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PAPER

New bis(aryloxy)–Ti(IV) complexes and their use for the selective dimerization of ethylene to 1-butene†‡

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New titanium complexes of general formula $[(ArO)_nTi(O\textit{i}\text{-}Pr)_{(4-n)}]$ were synthesized and used as pre-catalysts for the selective dimerization of ethylene to 1-butene. The complexes were prepared in cyclohexane using $[Ti(O\textit{i}\text{-}Pr)_4]$ and one or two equivalents of the corresponding phenols (ArOH) at room temperature. In this work, both monodentate and chelating phenols were evaluated. For alkyl-substituted phenols, it was demonstrated that large steric hindrance at both *ortho* and *ortho′* positions selectively yielded the mono-substituted complexes $[(ArO)Ti(O\textit{i}\text{-}Pr)_3]$. Substitution at only one of the *ortho* positions allowed both the mono- and the di-substituted Ti complexes to be isolated. When a heteroatom was introduced on the phenol backbone, di-substitution systematically occurred except with phenols presenting a hemilabile $–CH_2NR_2$ group at the *ortho* position. Upon activation with 3 equiv. of $AlEt_3$ at 20 bar and 60 °C, all the complexes selectively dimerized ethylene to 1-butene (>86% of butenes among which 99% of 1-butene). An increase of the steric bulk at the *ortho* position of the ligand or the introduction of a functional group led to decreased activity compared to $[Ti(O\textit{i}\text{-}Pr)_4]$.

Introduction

The selective catalytic oligomerization of ethylene for the production of short-chain linear α-olefins (1-butene, 1-hexene and 1-octene) is a subject of paramount interest from both industrial and academic viewpoints, these olefins being used as comonomers for the manufacture of HDPE and LLDPE.[1] Homogeneous catalyst precursors comprising a chromium centre and chelating bisphosphine ligands belong to the most efficient systems for the selective tri- and tetramerization of ethylene.[2] Recent work has also demonstrated the potential of Ti-based catalysts. When associated with a cyclopentadienyl derivative (η^5-C_5H_4–CMe_2Ph)[3] or a tridentate phenoxy-imine type ligand,[4] Ti-catalysts exhibit very selective production of 1-hexene. For the selective dimerization of ethylene to 1-butene, nickel complexes with bidentate {*N*,*N*},[5] {*N*,*P*},[6] or tridentate {*N*,*N*,*N*}[7] ligands can be used but owing to the higher quality of the 1-butene produced, titanium catalysts are preferred.[8]

Possible ligands for new catalysts in this area include aryloxy ligands.[9] They have proved to be good alternatives to the Cp ligand especially for olefin polymerization with for example the development of the ancillary phenoxy-imine systems which have raised a great deal of interest. Although the potential of their complexes for the polymerization and co-polymerization of ethylene is well known,[10] examples in the field of selective oligomerization remain scarce.[9,11] Furthermore, the use of aryloxy ligands in combination with alkoxy co-ligands is rare.[12] The strongly basic alkoxy moiety is often found bridging several metal centres, which results in multinuclear cage-like or cluster frameworks, which are likely to fragment into less well-defined species during catalysis.[12,13] In this contribution, we report on the synthesis of new bis(aryloxy)–Ti(IV) complexes and their use for the selective dimerization of ethylene to 1-butene. The influence of the *ortho* substituents of the phenols on the degree of substitution of the isopropoxy ligands from $[Ti(O\textit{i}\text{-}Pr)_4]$ was investigated. Purely steric effects will be revealed by the study of *ortho* alkyl-functionalized phenols whereas electronic effects will be examined by using heteroatom-based *ortho* functionalized phenols. These effects will be related to catalytic activities in the selective dimerization of ethylene to 1-butene.

Results and discussion

A set of phenols was selected to cover a diversity of steric situations, ranging from the simple phenol **1a** to the bulky 2,6-di-*tert*-butyl-4-methylphenol **1e** (Scheme 1).

The influence of additional donor groups with various coordinating strengths was also studied through phenols **1g–1o**.

Phenols **1a–1e**, **1g**, **1h** and **1j** are commercially available. Phenols **1f**,[9] **1i**,[9] **1k**,[14] **1l**,[14] **1m**,[14] **1n**[15,16] and **1o**[17,18] were

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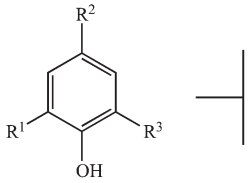
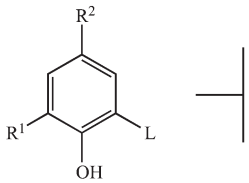
†Dedicated to Professor David Cole-Hamilton on the occasion of his retirement and for his outstanding contribution to transition metal catalysis.

‡Electronic supplementary information (ESI) available: Selected bond distances and angles for the structurally characterized complexes. CCDC 871140–871144. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30991b



Alkyl-substituted phenols

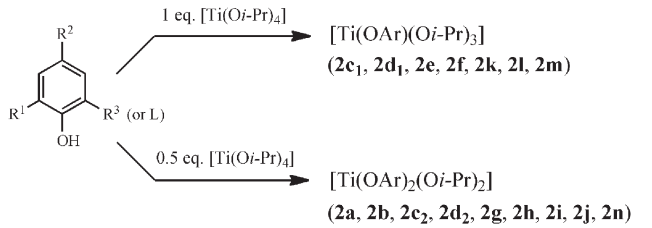
R = H, R^2 = H, R^3 = H (**1a**)
R^1 = Me, R^2 = Me, R^3 = H (**1b**)
R^1 = *t*-Bu, R^2 = Me, R^3 = H (**1c**)
R^1 = *t*-Bu, R^2 = *t*-Bu, R^3 = H (**1d**)
R^1 = *t*-Bu, R^2 = Me, R^3 = *t*-Bu (**1e**)
R^1 = *t*-Bu, R^2 = CMe_2Ph, R^3 = H (**1f**)



Phenols with donor substituents

R^1 = H, R^2 = H, L = OMe (**1g**)
R^1 = H, R^2 = Me, L = OMe (**1h**)
R^1 = *t*-Bu, R^2 = Me, L = CH_2OMe (**1i**)
R^1 = H, R^2 = H, L = N-heterocycle part of the 8-hydroxyquinoline (**1j**)
R^1 = Me, R^2 = Me, L = CH_2NMe_2 (**1k**)
R^1 = *t*-Bu, R^2 = Me, L = CH_2NMe_2 (**1l**)
R^1 = *t*-Bu, R^2 = Me, L = $CH_2N(C_4H_8)$ (**1m**)
R^1 = *t*-Bu, R^2 = *t*-Bu, L = PPh_2 (**1n**)
R^1 = *t*-Bu, R^2 = *t*-Bu, L = CH_2PPh_2 (**1o**)

Scheme 1 Set of phenols used in this work.



Scheme 2 Mono and bis-aryloxy-complexes obtained. The letters used in the numbering of the complexes refer to the ligand, as defined in Scheme 1. When appropriate, the subscript indicates the number of OAr substituents.

synthesized using protocols adapted from the literature. Complexes of general formula $[(ArO)_nTi(O\textit{i}\text{-}Pr)_{(4-n)}]$ (n = 1 or 2) were obtained in cyclohexane by direct alcohol exchange between $[Ti(O\textit{i}\text{-}Pr)_4]$ and the corresponding phenols.[13,19,20] Then the solvent and isopropanol were removed under reduced pressure, affording the titanium aryloxy complexes $[(ArO)_nTi(O\textit{i}\text{-}Pr)_{(4-n)}]$ (n = 1 or 2) in almost quantitative yields. The influence of the steric bulk of the phenol on the degree of substitution at the metal is illustrated by a comparison of the reaction products obtained with phenols **1a–1f**. When R^1 = R^2 = H or Me and R^3 = H (**1a**, **1b**), di-substitution occurred whereas when a bulky group was introduced at both *ortho* positions of the pro-ligand, as in phenol **1e**, only the mono-aryloxy complex was obtained (Scheme 2).

When two equivalents of phenol **1e** were engaged in the reaction, the ^{1}H NMR spectrum of the evaporated reaction mixture clearly showed that one equivalent of phenol remained unreacted. The other signals were consistent with the formation of the mono-aryloxy complex **2e**. Interestingly, when two equivalents of phenol **1d** having a *tert*-butyl group at only one *ortho* position were used, the ^{1}H NMR spectrum was consistent with the presence of the di-substituted complex $\mathbf{2d_2}$ as reported by Umare *et al.*[21] The ^{13}C NMR spectrum presented a doubling of the signals in the aromatic region. The same feature was observed when phenol **1c** was used.

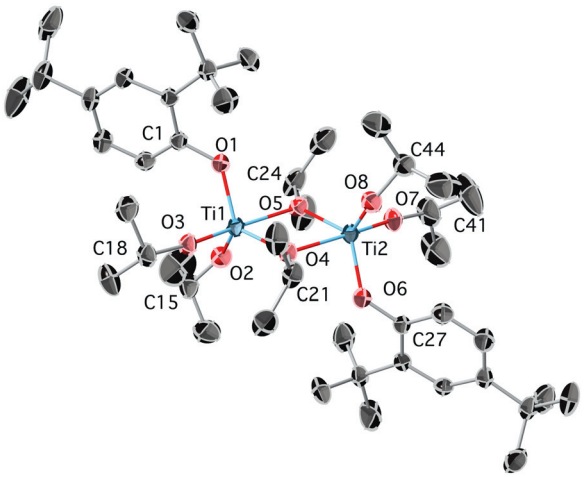


Fig. 1 ORTEP of the solid state structure of $\mathbf{2d_1}$. H atoms are omitted for clarity. Ellipsoids include 40% of the electron density. Selected bond distances [Å] and angles [°] are given for Ti1 only: Ti1–O1 1.874(2), Ti1–O2 1.785(2), Ti1–O3 1.7700(15), Ti1–O4 1.9423(15), Ti1–O5 2.117(2), O1–C1 1.361(3), O1–Ti1–O2 112.98(8), O1–Ti1–O3 96.87(8), O1–Ti1–O4 123.28(7), O1–Ti1–O5 84.98(7), O2–Ti1–O3 100.14(8), O2–Ti1–O4 117.45(8), O2–Ti1–O5 88.84(7), O3–Ti1–O4 98.24(7), O3–Ti1–O5 169.19(7), O4–Ti1–O5 72.08(6), Ti1–O4–Ti2 107.68(7), Ti2–O5–Ti1 107.91(7). For more data see ESI.‡

When only one equivalent of phenol **1d** was reacted with $[Ti(O\textit{i}\text{-}Pr)_4]$, the ^{1}H and ^{13}C NMR spectra showed different signals from those of the complex formed when two equivalents were used. The ^{13}C NMR spectrum presented only one set of signals and the ^{1}H NMR data are consistent with a mono-substitution (complex $\mathbf{2d_1}$). Yellow crystals grown from a saturated pentane solution were analyzed by X-ray diffraction (Table 1), which revealed that in the solid state, the complex $\mathbf{2d_1}$ is dinuclear, with two isopropoxy ligands bridging the two titanium centres (Fig. 1). The fact that the ^{1}H NMR spectrum revealed only one set of signals for the isopropoxy ligands may indicate a fast exchange in solution between the terminal and the bridging ligands. This structure is in agreement with that previously postulated by Mishra and Singh on the basis of NMR and FAB mass measurements.[22] On the basis of ^{1}H NMR, phenol **1c** is likely to lead to a similar mono-aryloxy structure (complex $\mathbf{2c_1}$). The dinuclear structure of $\mathbf{2d_1}$ shown in Fig. 1 is almost centrosymmetrical, so that the coordination geometry and metrical data around the two titanium centres are almost identical. The metal centres are separated by 3.2785(6) Å. The coordination geometry around the titanium centres can be viewed as distorted trigonal bipyramidal (considering O3 and O5 and O4 and O7 as the two apices of the bipyramid for Ti1 and Ti2, respectively). The bending of the aryloxy ligand suggests only little participation of the oxygen lone pairs in the titanium–oxygen bonding.[13] Consistently, the Ti–OAr bond length is slightly longer than in the mononuclear complex [(2-*tert*-butyl-4-methyl-6-(α,α-dimethylbenzyl)phenoxy)$Ti(O\textit{i}\text{-}Pr)_3$] reported previously.[9]

The dinuclear structure found for $\mathbf{2d_1}$ is sterically allowed because only one *ortho* position of the aryl group is substituted by a bulky *tert*-butyl group and the hydrogen atom at the other *ortho* position nicely points between the two terminal isopropoxy ligands. In contrast, substitution at the *ortho* and *ortho'*

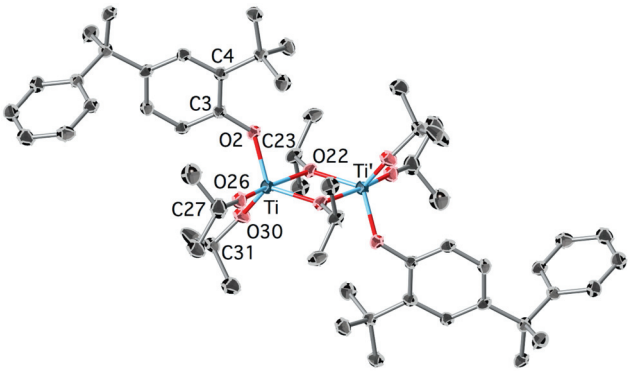


Fig. 2 ORTEP of the centrosymmetric structure of **2f** in the solid state. H atoms are omitted for clarity. Ellipsoids include 50% of the electron density. Selected bond distances [Å] and angles [°]: Ti–O2 1.8537(15), Ti–O22 1.9385(15), Ti–O26 1.777(2), Ti–O30 1.787(2), O22–Ti–O2 84.98(6), O22–Ti–O26 170.10(7), O2–Ti–O26 97.79(7), O22–Ti–O30 87.49(7), O2–Ti–O30 112.51(7), O26–Ti–O30 100.11(8), Ti–O2–C3 133.8(1). For more data see ESI.‡

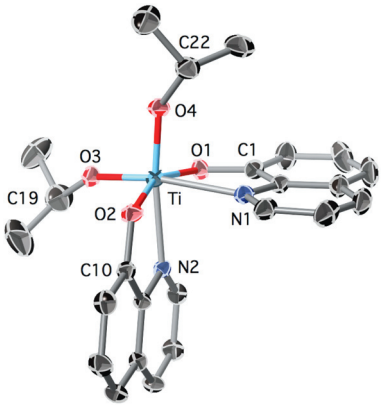


Fig. 3 ORTEP of the solid state structure of **2j**. H atoms are omitted for clarity. Ellipsoids include 40% of the electron density. Selected bond distances [Å] and angles [°]: Ti–O1 1.962(1), Ti–O2 1.959(1), Ti–O3 1.797(1), Ti–O4 1.795(1), Ti–N1 2.2514(15), O1–Ti–O2 155.21(5), O1–Ti–O3 94.37(6), O1–Ti–O4 100.88(6), O2–Ti–O3 101.62(6), O2–Ti–O4 94.03(6), O3–Ti–O4 102.56(6), O1–Ti–N1 75.93(5), O2–Ti–N1 84.56(5), O3–Ti–N1 165.77(6), O4–Ti–N1 89.65(6), N1–Ti–N2 79.43(5). For more data see ESI.‡

positions by bulky groups, as in **2e**, results in steric repulsion with the isopropoxy groups and thus in the formation of the mono-aryloxy titanium complex. Despite numerous attempts, no crystals were obtained in the case of the di-substitution by the phenol **1d** to obtain complex $\mathbf{2d_2}$. It has been suggested by Mishra and Singh that this di-substituted complex may also have a dinuclear structure with isopropoxy ligands bridging the two titanium centres, as observed in the case of $\mathbf{2d_1}$.[22] In view of its ^{13}C NMR spectrum, it is also conceivable that the di-substituted complex $\mathbf{2d_2}$ may be dinuclear but with the two bridging ligands being the aryloxy instead of the isopropoxy ligands. The duplication of the signals in the ^{13}C NMR spectrum could then be explained by a differentiation between the terminal and bridging aryloxy owing to slow or no exchange between them on the NMR time-scale. When one equivalent of phenol **1f** was reacted with [Ti(O*i*-Pr)$_4$], complex **2f** was obtained as a yellow solid. Its ^1H and ^{13}C NMR data are consistent with a mono-aryloxy derivative. Single crystals could be grown from a saturated pentane solution at −18 °C (Fig. 2) and the crystal structure analysis revealed a dinuclear structure very similar to that of complex $\mathbf{2d_1}$. In this centrosymmetrical structure, the titanium centres are separated by 3.2664(7) Å. The distances and angles in this molecule are similar to those in complex $\mathbf{2d_1}$.

The alcohol exchange reaction from [Ti(O*i*-Pr)$_4$] was then carried out with phenols **1g**, **1h**, **1j** and **1n**. According to the NMR spectra, the presence of a methoxy group directly linked to the *ortho* position of the phenol in **1g** and **1h** resulted in the formation of the di-substituted complexes **2g** and **2h**, respectively.

When the 8-hydroxyquinoline **1j** was used, yellow crystals of complex **2j** were isolated (Fig. 3). An X-ray diffraction analysis of **2j** confirmed the di-substitution and revealed a distorted octahedral geometry with the phenolic oxygen donor atoms *trans* to each other, the isopropoxy ligands *cis* to each other and the nitrogen atoms also *cis* to each other (Fig. 3). This result is in agreement with the structure reported by Zeng *et al.*[23]

Surprisingly, the use of the bulkier diphenylphosphino *ortho*-functionalized phenol **1n** also led to di-substitution, as shown by the ^1H NMR data and established by an X-ray diffraction study

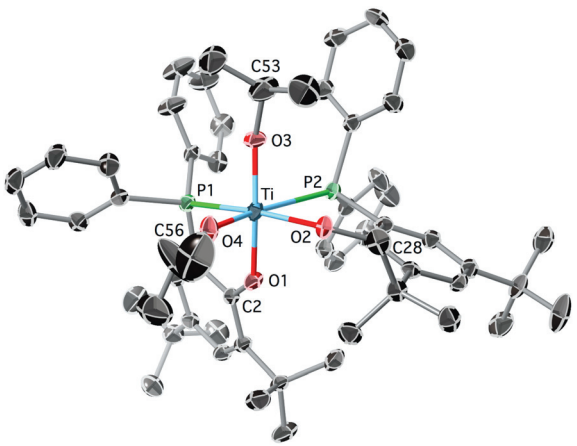


Fig. 4 ORTEP of the solid state structure of **2n**. H atoms are omitted for clarity. Ellipsoids include 40% of the electron density. Selected bond distances [Å] and angles [°]: Ti–O1 1.983(3), Ti–O2 1.874(3), Ti–O3 1.800(3), Ti–O4 1.777(3), Ti–P1 2.5967(15), Ti–P2 2.8764(15), O4–Ti–O3 100.50(17), O4–Ti–O2 103.50(15), O3–Ti–O2 100.37(15), O4–Ti–O1 96.30(16), O3–Ti–O1 157.02(16), O2–Ti–O1 90.75(14), O4–Ti–P1 97.68(12), O3–Ti–P1 88.49(12), O2–Ti–P1 155.02(11), O1–Ti–P1 73.74(10), O4–Ti–P2 174.26(12), O3–Ti–P2 82.74(12), O2–Ti–P2 71.13(10), O1–Ti–P2 81.94(11), P1–Ti–P2 87.10(5). For more data see ESI.‡

of complex **2n** (Fig. 4). The metal coordination geometry is distorted octahedral, with the phosphorus atoms *cis* to each other, likewise for the isopropoxy and the aryloxy oxygen atoms. This ligand arrangement around the titanium centre was also found in the complex [(2-diphenylphosphinophenoxy)$_2$TiCl$_2$] which has similar Ti–P and Ti–OAr bond lengths.[24] The difference of 0.36 Å between the covalent radii of phosphorus and nitrogen is almost equal to the difference between the shortest Ti–P bond length and the Ti–N bonds in complex **2j** (Fig. 3). However, the Ti–P2 length is 0.28 Å longer than Ti–P1, where P2 is *trans* to

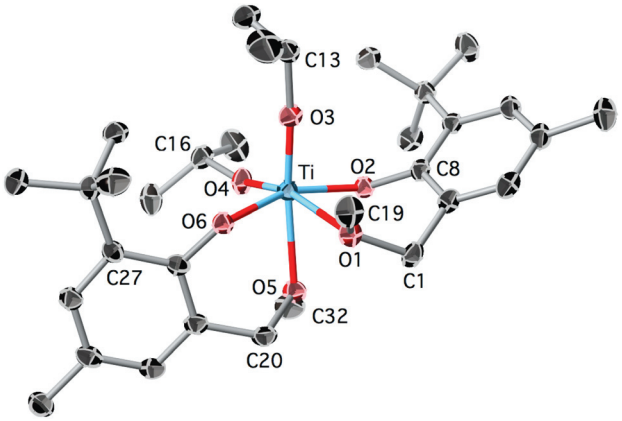


Fig. 5 ORTEP of the solid state structure of **2i**. H atoms are omitted for clarity. Ellipsoids include 40% of the electron density. There are two independent, but very similar molecules in the unit cell and data are given below for one of them. Selected bond distances [Å] and angles [°]: Ti2–O1 2.2321(15), Ti2–O2 1.9366(14), Ti2–O3 1.7627(14), Ti2–O4 1.7748(15), Ti2–O5 2.2689(14), Ti2–O6 1.9403(13); O1–Ti2–O2 80.84(6), O1–Ti2–O3 93.00(7), O1–Ti2–O4 162.29(6), O1–Ti2–O5 74.79(6), O1–Ti2–O6 81.40(6), O2–Ti2–O3 98.23(6), O2–Ti2–O4 95.72(6), O2–Ti2–O5 82.14(5), O2–Ti2–O6 158.23(6), O3–Ti2–O5 167.61(7), O3–Ti2–O6 95.16(6), O4–Ti2–O5 87.55(6), O4–Ti2–O6 97.38(7), O5–Ti2–O6 81.14(5), C8–O2–Ti2 129.7(1), C27–O6–Ti2 129.9(1). For more data see ESI.‡

the isopropoxy and P1 *trans* to the aryloxy oxygen, thus indicating a stronger *trans* influence of the isopropoxy ligands. Moreover, this rather long Ti–P2 bond may be caused by the steric hindrance of the two phenyl groups on the phosphorus. Consequently, the Ti–O–CAr angle values are larger than for **2j** and the Ti–OAr bond lengths are smaller. The ^{31}P NMR spectrum showed a broad signal at −3.5 ppm whereas the ^{31}P signal of the ligand was at −21.8 ppm. This indicated that in solution the phosphorous nucleus is still close to the titanium centre.

When the heteroatoms were shifted by one carbon from the *ortho* position of the phenol, different behaviour was observed in the isopropoxy substitution process. With phenol **1i** having a –CH_2OMe functional group in the *ortho* position, di-substitution occurred. Yellow crystals of complex **2i** were isolated and analyzed by X-ray diffraction (Fig. 5). The metal coordination geometry is distorted octahedral, with the isopropoxy ligands *cis* to each other, the oxygen atoms of the phenol *trans* to each other and the oxygen of the *ortho* groups also *trans* to each other. The Ti–OPh and the Ti–O^{i}Pr lengths are close to those found for the complex **2j** and the Ti–OMe and Ti–N bond lengths are also similar.

In contrast, the use of phenol **1l** with the CH_2NMe_2 functional group only resulted in the formation of the mono-aryloxy complex **2l**. The reaction mixture contained residual phenol, some titanium precursor and only a small amount of di-substituted complex. The hemilability of the side arm evidenced earlier by variable temperature ^{1}H NMR spectroscopy[9] may be responsible for the selective mono-substitution under these conditions. A distorted tetrahedral geometry as reported with phenols containing a bulky alkyl group at both *ortho* positions may be envisaged with aminomethyl functionalized aryloxy ligands. Similar behaviour was found for complexes **2k** and **2m**. The substitution process involving one or two equivalents of the phosphorus derivative **1o** led to mixtures of species that could not be separated (both mono and di-substitution appear to be present).

Catalytic oligomerization of ethylene with [(ArO)$_n$Ti(O*i*-Pr)$_{(4-n)}$] complexes

All the titanium complexes described in this work were used as pre-catalysts for the oligomerization of ethylene. Experiments were carried out under 20 bar, at 60 °C, in cyclohexane in the presence of $AlEt_3$ as an activator. The results showed that in all cases, good selectivity toward the formation of 1-butene was observed with variable activities. Results are summarized in Table 2. [Ti(O*i*-Pr)$_4$] (entries 1 and 2) was used as a reference. All complexes exhibited good selectivities for 1-butene. The substitution of two isopropoxy ligands by two aryloxy ligands (complex **2a**) led to a slight improvement of the activity.

This improvement may be the result of increased electrophilicity of the titanium due to the electron withdrawing effect of the aromatic rings. However, increasing the steric hindrance at the R^1 and R^3 positions of the ligand only led to a decrease in activity (entries 4–10). Mono-aryloxy complexes **2c$_1$** and **2d$_1$** led to better activities than their bis-aryloxy homologues **2c$_2$** and **2d$_2$** (entries 5–8). Thus, increasing the steric hindrance around the metal may disfavor ethylene coordination to the titanium centre. The presence of a methoxy group on the phenol (entries 11 and 12) also led to a decrease in activity. This is consistent with the expected detrimental effect of an *ortho* group larger than hydrogen. It was also shown that having a potentially stabilizing donor group, such as a methoxy, at the *ortho* position of a phenol did not compensate for the steric hindrance. Moreover, when increasing the spacer length (complex **2i**, entry 13), the activity tends to be even lower despite the increase in flexibility of the side arm. This may be due to a better coordination of the methoxy groups to titanium, as shown in Fig. 5, which decreases the electrophilicity of the titanium centre. The nitrogen-functionalized complexes displayed different catalytic behaviours than the oxygen-functionalized complexes. Indeed, complex **2j**, having a ligand with two carbon atoms between the oxygen and the nitrogen, was almost inactive whereas complexes **2k**, **2l** and **2m** with ligands having three carbon atoms between the oxygen and the nitrogen were among the most active catalysts screened (entries 14 to 17). The change of solvent was not responsible for that result since [Ti(O*i*-Pr)$_4$] in chlorobenzene was as active as in cyclohexane (despite a change in selectivities, entries 1 and 2). This appears to be in agreement with the behaviour of these ligands in the complexation process. Ligand **1j** strongly coordinates the titanium and leads to the di-substituted complex **2j** which may not be electrophilic enough to display good activity. However, phenols **1k**, **1l** and **1m** only led to the mono-substituted complexes with a titanium less hindered than in **2j** which favoured the catalytic activity. In addition, ligands which may exhibit hemilabile behaviour can stabilize the metal "on demand" and this could explain the better activities compared to **2b** or **2c$_1$**.[9] The increase of the steric bulk at the R^1 position slightly led to a decrease in activity (entries 15 and 16). No influence has been observed when the dimethylamino group was

Table 1 X-Ray crystallographic data for **2d$_1$**, **2f**, **2i**, **2j** and **2n**

Compound	**2d$_1$**	**2f**	**2i**	**2j**	**2n**
Lattice	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Formula	$C_{46}H_{84}O_8Ti_2$	$C_{56}H_{88}O_8Ti_2$	$C_{32}H_{52}O_6Ti$	$C_{24}H_{26}N_2O_4Ti$	$C_{58}H_{74}O_4P_2Ti$
Formula weight	860.93	985.0	580.64	454.37	944.32
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a (Å)	26.3870(6)	14.6692(9)	13.1940(4)	11.1702(2)	23.0760(8)
b (Å)	10.8511(3)	16.9750(10)	13.2380(3)	14.4223(5)	13.0154(6)
c (Å)	18.6970(3)	11.3986(7)	19.8430(8)	15.9597(5)	19.6086(9)
α (°)	90.00	90.00	78.242(1)	90.00	90.00
β (°)	103.080(1)	97.659(6)	76.0210(12)	114.419(2)	111.386(2)
γ (°)	90.00	90.00	85.2070(9)	90.00	90.00
Cell volume (Å^3)	5214.6(2)	2813.0(3)	3290.5(2)	2341.11(12)	5483.8(4)
Density	1.097	1.163	1.172	1.289	1.174
Z	4	2	4	4	4
F(000)	1872	1064	1256	952	2024
T (K)	173(2)	100(2)	173(2)	173(2)	173(2)
$\theta_{min} - \theta_{max}$ (°)	1.0, 27.5	3.4, 29.5	1.6, 30.0	1.0, 27.5	1.0, 27.5
μ (mm^{-1})	0.35	0.33	0.30	0.40	0.26
Measd. Reflections	30 806	38 164	28 319	17 236	38 963
Indep. reflections	11 827	7120	19 200	5361	12 528
R_{int}	0.053	0.049	0.034	0.039	0.209
$R[F^2 > 2\sigma(F^2)]$	0.144	0.061	0.059	0.042	0.163
w$R(F^2)$ $[F^2 > 2\sigma(F^2)]$	0.4	0.155	0.163	0.111	0.348
R (all data)	0.0880	0.0706	0.1134	0.0514	0.2702
w$R(F^2)$ (all data)	0.1594	0.1545	0.1630	0.1114	0.3480
S	1.03	0.94	1.03	1.03	1.51
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e Å^{-3})	−2.20, 2.34	−1.04, 1.17	−0.58, 0.55	−0.44, 0.75	−0.98, 1.17

Table 2 Ethylene dimerization by precatalysts **2a**–**2n**[a]

Entry	Precatalyst	Activity[b]	Sel. $C_4^=$(α)[c]	Sel. $C_6^=$[d]	Sel. HBP[e]
1	[Ti(O*i*-Pr)$_4$]	1400	93 (99+)	5	2
2[f]	[Ti(O*i*-Pr)$_4$]	1400	86 (99+)	12	2
3	**2a**	1700	93 (99+)	6	1
4	**2b**	1100	96 (99+)	2	1
5	**2c$_1$**	500	95 (99)	4	1
6	**2c$_2$**	400	95 (97)	1	4
7	**2d$_1$**	800	94 (99+)	4	2
8	**2d$_2$**	500	96 (98)	2	2
9	**2e**	300	95 (99+)	3	2
10	**2f**	600	93 (99)	4	3
11	**2g**	800	95 (99)	3	2
12	**2h**	1200	96 (99+)	3	1
13	**2i**	500	96 (99+)	3	1
14[f]	**2j**	200	96 (99+)	2	3
15	**2k**	1500	94 (99)	4	2
16	**2l**	1300	94 (99+)	5	1
17	**2m**	1300	93 (99+)	6	1
18	**2n**	<100	—	—	—

[a] Conditions: 0.15 mmol of Ti, 0.45 mmol of $AlEt_3$, 6 mL of cyclohexane, 20 bar C_2H_4, 60 °C, 1500 rpm, 25 min. [b] Expressed in $gC_2H_4/gTi/h$. [c] Amount of C4 dimers with respect to all products (α: amount of 1-butene in the C4 dimers). [d] Amount of C6 dimers with respect to all products. [e] Higher boiling products (essentially solid polyethylene with traces of C8 oligomers). [f] Chlorobenzene (6 mL) instead of cyclohexane.

replaced by a pyrrolidino group (entries 16 and 17). The study of the hexenes fraction revealed that the C6 products are only due to co-dimerization of 1-butene with ethylene. Indeed, a very small amount of 1-hexene was obtained and the major hexene isomer produced was 2-ethyl-1-butene. The high selectivity toward 1-butene and the formation of hexenes as by-products are consistent with a metallacyclic ethylene dimerization mechanism which is generally accepted for selective oligomerization using titanium catalysts.[2a,11]

Conclusions

New aryloxy-substituted titanium complexes of general formula $[(ArO)_nTi(O\textit{i}\text{-}Pr)_{(4-n)}]$ have been synthesized and characterized. It has been shown that both the steric hindrance and the nature of the heteroatom-based donor substituent of the phenol influenced the complexation process. A bulky alkyl group at both *ortho* positions of the aryl group prevents the formation of the di-substituted complex and selectively leads to the mono-aryloxy complex. A specific behaviour of the alkylaminomethyl *ortho*-functionalized phenols has been highlighted with selective formation of the mono-aryloxy complexes whereas all the other functionalizations introduced on the phenol ring led to bis-aryloxy complexes, as shown by ^{1}H NMR and X-ray diffraction analysis. Catalytic ethylene oligomerization studies with $AlEt_3$ as the activator revealed that all catalytic systems are active toward the selective dimerization of ethylene to 1-butene (with the exception of **2n** which is quite inactive). It was found that the larger the size of the *ortho* groups, the lower the activity. Incorporation of heteroatoms into the *ortho* groups did not compensate for the increase of the steric bulk, except for the alkylaminomethyl *ortho* functionalizations, possibly due to their hemilabile behaviour in solution.

Experimental section

General procedures

All experiments were performed under an argon atmosphere using standard Schlenk techniques. Anhydrous THF, Et_2O,

dichloromethane, pentane and toluene were purified by a solvent purification system (SPS-M-Braun) and cyclohexane was distilled over sodium. Their water content was determined by the Karl–Fischer method using a microcoulometer Methrom 756 KF. Anhydrous ethanol, methanol and chloroform were stored over 4 Å molecular sieves. All solvents were purchased from commercial sources. Reagents were purchased from Sigma-Aldrich or Strem and used without further purifications unless otherwise specified. [Ti(O*i*-Pr)$_4$] and Ph_2PCl were distilled and kept under argon.

NMR spectra were recorded on a Bruker AC 300 MHz at 293 K unless otherwise stated. Deuterated solvents ($CDCl_3$ and CD_2Cl_2) were purchased from Sigma-Aldrich or Eurisotop. They were freeze-pumped and stored over 4 Å molecular sieves under argon. All chemical shifts are reported in ppm *vs.* $SiMe_4$ and were determined with reference to residual solvent peaks.[25] ^{31}P NMR chemical shifts are reported in ppm related to an 85% H_3PO_4 solution in water reference. All coupling constants are given in Hertz.

GC analyses were performed on Agilent 6850 series II or Varian CP-3800 devices equipped with autosamplers and fitted with PONA columns. GC-MS analyses were performed on an Agilent 6890 N device equipped with an autosampler and fitted with a PONA or HP-5-MS column and an Agilent 5975B inert XL EI/CI MSD mass spectrometer.

Elemental analyses were performed by the Service Central d'Analyses of CNRS (Vernaison, France) or by the ICM-Université de Bourgogne (Dijon, France). The X-ray diffraction analyses performed in Strasbourg used a Kappa CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Data were collected using Ψ scans, the structures were solved by direct methods using the SHELX97 software,[26] 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). The diffraction data obtained at the Université Claude Bernard-Lyon I were collected on a Nonius KappaCCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) using Ψ scans and the structure was solved by direct methods using the SIR97 software and was refined by full-matrix least squares on F^2. No absorption correction was used.

Intermediates 2,4-di-*tert*-butyl-6-(hydroxymethyl)phenol,[17] 2,4-di-*tert*-butyl-6-(bromomethyl)phenol,[17] 2-bromo-4,6-di-*tert*-butyl phenol[15] as well as phenols **1i**,[9] **1l**,[9] **1m**,[9] and **1n**[16] were synthesized according to literature procedures.

Synthesis of 2-(*t*-butyl)-6-(2-phenylpropan-2-yl)phenol (1f). This ligand was synthesized similarly to 2-(*t*-butyl)-4-methyl-6-(2-phenylpropan-2-yl)phenol.[9] Starting from 2-(*t*-butyl)phenol (15.0 g, 0.10 mol, 1.0 equiv.), **1f** (19.9 g, 74%) was obtained as colourless crystals. MS (EI$^+$): (*m*/*z*) [M$^+$] = 268. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.38 (s, 9H, C–CH_3), 1.68 (s, 6H, C–CH_3), 3.88 (bs, 1H, OH), 6.55 (d, 1H, $^3J_{HH}$ = 8.2 Hz, O–C–CH), 6.90 (dd, 1H, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 2.4 Hz, O–C–CH–CH), 7.18 (d, 1H, $^5J_{HH}$ = 2.4 Hz, O–C–C–CH), 7.26 (m, 5H, CH). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ (ppm) 29.7 (C-(**C**H_3)$_3$), 31.0 (C(**C**H_3)$_2$), 34.7 (**C**(CH_3)$_3$), 42.5 (**C**(CH_3)$_2$), 116.0 (O–C–**C**H–CH), 125.3 (O–C–CH–**C**H), 125.4 (O–C–C–**C**H), 125.5 (CH), 126.8 (CH), 127.9 (CH), 135.2 (O–C–**C**), 142.6 (O–C–CH–CH–**C**), 151.1 (C), 151.9 (O–C). Anal. Calcd for $C_{19}H_{24}O$: C 85.03, H 9.01. Found: C 85.06, H 9.19.

Synthesis of 2-((dimethylamino)methyl)-4,6-dimethylphenol (1k). In a 500 mL round bottom flask were added paraformaldehyde (3.70 g, 123 mmol, 1.5 equiv.), dimethylamine (12.3 mL, 98.3 mmol, 1.2 equiv.) and an ethanol solution (250 mL) of 2,4-dimethylphenol (10.0 g, 81.9 mmol, 1 equiv.). The mixture was refluxed for 2 days to give a yellow solution. Volatiles were removed under reduced pressure to give **1k** as a dark orange oil (14.7 g, 99%). MS (EI$^+$): (*m*/*z*) [M$^+$] = 179. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 2.21 (s, 3H, O–C–C–CH_3), 2.22 (s, 3H, CH_3), 2.32 (s, 6H, N(CH_3)$_2$), 3.58 (s, 2H, CH_2), 6.62 (m, 1H, CH_2–C–C**H**), 6.87 (m, 1H, O–C–C–CH). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ (ppm) 15.7 (O–C–C–**C**H_3), 20.5 (CH_3), 44.5 (N(CH_3)$_2$), 63.0 (CH_2), 121.0 (O–C–**C**–CH_3), 124.6 (**C**–CH_2), 126.5 (CH_2–C–**C**), 127.5 (**C**–CH_3), 130.5 (CH), 153.7 (O–C). Anal. Calcd for $C_{11}H_{17}NO$: C 73.70, H 9.56. Found: C 74.03, H 9.69.

Synthesis of 2,4-di-*t*-butyl-6-((diphenylphosphino)methyl) phenol (1o). To a solution of 2-bromomethyl-4,6-(di-*t*-butyl)-phenol (4.00 g, 13.4 mmol, 1.0 equiv.) in Et_2O (70 mL) was added slowly *via* a syringe a 10% solution of diphenylphosphine in hexane (25.0 g, 13.4 mmol, 1.0 equiv.). The mixture turned cloudy and was refluxed for 40 min. The solid was separated and dissolved in water (30 mL) before a solution of sodium acetate (8.0 g, excess) in water (20 mL) was added. The aqueous phase was extracted with Et_2O (3 × 30 mL) and removal of the volatiles gave **1o** (3.0 g, 65%) as a white solid. This product was not further purified. MS (EI$^+$): (*m*/*z*) [M$^+$] = 404. ^1H NMR (300 MHz, CD_2Cl_2): δ (ppm) 1.12 (s, 9H, CH_3), 1.39 (s, 9H, O–C–C–C(CH_3)$_3$), 3.42 (s, 2H, CH_2), 5.35 (bs, 0.4H, OH), 6.59 (m, 1H, CH_2–C–C**H**), 7.11 (m, 1H, CH), 7.34 (m, 10H, CH). Impurities peaks: 1.16 (s, 0.3H), 1.29 (s, 1H), 2.03 (s, 0.6H), 3.43 (d, 0.4H), 4.40 (d, 0.2H), 6.37 (m, 0.1H), 7.16 (m, 0.1H). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ (ppm) 30.0 (O–C–C–C(**C**H_3)$_3$), 31.5 (CH_3), 32.2 (d, $^1J_{CP}$ = 12.5 Hz, CH_2), 34.3 (**C**-(CH_3)$_3$), 35.2 (O–C–C–**C**(CH_3)$_3$), 122.4 (d, $^5J_{CP}$ = 2.5 Hz, CH), 123.3 (d, $^2J_{CP}$ = 3.9 Hz, CH_2–**C**), 126.4 (d, $^3J_{CP}$ = 5.1 Hz, CH_2–C–**C**H), 128.8 (d, $^3J_{CP}$ = 6.6 Hz, P–C–CH–**C**H), 129.4 (P–C–CH–CH–**C**H), 133.2 (d, $^2J_{CP}$ = 17.8 Hz, P–C–**C**H), 137.0 (d, $^4J_{CP}$ = 1.6 Hz, O–C–**C**), 137.5 (d, $^1J_{CP}$ = 11.2 Hz, P–C), 142.8 (d, $^4J_{CP}$ = 1.8 Hz, C), 150.7 (d, $^3J_{CP}$ = 3.0 Hz, O–C). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ (ppm) −20.4. Impurities peaks: 15.7, 20.8, 38.3 (0.1P).

General procedure for the synthesis of complexes [(ArO)$_n$Ti(O*i*-Pr)$_{(4-n)}$]

The complexes **2e**, **2l** and **2m** were synthesized as described in the literature.[9] For other complexes, the procedure was the following: to a cyclohexane solution of the ligand (*n* equiv.) was added [Ti(O*i*-Pr)$_4$] (1.0 equiv.) at room temperature. The solution was stirred at room temperature overnight. Removal of the volatiles gave the complex [(ArO)$_n$Ti(O*i*-Pr)$_{(4-n)}$] in almost quantitative yield.

Synthesis of [(phenoxy)$_2$Ti(O*i*-Pr)$_2$] (2a). The general procedure was applied starting from **1a** (1.99 g, 21.1 mmol) and [Ti(O*i*-Pr)$_4$] (3.00 g, 10.5 mmol) yielding **2a** as a very viscous yellow to orange oil (3.7 g, 99%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) 1.17 (d, 12H, $^3J_{HH}$ = 4.9 Hz, CH_3), 4.59 (m, 2H; O–CH), 6.87 (m, 6H, O–C–C**H**–CH–C**H**), 7.14 (m, 4H, O–CH–C**H**). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ (ppm) 25.9 (CH_3), 79.1 (bs, O–CH), 119.8 (bs, O–C–**C**H), 121.3 (O–CH–CH–**C**H), 129.1 (O–CH–**C**H), 165.2 (O–C). Anal. Calcd for $C_{18}H_{24}O_4Ti$: C 61.38, H 6.87. Found: C, 60.92; H, 6.39.

Synthesis of [(2,4-dimethylphenoxy)$_2$Ti(O*i*-Pr)$_2$] (2b). The general procedure was applied starting from 2,4-dimethylphenol **1b** (4.28 g, 35.0 mmol) and [Ti(O*i*-Pr)$_4$] (5.00 g, 17.5 mmol) yielding **2b** (7.14 g, 99%) as a very viscous red oil. ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) 1.18 (d, 12H, $^3J_{HH}$ = 6.1 Hz, CH(C**H**$_3$)$_2$), 2.22 (s, 6H, O–C–C–CH_3), 2.25 (s, 6H, CH_3), 4.64 (sept., $^3J_{HH}$ = 6.1 Hz, 2H, O–CH), 6.83 (m, 4H, O–C–C**H**–C**H**), 6.89 (m, 2H, O–C–C–CH). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ (ppm) 16.9 (O–C–C–**C**H$_3$), 20.7 (CH_3), 25.9 (CH(**C**H$_3$)$_2$), 80.0 (bs, **C**H(CH$_3$)$_2$), 119.4 (O–C–**C**H), 126.1 (C–**C**H$_3$), 127.0 (O–C–CH–**C**H), 130.5 (O–C–**C**), 131.1 (O–C–C–**C**H), 162.6 (O–C). Anal. Calcd for $C_{22}H_{32}O_4Ti$: C 64.71, H 7.90. Found: C 64.40, H 7.69.

Synthesis of [(2-*tert*-butyl-4-methylphenoxy)Ti(O*i*-Pr)$_3$]$_2$ (2c$_1$). The general procedure was applied starting from 2-*t*-butyl-4-methylphenol **1c** (1.73 g, 10.5 mmol) and [Ti(O*i*-Pr)$_4$] (3.00 g, 10.5 mmol) leading to **2c$_1$** (4.08 g, 99%) as a yellow solid. ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) 1.28 (d, 18H, $^3J_{HH}$ = 6.4 Hz, CH(C**H**$_3$)$_3$), 1.41 (s, 9H, C(CH$_3$)$_3$), 2.26 (s, 3H, CH_3), 4.59 (bs, 3H, O–CH), 6.86 (m, 2H, O–C–C**H** and C**H**), 7.01 (bs, 1H, O–C–CH–C**H**). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ (ppm) 21.0 (CH_3), 26.7 (CH(**C**H$_3$)$_2$), 30.0 ((CH$_3$)$_3$), 34.9 (**C**(CH$_3$)$_3$), 78.3 (bs, O–CH), 121.5, 121.8 (O–C–**C**H–**C**H), 127.2, 127.5 (CH_3–**C**–**C**H–C), 136.4 (O–C–**C**), 152.7 (O–C).

Synthesis of [(2-*t*-butyl-4-methylphenoxy)$_2$Ti(O*i*-Pr)$_2$] (2c$_2$). The general procedure was applied starting from 2-*t*-butyl-4-methylphenol **1c** (5.75 g, 35.0 mmol) and [Ti(O*i*-Pr)$_4$] (5.00 g, 17.5 mmol) leading to **2c$_2$** (8.61 g, 99%) as a red oil. ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) 1.28 (d, 12H, $^3J_{HH}$ = 6.2 Hz, CH(C**H**$_3$)$_2$), 1.42 (s, 18H, C(CH$_3$)$_3$), 2.26 (s, 6H, CH_3), 4.71 (bs, 2H, O–CH), 6.89 (m, 4H, O–C–CH and O–C–C–CH), 7.05 (m, 2H, CH). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ (ppm) 21.0 (CH_3), 26.7 (CH(**C**H$_3$)$_2$), 30.1 (C(**C**H$_3$)$_3$), 34.9 (**C**(CH$_3$)$_3$), 80.3 (bs, O–CH), 120.4, 121.9, 122.4 (O–C–**C**H and O–C–C–**C**H), 127.2, 127.6 (O–C–CH–**C**H), 130.3, 131.3 (**C**–CH$_3$), 136.6 (O–C–**C**), 161.4, 161.8 (O–C).

Synthesis of [(2,4-di-*t*-butylphenoxy)Ti(O*i*-Pr)$_3$]$_2$ (2d$_1$). The general procedure was applied starting from 2,4-di-*t*-butylphenol **1d** (2.18 g, 10.5 mmol) and [Ti(O*i*-Pr)$_4$] (3.00 g, 10.5 mmol) leading to **2d$_1$** (4.51 g, 99%) as a yellow solid. Single crystals were grown from a cold saturated pentane solution. ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) 1.28 (d, 18H, $^3J_{HH}$ = 6.2 Hz, CH(C**H**$_3$)$_2$), 1.30 (s, 9H, C(CH$_3$)$_3$), 1.43 (s, 9H, O–C–C–C(CH$_3$)$_3$), 4.60 (bs, 3H, O–CH), 6.95 (m, 1H, O–C–CH–C**H**), 7.05 (m, 1H, O–C–CH), 7.24 (m, 1H, O–C–C–CH). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ (ppm) 26.8 (CH(**C**H$_3$)$_2$), 30.0 (O–C–C–C(**C**H$_3$)$_3$), 31.8 (C(**C**H$_3$)$_3$), 34.7 (O–C–C–**C**(CH$_3$)$_3$), 35.3 (**C**-(CH$_3$)$_3$), 78.3 (bs, O–CH), 121.1 (O–C–CH–**C**H), 121.5 (**C**–C(CH$_3$)$_3$), 123.4 (O–C–C–**C**H), 124.0 (O–C–**C**H), 135.9 (O–C–**C**), 152.8 (O–C). Anal. Calcd for $C_{23}H_{42}O_4Ti$: C 64.18; H 9.83. Found: C 63.44; H 9.81.

Synthesis of [(2,4-di-*t*-butylphenoxy)$_2$Ti(O*i*-Pr)$_2$] (2d$_2$). The general procedure was applied starting from 2,4-di-*t*-butylphenol **1d** (5.75 g, 35.0 mmol) and [Ti(O*i*-Pr)$_4$] (5.00 g, 17.5 mmol) leading to **2d$_2$** (10.0 g, 99%) as a red oil. ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) 1.34 (s, 18H, C(CH$_3$)$_3$), 1.37 (d, 12H, $^3J_{HH}$ = 5.2 Hz, CH(C**H**$_3$)$_2$), 1.50 (s, 18H, O–C–C–C(CH$_3$)$_3$), 4.75 (bs, 2H, O–CH), 7.00 (m, 2H, O–C–CH–C**H**), 7.13 (m, 2H, O–C–CH), 7.31 (m, 2H, CH). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ (ppm) 26.7 (CH(**C**H$_3$)$_3$), 27.3 (O–C–C–C(**C**H$_3$)$_3$), 30.1, 30.2 (O–C–C–**C**(CH$_3$)$_3$), 31.7, 31.8 (C(**C**H$_3$)$_3$), 34.7, 34.8 (O–C–C–**C**(CH$_3$)$_3$), 80.8 (bs, **C**H(CH$_3$)$_2$), 121.5, 122.0 (O–C–CH–**C**H), 123.6, 123.7, 124.0, 124.1 (CH); 135.8 (C); 143.7, 144.7 (O–C–**C**), 161.3, 161.6 (O–C). Anal. Calcd for $C_{34}H_{56}O_4Ti$: C 70.81; H 9.79. Found: C, 70.21; H, 9.78.

Synthesis of [(2-(*t*-butyl)-6-(2-phenylpropan-2-yl)phenoxy)Ti-(O*i*-Pr)$_3$] (2f). The general procedure was applied starting from **1f** (2.80 g, 10.5 mmol) and [Ti(O*i*-Pr)$_4$] (3.00 g, 10.5 mmol) leading to **2f** (5.17 g, 99%) as a yellow solid. Single crystals were grown from a cold saturated pentane solution. ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) 1.27 (d, 18H, $^3J_{HH}$ = 6.1 Hz, (CH$_3$)$_2$), 1.37 (s, 9H, C(CH$_3$)$_3$), 1.65 (s, 6H, CH(C**H**$_3$)$_2$), 4.58 (bs, 3H, O–CH), 6.87 (m, 2H, O–C–C–CH and O–C–CH–C**H**), 7.12 (m, 1H, CH), 7.15 (m, 1H, O–C–CH), 7.24 (bs, 2H, CH), 7.25 (m, 2H, CH). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ (ppm) 16.7 (CH(**C**H$_3$)$_2$), 30.0 (C(**C**H$_3$)$_3$), 31.0 ((CH$_3$)$_2$), 35.2 (**C**-(CH$_3$)$_3$), 42.8 (**C**(CH$_3$)$_2$), 78.5 (bs, O–CH), 121.1 (O–C–CH–**C**H), 124.8 (CH), 125.7 (O–C–C–**C**H), 127.0 (CH), 128.2 (CH), 132.3 (C), 135.8 (O–C–**C**), 142.4 (O–C–**C**H), 151.7 (C), 160.9 (O–C). Anal. Calcd for $C_{28}H_{44}O_4Ti$: C 68.28; H 9.00. Found: C, 66.84; H, 8.70. Despite many attempts, no better results could be obtained for the C analysis of this complex.

Synthesis of [(2-methoxyphenoxy)$_2$Ti(O*i*-Pr)$_2$] (2g). The general procedure was applied starting from guaiacol **1g** (4.34 g, 35.0 mmol) and [Ti(O*i*-Pr)$_4$] (5.00 g, 17.5 mmol) yielding **2g** (7.21 g, 99%) as a yellow solid. ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) 1.22 (d, 12H, $^3J_{HH}$ = 6.2 Hz, CH(C**H**$_3$)$_2$), 3.84 (s, 6H, CH_3), 4.81 (sept., 2H, $^3J_{HH}$ = 6.2 Hz, O–CH), 6.70 (m, 6H, O–C–C–C**H**–C**H**–C**H**), 6.91 (m, 2H, O–C–CH). Unattributed peaks at 3.78 (s, 0.2H) and 3.82 (s, 0.3H). Molar purity > 95%. $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ (ppm) 27.2 ((CH$_3$)$_2$), 58.6 (CH_3), 81.8 (O–CH), 111.6 (CH), 116.2 (CH), 119.8 (CH), 124.8 (O–C–CH), 151.1 (O–C–**C**), 155.6 (O–C). Anal. Calcd for $C_{20}H_{28}O_6Ti$: C, 58.26; H, 6.85. Found: C, 57.65; H, 6.52.

Synthesis of [(2-methoxy-4-methylphenoxy)$_2$Ti(O*i*-Pr)$_2$] (2h). The general procedure was applied starting from 2-methoxy-4-methylphenol **1h** (4.84 g, 35.0 mmol) and [Ti(O*i*-Pr)$_4$] (5.00 g, 17.5 mmol) leading to **2h** (7.70 g, 99%) as an orange viscous oil. ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) 1.21 (d, 12H, $^3J_{HH}$ = 5.1 Hz, CH(C**H**$_3$)$_2$), 2.25 (s, 6H, CH_3), 3.81 (s, 6H, O–CH_3), 4.78 (sept., 2H, $^3J_{HH}$ = 5.1 Hz, O–CH), 6.55 (m, 2H, O–C–CH), 6.60 (m, 2H, O–C–C–CH), 6.69 (m, 2H, O–C–CH–C**H**).

Unattributed peaks at 3.79 (s, 0.4H) and 3.72 (0.2H). Molar purity > 95%. $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ (ppm) 21.1 (CH_3), 25.7 (CH(**C**H_3)$_2$), 56.9 (O–CH_3), 79.9 (O–CH), 111.0 (O–C–C–**C**H), 114.0 (O–C–**C**H), 123.2 (O–C–CH–**C**H), 127.9 (**C**–CH_3), 149.3 (Ti–O–C), 152.0 (CH_3–O–**C**).

Synthesis of [(2-*t*-butyl-4-methyl-6-(methoxymethyl)-phenoxy)$_2$-Ti(O*i*-Pr)$_2$] (2i). The general procedure was applied but cyclohexane was replaced with Et_2O. Starting from **1i** (0.94 g, 4.56 mmol) and [Ti(O*i*-Pr)$_4$] (0.71 g, 2.23 mmol), complex **2i** (1.07 g, 83%) was obtained as a yellow solid after precipitation in cold pentane. Crystals suitable for X-ray diffraction were grown by slow crystallization from a cold saturated pentane solution. ^1H NMR (300 MHz, CD_2Cl_2): δ (ppm) 1.14 (d, $^3J_{HH}$ = 6.09 Hz, 12H, OCH(CH_3)$_2$), 1.51 (s, 18H, C(CH_3)$_3$), 2.27 (s, 6H, CH_3), 3.6 (s, 6H, OCH_3), 4.6 (s, 4H, Ar–CH_2OCH_3), 4.9 (m, 2H, OCH(CH_3)$_2$), 6.76–6.06 (2 d, $^4J_{HH}$ = 2 Hz, CH); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ (ppm) 20.3 (CH_3), 25.5 (OCH(CH_3)$_2$), 29.6 (C(CH_3)$_3$), 34.4 (C(CH_3)$_3$), 60.0 (ArCH_2OCH_3), 74.6 (OCH_2Ar), 78.0 (OCH(CH_3)$_2$), 124.2(C, Ph), 125.1 (C, Ph), 126.4 (CH, Ph), 127.2 (CH, Ph), 135.7 (C, Ph), 161.0 (C–O, Ph). Anal. Calcd for $C_{32}H_{52}O_6Ti$: C 66.20; H 9.03; Found: C 66.37; H 9.09.

Synthesis of [(quinolin-8-yloxy)$_2$Ti(O*i*-Pr)$_2$] (2j). The general procedure was applied starting from 8-hydroxyquinoline **1j** (3.10 g, 21.1 mmol) and [Ti(O*i*-Pr)$_4$] (3.00 g, 10.5 mmol) leading to **2j** (4.77 g, 99%) as a yellow solid. Single crystals were grown from a cold saturated pentane solution. ^1H NMR (300 MHz, CD_2Cl_2): δ (ppm) 0.91 & 1.13 (2d, 12H, $^3J_{HH}$ = 6.1 Hz, CH(C**H**$_3$)$_2$), 4.59 (sept., 2H, $^3J_{HH}$ = 6.1 Hz, O–CH), 6.99 (dd, 2H, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.0 Hz, C–C–CH), 7.09 (dd, 2H, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.0 Hz, O–C–CH), 7.17 (dd, 2H, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 4.7 Hz, N–CH–C**H**), 7.49 (m, 2H, O–C–CH–C**H**), 8.07 (dd, 2H, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.4 Hz, N–CH–CH–C**H**), 8.48 (dd, 2H, $^3J_{HH}$ = 4.7 Hz, $^4J_{HH}$ = 1.4 Hz, N–CH). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ (ppm) 25.3, 25.5 (CH_3), 78.3 (O–CH), 111.3 (C–C–**C**H), 114.5 (O–C–**C**H), 117.1 (N–CH–**C**H), 121.7 (N–C–**C**), 130.1 (O–C–CH–**C**H), 138.2 (N–CH–CH–**C**H), 141.9 (O–C–**C**), 145.5 (N–CH), 163.2 (O–C). Anal. Calcd for $C_{24}H_{26}O_4N_2Ti$: C, 63.45; H, 5.77; N, 6.17. Found: C, 63.37; H, 5.79; N, 6.23.

Synthesis of [(2-((dimethylamino)methyl)-4,6-dimethylphenoxy)Ti(O*i*-Pr)$_3$] (2k). The general procedure was applied starting from **1k** (3.13 g, 17.5 mmol) and [Ti(O*i*-Pr)$_4$] (5.00 g, 17.5 mmol) leading to **2k** (7.06 g, 99%) as a yellow oil. ^1H NMR (300 MHz, CD_2Cl_2): δ (ppm) 1.30 (d, 18H, $^3J_{HH}$ = 5.7 Hz, CH(C**H**$_3$)$_2$), 2.22 (s, 3H, O–C–C–CH_3), 2.25 (s, 3H, CH_3), 2.41 (s, 6H, N(CH_3)$_2$), 3.71 (s, 2H, CH_2), 4.91 (sept., 3H, $^3J_{HH}$ = 5.7 Hz, O–CH), 6.65 (m, 1H, CH_2–C–C**H**), 6.89 (m, 1H, CH). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ (ppm) 16.9 (O–C–C–**C**H_3), 20.6 (CH_3), 26.6 (CH(**C**H_3)$_2$), 47.5 (N(CH_3)$_2$), 62.9 (CH_2), 77.7 (O–CH), 123. 8 (CH_2–**C**), 125.0 and 127.1 (C), 127.7 (CH_2–C–**C**H), 2.9 (CH), 158.2 (O–C).

Synthesis of [(2,4-di-*t*-butyl-6-(diphenylphosphino)phenoxy)$_2$-Ti(O*i*-Pr)$_2$] (2n). The general procedure was applied with **1n** (0.50 g, 1.3 mmol) and [Ti(O*i*-Pr)$_4$] (0.20 g, 0.65 mmol) leading to **2n** (0.61 g, 99%) as a yellow solid. Single crystals were grown from a saturated pentane solution. ^1H NMR (300 MHz, CD_2Cl_2): δ (ppm) 0.96 (bs, 12H, CH(C**H**$_3$)$_2$), 1.19 (s, 18H, C-(CH_3)$_3$), 1.37 (s, 18H, O–C–C–C(CH_3)$_3$), 4.60 (bs, 2H, O–CH), 6.87 (bs, 2H, O–C–C–CH), 7.06 (bs, 12H, P–C–CH–C**H**–C**H**), 7.20 (m, 8H, P–C–CH), 7.33 (d, 2H, $^4J_{HH}$ = 2.5 Hz, CH). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ (ppm) 26.0 (CH(**C**H_3)$_2$), 29.8 (C(**C**H_3)$_3$), 31.7 (O–C–C–C(**C**H_3)$_3$), 34.6 (**C**(CH_3)$_3$), 35.5 (O–C–C–**C**(CH_3)$_3$), 79.1 (O–CH), 126.8, 128.1, 128.1, 128.2, 128.5, 128.9, 133.8, 133.9 and 136 (C and CH), 152.7 (C-1). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ (ppm) −3.5 (bs). Anal. Calcd for $C_{58}H_{74}O_4P_2Ti$: C 73.71, H 7.89. Found: C 69.88, H 7.83. Despite many attempts, no better results could be obtained for the C analysis of this complex.

Oligomerization experiments

All catalytic reactions were carried out in a mechanically stirred 35 mL stainless steel autoclave. In a classical procedure, the autoclave was first purged at 100 °C using "pressurization/depressurization" nitrogen cycles. After cooling down to room temperature, the pre-catalyst solution (0.15 mmol Ti) was introduced before adding the aluminium co-catalyst (0.45 mmol Al). The reactor was then sealed and fed with ethylene up to the desired pressure (20 bar) and temperature (60 °C). The stirrer was then set to 1500 rpm. During catalysis, the pressure was maintained constant at 20 bar. The ethylene uptake was monitored throughout the reaction time. After 25 min, the stirring was stopped and the autoclave cooled down to room temperature and depressurized. The liquid phase was collected (by a pipette after the autoclave was opened) and weighed. After quenching with a 10% H_2SO_4 solution in water (1 mL), the organic layer was analyzed by GC. The polymer formed was air-dried overnight and weighted. For more details, figures of reactors and reaction profiles are available in ESI.‡

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References

1 D. Vogt, Oligomerization of ethylene to higher linear alpha olefins, in *Applied Homogeneous Catalysis with Organometallic Compounds*, ed. B. Cornils and W. A. Hermann, Wiley-VCH, Weinheim, 1st edn, 2002, p. 245.
2 (*a*) D. S. McGuinness, *Chem. Rev.*, 2011, **111**, 2321; (*b*) J. T. Dixon, M. J. Green, F. M. Hess and D. H. Morgan, *J. Organomet. Chem.*, 2004, **689**, 3641; (*c*) T. Agapie, *Coord. Chem. Rev.*, 2011, **255**, 861; (*d*) P. W. N. M. van Leeuwen, N. D. Clément and M. J.-L. Tschan, *Coord. Chem. Rev.*, 2011, **255**, 1499.
3 P. J. W. Deckers, B. Hessen and J. H. Teuben, *Angew. Chem., Int. Ed.*, 2001, **40**, 2516.
4 Y. Suzuki, S. Kinoshita, A. Shibahara, S. Ishii, K. Kawamura, Y. Inoue and T. Fujita, *Organometallics*, 2010, **29**, 2394.

5 (*a*) C. T. Burns and R. F. Jordan, *Organometallics*, 2007, **26**, 6726; (*b*) J. G. Yu, X. Q. Hu, Y. N. Zeng, L. P. Zhang, C. H. Ni, X. A. Hao and W. H. Sun, *New J. Chem.*, 2011, **35**, 178.

6 (*a*) K. Song, H. Gao, F. Liu, J. Pan, L. Guo, S. Zai and Q. Wu, *Eur. J. Inorg. Chem.*, 2009, 3016; (*b*) J. Flapper, H. Kooijman, M. Lutz, A. L. Spek, P. W. N. M. van Leeuwen, C. J. Elsevier and P. C. J. Kamer, *Organometallics*, 2009, **28**, 3272.

7 (*a*) K. F. Wang, R. Gao, W. Hao and W. H. Sun, *Catal. Commun.*, 2009, **10**, 1730; (*b*) W. H. Sun, K. Wang, K. Wedeking, D. Zhang, S. Zhang, J. Cai and Y. Li, *Organometallics*, 2007, **26**, 4781.

8 (*a*) H. Olivier-Bourbigou, A. Forestière, L. Saussine, L. Magna, F. Favre and F. Hugues, *Oil & Gas, Eur. Mag.*, 2010, **36**, 97; (*b*) *Petrochemical Processes; Hydrocarbon Processing*, Gulf Publishing Company ed., Houston (TX), 2010.

9 J.-B. Cazaux, P. Braunstein, L. Magna, L. Saussine and H. Olivier-Bourbigou, *Eur. J. Inorg. Chem.*, 2009, 2942.

10 V. C. Gibson and S. K. Spitzmesser, *Chem. Rev.*, 2003, **103**, 283.

11 J. A. Suttil, D. S. McGuinness, M. Pichler, M. G. Gardiner, D. H. Morgan and S. J. Evans, *Dalton Trans.*, 2012, **41**, 6625.

12 M. K. Panda, S. Kaur, A. R. Reddy, M. M. Shaikh, R. J. Butcher, V. Gupta and P. Ghosh, *Dalton Trans.*, 2010, **39**, 11060.

13 D. C. Bradley, R. C. Mehrotra, I. P. Rothwell and A. Singh, *Alkoxo and Aryloxo Derivatives of Metals*, Academic Press, 2001.

14 T. Maki, Y. Araki, Y. Ishida, O. Onomura and Y. Matsumura, *J. Am. Chem. Soc.*, 2001, **123**, 3371.

15 T. Agapie and J. E. Bercaw, *Organometallics*, 2007, **26**, 2957.

16 J. Heinicke, R. Kadyrov, M. K. Kindermann, M. Koesling and P. G. Jones, *Chem. Ber.*, 1996, **129**, 1547.

17 A. Sokolowski, J. Muller, T. Weyhermuller, R. Schnepf, P. Hildebrandt, K. Hildenbrand, E. Bothe and K. Wieghardt, *J. Am. Chem. Soc.*, 1997, **119**, 8889.

18 M. E. Van Der Boom, S. Y. Liou, Y. Ben-David, L. J. W. Shimon and D. Milstein, *J. Am. Chem. Soc.*, 1998, **120**, 6531.

19 S. Groysman, E. Sergeeva, I. Goldberg and M. Kol, *Inorg. Chem.*, 2005, **44**, 8188.

20 L. Lavanant, T.-Y. Chou, Y. Chi, C. W. Lehmann, L. Toupet and J.-F. Carpentier, *Organometallics*, 2004, **23**, 5450.

21 P. S. Umare, A. J. Tiwari, R. Antony, G. L. Tembe and B. Trivedi, *Appl. Organomet. Chem.*, 2007, **21**, 652.

22 S. Mishra and A. Singh, *Transition Met. Chem.*, 2005, **30**, 163.

23 W. F. Zeng, Y. H. Chen, M. Y. Chiang and C. P. Cheng, *Polyhedron*, 2007, **26**, 1303.

24 R. J. Long, V. C. Gibson, A. J. P. White and D. J. Williams, *Inorg. Chem.*, 2006, **45**, 511.

25 G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176.

26 (*a*) Kappa CCD Operation Manual; Netherlands, 1997 (*b*) University of Göttingen Program for the refinement of crystal structures; Germany, 1997.

