Novel Routes to Bidentate Cyclopentadienyl−Alkoxide Complexes of Titanium: Synthesis of (η^5-σ-$C_5R^1_4CHR^2CH_2CR^3R^4O$)$TiCl_2$

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Reaction of $C_5R^1_4(SiMe_3)CHR^2CH_2CR^3R^4OR^5$ with titanium tetrachloride gives the bidentate η^5-σ-cyclopentadienyl−alkoxide complexes of titanium (η^5-σ-$C_5R^1_4CHR^2CH_2CR^3R^4O$)-$TiCl_2$ through elimination of chlorotrimethylsilane and RCl (R = $SiMe_3$, CH_2Ph, CMe_3). A potentially tridentate system (R^1, R^2, R^3 = H, R^4 = $-(CH_2)_2OMe$) was synthesized in optically pure form and its structure determined by X-ray diffraction. The pendant ether oxygen does not coordinate to the metal, and hydride transfer reactions catalyzed by the complex gave racemic products. Efficient routes to tetramethylcyclopentadienyl-substituted ligands (R^1 = Me) were developed on the basis of the addition of 2-butenylmagnesium bromide to γ-lactones to give the dienyl alcohols $[C(CH_3)=CH(CH_3)]_2C(OH)CHR^2(CH_2)_2OH$, which could be functionalized on the primary alcohol before acid-catalyzed cyclization to afford the 3-alkoxypropyl-substituted tetramethylcyclopentadienes.

Introduction

Bis(cyclopentadienyl) complexes of group IV metals (metallocenes) are an important class of organometallics with many applications as polymerization catalysts,[1] as well as in catalytic and stoichiometric organic synthesis.[2] Examples with linked cyclopentadienyl ligands have proved particularly valuable for polymerization[1] and asymmetric synthesis.[2b] The search for new or modified reactivity prompts the investigation of alternative supporting ligand systems for the metal, for example diaryloxy and diamido complexes.[3] Complexes containing both η^5-cyclopentadienyl and σ-heteroatom components,[4] particularly where these are linked, should have special reactivities. Linked amido−cyclopentadienyl complexes of group 4 transition metals have been synthesized by several groups[5] and show unique polymerization properties.[6] Only a few linked alkoxy−cyclopentadienyl complexes of group 4 transition metals have been reported.[7] Complexes containing a cyclopentadienyl ligand with a coordinating tether are also of current interest.[8]

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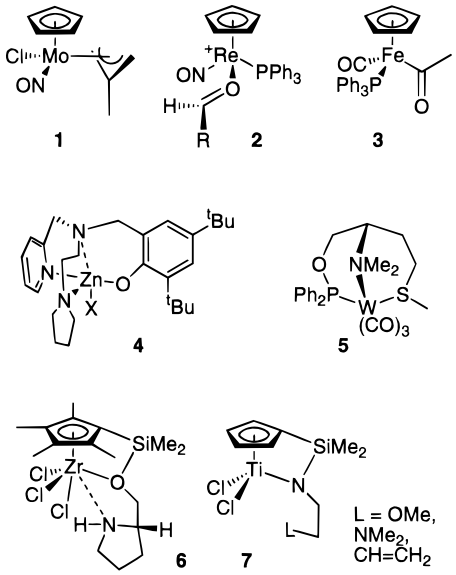
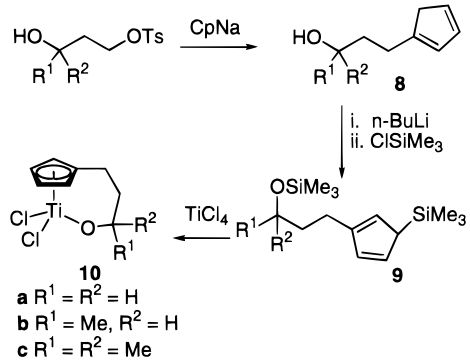
Complexes with metal-centered asymmetry have great potential in chiral organic synthesis. Several "chiral at metal" complexes have been used stoichiometrically, including **1**−**3**,[9] but the need for resolution in their



synthesis makes them expensive. A more serious problem is that in catalytic reactions where bonds are broken/remade to the metal, racemization is very likely. An elegant solution to both problems would be to induce the metal-centered chirality on complexation of a ligand containing three different coordinating groups. The complexes **4**[10] and **5**[11] are examples, although the concept has not been systematically investigated. Ligands containing linked cyclopentadienyl groups, an anionic center, and a coordinating group seem ideal to investigate the area, particularly with group 4 transition metals. Several examples of this type of complex have been reported, including **6**[12] and **7**.[13] Recently chiral tridentate ligands consisting of a cyclopentadiene and two different phosphines have been reported together with their molybdenum and iron complexes.[14] We report below our work towards the synthesis of linked cyclopentadienyl−alkoxide[7] complexes of titanium.

Results and Discussion

It was our intention to bind both cyclopentadienyl and alkoxy ends of the ligand to the metal in one operation, as has been used in the synthesis of bidentate cyclopentadienyl−imido complexes of niobium.[15] The synthesis of mono(cyclopentadienyl) complexes has greatly benefited from the use of (trimethylsilyl)cyclopentadiene as a mild and effective reagent for the transfer of a cyclopentadienyl ring to the metal.[16] Since phenoxide has also been efficiently transferred to group 4 metals *via* its trimethylsilyl ether,[17] we expected that a bis-$SiMe_3$ compound of type **9** would be effective in generating the desired complexes. During the course of our work Teuben reported an identical approach.[7a] The alcohol **8a** was synthesized from propane-1,3-diol *via* reaction of the derived mono(4-methylbenzenesulfonate) with excess sodium cyclopentadienide. Double deprotonation with *n*-butyllithium and quenching with excess chlorotrimethylsilane gave the required ligand precursor **9a**. Reaction with titanium tetrachloride in dichloromethane at 0 °C produced the desired complex **10a** as a yellow-brown solid. Obtaining the pure complex **10a** was hampered by the presence of titanium tetrachloride as an impurity. We found that either exposing the crude product to air followed by extracting into toluene or washing a solution of the complex in dichloromethane with 6 M hydrochloric acid was effective in removing the contaminant and gave bright yellow air-stable crystals of **10a** in 65% yield. Analytically pure material was obtained by sublimation (100 °C at 0.1 mbar, 31% overall yield) or recrystallization (dichloromethane/hexane, 32%). Teuben published a very similar route to **10a** during the course of this work.[7a]



In a similar fashion 1,3-butanediol lead to the asymmetric complex **10b** with a secondary alcohol bound to the metal center. Reaction of the ligand precursor **9c**

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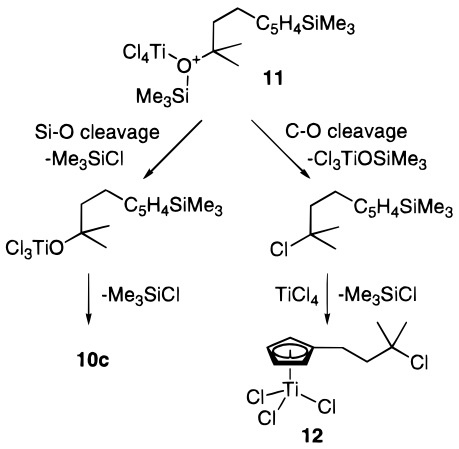
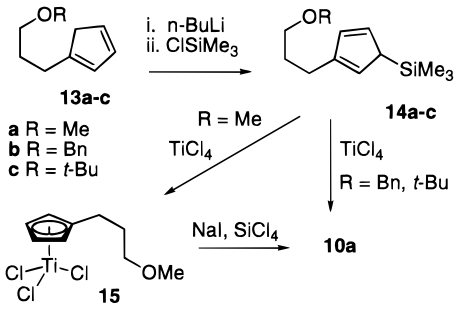
containing a silylated tertiary alcohol with titanium tetrachloride gave a 1:1 mixture of the expected complex **10c** and the complex **12**, resulting from cleavage of the



carbon−oxygen bond. The ratio of **10c** to **12** did not change on standing, showing that **10c** is not a precursor of **12**. A likely route to **10c** and **12** is *via* the intermediate **11**, where the rates of cleavage of O−Si and O−C bonds are similar. Titanium tetrachloride is known to cleave *tert*-butyl ethers and to convert tertiary alcohols into chlorides.[18] Although **12** could not be separated from **10c**, the following data allowed identification. In the bidentate complexes **10** the cyclopentadiene ring protons are well-separated in the proton NMR (δ 6.9 and 6.1), whereas in simple mono(cyclopentadienyl)-titanium complexes, such as **12**, they are much closer (δ 7.0 and 6.9). The proton and carbon-13 chemical shifts of **12** in the RCH_2CMe_2Cl region are in excellent agreement with models (e.g. δ_C 69.7 (C), 32.6 (Me) in **12**; δ_C 71.3 (C), 32.4 (Me) in 2-chloro-2-methylheptane[19]). The complex **10c** could be obtained free of **12** by selective hydrolysis of the latter followed by extraction of **10c** into hexane.

Attempts to improve the moderate yields of **10** were frustrating. The most likely problem is that reaction of the $OSiMe_3$ unit with the metal chloride is faster than reaction of the $C_5H_4RSiMe_3$ moiety, leading to some $(Me_3SiC_5H_3(CH_2)_3O)_2TiCl_2$ and hence oligomeric structures. A solution would be to protect the hydroxyl group with a more robust ether, encouraging initial reaction between the silylated cyclopentadiene and the metal halide. The cyclopentadiene **13a**, carrying a 3-methoxypropyl side chain, was readily synthesized. Silylation to give **14a** followed by reaction with titanium tetrachloride produced **15** in excellent yield. The carbon and proton NMR signals for the CH_2OMe moiety change by less than 0.5 and 0.05 ppm, respectively, on complexation, indicating no coordination between the oxygen and titanium. The cyclopentadienyl proton signals in **8** appeared close together (δ_H 6.9 and 6.8), also typical for a nonchelated side chain. Reaction with sodium iodide/silicon tetrachloride in dichloromethane/acetonitrile[20]



produced **10a**, but the yield was poor and the product contaminated with chloride/iodide exchange products.

We next examined benzyl as a protecting group for the ligand oxygen, in the expectation that it could be cleaved by hydrogenation. The required substituted cyclopentadiene **13b** was readily prepared, and deprotonation/chlorotrimethylsilane quench gave the ligand precursor **14b**. Surprisingly, when butyllithium was used for the deprotonation, a small amount of the benzyloxy substituent was eliminated[21] (5−10%) to give allyl(trimethylsilyl)cyclopentadienes, a problem which could be minimized by rapid addition of the chlorotrimethylsilane quench. We were surprised (and delighted!) to find that attempted complexation of **14b** to titanium tetrachloride gave the required bidentate complex **10a** directly, in excellent yield (76%, >90% pure by NMR), together with benzyl chloride. There was no sign of the complex analogous to **15**. Recrystallization of the crude product from toluene/pentane gave analytically pure **10a** in 49% yield.

The C−O bond cleavage observed in the reaction of **9c** with titanium tetrachloride suggested the use of a *tert*-butyl ether as an *in situ* cleavable protecting group for the oxygen. The ligand precursor **13c** was synthesized, and silylation was quantitative to give **14c**. Addition of titanium tetrachloride to **14c** gave the required bidentate complex **10a** in reasonable crude yield, but the reaction was not as clean as was observed with **14b** and pure complex was isolated in only 15% yield. We believe that the high yields and pure complex produced from the benzyl-protected ligand precursor **14b** are due to benzyl elimination occurring only after the cyclopentadiene is bound to the metal. The activation required for nucleophilic cleavage of the benzyl−oxygen bond by chloride is provided by intramolecular coordination of the benzyl ether oxygen to the metal center. The trimethylsilyl and *tert*-butyl ethers in the ligand precursors **9a** and **14c** may be cleaved by titanium tetrachloride before complexation of the cyclopentadiene, allowing oligomeric byproducts to form which make purification difficult. To favor the initial formation of the cyclopentadienyl−titanium bond **13c** was deprotonated with butyllithium, and the anion

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(21) Deprotonation with potassium hydride or sodium hydride/catalytic imidazole avoided elimination of the benzyloxy group, but the chlorotrimethylsilane quench gave only moderate yields of the required **14b** together with substantial amounts of recovered **13b**. Deprotonation went to completion as judged by methyl iodide quench; therefore, the problem is probably associated with rapid proton exchange between **14b** and residual Li-**13b** during the chlorotrimethylsilane quench. The elimination of the benzyloxy group probably occurs *via* deprotonation of one of the benzylic hydrogens followed by *syn*-elimination *via* a [2,3]-sigmatropic reaction. Treatment of 1-(benzyloxy)octane with excess butyllithium at 0 °C cleanly gave 1-octene in <1 min.

reacted with titanium tetrachloride to give a slightly improved 22% yield of **10a**.[22]

The discovery that benzyl and *tert*-butyl ethers could be used instead of the more labile trimethylsilyl ethers as alkoxide equivalents in complexation makes the synthesis of more elaborate systems easier. With our interest in potentially tridentate systems we synthesized the complexes **19** and **23** using the elimination of benzyl and *tert*-butyl groups, respectively.

Mesylation of **16** followed by reaction with sodium cyclopentadienide gave the ligand precursor **17**. Formation of the trimethylsilyl derivative **18** and reaction with titanium tetrachloride gave the asymmetric complex **19** in good yield. There was no sign by NMR of coordination of the alkene moiety to the metal center.[23]

Synthesis of a complex with an oxygen as a third coordinating group started with the regioselective cleavage of the acetonide **20** with trimethylaluminum.[24] The alcohol **21** could be resolved by enzyme-catalyzed enantioselective acylation using vinyl acetate. Of the many enzymes tested, Lipase-AK from *Pseudomonas* sp.[25] gave the best results, leaving alcohol of >99% ee after 65% conversion to the acetate. Mesylation, displacement with sodium cyclopentadienide, silylation, and addition of titanium tetrachloride gave the complex **23**. The complexation was low-yielding (10−30%) and erratic.[26] The main problem seemed to be excess titanium tetrachloride binding to the complex and causing decomposition on attempted purification (crude NMR yields were around 60%). The proton NMR signals for the CH_2OMe moiety changed by +0.07 (CH_2) and +0.03 and the carbon by +0.7 (CH_2) and +0.4, respectively, on complexation, indicating no significant coordination between the oxygen and titanium. We also obtained a crystal structure determination of **23** (Figure 1), which confirmed that the OMe unit does not coordinate to the metal. Details of the structure determination are given in the Experimental Section and in Table 1. Selected

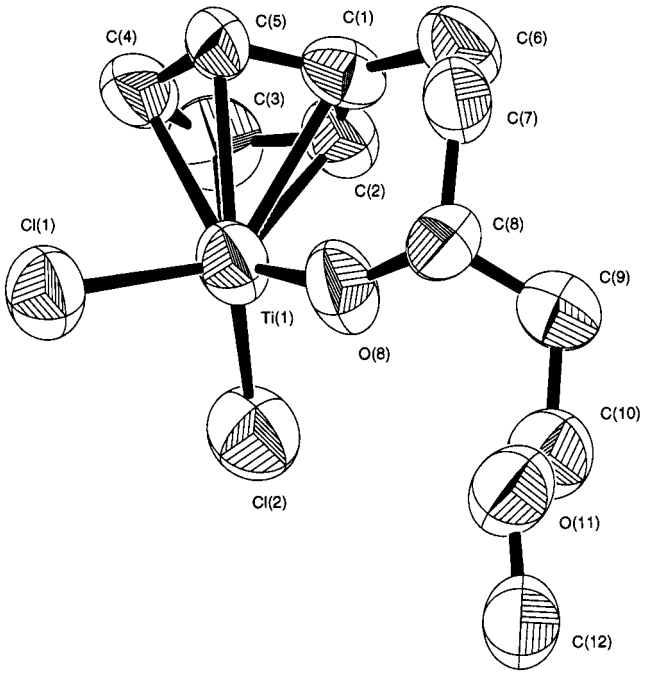

Figure 1. ORTEP diagram of **23** (ellipsoids drawn at 50% probability level).

Table 1. Crystallographic Data for 23

empirical formula	$C_{11}H_{16}O_2Cl_2Ti$
fw	299.05
crystal syst	triclinic
space group	$P\bar{1}$ (No. 2)
a, Å	9.902(5)
b, Å	10.526(6)
c, Å	6.954(4)
α, deg	99.38(6)
β, deg	109.93(4)
γ, deg	101.57(5)
V, Å^3	646.1(7)
Z	2
D_{calcd}, g cm^{-3}	1.537
temp, K	273
no. of measd rflns	2046
no. of unique rflns	1915 (R_{int} = 0.152)
no. of observns ($I > 2.00\sigma(I)$)	569
no. of variables	145
residuals: *R*; R_w[a]	0.052; 0.044
largest diff peak and hole, e Å^{-3}	0.36, −0.24

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [(\sum w|F_o| - |F_c|)^2/\sum wF_o^2)]^{1/2}$.

(22) Cyclopentadienides of electropositive metals such as Na^+ and Li^+ generally give low yields of monocyclopentadienyl complexes with titanium tetrachloride. Good yields may obtained with less electropositive metals, e.g.: Sloan, C. L.; Barber, W. A. *J. Am. Chem. Soc.* **1959**, *81*, 13.

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(24) (a) Takano, S.; Ohkawa, T.; Ogasawara, K. *Tetrahedron Lett.* **1988**, *29*, 1823. (b) Luh, T.-Y. *Synlett* **1996**, 201. The regiochemistry follows from complexation of the Lewis acid to the less hindered primary oxygen, leading to cleavage of the bond between this and the Me_2COR fragment, and indicates that a possible chelate between the Lewis acid, secondary oxygen, and the methoxy group does not have a significant effect. For comparison the acetonide of 1-(benzyloxy)-2,3-propanediol gives mostly $^tBuOCH_2CHOHCH_2OBn$.

(25) Burgess, K.; Jennings, L. D. *J. Am. Chem. Soc.* **1991**, *113*, 6129. Morgan, B.; Dodds, D. R.; Zaks, A.; Andrews, D. R.; Klesse, R. *J. Org. Chem.* **1997**, *62*, 7736.

(26) A ligand analogous to **22** was synthesized with a benzyl rather than *tert*-butyl protecting group on the secondary alcohol. Unfortunately, deprotonation and reaction with chlorotrimethylsilane was complicated by substantial elimination of the benzyloxy group. Partially purifed trimethylsilylated ligand was reacted with titanium tetrachloride, but the overall yields of **23** were lower than for the *tert*-butyl case (5−10%).

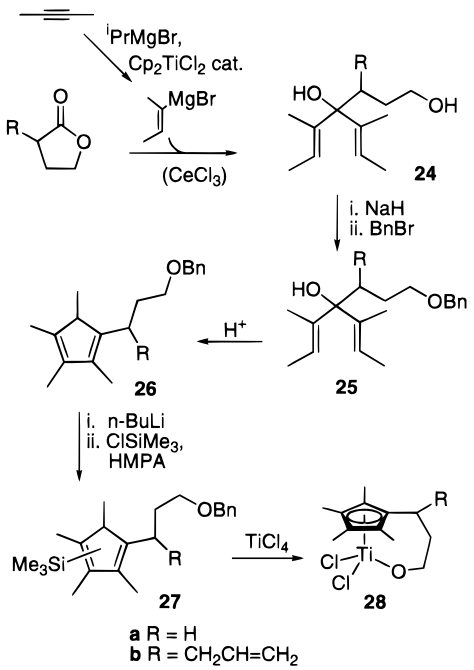
Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 23

Ti−Cl(1)	2.273(4)	Ti−C(5)	2.33(1)
Ti−Cl(2)	2.255(5)	O(8)−C(8)	1.42(2)
Ti−O(8)	1.73(1)	C(1)−C(6)	1.49(2)
Ti−C(1)	2.35(1)	C(6)−C(7)	1.53(2)
Ti−C(2)	2.30(1)	C(7)−C(8)	1.52(2)
Ti−C(3)	2.34(1)	Ti−Cp(centroid)	2.996
Ti−C(4)	2.30(1)		

Cl(1)−Ti−Cl(2)	104.2(2)	C(1)−C(6)−C(7)	114(1)
Cl(1)−Ti−O(8)	103.5(3)	C(6)−C(7)−C(8)	115(1)
Cl(2)−Ti−O(8)	103.8(4)	O(8)−C(8)−C(7)	112(1)
Ti−O(8)−C(8)	149.6(9)		

bond lengths and angles are given in Table 2. The structure is very similar to that reported for **10a** by Teuben.[7a] Of note is that the bond lengths and angles in the three-carbon tether connecting the cyclopentadiene to the coordinating alkoxy group indicate no significant strain. There is no tilting of the cyclopentadienyl ring, and the Ti−Cp centroid, Ti−O bond length, and Ti−O−C bond angles are very similar to those of the nonlinked analogues $CpTiCl_2(O\text{-}c\text{-}C_6H_{12})$[4k] (2.020 Å, 1.722 Å, and 156°, respectively) and $CpTiCl_2(O^iPr)$[4l] (2.018 Å, 1.711 Å, and 157°, respectively).

The discovery that a benzyloxy group acts as a masked alkoxide allowed us to develop an efficient synthesis of **28a**, the tetramethylcyclopentadienyl analogue of **10a**. Hydromagnesiation of 2-butyne gave (*E*)-2-butenylmagnesium bromide,[27] which was reacted with butyrolactone to give the diol **24a** in 65% yield. The



preparation could be easily carried out on a large scale, the diol being isolated by crystallization from the crude product.[28] Benzylation of the terminal hydroxyl group followed by acid-catalyzed dehydration/cyclization[29] gave the tetramethylcyclopentadiene **26a** in excellent yield. The dehydration/cyclization failed when either the unprotected primary alcohol **24a** or its trimethylsilyl ether was used, indicating the importance of our discovery that a benzyl ether could act as an alkoxide equivalent. The required complex precursor **16a** was formed by deprotonation of **26a** with *n*-butyllithium at 0 °C followed by an immediate quench with chlorotrimethylsilane in the presence of hexamethylphosphoramide (HMPA). The short deprotonation time minimized elimination of the benzyl ether, and in the absence of HMPA the lithium salt did not react with the electrophile (potassium salts of heavily substituted cyclopentadienes have previously been used).[30] Removal of HMPA from the crude product by filtration through silica gave **27a** contaminated with 10−20% of **26a**, the mixture being used in the next step. Addition of **27a** to titanium tetrachloride gave the bidentate complex **28a**, together with benzyl chloride. Recrystallization from petroleum ether gave orange crystals of **28a** in 45% yield with respect to **26a**. The complex **28a** has previously been synthesized by thermolysis at 155 °C of $[MeO(CH_2)_3C_5Me_4TiCl_2(CH_2PPh_3)]$[7b] or at 225 °C of $[MeO(CH_2)_3C_5Me_4TiCl_3]$.[7c]

Since substituted γ-lactones are readily available, extension of the above method to give more complex titanium complexes seemed reasonable. Reaction of 2-allylbutyrolactone with 2-magnesio-2-butene required the addition of 1 equiv of anhydrous cerium trichloride[31] for high yields to give the diol **24b**, which was not amenable to purification. The crude trialkene was deprotonated with sodium hydride and then quenched with benzyl bromide to afford the monoprotected alcohol **25b** in 81% yield over the two steps. Cyclization using 4-methylbenzenesulfonic acid in chloroform gave the substituted cyclopentadiene **26b** in excellent yield. Deprotonation (*n*-BuLi) and chlorotrimethylsilane/HMPA quench gave the required complex precursor **27b** (60−85% yield) contaminated with the product of elimination of the benzyloxy group. After purification by chromatography, reaction with titanium tetrachloride gave the desired allyl-substituted mono(cyclopentadienyl)titanium complex **28b** (62%) as orange crystals. As with **19**, there was no indication of coordination of the alkene to the metal center.

Catalytic Studies. We briefly examined the properties of complex **10a** and the chiral form of the complex **23** as catalysts in a variety of reactions. Both **10a** and **23** (5 mol %, activated with 4 equiv of *n*-butyllithium) were catalysts for the hydrosilation of acetophenone[32] and hydrogenation of 2-phenylpyrrolidine[33] and 2-phenylbutene,[34] with activities comparable to those of ti-

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(28) The readily available diol **24a** proves to be an excellent precursor for a variety of tetramethylcyclopentadienyl ligands substituted with a functionalized chain. In addition to benzylation, the primary alcohol may be methylated and ethylated and the methoxymethyl ether formed, leading to the corresponding cyclopentadienes on acid treatment in excellent yield. The primary alcohol may also be converted to the methanesulfonate and displaced with PhS^-, Ph_2P^-, phthalimide, or cyanide to give the corresponding substituted ligands on treatment with acid: Christie, S. D. R.; Whitby, R. J. Unpublished work.

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(30) Reaction of Me_5C_5Li with $ClSiMe_3$ required 150 °C and 3−4 days: Jutzi, P.; Saleske, H.; Dittmar, Bühl, D.; Grohe, H. *J. Organomet. Chem.* **1983**, *252*, 29.

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tanocene dichloride. Using the chiral form of **23**, racemic products were produced. The most likely reason is the failure of the pendant methoxy group in **16** to coordinate to the metal of the titanium(III)-hydride species, which is probably the key intermediate in the reactions.

Complex **10a** was also a good catalyst for the polymerization of styrene when activated with 10 equiv of methylalumoxane (activity = 2.8×10^6 g of PS/((mol of Ti)(mol of styrene)h)] using the method of Qian.[35] The complexes $CpTiCl_3$ and $CpTiCl_2(O^iPr)$ had similar activities. In the pinacol coupling of benzaldehyde (Zn as stoichiometric reductant) by the method of Gansauer[36] **10a** was less active than titanocene dichloride and gave very different ratios of *meso*- to *rac*-1,2-dihydroxy-1,2-diphenylethane (1:1.3; *cf*. 1:3.8). Surprisingly **10a** was completely inactive in the catalytic intramolecular hydroamination of alkynes as reported by Livinghouse[37] using $CpTiCl_3$ as the catalyst. Under stoichiometric conditions cyclization of 1-amino-4-octyne gave *ca*. 50% conversion (by NMR) to 5-butyl-3,4-dihydro-2*H*-pyrrole after refluxing in THF with 1 equiv of $[C_5H_4(CH_2)_3O]TiMe_2$ for 2 days. For comparison the same reaction using $CpTiMe_2Cl$ was fast at 25 °C.[37]

Conclusions

We have developed the synthesis of bidentate cyclopentadienyl−alkoxide ligands and methods for their complexation to titanium. In particular, the use of benzyl and *tert*-butyl ethers as spontaneously cleaved masked alkoxides was discovered. Several complexes of potentially tridentate ligands were formed. The most promising, incorporating a pendant ether coordinating group, was synthesized in optically pure form but gave racemic products in hydrogenation and hydrosilation reactions. We have also developed a convenient route to tetramethylcyclopentadienes carrying a tethered ether or other functional group.

Experimental Section

^1H and ^{13}C NMR spectra were recorded on JEOL JNM-GX270 and Bruker AC300, AM360, and AM400 spectrometers and referenced to tetramethylsilane or residual solvent. The number of directly attached protons in carbon spectra were determined by DEPT experiments. Electron impact (EI) and chemical ionization (using NH_3, CI) mass spectra, including accurate masses, were recorded on a VG Analytical 70-250-SE double-focusing mass spectrometer at 70 eV. Electrospray (ES^+ or APCI) spectra were recorded on a VG Platform spectrometer in acetonitrile using positive ion or APCI techniques. ES spectra generally gave MH^+ as the only significant peak. Mass spectra of titanium complexes are reported for the $^{48}Ti^{35}Cl$ isotopomer. Peaks showed the calculated isotope pattern. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer as films or solutions between sodium chloride plates or in KCl disks. Peaks are described as s (strong), m (medium), w (weak), and/or br (broad). Elemental analyses were performed by the University College London Microanalysis Service. Melting points were measured on a Gallemkamp type apparatus and are uncorrected. Organometallic reactions were performed under an argon atmosphere using standard Schlenk, syringe, and vacuum line techniques. Column chromatography was performed on silica (230−400 mesh), under slight positive pressure. Solvent ratios are described as volumes before mixing. Diethyl ether, THF, benzene, and hexane were freshly distilled from sodium/benzophenone, the last solvent containing added tetraethylene glycol dimethyl ether. Dichloromethane and triethylamine were distilled from calcium hydride. Petrol refers to the petroleum ether fraction with bp 40−60 °C and was distilled through a Vigreaux column before use. All monosubstituted cyclopentadienes were isolated as a 3:2 mixture of tautomers, with a third just visible. The trimethylsilylated monosubstituted cyclopentadienes were formed as >80% of one regioisomer and tautomer but gave broad signals in the cyclopentadienyl region of the proton NMR, probably due to 1,5-silyl shifts.[38]

$[\eta^5$-σ-$C_5H_4(CH_2)_3O]TiCl_2$ (10a) from 9a. To sodium cyclopentadienide (100 mmol) in THF (100 mL) at 0 °C was slowly added 3-(hydroxypropyl)-4-methyl-1-benzenesulfonate[39] (8.28 g, 35.9 mmol) in THF (20 mL), and the mixture was stirred overnight at room temperature. The reaction mixture was poured into saturated NH_4Cl solution (100 mL) and extracted into diethyl ether (100 mL). The ethereal extract was washed with $NaHCO_3$ saturated solution (2 × 100 mL), 2 M NaOH (100 mL), and brine (100 mL) and dried with anhydrous $MgSO_4$ and the solvent removed *in vacuo*. Column chromatography (25% diethyl ether in petroleum ether) gave 3-cyclopentadienyl-1-propanol (**8a**) as a yellow oil (2.71 g, 61%). Proton NMR was consistent with literature values.[40] ^1H NMR (300 MHz, $CDCl_3$): δ 6.36 (1.6H, m), 6.20 (0.4H, br d, J = 5 Hz), 6.12 (0.4H, br s), 5.98 (0.6 H, br s), 3.70 (2H, t, J = 7 Hz), 2.90 (1.2H, br s), 2.83 (0.8H, br s), 2.45 (2H, m), 1.85 (2H, m), 1.35 (1H, s, OH).^{13}C NMR (67.5 MHz, $CDCl_3$): δ 149.25 (C), 146.62 (C), 134.70 (CH), 134.20 (CH), 132.56 (CH), 130.95 (CH), 126.82 (CH), 126.40 (CH), 62.86 (CH_2), 43.44 (CH_2), 41.46 (CH_2), 32.73 (CH_2), 31.88 (CH_2), 27.14 (CH_2), 26.28 (CH_2).

To a solution of **8a** (2.515 g, 20.2 mmol) in THF (50 mL) at 0 °C under argon was added slowly butyllithium (20.2 mL of a 2.5 M solution in hexanes, 50.5 mmol). The reaction mixture was stirred at 0 °C for 15 min and then allowed to attain room temperature. After 15 min the reaction mixture was cooled to 0 °C and quenched with chlorotrimethylsilane (10 mL, 78.8 mmol). After the mixture was stirred for 30 min at 0 °C, pentane (30 mL) was added and the mixture filtered through a sinter. Solvent was removed from the filtrate, pentane (30 mL) added, the mixture filtered, and solvent removed from the filtrate to afford trimethylsilyl [3-(3-(trimethylsilyl)-1,4-cyclopentadienyl)propyl] ether (**9a**) as a pale yellow oil (5.49 g, 100%). Kugelrohr distillation (100 °C, 1 mbar) of 1.258 g gave 1.089 g (86% yield) of **9a** as a colorless clear oil, the NMR of which was consistent with literature values.[7a] ^1H NMR (300 MHz, $CDCl_3$): δ 6.4−6.5 (2H, m), 6.10 (1H, br s), 3.62 (2H, t, J = 6.6 Hz), 3.26 (1H, br s), 2.46 (2H, t, J = 7.5 Hz), 1.81 (2H, quintet, J = 7.0 Hz), 0.13 (9H, s), −0.03 (9H, s). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 144.92 (C) 134.06 (CH), 132.64 (CH), 127.28 (CH), 62.58 (CH_2), 51.10 (CH), 32.96 (CH_2), 26.19 (CH_2), −0.29 (CH_3), −1.89 (CH_3).

To a stirred solution of freshly distilled bis(trimethylsilyl) ligand **8a** (1.089 g, 4.06 mmol) in dichloromethane (10 mL), under an argon atmosphere at 0 °C, was added dropwise titanium tetrachloride (4.06 mmol, 4.06 mL, 1 M solution in dichloromethane). The reaction mixture was stirred at 0 °C under an inert atmosphere and allowed to attain room temperature overnight. Removal of solvent gave a dark brown solid

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which was extracted into chloroform (30 mL) in air. Solvent was removed, the residue dissolved in chloroform (2−3 mL), and the solution filtered through cotton wool plugs until it was clear. Removal of solvent gave (η^5-σ-$C_5H_4(CH_2)_3O$)$TiCl_2$ (**10a**) as a bright yellow solid (0.636 g, 65%) that was found to be pure by NMR. Sublimation at 100 °C, 0.2 mbar gave analytically pure material. The NMR of the product obtained is comparable to literature values.[7a] ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.94 (2H, t, J = 2.6 Hz), 6.13 (2H, t, J = 2.7 Hz), 4.29 (2H, t, J = 5.2 Hz), 2.89 (2H, t, J = 6.1 Hz), 2.31 (2H, quintet, J = 5.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.47 (C), 121.47 (CH), 117.29 (CH), 76.80 (CH_2), 33.35 (CH_2), 25.54 (CH_2). IR (KBr): 2946 (s), 1643 (s), 1490 (m), 1189 (s), 1065 (s) 1013 (m), 939 (s), 826 (s) cm^{-1}. MS (EI): *m/z* 240 (M$^+$, 47%), 210 (56%), 174 (100%), 148 (9%), 118 (9%), 95 (12%), 78 (18%). Anal. Calcd for $C_8H_{10}Cl_2OTi$: C, 39.88; H, 4.18. Found: C, 40.24; H, 4.06.

[η^5-σ-$C_5H_4(CH_2)_2CHMeO$]$TiCl_2$ (10b). By the same method as for **8a** 3-(hydroxybutyl)-4-methyl-1-benzenesulfonate[41] (2.70 g, 11.0 mmol) gave 4-cyclopentadienyl-2-butanol (**8b**; yellow oil, 1.002 g, 66%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.45 (1.6H, m), 6.25 (0.4H, d + fs, J = 5 Hz), 6.18 (0.4H, br s), 6.00 (0.6H, br s), 3.82 (1H, sextet, J = 6.4 Hz), 2.96 (1.2H, br s), 2.90 (0.8H, br s), 2.61−2.37 (2H, m), 1.70 (2H, m), 1.61 (1H, s, OH), 1.22 (3H, d, J = 6.1 Hz). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 149.45 (C), 146.82 (C), 134.73 (CH), 134.16 (CH), 132.55 (CH), 130.89 (CH), 126.66 (CH), 126.21 (CH), 68.03 (CH), 68.00 (CH), 43.45 (CH_2), 41.44 (CH_2), 39.15 (CH_2), 38.31 (CH_2), 27.17 (CH_2), 26.34 (CH_2), 23.66 (CH_3). IR (film): 3330 (s, br), 2935 (s), 2875 (m), 1442 (m), 1365 (m), 1055 (s), 897 (m), 676 (m) cm^{-1}. MS (EI): *m/z* 138 (M$^+$, 50%), 120 (51%), 105 (94%), 91 (72%), 80 (100), 77 (56%), 71 (15%), 65 (16%), 55 (18%), 51 (5%), 45 (26%), 39 (21%), 28 (15%).

By the same method as for **9a**, **8b** (0.962 g, 7.0 mmol) gave crude 1-methyl-3-[3-(trimethylsilyl)-1,4-cyclopentadienyl]-propyl trimethylsilyl ether (**9b**; 2.16 g, >100%) as a yellow oil. Kugelrohr distillation (120 °C, 0.5 mbar) of 0.527 g of the crude product gave 0.457 g (95% overall yield) of pure **9b**. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.44 (2H, m), 6.08 (1H, br s), 3.80 (1H, sextet, J = 6.4 Hz), 3.26 (1H, br s), 2.51−2.37 (2H, m), 1.71 (2H, m), 1.18 (3H, d, J = 6.1 Hz), −0.04 (9H, s), −0.18 (9H, s). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 145.69 (C), 134.05 (CH), 132.32 (CH), 127.13 (CH), 68.51 (CH), 51.06 (CH), 39.77 (CH_2), 26.45 (CH_2), 23.97 (CH_3), 0.46 (CH_3), −1.90 (CH_3). IR (film): 2956 (s), 2859 (s), 1448 (w), 1409 (w), 1373 (m), 1248 (s), 1134 (s), 1085 (s, br), 1037 (s, br), 985 (s) cm^{-1}. MS (EI): *m/z* 282 (M$^+$, 5%), 224 (4%), 192 (8%), 152 (25%), 147 (15%), 117 (13%), 84 (17%), 73 (100%), 59 (5%), 45 (6%). HRMS (CI): calcd for $C_{15}H_{30}OSi_2$ (M$^+$) *m/z* 282.1835, found (M$^+$) *m/z* 282.1838.

To a stirred solution of **9b** (0.430 g, 1.53 mmol) in dichloromethane at 0 °C under argon was added dropwise titanium tetrachloride (1.37 mL of a 1 M solution in dichloromethane, 1.37 mmol). The reaction mixture was stirred at room temperature overnight and then filtered through Celite, and solvent was removed *in vacuo* to give the crude complex (0.449 g). Sublimation of the crude product (100 °C, 0.3 mbar for 3 h) gave the *title complex* **10b** as a yellow solid (0.081 g, 21% yield). Mp: 84−85 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.92 (2H, m), 6.14 (2H, m), 4.44 (1H, m, CH), 3.01 (1H, ddd, J = 3.1, 6.8, 14.7 Hz), 2.74 (1H, ddd, J = 3.1, 7.9, 14.7 Hz), 2.37 (1H, ddt, J = 14, 7, 3.5 Hz), 2.01 (1H, dddd, J = 14, 10.8, 8.6, 3.1 Hz), 1.27 (3H, d, J = 6.1 Hz). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 132.47 (C), 121.57 (CH), 121.27 (CH), 118.42 (CH), 116.24 (CH), 82.85 (CH), 39.61 (CH_2), 24.43 (CH_2), 21.79 (CH_3). IR (KBr): 1684 (w), 1623 (w), 1414 (w), 1057 (s), 968 (s), 831 (s), 764 (m), 612 (m) cm^{-1}. MS (EI): *m/z* 254 (M$^+$, 45%), 239 (28), 210 (51), 174 (100), 148 (14), 118 (12), 91 (15), 78 (23). Anal. Calcd for $C_9H_{12}Cl_2OTi$: C, 42.39; H, 4.74; M$^+$, *m/z* 253.9745. Found: C, 42.61; H, 4.82; M$^+$, *m/z* 253.9752.

[η^5-σ-$C_5H_4(CH_2)_2CMe_2O$]$TiCl_2$ (10c). In a similar way to the preparation of **8a**, 3-hydroxy-3-(methylbutyl)-4-methyl-1-benzenesulfonate[42] (8 g, 31 mmol) gave 4-cyclopentadienyl-2-methyl-2-butanol (**9c**; yellow oil, 2.534 g, 54%) after column chromatography (eluent 25% diethyl ether in petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.45 (1.6H, m), 6.28 (0.4H, dq, J = 5.3, 1.5 Hz), 6.19 (0.4H, septet, J = 1.5 Hz), 6.05 (0.6H, septet, J = 1.5 Hz), 2.96 (1.2H, septet, J = 1.5 Hz), 2.90 (0.8H, q, J = 1.5 Hz), 2.50 (2H, m), 1.75 (2H, m), 1.52 (1H, s, OH). 1.25 (6H, s). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 149.89 (C), 147.25 (C), 134.83 (CH), 134.09 (CH), 132.56 (CH), 130.80 (CH), 126.31 (CH), 125.81 (CH), 71.08 (C), 71.05 (C), 43.57 (CH_2), 43.50 (CH_2), 42.79 (CH_2), 41.42 (CH_2), 29.39 (CH_3), 25.70 (CH_2), 24.91 (CH_2). IR (film): 3356 (s, br), 3057 (m), 2967 (s), 2925 (s), 1601 (m), 1468 (s), 1363 (s), 1292 (m), 1207 (s), 1149 (s), 930 (s), 897 (s), 674 (s) cm^{-1}. MS (EI): *m/z* 152 (M$^+$, 20%), 134 (61%), 119 (98%), 105 (12%), 96 (15%), 91 (38%), 79 (100%), 69 (24%), 59 (56%).

By a method similar to the preparation of **9a**, **8c** (1.659 g, 10.9 mmol) gave crude 1,1-dimethyl-3-[3-(trimethylsilyl)-1,4-cyclopentadienyl]propyl trimethylsilyl ether (**10c**; 3.27 g) as a brown oil. A 1.682 g portion was Kugelrohr-distilled (120 °C, 0.3 mbar) to give 1.154 g (69% yield) of pure **10c**. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.35 (2H, m), 6.00 (1H, m), 3.12 (1H, br s), 2.35 (2H, m), 1.58 (2H, m), 1.15 (6H, s), 0.00 (9H, s), −0.15 (9H, s). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 146.05 (C), 133.95 (CH), 132.44 (CH), 126.67 (CH), 73.99 (C), 51.03 (CH), 44.94 (CH_2), 30.04 (CH_3), 24.83 (CH_2), 2.76 (CH_3), −1.89 (CH_3). IR (film): 2958 (s), 1453 (s), 1380 (s), 1250 (s), 1152 (s), 1049 (s), 837 (s), 755, (s), 689 (s), 620 (s) cm^{-1}. MS (EI): *m/z* 296 (M$^+$, 6%), 281 (42%), 224 (7%), 206 (53%), 191 (48%), 175 (11%), 147 (62%), 131 (94%), 117 (11%), 91 (9%), 73 (100%), 59 (8%), 45 (23%). HRMS (EI): calcd for $C_{16}H_{32}OSi_2$ (M$^+$) *m/z* 296.1991, found (M$^+$) *m/z* 296.1977.

To a stirred solution of freshly distilled **9c** (0.426 g, 1.43 mmol) in dichloromethane (10 mL), under an argon atmosphere at 0 °C, was added dropwise titanium tetrachloride (0.86 mL of a 1 M solution in dichloromethane, 0.86 mmol). After the mixture was stirred at room temperature overnight solvent was removed *in vacuo* to afford crude product (0.224 g) as a 1:1 mixture of **10c** and **12**. Exposure of the mixture to moist air to decompose **12** followed by extraction into ether and recrystallization from ether/pentane allowed the isolation of **10c** as a yellow powder (65 mg, 17%) still containing 7% **12**. Further treatment of a 20 mg portion of the mixture with water followed by extraction into ether/hexane and crystallization gave pure **10c** (3 mg). Mp: 109−110 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.90 (2H, t, J = 2.6 Hz), 6.12 (2H, t, J = 2.6 Hz), 2.90 (2H, t, J = 6.3 Hz), 2.19 (2H, t, J = 6.3 Hz), 1.31 (6H, s). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 132.12 (C), 121.39 (CH), 117.18 (CH), 83.89 (C), 43.76 (CH_2), 28.15 (CH_3), 22.79 (CH_2). IR (KBr disk): 2971 (m), 1635 (w), 1366 (w), 1262 (w), 1141 (m), 1114 (m), 985 (s), 824 (s), 779 (s), 754 (s), 591 (m) cm^{-1}. MS (EI): *m/z* 268 (M$^+$, 60%), 232 (30), 210 (37), 199 (7), 174 (100), 140 (16), 118 (15), 99 (13), 91 (20), 78 (37). HRMS (EI): calcd for $C_{10}H_{14}Cl_2OTi$ (M$^+$) *m/z* 267.9901, found (M$^+$) *m/z* 267.9904.

The following data could be obtained for **12** from the mixture with **10c**. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.97 (2H, t, J = 2.6 Hz), 6.88 (2H, t, J = 2.6 Hz), 3.12 (2H, t, J = 8.4 Hz), 2.12 (2H, t, J = 8.4 Hz), 1.66 (6H, s, Me). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 143.94 (C), 123.83 (CH), 123.02 (CH), 69.69 (C), 45.02 (CH_2), 32.59 (CH_3), 27.71 (CH_2).

[η^5-σ-$C_5H_4(CH_2)_3O$]$TiCl_2$ 10a *via* [η^5-$C_5H_4(CH_2)_3OMe$]-$TiCl_3$ (15; Loss of Me_3SiCl and MeI). By a method similar to the preparation of **8a** 3-(methoxypropyl)-4-methyl-1-benzenesulfonate[43] (12.70 g, 52.0 mmol) gave 3-cyclopentadienylpropyl methyl ether (**13a**) as a yellow oil (7.120 g, 99%), ^{1}H

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NMR was consistent with that previously reported.[44] ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.44 (1.6H, m), 6.25 (0.4H, dq, J = 5.3, 1.5 Hz), 6.17 (0.4H, septet, J = 1.5 Hz), 6.03 (0.6H, septet, J = 1.5 Hz), 3.40 and 3.41 (2H, 2 t, J = 6.6 Hz), 3.35 (3H, s, OMe), 2.94 (1.2H, septet, J = 1.5 Hz), 2.89 (0.8H, q, J = 1.5 Hz), 2.43 (2H, m), 1.82 (2H, m). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 149.31 (C), 146.66 (C), 134.80 (CH), 133.92 (CH), 132.56 (CH), 130.75 (CH), 126.65 (CH), 126.22 (CH), 72.49, (CH_2), 58.69 (CH_3), 43.40 (CH_2), 41.39 (CH_2), 29.77 (CH_2), 28.94 (CH_2), 28.51 (CH_2), 27.31 (CH_2). IR (film): 2921 (s), 2869 (s), 2341 (s), 1448 (m), 1384 (m), 1189 (m), 1119 (s), 1023 (m, br), 948 (m), 898 (s) cm^{-1}. MS (EI): m/z 138 (M^+, 78%), 120 (34%), 106 (97%), 91 (50%), 80 (100%). HRMS (EI): calcd for $C_9H_{14}O$ (M^+) m/z 138.1045, found (M^+) m/z 138.1052.

To a solution of 3-cyclopentadienylpropyl methyl ether (**13a**; 5.663 g, 37.2 mmol) in THF (50 mL) stirred at 0 °C under argon was slowly added butyllithium (22.3 mL of a 2.5 M solution in hexanes, 55.8 mmol). After 15 min the reaction mixture was warmed to room temperature for 15 min before it was recooled to 0 °C and quenched with chlorotrimethylsilane (73.3 mmol, 9.3 mL). Workup as for **2a** gave methyl 3-[3-(trimethylsilyl)-1,4-cyclopentadienyl]propyl ether (**14a**) as a yellow oil (8.367 g crude yield). Kugelrohr distillation of a 0.994 g portion gave 0.764 g (76% yield) of **14a** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.45 (2H, m), 6.13 (1H, br s), 3.45 (2H, t, J = 6.5 Hz), 3.38 (3H, s), 3.26 (1H, br s), 2.51 (2H, t, J = 7.1 Hz), 1.85 (2H, quintet, J = 7.0 Hz), 0.03 (9H, s). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 145.05 (C), 134.07 (CH), 132.21 (CH), 127.40 (CH), 72.61 (CH_2), 58.71 (CH_3), 51.13 (CH), 29.99 (CH_2), 26.37 (CH_2), −1.90 (CH_3). IR (film): 2951 (s), 2868 (s), 1448 (w), 1384 (w), 1248 (s), 1120 (s) 982 (m), 959 (m) cm^{-1}. MS (EI): m/z 210 (M^+, 12%), 152 (32%), 106 (15%), 91 (25%), 78 (26%), 73 (100%). HRMS (CI): calcd for $C_{12}H_{22}OSi$ (M^+) m/z 210.1440, found (M^+) m/z 210.1439**.**

To a solution of **14a** (0.427 g, 2.03 mmol) in dichloromethane (10 mL) under argon at 0 °C was added dropwise titanium tetrachloride (1.83 mL of a 1 M solution in dichloromethane, 1.83 mmol). After the mixture was stirred at room temperature overnight, it was filtered under argon through Celite on a sinter. Removal of solvent *in vacuo* gave (η^5-$C_5H_4(CH_2)_3OMe$)-$TiCl_3$ (**15)** as a yellow oil (0.514 g, 87%). The complex proved too unstable for us to obtain mass spectrometric or analytical data. ^{1}H NMR (270 MHz, $CDCl_3$): δ 6.95 (2H, t, J = 2.6 Hz), 6.86 (2H, t, J = 2.6 Hz), 3.45 (2H, t, J = 6.2 Hz), 3.36 (3H, s, OMe), 2.96 (2H, dd, J = 7.7, 7.9 Hz), 1.85 (2H, m). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 144.50 (C), 123.80 (CH), 123.31 (CH), 72.92 (CH_2), 59.05 (CH_3), 29.66 (CH_2), 28.66 (CH_2). IR ($CDCl_3$): 2928 (s), 2871 (s), 1488 (m), 1448 (m), 1262 (s), 1114 (s), 919 (s), 836 (s) cm^{-1}.

The titanium complex **15** (0.359 g, 1.23 mmol) and NaI (0.202 g, 1.35 mmol) were dissolved in dichloromethane/acetonitrile (1:1; 20 mL). Silicon tetrachloride (1.35 mmol, 0.15 mL) was added slowly at room temperature to the stirred solution before refluxing the mixture.[20] The progress of the reaction was followed by NMR of aliquots; 3 days were required to reach completion. Removal of volatiles, extraction into chloroform (2 × 20 mL), removal of solvent, and then extraction into chloroform in air, filtration, and removal of solvent, gave the crude product shown by NMR to be around 70% **10a**, but with several other signals suggesting products from Cl/I exchange.

[η^5-,σ-$C_5H_4(CH_2)_3O$]$TiCl_2$ (10a) *via* Loss of Me_3SiCl and $PhCH_2Cl$. By a method similar to the preparation of **13a**, 3-((benzyloxy)propyl)-4-methyl-1-benzenesulfonate[45] (3.204 g, 10 mmol) gave benzyl 3-cyclopentadienylpropyl ether (**13b**) as a yellow oil (2.135 g, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40−7.20 (5H, m), 6.45 (1.6H, m), 6.28 (0.4H, dq, J = 5.3, 1.5 Hz), 6.19 (0.4H, septet, J = 1.5 Hz), 6.05 (0.6H, septet, J = 1.5 Hz), 4.55 (2H, s), 3.539 and 3.533 (2H, 2t, J = 6.4 Hz), 2.975 (1.2H, septet, J = 1.5 Hz), 2.911 (0.8H, q, J = 1.5 Hz), 2.50 (2H, m), 1.90 (2H, m). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 149.39 (C), 146.73 (C), 138.82 (C), 134.82 (CH), 133.95 (CH), 132.60 (CH), 130.78 (CH), 128.53 (CH), 127.81 (CH), 127.68 (CH), 126.69 (CH), 126.29 (CH), 73.12 (CH_2), 73.07 (CH_2), 70.18 (CH_2), 70.12 (CH_2), 43.47 (CH_2), 41.45 (CH_2), 29.94 (CH_2), 29.11 (CH_2), 27.47 (CH_2), 26.59 (CH_2). IR (film): 2935 (s), 2851 (s), 1494 (w), 1453 (m), 1363 (s), 1203 (w), 1101 (s, br), 1027 (m), 898 (s) cm^{-1}. MS (EI): m/z 214 (M^+, 18%), 170 (6), 151 (6), 123 (54), 105 (21), 91 (100), 79 (37). HRMS (EI): calcd for $C_{15}H_{18}O$ (M^+) m/z 214.1357, found (M^+) m/z 214.1353.

To a solution of benzyl 3-cyclopentadienylpropyl ether (**13b**; 2.135 g, 10 mmol) in THF (20 mL) at 0 °C under argon was added quickly (∼5 s) BuLi (4 mL of a 2.5 M solution in hexane, 10 mmol). After the mixture was stirred for ∼30 s, chlorotrimethylsilane (1.9 mL, 15 mmol) was added and the mixture stirred at room temperature for 2 h. The reaction mixture was diluted with pentane (30 mL) and filtered through a No. 3 sinter and the solvent removed *in vacuo* to give a cloudy oil. Pentane (30 mL) was added, the mixture was filtered, and volatiles were removed from the solution to give benzyl 3-[3-(trimethylsilyl)-1,4-cyclopentadienyl]propyl ether (**14b**; 2.819 g, 98%) as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38−7.31 (5H, m), 6.45 (2H, m), 6.11 (1H, br s), 4.55 (2H, s), 3.55 (2H, t, J = 7 Hz), 3.30 (1H, br s), 2.53 (2H, t, J = 7.6 Hz), 1.81 (2H, quintet, J = 7.2 Hz), 0.02 (9H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.21 (C), 138.93 (C), 134.20 (CH), 132.38 (CH), 128.64 (CH), 127.95 (CH), 127.79 (CH), 127.57 (CH), 73.22 (CH_2), 70.37 (CH_2), 51.27 (CH), 30.26 (CH_2), 26.58 (CH_2), −1.76 (CH_3). IR (film): 2926 (m), 1597 (m), 1462 (m), 1359 (s), 1291 (s), 1176 (s), 1121 (s), 1028 (s), 947 (s), 838 (s), 753 (s), 665 (s) cm^{-1}. MS (EI): m/z 286 (M^+, 12%), 195 (11%), 167 (6%), 152 (43%), 106 (17%), 91 (83%), 79 (15%), 73 (100%), 65 (7%), 45 (7%). HRMS: calcd for $C_{18}H_{26}OSi$ (M^+) m/z 286.1753, found 286.1756.

To a solution of benzyl 3-[3-(trimethylsilyl)-1,4-cyclopentadienyl]propyl ether (**14b**; 0.95 g, 3.32 mmol) in dichloromethane (40 mL) stirred at 0 °C under argon was added titanium tetrachloride (3.0 mL of a 1 M solution in dichloromethane, 2.98 mmol) dropwise over 1 h. The initial pale yellow solution turned bright yellow on addition of titanium tetrachloride. After the last drop of titanium tetrachloride was added, the solvent was removed by vacuum transfer and the crude product left at 0.1 mbar for 3 h. The residue was dissolved in toluene (5 mL) and pentane (35 mL) layered on top. Storage at −20 °C overnight gave pure **10a** as a yellow crystalline solid (0.392 g, 49%).

[η^5-$C_5H_4(CH_2)_3O$]$TiCl_2$ (10a) *via* Loss of Me_3SiCl and Me_3CCl. By a method similar to that for **13a** 3-((*tert*-butyloxy)-propyl)-4-methyl-1-benzenesulfonate[46] (21.312 g, 99.50 mmol) gave *tert*-butyl 3-cyclopentadienylpropyl ether (**13c**) as a yellow oil (14.252 g, 79%). ^{1}H NMR (270 MHz, $CDCl_3$): δ 6.45 (1.6H, m), 6.25 (0.4H, d + fs, J = 5.1 Hz), 6.18 (0.4H, br s), 6.00 (0.6H, br s), 3.35 (2H, t, J = 6.5 Hz), 2.95 (1.2H, br s), 2.90 (0.8H, br s), 2.42 (2H, quintet, J = 7.3 Hz), 1.78 (2H, m), 1.19 (9H, s). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 149.72 (C), 146.96 (C), 134.92 (CH), 133.79 (CH), 132.56 (CH), 130.63 (CH), 126.46 (CH), 126.04 (CH), 72.66 (C), 61.35 (CH_2), 61.29 (CH_2), 43.45 (CH_2), 41.37 (CH_2), 30.67 (CH_2), 29.85 (CH_2), 27.74 (CH_3), 27.53 (CH_2), 26.63 (CH_2). IR (film): 2995 (s), 1468 (m), 1423 (s), 1362 (s), 1223 (m), 1187 (s), 880 (s), 872 (m), 702 (m), 656 (m) cm^{-1}.

By a method similar to that for **14a** *tert*-butyl 3-cyclopentadienylpropyl ether (**13c**; 0.528 g, 2.93 mmol) gave *tert*-butyl 3-[3-(trimethylsilyl)-1,4-cyclopentadienyl]propyl ether (**14c**) as a yellow oil (0.744 g, 100%). ^{1}H NMR (270 MHz, $CDCl_3$): δ

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6.45 (2H, m), 6.1 (1H, br s), 3.37 (2H, t, J = 6.7 Hz), 3.25 (1H, br s), 2.46 (2H, t, J = 7.0 Hz), 1.77 (2H, quintet, J = 6.8 Hz), 1.19 (9H, s, t-Bu), −0.07 (9H, s). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 145.38 (C), 133.94 (CH), 132.34 (CH), 127.25 (CH), 72.64 (C), 61.48 (CH_2), 51.07 (CH), 30.89 (CH_2), 27.77 (CH_3), 26.56 (CH_2), −1.89 (CH_3). IR (film): 2972 (s), 1360 (s), 1249 (s), 1197 (s), 1083 (s), 981 (s), 867 (s) 838 (s) cm^{-1}. MS (EI): m/z 252 (M^+, 7%), 195 (12%), 181 (6%), 152 (27%), 103 (24%), 91 (11%), 79 (22%), 73 (100%), 57 (42%), 41 (9%), 29 (6%). HRMS (CI): calcd for $C_{15}H_{28}OSi$ (M^+) m/z 252.1909, found (M^+) m/z 252.1921.

To a solution of **14c** (1.033 g, 4.11 mmol) in dichloromethane (30 mL, dried over CaH_2) stirred under argon at 0 °C was added dropwise titanium tetrachloride (3.70 mmol, 3.70 mL, 1 M solution in dichloromethane). After it was stirred at room temperature overnight, the reaction mixture was filtered through Celite on a sinter; then the solvent was removed *in vacuo* to give a yellow oil (NMR yield of **10a** using an internal standard was 60%). The oil was dissolved in toluene (15 mL), pentane (40 mL) was layered on top, and the mixture was left to crystallize at −20 °C. The complex **10a** (0.15 g, 15%) was isolated as a yellow crystalline solid.

[η^5-σ-$C_5H_4(CH_2)_3O$]$TiCl_2$ (10a) *via* Loss of LiCl and Me_3CCl. A solution of Li-**13c** was prepared from *tert*-butyl 3-cyclopentadienylpropyl ether (**13c**; 0.157 g, 0.87 mmol) and butyllithium (0.87 mmol, 0.35 mL of a 2.5 M solution in hexanes) in toluene (10 mL) at −78 °C. The anion solution was slowly added to a mixture of toluene (10 mL) and $TiCl_4$ (0.78 mmol, 0.78 mL of a 1 M solution in dichloromethane) at −78 °C. After 90 min the reaction mixture was warmed to room temperature, giving a brown solution. Filtration through a sinter lined with Celite under argon, removal of solvent, and washing with pentane (2 × 3 mL) gave pure **10a** (0.042 g, 22%) as a yellow crystalline solid.

Preparation of [η^5-σ-$C_5H_4CH(CH_2CH{=}CH_2)(CH_2)_2O$]-$TiCl_2$ (19). To a solution of 1-(benzyloxy)-5-hexen-3-ol (**16**;[47] 0.509 g, 2.47 mmol) in dichloromethane (30 mL) stirred at −40 °C under argon was added triethylamine (0.48 mL, 3.45 mmol) and methanesulfonyl chloride (0.23 mL, 2.96 mmol). After it was warmed to −20 °C over 60 min, the reaction mixture was poured into saturated NaCl (50 mL) and extracted with dichloromethane (50 mL). The organic layer was washed with brine (50 mL) and then dried over Na_2SO_4 and solvent removed *in vacuo* to yield [1-(2-(benzyloxy)ethyl)-3-butenyl]methanesulfonate as a yellow oil (0.665 g, 95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35 (5H, m), 5.82 (1H, ddt, J = 16.9, 9.6, 7.0 Hz), 5.18 (2H, m), 4.95 (1H, ddt, J = 7.3, 5.1, 5.9 Hz), 4.544 and 4.495 (2 × 1H, d, J = 11.8 Hz, strongly distorted), 3.60 (2H, t, J = 7 Hz), 2.96 (3H, s), 2.54 (2H, m), 1.98 (2H, m).^{13}C NMR (67.5 MHz, $CDCl_3$): δ 138.19 (C), 132.47 (CH), 128.62 (CH), 128.02 (CH), 127.92 (CH), 119.37 (CH_2), 80.04 (CH), 73.31 (CH_2), 65.82 (CH_2), 39.75 (CH_2), 38.50 (CH_3), 34.39 (CH_2). IR (film): 2935 (s), 2940 (s), 1641 (w), 1355 (s), 1173 (s), 1096 (s), 912, (s), 738 (m), 699 (m) cm^{-1}.

To sodium cyclopentadienide (10.5 mmol) in THF at 0 °C was slowly added a solution of [1-(2-(benzyloxy)ethyl)-3-butenyl]methanesulfonate (0.996 g, 3.5 mmol) in THF (10 mL). After it was stirred at room temperature for 16 h, the reaction mixture was poured into saturated NH_4Cl (100 mL) and diethyl ether (100 mL) added. The ethereal extract was washed with saturated $NaHCO_3$ (2 × 100 mL), 2 M NaOH (100 mL), and brine (100 mL) and dried with anhydrous $MgSO_4$ and the solvent removed *in vacuo*. Column chromatography (silica, eluent 2−10% diethyl ether in petroleum ether) gave benzyl 3-cyclopentadienyl-5-hexenyl ether (**17**) as a yellow oil (0.645 g, 72%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36 (5H, m), 6.49 (0.6H, dq, J = 5, 1.5 Hz), 6.44 (1H, m), 6.28 (0.4 H, dq, J = 5.5, 1.5 Hz), 6.18 (0.4H, br s), 6.01 (0.6H, br s), 5.77 (1H, m), 4.95−5.03 (2H, m), 4.49 (2H, s), 3.35−3.50 (2H, m), 2.95 (1.2H, br s), 2.87 (0.8H, br s), 2.68 (1H, m), 2.15 (2H, m), 1.93 (1H, ddt, J = 13.8, 5.0, 7.2 Hz), 1.75 (1H, m). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 151.93 (C), 149.46 (C), 138.85 (C), 138.78 (C), 137.22 (CH), 134.03 (CH), 133.04 (CH), 132.25 (CH), 130.94 (CH), 128.51 (CH), 127.83 (CH), 127.69 (CH), 127.65 (CH), 127.51 (CH), 127.60 (CH), 126.89 (CH), 116.07 (CH_2), 115.98 (CH_2), 73.13 (CH_2), 73.07 (CH_2), 68.72 (CH_2), 68.67 (CH_2), 41.17 (CH_2), 40.89 (CH_2), 40.89 (CH_2), 39.59 (CH_2), 37.74 (CH), 36.83 (CH), 35.23 (CH_2), 34.15 (CH_2). IR (film): 2927 (m), 2855 (m), 1639 (m), 1601 (w), 1453 (m), 1364 (s), 1102 (s), 904 (s), 734 (s), 696 (s) cm^{-1}. MS (EI): m/z 254 (M^+, 7%), 213 (9%), 163 (46%), 146 (13%), 119 (23%), 105 (19%), 91 (100%).

To a solution of **17** (0.166 g, 0.68 mmol) in THF (15 mL) stirred at 0 °C under an inert atmosphere was added butyllithium (0.31 mL, 0.68 mmol). The reaction mixture was stirred at 0 °C for 5 min and then quenched with chlorotrimethylsilane (0.26 mL, 2.04 mmol). The mixture was stirred and warmed to room temperature over 30 min. To the reaction mixture was added pentane (30 mL), which produced a white precipitate of LiCl that was filtered and washed with diethyl ether. Pentane (30 mL) was again added to remove more precipitate, and the mixture was filtered and washed with ether. The solvent was removed *in vacuo* to give benzyl 3-[3-(trimethylsilyl)-1,4-cyclopentadienyl]-5-hexenyl ether (**18**) as a yellow oil (0.190 g, 86%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36 (5H, m), 6.50 (2H, m), 6.10 (1H, br s), 5.75 (1H, m), 5.00 (2H, m), 4.49 (2H, s), 3.45 (2H, m), 3.30 (1H, br s), 2.78 (1H, m), 2.30 (2H, m), 1.95 (1H, m), 1.75 (1H, m), 0.00 (9H, s). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 148.30 (C), 148.17 (C), 138.84 (C), 137.57 (CH), 134.43 (CH), 130.80 (CH), 130.61 (CH), 128.49 (CH), 127.82 (CH), 127.72 (CH), 127.63 (CH), 115.90 (CH_2), 73.07 (CH_2), 68.88 (CH_2), 50.82 (CH), 40.44 (CH_2), 36.87 (CH), 34.92 (CH_2), −1.73 (CH_3). IR (film): 3043 (w), 2927 (m), 2855 (m), 1639 (m), 1601 (w), 1453 (m), 1364 (m), 1102 (s), 910 (m), 734 (s), 696 (s) cm^{-1}. MS (EI): m/z 326 (M^+, 14%), 285 (6%), 257 (5%), 235 (9%), 192 (28%), 145 (5%), 117 (11%), 103 (12%), 91 (100%), 73 (87%). HRMS (EI): calcd for $C_{21}H_{30}OSi$ (M^+) m/z 326.2066, found (M^+) m/z 326.2064.

To a solution of **18** (0.190 g, 0.58 mmol) in dichloromethane (15 mL) stirred at 0 °C under argon was added $TiCl_4$ (1 M solution in dichloromethane, 0.47 mL, 0.47 mmol) dropwise very slowly. The reaction mixture was stirred at 0 °C for 2 h and then the solvent removed by vacuum transfer. Dry diethyl ether (10 mL) was added, and the product was filtered through a sinter lined with Celite into another dry flask under argon. The diethyl ether was removed using vacuum transfer and fresh diethyl ether (1 mL) added. Pentane (5 mL) was then layered on the diethyl ether solution and the flask placed at −20 °C overnight, forming the *title complex* **19** as a yellow solid (0.030 g, 18%). Mp: 107−108 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.97 (1H, q, J = 2.8 Hz), 6.92 (1H, q, J = 2.8 Hz), 6.13 (2H, t, J = 2.6 Hz), 5.74 (1H, ddt, J = 17.3, 9.8, 7.2 Hz), 5.10 (2H, m), 4.40 (1H, ddd, J = 3.1, 4.2, 12.5 Hz), 4.29 (1H, dt, J = 3.0, 12.5 Hz), 2.85 (1H, dtd, J = 11, 7.4, 3 Hz), 2.47 (2H, t, J = 7.0 Hz), 2.36 (1H, dq, J = 14.5, 3 Hz), 2.12 (1H, dtd, J = 14.5, 11, 4.6 Hz). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 135.66 (C), 135.06 (CH), 121.67 (CH), 120.89 (CH), 119.06 (CH), 118.12 (CH_2), 113.74 (CH), 77.53 (CH_2), 40.60 (CH_2), 39.38 (CH_2), 37.40 (CH). MS (EI): m/z 280 (M^+, 14%), 239 (100%), 209 (84%), 173 (38%), 137 (10%), 118 (15%), 103 (8%), 91 (24%), 77 (12%), 65 (14%), 51 (6%), 39 (18%), 27 (5%). Anal. Calcd for $C_{11}H_{14}Cl_2OTi$: C, 47.01; H, 5.02; M^+ (EI), m/z 279.9901. Found: C, 46.68; H, 4.78; M^+, m/z 279.9900.

Preparation of [η^5-σ-$C_5H_4(CH_2)_2CH(CH_2CH_2OMe)O$]-$TiCl_2$ (23). To a stirred suspension of sodium hydride (2.336 g, of a 60% dispersion in mineral oil, 58.41 mmol, from which mineral oil had been removed by washing with pentane) in THF (30 mL) at 0 °C under a nitrogen atmosphere was added a solution of 2-(2,2-dimethyl-1,3-dioxan-4-yl)-1-ethanol[48] (4.679 g, 29.21 mmol) in THF (20 mL). The reaction mixture was

(47) Coppi, L.; Ricci, A.; Taddei, M. *J. Org. Chem.* **1988**, *53*, 911.

(48) Mori, K.; Ikunaka, M. *Tetrahedron* **1987**, *43*, 45.

stirred at room temperature for 5 h and then quenched with iodomethane (3.65 mL, 58.6 mmol) and stirred overnight. The reaction mixture was poured into saturated $NaHCO_3$ (100 mL), and ether (100 mL) was added. The ether layer was separated, washed with brine (100 mL), and dried over Na_2SO_4 and the solvent removed *in vacuo* to yield 4-(2-methoxyethyl)-2,2-dimethyl-1,3-dioxane (**20**) as a yellow oil (4.385 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.96 (1H, m), 3.91 (1H, dt, J = 2.9, 12.0 Hz), 3.77 (1H, ddd, J = 1.7, 5.5, 11.9 Hz), 3.40 (2H, m), 3.27 (3H, s), 1.74−1.47 (4H, m), 1.39 (3H, s), 1.35 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 98.15 (C), 68.49 (CH_2), 66.08 (CH), 60.26 (CH_2), 58.56 (CH_3), 36.42 (CH_2), 31.02 (CH_2), 29.89 (CH_3), 19.16 (CH_3). IR (film): 2991 (s), 2945 (s), 2868 (s), 1461 (m), 1380 (s), 1198 (s), 1098 (s), 969 (m), 861 (m) cm^{-1}. MS (GCMS) *m*/*z*: 174 (M^+, 1%), 159 (M^+ − Me, 100%), 127 (10%), 115 (17%), 99 (10%), 97 (8%), 85 (25%), 71 (23%), 67 (63%), 59 (41%).

To a solution of 4-(2-methoxyethyl)-2,2-dimethyl-1,3-dioxane (**20**; 5.011 g, 28.8 mmol) stirred in dichloromethane (20 mL) at 0 °C under a nitrogen atmosphere was added a solution of trimethylaluminum (72 mL of a 2.0 M solution in hexane, 144.0 mmol) dropwise, and the mixture was stirred overnight.[24] The reaction was quenched by adding dropwise propan-2-ol until gas evolution stopped and then adding methanol and finally NaOH(aq). The reaction mixture was poured into ether (100 mL), the layers were separated, and the aqueous layer was extracted with ether (2 × 100 mL). The organic fractions were combined, washed with brine (200 mL), and dried over Na_2SO_4, and solvent was removed *in vacuo*. Purification by column chromatography (silica; eluent 25−50% ether in pentane) gave 3-*tert*-butoxy-5-methoxy-1-pentanol (**21**) as a light yellow oil (4.234 g, 77%). Kugelrohr distillation (135 °C at 1 mbar) of a small sample gave colorless analytically pure material. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.92 (1H, dt, J = 11.4, 5.3 Hz), 3.81 (1H, ddd, J = 4.1, 8.6, 11.4 Hz), 3.66 (1H, ddd, J = 4.8, 5.5, 10.7 Hz), 3.39 (2H, m), 3.28 (3H, s), 1.7−1.9 (3H, m), 1.59 (1H, dddd, J = 19.6, 7.6, 6.9, 5.4 Hz), 1.40 (1H, s, OH), 1.19 (9H, s). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 74.40 (C), 69.44 (CH_2), 68.15 (CH), 60.17 (CH_2), 58.56 (CH_3), 37.16 (CH_2), 35.73 (CH_2), 28.59 (CH_3). IR (film): 3429 (br), 2973 (s), 2874 (s), 1462 (br), 1389 (s), 1364 (s), 1194 (s), 1119 (s, br), 1040 (s), 1006 (s) cm^{-1}. MS (CI): *m*/*z* 191 (MH^+, 72%), 173 (5), 147 (6), 135 (100), 117 (11), 99 (10), 89 (16), 57 (40). Anal. Calcd for $C_{10}H_{22}O_3$: C, 63.12; H, 11.65; MH^+ (CI), *m*/*z* 191.1647. Found: C, 63.09; H, 11.60; MH^+, *m*/*z* 191.1656.

Chiral 3-*tert*-butoxy-5-methoxy-1-pentanol (**21**) was produced by enzymic kinetic resolution. To a solution of 3-*tert*-butoxy-5-methoxy-1-pentanol (1.001 g, 5.26 mmol) in toluene (100 mL) was added vinyl acetate (0.98 mL, 10.52 mmol) and lipase AK (Amano International Enzyme Co., 0.2 g), and the mixture was stirred at room temperature for 19 h. The mixture was filtered through a Celite-lined sinter and the solvent removed *in vacuo*. The product was purified by column chromatography (silica; eluent 20−100% ether/pentane) to afford the acetate (0.549 g, 49%) and recovered chiral starting alcohol (0.349 g, 35%, ee >99% by GC on a Hewlett-Packard 6890 machine using ChemStation software with a Macherey-Nagel FS-Hydrodex-β-3p 25 m × 0.25 mm column, 120 °C, 2 mL/min He carrier gas, retention times 10.14 and 10.71 (major) min).

To a solution of 3-*tert*-butoxy-5-methoxy-1-pentanol (**21**; 3.401 g, 17.78 mmol) in dichloromethane (20 mL) stirred at −40 °C under a nitrogen atmosphere was added methanesulfonyl chloride (1.66 mL, 21.44 mmol) and triethylamine (3.49 mL, 25.02 mmol). The reaction mixture was stirred and warmed to −20 °C over 1 h. The reaction mixture was poured into saturated $NaHCO_3$ (100 mL) and dichloromethane (100 mL) added. The organic layer was separated and washed with brine (100 mL), dried over Na_2SO_4 and solvent removed *in vacuo* to yield 3-*tert*-butoxy-5-methoxypentyl methanesulfonate as a yellow oil (3.997 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.30 (2H, t, J = 6.6 Hz), 3.79 (1H, tt, J = 5.7, 5.9 Hz), 3.39 (2H, m), 3.28 (3H, s), 2.98 (3H, s), 1.99−1.63 (4H, m), 1.19 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 74.08 (C), 69.15 (CH_2), 67.57 (CH_2), 65.09 (CH), 58.69 (CH_3), 37.45 (CH_3), 36.54 (CH_2), 35.78 (CH_2), 28.71 (CH_3). IR (liquid film): 2973 (s), 1469 (m), 1355 (s), 1174 (s), 1116 (s, br), 957 (s, br), 915 (s, br), 838 (m), 794 (m) cm^{-1}. MS (GCMS): *m*/*z* 253 (M^+ − CH_3, 4%), 209 (6%), 195 (8%), 179 (1%), 163 (5%), 153 (20%), 141 (2%), 124 (6%), 115 (10%), 89 (22%), 79 (16%), 57 (100%), 55 (10%).

A solution of 3-*tert*-butoxy-5-methoxypentyl methanesulfonate (3.868 g, 14.41 mmol) in THF (30 mL) was added to the solution of sodium cyclopentadienide (115 mmol) in THF (80 mL) at 0 °C, and then the mixture was stirred overnight at room temperature. The reaction mixture was poured into saturated NH_4Cl (200 mL) and ether (150 mL) added. The ethereal extract was washed with saturated $NaHCO_3$ (100 mL), 2 M NaOH (100 mL), and brine (100 mL) and dried over Na_2SO_4 and solvent removed *in vacuo* to yield the crude product. Purification by column chromatography (silica; eluent pentane) gave 3-*tert*-butoxy-1-cyclopentadienyl-5-methoxypentane (**22**) as a light yellow oil (3.006 g, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.42 (1.6H, m), 6.24 (0.4H, br d, J = 5.3 Hz), 6.15 (0.4H, br s), 6.00 (0.6H, br s), 3.68 (1H, quintet, J = 6.8 Hz), 3.43 (2H, m), 3.32 (3H, s), 2.94 (1.2H, br s), 2.87 (0.8H, br s), 2.42 (2H, m), 1.72 (4H, m), 1.19 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.96 (C), 147.23 (C), 134.93 (CH), 133.83 (CH), 132.57 (CH), 130.55 (CH), 126.17 (CH), 125.70 (CH), 73.55 (C), 69.63 (CH_2), 68.02 (CH), 58.31 (CH_3), 43.52 (CH_2), 41.35 (CH_2), 36.62 (CH_2), 36.17 (CH_2), 35.83 (CH_2), 28.85 (CH_3), 26.58 (CH_2), 25.76 (CH_2). IR (film): 2948 (s), 2868 (s), 1495 (m), 1453 (s), 1247 (s), 1198 (m), 1117 (s), 1066 (s), 1027 (m) cm^{-1}. MS (EI): *m*/*z* 238 (M^+, 5%), 182 (19), 164 (100), 132 (31), 89 (32), 57 (62). HRMS (EI): calcd for $C_{15}H_{26}O_2$ requires (M^+) *m*/*z* 238.1933, found (M^+) *m*/*z* 238.1933.

To a solution of **22** (2.894 g, 12.14 mmol) in THF (30 mL) stirred at 0 °C under a nitrogen atmosphere was added dropwise butyllithium (22.76 mL of a 1.6 M solution in hexane, 36.42 mmol). The reaction mixture was stirred for 30 min and then quenched with TMSCl (6.2 mL, 48.56 mmol). To the reaction mixture was added saturated $NaHCO_3$ (100 mL) and ether (100 mL). The ethereal layer was separated, washed with brine (100 mL), and dried over Na_2SO_4 and solvent removed *in vacuo* to yield the crude product. Purification by column chromatography (silica; eluent 100% pentane) gave [3-(3-*tert*-butoxy-5-methoxypentyl)-2,4-cyclopentadienyl]trimethylsilane as a light yellow oil (3.242 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.49 (2H, m), 6.10 (1H, br s), 3.67 (1H, m), 3.44 (2H, m), 3.31 (3H, s), 3.23 (1H, br s), 2.43 (2H, m), 1.71 (4H, m), 1.19 (9H, s), 0.06 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.30 (C), 133.98 (CH), 132.19 (CH), 126.88 (CH), 73.29 (C), 69.40 (CH_2), 67.88 (CH), 58.38 (CH_3), 51.02 (CH), 36.88 (CH_2), 36.05 (CH_2), 28.86 (CH_3), 25.80 (CH_2), −1.91 (CH_3). IR (film): 2959 (s), 1587 (w), 1454 (m, br), 1388 (m), 1362 (s), 1248 (s), 1195 (s), 1120 (s), 1040 (s), 838 (s), 806 (s) cm^{-1}. MS (GCMS): *m*/*z* 310 (M^+, 1%), 281 (1%), 253 (3%), 236 (15%), 221 (2%), 195 (3%), 177 (8%), 152 (13%), 131 (20%), 117 (19%), 89 (27%), 73 (100%), 57 (39%).

To a solution of [3-(3-*tert*-butoxy-5-methoxypentyl)-2,4-cyclopentadienyl]trimethylsilane (0.127 g, 0.40 mmol) in dichloromethane (1 mL) stirred at 0 °C under an argon atmosphere was added slowly $TiCl_4$ (0.36 mmol, 0.36 mL of a 1 M solution in dichloromethane), and the mixture was stirred overnight. The solvent was removed *in vacuo* and diethyl ether (10 mL) added to dissolve the crude product, filtering off insoluble impurities. The organic layer was concentrated to ∼2 mL and stored at −20 °C overnight. Recrystallization (diethyl ether) of the deposited material gave the *title complex* **23** as a yellow crystalline solid (0.030 g, 28%). Mp: 93−94 °C (racemate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.938 (1H, ddd, J = 3.6, 2.9, 2.2 Hz), 6.903 (1H, dt, J = 2.2, 3.5 Hz), 6.135 (1H, q, J = 2.5 Hz), 6.119 (1H, q, J = 2.5 Hz), 4.44 (1H, ddt, J = 3.5, 4.8, 8.1 Hz)

[3.537 (1H, ddd, J = 9.6, 7.6, 5.7 Hz), 3.498 (1H, dt, J = 9.6, 5.6), strongly distorted on 9.6 Hz coupling], 3.34 (3H, s), 3.01 (1H, ddd, J = 3.2, 7.3, 14.8 Hz), 2.74 (1H, ddd, J = 3.2, 10.9, 14.8 Hz), 2.36 (1H, tdd, J = 3.2, 7.1, 14.3 Hz), 2.08 (1H, dddd, J = 3.2, 8.3, 11.5, 17.6 Hz) [1.794 (1H, dddd, J = 14.2, 7.4, 5.9, 4.7 Hz), 1.747 (1H, ddt, J = 14.2, 7.6, 5.3), strongly distorted on 14.2 Hz coupling]. ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.57 (C), 121.52 (CH), 120.95 (CH), 118.16 (CH), 116.16 (CH), 83.48 (CH), 68.63 (CH_2), 58.84 (CH_3), 37.91 (CH_2), 36.14 (CH_2), 24.29 (CH_2). IR (KBr): 2954 (s), 2886 (s), 1494 (m), 1457 (m), 1440 (m), 1098 (s), 1027 (s), 993 (s), 944 (s), 836 (s) cm^{-1}. MS (EI): m/z 298 (M^+, 4%), 262 (100%), 239 (55%), 230 (40%), 203 (59%), 174 (53%), 112 (18%), 99 (9%), 78 (71%), 65 (11%), 58 (17%), 45 (64%), 39 (16%), 27 (9%). HRMS (EI): calcd for $C_{11}H_{16}Cl_2O_2Ti$ (M^+) m/z 298.0007, found (M^+) m/z 298.0000.

Crystal Structure Determination of Complex 23. A summary of crystal data, intensity collection, and refinement parameters is reported in Table 1. A yellow needlelike crystal of **23** of dimensions 0.1 × 0.1 × 0.25 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC7S diffractometer with graphite-monochromated Cu Kα radiation (λ = 1.541 78 Å). Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range 32.96° < 2θ < 56.56°. The data were collected at a temperature of 20 ± 1 °C using the ω-scan technique to a maximum 2θ value of 120.4°. The intensities of 3 representative reflections were measured after every 150 reflections. Over the course of data collection, the standards decreased by 16.6%. A linear correction factor was applied to the data to account for this phenomenon. An empirical absorption correction using the program DIFABS[49] was applied, which resulted in transmission factors ranging from 0.40 to 1.00. The data were corrected for Lorentz and polarization effects. The structure was solved using direct methods[50] and expanded using Fourier techniques[51] and the non-hydrogen atoms refined anisotropically using full-matrix least squares on $\sum w(|F_o| - |F_c|)^2$ to give satisfactory R factors (Table 1). Hydrogens were included in calculated positions but not refined. Full details are given in the Supporting Information.

(*E*)-5-Methyl-4-[(*E*)-1-methyl-1-propenyl]-5-heptene-1,4-diol (24a). 2-Butyne (8.1 mL, 0.1 mol) was dissolved in diethyl ether (100 mL) and the solution cooled to 0 °C. Titanocene dichloride (0.5 g, 2 mol %) was added, followed by the dropwise addition of isobutylmagnesium bromide (45 mL of a 2 M solution in ether, 0.09 mol) to give a brown solution. The reaction mixture was warmed to room temperature and stirred for 2 h before γ-butyrolactone (3.4 mL, 0.045 mol) was added slowly dropwise (vigorous reaction!). As the addition was completed, magnesium salts began to precipitate from solution. The reaction mixture was stirred for 4 h and then quenched by slow addition of water. The layers were separated, and the aqueous layer was extracted twice with ether (50 mL). The combined organic layers were dried ($MgSO_4$) and filtered, and the majority of the ether was evaporated. Petroleum ether was added until the product started to precipitate; then the solution was stored at −20 °C for 3 h. Filtration gave the title diol **24a** (5.97 g, 65%) as a pale yellow or white fluffy solid, mp 64−65 °C (from petroleum ether), which could be stored in a freezer for several months without decomposition. ^{1}H NMR (270 MHz, $CDCl_3$): δ 5.6 (2H, qq, J = 6.8, 1.3 Hz), 3.63 (2H, t, J = 6.1 Hz), 2.1 (2H, br s, 2 × OH), 1.81 (2H, t, J = 7.3 Hz), 1.63 (6H, dq, J = 6.8, 1 Hz), 1.53 (2H, tt, J = 7.3, 6.1 Hz), 1.46 (6H, quintet, J = 1 Hz). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 138.2 (C), 119.4 (CH), 80.5 (C), 63.7 (CH_2), 33.1 (CH_2), 27.2 (CH_2), 13.6 (CH_3), 12.6 (CH_3). IR (liquid film): 3247 (br, s), 2958 (s), 2920 (s), 2858 (s), 1462 (s), 1376 (w), 1206 (w), 1072 (s), 976 (w), 815 (w) cm^{-1}. MS (APCI + ve): m/z 181 ($MH^+ - H_2O$) cyclized in MS. HRMS: calcd for $C_{12}H_{22}O_2$ (M^+) m/z 198.1620, found (M^+) m/z 198.1631.

Preparation of [η^5-σ-$Me_4C_5(CH_2)_3O$]$TiCl_2$ (28a). Sodium hydride (1.2 g of a 60 wt % suspension, 30 mmol) was washed with pentane to remove oil. THF (50 mL) was added and the slurry cooled to 0 °C. The diol **24a** (2.5 g, 13 mmol) was added dropwise as a THF solution (10 mL). The resulting solution was stirred at 0 °C for 1 h, and then benzyl bromide (1.8 mL, 15 mmol) was added. After the mixture was stirred for 1 h, the reaction was quenched by careful addition of water. The layers were separated, the aqueous layer was extracted with ether (2 × 20 mL), the combined organic layers were washed with brine, dried ($MgSO_4$), and filtered, and the solvent was evaporated to give (2*E*,5*E*)-4-[3-(benzyloxy)propyl]-3,5-dimethyl-2,5-heptadien-4-ol (**25a**) as a yellow oil (3.505 g, 98%). ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.2 (5H, m), 5.61 (2H, qq, J = 7, 1 Hz), 4.51 (2H, s), 3.49 (2H, t, J = 6.3 Hz), 2.06 (1H, br. s, OH), 1.82 (2H, t, J = 7.5 Hz), 1.64 (6H, dq, J = 7, 1 Hz), 1.58 (2H, m), 1.47 (6H quintet, J = 1 Hz). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 138.7 (C), 138.4 (C), 128.5 (CH), 127.8 (CH), 127.7 (CH), 119.1 (CH), 80.3 (C), 73.0 (CH_2), 71.2 (CH_2), 33.4 (CH_2), 24.2 (CH_2), 13.6 (CH_3), 12.6 (CH_3). IR (liquid film): 3448 (br, s), 3059 (m), 3027 (m), 2916 (s), 2857 (s), 1494 (w), 1452 (m), 1378 (m), 1369 (m), 1203 (m), 1099 (s), 1026 (m), 1001 (m) cm^{-1}. MS (APCI + ve): m/z 271.2 ($MH^+ - H_2O$).

The diene **25a** (3 g, 10.4 mmol) was dissolved in chloroform (30 mL) at room temperature and 4-methylbenzenesulfonic acid (50 mg) added. After 0.5 h saturated aqueous sodium carbonate solution (30 mL) was added and the layers were separated. The aqueous layer was extracted with dichloromethane (20 mL), the organic layers were combined, dried ($MgSO_4$), and filtered, and the solvent was evaporated to give 1-[3-(2,3,4,5-tetramethyl-2,4-cyclopentadienyl)propoxy]methylbenzene (**26a**) as a yellow oil (2.8 g, 100%). The product exists as a mixture of three tautomers. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.3−7.4 (5H, m), 4.5−4.6 (2H, m), 3.4−3.5 (2H, m), 2.2−2.7 (3H, m), 1.6−1.9 (∼10.5H, m), 1.2 (∼0.5H, m), 1.02 (∼3H, d, J = 7 Hz). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 138.9 (C), 128.5 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 73.1 (CH_2), 72.9 (CH_2), 71.2 (CH_2), 70.4 (CH_2), 70.1 (CH_2), 55.9 (CH), 51.7 (CH), 49.6 (CH), 30.7 (CH_2), 29.8 (CH_2), 23.9 (CH_2), 22.9 (CH_2), 22.3 (CH_2), 14.5 (CH_3), 14.3 (CH_3), 11.9 (CH_3), 11.8 (CH_3), 11.3 (CH_3), 11.2 (CH_3). IR (liquid film): 2923 (s), 2848 (s), 1654 (w), 1494 (m), 1451 (s), 1362 (s), 1205 (m), 1098 (s), 1027 (m), 906 (s) cm^{-1}. MS (APCI + ve): m/z 271.2 (MH^+).

The cyclopentadiene **26a** (2.5 g, 9.2 mmol) was dissolved in THF (30 mL) and the solution cooled to 0 °C. HMPA was added (1.7 mL, 10 mmol) followed by n-BuLi (4 mL of a 2.5 M solution in hexane, 10 mmol) to give a red solution. The reaction was quenched after 1 min with chlorotrimethylsilane (2.5 mL, 20 mmol); the red color disappeared, and the reaction mixture was stirred for 10 min. Saturated sodium carbonate was carefully added and the layers were separated. The aqueous layer was extracted with ether (20 mL), and the combined organic layers were washed with brine (3 × 20 mL). The organic layer was dried ($MgSO_4$) and filtered and the solvent removed to give an orange oil, which was passed through a short column of silica (8/1 petrol/ether as eluant) to remove residual HMPA. The solvent was evaporated to give (Me_3Si)-$Me_4C_5(CH_2)_3OCH_2Ph$ (**27a**) as a yellow oil. (2.95 g, 90%). Complete silylation was indicated in the ^{1}H NMR by the absence of a methyl doublet at δ 0.95 and by the trimethylsilyl resonance at δ −0.15. The product exists as a mixture of three isomers. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.1−7.5 (5H, m), 4.4−4.6 (2H, m), 3.4−3.6 (2H, m), 2.05−2.8 (2H, m), 1.5−1.95, (14H, m), −0.15 (9H, br s). IR (liquid film): 2924 (s), 2856 (s), 1453 (s), 1378 (m), 1364 (m), 1247 (s), 1113 (s), 839 (s) cm^{-1}. MS

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(APCI + ve): *m*/*z* 343.2 (MH^+). HRMS (CI): calcd for $C_{22}H_{34}OSi$ (M^+) *m*/*z* 342.2379, found (M^+) *m*/*z* 342.2372.

To the (trimethylsilyl)cyclopentadiene **27a** (0.5 g, 1.5 mmol) in dichloromethane (15 mL) at 0 °C was added slowly dropwise titanium tetrachloride (1.5 mL of a 1.0 M solution in dichloromethane, 1.5 mmol). The reaction mixture turned brown and eventually red-brown after 0.5 h. The mixture was stirred at room temperature for 12 h, and then the volatile components were evaporated to give a red solid. Recrystallization from ether/petrol gave yellow crystals of (η^5-σ-$Me_4C_5(CH_2)_3O)TiCl_2$ (**28a**; 195 mg, 45%), NMR data are consistent with that those previously reported.[7b] ^{1}H NMR (270 MHz, $CDCl_3$): δ 4.34 (2H, t, J = 5.1 Hz), 2.8 (2H, t, J = 6.3 Hz), 2.32 (6H, s), 2.30 (2H, m), 2.01 (6H, s). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 132.3 (C). 132.2 (C), 125.9 (C), 75.2 (CH_2), 35.0 (CH_2), 22.3 (CH_2), 13.1 (CH_3), 12.9 (CH_3). MS (APCI + ve): *m*/*z* 302.1 (M^+ − Cl + MeCN). Anal. Calcd for $C_{12}H_{18}Cl_2OTi$: C, 48.52; H, 6.11. Found: C, 48.31; H, 5.97.

Preparation of (η^5-σ-$Me_4C_5CH(CH_2CH{=}CH_2)(CH_2)_2O)TiCl_2$ (28b). 2-Butyne (3.5 mL, 45 mmol) was dissolved in diethyl ether (45 mL) and cooled to 0 °C. Titanocene dichloride (150 mg, 5 mol %) was added, and to the resulting red suspension was added, dropwise, isobutylmagnesium bromide (19 mL of a 2 M solution in ether, 38 mmol). During the course of the addition, the solution turns brown. The reaction mixture was warmed to room temperature and stirred for 2 h to give 2-butenylmagnesium bromide. Dry cerium trichloride (3.5 g, 14 mmol) was slurried in THF (45 mL), the slurry was stirred at room temperature for 0.5 h and then cooled to −78 °C, and 2-butenylmagnesium bromide was added *via* cannula. After this mixture was stirred at −78 °C for 0.5 h, 3-allyltetrahydro-2-furanone[52] (1.7 g, 14 mmol) in THF (20 mL) was added slowly dropwise. The reaction mixture was warmed slowly to room temperature overnight before being quenched by the slow addition of water. The layers were separated, and the aqueous layer was extracted twice with ether (50 mL). The organic layers were combined, dried ($MgSO_4$), and filtered, and the ether was evaporated to afford crude (*E*)-3-allyl-5-methyl-4-[(*E*)-1-methyl-1-propenyl]-5-heptene-1,4-diol (**24b**; 4 g), which was used in the next step without purification.

The crude diol **24b** (4 g) was monobenzylated as described for **24a** to give (2*E*)-5-[2-(benzyloxy)ethyl]-3-methyl-4[(*E*)-1-methyl-1-propenyl]-2,7-octadien-4-ol (**25b**) as a clear oil (3.72 g, 81%) after chromatography on silica (6/1 petrol/ether). ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.25−7.45 (5H, m), 5.82 (1H, dddd, J = 5, 8, 10, 16 Hz), 5.56 (2H, overlapping qq, J = 7, 1 Hz), 4.94−5.02 (2H, m), 4.50 (2H, AB q, J = 12 Hz, OCH_2Ph), 3.6 (1H, ddd, J = 5, 8, 10 Hz), 3.46 (1H, ddd, J = 5, 6, 10 Hz), 3.0 (1H, s, OH), 2.02 (1H, m), 2.3 (2H, m), 1.78 (2H, m), 1.64 (3H, dq, J = 7, 1 Hz), 1.63 (3H, dq, J = 7, 1 Hz), 1.48 (3H, quintet, J = 1 Hz), 1.45 (3H, quintet, J = 1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): 138.8 (CH), 138.3 (C), 137.6 (C), 137.1 (C), 128.5 (CH), 127.7 (CH), 119.05 (CH), 119.00 (CH), 115.7 (CH_2), 83.6 (C), 72.9 (CH_2), 68.0 (CH_2), 38.0 (CH), 33.4 (CH_2), 28.4 (CH_2), 13.75 (CH_3), 13.70 (CH_3), 12.35 (CH_3), 12.30 (CH_3) (missing aromatic CH probably degenerate with the 127.7 signal). IR (film): 3399 (m, br), 3061 (m), 3027 (m), 2916 (s), 2853 (s), 1637 (m), 1453 (s), 1379 (s), 1097 (s), 998 (s), 909 (s) cm^{-1}. MS (APCI +ve): *m*/*z* 329.2 (MH^+, 9%), 311.2 ($MH^+ - H_2O$, 100).

The diene **25b** (2 g, 6 mmol) was cyclized as described for **25a** to give 6-(benzyloxy)-4-(2,3,4,5-tetramethylcyclopentadienyl)-1-hexene (**26b**) as a yellow oil (1.85 g, 100%). The product exists as a mixture of tautomers and diastereoisomers, making NMR characterization difficult. IR (film): 3062 (w), 3028 (w), 2925 (s), 2854 (s), 1639 (w), 1453 (m), 1363 (w), 1102 (s), 908 (m) cm^{-1}. MS (APCI + ve): *m*/: 311.3 (MH^+).

The crude cyclopentadiene **26b** (1.06 g, 3.4 mmol) was lithiated, and this compound was reacted with trimethylsilyl chloride as described for **26a** to give 6-(benzyloxy)-4-[(trimethylsilyl)-2,3,4,5-tetramethylcyclopentadienyl]-1-hexene (**27b**) as a yellow oil (0.8 g, 72%). The Me_3Si peak at δ_H −0.1 and MS confirmed silylation. IR (film): 2929 (s), 2856 (s), 1638 (m), 1452 (s), 1376 (m), 1361 (m), 1246 (s), 1102 (s), 908 (s), 836 (s) cm^{-1}. MS (APCI + ve): *m*/*z* 383.3 (MH^+).

The crude (trimethylsilyl)cyclopentadienyl compound **27b** (0.8 g, 2.4 mmol) was complexed to titanium as described for **27a** to give a crude brown solid. Recrystallization from toluene/pentane gave the *title complex* **28b** (0.50 g, 62%, >90% pure by NMR). An analytically pure sample (bright yellow) was obtained by sublimation (130 °C at 3×10^{-4} mbar). ^{1}H NMR (270 MHz, $CDCl_3$): δ 5.68 (1H, ddt, J = 17.3, 9.9, 7.2 Hz), 4.95−5.2 (2H, m), 4.47 (1H, ddd, J = 12.1, 4.5, 2.3 Hz), 4.35 (1H, ddd, J = 12.1, 10.2, 4.5 Hz), 2.96 (1H, m), 2.49−2.55 (2H, m), 2.31 (3H, s, Me), 2.3 (3H, s, Me), 2.28−2.37 (2H, m), 2.08 (3H, s, Me), 1.95 (3H, s, Me). ^{1}H NMR (270 MHz, C_6D_6): δ 5.38 (1H, ddt, J = 17.0, 10.0, 7.1 Hz), 4.83 (2H, m), 3.93 (1H, ddd, J = 12.1, 4.6, 1.7 Hz), 3.76 (1H, td, J = 12.1, 2.5 Hz), 2.38 (1H, dddd, J = 12.1, 8.5, 7.5, 3.4 Hz), 2.12 (3H, s, Me), 2.10 (3H, s, Me), 2.05 (2H, m), 1.79 (3H, s), 1.77 (1H, m), 1.67 (3H, s), 1.52 (1H, dddd, J = 13.8, 3.5, 2.5, 1.5 Hz). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 135.7 (CH), 133.3 (C), 132.8 (C), 132.5 (C), 129.9 (C), 126.6 (C), 117.1 (CH_2), 76.5 (CH_2), 38.9 (CH_2), 38.2 (CH_2), 36.2 (CH), 15.1 (CH_3), 13.3 (CH_3), 13.1 (CH_3), 12.8 (CH_3). IR (CH_2Cl_2 solution): 2956 (m), 2924 (m), 2858 (m), 1643 (w), 1447 (m), 1374 (m), 1234 (m), 1069 (s), 1019 (s), 896 (m) cm^{-1}. MS (APCI + ve): *m*/: 342.1 (M^+ − Cl + MeCN). Anal. Calcd for $C_{15}H_{22}Cl_2OTi$: C, 53.61; H, 6.54. Found: C, 53.62; H, 6.61.

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Supporting Information Available: Full details of the X-ray structure determination of **23**, including tables of positional parameters, displacement parameters, and bond lengths and angles, and ^{1}H and ^{13}C NMR spectra of **10c** and **23** (14 pages). Ordering and Internet access information is given on any current masthead page.

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