 mL and cooled to −30 °C. A second crop was isolated, weighing 0.091 g (32% combined yield, not optimized). ^{1}H NMR (C_6D_6): δ 7.45 (1H, s), 7.33 (1H, d, $J = 2.5$ Hz), 7.29 (1H, d, $J = 2.2$ Hz), 7.15 (3H, m), 7.10 (1H, d, $J = 2.5$ Hz), 6.37 (1H, s), 6.04 (1H, s), 4.61 (1H, q, $J = 7.1$ Hz), 1.53 (3H, d, $J = 7.1$ Hz), 1.31 (9H, s), 1.29 (9H, s), 1.24 (9H, s), 1.23 (9H, s), 1.17 (9H, s). ^{13}C{^{1}H} NMR (C_6D_6): δ 150.10, 149.84, 147.91, 144.57, 143.33, 143.18, 136.04, 135.95, 132.26, 131.96, 125.68, 122.43, 122.35, 122.01, 121.76, 34.65, 34.62, 34.43, 34.18, 34.08, 31.95, 31.59, 31.31, 31.12, 30.02, 29.99, 20.24. Mass spectrum ((+)-FAB, NBA): 601 (9%, MH^+), 600 (8%, M^+), 586 (7%), 394 (72%), 233 (99%), 217 (68%), 203 (40%), 189 (100%), 133 (68%). Anal. Calcd for $C_{41}H_{60}O_3$: C, 81.95; H, 10.06. Found: C, 81.27; H, 10.06.

Ti$_2$(chiral trisphenolate)$_2$(O-*t*-Bu)$_2$ (6b). In a 20 mL vial, **1b** (150 mg, 0.25 mmol) was dissolved in toluene (1 mL). Titanium(IV) *tert*-butoxide (85 mg, 0.25 mol) was added dropwise as a solution in toluene (2 mL), and the resultant orange solution was stirred at room temperature for 24 h. The solution was concentrated by rotary evaporation to an orange glassy residue. The residue was dissolved in pentane (5 mL) and concentrated by rotary evaporation to an orange solid, and these dissolution and concentration steps were repeated two additional times. The residue was concentrated under vacuum for an additional 1 h, and then it was dissolved in pentane (2 mL) and cooled to −30 °C for 72 h. A yellow powder was isolated by vacuum filtration (20 mg), and ^{1}H NMR spectroscopy indicated that it was the minor isomer. An additional crystalline solid was isolated after concentration of the mother liquors, crystallization at −30 °C, and filtration (14 mg), and ^{1}H NMR spectroscopy again indicated that it was the minor isomer (19% combined yield). The mother liquors were concentrated to an orange residue (12 mg), the ^{1}H NMR spectrum of which indicated that it was predominantly the major isomer. ^{1}H NMR (C_6D_6, major isomer): δ 7.64 (2H, d, $J = 2.7$ Hz), 7.59 (2H, d, $J = 2.5$ Hz), 7.55 (2H, d, $J = 3.0$ Hz), 7.37 (2H, d, $J = 2.5$ Hz), 7.28 (2H, d, $J = 2.5$ Hz), 6.47 (2H, d, $J = 2.2$ Hz), 5.48 (2H, d, $J = 17.0$ Hz), 4.33 (2H, q, $J = 7.3$ Hz), 4.28 (2H, d, $J = 16.8$ Hz), 1.81 (18H, s), 1.62 (18H, s), 1.41 (18H, s), 1.40 (18H, s), 1.38 (18H, s) (chiral trisphenolate methyl group not identified, due to impure sample). ^{1}H NMR (C_6D_6, minor isomer): δ 7.66 (2H, d, $J = 2.5$ Hz), 7.58 (2H, d, $J = 1.9$ Hz), 7.47 (2H, d, $J = 2.2$ Hz), 7.33 (2H, d, $J = 2.5$ Hz), 7.08 (2H, d, $J = 2.2$ Hz), 6.70 (2H, d, $J = 2.2$ Hz), 5.41 (2H, d, $J = 17.0$ Hz), 5.13 (2H, q, $J = 6.9$ Hz), 4.16 (2H, d, $J = 17.6$ Hz), 1.69 (6H, d, $J = 7.0$ Hz), 1.64 (18H, s), 1.55 (18H, s), 1.32 (18H, s), 1.24 (18H, s), 1.19 (18H, s), 1.14 (18H, s).

Al$_2$(trisphenolate)$_2$ (8a). In a 100 mL round-bottomed flask in the drybox was dissolved **1a** (1.00 g, 0.170 mmol) in toluene (15 mL). The colorless solution was cooled to −30 °C for 1 h, removed from the drybox freezer, and stirred, and trimethylaluminum (0.163 mL, 0.170 mmol) was added dropwise by syringe. Gas evolution was immediately apparent and the reaction mixture was allowed to warm to room temperature, during which time the solution turned pale yellow. After 1 h, the reaction mixture was concentrated by rotary evaporation to a pale yellow foam. The residue was dissolved in a mixture of pentane (5 mL) and THF (1 mL) and cooled to −30 °C. The first crop was isolated by filtration (0.202 g), and the filtrate was concentrated to a pale yellow film and dissolved in pentane (5 mL) to yield a second crop (27 mg, 22% combined yield). The liquors were concentrated to a pale yellow residue that was impure by NMR (0.145 g). ^{1}H NMR (C_6D_6): δ 7.14 (4H, s), 7.13 (8H, m), 4.65 (4H, d, $J = 16.8$), 3.64 (4H, d, $J = 16.8$), 1.23 (36H, s), 1.13 (18H, s), 0.85 (36H, s). ^{13}C{^{1}H} NMR (C_6D_6): δ 151.43, 147.88, 146.62, 141.70, 138.25, 129.02, 128.65, 126.30, 124.20, 122.85, 34.77, 34.27, 34.09, 33.09, 31.78, 31.27, 29.19. Mass spectrum ((+)-FAB, NBA): 1221 (26, $M^{+\bullet}$), 587 (23), 381 (40), 325 (26), 219 (100), 203 (34), 175 (65), 163 (31), 147 (25), 119 (33).

X-ray Crystallography. X-ray crystallographic studies were carried out using a Bruker SMART system (**6a**) or Siemens SMART system (**8a**) at 173(2) K using Mo Kα radiation (graphite monochromatized, $\lambda = 0.71073$ Å). A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 39 (**6a**) or 348 (**8a**) reflections. Final cell constants were calculated from a set of 5804 (**6a**) or 5858 (**8a**) strong reflections from the actual data collection.[23]

The data collection technique used for these crystals is generally known as a hemisphere collection. A randomly oriented region of reciprocal space was surveyed to the extent of 1.3 (**6a**) or 1.5 (**8a**) hemispheres and to a resolution of 0.77 Å (**6a**) or 0.84 Å (**8a**). Three major sections of frames were collected with 0.30° steps in ω, and additionally at three different ϕ settings and a detector position of −28° in 2θ for compound **6a**. The intensity data were corrected for absorption.[24]

The space groups $P\bar{1}$ (**6a**) and *Pbcn* (**8a**) were determined by the lack of (for **6a**) or presence of (for **8a**) systematic absences and intensity statistics.[25] A direct-methods solution was calculated, which provided most non-hydrogen atoms from the *E*-map. Full-matrix least squares and difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen

(23) Bruker. *SAINT Version 6.01*; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 1999.
(24) (a) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−38. (b) Sheldrick, G. M. *SADABS*; University of Göttingen: Göttingen, Germany, 1999.
(25) Bruker. *SHELXTL-Plus Version 5.4*; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 1997.

atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with individual (or group if appropriate) isotropic displacement parameters. The final full-matrix least squares refinements converged to the *R* values reported in Table 1. The high *R* values can be attributed to the presence of large voids in the crystals, which allowed for disorder of the incorporated solvents.

The structure of **6a** was found to be a dimer with seven solvent molecules (THF) per unit cell (per dimer). Disorder was modeled for two *tert*-butyl groups of the trisphenolate ligand. SADI instructions were applied to restrain C−C distances to be similar. One THF molecule is disordered over two positions (53:47). SAME instructions were applied to restrain the geometry of the two sites to be similar. One THF molecule is disordered over a special position.

The structure of **8a** was found with several toluene solvent molecules. Half of the molecule of interest is unique, being related by a 2-fold rotation axis parallel to *b*. Both Al atoms are located on the 2-fold rotation axis. Two solvent molecules were found with confidence. One is disordered head-to-tail in a cavity. A region containing some additional badly disordered solvent was identified with PLATON/SQUEEZE.[26] This void could potentially hold up to 8−12 more molecules of toluene per unit cell. The potential solvent volume was determined to be 1537.3 Å^3 in the unit cell volume of 10901.2 Å^3. The total electron count was determined to be 377 in the cell (this number corresponds to about 8 extra disordered toluene molecules per unit cell). The *R* value improved about 6% after the data were corrected for the disordered solvent. One hundred eighty-two restraints were applied to assist in a sensible refinement of the head-to-tail disordered toluene.

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Supporting Information Available: X-ray crystal structure data for **6a** and **8a**, including tables of crystal data, positional and thermal parameters, and bond distances and angles (CIF file), two-dimensional NMR data for **6a** and **6b**, and ^{1}H NMR spectra of all reported compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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