

Stoichiometric olefin insertion into the Ti–C bond of four-coordinate cationic bis(phenolate) titanium aryl and benzyl complexes[☆]

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Abstract

A series of five-coordinate bis(phenolate) titanium hydrocarbyl complexes (MBP)Ti(η^2 -R)R' was prepared, with MBP = 2,2'-methylenebis(4-methyl-6-*tert*-butylphenolate), R = C₆H₄(*o*-CH₂NMe₂); R' = Cl, OSO₂CF₃, Me, CH₂CMe₃ or R = CH₂C₆H₄(*o*-NMe₂); R' = Cl, Me. A structure determination of (MBP)Ti[η^2 -C₆H₄(*o*-CH₂NMe₂)]OSO₂CF₃ showed the metal to have a distorted trigonal bipyramidal coordination geometry. Cationic four-coordinate derivatives [(MBP)Ti(η^2 -R)]⁺ were generated by reacting the R' = Me derivatives with the Lewis acid B(C₆F₅)₃. These cations were found to undergo stoichiometric insertions of ethene and propene into the Ti–C bond, as seen by 1D and 2D-NMR spectroscopy and quenching reactions with CD₃OD. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Olefin insertion; Titanium alkyls; Cationic complexes

1. Introduction

Bis(phenolates) of the type 2,2'-X-bis(4-methyl-6-*tert*-butylphenolate) (X = CH₂, CH₂CH₂, S) have been found to be useful dianionic ancillary ligands for Group 4 transition metals. In particular, it was observed that the bis(phenolate)MCl₂/MAO combinations (M = Ti, Zr) are reasonably active catalysts for the catalytic polymerisation of ethene, α -olefins and butadiene [1,2], the copolymerisation of ethene and styrene [1,3], and the polymerisation of styrene to syndiotactic polystyrene [4]. Recent theoretical studies [5] indicated that the higher catalytic activities observed for the bis(phenolates) with a bridging group X that has coordinative ability (e.g. S) may stem from a destabilisation of the olefin adduct of the bis(phenolate)TiR cation (which is now four coordinate rather than three coordinate), thus lowering the activation barrier to subse-

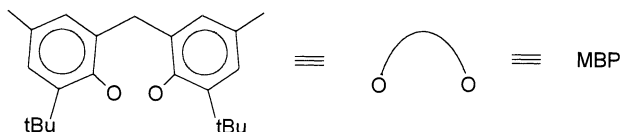
quent insertion. It appeared to us that the bis(phenolate) Ti system would be very interesting and suitable for studies on well-defined cationic hydrocarbyl species. For a bis(naphtholate) Zr system a well-defined cationic hydrocarbyl complex has been generated and characterised [2], but this appears to be much more difficult for the Ti systems. Recently, a well-characterised cationic Ti species was reported with highly substituted phenolate ancillary ligands, [(ArO)₂TiCH₂Ph]-[η^6 -PhCH₂B(C₆F₅)₃] with ArO = 2,6-diphenyl-3,5-dimethyl-phenolate [6].

We sought to obtain stable cationic four-coordinate bis(phenolate)TiR species by using aryl or benzyl groups R with an additional Lewis base functionality attached, R = C₆H₄(*o*-CH₂NMe₂) and CH₂C₆H₄(*o*-NMe₂). In this paper, we report the synthesis of the neutral complexes (MPB)Ti(η^2 -R)R' (MBP = 2,2'-methylenebis(4-methyl-6-*tert*-butylphenolate); R' = Cl, OSO₂CF₃, Me, CH₂CMe₃) and their cationic derivatives [(MBP)Ti(η^2 -R)]⁺. When studying the reactivity of the cationic derivatives towards ethene and propene, we observed stoichiometric single insertion of the olefin into the titanium–carbon bond in all cases.

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2. Synthesis of (MBP)Ti(η^2 -R)R' complexes

A convenient starting material for this chemistry is the bis(phenolate) dichloride (MBP)TiCl₂ (**1**), from which the dimethyl derivative (MBP)TiMe₂ was also reported [7,8]. Complexes (MBP)Ti(η^2 -R)Cl (**2a**, R = C₆H₄(*o*-CH₂NMe₂); **2b**, R = CH₂C₆H₄(*o*-NMe₂)) were obtained by reaction of **1** with stoichiometric amounts of the appropriate RLi reagent. The compounds are yellow solids, thermally stable at ambient temperature both in the solid state and in solution, and they appear

to be insensitive to room light. Reaction of **2a** with AgO₃SCF₃ in THF yielded the triflate (MBP)Ti[η^2 -C₆H₄(*o*-CH₂NMe₂)]OSO₂CF₃ (**3**), which was structurally characterised. The molecular structure of **3** (Fig. 1, selected interatomic distances and angles in Table 1) shows the metal to have a distorted trigonal bipyramidal five-coordinate geometry. One of the MBP oxygens, O(2), and the dimethylamino functionality of the η^2 -C₆H₄(*o*-CH₂NMe₂) group are located in the axial positions, and the triflate group is η^1 -bound to the metal.

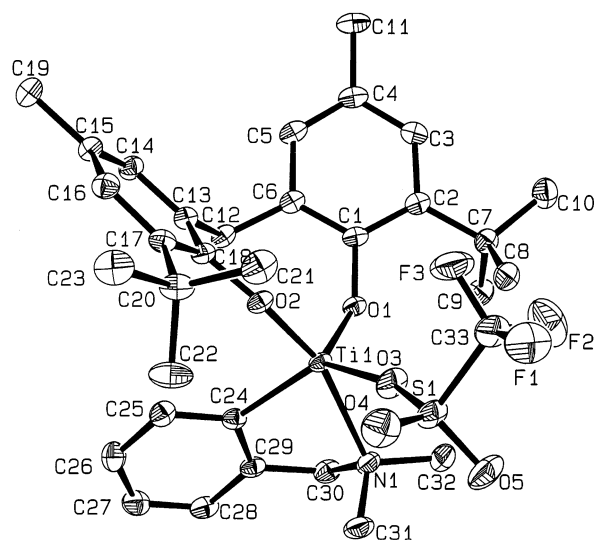
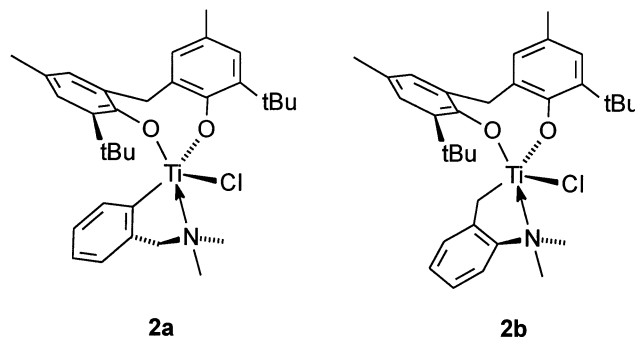


Fig. 1. Molecular structure of **3**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

Table 1
Selected interatomic distances (Å) and angles (°) for **3**

Interatomic distances			
Ti(1)–O(1)	1.792(2)	S(1)–O(3)	1.488(2)
Ti(1)–O(2)	1.784(2)	S(1)–O(4)	1.414(2)
Ti(1)–O(3)	1.999(2)	S(1)–O(5)	1.426(2)
Ti(1)–C(24)	2.116(2)	S(1)–C(33)	1.820(3)
Ti(1)–N(1)	2.298(2)		
Interatomic angles			
O(1)–Ti(1)–O(2)	102.43(7)	O(1)–Ti(1)–N(1)	94.00(7)
O(1)–Ti(1)–O(3)	113.71(7)	O(3)–Ti(1)–N(1)	82.88(7)
O(2)–Ti(1)–N(1)	161.48(7)	Ti(1)–O(1)–C(1)	137.1(1)
N(1)–Ti(1)–C(24)	74.89(7)	Ti(1)–O(2)–C(18)	156.1(1)
O(1)–Ti(1)–C(24)	108.47(8)	Ti(1)–O(3)–S(1)	164.2(1)
O(3)–Ti(1)–C(24)	133.26(8)		

When compared with the octahedral [2,2'-thiobis(4-methyl-6-*tert*-butylphenolate)]Ti(η^2 -C₆H₄(*o*-CH₂NMe₂))Cl [9], the Ti–O and Ti–C distances in **3** are somewhat shorter, as expected for the lower coordination number, although the Ti–N distances are similar in both complexes. As the N–Ti–C(24) angle of the η^2 -R group in **3** is rather small with 74.89(7)°, the MBP O(1)–Ti–O(2) angle (102.43(7)°) and the O(3)–Ti–C(24) angle (133.26(8)°) open up somewhat, making **3** considerably more distorted than the *tbp* five-coordinate complex (MBP)TiCl₂(THF) [8], which has an MBP O–Ti–O angle of 96.2(1)°.

Compounds **2** react with either MeLi or MgMgI to give the corresponding monomethyl derivatives (MBP)Ti(η^2 -R)Me (**4a**, R = C₆H₄(*o*-CH₂NMe₂); **4b**, R = CH₂C₆H₄(*o*-NMe₂)). These yellow air-sensitive compounds seem to be stable in the solid state at ambient temperature, but gradually decompose in solution, liberating methane. The reaction of **2a** with LiCH₂CMe₃ resulted in the formation of the neopentyl derivative (MBP)Ti[η^2 -C₆H₄(*o*-CH₂NMe₂)]CH₂CMe₃ (**5**). The solution behaviour of compounds **2**, **4** and **5** was studied by NMR spectroscopy. At or above ambient temperature the ¹H-NMR spectra show a C_s symmetrically averaged structure with equivalent MBP *tert*-butyl and methyl resonances and dimethylamino methyl groups. At low temperatures the spectra indicate an asymmetric structure as expected for the *tbp*-type complex seen in the solid state for **3**. From the coalescence temperatures of the MBP methyl resonances, free energies of activation can be estimated (shown in Table 2). For the observed fluxional behaviour two pathways are available: (A) dissociation of the NMe₂-functionality followed by rotation around the Ti–C bond (as

Table 2

^1H -NMR (500 MHz) coalescence temperatures of the MBP methyl protons of $(\text{MBP})\text{Ti}(\eta^2\text{-R})\text{R}'$ and derived free energies of activation (standard deviations in parentheses)

Compound	T_c (K)	$\Delta G^\ddagger_{T_c}$ (kJ mol $^{-1}$)
2a	261	51.3(4)
2b	233	45.5(5)
4a	227	44.3(3)
4b	< 200	n.d.
5	261	53.0(3)

suggested for the octahedral $[2,2'\text{-thiobis}(4\text{-methyl-6-}t\text{-tert-butylphenolate})]\text{Ti}(\eta^2\text{-C}_6\text{H}_4(o\text{-CH}_2\text{NMe}_2)\text{Cl}$ [9]), or (B) by a non-dissociative pseudorotation process. It is clear that the activation barrier for symmetrisation is dependent both on R and R'. The observations are that $\Delta G^\ddagger$ is smaller for R' = Me than for R' = Cl, and smaller for R = $\text{CH}_2\text{C}_6\text{H}_4(o\text{-NMe}_2)$ than for R = $\text{C}_6\text{H}_4(o\text{-CH}_2\text{NMe}_2)$. The latter could be due to a reduced Lewis acidity of the NMe_2 functionality in the arylamine relative to the alkylamine (suggesting pathway A), or due to reduced steric encumbrance of the metal centre in the benzylic species relative to the σ -aryl species (suggesting pathway B). The dependance on R' could be due to a reduced Lewis acidity of the metal in the methyl derivatives (suggesting pathway A). However, increasing the steric bulk of R to neopentyl slows down the process, more in line with pathway B, although this could also derive from hindered rotation around the Ti-aryl σ -bond in **5** after amine dissociation. Thus, based on the present set of data, it is difficult to attribute the observed fluxionality in these neutral five-coordinate compounds unequivocally to one specific pathway. It has to be noted that the THF molecule in $(\text{MBP})\text{TiCl}_2(\text{THF})$ is readily lost on warming in vacuo, and that the related dibromide and diiodide derivatives do not form isolable THF adducts [8].

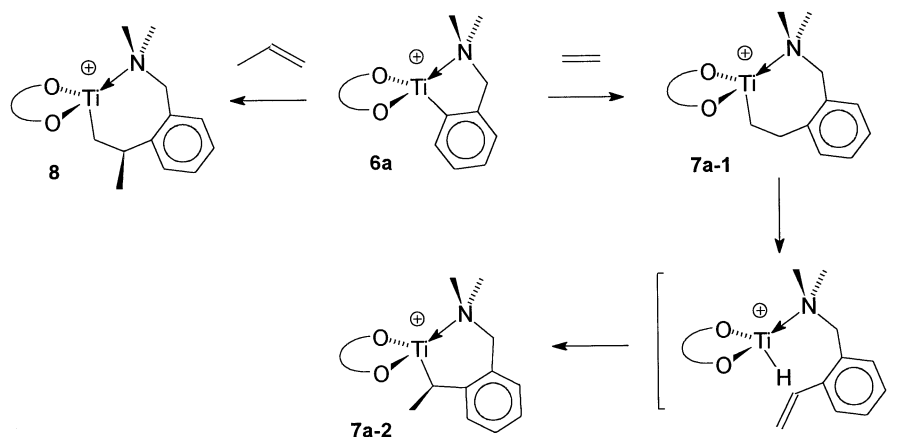
This was attributed to the large steric requirement of the MBP ligand.

3. Generation and reactivity of $(\text{MBP})\text{Ti}(\eta^2\text{-R})$ -cations

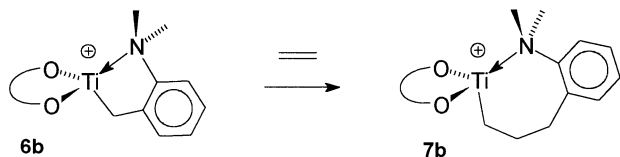
Compound **4a** reacts with the Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ in bromobenzene- d_5 solvent to give the ionic species $\{(\text{MBP})\text{Ti}[\eta^2\text{-C}_6\text{H}_4(o\text{-CH}_2\text{NMe}_2)]\}[\text{MeB}(\text{C}_6\text{F}_5)_3]$ (**6a**) cleanly, as seen by NMR spectroscopy. The ^{19}F -NMR spectrum indicates that the $\text{MeB}(\text{C}_6\text{F}_5)_3$ -anion is non-coordinating, with $\Delta\delta(p-m) = 2.7$ ppm [10]. The ^1H - and ^{13}C -NMR spectra suggest a C_s symmetry for the cation, in which the metal centre is likely to be pseudotetrahedrally coordinated. Characteristic differences in the NMR spectra of **6a** relative to neutral **4a** include a 1 ppm upfield shift of the MBP methylene protons and a 6 ppm downfield shift of the Ti- C_{ipso} resonance.

The benzyl complex **4b** reacts similarly with $\text{B}(\text{C}_6\text{F}_5)_3$ in bromobenzene- d_5 to give the ionic species $\{(\text{MBP})\text{Ti}[\eta^2\text{-CH}_2\text{C}_6\text{H}_4(o\text{-NMe}_2)]\}[\text{MeB}(\text{C}_6\text{F}_5)_3]$ (**6b**). In contrast to **6a**, the ^1H - and ^{13}C -NMR spectra of **6b** suggest some kind of fluxional behaviour (temperature-dependent broadening of resonances), although this could not be frozen out above the freezing point of bromobenzene. This fluxionality may be associated with a folded envelope geometry of the Ti-C-C-N ring due to additional interaction of the electron-deficient metal centre with the aryl moiety. Again, the $\text{MeB}(\text{C}_6\text{F}_5)_3$ anion appears to be non-coordinating.

Addition of an excess of ethene to a solution of **6a** in bromobenzene- d_5 , monitored by ^1H -NMR spectroscopy, initially shows formation of a product with two new triplet resonances ($J = 6.7$ Hz) at δ 3.41 and 2.6 ppm (2H each), suggestive of a single insertion of ethene into the Ti-aryl bond (**7a-1**, Scheme 1). However, this product rearranges over a period of 15 min to an asymmetric species containing a Ti-CH(Me)-Ar moiety (**7a-2**). This is seen in the ^1H -NMR spectrum from two new resonances, a doublet (δ 1.60 ppm,



Scheme 1.



Scheme 2.

$J = 6.4$ Hz, 3H) and a quartet (δ 3.32 ppm, $J = 6.4$ Hz, 1H), and in the ^{13}C -NMR spectrum by resonances at δ 16.80 ppm (q, $J = 126.7$ Hz) and δ 110.78 ppm (d, $J = 121.3$ Hz). No subsequent reaction with ethene was observed, and quenching with methanol- d_4 liberates the $\text{MeCHDC}_6\text{H}_4\text{CH}_2\text{NMe}_2$ fragment, as seen by GC–MS (164 m/e). Thus, it appears that initial insertion of ethene into the Ti–aryl bond is followed by a rearrangement that is likely to proceed through β -H elimination and 2,1-reinsertion of the substituted styrene ligand thus formed. Styrenes are known to have an electronic preference for secondary insertion (as seen, for example, in the catalytic formation of syndiotactic polystyrene with organo-titanium catalysts [11]).

This rearrangement to give a complex with a secondary carbon attached to Ti could be a reason why only stoichiometric, not catalytic, reactivity with ethene is observed. The observation that this rearrangement is substantially slower than the initial insertion of ethene into the Ti–aryl bond makes this unlikely, however. Indeed, upon reaction of the cationic benzyl species **6b** with ethene a stoichiometric reaction is observed also, producing the $(\text{MBP})\text{Ti}[\eta^2\text{-CH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4(o\text{-NMe}_2)]\text{-cation}$ (**7b**, Scheme 2). $^1\text{H}, ^1\text{H}$ -COSY-NMR clearly indicates the presence of a linear $(\text{CH}_2)_3$ moiety, and in this case no subsequent rearrangement occurs. This shows that the rearrangement observed in **7a** is driven by the formation of a thermodynamically more favourable benzylic species.

As with ethene, the reaction of **6a** with an excess of propene also shows the stoichiometric insertion of one molecule of the olefin into the Ti–C bond, leading to the product **8** (Scheme 1). Again, the formation of the product shown was deduced from the $^1\text{H}, ^1\text{H}$ -COSY and ^{13}C -NMR spectra and from quenching reactions with methanol- d_4 to give $\text{CH}_2\text{DCH}(\text{Me})\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2$ (178 m/e , GC–MS). In this case, the reaction product of **6a** with the olefin does not give a subsequent rearrangement. Apparently, the generation after such a rearrangement of a tertiary carbon centre attached to titanium is sufficiently unfavourable to offset the formation of a benzylic species here.

4. Discussion

Due to the Lewis acidity and the low coordination number of the metal centre in the cationic four-coordi-

nate species $[(\text{MBP})\text{Ti}(\eta^2\text{-R})]^+$ **6a** and **6b**, it is likely that the observed olefin insertion into the Ti–C bonds of these complexes takes place through initial coordination of the olefin to the four-coordinate metal centre. Indeed, from the calculations by Morokuma et al. on olefin insertion into the Ti–Me bond of the four-coordinate $[2,2'\text{-thiobis(4-methyl-6-tert-butylphenolate)}]\text{TiMe}$ complex [5], it seems likely that this is a relatively facile process. However, unlike the case of this thiobis(phenolate) system, the position of the Lewis base functionality in the $[(\text{MBP})\text{Ti}(\eta^2\text{-R})]^+$ complex is not constrained relative to the bis(phenolate) ligand. Due to the small C–Ti–N ‘bite’ angle of the $\eta^2\text{-R}$ group in **6** the metal centre is relatively open, allowing the incoming olefin easy access. A single olefin insertion causes a significant increase in this angle. Thus, the approach of a second olefin molecule to the metal centre of the insertion products **7** and **8** is expected to be much more difficult. This, combined with the affinity of the highly Lewis acidic metal centre for the dimethylamino functionality (which makes dissociation of the base unfavourable) is a possible cause for the occurrence of stoichiometric, rather than catalytic reactivity of the cations **6** with olefins.

Several cationic zirconocene systems are known that either will effect only stoichiometric olefin insertion (e.g. $[\text{Cp}_2\text{Zr}(2\text{-pyridyl})(\text{THF})]^+$ [12] and $[\text{Cp}_2\text{Zr}(\text{lutidyl})]^+$ [13]), or will polymerise olefins at or above ambient temperature, but allow the product of the first olefin insertion to be observed at lower temperatures, such as the zwitterionic reaction products of $\text{Cp}_2\text{Zr}(\text{butadiene})$ with $\text{B}(\text{C}_6\text{F}_5)_3$ [14]. For more electron-deficient non-metallocene cationic systems, stoichiometric olefin insertions have so far only been observed into M–benzyl bonds, where η^6 -coordination to the metal centre of the benzyl aryl group in the first olefin insertion product quenches the electron deficiency of the metal centre [6,15]. In the cationic bis(phenolate) titanium complexes presented here, the metal centre in the first insertion products **7** and **8** is formally still sufficiently electron deficient to allow olefin complexation and insertion without the need for dissociation of the NMe_2 -group. There is no evidence for η^6 -coordination of the R-aryl moiety in these compounds (a typical NMR feature of which is the presence of one or several upfield shifted aryl H resonances with $\delta < 6.5$ ppm [6,15]), although it is difficult to exclude interaction of a part of the aromatic system with the metal centre (e.g. of the C–C bond between the two substituted carbons), as the aromatic region of the ^{13}C -NMR spectra of **7** and **8** is difficult to analyse. It could be that in this system the geometry around the metal centre enforced by the ligands in **7** and **8** (an eight-membered MBP–Ti ring and a six- or seven-membered $(\eta^2\text{-C}_2\text{R})\text{-Ti}$ ring) is sufficient to block further olefin insertion.

5. Experimental

5.1. General considerations

All experiments were performed under nitrogen using standard Schlenk, glovebox and vacuum-line techniques. Diethyl ether, toluene, benzene- d_6 and pentane were distilled from Na/K or Na prior to use. Bromobenzene- d_5 (Aldrich) was degassed, dried on molecular sieves (4 Å) and stored and used in a dry-box. The compounds **1** [7,8], $\text{LiC}_6\text{H}_5(o\text{-CH}_2\text{NMe}_2)$ and $\text{LiCH}_2\text{C}_6\text{H}_4(o\text{-NMe}_2)$ [16] and $\text{B}(\text{C}_6\text{F}_5)_3$ [17] were prepared according to published procedures. Ethene and propene (Ucar 99.5%) were used as received. NMR spectra were recorded on Varian Unity-500 (^1H and ^{13}C) and Gemini-200 (^{19}F) spectrometers. GC–MS analyses were performed using an HP 5973 mass-selective detector attached to a HP 6890 GC equipped with a HP-1 dimethylpolysiloxane column. Elemental analyses were performed at the Micro-Analytical Department of the University of Groningen. Listed values are the average of at least two independent determinations. It was noted that most of the bis(phenolate) hydrocarbyl species give carbon analyses that are persistently and reproducibly too low (by up to 1.5%, as in the case for **4b**), whereas correct H and Ti values are obtained. It is possible that formation of inert Ti–carbides during the combustion analysis (as seen by the formation of non-white residual ashes) is responsible for this.

5.2. Synthesis of $(\text{MBP})\text{Ti}[\eta^2\text{-C}_6\text{H}_4(o\text{-CH}_2\text{NMe}_2)]\text{Cl}$ (**2a**)

To a mixture of solid **1** (6.38 g, 14.0 mmol) and $\text{LiC}_6\text{H}_5(o\text{-CH}_2\text{NMe}_2)$ (2.00 g, 14.2 mmol) was added a 150 ml portion of cold (-80°C) ether. The orange suspension was warmed to -30°C and stirred for 3.5 h. The mixture was subsequently warmed to ambient temperature and stirred overnight. The suspension was filtered, and the solvent was removed in vacuo. Extracting the product with an ether–pentane (1:1) mixture and cooling to -80°C yielded orange crystalline **2a** (5.22 g, 9.39 mmol, 67%). ^1H -NMR (C_6D_6 , 25°C) δ 7.86 (d, $J = 7.3$ Hz, 1H, R–Ar H), 7.04 and 6.99 (s, 2H each, MBP–Ar H), 6.92 (d, $J = 7.3$ Hz, 1H, R–Ar H), 6.7 (m, 2H, R–Ar H), 4.87 and 3.44 (d, $J = 13.4$ Hz, 1H each, MBP– CH_2), 3.71 (br.s, 2H, NCH_2), 2.76 (s, 6H, NMe_2), 2.10 (s, 6H, MBP– CH_3), 1.53 (s, 18H, MBP– CMe_3). ^{13}C -NMR (C_6D_6 , 25°C) δ 196.36 (s, Ti– C_{ipso}), 161.91 (s, O– ArC_{ipso}), 143.62 (s, $\text{NCH}_2\text{--C}_{\text{ipso}}$), 137.4 (br. s, $2 \times \text{MBP--C}_{\text{ipso}}$), 132.52 (d, $J = 158.8$ Hz, R–Ar CH), 131.55 (s, MBP– C_{ipso}), 130.24 (d, $J = 161.1$ Hz, R–Ar CH), 129.10 (d, $J = 158.7$ Hz, MBP–Ar CH), 125.98 (d, $J = 155.0$ Hz, MBP–Ar CH), 125.74 (d, $J = 159.9$ Hz, R–Ar CH), 124.56 (d, $J = 157.5$ Hz, R–Ar CH), 67.78 (t, $J = 137.3$ Hz, NCH_2), 49.48 (q,

$J = 136.2$ Hz, NMe_2), 35.74 (t, $J = 127.0$ Hz, MBP CH_2), 35.19 (s, CMe_3), 30.63 (q, $J = 126.1$ Hz, $\text{C}(\text{CH}_3)_3$), 21.13 (q, $J = 126.1$ Hz, MBP Me). Anal. Found: C, 68.50; H, 8.20; Ti, 8.52. Calc. for $\text{C}_{32}\text{H}_{42}\text{ClNO}_2\text{Ti}$: C, 69.12; H, 7.61; Ti, 8.61.

5.3. Synthesis of $(\text{MBP})\text{Ti}[\eta^2\text{-CH}_2\text{C}_6\text{H}_4(o\text{-NMe}_2)]\text{Cl}$ (**2b**)

To a mixture of solid **1** (12.36 g, 27.0 mmol) and $\text{LiCH}_2\text{C}_6\text{H}_5(o\text{-NMe}_2)$ (4.64 g, 32.9 mmol) was added a 300 ml portion of cold (-80°C) ether. The orange suspension was warmed to -30°C and stirred for 3.5 h. The mixture was subsequently warmed to ambient temperature and stirred overnight. The suspension was filtered, and the solvent was removed in vacuo. Extracting the product with ether and cooling to -80°C yielded orange crystalline **2b** (6.99 g, 12.6 mmol, 47%). ^1H -NMR (C_6D_6 , 25°C) δ 7.03 and 6.98 (s, 2H each, MBP–Ar H), 6.90 (m, 1H, R–Ar H), 6.8 (m, 2H, R–Ar H), 6.73 (m, 1H, R–Ar H), 4.70 and 3.41 (d, $J = 13.8$ Hz, 1H each, MBP CH_2), 3.05 (s, 6H, NMe_2), 2.92 (br.s, 2H, TiCH_2), 2.12 (s, 6H, MBP– CH_3), 1.50 (s, 18H, MBP– CMe_3). ^{13}C -NMR (C_6D_6 , 25°C) δ 163.11 (s, O– ArC_{ipso}), 150.73 (s, R–Ar C_{ipso}), 140.01 (s, R–Ar C_{ipso}), 137.11, 136.84 and 131.42 ($3 \times \text{MBP--C}_{\text{ipso}}$), 129.23 (d, $J = 158.7$ Hz, MBP–Ar CH), 129.12 (d, $J = 158.7$ Hz, R–Ar CH), 127.74 (d, $J = 158.7$ Hz, R–Ar CH), 126.32 (d, $J = 161.1$ Hz, R–Ar CH), 125.77 (d, $J = 152.6$ Hz, MBP–Ar CH), 117.67 (d, $J = 156.9$ Hz, R–Ar CH), 79.02 (t, $J = 131.8$ Hz, TiCH_2), 49.48 (q, $J = 138.6$ Hz, NMe_2), 35.25 (t, $J = 127.0$ Hz, MBP CH_2), 35.18 (s, CMe_3), 30.57 (q, $J = 125.7$ Hz, $\text{C}(\text{CH}_3)_3$), 21.67 (q, $J = 125.7$ Hz, MBP Me). Anal. Found: C, 68.47; H, 7.60; Ti, 8.50. Calc. for $\text{C}_{32}\text{H}_{42}\text{ClNO}_2\text{Ti}$: C, 69.12; H, 7.61; Ti, 8.61.

5.4. Synthesis of $(\text{MBP})\text{Ti}[\eta^2\text{-C}_6\text{H}_4(o\text{-CH}_2\text{NMe}_2)]\text{OSO}_2\text{CF}_3$ (**3**)

To an orange solution of **2a** (4.73 g, 8.51 mmol) in 50 ml of THF, $\text{AgOSO}_2\text{CH}_3$ (2.05 g, 7.98 mmol) was added at room temperature. The solution turned red instantaneously, and AgCl precipitated. After stirring for 2 h, the solution was filtered and the solvent removed in vacuo. The resulting red oil was dissolved in 40 ml of ether. Cooling to -30°C yielded orange crystalline **3**· $(\text{Et}_2\text{O})_{0.5}$ (4.80 g, 6.79 mmol, 85%). ^1H -NMR (C_6D_6 , 25°C) δ 7.69 (d, $J = 7.3$ Hz, 1H, R–Ar H), 6.91 (br s, 4H MBP–Ar H), 6.85 (t, $J = 7.6$ Hz, 1H, R–Ar H), 6.63 (d, $J = 7.8$ Hz, 1H, R–Ar H), 6.60 (t, $J = 7.3$ Hz, 1H, R–Ar H), 4.78 and 3.24 (d, $J = 13.7$ Hz, 1H each, MBP CH_2), 3.67 (br.s, 2H, NCH_2), 2.68 (s, 6H, NMe_2), 2.02 (s, 6H, MBP– CH_3), 1.45 (s, 18H, MBP– CMe_3). ^{19}F -NMR (C_6D_6 , 25°C) δ -77.57 . The diethyl ether in the crystal lattice appears to be rela-

tively loosely incorporated. Solvent-free solid **3** for elemental analysis was obtained by finely grinding the crystalline material followed by drying overnight at ambient temperature under diffusion-pump vacuum. Anal. Found: C, 58.15; H, 6.39; Ti, 7.26. Calc. for $C_{33}H_{42}F_3NO_5STi$: C, 59.19; H, 6.32; Ti, 7.15.

5.5. Synthesis of $(MBP)Ti[\eta^2-C_6H_4(o-CH_2NMe_2)]Me$ (**4a**)

To a red suspension of **2a** (5.18 g, 8.74 mmol) in 100 ml of ether, cooled to $-80^\circ C$, 3.3 ml of a 2.7 M MeLi solution in ether was added dropwise. After 2 h the mixture was allowed to warm to ambient temperature and stirred for a further hour. Subsequently, 5 g of dried Celite was added. The mixture was filtered, and the solution concentrated to 40 ml. Cooling to $-80^\circ C$ yielded yellow microcrystalline **4a** (3.58 g, 6.70 mmol, 76%). 1H -NMR (C_6D_6 , $25^\circ C$) δ 7.91 (d, $J = 7.2$ Hz, 1H, R-Ar H), 7.05 (br.s, 4H, MBP-Ar H), 7.00 (d, $J = 7.4$ Hz, 1H, R-Ar H), 6.8 (m, 2H, R-Ar H), 4.16 and 3.42 (d, $J = 13.5$ Hz, 1H each, MBP CH_2), 3.57 (br.s, 2H, NCH_2), 2.60 (s, 6H, NMe_2), 2.14 (s, 6H, MBP- CH_3), 1.59 (s, 18H, MBP- CMe_3), 1.46 (s, 3H, Ti-Me). ^{13}C -NMR (selected data, C_6D_6 , $25^\circ C$) δ 191.39 (s, Ti- C_{ipso}), 62.72 (q, $J = 120.9$ Hz, Ti- CH_3). Anal. Found: C, 73.76; H, 8.75; Ti, 8.83. Calc. for $C_{33}H_{45}NO_2Ti$: C, 74.00; H, 8.47; Ti, 8.94.

5.6. Synthesis of $(MBP)Ti[\eta^2-CH_2C_6H_4(o-NMe_2)]Me$ (**4b**)

To a red suspension of **2b** (1.34 g, 2.41 mmol) in 100 ml of ether, cooled to $-80^\circ C$, 2.2 ml of a 1.32 M MeMgI solution in ether was added dropwise. After 3 h the mixture was allowed to warm to ambient temperature and stirred for another 2 h. To the yellow–orange solution 0.25 ml (2.90 mmol) of 1,4-dioxane was added, precipitating a white solid. After addition of 5 g of dried Celite the solution was filtered. Concentrating the solution and cooling to $-80^\circ C$ yielded yellow **4b** (0.75 g, 1.40 mmol, 58%). 1H -NMR (C_6D_6 , $25^\circ C$) δ 7.06 and 7.02 (s, 2H each, MBP-Ar H), 6.9 (m, 3H, R-Ar H), 6.85 (m, 1H, R-Ar H), 4.18 and 3.43 (d, $J = 13.7$ Hz, 1H each, MBP CH_2), 2.87 (s, 6H, NMe_2), 2.75 (br.s, 2H, $TiCH_2$), 2.16 (s, 6H, MBP- CH_3), 1.55 (s, 18H, MBP- CMe_3), 1.12 (s, 3H, Ti-Me). ^{13}C -NMR (selected data, C_6D_6 , $25^\circ C$) δ 69.32 (t, $J = 130.6$ Hz, Ti- CH_2), 56.39 (q, $J = 120.5$ Hz, Ti- CH_3). Anal. Found: C, 72.38; H, 8.45; Ti, 8.95. Calc. for $C_{33}H_{45}NO_2Ti$: C, 74.00; H, 8.47; Ti, 8.94.

5.7. Synthesis of $(MBP)Ti[\eta^2-C_6H_4(o-CH_2NMe_2)]-CH_2CMe_3$ (**5**)

To a red suspension of **2a** (2.08 g, 3.74 mmol) in 60 ml of ether, cooled to $-80^\circ C$, 0.40 g (5.12 mmol) of

solid $LiCH_2CMe_3$ was added. The mixture was stirred for 2 h, warmed to ambient temperature and then stirred for a further 20 min. The solvent was removed in vacuo and residual solvent was removed from the dark yellow residue by stirring with 30 ml of pentane, which was subsequently pumped off. Extraction with pentane and evaporation of the solvent resulted in a yellow solid that was rinsed with cold pentane and dried in vacuo. Yield: 1.30 g (2.20 mmol, 59%) of **5**. 1H -NMR (C_7D_8 , $-40^\circ C$) δ 8.14 (d, $J = 7.8$ Hz, 1H, R-Ar H), 6.8 (m, 3H, Ar H), other aromatic protons overlapped by solvent, 4.23 and 2.84 (d, $J = 13$ Hz, 1H each, NCH_2), 3.37 and 3.17 (d, $J = 13.8$ Hz, 1H each, MBP CH_2), 2.74 and 2.20 (s, 3H each, NMe_2), 2.66 and 1.29 (d, $J = 10.7$ Hz, 1H each, $TiCH_2$), 2.17 and 2.05 (s, 3H each, MBP- CH_3), 1.74 and 1.65 (s, 9H each, MBP- CMe_3), 1.23 (s, 9H, CMe_3). ^{13}C -NMR (selected data, C_6D_6 , $25^\circ C$) δ 192.22 (s, Ti- C_{ipso}), 108.68 (t, $J = 114.2$ Hz, Ti- CH_2). Anal. Found: C, 74.31; H, 9.34; Ti, 7.92. Calc. for $C_{37}H_{53}NO_2Ti$: C, 75.10; H, 9.03; Ti, 8.09.

5.8. Generation of $\{(MBP)Ti[\eta^2-C_6H_4(o-CH_2NMe_2)]-[MeB(C_6F_5)_3]\}$ (**6a**)

A solution of **4a** (43.2 mg, 80.7 mmol) in 0.25 ml of bromobenzene- d_5 was added to a solution of $B(C_6F_5)_3$ (45.2 mg, 88.3 mmol) in 0.25 ml of bromobenzene- d_5 . The solution immediately turned wine-red, and NMR spectroscopy showed formation of **6a** as the only product. 1H -NMR (C_6D_5Br , $-35^\circ C$) δ 7.0 (m, 2H, R-Ar H), 6.85 and 6.72 (s, 2H each, MBP-Ar H), 6.80 (m, 2H, R-Ar H), 4.11 (br.s, 2H, NCH_2), 3.46 and 2.57 (d, $J = 13.9$ Hz, 1H each, MBP CH_2), 2.50 (s, 6H, NMe_2), 2.09 (s, 6H, MBP- CH_3), 1.26 (s, 18H, MBP- CMe_3), 1.09 (br.s, 3H, B-Me). ^{13}C -NMR (C_6F_5 resonances omitted, C_6D_5Br , $-35^\circ C$) δ 197.30 (s, Ti- C_{ipso}), 162.64 (s, O-Ar C_{ipso}), 142.58 (s, NCH_2-C_{ipso}), 136.62 (s, MBP- C_{ipso}), 132.96 (s, MBP- C_{ipso}), 132.43 (d, $J = 138.0$ Hz, R-Ar CH), 131.91 (d, $J = 167.7$ Hz, R-Ar CH), 128.07 (s, MBP- C_{ipso}), 127.67 (d, $J = 155.0$ Hz, R-Ar CH), three other aryl resonances overlapped by solvent, 65.21 (t, $J = 145.5$ Hz, NCH_2), 49.53 (q, $J = 142.4$ Hz, NMe_2), 35.02 (s, CMe_3), 32.63 (t, $J = 125.0$ Hz, MBP CH_2), 30.68 (q, $J = 126.1$ Hz, $C(CH_3)_3$), 21.16 (q, $J = 126.2$ Hz, MBP Me), 11.21 (br.q, $J = 115$ Hz, B-Me). ^{19}F -NMR (C_6D_5Br , $25^\circ C$) δ -167.66 (m-F), -164.96 (p-F), -133.29 (o-F).

5.9. Generation of $\{(MBP)Ti[\eta^2-CH_2C_6H_4(o-NMe_2)]-[MeB(C_6F_5)_3]\}$ (**6b**)

A solution of **4b** (31.6 mg, 59.0 mmol) in 0.25 ml of bromobenzene- d_5 was added to a solution of $B(C_6F_5)_3$

(31.7 mg, 61.9 mmol) in 0.25 ml of bromobenzene- d_5 . The solution immediately turned wine-red, and NMR spectroscopy showed formation of **6b** as the sole product. ^1H -NMR ($\text{C}_6\text{D}_5\text{Br}$, 30°C) δ 7.35 (m, 2H, R–Ar H), 7.12 and 6.93 (s, 2H each, MBP–Ar H), 7.09 (m, 2H, R–Ar H), 3.66 (d, $J = 13.7$ Hz, 1H, MBP CHH), 3.2 (br, 3H, MBP CHH and TiCH $_2$), 2.94 (br.s, 6H, NMe $_2$), 2.20 (s, 6H, MBP–CH $_3$), 1.16 (s, 18H, MBP–CMe $_3$), 1.08 (br.s, 3H, B–Me). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6F_5 resonances omitted, $\text{C}_6\text{D}_5\text{Br}$, 30°C) δ 162.29 (s, O–ArC $_{ipso}$), 149.11 (s, R–Ar C $_{ipso}$), 147.11 (s, R–Ar C $_{ipso}$), 135.95 and 134.39 ($2 \times$ MBP–C $_{ipso}$), 131.81, 121.88, 119.86, 112.86, 90.60, 69.80 (assignment ambiguous), 46.67 (NMe $_2$), 34.66 (s, CMe $_3$), 33.81 (MBP CH $_2$), 29.96 (C(CH $_3$) $_3$), 21.01 (MBP Me), 10.92 (br, B–Me). ^{19}F -NMR ($\text{C}_6\text{D}_5\text{Br}$, 25°C) δ –168.09 (*m*-F), –165.46 (*p*-F), –133.45 (*o*-F).

5.10. Reaction of **6a** with ethene

A solution of **6a** in bromobenzene- d_5 , prepared as above using 48.8 mg (91.1 mmol) of **4a** and 49.8 mg (97.3 mmol) of $\text{B}(\text{C}_6\text{F}_5)_3$, was placed in an NMR tube equipped with a Teflon (Young) valve and attached to a vacuum line. The solution was frozen in liquid nitrogen and evacuated. Subsequently, 91 mmol of ethene was condensed into the mixture. The valve was closed and the mixture was thawed out, resulting in an orange–red solution. A ^1H -NMR spectrum was immediately recorded which showed formation of **7a–1**. ^1H -NMR ($\text{C}_6\text{D}_5\text{Br}$, 25°C) δ 7.31 and 7.18 (t, $J = 7.3$ Hz, 1H each, R–Ar H), 7.14 and 6.95 (s, 2H each, MBP–Ar H), 7.06 and 6.99 (d, $J = 7.3$ Hz, 1H each, R–Ar H), 3.78 (br.s, 2H, NCH $_2$), 3.59 (d, $J = 14.2$ Hz, 1H, MBP CHH), 3.41 (t, $J = 6.7$ Hz, 2H, CH $_2$), 2.6 (3H, Ti–CH $_2$ and MBP CHH) 2.44 (s, 6H, NMe $_2$), 2.20 (s, 6H, MBP–CH $_3$), 1.30 (s, 18H, MBP–CMe $_3$), 1.10 (br.s, 3H, B–Me). Upon standing at ambient temperature, rearrangement of the initial product took place. After 15 min, conversion to **7a–2** was complete. ^1H -NMR ($\text{C}_6\text{D}_5\text{Br}$, 25°C) δ 7.56 and 7.26 (t, $J = 7.8$ Hz, 1H each, R–Ar H), 7.36 and 7.10 (d, $J = 7.8$ Hz, 1H each, R–Ar H), 7.14, 7.04, 7.00 and 6.86 (s, 1H each, MBP–Ar H), 4.59 and 3.47 (d, $J = 13.7$ Hz, 1H each, MBP CH $_2$), 3.53 and 1.81 (d, $J = 14.2$ Hz, NCH $_2$), 3.32 (q, $J = 6.4$ Hz, 1H, Ti–CH), 2.63 (s, 3H, NMe), 2.2 (s, 6H, NMe and MBP–CH $_3$), 2.13 (s, 3H, MBP–CH $_3$), 1.60 (d, $J = 6.4$ Hz, 3H TiCHMe), 1.52 and 1.06 (s, 9H each, MBP–CMe $_3$), 1.10 (br.s, 3H, B–Me). ^{13}C -NMR (selected data, $\text{C}_6\text{D}_5\text{Br}$, 25°C) δ 162.84 and 162.16 (s, O–ArC $_{ipso}$), 110.78 (d, $J = 121.3$ Hz, Ti–CH), 65.35 (t, $J = 141.8$ Hz, NCH $_2$), 49.15 (q, $J = 142.7$ Hz, NMe), 44.23 (q, $J = 146.5$ Hz, NMe), 35.06 (t, $J = 125.5$ Hz, MBP CH $_2$), 34.96 and 34.71 (s, CMe $_3$), 30.53 (q, $J = 121.3$ Hz, C(CH $_3$) $_3$), 29.65 (q, $J = 126.7$ Hz, C(CH $_3$) $_3$), 21.03 and 20.88 (q, $J = 126.7$ Hz, MBP Me), 16.80 (q,

$J = 126.7$ Hz, TiCHCH $_3$), 11.16 (br, B–Me). Similar reactions in which an excess of ethene was used did not lead to subsequent ethene insertions or polymerisation.

5.11. Reaction of **6b** with ethene

A solution of **6b** in bromobenzene- d_5 , prepared as above using 40.8 mg (76.2 mmol) of **4b** and 41.4 mg (80.1 mmol) of $\text{B}(\text{C}_6\text{F}_5)_3$, was placed in an NMR tube equipped with a Teflon (Young) valve and attached to a vacuum line. The solution was frozen in liquid nitrogen and evacuated. Subsequently, 76 mmol of ethene was condensed into the mixture. The valve was closed and the mixture was thawed out resulting in an orange–red solution. NMR spectroscopy indicated formation of **7b**. ^1H -NMR ($\text{C}_6\text{D}_5\text{Br}$, 45°C) δ 7.22 (m, 2H, R–Ar H), 7.16 and 6.94 (s, 2H each, MBP–Ar H), 7.09 (t, $J = 7.3$ Hz, 1H, R–Ar H), 6.86 (d, $J = 8.3$ Hz, 1H, R–Ar H), 3.60 and 3.00 (d, $J = 13.8$ Hz, 1H, MBP CH $_2$), 3.12 (t, $J = 6.3$ Hz, 2H, Ti–CH $_2$), 2.81 (s, 6H, NMe $_2$), 2.65 (m, 2H, –CH $_2$ –), 2.20 (s, 6H, MBP–CH $_3$), 2.18 (t, $J = 6.8$ Hz, 2H, R–Ar–CH $_2$), 1.24 (s, 18H, MBP–CMe $_3$), 1.05 (br.s, 3H, B–Me). ^{13}C -NMR (selected data, $\text{C}_6\text{D}_5\text{Br}$, 45°C) δ 162.46 (s, O–ArC $_{ipso}$), 91.73 (t, $J = 137.1$ Hz, Ti–CH $_2$), 47.51 (q, $J = 141.8$ Hz, NMe $_2$), 34.61 (s, CMe $_3$), 34.56 (t, $J = 126.8$ Hz, MBP CH $_2$), 32.37 (t, $J = 125.0$ Hz, –CH $_2$ –), 30.30 (t, $J = 133.6$, R–Ar–CH $_2$), 30.09 (q, $J = 125.6$ Hz, C(CH $_3$) $_3$), 20.93 (q, $J = 126.2$ Hz, MBP Me), 10.68 (br, B–Me). Similar reactions in which an excess of ethene was used did not lead to subsequent ethene insertions or polymerisation.

5.12. Reaction of **6a** with propene

A solution of **6a** in bromobenzene- d_5 , prepared as above using 55.5 mg (103.6 mmol) of **4a** and 56.3 mg (110.0 mmol) of $\text{B}(\text{C}_6\text{F}_5)_3$, was placed in an NMR tube equipped with a Teflon (Young) valve and attached to a vacuum line. The solution was frozen in liquid nitrogen and evacuated. Subsequently, 104 μmol of propene was condensed into the mixture. The valve was closed and the mixture was thawed out, resulting in a deep red solution. NMR spectroscopy indicated formation of **8a**. ^1H -NMR ($\text{C}_6\text{D}_5\text{Br}$, 25°C) δ 7.42 and 7.20 (t, $J = 7.8$ Hz, 1H each, R–Ar H), 7.24 (d, $J = 7.8$ Hz, 1H, R–Ar H), 7.16, 7.12 and 6.90 (s, 1H each, MBP–Ar H), 7.0 (2H, MBP–Ar H and R–Ar H), 4.42 and 3.18 (d, $J = 13.7$ Hz, 1H each, MBP CH $_2$), 3.61 and 2.72 (d, $J = 14.2$ Hz, NCH $_2$), 3.51 (m, 1H, CH), 2.95 (dd, $J = 11.7$ Hz and 3.4 Hz, 1H, Ti–CHH), 2.63 (ps.t, $J = 11.7$ Hz, 1H, Ti–CHH), 2.60 and 2.34 (s, 3H each, NMe), 2.23 and 2.18 (s, 3H each, MBP–CH $_3$), 1.45 and 1.08 (s, 9H each, MBP–CMe $_3$), 1.43 (d, $J = 6.4$ Hz, 3H, CHMe) 1.10 (br.s, 3H, B–Me). ^{13}C -NMR (selected data, $\text{C}_6\text{D}_5\text{Br}$, 25°C) δ 163.20 and 162.73 (s,

O–ArC_{ipso}), 104.56 (t, $J = 135.5$ Hz, Ti–CH₂), 64.75 (t, $J = 143.9$ Hz, NCH₂), 49.50 (q, $J = 140.1$ Hz, NMe), 46.66 (q, $J = 140.1$ Hz, NMe), 34.85 and 34.51 (s, CMe₃), 34.45 (t, $J = 127.8$ Hz, MBP CH₂), 34.26 (d, $J = 128.4$ Hz, CH), 30.53 (q, $J = 125.8$ Hz, C(CH₃)₃), 30.09 (q, $J = 127.1$ Hz, C(CH₃)₃), 23.80 (q, $J = 129.1$ Hz, CHCH₃), 20.99 and 20.95 (q, $J = 126.6$ Hz, MBP Me), 10.84 (br, B–Me). Similar reactions in which an excess of propene was used did not lead to subsequent propene insertions or polymerisation.

5.13. Structure determination of **3**·(Et₂O)_{0.5}

Suitable single crystals were obtained by crystallisation from diethyl ether. From one orange crystal with approximate dimensions 0.20 × 0.40 × 0.56 mm, intensity data were recorded on an Enraf–Nonius CAD4-F diffractometer at 130 K using Mo–K_α radiation with $\lambda(\text{Mo–K}_{\alpha}) = 0.71073$ Å.

5.13.1. Crystal data

C₃₃H₄₂F₃N₁O₅STi·(C₄H₁₀O)_{0.5}, $M = 669.63$, triclinic, space group $P\bar{1}$, $a = 11.071(1)$, $b = 11.367(1)$, $c = 15.185(1)$ Å, $\alpha = 72.809(4)$, $\beta = 76.394(5)$, $\gamma = 87.217(5)^{\circ}$, $V = 1766.7(3)$ Å³, $Z = 2$, $D_{\text{calc.}} = 1.2588(2)$ g cm^{−3}, $\mu(\text{Mo–K}_{\alpha}) = 3.5$ cm^{−1}. Data (7689 unique reflections) were collected between $1.45 < \theta < 27.0^{\circ}$. The structure was solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors, as described previously [18]. A disordered solvent molecule was present (with the O-atom located at the inversion centre), which could not be fitted with a discrete model. The BYPASS procedure [19] was used to account for this electron density. Of the molecule of **3** all hydrogen atoms were located from the difference Fourier map and included in the refinement with isotropic temperature factors. Full refinement on F_o converged at $R_F = 0.038$ ($wR = 0.042$, $w = 1$) from 6623 reflections with $I \geq 2.5\sigma(I)$ and 566 parameters.

6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic

Data Centre, CCDC no. 126019 for compound **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (Fax: +44-1223-336-033 or e-mail deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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