

The synthesis, structure and ethene polymerization
activity of octahedral heteroligated
(salicylaldiminato)(β -enaminoketonato)titanium complexes:
The X-ray crystal structure of
 $\{3\text{-Bu}^t\text{-2-(O)C}_6\text{H}_3\text{CHN(Ph)}\}\{(\text{Ph)NC(Me)C(H)C(Me)O}\}\text{TiCl}_2$

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Abstract

Treatment of the mono(salicylaldiminato)titanium complexes $\{3\text{-Bu}^t\text{-2-(O)C}_6\text{H}_3\text{CHN(Ar)}\}\text{TiCl}_3(\text{THF})$ ($\text{Ar} = \text{C}_6\text{H}_5, 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ or C_6F_5) with the potassium β -enaminoketonates $(\text{C}_6\text{H}_5)\text{NC}(\text{CH}_3)\text{C}(\text{H})\text{C}(\text{R})\text{OK}$ ($\text{R} = \text{CH}_3, \text{CF}_3$) yielded the first examples of heteroligated (salicylaldiminato) (β -enaminoketonato)titanium dichloride complexes. The complex $\{3\text{-Bu}^t\text{-2-(O)C}_6\text{H}_3\text{CHN(C}_6\text{H}_5)\}\{(\text{C}_6\text{H}_5)\text{-NC}(\text{CH}_3)\text{C}(\text{H})\text{C}(\text{CH}_3)\text{O}\}\text{TiCl}_2$ was structurally characterized by X-ray diffraction and has an orientation with *trans*-O,O,*cis*-Cl,Cl, *cis*-N,N distorted octahedral geometry. These complexes polymerize ethene when activated with MAO; the highest productivity, 5650 kg PE $(\text{mol metal})^{-1} \text{h}^{-1} \text{atm}^{-1}$, was afforded by $\{3\text{-Bu}^t\text{-2-(O)C}_6\text{H}_3\text{CHN(C}_6\text{F}_5)\}\{(\text{C}_6\text{H}_5)\text{NC}(\text{CH}_3)\text{C}(\text{H})\text{C}(\text{CF}_3)\text{O}\}\text{TiCl}_2$ at 60 °C.
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1. Introduction

The development and mechanistic investigation of 1-alkene polymerization catalysis has long enjoyed a prominent position in the field of organometallic homogeneous catalysis. Pioneering work in the 1980s established that the active species in homogeneous group 4 metallocene catalysts was a metal alkyl cation [1]. Since the implicit recognition that the essential pre-requisite of an active catalyst is a vacant coordination site *cis* to a metal alkyl, a great variety of coordination complexes in combination with methylaluminumoxane and other alkylating and cation-generating

reagents have been studied as potential polymerization catalysts [2].

Octahedral group 4 metal complexes supported by two monoanionic bidentate ligands such as the bis(salicylaldiminato) (**I**, Chart 1) [3], bis(pyrrolylaldiminato) (**II**) [4] and bis(β -enaminoketonato) (**III**) [5] metal dichlorides are amongst the most successful of these new catalyst classes. Varying the electronic and steric properties of two identical ancillary ligands has proven effective in modifying important catalytic parameters, namely the productivity, comonomer incorporation and chain transfer rate. However, there is generally a trade-off such that, for example, whilst sterically hindered systems such as the *ortho-tert*-butyl substituted bis(salicylaldiminato)titanium complexes are extremely productive ethene homopolymer-

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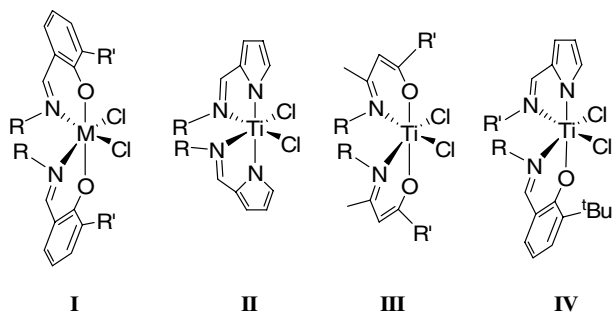


Chart 1.

ization catalysts, they are poor at incorporating bulky monomers. If the size of the substituent is reduced then comonomer incorporation improves at the expense of productivity [6]. Similarly, inherently more open catalysts, such as those derived from bis(pyrrolylaldiminato) or bis(β -enaminoketonato) pre-catalysts, tend to afford better comonomer incorporation but with lower productivities.

We reasoned that an alternative approach to varying the steric bulk of two equivalent ancillary ligands would be to produce octahedral hybrids with a combination of two different ligands, affording catalysts with unique steric and electronic properties [7]. We recently communicated the first example of a heteroligated octahedral pre-catalyst, whereby (salicylaldiminato)(pyrrolylaldiminato)titanium complexes (**IV**) combine the high productivity of the bis(salicylaldiminato) systems with the high monomer incorporation of the bis(pyrrolylaldiminato) catalysts [8]. The steric and electronic properties of the β -enaminoketonato ligand family provide an interesting comparison with the pyrrolylaldiminates and we report here the first (salicylaldiminato)(β -enaminoketonato)titanium complexes and a preliminary investigation of their catalytic behavior.

2. Results and discussion

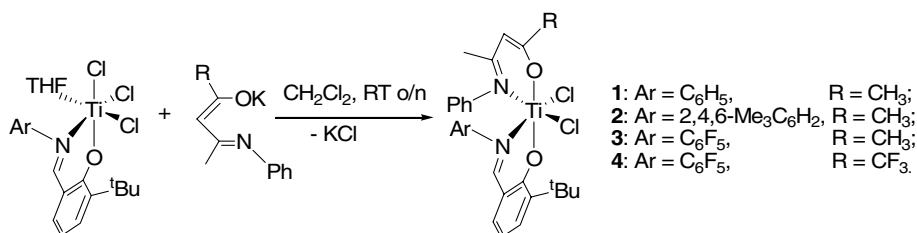
Obviously, the systematic synthesis of heteroligated complexes requires a stepwise approach through a mono(ligand) intermediate. The typical method for the preparation of both bis(salicylaldiminato) and bis(β -enaminoketonato) titanium complexes is the reaction between two equivalents of the lithiated ligand and TiCl_4 in ether or tetrahydrofuran solution [3a,5b]. However, we have shown

that treating TiCl_4 with one equivalent of a metallated salicylaldiminato ligand is not selective for the mono(ligand)titanium trichloride compound and affords a mixture of unreacted TiCl_4 , LTiCl_3 and L_2TiCl_2 . In contrast, treatment of $\text{TiCl}_4(\text{THF})_2$ with the trimethylsilyl ether derivative of an iminophenol provides a general and facile route to complexes $\{3\text{-Bu}^t\text{-2-(O)C}_6\text{H}_3\text{CHN(Ar)}\}\text{TiCl}_3(\text{THF})$ (where $\text{Ar} = \text{C}_6\text{H}_5$, $2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ or C_6F_5) [9]. Examples with sterically less demanding imine substituents than the mesityl group ($2,4,6\text{-Me}_3\text{C}_6\text{H}_2$) can also be prepared by direct reaction between the iminophenol and $\text{TiCl}_4(\text{THF})_2$ [7,9b]. Deprotonation of the β -enaminoketonates ($\text{C}_6\text{H}_5\text{NC}(\text{CH}_3)\text{C}(\text{H})\text{C}(\text{R})\text{OH}$ (where $\text{R} = \text{CH}_3$ or CF_3) with KH in dichloromethane solution affords the corresponding potassium salts. A series of heteroligated complexes (**1–4**) were subsequently prepared through overnight reactions in dichloromethane solution between mono(salicylaldiminato)titanium trichloride complexes and (β -enaminoketonato)potassium salts, giving dark red solids in yields of between 45% and 62% (Scheme 1).

Formulation of **1–4** as (salicylaldiminato)(β -enaminoketonato)titanium dichloride complexes is supported by the ^1H NMR spectra, which show a single set of resonances for titanium-bonded salicylaldiminato and β -enaminoketonato ligands in a 1:1 ratio. The ^{19}F NMR spectrum of compound **4** (Fig. 1) provides further evidence for its composition, with distinctive resonances for the CF_3 and C_6F_5 groups in the expected ratio. The ^{19}F NMR spectra of both **3** and **4** indicate sterically hindered rotation of the C_6F_5 groups rendering the *ortho*- and *meta*-fluorines inequivalent. Over a period of 24 h no spectral changes were observed in d_1 -chloroform solutions of **1–4** stored under an inert atmosphere at room temperature. We conclude that the complexes are resistant to ligand redistribution reactions that would generate the homo-ligated complexes.

There are a number of possible geometric isomers for octahedral complexes with two bidentate monoanionic ligands. The geometry calculated to be most stable for these systems is that in which the two anionic functions are *trans* to one another and the two chlorides *cis* [3a,3i]. This is the arrangement found in both bis(salicylaldiminato) and bis(β -enaminoketonato)metal dichlorides [3,5,10]. It is also the isomer found in the (salicylaldiminato)(pyrrolylaldiminato)titanium system [8,11].

Compounds **2–4** proved to be poorly crystalline, but the solid state structure of **1** was determined by X-ray crystallog-



Scheme 1.

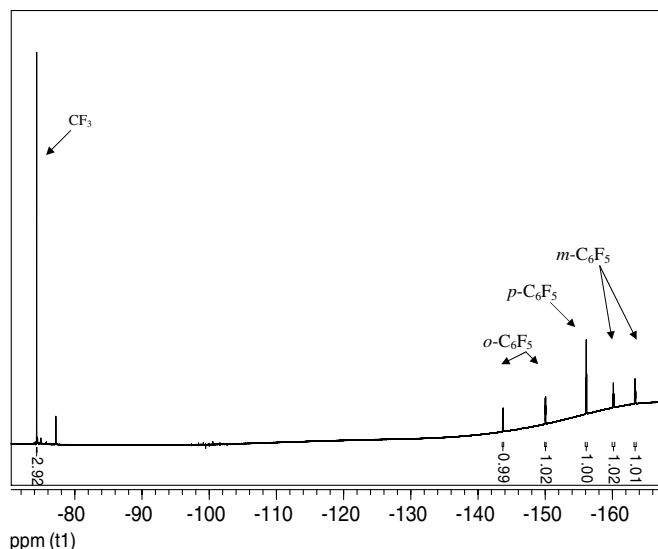


Fig. 1. The ^{19}F NMR spectrum of compound **4**.

raphy (Fig. 2, Table 1). As expected, **1** has an essentially octahedral geometry with a *trans*-O,O, *cis*-Cl,Cl ligand arrangement. Fig. 3 provides a comparison of the structures of **1**, the parent compound $\{3\text{-Bu}^t\text{-2-(O)C}_6\text{H}_3\text{CHN(C}_6\text{H}_5)\}_2\text{TiCl}_2$ (**1a**) [3f] and the very closely related $\{(4\text{-MeC}_6\text{H}_4)\text{-NC(CH}_3\text{)C(H)C(CH}_3\text{)O}\}_2\text{TiCl}_2$ (**IIIa**) [10b]. Whilst in all three cases the O–Ti–O angles are very similar, the Cl–Ti–Cl and N–Ti–N angles of the heteroligated compound more closely resemble those of the bis(β -enaminoketonato) than bis(salicylaldiminato) complexes. This is presumably a reflection of the relative steric congestion **1a** > **1**–**IIIa**. There is very little difference in the Ti–Cl bond lengths in **1**, **1a** and **IIIa**, while the Ti–O and Ti–N distances for the respective ligand types are remarkably similar to those found for the salicylaldiminato ligand in **1a** and the β -enaminoketonato ligand in **IIIa**.

When activated with 1000 equivalents of methylaluminoxane (MAO) at 20 °C, complex **1** forms a highly active catalyst for the polymerization of ethene to moderately high molecular weight linear polyethylene (run 1, Table 2). The

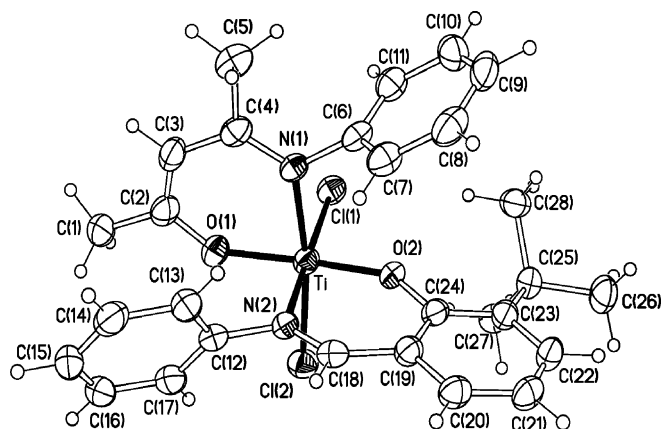


Fig. 2. Molecular structure of **1** with 50% probability displacement ellipsoids.

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

Ti–Cl(1)	2.3102(12)	Ti–Cl(2)	2.3090(12)
Ti–N(1)	2.145(3)	Ti–N(2)	2.213(3)
Ti–O(1)	1.890(3)	Ti–O(2)	1.828(3)
N(1)–C(4)	1.326(5)	N(1)–C(6)	1.448(5)
N(2)–C(12)	1.440(5)	N(2)–C(18)	1.293(5)
O(1)–C(2)	1.323(5)	O(2)–C(24)	1.341(4)
Cl(1)–Ti–Cl(2)	98.70(5)	Cl(1)–Ti–N(1)	90.48(9)
Cl(1)–Ti–N(2)	172.48(9)	Cl(1)–Ti–O(1)	95.16(9)
Cl(1)–Ti–O(2)	95.14(9)	Cl(2)–Ti–N(1)	168.80(9)
Cl(2)–Ti–N(2)	88.24(8)	Cl(2)–Ti–O(1)	90.08(9)
Cl(2)–Ti–O(2)	93.14(9)	N(1)–Ti–N(2)	82.96(11)
N(1)–Ti–O(1)	82.68(12)	N(1)–Ti–O(2)	92.41(12)
N(2)–Ti–O(1)	87.68(12)	N(2)–Ti–O(2)	81.52(11)
O(1)–Ti–O(2)	168.63(12)	Ti–N(1)–C(4)	128.7(3)
Ti–N(1)–C(6)	115.4(2)	C(4)–N(1)–C(6)	115.9(3)
Ti–N(2)–C(12)	120.4(2)	Ti–N(2)–C(18)	125.4(3)
C(12)–N(2)–C(18)	114.0(3)	Ti–O(1)–C(2)	139.5(3)
Ti–O(2)–C(24)	144.7(3)		

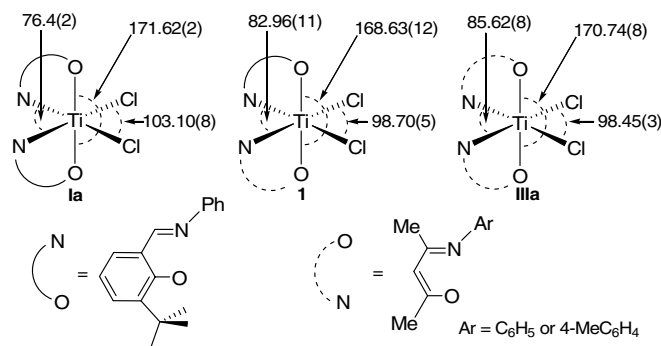


Fig. 3. Comparison of bond angles between complexes **1a**, **1** and **IIIa**.

productivity of the catalyst derived from **1** drops dramatically at 50 °C. Very similar behavior was found for the pre-catalyst with a pentafluorophenyl imine substituent, **3**. However, rather surprisingly in light of the propensity of catalysts with this ligand to yield high molecular weight polyethylene [3i], the molecular weight is somewhat lower than that of the simple phenyl derivative. Attempts to activate complex **2** for ethene polymerization yielded only traces of polyethylene. This result is consistent with our previous findings for complexes with mesityl-substituted sali-

Table 2
Ethene polymerization results

Run	Complex (μmol)	T (°C)	t (min)	Polymer (g)	Productivity ^b	M_w	Polydispersity
1	1 (10)	20	10	0.309	185	310,000	3.0
2	1 (10)	50	10	0.125	75	–	–
3	3 (10)	20	10	0.497	298	44,500	1.4
4	3 (10)	50	10	0.173	104	20,900	2.3
5	4 (3)	20	1.5	0.353	4710	391,000	1.5
6	4 (3)	50	1.5	0.424	5650	416,000	1.7

–, not determined.

^a In 50 cm³, 1 bar ethene pressure, 10 mmol MAO.

^b kg PE (mol metal)^{−1} h^{−1} atm^{−1}.

cylaldiminato ligands [12]. Despite first being described by Cavell and coworkers in 1998 [10a] there are no reports for ethene polymerization with the parent bis(β -enaminoketonato)titanium complex $\{(C_6H_5)NC(CH_3)C(H)C(CH_3)O\}_2TiCl_2$, while the zirconium analogue is an oligomerization catalyst when activated with an alkylaluminum reagent [5a]. The productivity of the most closely related pre-catalyst for which we have data, $\{(C_6H_5)(NCCH_3)C(H)C(C_6H_5)O\}_2TiCl_2$, at 120 kg PE (mol metal) $^{-1} h^{-1} atm^{-1}$ is similar to those found for **1** and **3** under conditions which are broadly comparable to those we have employed [5b]. At 20 °C, both the bis(salicylaldiminato)titanium parent complexes $\{3-Bu^t-2-(O)C_6H_3-CHN(C_6H_5)\}_2TiCl_2$ (**1a**) (5460 kg PE (mol metal) $^{-1} h^{-1} atm^{-1}$) and $\{3-Bu^t-2-(O)C_6H_3-CHN(C_6F_5)\}_2TiCl_2$ (**1b**) (35,900 kg PE (mol metal) $^{-1} h^{-1} atm^{-1}$) are over an order of magnitude more productive than **1** and **3** [3f,8].

The productivities for complex **4**, which has a pentafluorophenyl substituent on the salicylaldiminato ligand and a trifluoromethyl substituent on the β -enaminoketonato ligand, are considerably better than those of **1–3**. Pre-catalyst **4** afforded high molecular weight polyethylene with similar very high productivities at both 20 and 50 °C (runs 5 and 6). This value may be only one eighth of that observed for **1b** [8], but it is nearly five times higher than that of $\{(C_6H_5)NC(CH_3)C(H)C(CF_3)O\}_2TiCl_2$ (1080 kg PE (mol metal) $^{-1} h^{-1} atm^{-1}$) [5b]. The catalytic behavior of hybrid **4** can therefore be regarded as intermediate between those of the parent compounds.

3. Conclusion

Heteroligated (salicylaldiminato) (β -enaminoketonato)titanium dichloride complexes can be prepared through treatment of mono(salicylaldiminato)titanium complexes with potassium β -enaminoketonates. The complexes are stable with respect to isomerization and ligand redistribution reactions and crystallize with *trans*-O,O, *cis*-Cl,Cl, *cis*-N,N octahedral geometries. The polymerization productivities are intermediate between those of the parent homo-ligated pre-catalysts and thus differ from the behavior of (salicylaldiminato)(pyrrolylaldiminato)titanium mixed ligand complexes, some of which showed drastically enhanced productivities. We are currently examining whether these and related heteroligated complexes can combine very high productivities with high comonomer incorporation levels.

4. Experimental

4.1. General

Syntheses were performed under nitrogen using standard Schlenk techniques. Solvents were distilled over sodium/benzophenone (diethyl ether, THF), sodium (toluene), sodium–potassium alloy (light petroleum, b.p. 40–60 °C), or CaH₂ (dichloromethane). NMR solvents

(CDCl₃, C₆D₆) were dried over activated 4 Å molecular sieves and degassed by several freeze–thaw cycles. NMR spectra were recorded using a Bruker DPX300 spectrometer. Chemical shifts are reported in ppm and referenced to residual solvent resonances (¹H, ¹³C), ¹⁹F is relative to CFCl₃. Nitrogen, argon and ethene (BOC, 99.5%) were purified by passing through columns of supported P₂O₅ with moisture indicator, and activated 4 Å molecular sieves. GPC analyses were performed by RAPRA Technology Ltd. Elemental analyses were performed by the School of Chemical Sciences and Pharmacy Microanalysis Service.

$\{3-Bu^t-2-(O)C_6H_3-CHN(Ar)\}_2TiCl_3(THF)$ (where Ar = C₆H₅, 2,4,6-Me₃C₆H₂ or C₆F₅) [9b] and $(C_6H_5)NC(CH_3)C(H)C(R)OH$ (where R = CH₃ [11a] or CF₃ [4b]) were prepared according to the literature procedures. KH (40% mineral oil suspension) was purchased from Aldrich and washed with light petroleum.

4.1.1. $\{3-Bu^t-2-(O)C_6H_3-CHN(C_6H_5)\}_2\{(C_6H_5)NC(CH_3)C(H)C(CH_3)O\}_2TiCl_2$ (**1**)

A solution of $\{3-Bu^t-2-(O)C_6H_3-CHN(C_6H_5)\}_2TiCl_3(THF)$ (1.9 g, 4 mmol) in dichloromethane (20 ml) at –78 °C was treated with $(C_6H_5)NC(CH_3)C(H)C(CH_3)OK$ (0.85 g, 4 mmol). The reaction mixture was allowed to warm slowly to room temperature and stirred for 16 h, affording a dark red solution. The solution was filtered to separate KCl and the product isolated by concentration and cooling (1.35 g, 2.5 mmol, 62%). Fine red needles suitable for synchrotron X-ray diffraction were grown from a tetrahydrofuran/light petroleum solution held at –26 °C overnight. ¹H NMR (300 MHz, CDCl₃, 20 °C): δ 8.09 (s, 1H, CH=N), 7.60 (d, 1H, *J* = 7.78, Ar), 7.05–7.39 (m, 12H, Ar), 5.06 (s, 1H, CH), 2.31, (s, 3H, O–C–CH₃), 1.98 (s, 6H, N–C–CH₃) 1.63 (s, 9H, *t*-Bu). ¹³C NMR (75 MHz, CDCl₃, 20 °C): δ 178.3, 170.9, 166.1, 163.8, 160.0, 153.4, 150.7, 139.0, 133.1, 128.9, 128.8, 128.2, 126.4, 122.4, 108.2, 35.4, 30.2, 24.7, 23.7. Anal. Calc. for C₂₈H₃₀Cl₂N₂O₂Ti: C, 61.90; H, 5.19; N, 5.16; Cl, 13.05. Found: C, 61.62; H, 5.11; N, 5.01; Cl, 13.28%.

4.1.2. $\{3-Bu^t-2-(O)C_6H_3-CHN(2,4,6-Me_3C_6H_2)\}_2\{(C_6H_5)NC(CH_3)C(H)C(CH_3)O\}_2TiCl_2$ (**2**)

Following a similar procedure to that employed for the preparation of compound **1** $\{3-Bu^t-2-(O)C_6H_3-CHN(2,4,6-Me_3C_6H_2)\}_2TiCl_3(THF)$ (1.56 g, 3 mmol) was treated with $\{(C_6H_5)NC(CH_3)C(H)C(CH_3)OK\}$ (0.64 g, 3 mmol). The isolated solid was purified by recrystallization from a tetrahydrofuran/light petroleum solvent mixture at –26 °C yielding 0.79 g (1.35 mmol, 45%) of a very dark red microcrystalline solid. ¹H NMR (300 MHz, CDCl₃, 20 °C): δ 8.20 (s, 1H, CH=N), 7.52 (d, 1H, *J* = 6.43, Ar), 6.72–7.29 (m, 9H, Ar), 5.20 (s, 1H, CH), 2.49 (s, 3H, *p*-CH₃), 2.31 (s, 3H, *o*-CH₃), 2.10 (s, 3H, *o*-CH₃), 1.57 (s, 3H, O–C–CH₃), 1.47 (s, 3H, N–C–CH₃) 1.10 (s, 9H, *t*-Bu). ¹³C NMR (75 MHz, CDCl₃, 20 °C): δ 179.0, 171.7, 169.2, 161.4, 151.2, 150.2, 138.9, 136.2, 134.8, 133.6, 133.2, 130.4, 130.0, 129.2, 128.9, 128.7, 126.9, 126.5, 125.9, 122.6,

122.4, 108.2, 35.3, 29.9, 25.1, 23.3, 21.3, 21.0, 19.3. Anal. Calc. for $C_{31}H_{36}Cl_2N_2O_2Ti$: C, 63.38; H, 6.18; N, 4.77; Cl, 12.07. Found: C, 63.00; H, 6.15; N, 4.53; Cl, 12.78%.

4.1.3. $\{3-Bu^t-2-(O)C_6H_3CHN(C_6F_5)\}-\{(C_6H_5)NC(CH_3)C(H)C(CH_3)O\}TiCl_2$ (**3**)

Utilizing a similar method to that for compound **1** the reaction between $\{(C_6H_5)NC(CH_3)C(H)C(CH_3)OK\}$ (0.64 g, 3 mmol) and $\{3-Bu^t-2-(O)C_6H_3CHN(C_6F_5)\}-TiCl_3(THF)$ (1.71 g, 3 mmol) was conducted in dichloromethane (40 cm³) and gave a dark red solution. The crude product was purified by cooling a tetrahydrofuran/light petroleum solution to $-26^\circ C$ overnight yielding 0.97 g (1.53 mmol, 51%) of a red powder. ¹H NMR (300 MHz, CDCl₃, 20 °C): δ 8.26 (s, 1H, CH=N), 7.52 (d, 1H, $J=7.74$, Ar), 6.84–7.27 (m, 6H, Ar), 6.54 (d, 1H, $J=7.66$, Ar), 5.40 (s, 1H, CH), 1.81 (s, 3H, *p*-CH₃), 1.62 (s, 3H, *o*-CH₃), 1.23 (s, 9H, *t*-Bu). ¹³C NMR (75 MHz, CDCl₃, 20 °C): δ 177.4, 172.6, 171.6, 161.5, 150.6, 139.5, 136.5, 134.2, 129.6, 128.6, 126.4, 125.9, 125.4, 122.7, 122.1, 122.0, 107.3, 35.4, 30.1, 24.7, 23.8. ¹⁹F NMR (282.4 MHz, CDCl₃, 20 °C): δ 141.9 (d, 1F, $J_{FF}=23$ Hz, *o*-F), 149.4 (d, 1F, $J_{FF}=23$ Hz, *o*-F), 156.7 (t, 1F, $J_{FF}=23$ Hz, *p*-F), 161.0 (t, 1F, $J_{FF}=23$ Hz, *m*-F), 163.3 (t, 1F, $J_{FF}=23$ Hz, *m*-F). Anal. Calc. for $C_{28}H_{25}Cl_2F_5N_2O_2Ti$: C, 52.94; H, 3.97; N, 4.41; Cl, 11.16. Found: C, 52.83; H, 3.81; N, 4.34; Cl, 11.47%.

4.1.4. $\{3-Bu^t-2-(O)C_6H_3CHN(C_6F_5)\}-\{(C_6H_5)NC(CH_3)C(H)C(CF_3)O\}TiCl_2$ (**4**)

The preparation of compound **4** followed a similar procedure to that of **1**, $\{3-Bu^t-2-(O)C_6H_3CHN(C_6F_5)\}-TiCl_3(THF)$ (2.27 g, 4 mmol) was treated with $\{(C_6H_5)NC(CH_3)C(H)C(CF_3)OK\}$ (1.07 g, 4 mmol) in dichloromethane (40 ml) solution. Purification by precipitation from a dichloromethane/light petroleum at $-26^\circ C$ gave the title compound as a red powder (1.57 g, 2.28 mmol, 57%). ¹H NMR (300 MHz, CDCl₃, 20 °C): δ 8.26 (s, 1H, CH=N), 7.56 (d, 1H, $J=7.60$, Ar), 6.93–7.27 (m, 6H, Ar), 6.86 (d, 1H, $J=7.66$, Ar), 5.92 (s, 1H, CH), 1.81 (s, 3H, *p*-CH₃), 1.23 (s, 9H, *t*-Bu). ¹³C NMR (75 MHz, CDCl₃, 20 °C): δ 173.4, 139.2, 136.8, 134.3, 130.0, 128.7, 126.8, 126.0, 125.4, 123.6, 53.8, 35.6, 30.3, 25.1. ¹⁹F NMR (282.4 MHz, CDCl₃, 20 °C): δ -74.3 (s, 3F, CF₃), 143.7 (d, 1F, $J_{FF}=23$ Hz, *o*-F), 150.0 (d, 1F, $J_{FF}=23$ Hz, *o*-F), 156.0 (t, 1F, $J_{FF}=22$ Hz *p*-F), 160.1 (t, 1F, $J_{FF}=22$ Hz, *m*-F), 163.4 (t, 1F, $J_{FF}=22$ Hz, *m*-F). Anal. Calc. for $C_{28}H_{22}Cl_2F_8N_2O_2Ti$: C, 48.79; H, 3.22; N, 4.06; Cl, 10.28. Found: C, 49.01; H, 3.35; N, 3.90; Cl, 11.47%.

4.2. X-ray crystallography

Data for **1** were collected on a Bruker APEX2 diffractometer [13] at station 9.8 of the SRS, Daresbury Laboratory, UK, using synchrotron radiation with $\lambda = 0.6768 \text{ \AA}$, at 120 K [14]. Corrections were made for absorption and for incident beam decay on the basis of repeated and sym-

metry-equivalent reflections [15]. Standard methods were used for structure solution and refinement on F^2 , with anisotropic displacement parameters for non-H atoms, and with riding-model constraints for geometry and isotropic displacement parameters of H atoms [16]. The structure is ordered. Crystal data for **1**: $C_{28}H_{30}Cl_2N_2O_2Ti$, $M = 545.3$, monoclinic, space group $P2_1/c$, $a = 12.9376(17) \text{ \AA}$, $b = 13.9030(18) \text{ \AA}$, $c = 15.519(2) \text{ \AA}$, $\beta = 110.364(2)^\circ$, $V = 2617.0(6) \text{ \AA}^3$, $Z = 4$, $D_c = 1.384 \text{ g cm}^{-3}$, $\mu = 0.08 \text{ mm}^{-1}$ at 120 K; $R(F^2 > 2\sigma) = 0.0498$, $R_w(F^2, \text{ all data}) = 0.1310$, goodness-of-fit = 0.980 for all 4456 unique data (18,759 measured, $R_{int} = 0.0923$, $2\theta < 47^\circ$) and 322 refined parameters, all final difference map features are within $\pm 0.37 \text{ e \AA}^{-3}$.

4.3. Polymerization procedure

A solution of MAO in toluene (50 cm³) was saturated with ethene (1 bar) at the given temperature. Polymerization was initiated by addition of a toluene solution of pre-catalyst into the reactor under vigorous stirring (1000 rpm). Methanol (1 cm³) was added to terminate the polymerization. The polymeric product was precipitated and separated from aluminum residues by addition of methanol ($\sim 300 \text{ cm}^3$) and 2 M HCl ($\sim 5 \text{ cm}^3$). The polymer was collected by filtration, washed with methanol, 2 M HCl, distilled water and again with methanol before drying until constant mass at $80^\circ C$. Each run is the average of at least two polymerizations.

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Appendix A. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: CCDC No. 294633. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, fax: (internat.) +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2006.03.026](https://doi.org/10.1016/j.jorganchem.2006.03.026).

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