A chelating β-diketonate/phenoxide ligand and its coordination behavior toward titanium and scandium

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Dibenzoylmethane derivatives with one (L^1H_2) or both (L^2H_3, L^3H_3) benzenes linked at their *ortho* positions to 4,6-di-*tert*-butylphenol moieties by two-carbon linkers have been synthesized. The mono-β-diketone-monophenol ligand L^1H_2 is metalated by titanium alkoxides to form the homoleptic complex $(L^1)_2Ti$ and heteroleptic complexes $(L^1)Ti([OCH_2CH_2]_2NR)$ (R = H, CH_3), and reacts with Cp_3Sc to form $CpSc(L^1)$. These are the first examples of complexes of a β-diketonate ligand which is further chelating to a single metal center. Crystallographic analysis of $(L^1)_2Ti$ indicates that the 10-membered ring allows chelation of the phenoxide with little strain, and both *fac* and *mer* geometries are accessible in solution. Protonolysis of the second cyclopentadienyl ring of Cp_3Sc appears to take place by an indirect, Cp_3Sc-catalyzed pathway.

Introduction

β-Diketonates have been used as ligands for almost 120 years.[1,2] They form homo- or heteroleptic complexes with virtually every transition metal, *p*-block metal, and lanthanide. The great chemical stability and covalency of many of their complexes has led to them being particularly useful sources of volatile precursors for applications such as chemical vapor deposition.[3] A wide variety of β-diketonates with different substituents have been prepared, allowing one to tune properties of their complexes such as volatility, Lewis acidity, or aggregation state, and in the case of chiral β-diketonates, to achieve chiral recognition (as in chiral shift reagents[4]) or enantioselective catalysis.[5] The robustness of the complexes, and in particular the ability to chemically modify the diketonate ligand without destroying the metal complexes, has even earned these ligands an important place in chemical education.[6]

However, one important limitation of the β-diketonate ligand is that it can bind in no more than two sites; β-diketonates that are further chelating to a single metal center are unknown. In contrast to β-ketoiminates or β-diketiminates, where the nitrogen atom has a substituent which can easily link to another chelating group (as in the well-known tetradentate acacen ligand), the only sites for further elaboration on a diketone are pointed away from the site where the oxygen atoms bind to a metal. Thus, while polyketones[7] and bis(β-diketone) ligands,[8] as well as mixed diketone/phosphine ligands,[9] are known, their complexes are always bi- or polymetallic.

Based on our earlier observations of good hydrolytic stability of chelating polyphenoxide complexes of titanium(IV),[10] we anticipated that β-diketonate ligands containing dangling phenoxides would also allow the preparation of water-stable derivatives of the early transition metals. Here we report the preparation of dibenzoylmethane derivatives where one or both aryl groups are linked by two-carbon tethers to 4,6-di-*tert*-butylphenol groups.

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The ethylene-bridged diketone-monophenol L^1H_2 in particular readily forms chelates with early transition metals such as titanium and scandium, yielding stable and apparently largely unstrained complexes.

Results and discussion

Synthesis of β-diketones with dangling phenols

Because the substituents on the carbonyl carbons and the α-carbon of a β-diketone are directed away from the metal, any polydentate diketonate will require that the pendant groups form a rather large ring to allow chelation. Inspection of simple molecular models suggested that a dibenzoylmethane derivative joined to a phenoxide in the *ortho* position with a two-carbon tether would form a relatively unstrained 10-membered chelate ring, with the two-carbon linker in a fully extended conformation. A ring of this size would allow a nearly linear M–O–C angle at the phenoxide, as is typically observed in unconstrained early metal aryloxides.[11] Indeed, compatibility with such large angles and the consequent π-bonding has been adduced as a reason for the favorability of forming large-ring titanium aryloxide chelates.[12]

Synthesis of the ligand begins with construction of the phenoxide "arm" (Scheme 1). Horner–Wadsworth–Emmons condensation of dimethyl 2-bromobenzylphosphonate (**1**, prepared by an Arbuzov reaction of 2-bromobenzyl bromide) with 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde gives the 2′-bromostyrylphenol **2** in good yield and with complete *E*-selectivity. (The di-*tert*-butyl substitution pattern was chosen to give a bulky substituent *ortho* to the phenol and because of the commercial availability and moderate price of the appropriate salicylaldehyde.) The phenol group was protected as a *tert*-butyldimethylsilyl ether using TBSCl–DBU to give **3**, followed by lithium–halogen exchange and carboxylation to give the unsaturated carboxylic acid **4**. Protection of the phenol as a trimethylsilyl ether was tried, but the TMS group proved labile under the conditions used to prepare and isolate the carboxylic acid. The two-carbon linker could be reduced by diimide at this stage to provide the saturated acid **5**.
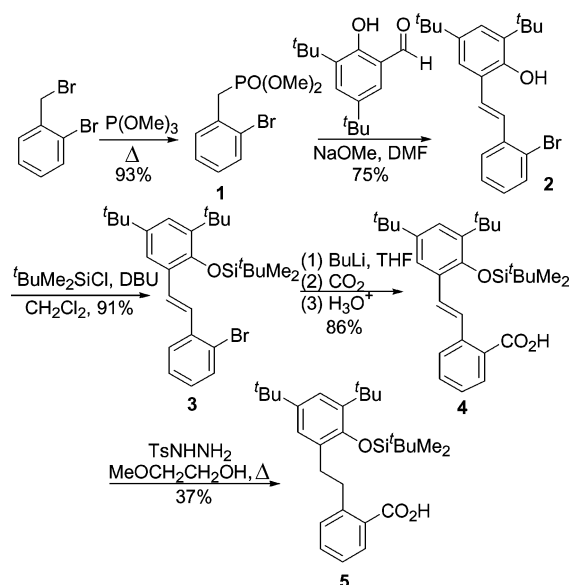
Scheme 1   Preparation of phenol "arms".

Formation of the carboxylic acid sets up the protected phenol for formation of the diketone by Claisen condensation.[13] To prepare a diketone-monophenol ligand (Scheme 2), the saturated acid **5** was converted to the acyl chloride and condensed with the lithium enolate of 4′-methylacetophenone in the presence of excess lithium bis(trimethylsilyl)amide. O-acylation is seen as a side product in this reaction at short reaction times,[14] but the O-acylated product is converted to the thermodynamic C-acylated product **6** upon heating or prolonged reaction at room temperature (preferably in the presence of excess lithium enolate). Desilylation with ice-cold tetrabutylammonium fluoride in THF furnishes the tridentate diketone-monophenol L^1H_2. Both unsaturated and saturated versions of bis(phenol)-diketone ligands were prepared by analogous routes (Scheme 3). In this case the unsaturated acid **4** was taken on to make both the acyl chloride **7** and, through treatment with methyllithium,[15] the protected phenol-bearing methyl ketone **8**, which were then coupled under basic conditions to form the unsaturated diketone **9**. Deprotection of **9** furnished the *trans*-alkene-bridged ligand L^2H_3, while the alkane-bridged analogue L^3H_3 was prepared by diimide reduction of the stilbenes either before or after desilylation of **9**.
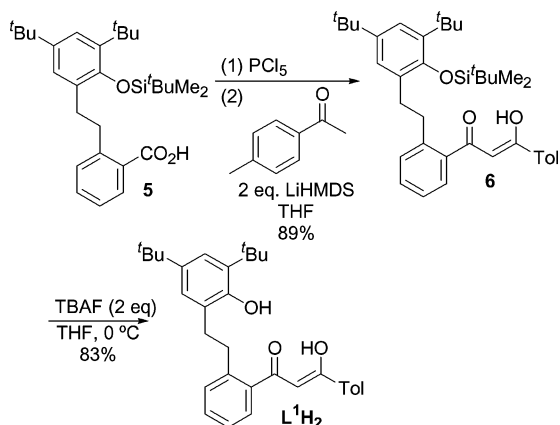
Scheme 2   Preparation of diketone-monophenol L^1H_2.
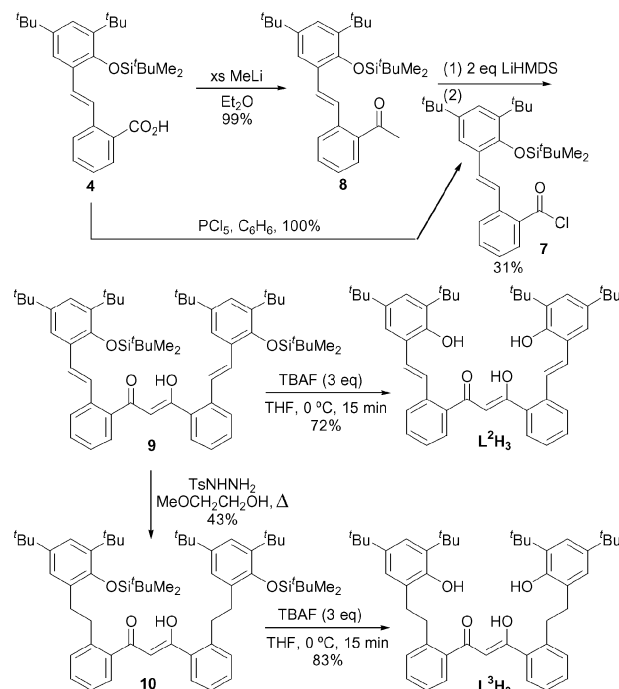
Scheme 3   Preparation of diketone-bis(phenol)s L^2H_3 and L^3H_3.

The structure of the β-diketone-bis(styrylphenol) ligand L^2H_3 was confirmed by X-ray crystallography (Table 1). The compound crystallizes as the *cis*-enol tautomer (Fig. 1), which also appears to predominate in solution, as judged from the downfield C–H proton at δ 6.33 and enol O–H proton at δ 17.01 (in C_6D_6). The structural details of the enolized dibenzoylmethane core, such as the presence of a strong intramolecular hydrogen bond, are very similar to those of other structurally characterized dibenzoylmethanes.[16]
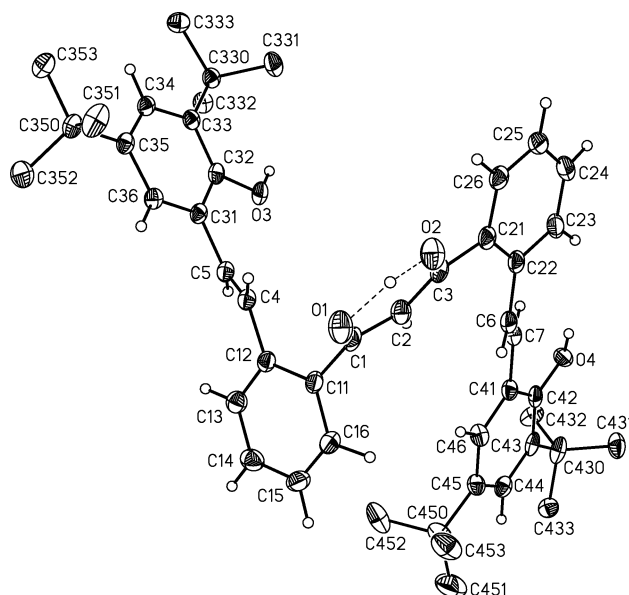
Fig. 1   Thermal ellipsoid plot of L^2H_3, with methyl hydrogens and minor disordered components omitted for clarity. Selected bond distances (Å) and angles: C1–O1, 1.269(3); C3–O2, 1.311(3); C1–C2, 1.411(3); C2–C3, 1.381(3); C4–C5, 1.338(3); C6–C7, 1.333(3); O1–C1–C2, 122.1(2)°; C1–C2–C3, 121.2(2)°; O2–C3–C2, 120.01(19)°.

Table 1 X-ray crystallographic details for L^2H_3 and $(L^1)_2Ti\cdot4CH_2Cl_2$

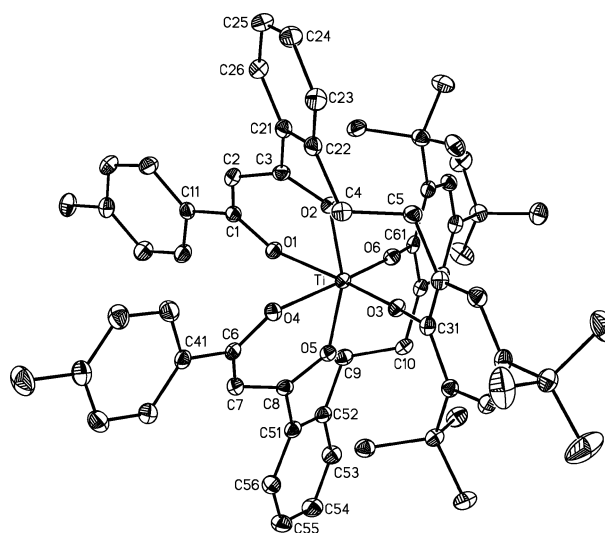|	L^2H_3	$(L^1)_2Ti\cdot4CH_2Cl_2$
Molecular formula	$C_{47}H_{56}O_4$	$C_{68}H_{80}Cl_8O_6Ti$
Formula weight	684.92	1324.82
T/K	100(2)	100(2)
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Total data collected	41961	65373
No. of ind. reflns	9525	16402
R_{int}	0.0438	0.0279
Obs. reflns $[I > 2\sigma(I)]$	7190	12632
$a/\text{Å}$	9.1032(4)	13.1693(5)
$b/\text{Å}$	11.9561(5)	14.4819(6)
$c/\text{Å}$	18.4632(8)	18.8272(8)
$\alpha/°$	104.741(2)	69.077(1)
$\beta/°$	96.902(3)	88.780(2)
$\gamma/°$	92.611(2)	89.507(2)
$V/\text{Å}^3$	1923.21(14)	3353.1(2)
Z	2	2
μ/mm^{-1}	0.073	0.496
No. refined param.	562	1068
$R1, wR2 [I > 2\sigma(I)]$	0.0696, 0.1880	0.0365, 0.0930

Both alkenes are *trans*, but the conformation implies substantial flexibility in the structure, with the aryl groups twisted out of the plane of the diketone moiety by substantial but widely varying amounts (89.0 and 31.5° for C11–C16 and C21–C26, respectively). Similarly, the alkenes are not coplanar with the arenes to which they are bonded, with angles of 37.7 and 52.4° between the C4–C5 olefin and the arene planes and 31.0 and 7.4° for the C6–C7 olefin. This structural variability suggested that the styryl- (or phenethyl-) phenol arms would have the flexibility required to chelate to a transition metal.

Titanium(IV) complexes of diketonate-phenoxide ligands

The diketone-monophenol ligand L^1H_2 reacts immediately at room temperature in a 2 : 1 molar ratio with titanium(IV) isopropoxide to form the air- and moisture-stable red complex $(L^1)_2Ti$ (eqn 1). ^1H NMR spectra of the reaction mixture in benzene-d_6 show a large number of sharp peaks, suggestive of formation of a monometallic complex that exists as several geometric isomers. The formulation of the complex as a monomer is supported by mass spectrometry, which shows peaks at the expected mass of 984 amu, and no sign of higher oligomers. Upon heating, the NMR spectrum changes, with some peaks disappearing and others growing, forming an equilibrium mixture within 16 h at 70 °C. ^1H and ^{13}C NMR spectra of the equilibrium mixture show three different L^1 environments, consistent with the presence of three symmetric isomers, or one symmetric and one unsymmetric isomer.

$$2\,L^1H_2 + Ti(O^iPr)_4 \rightarrow (L^1)_2Ti + 4\,^iPrOH \qquad (1)$$
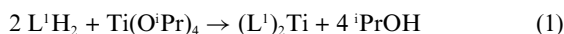
The ability of the linked phenoxide to chelate to the titanium is confirmed by the crystallization of the dichloromethane solvate of *cis-mer*-$(L^1)_2Ti$ (Fig. 2). The molecule possesses an approximate (non-crystallographic) twofold axis relating the two ligands and adopts the *cis* arrangement of diketonates that is universally observed in the alkoxide complexes (dike)$_2$Ti(OR)$_2$.[17] In order to accommodate the large Ti–O–C angles typical of titanium aryloxides,[12] the ethylene bridge in the 10-membered chelate ring adopts a fully extended conformation, with dihedral angles of

Fig. 2 Thermal ellipsoid plot of $(L^1)_2Ti\cdot4CH_2Cl_2$, with solvent molecules and hydrogen atoms omitted for clarity.

178.5 and 174.3° for the two bridges. The bond distances and angles of *cis-mer*-$(L^1)_2Ti$ are generally extremely similar to those of unconstrained (acac)$_2$Ti(O-2,6-$^iPr_2C_6H_3$)$_2$[18] (Table 2), though

Table 2 Selected bond distances (Å) and angles (°) in $(L^1)_2Ti\cdot4\,CH_2Cl_2$ and for comparison, analogous distances and angles in (acac)$_2$Ti(O-2,6-$^iPr_2C_6H_3$)$_2$[a]

	$(L^1)_2Ti\cdot4CH_2Cl_2$	(acac)$_2$Ti(O-2,6-$^iPr_2C_6H_3$)$_2$[a]
Ti–O1	2.0831(12)	2.046(5)
Ti–O4	2.0599(11)	
Ti–O2	1.9459(11)	1.985(5)
Ti–O5	1.9429(11)	
Ti–O3	1.8284(12)	1.834(5)
Ti–O6	1.8322(11)	
O1–C1	1.2805(19)	1.28(1)
O4–C6	1.2778(19)	
C1–C2	1.413(2)	1.41(1)
C6–C7	1.410(2)	
C2–C3	1.382(2)	1.38(1)
C7–C8	1.393(2)	
O2–C3	1.2948(19)	1.28(1)
O5–C8	1.2882(19)	
C4–C5	1.544(2)	*n/a*
C9–C10	1.546(2)	
O1–Ti–O2	81.27(5)	82.8(2)
O4–Ti–O5	81.16(5)	
O1–Ti–O4	80.87(5)	83.1(2)
O2–Ti–O5	160.81(5)	161.7(3)
O3–Ti–O6	101.15(5)	97.3(2)
O1–Ti–O5	84.39(5)	83.5(2)
O2–Ti–O4	84.03(4)	
O1–Ti–O3	168.83(5)	172.1(2)
O4–Ti–O6	168.46(5)	
O1–Ti–O6	89.37(5)	89.9(2)
O4–Ti–O3	89.05(5)	
O5–Ti–O3	98.88(5)	
O2–Ti–O3	92.98(5)	92.9(2)
O5–Ti–O6	91.84(5)	
Ti–O3–C31	165.86(10)	162.2(4)
Ti–O6–C61	163.25(11)	

[a] Ref. 18. The complex (acac)$_2$Ti(O-2,6-$^iPr_2C_6H_3$)$_2$ has crystallographic C_2 symmetry, so its bond distances and angles are listed next to the first of the pair of analogous distances or angles in $(L^1)_2Ti$. The numbering scheme is that of $(L^1)_2Ti$.

there are small distortions suggestive of increasing constraints in the chelated compound. One rather perceptible distortion in *cis-mer*-$(L^1)_2$Ti is the folding of the β-diketonate rings out of the plane defined by the titanium and the two bound oxygens. Both rings are markedly bent inwards, towards the molecular twofold axis, with "fold angles" between the diketonate planes and TiO$_2$ planes of 21.1 and 17.2°. This distortion is not significant in (acac)$_2$Ti(O-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$,[18] but it is quite common in other (dike)$_2$Ti complexes. For example, the six diketonates in the oxo cluster [(dbm)$_2$Ti]$_3$(Cp*Ti)$_2$(O)$_6$ (Hdbm = dibenzoylmethane)[19] show fold angles ranging from 2.7–24.1° with an average of 16°, emphasizing the low energetic cost of such moderate deviations from planarity. Thus, the structural data, in conjunction with the observation that monomers are strongly favored over oligomers, support the notion that the chelate ring linking the diketonate to the phenoxide is relatively unstrained.

When pure crystalline *cis-mer*-$(L^1)_2$Ti is redissolved in C$_6$D$_6$ at room temperature, it immediately equilibrates to the same mixture of isomers it contained before crystallization. This rapid isomerization is in contrast to the much slower isomerization rate displayed by the kinetic mixture of $(L^1)_2$Ti isomers, which requires hours of heating at 70° to effect complete isomerization to the thermodynamic mixture. Diketonatotitanium(IV) complexes are well known to undergo facile isomerizations *via* a trigonal twist mechanism.[20] Since there is only one possible isomer of $(L^1)_2$Ti with a meridional arrangement of the diketonate-phenoxide, the presence of multiple geometric isomers suggests that the intrinsic geometric preference of the ligand is rather small. In fact, a *fac* isomer would be expected to be somewhat more compact than the *mer*, with a distance from the (equatorial) carbonyl carbon to the phenoxide *ipso* carbon estimated from the crystal structure of only 4.57 Å, compared to 4.77 Å in the observed *mer* isomer (the corresponding distances in (acac)$_2$Ti(O-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$ are 4.38 and 4.87 Å, respectively[18]). Presumably chelation is sufficiently unstrained, and the backbone sufficiently flexible, that the energetic cost of increasing the chelate span from the *fac* to the *mer* isomer is small.

$$\text{Ti(O}^i\text{Pr)}_4 \xrightarrow[\text{(2) } \mathbf{L^1H_2}]{\text{(1) HO}\overset{R}{\underset{}{N}}\text{OH}} \qquad (2)$$
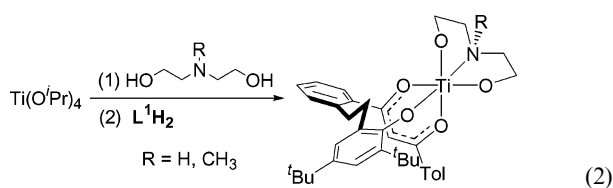
R = H, CH$_3$

The reaction of Ti(O^{i}Pr)$_4$ with diethanolamine or *N*-methyl-diethanolamine, followed by an addition of L^{1}H$_2$, results in the formation of the heteroleptic complexes (L^1)Ti([OCH$_2$CH$_2$]$_2$NR) (R = H, CH$_3$) (eqn 2). In both cases, yields of monometallic complexes are high, with no sign of formation of either polymetallic or homoleptic by-products. ^{1}H NMR spectra of the two compounds at room temperature show the presence of a mirror plane, but the broadness of many of the resonances suggests that this is due to a fluxional process. This has been confirmed for the diethanolamine complex by a variable-temperature NMR study, which shows that the static structure of the complex has no symmetry, as judged by the observation of twelve inequivalent protons due to the CH$_2$CH$_2$ hydrogens in diethanolamine and L^1 at temperatures below about −30 °C. Since the *mer* complex would have a mirror plane, the complexes apparently adopt a *fac* geometry, with the tertiary

amine presumed to be *trans* to the phenoxide on the basis of the *trans* influence. The fluxional process presumably corresponds to an interconversion between the two enantiomers of the chiral complex, which results in a time-averaged mirror plane. If this interconversion takes place by a trigonal twist mechanism, then it must proceed through the intermediacy of the unobserved *mer* isomer (Scheme 4), once again demonstrating the flexibility of the L^1 framework.
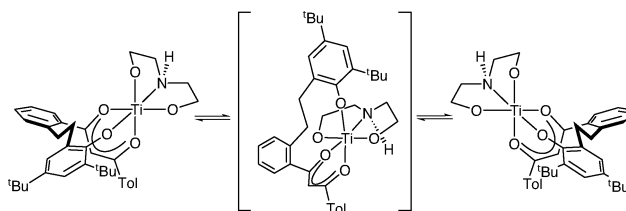

Scheme 4 Fluxionality of (L^1)Ti([OCH$_2$CH$_2$]$_2$NR).

In contrast to the straightforward preparative chemistry of L^{1}H$_2$, reaction of neither L^{2}H$_3$ nor L^{3}H$_3$ with titanium(IV) alkoxides has resulted in isolable complexes. Reactions carried out with comparable quantities of the ligand and titanium alkoxide appear to result in complex mixtures of bis(diketonato)titanium complexes, as judged by ^{1}H NMR and mass spectrometry. This result is consistent with the higher kinetic reactivity of β-diketones compared to phenols with titanium alkoxides.[20a] Reactions using a large excess of titanium also give ill-defined mixtures which decompose upon attempted removal of the excess titanium alkoxide by precipitation with water or vacuum distillation.

Cyclopentadienylscandium complexes of a β-diketonate-monophenoxide

Tricyclopentadienylscandium reacts readily with one equivalent of L^{1}H$_2$ to eliminate cyclopentadiene and form Cp$_2$Sc(L^{1}H), where the scandium is coordinated to the β-diketonate (Scheme 5). The regioselectivity is confirmed by the loss of the enol proton in the ^{1}H NMR, while the signal for the phenolic O–H is still observed at δ 4.99 in C$_6$D$_6$. The reaction of Cp$_2$Sc(L^{1}H) with a second equivalent of Cp$_3$Sc, or the direct reaction of L^{1}H$_2$ with two equivalents of Cp$_3$Sc, results in metalation of the phenol with
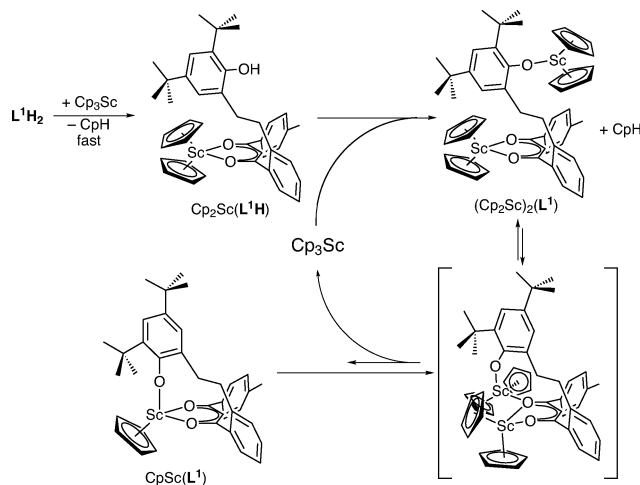
Scheme 5 Proposed pathway for metalation of L^{1}H$_2$ by Cp$_3$Sc.

a second Cp$_2$Sc group, forming (Cp$_2$Sc)$_2$L^1. The presence of two independent Cp$_2$Sc units is clearly indicated by the observation of two 10H cyclopentadienyl peaks in the ^{1}H NMR. Both Cp$_2$Sc(L^{1}H) and (Cp$_2$Sc)$_2$L^1 maintain a mirror plane, as confirmed by the equivalence of the geminal protons in the CH$_2$CH$_2$ group of the ethylene linker.

Protonolysis of a second cyclopentadienyl group by the pendant phenol in Cp$_2$Sc(L^{1}H) is extremely slow. The monoscandium complex can be heated in benzene at 70 °C for several days and only undergoes slow decomposition without any sign of metalation to form CpSc(L^1). This chelated complex can be prepared, but only when Cp$_2$Sc(L^{1}H) is heated in the presence of excess Cp$_3$Sc (or equivalently, with (Cp$_2$Sc)$_2$L^1, which forms rapidly under these conditions). Thus, Cp$_3$Sc effectively catalyzes the metalation of Cp$_2$Sc(L^{1}H). This preparative route results in the contamination of CpSc(L^1) with (Cp$_2$Sc)$_2$L^1, which has prevented isolation of CpSc(L^1) in its pure form, but *in situ* characterization by NMR clearly indicates that chelation has taken place. Cyclopentadiene is lost from the precursor Cp$_2$Sc(L^{1}H) and can be observed by NMR, leaving a single cyclopentadienyl peak due to the complex that integrates as 5H and is shifted substantially downfield of the usual Cp$_2$Sc moieties. Furthermore, the mirror plane characteristic of either scandocene complex is lost, with the ethylene bridge appearing as a CHH′CH″H‴ pattern.

The preference for the scandium-catalyzed reaction over direct protonolysis in the formation of CpSc(L^1) is remarkable. It is reasonable that proton transfer takes place only within the coordination sphere of scandium, as we have observed in reactions of titanium alkoxides.[21] If so, direct protonolysis of Cp$_2$Sc(L^{1}H) would require coordination of the bulky phenol to the scandium, which would be strongly disfavored by the bidentate coordination of the diketonate. In contrast, the phenoxide-ligated scandium in (Cp$_2$Sc)$_2$L^1 is still Lewis acidic and could potentially coordinate to one of the diketonate oxygens to form a bridging diketonate (Scheme 5). Cyclopentadienyl transfer between scandium atoms would then give Cp$_3$Sc and CpSc(L^1). This must be an equilibrium process, with the expulsion of Cp$_3$Sc thermodynamically uphill, since the addition of Cp$_3$Sc to CpSc(L^1) converts it into the discandium complex (Cp$_2$Sc)$_2$L^1. In the presence of the phenolic proton on Cp$_2$Sc(L^{1}H), however, the Cp$_3$Sc reacts irreversibly to release cyclopentadiene and complete the catalytic cycle. This metal-catalyzed reaction represents a very unusual pathway for achieving the "proton-coupled ligand substitution"[22] required to chelate the L^1 ligand.

Conclusions

Dibenzoylmethane derivatives with one or two sterically hindered pendant phenols have been prepared. The linkage employed, consisting of a two-carbon bridge between the *ortho* positions of the phenol and the benzoyl group, allows for the first time an additional chelation from a β-diketone to a single metal center. The crystal structure of (L^1)$_2$Ti indicates that the chelation is not accompanied by any significant distortions in bond distances and angles, and the relatively unstrained nature of the 10-membered chelate ring is further supported by its ability to form monomeric complexes with both *fac* and *mer* geometries of the three oxygen atoms.

Experimental

General procedures

Unless otherwise noted, procedures were carried out on the benchtop without precautions to exclude air or moisture. When dry THF was required, it was vacuum transferred from sodium benzophenone ketyl. Benzene and toluene were dried over sodium. Dry DMF was purchased from Aldrich and stored in a drybox. All other reagents were used without further purification. ^{1}H- and ^{13}C{^{1}H}-spectra were recorded on a Varian UnityPlus 300 FT-NMR or a Varian UnityPlus 600 FT-NMR spectrometer and are reported in ppm downfield of TMS. Infrared spectra were measured as evaporated films on KBr plates on a Perkin–Elmer Paragon 1000 FT-IR spectrometer and are reported in wavenumbers (cm^{-1}). Fast atom bombardment (FAB) mass spectra were measured in positive ion mode on a JEOL JMS-AX505HA mass spectrometer using 3-nitrobenzyl alcohol (NBA) or nitrophenyl octyl ether (NPOE) as the matrix. Elemental analyses were carried out by M–H–W laboratories (Phoenix, AZ, USA). In some cases, the sensitivity of compounds, or their immediate use as synthetic intermediates, prevented us from obtaining satisfactory analyses.

Preparation of ligands

Dimethyl 2-bromobenzylphosphonate (1). Into a 250 mL round bottom flask were placed 36.62 g of 2-bromobenzyl bromide (Aldrich, 0.147 mol), 38 mL of trimethyl phosphite (0.322 mol, 2.2 equiv.), and a stir bar. The flask was placed on a heating mantle on a stirring plate and capped with a condenser with an N$_2$ tee vented to a mineral oil bubbler. The colorless solution was stirred and purged for 30 min at room temperature. While purging, the solution was heated for 15 min using the heating mantle, at which point it started to effervesce vigorously as CH$_3$Br gas was released. The heating was switched off for about 15–20 min, during which time the solution was heated by the exothermic reaction. Heating was then resumed for another 45–50 min. The N$_2$ flow was stopped and the reaction mixture was allowed to cool to room temperature. The flask was detached from the condenser and connected to a distilling adapter affixed to a vacuum take-off adapter. The mixture was distilled under vacuum to remove the dimethyl methylphosphonate which forms as a side product, and the colorless residual liquid yielded 38.22 g (93%) of dimethyl (2-bromobenzyl)phosphonate. Spectroscopic data were in agreement with those reported in the literature.[23]

***trans*-2-Bromo-3′,5′-di-*tert*-butyl-2′-hydroxystilbene (2).** In a round bottom flask in the drybox, 13.40 g of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (Aldrich, 57.2 mmol) was dissolved in 150 mL dry DMF. To this stirred solution was added 9.23 g of solid sodium methoxide (Aldrich, 173 mmol, 3 equiv.). Dimethyl 2-bromobenzylphosphonate (19.15 g, 68.6 mmol, 1.2 equiv.) was dissolved in 20 ml DMF and the solution added in portions to the stirred reaction mixture over the course of 20 min. The flask was capped with a rubber septum and the solution stirred at RT under nitrogen for 16 h. After neutralizing the reaction mixture with 400 mL saturated aqueous NH$_4$Cl and 150 mL 1 M HCl, the aqueous phase was separated and extracted with 5 × 100 mL of Et$_2$O. The combined organic phases were dried with MgSO$_4$ and the solvent removed under reduced pressure. The crude product

was purified by column chromatography on silica gel, eluting with hexanes to give a crystalline material, which was washed with hexanes to yield 16.61 g of pure bromostyrylphenol (75%). ^{1}H NMR (CDCl$_3$): δ 7.68 (dd, 8.0, 1.5 Hz, 1H, *H*-3 or -6), 7.60 (dd, 8.0, 1.5 Hz, 1H, *H*-3 or -6), 7.37 (d, 16.5 Hz, 1H, alkene C*H*), 7.34 (td, 8.0, 1.5 Hz, 1H, *H*-4 or -5), 7.31 (s, 2H, *meta* to OH), 7.20 (d, 16.5 Hz, 1H, alkene C*H*), 7.15 (td, 8.0, 1.5 Hz, 1H, *H*-4 or -5), 5.21 (s, 1H, O*H*), 1.47, 1.35 (s, 9H each, C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 150.00 (*C*OH), 142.93, 137.54, 136.01, 133.25, 130.72, 129.16, 127.83, 127.38, 127.12, 124.65, 124.50, 124.20, 122.87, 35.03 (*C*(CH$_3$)$_3$), 34.58 (*C*(CH$_3$)$_3$), 31.79 (C(*C*H$_3$)$_3$), 30.15 (C(*C*H$_3$)$_3$). IR: 3538 (w, v_{OH}), 3400 (w), 2959 (s), 2904 (m), 2868 (m), 1627 (w), 1470 (m), 1441 (m), 1392 (m), 1362 (m), 1250 (m), 1235 (m), 1215 (m), 1189 (m), 1151 (m), 1117 (m), 1021 (m), 966 (w), 881 (w), 745 (m). FAB-MS: m/z = 386 (M+, [79]Br), 388 (M+, [81]Br). Anal.: Calcd for C$_{22}$H$_{27}$BrO: C, 68.22; H, 7.03; found C, 68.57; H, 6.70.

***trans*-2-Bromo-3′,5′-di-*tert*-butyl-2′-(*tert*-butyldimethylsilyloxy)-stilbene (3).** Into a round bottom flask were weighed 16.59 g (42.8 mmol) of bromostyrylphenol **2** and 13.02 g (86.4 mmol, 2 equiv.) of *tert*-butyldimethylsilylchloride. Dichloromethane (130 mL) and a stir bar were added and the flask was capped with a rubber septum. To the stirred solution 13.0 mL (13.3 g, 84 mmol, 2 equiv.) of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was added dropwise *via* a syringe over the course of 5 min. After stirring for 4 h the orange reaction mixture was poured into a separatory funnel and 80 mL of 1 M HCl was added. The aqueous layer was separated and extracted with 3 × 50 mL of Et$_2$O. The combined organic phases were dried with MgSO$_4$ and the solvent evaporated at reduced pressure. The residue was purified by column chromatography on silica gel, eluting with 1 : 1 mixture of hexanes : EtOAc to give 19.45 g of **3** (91%) as a colorless oil. ^{1}H NMR (CDCl$_3$): δ 7.60 (dd, 8.0, 1.5 Hz, 1H, *H*-3 or -6), 7.59 (dd, 8.0, 1.5 Hz, 1H, *H*-3 or -6), 7.43 (d, 2.5 Hz, 1H, *meta* to silyloxy), 7.35 (d, 2.5 Hz, 1H, *meta* to silyloxy), 7.31 (td, 8.0, 1.5 Hz, 1H, *H*-4 or -5), 7.26 (s, 2H, alkene C*H*), 7.11 (td, 8.0, 1.5 Hz, 1H, *H*-4 or -5), 1.43, 1.35 (s, 9H each, ArC(C*H*$_3$)$_3$), 0.98 (s, 9H, SiC(C*H*$_3$)$_3$), 0.21 (s, 6H, Si(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 150.66 (*C*–OSi), 143.36, 139.74, 137.93, 133.24, 131.05, 128.85, 128.56, 127.71, 126.96, 126.64, 125.68, 124.12, 122.12, 35.65 (Ar*C*(CH$_3$)$_3$), 34.55 (Ar*C*(CH$_3$)$_3$), 31.75 (ArC(*C*H$_3$)$_3$), 31.59 (ArC(*C*H$_3$)$_3$), 27.22 (SiC(*C*H$_3$)$_3$), 19.53 (Si*C*(CH$_3$)$_3$), −0.49 (Si(*C*H$_3$)$_2$). IR: 2958 (s), 2930 (s), 2903 (m), 2860 (m), 1625 (w), 1586 (w), 1467 (s), 1438 (s), 1412 (w), 1392 (w), 1362 (m), 1291 (w), 1255 (s), 1232 (m), 1202 (w), 1163 (w), 1126 (w), 1024 (w), 977 (w), 924 (m), 887 (m), 839 (m), 822 (m), 805 (m), 780 (m), 747 (m), 682 (w). FAB-MS: m/z = 500 (M+, [79]Br), 502 (M+, [81]Br).

***trans*-3′,5′-Di-*tert*-butyl-2′-(*tert*-butyldimethylsilyloxy)-stilbene-2-carboxylic acid (4).** Protected bromostilbene **3** (5.86 g, 11.7 mmol) was weighed into a three-neck round bottom flask. One neck was capped with a rubber septum and another with a glass stopper, and the flask was attached to the vacuum line through a needle valve inserted in the third neck. Dry THF (70 mL) was vacuum transferred into the flask and the solution chilled to −78 °C. To the stirred solution 15 mL (24 mmol, 2 equiv.) of a solution of *n*-butyllithium in hexanes (Strem, 1.59 M) was added over 15 min using a syringe. After stirring the solution for 1 h at −78 °C, the stopper was replaced under N$_2$ flow

by a hose adapter vented to a mineral oil bubbler. The reaction mixture was warmed to 0 °C and the rubber septum removed for short periods of time while dry ice was added to the reaction mixture. The bright yellow solution was poured into a separatory funnel and 70 mL of 1 M HCl was added. The aqueous phase was separated and extracted with 3 × 30 mL of Et$_2$O. The combined organic phases were dried with MgSO$_4$ and the solvents removed under reduced pressure. After standing uncapped in the hood overnight, a slightly yellow solid was obtained, which was washed with hexanes to give 4.70 g (86%) of the carboxylic acid. ^{1}H NMR (CDCl$_3$): δ 8.08 (dd, 8.0, 1.5 Hz, 1H, *H*-3), 7.86 (d, 16.0 Hz, 1H, alkene C*H*), 7.69 (dd, 8.0, 1.5 Hz, 1H, *H*-6), 7.56 (td, 8.0, 1.5 Hz, 1H, *H*-4 or -5), 7.45 (d, 3.0 Hz, 1H, *meta* to silyloxy), 7.34 (td, 8.0, 1.5 Hz, 1H, *H*-4 or -5), 7.34 (d, 3.0 Hz, 1H, *meta* to silyloxy), 7.26 (d, 16.0 Hz, 1H, alkene C*H*), 1.43, 1.33 (s, 9H each, ArC(C*H*$_3$)$_3$), 0.97 (s, 9H, SiC(C*H*$_3$)$_3$), 0.20 (s, 6H, Si(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 172.56 (*C*OOH), 150.64 (*C*–OSi), 143.29, 140.94, 139.66, 133.16, 131.81, 131.33, 129.13, 127.51, 127.23, 127.00, 126.45, 125.59, 122.32, 35.64 (Ar*C*(CH$_3$)$_3$), 34.54 (Ar*C*(CH$_3$)$_3$), 31.73 (ArC(*C*H$_3$)$_3$), 31.61 (ArC(*C*H$_3$)$_3$), 27.20 (SiC(*C*H$_3$)$_3$), 19.54 (Si*C*(CH$_3$)$_3$), −0.50 (Si(*C*H$_3$)$_2$). IR: 3061 (m), 2958 (s), 2926 (s), 2901 (m), 2862 (m), 2636 (w), 2532 (w), 1689 (s, v_{CO}), 1625 (w), 1597 (w), 1566 (w), 1475 (m), 1464 (m), 1436 (m), 1409 (m), 1360 (m), 1299 (m), 1260 (m), 1255 (m), 1237 (m), 1200 (w), 1164 (w), 1127 (w), 1079 (w), 976 (w), 925 (m), 885 (m), 839 (m), 805 (m), 780 (m), 746 (m). FAB-MS: m/z = 466 (M+). Anal.: Calcd for C$_{29}$H$_{42}$O$_3$Si: C, 74.63; H, 9.07; found C, 74.70; H, 9.22.

2-(3′,5′-Di-*tert*-butyl-2′-(*tert*-butyldimethylsilyloxy)phenethyl)-benzoic acid (5). In a two-neck round-bottom flask 0.893 g (1.91 mmol) of stilbenecarboxylic acid **4** was dissolved in 15 mL of methoxyethanol. One neck of the flask was capped with a rubber septum, the other with a reflux condenser capped with a hose adapter vented through a mineral oil bubbler. The apparatus was flushed with nitrogen (using a needle through the septum) for 15 min. The solution was heated to reflux and a solution of 0.891 g (4.78 mmol, 2.5 equiv.) of tosylhydrazide in 15 mL of methoxyethanol was added over the course of 45 min using a syringe. After heating the reaction mixture at reflux for 16 h under N$_2$, the solution was allowed to cool to room temperature and poured into a separatory funnel. 50 mL of saturated NaHCO$_3$ solution and 30 mL of Et$_2$O were added, and the aqueous phase was separated and extracted with 3 × 20 mL of Et$_2$O. The combined organic phases were dried with MgSO$_4$ and the solvents evaporated *in vacuo*. The residue was purified by column chromatography using silica gel, eluting first with hexanes, followed by a mixture of 10% EtOAc–hexanes. Evaporation of the eluate gave the product as a white crystalline solid (0.333 g, 37%). ^{1}H NMR (CDCl$_3$): δ 8.09 (dd, 7.5, 1.5 Hz, 1H, *H*-6), 7.37 (td, 7.5, 1.5 Hz, 1H, *H*-4 or -5), 7.28 (td, 7.5, 1.5 Hz, 1H, *H*-4 or -5), 7.17 (d, 2.5 Hz, 1H, *meta* to silyloxy), 7.02 (dd, 7.5, 1.5 Hz, 1H, *H*-3), 6.93 (d, 2.5 Hz, 1H, *meta* to silyloxy), 3.27 (t, 8.0 Hz, 2H, C*H*$_2$CH$_2$), 2.98 (t, 8.0 Hz, 2H, CH$_2$C*H*$_2$), 1.41, 1.25 (s, 9H each, ArC(C*H*$_3$)$_3$), 0.95 (s, 9H, SiC(C*H*$_3$)$_3$), 0.30 (s, 6H, Si(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 173.39 (*C*OOH), 149.73 (*C*–OSi), 145.30, 142.67, 138.66, 132.89, 131.92, 131.87, 130.96, 128.18, 126.14, 125.25, 122.79, 36.17, 35.63, 34.30, 33.53, 31.74 (ArC(*C*H$_3$)$_3$), 31.58 (ArC(*C*H$_3$)$_3$), 27.42 (SiC(*C*H$_3$)$_3$), 19.92 (Si*C*(CH$_3$)$_3$), −0.44 (Si(*C*H$_3$)$_2$). IR: 3072 (m), 2958 (s), 2900 (m),

2862 (m), 2636 (w), 2654 (w), 2553 (w), 1694 (s, v_{CO}), 1603 (w), 1576 (w), 1472 (m), 1440 (m), 1408 (m), 1392 (m), 1362 (m), 1300 (m), 1264 (s), 1234 (m), 1203 (w), 1167 (w), 1142 (w), 1123 (w), 1080 (m), 926 (m), 911 (m), 891 (m), 840 (m), 823 (m), 808 (m), 780 (m), 735 (m). FAB-MS: $m/z = 468$ (M$^+$).

2-(3′,5′-Di-*tert*-butyl-2′-(*tert*-butyldimethylsilyloxy)phenethyl)-benzoyl chloride. Into a round bottom flask was weighed 1.418 g of phenethylbenzoic acid **5** (3.04 mmol). 50 mL of dry toluene was vacuum transferred into the flask and the solution was taken into the drybox. In the drybox 0.633 g of phosphorus pentachloride (Aldrich, 3.04 mmol) was added and the reaction mixture stirred at RT for 4 h. The solvent was evaporated on the vacuum line and the crude product was used without further purification. ^{1}H NMR (CDCl$_3$): δ 8.18 (dd, 7.5, 1.5 Hz, 1H, *H*-6), 7.38 (td, 7.5, 1.5 Hz, 1H, *H*-4 or -5), 7.31 (td, 7.5, 1.5 Hz, 1H, *H*-4 or -5), 7.14 (d, 3.0 Hz, 1H, *meta* to silyloxy), 6.94 (dd, 7.5, 1.5 Hz, 1H, *H*-3), 6.74 (d, 3.0 Hz, 1H, *meta* to silyloxy), 3.11 (t, 7.5 Hz, 2H, C*H*$_2$CH$_2$), 2.91 (t, 7.5 Hz, 2H, CH$_2$C*H*$_2$), 1.39, 1.20 (s, 9H each, ArC(C*H*$_3$)$_3$), 0.93 (s, 9H, SiC(C*H*$_3$)$_3$), 0.28 (s, 6H, Si(C*H*$_3$)$_2$). IR: 2960 (s), 2861 (m), 1777 (s, v_{CO}), 1644 (w), 1600 (w), 1569 (w), 1474 (m), 1440 (m), 1361 (m), 1256 (m), 1234 (m), 1203 (w), 1186 (w), 1129 (w), 927 (m), 884 (m), 868 (m), 840 (m), 780 (m).

1-(2′-(3″,5″-Di-*tert*-butyl-2″-(*tert*-butyldimethylsilyloxy)phen-ethyl)phenyl)-3-*p*-tolylpropane-1,3-dione (6). In the drybox, 1.485 g of LiN(SiMe$_3$)$_2$ (Aldrich, 7.6 mmol, 2.5 equiv.) and 20 ml of dry THF were placed into a glass bomb. A solution of 0.489 g 4′-methylacetophenone (3.65 mmol, 1.2 equiv.) in 15 ml of dry THF was added and the mixture stirred at RT for 15 min. The acyl chloride prepared from 1.418 g of carboxylic acid **5** (3.04 mmol, assuming quantitative yield) was dissolved in 5 ml of dry THF and the solution was dropped into the reaction mixture, with stirring, over 10 min using a syringe. The bomb was closed and the reaction mixture stirred in a 65 °C oil bath for 4 h. The solution was cooled to room temperature, opened to the air, and poured into a separatory funnel. 40 mL of 1 M HCl and 20 mL of Et$_2$O were added, the phases separated, and the aqueous phase extracted with 3 × 20 mL of Et$_2$O. The combined organic phases were dried with MgSO$_4$ and the solvents evaporated under reduced pressure. The oily residue was chromatographed on silica gel with 2.5% EtOAc–hexanes to give diketone **6** as a pale red oil (1.587 g, 89%). NMR spectroscopy in acetone-d_6 indicates that the compound exists predominantly as the enol. ^{1}H NMR (CD$_3$COCD$_3$): δ 7.97 (d, 8.0 Hz, 2H, tolyl-*H meta* to CH$_3$), 7.66 (dd, 7.5, 1.5 Hz, 1H, *H*-6′), 7.39 (td, 7.5, 1.5 Hz, 1H, *H*-4′ or -5′), 7.36 (d, 8.0 Hz, 2H, tolyl-*H ortho* to CH$_3$), 7.32 (td, 7.5, 1.5 Hz, 1H, *H*-4′ or -5′), 7.19 (dd, 7.5, 1.5 Hz, 1H, *H*-3′), 7.18 (d, 2.5 Hz, 1H, *meta* to silyloxy), 6.90 (d, 2.5 Hz, 1H, *meta* to silyloxy), 6.74 (s, 1H, COC*H*CO), 3.13 (m, 2H, C*H*$_2$CH$_2$), 2.99 (m, 2H, CH$_2$C*H*$_2$), 2.42 (s, 3H, tolyl C*H*$_3$), 1.37, 1.19 (s, 9H each, ArC(C*H*$_3$)$_3$), 0.92 (s, 9H, SiC(C*H*$_3$)$_3$), 0.30 (s, 6H, Si(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (CD$_3$COCD$_3$): δ 188.95 (carbonyl), 185.77 (carbonyl), 150.93 (*C*OSi), 144.93, 143.85, 142.30, 139.71, 138.11, 133.62, 132.23, 132.19, 132.04, 130.82, 130.11, 128.68, 127.46, 126.22, 123.90, 98.11 (CO*C*HCO), 36.50, 36.06, 35.16, 35.03, 32.36 (Ar*C*(CH$_3$)$_3$), 32.22 (Ar*C*(CH$_3$)$_3$), 28.17 (SiC(*C*H$_3$)$_3$), 22.08 (Ar*C*H$_3$), 20.86 (Si*C*(CH$_3$)$_3$), 0.14 (Si*C*H$_3$). IR: 3060 (w), 3028 (w), 2954 (s), 2930 (s), 2903 (m), 2860 (m), 1604 (m), 1584 (m), 1562 (m), 1535 (m), 1501 (m), 1464 (m), 1439 (m), 1411 (m),

1391 (m), 1361 (m), 1298 (m), 1263 (m), 1255 (m), 1232 (m), 1204 (w), 1184 (w), 1166 (w), 1130 (w), 925 (w), 886 (w), 838 (w), 822 (w), 810 (w), 778 (w). FAB-MS: $m/z = 584$ (M$^+$), 527 ([M-^{t}Bu]$^+$).

1-(2′-(3″,5″-Di-*tert*-butyl-2″-hydroxyphenethyl)phenyl)-3-*p*-tolylpropane-1,3-dione (L^{1}H$_2$). Into a two-neck round bottom flask was placed 1.587 g (2.71 mmol) of the silylated diketone **6**. One neck was capped with a rubber septum and 200 mL of dry THF was vacuum transferred into the flask. The solution was chilled to 0 °C and 5.5 mL (5.5 mmol, 2 equiv.) of 1 M Bu$_4$NF in THF was added to the stirred solution *via* syringe. After stirring the reaction mixture at RT for 15 min, the solution was poured into a separatory funnel. Ether (40 mL) and 0.5 M aqueous HCl (100 mL) were added and the phases separated. The aqueous phase was extracted with 3 × 40 mL of Et$_2$O and the combined organic phases were dried over MgSO$_4$. The solvent was evaporated and the slightly yellow solid washed with hexanes. The hexane wash was chromatographed (7.5% EtOAc–hexanes, silica gel) and the purified fractions combined with the hexane-insoluble material to yield 1.057 g (83%) of L^{1}H$_2$ as a crystalline white solid. ^{1}H NMR (CD$_3$COCD$_3$): δ 16.91 (br s, 1H, enol O*H*), 7.99 (d, 8.0 Hz, 2H, tolyl-*H meta* to CH$_3$), 7.76 (dd, 7.5, 1.5 Hz, 1H, *H*-6′), 7.49 (td, 7.5, 1.5 Hz, 1H, *H*-4′), 7.44 (dd, 7.5, 1.5 Hz, 1H, *H*-3′), 7.37 (td, 8.0, 1.5 Hz, 1H, *H*-5′), 7.37 (d, 8.0 Hz, 2H, tolyl-*H ortho* to CH$_3$), 7.15 (d, 2.5 Hz, 1H, *meta* to OH), 6.98 (d, 2.5 Hz, 1H, *meta* to OH), 6.81 (s, 1H, COC*H*CO), 3.13 (m, 2H, C*H*$_2$CH$_2$), 2.99 (m, 2H, CH$_2$C*H*$_2$), 2.42 (s, 3H, tolyl C*H*$_3$), 1.41, 1.24 (s, 9H each, C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (CD$_3$COCD$_3$): δ 194.74 (carbonyl), 184.39 (carbonyl), 152.23 (Ar*C*–OH), 145.05, 142.76, 142.68, 138.02, 136.81, 133.01, 132.60 (2 overlapped resonances), 130.85, 130.43, 128.68, 128.24, 127.65, 126.19, 122.98, 98.05 (CO*C*HCO), 36.10, 36.08, 35.19, 35.02, 32.51 (C(*C*H$_3$)$_3$), 30.76 (C(*C*H$_3$)$_3$), 22.10 (tolyl *C*H$_3$). IR: 3470 (s, phenol v_{OH}), 2958 (s), 2869 (m), 1605 (s), 1579 (m), 1564 (m), 1510 (m), 1480 (m), 1445 (m), 1415 (m), 1391 (m), 1362 (m), 1308 (m), 1281 (m), 1214 (m), 1200 (m), 1186 (m), 1153 (w), 1122 (w), 1087 (w), 949 (w), 878 (w), 805 (w), 768 (w), 738 (w). FAB-MS: Exact mass for C$_{32}$H$_{38}$O$_3$ calcd 470.2805, obsd 470.2800. Anal.: Calcd for C$_{32}$H$_{38}$O$_3$: C, 81.66; H, 8.14; found C, 79.84; H, 8.49.

***trans*-3′,5′-Di-*tert*-butyl-2′-(*tert*-butyldimethylsilyloxy)-stilbene-2-carbonyl chloride (7).** Into a 100 mL round bottom flask was measured 6.925 g (14.8 mmol) of carboxylic acid **4**. In the drybox, 3.142 g of PCl$_5$ (15.1 mmol), 50 mL of dry benzene, and a stir bar were added to the flask. The flask was capped with a rubber septum and taken outside of the drybox. The yellow solution was stirred for 4 h at RT, while vented to a mineral oil bubbler to allow HCl to escape. The flask was opened and the solvent removed on a rotary evaporator to leave a thick yellow oil, which was evacuated on a vacuum line for 2 h to ensure complete removal of POCl$_3$ (as verified by the absence of a signal in the ^{31}P NMR). The viscous acyl chloride **7** (7.174 g, 100%) was stored in the drybox. ^{1}H NMR (CDCl$_3$): δ 8.08 (d, 8.0 Hz, 1H, *H*-3), 7.97 (d, 16.0 Hz, 1H, alkene C*H*), 7.84 (d, 2.4 Hz, 1H, *meta* to silyloxy), 7.67 (d, 2.4 Hz, 1H, *meta* to silyloxy), 7.56 (d, 8.0 Hz, 1H, *H*-6), 7.53 (d, 16.0 Hz, 1H, alkene C*H*), 7.14 (t, 7.5 Hz, 1H, *H*-4 or -5), 6.90 (t, 7.5 Hz, 1H, *H*-4 or -5), 1.65, 1.42 (s, 9H each, ArC(C*H*$_3$)$_3$), 1.07 (s, 9H, SiC(C*H*$_3$)$_3$), 0.24 (s, 6H, Si(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 167.74 (*C*OCl), 150.84 (*C*OSi), 143.47, 140.73, 139.83, 134.33, 133.81, 133.16, 131.43, 128.64, 127.53, 127.29, 126.13,

124.87, 122.09, 35.67 (ArC(CH$_3$)$_3$), 34.57 (ArC(CH$_3$)$_3$), 31.74 (ArC(CH_3)$_3$), 31.64 (ArC(CH_3)$_3$), 27.17 (SiC(CH_3)$_3$), 19.49 (SiC(CH$_3$)$_3$), −0.59 (Si(CH_3)$_2$). IR: 3061 (w), 3020 (w), 2959 (s), 2904 (s), 2861 (s), 1774 (s, v_{CO}), 1623 (m), 1595 (m), 1561 (w), 1471 (s), 1437 (s), 1412 (m), 1392 (m), 1362 (m), 1292 (m), 1256 (s), 1234 (s), 1203 (m), 1185 (m), 1166 (m), 1126 (m), 1104 (m), 1051 (w), 1006 (w), 975 (m), 924 (m), 882 (m), 869 (m), 839 (m), 801 (m), 780 (m). FAB-MS: 484 (M$^+$).

trans-2-Acetyl-3′,5′-di-_tert_-butyl-2′-(_tert_-butyldimethylsilyloxy)-stilbene (8). In a 100 mL round bottom flask 3.1845 g of carboxylic acid **4** (6.82 mmol) was dissolved in 40 mL of dry THF. In the drybox, 9.4 mL of methyllithium in Et$_2$O (Acros, 1.6 M, 2.2 equiv.) was syringed into the stirred solution. During the first 30 s, a gas evolves and the solution turns tan. After stirring for 2 h under N$_2$, the reaction was quenched with 20 mL of 1 M HCl and the cloudy light yellow mixture was transferred into a separatory funnel. The organic layer was separated and washed with 50 mL of saturated aqueous NH$_4$Cl. The aqueous layers were combined and extracted with 2 × 20 mL of ether. The combined organic layers were dried over MgSO$_4$, and the solvent was removed on a rotary evaporator to give a thick light yellow oil, which was dried _in vacuo_ for 2 h to give 3.1391 g of the ketone **8** (99%). ^{1}H NMR (CDCl$_3$): δ 7.66 (dd, 7.5, 1.0 Hz, 1H, H-3 or -6), 7.65 (dd, 8.0, 1.0 Hz, 1H, H-3 or -6), 7.49 (td, 7.5, 1.0 Hz, 1H, H-4 or -5), 7.47 (d, 16.0 Hz, 1H, alkene CH), 7.40 (d, 2.4 Hz, 1H, _meta_ to silyloxy), 7.34 (d, 2.7 Hz, 1H, _meta_ to silyloxy), 7.33 (td, 7.5, 1.0 Hz, 1H, H-4 or -5), 7.24 (d, 16 Hz, 1H, alkene CH), 2.62 (s, 3H, CH_3CO) 1.43, 1.35 (s, 9H each, ArC(CH_3)$_3$), 0.97 (s, 9H, SiC(CH_3)$_3$), 0.21 (s, 6H, Si(CH_3)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 202.57 (COCH$_3$), 150.60 (COSi), 143.27, 139.64, 137.89, 137.85, 131.63, 131.20, 129.04, 128.99, 127.46, 126.96, 126.03, 125.55, 122.03, 35.63 (ArC(CH$_3$)$_3$), 34.53 (ArC(CH$_3$)$_3$), 31.74 (ArC(CH_3)$_3$), 31.59 (ArC(CH_3)$_3$), 30.36 (COCH$_3$), 27.21 (SiC(CH_3)$_3$), 19.53 (SiC(CH$_3$)$_3$), −0.55 (Si(CH_3)$_2$). IR: 3062 (w), 3021 (w), 2958 (s), 2904 (s), 2861 (s), 1686 (s, v_{CO}), 1624 (w), 1595 (m), 1562 (m), 1474 (s), 1464 (s), 1438 (s), 1412 (m), 1392 (m), 1362 (s), 1296 (s), 1259 (s), 1237 (s), 1203 (m), 1164 (m), 1126 (m), 1070 (w), 1042 (w), 1007 (w), 975 (m), 954 (m), 924 (m), 889 (s), 839 (s), 823 (m), 806 (m), 781 (s), 756 (s). FAB-MS: 465 (M + H$^+$).

1,3-Bis(2′-(3″,5″-di-_tert_-butyl-2″-(_tert_-butyldimethylsilyloxy)-styryl)phenyl)-propane-1,3-dione (9). Into a 100 mL round bottom flask was measured 3.1931 g of acetylstilbene **8** (6.75 mmol). In the drybox, 2.2600 g of LiN(SiMe$_3$)$_2$ (13.5 mmol, 2 equiv.) and 15 mL of THF were added to the ketone. The very dark orange-brown solution was stirred for 15 min, then 2.9360 g of acyl chloride **7** (6.05 mmol, 0.90 equiv.) dissolved in 15 mL of THF was added, causing the solution to turn darker brown. The reaction mixture was stirred under N$_2$ for 3 d, then poured into a separatory funnel with 50 mL of 1 M HCl. The cloudy yellow organic layer was separated and washed with 50 mL of saturated aqueous NH$_4$Cl, and the combined aqueous layers were extracted with 2 × 20 mL of ether. The combined organic layers were dried over MgSO$_4$, filtered, and the solvent was removed on a rotary evaporator, giving a thick orange oil which solidified after a few minutes. The crude material was triturated with 20 mL of hexane and the precipitated product was filtered on a glass frit and air-dried for 1 h. Reduction of the volume of the filtrate and further addition of hexane yielded a second crop;

combined yield 1.7545 g, 31%. ^{1}H NMR (CDCl$_3$): δ 16.46 (br s, 1H, enol OH) 7.67 (d, 7.0 Hz, 2H, H-3′ or -6′), 7.59 (d, 8.0 Hz, 2H, H-3′ or -6′), 7.47 (d, 16.0 Hz, 2H, alkene CH), 7.44 (t, 2H, 7.0 Hz, H-4′ or -5′), 7.40 (d, 2.4 Hz, 2H, _meta_ to silyloxy), 7.31 (d, 3.0 Hz, 2H, _meta_ to silyloxy), 7.28 (d, 16.5 Hz, 2H, alkene CH), 7.22 (t, 8.0 Hz, 2H, H-4′ or -5′), 6.33 (s, 1H, COCHCO), 1.41, 1.28 (s, 18H each, ArC(CH_3)$_3$), 0.95 (s, 18H, SiC(CH_3)$_3$), 0.18 (s, 12H, Si(CH_3)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 188.60 (C=O), 150.57 (COSi), 143.37, 139.74, 137.55, 135.55, 131.25, 130.33, 129.17, 128.90, 127.17, 126.90, 125.63, 125.61, 121.76, 103.37 (COCHCO), 35.66 (ArC(CH$_3$)$_3$), 34.51 (ArC(CH$_3$)$_3$), 31.74 (ArC(CH_3)$_3$), 31.64 (ArC(CH_3)$_3$), 27.20 (SiC(CH_3)$_3$), 19.55 (SiC(CH$_3$)$_3$), −0.55 (Si(CH_3)$_2$). IR: 3066 (w), 3015 (w), 2956 (s), 2905 (m), 2862 (m), 1599 (m), 1578 (m), 1552 (w), 1472 (m), 1463 (m), 1434 (m), 1412 (w), 1392 (w), 1361 (m), 1294 (w), 1255 (s), 1233 (s), 1203 (w), 1163 (w), 1126 (w), 1075 (w), 1056 (w), 1031 (w), 1005 (w), 978 (w), 924 (m), 884 (m), 840 (m), 823 (w), 806 (w), 780 (m). FAB-MS: 913 (M$^+$). Anal.: Calcd for C$_{59}$H$_{84}$O$_4$Si$_2$: C, 77.58; H, 9.27; found C, 77.58; H, 9.32.

1,3-Bis(2′-(3″,5″-di-_tert_-butyl-2″-hydroxystyryl)phenyl)propane-1,3-dione (L^{2}H$_3$). In the drybox, 0.3385 g of protected diketone **9** (0.371 mmol) was dissolved in 15 mL of THF in a 50 mL round bottom flask to give a dark orange solution. The flask was capped with a rubber septum and taken out of the drybox. After stirring the solution for 30 min at 0 °C, Bu$_4$NF (3.7 mL, 1 M solution in THF, 3.7 mmol, 10 equiv.) was added with a syringe. The solution turned a very dark brown. It was stirred for 15 min at 0 °C and quenched with 15 mL of 1 M HCl. The organic layer of the orange mixture was separated and the aqueous layer extracted with 2 × 20 mL of ether. The combined organic layers were dried over MgSO$_4$, filtered, and the solvent removed on a rotary evaporator, leaving a thick dark orange oil. A few mL of hexane were added to it, swirled well and the mixture allowed to stand overnight to ensure complete precipitation of the light yellow product, which was filtered and air-dried for 1 h to give 0.1826 g of L^{2}H$_3$ (72%). ^{1}H NMR (C$_6$D$_6$): δ 17.01 (br s, 1H, enol OH), 7.65 (d, 16.0 Hz, 2H, alkene CH), 7.45 (d, 2.5 Hz, 2H, _meta_ to OH), 7.44 (dd, 7.0, 1.0 Hz, 2H, H-3′ or -6′), 7.37 (d, 2.5 Hz, 2H, _meta_ to OH), 7.33 (d, 7.0 Hz, 2H, H-3′ or -6′), 7.07 (td, 7.5, 1.0 Hz, 2H, H-4′ or -5′), 6.94 (td, 7.0, 1.0 Hz, 2H, H-4′ or -5′), 6.90 (d, 16.0 Hz, 2H, alkene CH), 6.33 (s, 1H, COCHCO), 5.38 (br s, 2H, phenol OH), 1.55, 1.26 (s, 18H each, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 188.40 (C=O), 150.15 (C–OH), 142.63, 137.60, 136.06, 135.17, 131.71, 130.80, 129.13, 127.85, 127.50, 127.34, 124.58, 124.27, 122.87, 102.65 (COCHCO), 35.10 (C(CH$_3$)$_3$), 34.51 (C(CH$_3$)$_3$), 31.77 (C(CH_3)$_3$), 30.14 (C(CH_3)$_3$). IR: 3498 (br, v_{OH}), 3397 (br, v_{OH}), 3066 (w), 2960 (s), 2905 (m), 2870 (m), 1601 (s), 1580 (s), 1557 (m), 1476 (s), 1444 (s), 1416 (w), 1391 (w), 1362 (m), 1296 (w), 1276 (w), 1250 (w), 1217 (s), 1190 (m), 1153 (w), 1119 (w), 1090 (w), 1076 (w), 1029 (w), 969 (w), 879 (w), 845 (w), 823 (w), 772 (w). FAB-MS: 685 (M + H$^+$) Anal.: Calcd for C$_{47}$H$_{56}$O$_4$: C, 82.42; H, 8.24; found C, 82.27; H, 7.93.

1,3-Bis(2′-(3″,5″-di-_tert_-butyl-2″-(_tert_-butyldimethylsilyloxy)-phenethyl)phenyl)propane-1,3-dione (10). In a two-neck round bottom flask 200 mg (0.219 mmol) of the unsaturated and protected diketone **9** was reduced with TsNHNH$_2$ (204 mg, 1.09 mmol, 5 equiv.) as described for the reduction of **4** to **5**. After workup, the residue was chromatographed on a short column of

silica gel, eluting with hexanes. The saturated, protected diketone **10** was isolated as a pale yellow oil; yield 87 mg (43%). ^{1}H NMR (acetone-d_6): δ 16.88 (s, 1H, enol OH), 7.64 (dd, 7.5, 1.5 Hz, 2H, H-6′), 7.36 (td, 7.5, 1.5 Hz, 2H, H-4′ or -5′), 7.29 (td, 7.5, 1.5 Hz, 2H, H-4′ or -5′), 7.20 (d, 2.5 Hz, 2H, *meta* to silyloxy), 7.12 (dd, 7.5, 1.5 Hz, 2H, H-3′), 6.92 (d, 2.5 Hz, 2H, *meta* to silyloxy), 6.41 (s, 1H, COCHCO), 3.14 (m, 4H, CH_2CH′$_2$), 3.02 (m, 4H, CH$_2$CH'_2), 1.40, 1.20 (s, 18H each, ArC(CH_3)$_3$), 0.93 (s, 18H, SiC(CH_3)$_3$), 0.31 (s, 12H, Si(CH_3)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 190.32 (C=O), 149.82 (COSi), 142.65, 141.57, 138.68, 136.32, 131.16, 130.89, 130.78, 128.80, 126.04, 125.03, 122.78, 101.38 (COCHCO), 35.60, 34.99, 34.32, 33.67, 31.75 (ArC(CH$_3$)$_3$), 31.50 (ArC(CH$_3$)$_3$), 27.49 (SiC(CH$_3$)$_3$), 20.01 (SiC(CH$_3$)$_3$), −0.36 (Si(CH$_3$)$_2$).

1,3-Bis(2′-(3″,5″-di-*tert*-butyl-2″-hydroxyphenethyl)phenyl)-propane-1,3-dione (L³H₃). The silylated compound **10** (87 mg, 0.095 mmol) was deprotected using Bu$_4$NF (0.3 mL, 0.3 mmol, 3 equiv.) as described for L²H₃. Washing the crude product with 0.5 mL of ethanol and 1 mL of 10% EtOAc in hexanes gave 55 mg (83%) L³H₃ as a slightly yellow solid. ^{1}H NMR (C$_6$D$_6$): δ 16.94 (s, 1H, enol O–H), 7.45 (d, 2.5 Hz, 2H, *meta* to OH), 7.19 (d, 7.5 Hz, 2H, H-3′ or -6′), 7.13 (d, 2.5 Hz, 2H, *meta* to OH), 7.04 (t, 7.5 Hz, 2H, H-4′ or -5′), 6.92 (t, 7.5 Hz, 2H, H-4′ or -5′), 6.87 (d, 7.5 Hz, 2H, H-3′ or -6′), 6.11 (s, 2H, phenol OH), 6.04 (s, 1H, COCHCO), 3.07 (m, 4H, CH_2CH′$_2$), 2.92 (m, 4H, CH$_2$CH'_2), 1.64, 1.38 (s, 18H each, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 190.80 (C=O), 151.85 (Ar C–OH), 142.45, 142.25, 136.32, 135.86, 132.10, 132.02, 129.96, 126.84, 126.73, 125.56, 122.90, 101.86 (COCHCO), 36.13, 35.75, 35.27, 34.77, 32.35 (C(CH$_3$)$_3$), 30.62 (C(CH$_3$)$_3$). IR: 3492 (m, ν_{OH}), 2956 (s), 2870 (m), 1673 (m, $\nu_{\text{C=O}}$), 1602 (m), 1480 (m), 1462 (m), 1415 (m), 1391 (m), 1362 (m), 1274 (m), 1214 (s), 1198 (s), 1222 (s), 877 (w), 820 (w), 752 (w). FAB-MS: Exact mass for C$_{47}$H$_{60}$O$_4$ calcd 688.4466, obsd 688.4470.

Preparation of metal complexes

Bis{1-[2′-(3″,5″-di-*tert*-butyl-2″-oxyphenethyl)phenyl]-3-*p*-tolylpropane-1,3-dionato}titanium(IV), (L¹)₂Ti. 100 mg L¹H₂ (0.213 mmol) was weighed into a glass bomb, a stir bar was added and 20 mL of dry benzene was added by vacuum transfer. In the drybox, 31.5 µL of titanium(IV) isopropoxide (Aldrich, 30.6 mg, 0.107 mmol) was added. The reaction mixture was stirred at 70 °C for 17 h. The solvent was evaporated to give the product in quantitative yield as a mixture of isomers. ^{1}H NMR (C$_6$D$_6$): δ 7.93 (d, 8.0 Hz), 7.64 to 7.50 (m), 7.44 to 7.01 (m), 6.77 (d, 7.0 Hz), 6.57 (s, COCHCO), 6.54 (s, COCHCO), 6.51 (s, COCHCO), 5.28 to 5.13 (m, ethylene-H), 4.80 to 4.62 (m, ethylene-H), 3.10 to 2.89 (m, ethylene-H), 1.79 (s, Me or *t*Bu), 1.70 (s, Me or *t*Bu), 1.63 (s, Me or *t*Bu), 1.61 (s, Me or *t*Bu), 1.38 (s, Me or *t*Bu), 1.37 (s, Me or *t*Bu), 1.30 (s, Me or *t*Bu). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 187.79 (carbonyl), 187.60 (carbonyl), 187.24 (carbonyl), 184.85 (carbonyl), 184.70 (carbonyl), 184.06 (carbonyl), 165.69 (phenoxide-C–O–Ti), 165.23 (phenoxide-C–O–Ti), 164.86 (phenoxide-C–O–Ti), 147.51, 145.27, 145.19, 143.49, 143.41, 143.31, 143.15, 139.22, 139.19, 139.14, 137.76, 137.69, 135.57, 135.51, 135.16, 134.66, 134.32, 134.26, 133.31, 132.77, 132.20, 132.12, 130.22, 129.95, 129.71, 129.64, 129.22, 128.98, 128.87, 128.81, 128.57, 128.50, 128.25, 128.18, 127.86, 127.56, 127.17, 126.83, 126.77, 126.68, 126.38, 122.30, 122.27, 122.21,

101.51 (COCHCO), 101.09 (COCHCO), 99.76 (COCHCO), 42.91, 40.38, 39.91, 39.73, 36.51, 36.16, 36.12, 36.07, 34.91, 34.87, 34.85, 34.79, 32.32 (C(CH_3)$_3$), 32.28 (C(CH_3)$_3$), 32.22 (C(CH_3)$_3$), 31.59 (C(CH_3)$_3$), 31.19 (C(CH_3)$_3$), 31.10 (C(CH_3)$_3$), 23.08 (tolyl CH_3), 21.54 (tolyl CH_3). IR: 2956 (s), 2925 (s), 2867 (m), 1601 (m), 1588 (s), 1551 (s), 1523 (s), 1495 (s), 1473 (m), 1447 (m), 1434 (m), 1410 (w), 1360 (s), 1322 (m), 1300 (m), 1283 (m), 1231 (s), 1202 (m), 1184 (w), 1165 (m), 1125 (m), 1093 (w), 1064 (w), 1047 (w), 1018 (w), 944 (w), 914 (w), 866 (m), 799 (w), 765 (m), 763 (w). FAB-MS: 984 (M$^+$). Anal.: Calcd for C$_{64}$H$_{72}$O$_6$Ti: C, 78.03; H, 7.37; found C, 77.84; H, 7.44.

[1-(2′-(3″,5″-Di-*tert*-butyl-2″-oxyphenethyl)phenyl)-3-*p*-tolylpropane-1,3-dionato](di(2-oxyethyl)amine)titanium(IV), (L¹)Ti[(OCH₂CH₂)₂-NH]. In the drybox, 4.5 mg (43 µmol) diethanolamine was weighed into a round bottom flask. A stir bar, 12.5 µL (12.1 mg, 43 µmol) of titanium(IV) isopropoxide and 3 mL of dry benzene were added. The reaction mixture was stirred for 20 min at RT. A solution of 20.0 mg (42 µmol) of L¹H₂ in 2 mL of benzene was then added dropwise to the stirred mixture over the course of 1 min using a syringe. The reaction mixture was stirred for 10 min at RT, and the solvent removed on the vacuum line. The orange residue was transferred into a vial, suspended in a small amount of hexanes and the vial placed in a freezer at −40 °C. After 16 h the solvent was removed using a syringe and the orange residue dried in vacuum. Yield 26 mg (98%). ^{1}H NMR (CD$_2$Cl$_2$, −60 °C, assignments by selective decoupling): δ 7.95 (d, 8.5 Hz, 2H, tolyl-H *meta* to -CH$_3$), 7.63 (d, 7.0 Hz, 1H, H-3′ or -6′), 7.40 (t, 7.0 Hz, 1H, H-4′ or -5′), 7.33 (d, 7.0 Hz, 1H, H-3′ or -6′), 7.32 (t, 7.0 Hz, 1H, H-4′ or -5′), 7.28 (d, 8.5 Hz, 2H, tolyl-H *ortho* to –CH$_3$), 7.12 (d, 2.5 Hz, 1H, *meta* to OTi), 6.97 (d, 2.5 Hz, 1H, *meta* to OTi), 6.83 (s, 1H, COCHCO), 4.68 (dt, 11.0, 5.5 Hz, 1H, CHH′O–Ti), 4.45 (dt, 11.0, 5.5 Hz, CHH'O–Ti), 4.41 (dt, 11.0, 5.5 Hz, 1H, CHH′O–Ti), 4.30 (dt, 11.0, 5.5 Hz, 1H, CHH'O–Ti), 3.68 (td, 12.5, 2.5 Hz, 1H, CHH′Ar), 3.39 (ddt, 11.5, 6.0, 5.5 Hz, 1H, NHCHH′), 3.28 (ddt, 12.0, 6.0, 5.5 Hz, 1H, NHCHH′), 3.17 (tt, 6.0, 5.5 Hz, 1H, NH), 3.10 (dq, 11.5, 5.5 Hz, NHCHH′), 2.93 (dq, 12.0, 5.5 Hz, 1H, NHCHH′), 2.62 (td, 12.5, 2.5 Hz, 1H, ArCHH′), 2.51 (td, 12.5, 5.5 Hz, 1H, ArCHH′), 2.38 (s, 3H, tolyl CH_3), 2.11 (td, 12.5, 5.5 Hz, 1H, ArCHH′), 1.55, 1.23 (s, 9H each, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 190.83 (carbonyl), 185.21 (carbonyl), 163.10 (phenoxide *ipso C*), 143.62, 142.95 (sl br), 142.79, 140.55 (v br), 139.57, 135.29, 134.04, 131.72, 130.63, 129.96, 128.83, 126.42 (2 overlapping resonances), 125.90, 122.18, 100.04 (COCHCO), 72.23 (N(CH$_2$$CH_2$O)$_2$), 53.18 (N($CH_2CH_2$O)$_2$), 38.70, 36.41, 35.21, 34.88, 32.38 (C(CH_3)$_3$), 30.57 (C(CH_3)$_3$), 21.82 (tolyl CH_3). IR: 3312 (w, ν_{NH}), 3176 (w), 2957 (s), 2920 (s), 2853 (s), 1602 (s), 1584 (s), 1547 (s), 1524 (s), 1499 (s), 1472 (s), 1446 (s), 1410 (s), 1361 (s), 1327 (s), 1304 (s), 1252 (s), 1237 (s), 1208 (m), 1185 (m), 1167 (m), 1101 (s), 1087 (s), 1061 (s), 1017 (w), 957 (m), 914 (m), 870 (s), 796 (m), 767 (s), 748 (m). FAB-MS: m/z = 619 (M$^+$).

[1-(2′-(3″,5″-Di-*tert*-butyl-2″-oxyphenethyl)phenyl)-3-*p*-tolyl-propane-1,3-dionato](*N*-methyldi(2-oxyethyl)amine)titanium(IV), (L¹)Ti[(OCH₂CH₂)₂NCH₃]. This complex was prepared using the procedure described for the diethanolamine derivative, using 5.1 mg (43 µmol) of *N*-methyldiethanolamine in place of the di-ethanolamine, to give 22 mg (81%) of (L¹)Ti[(OCH$_2$CH$_2$)$_2$NCH$_3$] as a yellow powder. ^{1}H NMR (C$_6$D$_6$): δ 7.96 (d, 8.0 Hz, 2H, tolyl-H,

meta to CH$_3$), 7.52 (d, 2.0 Hz, 1H, *meta* to aryl-O–Ti), 7.41 to 7.38 (m, 1H, *H*-4′ or -5′), 7.21 (d, 2.0 Hz, 1H, *meta* to aryl-O–Ti), 7.11 to 7.02 (m, 3H, *H*-3′, -6′, and -4′ or -5′), 6.95 (d, 8.0 Hz, 2H, tolyl-*H*, *ortho* to CH$_3$), 6.65 (s, 1H, COC*H*CO), 4.89 (br, 1H), 4.30 (br, 4H), 3.13 (br, 1H), 2.80 (br, 2H), 2.47 (br, 2H), 2.36 (br, 2H), 2.05 (s, 9H, C(C*H*$_3$)$_3$), 2.03 (s, 3H, tolyl- or N–C*H*$_3$), 1.99 (s, 3H, tolyl- or N–C*H*$_3$), 1.41 (s, 9H, C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 191.03 (carbonyl), 185.82 (carbonyl), 163.44 (phenoxide *ipso C*), 143.75, 142.93, 142.62 (sl br), 140.75 (v br), 139.47, 135.16, 134.14, 131.42, 130.50, 129.93, 128.92, 126.35 (2 overlapping resonances), 125.87, 122.14, 100.06 (COC*H*CO), 71.19 (*C*H$_2$O), 70.78 (*C*H$_2$O), 62.05 (N*C*H$_2$), 44.92, 38.54, 36.39, 35.32 (*C*(CH$_3$)$_3$), 34.89 (*C*(CH$_3$)$_3$), 32.37 (C(*C*H$_3$)$_3$), 31.56 (C(*C*H$_3$)$_3$), 21.79 (tolyl *C*H$_3$). IR: 2952 (m), 2861 (m), 1602 (m), 1583 (m), 1544 (s), 1526 (s), 1500 (s), 1473 (m), 1448 (m), 1410 (m), 1360 (s), 1328 (m), 1303 (m), 1252 (w), 1236 (m), 1206 (w), 1183 (w), 1167 (w), 1146 (w), 1113 (w), 1088 (s), 1070 (m), 1031 (w), 1017 (w), 989 (w), 916 (w), 871 (m). FAB-MS: 634 (M + H)$^+$.

[1 - (2′ - (3″,5″ - Di - *tert* - butyl - 2″-hydroxyphenethyl)phenyl)-3-*p*-tolylpropane - 1,3-dionato] di (η^5 - cyclopentadienyl) scandium(III), (L^{1}H)ScCp$_2$. Into an NMR tube 40.0 mg (85 μmol) of L^{1}H$_2$ was weighed. In the drybox 20.4 mg (85 μmol) of tricyclopentadienylscandium(III) and some benzene-*d$_6$* were added. After shaking the reaction mixture vigorously for 10 min, the tube was allowed to stand in the drybox at room temperature for 30 min. The reaction mixture was poured into a flask, a stir bar was added and the flask was attached to a needle valve. The solvent was evaporated on the vacuum line and inside the drybox the yellow residue was suspended in hexanes. The supernatant was removed using a pipet and transferred into a flask and the solvents evaporated *in vacuo* to give 41 mg (75%) of (L^{1}H)ScCp$_2$ as a yellow solid. ^{1}H NMR (C$_6$D$_6$): δ 7.81 (d, 8.0 Hz, 2H, tolyl-*H*, *meta* to CH$_3$), 7.34 (d, 2.5 Hz, 1H, *meta* to OH), 7.32 (dd, 7.0, 2.0 Hz, 1H, *H*-3′ or -6′), 7.07 (d, 2.5 Hz, 1H, *meta* to OH), 7.02 (d, 8.0 Hz, 2H, tolyl-*H*, *ortho* to CH$_3$), 7.00 to 6.93 (m, 2H, *H*-4′ and -5′), 6.75 (dd, 7.0, 2.0 Hz, 1H, *H*-3′ or -6′), 6.48 (s, 1H, COC*H*CO), 6.20 (s, 10H, Cp*H*), 4.99 (s, 1H, O*H*), 3.09 (t, 7.0 Hz, 2H, C*H*$_2$), 2.92 (t, 7.0 Hz, 2H, C*H*$_2$), 2.08 (s, 3H, tolyl C*H*$_3$), 1.47, 1.35 (s, 9H each, C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 190.47 (carbonyl), 185.23 (carbonyl), 151.57 (phenol-*C*–OH), 143.27, 142.56, 141.48, 139.41, 135.92, 135.72, 132.04, 130.12, 129.85, 128.93, 128.58, 126.82, 126.43, 125.37, 122.43, 113.27 (Cp), 100.37 (COC*H*CO), 35.49, 35.16, 33.13, 32.52, 32.31 (C(*C*H$_3$)$_3$), 30.43 (C(*C*H$_3$)$_3$), 21.77 (tolyl *C*H$_3$). IR: 3549 (w, *ν*$_{OH}$), 2952 (s), 2926 (m), 2863 (m), 1601 (w), 1584 (m), 1542 (s), 1536 (s), 1522 (s), 1499 (s), 1477 (s), 1445, 1410 (m), 1373 (s), 1361 (s), 1316 (m), 1301 (m), 1273 (m), 1232 (w), 1211 (w), 1185 (m), 1058 (w), 1042 (w), 1017 (m), 785 (s), 752 (m). FAB-MS: 645 (M + H)$^+$, 579 (M–Cp)$^+$.

[1-(2′-(3″,5″-Di-*tert*-butyl-2″-(oxydi-η^5-cyclopentadienylscandium-(III))phenethyl)phenyl)-3-*p*-tolylpropane-1,3-dionato]di(η^5-cyclopentadienyl)scandium(III), (L^1)[ScCp$_2$]$_2$. In the drybox 16 mg (25 μmol) of (L^{1}H)ScCp$_2$ and 6 mg (25 μmol) of tricyclopentadienylscandium(III) were weighed into a NMR tube. Benzene-*d$_6$* was added and the reaction mixture shaken vigorously. After standing at room temperature for 30 min, the reaction mixture was poured into a flask. A stir bar was added and the flask was attached to a needle valve. The solvents were evaporated on the vacuum line and the residue transferred into

a small vial. The crude product was suspended in some hexane and the vial was allowed to stand overnight at −40 °C. The solution was decanted from the residue and the yellow solid dried *in vacuo* to give 7.5 mg (37%) of (L^1)[ScCp$_2$]$_2$. ^{1}H NMR (C$_6$D$_6$): δ 7.83 (d, 8.0 Hz, 2H, tolyl-*H meta* to CH$_3$), 7.46 (s, 1H, *meta* to aryl-O–Sc), 7.45 (d, 7.0 Hz, 1H, *H*-3′ or -6′), 7.27 (s, 1H, *meta* to aryl-O–Sc), 7.19 (t, 7.0 Hz, 1H, *H*-4′ or 5′), 7.09 (t, 7.0 Hz, 1H, *H*-4′ or -5′), 7.08 (d, 7.0 Hz, 1H, *H*-3′ or -6′), 6.99 (d, 8.0 Hz, 2H, tolyl-*H ortho* to CH$_3$), 6.65 (s, 1H, COC*H*CO), 6.16 (s, 10H, Cp*H*), 6.12 (s, 10H, Cp*H*), 3.41 (t, 7.5 Hz, 2H, C*H*$_2$), 2.79 (t, 7.5 Hz, 2H, C*H*$_2$), 2.06 (s, 3H, tolyl-C*H*$_3$), 1.53, 1.40 (s, 9H each, C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 190.57 (carbonyl), 184.73 (carbonyl), 161.84 (phenoxide-*C*–OSc), 143.03, 141.64, 141.23, 139.08, 135.88, 134.71, 133.54, 132.95, 130.45, 130.17, 129.85, 128.49, 126.64, 124.09, 122.07, 115.86 (Cp), 113.12 (Cp), 100.63 (COC*H*CO), 42.08, 35.67, 34.82, 34.32, 32.54 (C(*C*H$_3$)$_3$), 31.57 (C(*C*H$_3$)$_3$), 21.76 (tolyl *C*H$_3$). IR (nujol mull): 1601 (m), 1584 (s), 1542 (s), 1523 (s), 1498 (s), 1411 (m), 1303 (s), 1272 (s), 1234 (m), 1185 (w), 1126 (w), 1015 (s), 855 (m), 789 (s).

1-(2′-(3″,5″-Di-*tert*-butyl-2″-oxyphenethyl)phenyl)-3-*p*-tolyl-propane-1,3-dionato-(η^5-cyclopentadienyl)scandium(III), L^{1}ScCp. Into an NMR tube were weighed 30 mg (64 μmol) of L^{1}H$_2$. The tube was taken into the drybox and 20 mg (83 μmol) of Cp$_3$Sc and benzene-*d$_6$* (0.5 mL) were added. The reaction mixture was shaken vigorously for 10 min and the tube was placed in an oil bath at 73 °C. After 5.5 h the heating was stopped and the tube was allowed to stand in the drybox overnight at RT. By ^{1}H NMR, the solution contained equimolar amounts of L^1(ScCp$_2$)$_2$ and L^{1}ScCp. Attempts to raise the yield of the monoscandium complex by adding more ligand or further heating of the reaction mixture led to decomposition of the product, which could thus be characterized only *in situ* by NMR. ^{1}H NMR (C$_6$D$_6$): δ 7.71 (d, 8.0 Hz, 2H, tolyl-*H*, *meta* to CH$_3$), 7.43 (d, 2.5 Hz, 1H, *meta* to aryl-O–Sc), 7.23 (d, 2.5 Hz, 1H, *meta* to aryl-O–Sc), 7.05 (m, 4H, *H*-3′,4′,5′,6′), 6.90 (d, 8.0 Hz, 2H, tolyl-*H*, *ortho* to CH$_3$), 6.64 (s, 5H, Cp–*H*), 6.41 (s, 1H, COC*H*CO), 3.12 to 2.91 (m, 2H, C*H*H′), 2.85 to 2.71 (m, 2H, C*H*″*H*‴), 1.99 (s, 3H, tolyl C*H*$_3$), 1.69, 1.43 (s, 9H each, C(C*H*$_3$)$_3$).

X-Ray crystallography

Crystals of L^{2}H$_2$ were grown as yellow blocks when the oily material formed after desilylation of **10** was allowed to stand overnight in hexane solution. Crystals of the *mer* isomer of (L^1)$_2$Ti were grown by allowing a concentrated solution of the complex (as a mixture of isomers) in dichloromethane–methanol to stand for two weeks at −20 °C. The crystals were placed in inert oil and transferred to the tip of a glass fiber in the cold N$_2$ stream of a Bruker Apex CCD diffractometer (*T* = 100 K). Data were reduced, correcting for absorption and decay, using the program SADABS.[24] The structures were solved using direct methods, with remaining non-hydrogen atoms found on difference Fourier maps. All heavy atoms were refined anisotropically. The OH groups in L^{2}H$_3$ were disordered unequally over the two *ortho* positions in each of the phenol rings, and one *tert*-butyl group in L^{2}H$_3$ was disordered over two orientations. All hydrogen atoms were located on difference maps and refined isotropically, except the hydrogens on the minor O–H groups and the *tert*-butyl hydrogens in L^{2}H$_3$. Calculations used SHELXTL (Bruker Analytical X-ray

Systems), with scattering factors and anomalous dispersion terms taken from the literature.[25] Further details about the individual structures are in Table 1. CCDC reference numbers 281977 and 281978. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b511915d

Acknowledgements

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