ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 591 (1999) 148–162

Journal of Organometallic Chemistry

Cationic Group 4 metal alkyl compounds containing aryloxide ligation: synthesis, structure, reactivity and polymerization studies

Matthew G. Thorn, Zac C. Etheridge, Phillip E. Fanwick, Ian P. Rothwell *

Department of Chemistry, 1393 Brown Building, Purdue University, West Lafayette, IN 47907-1393, USA

Received 2 June 1999; accepted 25 June 1999

Abstract

A series of bis(alkyl) derivatives of titanium and zirconium $[(ArO)_2MR_2]$ (M = Ti, Zr; R = Me, CH_2Ph; ArO = various 2,6-di-substituted phenoxides) has been synthesized and their reactivity towards the Lewis acid $[B(C_6F_5)_3]$ examined. The benzyl compounds generate stable zwitterionic species such as $[M(OC_6HPh_2\text{-}2,6\text{-}R_2\text{-}3,5)_2(CH_2Ph)][\eta^6\text{-}C_6H_5CH_2B(C_6F_5)_3]$ (M = Ti, R = H, **12**; Me, **13**: M = Zr, R = Me, **15**). Structural studies of **12** and **15** show the boron anion π-bound to the metal center through the original benzyl phenyl ring. In contrast, treatment of the benzyl compound $[Zr(OC_6H_3Bu^t_2\text{-}2,6)_2(CH_2Ph)_2]$ with $[B(C_6F_5)_3]$ leads to the cyclometallated compound $[Zr(OC_6H_3Bu^t\text{-}CMe_2CH_2)(OC_6H_3Bu^t_2\text{-}2,6)][\eta^6\text{-}C_6H_5CH_2B(C_6F_5)_3]$ **16** which was structurally characterized. In contrast to this behavior the bis(methyl) species react with $[B(C_6F_5)_3]$ to produce unstable methyl cationic intermediates which decompose to a mixture of $[Ti(OAr)_2(CH_3)(C_6F_5)]$ and $[CH_3B(C_6F_5)_2]$. The titanium zwitterionic benzyl compounds will react with alkynes and α-olefins to produce mono-insertion products such as $[Ti(OC_6H_3Ph_2\text{-}2,6)_2\{C(CH_3)C(Ph)CH_2(\eta^6\text{-}C_6H_5)\}][PhCH_2B(C_6F_5)_3]$ **24**. In these compounds 1,2-insertion of olefins occurs followed by chelation of the original benzyl group to the metal center. Spectroscopic studies show the boron anion is non-coordinated to the metal center. Despite their thermal instability, the methyl cations can be generated in situ in the presence of olefins to produce polymers (ethene and propene) and oligomers (1-hexene). Studies show that the molecular weight of the polymers or oligomers increases systematically with the bulk of the aryloxide ligand. Spectroscopic studies of the polypropylene indicate 1,2-insertion is occurring with β-hydrogen abstraction to produce vinylidene end groups as the termination step. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Titanium; Zirconium; Alkyl; Phenoxides; Zwitterionic polymerization

1. Introduction

There has been an explosive growth of research interest into the use of non-cyclopentadienyl ligation for supporting organometallic chemistry at early d-block metal centers [1]. The replacement of the ubiquitous cyclopentadiene ligands by 'hard' donor ligands such as amido [2], alkoxide [3], siloxide [4] and aryloxide [5] groups has generated both complementary and novel reactivity. One exciting development has been in the use of these ligands to carry out the polymerization of olefins by well-defined cationic catalyst systems [6]. In the case of amido ligation, new, living polymerization catalysts have been developed [7]. As part of our ongoing studies of bulky aryloxide ligation, we have investigated the potential of these monodentate ligands for carrying out olefin polymerization at Group 4 metal centers [8–10]. In this paper, we report on the formation and chemistry of a series of cationic alkyl derivatives of titanium and zirconium. Polymerization studies show that the polymer properties are dependent on the nature of the aryloxide ligands.

2. Results and discussion

2.1. Synthesis and characterization of alkyl precursors

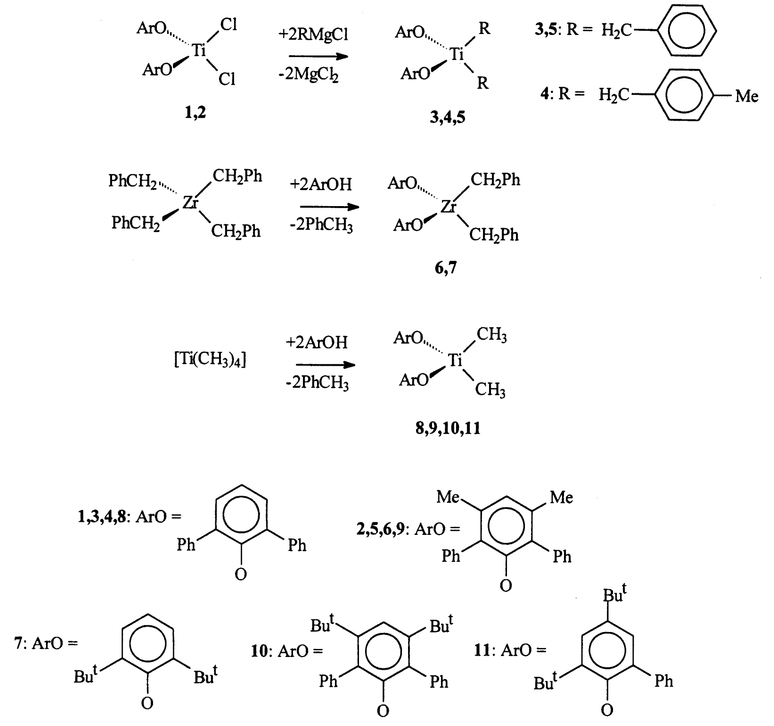
There are two synthetic strategies that have been developed for the generation of bis(alkyl), bis(aryloxides) of titanium and zirconium. The first method in-

---

* Corresponding author. Fax: + 1-765-494-0239.

E-mail address: rothwell@purdue.edu (I.P. Rothwell)

PII: S0022-328X(99)00409-X



Scheme 1.

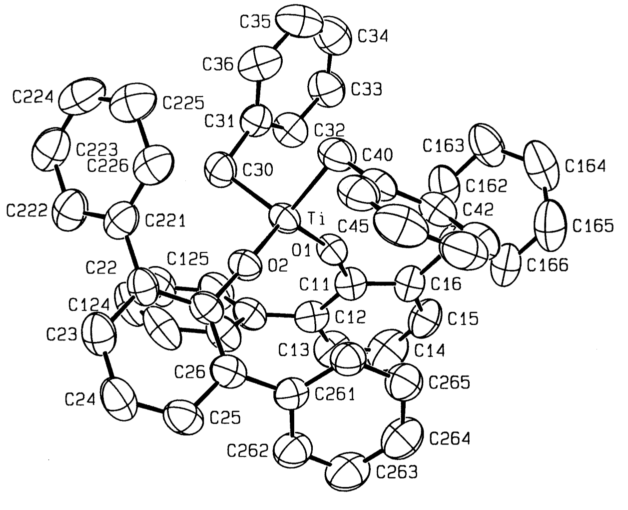


Fig. 1. ORTEP view of $[Ti(OC_6H_3Ph_2\text{-}2,6)_2(CH_2Ph)_2]$ (**3**).

volves the alkylation of di-chloride precursors such as **1** [11] and **2** (Scheme 1). By this method the titanium bis(benzyl) derivatives **3–5** can be obtained. A solid-state structure on **3** (Fig. 1 and Table 1) shows a pseudo-tetrahedral environment about the Ti metal center with both benzyl ligands being η^1-bound [12]. In the case of zirconium, corresponding di-chlorides are not available. Hence the bis(benzyl) compounds **6** and **7** can be generated by treatment of precursor $[Zr(CH_2Ph)_4]$ [13] with two equivalents of the corresponding parent phenol (Scheme 1). A series of dimethyl derivatives of titanium **8–11** has also been obtained by treatment of $[TiMe_4]$ generated in situ with two equivalents of phenol (Scheme 1) [14]. The solid-state structure of dimethyl **8** (Fig. 2 and Table 2) again shows a pseudo-tetrahedral metal environment. Some of the structural parameters for **3** and **8** will be discussed in more detail below.

Table 1
Selected bond distances (Å) and angles (°) for $[Ti(OC_6H_3Ph_2\text{-}2,6)_2(CH_2Ph)_2]$ **3**

Bond distances			
Ti–O(1)	1.797(3)	Ti–C(30)	2.078(5)
Ti–O(2)	1.784(3)	Ti–C(40)	2.091(5)
Bond angles			
O(1)–Ti–O(2)	122.6(1)	C(30)–Ti–C(40)	107.3(2)
O(1)–Ti–C(30)	106.0(2)	Ti–O(1)–C(11)	161.4(3)
O(1)–Ti–C(40)	109.0(2)	Ti–O(2)–C(21)	168.3(3)
O(2)–Ti–C(30)	108.0(2)	Ti–C(30)–C(31)	102.1(3)
O(2)–Ti–C(40)	103.2(2)	Ti–C(40)–C(41)	113.1(1)

2.2. Formation of cationic alkyl compound

Hydrocarbon solutions of the bis(benzyl) derivatives **3–7** react rapidly (^{1}H-NMR) with the reagent $[B(C_6F_5)_3]$ [15] to produce a series of zwitterionic organometallic species **12–16** (Scheme 2). Four of the compounds, **12–15**, are simply the result of abstraction of a benzyl ligand from the metal by the Lewis acidic boron reagent. However, in the case of **16** abstraction is followed by facile CH bond activation of an *ortho-tert-*

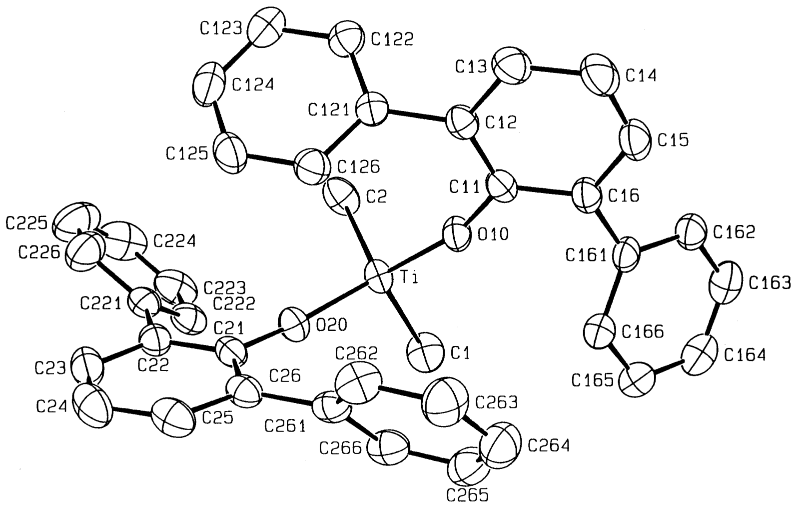
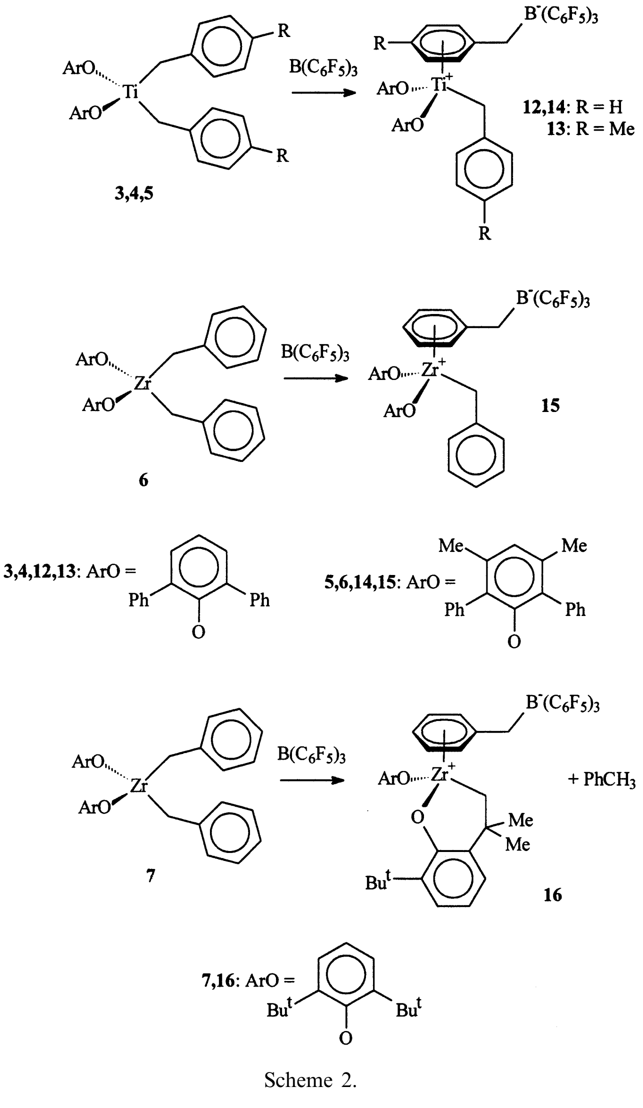


Fig. 2. ORTEP view of $[Ti(OC_6H_3Ph_2\text{-}2,6)_2(CH_3)_2]$ (**8**).

Table 2
Selected bond distances (Å) and angles (°) for $[Ti(OC_6H_3Ph_2\text{–}2,6)_2(CH_3)_2]$ **8**

Bond distances			
Ti–O(10)	1.795(1)	Ti–C(1)	2.069(2)
Ti–O(20)	1.791(1)	Ti–C(2)	2.052(2)
Bond angles			
O(10)–Ti–O(20)	126.19(7)	O(20)–Ti–C(2)	106.77(8)
O(10)–Ti–C(1)	107.06(9)	C(1)–Ti–C(2)	103.9(1)
O(10)–Ti–C(2)	106.67(8)	Ti–O(10)–C(11)	162.6(1)
O(20)–Ti–C(1)	104.29(9)	Ti–O(20)–C(21)	164.5(1)

butyl group leading to elimination of toluene and formation of a six-membered, oxa-metallacycle ring (Scheme 2). The cyclometallation of 2,6-di-*tert*-butylphenoxide by a variety of early d-block metal systems has been well documented and studied [16]. In all five compounds there is spectroscopic evidence for the presence of an $[(ArCH_2)B(C_6F_5)_3]^-$ anion π-bound to the metal center through the benzyl arene ring. Hence in the ^{1}H-NMR spectra of compounds **12**, **14** and **15** three multiplets are observed upfield of the aromatic region which can be assigned to the *ortho*, *meta* and *para* protons on the π-bound C_6H_5–CH_2B ring. In 4-methylbenzyl derivative **13** only a pair of doublets is observed due to the presence of the methyl substituent. The presence of equivalent *ortho* and *meta* protons combined with the presence of singlets for the Ti–CH_2Ar and ArCH_2B protons implies the presence of a mirror plane through the molecule in solution. This contrasts with the observed solid-state structures (vide infra), which would produce non-equivalent *ortho* and *meta* protons and diasterotopic methylene protons. Hence, either a higher symmetry structure is adopted in solution or more likely there is facile rotation of the π-bound arene on the NMR time-scale. In the case of the 2,6-di-*tert*-butylphenoxide derivative **16**, the presence of the cyclometallated ring results in non-equivalent *ortho* and *meta* aromatic protons and



Scheme 2.

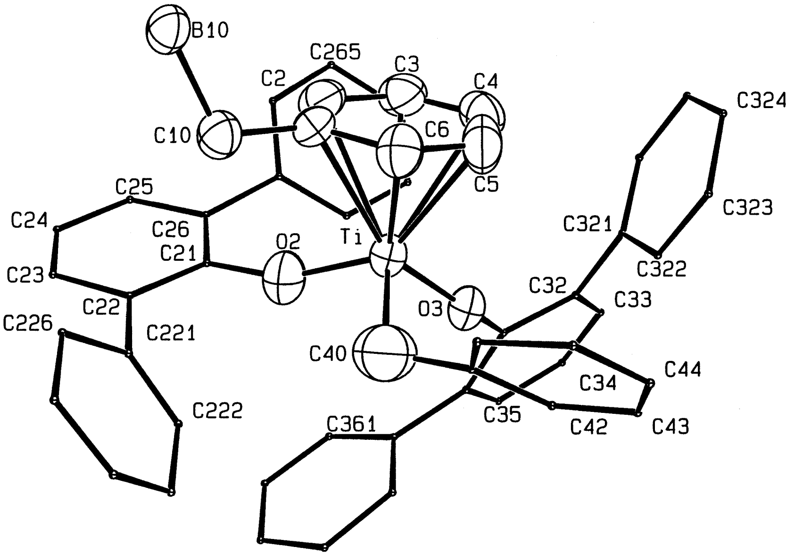


Fig. 3. ORTEP view of $[Ti(OC_6H_3Ph_2\text{-}2,6)_2(CH_2Ph)][\eta^6\text{-}C_6H_5CH_2B(C_6F_5)_3]$ (**12**) with C_6F_5 groups omitted for clarity.

diastereotopic $PhCH_2$–B protons for the π-bound anion. In this case even facile anion rotation cannot generate a mirror plane of symmetry.

In the ^{13}C-NMR spectra of the zwitterionic benzyl compounds **12–15**, the Ti–CH_2 carbon atom resonates only slightly downfield of its position for the neutral precursors. Hence this signal is found at δ 101.2 and 70.6 for Ti and Zr species **12** and **15** compared to δ 94.0 and 68.7 for corresponding precursors **3** and **6**. In the case of the cyclometallated compound **16**, the non-equivalence of the aryloxide ligands is demonstrated by the presence of two Zr–O–*C* resonances compared to only one corresponding signal in **12–15**.

The solid-state structures of the zwitterionic species **12**, **15** and **16** were determined (Figs. 3–5 and Tables 3–5). In all three compounds the anion can be seen to be π-bound to the metal center through the benzyl arene ring. However, the M–C distances in these d^0-complexes are much longer than reported for lower-valent arene derivatives of these metals. In the anion $[Ti(\eta^6\text{-}C_6H_5Ph)_2]^-$ the average Ti–C(arene) distance is 2.27(2) Å [17], while in the cation $[Ti(\eta^6\text{-}C_6H_3Pr^i_3)_2]^+$ the range is 2.27(2)–2.33(2) Å [18]. This compares with values of 2.538(7)–2.627(6) Å found for **12** (Table 3). These distances are comparable to the values of 2.46(1)–2.52(1) Å reported for $[(\eta^6\text{-}C_6Me_6)TiCl_3]^+$ cation [19]. For the 18-electron zirconium complex $[(\eta^6\text{-}C_6H_3Me_3)_2Zr(\mu\text{-}Cl)_2AlCl_2][Al_2Cl_7]$ [20] the average Zr–C(arene) distances are reported as 2.54 Å compared with the ranges of 2.653(4)–2.821(4) and 2.670(4)–2.851(3) Å for **15** and **16**, respectively [21]. It can also be seen that in all three compounds the metal to carbon(arene) distances are not equivalent. In the titanium compound **12** the Ti–C(*ipso*) distance of 2.627(6) Å is slightly longer than the values of 2.538(7)–2.566(7) Å found for the other five Ti–C distances. Similarly in **15** the Zr–C(*ipso*) distance of 2.821(4) Å is also longer than the other distances of 2.653(4)–2.764(4) Å. A similar assymmetry in the bonding of benzyl boron anions to zirconium metal centers in compounds $[Zr(CH_2Ph)_3\{\eta^6\text{-}PhCH_2B(C_6F_5)_3\}]$ [22] and $[CpZr(CH_2Ph)_2\{\eta^6\text{-}PhCH_2B(C_6F_5)_3\}]$ [23] has been noted. In one case the distortion was interpreted as representing an η^5-interaction. However, it can be seen in **16**, which contains the bulkiest aryloxide, that there is a definite elongation of two adjacent Zr–C(arene) distances, 2.803(3) and 2.851(3) Å compared with distances to other carbon atoms. It would, therefore, appear in these compounds that the non-symmetric bonding of the arene rings reflects simple steric factors with the rings slipping to minimize unfavorable interactions.

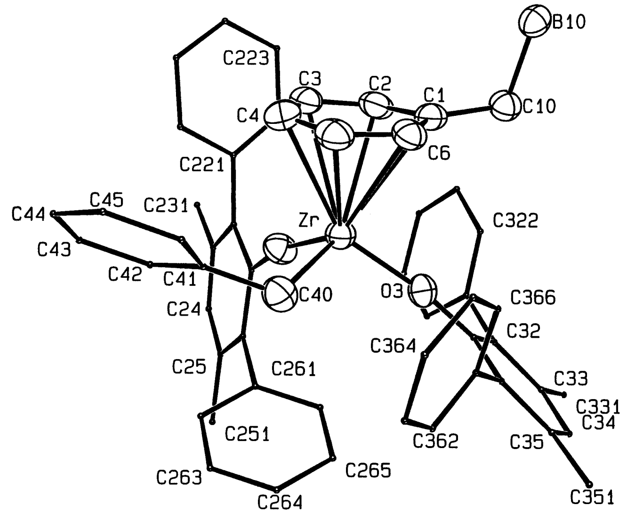


Fig. 4. ORTEP view of $[Zr(OC_6HPh_2\text{-}2,6\text{-}Me_2\text{-}3,5)_2(CH_2Ph)][\eta^6\text{-}C_6H_5CH_2B(C_6F_5)_3]$ (**15**) with C_6F_5 groups omitted for clarity.

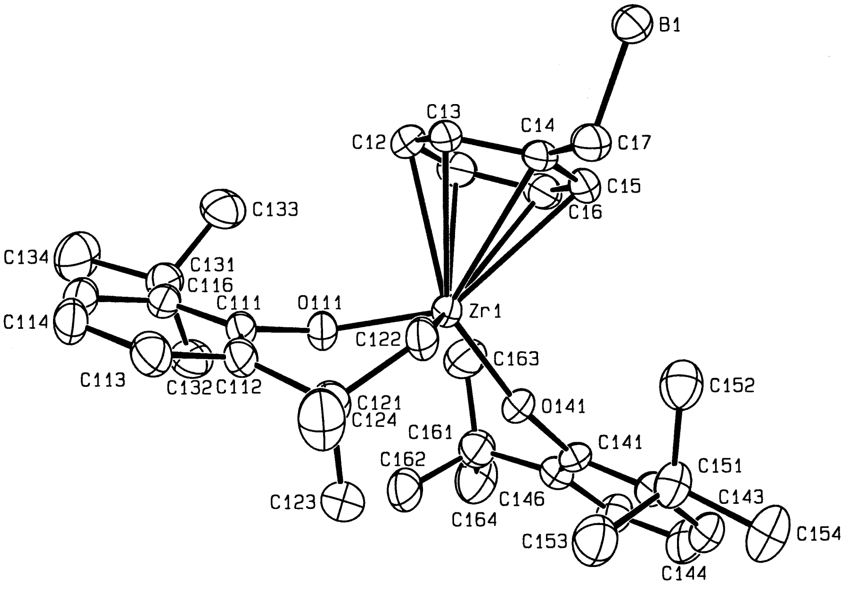


Fig. 5. ORTEP view of $[Zr(OC_6H_3Bu^t–CMe_2CH_2)(OC_6H_3Bu^t_2\text{-}2,6)][\eta^6\text{-}C_6H_5CH_2B(C_6F_5)_3]$ (**16**) with C_6F_5 groups omitted for clarity.

The M–OAr distances in the zwitterionic compounds **12** and **15** (Tables 3 and 4) are among the shortest for these types of ligands bound to titanium and zirconium. This presumably is a reflection of the high electrophilicity of the cationic metal center. In both the neutral precursors and zwitterionic compounds the M–O–Ar angles are almost linear. Previous work has shown that this parameter cannot be used as a measure of the amount of oxygen-p to metal-d π-bonding [24]. This is highlighted by the cyclometallated compound **16** (Table 5) where the chelated phenoxide, 137° (average for two independent molecules) angle, has an essentially identical Zr–O distance to that found for the terminal aryloxide which has a larger, 165° (av.), Zr–O–Ar angle.

The addition of $[B(C_6F_5)_3]$ to C_6D_6 solutions of the pale yellow dimethyl compounds **8** and **9** immediately results in formation of dark red solutions. Analysis by ^{1}H-NMR of these solutions showed the presence of the expected abstraction products **17** and **18** (Scheme 3). Equal intensity, broad resonances for the Ti–Me and Me–B protons were observed. However, both reaction mixtures contained varying amounts of other species. Over the course of 1 h at ambient temperature, peaks due to the initial abstraction compounds **17** and **18** were replaced by a set of signals due to three other species. In both cases an equimolar mixture of $[(ArO)_2Ti(Me)(C_6F_5)]$ (**20** or **23**) along with the boron compound $[MeB(C_6F_5)_2]$ **21** were observed as the major decomposition products (Scheme 3). These compounds arise via abstraction of a perfluorophenyl group from the $[MeB(C_6F_5)_3]^-$ anion by the electrophilic titanium metal center. The mono-methyl compounds **20** and **23** are characterized in the ^{1}H-NMR by a well-resolved

Table 3
Selected bond distances (Å) and angles (°) for $[Ti(OC_6H_3Ph_2\text{–}2,6)_2\text{-}(CH_2Ph)(\eta^6\text{–}C_6H_5CH_2B\{C_6F_5\}_3)]$ **12**

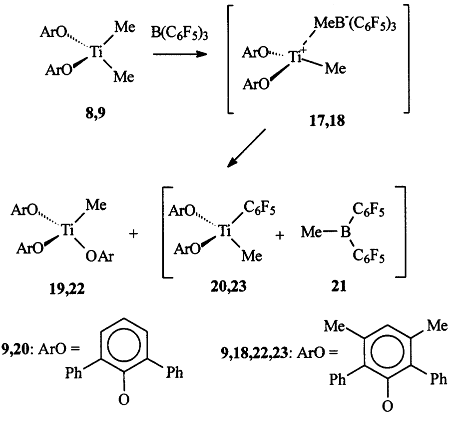
Bond distances			
Ti–O(2)	1.761(5)	Ti–C(5)	2.538(7)
Ti–O(3)	1.795(4)	Ti–C(6)	2.558(7)
Ti–C(40)	2.159(9)	C(40)–C(41)	1.53(1)
Ti–C(1)	2.627(6)	C(1)–C(10)	1.488(8)
Ti–C(2)	2.555(6)	C(10)–B(10)	1.692(9)
Ti–C(3)	2.543(7)	O(2)–C(21)	1.376(8)
Ti–C(4)	2.566(7)	O(3)–C(31)	1.374(7)
Bond angles			
O(2)–Ti–O(3)	110.0(2)		
O(2)–Ti–C(40)	96.6(3)	C(41)–C(40)–Ti	120.6(6)
O(3)–Ti–C(40)	97.8(3)	C(1)–C(10)–B(10)	116.5(5)
C(21)–O(2)– Ti	158.9(5)	C(10)–B(10)–C(111)	101.9(5)
C(31)–O(3)– Ti	158.8(4)		

Table 4
Selected bond distances (Å) and angles (°) for $[Zr(OC_6HPh_2\text{–}2,6\text{–}Me_2\text{–}3,5)_2(CH_2Ph)(\eta^6\text{–}C_6H_5CH_2B\{C_6F_5\}_3)]$ **15**

Bond distances			
Zr–O(2)	1.893(3)	Zr–C(5)	2.694(4)
Zr–O(3)	1.900(3)	Zr–C(6)	2.764(4)
Zr–C(40)	2.230(4)	C(40)–C(41)	1.495(6)
Zr–C(1)	2.821(4)	C(1)–C(10)	1.482(6)
Zr–C(2)	2.653(4)	C(10)–B(10)	1.691(6)
Zr–C(3)	2.662(4)	O(2)–C(21)	1.380(5)
Zr–C(4)	2.681(5)	O(3)–C(31)	1.365(5)
Bond angles			
O(2)–Zr–O(3)	113.6(1)		
O(2)–Zr–C(40)	99.4(2)	C(41)–C(40)–Zr	117.4(3)
O(3)–Zr–C(40)	99.6(1)	C(1)–C(10)–B(10)	111.4(3)
C(21)–O(2)–Zr	165.3(3)	C(10)–B(10)–C(111)	109.8(3)
C(31)–O(3)–Zr	170.5(3)		

Table 5
Selected bond distances (Å) and angles (°) for $[Zr(OC_6H_3Bu^t_2\text{-}2,6)(OC_6H_3Bu^t\text{-}2\text{-}\{CH_2CMe_2\}\text{-}6)(\eta^6\text{-}C_6H_5CH_2B\{C_6F_5\}_3)]$ **16**

Molecule 1			
Zr(1)–O(141)	1.920(2)	C(17)–B(1)	1.693(5)
Zr(1)–O(111)	1.922(2)		
Zr(1)–C(122)	2.240(4)	O(111)–Zr(1)–O(141)	114.4(1)
Zr(1)–C(11)	2.670(4)	O(111)–Zr(1)–C(122)	84.9(1)
Zr(1)–C(12)	2.671(4)	O(141)–Zr(1)–C(122)	103.9(1)
Zr(1)–C(13)	2.717(3)	Zr(1)–O(111)–C(111)	138.8(2)
Zr(1)–C(14)	2.851(3)	Zr(1)–O(141)–C(141)	166.5(2)
Zr(1)–C(15)	2.803(3)	Zr(1)–C(122)–C(121)	115.3(3)
Zr(1)–C(16)	2.725(4)	C(121)–C(112)–C(111)	122.4(3)
C(121)–C(122)	1.563(3)	C(112)–C(111)–O(111)	117.1(3)
Molecule 2			
Zr(2)–O(241)	1.916(2)	C(27)–B(2)	1.680(5)
Zr(2)–O(211)	1.907(2)		
Zr(2)–C(222)	2.236(4)	O(211)–Zr(2)–O(241)	111.4(1)
Zr(2)–C(21)	2.657(4)	O(211)–Zr(2)–C(222)	85.5(1)
Zr(2)–C(22)	2.721(4)	O(241)–Zr(2)–C(222)	107.3(1)
Zr(2)–C(23)	2.803(3)	Zr(2)–O(211)–C(211)	137.5(2)
Zr(2)–C(24)		Zr(2)–O(241)–C(241)	164.1(2)
Zr(2)–C(25)	2.722(3)	Zr(2)–C(222)–C(221)	115.3(2)
Zr(2)–C(26)	2.661(4)	C(221)–C(212)–C(211)	122.1(3)
C(221)–C(222)	1.574(5)	C(212)–C(211)–O(211)	116.6(3)



Scheme 3.

triplet for the Ti–*Me* protons, which are weakly coupled to the two *ortho*-F substituents of the adjacent perfluorophenyl group. In the boron compound $[MeB(C_6F_5)_2]$, it is possible to resolve a broad pentet structure for the methyl group, again due to coupling to four *ortho*-F substituents. A minor component of these reaction mixtures was identified as the mono-methyl compounds $[(ArO)_3TiMe]$ **19**, **22**. These compounds can be independently synthesized by adding one equivalent of phenol to dimethyl compounds **8** and **9**. Crystals of 2,6-diphenylphenoxide **19** were obtained from one of the reaction mixtures and structurally characterized (Fig. 6, Table 6). The origins of this decomposition by-product are presently unknown.

2.3. Stoichiometric reactivity towards olefins and alkynes

The zwitterionic compounds **12** and **14**, either isolated or generated in situ, will react stoichiometrically with one equivalent of added alkyne or olefin (Scheme 4). In all cases the resulting products are salts that contain the $[PhCH_2B(C_6F_5)_3]^-$ anion, whose B–C*H*$_2$ protons can be observed in the ^{1}H-NMR spectrum (C_6D_6) as a broad resonance at δ 3.1–3.3 ppm. Unfortunately all of these salt products have resisted all attempts at crystallization. However, the spectroscopic properties of their cations is consistent with their formulation as shown (Scheme 4). The mono-insertion of one equivalent of alkyne or olefin into the Ti^+–CH_2Ph bond has occurred followed by chelation to the cationic metal center by the phenyl ring originally contained in the benzyl ligand. There is excellent precedent in the literature for the formation of similar chelate rings. Specifically, the work of Pellechia et al. has shown that single insertion of α-olefins into the Zr–C bonds of cationic benzyls $[Zr(CH_2Ph)_3]^+$ and $[CpZr(CH_2Ph)_2]^+$ leads to analogous compounds. One such derivative $[Cp^*Zr\{CH_2CH(Me)CH_2(\eta^6\text{-}C_6H_5)\}(CH_2Ph)]$ $[PhCH_2B(C_6F_5)_3]$ was structurally characterized [25]. The phenyl ring was found to be η^6-bound to the zirconium metal center with Zr–C distances of 2.42(2)–2.69(2) Å. These distances are similar to those found in zwitterionic arene compounds such as **15** and **16**. Spectroscopically the insertion of phenylpropyne leads to cations **24** and **25** that contain a plane of symmetry. This generates three resolvable multiplets upfield of the normal aromatic region in the ^{1}H-NMR spectra for the *ortho*, *meta* and *para* protons of the π-bound phenyl ring. The presence of a single Ti–O–*C* resonance in the ^{13}C-NMR spectrum indicates equivalent aryloxide ligands. The Ti–*C*(Me)=C(Ph) carbon for **24** resonates at δ 231.6 ppm in the ^{13}C-NMR spectrum. This is a region typical for Ti–C(vinyl) groups. The proposed regiochemistry for **24** and **25** is based upon the upfield shift of the methyl protons within the alkyl chain. This is consistent with this methyl group being attached to the α-carbon, Ti–C(*Me*)=C(Ph), and being upfield shifted by the adjacent 2,6-diphenylphenoxide ligands in **24**. This signal is shifted even more upfield on changing the aryloxide ligands to the *meta*-methyl-substituted 2,6-diphenylphenoxide **25**. Previous studies have shown that the introduction of *meta*-substituents onto the central nucleus of 2,6-diphenylphenoxide ligands causes a decrease in conformation flexibility for the *ortho*-phenyl rings. This generates a greater amount of diamagnetic shielding by the *ortho*-phenyl ring of protons attached to other ligands within the coordination sphere [5c].

The addition of α-olefins to zwitterions **12** and **14** leads to cations **26–30**, where the alkyl chelate back-

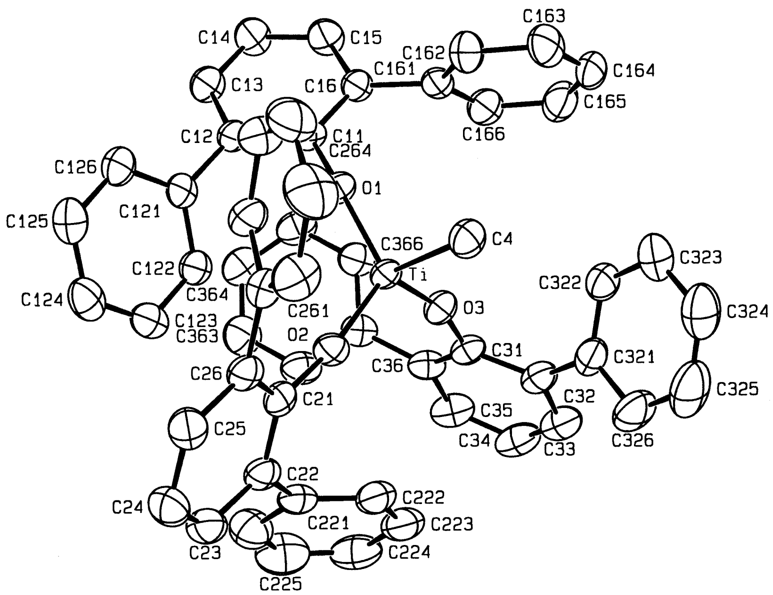


Fig. 6. ORTEP view of [Ti(OC$_6$H$_3$Ph$_2$-2,6)$_3$(CH$_3$)] (**19**).

Table 6
Selected bond distances (Å) and angles (°) for [Ti(OC$_6$H$_3$Ph$_2$-2,6)$_3$(CH$_3$)] **19**

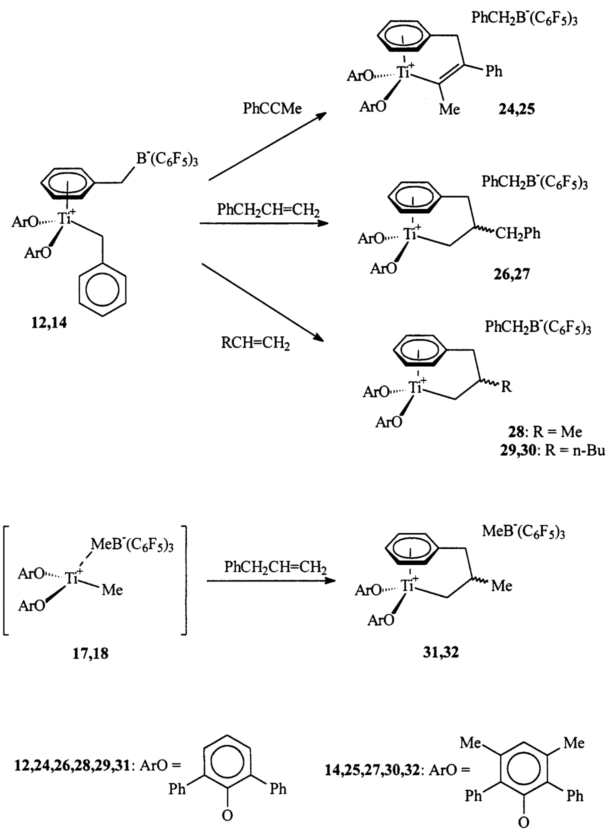
Bond distances			
Ti–O(1)	1.793(2)	Ti–O(3)	1.793(3)
Ti–O(2)	1.798(2)	Ti–C(4)	2.070(4)
Bond angles			
O(1)–Ti–C(4)	103.5(1)		
O(2)–Ti–C(4)	101.9(4)	O(2)–Ti–O(3)	113.7(2)
O(3)–Ti–C(4)	106.0(1)	Ti–O(1)–C(11)	159.8(2)
O(1)–Ti–O(2)	119.5(1)	Ti–O(2)–C(21)	169.7(2)
O(1)–Ti–O(3)	110.4(1)	Ti–O(3)–C(31)	162.5(2)

bone lacks a plane of symmetry. Hence in these species five multiplets can be resolved for the η^6-C$_6$H$_5$ protons in the ^{1}H-NMR spectrum. Two separate Ti–O–*C* signals are also present in the ^{13}C-NMR spectra due to non-equivalent aryloxides. The regiochemistry shown for α-olefin insertion is assigned due to the presence if Ti–*C*H$_2$ carbon resonances being observed in the ^{13}C-NMR spectra as well as the following results.

Although the methyl cations **17** and **18** undergo facile decomposition (Scheme 3), they can be intercepted by the addition of allylbenzene (Scheme 4). The resulting cations also contain chelated η^6-arene rings. The cation in **28** obtained by insertion of propene into the Ti$^+$–CH$_2$Ph bond of **12** is identical (NMR) to that within **31**, which is obtained by inserting allylbenzene into the Ti$^+$–Me bond of generated **17**. The only spectroscopic difference between **28** and **31** relates to the anions [PhCH$_2$B(C$_6$F$_5$)$_3$]$^-$ and [MeB(C$_6$F$_5$)$_3$]$^-$ present in each. The identical nature of the cations in **28** and **31** shows that the insertion of α-olefins is taking place in a 1,2-fashion

2.4. Polymerization studies

The zwitterionic benzyl species **12–16** fail to act as active catalysts for the polymerization of olefins. The reasons for this undoubtedly rest in the stability of the cations such as **26–30** (Scheme 4) formed after initial insertion of one equivalent of olefin. Although cationic methyl species such as **17** and **18** (Scheme 3) undergo facile decomposition, activation of the dimethyl compounds **8–11** with [B(C$_6$F$_5$)$_3$] in the presence of olefin does lead to the formation of polymers and oligomers. Table 7 contains information concerning the polymerization of ethylene and propene by these catalyst systems. In all cases it can be seen that the polydispersities are low and consistent with the presence of a single active site. Furthermore, the polymer molecular weight can be seen to be highly dependent on the nature of the aryloxide ligand within the catalyst precursor. As the bulk of the aryloxide increases, it can be seen that the polymer molecular weight increases. Analysis of the polypropylene polymers by ^{1}H- and ^{13}C-NMR shows the presence of vinylidene (*H$_2$C=C*) end groups. Specifically the protons resonate at δ 4.72 and 4.79 ppm while the two carbons resonate at δ 144.7 and 112.1 ppm. This is consistent with a 1,2-insertion pathway for polymer propagation with termination by β-hydrogen abstraction. This, combined with the similar activities (Table 7) implies that the aryloxide ligands that generate the highest molecular weights do so by slowing down β-hydrogen abstraction.



Scheme 4.

In the case of 1-hexene, catalysts derived from **8–10** were found to produce only oligomers (Table 8). The distribution of dimers to pentamers was determined by GC analysis. It can be seen (Table 8) that a similar trend is present to that obtained for the polymerization of ethylene and propylene. There is a definite increase in average oligomer molecular weight on moving down the series. In the case of **11**, a polymer of much higher molecular weight is obtained. The oligomerization of 1-hexene by chelating phenoxides activated by MAO has been reported.

3. Experimental

3.1. General

All operations were carried out under a dry nitrogen atmosphere using standard Schlenk Techniques [26]. The hydrocarbon solvents were distilled from sodium benzophenone and stored over sodium ribbons under nitrogen until use. Reagents were purchased from Aldrich Chemical Co., Inc. and used without further purification. The ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian Associates Gemini-200 spectrometer and referenced to protio impurities of commercial benzene-d_6 or deuterated chloroform as internal standards. Mass spectra, elemental analyses and molecular structures were obtained in-house at Purdue University.

3.2. [Ti(OC$_6$HPh$_2$-2,6-Me$_2$-3,5)$_2$Cl$_2$] (**2**)

A sample of 2,6-diphenyl-3,5-dimethylphenol (10.0 g, 36.5 mmol) was added to a solution containing [TiCl$_4$] (1.9 ml, 17.4 mmol) and benzene (40 ml). The resulting red solution was refluxed for 2 h to drive off HCl gas and then slowly allowed to cool, affording an orange–red solid. The solvent was decanted away from this solid, which was subsequently washed with hexane three times and dried under vacuum affording an orange solid (9.6 g, 90.0%). Anal. Calc. for $C_{40}H_{34}Cl_2O_2Ti$: C, 71.98; H, 5.15; Cl, 10.67. Found: C, 71.98; H, 4.89; Cl, 10.89. ^{1}H-NMR (C_6D_6, 30°C): δ 6.74 (s, *para-H*); 7.1–7.3 (other aromatics); 2.01 (s, C*H*$_3$).

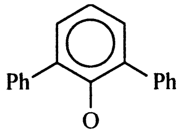
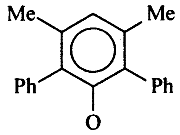
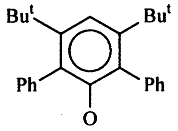
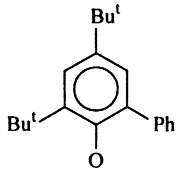
3.3. [Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$(CH$_2$Ph)$_2$] (**3**)

A sample of [Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$Cl$_2$] (1.00 g, 1.46 mmol) was dissolved in a benzene solution along with 1.3 equivalents of [Mg(CH$_2$Ph)$_2$(thf)$_2$] (0.66 g, 1.89 mmol). The dark red solution was stirred for several hours and then evacuated to dryness. The resulting red solid was redissolved in benzene, filtered, and evacuated to dryness, affording a red solid that was redissolved in a minimal amount of benzene and layered with hexane, affording red crystals (1.89 g, 89%). Anal. Calc. for $C_{50}H_{40}O_2Ti$: C, 83.32; H, 5.59; Found: C, 82.39; H, 5.44. ^{1}H-NMR (C_6D_6, 30°C): δ 6.70–7.30 (aromatics); 6.63 (d, *ortho*-CH$_2$*Ph*); 1.91 (s, Ti–C*H*$_2$). Selected ^{13}C-NMR (C_6D_6, 30°C): δ 159.8 (Ti–O–*C*); 94.0 (Ti–*C*H$_2$).

3.4. [Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$(CH$_2$C$_6$H$_4$-Me-4)$_2$] (**4**)

A sample of [Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$Cl$_2$] (3.00 g, 4.37 mmol) was dissolved in toluene and cooled to −78°C using dry ice–acetone. To this vigorously stirred orange solution was slowly added 4-methylbenzylmagnesiumchloride (10.9 ml, 10.9 mmol) (prepared as a 1 M solution in ether from the reaction of 4-methylbenzylchloride with 3 equivalents of magnesium). The solution turned a dark red color and was allowed to slowly warm to room temperature (r.t.) with continued stirring for 1 day. The solution was then evacuated to dryness and the resulting dark solid dissolved in benzene and filtered to remove MgCl$_2$. The filtrate was evacuated to dryness affording a red solid that was recrystallized from benzene–pentane, affording a red powder (2.72 g, 83%). Anal. Calc. for $C_{52}H_{44}O_2Ti$: C, 83.41; H, 5.92. Found: C, 80.09; H, 5.87. ^{1}H-NMR (C_6D_6, 30°C): δ 6.80–7.30 (aromatics); 6.57 [d, $^{3}J(^{1}H-^{1}H)$ 8.1 Hz, *ortho-Ph*Me)]; 2.09 (s, CH$_2$Ph*Me*); 1.90 (s, TiC*H*$_2$). Selected ^{13}C-NMR (C_6D_6, 30°C): δ 160.2 (Ti–O–*C*); 94.0 (Ti*C*H$_2$); 34.5 (*p*-*C*H$_3$).

Table 7
Polymer properties and catalyst activities for the polymerization of ethylene and propene by [$(ArO)_2TiMe_2$] activated by [$B(C_6F_5)_3$] [a]

Precursor		Polyethylene				Polypropylene			
	OAr	10^3 M_n	10^3 M_w	M_w/M_n	Activity [b]	10^3 M_n	10^3 M_w	M_w/M_n	Activity [b]
8		2.59	5.64	2.2	3	1.53	1.97	1.3	6
9		2.61	4.91	1.9	4	1.72	2.17	1.3	5
10		8.23	11.80	1.4	3	3.45	4.65	1.4	3
11		12.50	23.50	1.9	2	14.50	28.98	2.0	2

[a] Conditions: 0.089 mmol of **8–11**; 0.097 mmol of $B(C_6F_5)_3$; 3 ml of toluene; 0°C; 1 atm; 15 min reaction time.
[b] kg mol^{-1} h^{-1} atm^{-1}.

3.5. [$Ti(OC_6HPh_2$-2,6-Me_2-3,5$)_2(CH_2Ph)_2$] (**5**)

An identical procedure to that used in the synthesis of **3** was used for **5** starting with [$Ti(OC_6HPh_2$-2,6-Me_2-3,5$)_2Cl_2$] (1.00 g, 1.50 mmol). The synthesis afforded **5** as a red powder (1.04 g, 87%). Anal. Calc. for $C_{54}H_{48}O_2Ti$: C, 83.49; H, 6.23; Found: C, 83.15; H, 6.17. ^{1}H-NMR (C_6D_6, 30°C): δ 6.80–7.50 (aromatics); 6.64 (d, *ortho*-CH_2*Ph*); 2.13 (s, *meta* C*H*$_3$); 1.34 (s, Ti–C*H*$_2$). Selected ^{13}C-NMR (C_6D_6, 30°C): δ 160.8 (Ti–O–*C*); 92.7 [Ti–*C*H$_2$, $^1J(^{13}C–^1H) = 131$ Hz]; 20.8 (*meta* *C*H$_3$).

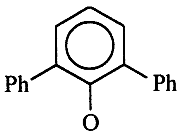
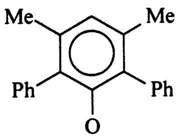
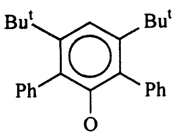
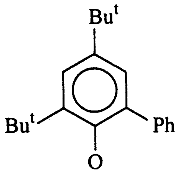
3.6. [$Zr(OC_6HPh_2$-2,6-Me_2-3,5$)_2(CH_2Ph)_2$] (**6**)

To a solution of [$Zr(CH_2Ph)_4$] (1.0 g, 2.20 mmol) in toluene (20 ml) was added 2,6-diphenyl-3,5-dimethylphenol (1.2 g, 4.40 mmol). The resulting mixture was stirred for 12 h before the solvent was removed in vacuo to yield the crude product. The crude product was recrystallized as a brown solid from a benzene solution layered with pentane (0.61 g, 34%). Anal. Calc. for $C_{54}H_{48}O_2Zr$: C, 79.08; H, 5.90. Found: C, 79.05; H, 6.09. ^{1}H-NMR (C_6D_6, 30°C): δ 6.8–7.3 (aromatics); 6.78 (s, *para*-CH); 6.44 (d, *ortho-Ph*); 2.13 (s, *meta*-C*H*$_3$); 1.05 (s, Zr–C*H*$_2$). Selected ^{13}C-NMR (C_6D_6, 30°C): δ 158.0 (Zr–O–*C*); 68.7 (Zr–*C*H$_2$); 21.3 (*meta* *C*H$_3$).

3.7. [$Ti(OC_6H_3Ph_2$-2,6$)_2(CH_3)_2$] (**8**)

A procedure identical to the one used for **9** was used to prepare **8**. The amounts of reagents used were as follows: [$TiCl_4$] (1 ml, 9.12 mmol); [MeLi] (26.1 ml, 36.5 mmol); 2,6-diphenylphenol (4.35 g, 17.1 mmol). **8** was isolated as a yellow solid (3.84 g, 74%). Recrystallization from benzene–hexane afforded X-ray quality crystal. Anal. Calc. for $C_{38}H_{32}O_2Ti$: C, 80.28; H, 5.67. Found: C, 80.14; H, 5.69. ^{1}H-NMR (C_6D_6, 30°C): δ 6.70–7.50 (aromatics); 0.60 (Ti–C*H*$_3$). Selected ^{13}C-NMR (C_6D_6, 30°C): 66.1 (Ti–*C*H$_3$, $^1J(^{13}C–^1H) = 125$ Hz).

Table 8
Oligomerization of 1–hexene by $[(ArO)_2TiMe_2]$ activated by $[B(C_6F_5)_3]$ [a]

Precursor		1–Hexene oligomers			
	Oar	% Dimer (C_{12})	% Trimer (C_{18})	% Tetramer (C_{24})	% Pentamer (C_{30})
8		62	24	13	–
9		42	32	18	7
10		34	34	21	11
11 [b]		–	–	–	–

[a] Conditions: 0.089 mmol of **54–57**; 0.097 mmol of $B(C_6F_5)_3$; 3 ml of toluene; 25°C; 2 ml (17.8 mmol) 1–hexene; 24 h reaction time.

[b] Catalyst precursor **57** gave too high M_w (^1H-NMR) to be measured by GC analysis.

3.8. $[Ti(OC_6HPh_2\text{-}2,6\text{-}Me_2\text{-}3,5)_2(CH_3)_2]$ (**9**)

A 1 l three-neck flask fitted with a nitrogen adapter was charged with distilled anhydrous diethylether (400 ml), $[TiCl_4]$ (2 ml, 18.2 mmol) and cooled to −78°C using dry ice–acetone. Once the desired temperature was achieved, 4 equivalents of [MeLi] (1.4 M in Et_2O, 52.11 ml, 73 mmol) was slowly added to the stirred solution. The solution turned red upon [MeLi] addition. After 15 min of stirring the dark solution at −78°C, 2 equivalents of 2,6-diphenyl-3,5-dimethylphenol (9.86 g, 36.0 mmol) were added with continued stirring. The dark solution was slowly allowed to warm to r.t. The diethyl ether was removed in vacuo and the resulting dark residue was dissolved in benzene, filtered to remove LiCl, and evacuated to dryness. The resulting dark solid was recrystallized from a benzene–hexane mixture (3:7) affording **9** as a dark green powder (5.61 g, 50%). ^1H-NMR (C_6D_6, 30°C): δ 6.90–7.40 (aromatics); 6.83 (s, *para*-OC_6H); 2.12 (s, *meta* CH_3); 0.24 (Ti–CH_3). Selected ^{13}C-NMR (C_6D_6, 30°C): δ 160.7 (Ti–O–C); 64.7 (Ti–CH_3); 21.2 (*meta* CH_3).

3.9. $[Ti(OC_6HPh_2\text{-}2,6\text{-}Bu^t_2\text{-}3,5)_2(CH_3)_2]$ (**10**)

A procedure identical to the one used for **9** was used to prepare **10**. The amounts of reagents used was as follows: $[TiCl_4]$ (1 ml, 9.12 mmol); [MeLi] (26.1 ml, 36.5 mmol); 3,5-di-*tert*-butyl-2,6-diphenylphenol (4.35 g, 17.1 mmol). $[Ti(OC_6HPh_2\text{-}2,6\text{-}Bu^t_2\text{-}3,5)_2(CH_3)_2]$ (**10**) was isolated as a yellow solid (3.84 g, 27%)). ^1H-NMR (C_6D_6, 30°C): δ 7.69 (s, *para*-OC_6H); 6.90–7.40 (aromatics); 1.31 [s, $C(CH_3)_3$]; 0.06 (s, Ti–CH_3). Selected ^{13}C-NMR (C_6D_6, 30°C): δ 162.4 (Ti–O–C); 64.9 (Ti–CH_3, $^1J(^{13}C–^1H) = 125.2$ Hz); 37.5 [$C(CH_3)_3$]; 33.1 [$C(CH_3)_3$].

3.10. $[Ti(OC_6HPh\text{-}2\text{-}Bu^t_2\text{-}4,6)_2(CH_3)_2]$ (**11**)

A procedure identical to the one used for **9** was used to prepare **11**. The amounts of reagents used was as follows: [TiCl$_4$] (1 ml, 9.12 mmol); [MeLi] (26.1 ml, 36.5 mmol); 4,6-di-*tert*-butyl-2-phenylphenol (4.35 g, 17.1 mmol). [Ti(OC$_6$HPh-2-Bu$^t_2$-4,6)$_2$(CH$_3$)$_2$] (**11**) was isolated as a green solid (3.84 g, 47%). ^{1}H-NMR (C$_6$D$_6$, 30°C): δ 7.59 (d), 7.33 (d, *meta-H*); 6.80–7.30 (aromatics); 1.71 [s, *ortho*-C(C*H*$_3$)$_3$]; 1.31 [s, *para*-C(C*H*$_3$)$_3$]; 1.10 (s,Ti–C*H*$_3$). Selected ^{13}C-NMR (C$_6$D$_6$, 30°C): δ 160.3 (Ti–O–*C*); 67.6 (Ti–*C*H$_3$, $^1J(^{13}\mathrm{C}–^1\mathrm{H}) = 124.0$ Hz); 35.9 [*ortho*-*C*(CH$_3$)$_3$]; 34.7 [*para*-C(*C*H$_3$)$_3$]; 31.8 [*ortho*-C(*C*H$_3$)$_3$]; 30.9 [*para*-*C*(CH$_3$)$_3$].

3.11. [Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$(CH$_2$Ph)][η^6-C$_6$H$_5$CH$_2$B(C$_6$F$_5$)$_3$] (**12**)

A sample of [Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$(CH$_2$Ph)$_2$] **3**. (1.00 g, 1.39 mmol) was placed in a solvent sealed flask along with 1.3 equivalents of [B(C$_6$F$_5$)$_3$] (0.92 g, 1.80 mmol) and benzene (5 ml). The reaction solution immediately turned red in color. The flask was left undisturbed for 12 h and then the solution was evacuated to dryness. The resulting red solid was re-dissolved in minimal benzene and layered with hexane, affording dark red crystals (1.07 g, 63%). Anal Calc. for C$_{68}$H$_{40}$BF$_{15}$O$_2$Ti: C, 66.26; H, 3.27. Found: C, 66.32; H, 3.28. ^{1}H-NMR (C$_6$D$_6$, 30°C): δ 6.75–7.30 (aromatics); 6.65 [d, $^3J(^1\mathrm{H}–^1\mathrm{H}) = 7.0$ Hz, *ortho* Ti–CH$_2$*Ph]*; 6.07 [d, $^3J(^1\mathrm{H}–^1\mathrm{H}) = 6.7$ Hz, *ortho* Ti-η^6-C$_6$*H*$_5$]; 4.78 [t, $^3J(^1\mathrm{H}–^1\mathrm{H}) = 7.5$ Hz, *meta* Ti–η^6–C$_6$*H*$_5$]; 4.43 [t, $^3J(^1\mathrm{H}–^1\mathrm{H}) = 7.3$ Hz, *para* Ti-η^6-C$_6$*H*$_5$]; 2.77 (br, B–C*H*$_2$); 2.12 (s, Ti–C*H*$_2$). Selected ^{13}C-NMR (C$_6$D$_6$, 30°C): δ 161.9 (Ti–O–*C*); 101.2 (Ti*C*H$_2$).

3.12. [Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$(CH$_2$C$_6$H$_4$-Me-4)][η^6-(C$_6$H$_4$Me-4)CH$_2$B(C$_6$F$_5$)$_3$] (**13**)

Procedure used was similar to that used in the synthesis of **12**. Anal Calc. for C$_{70}$H$_{44}$BF$_{15}$O$_2$Ti: C, 66.86; H, 3.47. Found: C, 63.73; H, 3.46. ^{1}H-NMR (C$_6$D$_6$, 30°C): δ 6.80–7.40 (aromatics); 6.65 (d), 6.15 [d, $^3J(^1\mathrm{H}–^1\mathrm{H}) = 7.7$, 8.0 Hz, *ortho*-Ti–CH$_2C_6$*H*$_4$Me-4]; 6.08 (d), 4.92 [d, $^3J(^1\mathrm{H}–^1\mathrm{H}) = 7.6$, 7.4 Hz, *ortho* and *meta* Ti-η^6-C$_6$*H*$_4$]; 2.95 (br, B–C*H*$_2$); 2.02 (s, Ti–CH$_2$-C$_6$H$_4$*Me*)); 1.35 (s, TiC*H*$_2$); 0.57 (s, Ti-η^6-C$_6$H$_4$*Me*). Selected ^{13}C-NMR (C$_6$D$_6$, 30°C): δ 161.7 (Ti–O–*C*); 101.6 (Ti*C*H$_2$); 20.7(Ti–CH$_2$C$_6$H$_4$*Me*); 18.7 (Ti-η^6-C$_6$H$_4$*Me*).

3.13. [Ti(OC$_6$HPh$_2$-2,6-Me$_2$-3,5)$_2$-(CH$_2$Ph)][η^6-C$_6$H$_5$CH$_2$B(C$_6$F$_5$)$_3$] (**14**)

An identical procedure to that used for the synthesis of **12** was attempted for the synthesis of **14** using **5** as the Ti starting material; however, only reddish oils could be isolated, which were found to have broad ^{1}H-NMR resonances with similar chemical shifts as that of **12**. ^{1}H-NMR (C$_6$D$_6$, 30°C): δ 6.60–7.40 (aromatics); 6.39 (d, *ortho* Ti–CH$_2$*Ph*); 5.85 (br, *ortho* Ti-η^6-C$_6$*H*$_5$); 4.75 (br t, *meta* Ti-η^6-C$_6$*H*$_5$); 3.49 (br, *para* Ti-η^6-C$_6$*H*$_5$); 2.93 (br, B–C*H*$_2$); 1.89 (s, Ti–C*H*$_2$); 1.86 (s, *meta* C*H*$_3$). For subsequent reactions **14** was generated in situ and found to undergo similar chemistry as solid **12**, thereby further confirming its synthesis here.

3.14. [Zr(OC$_6$HPh$_2$-2,6-Me$_2$-3,5)$_2$-(CH$_2$Ph)][η^6-C$_6$H$_5$CH$_2$B(C$_6$F$_5$)$_3$] (**15**)

A sample of [Zr(OC$_6$HPh$_2$-2,6-Me$_2$-3,5)$_2$(CH$_2$Ph)$_2$] (**6**) (200 mg, 0.24 mmol) was placed in a solvent sealed flask along with one equivalent of [B(C$_6$F$_5$)$_3$] (125 mg, 0.24 mmol) and benzene (1 ml). The flask was left undisturbed for 12 h and then the solution was evacuated to dryness. The resulting material was re-dissolved in a minimal amount of benzene and layered with hexane, affording yellow crystals (252 mg, 79%). Anal. Calc. for C$_{60}$H$_{56}$BF$_{15}$O$_2$Zr: C, 60.25; H, 4.72. Found: C, 55.47; H, 4.60. ^{1}H-NMR (C$_6$D$_6$, 30°C): δ 6.91 [t, $^3J(^1\mathrm{H}–^1\mathrm{H}) = 7.7$ Hz, *meta-Ph*)]; 6.72 [t, $^3J(^1\mathrm{H}–^1\mathrm{H}) = 7.4$ Hz, *para-Ph*)]; 6.34 [d, $^3J(^1\mathrm{H}–^1\mathrm{H}) = 7.2$ Hz, *ortho-Ph*)]; 6.10 [d, $^3J(^1\mathrm{H}–^1\mathrm{H}) = 7.3$ Hz, *ortho* Zr-η^6-C$_6$*H*$_5$]; 5.00 [t, $^3J(^1\mathrm{H}–^1\mathrm{H}) = 7.4$ Hz, *meta* Zr-η^6-C$_6$*H*$_5$]; 4.71 [t, $^3J(^1\mathrm{H}–^1\mathrm{H}) = 7.3$ Hz, *para* Zr-η^6-C$_6$*H*$_5$]; 2.97 [(br), BC*H*$_2$]; 1.88 (s, *meta*-C*H*$_3$); 0.83 (s, Zr–C*H*$_2$). Selected ^{13}C-NMR (C$_6$D$_6$, 30°C): δ 163.0 (Zr–O–*C*); 70.6 (Zr–*C*H$_2$); 20.7 (*meta* *C*H$_3$).

3.15. [Zr(OC$_6$H$_3$Bu^t–CMe$_2$CH$_2$)(OC$_6$H$_3$Bu$^t_2$–2,6)]-[η^6-C$_6$H$_5$CH$_2$B(C$_6$F$_5$)$_3$] (**16**)

A sample of [Zr(OC$_6$H$_3$Bu$^t_2$-2,6)$_2$(CH$_2$Ph)$_2$] (**7**) (180 mg, 0.29 mmol) and [B(C$_6$F$_5$)$_3$] (165 mg, 0.32 mmol) were dissolved in benzene (2 ml) in a solvent sealed flask forming a yellow solution. The solution was left undisturbed for 16 h and then evacuated to dryness, affording a yellow glassy solid. This solid was re-dissolved in fresh benzene and layered with pentane, affording **16** as yellow crystals (260 mg, 75%). Anal. Calc. for C$_{60}$H$_{56}$BF$_{15}$O$_2$Zr: C, 60.25; H, 4.72. Found: C, 58.85; H, 4.50. ^{1}H-NMR (C$_6$D$_6$, 30°C): δ 7.05–7.20 (aromatics); 6.98 (d), 6.87 [d, $^3J(^1\mathrm{H}–^1\mathrm{H}) = 7.7$ and 7.9 Hz, *ortho* Zr-η^6-C$_6$*H*$_5$]; 6.81 (t), 6.75 [t, $^3J(^1\mathrm{H}–^1\mathrm{H}) = 7.8$ and 7.9 Hz, *meta*-Ti–O–*Ph*)]; 6.16 (t), 5.89 (t), 5.66 [t, $^3J(^1\mathrm{H}–^1\mathrm{H}) = 7.6$, 7.6, and 7.3 Hz, *meta* and *para* Zr-η^6-C$_6$*H*$_5$]; 3.39 (br), 3.19 (br, B–C*H*$_2$); 1.98 (AB, 17.2 and 21.5 Hz); 1.23 (s), 1.18 (s, ^{t}*Bu*). Selected ^{13}C-NMR (C$_6$D$_6$, 30°C): δ 163.9, 161.2 (Zr–O–*C*); 82.0 (Zr–*C*H$_2$); 35.4, 35.3 [*C*–(CH$_3$)$_3$]; 32.3, 31.2 [C–(*C*H$_3$)$_3$].

3.16. [Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$(CH$_3$)][CH$_3$B(C$_6$F$_5$)$_3$] (**17**), [Ti(OC$_6$H$_3$Ph$_2$-2,6)$_3$(CH$_3$)] (**19**), [Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$(CH$_3$)(C$_6$F$_5$)] (**20**) and [CH$_3$B(C$_6$F$_5$)$_2$] (**21**)

Equimolar amounts of **8** and B(C$_6$F$_5$)$_3$ were placed in an NMR tube along with C$_6$D$_6$. Only small amounts of the initial abstraction product **17** were observed in the

^{1}H-NMR spectrum, which was dominated by the decomposition products **20** and **21** along with a small amount of **19**. $[Ti(OC_6H_3Ph_2\text{-}2,6)_2(CH_3)][CH_3B(C_6F_5)_3]$ (**17**): ^{1}H-NMR (C_6D_6, 30°C): δ 6.80–7.30 (aromatics); 1.22 (br, B–CH_3); 0.39 (br, Ti–CH_3). $[Ti(OC_6H_3Ph_2\text{-}2,6)_3(CH_3)]$ (**19**): ^{1}H-NMR (C_6D_6, 30°C): δ 6.75–7.30 (aromatics); −0.36 [s, $(ArO)_3TiCH_3$]. $[Ti(OC_6H_3Ph_2\text{-}2,6)_2(CH_3)(C_6F_5)]$ (**20**): ^{1}H-NMR (C_6D_6, 30°C): δ 6.75–7.30 (aromatics); 0.75 (t, $^5J(^{19}F–^1H) = 1.5$ Hz, Ti–CH_3). $[CH_3B(C_6F_5)_2]$ (**21**): ^{1}H-NMR (C_6D_6, 30°C): δ 1.27 [p, $^5J(^{19}F–^1H) = 1.7$ Hz, $CH_3B(C_6F_5)_2$].

*3.17. $[Ti(OC_6HPh_2\text{-}2,6\text{-}Me_2\text{-}3,5)_2(CH_3)][CH_3B(C_6F_5)_3]$ (**18**), $[Ti(OC_6HPh_2\text{-}2,6\text{-}Me_2\text{-}3,5)_3(CH_3)]$ (**22**) and $[Ti(OC_6HPh_2\text{-}2,6\text{-}Me_2\text{-}3,5)_2(CH_3)(C_6F_5)]$ (**23**)*

A sample of **9** was placed in an NMR tube along with $[B(C_6F_5)_3]$ and C_6D_6 forming a red solution of **18**: ^{1}H-NMR (C_6D_6, 30°C): δ 6.80–7.30 (aromatics); 6.77 (s, *para-H*); 1.92 (s, *meta*-CH_3); 1.27 (br, B–CH_3); 0.01 (br, Ti–CH_3). Within an hour, the decomposition products **23** and **21** had formed along with a minor amount of $[Ti(OC_6HPh_2\text{-}2,6\text{-}Me_2\text{-}3,5)_3(CH_3)]$ (**22**): ^{1}H-NMR-(C_6D_6, 30°C): δ 6.70–7.50 (aromatics); 1.90 (s, *meta* CH_3); −0.97 (s, Ti–CH_3). $[Ti(OC_6HPh_2\text{-}2,6\text{-}Me_2\text{-}3,5)_2(CH_3)(C_6F_5)]$ (**23**): ^{1}H-NMR (C_6D_6,30°C): δ 6.70–7.50 (aromatics); 2.04 (s, *meta* CH_3); 0.52 (t, $^5J(^{19}F–^1H) = 1.5$ Hz, Ti–CH_3).

*3.18. $[Ti(OC_6H_3Ph_2\text{-}2,6)_2\{C(CH_3)C(Ph)CH_2\text{-}(\eta^6\text{-}C_6H_5)\}][PhCH_2B(C_6F_5)_3]$ (**24**)*

A sample of $[Ti(OC_6H_3Ph_2\text{-}2,6)_2(CH_2Ph)][\eta^6\text{-}C_6H_5CH_2B(C_6F_5)_3]$ (**12**) (130 mg, 0.105 mmol) was dissolved in benzene (2 ml) in a round-bottomed flask. To this solution was added 1.0 equivalents of 1-phenylpropyne (13.2 µl, 0.105 mmol). The color of this solution slowly turned from red to orange over the course of an hour. This orange solution was evacuated to dryness, affording a red glassy solid (90 mg, 64%). Anal. Calc. for $C_{77}H_{48}BF_{15}O_2Ti$: C, 68.56; H, 3.59. Found: C, 65.59; H, 3.87. ^{1}H-NMR (C_6D_6, 30°C): δ 6.60–7.40 (aromatics); 6.29 [t, $^3J(^1H–^1H) = 7.6$ Hz, *meta* Ti-η^6-C_6H_5]; 5.82 [d, $^3J(^1H–^1H) = 7.4$ Hz, *ortho* Ti-η^6-C_6H_5]; 4.29 [t, $^3J(^1H–^1H) = 7.4$ Hz, *para* Ti-η^6-C_6H_5]; 3.22 (s, CH_2); 3.17 (s, B–CH_2); 1.87 (s, CH_3). Selected ^{13}C-NMR (C_6D_6, 30°C): δ 231.6 (Ti–$C\{CH_3\}$); 163.8 (Ti–O–C); 45.7 (CH_2); 34.3 (Ti–C$\{CH_3\}$). Attempts to isolate **24** as a crystalline solid have thus far been unsuccessful.

*3.19. $[Ti(OC_6HPh_2\text{-}2,6\text{-}Me_2\text{-}3,5)_2\{C(CH_3)C(Ph)CH_2\text{-}(\eta^6\text{-}C_6H_5)\}][PhCH_2B(C_6F_5)_3]$ (**25**)*

A sample of $[Ti(OC_6HPh_2\text{-}2,6\text{-}Me_2\text{-}3,5)_2(CH_2Ph)_2]$ (**5**) was placed in an NMR tube along with $[B(C_6F_5)_3]$ and C_6D_6. After several minutes excess 1-phenylpropyne was added. ^{1}H-NMR (C_6D_6, 30°C): δ 6.60–7.60 (aromatics); 6.53 [t, $^3J(^1H–^1H) = 8.0$ Hz, *meta* Ti-η^6-C_6H_5]; 5.99 [d, $^3J(^1H–^1H) = 6.0$ Hz, *ortho* Ti-η^6-C_6H_5]; 4.51 [t, $^3J(^1H–^1H) = 8.0$ Hz, *para* Ti-η^6-C_6H_5]; 3.32 (br s, B–CH_2); 3.21 (s, CH_2); 1.88 (s, *meta* CH_3); 1.03 (s, CH_3). Attempts to isolate **25** as a solid and not as an oil have thus far been unsuccessful.

*3.20. Synthesis of $[Ti(OC_6H_3Ph_2\text{-}2,6)_2\{CH_2CH\text{-}(CH_2Ph)CH_2(\eta^6\text{-}C_6H_5)\}][PhCH_2B(C_6F_5)_3]$ (**26**)*

A sample of $[Ti(OC_6H_3Ph_2\text{-}2,6)_2(CH_2Ph)]\text{-}[B(C_6F_5)_3(CH_2\{\eta^6\text{-}C_6H_5\})]$ (**12**) (20 mg, 0.016 mmol) was placed in an NMR tube along with deuterated benzene and 1.5 equivalents of allylbenzene (3.22 µl, 0.024 mmol), resulting in a red solution. ^{1}H-NMR (C_6D_6, 30°C): δ 6.50–7.50 (aromatics); 6.16 (d), 6.08 [d, $^3J(^1H–^1H) = 7.5$ and 7.6 Hz, *ortho* Ti-η^6-C_6H_5]; 5.43 (t), 5.27 (t), 5.12 [t, $^3J(^1H–^1H) = 6.9$, 7.8, and 7.4 Hz, *meta* and *para* Ti-η^6-C_6H_5]; 3.28 (s, B–CH_2Ph); 1.40–2.60 (aliphatics); 0.26 (dd, Ti–CH_2). Selected ^{13}C-NMR (C_6D_6, 30°C): δ 161.9, 161.6 (Ti–O–C); 58.3 (Ti–CH_2); 45.0 (Ti–CH_2CH); 40.5, 39.7 (CH_2Ph, $CH_2\{\eta^6\text{-}C_6H_5\}$); 32.7 (br, B–$CH_2$). Attempts to isolate **26** as a solid and not as an oil have thus far been unsuccessful.

*3.21. $[Ti(OC_6HPh_2\text{-}2,6\text{-}Me_2\text{-}3,5)_2\{CH_2CH\text{-}(CH_2Ph)CH_2(\eta^6\text{-}C_6H_5)\}][B(C_6F_5)_3(CH_2Ph)]$ (**27**)*

A sample of $[Ti(OC_6HPh_2\text{-}2,6\text{-}Me_2\text{-}3,5)_2(CH_2Ph)_2]$ (**5**) (200 mg, 0.026 mmol) and 1.3 equivalents of $[B(C_6F_5)_3]$ (171 mg, 0.33 mmol) were dissolved in benzene and after 10 min 1.1 equivalents of allylbenzene (37.5 ml, 0.28 mmol) were added to this stirred red solution. The solution was stirred for an additional 30 min and then evacuated to dryness, leaving a yellow–orange solid. ^{1}H-NMR (C_6D_6, 30°C): δ 6.65–7.40 (aromatics); 6.58 (d), 6.37 [d, $^3J(^1H–^1H) = 7.6$ and 7.0 Hz, *ortho* Ti-η^6-C_6H_5]; 6.14 (t), 5.63 (t), 5.03 [t, $^3J(^1H–^1H) = 6.8$, 7.7, and 6.9 Hz, *meta* and *para* Ti-η^6-C_6H_5]; 3.35 (s, B–CH_2Ph); 1.94 (s), 1.82 (s, *meta* CH_3); 1.40–2.50 (aliphatics); 0.00 (dd, Ti–CH_2). Selected ^{13}C-NMR (C_6D_6, 30°C): δ 162.5, 161.6 (Ti–O–C); 58.4 (Ti–CH_2); 44.9 (Ti–CH_2CH); 40.2 (CH_2Ph, $CH_2\{\eta^6\text{-}C_6H_5\}$); 20.8, 20.6 (*meta* CH_3).

*3.22. $[Ti(OC_6H_3Ph_2\text{-}2,6)_2\{CH_2CH(CH_3)\text{-}CH_2(\eta^6\text{-}C_6H_5)\}][PhCH_2B(C_6F_5)_3]$ (**28**)*

A sample of **12** was placed in an NMR tube along with C_6D_6, causing the formation of a red solution. Propene (1 atm) was added to the solution via a glass manifold, causing the solution to become orange in color after a few minutes. Excess propene was then removed by evacuation of the solution, leaving an orange oil. This oil was re-dissolved in C_6D_6. The ^{1}H-NMR spectrum matches exactly with the ^{1}H-NMR spectrum of **31** except for the signal for the boron-containing anion which was δ 3.28 for B–CH_2 for **28**.

3.23. Synthesis of $[Ti(OC_6H_3Ph_2\text{-}2,6)_2\{CH_2CH((CH_2)_3CH_3)CH_2(\eta^6\text{-}C_6H_5)\}][PhCH_2B(C_6F_5)_3]$ (*29*)

A sample of $[Ti(OC_6H_3Ph_2\text{-}2,6)_2(CH_2Ph)][B(C_6F_5)_3(CH_2\{\eta^6\text{-}C_6H_5\})]$ (**12**) (40 mg, 0.03 mmol) was placed in an NMR tube along with deuterated benzene and 2 equivalents of 1-hexene (8.1 µl, 0.06 mmol), resulting in an orange solution. ^{1}H-NMR (C_6D_6, 30°C): δ 6.50–7.50 (aromatics); 6.37 (d), 6.30 [d, $^3J(^1H\text{–}^1H) = 7.9$ and 7.8 Hz, *ortho* Ti-η^6-C_6H_5]; 5.63 (t), 5.16 (t), 4.86 [t, $^3J(^1H\text{–}^1H) = 7.6$, 7.4, and 7.6 Hz, *meta* and *para* Ti-η^6-C_6H_5]; 3.22 (s, B–CH_2Ph); 0.20–1.50 (aliphatics). Selected ^{13}C-NMR (C_6D_6, 30°C): δ 161.9, 161.4 (Ti–O–*C*); 58.7 (Ti–*C*H); 44.1 (*C*H$_2$CH$_2$$\{\eta^6$-$C_6H_5\}$); 39.7 (Ti–CH*C*H$_2$); 36.8 (CH$_2$*C*H$_2$$\{\eta^6$-$C_6H_5\}$); 29.8 (Ti–CHCH$_2$*C*H$_2$); 23.3 (Ti–CHCH$_2CH_2$*C*H$_2$); 14.3 (Ti–CHCH$_2$ CH$_2$CH$_2$*C*H$_3$).

3.24. $[Ti(OC_6HPh_2\text{-}2,6\text{-}Me_2\text{-}3,5)_2\{CH_2CH((CH_2)_3CH_3)CH_2(\eta^6\text{-}Ph)\}][PhCH_2B(C_6F_5)_3]$ (*30*)

A sample of $[Ti(OC_6HPh_2\text{-}2,6\text{-}Me_2\text{-}3,5)_2(CH_2Ph)_2]$ (**5**) (60 mg, 0.08 mmol) was placed in an NMR tube along with $[B(C_6F_5)_3]$ (50 mg, 0.10 mmol), deuterated benzene, and 2 equivalents of 1-hexene (19.3 µl, 0.15 mmol) resulting in a red solution. ^{1}H-NMR (C_6D_6, 30°C): δ 6.95–7.60 (aromatics); 6.77(s), 6.73 (s, *para* OC$_6$*H*); 6.87 (d), 6.58 [d, $^3J(^1H\text{–}^1H) = 7.3$ and 7.3 Hz, *ortho* Ti-η^6-C_6H_5]; 5.81 (t), 5.68 (t), 5.08 [t, $^3J(^1H\text{–}^1H) = 7.3$, 7.3, and 7.0 Hz, *meta* and *para* Ti-η^6-C_6H_5]; 3.37 (s, B–CH_2Ph); 1.94 (s), 1.87 (s, *meta* CH_3); 0.00–2.50 (aliphatics). Evacuation of this solution to dryness afforded a yellow–orange glassy solid, which only produced an oil from recrystallization attempts.

3.25. $[Ti(OC_6H_3Ph_2\text{-}2,6)_2\{CH_2CH(CH_3)CH_2(\eta^6\text{-}C_6H_5)\}][CH_3B(C_6F_5)_3]$ (*31*)

A sample of **8** (50 mg, 0.09 mmol) was placed in an NMR tube along with 2 equivalents of allylbenzene (24 µl, 0.18 mmol) and C_6D_6 (0.5 ml). To this solution was added $[B(C_6F_5)_3]$ (60 mg, 0.11 mmol) dissolved in C_6D_6 (0.5 ml) resulting in a dark red solution. ^{1}H-NMR (C_6D_6, 30°C): δ 6.80–7.50 (aromatics); 6.49 (d), 6.33 [d, $^3J(^1H\text{-}^1H) = 8.0$ and 7.8 Hz, *ortho* Ti-η^6-C_6H_5]; 5.79 (t), 5.24 (t), 4.79 [t, $^3J(^1H\text{–}^1H) = 7.7$, 7.3, and 7.5 Hz, *meta* and *para* Ti-η^6-C_6H_5]; 1.35 (m, CH_2Ph); 1.18 (m, C*H*CH$_3$); 0.98 (br, B–CH_3); 0.21 (m, Ti–CH$_2$); 0.21 [d, $^3J(^1H\text{–}^1H) = 5.9$ Hz, CHCH_3). Selected ^{13}C-NMR (C_6D_6, 30°C): δ 162.1, 161.3 (Ti–O–*C*); 70.4 (Ti–*C*H$_2$); 53.2 (Ti–CH$_2$*C*H); 33.2 (*C*H$_2$–η^6-C_6H_5); 24.5 (B–*C*H$_3$); 13.6 (CH*C*H$_3$).

3.26. $[Ti(OC_6HPh_2\text{-}2,6\text{-}Me_2\text{-}3,5)_2\{CH_2CH(CH_3)CH_2(\eta^6\text{-}C_6H_5)\}][CH_3B(C_6F_5)_3]$ (*32*)

A sample of **9** (50 mg, 0.08 mmol) was placed in an NMR tube along with 2 equivalents of allylbenzene (21 µl, 0.16 mmol) and C_6D_6 (0.5 ml). To this solution was added $[B(C_6F_5)_3]$ (50 mg, 0.10 mmol) dissolved in C_6D_6 (0.5 ml), resulting in a dark red solution. ^{1}H-NMR (C_6D_6, 30°C): δ 6.75–7.40 (aromatics); 6.66 (d), 6.52 [d, $^3J(^1H\text{–}^1H) = 7.7$ and 7.4 Hz, *ortho* Ti-η^6-C_6H_5]; 5.71 (t),

Table 9
Crystal data and data collection parameters

	3	8	12	15	16	19
Formula	$TiO_2C_{50}H_{40}$	$TiO_2C_{38}H_{32}$	$TiBF_{15}O_2C_{60}H_{40}$	$ZrBF_{15}O_2C_{84}H_{55}$	$ZrBF_{15}O_2C_{56}H_{51}$	$TiO_3C_{55}H_{42}$
Formula weight	720.78	568.58	1232.76	1483.38	1143.04	798.85
Space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	10.4608(9)	9.8108(3)	12.917(2)	13.3579(17)	15.5437(2)	10.3321(3)
b (Å)	18.8946(17)	10.7880(5)	13.045(2)	14.722(4)	19.0909(3)	20.6823(8)
c (Å)	19.9761(15)	14.9475(6)	19.600(2)	20.596(7)	36.6115(6)	20.2955(8)
α (°)	90	93.1218(18)	84.757(12)	71.45(2)	90	90
β (°)	97.118(5)	106.605(2)	77.580(12)	77.548(19)	101.1696(8)	103.376(2)
γ (°)	90	93.597(2)	61.871(13)	72.175(17)	90	90
V (Å^3)	3917.9(10)	1508.7(2)	2844.0(8)	3624.1(17)	10658.4(5)	4219.3(5)
Z	4	2	2	2	8	4
ρ_{calc} (g cm^{-3})	1.222	1.252	1.444	1.359	1.425	1.257
Temperature (K)	203.	203.	295.	203.	203.	203.
Radiation (wavelength)	Mo–K$_\alpha$ (0.71073 Å)	Mo–K$_\alpha$ (0.71073 Å)	Mo–K$_\alpha$ (0.71073 Å)	Mo–K$_\alpha$ (0.71073 Å)	Mo–K$_\alpha$ (0.71073 Å)	Mo–K$_\alpha$ (0.71073 Å)
R	0.080	0.050	0.069	0.055	0.055	0.093
R_W	0.168	0.113	0.178	0.160	0.135	0.226

5.52 (t), 5.30 [t, $^3J(^1H–^1H) = 8.0$, 6.7, and 7.3 Hz, *meta* and *para* Ti-η^6-C_6H_5]; 1.93 (s), 1.89 (s, *meta* CH_3); 0.98 (br, B–CH_3); 0.00–2.10 (other aliphatics). Selected ^{13}C-NMR (C_6D_6, 30°C): δ 162.1, 161.7 (Ti–O–*C*); 70.5 (Ti–CH_2); 53.1 (Ti–CH_2CH); 33.2 (CH_2-η^6-C_6H_5); 24.5 (B–CH_3); 24.0 ($CHCH_3$); 20.8, 20.5 (*meta* CH_3).

3.27. Oligomerization of 1-hexene by $[(ArO)_2TiMe][MeB(C_6F_5)_3]$

In the drybox a sample of $[(ArO)_2TiMe_2]$ (**8–11**) (0.089 mmol) was dissolved toluene in (0.5 ml) along with 200 equivalents of 1-hexene (2 ml). This solution was stirred as $[B(C_6F_5)_3]$ (0.097 mmol) dissolved in toluene (1 ml) was quickly added. The mixture was stirred for 24 h and analyzed by gas chromatography using the parent phenol as an internal reference to determine product distribution. The heavier polyhexene samples were isolated as described for polyethylene and polypropylene in heading 6.3.22 and subsequently analyzed by ^1H- and ^{13}C-NMR in order to determine end groups. For lighter polyhexene samples the original solutions were dried on a rotary evaporator and analyzed by NMR.

3.28. Polymerization of ethene and propene by $[(ArO)_2TiMe][MeB(C_6F_5)_3]$

In the drybox a solvent sealed flask containing a stir bar was charged with a sample of $[(ArO)_2TiMe_2]$ (**8–11**) (0.089 mmol), toluene (3 ml) and $[B(C_6F_5)_3]$ (0.097 mmol). The flask was quickly brought out of the drybox and chilled to 0°C using an ice–acetone bath. One atmosphere of monomer was placed upon the contents of the flask for 15 min while the mixture was vigorously stirred. After this time methanol was added to quench the reaction and precipitate any polymer formed. The polymers that formed were washed with methanol and dried under vacuum, affording either viscous colorless oils (polypropylene) or white solids (polyethylene).

3.29. Crystallographic studies

Crystal data and data collection parameters are contained in Table 9. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 127153 (**3**), 127154 (**8**), 127155 (**12**), 127156 (**15**), 12757 (**16**) and 12758 (**19**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ (fax +44(1223)336-033 or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

The authors wish to thank the National Science Foundation (Grant CHE-9700269) for financial support of this research.

References

[1] (a) G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem. Int. Ed. Engl. 38 (1999) 428 and references therein. (b) V.C. Gibson, Angew. Chem. Int. Ed. Engl. 33 (1994) 1565.

[2] (a) Polyhedron Symposium in Print #19 (M.H. Chisholm, Ed.) Polyhedron, 17 (1998) 623–1034. (b) M.F. Lappert, P.P. Power, A.R. Sanger, R.C. Srivastava, Metal and Metalloid Amides, John Wiley, New York, 1980.

[3] (a) Polyhedron Symposium in Print #16 (M.H. Chisholm, I.P. Rothwell, Eds.) Polyhedron, 14 (1995) 3177–3366. (b) D.C. Bradley, R.C. Mehrotra, D.P. Gaur, Metal Alkoxides, Academic Press, New York, 1978. (c) M.H. Chisholm, Chemtracts 4 (1992) 273.

[4] P.T. Wolczanski, Polyhedron 14 (1995) 3335.

[5] (a) I.P. Rothwell, Chem. Commun. (Cambridge) (Feature Article) (1997) 1331. (b) V.M. Visciglio, J.R. Clark, M.T. Nguyen, D.R. Mulford, P.E. Fanwick, I.P. Rothwell, J. Am. Chem. Soc. 119 (1997) 3490. (c) J.S. Vilardo, M.A. Lockwood, L.G. Hanson, J.R. Clark, B.C. Parkin, P.E. Fanwick I.P. Rothwell, J. Chem. Soc. Dalton Trans. (1997) 3353. (d) M.G. Thorn, J.E. Hill, S.A Waratuke, E.S. Johnson, P.E. Fanwick, I.P. Rothwell, J. Am. Chem. Soc. 119 (1997) 8630. (e) E.S. Johnson, G.J. Balaich, I.P. Rothwell, J. Am. Chem. Soc. 119 (1997) 7685.

[6] (a) M. Bochmann, J. Chem. Soc. Dalton Trans. (1996) 255. (b) H.-H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, Angew. Chem. Int. Ed. Engl. 34 (1995) 1143. (c) P.C. Möhring, N.J. Coville, J. Organomet. Chem. 479 (1994) 1. (d) W. Kaminsky, K. Kulper, H.H. Brintzinger, Angew. Chem. Int. Ed. Engl. 24 (1985) 507.

[7] (a) J.D. Scollard, D.H. McConville, J. Am. Chem. Soc. 118 (1996) 10008. (b) R. Baumann, W.M. Davis, R.R. Schrock, J. Am. Chem. Soc. 119 (1997) 3830.

[8] For the polymerization of olefins by bidentate aryloxides see (a) T. Miyatake, K. Mizunuma, M. Kakugo, Marcomol. Chem. Macromol. Symp. 66 (1993) 203. (b) A. van der Linden, C.J. Schaverien, N. Meijboom, C. Grant, A.G. Orpen, J. Am. Chem. Soc. 117 (1995) 3008. (c) S. Fokken, T.P. Spaniol, H.-C. Kang, W. Massa, J. Okuda, Organometallics 15 (1996) 5069. (d) For cationic zirconium alkyls supported by chelating phenoxides see P.G. Cozzi, E. Gallo, C. Floriani, A. Chiesi-Villa, C. Rizzoli, Organometallics 14 (1995) 4994.

[9] M.G. Thorn, Z.C. Etheridge, P.E. Fanwick, I.P. Rothwell, Organometallics 17 (1998) 3636.

[10] Mixed cyclopentadienyl aryloxide compounds have also been studied, see (a) K. Nomura, N. Naga, M. Miki, K. Yanagi, Macromolecules 31 (1998) 7588. (b) S.W. Ewart, M.J. Sarsfield, D. Jeremic, T.L. Tremblay, E.F. Williams, M.C. Baird, Organometallics 17 (1998) 1502. (c) M.J. Sarsfield, S.W. Ewart, T.L. Tremblay, A.W. Roszak, M.C. Baird, J. Chem. Soc. Dalton Trans. (1997) 3097. (d) T.L. Tremblay, S.W. Ewart, M.J. Sarsfield, M.C. Baird, Chem. Commun. (Cambridge) (1997) 831. (e) For linked Cp-phenoxide derivatives see Y.-X. Chen, P.-F. Fu, C.L. Stern, T.J. Marks, Organometallics 16 (1997) 5958. (f) J.S. Vilardo, M.G. Thorn, P.E. Fanwick, I.P. Rothwell, Chem. Commun. (Cambridge) (1998) 2425. (g) M.G. Thorn, J.S. Vilardo, P.E. Fanwick, I.P. Rothwell, Chem. Commun. (Cambridge) (1998) 2427.

[11] J.R. Dilworth, J. Hanich, M. Krestel, J. Organomet. Chem. 315 (1986) 9.
[12] S.L. Latesky, A.K. McMullen, I.P. Rothwell, J.C. Huffman, Organometallics 4 (1985) 902.
[13] (a) G.R. Davies, J.A.J. Jarvis, B.T. Kilbourn, A.J.P. Piols, J. Chem. Soc. Chem. Commun. (1971) 677. (b) G.R. Davies, J.A.J. Jarvis, B.T. Kilbourn, J. Chem. Soc. Chem. Commun. (1971) 1511.
[14] R.W. Chesnut, L.D. Durfee, P.E. Fanwick, I.P. Rothwell, K. Folting, J.C. Huffman, Polyhedron 6 (1987) 2019.
[15] (a) X. Yang, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 116 (1994) 10015. (b) J.A. Ewen, M. Elder, J. Chem. Abstr. 115 (1991) 136998g. (c) A.G. Massey, A.J. Park, J. Organomet. Chem. 2 (1964) 245. (d) M. Bochmann, S.J. Lancaster, M.B. Hursthouse, K.M.A. Malik, Organometallics 13 (1994) 2235. (e) D.J. Gillis, M.-J. Tudoret, M.C. Baird, J. Am. Chem. Soc. 115 (1993) 2543. (f) C. Pellecchia, D. Pappalardo, L. Oliva, A. Zambelli, J. Am. Chem. Soc. 117 (1995) 6593.
[16] I.P. Rothwell, Acc. Chem. Res. 21 (1988) 153.
[17] D.W. Blackburn, D. Britton, J.E. Ellis, Angew. Chem. Int. Ed. Engl. 31 (1992) 1495.
[18] F. Calderazzo, I. Ferri, G. Pamploni, U. Englert, M.L.H. Green, Organometallics 16 (1997) 3100.
[19] E. Solari, C. Floriani, A. Chiesi-Villa, C. Guastini, J. Chem. Soc. Chem. Commun. (1989) 1747.
[20] S. Troyanov, A. Pisarevsky, Y.T. Struchov, J. Organomet. Chem. 494 (1995) C4.
[21] For other high valent arene derivatives of the Group 4 metals see (a) S.J. Lancaster, O.B. Robinson, M. Bochmann, S.J. Coles, M.B. Hurshouse, Organometallics 14 (1995) 2456. (b) D.J. Gillis, R. Quyoum, M.-J. Tudoret, Q. Wang, D. Jeremic, A.W. Roszak, M.C. Baird, Organometallics 15 (1996) 3600.
[22] C. Pellecchia, A. Grassi, A. Immirzi, J. Am. Chem. Soc. 115 (1993) 1160.
[23] C. Pellecchia, A. Immirzi, A. Grassi, A. Zambelli, Organometallics 12 (1993) 4473.
[24] B.D. Steffey, P.E. Fanwick, I.P. Rothwell, Polyhedron 9 (1990) 963.
[25] C. Pellecchia, A. Immirzi, A. Zambelli, J. Organomet. Chem. 479 (1994) C9.
[26] D.F. Shriver, M.A. Drezdzon, The Manipulation of Air-Sensitive Compounds, Wiley–Interscience, New York, 1986.