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Mono(aryloxido)Titanium(IV) Complexes and Their Application in the Selective Dimerization of Ethylene

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We report on the synthesis of mono(aryloxido)titanium(IV) complexes of general formula {Ti[O(*o*-R)Ar]X_3}, with X = O*i*Pr, ArO = 2-*tert*-butyl-4-methylphenoxy and R = CMe_3 (**2a**), CMe_2Ph (**2b**) and CH_2NMe_2 (**2c**). Attempts to reach pure mono(aryloxido) complexes when R = $CH_2NMe(CH_2Ph)$ (**2d**) or $CH_2N(CH_2Ph)_2$ (**2e**) were unsuccessful. When R = CH_2OMe, the analogous mononuclear complex was not obtained, and instead, a dinuclear complex [(2-*tert*-butyl-4-methyl-6-methoxymethylphenoxy) TiCl(O*i*Pr)(μ_2-O*i*Pr)$_2$TiCl-(O*i*Pr)$_2$] (**3**) was formed. Complexes **2b** and **3** were characterized by single-crystal X-ray diffraction. The former contains a tetrahedrally coordinated Ti^{IV} centre, whereas in the latter the aryloxido ligand behaves as a chelating–bridging ligand between the two, chemically very different metal centres that form two face-sharing octahedra. Different synthetic approaches starting from [Ti(O*i*Pr)$_4$] or [TiCl(O*i*Pr)$_3$] were evaluated and are discussed. The hemilabile behaviour of the aryloxido ligand resulting from reversible coordination of its side arm was studied by variable-temperature ^{1}H NMR spectroscopy for **2c** (R = CH_2NMe_2). Complexes **2a–d** were contacted with ethylene and $AlEt_3$ as cocatalyst. When activated with $AlEt_3$ (3 equiv.) at 20 bar and 60 °C, complex **2c** exhibits interesting activity (2100 g/gTi/h) for the selective dimerization of ethylene to 1-butene (92 % $C_4^=$; 99$^+$% $C_4^{=1}$). Noticeable differences in catalyst activity were observed when the R group was modified.

Introduction

The catalytic oligomerization of ethylene represents the main industrial source of α-olefins.[1] Processes based on this reaction yield olefins with an even number of carbon atoms and a more or less tuneable chain length distribution. Among these products, short-chain linear α-olefins (1-butene, 1-hexene, 1-octene) are of particular interest because of their use, for example, in the synthesis of linear low-density polyethylene. The development of efficient catalyst systems for the selective production of these olefins has recently triggered intensive research in both academia and industry. For this purpose, titanium- and chromium-based catalysts have attracted much attention.[2] Homogeneous chromium catalysts play a major role in ethylene trimerization[3–13] and tetramerization reactions.[14–22] Titanium catalysts are preferred catalysts for the selective dimerization of ethylene to 1-butene.[23–26] The conventional industrial production of 1-butene is realized by extraction from the C4 fraction of steam cracker plants. Butadiene and isobutene also present in the C4 fraction have a boiling point very close to that of 1-butene and separation by superfractionation is almost impossible. Chemical extraction is industrially used but the 1-butene obtained contains 1,3-butadiene and isobutene impurities, which are very detrimental in polyethylene processes. On the contrary, selective ethylene dimerization, which is industrially operated in the IFP Alphabutol processes,[26] has the main advantage to provide 1-butene with a much better quality associated with a low investment. Today, 24 Alphabutol units have been licensed, for a cumulated 1-butene production capacity of 500000 t/y, nearly 25% of the world's 1-butene consumption as co-monomer in polyethylene.

Another source of 1-butene results from its co-production in the ethylene oligomerization processes leading to higher, linear α-olefins (Ineos, Chevron-Phillips, Idemitsu processes). However, 1-butene appears as a byproduct in these processes, and the amount available is directly dependent on the market for the higher linear α-olefins. When these two sources cannot be envisaged, a polyethylene manufacturer may either import 1-butene, which implies transportation and storage costs, or produce 1-butene on-site by a dedicated process. Titanium complexes also appeared recently as good catalysts for the selective trimerization of ethylene to 1-hexene. This new catalyst comprises a titanium cyclopentadienyl (Cp) system with an aromatic side arm grafted onto the Cp ligand.[27–29] The addition of this

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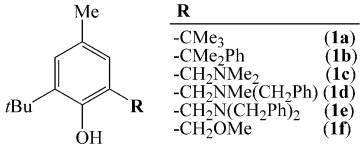
functionality to Cp dramatically changes the selectivity of the known ethylene polymerization system [$CpTiCl_3$]-MAO. DFT studies were conducted on this catalytic system and essentially confirmed the role of the arene side arm on this surprising reactivity.[30–33] In a further modification of this titanium-based catalyst, Huang et al. replaced the pendant arene with a thienyl[34] or ether pendant group[35] and observed again selectivity toward 1-hexene. Over the past decade, there has been much interest for catalysts based on post-metallocene group 4 complexes.[36–38] In this context, aryloxido-based ligands[39,40] have proved to be good alternatives to the Cp ligand. In particular, ancillary phenoxyimine systems have raised a great deal of interest.[41,42] The use of other functionalized aryloxido ligands in group 4 metal complexes remains scarce.[43–46] Most of these aryloxido/group 4 systems were developed for ethylene polymerization and contain ligands presenting a constrained geometry for better polymer selectivity. In comparison with these systems, complexes containing one aryloxido ligand with a π-electron donor pendant group remain underrepresented.[47] Owing to the expected reversible coordination of the pendant group, such ligands could stabilize highly reactive electrophilic metal centres until the substrate coordinates and replaces the pendant group. The aim of the present work was to design monoanionic bidentate phenoxido ligands capable of generating hemilabile behaviour in association with a titanium complex. This feature should lead to more flexibility in the ligand-coordinating ability and could affect both the stability and the reactivity of the complexes for the selective dimerization of ethylene.

Results and Discussion

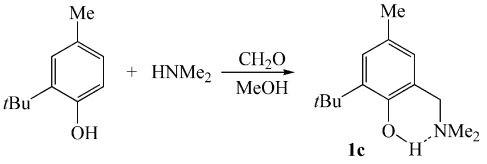
Synthesis of the Substituted Aryloxido Ligands

The *ortho* position of 2-*tert*-butyl-4-methylphenol was functionalized with various R groups (Scheme 1). These side chains cover a wide panel of coordinating abilities, ranging from the bulky non-coordinating *tert*-butyl group to the stronger donor amine chain, through an aromatic group able to donate up to 6π electrons to the titanium centre. The influence of steric factors was also studied by comparing several aminophenols.



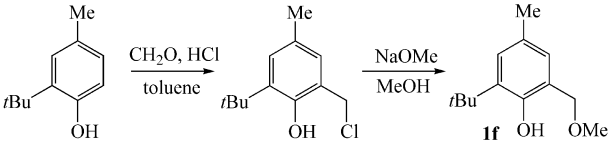
Scheme 1. *o*-Functionalized aryloxido ligands.

Ligand **1b** was obtained by an acid-catalyzed alkylation reaction by following a procedure described for the synthesis of 2,6-di-*tert*-butylphenol.[48] The use of *ortho*/*para*-substituted phenol as the starting material prevented the formation of bisalkylation products and facilitated the isolation of the desired compound (43% yield after distillation and recrystallization from pentane). Aminophenols **1c**–**e** were synthesized by using a Mannich-type condensation, as described for **1c**[49] [Equation (1)], and they were obtained as white crystalline solids in 85, 76 and 57% yield, respectively, depending on the steric hindrance of the precursor amine.



(1)

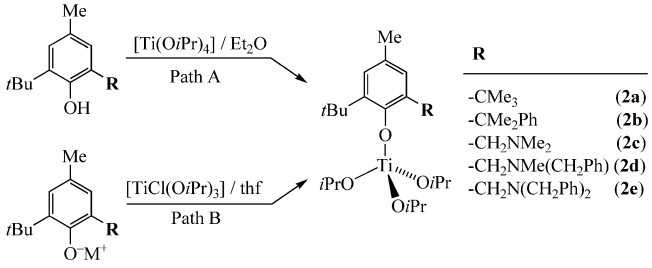
The synthesis of ligand **1f** was achieved in a two-step reaction involving the synthesis of the chloromethylphenol intermediate and its reaction with sodium methoxide [Equation (2)]. Ligand **1f** was isolated as a white solid that melts at room temperature (52% yield).



(2)

Synthesis of the [Ti(OAr)(O*i*Pr)$_3$] Complexes

We used two different approaches to access the mono(aryloxido) complexes shown in Scheme 2. The most suitable synthetic route (path A, Scheme 2) involved ligand exchange between the tetraalkoxide Ti^{IV} precursor [Ti(O*i*Pr)$_4$] and the phenol.[39,50–52] This route led to readily isolable species, as the only byproduct was an alcohol that could be easily removed under reduced pressure. These mono(aryloxido) complexes could also be obtained by transmetallation, starting from the metallated phenol (Na, Li) and the [$TiCl(OiPr)_3$] precursor (path B, Scheme 2).



Scheme 2. General synthesis of [Ti{O(*o*-R)Ar}(O*i*Pr)$_3$].

When 2,6-di-*tert*-butyl-4-methylphenol was treated with [Ti(O*i*Pr)$_4$], expected mono(aryloxido)titanium(IV) complex **2a** was obtained and isolated in good yield after crystallization from cold pentane (off white solid, 78%). The same synthetic route applied to the aminophenol series gave less satisfactory results. The desired mono(aryloxido) complex was only obtained starting from **1c** with nevertheless the presence of residual phenol characterized by ^{1}H

NMR spectroscopy. Owing to the oily nature of **2c** and its high solubility in common organic solvents, we were not able to isolate this complex pure. Moreover, it became increasingly difficult to obtain pure compounds when the steric bulk of the *N*-substituents increased. Benzylmethylaminomethyl derivative **2d** could only be obtained with in 90% purity, and bulkier dibenzylaminomethyl derivative **2e** was only observable in a very complex mixture [free phenol **1e**, residual [Ti(O*i*Pr)$_4$], mono- and bis(aryloxido) complexes]. Path B was then evaluated to overcome these difficulties. The reaction of the sodium phenoxide derived from **1c** with [TiCl(O*i*Pr)$_3$] afforded **2c** in high yields as a bright-yellow oil. None of the various crystallization attempts afforded a crystalline product. Unfortunately, the reaction of the phenoxide derived from **1e** with [TiCl(O*i*Pr)$_3$] yielded a complicated mixture of products. The relatively large amount of bis(aryloxido) complex formed suggests the occurrence of a ligand redistribution in solution [Equation (3)].

$$2\ [Ti(OAr)(OiPr)_3] \longrightarrow [Ti(OAr)_2(OiPr)_2] + [Ti(OiPr)_4] \quad (3)$$

Following path B, complex **2b** was also isolated in high yield as a pure crystalline compound that easily formed large, colourless crystals suitable for X-ray diffraction. A view of the molecular structure of **2b** is shown in Figure 1 and selected bond lengths and angles are collected in Tables 1 and 2, respectively. In complex **2b**, the tetrahedral coordination geometry around the metal centre is slightly distorted and the bulky aryloxido unit is further away from the metal than the isopropoxido ligands, Ti–O(3) < Ti–O(4) < Ti–O(2) < Ti–O(1), indicating a weaker interaction of the aryloxido oxygen lone pairs with the titanium d orbitals. Furthermore, the position of the aromatic side chain induces a widening of the tetrahedral cone angle Ti-{O(1),O(2),O(3)}. This results in a relatively short distance of 0.550 Å between Ti and the {O(1),O(2),O(3)} plane (materialized by a dashed plane in Figure 1). The distances between the titanium and the other {O(*x*),O(*y*),O(*z*)} planes are much longer: Ti-{O(1),O(3),O(4)} = 0.583 Å, Ti-{O(1),O(2),O(4)} = 0.613 Å and Ti-{O(2),O(3),O(4)} = 0.635 Å. The titanium atom is not at the centre of the tetrahedron but slightly displaced towards the aromatic side chain. However, when considering the interatomic distances, the aromatic group appears too far from the metal to interfere significantly with its coordination sphere [C(15)–Ti ≈ 3.6 Å].

Difficulties observed for the selective synthesis of mono(aryloxido)titanium(IV) complexes **2c**–**e** were also observed with ether-functionalized phenol ligand **1f**. The reaction of **1f** with [Ti(O*i*Pr)$_4$] and that of the sodium derivative of **1f** with [TiCl(O*i*Pr)$_3$] led to redistribution of the ligands, and the only isolated product was the bis(aryloxido) species. Another approach (Scheme 3) was attempted with **1f** that involved the use of its trimethylsilyl derivative.[40,53]

However, this reaction did not afford the expected complex of type **2**; instead, binuclear complex **3** was obtained in low yield as red crystals, suitable for X-ray diffraction analysis (Figure 2). In this compound, the Ti1 atom is at the centre of a distorted octahedron formed by a terminal chloride ion, a terminal alkoxido group, two bridging alkoxido ligands, the terminally bound ether oxygen atom of the aryloxido group and the bridging oxygen atom of the aryloxido ligand. The Ti2 centre displays a distorted structure between trigonal-bipyramidal and octahedral when considering the terminal chloride ion, the two terminal alkoxido groups, the two bridging alkoxido groups and the methoxy group of the aryloxido ligand. The structure of this dinuclear complex can therefore be viewed as that of

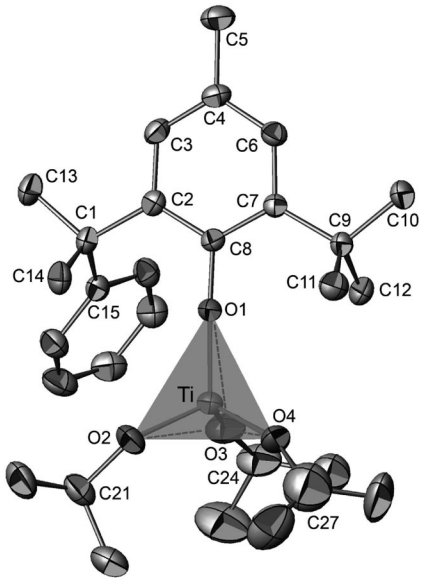


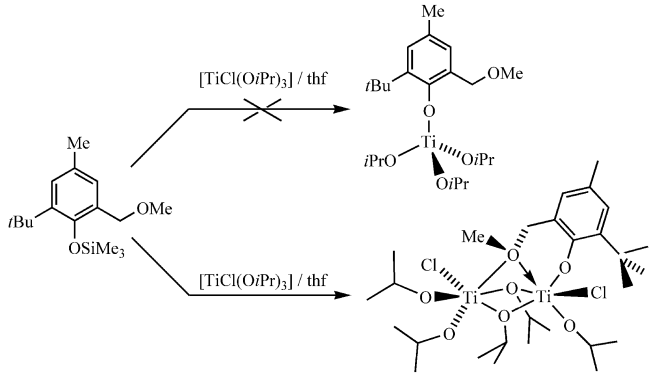
Figure 1. ORTEP view and atom numbering of **2b**. H atoms omitted for clarity. Thermal ellipsoids include 50% of the electron density.

Table 1. Selected bond lengths for **2b**.

Atom 1	Atom 2	Bond length [Å]
Ti	O1	1.825(1)
Ti	O2	1.793(2)
Ti	O3	1.754(2)
Ti	O4	1.774(2)
O1	C8	1.360(2)
O2	C21	1.423(2)
O3	C24	1.421(3)
O4	C27	1.383(3)

Table 2. Selected bond angles for **2b**.

Atom 1	Atom 2	Atom 3	Bond angle [°]
O1	Ti	O2	110.77(7)
O1	Ti	O3	113.21(7)
O1	Ti	O4	108.92(7)
O2	Ti	O3	109.04(8)
O2	Ti	O4	107.29(7)
O3	Ti	O4	107.40(9)
C8	O1	Ti	170.3(2)
C21	O2	Ti	145.0(2)
C24	O3	Ti	158.7(2)
C27	O4	Ti	157.8(2)



Scheme 3.

two face-sharing octahedra. It clearly illustrates the bending induced by the coordination of the ether group (Tables 3 and 4). As shown, the selective synthesis of *N*- or *O*-functionalized mono(aryloxido)titanium complexes appears rather difficult. We first thought that steric factors (in the case of the aminophenol series) were responsible for the ligand redistribution reactions. However, we did not observe them with **2a** and **2b**, where a strong *ortho* donor group is not present. It is conceivable that a strong donor group induces ligand redistribution via some dinuclear intermediate, but if this donor binds tightly to the titanium in the mononuclear species, then this pathway for ligand redistribution is blocked.

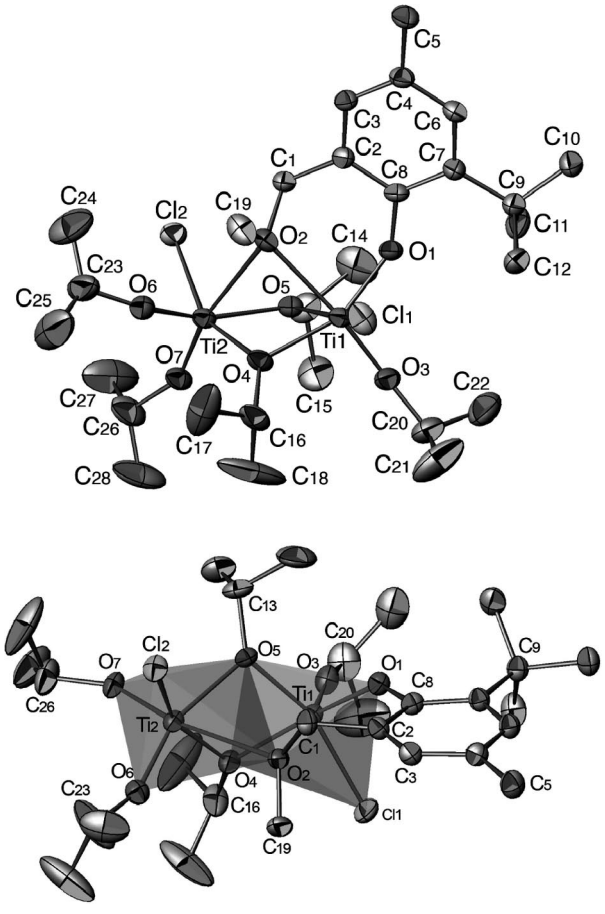


Figure 2. ORTEP views of **3**. H atoms omitted for clarity. Thermal ellipsoids include 50% of the electron density. The bottom view emphasizes the metal coordination polyhedra forming face-sharing octahedra.

Table 3. Selected bond lengths for **3**.

Atom 1	Atom 2	Bond length [Å]
Ti1	O1	1.842(3)
Ti1	O2	2.382(3)
Ti1	O3	1.751(3)
Ti1	O4	2.028(3)
Ti1	O5	1.979(2)
Ti1	Cl1	2.334(1)
Ti2	Cl2	2.346(1)
Ti2	O2	2.554(2)
Ti2	O4	1.997(2)
Ti2	O5	2.055(3)
Ti2	O6	1.771(3)
Ti2	O7	1.755(3)
O1	C8	1.361(4)
O2	C1	1.466(5)
O2	C19	1.455(5)
O3	C20	1.428(6)
O4	C16	1.454(5)
O5	C13	1.443(5)
O6	C23	1.389(7)
O7	C26	1.427(5)

Table 4. Selected bond angles for **3**.

Atom 1	Atom 2	Atom 3	Bond angle [°]
O1	Ti1	O4	155.6(1)
O2	Ti1	O3	172.31(1)
O5	Ti1	Cl1	157.5(1)
O2	Ti2	O7	166.4(1)
O4	Ti2	Cl2	153.3(1)
O5	Ti2	O6	156.8(1)
C8	O1	Ti1	136.0(2)
C20	O3	Ti1	169.8(3)
C16	O4	Ti2	132.6(2)
C16	O4	Ti1	124.7(2)
C13	O5	Ti1	133.4(3)
C13	O5	Ti2	124.0(2)
C23	O6	Ti2	151.8(5)
C26	O7	Ti2	147.6(4)

Hemilabile Properties of the –CH_2NMe_2 Group in Complex 2c

The ^{1}H NMR spectrum of complex **2c** in the methylene region suggests a loose coordination of the amine side chain to the metal centre. The two CH protons display a very broad signal at room temperature, which can be explained by a dynamic exchange involving reversible coordination of the amine, typical of hemilabile behaviour.[54] The ^{1}H NMR resonances of the methylene protons are diagnostic for the formation of metallocycles.[55] Therefore, the variable-temperature ^{1}H NMR study performed in [D_8]toluene between 193 and 353 K allowed us to follow the evolution of the broad signal observed for the methylene protons at 293 K (Figure 3).

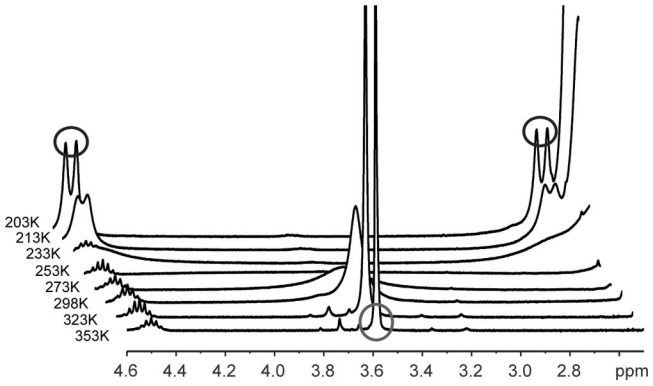


Figure 3. ^{1}H NMR study of complex **2c** as a function of temperature.

The resonance of the methylene protons at 3.6 ppm sharpens when the temperature is raised from 293 to 353 K. On the contrary, the broad signal observed at 293 K progressively disappears when the sample is cooled down, until two doublets appear at 2.7 and 4.5 ppm, indicative of the presence of an AX spin system. This pattern is attributed to the two geminal protons of the species with the amine nitrogen coordinated to titanium in a titanaoxoazacyclohexane. This reversible "opening–closing" phenomenon indicates a high stability of the compound over this temperature range. The free energy of activation associated with this process was calculated to be 50.4 kJ/mol.[56] The same NMR spectroscopic study was performed for complex **2b**. In that case, no evolution of the ^{1}H NMR spectrum was detected from 203 to 353 K. If thermal stability of complex **2b** is then demonstrated, this result indicates the absence of dynamic equilibrium involving the pendant aromatic ring.

Catalysis

The catalytic properties of complexes **2a**–**d** were investigated for ethylene oligomerization. [Ti(O*i*Pr)$_4$] was used as a reference for comparison of ligand effects. Experiments were carried out in heptane at 60 °C in the presence of $AlEt_3$ as cocatalyst. The ethylene pressure was maintained constant at 20 bar throughout the catalytic run (1 h). Results are summarized in Table 5.

With [Ti(O*i*Pr)$_4$], the catalyst activity was estimated at 1600 g/gTi/h. The ethylene consumption remained constant during the test. The selectivity for dimerization products was 93% with more than 99% of 1-butene. Under the same reactions conditions, complex **2c** exhibited an activity of 2100 g/gTi/h for the selective dimerization of ethylene to 1-butene (92% $C_4^=$; 99$^+$% $C_4^{=1}$). A small amount of $C_6^=$ byproducts were also obtained, which contained (GC analysis) 3-methyl-1-pentene (30%), 2-ethyl-1-butene (57%) and linear hexenes (10%). The nature of these products and the high selectivity for 1-butene can be explained by a metallacyclic mechanism, and byproducts result from a codimerization process reported earlier.[57] The influence of the $AlEt_3$/Ti ratio was also evaluated for complex **2c**. By increasing this ratio from 3 to 5, the activity decreased dramatically and the amount of polyethylene formed increased from ca. 1 to 36 wt.-%, but the selectivity for 1-butene in the butenes was not affected. This loss of activity can be related to the presence of free $AlEt_3$, which promotes the transfer of the aryloxido ligand to aluminum, resulting in inactive aluminum species.[58] Noticeable differences of activity were observed when the side group of the aryloxido ligand was modified. Substitution of the nitrogen with a benzyl group in **2d** reduced the catalytic activity. A similar comment can be made for complex **2b**, which displays a somewhat higher activity than **2a**. This could result from a weak coordination of the aromatic side chain to the titanium centre in the activated species. If the catalytic activity is enhanced by the aromatic side chain, the selectivity for the dimerization products is lowered. Indeed, this catalyst yields a mixture of 1-butene and $C_6^=$ isomers with a lower selectivity for butenes (less than 70%) than **2c** and a distribution of hexene isomers typical of a codimerization process (the main products being 2-ethyl-1-butene and 3-methyl-1-pentene). This observation suggests an increase in the rate of codimerization reaction. Complementary experiments were conducted with aluminoxane derivatives or chlorinated aluminum alkyls as cocatalysts.[59] These activators switch the reactivity from dimerization to polymerization.

Conclusions

New titanium monoanionic aryloxido complexes were synthesized and characterized. The interaction of the aryloxido *ortho*-substituent R with titanium could be evidenced, and the resulting hemilabile behaviour demonstrated through variable-temperature ^{1}H NMR spectroscopic analyses on complex **2c**. When the *ortho*-substituent

Table 5. Oligomerization of C_2H_4 with complexes **2a**–**d** and $AlEt_3$ as cocatalyst.[a]

Catalyst	Al/Ti ratio	Productivity (g/gTi/h)[b]	Sel. $C_4^=$(α[c])	Sel. $C_6^=$(α[d])	Sel. $C_{8+}^=$	PE[e]
[Ti(O*i*Pr)$_4$]	3	1600	93 (99$^+$)	6 (13)	<1	≈1
2a	3	170	91 (99)	2 (5)	4	2
2b	3	380	69 (99$^+$)	27 (2)	3	≈1
2c	3	2100	92 (99$^+$)	7 (11)	<1	≈1
2c	5	320	53 (98)	9 (16)	2	36
2d	3	100	91 (98)	8 (1)	<1	–

[a] Ti precursor (0.15 mmol), heptane (6 mL), 20 bar C_2H_4, 60 °C, stirring rate: 1000 rpm, reaction time: 1 h. [b] Expressed in grams of products per gram of Ti per hour. [c] 1-Butene vs. total butenes formed. [d] 1-Hexene vs. total hexenes formed. [e] Calculated from the solid isolated (insoluble in heptane).

R was CH_2OMe, dinuclear complex **3** was obtained and characterized by X-ray diffraction. The Ti centres are in very different coordination environments and only one mono(aryloxido) ligand is present, which acts as a chelating–bridging ligand. The activation of these complexes with $AlEt_3$ as cocatalyst was performed to evaluate their performances as ethylene selective dimerization catalysts. The donating ability as well as the steric bulk of the R group have a significant influence on the catalytic performances, as shown by the dimethylamine-functionalized compound **2c**, which selectively dimerizes ethylene with good productivity, whereas the benzylmethylamine and α,α-dimethylbenzyl derivatives (**2d** and **2b**, respectively) are less active. The influence of the aluminum-based cocatalyst was evaluated and appears critical for the type of mechanism involved. Whereas $AlEt_3$ generally implies selective ethylene dimerization, chlorinated cocatalysts or aluminoxane derivatives systematically lead to polymerization catalysis.

Experimental Section

General Methods: All manipulations were performed under an argon atmosphere by using standard Schlenk techniques. Ethyl ether and thf were distilled from Na/benzophenone prior to use. Pentane, heptane, *o*-xylene and toluene were distilled from a sodium suspension and dichloromethane over calcium hydride. The water contents of these solvents were periodically controlled by Karl-Fischer coulometry by using a Methrom 756 KF apparatus. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded with a Bruker AC 300 MHz instrument. Deuterated solvents (CD_2Cl_2, $CDCl_3$, D_2O) were purchased from Aldrich or Eurisotop. CD_2Cl_2 and $CDCl_3$ were degassed by freeze–thaw–vacuum cycles and stored over 3 Å molecular sieves. Chemical shifts are reported in ppm vs. $SiMe_4$ and were determined by reference to the residual solvent peaks. All coupling constants are given in Hertz. Elemental analyses of the ligands were performed by the Service Central d'Analyses of the CNRS (Vernaison, France) or by the ICMUB Université de Bourgogne (Dijon, France). Elemental analyses of the complexes were performed by Mikroanalitisches Labor Pascher (Remagen, Germany). Mass spectra analyses were performed by using an Agilent 5975 B instrument, in a chemical ionization mode with methane as gas. The samples, liquids or solids, were introduced by using a SIM automated direct inlet probe system with temperature control. Ion mass (*m*/*z*) signals are reported as values in atomic mass units. Ligand **1a** (2,6-di-*tert*-butyl-3-methylphenol) and all reagents were obtained from commercial sources and used as received unless otherwise indicated.

2-*tert*-Butyl-4-methyl-6-(α,α-dimethylbenzyl)phenol (1b): A solution of triethylaluminum (1.3 mL, 1.16 g, 10 mmol) in *n*-heptane (15 mL) was added dropwise to 2-*tert*-butyl-4-methylphenol (16.4 g, 198 mmol). The reaction mixture was then heated to 60 °C before α-methylstyrene (13 mL, 11.8 g, 100 mmol) was added. The reaction mixture was stirred for 1.5 h at 60 °C and then cooled to room temperature. The organics were diluted with heptane/ethyl ether (70:30, 150 mL) and washed with 5% aqueous HCl (20 mL), distilled water (2 × 20 mL), 5% NaOH (20 mL) and then water (2 × 20 mL). The organic phase was then dried with $MgSO_4$ and filtered, and the solvents were removed under vacuum. Distillation of the oily residue under reduced pressure (4.10^{-2} mbar, 80 °C) and crystallization from *n*-pentane yielded **1b** (12.1 g, 42.7%) as white cubic crystals. MS (CI+): *m*/*z* = 282 [M]$^+$. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 1.30 [s, 9 H, $C(CH_3)_3$], 1.69 [s, 6 H, $C(CH_3)_2$], 2.37 (s, 3 H, CH_3), 4.83 (s, 1 H, OH), 7.07 and 7.22 (2 d, $^4J_{H,H}$ = 2 Hz, 2 H, CH from ArOH), 7.35 (m, 1 H, *p*-CHAr), 7.38 (m, 4 H, *o*- and *m*-CHAr) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 298 K): δ = 21.31 (s, C-CH_3), 29.9 [s, $C(CH_3)_3$], 30.1 [s, $C(CH_3)_2$], 34.9 [s, $C(CH_3)_3$], 42.2 [s, $C(CH_3)_2$], 115.8 (s, *p*-C from ArOH), 125–130 (s, 5 CH), 135.8 and 138.0 (s, *o*-C from ArOH), 148.6 (s, C-OH), 150.8 [s, CArOH-$C(CH_3)_2$-CAr] ppm. $C_{20}H_{26}O$ (282,42): calcd. C 85.06, H 9.28, O 5.67; found C 84.81, H 9.52, O 5.46.

2-*tert*-Butyl-4-methyl-6-(*N*-dimethylaminomethyl)phenol (1c): This compound was synthesized following the procedure described in the literature.[49] A solution of 2-*tert*-butyl-4-methylphenol (10.6 g, 64.6 mmol) in ethanol (200 mL) was heated at reflux overnight with paraformaldehyde (3.06 g, 102 mmol) and 40% aqueous dimethylamine (9.0 g, 78.3 mmol). The volatiles were then removed under reduced pressure. The viscous residue was purified by crystallization from cold ethanol, yielding **1c** (12.2 g, 85%) as white crystals. MS (CI+): *m*/*z* = 221 [M]$^+$. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 1.28 [s, 9 H, $C(CH_3)_3$], 2.12 (s, 3 H, CH_3), 2.18 [s, 6 H, $N(CH_3)_2$], 3.46 (s, 2 H, NCH_2Ph), 6.55 and 6.87 (2 s, 2 H, aromatic), 11 (br. s, 1 H, OH) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 298 K): δ = 20.8 (s, CH_3), 29.07 [s, $C(CH_3)_3$], 34.2 [s, $C(CH_3)_3$], 44.34 [s, $N(CH_3)_2$], 63.45 (s, NCH_2Ph), 122.5 (s, 1 C), 126.7 (s, CH), 127.1 (s, 1 C), 127.22 (s, CH), 136.3 (s, 1 C), 155 (s, C-OH) ppm. $C_{14}H_{23}NO$ (221,34): calcd. C 75.97, H 10.47, N 6.33, O 7.23; found C 75.79, H 10.63, N 6.08, O 7.48.

2-*tert*-Butyl-4-methyl-6-(*N*-benzylmethylaminomethyl)phenol (1d): This compound was synthesized following the procedure described for **1c**. A solution of 2-*tert*-butyl-4-methylphenol (4.5 g, 27.4 mmol) in toluene (100 mL) was heated at 80 °C for 6 h with paraformaldehyde (1.0 g, 33 mmol) and methylbenzylamine (3.5 mL, 27.1 mmol). After cooling to room temperature, water (100 mL) was poured into the reaction mixture. The organic layer was collected, and the aqueous phase was extracted with ethyl acetate (200 mL). The combined organic phase was dried with $MgSO_4$, and the volatiles were removed under reduced pressure. The viscous residue was purified by crystallization from cold methanol, yielding **1d** (6.14 g, 76%) as white crystals. MS (CI+): *m*/*z* = 298 [M]$^+$. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 1.42 [s, 9 H, $CC(CH_3)_3$], 2.20–2.24 (2 s, 2 × 3 H, CH_3 and N-CH_3), 3.54 (s, 2 H, NCH_2Ph), 3.70 (s, 2 H, NCH_2Ar), 6.71 and 7.00 (2 d, $^4J_{H,H}$ = 1.9 Hz, 2 H, CH from ArOH), 7.73 (m, 5 H, CH Ph), 11.0 (br. s, 1 H, OH) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 298 K): δ = 20.8 (s, CH_3), 29.7 [s, $C(CH_3)_3$], 34.8 [s, $CC(CH_3)_3$], 41.1 (s, NCH_3), 61.1 and 61.8 (s, 2 NCH_2), 126.94, 127.6, 127.8, 128.8 and 129.8 (s, CH), 122.5, 127.4, 136.5, 137.7 (s, 1 C), 154.7 (s, C-OH) ppm. $C_{20}H_{27}NO$ (297.43): calcd. C 80.76, H 9.15, N 4.71; found C 80.3, H 9.14, N 4.89.

2-*tert*-Butyl-4-methyl-6-(*N*-dibenzylaminomethyl)phenol (1e): The procedure described above for **1c** was used, starting from 2-*tert*-butyl-4-methylphenol (4.43 g, 27 mmol) in toluene (170 mL), paraformaldehyde (1.0 g, 33 mmol) and dibenzylamine (5.4 mL, 27.9 mmol). Ligand **1e** (5.57 g, 57%) was obtained as white crystals. MS (CI+): *m*/*z* = 373 [M + 1]$^+$. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 1.43 [s, 9 H, $CC(CH_3)_3$], 2.24 (s, 3 H, CH_3), 2.62 (m, 4 H, CH_2), 3.59 (s, 4 H, NCH_2Ph), 3.70 (s, 2 H, NCH_2Ar), 6.70 and 6.99 (2 d, $^4J_{H,H}$ = 1.9 Hz, 2 H, H from Ar), 7.73 (m, 10 H, H benzyl), 10.6 (s, 1 H, OH) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 298 K): δ = 20.8 (s, CH_3), 29.7 [s, $CC(CH_3)_3$], 34.8 [s, $CC(CH_3)_3$], 57.8 and 57.9 (s, 3 NCH_2), 127.0, 127.86, 127.99, 128.86 and 130.02 (s, CH), 122.6, 127.6, 136.5 and 137.7 (s, 1 C), 154.2 (s, C-OH) ppm. $C_{26}H_{31}NO$ (373,53): calcd. C 83.60, H 8.37, N 3.75; found C 82.98, H 8.38, N 3.97.

2-*tert*-Butyl-4-methyl-6-(methoxymethyl)phenol (1f): Gaseous HCl (Air Liquide, 99^{+}%) was bubbled for 5 min through a cold (0 °C) solution of 2-*tert*-butyl-4-methylphenol (15.3 g, 93.2 mmol) in toluene (60 mL). Paraformaldehyde powder (3.63 g, 121 mmol) was then added in small portions. Bubbling of gaseous HCl was maintained for 1 h at room temperature. The solution was further stirred for 1 h while a second phase appeared in the flask. The organic phase was washed three times with cold water (10 mL) and then dried with K_2CO_3. After removing the volatiles under vacuum, the chlorinated intermediate was obtained (18.83 g, 92.4%). Without further purification, it was treated in methanol (30 mL) with an excess amount of sodium methoxide in methanol. The temperature of the mixture was brought to 25 °C and then reflux was maintained for 3 h. After addition of distilled water (100 mL), the reaction mixture was extracted with dichloromethane (3 × 50 mL). The organic layers were collected, dried with K_2CO_3, filtered and concentrated under vacuum to leave a yellow oily residue. Purification of this residue by distillation under vacuum (4×10^{-2} mbar, 60 °C) yielded **1f** (10.21 g, 52.4%) as a colourless viscous oil. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 1.45 [s, 9 H, $CC(CH_3)_3$], 2.29 (s, 3 H, CH_3), 3.47 (s, 3 H, O-CH_3), 4.6 (s, 2 H, CH_2OMe), 6.76 and 6.09 (2 d, $^4J_{H,H}$ = 2 Hz, 2 H, Ar-H), 7.65 (s, 1 H, OH) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 298 K): δ = 20.8 (s, CH_3), 29.8 [s, $CC(CH_3)_3$], 34.9 [s, $CC(CH_3)_3$], 58.3 (s, OCH_3), 75.0 (s, OCH_2Ar), 122.7 (s, CH, Ph), 127.0 (s, CH, Ph), 127.9 (s, CH, Ph), 128.4–136.9 (s, Ph-C), 153.4 (s, C-OH, Ph) ppm. $C_{13}H_{20}O_2$ (208,30): calcd. C 74.96, H 9.68, O 15.36; found C 74.87, H 9.42, O 15.69.

[Ti(2,6-di-*tert*-Butyl-4-methylphenoxy)(O*i*Pr)$_3$] (2a): To a cold solution (–30 °C) of 2,6-bis(*tert*-butyl)-4-methylphenol (1.10 g, 5.0 mmol) in Et_2O (15 mL) was added [Ti(O*i*Pr)$_4$] (1.5 mL, 1.45 g, 5.0 mmol) in Et_2O (20 mL). The mixture turned yellow and was then warmed to 20 °C and stirred overnight. The solvent was then removed under vacuum, leading to an oily yellow residue (2.26 g, 99% crude yield). This residue was then crystallized from cold pentane (5 mL, –78 °C), yielding **2a** (1.77 g, 78%) as an off-white solid. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 1.28 [d, 18 H, $OCH(CH_3)_2$], 1.49 [s, 9 H, $C(CH_3)_3$], 2.29 (s, 3 H, CH_3), 4.67 [m, 3 H, $OCH(CH_3)_2$], 7.0 (s, 2 H, CH) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 298 K): δ = 21.3 (s, CH_3), 26.3 [s, $OCH(CH_3)_2$], 30.7 [s, $C(CH_3)_3$], 34.8 [s, $C(CH_3)_3$], 78.2 [s, $OCH(CH_3)_2$], 125.3, 127.6, 138.8 and 162.2 (s, CO) ppm for the aromatics.

[Ti{2-*tert*-Butyl-4-methyl-6-(α,α-dimethylbenzyl)phenoxy}(O*i*Pr)$_3$] (2b): A solution of *n*BuLi (1.7 M in pentane, 7 mL, 12 mmol) was added dropwise to a solution of **1b** (2.9 g, 10 mmol) in thf (40 mL). After the mixture was stirred overnight, a white precipitate was formed. The volatiles were then removed under reduced pressure, and the residue was washed twice with pentane (20 mL). After drying under vacuum, the phenoxide derived from **1b** was obtained as a white solid (3.43 g, 92%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 1.03 [s, 9 H, $C(CH_3)_3$], 1.71 [s, 6 H, $CC(CH_3)_2C$], 1.85 [m, 4 H, $O(CH_2CH_2)_2$, thf], 2.28 (s, 3 H, CH_3), 3.71 [m, 4 H, $O(CH_2CH_2)_2$, thf], 6.92–7.1 (2 d, $^3J_{H,H}$ = 2.3 Hz, 2 H, 2CH ArO), 7.2 (tt, $^3J_{H,H}$ = 7.18 Hz, $^4J_{H,H}$ = 1.6 Hz, 1 H, Ph, *p*-H), 7.33 (m, 4 H, Ph, *o*-H and *m*-H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ = 20.6 (CH_3), 25.4 [$O(CH_2CH_2)_2$, thf], 31.0 [s, $C(CH_3)_3$ and $C(CH_3)_2$], 33.0 [$C(CH_3)_3$], 42.0 [$C(CH_3)_2$], 67.5 [$O(CH_2CH_2)_2$, thf], 125.1 and 125.4 (2 s, CH ArO), 126.4 (*p*-CH, Ph), 124.3 and 129.2 (*m*- and *o*-CH, Ph), 120.6, 136.3, 137.8, 153.4, 159.6 (5 C, Ph) ppm. To a suspension of the metallated form of **1b** (3.43 g, 9.51 mmol) in thf (25 mL) was added [TiCl(O*i*Pr)$_3$] (2.4 g, 9.2 mmol) in thf (15 mL). The mixture was stirred overnight and the volatiles were removed under vacuum. The residue was crystallized from *n*-pentane at 25 °C to yield **2b** (3.63 g, 86.8%) as white crystals. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 1.1 [d, 18 H, $OCH(CH_3)_2$], 1.31 [s, 9 H, $C(CH_3)_3$], 1.61 [s, 6 H, $CC(CH_3)_2C$], 2.2 (s, 3 H, CH_3), 4.35 [m, 3 H, $OCH(CH_3)_2$], 6.9 (2 d, 2 H, 2CH ArO), 7.0 (m, 1 H, *p*-H, Ph), 7.1 (m, 4 H, *m*- and *o*-H, Ph) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 298 K): δ = 20.2 (s, CH_3), 25.3 [s, $OCH(CH_3)_2$], 29.8 and 30.4 [s, $C(CH_3)_3$, $CC(CH_3)_2C$], 33.8 [s, $C(CH_3)_3$], 42.0 [s, $C(CH_3)_2$], 77.2 [s, $OCH(CH_3)_2$], 124.2, 124.8, 125.3, 125.4, 126.5, 126.9, 136.9, 138.2, 149.7 (10 C, Ph), 160.7 (s, CO). $C_{29}H_{46}O_4Ti$ (506.54): calcd. C 68.76, H 9.15, Ti 9.45; found C 68.93, H 9.42, Ti 9.69.

[Ti{2-*tert*-Butyl-4-methyl-6-(*N*,*N*-dimethylaminomethyl)phenoxy}(O*i*Pr)$_3$] (2c)

Path A: To a cold solution of [Ti(O*i*Pr)$_4$] (0.73 mL, 0.71 g, 2.5 mmol) in Et_2O (5 mL) was added a solution of **1c** (0.55 g, 2.5 mmol) in Et_2O (10 mL). The reaction mixture immediately turned yellow. After warming the solution to room temperature, the reaction mixture was vigorously stirred overnight. The volatiles were then removed under vacuum, yielding **2c** (1.02 g, 92%) as a yellow oil. Attempts to obtain a crystalline compound were unsuccessful. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 1.27 [d, 18 H, $OCH(CH_3)_2$], 1.44 [s, 9 H, $C(CH_3)_3$], 2.24 (s, 3 H, CH_3), 2.35 [s, 6 H, $N(CH_3)_2$], 3.7 (br. s, 2 H, $ArCH_2N$), 4.9 [m, 3 H, $OCH(CH_3)_2$], 6.67–6.95 (2 d, $^4J_{H,H}$ = 2 Hz, CH) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 298 K): δ = 20.3 (s, CH_3), 26.3 [s, $OCH(CH_3)_2$], 29.2 [s, $C(CH_3)_3$], 34.4 [s, $C(CH_3)_3$], 46.8 [s, $N(CH_3)_2$], 62.5 [s, $ArCH_2N(CH_3)_2$], 77.0 [s, $OCH(CH_3)_2$], 124.9, 126.2, 126.3, 127.6, 135.9 (5 C), 158.3 (s, CO) ppm. $C_{23}H_{43}N_1O_4Ti$ (445.46): calcd. C 62.01, H 9.73, N 3.14, Ti 10.75; found C 61.87, H 9.66, N 3.30, Ti 11.30.

Path B: This complex was synthesized following the procedure described for **2b**. To a solution of **1c** (1.1 g, 5.0 mmol) in thf (40 mL) was added dropwise *n*BuLi (1.7 M in pentane, 4 mL, 6.8 mmol). The mixture was stirred for 12 h at room temperature. The volatiles were then removed under reduced pressure, yielding a yellow oil that was used without further purification. To this crude adduct of ArOLi·thf was added [TiCl(O*i*Pr)$_3$] (1.3 g, 5.0 mmol) in thf (10 mL). The resulting yellow slurry was stirred overnight at room temperature. After the volatiles were removed under reduced pressure, the yellow residue was extracted with pentane (30 mL) and dried under vacuum to yield the desired compound as a yellow viscous oil (1.9 g, 85% yield). Characterization data are the same as for **2c** isolated from path A.

[Ti{2-*tert*-Butyl-4-methyl-6-(*N*,*N*-benzylmethylaminomethyl)phenoxy}(O*i*Pr)$_3$] (2d): To a cold solution of [Ti(O*i*Pr)$_4$] (1.0 mL, 3.4 mmol) in Et_2O (5 mL, –30 °C) was added ligand **1d** (0.51 g, 1.72 mmol) in Et_2O (10 mL). The mixture instantly turned yellow and was then warmed to 20 °C and stirred for 1 h. The volatiles were removed under vacuum at 40 °C. The resulting yellow oil was a mixture of desired compound **2d** with some residual phenol as well as unreacted [Ti(O*i*Pr)$_4$]. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 1.30 [d, 18 H, $OCH(CH_3)_2$], 1.45 [s, 9 H, $C(CH_3)_3$], 2.22 (s, 3 H, CH_3), 2.25 (s, 3 H, NCH_3), 3.72 (s, 2 H, $ArCH_2N$), 4.12 (s, 2 H, NCH_2Ph), 4.93 [m, 3 H, $OCH(CH_3)_2$], 6.57–6.97 (2 d, $^4J_{H,H}$ = 2 Hz, CH), 7.20–7.34 (2 m, 5 H, CH_2Ph) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 298 K): δ = 20.3 (s, CH_3), 26.3 [s, $OCH(CH_3)_2$], 29.2 [s, $C(CH_3)_3$], 34.4 [s, $C(CH_3)_3$], 41.4 [s, $N(CH_3)$], 56.9 (s, NCH_2Ph), 58.4 [s, $ArCH_2N(CH_3)$benzyl], 77.2 [s, $OCH(CH_3)_2$], 124.4, 126.2, 126.4, 127.3, 127.6, 128.1, 132.0, 133.5 and 136.1 (C, Ph), 158.6 (s, CO) ppm.

[Ti{2-*tert*-Butyl-4-methyl-6-(*N*,*N*-dibenzylaminomethyl)phenoxy}(O*i*Pr)$_3$] (2e): To a cold solution of [Ti(O*i*Pr)$_4$] (1.0 mL,

3.4 mmol) in Et_2O (5 mL, –30 °C) was added ligand **1e** (0.51 g, 1.72 mmol) in Et_2O (10 mL). The mixture instantly turned yellow and was then warmed to 20 °C and stirred for 1 h. The volatiles were removed under vacuum at 40 °C. The resulting yellow oil was a mixture of desired compound **2e** with some residual phenol as well as unreacted [Ti(O*i*Pr)$_4$].

[(2-*tert*-Butyl-4-methyl-6-methoxymethylphenoxy)TiCl(O*i*Pr)(μ$_2$-O*i*Pr)$_2$TiCl(O*i*Pr)$_2$] (3): To a stirred solution of ligand **1f** (1.34 g, 6.43 mmol) in thf (30 mL) was added solid Na (0.50 g, 21.7 mmol). The reaction mixture was heated at reflux for 2 h. Trimethylsilyl chloride (2.5 mL, 2.17 g, 20 mmol) was then poured into this solution, and the mixture was heated at reflux for 2 d. After cooling to room temperature, the volatiles were removed, and the residue was extracted with pentane (10 mL) and dichloromethane (10 mL). The organics were collected and concentrated, and the silyl ether derived from **1f** was obtained as a yellow viscous oil (1.70 g, 94.2%). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 0.37 [s, 9 H, Si(CH$_3$)$_3$], 1.4 [s, 9 H, C(CH$_3$)$_3$], 2.29 (s, 3 H, CH$_3$), 3.4 (s, 3 H, OCH$_3$), 4.4 (s, 2 H, ArCH$_2$OCH$_3$), 7.03–7.1 (2 d, $^4J_{H,H}$ = 2.3 Hz, CH) ppm. The silyl ether derivative was then added to a thf solution (20 mL) of [TiCl(O*i*Pr)$_3$] (1.57 g, 6.0 mmol). The solution instantly turned red. It was then stirred overnight at room temperature, the solvent was removed under vacuum, leaving a red oil from which a crystalline compound was obtained through crystallization from *n*-pentane at –18 °C (17% isolated yield). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 1.3–1.5 [m, 40 H, C(CH$_3$)$_3$ and 5 OCH(CH$_3$)$_2$], 2.30 (s, 3 H, CH$_3$), 3.65 (s, 3 H, OCH$_3$), 4.0 and 5.7 (2 d, $^2J_{H,H}$ = 12.7 Hz, ArCH$_2$OCH$_3$, 0.63H each), 4.78, 5.09 and 5.25 [3 m, ratios 1:2:2, OCH(CH$_3$)$_2$], 6.83 and 7.14 (2 d, CH) ppm. $C_{28}H_{54}Cl_2O_7Ti_2$ (669.36): calcd. C 50.24, H 8.13; found C 50.44, H 8.09.

X-ray Data Collection, Structure Solution and Refinement for Compounds 2b and 3: Suitable crystals for X-ray analysis were obtained as described above. Diffraction data were collected at 173(2) K with a Kappa CCD diffractometer by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Data were collected by using ϕ scans, the structures were solved by direct methods by using the SHELX97 software,[60,61] and the refinement was by full-matrix least-squares on F^2. No absorption correction was used. All non-hydrogen atoms were refined anisotropically, with H atoms introduced as fixed contributors (d_{C-H} = 0.95 Å, U_{11} = 0.04). Crystallographic and experimental details for the structures are summarized in Table 6. CCDC-727372 (for **2b**) and -727373 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Oligomerization Studies: All catalytic reactions were carried out in a magnetically stirred (≈1000 rpm) 120-mL stainless steel autoclave. The evacuated reactor was charged with 1 atm ethylene and heated to the reaction temperature. The cocatalyst was introduced before adding the catalyst precursor. The reactor was then sealed and fed with ethylene up to the desired pressure. During the catalysis, the pressure was maintained constant through a continuous feed from a bottle placed on a balance used to monitor the ethylene uptake. At the end of the test, the catalyst was quenched in situ by addition of water or methanol and the reactor rapidly cooled down to 25 °C. The gaseous effluents were then collected in a 15 L polyethylene bottle filled with water. The liquid effluents were collected, washed with H_2SO_4 (10 vol.-%) and weighted. The polymer formed was collected, washed with methanol, dried under vacuum and weighed. Aliquots of gaseous and liquid effluents were then analyzed by gas chromatography. Catalytic runs were performed for 1 h at 60 °C, 20 bar ethylene in 5 mL heptane (unless otherwise stated).

Table 6. Crystallographic data and structure refinement details for **2b** and **3**.

	2b	**3**
Formula	$C_{29}H_{46}O_4Ti$	$C_{28}H_{51}Cl_2O_7Ti_2$
Formula weight	506.56	666.39
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	Cc
a [Å]	9.8570(4)	13.7950(3)
b [Å]	10.6790(5)	17.2200(5)
c [Å]	14.5330(7)	15.6480(4)
α [°]	86.633(3)	90
β [°]	86.380(3)	108.27
γ [°]	73.882(2)	90
V [Å^3]	1465.37(12)	3529.88(16)
Z	2	4
$\rho_{calcd.}$ [g cm^{-3}]	1.148	1.254
μ (Mo-K_α) [mm^{-1}]	0.321	0.641
F(000)	548	1412
Temperature [K]	173(2)	173(2)
$\theta_{min-max}$	2.77–30.06	2.94–30.04
Dataset [h, k, l]	–13/12 –15/15 –20/20	19/19 –19/24 –22/22
Total, unique data, R(int)	13051, 8544, 0.0271	8607, 8605, 0.0185
Observed data	5994	6524
N reflections, N parameters	8544, 307	8605, 352
R_1, R(all)	0.0586, 0.0917	0.0540, 0.0794
wR_2, wR(all)	0.1492, 0.1679	0.1269, 0.1416
GOF	1.070	1.011
Max. and Av. shift/error	0.001, 0.000	0.016, 0.001
Min, max. resd dens. [e Å^{-3}]	–0.946, 1.008	–0.352,0.477

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