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Synthesis and catalytic activity of dinuclear imido titanium complexes: the molecular structure of $[Ti(NPh)Cl(\mu\text{-}Cl)(THF)_2]_2$

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Abstract

Reaction of $TiCl_4$ with the reagents $RN(SiMe_3)_2$ in dichloromethane precipitates red to black powders (R = 1-adamantyl, phenyl, pentafluorophenyl, 3,5-bis(trifluoromethyl)phenyl), which on treatment with tetrahydrofuran gives the new THF adducts $[Ti(NR)Cl(\mu\text{-}Cl)(THF)_2]_2$. The complexes are dimeric in the solid state with bridging chloride and terminal imido ligands. Activation with MAO (methylaluminoxane) gives ethene polymerisation catalysts with productivities of up to 31 kg PE [(mol complex) h bar]$^{-1}$.

Keywords: Titanium; Imido; Catalysis; Polymerisation; Methylaluminoxane

1. Introduction

Metal imido complexes are known to adopt a number of structural motifs [1]. For example, titanium forms complexes in which imido ligands adopt either bridging (for example **I**, Chart 1) [2] or terminal (**II**) [3] bonding modes [4]. We recently reported the synthesis and structure of $[Ti(\mu\text{-}NAr^P)Me_2(THF)]_2$ (**III**) ($Ar^P = m\text{-}C_6H_4P(3,5\text{-}(CF_3)_2C_6H_3)_2$) in which the imido ligand is bridging [5]. This result contrasts with Nielson's 2-*tert*-butyl- (**IV**) and 2-phenyl-phenylimido complexes which form chloride-bridged dimers [6] and Carmalt's exclusively chloride-bridged tetramer (**V**) [7]. In the absence of basic co-ligands structures with even higher nuclearity have been observed [8–10]. We continue to be interested in the factors dictating whether the imido ligand adopts a bridging or terminal bonding mode and the implications for alkene polymerisation catalysis using titanium imido precatalysts [6,11]. We report here the synthesis, structure and polymerisation activity of compounds of the type $[Ti(NR)Cl_2(THF)_2]$.

2. Results and discussion

Most commonly imidotitanium complexes are prepared through an imido exchange reaction between $[Ti(NBu^t)Cl_2(L)_x]$ and the corresponding primary amine [6]. We chose to employ an alternative dehalosilylation methodology in order to access the base-free compounds [12]. The ligand precursors $RN(SiMe_3)_2$ (**1a**–**g**) were readily prepared by the step-wise deprotonation of the parent amine and reaction with trimethylsilylchloride (Scheme 1). Treating $TiCl_4$ with **1a**–**d** in dichloromethane solution led to the precipitation of sparingly soluble red to black solids (Scheme 2). Unfortunately the poor solubility of these crude materials in non-basic

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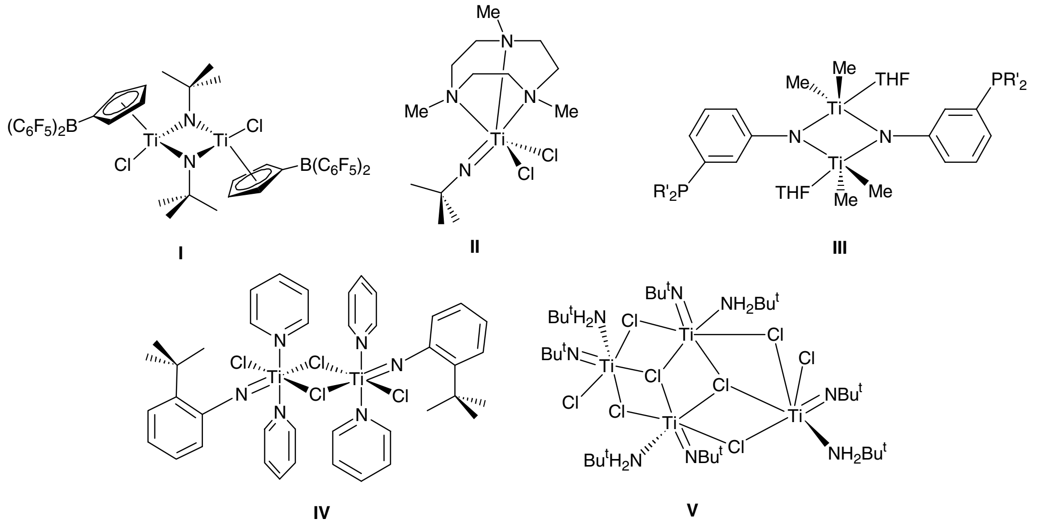
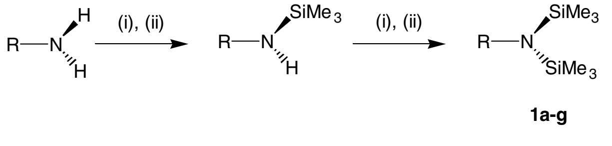


Chart 1.

solvents, which presumably reflects high nuclearity, precluded spectroscopic characterisation or attempts to obtain X-ray quality crystals. However, the solids reacted exothermically on dissolution in tetrahydrofuran and could be isolated as THF adducts **2a**–**d** on crystallisation from THF/light petroleum mixtures. ^{1}H NMR spectroscopy of **2a**–**d** confirmed that quantitative dehalosilylation had taken place and indicated a ligand RN:THF ratio of 1:2, which was supported by the elemental analysis. This composition differs from that observed for [Ti(μ-NAr^P)Cl$_2$(THF)]$_2$ where the ligand RN:THF ratio is 1:1 [5], but is consistent with a formulation analogous to complex **IV**, which has a chloride-bridged structure with terminal imido ligands. While the dehalosilylation route is effective for the introduction of *meta*-substituted aryl imido ligands, the *ortho* disubstituted reagents **1e** and **1f** failed to react with TiCl$_4$, even after refluxing in toluene, presumably as a consequence of steric encumbrance. However, the mononuclear complex [Ti(NAr″)Cl$_2$(py)$_3$] (Ar″ = 2,6-diisopropylphenyl, py = pyridine) is accessible through an imido exchange reaction [3c]. The *o*-OMe compound **1g** reacted with TiCl$_4$ but the resulting product was intractable and could not be isolated even after treatment with THF.

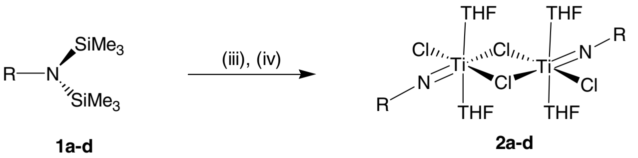
The structure of **2b** (Fig. 1) was determined by X-ray crystallography and confirmed as a chloride-bridged dimer with two edge-sharing octahedral metal coordination spheres. Each distorted octahedron is completed by terminal chloride and imido ligands opposite the bridging chlorides and two mutually *trans* THF ligands. The geometry resembles the 2-*tert*-butylphenyl imido complex **IV**, which has *trans* pyridine ligands.

Selected bond lengths and angles for complex **2b** are shown in Table 1. While the terminal imido bond length is insensitive to the differences between **2b**, **IV** and the mononuclear complex [Ti(NC$_6$H$_5$)Cl$_2$(py)$_3$] at 1.710(2), 1.702(2) and 1.714(2) Å, respectively, the C1–N1–Ti1 angle decreases from the almost linear, 177.5(2)°, in [Ti(NC$_6$H$_5$)Cl$_2$(py)$_3$] to 167.5(2)° in **2b** and 165.9(2)° in **IV**, which reflects the increase in steric crowding.



a, R = 1-adamantyl;
b, R = phenyl;
c, R = pentafluorophenyl;
d, R = 3,5-bis(trifluoromethyl)phenyl;
e, R = 2,4,6-trimethylphenyl
f, R = 2,6-diisopropylphenyl
g, R = 2-methoxyphenyl

Scheme 1. *Reagents and conditions*: (i) *n*-BuLi, THF, −78 °C to room temperature; (ii) SiClMe$_3$, THF, −78 °C to room temperature.



a, R = 1-adamantyl;
b, R = phenyl;
c, R = pentafluorophenyl;
d, R = 3,5-bis(trifluoromethyl)phenyl;

Scheme 2. *Reagents and conditions*: (iii) TiCl$_4$, CH$_2$Cl$_2$, room temperature; (iv) tetrahydrofuran, room temperature.

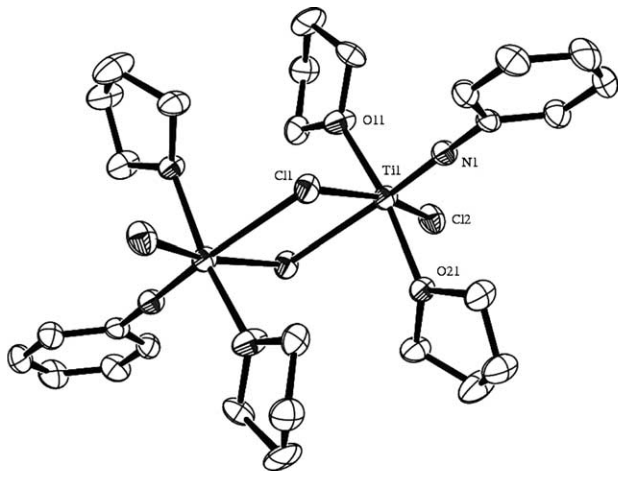


Fig. 1. The molecular structure of **2b** with thermal ellipsoids at 50% probability and the hydrogen atoms, the solvent THF and one half of the co-ordinated disordered THF removed for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for **2b**

Bond lengths			
Cl1–Ti1	2.4845(9)	Cl2–Ti1	2.3734(9)
Cl1–Ti1	2.6408(8)	Ti1–N1	1.710(2)
Ti1–O11	2.085(2)	Ti1–O21	2.114(2)
Ti1–Cl1^{i}	2.6408(8)	C1–N1	1.387(3)
Bond angles			
Ti1–Cl1–Ti1^{i}	103.21(3)	N1–Ti1–O11	97.18(10)
N1–Ti1–Cl2	103.90(9)	O11–Ti1–O21	168.94(8)
O21–Ti1–Cl2	87.87(6)	O11–Ti1–Cl2	87.96(7)
O11–Ti1–Cl1	89.54(7)	N1–Ti1–Cl1	90.84(9)
Cl2–Ti1–Cl1	165.24(3)	O21–Ti1–Cl1	91.90(6)
O11–Ti1–Cl1^{i}	85.18(6)	N1–Ti1–Cl1^{i}	167.42(9)
Cl2–Ti1–Cl1^{i}	88.51(3)	O21–Ti1–Cl1^{i}	84.48(6)
C1–N1–Ti1	167.5(2)	Cl1–Ti1–Cl1^{i}	76.79(3)

Symmetry transformations used to generate equivalent atoms: (i) $-x + 3/2$, $-y + 1/2$, $-z + 1$.

Since complexes **2b**, **IV** and $[Ti(NCMe_3)Cl(\mu\text{-}Cl)(NH_2CMe_3)_2]_2$ [6] all adopt similar dimeric structures with bridging chlorides, its seems likely that the remaining examples **2a,c,d,** which all have two THF ligands per metal centre, have a similar structure. Our complexes are consistent with the pattern illustrated by **II** and **IV**, whereas bridging imido ligands are preferred to bridging chloride ligands only in relatively electron rich complexes, with low steric hindrance.

We reasoned that exchanging the chloride for methyl ligands in complexes **2a**–**2d** might result in structural analogues to **III**. Unfortunately, attempts to isolate the products of treating **2a**–**d** with the alkylating agents LiMe, MgClMe and $ZnMe_2$ were unsuccessful, yielding only black tars.[1] This is in sharp contrast to the reaction of $[Ti(\mu\text{-}NAr^{P})Cl_2(THF)]_2$ with LiMe which proceeds smoothly in diethyl ether at 0 °C to give **III**. Nevertheless, it remains possible that dinuclear imido-bridged complexes are formed during the reaction of **2a**–**d** with the catalyst activator methylaluminoxane (MAO).

3. Polymerisation studies

Complexes **2a**–**d** were screened as ethene polymerisation pre-catalysts in combination with MAO (methylaluminoxane) and the results are presented in Table 2. The productivities are in the region of 10 kg [(mol complex) h bar]$^{-1}$, and there is no suggestion of mass transport limitation. The gel permeation chromatography (GPC) traces indicated bi- or polymodal distributions preventing the assignment of meaningful polydispersities and implying the formation of more than one active species. In each of the systems studied increasing the polymerisation temperature from 20 to 60 °C resulted in significantly lower molecular weight polymer. The effect of raising the polymerisation temperature on the productivity appears to be highly dependent on the nature of the imido substituent, such that **2a** and **2d** showed a modest increase in productivity, while in contrast **2b** and **2c** showed a decrease, possibly as a result of catalyst decomposition. Mountford has recently reported a dramatic productivity dependence on polymerisation temperature for imido titanium catalysts of the type illustrated by **II** [11b]. Our results are broadly comparable with those observed for $[Ti(NC_6H_4\text{–}Ph\text{-}2)Cl(\mu\text{-}Cl)(tmeda)]_2$ (12.7 kg PE [(mol complex) h bar]$^{-1}$ at 20 °C) [6] but they do not approach the 1.1×10^6 g PE [(mol complex) h bar]$^{-1}$ we obtained with **III**/MAO [5].

4. Conclusion

Titanium tetrachloride undergoes a facile dehalosilylation reaction with the relatively unhindered bis(silyl)amines **1a**–**1d** but fails to react with 2,6-substituted silyl anilines (**1f, 1g**). The resulting products react with tetrahydrofuran to give the adducts $[Ti(NR)Cl(\mu\text{-}Cl)(THF)_2]_2$ (**2a**–**2d**). **2a**–**d** are chloride-bridged dimers with terminal imido ligands. Activation of **2a**–**2d** with MAO (methylaluminoxane) gives ethene polymerisation catalysts with moderate productivity.

5. Experimental

5.1. General

Syntheses were performed under nitrogen using standard Schlenk techniques. Solvents were distilled over sodium–benzophenone (diethyl ether, tetrahydrofuran), sodium (toluene), sodium–potassium alloy

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[1] Similar difficulties were reported in [6].

Table 2
Ethene polymerisation results for **2a**–**d**/MAO[a]

Run	Complex (μmol)	MAO (mmol)	T (°C)	t (min)	Polymer yield (g)	Productivity[b]	M_w
1	**2a**(10)	10	20	30	0.078	16	370 000
2	**2a**(10)	10	60	30	0.150	30	23 000
3	**2b**(10)	10	20	30	0.040	8	270 000
4	**2b**(10)	10	60	30	0.004	0.7	150 000
5	**2c**(10)	10	20	10	0.052	31	220 000
6	**2c**(10)	10	60	10	0.013	8	83 000
7	**2d**(10)	10	20	10	0.009	5.5	270 000
8	**2d**(10)	10	60	10	0.028	17	23 000

[a] In 50 cm^3, 1 bar ethene pressure.

[b] In kg PE [(mol complex) h bar]$^{-1}$.

(light petroleum, b.p. 40–60 °C), or CaH_2 (dichloromethane). NMR solvent ($CDCl_3$) was dried over activated 4 Å molecular sieves and degassed by several freeze thaw cycles. NMR spectra were recorded using a Bruker DPX300 spectrometer. Data are reported in ppm and referenced to residual solvent resonances (^1H, ^{13}C); ^{19}F is relative to $CFCl_3$. IR spectra were measured as nujol mulls on a Perkin–Elmer Spectrum 1000 FT IR spectrometer in the range of 600–4000 cm^{-1}. Nitrogen and ethene (BOC, 99.5%) were purified by passing through columns of supported P_2O_5 with moisture indicator, and activated 4 Å molecular sieves. MAO was purchased from Witco as a 10% solution in toluene and used as received. GPC analyses were performed on a Polymer Labs PL-GPC-220 chromatograph. Elemental analyses were performed by the School Microanalysis Service.

5.2. Ligand synthesis

5.2.1. (1-Adamantyl)N(SiMe$_3$)$_2$ (**1a**)

To a stirred solution of 1-adamantylamine (4.6 cm^3, 50 mmol) in tetrahydrofuran (100 cm^3), held at −78 °C, was slowly added *n*-butyllithium (31.3 cm^3 of a 1.6 M hexane solution, 50 mmol). The reaction was stirred for 2 h at room temperature before slow addition of trimethylsilylchloride (6.4 cm^3, 50 mmol). The resulting mixture was stirred for 2 h at room temperature before cooling to −78 °C and treatment with a second portion of *n*-butyllithium (31.3 cm^3 of a 1.6 M hexane solution, 50 mmol). This suspension was stirred for 2 h at room temperature before adding further trimethylsilylchloride (6.4 cm^3, 50 mmol) and stirring for 2 h to ensure complete reaction. The volatiles were removed under reduced pressure and the product extracted with light petroleum (2 × 50 cm^3). The product was purified by vacuum distillation, 65 °C at 0.1 mbar to give a colourless oil in 80% yield. ^1H NMR (300 MHz, 293 K, $CDCl_3$): δ 0.51 (br m, 3H, $(CH)_3$), 0.18 (br m, 6H $(CH_2)_3$), 0.1 (br m, 6H $(CH_2)_3$), 0.08 (s, 18H, $Si(CH_3)_3$). ^{13}C NMR (75.5 MHz, 293 K, $CDCl_3$): δ 36.7 (CH), 30.4 (CH_2), 30.1 (CH_2), 3.3 ($Si(CH_3)_3$).

5.2.2. $C_6H_5N(SiMe_3)_2$ (**1b**)

1b was prepared from aniline following the procedure outlined for **1a**. The product was purified by vacuum distillation, 81 °C at 15 mbar giving the product as a colourless oil in 80% yield. ^1H NMR (300 MHz, 293 K, $CDCl_3$): δ 7.26 (t, 2H, J = 7.0 Hz, Ar), 7.11 (t, 1H, J = 7.3 Hz, Ar), 6.96 (d, 2H, J = 6.9 Hz, Ar), 0.14 (s, 18H, $Si(CH_3)_3$). ^{13}C NMR (75.5 MHz, 293 K, $CDCl_3$): δ 148.4, 130.6, 128.7, 123.9 (Ar), 2.5 ($Si(CH_3)_3$).

5.2.3. $C_6F_5N(SiMe_3)_2$ (**1c**)

1c was prepared from pentafluoroaniline following the procedure outlined for **1a**. The product was purified by vacuum distillation, 75 °C at 15 mbar to give a colourless oil in 90% yield. ^1H NMR (300 MHz, 293 K, $CDCl_3$): δ 0.13 (s, 18H, $Si(CH_3)_3$). ^{13}C NMR (75.5 MHz, 293 K, $CDCl_3$): δ 146.4 (d, $J_{C–F}$ = 242 Hz, *o*-C), 138.0 (d, $J_{C–F}$ = 249 Hz, *m*-C), 127.9 (*i*-C), 1.6 ($Si(CH_3)_3$). ^{19}F NMR (283.4 MHz, 293 K, $CDCl_3$): δ −147.5 (d, 2F, $J_{F–F}$ = 20 Hz, *o*-F), −162.5 (tr, 1F, $J_{F–F}$ = 20 Hz, *p*-F), −165.0 (tr, 2F, $J_{F–F}$ = 20 Hz, *m*-F).

5.2.4. $C_6H_3(CF_3)_2N(SiMe_3)_2$ (**1d**)

1d was prepared from 3,5-bis(trifluoromethyl)aniline following the procedure outlined for **1a**. The product was purified by vacuum distillation, 70 °C at 20 mbar to give a colourless oil in 80% yield. ^1H NMR (300 MHz, 293 K, $CDCl_3$): δ 7.60 (s, 1H, *p*-H), 7.34 (s, 2H, *o*-H), 0.12 (s, 18H, $Si(CH_3)_3$). ^{13}C NMR (75.5 MHz, 293 K, $CDCl_3$): δ 150.9 (*p*-C), 132.2 (q, $J_{C–F}$ = 33 Hz, *m*-C(CF_3)), 130.2 (*o*-C), 123.7 (q, $J_{C–F}$ = 273 Hz, CF_3), 117.5 (*i*-C), 2.2 ($Si(CH_3)_3$). ^{19}F NMR (283.4 MHz, 300 K, $CDCl_3$): δ −63.5 (s, 6F, CF_3).

5.2.5. $C_6H_2Me_3N(SiMe_3)_2$ (**1e**)

1e was prepared from 2,4,6-trimethylaniline following the procedure outlined for **1a**. The product was purified by vacuum distillation, 95 °C at 15 mbar to give a colourless oil in 80% yield. ^1H NMR (300 MHz, 293 K, $CDCl_3$): δ 6.89 (s, 2H, *m*-H), 2.31 (s, 6H, *o*-CH_3), 2.31 (s, 3H, *p*-CH_3), 0.18 (s, 18H, $Si(CH_3)_3$). ^{13}C NMR (75.5 MHz, 293 K, $CDCl_3$): δ 143.5 (*p*-C), 136.8

(*m*-C), 132.7 (*i*-C), 129.5 (*o*-C), 21.2 (*p*-CH_3), 20.8 (*o*-CH_3), 2.9 ($Si(CH_3)_3$).

5.2.6. $C_6H_3{}^iPr_2N(SiMe_3)_2$ (*1f*)

1f was prepared from 2,6-di(isopropyl)aniline following the procedure outlined for **1a**. The product was purified by crystallisation from light petroleum at −30 °C to give white crystals in 90% yield. ^1H NMR (300 MHz, 293 K, $CDCl_3$): δ 7.07 (m, 3H, Ar), 3.49 (sep, 2H, $J = 6.9$, C*H*$(CH_3)_2$), 1.21 (d, 12H, $J = 6.9$ Hz, $CH(CH_3)_2$), 0.11 (s, 18H, $Si(CH_3)_3$). ^{13}C NMR (75.5 MHz, 293 K, $CDCl_3$): δ 147.4 (*m*-C), 143.6 (*p*-C), 124.5 (*i*-C), 123.9 (*o*-C), 27.9 ($CH(CH_3)_2$), 25.5 ($CH(C_3)_2$), 2.9 ($Si(CH_3)_3$).

5.2.7. $C_6H_4OMeN(SiMe_3)_2$ (*1g*)

1g was prepared from 2-methoxyaniline following the procedure outlined for **1a**. The product was purified by vacuum distillation, 85 °C at 15 mbar to give a colourless oil in 80% yield. ^1H NMR (300 MHz, 293 K, $CDCl_3$): δ 7.09 (t, 1H, $J = 6.0$ Hz, Ar), 6.98 (d, 1H, $J = 6.3$ Hz, Ar), 6.88 (m, 2H, $J = 6.2$ Hz, Ar), 3.80 (s, 1H, OCH_3), 0.12 (s, 18H, $Si(CH_3)_3$). ^{13}C NMR (75.5 MHz, 293 K, $CDCl_3$): δ 157.5, 137.4, 131.5, 124.8, 120.6, 110.9 (Ar), 55.2 (OCH_3), 2.3 ($Si(CH_3)_3$).

5.3. Complex synthesis

5.3.1. $[Ti(N\text{-}1\text{-}adamantyl)Cl(\mu\text{-}Cl)(THF)_2]_2$ (*2a*)

To a stirred solution of $TiCl_4$ (0.54 cm^3, 5 mmol) in dichloromethane (40 cm^3), **1a** (1.4 g, 5 mmol) was added drop wise and stirred for 2 h. The volatiles were removed under reduced pressure and the resulting red solid was washed with light petroleum (2×20 cm^3). The product was crystallised from a tetrahydrofuran (20 cm^3)/light petroleum (5 cm^3) solvent mixture at −30 °C to give yellow needle-shaped crystals in 65% yield. ^1H NMR (300 MHz, 293 K, $CDCl_3$): δ 4.57 (m, 4H, THF), 2.10 (m, 4H, THF), 1.88 (br m, 3H, $(CH)_3$), 1.66 (br m, 6H, $(CH_2)_3$), 1.44 (br m, 6H, $(CH_2)_3$). ^{13}C NMR (75.5 MHz, 293 K, $CDCl_3$): δ 75.6 (THF), 45.2 ($(CH)_3$), 41.4 ($(CH_2)_3$), 29.9 ($(CH_2)_3$), 26.0 (THF). IR (cm^{-1}): 1278s, 1170m, 1039m, 1024s, 926w, 864m, 698w, 682w. *Anal.* Calc. for $C_{34}H_{62}N_2Cl_4O_4Ti_2$: C, 51.02; H, 7.81; N, 3.50; Cl, 17.72. Found: C, 50.81; H, 7.30; N, 3.42; Cl, 17.56%.

5.3.2. $[Ti(NPh)Cl(\mu\text{-}Cl)(THF)_2]_2$ (*2b*)

2b was prepared following a similar procedure to **2a** from $TiCl_4$ (1.1 cm^3, 10 mmol) and **1b** (2.4 g, 10 mmol) giving a black powder. Tetrahydrofuran (20 cm^3) was added and stirred for 5 min. An exothermic reaction took place to give a red solution. The product was crystallised from a tetrahydrofuran (20 cm^3)/light petroleum (5 cm^3) mixture at −30 °C to give red block crystals suitable for X-ray crystallography in 95% yield. ^1H NMR (300 MHz, 293 K, $CDCl_3$): δ 7.05 (t, 2H, $J = 7.7$ Hz, Ar), 6.80–6.88 (m, 3H, Ar), 4.47 (m, 8H, THF), 2.11 (m, 8H, THF). ^{13}C NMR (75.5 MHz, 293 K, $CDCl_3$): δ 128.0 (Ar), 123.5 (Ar), 123.1 (Ar), 75.3 (THF), 25.5 (THF). IR (cm^{-1}): 1576m, 1342m, 1315s, 1246m, 1172w, 1066m, 1042m, 1017s, 970m, 825m, 860s, 772s, 684m, 649w, 619w. *Anal.* Calc. for $C_{28}H_{42}N_2Cl_4O_4Ti_2$: C, 47.48; H, 5.98; N, 3.96; Cl, 20.02. Found: C, 46.20; H, 6.02; N, 3.40; Cl, 19.31%.

5.3.3. $[Ti(NC_6F_5)Cl(\mu\text{-}Cl)(THF)_2]_2$ (*2c*)

2c was prepared following a similar procedure to **2a** from $TiCl_4$ (0.54 cm^3, 5 mmol) and **1c** (1.6 g, 5 mmol) giving a red solid. The product was crystallised from a tetrahydrofuran (20 cm^3)/petroleum (5 cm^3) mix at −30 °C to give dark red block crystals in 70% yield. ^1H NMR (300 MHz, 293 K, $CDCl_3$): δ 4.50 (m, 4H, THF), 2.15 (m, 4H, THF). ^{13}C NMR (75.5 MHz, 293 K, $CDCl_3$): δ 76.4 (THF), 26.0 (THF). ^{19}F NMR (283.4 MHz, 293 K, $CDCl_3$): δ −152.8 (d, 2F, *o*-F), −164.7 (t, 1F, *p*-F), −165.5 (d, 2F, *m*-F). IR (cm^{-1}): 1525m, 1505s, 1334m, 1216w, 1171w, 1377w, 1350s, 1014m, 988m, 949w, 920w, 852m. *Anal.* Calc. for $C_{28}H_{32}F_{10}N_2Cl_4O_4Ti_2$: C, 37.87; H, 3.63; N, 3.15; Cl, 15.97. Found: C, 37.26; H, 3.66; N, 3.10; Cl, 15.53%.

5.3.4. $[Ti(NC_6H_3(CF_3)_2\text{-}3,5)Cl(\mu\text{-}Cl)(THF)_2]_2$ (*2d*)

2d was prepared following a similar procedure to **2a** from $TiCl_4$ (1.1 cm^3, 10 mmol) and **1d** (3.7 g, 10 mmol) giving a red solid. The product was crystallised from a tetrahydrofuran (20 cm^3)/petroleum (5 cm^3) mix at −30 °C to give bright red/orange needle-shaped crystals in 75% yield. ^1H NMR (300 MHz, 293 K, $CDCl_3$): δ 7.29 (s, 1H, *o*-H), 7.25 (s, 2H, *p*-H), 4.44 (m, 4H, THF), 2.09 (m, 4H, THF). ^{13}C NMR (75.5 MHz, 293 K, $CDCl_3$): δ 158.7 (Ar), 132.0 (q, $J_{C\text{–}F} = 33$ Hz, *m*-$C(CF_3)$), 129.0 (Ar), 123.8 (Ar), 123.5 (q, $J_{C\text{–}F} = 271$ Hz, CF_3), 116.2 (Ar), 76.0 (THF), 26.0 (THF). ^{19}F NMR (283.4 MHz, 300 K, $CDCl_3$): δ −63.5 (s, 6F, CF_3). IR (cm^{-1}): 1229m, 1089m, 1021s, 920w, 864m, 672w. *Anal.* Calc. for $C_{32}H_{38}F_{12}N_2Cl_4O_4Ti_2$: C, 39.21; H, 3.91; N, 2.86; Cl, 14.47. Found: C, 39.31; H, 3.97; N, 3.60; Cl, 14.72%.

5.4. Polymerisation procedure

A solution of MAO in toluene (50 cm^3) was saturated with ethene (1 bar) at the given temperature. Polymerisation was initiated by addition of a toluene solution of pre-catalyst into the reactor under vigorous stirring (1000 rpm). Methanol (1 cm^3) was added to terminate the polymerisation. The polymeric product was precipitated and separated from aluminium residues by addition of methanol (~300 cm^3) and 2 M HCl (~5 cm^3). The polymer was collected by filtration, washed with methanol, 2 M HCl, distilled water and again with methanol before drying until constant mass at 80 °C. Each run is the average of at least two polymerisations.

6. Crystal structure analysis

Intensity data were recorded at the EPSRC National Crystallography Service at the University of Southampton on a Nonius Kappa CCD diffractometer (with Mo Kα radiation and graphite monochromator).

From a sample of orange block crystals of **2b** under oil, one, $0.44 \times 0.38 \times 0.22$ mm was mounted on a glass fibre and fixed in the cold nitrogen stream.

The cell was determined using DirAx [13]. Data were collected using Collect [14] and processed using the DENZO program [15]. The absorption was correction using SORTAV [16]. The structure was determined by the direct methods routines in the SHELXS [17] program and refined by full-matrix least-squares methods, on F^2's, in SHELXL [18]. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealised positions and their U_{iso} values were set to ride on the U_{eq} values of the parent carbon atoms.

Crystal data for **2b**: $C_{32}H_{50}Cl_4N_2O_5Ti_2$, Mr = 780.34, $T = 120(2)$ K, monoclinic, space group $C2/c$, $a = 19.5782(8)$ Å, $b = 9.0622(4)$ Å, $c = 31.5335(9)$ Å, $\beta = 107.507(2)°$, $V = 3643.5(3)$ Å^3, $\rho_{(calc)} = 1.423$ Mg/m^3, $\mu = 0.772$ mm^{-1}, $Z = 4$, reflections collected: 19 476, independent reflections: 4079 ($R_{int} = 0.0554$), completeness (to $\theta = 27.48°$) = 97.8%, final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0461$, $wR_2 = 0.1148$, R indices (all data): $R_1 = 0.0638$, $wR_2 = 0.1248$.

7. Supplementary material

Crystallographic data (excluding structure factors) for structure **2b** have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC-251697. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk, or www at http://www.ccdc.cam.ac.uk].

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