

Tetrabenzo[*a,c,g,i*]fluorenyllithium and η^5 -Tetrabenzo[*a,c,g,i*]fluorenyltitanium Complexes

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Tetrabenzo[*a,c,g,i*]fluorene (Tbf-H, **4**) was deprotonated with *n*-butyllithium, leading to ionic Tbf-Li_{*n*} complexes **5** and **6**, consisting of well-separated cations (Li(THF)₄ (**5**), Li(DME)₃ (**6**)) and Tbf anions. Subsequent reactions with chlorotitanium alkoxides Cl₂Ti(O^{*i*}Pr)_{4-*x*} (*x* = 1, 3) and chlorotitanium phenoxides {ClTi(OR)₃(THF)}₂ (R = C₆H₅ (**12**), 4-MeC₆H₄ (**13**), 4-BuC₆H₄ (**14**)) give a series of η^5 -tetrabenzo[*a,c,g,i*]fluorenyltitanium complexes (TbfTiCl₂(O^{*i*}Pr) (**11**) and TbfTi(OR)₃ [R = ^{*i*}Pr (**10**), C₆H₅ (**15**), 4-MeC₆H₄ (**16**), 4-BuC₆H₄ (**17**)]), which were characterized by NMR, MS, and IR measurements and X-ray crystallography. Additionally, the compounds' properties regarding the syndiospecific polymerization of styrene when activated with MAO were explored. The activities increase in the following order [kg sPS/(mol Ti × mol styrene × h)]: **11** (1420) < **17** (3400) < **16** (3740) < **10** (6040) < **15** (6720).

Introduction

The cyclopentadienide anion and its derivatives are widely used ligands in coordination and organometallic chemistry. It has been recognized that the replacement of hydrogen atoms on the cyclopentadienyl ring by substituents influences the physical and chemical properties of the corresponding metal complexes.¹ In addition to the well-known permethylated ligand Cp*, a broad range of other Cp substituents are used to prepare sterically demanding Cp ligands. On one hand, bulky Cp ligands become available by pentasubstitution employing isopropyl,² benzyl,^{3,4} phenyl,⁵ and ferrocenyl ligands directly⁶ or indirectly attached to the five-membered ring.⁷ On the other hand, more bulky Cp ligands become available by using fused aromatic ring

systems, such as indenyl,⁸ fluorenyl,⁹ or corannulenes,¹⁰ the last one being understood as a formal part of a C₆₀ molecule.¹¹ By modification of the steric and electronic requirements the complex properties can be tuned in an excellent way, e.g., in order to obtain better solubilities and thermal stabilities or to avoid subsequent reactions.¹² Particularly, the fine-tuning of the steric and electronic properties of these complexes is of interest in order to optimize properties in catalytic applications such as the stereoregular polymerization of olefins,¹³ hydroamination, or hydroformylation.¹⁴ Particularly, half-sandwich titanium(IV) complexes are useful in the syndiotactic polymerization of styrene.¹⁵ It was shown that monocyclopentadienyl titanium derivatives show increasing catalytic activities with increasing steric size of the spectator ligands. In such a way titanium complexes with 2-phenylcyclopenta[*l*]phenanthrene¹⁶ (**1**), 2methylbenz[*e*]indene¹⁷ (**2**), or 1,2,3,4,5,6,7,8-octahydrofluorene¹⁸ (**3**) are important catalysts for styrene polymerization (Chart 1).

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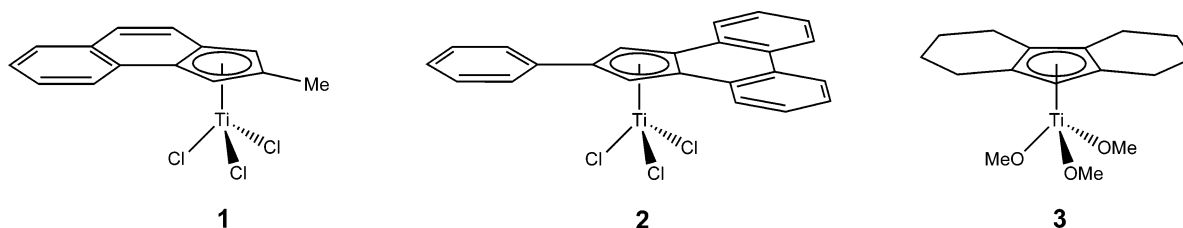
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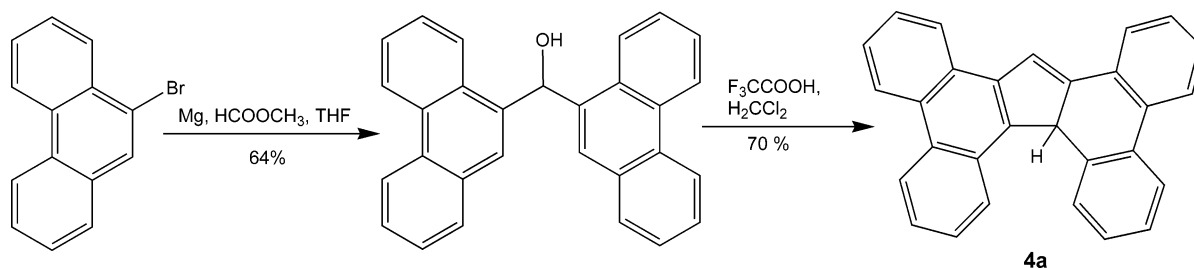
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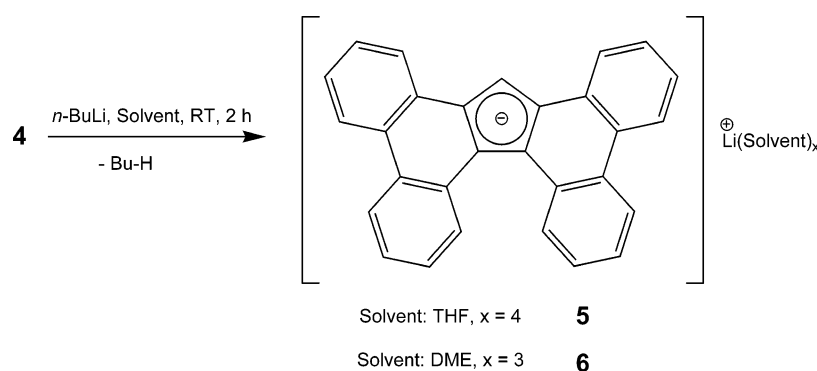
Chart 1



Scheme 1



Scheme 2



Prompted by these developments, we were interested in developing a nearly planar Cp ligand system with an increasing number of annulated benzene rings and subsequently tried to synthesize a novel type of titanium complexes bearing tetrabenzo[*a,c,g,i*]fluorenyl (Tbf) as ligand. The corresponding protonated hydrocarbon *8bH*-tetrabenzo[*a,c,g,i*]fluorene (Tbf-H **4a**) is easily available starting from 9-bromophenanthrene in a classical procedure with slight modifications to the protocol (Scheme 1).¹⁹

The tetrabenzo[*a,c,g,i*]fluorene moiety has not been widely used in organometallic chemistry so far. Originally, derivatives of **4** were developed as protecting groups, which exhibit an increased affinity for charcoal and thus have been applied in the purification of peptides, proteins, and oligonucleotides.²⁰ Later on, it was also used as an anchor group for solution phase supported organic synthesis,¹⁹ and there was an attempt to use it in main group organometallic chemistry, e.g., as a polyaromatic tag for organotin compounds.²¹ Here we wish to report the synthesis and characterization of tetrabenzo[*a,c,g,i*]fluorenyllithium and η^5 -tetrabenzo[*a,c,g,i*]fluorenyltitanium complexes.

Furthermore, the applications of the titanium complexes in the syndiospecific polymerization of styrene, activated with MAO, are examined.

Results and Discussion

Synthesis and Characterization of Tetrabenzo[*a,c,g,i*]fluorenyllithium. *8bH*-Tetrabenzo[*a,c,g,i*]fluorene (Tbf-H, **4**)¹⁹ can be deprotonated with *n*-butyllithium in THF to give Tbfl-Li(THF)₄ (**5**) as blocky yellow crystals when stored at -80°C (Scheme 2). The substance is soluble in THF, aromatic solvents, and cyclohexane and exhibits sensitivity to air and moisture, but is not pyrophoric, in contrast to common lithium cyclopentadienides. In the case of **5**, a low melting point without decomposition of 81°C is found.

The crystals obtained are suitable for X-ray structure analysis; **5** crystallizes in space group *P*1; the triclinic unit cell contains four separated ion pairs. As seen in the ORTEP plot (Figure 1), the tetrabenzo[*a,c,g,i*]fluorenyl anion is not planar but exhibits a slightly helical distortion due to steric repulsion of the aromatic ring protons.

These results raise the question, whether tetrabenzo[*a,c,g,i*]fluorenyllithium also forms separated ion pairs in the solid state, when other coordinating solvents, such as dimethoxyethane (DME), are used. Therefore, tetrabenzo[*a,c,g,i*]fluorenyllithium was prepared by deprotonation of Tbf-H by *n*-butyllithium in toluene. The white precipitate was filtered and redissolved in DME (Scheme 2). Cooling the resulting yellow solution to -80°C yields blocky yellow crystals (mp 98°C), suitable for X-ray

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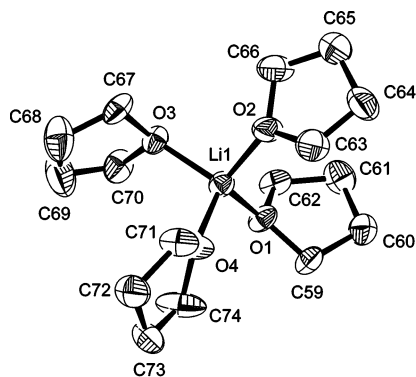


Figure 1. ORTEP plot of the solid-state molecular structure of **5**. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [deg]: C(1)–C(2) 1.404(3), C(1)–C(5) 1.406(3), C(2)–C(3) 1.431(3), C(3)–C(4) 1.431(3), C(4)–C(5) 1.425(3), C(17)–C(3)–C(4)–C(29) 30.4(4).

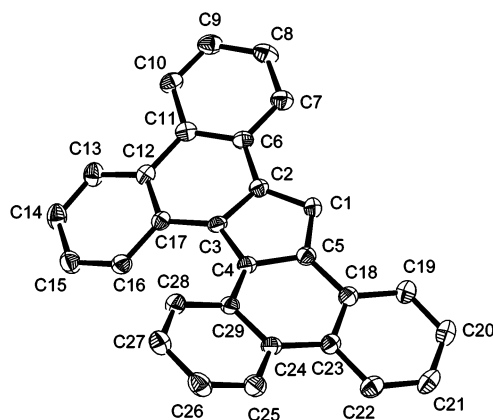


Figure 2. ORTEP plot of the solid-state molecular structure of **6**. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [deg]: C(1)–C(2) 1.403(2), C(1)–C(5) 1.397(2), C(2)–C(3) 1.425(2), C(3)–C(4) 1.432(2), C(4)–C(5) 1.437(2), C(17)–C(3)–C(4)–C(18) 22.2(3).

diffraction. Like **5**, $\text{TbfLi}(\text{DME})_3$ (**6**) crystallizes in space group $P\bar{1}$; the triclinic unit cell contains 0.25 equiv of DME in addition to four separated ion pairs of **6**. Like in the case of **5**, also for **6** two symmetry-independent molecules are found in the unit cell. However, the structural data are identical with respect to the standard deviation; for that reason only one molecule is discussed. The Li–O distances are found shorter in the tetrahedral cation **5** (1.876–1.930 Å, av 1.90 Å) compared to the octahedral cation **6** (2.096–2.190 Å, av 2.13 Å). These values are in the expected range of Li–O distances.^{22,23}

The packing diagrams of **5** (Figure 3) and **6**²⁴ show no bonding contacts between the lithium cations and tetrabenzofluorenyl anions, respectively. Two types of rhombic arrangements (**a**, **b** and **d**, **e**) of the anions (center of the five-membered

ring) and Li cations are found, exhibiting Ct–Li distances (av) of 5.9/7.2 and 5.8/7.2 Å. Between this Li–Tbf ensemble, distances (av *c*, *f*) of 5.55 Å are found. The Tbf anions fulfill a honeycomb-like arrangement, showing Tbf molecules alternating in a horizontal and in a orthogonal arrangement. The C17 atoms of the Tbf molecules are orientated in an alternative manner—one molecule ahead, the next reverse—forming a point to face (T-shaped) interaction in **5** (2.618 Å shortest contact H21 center of C47–C52) and in **6** (2.803 Å shortest contact H13 center of C59–C64).²⁵

NMR experiments were performed on **6** in order to inspect if the compound also exists as separated ion pairs in solution, especially in nonpolar solvents such as C_6D_6 . NOE measurements do not reveal any coupling between the protons of the DME molecules coordinated to the lithium cation and the protons of the Tbf anion. Therefore, it is assumed that even in nonpolar solvents separated ion pairs are formed due to the strong delocalization of the negative charge on the anions' aromatic ring system.

The tetrabenzofluorenyl complexes **5** and **6** represent rare examples of η^0 -coordinated carbanions employing "simple" Lewis bases, such as THF or DME, instead of crown ethers, for coordinative saturation of the cation.^{22,26}

Synthesis and Characterization of Tetrabenzofluorenyltitanium Complexes. Standard procedures for the synthesis of half-sandwich titanocene complexes proved not to be successful with the tetrabenzofluorenyl ligand system. For instance, reacting **5** with $\text{TiCl}_4(\text{THF})_2$ in different solvents such as THF, toluene, and *n*-hexane leads to dimerization of the ligand, forming bis(17-tetrabenzofluorene) (**7**) (Scheme 3), a reaction pathway that is known for fluorenyltitanium compounds and involves oxidation of the ligand anion and its subsequent radical coupling while reducing the metal center.²⁷ The low solubility of **7** prohibits NMR measurements, whereas in the EI mass spectra the molecular peak can be observed (*m/z* 730.2).

Bis(17-tetrabenzofluorene) (**7**) is poorly soluble in any organic solvent and proves to be highly temperature resistant for an aromatic compound, as it decomposes without melting at 363 °C. The compound crystallizes from dichloromethane in

(22) Li–O distances [Å]: $[\text{Li}(\text{DIGLYME})_2]^+$ 2.043(5)–2.228(5),²² $[\text{Li}(\text{THF})_3]^+$ 1.893–1.955,^{23a} $[\text{Li}(\text{THF})_4]^+$ 1.924–1.954,^{23b} $[\text{Li}(\text{DME})_3]^+$ 2.082–2.271.^{23c} Neander, S.; Körmich, J.; Olbrich, F. *J. Organomet. Chem.* **2002**, 656, 89–96.

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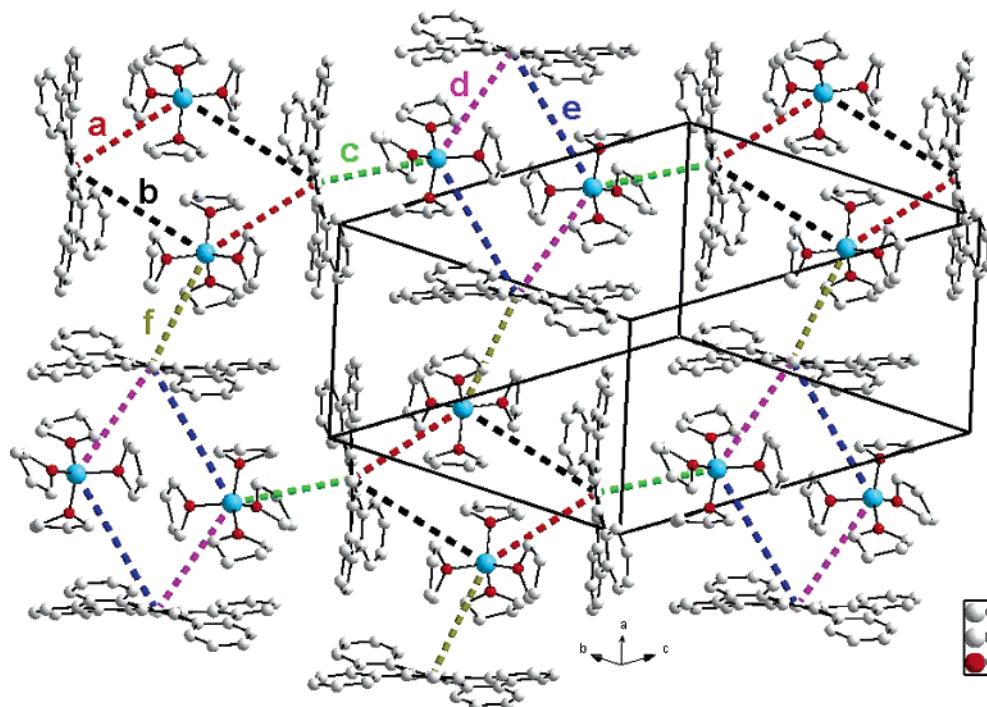
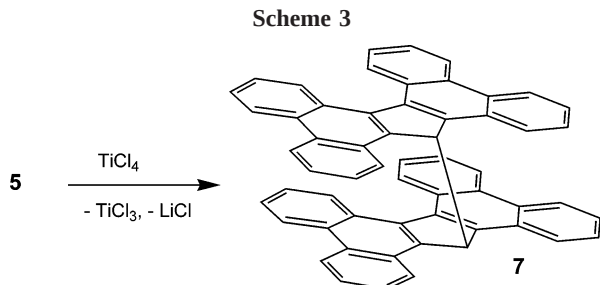


Figure 3. Packing diagram of **5**. Hydrogen atoms are omitted for clarity (values of **6** in brackets). Selected distances [Å]: **a** (red) 5.902 (6.854), **b** (black) 7.173 (6.829), **c** (green) 5.469 (6.276), **d** (pink) 5.835 (7.081), **e** (blue) 7.209 (7.217), **f** (dark yellow) 5.586 (6.167).

Scheme 3



space group $P2_1/n$; the monoclinic cell unit contains four molecules of $(\text{Tbf})_2$ along with 4 equiv of dichloromethane (Figure 4). An extraordinarily long C–C single bond between C1–C30 (1.615(2) Å) is found, nearly identical to the corresponding C–C bond in a comparable compound described by Malaba and Youngs.²⁸ A nearly perfect face-to-face π – π stacking of the C5/C24 and C31/C41 rings is observed (distance of the ring centers 3.422 Å).²⁵

However, as also alternative reactions of Tbf-SiMe_3 ²⁴ and TiCl_4 failed, resulting only in unidentified products,²⁹ we were forced to choose an alternative synthetic path, employing titanium alkoxides in order to increase the electron density on the metal center.³⁰ Thus for fluorenyltitanium complexes an sufficient thermal stability is observed.³¹ Reacting a solution of **5** in toluene with $\text{ClTi}(\text{O}^i\text{Pr})_3$ (**8**) at ambient temperature and subsequent crystallization from *n*-hexane (–60 °C) yields yellow crystals of **10** (Scheme 4), which can be isolated in acceptable yields (68%). The Tbf complex **10** melts at 135 °C and shows good solubilities in common organic solvents. Of high diagnostic

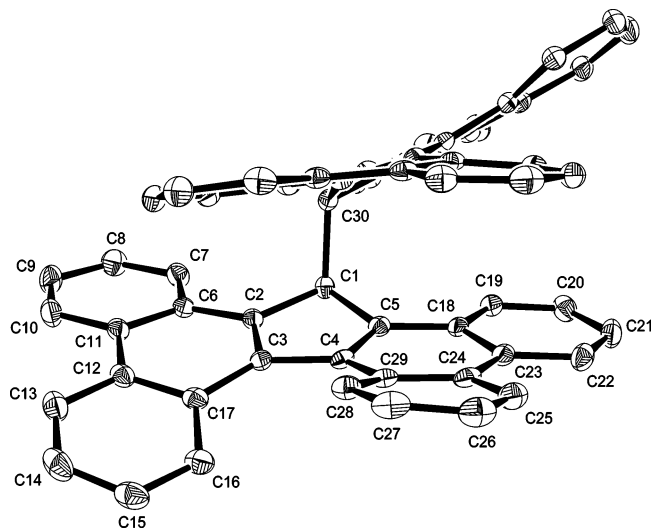


Figure 4. ORTEP plot of the solid-state molecular structure of **7**. Hydrogen atoms and one molecule of CH_2Cl_2 are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [deg]: C(1)–C(30) 1.615(2), C(1)–C(2) 1.509(2), C(1)–C(5) 1.512(2), C(2)–C(3) 1.366(2), C(3)–C(4) 1.474(2), C(4)–C(5) 1.370(2), C(17)–C(3)–C(4)–C(29) 19.3.

value is the ^1H NMR shift of H17 in **10** (δ 7.6 ppm) (Figure 6). The other signals are in the expected range; further details are given later on. The crystals obtained were also suitable for X-ray diffraction (Figure 5). The orthorhombic crystals contained eight molecules of compound **10** in the unit cell (space group $Pbca$). The distance Ti(1)–Ct(1) measures 2.120 Å and is nearly identical to the Ti–Ct distance in $(\eta^5\text{-Flu})(\eta^1\text{-Flu})\text{Ti}(\text{O}^i\text{Pr})_2$ (Flu: fluorenyl, 2.122 Å),³¹ but longer than in CpTiCl_3 (2.01 Å)³² or $(\eta^5\text{-Ind})\text{TiCl}_3$ (2.032 Å).³³

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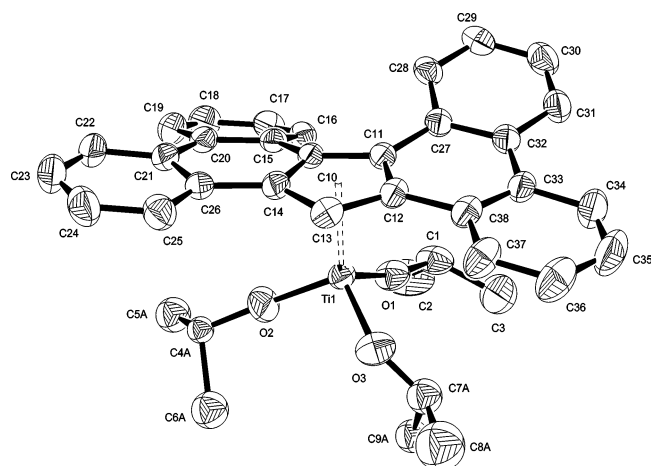
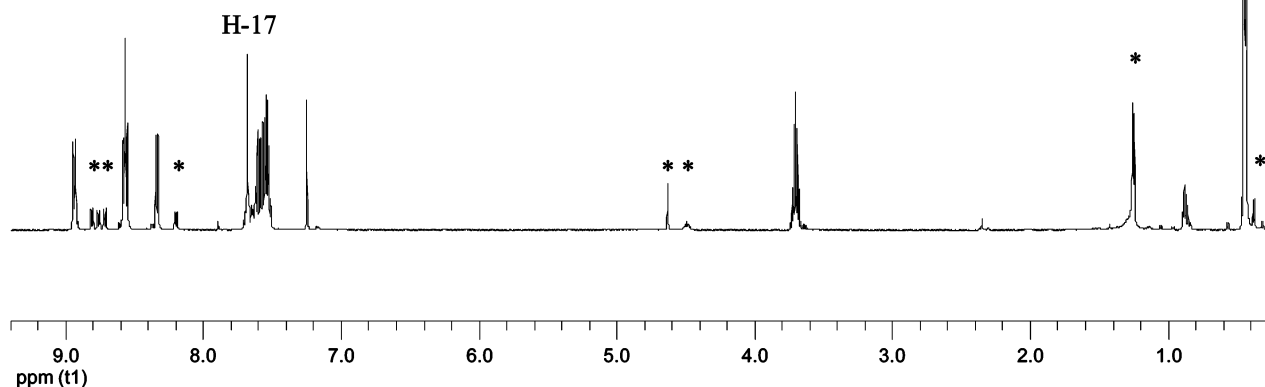


Figure 5. ORTEP plot of the solid-state molecular structure of **10**. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [deg]: Ti(1)–Cl(1) 2.120, Ti(1)–O(1) 1.775(8), Ti(1)–O(2) 1.768(8), Ti(1)–O(3) 1.823(2), O(1)–C(1) 1.396(3), O(2)–C(4) 1.394(3), O(3)–C(7) 1.319(9), C(10)–C(11) 1.435(3), C(10)–C(14) 1.417(4), C(11)–C(12) 1.418(4), C(12)–C(13) 1.409(4), Ti(1)–O(1)–C(1) 165.0(5), Ti(1)–O(2)–C(4) 169.2(2), Ti(1)–O(3)–C(7) 137.4(5), C(15)–C(10)–C(11)–C(27) 22.4(4).

Two of the OⁱPr groups show short Ti–O distances (av 1.77 Å), whereas a larger value of 1.823(2) Å is found for the third group. This corresponds with short C–O distances (av 1.39 Å) and large Ti–O–C angles (av 167°) for the first two alkoxide ligands, indicative of higher Ti–O bond orders. On the other hand, a shorter C(7)–O(3) bond (1.319(9) Å) as well as a smaller Ti(1)–O(3)–C(7) angle (137.4(5)°) is found.

polar solvent



non-polar solvent

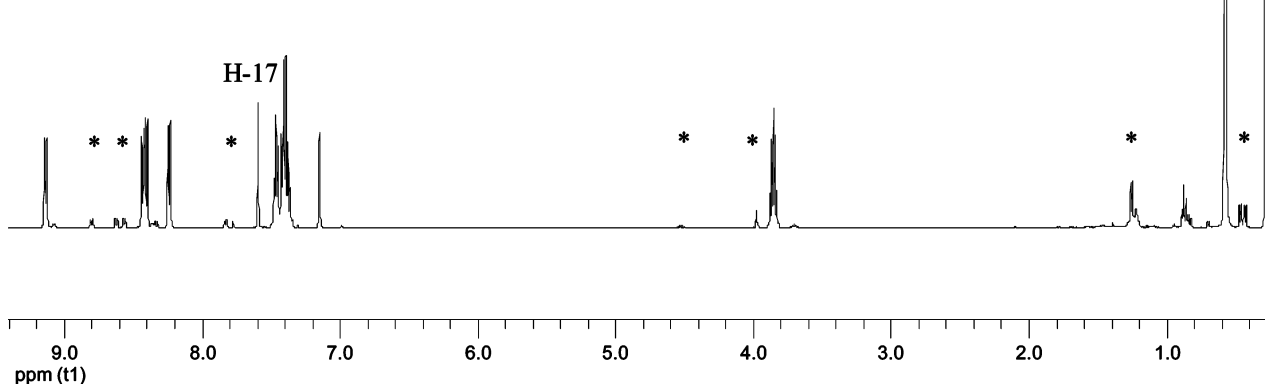
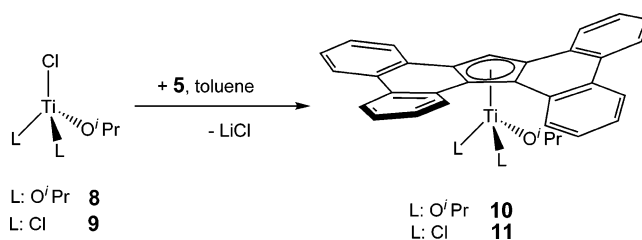
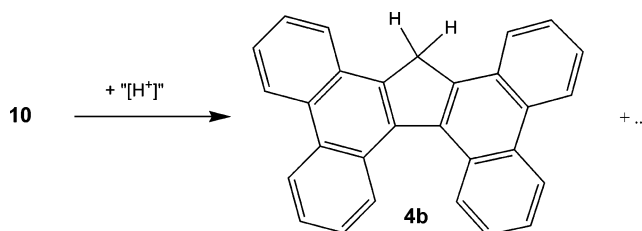


Figure 6. ¹H NMR spectrum (500.13 MHz, 300 K) of **10** in CDCl₃ (polar solvent) and C₆D₆ (nonpolar solvent). The asterisks demark subsequent products.

Scheme 4



Scheme 5



Being stable as a solid compound, **10** shows some decomposition, mainly more in polar solvents than in nonpolar ones (Scheme 5).

As one subsequent product the hydrocarbon 17*H*-tetrabenzob[*a,c,g,i*]fluorene (**4b**) is identified, besides an unknown titanium-containing species.²⁴ The 17*H*-isomer **4b** is the thermodynamically preferred one, compared to 8*bH*-tetrabenzob[*a,c,g,i*]fluorene (**4a**) as the kinetic one.²¹ The former can be easily obtained as needle-shaped monoclinic crystals, suitable for X-ray diffraction, directly from solutions of **10**. 17*H*-Tetrabenzob[*a,c,g,i*]fluorene (**4b**) crystallizes in space group *P2/c* with four molecules per unit cell (Figure 7).

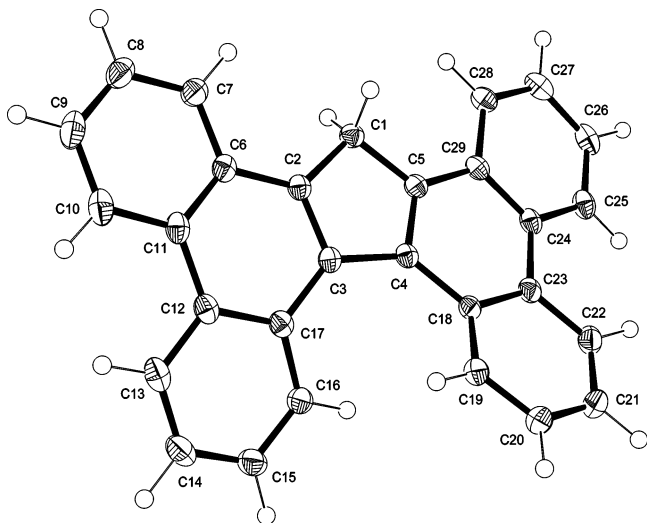


Figure 7. ORTEP plot of the solid-state molecular structure of 17*H*-tetrabenzofluorene (**4b**). All protons are freely refined; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [deg]: C(1)–C(2) 1.5022(16), C(2)–C(3) 1.3718(16), C(3)–C(4) 1.4809(16), C(4)–C(5) 1.3719(15), C(1)–C(5) 1.4971(16), C(17)–C(3)–C(4)–C(18) 22.3(2).

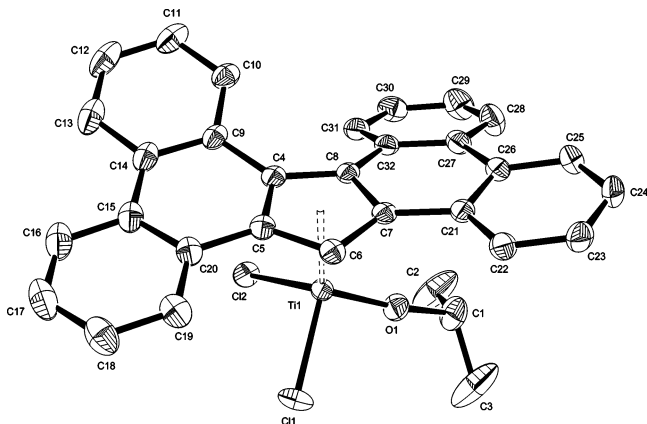


Figure 8. ORTEP plot of the solid-state molecular structure of **11**. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [deg]: Ti(1)–Ct(1) 2.049, Ti(1)–O(1) 1.733(3), Ti(1)–Cl(1) 2.284(9), Ti(1)–Cl(2) 2.285(7), O(1)–C(1) 1.426(3), C(4)–C(5) 1.417(3), C(4)–C(8) 1.446(3), C(5)–C(6) 1.422(3), C(6)–C(7) 1.416(3), C(7)–C(8) 1.423(3), Ti(1)–O(1)–C(1) 173.25(1), C(9)–C(4)–C(8)–C(32) 21.3(4).

The formation of 17*H*-tetrabenzofluorene (**4b**) also occurs by deliberately protonating **10**, which leads to the assumption that the decomposition process in polar solvents might employ an intramolecular proton transfer, e.g., due to the potential acidity of the *O*^{*i*}Pr group. Reacting **9** with **5** in toluene, the Tbf complex **11** can be isolated as red crystals (mp 208 °C). Suitable crystals for X-ray structure determination are obtained by layering the mother liquor with *n*-hexane (Figure 8). Being in space group *P*₂₁/*c*, the cell unit contains four molecules. The decrease of electron density on the titanium center leads to a significantly shortened Ti(1)–Ct(1) distance of 2.049 Å, as opposed to compound **10**, and therefore to a tighter bond between titanium and the spectator ligand. The Ti(1)–O(1) distance (1.733(3) Å) is indicative of an expected *d*π–*p*π interaction, leading to a large Ti–O–C angle of 173.25(1)°. As opposed to **10**, compound **11** is stable in all solvents.

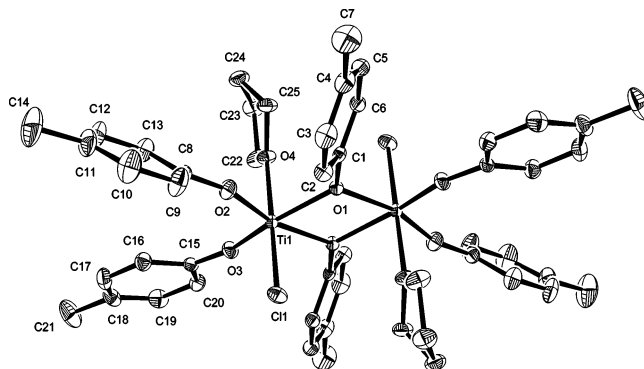
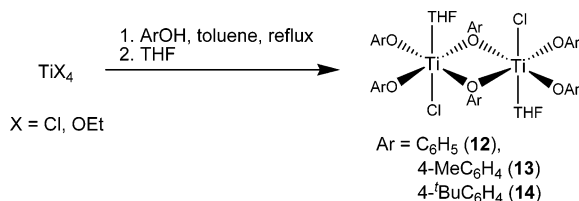


Figure 9. ORTEP plot of the solid-state molecular structure of **13**. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [deg]: Ti(1)–Cl(1) 2.343(4), Ti(1)–O(1) 2.056(3), Ti(1)–O(2) 1.789(8), Ti(1)–O(3) 1.808(4), Ti(1)–O(4) 2.142(4), O(1)–C(1) 1.383(4), O(2)–C(8) 1.354(3), O(3)–C(15) 1.351(0), Ti(1)–O(1)–C(1) 125.94(8), Ti(1)–O(2)–C(8) 164.01(1), Ti(1)–O(3)–C(15) 164.44(1).

Scheme 6



The preparation of Tbf-titanium phenoxides involved the development of a suitable type of chlorotitanium aryloxy as starting material since most complexes of the general formula ClTi(OAr)₃X_{*n*} (Ar = any phenyl, X = Lewis base, *n* = 0–2) are often only obtained as highly viscous oils or gums and would thus be quite inconvenient to handle.³⁴ In comparison to the corresponding aliphatic alkoxides titanium aryloxides are more Lewis-acidic due to a σ^{*n*} → π* interaction between the lone pair of the oxygen atom and an antibonding orbital of the aryl-ring system.³⁵ They can easily be reacted with Lewis bases to form adducts.^{36,37} In our search for a convenient starting material for the preparation of TbfTi(OAr)₃ complexes, TiCl₄ or Ti(OEt)₄ was refluxed with different phenols (phenol, 4-methylphenol, and 4-*tert*-butylphenol) in toluene (Scheme 6). After evaporation of all volatiles the resulting residues were redissolved in THF and layered with *n*-hexane to give red to orange crystalline compounds {ClTi(OAr)₃(THF)}₂ (**12**–**14**). The nearly air-stable and crystalline aryloxides **12** (mp 94 °C), **13** (mp 109 °C), and **14** (mp 125 °C) are highly soluble in common solvents with the exception of *n*-hexane.

Suitable crystals of **13** for X-ray diffraction were obtained from a THF solution layered with *n*-hexane. Compound **13** crystallized as monoclinic red-orange crystals in space group *P*₂₁/*c*. The phenoxide **13** is characterized by the formation of two equivalent molecule parts, bridged by phenolate ligands (Figure 9). Each titanium atom is coordinated in an octahedral

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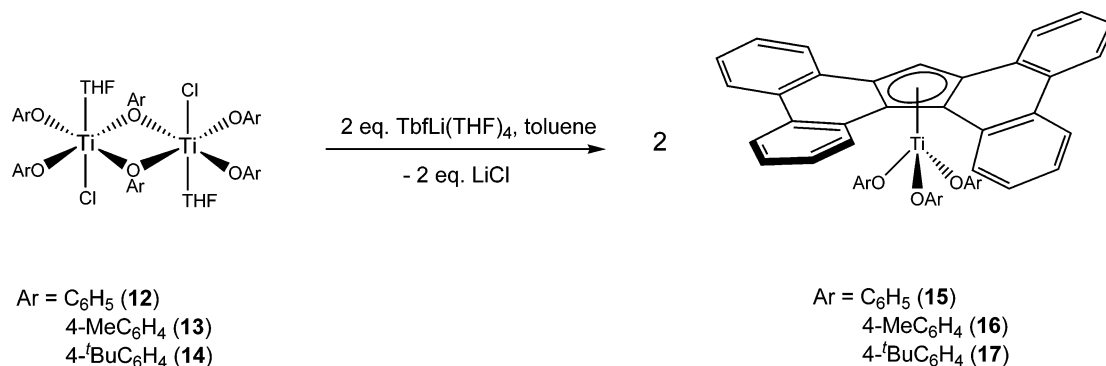
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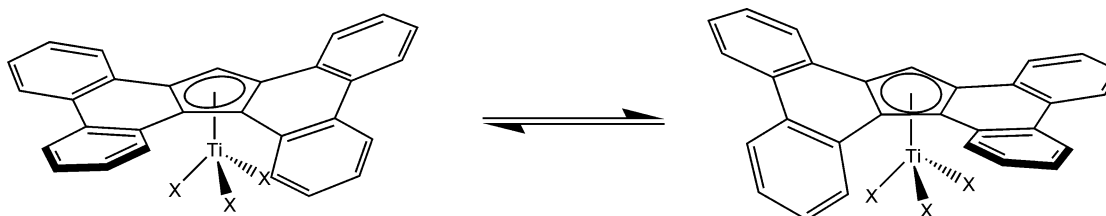
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Scheme 7



Scheme 8



fashion; the Ti(1)–O(1) (2.056(3) Å) bond is found to be longer than Ti(1)–O(2) (1.789(8) Å) and Ti(1)–O(3) (1.808(4) Å). The Ti(1)–Cl(1) bond (2.343(4) Å) is longer than expected (2.305 Å),³⁸ whereas the bond length to the coordinated THF molecule is in the typical range (2.142(4) Å).

Reacting the chlorotitanium triphenoxides **12**, **13**, and **14** with **5** in cyclohexane or toluene at ambient temperature yields mononuclear tetrabenzofluorenyltitanium triaryloxides TbfTi(OAr)₃ (Ar = C₆H₅ (**15**), 4-MeC₆H₄ (**16**), 4-tBuC₆H₄ (**17**)). These Tbf-titanium aryloxides are obtained as red crystalline solids (mp 153 °C (**15**), 154 °C (**16**), 173 °C (**17**)) showing acceptable solubilities in common solvents with the exception of *n*-hexane. Layering the mother liquors with *n*-hexane yielded crystals suitable for X-ray diffraction of compounds **15** and **16** (Figures 10, 11). Any attempts to obtain crystals of compound **17** that would have been suitable for X-ray diffraction have not been successful so far. Compound **15** crystallizes in the monoclinic space group *P*2₁/*n* with four molecules per unit cell, whereas **16** crystallizes in the triclinic space group *P* $\bar{1}$ with two molecules per unit cell.

The Tbf complexes **15** and **16** are characterized by the formation of a tetrahedral-coordinated titanium center. The Ti(1)–O distances in **15** (2.069 Å) and **16** (2.067 Å) are shorter than those in **10** (2.120 Å). Similar to **10**, also for **15** two shorter (av 1.80 Å) and one longer Ti(1)–O(1) bond (1.851(6) Å) are found. The short distances correlate also as in **10** to the Ti–O–C angles. For **16** three different Ti–O bond lengths are found. Short contacts of the aromatic rings (center of C(18)/C(23) and C(42)/C(47) 3.78 Å) in **15** are indicative again of a face-to-face π – π stacking.²⁵

Due to the helical shape of the ligand, all η^5 -tetrabenzofluorenyltitanium complexes exhibit C₁-symmetry, giving two optical isomers, both of which crystallize as a racemate leading to centrosymmetric space groups (Table 5).

NMR spectroscopy reveals that in solution both isomers rapidly interconvert, as instead of a 2-fold signal set, which would be indicative of two isomers, only half the signal set can be observed at ambient temperature. Thus temperature-

dependent NMR experiments were conducted in order to determine the energetic barrier for interconversion of both isomers (Figure 12). A sample of compound **16**, which was chosen due to its good solubility and stability, was dissolved in CDCl₃, and measurements were taken within a temperature range of 300–203 K in the attempt to “freeze in” the flipping movement of the benzo-fused rings. Unfortunately, a complete stoppage and thus a 2-fold signal set could not be achieved. The spectra show only what seems to be a deceleration of the interconversion movement as the doublet for the H-8/H-9 protons—which cause the ligand to twist helically due to their steric repulsion—is shifted upfield with decreasing temperature.

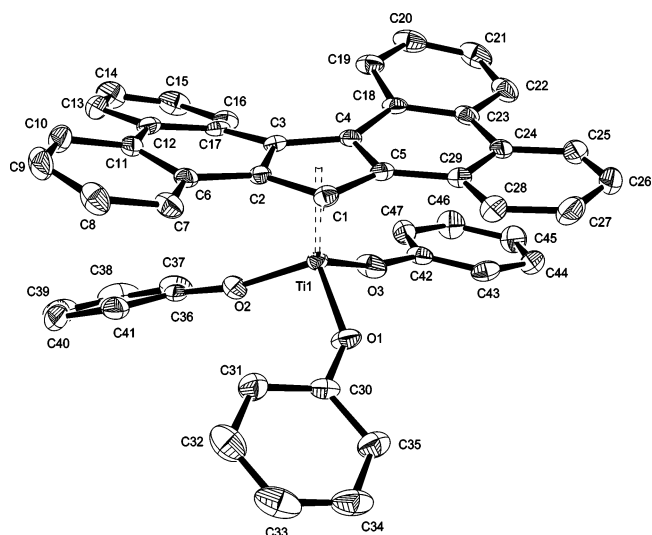


Figure 10. ORTEP plot of the solid-state molecular structure of **15**. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [deg]: Ti(1)–O(1) 2.069, Ti(1)–O(2) 1.799(3), Ti(1)–O(3) 1.806(9), O(1)–C(30) 1.358(8), O(2)–C(36) 1.348(7), O(3)–C(42) 1.356(3), C(1)–C(2) 1.402(3), C(1)–C(5) 1.424(4), C(2)–C(3) 1.438(3), C(3)–C(4) 1.452(4), C(4)–C(5) 1.431(3), Ti(1)–O(1)–C(30) 142.76(1), Ti(1)–O(2)–C(36) 166.11(1), Ti(1)–O(3)–C(42) 161.52(1), C(17)–C(3)–C(4)–C(18) 11.7(5).

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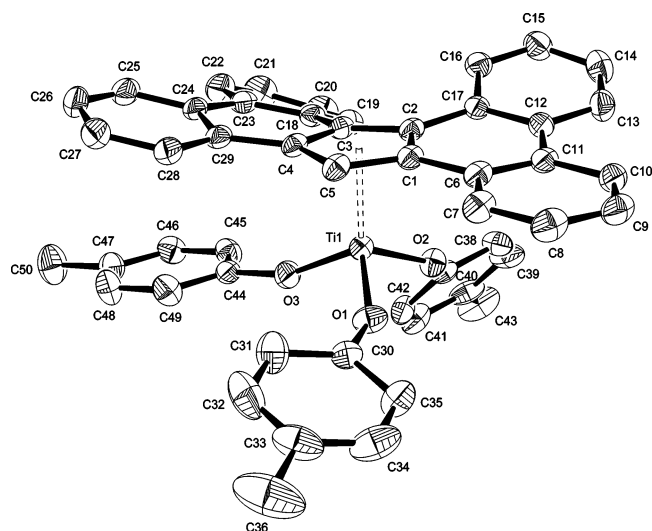


Figure 11. ORTEP plot of the solid-state molecular structure of **16**. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [deg]: Ti(1)–Ct(1) 2.067, Ti(1)–O(1) 1.829(9), Ti(1)–O(2) 1.844(5), Ti(1)–O(3) 1.800(0), O(1)–C(30) 1.353(2), O(2)–C(37) 1.359(2), O(3)–C(44) 1.361(2), C(1)–C(2) 1.431(2), C(1)–C(5) 1.418(3), C(2)–C(3) 1.437(3), C(3)–C(4) 1.433(3), C(4)–C(5) 1.417(3), Ti(1)–O(1)–C(30) 150.10(1), Ti(1)–O(2)–C(37) 141.72(1), Ti(1)–O(3)–C(44) 160.28(1), C(18)–C(3)–C(19)–C(17) 13.3(4).

When comparing the NMR data of the different η^5 -tetrabenzofluorenyltitanium complexes (Table 2), one difference between the compounds measured in CDCl_3 is striking: Whereas the proton signals of H-1/H-16, H-4/H-13, H-5/H-12, and H-17

Table 1. Selected ^1H (ppm, C_6D_6 , 500.13 MHz, 300 K) NMR Data of Compounds **5** and **6**

	5	6
H-1/H-16	8.48	8.49
H-2/H-15	7.53	7.55
H-3/H-14	7.40	7.41
H-4/H-13	8.59	8.60
H-5/H-12	8.60	8.62
H-6/H-11	7.35	7.36
H-7/H-10	7.48	7.48
H-8/H-9	9.30	9.28
H-17	7.690	7.670

for the triaryloxide derivatives all fall in the same range the above-mentioned proton signals of compound **11** are shifted downfield about 0.2 ppm. Most interestingly, this shift correlates with different Ti–Ct bond lengths and twist angles of the helically shaped ligand found in X-ray crystal structures (Table 3). The torsion angle between the carbon atoms denoted a, b, c, and d can be taken as indicative of the ligands' helical twisting. Interestingly, this torsion angle is almost identical in 17H-Tbf (**4b**), in the anion of **6**, and in the complexes **10** and

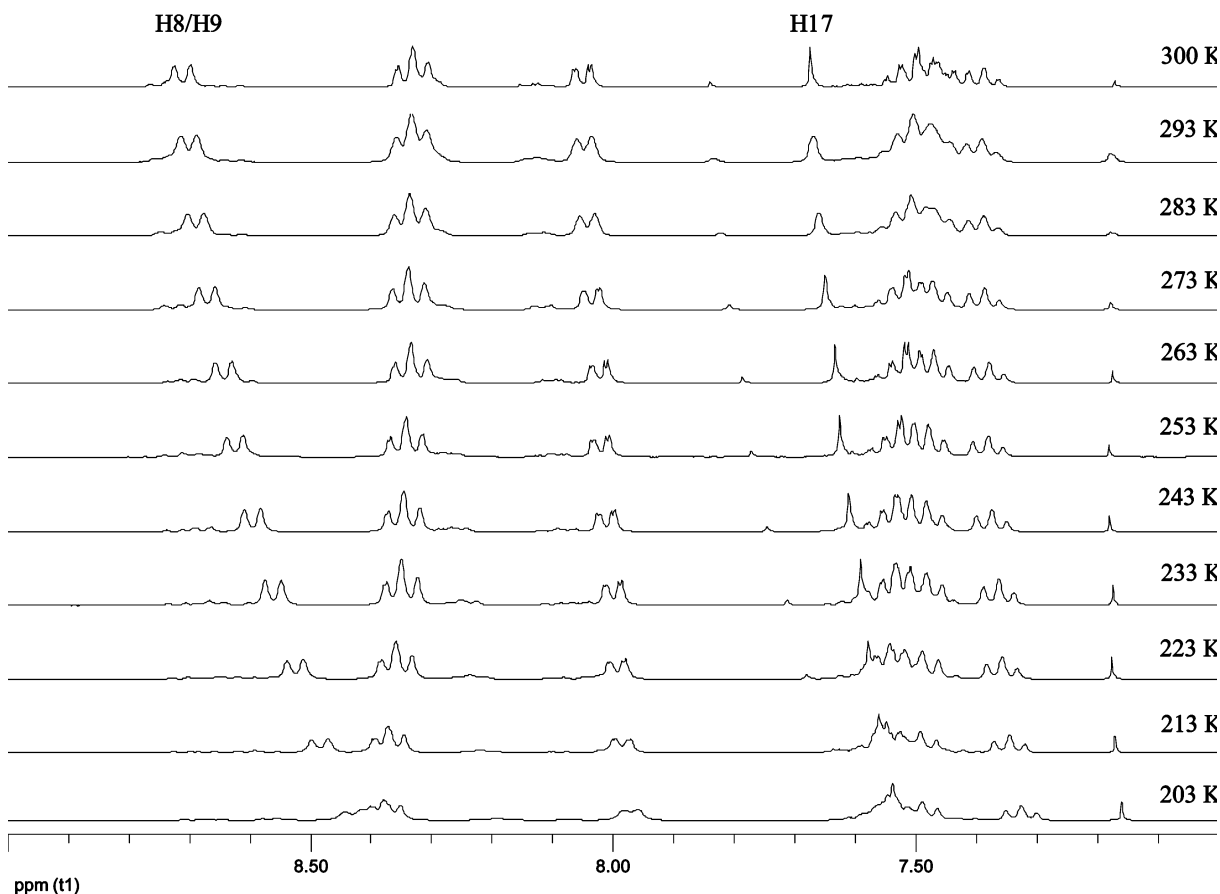


Figure 12. Variable-temperature ^1H NMR spectrum (300.13 MHz, CDCl_3) of **16**. Only the range relevant for the tetrabenzofluorenyl ligand is shown.

Table 2. Selected ^1H NMR Data (500.13 MHz, 300 K) of Compounds **10, **11**, and **15–17** (numbering scheme in accordance with Table 1)**

	10	11	15	16	17
solvent	C_6D_6	CDCl_3	CDCl_3	CDCl_3	CDCl_3
H-1/H-16	8.24	8.39	8.14	8.16	8.14
H-2/H-15	7.47	<i>a</i>	7.60	7.63	7.58
H-3/H-14	<i>a</i>	<i>a</i>	7.53	7.56	7.51
H-4/H-13	8.41	8.60	8.38	8.43	8.33
H-5/H-12	8.43	8.63	8.41	8.45	8.36
H-6/H-11	<i>a</i>	<i>a</i>	7.48	7.50	7.48
H-7/H-10	<i>a</i>	7.60	7.56	7.59	7.54
H-8/H-9	9.14	8.85	8.81	8.83	8.81
H-17	7.596	8.014	7.800	7.795	7.793

^a Signals could not be clearly assigned.

11 despite their different electronic situations. In the triaryloxide complexes **15** and **16** the torsion angle declines from an average 22° (**6**, **10**, **11**) to $11.7(5)^\circ$ (**15**) and $13.3(4)^\circ$ (**16**), respectively.

Comparison of bond lengths in the Tbf moiety reveals that the C–C distances of the five-membered ring are strongly influenced by the charge of the molecule. In the Li salts **5** and **6** the C17–C18 and C17–C29 bonds (av 1.40 Å, numbering in accordance with Table 1) are found to be shorter than in the neutral compounds **4b** and **7** (av 1.50 Å). A similar shortening is observed for the titanium complexes **10**, **11**, **15**, and **16** (av 1.41 Å). The C24–C29 as well as the C18–C23 bond is elongated comparing the neutral (av 1.37 Å), ionic, and titanium derivatives (av 1.43 Å). Also the C23–C24 distances are influenced, as expected, for the neutral derivatives, 1.40 Å (av), the lithium salts, 1.43 Å (av), and the titanium complexes, 1.44 Å (av). The other C–C distances are less influenced by electronic effects. However, an increasing aromatic character of the annelated rings is found comparing **4b** and **7** with the lithium as well as the titanium complexes. In such a way the C–C distances C20–C21, C26–C27 (**x**); C18–C19, C28–C29 (**y**), and C23–C22, C24–C25 (**z**) of the central six-membered rings increase significantly from the neutral to the lithium up to the titanium Tbf derivatives (**x**, av: neutral 1.45, Li 1.46, Ti 1.47 Å; **y**, av: neutral 1.42, Li: 1.44, Ti 1.45 Å; **z**, av: neutral 1.45, Li 1.45, Ti 1.46 Å).

Styrene Polymerization. To assess the capability of the complexes as catalysts in polymerization reactions, the coordination polymerization of styrene as a monomer was investigated in the presence of the η^5 -tetrabenzobenzofluorenyltitanium complexes. Methylalumoxane (MAO) was selected as a cocatalyst and was used in relatively low concentrations with regard to the transition metal, corresponding to a molar ratio MAO/Ti = 110/1. In addition, triisobutylaluminum (TIBA) was used as a strong reducing agent for the titanium compound and was added in a molar ratio of TIBA/Ti = 25/1. The polymerizations were initiated at a high molar ratio styrene/Ti = 700 000/1 by addition of the catalyst premix solution to the styrene monomer at 30°C . The polymerization results (Table 4) indicate a significant activity of all η^5 -tetrabenzobenzofluorenyltitanium complexes as catalysts in the coordination polymerization of styrene with MAO as cocatalyst. However, the polymerization activity of the different complexes varies depending on the kind of ancillary ligands in addition to the η^5 -tetrabenzobenzofluorenyl group. The activity increases in the following order: **11** (1420 kg sPS/(mol Ti $\times$ mol styrene $\times$ h)) < **17** (3400) < **16** (3740) < **10** (6040) < **15** (6720). On the other hand, the stereospecificity of the complexes as catalysts in the coordination polymerization of styrene can be determined by investigation of the melting points of the polystyrenes received by DSC (Table 4). All polymer samples obtained exhibited high melting points,

indicating syndiotactic polymers. Furthermore, on the basis of the melting points the polystyrenes show a very high degree of syndiotacticity, comparable to about 100% of the rrrrr-hexad fraction via ^{13}C NMR, in comparison to, for example, syndiotactic polystyrene of a melting point of 257°C and a rrrrr-hexad fraction of 89% received with CpTiCl_3 as catalyst.³⁹

Conclusions

The efficient synthesis of **4a** allows an effective access to the organometallic chemistry of the tetrabenzobenzofluorenyl moieties. Using the remarkable η^0 -coordinated lithium salts **5** and **6** monosubstituted titanium(IV) alkoxides and aryloxides become available. The tetrabenzobenzofluorenyl moiety is coordinated as a sterically demanding Cp derivative in a η^5 -fashion to the titanium centers. The formal benzannulation of the fluorenyl system, as present in the Tbf titanium complexes, leads to large mono-Cp complexes of high thermal stability compared to η^5 -fluorenyl titanium derivatives. Due to its helical twist, the η^5 -coordinated tetrabenzobenzofluorenyl ligands show C_1 -symmetry in the solid state but seem to interconvert in solution. Additionally, the titanium complexes were subjected to polymerization experiments of styrene to some extent.

Experimental Section

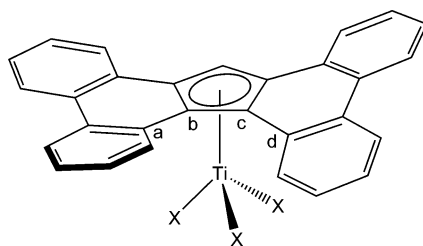
Reagents and General Techniques. All operations were performed in a nitrogen atmosphere with rigorous exclusion of oxygen and moisture using glovebox or Schlenk techniques. All chemicals used were reagent grade or higher and purified according to standard protocols. Nonchlorinated solvents were distilled over Na/K alloy and benzophenone under nitrogen atmosphere. Dichloromethane was distilled over CaH_2 under nitrogen atmosphere. Trichlorotitanium isopropoxide (**9**) was prepared according to literature.⁴⁰ ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 500 (^1H , 500.13 MHz; ^{13}C , 125.75 MHz) spectrometer. Variable-temperature NMR experiments were conducted on a Bruker Avance 300 (^1H , 300.13 MHz) spectrometer. ^1H chemical shifts are referenced to residual solvent protons; ^{13}C spectra were referenced to CDCl_3 or C_6D_6 . Signal assignment was done according to H,H- and C,H-COSY and NOE measurements. Electron impact (EI) mass spectra were taken on a Finnigan-MAT 95 spectrometer. IR spectra were recorded on a BIO-RAD FTS-7 spectrometer using KBr pellets. Elemental analyses were carried out by the Analytische Laboratorien GmbH, Lindlar (Germany). Melting points were determined using a "Mel-Temp" by Laboratory Devices, Cambridge.

X-ray Diffraction. Single-crystal experiments were performed on a Stoe IPDS diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct phase determination and refined by full-matrix least-squares techniques against F^2 with the SHELXL-97 program system.⁴¹ Crystallographic details are given in Table 5.

Modified Synthesis of Bis(phenanthren-9-yl)methanol.¹⁹ A solution of 50 g (194 mmol) of 9-bromophenanthrene in 80 mL of THF is dropped within 20 min onto a 4.7 g (196 mmol) portion of magnesium turnings under vigorous stirring. Heat evolves, and for reaction's completeness the mixture is stirred overnight. Subsequently, a solution of 6.1 mL (99 mmol) of methylformiate in 25 mL of THF is added to the reaction mixture within 20 min, whereupon the solution turned from green to brown. After 2 h the reaction mixture is poured into 200 mL of 2 M HCl, yielding a

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Table 3. Comparison of Selected Bond Lengths and Torsion Angles



	4b	5	6	10	11	15	16
a, b, c, d [deg]	22.3(2)	30.4(4)	22.2(3)	22.4(4)	21.3(4)	11.7(5)	13.3(4)
Cr–Ti [Å]				2.120	2.049	2.069	2.067

Table 4. Polymerization of Styrene (30 °C, styrene/MAO/TIBA/Ti = 700 000/110/25/1)

run no.	catalyst	polymerization time [min]	activity ^a	melting point ^b [°C]
1	11	120	1420	267.2
2	10	120	6040	268.0
3	15	60	6720	266.2
4	15	120	4720	265.6
5	16	60	3740	266.4
6	16	120	2000	266.2
7	17	60	3400	266.0
8	17	120	2000	267.0

^a Activity in kg sPS/(mol Ti × mol styrene × h). ^b Melting point of the polymer.

sticky white precipitate, which is filtered and washed with 100 mL of water and 200 mL of diethyl ether. Afterward the product is dried in vacuo, giving 31.6 g (82.2 mmol, 84. 6%) of bis-(phenanthren-9-yl)methanol. Mp: 235 °C. ¹H NMR (CDCl₃, 500.13 MHz, 300 K) [ppm]: δ 8.78 (d, 2 H, H-5, H-5b), 8.70 (d, 2 H, H-4, H-4b), 8.12 (d, 2 H, H-8, H-8b), 7.811 (s, 2 H, H-10, H-10b), 7.74 (d, 2 H, C-1, C-1b), 7.68–7.64 (m, 4 H, H-), 7.54 (m, 4 H), 7.308 (s, 1 H, CHOH). ¹³C NMR (CDCl₃, 124.75 MHz, 300 K) [ppm]: δ 136.4 (C-14, C-14b), 131.4 (C-11, C-11b), 131.0 (C-13, C-13b), 130.5 (C-12, C-12b), 130.1 (C-9, C-9b), 129.1 (C-1, C-1b), 127.0, 126.8 (C-2, C-2b, C-7, C-7b), 126.5 (C-3, C-3b, C-5, C-5b), 126.2 (C-10, C-10b), 124.4 (C-8, C-8b), 123.3 (C-5, C-5b), 122.5 (C-4, C-4b), 69.9 (CHOH). IR (KBr) [cm⁻¹]: ν̄ 3540 (s), 3464 (s), 3072 (s), 1938 (m), 1802 (m), 1604 (s), 1489 (m), 1441 (m), 1401 (m), 1243 (m), 1210 (m), 1066 (s), 1036 (s), 965 (m), 906 (m), 889 (m), 802 (m), 751 (s), 718 (s). MS (EI, 70 eV): *m/z* (relative intensity) 384.1 (70) [M⁺], 365.1 (10) [M – OH], 205.2 (100), 178.2 (50).

Modified Synthesis of 8bH-Tetrabenzo[*a,c,g,i*]fluorene (4a).¹⁹ To a suspension of 28.9 g (75.14 mmol) of bis(phenanthren-9-yl)methanol in 250 mL of dichloromethane is added 50 mL of trifluoroacetic acid within 20 min. After stirring overnight the yellow suspension is evaporated to dryness and 200 mL of chloroform is added. The mixture is refluxed for 30 min and filtered after cooling to ambient temperature in order to remove residual trifluoroacetic acid. The yellow precipitate is dried in vacuo, yielding 18.7 g of product (51 mmol, 68%). Mp: 277 °C. ¹H NMR (CDCl₃, 500.13 MHz, 300 K) [ppm]: δ 8.79 (m, 2 H, H-12, H-13), 8.26 (m, 1 H, H-16), 8.09 (dd, 1 H, ³*J*_{HH} = 7.4 Hz, ⁴*J*_{HH} = 1.5 Hz, H-9), 7.97 (m, 1 H, ³*J*_{HH} = 7.4 Hz, ⁴*J*_{HH} = 1.2 Hz, H-4), 7.84 (m, 1 H, ³*J*_{HH} = 7.5, H-5), 7.72 (dd, 1 H, ³*J*_{HH} = 7.2 Hz, ⁴*J*_{HH} = 1.6 Hz, H-1), 7.70–7.68 (m, 2 H, H-10, H-15), 7.66–7.63 (m, 2 H, H-11, H-14), 7.46 (m, 1 H, ³*J*_{HH} = 7.7 Hz, H-8), 7.46 (d, 1 H, ⁴*J*_{HH} = 2.2 Hz, H-16), 7.42 (ddd, 1 H, ³*J*_{HH} = 7.4 Hz, ³*J*_{HH} = 7.4 Hz, ⁴*J*_{HH} = 1.5 Hz, H-3), 7.39 (ddd, 1 H, ³*J*_{HH} = 7.4 Hz, ³*J*_{HH} = 7.4 Hz, ⁴*J*_{HH} = 1.3 Hz, H-2), 7.32 (dd, 1 H, ³*J*_{HH} = 7.4 Hz, ³*J*_{HH} = 7.5 Hz, H-6), 7.11 (m, 1 H, ³*J*_{HH} = 7.5 Hz, ³*J*_{HH} = 7.5 Hz, H-7), 5.39 (m, 1 H, H-23). ¹³C NMR (CDCl₃, 124.75 MHz, 300 K) [ppm]: δ 148.5 (C-18), 141.4 (C-29), 137.5 (C-24), 135.5, 135.4 (C-21,

C-22), 134.2 (C-5), 133.3 (C-19), 130.8 (C-27), 130.5 (C-25), 129.5 (C-26), 128.5 (C-3), 128.3 (C-2), 127.6 (C-28), 127.3 (C-7), 127.0, 127.0 (C-6, C-8), 126.7 (C-14, C-15), 126.4 (C-10), 126.3 (C-9), 125.9 (C-5), 125.2 (C-11), 125.0 (C-1), 124.7 (C-16), 123.7 (C-4), 123.6, 123.3 (C-13, C-12), 121.3 (C-17), 53.2 (C-23). IR (KBr) [cm⁻¹]: ν̄ 3057 (m), 933 (m), 1690 (m), 1603 (m), 1497 (s), 1436 (m), 1381 (m), 1324 (m), 1264 (m), 1228 (m), 1160 (w), 1094 (w), 1040 (w), 933 (w), 856 (w), 742 (s), 618 (w), 517 (w), 436 (w). MS (EI, 70 eV): *m/z* (relative intensity) 366.0 (100) [M⁺], 181.9 (30), 175.4 (10).

Synthesis of TbLi(THF)₄ (5). To a suspension of 2.5 g (6.82 mmol) of 8bH-tetrabenzo[*a,c,g,i*]fluorene (4a) in 50 mL of THF is added 4.4 mL (7.04 mmol) of *n*-butyllithium in *n*-hexane (1.6 M), whereupon a dark orange solution is formed, which is cooled to –80 °C to give 7.93 g of 4 as orange-yellow crystals (11.04 mmol, 81%). Mp: 81 °C. ¹H NMR (C₆D₆, 500.13 MHz, 300 K) [ppm]: δ 9.30 (d, 2 H, ³*J*_{HH} = 8.2 Hz, H-8, H-9), 8.60 (d, 2 H, ³*J*_{HH} = 9.8 Hz, H-5, H-12), 8.59 (d, 2 H, H-4, H-13), 8.48 (d, 2 H, ³*J*_{HH} = 7.7 Hz, H-1, H-16), 7.690 (s, 1 H, H-17), 7.53 (m, 2 H, H-2, H-15), 7.48 (m, 2 H, H-7, H-10), 7.40 (m, 2 H, H-3, H-14), 7.35 (m, 2 H, H-6, H-11), 2.95 (t, 16 H, ³*J*_{HH} = 7.4 Hz, OCH₂), 1.04 (t, 16 H, ³*J*_{HH} = 7.4 Hz, OCH₂CH₂). ¹³C NMR (C₆D₆, 124.75 MHz, 300 K) [ppm]: δ 133.0 (C-22, C-25), 131.8 (C-19, C-28), 129.3 (C-20, C-27), 128.3 (C-21, C-26), 126.4 (C-2, C-15), 126.2 (C-7, C-10), 125.4 (C-18, C-29), 124.8 (C-8, C-9), 124.2 (C-5, C-12), 123.7 (C-1, C-16), 123.6 (C-4, C-13), 123.4 (C-3, C-14), 122.2 (C-6, C-11), 112.6 (C-23, C-24), 87.4 (C-17), 67.7 (OCH₂CH₂), 25.2 (OCH₂CH₂). Anal. Calcd for C₄₅H₄₉LiO₄: C, 81.79; H, 7.47. Found: C, 82.04; H, 7.34.

Synthesis of TbLi(DME)₃ (6). To a solution of 1 g (2.73 mmol) of 8bH-tetrabenzo[*a,c,g,i*]fluorene (4a) in 160 mL toluene is added 1.9 mL (3.04 mmol) of *n*-butyllithium in *n*-hexane. The reaction mixture is stirred overnight, and the white precipitate is filtered off, washed two times with 20 mL of toluene, and dried in vacuo. Subsequently 300 mg (0.94 mmol) of tetrabenzo[*a,c,g,i*]fluorenyllithium is dissolved in 80 mL of DME to form a bright yellow solution, which is cooled to –20 °C to yield 315 mg (0.47 mmol, 50%) of yellow crystals. Melting point: 98 °C. ¹H NMR (C₆D₆, 500.13 MHz, 300 K) [ppm]: δ 9.28 (d, 2 H, ³*J*_{HH} = 8.3 Hz, H-8, H-9), 8.62 (d, 2 H, ³*J*_{HH} = 7.8 Hz, H-5, H-12), 8.60 (d, 2 H, ³*J*_{HH} = 7.8 Hz, H-4, H-13), 8.49 (d, 2 H, ³*J*_{HH} = 7.8 Hz, H-1, H-16), 7.67 (s, 1 H, H-17), 7.55 (m, 2 H, H-2, H-15), 7.48 (m, 2 H, H-7, H-10), 7.41 (m, 2 H, H-4, H-14), 7.36 (m, 2 H, H-6, H-11), 2.72 (s, 12 H, CH₂), 2.64 (s, 18 H, CH₃). ¹³C NMR (C₆D₆, 124.75 MHz, 300 K) [ppm]: δ 137.5 (C-17), 132.9 (C-22, C-25), 131.6 (C-19, C-28), 129.3 (C-20, C-26), 128.0 (C-21, C-27), 126.6 (C-2, C-15), 125.5 (C-18, C-29), 125.4 (C-7, C-10), 124.9 (C-8, C-9), 124.3 (C-5, C-12), 123.7, 123.7, 123.6 (C-1, C-16, C-4, C-13, C-3, C-14), 122.4 (C-6, C-11), 112.5 (C-23, C-24). Anal. Calcd for C₄₁H₄₇LiO₃: C, 76.61; H, 7.37. Found: C, 78.19; H, 6.40.

Formation of Bis(17-tetrabenzo[*a,c,g,i*]fluorene) (7) by Reaction of 4 with TiCl₄(THF)₂. To a solution of 455 mg (1.40 mmol) of TiCl₄(THF)₂ in 50 mL of THF is added 925 mg (1.40 mmol) of

Table 5. Crystal Structure Data for Compounds 4b, 5–7, 10, 11, 13, 15, and 16

	4b	5	6	7	10	11	13	15	16
empirical formula	C ₂₉ H ₁₈	C ₄₅ H ₄₉ LiO ₄	C ₄₁ H ₄₇ LiO ₆ ·0.25C ₄ H ₁₀ O ₂	C ₅₈ H ₃₄ ·C ₂ H ₂ Cl ₂	C ₃₈ H ₃₈ O ₃ Ti	C ₃₂ H ₂₄ Cl ₂ OTi	C ₅₀ H ₅₈ Cl ₂ O ₈ Ti	C ₄₇ H ₃₂ O ₃ Ti	C ₅₀ H ₃₈ O ₃ Ti
fw	366.43	660.78	665.26	815.78	590.58	543.31	953.66	692.63	734.70
color	yellow	yellow	orange-yellow	yellow	yellow	red	orange-red	yellow	yellow
cryst dimens, mm	1.20 × 0.19 × 0.10	0.50 × 0.34 × 0.33	1.10 × 0.45 × 0.15	0.30 × 0.24 × 0.18	0.45 × 0.43 × 0.42	0.40 × 0.31 × 0.28	0.55 × 0.29 × 0.24	0.28 × 0.21 × 0.09	0.32 × 0.20 × 0.19
cryst syst	monoclinic	triclinic	triclinic	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic	triclinic
space group	<i>P</i> 2/ <i>c</i>	<i>P</i> 1	<i>P</i> 1	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> bca	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1
<i>a</i> , Å	18.4562(14)	12.8899(11)	12.2073(6)	13.8807(8)	16.4719(8)	12.9702(6)	11.9750(4)	14.2737(9)	10.0203(5)
<i>b</i> , Å	5.0962(2)	17.0343(13)	13.4821(7)	20.0576(8)	17.0792(7)	10.6352(7)	23.7536(7)	15.7569(8)	13.5219(8)
<i>c</i> , Å	19.1459(16)	18.0571(13)	23.8558(14)	14.8992(10)	22.1152(14)	18.6582(9)	8.4337(2)	15.2020(8)	14.6028(8)
α , deg	90	106.810(8)	75.144(6)	90	90	90	90	90	87.455(7)
β , deg	91.022	96.169(9)	76.299(6)	110.980	90	93.630(6)	92.273	99.529(7)	75.017(6)
γ , deg	90	105.422(9)	82.717(6)	90	90	90	90	90	77.620(6)
<i>V</i> , Å ³	1800.5(2)	3585.0(5)	3677.8(3)	3873.1(4)	6221.6(6)	2568.6(2)	2397.07(12)	3371.9(3)	1866.75(18)
<i>Z</i>	4	4	4	4	8	4	2	4	2
<i>D</i> _{calcd} , g cm ³	1.352	1.224	1.201	1.399	1.261	1.404	1.321	1.364	1.307
μ , mm ^{−1}	0.077	0.076	0.079	0.212	0.311	0.566	0.496	0.299	0.274
<i>T</i> , K	153	153	153	153	153	153	153	153	153
θ range, deg	1.38 to 26.00	2.25 to 26.05	2.10 to 26.04	2.50 to 26.05	2.47 to 25.99	2.21 to 26.03	2.42 to 26.00	2.14 to 26.04	2.10 to 26.10
no. of rflns collected	14 846	40 561	45 760	31 892	49 297	21 824	23 709	33 096	23 098
no. of indep rflns	3328 [<i>R</i> (int) = 0.0446]	13 147 [<i>R</i> (int) = 0.0807]	13 458 [<i>R</i> (int) = 0.0572]	7507 [<i>R</i> (int) = 0.0617]	5898 [<i>R</i> (int) = 0.0805]	4713 [<i>R</i> (int) = 0.0538]	4497 [<i>R</i> (int) = 0.0387]	6618 [<i>R</i> (int) = 0.1291]	6847 [<i>R</i> (int) = 0.0598]
no. of rflns <i>I</i> > 2 σ (<i>I</i>)	2514	6785	8856	4918	3801	3416	3793	3348	4553
abs corr	none	none	none	numerical	numerical	numerical	numerical	none	numerical
max., min. transmn	0.9924 and 0.9137	0.9754 and 0.9630	0.9882 and 0.9180	0.9628 and 0.9390	0.8805 and 0.8727	0.8577 and 0.8054	0.8902 and 0.7720	0.9736 and 0.9210	0.9498 and 0.9175
final <i>R</i> indices		<i>R</i> 1 = 0.0463, w <i>R</i> 2 = 0.0910	<i>R</i> 1 = 0.0383, w <i>R</i> 2 = 0.0826	<i>R</i> 1 = 0.0364, w <i>R</i> 2 = 0.0763	<i>R</i> 1 = 0.0472, w <i>R</i> 2 = 0.1193	<i>R</i> 1 = 0.0321, w <i>R</i> 2 = 0.0742	<i>R</i> 1 = 0.0298, w <i>R</i> 2 = 0.0822	<i>R</i> 1 = 0.0399, w <i>R</i> 2 = 0.0608	<i>R</i> 1 = 0.0363, w <i>R</i> 2 = 0.0758
<i>R</i> indices (all data)		<i>R</i> 1 = 0.1059, w <i>R</i> 2 = 0.1054	<i>R</i> 1 = 0.0676, w <i>R</i> 2 = 0.0906	<i>R</i> 1 = 0.0668, w <i>R</i> 2 = 0.0835	<i>R</i> 1 = 0.0779, w <i>R</i> 2 = 0.1306	<i>R</i> 1 = 0.0517, w <i>R</i> 2 = 0.0796	<i>R</i> 1 = 0.0369, w <i>R</i> 2 = 0.0847	<i>R</i> 1 = 0.1121, w <i>R</i> 2 = 0.0732	<i>R</i> 1 = 0.0646, w <i>R</i> 2 = 0.0823

solid **5** at -78 °C. The reaction mixture was slowly warmed to ambient temperature, whereupon **7** precipitated nearly quantitatively as an orange-yellow solid, which was isolated on a glass frit and dried in vacuo. Crystals suitable for X-ray diffraction were obtained by recrystallization from dichloromethane. Mp: 363 °C dec. IR (KBr) [cm^{-1}]: $\tilde{\nu}$ 3070 (m), 2920 (w), 2327 (w), 1931 (w), 1701 (w), 1606 (w), 1495 (m), 1423 (m), 1327 (m), 1263 (m), 1232 (m), 1157 (m), 1107 (m), 1040 (m), 935 (w), 857 (w), 727 (s), 617 (w), 521 (w), 433 (w). MS (EI, 70 eV): m/z (relative intensity) 730.2 (40) [M^+], 365.2 (100) [M^{2+}].

Synthesis of $\text{Tb}(\text{O}^i\text{Pr})_3$ (10**).** A portion of 660 mg (1.00 mmol) of **5** and 260 mg (1.00 mmol) of $\text{ClTi}(\text{O}^i\text{Pr})_3$ are mixed as solids, and 60 mL of toluene is added. After stirring overnight the reaction mixture is taken to dryness and the residue is extracted with 60 mL of *n*-hexane. Cooling the yellow solution to -80 °C yields 402 mg (0.68 mmol, 68%) of **7** as yellow crystals. Mp: 135 °C. ^1H NMR (C_6D_6 , 500.13 MHz, 300 K) [ppm]: δ 9.14 (d, 2 H, $^3J_{\text{HH}} = 7.9$ Hz, H-8, H-9), 8.43 (d, 2 H, $^3J_{\text{HH}} = 7.9$ Hz, H-5, H-12), 8.41 (d, 2 H, $^3J_{\text{HH}} = 8.1$ Hz, H-4, H-13), 8.24 (d, 2 H, $^3J_{\text{HH}} = 7.7$ Hz, H-1, H-16), 7.596 (s, 1 H, H-17), 7.47 (m, 2 H, $^3J_{\text{HH}} = 7.3$ Hz, H-2, H-15), 7.43–7.37 (m, 6 H, H-3, H-6, H-7, H-10, H-14, H-11), 3.86 (q, 3 H, $^3J_{\text{HH}} = 6.1$ Hz, $\text{OCH}(\text{CH}_3)_2$), 0.58 (d, 18 H, $^3J_{\text{HH}} = 6.1$ Hz, $\text{OCH}(\text{CH}_3)_2$). ^{13}C NMR (C_6D_6 , 124.75 MHz, 300 K) [ppm]: δ 131.2 (C-19, C-28), 130.6 (C-22, C-26), 129.5 (C-20, C-27), 128.3 (C-21, C-26), 127.4 (C-8, C-9), 127.1 (C-2, C-15), 126.7, 126.1, 125.7 (C-3, C-6, C-7, C-10, C-11, C-14), 125.6 (C-18, C-29), 124.9 (C-1, C-16), 124.2 (C-5, C-12), 123.6 (C-4, C-13), 116.9 (C-23, C-24). MS (EI, 70 eV): m/z (relative intensity) 598.8 (90) [$\text{M} - \text{H}$], 531 (20), 472.8 (30), 428.7 (35), 365.8 (95), 268.9 (100), 224.9 (45), 180.9 (30), 138.9 (25). IR (KBr) [cm^{-1}]: $\tilde{\nu}$ 3077 (m), 2966 (s), 2923 (s), 2856 (m), 1604 (m), 1510 (m), 1434 (s), 1373 (m), 1326 (s), 977 (s), 848 (s), 794 (m), 751 (s), 721 (s), 594 (s). Anal. Calcd for $\text{C}_{38}\text{H}_{38}\text{O}_3\text{Ti}$: C, 77.28; H, 6.49; O, 8.13. Found: C, 77.30; H, 5.21.

Synthesis of $\text{Tb}(\text{TiCl}_2(\text{PrO}))$ (11**).** A portion of 661 mg (1.00 mmol) of **5** and 213 mg (1.00 mmol) of $\text{Cl}_3\text{Ti}(\text{O}^i\text{Pr})$ (**9**) are mixed as solids, and 40 mL of toluene is added, whereupon a red suspension is formed immediately. After 2 h the reaction mixture is filtered through a P4 glass frit. Layering the solution with 40 mL of *n*-hexane afforded red crystals of **11** (124 mg, 23%). Mp: 208 °C. ^1H NMR (CDCl_3 , 500.13 MHz, 300 K) [ppm]: δ 8.85 (d, 2 H, $^3J_{\text{HH}} = 8.1$ Hz, H-8, H-9), 8.63 (d, 2 H, $^3J_{\text{HH}} = 8.2$ Hz, H-5, H-12), 8.60 (d, 2 H, $^3J_{\text{HH}} = 5.3$ Hz, H-4, H-13), 8.39 (d, 2 H, $^3J_{\text{HH}} = 8.4$ Hz, H-1, H-16), 8.014 (s, 1 H, H-17), 7.72–7.67 (m, 6 H, H-2, H-3, H-6, H-11, H-14, H-15), 7.60 (m, 2 H, $^3J_{\text{HH}} = 7.6$ Hz, H-7, H-10), 3.42 (q, 1 H, $^3J_{\text{HH}} = 6.1$ Hz, $\text{OCH}(\text{CH}_3)_2$), 0.41 (d, 6 H, $^3J_{\text{HH}} = 6.1$ Hz, $\text{OCH}(\text{CH}_3)_2$). ^{13}C NMR (CDCl_3 , 124.75 MHz, 300 K) [ppm]: δ 131.7 (C-19, C-28), 131.2 (C-22, C-25), 128.6 (C-21, C-26), 127.9 (C-8, C-9), 127.6 (C-20, C-27), 127.5 (C-18, C-29), 126.3 (C-7, C-10), 125.1 (C-1, C-16), 124.3 (C-5, C-12), 123.6 (C-4, C-13), 122.3 (C-23, C-24), 101.3 (C-17), 85.4 ($\text{OCH}(\text{CH}_3)_2$), 23.2 ($\text{OCH}(\text{CH}_3)_2$). MS (EI, 70 eV): m/z (relative intensity) 541.7 (20) [M^+], 364.9 (100). IR (KBr) [cm^{-1}]: $\tilde{\nu}$ 3076 (w), 2986 (w), 2924 (w), 1507 (w), 1430 (w), 1164 (w), 1107 (s), 1017 (s), 862 (w), 818 (w), 754 (s), 721 (m), 607 (w), 426 (w). Anal. Calcd for $\text{C}_{32}\text{H}_{24}\text{Cl}_2\text{OTi}$: C, 77.28; H, 6.49; O, 8.13. Found: C, 74.68 (lowered by TiC formation); H, 5.92. Isotope pattern for $\text{C}_{32}\text{H}_{24}\text{Cl}_2\text{OTi}$ m/z (relative intensity): calcd 542.1 (100), 544.1 (72), 543.1 (48), 545.1 (29); found 542.1 (100), 544.1 (75), 544.1 (50), 545.1 (30).

Synthesis of $[(\text{C}_6\text{H}_5\text{O})_3\text{Ti}(\text{Cl})(\text{THF})_2]$ (12**).** To 4.56 g (20 mmol) of titanium tetraethoxide is added a solution of 7.53 g (80 mmol) of phenol, and the resulting ethanol is distilled from the reaction mixture. The red solution is taken to dryness, the residue is dissolved in 80 mL of dichloromethane, and the color deepens as 0.73 mL (6.67 mmol) of TiCl_4 is added. After stirring for 2 h all volatiles are evaporated and 40 mL of THF is added. Layering the deep red

solution with 40 mL of *n*-hexane yields 5.30 g (10.5 mmol, 39%) of **12** as dark red crystals. Mp: 95 °C. ^1H NMR (CDCl_3 , 500.13 MHz, 300 K) [ppm]: δ 7.16 (t, 6 H, $^3J_{\text{HH}} = 6.9$ Hz, H_{meta}), 6.98–6.93 (m, 9 H, H_{para} , H_{ortho}), 4.14 (t, 4 H, $^3J_{\text{HH}} = 6.2$ Hz, OCH_2CH_2), 1.95 (q, 4 H, $^3J_{\text{HH}} = 6.2$ Hz). ^{13}C NMR (CDCl_3 , 124.75 MHz, 300 K) [ppm]: δ 166.5, 166.4, 166.3 (C_{ipso}), 128.9 (C_{meta}), 128.0, 127.8, 127.6, 123.1 (C_{para}), 119.4 (C_{ortho}), 71.2 (OCH_2CH_2), 25.5 (OCH_2CH_2). MS (EI, 70 eV): m/z (relative intensity) 419.7 (100), 361.7 (95), 236.8 (55), 268.8 (35), 232.8 (60), 156.8 (15), 93.9 (50), 76.9 (15). IR (KBr) [cm^{-1}]: $\tilde{\nu}$ 2970 (m), 1939 (w), 1586 (s), 1477 (s), 1362 (s), 1160 (m), 1068 (s), 1020 (s), 999 (s), 900 (s), 820 (s), 756 (s), 688 (s), 667 (s), 617 (s), 559 (s), 486 (s), 459 (s), 444 (s). Anal. Calcd for $\text{C}_{44}\text{H}_{46}\text{Cl}_2\text{O}_8\text{Ti}_2$: C, 60.78; H, 5.33. Found: C, 60.51; H, 5.46.

Synthesis of $[(4\text{-MeC}_6\text{H}_4\text{O})_3\text{Ti}(\text{Cl})(\text{THF})_2]$ (13**).** To a solution of 10.00 g (92.47 mmol) of 4-methylphenol in 50 mL of toluene is added 3.40 mL (30.82 mmol) of TiCl_4 , and the mixture is refluxed overnight. The deep red reaction mixture is taken to dryness, and the residue is dissolved in a minimum amount (ca. 80 mL) of THF. Layering the solution with 80 mL of *n*-hexane affords 11.56 g (12.13 mmol, 82.7%) of **13** as deep red crystals suitable for X-ray diffraction. Mp: 109 °C. ^1H NMR (CDCl_3 , 500.13 MHz, 300 K) [ppm]: δ 6.95 (d, 6 H, $^3J_{\text{HH}} = 7.6$ Hz, H_{meta}), 6.84 (m, 6 H, H_{ortho}), 4.12 (t, 4 H, $^3J_{\text{HH}} = 6.2$ Hz, OCH_2CH_2), 2.228 (s, 9 H, CH_3), 1.94 (q, 4 H, $^3J_{\text{HH}} = 6.2$ Hz). ^{13}C NMR (CDCl_3 , 124.75 MHz, 300 K) [ppm]: δ 164.9 (C_{ipso}), 129.2 (C_{meta}), 119.1 (C_{ortho}), 70.9 (OCH_2CH_2), 25.5 (OCH_2CH_2), 20.8 (CH_3). MS (EI, 70 eV): m/z (relative intensity) 476.0 (25), 403.9 (100), 368.9 (15), 331.8 (30), 296.9 (30), 260.9 (20), 204.9 (10), 107.0 (90), 91.0 (35), 77.0 (25), 65.0 (10), 51.0 (10). IR (KBr) [cm^{-1}]: $\tilde{\nu}$ 2915 (m), 1603 (m), 1577 (m), 1498 (s), 1251 (s), 1206 (s), 1165 (m), 1101 (m), 1025 (m), 903 (s), 831 (s), 787 (s), 757 (m), 643 (w), 592 (s), 575 (s), 558 (s), 463 (s), 416 (s). Anal. Calcd for $\text{C}_{50}\text{H}_{58}\text{Cl}_2\text{O}_8\text{Ti}_2$: C, 62.97; H, 6.13. Found: C, 62.96; H, 6.40.

Synthesis of $[(4\text{-}^t\text{BuC}_6\text{H}_4\text{O})_3\text{Ti}(\text{Cl})(\text{THF})_2]$ (14**).** To a solution of 3.25 g (21.64 mmol) of 4-*tert*-butylphenol in 40 mL of toluene is added 0.80 mL (7.11 mmol) of TiCl_4 , and the mixture is refluxed overnight. The deep red reaction mixture is evaporated to dryness and the residue dissolved in 40 mL of THF. Layering the solution with 40 mL of *n*-hexane yielded 2.73 g (2.27 mmol, 63.8%) of **14** as red microcrystals. Mp: 125 °C. ^1H NMR (CDCl_3 , 500.13 MHz, 300 K) [ppm]: δ 7.09 (d, 8 H, $^3J_{\text{HH}} = 6.2$ Hz, H_{meta}), 7.00 (d, 4 H, $^3J_{\text{HH}} = 7.8$ Hz, $\text{H}_{\text{meta bridge}}$), 6.77 (m, 8 H, H_{ortho}), 6.55 (d, 2 H, $^3J_{\text{HH}} = 6.2$ Hz, $\text{H}_{\text{ortho bridge}}$), 6.48 (d, 2 H, $\text{H}_{\text{ortho bridge}}$), 4.00 (t, 8 H, $^3J_{\text{HH}} = 6.4$ Hz, OCH_2CH_2), 1.90 (q, 8 H, $^3J_{\text{HH}} = 6.4$ Hz, OCH_2CH_2), 1.243 (s, 36 H, ^tBu), 1.221 (s, 9 H, $^t\text{Bu bridge}$), 1.209 (s, 9 H, $^t\text{Bu bridge}$). ^{13}C NMR (CDCl_3 , 124.75 MHz, 300 K) [ppm]: δ 164.8 (C_{ipso}), 145.9 (C_{para}), 145.8 ($\text{C}_{\text{para bridge}}$), 125.5 (C_{meta}), 125.4 ($\text{C}_{\text{meta bridge}}$), 118.8 (C_{ortho}), 118.7 ($\text{C}_{\text{ortho bridge}}$), 70.3 (OCH_2CH_2), 34.3 ($\text{C}(\text{CH}_3)_3$), 31.5 ($\text{C}(\text{CH}_3)_3$), 25.5 (OCH_2CH_2). MS (EI, 70 eV): m/z (relative intensity) 643.9 (55), 628.9 (55), 529.8 (30), 514.9 (90), 400.8 (15), 341.0 (45), 306.9 (30), 249.9 (15), 232.8 (10), 150.0 (25), 135.0 (100), 107.0 (25), 95.0 (10). IR (KBr) [cm^{-1}]: $\tilde{\nu}$ 3252 (m), 2961 (s), 2900 (m), 2865 (m), 1599 (w), 1503 (s), 1459 (m), 1391 (w), 1362 (m), 1256 (s), 1219 (m), 1175 (m), 1110 (m), 1019 (m), 910 (s), 869 (s), 831 (s), 721 (m), 681 (w), 641 (w), 577 (m), 549 (m), 527 (s), 475 (w), 446 (w). Anal. Calcd for $\text{C}_{68}\text{H}_{94}\text{Cl}_2\text{O}_8\text{Ti}_2$: C, 67.72; H, 7.86. Found: C, 67.52; H, 7.72.

Synthesis of $\text{Tb}(\text{OC}_6\text{H}_5)_3$ (15**).** A portion of 330 mg (0.50 mmol) of **5** and 220 mg (0.25 mmol) of **12** are mixed as solids and suspended in 30 mL of cyclohexane. The reaction mixture is stirred overnight and filtered through a glass frit. Layering the orange solution with 30 mL of *n*-hexane yielded 121 mg (0.18 mmol, 35%) of **15** as red crystals suitable for X-ray diffraction. Mp: 153 °C. ^1H NMR (CDCl_3 , 500.13 MHz, 300 K) [ppm]: δ 8.81 (d, 2 H, $^3J_{\text{HH}} = 8.0$ Hz, H-8, H-9), 8.41 (d, 2 H, $^3J_{\text{HH}} = 8.0$ Hz, H-5, H-12), 8.38 (d, 2 H, $^3J_{\text{HH}} = 8.0$ Hz, H-4, H-13), 8.14 (d, 2 H, $^3J_{\text{HH}} = 6.9$

Hz, H-1, H-16), 7.80 (s, 1 H, H-17), 7.60 (m, 2 H, H-2, H-15), 7.56 (m, 2 H, H-7, H-10), 7.53 (m, 2 H, H-3, H-14), 7.48 (m, 2 H, H-6, H-11), 6.85 (dd, 6 H, $^3J_{\text{HH}} = 7.7$ Hz, H_{meta}), 6.68 (t, 3 H, $^3J_{\text{HH}} = 7.7$ Hz, H_{para}), 5.95 (d, 6 H, $^3J_{\text{HH}} = 7.7$ Hz, H_{ortho}). ^{13}C NMR (CDCl_3 , 124.75 MHz, 300 K) [ppm]: δ 164.9 (C_{ipso}), 131.5 (C-22, C-25), 131.2 (C-19, C-28), 128.5 (C_{meta}), 128.0 (C-20, C-27), 127.5 (C-21, C-26), 127.5 (C-2, C-15), 127.3 (C-7, C-10), 127.3 (C-18, C-29), 127.2 (C-8, C-9), 127.2 (C-5, C-12), 126.0 (C-1, C-16), 124.7 (C-4, C-13), 124.3 (C-3, C-14), 123.6 (C-6, C-11), 120.8 (C_{para}), 119.4 (C-23, C-24), 118.3 (C_{ortho}), 97.4 (C-17). MS (EI, 70 eV): m/z (relative intensity) 692.2 (10) [M^+], 420.1 (65), 366.1 (100) [Tb^+], 327.1 (45), 233.0 (50), 94.0 (15) [PhO^+], 77.0 (30) [C_6H_5^+], 63.9 (40). IR (KBr) [cm^{-1}]: $\tilde{\nu}$ 3058 (w), 2962 (w), 2921 (w), 2849 (w), 1577 (s), 1477 (s), 1245 (s), 1153 (m), 1098 (m), 1060 (m), 1020 (m), 896 (s), 869 (s), 816 (m), 750 (s), 685 (m), 643 (s). Anal. Calcd for $\text{C}_{47}\text{H}_{32}\text{O}_3\text{Ti}$: C, 81.50; H, 4.66; O, 6.93. Found: C, 80.68; H, 5.93.

Synthesis of $\text{TbTi}(\text{4-MeC}_6\text{H}_4\text{O})_3$ (16**).** A portion of 330 mg (0.50 mmol) of **5** and 240 mg (0.25 mmol) of **13** are mixed as solids and suspended in 30 mL of cyclohexane. The reaction mixture is stirred overnight and filtered through a glass frit. Layering the orange solution with 30 mL of *n*-hexane yielded 105 mg (105 mg, 29%) of **16** as red crystals suitable for X-ray diffraction. Mp: 154 °C. ^1H NMR (CDCl_3 , 500.13 MHz, 300 K) [ppm]: δ 8.83 (d, 2 H, $^3J_{\text{HH}} = 8.0$ Hz, H-8, H-9), 8.45 (d, 2 H, $^3J_{\text{HH}} = 8.2$ Hz, H-5, H-12), 8.43 (d, 2 H, $^3J_{\text{HH}} = 8.3$ Hz, H-4, H-13), 8.16 (d, 2 H, $^3J_{\text{HH}} = 7.8$ Hz, H-1, H-16), 7.795 (s, 1 H, H-17), 7.63 (m, 2 H, H-2, H-15), 7.59 (m, 2 H, H-7, H-10), 7.56 (m, 2 H, H-3, H-14), 7.50 (m, 2 H, H-6, H-11), 6.66 (d, 6 H, $^3J_{\text{HH}} = 8.1$ Hz, H_{meta}), 5.88 (d, 6 H, $^3J_{\text{HH}} = 8.1$ Hz, H_{ortho}), 2.19 (s, 9 H, CH_3). ^{13}C NMR (CDCl_3 , 125.75 MHz, 300 K) [ppm]: δ 164.9 (C_{ipso}), 131.5 (C-22, C-25), 131.2 (C-19, C-28), 128.5 (C_{meta}), 128.0 (C-20, C-27), 127.5 (C-21, C-26), 127.5 (C-2, C-15), 127.3 (C-7, C-10), 127.3 (C-18, C-29), 127.2 (C-8, C-9), 127.2 (C-5, C-12), 126.0 (C-1, C-16), 124.7 (C-4, C-13), 124.3 (C-3, C-14), 123.6 (C-6, C-11), 120.8 (C_{para}), 119.1 (C-23, C-24), 117.9 (C_{ortho}), 97.4 (C-17), 26.9 (CH₃). MS (EI, 70 eV): m/z (relative intensity) 629.0 (20), 579.0 (20), 479.0 (15), 366.1 (15) [Tb^+], 276.0 (45), 151.0 (40), 84.1 (100). IR (KBr) [cm^{-1}]: $\tilde{\nu}$ 3019 (w), 2918 (w), 2853 (w), 1603 (w), 1499 (s), 1434 (m), 1275 (s), 1251 (s), 1163 (m), 1099 (m), 928 (w), 880 (s), 819 (m), 781 (m), 755 (m), 723 (m), 642 (w), 582 (m), 510 (m), 418 (w). Anal. Calcd for $\text{C}_{50}\text{H}_{38}\text{O}_3\text{Ti}$: C, 81.74; H, 5.21; O, 6.53. Found: C, 81.42; H, 5.15.

Synthesis of $\text{TbTi}(\text{4-BuC}_6\text{H}_4\text{O})_3$ (17**).** A portion of 330 mg (0.50 mmol) of **5** and 300 mg (0.25 mmol) of **14** are mixed as solids and suspended in 30 mL of cyclohexane. The reaction mixture is stirred overnight and filtered through a P4 glass frit. Layering the orange solution with 30 mL of *n*-hexane yielded 114 mg (0.13 mmol, 27%) of **17** as orange microcrystals. Mp: 173 °C. ^1H NMR (CDCl_3 , 500.13 MHz, 300 K) [ppm]: δ 8.81 (d, 2 H, $^3J_{\text{HH}} = 7.4$ Hz, H-8, H-9), 8.36 (d, 2 H, $^3J_{\text{HH}} = 8.0$ Hz, H-5, H-12), 8.33 (d, 2 H, $^3J_{\text{HH}} = 7.7$ Hz, H-4, H-13), 8.14 (d, 2 H, $^3J_{\text{HH}} = 7.0$ Hz, H-1, H-16), 7.793 (s, 1 H, H-17), 7.58 (m, 2 H, H-2, H-15), 7.54 (m, 2 H, H-7, H-10), 7.51 (m, 2 H, H-3, H-14), 7.48 (m, 2 H, H-6, H-11), 6.83 (d, 6 H, $^3J_{\text{HH}} = 8.6$ Hz, H_{meta}), 5.89 (d, 6 H, $^3J_{\text{HH}} = 8.6$ Hz,

H_{para}), 1.228 (s, 27 H, $\text{C}(\text{CH}_3)_3$). ^{13}C NMR (CDCl_3 , 125.75 MHz, 300 K) [ppm]: δ 162.8 (C_{ipso}), 143.2 (C_{para}), 131.4 (C-22, C-25), 131.2 (C-19, C-28), 128.6 (C-20, C-27), 127.7 (C-21, C-26), 127.4 (C-2, C-15), 127.3 (C-7, C-10), 127.2 (C-18, C-29), 127.1 (C-8, C-9), 127.0 (C-5, C-12), 125.8 (C-1, C-16), 125.1 (C_{meta}), 124.8 (C-4, C-13), 124.2 (C-3, C-14), 123.5 (C-7, C-10), 119.1 (C-23, C-24), 117.6 (C_{ortho}), 97.2 (C-17), 34.1 ($\text{C}(\text{CH}_3)_3$), 31.6 ($\text{C}(\text{CH}_3)_3$). MS (EI, 70 eV): m/z (relative intensity) 679 (10), 617 (10), 366.1 (35) [Tb^+], 150.1 (25) [$4\text{-BuC}_6\text{H}_5\text{O}^+$], 135.1 (100), 107.1 (20). IR (KBr) [cm^{-1}]: $\tilde{\nu}$ 3030 (w), 2958 (m), 2902 (m), 2864 (m), 1599 (m), 1502 (s), 1460 (m), 1438 (m), 1248 (s), 1248 (m), 1174 (s), 1108 (m), 908 (m), 834 (s), 807 (m), 756 (s), 721 (s), 567 (m), 550 (m), 430 (w). Anal. Calcd for $\text{C}_{59}\text{H}_{56}\text{O}_3\text{Ti}$: C, 82.31; H, 6.56. Found: C, 82.52; H, 6.72.

Styrene Polymerization. A catalyst premix solution was prepared by using the corresponding transition metal catalyst together with methylalumoxane (MAO) as cocatalyst with a molar ratio of MAO/triisobutylaluminum (TIBA)/Ti = 110/25/1. The mixture was composed in a drybox under argon atmosphere in a 5 mL volumetric flask by adding sequentially 1.17 mL of 1.41 M MAO solution in toluene, 0.38 mL of a 1 M TIBA solution in toluene, 14.9 μmol of neat tetrabenzotriisobutylfluorenyltitanium catalysts (**10**, **11**, **15**, **16**, **17**), and sufficient additional toluene to 5 mL volume. To run the polymerization trials, glass ampoules were charged in a drybox with 10 mL of styrene that had previously been deoxygenated by sparging with nitrogen, passed through activated alumina, and hydrogenated using Pd on alumina to remove phenylacetylene. After removal from the drybox the septum-capped, crimp-sealed ampoules were placed in a water bath and equilibrated for 10 min at the polymerization temperature of 30 °C. Polymerizations were initiated at a molar ratio styrene/Ti = 700 000/1, by addition of 41.6 μL of the catalyst premix solution described above via microliter syringe. After the desired polymerization time of 60 or 120 min, respectively, the polymerization reactions were quenched by the addition of methanol. The resulting polymer was isolated and dried under vacuum for 30 min at 150 °C followed by 30 min at 250 °C. The samples were weighed and melting points were determined by DSC.

Additional crystallographic data for the structures **4b**, **5**, **6**, **7**, **10**, **11**, **13**, **15**, and **16** have been deposited with the Cambridge Data Centre as supplementary publications nos. CCDC 601752 (**4b**), CCDC 601753 (**5**), CCDC 601749 (**6**), CCDC 601754 (**7**), CCDC 601751 (**10**), CCDC 601750 (**11**), CCDC 601746 (**13**), CCDC 601748 (**15**), and CCDC 601747 (**16**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax (+44)1223-336-033; e-mail deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Additional crystallographic data for the structures **4b**, **5**, **6**, **7**, **10**, **11**, **13**, **15**, and **16** are available free of charge via the Internet at <http://pubs.acs.org>.

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