FULL PAPER

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Synthesis, stereochemistry, bonding and fluxionality of 2-(inden-3-yl)phenols and their cyclopentadienyl titanium derivatives

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The phenolic reagents 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 have been obtained. The solid-state structures of **2**, **3** and **4** have been determined by X-ray diffraction and torsion angles (between the vinyl group and phenoxy ring) of 57, 61 and 79° measured. Both the (a*R*) and (a*S*) forms of the ligands are present in the solid state. Solution ^{1}H NMR spectra show that rotation about the indenyl–phenoxy bond is facile for **1** but introduction of the 2-methyl substituent leads to restricted rotation on the NMR timescale. In the crystals of **3** analyzed, only the (a*S*,*S*) and (a*R*,*R*) forms were present, with the 1-methyl group pointing away from the OH group. In the ^{1}H and ^{13}C NMR spectra of **3** and **5** there are two, equal intensity sets of signals. Hence, both diastereoisomeric forms are present in equal concentrations in solution and two sharp O*H* singlets are observed for **3** even at 130 °C in *p*-xylene-d_{10}. Reaction of the phenols **1**–**4** with [CpTiCl$_3$] in the presence of pyridine has previously generated the corresponding mono-aryloxides **7**–**10** with no evidence of the de-protonation of the indenyl ring in these reactions. In all four compounds both the (a*R*) and (a*S*) forms are present within the unit cells. Variable temperature NMR studies of **7** allow the barrier to inden-3-yl rotation (enantiomer interconversion) to be estimated at 13.9(5) kcal mol^{-1} (at 20 °C). In solution only one major set of ^{1}H and ^{13}C NMR resonances were observed for 1,2-dimethyl derivative **9**. Hence, it appears that replacement of the phenolic proton by the much bulkier [CpTiCl$_2$] unit destabilizes the (a*S*,*R*) and (a*R*,*S*) forms in solution. Attempted de-protonation of the inden-3-yl ring in **7** by treatment with n-BuLi or MeLi did not lead to the formation of chelate rings. Instead formation of a Ti(III) dinuclear compound **11** and dimethyl derivative **12** occurred. The barrier to indenyl rotation in **12** can be estimated to be 13.4(5) kcal mol^{-1} at −5 °C, slightly lower than that measured for the dichloride **7**. Reaction of [CpTiCl$_3$] with the di-lithio (doubly deprotonated ligand) did lead to the formation of a chelated indenyl-phenoxide derivative **13**. In the solid state only the (p*S*,*R*) and (p*R*,*S*) forms were observed (indenyl oriented towards the Cp group, and in solution only one set of ^{1}H and ^{13}C NMR signals were observed indicating the presence of this single diastereoisomer. The bonding of the indenyl group and Cp ligands in **13** have been compared.

Introduction

The initial development by Bercaw, Shapiro *et al.*[1] of bridged amido-cyclopentadienyl ligands for early transition organometallic chemistry has been followed by intense research interest into these and related "constrained geometry" systems.[2] This interest has been stimulated by the high activity of single component olefin polymerization catalysts that can be generated with such ligands. Although the amido linked systems dominate the literature, some related alkoxo(aryloxo)-cyclopentadienyl ligands have been developed and studied. In this context we have begun an exploration of the chemistry associated with the ligand 2-(inden-3-yl)-4,6-di-*tert*-butylphenol **1**. This particular ligand architecture was chosen for a number of reasons. Firstly a great deal of discussion has appeared in the literature concerning the chemistry of indenyl ligands compared to their cyclopentadienyl counterparts. The basis of the so-called "indenyl effect"[3] 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.[4,5] Furthermore the indenyl group is an integral part of many chiral *ansa*-metallocenes[6] and bis(2-*R*-indenyl)metallocenes[7] where the ligands control the morphology (and properties) of generated polymers. Secondly this ligand is intriguing given the fact that chelation to a metal center *via* CH bond activation will generate a constrained geometry, indenyl-aryloxide system which is inherently chiral.[8–10] In this initial full paper we report on the synthesis of a variety of these ligands as well as their cyclopentadienyl-titanium derivatives.[11] This study pays particular attention to the stereochemistry and fluxionality of the ligands as well as observed bonding modes to the metal center.[12,13]

Results and discussion

Ligand synthesis and stereochemistry

The treatment of 2-bromo-4,6-di-*tert*-butyl phenol with two equivalents of Bu^{n}Li in diethyl ether leads to a solution of the corresponding di-lithio species. Addition of 1-indanone to this solution produces 2-(inden-3-yl)-4,6-di-*tert*-butylphenol **1** in moderate yield (Scheme 1). A similar procedure has been used to prepare 2-(1-naphthyl)-4,6-di-*tert*-butylphenol from tetralone. Analysis of the crude reaction mixture by GC/MS showed the presence of 2,4-di-*tert*-butyl phenol and unreacted 1-indanone as the major impurities. During one synthesis a few large white crystals were obtained directly from the product mixture and shown by X-ray diffraction to contain a 1 : 1 mixture of 2,4-di-*tert*-butyl phenol and an aldol condensation product of 1-indanone (Scheme 1). The use of methyl substituted 1-indanones has allowed the isolation of the corresponding methyl substituted ligands **2**–**5** (Scheme 1). The

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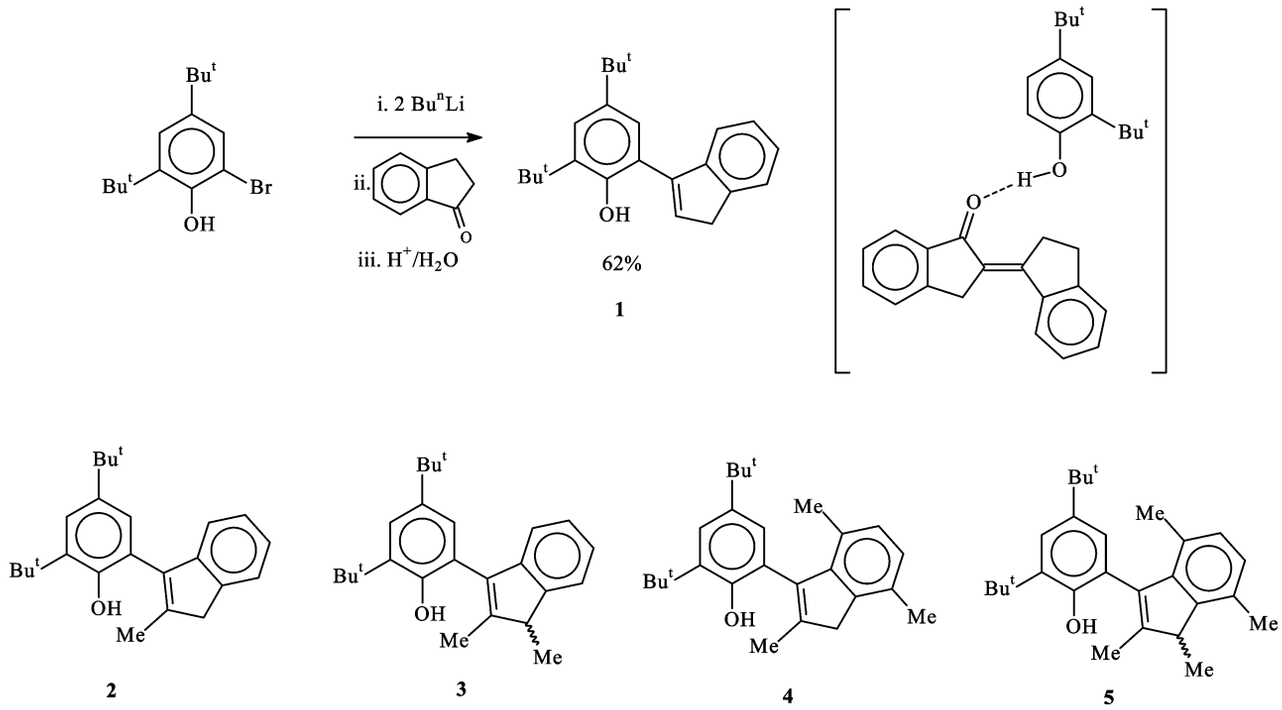


Scheme 1

position of the methyl substituents was chosen to have an impact on both the dynamics and inherent stereochemistry of these phenols.

Any restricted rotation about the sp^2–sp^2 (phenoxy-indenyl) bond in ligands **1**–**5** has important stereochemical consequences. The solid-state structures of **2**, **3** and **4** have been determined by X-ray diffraction. An ORTEP view of the 1,2-dimethyl compound **3** is shown in Fig. 1. In all three compounds the indenyl and phenoxy rings are twisted (non-coplanar) with torsion angles (between the vinyl group and phenoxy ring) of 57, 61 and 79° for **2**–**4**, respectively. This geometry leads to atropisomerism for the indenyl-phenoxide nucleus, a situation commonly encountered for bi-aryl systems.[14] The two enantiomers formed by restricted rotation about this bond (axial symmetry) are shown in Scheme 2. The assignment of the (a*R*) and (a*S*) forms is based upon the Cahn–Ingold–Prelog rules applied to bi-aryls.[15] In the crystals of **2**, **3** and **4** both enantiomers are present. Hence, the structures were modeled with a disordered OH group. The position of the hydroxy group also has an impact upon the conformation adopted by the *tert*-butyl groups. Typically, a disorder of two rotamers is present with one of the methyl groups pointing either towards or away from the indenyl group. An adjacent hydroxy group would be expected to lead to a preference for the methyl away rotamer.

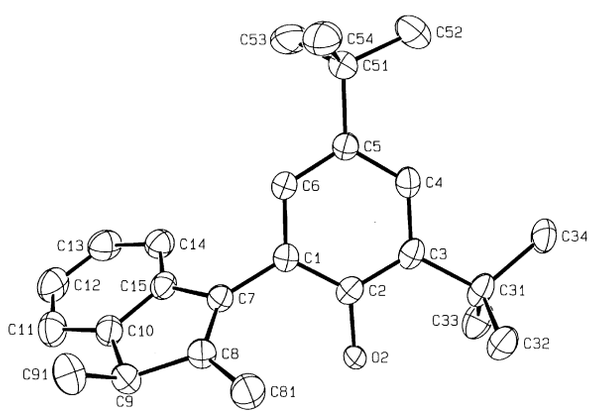
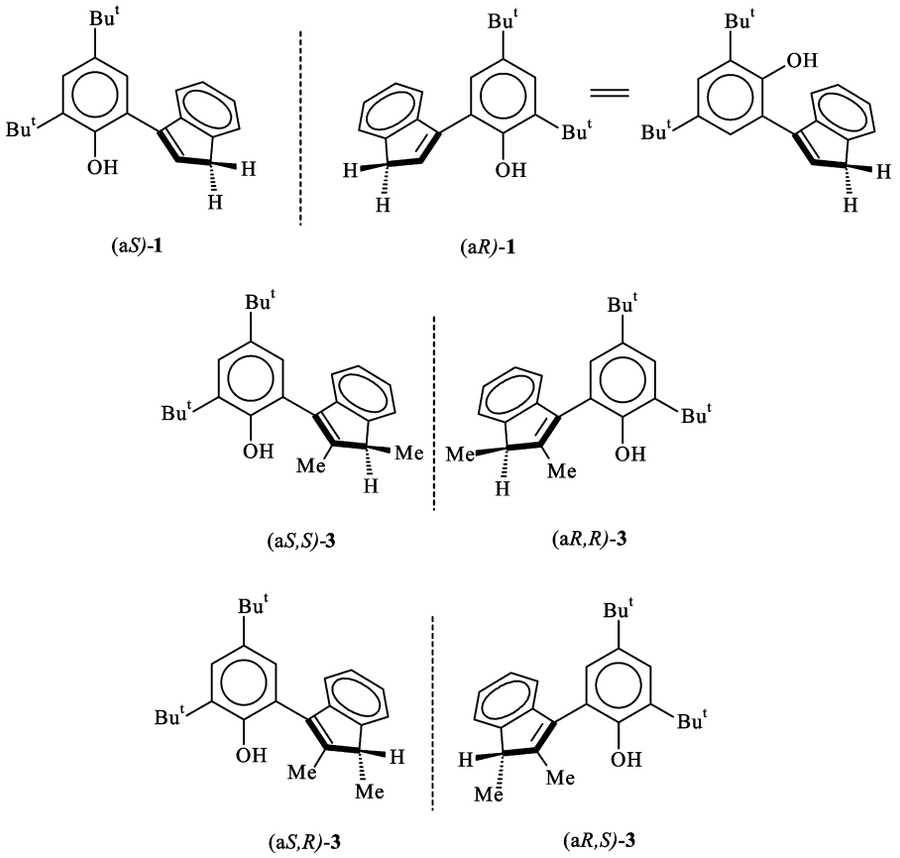


Fig. 1 Molecular structure of $HOC_6H_2\{C_9H_5Me_2$-1,2$\}$-2-Bu^t_2-4,6, **3**. The (a*R*,*R*) form is shown.

The ^{1}H NMR spectrum of **1** is consistent with the tautomer shown (Scheme 1), the indenyl ring protons appearing as a distinct doublet and triplet at δ 3.69 and 6.78 ppm, respectively. Futhermore, cooling a toluene-d_8 solution of **1** to −75 °C does not lead to splitting of the diastereotopic methylene protons. Hence, it appears that rotation about the phenoxy–indenyl bond is rapid on the NMR timescale (although it has to be recognized that there may not be a resolvable difference in chemical shifts). Previous NMR studies of 2,6-di(1-naphthyl)-phenol have shown the barrier to naphthyl rotation in this molecule can be estimated as 18.0(5) kcal mol^{-1} at 67 °C.[16] Hence, rotation appears to be more facile for the indenyl group (5-membered ring) compared to the naphthyl case. The introduction of a methyl group into the 2-position of the indenyl ring (**2**) does not lead to well resolved CH_2 protons, but the ambient ^{1}H NMR spectrum of **4** (methyl groups in the 2- and 4-positions) does show a well resolved AB pattern, consistent with a significant barrier to rotation in this case.

More information is obtained by analysis of the spectra for the 1-methyl substituted compounds **3** and **5**. This substituent introduces a second chiral element to the molecule so that there are now four distinct isomers (two enantiomeric pairs of diastereomers, Scheme 2). In the crystals of **3** analyzed, only the (a*S*,*S*) and (a*R*,*R*) (the latter shown in Fig. 1) forms were observed. This isomer has the 1-methyl group away from the OH group. In the ^{1}H and ^{13}C NMR spectra of **3** and **5** there are two, equal intensity sets of signals. Hence, both diastereoisomeric forms are present in equal concentrations in solution. Two sharp singlets are observed for the O*H* resonances (Fig. 2 shows the ^{1}H NMR of **3**). Even at 130 °C in *p*-xylene-d_{10}, the two O*H* resonances for **3** are only broadened slightly. Hence, we can conclude from this result that there is a significant barrier to rotation about the indenyl–phenoxide bond, resulting in slow interconversion of diastereoisomers on the NMR time-scale. This barrier is estimated to be greater than 20.1(5) kcal mol^{-1} at 130 °C (which would lead to coalescence of the O*H* resonances).

It should be pointed out that tautomerism *via* 1,3 hydrogen shifts within these indenyl phenols will not directly lead to racemization. This is based upon the assumption that the hydrogen shift occurs in a confacial fashion. The inden-3-yl ring is sufficiently acidic to be de-protonated. Hence, treatment of a



Scheme 2

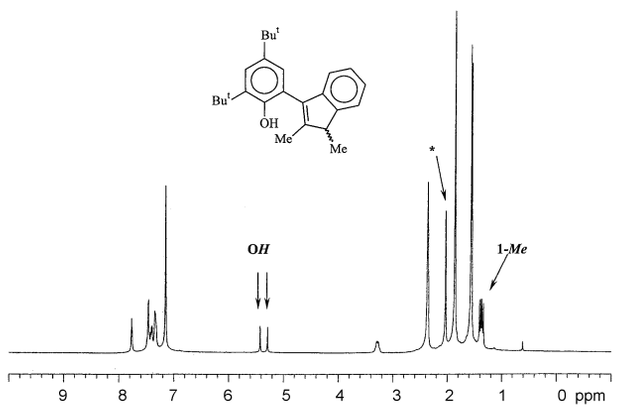


Fig. 2 ^{1}H NMR (*p*-xylene-d_{10}, 20 °C) spectrum of $HOC_6H_2\{C_9H_5Me_2$-2,3$\}$-2-Bu^t_2-4,6, **3**. * Protio impurity.

pentane solution of **1** with two equivalents of Bu^nLi in hexane led to the di-lithio salt **6** as a white powder.

Synthesis of Cp–titanium derivatives of 2-(1-indenyl)-4,6-di-*tert*-butylphenoxides

Reaction of the phenols with $[CpTiCl_3]$[17] in the presence of pyridine has previously been used to generate a variety of corresponding mono-aryloxides.[16d] Reaction with **1**–**4** leads to formation of the corresponding di-chlorides **7**–**10** in good yield (Scheme 3). No evidence was obtained for the de-protonation of the indenyl ring in these reactions. The spectroscopic and structural data on **7**–**10** are consistent with the presence of an inden-3-yl ring in all cases. All four compounds were structurally characterized (Tables 1–4) and ORTEP views of **8** and **9** are shown in Fig. 3 and 4. In all four compounds both the (a*R*) and (a*S*) forms are present within the unit cells (Scheme 3). The structural parameters are comparable and similar to those reported for previously isolated $[CpTi(OAr)Cl_2]$ compounds.[16,18] The Ti–O–Ar angles in **7**–**10** span the narrow range of 157–160°. Large M–O–Ar angles are a common feature of early d-block metal aryloxide compounds.[19] In all four compounds a conformation is adopted in the solid state in which the plane of the phenoxy ring is oriented approximately co-planar

Table 1 Selected bond distances (Å) and angles (°) for $[CpTi(OC_6H_2\{C_9H_7\}$-2-Bu^t_2-4,6$)Cl_2]$, **7**

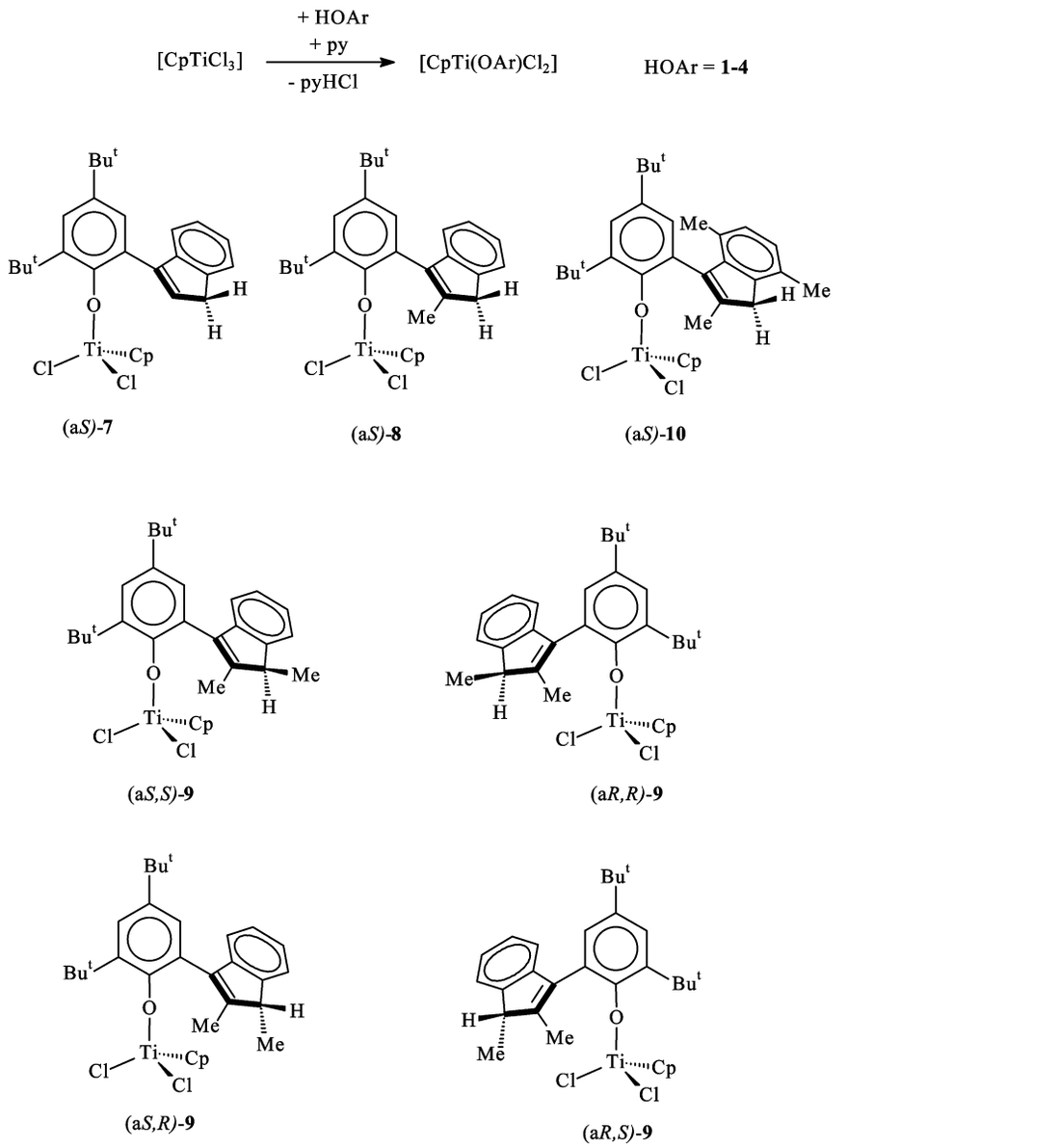
Ti–O(1)	1.785(2)	Ti–Cl(2)	2.2554(8)
Ti–Cp	2.023(3)	Ti–Cl(1)	2.2581(8)
Cl(1)–Ti–Cl(2)	100.24(4)	O(1)–Ti–Cp	118.1(1)
O(1)–Ti–Cl(1)	103.74(6)	Cl(1)–Ti–Cp	113.36(9)
O(1)–Ti–Cl(2)	104.89(6)	Cl(2)–Ti–Cp	114.41(8)
Ti–O(1)–C(11)	158.7(1)		

Table 2 Selected bond distances (Å) and angles (°) for $[CpTi(OC_6H_2\{C_9H_6Me$-2$\}$-2-Bu^t_2-4,6$)Cl_2]$, **8**

Ti–O(1)	1.784(1)	Ti–Cl(2)	2.2575(6)
Ti–Cp	2.030(2)	Ti–Cl(1)	2.2574(6)
Cl(1)–Ti–Cl(2)	100.87(2)	O(1)–Ti–Cp	118.00(8)
O(1)–Ti–Cl(1)	106.08(5)	Cl(1)–Ti–Cp	113.95(7)
O(1)–Ti–Cl(2)	102.83(4)	Cl(2)–Ti–Cp	113.20(7)
Ti–O(1)–C(11)	157.8(1)		

Table 3 Selected bond distances (Å) and angles (°) for $[CpTi(OC_6H_2\{C_9H_5Me_2$-1,2$\}$-2-$Bu^t_2$-4,6$)Cl_2]$, **9**

Ti–O(1)	1.788(2)	Ti–Cl(1)	2.2621(8)
Ti–Cp	2.030(3)	Ti–Cl(2)	2.2581(8)
Cl(1)–Ti–Cl(2)	99.59(3)	O(1)–Ti–Cp	117.6(1)
O(1)–Ti–Cl(1)	107.15(6)	Cl(1)–Ti–Cp	113.1(1)
O(1)–Ti–Cl(2)	103.44(6)	Cl(2)–Ti–Cp	114.1(1)
Ti–O(1)–C(11)	157.7(2)		



Scheme 3

Table 4 Selected bond distances (Å) and angles (°) for [CpTi(OC$_6$H$_2${C$_9$H$_4$Me$_3$-2,4,7}-2-Bu$^t_2$-4,6)Cl$_2$], **10**

Ti–O(1)	1.789(2)	Ti–Cl(1)	2.2634(8)
Ti–Cp	2.020(3)	Ti–Cl(2)	2.2597(8)
Cl(1)–Ti–Cl(2)	100.80(3)	O(1)–Ti–Cp	118.7(1)
O(1)–Ti–Cl(1)	101.97(6)	Cl(1)–Ti–Cp	113.23(9)
O(1)–Ti–Cl(2)	107.43(6)	Cl(2)–Ti–Cp	112.8(1)
Ti–O(1)–C(11)	159.9(2)		

with the Cp ring. An identical geometry is adopted for all other reported [CpTi(OAr)Cl$_2$] compounds.[16] In **7**–**10** the indenyl ring packs pointing towards the Cp ring, making torsion angles with the phenoxy ring of 56, 73, 71 and 75° for **7**–**10**, respectively.

At ambient temperatures the potentially diastereotopic methylene protons in the *ortho*-inden-3-yl groups of **7** appear as a broad singlet in the ^{1}H NMR spectra due to indenyl rotation on the NMR timescale. At lower temperatures this signal broadens and resolve into the AB pattern expected for the static structure. Variable temperature NMR studies of **7** in toluene-d$_8$ allow the barrier to inden-3-yl rotation (enantiomer interconversion) to be estimated at 13.9(5) kcal mol^{-1} (at 20 °C). In contrast the 2-methyl derivative **8** (Fig. 5) and 2,4,7-trimethyl substituted compound **10** show sharp, well-resolved AB patterns for these methylene protons at ambient temperature.

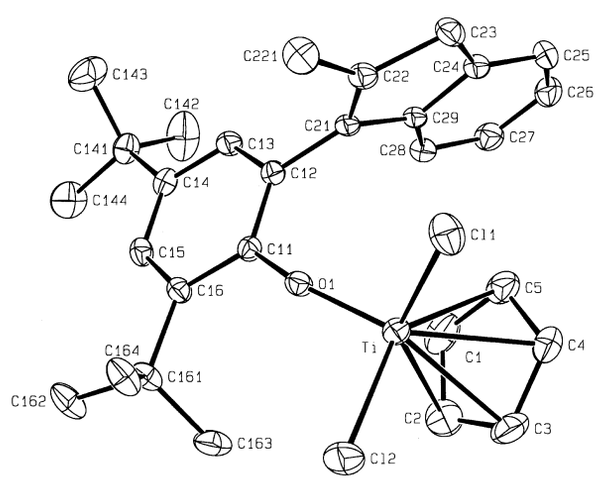


Fig. 3 Molecular structure of [CpTi(OC$_6$H$_2${C$_9$H$_6$Me-2}-2-Bu$^t_2$-4,6)Cl$_2$], **8**.

In the case of the 1,2-dimethyl substituted **9**, two enantiomeric pairs of diastereomers are possible. In the solid state only the (a*S*,*S*) and (a*R*,*R*) forms were observed, with the 1-methyl group pointing away from the titanium coordination sphere. In solution only one major set of ^{1}H and ^{13}C NMR resonances

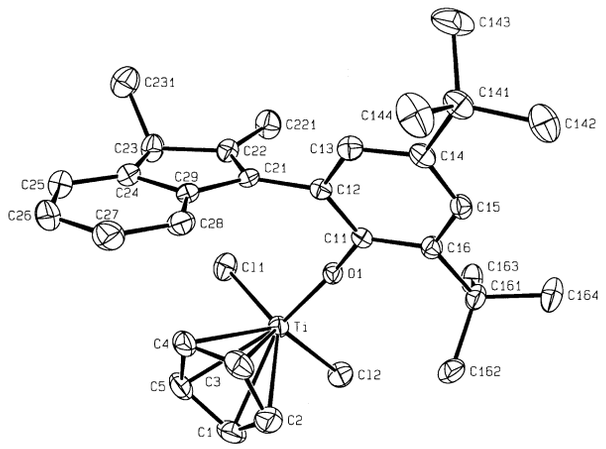


Fig. 4 Molecular structure of [CpTi(OC_6H_2{$C_9H_5Me_2$-1,2}-2-Bu^t_2-4,6)Cl_2], **8**.

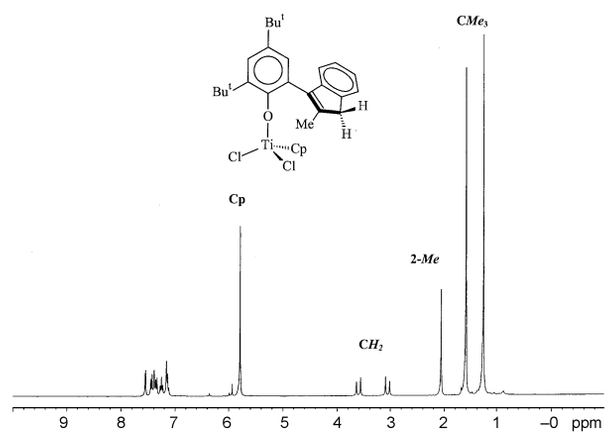


Fig. 5 ^{1}H NMR (C_6D_6) spectrum of [CpTi(OC_6H_2{C_9H_6Me-2}-2-Bu^t_2-4,6)Cl_2], **8**.

were observed. Hence, it appears that replacement of the phenolic proton by the much bulkier [$CpTiCl_2$] unit destabilizes the (a*S*,*R*) and (a*R*,*S*) forms in solution.

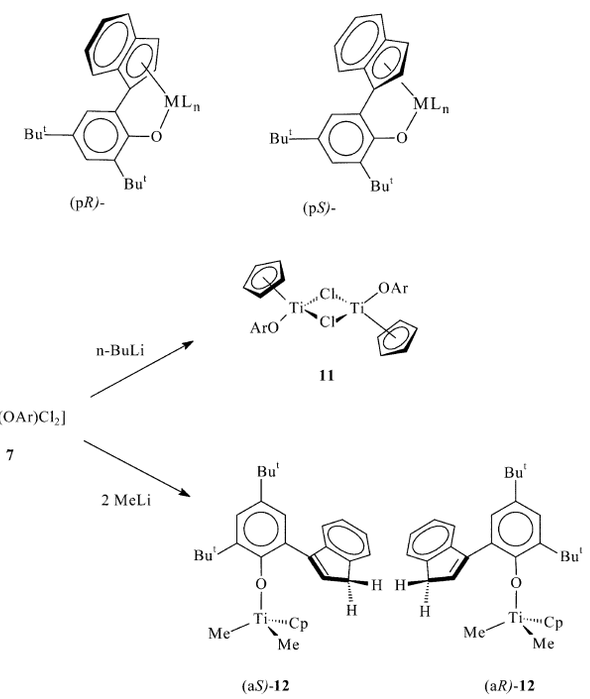
Attempted deprotonation and formation of a constrained geometry chelate ring

The indenyl ring of the ligand used in this study has enantiotopic faces. Hence, metallation of the indenyl ring (deprotonation and metal binding) can lead to two enantiomeric complexes. The nomenclature used to define the planar chirality of the chelates thus obtained is based upon that used for ansa-metallocenes.[20] The planar chirality of the indenyl ring is assigned (p*R*) or (p*S*) based on the Cahn–Ingold–Prelog configuration of the 1-position of the metal bound ring (Scheme 4). In this case, the 1-position is the stereogenic center bound to the *ortho*-position of the phenoxide nucleus. The (a*R*) and (a*S*) forms of the parent ligand lead directly to the (p*R*) and (p*S*) chelates, respectively. It should also be noted that the chirality 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.

Attempted de-protonation of the inden-3-yl ring in **7** by treatment with n-BuLi or MeLi did not lead to the formation of chelate rings. Instead n-BuLi resulted in reduction of the metal center and formation of a compound **11** containing two d^1-Ti(III) metal centers linked by chloride bridges (Scheme 4). The solid-state structure of **11** (Table 5, Fig. 6) shows a transoid arrangement of Cp and aryloxide ligands similar to that found in related compounds.[16] Each molecule (Fig. 6) can be seen to contain both (a*R*) and (a*S*) forms of the ligand (crystallographic inversion center). This reduction process presumably

Table 5 Selected bond distances (Å) and angles (°) for [CpTi(OC_6H_2{C_9H_7}-2-Bu^t_2-4,6)(μ-Cl)]$_2$, **11**

Ti–O(1)	1.819(2)	Ti–Cl	2.420(1)
Ti–Cp	2.028(5)	Ti–Cl(1)	2.430(1)
Cl–Ti–Cl	89.96(3)	Ti–Cl–Ti	90.04(3)
Cl–Ti–O(1)	104.45(7)	Cl–Ti–O(1)	102.44(9)
Cl–Ti–Cp	118.0(1)	Cl–Ti–Cp	116.9(2)
O(1)–Ti–Cp	120.1(1)	Ti–O(1)–C(11)	154.7(2)



Scheme 4

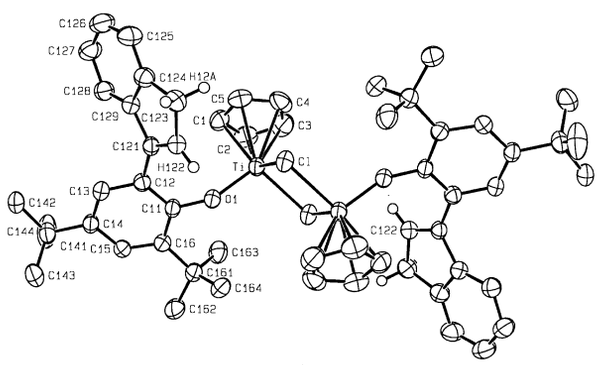


Fig. 6 Molecular structure of [CpTi(OC_6H_2{C_9H_7}-2-Bu^t_2-4,6)-(μ-Cl)]$_2$, **11**.

involves alkylation at the Ti–Cl bond followed by a β-hydrogen abstraction/elimination pathway leading to an unstable hydride intermediate. The reaction with methyl lithium also leads to alkylation of the Ti–Cl bonds and formation of the dimethyl compound **12** (Scheme 4). Both Ti–*Me* groups in **12** appear as one broad singlet in both the ^{1}H and ^{13}C NMR spectra at ambient temperatures but appear as two well-resolved resonances at lower temperatures (Fig. 7). From the coalescence temperature the barrier to indenyl rotation can be estimated to be 13.4(5) kcal mol^{-1} at −5 °C, slightly lower than that measured for the dichloride **7**. These barriers are much lower than that measured for corresponding 2-(1-naphthyl)phenoxides. In the case of the direct 2-(1-naphthyl-4,6-di-*tert*-butlyphenoxide analogue of **12**, two sharp, distinct Ti–Me resonances are observed in the ^{1}H NMR spectrum even at 90 °C.[16b]

Reaction of [$CpTiCl_3$] with the di-lithio (doubly deprotonated ligand) compound **6** did lead to the formation of a

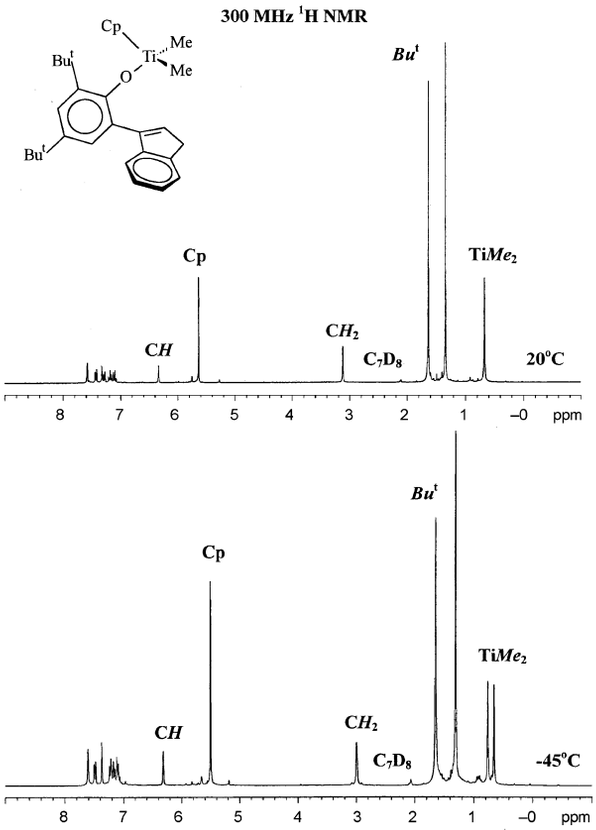
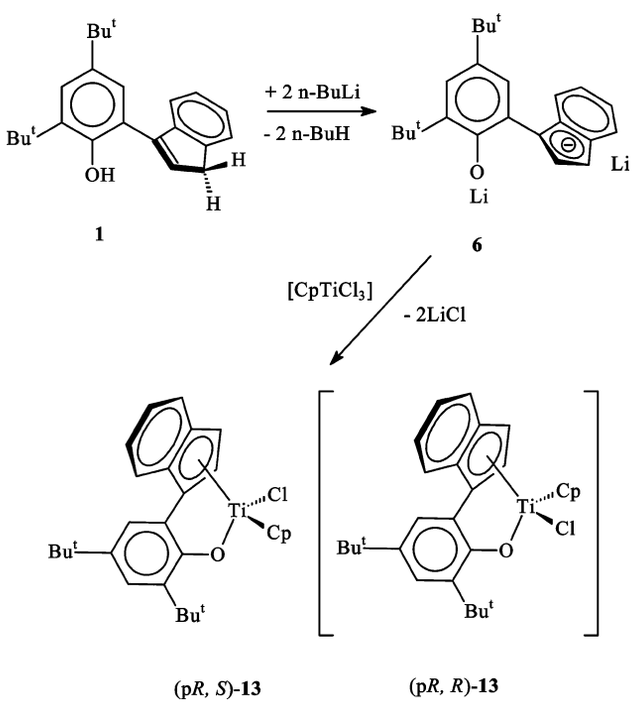


Fig. 7 ^{1}H NMR (toluene-d$_8$) spectrum of [CpTi(OC$_6$H$_2${η^5-C$_9$H$_7$}-2-Bu$^t_2$-4,6)Me$_2$], **12**, at 20 and −45 °C.



Scheme 5

chelated indenyl-phenoxide derivative **13** (Scheme 5). The compound was structurally characterized and an ORTEP view is shown in Fig. 8 with selected bond distances and angles in Table 6. The chelation also introduces a further stereochemical element in that the pseudo-tetrahedral titanium now becomes a chiral center. Hence, there are two diastereoisomers possible for **13** with the plane of the indenyl ring pointing either towards or away from the Cp substituent (Scheme 5). In the solid state only the (p*S*,*R*) and (p*R*,*S*) forms were observed (indenyl oriented

Table 6 Selected bond distances (Å) and angles (°) for [CpTi(OC$_6$H$_2${η^5-C$_9$H$_6$}-2-Bu$^t_2$-4,6)Cl], **13**

Ti(1)–O(1)	1.915(3)	Ti(2)–O(2)	1.908(3)
Ti(1)–C(111)	2.365(5)	Ti(2)–C(221)	2.366(4)
Ti(1)–C(112)	2.334(5)	Ti(2)–C(212)	2.348(4)
Ti(1)–C(113)	2.370(5)	Ti(2)–C(213)	2.378(4)
Ti(1)–C(114)	2.398(5)	Ti(2)–C(214)	2.420(4)
Ti(1)–C(115)	2.386(5)	Ti(2)–C(215)	2.397(4)
Ti(1)–Cl(1)	2.375(1)	Ti(2)–Cl(2)	2.385(1)
Ti(1)–C(121)	2.332(4)	Ti(2)–C(221)	2.366(4)
Ti(1)–C(122)	2.363(4)	Ti(2)–C(222)	2.363(4)
Ti(1)–C(123)	2.399(5)	Ti(2)–C(223)	2.374(4)
Ti(1)–C(124)	2.514(5)	Ti(2)–C(224)	2.491(4)
Ti(1)–C(129)	2.414(4)	Ti(2)–C(229)	2.433(4)
O(1)–Ti(1)–Cl(1)	92.20(9)	O(2)–Ti(2)–Cl(2)	95.38(9)
Ti(1)–O(1)–C(11)	124.8(3)	Ti(2)–O(2)–C(21)	127.3(3)

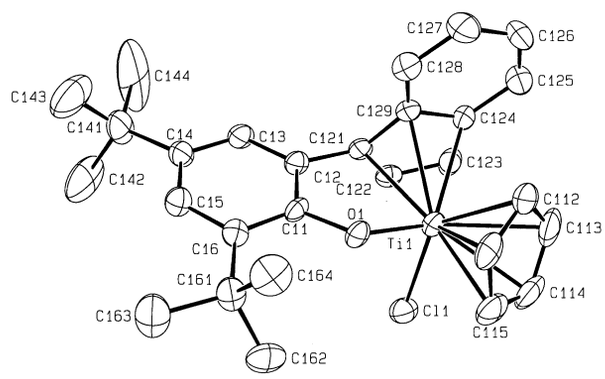


Fig. 8 Molecular structure of [CpTi(OC$_6$H$_2${η^5-C$_9$H$_6$}-2-Bu$^t_2$-4,6)Cl], **13**.

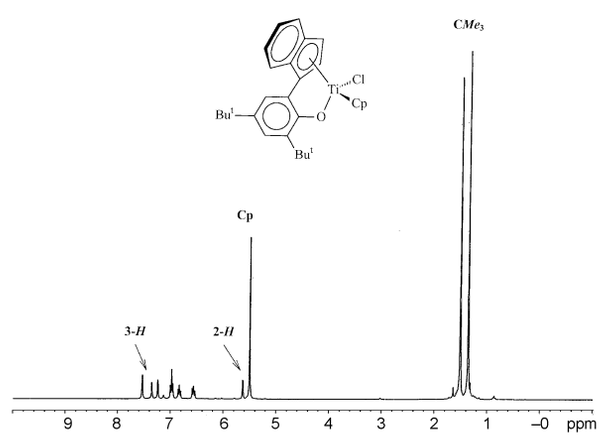


Fig. 9 ^{1}H NMR (C$_6$D$_6$) spectrum of [CpTi(OC$_6$H$_2${η^5-C$_9$H$_6$}-2-Bu$^t_2$-4,6)Cl], **13**.

towards the Cp group, Fig. 8). In solution only one set of ^{1}H (Fig. 9) and ^{13}C NMR signals were observed indicating the presence of this single diastereoisomer.

Besides its inherent stereochemistry, compound **13** also is of interest as it contains both a "regular" cyclopentadienyl group and the new, chelated indenyl group bound to the same metal center. The structural parameters for the bonding of these two groups are highlighted in a "radar plot" of Ti–C distances in Fig. 10. The crystal contains two independent molecules within the unit cell. The Cp ligand is symmetrically bound to the titanium metal with equal Ti–C distances. The Ti–C(indenyl) distances are more irregular. The Ti–C(1) (*ipso* carbon bound to the phenoxy ring) distance is the shortest contact with the longest being to the aromatic carbon atoms, C(4) and C(5). The "slip value" has been defined as [Δ = avg. d{M–C(3a),(7a)} − avg. d{M–C(1),(3)}].[21] This corresponds to [Δ = avg. d{M–C(124),(129)} − avg. d{M–C(121),(123)] in the labeling used

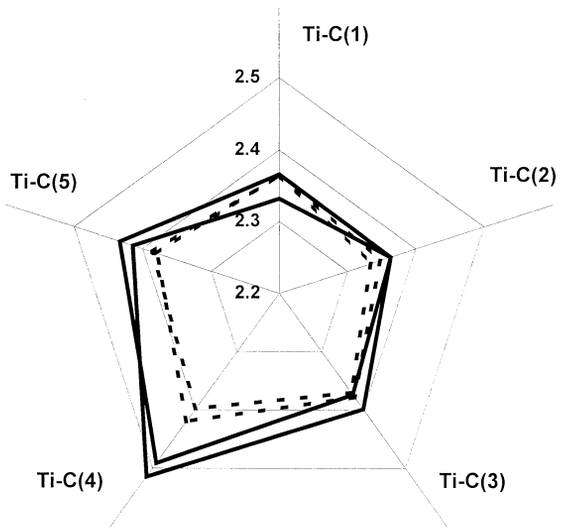


Fig. 10 "Radar" plot of the Ti–C(indenyl) (solid line) and Ti–Cp (dashed line) distances in compound **13** (two independent molecules within the unit cell). The coordination is exaggerated by using a plot scale of 2.2–2.5 Å from the metal center.

here. For compound **13** the value of $\Delta = 0.092$ and 0.028 Å for the two independent molecules. 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.[21] Hence, based upon this parameter, there is only minor slippage away from η^5-bonding. The electronic configuration of the Ti metal center in **13** is formally 16-electron. The Ti–O–C angle for the chelated indenyl-phenoxide in **13** is 125 and 127° (Table 6). The Ti–O distances of 1.915(3) and 1.908(3) Å are significantly longer than the 1.78 Å found in electronically less saturated **7**–**10** (Tables 1–4), indicating that there is decreased oxygen-p to metal-d, π-donation.

Experimental

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 ^{1}H 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.

Synthesis of 2-(inden-3-yl)-4,6-di-*tert*-butylphenol (1)

A sample of 2-bromo-4,6-di-*tert*-butyl phenol (143 g, 0.50 mol) was dissolved in diethyl ether (500 mL) and cooled to 0 °C using an ice/acetone bath. Under a nitrogen atmosphere Bu^{n}Li was added (400 mL of a 2.5M hexane solution, 1.0 mol). The solution became white in color and was allowed to slowly warm to room temperature over the course of 2 h. To this solution was slowly added 1-indanone (66.3 g, 0.50 mol) dissolved in ether and the yellow solution was allowed to stir overnight. The solution was then hydrolyzed with 6 M HCl (300 mL) and allowed to stir for 1 h. The orange ether layer was separated from the aqueous layer, washed three times with water (500 mL), dried with $MgSO_4$, and evaporated to dryness affording a brown oil. This oil was vacuum distilled to 150 °C to remove 1-indanone and 2,4-di-*tert*-butylphenol leaving a brown oil (100 g, 62%). Elution of this oil on silica-gel with hexane afforded a yellow oil that gave white crystalline material from cold pentane. Anal. Calcd for $C_{23}H_{28}O$: C, 86.20; H, 8.81. Found: C, 86.23; H, 8.72%. (HRMS): calcd: 320.2140, found: 320.2139. ^{1}H NMR ($CDCl_3$, 30 °C): δ 7.27–7.67 (aromatics); 6.78 [t, $^3J(^1H–^1H)$ = 2.1 Hz, C*H*]; 5.68 (s, O*H*); 3.69 [d, $^3J(^1H–^1H)$ = 1.6 Hz, CH_2]; 1.57 (s), 1.44 (s, CMe_3). ^{13}C NMR ($CDCl_3$, 30 °C): δ 149.3 (O–*C*); 144.4, 144.2, 141.7, 141.5, 135.3, 132.7, 126.5, 125.5, 124.1, 123.9, 123.8, 121.2, 120.9 (unsaturated *C*); 38.7 (*C*H$_2$); 35.1, 34.3 (*C*Me$_3$); 31.7, 29.7 (C*Me*$_3$).

Synthesis of 2-(1-methylinden-3-yl)-4,6-di-*tert*-butylphenol (2)

A solution of 2-bromo-4,6-di-*tert*-butylphenol (105 g, 0.368 mol) in 500 mL of diethyl ether was cooled to 0 °C under an atmosphere of nitrogen. To the stirred solution was slowly added Bu^{n}Li (305 mL of a 2.5M hexane solution, 0.77 mol). The solution was slowly warmed to room temperature with magnetic stirring for 5 h. The white solution was then cooled to 0 °C in an ice bath, and freshly distilled 2-methylindanone (49 g, 0.34 mol) in diethyl ether was added dropwise over 30 min *via* an addition funnel. The yellow solution was allowed to warm to room temperature followed by stirring overnight. The reaction mixture was quenched with 100 mL of a saturated ammonium chloride solution and poured into a 2000 mL Erlenmeyer flask containing 500 g of ice and 100 mL of concentrated HCl. The mixture was stirred for 30 min and the aqueous layer extracted three times with 100 mL portions of diethyl ether. The ether extracts were combined and washed three times with water (200 mL), dried with $MgSO_4$, and evaporated to dryness to produce a brown oil. The crude material was vacuum distilled (0.5 mmHg) at 150 °C to remove indanone and 2,4-di-*tert*-butylphenol to afford a reddish brown crystalline residue. Dissolution of this material in 300 mL of pentane followed by cooling to −20 °C produced a white crystalline material overnight (27 g, 24%). Anal. Calcd for $C_{24}H_{30}O$: C, 86.18; H, 9.04. Found: C, 86.21; H, 8.88%. (HRMS): calcd: 334.2297, found: 334.2302. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.09–7.51 (m, aromatics); 5.16 (s, O*H*); 3.56 (s, CH_2); 2.12 [s, CH_3]; 1.48 (s), 1.35 (s, C*Me*$_3$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 149.2 (O–*C*); 145.8, 143.9, 142.7, 141.6, 135.0, 134.7, 126.5, 124.5, 124.3, 123.5, 123.4, 123.3, 119.9, 112.3 (unsaturated *C*); 43.1 (*C*H$_2$); 35.1, 34.3 (*C*Me$_3$); 31.7, 29.6 (C*Me*$_3$); 15.2 (*C*H$_3$).

Synthesis of 2-(1,2-dimethylinden-3-yl)-4,6-di-*tert*-butylphenol (3)

Using an identical procedure as for **1**, 65 g of 2-bromo-4,6-di-*tert*-butylphenol (0.22 mol) was treated with Bu^{n}Li (180 mL of a 2.5 M hexane solution, 0.45 mol), followed by addition of 35 g of 2,3-dimethylindanone (0.21 mol). Hydrolysis and work-up of the reaction mixture produced a brown oil that was vacuum distilled at 150 °C to remove indanone and 2,4-di-*tert*-butylphenol. The reddish brown residue was dissolved in 400 mL of pentane and cooled to −20 °C to produce a light yellow crystalline material overnight (22 g, 30%). Anal. Calcd for $C_{25}H_{32}O$: C, 86.15; H, 9.25. Found: C, 85.99; H, 9.26%. (HRMS): calcd: 348.2453, found: 348.2454. ^{1}H NMR (C_6D_6, 25 °C): δ 7.10–7.61 (m, aromatics); 5.23 (s), 5.11 (s, O*H*); 3.01 (m, C*H*); 1.72 (s), 1.71 (s, CH_3); 1.66 (s), 1.65 (s), 1.33 (s), 1.32 (s, C*Me*$_3$); 1.09 (d), 0.99 [d, $^3J(^1H–^1H)$ = 7.5 Hz, CH_3]. ^{13}C NMR ($CDCl_3$, 25 °C): δ 149.2, 149.0 (O–*C*); 148.9, 148.5, 144.4, 141.6, 134.9, 133.3, 126.6; 124.8, 124.7, 124.5, 124.3, 123.4, 122.6,, 120.5, 120.4, 119.8; (unsaturated *C*); 47.7, 47.4 (*C*H); 35.0, 34.3 (*C*Me$_3$); 31.7, 29.6 (C*Me*$_3$); 16.2, 15.9, 13.3, 13.2 (*C*H$_3$).

Synthesis of 2-(2,4,7-trimethylinden-3-yl)-4,6-di-*tert*-butylphenol (4)

Using an identical procedure as for **1**, 68 g of 2-bromo-4,6-di-*tert*-butylphenol (0.22 mol) was treated with Bu^{n}Li (180 mL of a 2.5 M hexane solution, 0.45 mol), followed by addition of 35 g of 2,4,7-trimethylindanone (0.20 mol). Hydrolysis and work-up of the reaction mixture produced a brown oil that was

vacuum distilled at 150 °C to remove indanone and 2,4-di-*tert*-butylphenol. The reddish brown residue was dissolved in 300 mL of pentane and cooled to −20 °C to produce a white crystalline material overnight (25 g, 34%). Anal. Calcd for $C_{26}H_{34}O$: C, 86.13; H, 9.45. Found: C, 85.90; H, 9.19%. (HRMS): calcd: 362.2610, found: 362.2609. ^{1}H NMR (C_6D_6, 25 °C): δ 7.56 (d), 7.16 (s), 6.93 (s, aromatics); 5.09 (s, O*H*); 2.80 (d), 2,84 [d, $^2J(^1H–^1H)$ = 13 Hz, CH_2); 2.20 (s), 2.06 (s), 1.75 (s, CH_3); 1.65 (s), 1.33 (s, CMe_3). ^{13}C NMR (C_6D_6, 25 °C): δ 150.7, 150.12, 144.8, 142.1, 141.9, 141.4, 135.6, 135.2, 135.0, 130.1, 130.0, 128.8, 128.3, 127.8, 127.3, 126.1, 125.2, 124.4, 123.4 (unsaturated *C*); 41.7 (*C*H$_2$); 35.3, 34.4 (*C*Me$_3$); 31.8, 29.9 (C*Me*$_3$); 18.7, 18.4, 14.5 (*C*H$_3$).

Synthesis of 2-(1,2,4,7-tetramethylinden-3-yl)-4,6-di-*tert*-butylphenol (5)

Using an identical procedure as for **1**, 38 g of 2-bromo-4,6-di-*tert*-butylphenol (0.13 mol) was treated with Bu^{n}Li (110 mL of a 2.5 M hexane solution, 0.28 mol), followed by addition of 23 g of 2,4,7-trimethylindanone (0.20 mol). Hydrolysis and work-up of the reaction mixture produced a brown oil that was vacuum distilled at 150 °C. The reddish brown residue was eluted over silica gel with hexane to afford an orange powder (9.5 g, 21%). Anal. Calcd for $C_{26}H_{34}O$: C, 86.11; H, 9.64. Found: C, 85.08; H, 9.74%. (HRMS): calcd: 376.2766, found: 376.2758. ^{1}H NMR (C_6D_6, 25 °C): δ 7.55 (s), 6.70 (s, aromatics); 5.20 (s), 5.06 (s, O*H*); 3.10–2.91 (m, C*H*); 2.27 (s), 2.25 (s), 2.04 (s), 1.68 (s, CH_3); 1.66 (s), 1.31 (s, CMe_3); 1.13 (d), 0.99 [d, $^3J(^1H–^1H)$ = 7.5 Hz, CH_3]. ^{13}C NMR (C_6D_6, 25 °C): δ 150.8, 150.2 (O–*C*); 150.1, 150.0, 147.3, 147.2, 142.2, 141.6, 135.0, 134.4, 133.5, 130.8, 130.3, 127.8, 127.3, 126.1, 125.2, 124.4, 123.4 121.7 (unsaturated *C*); 47.0, 46.8 (*C*H$_2$); 35.3, 34.4 (*C*Me$_3$); 31.8, 29.9 (C*Me*$_3$); 18.8, 18.6, 15.2, 14.0, 12.7, 12.6 (*C*H$_3$).

Synthesis of [Li$_2$(OC$_6$H$_2$-Ind-2-Bu^t-4,6)] (6)

To a stirred pentane (200 mL) solution of **1** (10 g, 34 mmol) was slowly added Bu^{n}Li (30 mL of a 2.5M hexane solution, 75 mmol). A yellow precipitate was formed upon complete addition of Bu^{n}Li, and stirring was continued for an additional 45 min. The yellow solid was rinsed five times with pentane then dried under vacuum affording a yellow powder that was used without further purification (9.0 g, 87%).

Synthesis of [CpTi(OC$_6$H$_2${C$_9$H$_7$}-2-Bu$^t_2$-4,6)Cl$_2$] (7)

A sample of [CpTiCl$_3$] (3.0 g, 13.7 mmol) was dissolved in benzene along with pyridine (1.7 mL, 21.0 mmol). To this solution was added 2-(inden-3-yl)-4,6-di-*tert*-butylphenol (4.4 g, 13.7 mmol) causing the solution to immediately to turn red and a precipitate to form. The mixture was stirred overnight and filtered to remove pyridinium chloride. The filtrate was evacuated to dryness giving a red glassy solid that was dissolved in a minimal amount of benzene/pentane. After sitting undisturbed overnight red crystals (1/2 benzene per Ti) formed which were washed with pentane and dried *in vacuo* (6.5 g, 94%). Anal. Calcd for $C_{28}H_{32}Cl_2OTi$: C, 66.81; H, 6.41. Calcd for $C_{31}H_{35}Cl_2Oti$ (1/2 benzene per Ti): C, 68.65; H, 6.50. Found: C, 67.79; H, 6.42%. ^{1}H NMR (C_6D_6, 30 °C): δ 7.13–7.61 (aromatics); 6.61 (t, C*H*); 5.81 (s, C$_5H_5$); 3.36 (br, CH_2); 1.61 (s), 1.28 [s, C(CH_3)$_3$]. ^{1}H NMR (C_7D_8, −30 °C): δ 6.72–7.58 (aromatics); 6.60 (br, C*H*); 5.67 (s, C$_5H_5$); 3.48 (d), 3.12 [d, $^2J(^1H–^1H)$ = 13.8 Hz, CH_2); 1.58 (s), 1.25 (s, CMe_3). Selected ^{13}C NMR (C_6D_6, 30 °C): δ 165.5 (Ti–O–*C*); 121.0 (*C*$_5$H$_5$); 38.7 (CH_2); 35.9, 34.7 (*C*Me$_3$); 31.5, 30.6 (CMe_3).

Synthesis of [CpTi(OC$_6$H$_2${C$_9$H$_6$Me-2}-2-Bu$^t_2$-4,6)Cl$_2$] (8)

A flask was charged with [CpTiCl$_3$] (1.60 g, 7.29 mmol), pyridine (2.0 mL, 25 mmol), and toluene (~50 mL). As this mixture was stirring **2** (2.44 g, 7.29 mmol) dissolved in toluene was slowly added. The solution slowly turned deep red and stirring was continued overnight. Filtration of the pyridinium chloride, followed by removal of the solvent under vacuum afforded an orange–red powder. Dissolution of the crude material in hot hexane produced deep red crystals of **8** on cooling (2.20 g, 58.4%). Anal. Calcd for $C_{29}H_{34}Cl_2OTi$: C, 67.32; H, 6.62. Found: C, 67.21; H, 6.58%. ^{1}H NMR (C_6D_6, 25 °C): δ 7.55 (d), 7.33–7.45 (m), 7.25 (t), 7.11–7.16 (m, aromatics); 5.79 (s, C$_5H_5$); 3.59, 3.05 (AB, $^2J(^1H–^1H)$ = 12.8 Hz, CH_2); 2.05 (s, CH_3); 1.59 (s), 1.26 (s, CMe_3). ^{13}C NMR (C_6D_6, 25 °C): δ 165.5 (Ti–O–*C*); 148.0, 146.8, 146.2, 143.5, 138.5, 135.2, 126.8, 125.7, 124.4, 123.0, 121.2, 118.6 (unsaturated *C*); 42.8 (*C*H$_2$); 35.8, 34.7 (*C*Me$_3$); 31.5, 30.7 (C*Me*$_3$); 15.9 (*C*H$_3$).

Synthesis of [CpTi(OC$_6$H$_2${C$_9$H$_5$Me$_2$-1,2}-2-Bu$^t_2$-4,6)Cl$_2$] (9)

A flask was charged with [CpTiCl$_3$] (1.12 g, 5.11 mmol), pyridine (1.5 mL, 19 mmol), and toluene (~50 mL). As this mixture was stirring **3** (1.78 g, 5.11 mmol) dissolved in toluene was slowly added. The solution slowly turned deep red and stirring was continued overnight. Filtration of the pyridinium chloride, followed by removal of the solvent under vacuum afforded an orange–red powder. Dissolution of the crude material in hot hexane produced deep red crystals of a single diastereomer of **9** on cooling (1.00 g, 36.9%). X-ray diffraction analysis of the isolated crystals established the configuration as the epimeric (a*S*,*S*)/(a*R*,*R*) isomers. Anal. Calcd for $C_{30}H_{36}Cl_2OTi$: C, 67.81; H, 6.83. Found: C, 67.61; H, 6.86%. ^{1}H NMR (C_6D_6, 25 °C): δ 7.55 (d), 7.32–7.45 (m), 7.24 (t), 7.15 (t, aromatics); 5.80 (s, C$_5H_5$); 3.64 (q, $^3J(^1H–^1H)$ = 7.5 Hz, C*H*–Me); 2.04 (s, 2-CH_3); 1.59 (s), 1.25 (s, CMe_3); 1.15 (d, $^3J(^1H–^1H)$ = 7.5 Hz, CH–*Me*). ^{13}C NMR (C_6D_6, 25 °C): δ 165.6 (Ti–O–*C*); 151.9, 149.2, 146.6, 146.3, 138.6, 133.9, 127.1, 125.9, 124.7, 123.6, 123.1, 121.2, 121.1, 118.6 (unsaturated *C*); 47.3 (*C*H$_2$); 35.8, 34.7 (*C*Me$_3$); 31.5, 30.7 (C*Me*$_3$); 15.4, 13.9 (*C*H$_3$).

Synthesis of [CpTi(OC$_6$H$_2${C$_9$H$_4$Me$_3$-2,4,7}-2-Bu$^t_2$-4,6)Cl$_2$] (10)

A flask was charged with [CpTiCl$_3$] (1.22 g, 5.56 mmol), pyridine (1.5 mL, 19 mmol), and toluene (~50 mL). As this mixture was stirring **4** (2.02 g, 5.56 mmol) dissolved in toluene was slowly added. The solution slowly turned deep red and stirring was continued overnight. Filtration of the pyridinium chloride, followed by removal of the solvent under vacuum afforded an orange–red powder. Dissolution of the crude material in hot hexane produced deep red crystals of **10** on cooling (2.11 g, 69.6%). Anal. Calcd for $C_{31}H_{38}Cl_2OTi$: C, 68.27; H, 7.02. Found: C, 68.00; H, 6.90%. ^{1}H NMR (C_6D_6, 25 °C): δ 7.48 (d), 7.24 (d), 6.97 (q, aromatics); 5.93 (s, C$_5H_5$); 3.44, 2.90 (AB, $^2J(^1H–^1H)$ = 13.0 Hz, CH_2); 2.25, 2.23, 2.01 (s, CH_3); 1.56 (s), 1.24 (s, CMe_3). ^{13}C NMR (C_6D_6, 25 °C): δ 165.3 (Ti–O–*C*); 146.2, 145.7, 144.5, 142.4, 138.7, 136.3, 131.3, 130.8, 130.3, 127.3, 126.9, 125.8, 123.1, 122.7, 122.1, 121.0, 119.6 (unsaturated *C*); 41.7 (*C*H$_2$); 35.8, 34.7 (*C*Me$_3$); 31.5, 30.7 (C*Me*$_3$); 20.2, 18.5, 15.9 (*C*H$_3$).

Synthesis of [CpTi(OC$_6$H$_2${C$_9$H$_7$}-2-Bu$^t_2$-4,6)Me$_2$] (12)

A sample of [CpTi(OC$_6$H$_2${C$_9$H$_7$}-2-Bu$^t_2$-4,6)Cl$_2$] (470 mg, 0.93 mmol) was dissolved in benzene and MeLi (51 mg, 2.3 mmol) slowly added with stirring. The solution was stirred for 6 h, filtered, and the filtrate evacuated to dryness affording a yellow oil that was very soluble in hydrocarbon solvents. ^{1}H NMR (C_6D_6, 30 °C): δ 7.57 (d), 7.33 [d, $^4J(^1H–^1H)$ = 2.4 Hz, *meta* C$_6H_2$]; 7.04–7.55 (other aromatics); 6.29 (t, C*H*); 5.59 (s, C$_5H_5$); 3.05 (d, CH_2); 1.60 (s), 1.28 (s, CMe_3); 0.64 (br, Ti–*Me*). Selected ^{13}C NMR (C_6D_6, 30 °C): δ 161.7 (Ti–O–*C*); 114.3 (*C*$_5$H$_5$); 57.7 (br, Ti–*Me*); 38.4 (CH_2); 35.7, 34.5 (*C*Me$_3$); 31.7, 30.5 (C*Me*$_3$). ^{1}H NMR (C_7D_8, −45 °C): δ 6.97–7.61 (aromatics); 6.31 (d, C*H*); 5.50 (s, C$_5H_5$); 2.90 (d), 3.10 [d, $^2J(^1H–^1H)$ = 13

Table 7 Crystal data and data collection parameters

Compound	**1**	**2**	**3**	**4**	**7**·1/2C_6H_6	**8**	**9**	**10**	**11**·C_5H_{12}	**13**
Formula	$C_{32}H_{36}O_2$	$C_{24}H_{30}O$	$C_{25}H_{32}O$	$C_{26}H_{34}O$	$C_{31}H_{35}Cl_2OTi$	$C_{29}H_{34}Cl_2OTi$	$C_{30}H_{36}Cl_2OTi$	$C_{31}H_{38}Cl_2OTi$	$C_{61}H_{76}Cl_2O_2Ti_2$	$C_{28}H_{31}ClOTi$
Formula weight	452.64	334.00	348.53	362.56	542.43	517.40	531.43	545.45	1007.99	466.91
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a/Å	8.2956(2)	20.0248(5)	9.4964(4)	41.2752(17)	12.2422(4)	13.1454(2)	13.2652(2)	13.5218(2)	10.2296(8)	9.5121(4)
b/Å	10.0981(3)	10.2632(2)	10.5345(3)	6.1782(3)	12.6093(4)	11.4807(2)	11.7696(3)	9.8978(2)	10.7280(10)	14.3700(5)
c/Å	15.7158(6)	9.9894(2)	11.9256(4)	18.8466(10)	18.9505(6)	18.2793(4)	18.5253(5)	21.7332(3)	13.6638(14)	18.6606(7)
α/°	102.3307(11)	90	107.9647(18)	90	90	90	90	90	102.861(5)	80.576(2)
β/°	93.1236(11)	100.5259(7)	106.6234(15)	112.707(2)	102.5167(19)	103.5146(8)	104.9462(8)	94.395(1)	102.520(5)	84.799(2)
γ/°	91.625(2)	90	98.9550(15)	90	90	90	90	90	96.692(6)	86.506(1)
V/Å^3	1283.2(1)	2018.46(8)	1047.79(14)	4433.5(7)	2855.8(3)	2682.30(9)	2794.4(1)	2900.13(8)	1405.6(5)	2503.2(3)
Z	2	4	2	8	4	4	4	4	1	4
T/K	150	150	150	150	203	150	150	150	203	150
R	0.048	0.046	0.054	0.048	0.045	0.041	0.054	0.050	0.074	0.061
R_w	0.113	0.123	0.135	0.118	0.111	0.095	0.122	0.119	0.192	0.112

Hz, CH_2]; 1.64 (s), 1.30 (s, CMe_3); 0.76 (s), 0.65 (s, Ti–*Me*). Selected ^{13}C NMR (C_7D_8, −45 °C): δ 161.6 (Ti–O–*C*); 114.3 (C_5H_5); 58.8, 56.8 (Ti–*Me*); 38.3 (CH_2); 35.8, 34.6 (*C*Me$_3$); 31.7, 30.3 (CMe_3).

Synthesis of [CpTi(OC$_6$H$_2$-{η^5-Ind}-2-Bu^t-4,6)Cl] (13)

A flask was charged with [$CpTiCl_3$] (1.55 g, 7.07 mmol) and benzene (100 mL). As this mixture was stirring, solid [Li_2(OC$_6$H$_2$–{C_9H_6}-2-Bu$^t_2$-4,6)] (2.35 g, 7.07 mmol) was slowly added. The solution immediately turned deep red and stirring was continued overnight. Filtration of the crimson product mixture over Celite®, followed by removal of the solvent under vacuum, afforded glassy red solid. Dissolution of the crude material in minimal pentane produced crimson blocks of a single diastereomer of **13** on standing for days (1.05 g, 31.8%). X-ray diffraction analysis of the crystals established the configuration as the (p-*R*,*S*)/(p-*S*,*R*) isomers. Anal. Calcd for $C_{28}H_{31}ClOTi$: C, 72.03; H, 6.69. Found: C, 72.07; H, 6.81%. ^{1}H NMR (C_6D_6, 25 °C): δ 7.55 (d), 7.25 (d), 6.99 (t), 6.84 (t), 6.57 (t, aromatics); 7.37 (d), 5.64 [d, $^3J(^1H–^1H)$ = 3.3 Hz, η^5-C*H*]; 5.50 (s, C_5H_5); 1.50 (s), 1.35 (s, CMe_3). ^{13}C NMR (C_6D_6, 25 °C): δ 176.7 (Ti–O–*C*); 144.1, 139.0, 138.6, 134.8, 128.4, 127.4, 127.1, 126.1, 125.8, 125.2, 124.8, 124.0, 123.4, 122.5 (unsaturated *C*); 119.3 (C_5H_5); 98.8 (η^5-*C*H); 35.2, 34.6 (*C*Me$_3$); 31.9, 30.0 (CMe_3).

X-ray data collection and reduction

Crystal data and data collection parameters are contained in Table 7. 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 MoKα radiation (λ = 0.71073 Å) on a Nonius Kappa CCD. Lorentz and polarization corrections were applied to the data.[22] An empirical absorption correction using SCALEPACK was applied.[23] Intensities of equivalent reflections were averaged. The structure was solved using the structure solution program PATTY in DIRDIF92.[24] The remaining atoms were located in successive difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The structures were refined by full-matrix least-squares using observed data where the function minimized was $\Sigma w(|F_o|^2 - |F_c|^2)^2$ 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 factors were taken from the *International Tables for Crystallography*.[25] Refinement was performed on a AlphaServer 2100 using SHELX-97.[26] Crystallographic drawings were done using ORTEP.[27]

CCDC reference numbers 218466–218475.

See http://www.rsc.org/suppdata/dt/b3/b310415j/ for crystallographic data in CIF or other electronic format.

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