Tetrabenzo[*a,c,g,i*]fluorenyltitanium(III) and -(IV) Complexes: Syntheses, Reactions, and Catalytic Application

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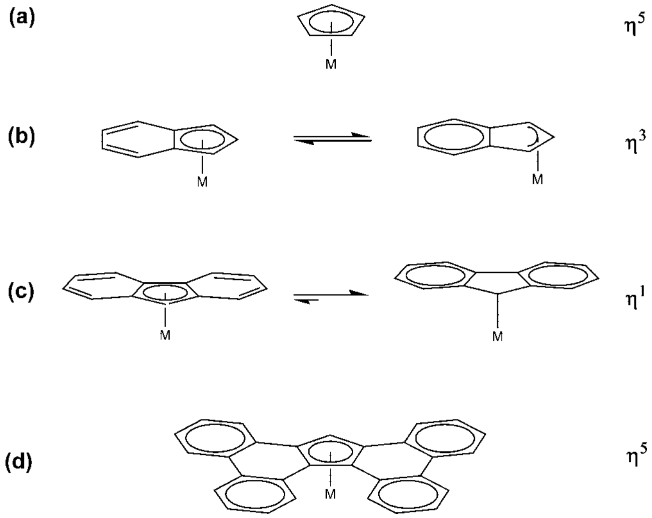
Reacting tetrabenzo[*a,c,g,i*]fluorenyllithium {TbfLi(THF)$_4$ (**1**)} with TiCl$_3$(THF)$_3$ (**2**) leads to the formation of the η^5-tetrabenzo[*a,c,g,i*]fluorenyltitanium(III) derivative TbfTiCl$_2$(THF) (**3**), which can be conveyed to the titanium(IV)complex TbfTiCl$_3$ (**4**) by oxidative chlorination with CCl$_4$. Subsequent reaction with various lithium phenoxides gives a series of titanium complexes of the type TbfTiCl$_2$(OAr) (Ar = 4-^{t}BuC$_6$H$_4$ (**5**), 2,6-Me$_2$C$_6$H$_3$ (**6**), 2,4,6-Me$_3$C$_6$H$_2$ (**7**), 2,6-^{i}PrC$_6$H$_3$ (**8**), 2,6-Ph$_2$C$_6$H$_3$ (**9**)). Furthermore, **3** was reacted with radicals or radical-generating peroxides to form the complexes TbfTiCl$_2$TEMPO (**10**) and TbfTiCl$_2$O^{t}Bu (**11**). All compounds were characterized by IR, MS, and NMR measurements and X-ray crystallography. Finally, compounds **6**, **8**, **9**, and **10** were subjected to ethylene polymerization experiments using d-MAO. The activities increase in the following order [kG(PE)mol(Ti)$^{-1}$ h^{-1} bar^{-1}]: **6** (320) < **8** (320) < **10** (760) < **9** (1000).

Introduction

The cyclopentadienide anion and its derivatives are widely used in organometallic and coordination chemistry, especially because replacing the hydrogen atoms on the cyclopentadienyl ring by substituents easily alters the chemical and physical properties of their corresponding complexes.[1] Particularly, benzo-fused Cp derivatives such as indene and fluorene had a serious impact in the development of catalyst precursors for stereospecific olefin polymerization.[2] However, fusing aromatic ring systems to the cyclopentadienyl ring can sometimes cause problems with regard to the bonding situation between metal and ligand, due to the tendency of the benzo-fused ring to preserve its aromatic six-electron system, leading to a haptotropic shift as depicted in Scheme 1.

Ring-slippage can occur on all Cp-type ligand systems, and this greatly adds to their chemical variety;[3] however, for the above-mentioned reason with (**b**) indenyl[4] and (**c**) fluorenyl ligands (Flu)[5] this is more likely to take place. Especially the fluorenyl moiety usually not only refuses to form η^5-complexes even in its *ansa*-bridged specimen[6] but often dimerizes in a redox reaction with the metal.[7] As a natural consequence, only very few unsubstituted fluorenyl transition metal complexes are known such as FluMn(CO)$_3$[8] and FluTi(O^{i}Pr)$_2$.[9]

Scheme 1



By further adding benzo-fused rings to the fluorenyl moiety complex stability significantly improves by forming the anionic five-membered ring; none of the six-electron ring systems are

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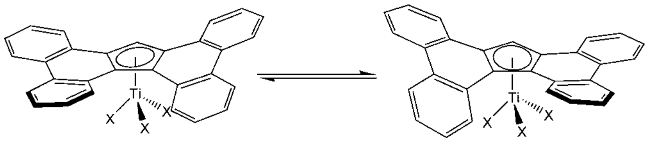
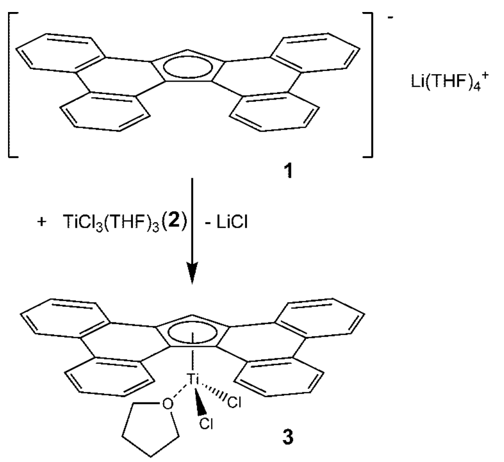
10.1021/om7012293 CCC: $40.75

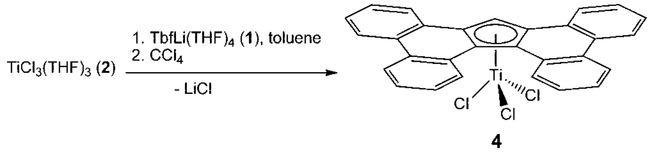
Scheme 2



Scheme 3



Scheme 4



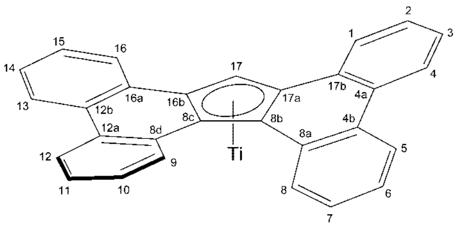
disturbed like in the (**d**) tetrabenbenzo[*a,c,g,i*]fluorenyl (Tbf) ligand,[10] which is also depicted in Scheme 1. Originally developed as a protecting anchor group for the synthesis of oligonucleotides,[11] polypeptides,[12] and proteins[13] it proved to be a useful spectator ligand in half-sandwich complexes intended for syndiospecific styrene polymerization.[10] Furthermore, the sterical repulsion between the benzo-fused rings leads to a slight helical distortion, which makes the tetrabenzo[*a,c,g,i*]fluorenyl moiety intrinsically chiral (see Scheme 2). However due to a very low racemization barrier in solution, only half the signal set can be observed in the NMR.[14]

In this article we wish to report the synthesis of the tetrabenzo[*a,c,g,i*]fluorenyltitanium half-sandwich complexes $\mathrm{TbfTi^{III}Cl_2(THF)}$ and $\mathrm{TbfTi^{IV}Cl_3}$ and their subsequent reactions leading to organometallic complexes of the general formula $\mathrm{TbfTi^{IV}Cl_2OR}$.

Results and Discussion

One of the standard procedures for the synthesis of half-sandwich cyclopentadienyltitanium trichlorides involves the use of silylated cyclopentadienyl[15] derivatives in cases where the use of lithiated compounds leads to reduction of the metal center.[7]

Chart 1. Numbering Scheme for Tetrabenzo[*a,c,g,i*]fluorenyltitanium Complexes



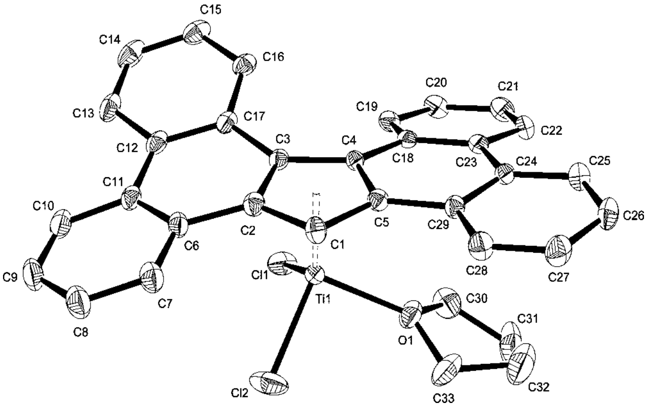


Figure 1. ORTEP plot of the solid state molecular structure of **3**. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [deg]: Ti(1)−Ct 2.0340, Ti(1)−Cl(1) 2.3006(5), Ti(1)−Cl(2) 2.3115(5), Ti(1)−O(1) 2.0536(12), Cl(1)−Ti(1)−Cl(2) 103.19(3), Cl(1)−Ti(1)−O(1) 96.81(4), Cl(2)−Ti(1)−O(1) 92.99(4), C17−C3−C4−C19 −18.486(290).

As mentioned in a previous article,[10] directly reacting $\mathrm{TbfLi(THF)_4}$ (**1**) with $\mathrm{TiCl_4(THF)_2}$ ended up in the reduction of the metal center and coinstantaneous oxidative coupling of the ligand, leading to the well-crystallizing Tbf−Tbf hydrocarbon coupled in the C17 position (Chart 1). As a natural consequence, the synthesis of tetrabenzo[*a,c,g,i*]fluorenyltitanium trichloride via a silylated tetrabenzo[*a,c,g,i*]fluorene derivative was approached, but it did not yield any identifiable products so far.[16] Thus it was tried to use reactants with an increased electron density on the titanium center such as Ti(III) complexes.

Synthesis of Tetrabenzo[*a,c,g,i*]fluorenyltitanium Chloride Complexes. Reacting $\mathrm{TbfLi(THF)_4}$ (**1**) with $\mathrm{TiCl_3(THF)_3}$ (**2**) in toluene formed a green solution, which was left for crystallization after 1 min of stirring. After 2 days dark green crystals of $\mathrm{TbfTiCl_2(THF)}$ (**3**) were afforded in acceptable yield (64%), which were suitable for X-ray diffraction (Figure 1). The compound proved to be extremely air and moisture sensitive and is hardly soluble in organic solvents with the exception of THF. In the solid state the compound decomposes without prior melting at 120 °C.

Compound **3** crystallizes in a monoclinic system; the space group is *C*2/*c* with eight molecules per unit. The distance between Ti(1)−Ct(1) measures 2.0340 Å, which is considerably longer than the Ti−Ct distance in the analogous cyclopentadienyl titanium complex $\mathrm{CpTiCl_2(THF)}$ (2.014 Å), which to our best knowledge is the only other example where a monomeric

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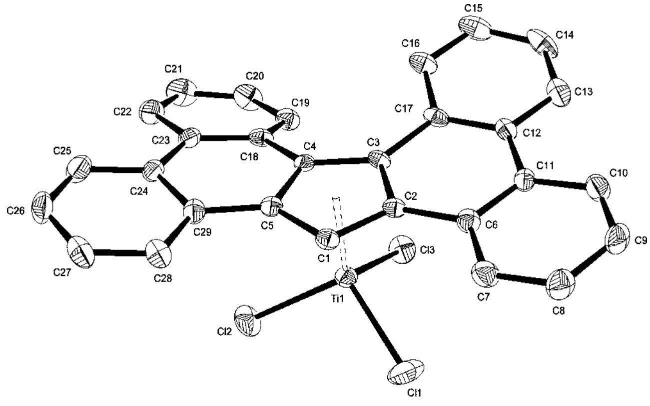

Figure 2. ORTEP plot of the solid state molecular structure of **4**. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [deg]: Ti(1)−Ct 2.0357, Ti(1)−Cl(1) 2.2303(11), Ti(1)−Cl(2) 2.2173(11), Ti(1)−Cl(3) 2.2512(11), Cl(1)−Ti(1)−Cl(2) 103.07(4), Cl(2)−Ti(1)−Cl(3) 106.57(4), Cl(1)−Ti(1)−Cl(3) 102.15(5), C18−C4−C3−C17 15.710(626).

Cp-type titanium(III) chloride compound could be isolated.[17,18] Bis THF adducts, as described for CpTiCl$_2$(THF)$_2$, are not found in the case of **3**.[17]

In order to synthesize a tetrabenzo[*a,c,g,i*]fluorenyltitanium(IV) species from compound **3**, oxidative chlorination with CCl$_4$ promised to be successful.[19] Reacting TiCl$_3$(THF)$_3$ with TbfLi(THF)$_4$ in toluene with subsequent extraction and thus simultaneous oxidative chlorination using CCl$_4$ afforded TbfTiCl$_3$ (**4**) in an acceptable overall yield of 66%. The dark purple compound is quite insensitive to air and moisture. In contrast to its moderate solubility in dichloromethane and THF, **4** is poorly soluble in toluene and completely insoluble in diethyl ether and aliphatic solvents; therefore crystals of **4** suitable for X-ray diffraction could easily be obtained by layering a solution in dichloromethane with an equal amount of *n*-hexane.

The dark violet needle-shaped crystals contain four molecules of **4** per unit cell along with 2 equiv of solvent. The crystal system is monoclinic with space group $P2_1/n$. As shown in Figure 2 the titanium atom is coordinated in a pseudotetrahedral fashion with the tetrabenzo[*a,c,g,i*]fluorenyl moiety in the apical position, with a Ct−Ti(1) distance of 2.0357 Å, which is about the same distance as in TbfTiCl$_2$(THF) within the accuracy of measurement. The bond lengths between titanium and the three chloride atoms amount to an average of 2.23 Å.

Table 2 gives a comparative survey of the most important structural data of compound **4** and similar organometallic complexes like CpTiCl$_3$[20] and IndTiCl$_3$.[21] It can be easily seen that all Ti−Cl bond lengths and Cl−Ti−Cl angles are almost alike in all three complexes, thus leaving the Ti−Ct distance in CpTiCl$_3$ at 2.01 Å as the only major difference from **4** and IndTiCl$_3$, in whose molecular structures the Ti−Ct distances amount to 2.03 Å. These crystallographic data and its dark violet color suggest that compound **4** is electronically quite similar to IndTiCl$_3$.

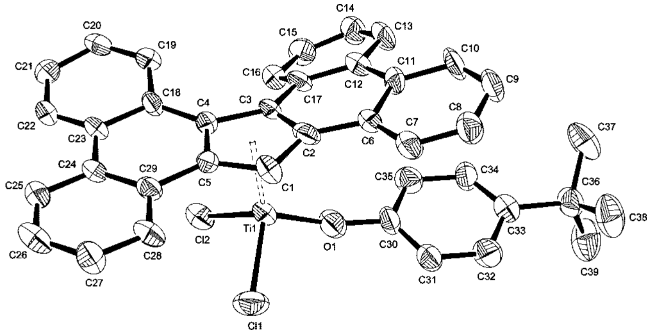

Figure 3. ORTEP plot of the solid state molecular structure of **5**. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [deg]: Ti(1)−Ct 2.0665, Ti(1)−Cl(1) 2.274(3), Ti(1)−Cl(2) 2.257(3), Ti(1)−O(1) 1.782(6), Ti(1)−O(1)−C(30) 161.1(5), O(1)−Ti(1)−Cl(1) 101.6(2), O(1)−Ti(1)−Cl(2) 105.1(2), Cl(1)−Ti(1)−Cl(2) 102.95(10), C18−C4−C3−C17 −13.722(1594).

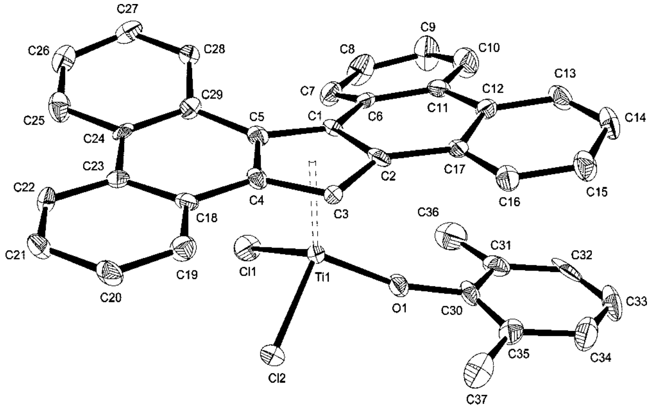

Figure 4. ORTEP plot of the solid state molecular structure of **6**. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [deg]: Ti(1)−Ct 2.0701, Ti(1)−Cl(1) 2.2766(16), Ti(1)−Cl(2) 2.2637(17), Ti(1)−O(1) 1.779(3), Ti(1)−O(1)−C(30) 159.7(3), Cl(1)−Ti(1)−O(1) 105.97(12), Cl(2)−Ti(1)−O(2) 100.72(12), Cl(1)−Ti(1)−Cl(2) 102.32(7), C29−C5−C1−C6 12.825(946).

Synthesis of Tetrabenzo[*a,c,g,i*]fluorenyltitanium Monophenoxide Complexes. Standard synthetic procedures for the synthesis of Cp-type titanium monophenoxide complexes from their trichloride precursors involve the use of either lithiumphenoxides[22] or phenols in conjunction with an organic base in order to absorb the HCl released.[23]

As depicted in Scheme 5 compound **4** was reacted with lithium phenoxides in a toluene slurry to form an array of tetrabenzo[*a,c,g,i*]fluorenyltitanium monophenoxides of the general formula TbfTiCl$_2$OAr. Generally, working up the reaction mixtures included evaporation of the solvent with subsequent extraction of the residue with dichloromethane with the exception of TbfTiCl$_2$(2,6-Ph$_2$C$_6$H$_3$O) (**9**), which was filtered directly in order to remove LiCl. All solutions obtained were layered with *n*-hexane to induce crystallization of the product complexes. This way crystals suitable for X-ray diffraction are obtained on a regular basis.

TbfTiCl$_2$(4-^{t}BuC$_6$H$_4$O) (**5**) is well soluble in dichloromethane and THF, of low solubility in toluene, and completely insoluble

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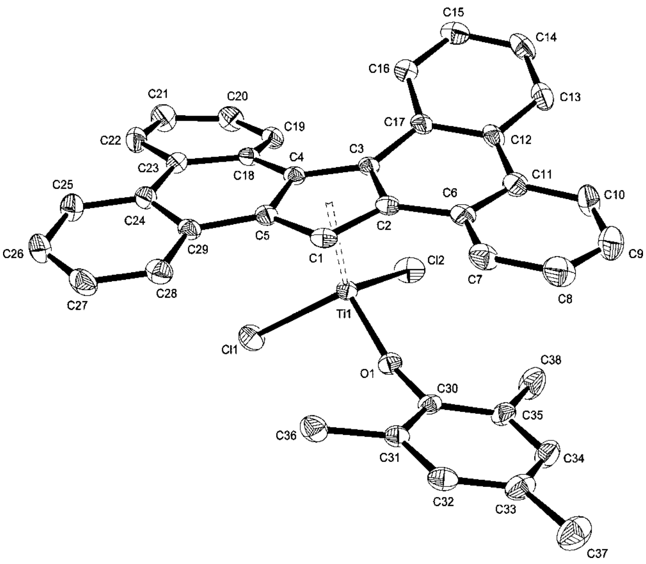


Figure 5. ORTEP plot of the solid state molecular structure of **7**. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [deg]: Ti(1)−Ct 2.0589, Ti(1)−Cl(1) 2.2508(6), Ti(1)−Cl(2) 2.2614(7), Ti(1)−O(1) 1.7737(16), Ti(1)−O(1)−C(30) 158.94(13), Cl(1)−Ti(1)−O(1) 102.79(5), Cl(2)−Ti(1)−O(1) 103.36(5), Cl(1)−Ti(1)−Cl(2) 103.45(3), C18−C4−C3−C17 12.510(412).

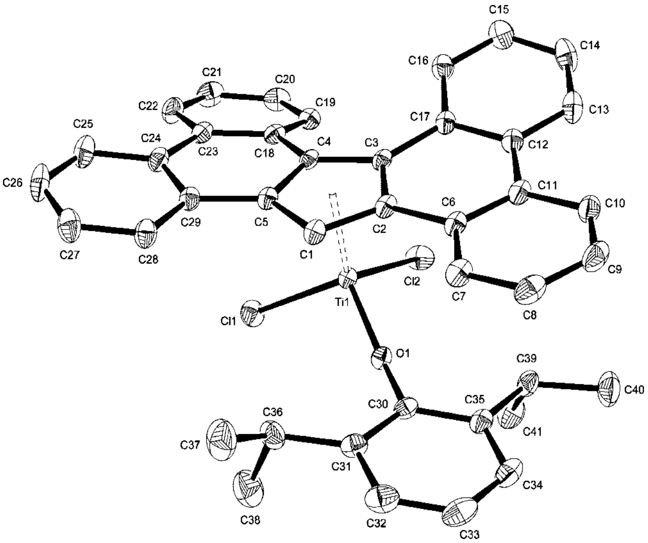


Figure 6. ORTEP plot of the solid state molecular structure of **8**. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [deg]: Ti(1)−Ct 2.0544, Ti(1)−Cl(1) 2.2467(6), Ti(1)−Cl(2) 2.2545(7), Ti(1)−O(1) 1.7751(14), Ti(1)−O(1)−C(30) 159.17(13), Cl(1)−Ti(1)−O(1) 102.28(5), Cl(2)−Ti(1)−O(1) 102.57(5), Cl(1)−Ti(1)−Cl(2) 104.45(2), C18−C4−C3−C17 14.966(406).

in aliphatic solvents. It could be obtained in 23% yield as deep red crystals with two molecules per unit cell in the triclinic crystal system $P\bar{1}$. The Ti(1)−Ct distance measures 2.0665 Å, the Ti(1)−Cl bond lengths amount to an average 2.266 Å (Figure 3). The distance between centers of the benzo-fused tetrabenzo[*a,c,g,i*]fluorene ring C6−C11 and the phenoxide ring C30−C35 measures 3.841 Å, and therefore it is assumed that face-to-face π-stacking interactions take place.[24]

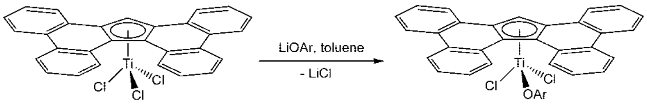
Table 1. Comparison of Selected Bond Length and Angles between Compound 3 and $CpTiCl_2(THF)$[17]

	$TbfTiCl_2(THF)$ (**3**)	$CpTiCl_2(THF)$
	Bond Lengths [Å]	
Ti(1)−Ct	2.0340	2.014
Ti(1)−Cl(1)	2.3006(5)	2.310(2)
Ti(1)−Cl(2)	2.3115(5)	2.339(3)
Ti(1)−O(1)	2.0536(12)	2.065(4)
	Bond Angles [deg]	
Cl(1)−Ti(1)−Cl(2)	103.19(3)	105.6(1)
Cl(1)−Ti(1)−O(1)	96.81(4)	93.7(1)
Cl(2)−Ti(1)−O(1)	92.99(4)	94.4(1)

Table 2. Comparison of Selected Bond Lengths and Angles between Compound 4, $CpTiCl_3$,[20] and $IndTiCl_3$[21]

	$TbfTiCl_3$ (**4**)	$CpTiCl_3$	$IndTiCl_3$
	Bond Lengths [Å]		
Ti(1)−Ct	2.0357	2.01	2.032
Ti(1)−Cl(1)	2.2303(11)	2.201(5)	2.2248(8)
Ti(1)−Cl(2)	2.2173(11)	2.248(5)	2.2319(8)
Ti(1)−Cl(3)	2.2512(11)	2.221(2)	2.2355(8)
	Bond Angles [deg]		
Cl(1)−Ti(1)−Cl(2)	103.07(4)	102.2(2)	102.44(3)
Cl(2)−Ti(1)−Cl(3)	106.57(4)	104.1(2)	104.09(3)
Cl(1)−Ti(1)−Cl(3)	102.15(5)	102.3(3)	103.32(3)

Scheme 5



Ar = 4-$^{t}BuC_6H_4$ (**5**), 2,6-$Me_2C_6H_3$ (**6**), 2,4,6-$Me_3C_6H_2$ (**7**), 2,6-$^{i}Pr_2C_6H_3$ (**8**), 2,6-$Ph_2C_6H_3$ (**9**)

$TbfTiCl_2(2,6\text{-}Me_2C_6H_3O)$ (**6**) is well soluble in dichloromethane and THF, of low solubility in toluene, and completely insoluble in aliphatic solvents. It could be isolated in 21% yield as red crystals with four molecules per unit cell in the monoclinic crystal system $P2_1/c$. As listed in Table 3 the Ti−Ct distance measures 2.0701 Å and the Ti−Cl bond lengths amount to an average 2.270 Å (Figure 4). Like in compound **5**, in **6** it is assumed that face-to-face π-stacking interactions take place between the benzo-fused ring C12−C17 and the phenoxide ring C30−C35, as the distance between their respective centroids measures 3.62 Å.

Interestingly, in contrast to complex **6**, $TbfTiCl_2(2,4,6\text{-}Me_3C_6H_2O)$ (**7**) does not show any $\pi-\pi$ interactions between the phenoxide and any of the benzo-fused rings, although they only differ by one methyl group in the *para*-position of the phenoxide ligand. It is not known if this is due to a slightly different electronic structure or a phenomenon of different packing in the crystal.

With regard to its solubility and its other physical properties, compound **7** is very similar to complex **6**. It crystallizes in the monoclinic space group $P2_1/n$ with four molecules per crystal cell. The Ti−Ct bond length measures 2.0589 Å and is thus slightly shorter than in **6**, whereas the Ti−O bond length and the Ti−O−C angle are almost identical (Figure 5).

Like all other tetrabenzo[*a,c,g,i*]fluorenyltitanium monophenoxide complexes mentioned so far, $TbfTiCl_2(2,6\text{-}^{i}Pr_2C_6H_3O)$ (**8**) is well soluble in dichloromethane and THF, to a lesser extent in aromatic solvents, and completely insoluble in aliphatic solvents. It can be obtained in 34% yield as red crystals in the monoclinic space group $P2_1/n$ with four molecules per unit cell (Figure 6).

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Table 3. Comparison of Selected Bond Lengths and Angles between Compounds 5, 6, 7, 8, and 9

	5	6	7	8	9
			Bond Lengths [Å]		
Ti(1)−Ct	2.0665	2.0701	2.0589	2.0544	2.0554
Ti(1)−Cl(1)	2.274(3)	2.2766(16)	2.2508(6)	2.2467(6)	2.2509(6)
Ti(1)−Cl(2)	2.257(3)	2.2637(17)	2.2614(7)	2.2545(7)	2.2570(7)
Ti(1)−O(1)	1.782(6)	1.779(3)	1.7737(16)	1.7751(14)	1.7913(15)
			Bond Angles [deg]		
Ti(1)−O(1)−C	161.1(5)	159.7(3)	158.94(13)	159.17(13)	154.61(12)
Cl(1)−Ti(1)−Cl(2)	102.95(10)	102.32(7)	103.45(3)	104.45(2)	104.08(3)

In contrast to the excellent catalyst precursor Cp*$TiCl_2(2,6\text{-}{}^iPr_2C_6H_3O)$[25] the Ti−O−C bond angle in compound **8** exhibits only a relatively small value of 159.17°.

As opposed to the TbfTiCl_2(OAr) complexes **5**−**8**, TbfTi$Cl_2(2,6\text{-}Ph_2C_6H_3O)$ (**9**) is well soluble in aromatic solvents. Its red crystals can be obtained from a toluene solution in 34% yield, and the compound crystallizes in the triclinic space group $P\bar{1}$ with two molecules of **9** and one molecule of toluene per unit cell (Figure 7).

Like in Figure 6 and Figure 7 it can be seen that one of the phenoxide's *ortho* substituents locks into the cavity in front of the cyclopentadienyl ring formed by two benzo-fused rings. With compound **9** it is assumed that this occurs not only in the solid state but also in solution, as the single proton on the cyclopentadienyl ring is located in the anisotropic cone of the phenyl ring and thus is shifted upfield in the proton NMR.

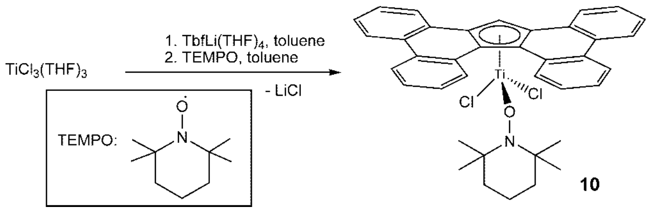
Reaction of TbfTi^{III}Cl$_2$(THF) with Radicals. Another possible synthetic route to introduce ligands into an organometallic complex is the reaction of one of its low-valent species with radicals. Thus an O- or N-centered radical is reduced to a monoanionic ligand while the metal center is oxidized. However, some applications of the radical-like properties of titanium(III) species are known in the literature. In that way the free-radical-like properties of CpTi^{III}Cl$_2$ derivatives are observed in reactions, for example, with quinones[26] as well as with azo and diazo compounds,[17] whereas the intermediately generated $Cp_2Ti^{III}Cl$ reagent is well introduced in organic reactions.[27]

A variety of persistent nitroxyl radicals such as TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl) or di-*tert*-butyl nitroxide have been used to synthesize an array of different metal complexes, including s-block metalloids,[28] early transition metals,[29] and lanthanoids.[30]

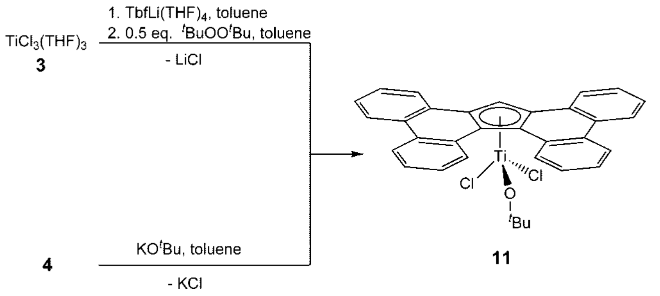
As depicted in Scheme 6 compound **3** was synthesized *in situ* and subsequently reacted with TEMPO at ambient temperature to form a burgundy red reaction mixture. Filtration and cooling of the solution to −10 °C afforded crystals of TbfTiCl_2TEMPO (**10**) in 51% yield.

Compound **10** is well soluble with the exception of aliphatic solvents and crystallizes in the triclinic space group $P\bar{1}$ with two molecules of **10** and one molecule of toluene per unit cell (Figure 8). In comparison to the TbfTiCl_2(OAr) complexes **5–9** the Ti−Ct distance is slightly elongated to 2.0875 Å, probably due to a higher electron density donated by the nitroxide moiety, as the Ti−O−N bond angle of 167.04° implies better dπ−pπ interactions between the oxygen and the titanium atom.[31]

Scheme 6



Scheme 7



Not only persistent radicals can be reacted with low-valent metal complexes but also those that are generated *in situ* by thermal cleavage of peroxides. To our best knowledge, so far only samarium[32] and ytterbium[33] compounds were reported into which a *tert*-butoxide moiety was introduced by reduction of di-*tert*-butylperoxide by the metal center. Here we report the first Cp-type titanium monoalkoxide complex synthesized by reacting a titanium(III) species with di-*tert*-butylperoxide.

As depicted in Scheme 7 the titanium(III) compound **3** was prepared *in situ*, and half an equivalent of di-*tert*-butylperoxide was added. Heating the reaction mixture fast until reflux affords a deep red suspension, which was taken to dryness. The residue was extracted with dichloromethane and filtered. Layering the solution with *n*-hexane afforded deep red crystals of TbfTi$Cl_2(O^tBu)$ (**11**) in only 10% yield. This is strongly associated with thermal decay of the monomeric titanium(III) species at those elevated temperatures.

In order to obtain higher yields a more conventional synthetic path was explored: Compound **4** was reacted with potassium *tert*-butoxide in a toluene suspension. Workup of the reaction mixture was identical and afforded crystals of **11** in 27% yield.

Compound **11** is well soluble in chlorinated solvents and THF and to a lesser extent in aromatic solvents. It crystallizes in the

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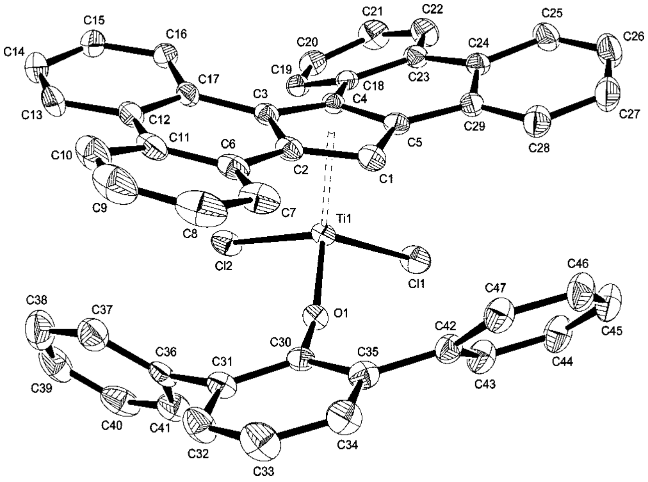

Figure 7. ORTEP plot of the solid state molecular structure of **9**. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [deg]: Ti(1)−Ct 2.0554, Ti(1)−Cl(1) 2.2509(6), Ti(1)−Cl(2) 2.2570(7), Ti(1)−O(1) 1.7913(15), Ti(1)−O(1)−C(30) 154.61(12), Cl(1)−Ti(1)−O(1) 103.98(5), Cl(2)−Ti(1)−O(1) 102.78(5), Cl(1)−Ti(1)−Cl(2) 104.08(3), C18−C4−C3−C17 −10.506(390).

monoclinic space group $P2_1/c$ with four molecules per unit cell (Figure 9). The Ti−Ct distance measures 2.0683 Å, and the Ti−O−C bond angle of 165.38° is very similar to the one in $TbfTiCl_2(O^iPr)$ reported previously.[10]

Common to all compounds discussed above are intermolecular face-to-face π-stacking interactions[24] in the solid state between the tetrabenzo[*a,c,g,i*]fluorenyl ligands of the titanium complexes, resulting in the above-mentioned low solubility of the compounds. This phenomenon is found in all solid state structures discussed so far and is most intense in the solid state structure of compound **4** (see Figure 10), in which the distance between the centroids of the five-membered ring and one of the six-membered rings amounts to 3.471 Å, being indicative of strong face-to-face π-interactions. This correlates with the compound's solubility, which is the lowest of all compounds described here. In the solid state structures of all other compounds this phenomenon occurs to a lesser extent, which should be the reason why they are more soluble.

Polymerization Experiments. Cyclopentadienyltitanium monophenoxide complexes of the general formula $CpR_5TiCl_2(OAr)$ (with R = H, Me) have been established as extraordinarily versatile catalysts for the homo- and copolymerization of ethylene, propylene, *n*-hexene, and norbornene by the works of Nomura. In particular, the compounds $CpTiCl_2(2,6\text{-}^iPr_2C_6H_3O)$ and $Cp^*TiCl_2(2,6\text{-}RC_6H_3O)$ (R = Me, ^{i}Pr) were proven to be quite potent catalysts for the homopolymerization of ethylene when activated with dried MAO (d-MAO).[22a,34] In contrast to commercially available methylalumoxane, d-MAO contains no free trimethylaluminum, which due to its high oxophilicity would potentially attack the Ti−O bond in the titanium monophenoxide complexes, resulting in the decomposition of the ligand framework.[35]

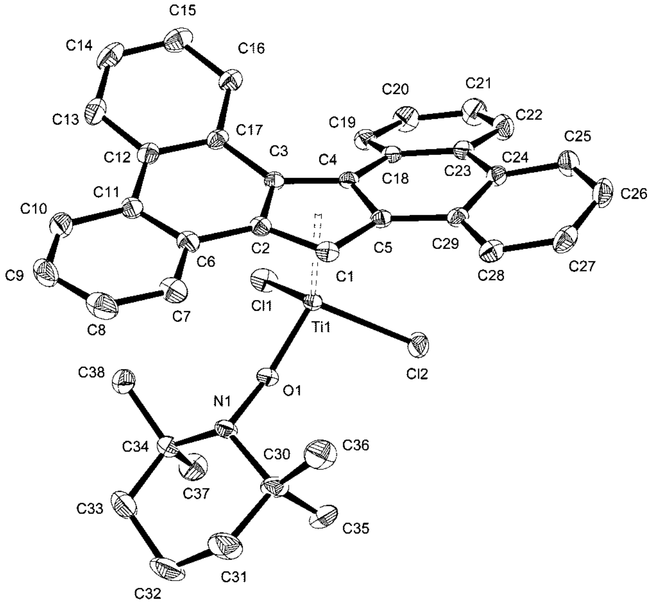

Figure 8. ORTEP plot of the solid state molecular structure of **10**. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [deg]: Ti(1)−Ct 2.0875, Ti(1)−Cl(1) 2.2940(5), Ti(1)−Cl(2) 2.2789(6), Ti(1)−O(1) 1.7549(14), Ti(1)−O(1)−N(1) 167.04(12), Cl(1)−Ti(1)−O(1) 101.13(4), Cl(2)−Ti(1)−O(1) 101.49(5), Cl(1)−Ti(1)−Cl(2) 104.63(3), C18−C4−C3−C17 −21.040(413).

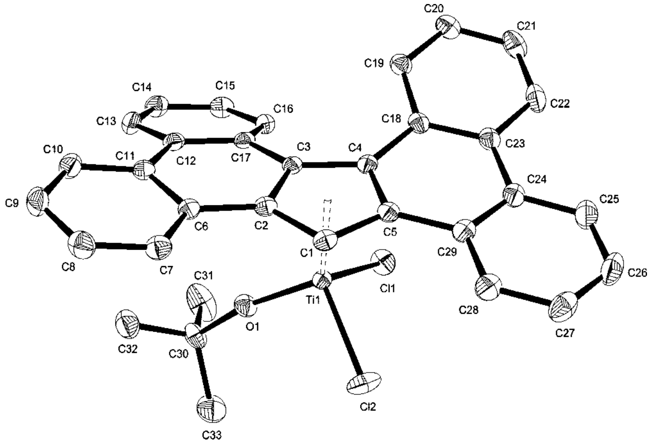

Figure 9. ORTEP plot of the solid state molecular structure of **11**. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [deg]: Ti(1)−Ct 2.0683, Ti(1)−Cl(1) 2.2808(5), Ti(1)−Cl(2) 2.2817(5), Ti(1)−O(1) 1.7414(11), Ti(1)−O(1)−C(30) 165.38(12), Cl(1)−Ti(1)−O(1) 103.22(4), Cl(2)−Ti(1)−O(1) 100.25(4), Cl(1)−Ti(1)−Cl(2) 103.44(2), C18−C4−C3−C17 19.489(298).

After achieving good results with tetrabenzo[*a,c,g,i*]fluorenyltitanium complexes in the syndiospecific polymerization of styrene,[10] we were eager to test the tetrabenzo[*a,c,g,i*]fluorenyltitanium complexes for their potential to polymerize other olefin monomers, e.g., ethylene.

In the course of the following studies, the compounds **6**, **8**, **9**, and **10** were subjected to ethylene polymerization experiments. Generally, the catalytic ethylene polymerization reactions were performed in a stainless steel 1 L autoclave (Medimex) in semibatch mode (ethylene was added by replenishing flow to keep the pressure constant). The reactor was temperature and pressure controlled and equipped with separated toluene, catalyst, and cocatalyst injection systems and a sample outlet

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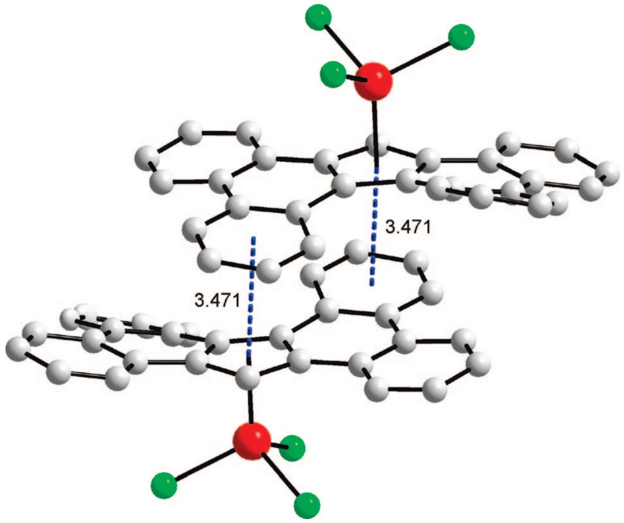

Figure 10. Intermolecular face-to-face π-stacking interactions (3.471 Å) in the solid state between the tetrabenzo[*a,c,g,i*]fluorenyl ligands in the example of compound **4** (titanium: red; chloride: green; carbon: gray).

Table 4. Ethylene Polymerization Runs Catalyzed by TbfTiCl$_2$(OAr)/MAO[a]

run no.	catalyst	cocat.	*T* [C°]	PE [g]	productivity[b]	M_w	M_w/M_n
1	**8**	d-MAO	30	0.5	200	491600	21.1
2	**8**	d-MAO	50	0.8	320	467000	10.0
3	**8**	d-MAO	80	0.7	280	122800	13.3
4	**8**	PMAO	80	0.3	120	59700	16.0
5	**9**	d-MAO	50	2.5	1000	619600	11.1
6	**9**	d-MAO	80	1.6	640	484400	8.4
7	**10**	d-MAO	50	1.9	760	590300	2.9
8	**10**	d-MAO	80	1.8	720	342100	2.4
9	**6**	d-MAO	50	0.8	320	478400	37.3
10	**6**	d-MAO	80	0.6	240	431200	19.5

[a] 2 μmol of cat., Ti:Al = 1:500 (m/m), 260 mL of toluene solvent, 5 bar of ethylene, 15 min run time. [b] kg(PE) × mol(Ti)$^{-1}$ h^{-1} bar^{-1}.

for continuous reaction monitoring. At 5 bar of ethylene pressure multiple injection of the catalyst with a pneumatically operated catalyst injection system was used. During a polymerization run the pressure, the ethylene flow, the inner and the outer reactor temperature, and the stirrer speed were monitored continuously. In a typical semibatch experiment, the autoclave was evacuated and heated for 1 h at 125 °C prior to use. The reactor was then brought to the desired temperature, stirred at 600 rpm, and charged with 230 mL of toluene together with d-MAO (0.058 g, Ti:Al = 1:500 (m/m)). After pressurizing with ethylene to reach 5 bar total pressure the autoclave was equilibrated for 5 min. Subsequently 1 mL of a 0.002 M stock solution of the titanium complex in toluene was injected together with 30 mL of toluene, to start the reaction. During the run the ethylene pressure was kept constant to within 0.2 bar of the initial pressure by replenishing flow. After the desired reaction time the reactor was vented and the residual PMAO/d-MAO was destroyed by addition of 20 mL of ethanol. Polymeric product was collected, stirred for 30 min in acidified ethanol, and rinsed with ethanol and acetone on a glass frit. The polymer was initially dried in air and subsequently in vacuum at 80 °C.

The polymerization results are given in Table 4. Compounds **6** and **8** are of only low productivity, ranging between 200 and 320 kg(PE) × mol(Ti)$^{-1}$ h^{-1} bar^{-1} when activated with d-MAO at all polymerization temperatures applied. The molecular weight of the polyethylene produced is quite high, with an average 467 000 g mol^{-1} with the exception of polymerization run 4, where the higher temperature of 80 °C leads to a significant decrease in polymer weight. On run 5 the effect of residual trimethylaluminum in commercial PMAO is seen, resulting in a further deterioration of catalyst productivity and polymer weight.

In contrast to their both aforementioned brethren complexes **9** and **10** deliver a considerably higher productivity in ethylene polymerization at both 50 and 80 °C when activated with d-MAO ranging from 640 to 1000 kg(PE) × mol(Ti)$^{-1}$ h^{-1} bar^{-1}, which is quite high for cyclopentadienyl-type titanium monophenoxide complexes and comparable to Nomura's complexes mentioned above. The weights of the polymers synthesized are higher at 50 °C and are again very similar to those prepared with CpR$_5$TiCl$_2$(2,6-^{i}Pr$_2$C$_6$H$_3$O) (R = H, Me). With the exception of complex **10**, all TbfTi complexes produced ethylene polymers with a quite broad molecular weight distribution, which in the literature is believed to originate from nonuniform active species.

Conclusion

Employing the tetrabenzo[*a,c,g,i*]fluorenyl ligand as a benzannelated fluorene system, a broad range of Tbf titanium complexes of high thermal stability becomes available. In order to obtain TbfTi^{IV}Cl$_3$ the primary synthesis of TbfTi^{III}Cl$_2$ is the best way in order to prevent Wurtz-type C−C coupling reactions, as observed by direct use of titanium(IV) starting materials. Radical-type coupling reactions of TbfTiCl$_2$ intermediates with free radicals (TEMPO) as well as radical-generating substrates (^{t}Bu-OO-Bu^t) are used as an efficient preparative tool for the formation of titanium(IV) complexes. All of the titanium complexes show η^5-coordinated Tbf ligands.

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.

For polymerization purposes toluene (Aldrich, anhydrous, 99.8%) was passed over columns of Al$_2$O$_3$ (Fluka), BASF R3-11-supported Cu oxygen scavenger, and molecular sieves (Aldrich, 4 Å). Ethylene (AGA polymer grade) was passed over BASF R3-11-supported Cu oxygen scavenger and molecular sieves (Aldrich, 4 Å). PMAO (4.9 wt % Al in toluene, Akzo Nobel) was used as received. d-MAO was prepared by removal of all volatiles from PMAO under vacuum.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 500 (^{1}H, 500.13 MHz; ^{13}C, 125.75 MHz) spectrometer. Variable-temperature NMR experiments were conducted on a Bruker Advance 300.1 MHz spectrometer. ^{1}H chemical shifts are referenced to residual solvent protons; ^{13}C spectra were referenced to CDCl$_3$ or C$_6$D$_6$, respectively (signal assignment based on NOE measurements). Electron impact (EI) and chemical ionization (CI) 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.

Gel permeation chromatography (GPC) analysis was carried out on a Polymer Laboratories Ltd. (PL-GPC210) chromatograph at 150 °C using 1,2,4-trichlorobenzene as the mobile phase. The samples were prepared by dissolving the polymer (0.1% weight/

Table 5

	3	**4**	**5**	**6**	**7**
empirical formular	$C_{33}H_{25}Cl_2OTi$	$C_{29}H_{17}Cl_3Ti$ × 0.5 CH_2Cl_2	$C_{39}H_{30}Cl_2OTi$	$C_{37}H_{26}Cl_2OTi$	$C_{38}H_{28}Cl_2OTi$
fw	556.23	562.14	633.43	605.38	619.40
color habit	green	dark violet	red	red	red
cryst dimens, mm	0.80 × 0.55 × 0.41	0.70 × 0.10 × 0.03	0.50 × 0.07 × 0.04	0.27 × 0.10 × 0.02	0.30 × 0.22 × 0.16
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	*C*2/c	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a, Å	21.9397(7)	10.5761(6)	10.5863(18)	14.6198(14)	10.3873(3)
b, Å	16.9151(6)	18.6258(10)	10.7139(14)	10.0172(5)	18.6488(9)
c, Å	13.7806(6)	12.9464(10)	14.898(3)	19.524(2)	14.7521(6)
α, deg	90	90	109.84(2)	90	90
β, deg	93.952(4)	110.549(8)	97.97(2)	102.673(11)	96.188(4)
γ, deg	90	90	99.321	90	90
V, $Å^3$	5102.0(3)	2388.0(3)	1533.9(5)	2789.7(4)	2841.0(2)
Z	8	4	2	4	4
D_{calcd}, g cm^3	1.449	1.564	1.371	1.441	1.448
μ, mm^{-1}	0.571	0.825	0.484	0.529	0.521
T, K	153	153	153	153	153
θ range, deg	2.17 to 25.98	2.15 to 26.10	2.53 to 25.35	2.14 to 26.10	2.25 to 25.98
no. of rflns collected	30033	22619	16264	22446	26786
no. of indep rflns $I > 2\sigma(I)$	4692 [*R*(int) = 0.0479]	4384 [*R*(int) = 0.1049]	5677 [*R*(int) = 0.2063]	5147 [*R*(int) = 0.2116]	5235 [*R*(int) = 0.0792]
abs corr	none	numerical	none	numerical	none
max., min. transmn	0.7995 and 0.6579	0.9757 and 0.5960	0.9809 and 0.7937	0.9895 and 0.8703	0.9212 and 0.8593
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0288, wR2 = 0.0742	R1 = 0.0388, wR2 = 0.0618	R1 = 0.0675, wR2 = 0.1272	R1 = 0.0492, wR2 = 0.0786	R1 = 0.0331, wR2 = 0.0593
R indices (all data)	R1 = 0.0383, wR2 = 0.0770	R1 = 0.0908, wR2 = 0.0712	R1 = 0.2285, wR2 = 0.1752	R1 = 0.1432, wR2 = 0.1017	R1 = 0.0661, wR2 = 0.0649

	8	**9**	**10**	**11**	
empirical formular	$C_{41}H_{34}Cl_2OTi$	$C_{47}H_{40}Cl_2OTi$ × 0.5 C_7H_8	$C_{38}H_{35}Cl_2NOTi$ × 0.5 C_7H_8	$C_{33}H_{26}Cl_2OTi$	
fw	661.48	775.58	686.54	557.34	
color habit	red	red	red	red	
cryst dimens, mm	0.45 × 0.27 × 0.19	0.45 × 0.44 × 0.18	0.80 × 0.41 × 0.11	0.40 × 0.11 × 0.08	
cryst syst	monoclinic	triclinic	triclinic	monoclinic	
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	
a, Å	12.9695(7)	9.5715(8)	10.2441(5)	13.3823(6)	
b, Å	14.7973(7)	12.8182(10)	14.2527(7)	10.8547(3)	
c, Å	17.2211(11)	16.3538(14)	14.5183(7)	18.1479(9)	
α, deg	90	92.982(10)	62.460(5)	90	
β, deg	100.068(7)	95.251(10)	75.719(6)	92.797(6)	
γ, deg	90	109.988(10)	70.775(6)	90	
V, $Å^3$	3254.1(3)	1870.2(3)	1763.42(18)	2633.04(19)	
Z	4	2	2	4	
D_{calcd}, g cm^3	1.350	1.377	1.293	1.406	
μ, mm^{-1}	0.460	0.412	0.428	0.554	
T, K	153	153	153	153	
θ range, deg	2.11 to 26.03	2.02 to 26.06	2.34 to 26.16	2.19 to 26.11	
no. of rflns collected	29371	17200	22004	27879	
no. of indep rflns $I > 2\sigma(I)$	6002 [*R*(int) = 0.0787]	6865 [*R*(int) = 0.0362]	6508 [*R*(int) = 0.0384]	5010 [*R*(int) = 0.0462]	
abs corr	none	numerical	numerical	numerical	
max., min. transmn	0.9177 and 0.8198	0.9296 and 0.8364	0.9545 and 0.7261	0.9570 and 0.8089	
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0343, wR2 = 0.0793	R1 = 0.0401, wR2 = 0.1083	R1 = 0.0392, wR2 = 0.1075	R1 = 0.0266, wR2 = 0.0589	
R indices (all data)	R1 = 0.0562, wR2 = 0.0853	R1 = 0.0534, wR2 = 0.1141	R1 = 0.0492, wR2 = 0.1119	R1 = 0.0427, wR2 = 0.0625	

volume) in the mobile phase solvent in an external oven and were run without filtration. The molecular weight was referenced to polyethylene (M_w = 50 000 g/mol) and polystyrene (M_w = 100 000–500 000 g/mol) standards. The reported values are the average of at least two independent determinations.

X-ray Diffraction. Single-crystal experiments were performed on a Stoe IPDS diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). 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.[36]

Synthesis of TbfTi(III)Cl$_2$(THF) (3). To a solution of 330 mg (0.50 mmol) of TbfLi(THF)$_4$ in 30 mL of toluene was added 185 mg (0.50 mmol) of TiCl$_3$(THF)$_3$ to form a dark green solution, which after 1 min of stirring was left for crystallization. Dark green, extremely air-sensitive crystals of **2** (179 mg, 0.32 mmmol, 64%) were obtained that were also suitable for X-ray diffraction. Mp: 120 °C (dec). MS (CI, isobutane): *m/z* (relative intensity) 556.6 (5) [MH$^+$], 420.8 (15), 366.8 (100) [TbfH$^+$], 302.8 (15), 264.7 (55), 111.0 (50). Anal. Calcd for C$_{33}$H$_{25}$Cl$_2$OTi: C, 71.25; H, 4.53. Found: C, 71.01; H, 4.46.

Synthesis of TbfTiCl$_3$ (4). TbfLi(THF)$_4$ (3.932 g, 5.95 mmol) and 2.205 g (5.95 mmol) of TiCl$_3$(THF)$_3$ were mixed as solids, and 20 mL of toluene was added to form a green suspension. After stirring overnight the reaction mixture was evaporated to dryness and the green residue was continuously extracted from a frit with 30 mL of CCl$_4$. The extract was filtered to give 2.046 g of **4** (3.94 mmol, 66%) as a dark violet microcrystalline solid. Crystals suitable for X-ray diffraction were prepared by layering a concentrated solution of **4** in 20 mL of dichloromethane with 40 mL of *n*-hexane. Mp: 279 °C. ^{1}H NMR (CDCl$_3$, 500.13 MHz, 300 K) [ppm]: δ 8.91 (d, 2 H, $^3J_{HH}$ = 7.9 Hz, H-8, H-9), 8.66 (d, 2 H, $^3J_{HH}$ = 8.0 Hz, H-5, H-12), 8.61 (d, 2 H, $^3J_{HH}$ = 7.6 Hz, H-4, H-13), 8.47 (d, 2 H, $^3J_{HH}$ = 6.8 Hz, H-1, H-16), 8.41 (s, 1 H, H-17), 7.76 (m, 6 H, J_{HH} = 7.4 Hz, H-2, H-3, H-6, H-11, H-14, H-15), 7.66 (t, 2 H, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 7.1 Hz, H-7, H-10). IR (KBr pellet) [cm^{-1}]: $\tilde{\nu}$ 3106 (m), 2962 (m), 1603 (m) 1508 (m), 1422 (m), 1397 (m), 1261 (m), 1164 (m), 1020 (m), 801 (m), 756 (s), 721 (s), 425 (s). MS (EI, 70 eV): *m/z* (relative intensity) 520.0 (10) [M$^+$], 365.1 (100) [Tbf$^+$], 182.1 (35). Anal. Calcd for C$_{29}$H$_{17}$Cl$_3$Ti: C, 67.03; H, 3.30. Found: C, 67.38; H, 3.10.

Synthesis of TbfTiCl$_2$(4-^{t}BuC$_6$H$_4$O) (5). **4** (260 mg, 0.50 mmol) and 50 mg of 4-^{t}BuC$_6$H$_4$OLi were mixed as solids, and 30 mL of toluene was added to give a dark violet suspension, which turned dark red upon stirring overnight. The reaction mixture was evaporated to dryness, and the residue was extracted with 30 mL of dichloromethane in order to remove LiCl. The resulting dark red solution was layered with 30 mL of *n*-hexane to afford 73 mg (0.11 mmol, 23%) of **5** as dark red crystals suitable for X-ray diffraction. Mp: 261 °C. ^{1}H NMR (CDCl$_3$, 500.13 MHz, 300 K) [ppm]: δ 8.85 (d, 2 H, $^3J_{HH}$ = Hz, H-8, H-9), 8.44−8.41 (m, 4 H, could not be clearly assigned), 8.37−8.35 (m, 2 H)*, 8.118 (s, 1 H, H-17), 8.69−7.59 (m, 8 H, could not be clearly assigned), 6.67 (d, 2 H, $^3J_{HH}$ = 8.6 Hz, *meta*-H), 5.61 (d, 2 H, $^3J_{HH}$ = 8.6 Hz, *ortho*-H), 1.146 (s, 9 H, C(C*H*$_3$)$_3$). ^{13}C NMR (CDCl$_3$, 124.75 MHz, 300 K) [ppm]: δ 162.9 (*ipso*-C), 140.1 (*para*-C), 131.3 (C-8a, C-8d), 130.2 (C-17b, C-16a), 128.7 (C-4a, C-12b), 128.3 (C-4b, C-12a), 128.2 (C-2, C-15), 127.8 (C-7, C-10), 127.3 (C-16b, C-17a), 127.1 (C-8, C-9), 127.0 (C-5, C-12), 125.1 (*meta*-C), 124.3 (C-4, C-13), 123.6 (C-7, C-10), 123.6, 123.3, 123.2 (could not be clearly assigned), 118.1 (*ortho*-C), 34.2 ($\underline{\mathrm{C}}$(CH$_3$)$_3$), 31.5 (C($\underline{\mathrm{C}}$H$_3$)$_3$). MS (EI, 70 eV): *m/z* (relative intensity) 661.9 (70) [M$^+$], 526.8 (70), 487.8 (10), 366.0 (100) [Tbf$^+$], 294.8 (65), 258.9 (15).

Synthesis of TbfTiCl$_2$(2,6-Me$_2$C$_6$H$_3$O) (6). **4** (260 mg, 0.50 mmol) and 65 mg (0.50 mmol) of 2,6-MeC$_6$H$_3$OLi were mixed as solids, and 30 mL of toluene was added to give a dark violet suspension, which turned dark red upon stirring overnight. The reaction mixture was evaporated to dryness, and the residue was extracted with 30 mL of dichloromethane in order to remove LiCl. The resulting dark red solution was layered with 30 mL of *n*-hexane to afford 63 mg (0.11 mmol, 21%) of **6** as dark red crystals suitable for X-ray diffraction. Mp: 257 °C. ^{1}H NMR (CDCl$_3$, 500.13 MHz, 300 K) [ppm]: δ 9.04 (d, 2 H, $^3J_{HH}$ = 7.8 Hz, H-8, H-9), 8.58 (d, 2 H, $^3J_{HH}$ = 7.8 Hz, H-5, H-12), 8.52 (d, 2 H, $^3J_{HH}$ = 8.2 Hz, H-4, H-13), 8.10 (d, 2 H, $^3J_{HH}$ = 8.0 Hz, H-1, H-16), 7.856 (s, 1 H, C-17), 7.71 (t, 2 H, $^3J_{HH}$ = 8.0 Hz, H-7, H-10), 7.66 (t, 4 H, $^3J_{HH}$ = 8.00 Hz, H-3, H-6, H-11, H-14), 7.52 (t, 2 H, $^3J_{HH}$ = 7.2 Hz, H-2, H-15), 6.72−6.67 (m, 3 H, phenyl), 1.638 (s, 6 H, 2-C*H*$_3$). ^{13}C NMR (CDCl$_3$, 124.75 MHz, 300 K) [ppm]: δ 131.4, 129.2, 128.7, 128.6, 128.2, 128.1, 128.0, 127.8, 127.8, 127.3, 126.7, 126.6, 124.5, 124.4, 123.7, 123.7, 122.9, 120.1, 100.1. IR (KBr) [cm^{-1}]: $\tilde{\nu}$ 3045 (w), 2916 (w), 1454 (m), 1437 (m), 1401 (m), 1262 (m), 1200 (s), 1165 (s), 1098 (m), 1084 (m), 909 (s), 801 (m), 753 (s), 721 (s), 425 (m). MS (EI, 70 eV): *m/z* (relative intensity) 603.8 (15) [M$^+$], 364.9 (100) [Tbf$^+$], 181.9 (15). Anal. Calcd for C$_{37}$H$_{26}$Cl$_2$OTi C, 73.41; H, 4.33. Found: C, 73.15; H 4.23.

Synthesis of TbfTiCl$_2$(2,4,6-Me$_3$C$_6$H$_2$O) (7). **4** (260 mg, 0.50 mmol) and 71 mg (0.50 mmol) of 2,4,6-MeC$_6$H$_2$OLi were mixed as solids, and 30 mL of toluene was added to give a dark violet suspension, which turned dark red upon stirring overnight. The reaction mixture was evaporated to dryness and extracted with 30 mL of dichloromethane in order to remove LiCl. The resulting dark red solution was layered with 30 mL of *n*-hexane to afford 70 mg (0.11 mmol, 23%) of **7** as dark red crystals suitable for X-ray diffraction. Mp: 251 °C. ^{1}H NMR (CDCl$_3$, 500.13 MHz, 300 K) [ppm]: δ 9.03 (d, 2 H, $^3J_{HH}$ = 8.0 Hz, H-8, H-9), 8.58 (d, 2 H, $^3J_{HH}$ = 8.0 Hz, H-5, H-12), 8.52 (d, 2 H, $^3J_{HH}$= 8.2 Hz, H-4, H-13), 8.09 (d, 2 H, $^3J_{HH}$ = 7.5 Hz, H-1, H-16), 7.814 (s, 1 H, H-17), 7.71 (dt, 2 H, $^3J_{HH}$ =, H-7, H-10), 7.67−7.63 (m, 4 H, H-3, H-6, H-14, H-11), 7.51 (t, 2 H, $^3J_{HH}$ = 7.5 Hz, H-2, H-15), 6.477 (s, 2 H, *meta*-H), 2.913 (s, 3 H, *para*-CH$_3$), 1.609 (s, 6 H, *ortho*-CH$_3$). ^{13}C NMR (CDCl$_3$, 124.75 MHz, 300 K) [ppm]: δ 131.9 (C-17b, C-16a), 131.4 (C-8a, C-8d), 129.5, 129.1, 128.9 (could not be clearly assigned), 128.7 (C-4b, C-12a), 128.6, 128.2, 128.1, 127.8 (could not be clearly assigned), 127.2 (C-16b, C-16b), 126.5, 124.5, 124.4 (could not be clearly assigned), 124.0 (C-8b, C-8c), 123.7 (could not be clearly assigned), 99.8 (C-17), 20.8 (*para*-$\underline{\mathrm{C}}$H$_3$), 16.55 (*ortho*-$\underline{\mathrm{C}}$H$_3$). IR (KBr) [cm^{-1}]: $\tilde{\nu}$ 3042 (w), 2945 (w), 1603 (w), 1496 (m), 1438 (m), 1399 (m), 1374 (m), 1212 (s), 1153 (s), 957 (m), 886 (s), 859 (m), 809 (m), 754 (s), 720 (s), 433 (m), 408 (m). MS (EI, 70 eV): *m/z* (relative intensity) 617.7 (15) [M$^+$], 364.9 (100) [Tbf$^+$]. Anal. Calcd for C$_{38}$H$_{28}$Cl$_2$OTi: C, 73.69; H, 4.56. Found: C, 73.44; H, 4.57.

Synthesis of TbfTiCl$_2$(2,6-^{i}Pr$_2$C$_6$H$_3$O) (8). **4** (260 mg, 0.50 mmol) and 92 mg (0.50 mmol) of 2,6-^{i}PrC$_6$H$_3$OLi were mixed as solids, and 30 mL of toluene was added to give a dark violet suspension, which turned dark red upon stirring overnight. The reaction mixture was evaporated to dryness and extracted with 30 mL of dichloromethane in order to remove LiCl. The resulting dark red solution was layered with 30 mL of *n*-hexane to afford 110 mg (0.17 mmol, 34%) of **8** as dark red crystals suitable for X-ray diffraction. Mp: 253 °C. ^{1}H NMR (CDCl$_3$, 500.13 MHz, 300 K) [ppm]: δ 9.06 (d, 2 H, $^3J_{HH}$ = 8.3 Hz, H-8, H-9), 8.60 (d, 2 H, $^3J_{HH}$ = 7.9 Hz, H-5, H-12), 8.55 (d, 2 H, $^3J_{HH}$ = 8.2 Hz, H-4, H-13), 7.97 (d, 2 H, $^3J_{HH}$ = 7.5 Hz, H-1, H-16), 7.72 (ddd, 2 H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.0 Hz, H-7, H-10), 7.690 (s, 1 H, H-17), 7.67−7.63 (m, 4 H, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.0 Hz, H-3, H-6, H-11, H-14), 7.48 (ddd, 2 H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ =1.0 Hz, H-2, H-15), 6.95−6.89 (m, 3 H, phenyl), 2.48 (q, 2 H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 0.94 (d, 12 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$). ^{13}C NMR (CDCl$_3$, 124.75 MHz, 300 K) [ppm]: δ 163.4 (*ipso*-C), 139.4 (*para*-C), 131.9 (C-17b, C-16a), 131.4 (C-8a, C-8d), 129.7, 129.2, 128.8 (C-4b, C-8d), 128.7 (C-7, C-10), 128.1 (C-8, C-9), 127.7

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[36] Sheldrick, G. M. *SHELXL-97. A Program for Refining Crystal Structures*; University of Göttingen: Germany, 1997.

(C-2, C-15), 127.3 (C-16b, C-17a), 126.5 (C-6, C-14), 124.4 (C-5, C-12), 124.3 (C-1, C-16), 123.8 (C-8b, C-8c), 123.7 (C-4, C-13), 122.6 (*meta*-C, *para*-C), 99.2 (C-17), 26.8 ($\underline{C}H(CH_3)_2$), 23.7 ($CH(\underline{C}H_3)_2$). IR (KBr) [cm^{-1}]: $\tilde{\nu}$ 2959 (m), 2861 (w), 1509 (w), 1456 (w), 1424 (m), 1382 (m), 1361 (m), 1324 (m), 1247 (m), 1193 (s), 1115 (m), 1092 (m), 914 (s), 811 (m), 793 (s), 723 (s). MS (EI, 70 eV): *m*/*z* (relative intensity) 659.9 (10) [M$^+$], 603.9 (10), 365.0 (100), 182.0 (10). Anal. Calcd for $C_{41}H_{34}Cl_2OTi$: C, 74.44; H, 5.18. Found: C, 73.24; H 5.13.

Synthesis of TbfTiCl$_2$(2,6-Ph$_2$C$_6$H$_3$O) (9). **4** (260 mg, 0.50 mmol) and 252 mg (0.50 mmol) of 2,6-PhC$_6$H$_3$OLi were mixed as solids, and 30 mL of toluene was added to give a dark violet suspension, which turned dark red upon stirring overnight. The reaction mixture was filtered in order to remove LiCl, and the resulting dark red solution was layered with 30 mL of *n*-hexane to afford 119 mg (0.16 mmol, 33%) of **9** as dark red crystals suitable for X-ray diffraction. Mp: 252 °C. ^{1}H NMR (CDCl$_3$, 500.13 MHz, 300 K) [ppm]: δ 8.89 (d, 2 H, $^3J_{HH}$ = 8.2 Hz, H-8, H-9), 8.47 (d, 2 H, $^3J_{HH}$ = 8.3 Hz, H-5, H-12), 8.45 (d, 2 H, $^3J_{HH}$ = 8.3 Hz, H-4, H-13), 7.61 (m, 2 H, H-3, H-14), 7.60 (m, 2 H, H-6, H-11), 7.51 (m, 2 H, H-7, H-10), 7.29−7.20 (m, 14 H, H-1, H-2, H-15, H-16, H-35, H-35′, H-36, H-36′, H-37, H-37′, H-38, H-38′, H-39, H-39′), 7.18−7.12 (m, 3 H, H-32, H-32′, H-33), 6.450 (s, 1 H, H-17). ^{13}C NMR (CDCl$_3$, 124.75 MHz, 300 K) [ppm]: δ 161.8 (C-30), 137.8 (C-31, C-31′), 134.5 (C-34, C-34′), 131.5 (C-4b, C-12a), 131.2 (C-4a, C-12b), 130.1 (C-32, C-32′), 130.0 (C-16b, C-17a, C-35, C-35′, C-39, C-39′), 128.8 (C-3, C-14), 128.6 (C-36, C-36′, C-38, C-38′), 128.5 (C-8a, C-8d), 128.4 (C-6, C-11), 128.2 (C-8, C-9), 127.3 (C-37, C-37′), 126.8 (C-2, C-15), 126.7 (C-17b, C-16a), 126.1 (C-7, C-10), 124.5 (C-1, C-16), 124.2 (C-8b, C-8c), 123.9 (C-5, C-12), 123.8 (C-33), 123.3 (C-4, C-13), 99.8 (C-17). IR (KBr) [cm^{-1}]: $\tilde{\nu}$ 3023 (m), 1494 (w), 1451 (m), 1439 (m), 1402 (s), 1221 (s), 900 (s), 810 (m), 754 (s), 714 (s), 696 (s). MS (EI, 70 eV): *m*/*z* (relative intensity) 729.8 (15) [M$^+$], 607.8 (15), 364.9 (100) [Tbf$^+$], 182.0. Anal. Calcd for $C_{47}H_{30}Cl_2OTi \times 0.5\ C_7H_8$: C, 77.38; H, 4.14. Found: 78.05; H 4.48.

Synthesis of TbfTiCl$_2$TEMPO (10). TiCl$_3$(THF)$_3$ (370 mg, 1.00 mmol) and 661 mg (1.00 mmol) of TbfLi(THF)$_4$ (**1**) were mixed as solids, and 20 mL of toluene was added to give a green suspension, which immediately turned dark red upon adding a solution of 156 mg (1.00 mmol) of TEMPO in 5 mL of toluene after 2 h. The reaction mixture was filtered in order to remove LiCl, and leaving the solution at −10 °C afforded 324 mg (0.51 mmol, 51%) of **10** as dark red crystals suitable for X-ray diffraction. Mp: 264 °C (dec). ^{1}H NMR (CDCl$_3$, 500.13 MHz, 300 K) [ppm]: δ 9.04 (d, 2 H, $^3J_{HH}$ = 8 Hz, H-8, H-9), 8.61 (d, 2 H, $^3J_{HH}$ = 8.0 Hz, H-5, H-12), 8.59 (dd, 2 H, $^3J_{HH}$ = 4.5 Hz, H-4, H-13), 8.22 (dd, 2 H, $^3J_{HH}$ = 4.5 Hz, H-1, H-16), 7.69−7.63 (m, 6 H, H-2, H-3, H-6, H-11, H-14, H-15), 7.62 (s, 1 H, H-17), 7.62 (dd, 2 H, $^3J_{HH}$ = 8.0 Hz, H-7, H-10), 1.285 (s, 6 H), 0.872 (s, 12 H, CH_3). ^{13}C NMR (CDCl$_3$, 124.75 MHz, 300 K) [ppm]: δ 131.7 (C-17b, C-16a), 131.5 (C-8a, C-8d), 129.0 (could not be clearly assigned), 128.6 (C-4b, C-12a), 128.2, 128.1 (could not be clearly assigned), 128.0 (C-8, C-9), 127.6 (C-16b, C-17a), 127.5 (could not be clearly assigned), 126.2 (C-7, C-10), 125.1 (C-1, C-16), 124.2 (C-5, C-12), 123.7 (C-4, C-13), 123.3 (C-8b, C-8c), 98.0 (C-17), 64.4, 39.7, 26.2 (4 $\underline{C}H_3$), 16.4 (CH$_2$). IR (KBr) [cm^{-1}]: $\tilde{\nu}$ 2964 (w), 2930 (w), 1454 (w), 1434 (w), 1401 (w), 1364 (w), 1260 (m), 1242 (w), 1174 (m), 1091 (m), 1047 (m), 1020 (m), 818 (m), 754 (s), 722 (s), 421 (w). MS (EI, 70 eV): *m*/*z* (relative intensity) 366.1 (100) [Tbf$^+$], 182.0 (16), 126.1 (25), 58.1 (20). Anal. Calcd for $C_{38}H_{35}Cl_2NOTi \times 0.5C_7H_8$: C, 72.60; H, 5.73. Found: C, 72.44; H, 5.56.

Synthesis of TbfTiCl$_2$O^{t}Bu (11). Method a. TiCl$_3$(THF)$_3$ (370 mg, 1.00 mmol) and 661 mg (1.00 mmol) of TbfLi(THF)$_4$ (**1**) were mixed as solids, and 20 mL of toluene was added to give a green suspension. After 2 h a solution of 0.92 mL (0.50 mmol) of ^{t}BuOO^{t}Bu in 5 mL of toluene was added, and the reaction mixture turned dark upon heating until reflux occurred. After cooling to ambient temperature the reaction mixture was evaporated to dryness and extracted with 50 mL of dichloromethane in order to remove LiCl. Layering the dark red solution with 50 mL of *n*-hexane afforded 50 mg (0.1 mmol, 10%) of dark red crystals of **11** suitable for X-ray diffraction.

Method b. TbfTiCl$_3$(**4**) (520 mg, 1.00 mmol) and 112 mg (1.00 mmol) KO^{t}Bu were mixed as solids, and 50 mL of Toluol were added to form a violet suspension, which was vigorously stirred overnight. The reaction mixture was evaporated to dryness and extracted with 60 mL of dichloromethane in order to remove LiCl. The dark red solution was layered with 60 mL of *n*-hexane to afford 135 mg (0.27 mmol, 27%) of dark red crystals of **11**. Mp: 254 °C. ^{1}H NMR (CDCl$_3$, 500.13 MHz, 300 K) [ppm]: δ 8.89 (d, 2 H, $^3J_{HH}$ = 8.2 Hz, H-8, H-9), 8.64 (d, 2 H, $^3J_{HH}$ = 8.2 Hz, H-5, H-12), 8.61 (dd, 2 H, $^3J_{HH}$ = 6.0 Hz, H-4, H-13), 8.43 (dd, 2 H, $^3J_{HH}$ = 6.0 Hz, H-1, H-16), 8.079 (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 (dd, 2 H, $^3J_{HH}$ = 7.2 Hz, H-7, H-10), 1.265 (s, 9 H, OC(CH_3)$_3$).). ^{13}C NMR (CDCl$_3$, 124.75 MHz, 300 K) [ppm]: δ 131.7 (C-17b, C-16a), 131.1 (C-8a, C-8d), 128.8 (C-4b, C-12a), 128.7 (could not be clearly assigned), 128.1 (C-8, C-9), 128.0 (could not be clearly assigned), 127.9 (C-4a, C-12b), 127.8 (could not be clearly assigned), 126.2 (C-7, C-10), 125.2 (C-1, C-16), 124.3 (C-5, C-12), 123.6 (C-4, C-13), 122.6 (C-8b, C-8c), 101.1 (C-17), 31.2 ($O\underline{C}(CH_3)_3$), 29.3 ($OC(\underline{C}H_3)_3$).). IR (KBr) [cm^{-1}]: $\tilde{\nu}$ 3077 (w), 2970 (m), 2925 (w), 1507 (w), 1454 (m), 1431 (m), 1363 (m), 1262 (w), 1235 (w), 1159 (s), 1109 (m), 999 (s), 819 (m), 754 (s), 722 (s), 666 (w), 479 (w), 426 (m), 406 (m). MS (EI, 70 eV): *m*/*z* (relative intensity) 556.1 (5) [M$^+$], 501.0 (20), 365.1 (100), 182.1 (15), 56.0 (45). Anal. Calcd for $C_{33}H_{26}Cl_2OTi$: C, 71.12; H, 4.70. Found: 70.93; H, 4.60.

Supporting Information Available: Additional crystallographic data for structures **3**−**11** have been deposited with the Cambridge Data Centre as supplementary publications nos. CCDC 670166 (**3**), CCDC 670167 (**4**), CCDC 670171 (**5**), CCDC 670165 (**6**), CCDC 670170 (**7**), CCDC 670168 (**8**), CCDC 670169 (**9**), CCDC 670172 (**10**), and CCDC 670173 (**11**). Copies of the data can be obtained free of charges on application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax(+44)1223-336-033; e-mail deposit@ccdc.cam.ac.uk), or free of charge via the Internet at http://pubs.acs.org.

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