Dalton Transactions

RSC Publishing

PAPER

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Cite this: *Dalton Trans.*, 2013, **42**, 4185

Ethylene polymerisation and oligomerisation with arene-substituted phenoxy-imine complexes of titanium: investigation of multi-mechanism catalytic behaviour†

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Received 20th September 2012,
Accepted 30th January 2013

DOI: 10.1039/c3dt32183e

www.rsc.org/dalton

A range of unsubstituted (**1,2**) and 6-substituted (**3–5**) *ortho*-phenoxy-imine ligands have been prepared and converted to their silyl ether derivatives (**6–10**). Reaction of silyl ethers with $TiCl_4(thf)_2$ in the case of the unsubstituted species yields bis-ligated complexes while the substituted species react cleanly to yield complexes of the form [Ti(O^NR)Cl_3(thf)]. In most cases the complexes have been characterised by X-ray crystallography. Testing of the complexes for ethylene oligomerisation and polymerisation has been undertaken employing alkylaluminium co-catalysts ($AlEt_3$, MAO). In all cases the predominant product formed is polyethylene however careful analysis of the liquid phase reveals a complex process by which 1-butene is most likely formed *via* Cossee mechanism while 1-hexene results from a metallacyclic process.

Introduction

The oligomerisation and polymerisation of olefins into higher olefin feedstocks and polyolefin resins continues to be an area that receives much attention from both industry and academia. Of particular interest is the selective oligomerisation of ethylene to co-monomer grade linear alpha olefins (LAOs, such as 1-butene, 1-hexene and 1-octene), a process by which excessive formation of lower value, higher molecular weight fractions can be avoided.[1–8] As such, there is significant drive in developing new selective oligomerisation technologies and understanding the mechanism by which they function.[2,9–28] In recent years, early transition metal complexes, in combination with alkyl aluminium activators such as methylaluminoxane (MAO), that selectively di-, tri- and tetramerise ethylene have become well established in the literature.[1–6] While the most prevalent metal employed for selective trimerisation is undoubtedly Cr, more examples of well characterised selective Ti complexes are being reported.

One such example is the highly active and selective ethylene trimerisation catalyst described by Hessen and coworkers in 2001 (**I**). While selective ethylene dimerisation systems based on titanium were previously known, this was the first reported selective trimerisation system for this metal.[29] Early reports by Pellecchia *et al.* showed that Cp*$TiMe_3$-$B(C_6F_5)_3$ in toluene generated butyl-branched polyethylene along with 1-hexene when exposed to ethylene, demonstrating the catalyst's ability to catalyse both trimerisation and co-polymerisation.[30,31] In light of this result, Hessen and coworkers recognised the ability of the aromatic solvent toluene to stabilise the catalytic species yielding trimerisation selectivity. By modifying the cyclopentadienyl ring to incorporate a pendant arene functionality, they were able to efficiently convert the mono(cyclopentadienyl) polymerisation system into an ethylene trimerisation system yielding selectivity of up to 93% 1-hexene with excellent activity.[32] Through a series of systematic ligand modifications, the authors were able to demonstrate that a careful balance between steric influences of the ligand, the nature of the Cp/arene bridging atom and electronics is required to achieve both high selectivity and activity.[32–35] It has been hypothesised that the exceptional selectivity is a result of the arene functionality's ability to interact with the metal centre in a hemilabile fashion yielding a number of coordination geometries that work to stabilise the various stages of the metallacycle mechanism.[10,13,20,35–37] Since this initial discovery, several other reports have been published investigating the effect of electron withdrawing groups on the arene ring, varying the arene functionality to thienyl, thioether and ether substituted

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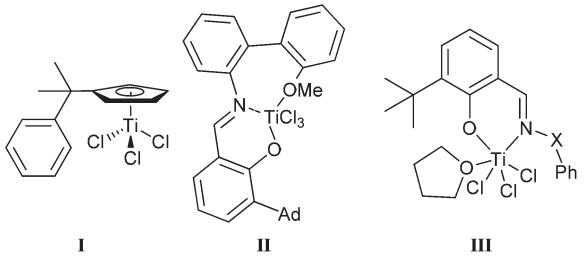
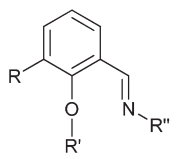
†Electronic supplementary information (ESI) available: Details of 1-butene and 1-hexene isotopomer analysis and X-ray structure of **13** and dichlorobis(3-*tert*-butyl-2-oxybenzoyl) titanium(IV). CCDC 902037–902043. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt32183e

derivatives and changing the metal to zirconium and hafnium; although benchmarks equal to that of the original systems have not been achieved.[38–41]

More recently, researchers from Mitsui Chemicals have demonstrated the conversion of the highly efficient phenoxy-imine (FI)[42] ethylene polymerisation motif to give selective ethylene trimerisation systems capable of exceptionally high activities.[43] The switching of selectivity was achieved by employing only a mono-ligated titanium centre, instead of the normal bis-arrangement that yields polymerisation, and incorporation of an additional donor atom to yield a tridentate complex (**II**).





R = H, R' = H, R'' = cumyl, **1**
R = H, R' = H, R'' = CH_2CH_2Ph, **2**
R = *t*-Bu, R' = H, R'' = cumyl, **3**
R = *t*-Bu, R' = H, R'' = $C(Me)_2CH_2Ph$, **4**
R = *t*-Bu, R' = H, R'' = CH_2CH_2Ph, **5**
R = H, R' = $SiMe_3$, R'' = cumyl, **6**
R = H, R' = $SiMe_3$, R'' = CH_2CH_2Ph, **7**
R = *t*-Bu, R' = $SiMe_3$, R'' = cumyl, **8**
R = *t*-Bu, R' = $SiMe_3$, R'' = $C(Me)_2CH_2Ph$, **9**
R = *t*-Bu, R' = $SiMe_3$, R'' = CH_2CH_2Ph, **10**

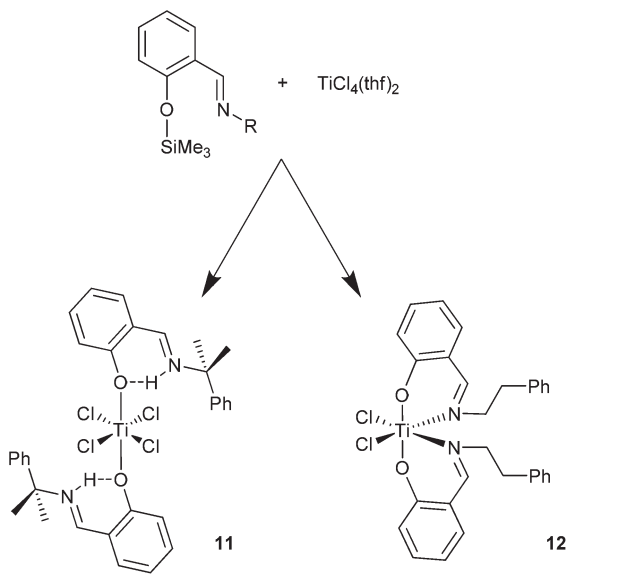
Given these more recent findings, we were interested in combining aspects of both Hessen's catalyst and the Mitsui system, namely the introduction of an arene functionality to phenoxy-imine catalysts, to yield novel precatalysts with potentially interesting ethylene oligomerisation properties. Previous reports on other mono-ligand phenoxy-imine catalysts bearing a phenyl substituent on the nitrogen have shown they have a propensity for polymer formation, although none of these reports comment on analyses of the oligomers that may have formed in the liquid phase.[44–46] Given these previous findings, our focus was on ligand systems employing a bridging atom between the nitrogen and arene functionalities, akin to the Hessen system (**III**, X = ethyl, α,α-dimethylethyl). Herein we report the preparation and characterisation of a range of both bis- and mono(salicylaldiminato) Ti complexes as well as their oligomerisation and polymerisation behaviour when activated with MAO.

Results and discussion

Synthesis and structures

The preparation of mono(salicylaldiminato) titanium complexes has been previously demonstrated for many combinations of either salicylaldimines or silyl ethers of salicylaldimines with titanium tetrachloride or titanium tetrachloride tetrahydrofuran adduct. The resulting stoichiometry of the complexes seems to be highly dependent upon the choice of starting reactants and the steric bulk of both the 6-position of the phenol and the nitrogen substituent.[44–51] The most broadly applicable and consistent of the literature methods was first reported by Lancaster and coworkers in 2003 and involves the silylation of the salicylaldimine precursor and subsequent dehalosilylation reaction with $TiCl_4(thf)_2$.[45,46] This methodology has since been widely employed to prepare heteroligated titanium precatalysts bearing at least one salicylaldiminato ligand; such catalysts are of interest in ethylene/alkene co-polymerisation reactions as they combine the exceptional activities of FI catalysts with the higher alkene incorporation of other systems.[52–62] Additionally, the resulting complexes should be facile towards activation for ethylene oligomerisation and polymerisation employing alkyl aluminium activators, as they contain easily exchangeable chloro ligands. As such, this methodology has been employed to prepare a series of novel (salicylaldiminato)-titanium complexes.

The starting salicylaldimines **1–5** and the subsequent silyl ethers **6–10** were prepared in moderate to good yields *via* a variety of modified literature procedures.[45,46] These species were characterised by ^1H and ^{13}C NMR spectroscopy and in most cases MS; where the silyl ether pre-ligands bore no substituent on the 6-position only the hydrolysed species could be observed by MS indicating substantial capacity for hydrolysis. Initial complex synthesis focused on the pre-ligands **6** and **7** which have an unsubstituted 6-position in the phenol. In both cases addition of the ligand to $TiCl_4(thf)_2$ yield dark red solutions after stirring for 24 hours. Upon work up bis(salicylaldiminium)titanium complex **11** and bis(salicylaldiminato) titanium complex **12** (Scheme 1) were obtained regardless of an initial 1 : 1 metal to ligand ratio. The ^1H and ^{13}C NMR spectra of **11** shows a single set of signals for the two symmetry equivalent ligands. The aldimine –C*H*=N(H)– resonance



Scheme 1 Synthesis of complexes **11** and **12**.

is observed in the ^{1}H NMR spectra as a doublet at δ 8.03 (^3J = 7.8 Hz) while the broad =N(*H*)– resonance is present at δ 12.97. These NMR features are consistent with the previously reported analogue tetrachlorobis(2,6-diisopropylphenylsalicylaldiminium)titanium(IV) and confirm that the proton is formally bound to the nitrogen atom yielding an overall neutrally charged ligand with zwitterionic character.[63] Crystals suitable for X-ray diffraction were obtained by slow diffusion of petroleum spirits into a dichloromethane solution of the complex. The solid state structure shows a distorted octahedral geometry with the oxygen atoms arranged *trans*-bound to the titanium atom with the chloride ligands adopting the equatorial positions (Fig. 1). Key bond length and angles are in general agreement with the analogous structure reported by Strauch *et al.*[63] Various reports of such compounds have previously been published in the literature, however they are typically prepared by reaction of salicylaldimines with titanium tetrachloride.[63–68] Given that the solvents were rigorously dried and stored, the source of the proton in our case is currently unclear.

Attempts to isolate complex **12** initially gave an intractable mixture of products but upon standing for an extended period crystallises from a mixture of tetrahydrofuran and petroleum spirits as dark red crystals. ^{1}H and ^{13}C NMR spectroscopy (CD_2Cl_2) show only a single set of resonances indicating the formation of only a single isomer. X-ray crystallography data again reveals an octahedral complex wherein the anionic oxygens adopt a *trans*-geometry while the remaining nitrogen donors and chloro ligands are in a *cis*-arrangement to each other (Fig. 2). The geometry, bond lengths and angles are broadly consistent with a previously reported titanium FI analogue bearing a benzyl N-substituent.[69] Furthermore, this geometry is in complete agreement with previously reported computational predictions on FI polymerisation catalysts, which suggest that for analogous complexes with low steric bulk that a *trans*-arrangement of the oxygen atoms and *cis*-arrangement of the nitrogen donors and chloro ligands is the most energetically favourable isomer for such a 2 : 1 complex.[70]

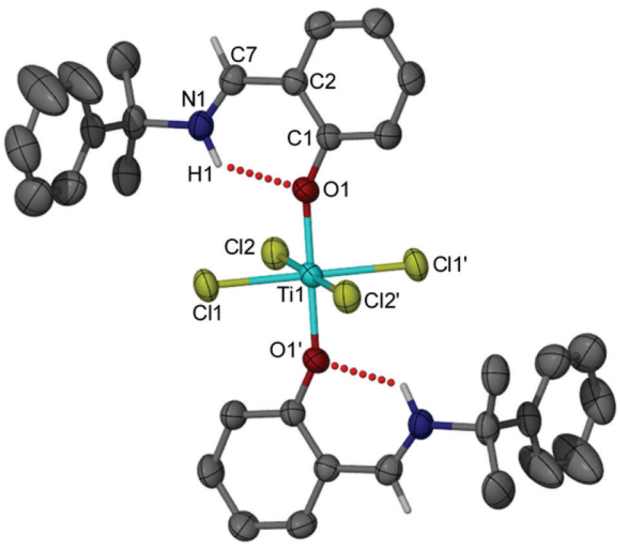


Fig. 1 Molecular structure of **11** (′ denotes symmetry operator 1 – *x*, –*y*, –*z*). Thermal ellipsoids are shown at the 50% probability level. Diffuse lattice solvent was removed in the refinement. All methyl and aromatic-ring hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ti1–O1,Cl1,Cl2 1.868(2), 2.3567(7), 2.3768(8), C2–C7 1.441(4), C7–N1 1.270(4), N1–H1 0.90(4), Cl1–Ti1–Cl2,Cl2′ 88.13(3), 91.87(3), O1–Ti1–Cl 88.60(6)–91.40(6), C1–O1–Ti1 152.35(18), C2–C7–N1 127.8(3).

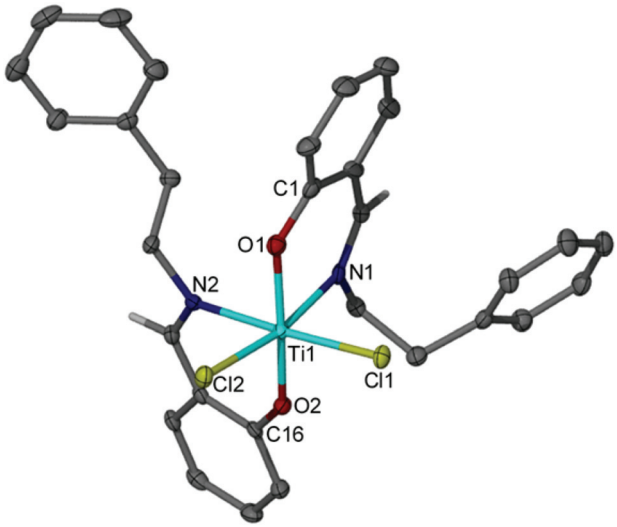
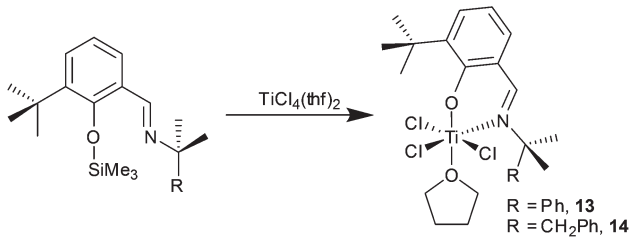
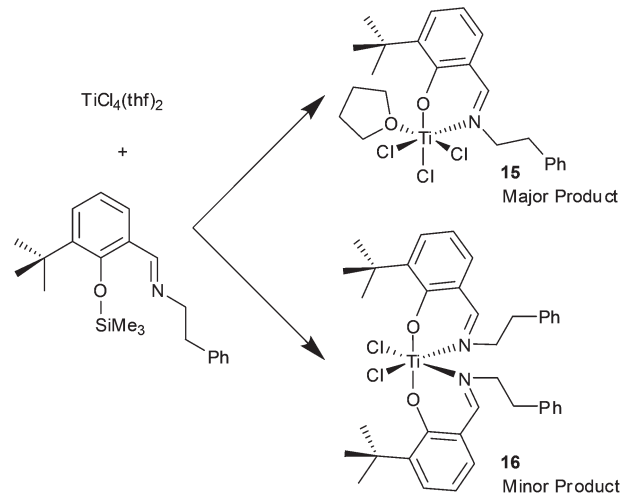


Fig. 2 Molecular structure of **12**. Thermal ellipsoids are shown at the 50% probability level. All methyl, methylene and aromatic-ring hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ti1–O1,O2,N1,N2, Cl1,Cl2 1.884(2), 1.851(2), 2.200(3), 2.181(3), 2.3006(10), 2.3211(11), O1, O2–Ti1–N1,N2$_{\text{chelate ring}}$ 82.61(10), 82.85(10), X–Ti1–Y$_{cis(\text{acyclic}),trans}$ 83.49(10)–99.61 (4), 168.88(11)–172.94(8), C1–O1–Ti1 138.1(2), C16–O2–Ti1 141.9(2).

Given these results, focus was shifted towards ligands bearing sterically bulky groups on the phenol 6-position. Complexes **13–15** were prepared by the method published by Lancaster and coworkers as red to dark red solids (Schemes 2 and 3) which were all moisture and air sensitive but thermally stable.[45,46] The crystal structure of a phenoxyaldehyde hydrolysis product are shown in the ESI.† All the complexes have been characterised by ^{1}H and ^{13}C NMR and microanalysis and in all cases could be recrystallised from tetrahydrofuran–petroleum spirit mixtures to yield crystals suitable for X-ray diffraction. Complex **14** adopts a distorted octahedral geometry with the electronically favourable mutually *trans*-oxygen arrangement while the chloride ligands are meridionally arranged around the titanium centre (Fig. 3). This geometry is consistent with previously reported low steric bulk mono(salicylaldiminato) titanium complexes.[45,46] Complex **13** is structurally similar to **14** and is shown in the ESI.† In both **13** and **14** the N-substituent is tertiary. Interestingly, complex **15** adopts an arrangement in which the ligating oxygen atoms now form a *cis*-arrangement while the chloride ligands are facially arranged (Fig. 4). Previously, it has been reported that this geometry is favoured for complexes with sterically bulky nitrogen substituents however in our case the bulk at the α-C (primary



Scheme 2 Synthesis of complexes **13** and **14**.



Scheme 3 Synthesis of complexes **15** and **16**.

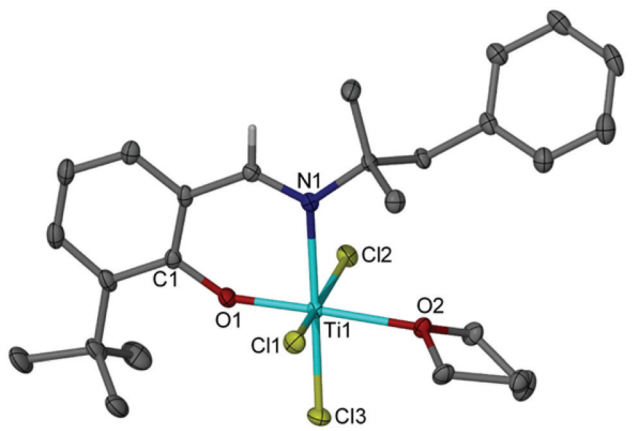


Fig. 3 Molecular structure of **14**. Thermal ellipsoids are shown at the 50% probability level. All methyl, methylene and aromatic-ring hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ti1–O1,O2 1.7806 (16), 2.2020(16), Ti1–N1 2.3028(19), Ti1–Cl 2.2944(7)–2.3073(8), O1–Ti1–N1 84.42(7), X–Ti1–$Y_{cis(acyclic),trans}$ 82.86(5)–96.85(3), 166.78(3)–179.29(5), C1–O1–Ti1 145.33(14).

substitution) from the nitrogen has significantly decreased bulk in comparison to complexes **13** and **14** (tertiary substitution).[46] Complex **15** shows a somewhat broadened ^{1}H NMR spectrum, particularly for the tetrahydrofuran signals, which

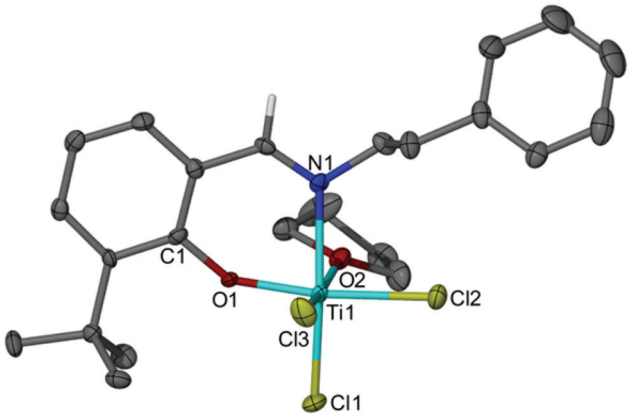


Fig. 4 Molecular structure of **15**. Thermal ellipsoids are shown at the 50% probability level. Disorder in the THF is omitted for clarity, as are all methyl, methylene and aromatic-ring hydrogen atoms. Selected bond lengths (Å) and angles (°): Ti1–O1,O2 1.776(4), 2.095(4), Ti1–N1 2.158(5), Ti1–Cl 2.242(2)–2.2900(18), O1–Ti1–N1 82.55(18), X–Ti1–$Y_{cis(acyclic),trans}$ 80.25(17)–101.98(8), 167.43(14)–172.42(15), C1–O1–Ti1 143.4(4).

may be indicative of a dynamic process in solution. This, combined with the decreased sterics at the α-C position, may suggest a less rigid N/Ph ethyl linker and in turn a more facile dynamism between different conformers of this group (relative to **13** and **14**). Alternatively a rapid isomerisation between the facial and meridional ligand arrangements could also account for this observation; this has not been explored any further however.

In addition, a small amount of crystalline bis-ligated complex **16** was isolated as a by-product of the preparation of **15**. X-ray crystallography reveals the expected *trans*-oxygen arrangement with mutually *cis*-nitrogen and chloride ligands (Fig. 5).[70] This structure confirms the computational predictions of Repo and co-workers.[69]

Ethylene oligomerisation and polymerisation

The bis-ligated and mono(salicylaldiminato) titanium complexes **11–15** were screened for ethylene oligomerisation/polymerisation activity in combination with methylaluminoxane (MAO). Table 1 shows that in all cases (entries 1–5), upon activation, ethylene polymerisation is the dominant mode of catalysis with polyethylene selectivity ranging from 95.9 to 99.9% polymer and with moderate productivity. For precatalysts **11** and **12** the moderate productivity (entries 1 and 2) is somewhat surprising given that they are direct analogues of the highly active FI catalysts. However, this result may be attributed to the lack of steric bulk at the *ortho*-position of the phenol ring; which has been shown to significantly improve productivity.[71] It was also suggested by a referee that ligand transfer to Al might be more facile without this steric protection, although we did not investigate this possibility. Compounds **13–15** show productivities (entries 3–5) broadly comparable with those previously published by Lancaster and coworkers and Owiny *et al.*, but, as these authors have previously highlighted, these

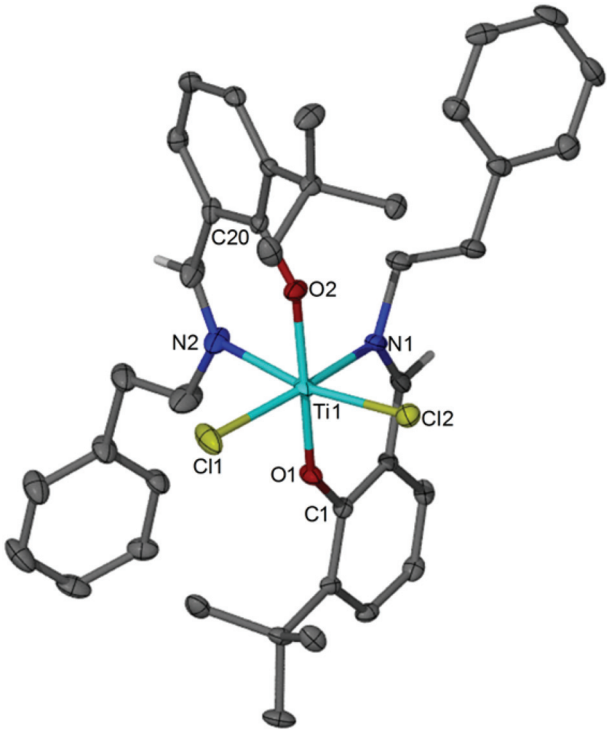


Fig. 5 Molecular structure of **16**. Thermal ellipsoids are shown at the 50% probability level. All methyl, methylene and aromatic-ring hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ti1–O1,O2,N1,N2, Cl1,Cl2 1.844(2), 1.856(2), 2.205(3), 2.192(3), 2.3144(10), 2.3087(10), O1,O2–Ti1–N1,$N2_{chelate\ ring}$ 81.63(9), 81.35(10), X–Ti1–$Y_{cis(acyclic),trans}$ 79.12(11)–98.57(4), 166.51(8)–170.41(11), C1–O1–Ti1 145.5(2), C20–O2–Ti1 144.3(2).

Table 1 Ethylene oligomerisation/polymerisation with **11–15** and MAO[a]

Entry	Catalyst	Productivity[b]	PE (wt%)	Olig (wt%)
1	**11**	7.6	99.9	0.1
2	**12**	6.0	99.9	0.1
3	**13**	29.2	99.6	0.4
4	**14**	7.7	99.6	0.4
5	**15**	9.8	95.9	4.1
6[c]	**15**	0.1	83.0	17.0

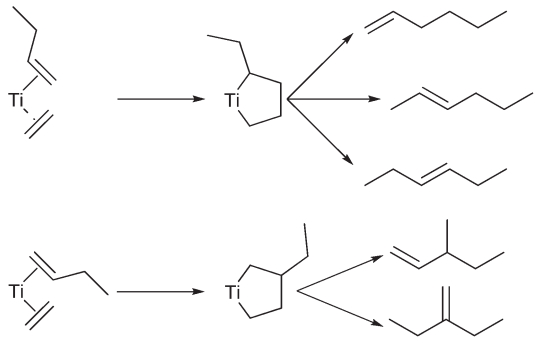
[a] Conditions: 20 μmol catalyst loading, toluene (50 mL), 300 equiv. MAO, 10 bar ethylene, 30 °C, 30 min. [b] kg product {(mol metal) bar}$^{-1}$. [c] 75 μmol catalyst loading, toluene (50 mL), 5 equiv. $AlEt_3$ in place of MAO, 20 bar ethylene, 55 °C, 30 min.

productivities are still orders of magnitudes less than their group IV metallocene or FI counterparts.[44–46]

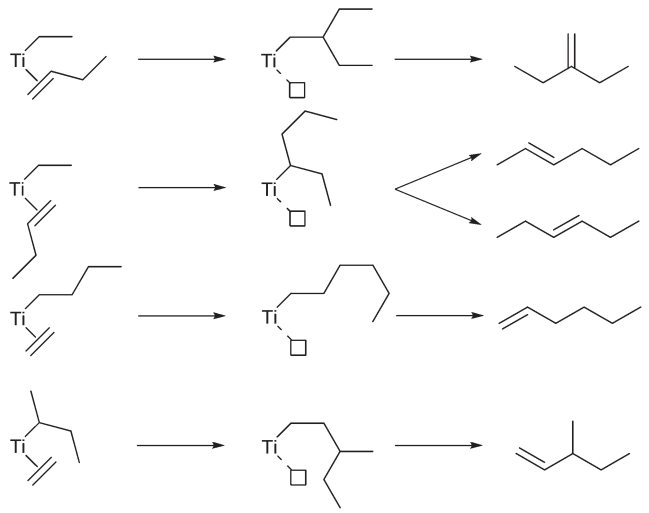
Even though these precatalysts clearly act predominantly as polymerisation systems; careful analysis of the liquid oligomer phase has been undertaken and yielded some interesting mechanistic insights. Precatalysts **11**, **12**, **14** and **15** all show a Schulz–Flory type distribution of even-carbon numbered linear alpha olefins in addition to some C_6 isomers and branched C_{10} products when activated with MAO. However, the Schulz–Flory constant for 1-butene/1-hexene ranges from 0.50–0.69 while the constants for 1-hexene/1-octene and 1-octene/1-decene are in the range of 0.15–0.38; this suggests that the formation of 1-butene is somewhat retarded compared to longer LAO's. We have previously reported a similar trend for a series of tridentate carbene/pyridine/carbene chromium complexes which oligomerise *via* an extended metallacycle mechanism (it should be noted that this observation is not a result of butene loss prior to analysis, see Experimental section).[72] In this and other studies, it has been proposed that for a metallacyclic mode of oligomerisation the sterically strained metallacyclopentane cannot adopt the required geometry for β-hydrogen shift and as such ring growth is kinetically favoured.[10,13,20,73–75] However, given the presence of a significant amount of C_6 isomers, most likely the result of ethylene/1-butene co-dimerisation which has been recently shown to result from a Cossee mechanism of dimerisation,[76] a process by which 1-butene and 1-hexene are formed by different modes of catalysis cannot be ruled out (discussed below).

Conversely, for precatalyst **13**, analysis of the liquid phase shows 14% 1-butene, 65% 1-hexene, 4% C_6 isomers, 5% 1-octene and the remainder as trace higher oligomers (C_{10+}). As previously discussed, studies by Hessen and co-workers have shown that cumyl-bearing mono(cyclopentadienyl) titanium complexes can undergo hemilabile metal–arene ring interactions that can effectively stabilise the key steps in the metallacycle mechanism which in turns yields a highly active and selective ethylene trimerisation catalysts.[29,32,34] While **13**, which also contains a nitrogen bearing cumyl functionality, does yield almost exclusively polymer, it is possible that a similar Ti–arene interaction is occurring within this system to give the liquid phase selectivity to 1-hexene.

Given that **15** yielded the highest amount of oligomers (Table 1, entry 5) and that the oligomeric distribution it displays is representative of the majority of catalysts discussed herein, it was selected for detailed mechanistic analysis. Here again we see evidence for metallacyclic oligomerisation. While the majority of the liquid phase C_6 fraction was 1-hexene (88%), a number of other products were determined by GC-FID and GC-MS. 3-Ethylbut-1-ene (5%), 3-methylpent-1-ene (2%), an unidentified internal hexene (2%), a unidentified hexadiene (1%), 3-methylpentane (1%), methylcyclopentane (1%) and trace hexane were also quantified. The majority of the C_6 products can be rationalised by the co-dimerisation of one unit of ethylene with one unit of 1-butene, as has been previously reported for other group IV catalysts such as the industrially relevant Alphabutol system ($Ti[OBu]_4/AlEt_3$).[1,2] However, from a mechanistic view point, this distribution can be readily ratified by either a metallacycle (Scheme 4) or a Cossee mechanism (Scheme 5). The presence of a hexadiene and methylcyclopentane are harder to reconcile. Hexadienes have previously been reported, in conjunction with the other co-dimers, as part of the Alphabutol co-dimer distribution (which occurs *via* a Cossee mechanism).[76,77] While methylcyclopentane has been shown to form during ethylene tri- and tetramerisation with PNP-Cr catalysts (*via* metallacycles).[21,78] Additionally, the alkanes 3-methylpentane and hexane most likely result from chain transfer from Ti to Al and then quenching during hydrolytic work up of the catalytic mixture. Finally, a proportion of



Scheme 4 Co-dimerisation of ethylene and 1-butene *via* a metallacycle mechanism.



Scheme 5 Co-dimerisation of ethylene and 1-butene *via* a Cossee mechanism.

branched C_{10} oligomers consisting of two isomers of 4-ethyl-octene and 5-methylnon-1-ene were detected; such species have previously been observed for other Ti and Cr catalysts and result from the co-trimerisation of ethylene/1-hexene *via* a metallacycle mechanism.[14,29,32,43] It is clear that this product distribution, which cannot be fully accounted for by either a Cossee or metallacycle mechanism, is highly suggestive of multiple modes of catalysis or multiple catalytically active species. Indeed, such a hypothesis has been previously suggested for polymerisation catalysts including mono(salicylaldiminato),[44,46] FI catalysts[79] and other analogous systems[80,81] in combination with MAO.

Given these results we were interested in exploring the possible mechanisms involved in the formation of various oligomers. The simplest method for probing oligomerisation catalysts involves the co-oligomerisation of a 1 : 1 mixture of ethylene : perdeuteroethylene.[9,19] Under these conditions a Cossee based mechanism will yield an isotopomer distribution containing H/D scrambling as a result of the β-hydride elimination and product release. Conversely, no H/D transfer between oligomers occurs in the metallacycle mechanism, and as such no H/D scrambled isotopomers are formed. In our

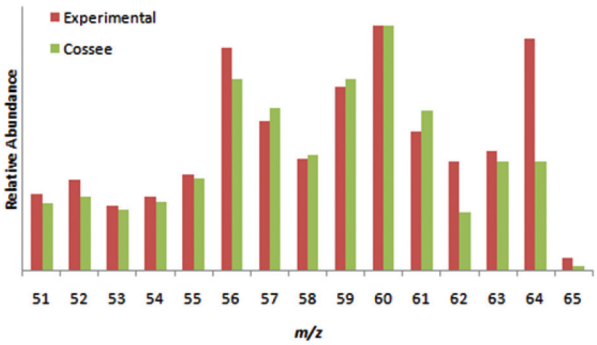


Fig. 6 Experimental and predicted mass spectrum of 1-butene produced from C_2H_4/C_2D_4 with **15**/MAO. Data normalised to mol. Ion *m*/*z* 60.

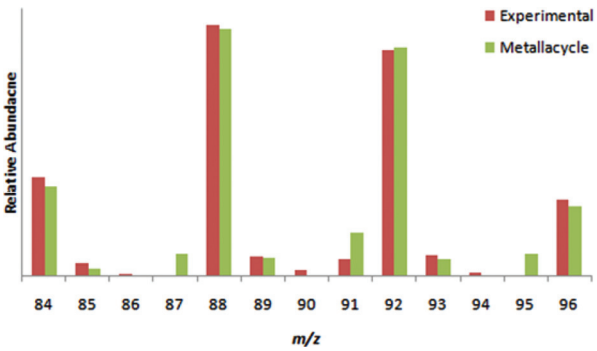


Fig. 7 Experimental and predicted mass spectrum of 1-hexene produced from C_2H_4/C_2D_4 with **15**/MAO.

work, we have tested the co-oligomerisation of 1 : 1 $H_2C{=}CH_2$ and $D_2C{=}CD_2$ with **15** in conjunction with MAO focusing on the 1-butene and 1-hexene formed. In the case of 1-butene, the theoretical mass spectrum resulting from a Cossee mechanism and the experimentally observed ion distribution are shown in Fig. 6 (see ESI† for the derivation of the theoretical mass spectrum). A very good match between the theoretical and experimental distribution exists, indicating that the formation of 1-butene with this catalytic system occurs by a Cossee mechanism. Significant over expression does result for ions *m*/*z* 64 and 62, which is consistent with *m*/*z* for fully deuterated 1-butene and loss of one deuteron from this species. This has been confirmed as a d_8-1-butene impurity in the perdeuteroethylene. Conversely, GC-MS analysis of the 1-hexene formed from the same experiment is shown in Fig. 7. Comparison of the theoretical mass spectrum for a metallacycle mechanism with the experimentally observed data shows a strong correlation indicating that this oligomer most likely results from a metallacyclic mechanism (see ESI† for the derivation of the theoretical mass spectrum). These results show that a myriad of catalytic species can form from a well characterised precatalyst system upon activation, each yielding a different mode of catalysis and hence a different selectivity for ethylene conversion.

As a significant amount of dimers and co-dimers were formed with a distribution consistent with that of an Alphabutol-type catalytic system, and as we have shown that

the mechanism of dimerisation of our system is the same, it was of interest to see how **15** would compare under similar conditions used in the Alphabutol process ($AlEt_3$ activation) and that if by changing the co-catalyst a more selective system could be realised. Testing of **15** with triethylaluminium co-catalyst (Table 1, entry 6) gave high percentages of polymer (83%) and a poor productivity. The 17% yield of liquid phase oligomers consisted of only 1-butene (85%) and co-dimers (15%) and no higher fractions. In the light of this result it is plausible to suggest that in earlier runs the 1-butene and co-dimers most likely result from activation with the free trimethylaluminium in MAO, yielding a species that dimerises by a Cossee mechanism. The 1-hexene, and also the higher LAOs, which are not present in the absence of MAO, most likely result from activation with MAO and the probable formation of a cationic active species.

Conclusions

A series of Ti(IV) complexes bearing either one or two phenoxy-imine ligands have been prepared and characterised. X-ray crystallography on a range of complexes has shown structural features in agreement with previously reported complexes.

Activation with MAO gives catalytic species with moderate activities for ethylene oligomerisation and polymerisation. While it is clear that polyethylene formation is the dominant process, with over 95% polymer formation in all cases of MAO activation, close examination of the short chained oligomers reveals a variety of operative mechanisms. Complexes **11**, **12**, **14** and **15** all show Schulz–Flory distributions with reduced 1-butene formation while complex **13** shows a similar distribution but significantly enriched in 1-hexene. We have suggested that this enrichment could result from a metallacyclic mechanism, aided by an arene–Ti interaction similar to systems reported by Hessen and co-workers.

Complexes **11**, **12**, **14** and **15** also show a series of C_6 isomers consistent with the co-dimerisation of ethylene and 1-butene. Deuterium labelling studies with complex **15** have shown that the 1-butene formed by the catalyst most likely results from a Cossee mechanism while the isotopomer distribution of 1-hexene from the same experiment supports a metallacycle mechanism. These experiments clearly show that even from a well characterised precatalyst species, upon activation, a range of catalytic species can form each with a different mode of catalysis. These results show that certain classes of titanium catalysts have a propensity for metallacyclic oligomerisation, as has been established for chromium, but the key to selectivity is suppression of polymer formation. However, it is still not well understood which factors control the switch from selective oligomerisation to polymerisation.

Experimental

General

All manipulations were performed under an atmosphere of UHP argon (BOC gases) using standard Schlenk techniques or in an MBraun glovebox unless otherwise stated. Solvents, excluding dichloromethane, were purified by passage through an Innovative Technologies purification system and, where appropriate, stored over a sodium mirror. Anhydrous dichloromethane was purchase from Sigma-Aldrich and stored over 3 Å molecular sieves. CP grade ethylene (BOC gases) was purified by passage through a column of activated 3 Å molecular sieves and alumina. NMR spectra were recorded on a Varian Mercury Plus NMR spectrometer operating at 300 MHz (^{1}H) or 75 MHz (^{13}C) at room temperature. MAO was supplied by Ablemarle as a 10% solution in toluene.

Preparation of 2-(OH)C_6H_4C═N(cumyl) (1). Cumyl amine (0.63 g, 4.67 mmol) taken up in 15 mL of diethyl ether and stirred over molecular sieves. Salicylaldehyde (0.57 g, 4.67 mmol) in 15 mL of diethyl ether was added as a stream. The reaction mixture was stirred overnight. Diethyl ether was removed *via* canula filtration and the molecular sieves washed with 2 × 8 mL of diethyl ether. The supernatant and washings were combined and the volatiles removed *in vacuo* to yield a yellow residue. The residue was recrystallised from 10 mL petroleum spirits at −20 °C to give the title compound as long yellow needles which were dried under reduced pressure with an 87% yield (0.98 g, 4.07 mmol). ^{1}H NMR (CD_2Cl_2, 299.89 MHz): δ 13.99 (s, 1H, O*H*), 8.31 (s, 1H, C*H*═N), 7.23–7.42 (m, 7H, *aryl-H*), 6.84–6.94 (m, 2H, *aryl-H*), 1.69 (s, 6H, C(CH_3)$_2$). ^{13}C NMR (CD_2Cl_2, 75.41 MHz): δ 162.4 (*C*═N), 161.9 (*C*–OH), 147.3, 119.6 (*aryl-C$_{ipso}$*), 117.3, 118.9, 126.5, 127.3, 128.9, 132.2, 132.6 (*aryl-C*), 63.1 (*C*(CH$_3$)$_2$), 30.0 (C(*C*H$_3$)$_2$). MS (electron ionisation): *m*/*z* 239 [M]$^+$.

Preparation of 2-(OH)C_6H_4C═N(CH_2CH_2Ph) (2). To 2-phenethylamine (2.53 g, 20.7 mmol) was added salicylaldehyde (2.51 g, 20.7 mmol) at 120 °C with stirring. The resulting yellow liquid was stirred overnight and then extracted with 40 mL petroleum spirits. The volatiles were removed under reduced pressure and the residue flash distilled under full pump vacuum at 190 °C (oil bath temperature) to give the title product as a yellow liquid, in 86% yield (4.03 g, 17.9 mmol), which solidified upon standing. ^{1}H NMR (CD_2Cl_2, 299.89 MHz): δ 13.36 (s, 1H, O–*H*), 8.25 (s, 1H, N═C*H*), 7.19–7.34 (m, 7H, *aryl-H*), 6.85–6.92 (m, 2H, *aryl-H*), 3.84 (td, *J* = 1.2, 6.90 Hz, 2H, NCH_2), 3.00 (t, *J* = 6.90 Hz, 2H, PhCH_2). ^{13}C NMR (C_6D_6, 75.41 MHz): δ 165.7 (*C*═N), 162.4 (*C*–OH), 140.0, 119.6 (*aryl-C$_{ipso}$*), 117.9, 118.8, 126.9, 129.0, 129.5, 131.8, 132.8 (*aryl-C*), 61.6 (N*C*H$_2$), 37.8 (Ph*C*H$_2$). MS (electron ionisation): *m*/*z* 225 [M]$^+$.

Preparation of 2-(OH)-3-(*t*-butyl)C_6H_3C═N(cumyl) (3). To 3-*t*-butylsalicylaldehyde (0.46 g, 2.57 mmol) in 8 mL of diethyl ether over 3 Å molecular sieves was added cumylamine (0.35 g, 2.57 mmol) in 8 mL of diethyl ether with stirring. The bright yellow reaction mixture was stirred overnight. The resulting solution was separated *via* canula filtration and the residue extracted with 2 × 10 mL of diethyl ether. The organic portions were combined and concentrated under reduced pressure to yield a pale yellow solid. The product was purified by recrystallisation from hot petroleum spirits followed by flash distillation at 240 °C (oil bath temperature) under full vacuum to give

3 as a pale yellow solid in 68% yield (0.52 g, 1.74 mmol). ^{1}H NMR (CD_2Cl_2, 299.89 MHz): δ 14.60 (s, 1H, O*H*), 8.29 (s, 1H, N=C*H*), 7.07–7.44 (m, 6H, *aryl-H*), 7.08 (dd, J = 1.80, 7.50 Hz, 1H, *aryl-H*), 6.79 (t, J = 7.50, 1H, *aryl-H*), 1.70 (s, 6H, C(CH_3)$_2$), 1.42 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (CD_2Cl_2, 75.41 MHz): δ 163.2 (N=*C*H), 119.2, 137.7, 147.2, 161.1 (*aryl-C*$_{ipso}$), 118.0, 126.4, 127.2, 128.8, 129.6, 130.4 (*aryl-C*), 62.7 (*C*(CH_3)$_2$), 35.1 (*C*(CH_3)$_3$), 29.9 (C(*C*H_3)$_2$), 29.5 (C(*C*H_3)$_3$). MS (electron ionisation): m/z 295 [M]$^+$.

Preparation of 2-(OH)-3-(*t*-butyl)C_6H_3C=N(CMe_2CH_2Ph) (4). To 3-*t*-butylsalicylaldehyde (1.06 g, 5.92 mmol) in 3 mL of petroleum spirits was added 2-methyl-3-phenylpropyl-2-amine (0.88 g, 5.92 mmol) with stirring to generate a bright yellow solution. The mixture was heated to 80 °C for 1 hour and then increased to 120 °C overnight. The bright yellow residue was extracted with 20 mL of petroleum spirits, concentrated under reduced pressure and purified by flash distillation at 216 °C under full vacuum to give **4** as a bright yellow liquid in 72% yield (1.31 g, 4.25 mmol). ^{1}H NMR (CD_2Cl_2, 299.89 MHz): δ 14.76 (s, 1H, O*H*), 8.13 (s, 1H, N=C*H*), 7.04–7.32 (m, 7H, *aryl-H*), 6.77 (t, J = 8.10 Hz, 1H, *aryl-H*), 2.91 (s, 2H, CH_2), 1.44 (s, 9H, C(CH_3)$_3$), 1.32 (s, 6H, C(CH_3)$_2$). ^{13}C NMR (CD_2Cl_2, 75.41 MHz): δ 161.7 (N=*C*H), 119.1, 137.7, 138.1, 161.3 (*aryl-C*$_{ipso}$), 117.8, 126.7, 128.1, 129.4, 130.1, 131.1 (*aryl-C*), 60.4 (*C*(CH_3)$_2$), 50.0 (*C*H_2), 35.1 (*C*(CH_3)$_3$), 29.5 (C(*C*H_3)$_3$), 27.0 (C(*C*H_3)$_2$). MS (electron ionisation): m/z 309 [M]$^+$.

Preparation of 2-(OH)-3-(*t*-butyl)C_6H_3C=N(CH_2CH_2Ph) (5). To 3-*t*-butylsalicylaldehyde (0.44 g, 2.46 mmol) was added 2-phenethylamine (0.30 g, 2.46 mmol) with stirring at 120 °C. The resulting bright yellow liquid was stirred overnight and then purified *via* flash distillation at 215 °C under full vacuum to give the title compound **5** in 73% yield (0.50 g, 1.78 mmol). ^{1}H NMR ($CDCl_3$, 299.89 MHz): δ 13.58 (s, 1H, O*H*), 8.28 (s, 1H, N=C*H*), 7.16–7.34 (m, 7H, *aryl-H*), 6.79 (t, J = 7.80, 1H, *aryl-H*), 3.76 (t, J = 7.20 Hz, 2H, NCH_2), 2.99 (t, J = 7.20 Hz, 2H, PhCH_2), 1.41 (s, 9H, C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, 75.41 MHz): δ 166.3 (N=*C*H), 118.7, 126.7, 128.8, 129.1, 129.5, 131.0, 160.6, 164.9 (*aryl-C*), 100.1 (N*C*H_2), 37.1 (Ph*C*H_2), 35.1 (*C*(CH_3)$_3$), 29.6 (C(*C*H_3)$_3$). MS (electrospray ionisation): m/z 382.2 [M]$^+$.

Preparation of 2-($OSiMe_3$)C_6H_4C=N(cumyl) (6). Compound **1** (0.98 g, 4.07 mmol) was taken up in 40 mL of petroleum spirits and cooled to −95 °C with stirring. *n*-Butyllithium (2.6 mL, 1.6 M in hexanes, 4.07 mmol) was added dropwise. The mixture was allowed to return to room temperature and stirred for four hours. The supernatant was removed *via* canula filtration and the precipitated lithium salt washed with 10 mL of petroleum spirits. The white solid was dried under reduced pressure and then taken up in 30 mL of tetrahydrofuran. Trimethylsilyl chloride (5 mL) was added and the mixture heated to 55 °C overnight. The volatiles were removed *in vacuo* and the remaining residue extracted with 3 × 5 mL petroleum spirits. The resulting yellow solution was concentrated and the resulting yellow residue purified by flash distillation at 240 °C under full vacuum to give the title compound as a colourless liquid in 52% yield (0.66 g, 2.12 mmol). Attempts to obtain mass spectroscopy of the product yielded only the hydrolysed species. ^{1}H NMR (CD_2Cl_2, 299.89 MHz): δ 8.53 (s, 1H, C*H*=N), 8.00 (dd, 1H, J = 1.8, 6.0 Hz, *aryl-H*), 7.20–7.45 (m, 6H, *aryl-H*), 7.02 (t, 1H, J = 7.5 Hz, *aryl-H*), 6.83 (dd, 1H, J = 1.2, 6.9 Hz, *aryl-H*), 1.63 (s, 6H, C(CH_3)$_2$), 0.20 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR (CD_2Cl_2, 75.41 MHz): δ 148.8, 155.7, 162.5 (*aryl-C*$_{ipso}$), 153.9 (*C*=N), 120.7, 122.2, 126.8, 127.5, 128.6, 128.9, 131.9 (*aryl-C*), 63.3 (*C*(CH_3)$_2$), 30.0 (C(*C*H_3)$_2$), 0.4 (Si(*C*H_3)$_3$).

Preparation of 2-($OSiMe_3$)C_6H_4C=N(CH_2CH_2Ph) (7). Compound **2** (4.03 g, 17.9 mmol) in 80 mL of petroleum spirits was cooled to −95 °C with stirring and *n*-butyllithium (11.2 mL, 1.6 M in hexanes, 17.9 mmol) was added dropwise. The white suspension was allowed to return to room temperature and stirred for five hours. The supernatant was removed *via* canula filtration and the remaining off-white solid was washed with 2 × 10 mL of petroleum spirits and dried briefly *in vacuo*. The white solid was taken up in 50 mL of tetrahydrofuran at 0 °C and 5 mL trimethylsilyl chloride added. The mixture was heated to 55 °C overnight. The volatiles were removed under reduced pressure and the residue extracted with 3 × 10 mL of petroleum spirits. The extracts were condensed and the remaining residue was flash distilled under full pump vacuum at 220 °C (oil bath temperature) to give **7** as a colourless liquid in 63% yield (3.35 g, 11.3 mmol). Attempts to obtain mass spectroscopy of the product yielded only the hydrolysed species. ^{1}H NMR (CD_2Cl_2, 299.89 MHz): δ 8.53 (s, 1H, N=C*H*), 7.92 (dd, J = 1.80, 6.00 Hz, 1H, *aryl-H*), 7.19–7.33 (m, 6H, *aryl-H*), 7.01 (t, J = 7.80 Hz, 1H, *aryl-H*), 6.84 (dd, J = 1.20, 6.90 Hz, 1H, *aryl-H*), 3.86 (td, J = 1.2, 7.20 Hz, 2H, NCH_2), 3.00 (t, J = 7.20 Hz, 2H, PhCH_2), 0.26 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR (CD_2Cl_2, 75.41 MHz): δ 140.9, 155.6, 165.7 (*aryl-C*$_{ipso}$), 157.8 (N=*C*H), 120.6, 122.2, 126.5, 127.8, 128.8, 129.5, 132.0 (*aryl-C*), 64.0 (N*C*H_2), 38.1 (Ph*C*H_2), 0.47 (Si(*C*H_3)$_3$).

Preparation of 2-($OSiMe_3$)-3-(*t*-butyl)C_6H_3C=N(cumyl) (8). Compound **3** (1.13 g, 3.83 mmol) was taken up in 20 mL of petroleum spirits and cooled to −95 °C with stirring. *n*-Butyllithium (2.4 mL, 1.6 M in hexanes, 3.83 mmol) was added dropwise, upon complete addition the mixture was allowed to return to room temperature and stirred for six hours. The resulting white solid was isolated by canula filtration and dried under reduced pressure. The solid was then taken up in 15 mL of tetrahydrofuran and 2.6 mL of trimethylsilyl chloride was added before heating the mixture to 60 °C overnight. Upon cooling, the volatiles were removed *in vacuo* and the yellow residue was extracted with 20 mL of petroleum spirits to remove any lithium chloride. The organic phase was concentrated and the resulting yellow residue recrystallised from 7 mL of petroleum spirits at −40 °C to give **8** as a pale yellow solid in 72% yield (1.01 g, 2.76 mmol). ^{1}H NMR (CD_2Cl_2, 299.89 MHz): δ 8.50 (s, 1H, N=C*H*), 7.90 (dd, J = 2.01, 7.20 Hz, 1H, *aryl-H*), 7.21–7.44 (m, 6H, *aryl-H*), 6.95 (t, J = 7.20 Hz, *aryl-H*), 1.64 (s, 6H, C(CH_3)$_2$), 1.39 (s, 9H, (C(CH_3)$_3$), 0.22 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR (CD_2Cl_2, 75.41 MHz): δ 129.4, 141.4, 149.1, 154.8 (*aryl-C*$_{ipso}$), 154.7 (N=*C*H), 121.6, 126.5, 126.6, 126.7, 128.5, 129.9 (*aryl-C*), 63.2 (*C*(CH_3)$_2$), 35.2 (*C*(CH_3)$_3$), 30.8

($C(CH_3)_3$), 30.1 ($C(CH_3)_2$), 1.98 ($Si(CH_3)_3$). MS (electron ionisation): m/z 352 $[M]^+$.

Preparation of 2-($OSiMe_3$)-3-(*t*-butyl)$C_6H_3C{=}N(CMe_2CH_2Ph)$ (9). Compound **9** was prepared according to the procedure outlined for compound **10**, upon extraction with petroleum spirits and removal of the volatiles *in vacuo* a white viscous liquid was isolated and identified as the title compound. 52% yield (0.85 g, 2.23 mmol). ^{1}H NMR (CD_2Cl_2, 299.89 MHz): δ 8.27 (s, 1H, N=C*H*), 7.88 (dd, J = 1.80 Hz, 6.00 Hz, 1H, *aryl-H*), 7.38 (dd, J = 1.80 Hz, 6.00 Hz, 1H, *aryl-H*), 7.10–7.22 (m, 5H, *aryl-H*), 6.96 (td, J = 0.90 Hz, 7.65 Hz, 1H, *aryl-H*), 2.91 (s, 2H, CH_2), 1.39 (s, 9H, $C(CH_3)_3$), 1.26 (s, 6H, $C(CH_2)_2$), 0.22 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR (CD_2Cl_2, 75.41 MHz): δ 129.5, 139.2, 141.4, 154.8 (*aryl-*C_{ipso}), 153.0 (N=*C*H), 121.6, 126.3, 126.5, 127.9, 129.7, 131.2 (*aryl-C*), 61.3 ($C(CH_3)_2$), 50.5 (CH_2), 35.1 ($C(CH_3)_3$), 30.8 ($C(CH_3)_3$), 27.3 (($C(CH_3)_2$), 2.06 ($Si(CH_3)_3$). MS (electron ionisation): m/z 382 $[M - H]^+$.

Preparation of 2-($OSiMe_3$)-3-(*t*-butyl)$C_6H_3C{=}N(CH_2CH_2Ph)$ (10). Compound **5** (0.50 g, 1.78 mmol) was taken up in 6 mL of petroleum spirits and cooled to −95 °C with vigorous stirring. *n*-Butyllithium (1.12 mL, 1.6 M in hexanes, 1.78 mmol) was added dropwise to generate a white suspension. The mixture was allowed to return to room temperature and stirred for two hours. The supernatant was removed *via* canula filtration and the remaining white solid was dried *in vacuo*. The solid was taken up in 5 mL of tetrahydrofuran and 1.2 mL trimethylsilyl chloride added before heating to 55 °C overnight. The volatiles were removed under reduced pressure and the remaining yellow residue was extracted with 2 × 3 mL of petroleum spirits. The organic extracts were concentrated and the residue recrystallised at −80 °C from petroleum spirits to give **10** as a white solid in 32% yield (0.20 g, 0.57 mmol). ^{1}H NMR (CD_2Cl_2, 299.89 MHz): δ 8.48 (s, 1H, N=C*H*), 7.65 (d, J = 7.80 Hz, 1H, *aryl-C*), 7.38 (d, J = 7.80 Hz, 1H, *aryl-C*), 7.16–7.32 (m, 5H, *aryl-C*), 6.94 (t, J = 7.80 Hz, 1H, *aryl-C*), 3.85 (t, J = 7.50 Hz, 2H, NCH_2), 3.01 (t, J = 7.50 Hz, 2H, $PhCH_2$), 1.39 (s, 9H, $C(CH_3)_3$), 0.25 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR (CD_2Cl_2, 75.41 MHz): δ 159.8 (N=*C*H), 121.7, 126.4, 128.7, 129.1, 129.4, 129.9, 140.8, 141.4 (*aryl-C*), 63.7 (NCH_2), 38.0 ($PhCH_2$), 35.1 ($C(CH_3)_3$), 30.6 ($C(CH_3)_3$), 1.90 ($Si(CH_3)_3$). MS (electrospray ionisation): m/z 354.3 $[M]^+$.

Preparation of complex 11. Compound **6** (0.21 g, 0.66 mmol) was taken up in 6 mL of dichloromethane and added dropwise to $TiCl_4(thf)_2$ (0.22 g, 0.66 mmol) in 6 mL of dichloromethane at −95 °C with stirring. The reaction mixture was stirred overnight at room temperature. The volatiles were removed from the dark red solution at reduced pressure and the resulting red solid was washed with 2 × 10 mL of petroleum spirits and 12 mL of dichloromethane. The remaining red powder was dried *in vacuo* to give **11** in 26% yield (0.06 g, 0.07 mmol). The complex was crystallised from a dichloromethane solution by slow diffusion of petroleum spirits to give large red needles suitable for X-ray diffraction. ^{1}H NMR (CD_2Cl_2, 299.89 MHz): δ 12.97 (br s, 2H, N^+–*H*–O^-), 8.03 (d, J = 7.80 Hz, 2H, *aryl*-H), 7.84 (s, 2H, C*H*=N), 7.42–7.79 (m, 10H, *aryl-H*), 7.22 (dd, J = 1.80, 6.30 Hz, 2H, *aryl-H*), 7.00 (td, J = 1.20, 6.90, 2H, *aryl-H*), 2.10 (s, 12H, $C(CH_3)_2$). ^{13}C NMR (CD_2Cl_2, 75.41 MHz): δ 115.2, 141.7, 170.5 (*aryl-*C_{ipso}), 166.4 (*C*=N), 121.2, 126.9, 127.3, 129.5, 129.8, 135.7, 140.4 (*aryl-C*), 66.1 ($C(CH_3)_2$), 29.6 ($C(CH_3)_2$), 0.4 ($Si(CH_3)_3$). Anal. calcd for $C_{32}H_{34}N_2O_2TiCl_4$: C 57.51, N 4.19, H 5.13. Found: C 57.40, N 3.93, H 5.43.

Preparation of complex 12. $TiCl_4(thf)_2$ (0.70 g, 2.10 mmol) was taken up in 15 mL of dichloromethane and cooled to −95 °C with stirring. Compound **7** (0.62 g, 2.10 mmol) in 15 mL of dichloromethane was added dropwise and upon complete addition the resulting orange solution was allowed to warm to room temperature and stirred overnight. The volatiles were removed from the resulting deep red solution under reduced pressure to yield a dark red honeycomb which was crushed and washed with 3 × 10 mL of petroleum spirits. The resulting red solid was dried *in vacuo* for 3.5 hours. The solid was then taken up in 3 mL of tetrahydrofuran and petroleum spirits added until precipitation began, the mixture was then cooled to −20 °C to generate a red oil. The mother liquor was decanted, concentrated and upon standing generated the title compound in 20% yield (0.12 g, 0.21 mmol) as a dark red crystalline solid suitable for X-ray crystallography. ^{1}H NMR (CD_2Cl_2, 299.89 MHz): δ 7.87 (s, 2H, N=C*H*), 7.61 (t, J = 3.60 Hz, 2H, *aryl-H*), 6.96–7.32 (m, 16H, *aryl-H*), 3.82 (m, 4H, NCH_2), 3.07 (m, 4H, $PhCH_2$). ^{13}C NMR (CD_2Cl_2, 75.41 MHz): δ 166.5 (N=*C*H), 117.0, 122.5, 124.3, 127.0, 128.9, 129.4, 129.9, 134.6, 136.8, 138.7 (*aryl-C*), 65.4 (NCH_2), 37.6 ($PhCH_2$). Anal. calcd for $C_{30}H_{28}N_2O_2TiCl_2$: C 46.13, N 3.36, H 5.81. Found: C 46.39, N 3.31, H 5.68.

Preparation of complex 13. Compound **8** (0.04 g, 1.09 mmol) was taken up in 15 mL of tetrahydrofuran and added to $TiCl_4(THF)_2$ (0.36 g, 1.09 mmol) in 15 mL of tetrahydrofuran at −95 °C with vigorous stirring. The reaction mixture was allowed to return to room temperature and stirred overnight. The volatiles were removed under reduced pressure from the dark red reaction mixture to yield a dark red honeycomb. The honeycomb was washed with 15 mL of petroleum spirits and then precipitated from tetrahydrofuran with petroleum spirits. The supernatant was decanted and the remaining dark red solid dried *in vacuo* to give **13** in 57% yield (0.33 g, 0.63 mmol). Crystals suitable for X-ray diffraction were prepared by recrystallisation of **13** from hot a mixture of petroleum spirits and tetrahydrofuran. ^{1}H NMR (CD_2Cl_2, 299.89 MHz): δ 8.22 (s, 1H, N=C*H*), 7.14–7.37 (m, 8H, *aryl-H*), 3.92 (m, 4H, $O(CH_2)_2(CH_2)_2$), 2.08 (s, 6H, $C(CH_3)_2$), 1.87 (m, 4H, $O(CH_2)_2(CH_2)_2$), 1.52 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (CD_2Cl_2, 75.41 MHz): δ 169.4 (N=*C*H), 127.5, 137.4, 148.6, 168.0 (*aryl-*C_{ipso}), 125.7, 126.9, 128.1, 129.3, 133.5, 134.1 (*aryl-C*), 72.7 ($C(CH_3)_2$), 70.4 $O(CH_2)_2(CH_2)_2$), 35.4 ($C(CH_3)_3$), 31.3 $O(CH_2)_2(CH_2)_2$), 29.6 ($C(CH_3)_3$), 25.9 ($C(CH_3)_2$). Anal. calcd for $C_{24}H_{32}NO_2TiCl_3$: C 55.36, N 2.69, H 6.19. Found: C 55.38, N 2.43, H 5.91.

Preparation of complex 14. To $TiCl_4(thf)_2$ (0.66 g, 1.99 mmol) in 15 mL of tetrahydrofuran was added dropwise compound **9** (0.76 g, 1.99 mmol) in 15 mL of tetrahydrofuran at −95 °C with vigorous stirring. The reaction was gradually

allowed to return to room temperature and stirred overnight. The resulting dark red solution was concentrated and petroleum spirits added to precipitate a dark brown powder. The powder was isolated by filtration and dried under reduced pressure. The dark brown powder was recrystallised from hot tetrahydrofuran/petroleum spirits to give the title product in 35% yield (0.37 g, 0.69 mmol) as dark red crystals suitable for x-ray diffraction. ^{1}H NMR (CD_2Cl_2, 299.89 MHz): δ 7.70 (s, 1H, N=C*H*), 7.72 (dd, J = 1.50, 7.95 Hz, 1H, *aryl-H*), 7.14–7.29 (m, 6H, *aryl-H*), 7.00 (dd, J = 1.20, 7.65 Hz, 1H, *aryl-H*), 3.91 (m, 4H, O(CH_2)$_2$(CH_2)$_2$), 3.23 (s, 2H, CH_2), 1.88 (m, 4H, O(CH_2)$_2$(CH_2)$_2$), 1.76 (s, 6H, C(CH_3)$_2$), 1.52 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (CD_2Cl_2, 75.41 MHz): δ 165.4 (N=*C*H), 125.9, 127.6, 128.4, 128.7, 129.4, 131.0, 131.6, 133.5, 133.8, 136.9 (*aryl-C*), 70.3 (*C*(CH_3)$_2$), 68.2 (O(*C*H_2)$_2$(CH_2)$_2$), 48.5 (*C*H_2), 35.5 (C(*C*H_3)$_3$), 29.8 ((C(*C*H_3)$_2$), 29.2 (O(CH_2)$_2$(*C*H_2)$_2$), 26.0 (C(*C*H_3)$_3$). Anal. calcd for $C_{25}H_{34}NO_2TiCl_3$: C 56.27, N 2.63, H 6.42. Found: C 56.12, N 2.61, H 6.37.

Preparation of complex 15. Compound **10** (0.37 g, 1.04 mmol) was taken up in 7 mL of dichloromethane and added dropwise to $TiCl_4(thf)_2$ (0.35 g, 1.04 mmol) in 6 mL of dichloromethane at −95 °C with vigorous stirring. The reaction mixture slurry was allowed to return to room temperature and stirred overnight. The volatiles were removed under reduced pressure and the resulting dark red honeycomb was crushed and washed with 3 × 15 mL portions of petroleum spirits. The residual solvent was removed *in vacuo* and the resulting red solid was taken up in 5.5 mL dichloromethane with one drop of tetrahydrofuran added. 4 mL of petroleum spirits was added to precipitate a red solid which was isolated *via* canula filtration and dried under reduced pressure to give **15** in 49% yield (0.26 g, 0.51 mmol). Large red block crystals suitable for X-ray diffraction were grown by vapour diffusion of petroleum spirits into a tetrahydrofuran solution of **15**. Additionally, layering of the supernatant with petroleum spirits yielded a small quantity of dark red needles which were suitable for X-ray diffraction and determined to be the bis-ligand complex **16**. ^{1}H NMR (CD_2Cl_2, 299.89 MHz): δ 7.95 (s, 1H, N=C*H*), 7.61 (dd, J = 1.80, 5.70 Hz, 1H, *aryl-H*), 7.09–7.31 (m, 7H, *aryl-H*), 4.27 (t, J = 7.20 Hz, 2H, NCH_2), 4.18 (bs, 4H, O(CH_2)$_2$(CH_2)$_2$), 3.20 (t, J = 7.20 Hz, 2H, PhCH_2), 1.94 (bs, 4H, O(CH_2)$_2$(CH_2)$_2$), 1.51 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (CD_2Cl_2, 75.41 MHz): δ 167.1 (N=*C*H), 129.5, 137.9, 138.9 (*aryl-C$_{ipso}$*), 124.3, 127.1, 129.0, 129.7, 132.7, 133.8 (*aryl-C*), 74.3 (N*C*H_2), 65.9 (O(*C*H_2)$_2$(CH_2)$_2$), 37.8 (Ph*C*H_2), 35.3 (*C*(CH_3)$_3$, 29.7 (O(CH_2)$_2$(*C*H_2)$_2$), 25.9 (C(*C*H_3)$_3$). Anal. calcd for $C_{23}H_{30}NO_2TiCl_3$: C 54.52, N 2.76, H 5.97. Found: C 54.57, N 2.61, H 5.95.

Ethylene polymerisation/oligomerisation

A 0.3 L stainless steel Parr 5500 Compact Mini Reactor was preheated to 120 °C and flushed with four vacuum/argon cycles and two ethylene purges. The reactor was cooled to the appropriate temperature and charged with toluene (total solvent volume of 50 mL). The catalyst (20 μmol) in 10 mL of toluene was then activated, in a Schlenk to observe any colour changes, with 300 equivalents of MAO before injection into the reactor. During the reaction, the pressure was kept constant with a replenishing flow of ethylene. After 30 minutes run time the replenishment of ethylene was ceased and the reactor cooled to <10 °C before venting of excess ethylene to atmospheric pressure and injection of a weighed amount of nonane standard. We have previously[72] established that negligible 1-butene is lost under these conditions; as such analysis of the vented ethylene for 1-butene is unnecessary. Residual MAO was quenched with ~10% HCl solution and samples of the reaction mixture were taken for analysis and quantification of soluble analytes *via* GC and where appropriate GC-MS. Any polymer formed was removed *via* filtration and washed with 10% HCl and methanol before drying at ~60 °C for 3 days. CH_2CH_2/CD_2CD_2 studies were performed *via* the method outlined above utilising a mixture of 1 : 1 ethylene–deuteroethylene.

X-ray crystallography

Data for **11** were collected at −173 °C on crystals mounted on a Hampton Scientific cryoloop at the MX2 beamline of the Australian Synchrotron, while the remaining structures were collected on MX1.[82] Data completeness is limited by the single axis goniometer on the MX beamlines at the Australian Synchrotron. The structures were solved by direct methods with SHELXS-97, refined using full-matrix least-squares routines against F^2 with SHELXL-97,[83] and visualised using X-SEED.[84] All non-hydrogen atoms were refined anisotropically. The structure of **15** featured a conformational disorder in the THF ring involving the remote carbon atoms that was modelled as a two site complementary occupancy with the use of EADP/EXYZ cards to assist in modelling of the associated hydrogen atom disorder that extends over most of the THF ring. Disordered DCM lattice solvent was apparent for **11** that could not be adequately modelled and required the use of SQUEEZE to remove its contribution. Details of the disorder modelling are provided in the cif files and summarised in the figure captions. Iminium and aldehyde protons were located and positionally refined. All other hydrogen atoms were placed in calculated positions and refined using a riding model with fixed C–H distances of 0.95 Å (sp^2CH), 0.99 Å (CH_2), 0.98 Å (CH_3). The thermal parameters of all hydrogen atoms were estimated as U_{iso}(H) = 1.2U_{eq}(C) except for CH_3 where U_{iso}(H) = 1.5U_{eq}(C). A summary of crystallographic data given below.

Crystal data for **11**: $C_{32}H_{34}Cl_4N_2O_2Ti$, M = 668.31, trigonal, a = 22.5011(13), c = 18.1552(13) Å, U = 7960.5(9) Å^3, T = 100 K, space group $R\bar{3}$ (no. 148), Z = 9, 56 709 reflections measured, 5600 unique (R_{int} = 0.0832), 4234 > 4σ(F), R = 0.0787 (observed), R_w = 0.2290 (all data). Crystal data for **12**: $C_{30}H_{28}Cl_2N_2O_2Ti$, M = 567.34, monoclinic, a = 7.1820(12), b = 25.1880(16), c = 14.674(4) Å, β = 90.750(3)°, U = 2654.3(8) Å^3, T = 100 K, space group $P2_1/n$ (no. 14), Z = 4, 23 158 reflections measured, 3535 unique (R_{int} = 0.0887), 3227 > 4σ(F), R = 0.0696 (observed), R_w = 0.1733 (all data). Crystal data for **13**: $C_{24}H_{32}Cl_3NO_2Ti$, M = 520.76, orthorhombic, a = 28.069(3), b = 8.6610(12), c = 20.8230(11) Å, U = 5062.2(9) Å^3, T = 100 K, space group $Pna2_1$ (no. 33), Z = 8, 80 972 reflections measured, 12 185 unique

(R_{int} = 0.0643), 11 468 > 4$\sigma(F)$, R = 0.0957 (observed), R_w = 0.2533 (all data). Crystal data for **14**: $C_{25}H_{34}Cl_3NO_2Ti$, M = 534.78, orthorhombic, a = 25.105(3), b = 10.6280(12), c = 9.7480(15) Å, U = 2600.9(6) Å^3, T = 100 K, space group $Pna2_1$ (no. 33), Z = 4, 42 641 reflections measured, 6238 unique (R_{int} = 0.0477), 5874 > 4$\sigma(F)$, R = 0.0372 (observed), R_w = 0.0961 (all data). Crystal data for **15**: $C_{23}H_{30}Cl_3NO_2Ti$, M = 506.73, orthorhombic, a = 20.373(3), b = 16.4210(15), c = 13.9580(16) Å, U = 4669.6(9) Å^3, T = 100 K, space group *Pbca* (no. 61), Z = 8, 50 366 reflections measured, 3624 unique (R_{int} = 0.0899), 3310 > 4$\sigma(F)$, R = 0.0786 (observed), R_w = 0.1741 (all data). Crystal data for **16**: $C_{38}H_{44}Cl_2N_2O_2Ti$, M = 679.55, monoclinic, a = 14.1400(10), b = 7.6160(10), c = 31.9980(19) Å, β = 100.824(2)°, U = 3384.6(5) Å^3, T = 100 K, space group $P2_1/n$ (no. 14), Z = 4, 18 966 reflections measured, 5287 unique (R_{int} = 0.0330), 4501 > 4$\sigma(F)$, R = 0.0507 (observed), R_w = 0.1203 (all data). Crystal data for **dichlorobis(3-*tert*-butyl-2-oxybenzoyl) titanium(IV)**: $C_{22}H_{26}Cl_2O_4Ti$, M = 473.23, monoclinic, a = 9.9030(9), b = 22.683(2), c = 10.1360(10) Å, β = 90.781(2)°, U = 2276.6(4) Å^3, T = 100 K, space group $P2_1/n$ (no. 14), Z = 4, 30 459 reflections measured, 4589 unique (R_{int} = 0.0559), 4390 > 4$\sigma(F)$, R = 0.0340 (observed), R_w = 0.0913 (all data).

Acknowledgements

The Australian Research Council is thanked for financial support through grant FT100100609 to DSM and an Australian Postgraduate Award to JAS. We thank Sasol Technology Ltd for funding and permission to publish this work. Albemarle Asia Pacific is thanked for donating the MAO solution. Noel Davies and Thomas Rodemann of the UTas Central Science Laboratory are thanked for MS and elemental analysis measurements respectively. Data for the structures of complexes **11–16** were obtained on the MX1/MX2 beamlines at the Australian Synchrotron, Victoria, Australia.

Notes and references

1 A. W. Al-Sa'doun, *Appl. Catal., A*, 1993, **105**, 1.
2 Y. Chauvin and H. Olivier, in *Applied Homogeneous Catalysis with Organometallic Compounds*, ed. B. Cornils and W. A. Herrmann, VCH, Weinheim, 1996, vol. 1, pp. 258–268.
3 J. T. Dixon, M. J. Green, F. M. Hess and D. H. Morgan, *J. Organomet. Chem.*, 2004, **689**, 3641.
4 D. S. McGuinness, *Chem. Rev.*, 2011, **111**, 2321.
5 P. W. N. M. van Leeuwen, N. D. Clément and M. J.-L. Tschan, *Coord. Chem. Rev.*, 2011, **255**, 1499.
6 T. Agapie, *Coord. Chem. Rev.*, 2011, **255**, 861.
7 G. P. Belov, *Pet. Chem.*, 2012, **52**, 139.
8 D. F. Wass, *Dalton Trans.*, 2007, 816.
9 T. Agapie, J. A. Labinger and J. A. Bercaw, *J. Am. Chem. Soc.*, 2007, **129**, 14281.
10 A. N. J. Blok, P. H. M. Budzelaar and A. W. Gal, *Organometallics*, 2003, **22**, 2564.
11 A. Brückner, J. K. Jabor, A. E. C. McConnell and P. B. Webb, *Organometallics*, 2008, **27**, 3849.
12 P. H. M. Budzelaar, *Can. J. Chem.*, 2009, **87**, 832.
13 T. J. M. de Bruin, L. Magna, P. Raybaud and H. Toulhoat, *Organometallics*, 2003, **22**, 3404.
14 L. H. Do, J. A. Labinger and J. E. Bercaw, *Organometallics*, 2012, **31**, 5143.
15 W. Janse van Rensberg, C. Grove, J. P. Steynberg, K. B. Stark, J. J. Huyser and P. J. Steynberg, *Organometallics*, 2004, **23**, 1207.
16 W. Janse van Rensberg, J.-A. van den Berg and P. J. Steynberg, *Organometallics*, 2007, **26**, 1000.
17 I. Y. Skobelev, V. N. Panchenko, O. Y. Lyakin, K. P. Bryliakov, V. H. Zakharov and E. P. Talsi, *Organometallics*, 2010, **29**, 2943.
18 J. A. Suttil, D. S. McGuinness, M. Pichler, M. G. Gardiner, D. H. Morgan and S. J. Evans, *Dalton Trans.*, 2012, **41**, 6625.
19 T. Agapie, S. J. Schofer, J. A. Labinger and J. A. Bercaw, *J. Am. Chem. Soc.*, 2004, **126**, 1304.
20 S. Tobisch and T. Ziegler, *Organometallics*, 2003, **22**, 5392.
21 J. M. Overett, K. Blann, A. Bollmann, J. T. Dixon, D. Hassbroek, E. Killian, H. Maumela, D. S. McGuinness and D. H. Morgan, *J. Am. Chem. Soc.*, 2005, **127**, 10723.
22 S. J. Schofer, M. W. Day, L. M. Henling, J. A. Labinger and J. E. Bercaw, *Organometallics*, 2006, **25**, 2743.
23 A. J. Rucklidge, D. S. McGuinness, R. P. Tooze, A. M. Z. Slawin, J. D. A. Pelletier, M. J. Hanton and P. B. Webb, *Organometallics*, 2007, **26**, 2782.
24 A. Jabri, C. B. Mason, Y. Sim, S. Gambarotta, T. J. Burchell and R. Duchateau, *Angew. Chem., Int. Ed.*, 2008, **47**, 9717.
25 I. Vidyarante, G. B. Nikiforov, S. I. Gorelsky, S. Gambarotta, R. Duchateau and I. Korobkov, *Angew. Chem., Int. Ed.*, 2009, **48**, 6552.
26 D. S. McGuinness, D. B. Brown, R. P. Tooze, F. M. Hess, J. T. Dixon and A. M. Z. Slawin, *Organometallics*, 2006, **25**, 3605.
27 A. Jabri, C. Temple, P. Crewdson, S. Gambarotta, I. Korobkov and R. Duchateau, *J. Am. Chem. Soc.*, 2006, **128**, 9238.
28 Y. Yang, Z. Liu, L. Zhong, P. Qiu, Q. Dong, R. Cheng, J. Vanderbilt and B. Liu, *Organometallics*, 2011, **30**, 5297.
29 P. J. W. Deckers, B. Hessen and J. H. Teuben, *Angew. Chem., Int. Ed.*, 2001, **40**, 2516.
30 C. Pellecchia, D. Pappalardo and G.-J. Gruter, *Macromolecules*, 1999, **32**, 4491.
31 C. Pellecchia, D. Pappalardo, L. Oliva, M. Mazzeo and G.-J. Gruter, *Macromolecules*, 2000, **33**, 2807.
32 P. J. W. Deckers, B. Hessen and J. H. Teuben, *Organometallics*, 2002, **21**, 5122.
33 H. Hagen, W. P. Kretschmer, F. R. van Buren, B. Hessen and D. A. van Oeffelen, *J. Mol. Catal. A: Chem.*, 2006, **248**, 237.
34 B. Hessen, *J. Mol. Catal. A: Chem.*, 2004, **213**, 129.

35 E. Otten, A. A. Batinas, A. Meetsma and B. Hessen, *J. Am. Chem. Soc.*, 2009, **131**, 5298.
36 T. J. M. de Bruin, P. Raybaud and H. Toulhoat, *Organometallics*, 2008, **27**, 4864.
37 H. Hagen, *Ind. Eng. Chem. Res.*, 2006, **45**, 3544.
38 C. Wang and J. Huang, *Chin. J. Chem.*, 2006, **24**, 1397.
39 J. Huang, T. Wu and Y. Qian, *Chem. Commun.*, 2003, 2816.
40 T. Wu, Y. Qian and J. Huang, *J. Mol. Catal. A: Chem.*, 2004, **214**, 227.
41 J. A. Suttil, D. S. McGuinness and S. J. Evans, *Dalton Trans.*, 2010, **39**, 5278.
42 M. Mitani, J. Saito, S. Ishii, Y. Nakayama, H. Makio, N. Matsukawa, S. Matsui, J. Mohri, R. Furuyama, H. Terao, H. Bando, H. Tanaka and T. Fujita, *Chem. Rec.*, 2004, **4**, 137.
43 Y. Suzuki, S. Kinoshita, A. Shibahara, S. Ishii, K. Kawamura, Y. Inoue and T. Fujita, *Organometallics*, 2010, **29**, 2394.
44 D. Owiny, S. Parkin and F. T. Ladipo, *J. Organomet. Chem.*, 2003, **678**, 134.
45 D. A. Pennington, D. L. Hughes, M. Bochmann and S. J. Lancaster, *Dalton Trans.*, 2003, 3480.
46 D. A. Pennington, W. Clegg, S. J. Coles, R. W. Harrington, M. B. Hursthouse, D. L. Hughes, M. E. Light, M. Schormann, M. Bochmann and S. J. Lancaster, *Dalton Trans.*, 2005, 561.
47 S. A. Pardhy, S. S. Deshpande, S. Gopinathan and C. Gopinathan, *Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem.*, 1981, **21**, 173.
48 S. J. Coles, M. B. Hursthouse, D. G. Kelly and A. J. Toner, *Polyhedron*, 2000, **19**, 177.
49 M. Goyal, S. Mishra and A. Singh, *Synth. React. Inorg. Met.-Org. Chem.*, 2001, **31**, 1705.
50 M. R. Salata and T. J. Marks, *Macromolecules*, 2009, **42**, 1920.
51 T. Xu, *J. Coord. Chem.*, 2011, **64**, 3652.
52 A. F. Mason and G. W. Coates, *J. Am. Chem. Soc.*, 2004, **126**, 10798.
53 D. A. Pennington, S. J. Coles, M. B. Hursthouse, M. Bochmann and S. J. Lancaster, *Chem. Commun.*, 2005, 3150.
54 D. A. Pennington, S. J. Coles, M. B. Hursthouse, M. Bochmann and S. J. Lancaster, *Macromol. Rapid Commun.*, 2006, **27**, 599.
55 D. A. Pennington, R. W. Harrington, W. Clegg, M. Bochmann and S. J. Lancaster, *J. Organomet. Chem.*, 2006, **691**, 3183.
56 K. P. Bryliakov, E. A. Kravtsov, L. Broomfield, E. P. Talsi and M. Bochmann, *Organometallics*, 2007, **26**, 288.
57 L. M. Broomfield, Y. Sarazin, J. A. Wright, D. L. Hughes, W. Clegg, R. W. Harrington and M. Bochmann, *J. Organomet. Chem.*, 2007, **692**, 4603.
58 Y. Nie, J. Sun, Z. Cheng and L. Wang, *J. Wuhan Univ. Technol., Mater. Sci. Ed.*, 2008, 821.
59 Y. Y. Long, W. P. Ye, X. C. Shi and Y. S. Li, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 6072.
60 Y. Y. Long, Y. X. Wang, J. Y. Liu, X. F. Li and Y. S. Li, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, **47**, 4626.
61 Y. Y. Long, W. P. Ye, P. Tao and Y. S. Li, *Dalton Trans.*, 2011, **40**, 1610.
62 Y. Y. Long, Y. X. Wang, J. Y. Liu, X. F. Li and Y. S. Li, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 638.
63 J. Strauch, T. H. Warren, G. Erker, R. Frolich and P. Saarenketo, *Inorg. Chim. Acta*, 2000, **300–302**, 810.
64 V. A. Kogan, O. A. Osipov, V. I. Minkin and V. P. Sokolov, *Russ. J. Inorg. Chem.*, 1965, **10**, 45.
65 V. P. Sokolov, V. A. Kogan, O. A. Osipov and M. I. Rumyantseva, *Zh. Obshch. Khim.*, 1968, **38**, 2489.
66 D. Negoiu and A. Kriza, *An. Univ. Bucuresti, Chim.*, 1970, **19**, 113.
67 D. Negoiu and A. Kriza, *An. Univ. Bucuresti, Chim.*, 1971, **20**, 1971.
68 A. Sousa, F. de la Fuente, M. Gayoso and R. Bastida, *An. Quim., Ser. B: Quim. Inorg.*, 1982, **78**, 46.
69 A. Pärssinen, T. Luhtanen, M. Klinga, T. Pakkanen, M. Leskelä and T. Repo, *Organometallics*, 2007, **26**, 3690.
70 S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, N. Matsukawa, Y. Takagi, K. Tsuru, M. Nitabaru, T. Nakano, H. Tanaka, N. Kashiwa and T. Fujita, *J. Am. Chem. Soc.*, 2001, **123**, 6847.
71 R. Furuyama, J. Saito, S. Ishii, M. Mitani, S. Mitsui, Y. Tohi, H. Makio, N. Matsukawa, H. Tanaka and T. Fujita, *J. Mol. Catal. A: Chem.*, 2003, **200**, 31.
72 D. S. McGuinness, J. A. Suttil, M. G. Gardiner and N. W. Davies, *Organometallics*, 2008, **27**, 4238.
73 R. Emrich, O. Heinemann, P. W. Jolly, C. Krüger and G. P. J. Verhovnik, *Organometallics*, 1997, **16**, 1511.
74 J. X. McDermott, J. F. White and G. M. Whitesides, *J. Am. Chem. Soc.*, 1973, **95**, 4451.
75 J. X. McDermott, J. F. White and G. M. Whitesides, *J. Am. Chem. Soc.*, 1976, **98**, 6521.
76 J. A. Suttil and D. S. McGuinness, *Organometallics*, 2012, **31**, 7004.
77 A. Bre, Y. Chauvin and D. Commereuc, *Nouv. J. Chim.*, 1986, **10**, 535.
78 A. Bollmann, K. Blann, J. T. Dixon, F. M. Hess, E. Killian, H. Maumela, D. S. McGuinness, D. H. Morgan, A. Neveling, S. Otto, M. Overett, A. M. Z. Slawin, P. Wasserscheid and S. Kuhlmann, *J. Am. Chem. Soc.*, 2004, **126**, 14712.
79 Y. Tohi, H. Makio, S. Matsui, M. Onda and T. Fujita, *Macromolecules*, 2003, **36**, 523.
80 R. K. J. Bott, D. L. Hughes, M. Schormann, M. Bochmann and S. J. Lancaster, *J. Organomet. Chem.*, 2003, **665**, 135.
81 D. Liguori, R. Centore, A. Tuzi, F. Grisi, I. Sessa and A. Zambelli, *Macromolecules*, 2003, **36**, 5451.
82 T. M. McPhillips, S. E. McPhillips, H. J. Chiu, A. E. Cohen, A. M. Deacon, P. J. Ellis, E. Garman, A. Gonzalez, N. K. Sauter, R. P. Phizackerly, S. M. Soltis and P. Kuhn, *Synchotron Radiat.*, 2009, **9**, 401.
83 G. M. Sheldrick, *SHELX97, Progreams for Crystal Structure Analysis*, Universität Göttingen, Germany, 1998.
84 L. J. Barbour, *J. Supramol. Chem.*, 2001, **1**, 189.

