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Synthesis, Isolation and Structural Characterisation of Alkoxytitanium Triflate Complexes

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Treatment of [Ti(O*i*Pr)$_4$] with trimethylsilyl triflate results in the formation of [Ti(O*i*Pr)$_3$(OTf)] (**2**) in high yield. Subsequent treatment of the triflate derivative **2** with a series of facially coordinating N$_3$-donor ligands results in the production of a series of charge-separated metal alkoxide salts of the general formula [{L}Ti(O*i*Pr)$_3$][OTf] {L = tris(pyrazolyl)methane (**3a**), 1,3,5-triethyl-1,3,5-triazacyclohexane (**3b**), 1,3,5-tribenzyl-1,3,5-triazacyclohexane (**3c**), 1,3,5-tris(*p*-fluorobenzyl)-1,3,5-triazacyclohexane (**3d**), and 1,3,5-tris[(1*S*)-1-phenylethyl]-1,3,5-triazacyclohexane (**3e**)}. The products were characterized by ^{1}H and ^{13}C NMR spectroscopy and in the case of **3a**–**c** by single-crystal X-ray diffraction. Reaction of **2** with 1,3,5-triphenyl-1,3,5-triazacyclohexane results in the formation of complex **4** [{L′}$_2$Ti(O*i*Pr)$_2$(OTf)$_2$], which contains two 3,4-dihydroquinazoline ligands (L′), a result of catalytic activation of the triazacyclohexane ligands by [Ti(O*i*Pr)$_3$(OTf)] towards electrophilic aromatic substitution.

Introduction

Titanium(IV) compounds of the general form [TiX$_4$] have been employed extensively as Lewis acid catalysts in a wide range of synthetic organic transformations.[1] Fine-tuning of the Lewis acidity of these systems can be achieved by the careful selection of X from alkoxide, halide, phenolate or triflate ligands.[2] Of these systems, it is the Lewis acid complexes based on weakly coordinating anions[3] such as triflate (trifluromethanesulfonate, [OTf]$^-$) that have received the most attention.[4] In the vast majority of cases, preparation of the metal triflate complex involves a salt metathesis and elimination, e.g. reaction of [Ti(O*i*Pr)$_3$Cl] with [Ag{OSO$_2$CF$_3$}] ([Ag{OTf}]) to form [Ti(O*i*Pr)$_3$OTf].[5] Such compounds are also subject to spontaneous/solvent-induced ligand redistribution; e.g., reaction of [Ti(O*t*Bu)$_3$Cl] with [Ag{OTf}] in tetrahydrofuran (thf) results in the formation of [Ti(O*t*Bu)$_2$(OTf)$_2$(thf)$_2$] rather than the expected [Ti(O*t*Bu)$_3$(OTf)].[6] A major disadvantage of such systems is, as the scale of reaction increases, the difficulty and disadvantage of being air- and moisture-sensitive liquids requiring storage and manipulation under inert conditions. Furthermore, in significant quantities, compounds such as TiCl$_4$ can present a considerable caustic and corrosive hazard.[7] Therefore, the design of new titanium-based reagents that are convenient to use yet retain high catalytic activity is of considerable importance to the synthetic community. One alternative synthetic methodology for the incorporation of weakly coordinating ligands such as triflate (OTf) into complexes has been the utility of Me$_3$SiOTf,[8] which reacts with M–OR and M–Cl functionalities to form the corresponding M–OTf complex and Me$_3$SiOR or Me$_3$SiCl, respectively.[2b,9] As part of a continuing study of the chemistry of titanium alkoxide and aryloxide chemistry and their activities in Lewis acid mediated organic transformations, we have previously described the synthesis of air- and moisture-stable Ti^{IV} triflate complexes of *C*$_3$-symmetric aminetris(phenolato) ligands and their activity as catalysts for aza-Diels–Alder reactions.[2b,10] More recently, we have described the interaction of strong organic acids such as bis(trifluoromethylsulfonyl)amide, with titanium alkoxide complexes and the structural chemistry of the products.[11]

Herein we report an initial study of the coordination chemistry of the titanium triflate complex [Ti(O*i*Pr)$_3$(OTf)] (**2**) with a range of neutral facially coordinating N$_3$-donor ligands, synthesised by using a salt-free process, with the aim of investigating the coordination chemistry of these systems.

Results and Discussion

Our interest in the development of the stoichiometric and catalytic chemistry of *C*$_3$-symmetric[12] titanium triflate compounds[2b,10] prompted us to explore the reactions of representative *fac*-N$_3$ donor ligands with compounds [Ti(O*i*Pr)$_3$OTf] to establish a framework for future studies. The N$_3$ donor ligands, selected on the basis of their synthetic utility and availability, are shown in Figure 1. In both cases the triazacyclohexane (TAC) and the tris(pyrazolyl)methane [HC(Pz)$_3$] ligand systems are known to coordinate to metal centres through a facial coordination arrangement, with titanium systems containing triazacyclohexane,[13] tri-

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azacyclononane,[13a] tris(pyrazolyl)methane[14] and tris(pyrazolyl)borate[15] ligands having previously been exploited in the synthesis of complexes for use in α-olefin polymerization, styrene polymerization, and as models for bioinorganic systems.

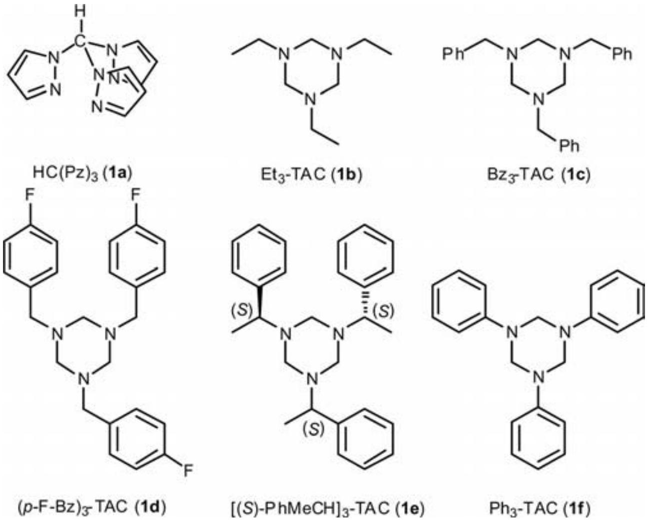
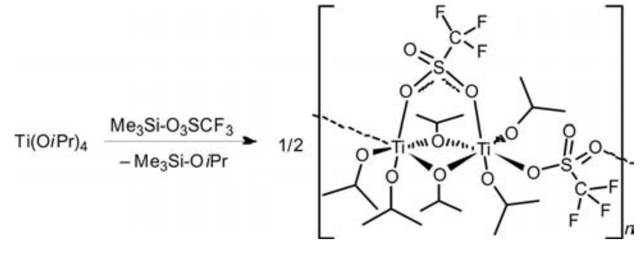


Figure 1. Ligands used in the course of this study.

Synthesis and Characterisation

The reaction of $[\mathrm{Ti(O}i\mathrm{Pr)_4}]$ with 1 equiv. of $[\mathrm{Me_3SiOSO_2CF_3}]$ (TMS-OTf) in toluene under an inert gas proceed rapidly at room temperature to afford $\mathrm{Me_3SiO}i\mathrm{Pr}$ and the highly air- and moisture-sensitive titanium triflate complex $[\mathrm{Ti(O}i\mathrm{Pr)_3(OTf)}]_n$ (**2**) in high yield (Scheme 1).



Scheme 1. Proposed equation for the synthesis of **2**, indicating the polymeric nature of **2** observed in the solid state.

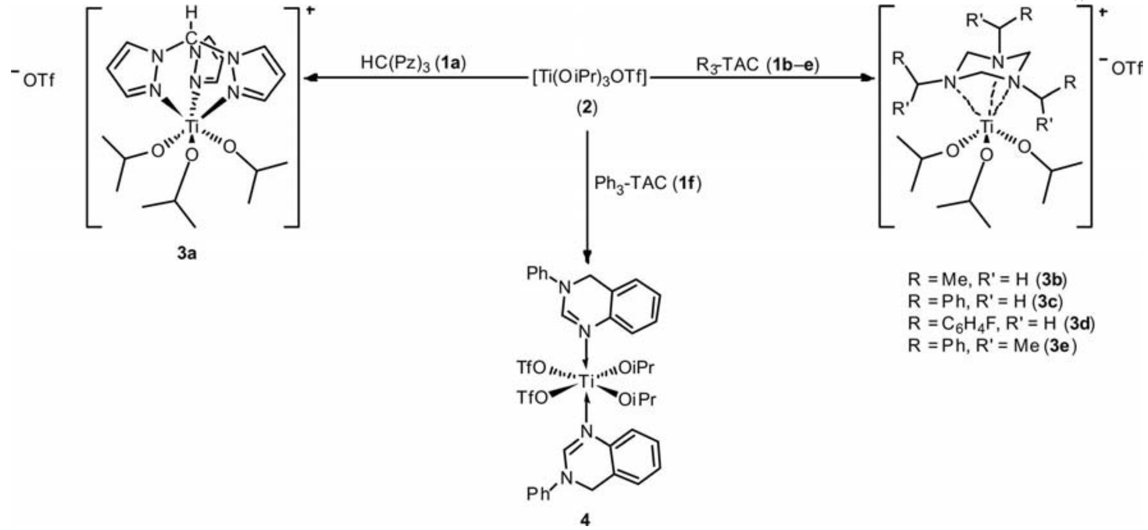
Complex **2** can be isolated as an analytically pure crystalline solid by recrystallization from concentrated toluene solutions.

Although crystals of **2** suitable for single-crystal X-ray diffraction were grown from both toluene and benzene, it has not been possible to find a suitable model for the considerable disorder that is present in the solid-state structure of **2**. After collecting and partially solving several data sets, we are confident the geometry of the complex obtained is that shown in Scheme 1. The asymmetric unit cell (ASU) consists of a complex with a dimetallic $\{\mathrm{Ti(\mu\text{-}O}i\mathrm{Pr)_2(O}i\mathrm{Pr)_4}\}$ core, in which the titanium centres are bridged by two alkoxido ligands. The dimetallic fragment is also bridged apically by a disordered triflate group. The second triflate group and one of the terminal alkoxide units are disordered over the two titanium centres, but the second triflate's coordination environment is such that this group serves to bridge adjacent dimetallic units to form an extended polymeric system. The ^{1}H NMR spectrum of **2** shows all three isopropoxide units to be equivalent on the NMR time scale, with the presence of a single set of broad resonances for both the C*H*(Me)$_2$ and CH(*Me*)$_2$ moieties on the isopropoxide groups. Low-temperature ^{1}H NMR studies (–60 °C) on **2** showed only a sharpening of the signals to well-defined doublet and septet resonances. Complex **2** has previously been synthesized by the reaction of $[\mathrm{ClTi(O}i\mathrm{Pr)_3}]$ with [Ag(OTf)] and reported by Jørgensen et al., although no characterization data was provided.[5] In the absence of donor solvents, e.g. thf, complex **2** appears to be stable to spontaneous ligand rearrangement and formation of the bis(triflate) complex $[\mathrm{Ti(O}i\mathrm{Pr)_2(OTf)_2}]$, although the effect of solvent on such spontaneous rearrangements has not been investigated by us.

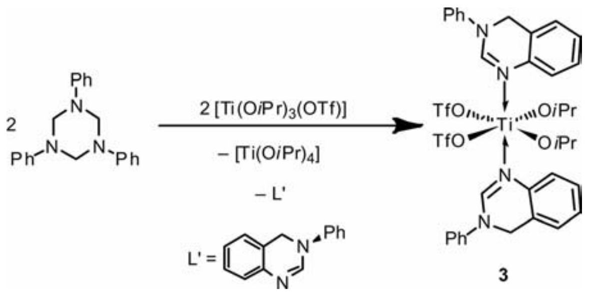
The reactions of **2** with the *fac*-N$_3$-donor ligands HC(Pz)$_3$ [tris(pyrazolyl)methane, **1a**], Et$_3$-TAC (1,3,5-triethyl-1,3,5-triazacyclohexane, **1b**), Bz$_3$-TAC (1,3,5-tribenzyl-1,3,5-triazacyclohexane, **1c**), (*p*-F-Bz)$_3$-TAC [1,3,5-tris(*p*-fluorobenzyl)-1,3,5-triazacyclohexane, **1d**], [(*S*)-Ph(Me)CH]$_3$-TAC {1,3,5-tris[(*S*)-1-phenylethyl]-1,3,5-triazacyclohexane, **1e**} and Ph$_3$-TAC (1,3,5-triphenyl-1,3,5-triazacyclohexane, **1f**) are summarized in Scheme 2. The reaction with 1 equiv. of the appropriate *fac*-N$_3$ donor proceeded smoothly in a 24–84% yield in toluene to give the products **3a**–**e** and **4** as analytically and spectroscopically pure solids.

The ^{1}H NMR spectra of **3a** and **3b**–**e** at room temperature all feature characteristic resonances in the region of $\delta = 1.1\text{–}1.4$ ppm and $\delta = 4.4\text{–}4.9$ ppm, respectively, corresponding to the isopropoxide ligands. Despite the difference in ligand systems used in complexes **3a**–**e**, ^{1}H NMR spectroscopy reveals little change in the characteristic resonances for the methine hydrogen atom, suggesting that any *trans* effect experienced by the isopropoxide group, originating from the N atom in the Pz$_3$CH or TAC ligands is not significant. The resonances for the coordinated *fac*-N$_3$-donor ligands were as expected on the basis of previous studies and were consistent with the C_s symmetry proposed in Scheme 3 (see Exp. Section for further details). For the TAC complexes **3b**–**e** coordination of the TAC ligand to the titanium centre results in a resolution of the (NCH$_2$)$_3$ ring methylene signals into two well-separated doublets ($\delta = 3.48$ and 4.21 ppm for **3c**; $\delta = 3.49$ and 4.20 ppm for **3d**; $\delta = 2.56$ and 4.54 ppm for **3e**) for the axial and equatorial hydrogen atoms. In the case of complex **3b** the signals are coincidental, and appear in the ^{1}H NMR spectrum as overlapping doublets ($\delta \approx 4.03$ ppm). This signal resolution is probably the best evidence for κ^3-coordination of the *fac*-N$_3$ ligand to the metal atom and indicates that the titanium centres appears to remain coordinated to the N-donor ligand in solution.

As with closely related triflate complexes, ^{19}F NMR experiments on **3a**–**e** provide little information on the coordi-



Scheme 2. Schematic illustration of the synthesis of complexes **3a**–**e** and **4**.



Scheme 3. Proposed equation for the synthesis of complex **4**.

nation state of the triflate anion, $[OTf]^-$, in the solution state.[13e]

In an attempt to produce an analogous cationic complexes with the 1,3,5-triphenyl-1,3,5-triazocyclohexane ligand **1f**, $[Ti(OiPr)_3(OTF)]$ (**2**) was treated with Ph$_3$-TAC in a manner analogous to that of previous reactions. Addition resulted in an immediate colour change (from colourless to orange), and standing overnight at room temperature resulted in the formation of a crop of orange crystals.

Analysis of the crystalline material by ^{1}H NMR spectroscopy showed the presence of a doublet and a septet at δ = 1.82 and 5.31 ppm, respectively, in the ^{1}H NMR spectrum, corresponding to isopropoxide ligands, which appear at significantly higher ppm values than those found for complexes **2a**–**e**. The ^{1}H NMR spectrum also showed the presence of several other resonances, but specifically a sharp singlet and doublet at δ = 8.62 and 8.46 ppm, respectively. The isolated crystalline solid of **4** was found to show only limited solubility in chlorinated and inert organic solvents. As a result ^{13}C{^{1}H} NMR spectroscopic data for **4** could not be obtained. Analysis by single-crystal X-ray diffraction was therefore relied upon to identify the nature of complex **4**. The molecular structure will be discussed at a later point, but studies showed the product to be a titanium bis(alkoxide) bis(triflate) system coordinated by two 3-phenyl-3,4-dihydroquinazoline ligands.

3,4-Dihydroquinazoline systems are typically prepared by condensation reactions between aniline derivatives and formaldehyde and have previously been isolated as intermediates in the synthesis of Tröger's base.[16] The precise mechanism by which complex **4** is formed is unknown, but it is possible to suggest that the formation of the 3,4-dihydroquinazoline system is a result of activation of the Ph$_3$-TAC ligand by a strong Lewis acid {i.e. $[Ti(OiPr)_3(OTf)]$} followed by electrophilic aromatic substitution. The reaction of triazacyclohexane systems with strong Lewis acids (such as $TiCl_4$ and $SnCl_4$) has previously been shown to produce *N*-methyleneamine derivatives in situ.[17] In the case of 1,3,5-triphenyl-1,3,5-triazacyclohexane, reaction with strong Lewis acids are known to produce *N*-methylideneaniline ($Ph{-}N{=}CH_2$), the initial product in the reaction of aniline and formaldehyde,[17a] and activate the methyleneamide derivative towards electrophilic aromatic substitution. It is therefore possible to hypothesise that the 3,4-dihydroquinazoline ligand results from such activation, and that ligand scrambling within the reaction mixture results in the formation of **4** along with half an equivalent of $[Ti(OiPr)_4]$ as shown in Scheme 3. Similar ligand rearrangement reactions have previously been reported for related tris(alkoxy)metal triflate systems,[11,18] but we believe the monodentate nature of the dihydroquinazoline ligand promotes a ligand redistribution, just as the *fac*-N$_3$ ligands appear to stabilise the $[Ti(OiPr)_3]^+$ cation against ligand redistribution.

Attempts to monitor the reaction by ^{1}H NMR spectroscopy were not wholly successful, but the ^{1}H NMR spectrum of the reaction mixture does show the presence of both free 3-phenyl-3,4-dihydroquinazoline and resonances that correspond to a second isopropoxide-containing species, although the relative integrals of these species do not provide conclusive support for the proposed reaction scheme.

Importantly, throughout this study a second, in situ, method for the synthesis of compounds **3a**–**3e** and **4** has also been evaluated. Stoichiometric amounts of Me_3SiOTf were added to a toluene solution of [Ti(O*i*Pr)$_4$] in the presence of the *fac*-N_3 nitrogen ligands **1a**–**f** in order to investigate any possible effect on the complex formation and to reveal any differences between the products formed by the two methods, i.e. stoichiometries, different ligand coordination modes, different polymorphs, etc. Our investigation has shown that for the compounds discussed here, both methodologies were equally effective, and for comparable experiments, the products were found to be identical by multinuclear NMR spectroscopy, elemental analysis and unit cell determination. This observation could have a significant effect on any future utility of these complexes, as there will be no need to preform the catalytic species, thereby saving time.

Attempts to synthesize the bis- and tris(triflate) complexes, i.e. [Ti(O*i*Pr)$_2$(OTf)$_2$] and [Ti(O*i*Pr)(OTf)$_3$], respectively, by reaction of stoichiometric amounts of Me_3SiOTf with [Ti(O*i*Pr)$_4$] in toluene, have to date been unsuccessful, forming only intractable, insoluble materials. The addition of donor solvents such as thf or pyridine to these systems results in the formation of a series of soluble complexes, which have yet to be fully and properly characterised.

Solid State Molecular Structures

Crystal data for complexes **3a**–**c** are shown in Table 3. In all cases, the complexes are ionic, comprising of well separated titanium-based cations, and triflate anions. The molecular structures of the cationic component of **3a**, **3b** and **3c** are shown in Figures 2, 3 and 4 respectively. Within all three cations the titanium centres are situated in a *pseudo* octahedral environment coordinated by the tridentate tris(pyrazol)methane [HC(Pz)$_3$] (**3a**), or a tridentate trialkyltriazacyclohexane (R_3-TAC) (**3b**; R = Et, **3c**; R = CH_2Ph) and three isopropoxide groups, which are orientated in a *transoid* fashion to the nitrogen atoms of the respective donor ligands.

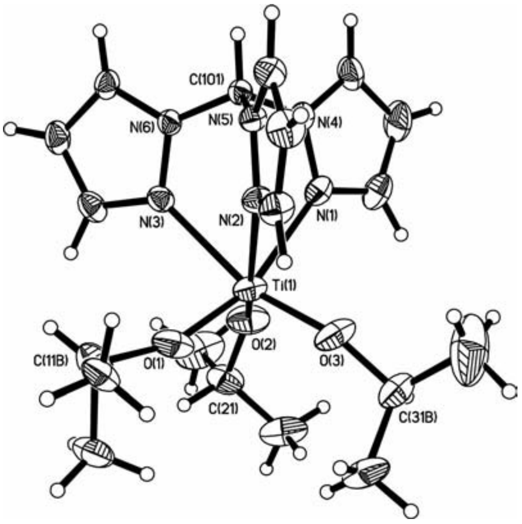


Figure 2. Diagram showing the molecular structures of the cationic component of [{H(Pz)$_3$}Ti(O*i*Pr)$_3$][OTf] (**3a**) (30% probability ellipsoids). Disordered based on O(1) and O(3) have been omitted and the major component shown only.

Complex **3a** crystallizes in the monoclinic space group *P*2$_1$/*c*, with one independent molecule per asymmetric unit. The tris(pyrazolyl)methane ligand is coordinated in a κ^3-fashion, with the lone pairs of the tris(pyrazolyl)methane pointing towards the Ti centre in approximately the same direction as the Ti–N bond. The Ti–N distances lying in the range 2.27–2.89 Å, which are comparable to those found in [Ti(N*t*Bu){C(Me$_2$Pz)$_3$}Cl(thf)][14b] [2.358(3)–2.16(9) Å], which contains the anionic ligand [C(Me$_2$Pz)$_3$]$^-$, (Me$_2$Pz = 3,5-dimethylpyrazole), and related Ti–tris(pyrazolyl)borate complex, such as [Ti{HB(Mes$_2$Pz)$_3$}Cl$_2$(O*t*Bu)], (2.17–2.25 Å).[19] The N–Ti–N "bite angles" in **3b** (N–Ti–N$_{av.}$ 75.61°) are slightly smaller than "bite angle" observed in [Ti(N*t*Bu){C(Me$_2$Pz)$_3$}Cl(thf)], (N–Ti–N$_{av.}$ 80.52°). This compression is accompanied by a small lengthening of the Ti···CH distance to 3.406(2) Å {cf. 3.332(3)° in [Ti(N*t*Bu){C(Me$_2$Pz)$_3$}Cl(thf)]}, but not at the expense of Ti–N contact. The steric demands of the three O*i*Pr groups about the Ti atom are presumably the cause of this displacement of the {HC(Pz)$_3$} ligand, an observation that is supported by the large O–Ti–O angles shown in Table 1. As a result the *cis*- and *trans*-N–Ti–O angles deviate considerably from the ideal.

Table 1. Selected geometric data for the complexes **3a**, **3b** and **3c**.

	3a	**3b**	**3c**
Bond lengths [Å]			
Ti(1)–O(1)	1.765(2)	1.7848(10)	1.787(3)
Ti(1)–O(2)	1.8066(19)		1.766(3)
Ti(1)–O(3)	1.7643(19)		1.780(3)
Ti(1)–N(1)	2.271(2)	2.3006(11)	2.350(3)
Ti(1)–N(2)	2.2877(18)		2.319(3)
Ti(1)–N(3)	2.2798(18)		2.339(3)
Bond angles [°]			
O(1)–Ti(1)–O(2)	102.02(10)	106.09(4)	109.23(14)
O(1)–Ti(1)–O(3)	103.03(10)		105.76(14)
O(2)–Ti(1)–O(3)	102.63(10)		105.30(13)
N(1)–Ti(1)–N(2)	75.04(6)	60.16(5)	59.61(10)
N(1)–Ti(1)–N(3)	76.46(6)		59.66(10)
N(2)–Ti(1)–N(3)	75.32(6)		59.41(9)
O(1)–Ti(1)–N(1)	161.69(8)	147.89(4)	146.55(12)
O(2)–Ti(1)–N(2)	157.97(8)		148.37(11)
O(3)–Ti(1)–N(3)	161.49(8)		145.86(11)
Additional distances [Å]			
Δ values	–	0.145 [C(101)]	0.070 [C(101)] 0.057 [C(201)] 0.203 [C(301)]

Complex **3b**, which crystallises in the cubic space group *P*2$_1$*3* with a third of a molecule per asymmetric unit (the Ti atom of the cation and the carbon and sulfur of the triflate anion residing on centre of threefold symmetry, the rest of the molecule is generated by symmetry operations) is revealed to possess an all *syn*-conformation in the solid state (Figure 3).

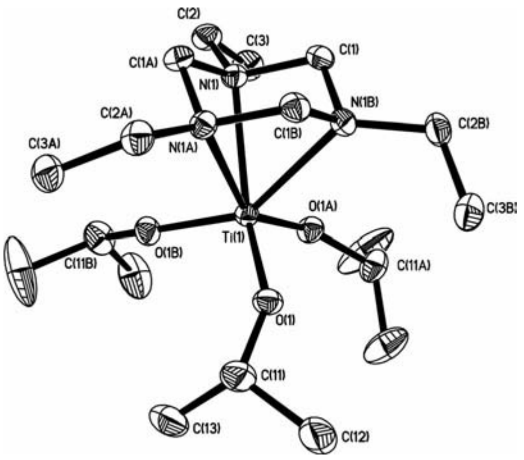


Figure 3. Diagram showing the molecular structures of the cationic component of [{Et$_3$-TAC}Ti(O*i*Pr)$_3$][OTf] (**3b**) (30 % probability ellipsoids). Hydrogen atoms have been omitted for clarity. Disordered based on O(1) has been omitted and the major component shown only. Symmetry transformations used to generate equivalent atoms: #A = *y*,*z*,*x* #B = *z*,*x*,*y*.

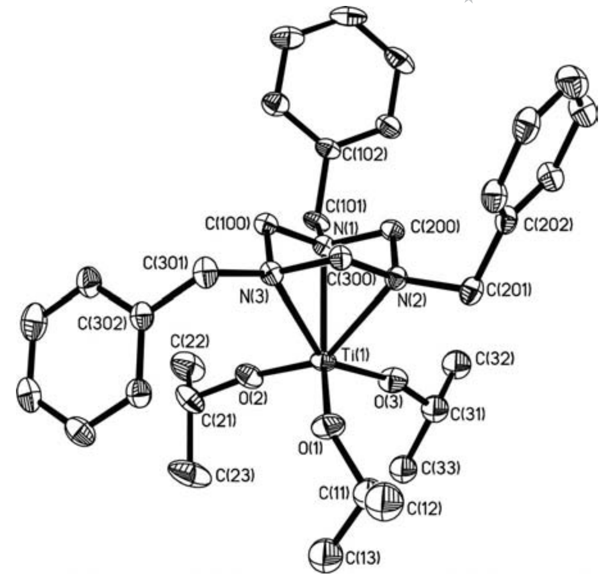


Figure 4. Diagram showing the molecular structures of the cationic component of [{Bz$_3$-TAC}Ti(O*i*Pr)$_3$][OTf] (**3c**) (30 % probability ellipsoids). Disordered based on O(1) and O(3) have been omitted and the major component shown only.

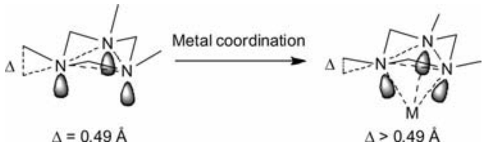
Complex **3c**, which crystallises in the orthorhombic space group *Pc*2$_1$*b*, with one molecule per asymmetric unit, shows an *anti*,*anti*,*syn* configuration of the benzyl groups of the TAC ligand (Figure 3). An examination of the Ti–N bond lengths with in the two complexes shows the two complexes to be comparable, within experimental error; the only significant differences being the relative conformations of the ethyl and benzyl substituents of the TAC ligands.

Structural parameters for the coordination environment around titanium in the cations [(R$_3$-TAC)Ti(O*i*Pr)$_3$]$^+$ (Figures 3 and 4) are summarised in Table 1. In both complexes the Ti–N bond length of [**3b**: 2.3006(11) Å] and {**3c**: 2.350(3) Å [N(1)], 2.319(3) Å [N(2)] & 2.339(3) Å [N(3)]} and bite angle {**3b**: 60.16(5)° [N(1)–Ti(1)–N(1*)] and **3c**: 59.56(10)° (av. N–Ti–N)} are comparable those found in the related complexes [{TAC}TiCl$_3$]$^+$ and [{TAC}Ti(N*t*Bu)-Cl$_2$].[13e,14b] As in other triazocyclohexanes complexes, the facial κ^3-coordination of the ligand results in a *mis*-direction of the nitrogen lone pairs, and results in a reduced bonding situation. However, bonding can be improved by bending of the N-substituent towards the {N$_3$}-plane and therefore the lone pair towards the metal.[13e]

This bending can be expressed by the distance Δ of the α-C atom of the nitrogen substituent above the {N$_3$} plane. For a perfect tetrahedral angle a value of Δ = 0.49 Å is expected. Any reduction of this value indicates a bending of the N-lone pair towards the metal centre. The observed Δ values for **3b** and **3c** are shown in Table 2 and fall into two groups. For substituents in the *syn*-orientation Δ values range between 0.14–0.20 Å, and for *anti*-oriented substituents the bending is significantly greater with values between 0.05–0.07 Å (Scheme 4).

Table 2. Selected geometric data for the complexes **4**.

Bond lengths [Å]			
Ti(1)–O(1)	1.757(3)	Ti(1)–N(1)	2.172(3)
Ti(1)–O(2)	1.757(3)	Ti(1)–N(2)	2.178(3)
Ti(1)–O(3)	2.142(3)		
Ti(1)–O(6)	2.105(3)		
Bond angles [°]			
O(1)–Ti(1)–O(2)	101.32(13)	O(1)–Ti(1)–O(3)	167.31(12)
O(1)–Ti(1)–O(6)	91.64(12)	O(2)–Ti(1)–O(6)	166.76(12)
O(2)–Ti(1)–O(3)	91.08(12)	N(1)–Ti(1)–N(3)	
O(3)–Ti(1)–O(6)	76.11(11)		



Scheme 4. A diagrammatic representation of the effect of metal coordination to the TAC ligands **1b**–**e**.

Complex **4** crystallises in the triclinic space group $P\bar{1}$ with two molecules of complex and two molecules of disordered toluene per asymmetric unit. The two molecules in the asymmetric unit cell (ASU) differ only in the relative orientations of the dihydroquinazoline ligands and the isopropoxide ligands and are equivalent, within experimental error, to each other. Figure 5 shows the molecular structure of one of the two molecules in the ASU, and is taken as representative of both molecules that are present. Selected bond lengths and angles for **4** are reported in Table 2.

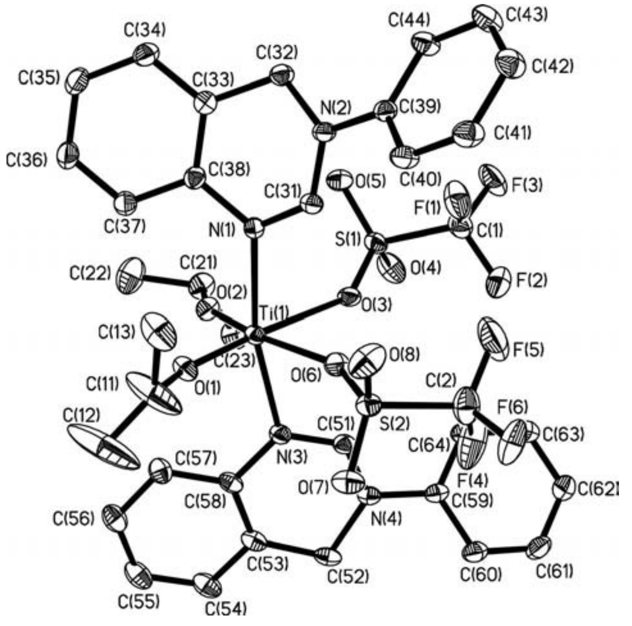


Figure 5. Diagram showing the molecular structures of the complex [Ti(O*i*Pr)$_2$(OTf)$_2$(L)$_2$] (**4**) (L = *N*-phenyl-3,4-dihyroquinazoline) (30% probability ellipsoids). Solvent of crystallisation has been omitted for clarity.

For both molecules within the asymmetric unit cell the titanium centre adopts a pseudo octahedral geometry with a, *cis*-alkoxide, *cis*-triflate *trans*-dihydroquinazoline arrangement. The gross structural arrangement is comparable to the related titanium-bis(isopropoxide) bis(triflamide) complex previously reported by Johnson et al.,[11] with the alkoxide ligands arranged in a *transoidal* configuration with respect to the "weakly coordinated" triflate groups.

The Ti–O*i*Pr bond lengths in **4** are only marginally smaller [Ti–O$_{av.}$ 1.757(3) Å] than those found in complexes **3a**–**c**, indicating the absence of any significant *trans*-influence. Not unsurprisingly the Ti–OTf bonds [Ti–O$_{av.}$ 2.124(3) Å] are also comparable to complexes with a *trans*-triflate, oxygen ligand arrangement.[20]

The two dihydroquinazoline ligands occupy the axial positions about the titanium centre [Ti–N$_{av.}$ 2.175(3) Å] but the N–Ti–N axis is bent [N–Ti–N 167.57(12)°] at the metal centre with the corresponding vectors resulting in a displacement of the ligands away from the alkoxide ligands, presumably to reduce steric interaction between the isopropoxide ligands and the C–H groups at C(37) and C(57). This is accompanied by a significant widening of the *i*PrO–Ti–O*i*Pr angle [O(1)–Ti(1)–O(2) 101.32(13)°] and a reduction in the TfO–Ti–OTf angle [O(3)–Ti(1)–O(6) 76.11(11)°].

The bond lengths and angles within the dihydroquinazoline ligands are directly comparable with previously described dihydroquinazoline derivatives;[16a,21] Figure 6 shows a diagram highlighting the localisation of bonding within the {C$_3$NCN} section of the dihydroquinazoline ligand found in **4**. The bond lengths are taken as exemplars for the other ligands found within the ASU which show identical trends. An examination of the N–C bond lengths within the {NCN} section of the ligand highlights a significant degree of delocalisation over this section of the ligand. An observation that is further supported by examining the angles about the amine nitrogen [average ΣN = 359.4(3)°] which suggest sp^2-hybridisation at this atom.

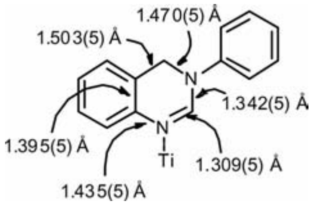


Figure 6. Diagram highlighting the bond localisation in the {C$_3$NCN} portion of the dihydroquinazoline ligand. The bond lengths shown are for the ligand based on [N(1),N(2),C(31)–C(44)].

Conclusions

In this paper we have described effective synthetic routes to the first-reported cationic titanium alkoxide compounds containing tris(pyrazolyl)methane and triazacyclohexane ligands. These compounds form the basis for a comprehensive study of the stoichiometric chemistry of cationic titanium complexes derived from face-capping ligands. In addition, we have found that the *mono*-triflate complex **2** is sufficiently Lewis-acidic to be capable of catalyzing electrophilic aromatic substitution reactions and synthesising dihydroquinazoline systems in a Mannich-type reaction. Reports on the further chemistry of these new complexes and their selected activity in Lewis acid catalysed reactions, such as the catalytic formation of dihydroquinazoline systems will be described at a later date.

Experimental Section

General Remarks: All manipulations were carried out under an atmosphere of dry argon using standard Schlenk and glove-box techniques. Solvents were purified by conventional procedures and distilled prior to use. Ti(O*i*Pr)$_4$ was purchased from Aldrich and used as received, without further purification. The *fac*-N$_3$ ligands HC(Pz)$_3$ (tris(pyrazolyl)methane, **1a**),[22] (tris(*p*-fluorobenzyl)-1,3,5-triazacyclohexane, **1d**)[13e] and (tris-*s*-phenylethyl-1,3,5-triazacyclohexane, **1e**)[23] were synthesised according to literature techniques. Et$_3$-TAC (triethyl-1,3,5-triazacyclohexane, **1b**), Bz$_3$-TAC (tribenzyl-1,3,5-triazacyclohexane, **1c**), and Ph$_3$-TAC (triphenyl-1,3,5-triazacyclohexane, **1f**) were purchased from Aldrich and used as received.

Solution ^{1}H, and ^{13}C{^{1}H} NMR experiments were performed at ambient temperature using a Bruker Advance-300. ^{1}H NMR spectroscopic data are referenced to residual non-deuterated solvent. Elemental analyses were performed externally by Elemental Microanalysis Ltd., Okehampton, UK.

[Ti(O*i*Pr)$_3$(OTf)] (2): Neat trimethylsilyl triflate (1.8 mL, 2.22 g, 10 mmol) was added to a solution of [Ti(O*i*Pr)$_4$] (3.1 mL, 10 mmol) in 50 mL of toluene. The mixture was stirred for 3 h at room temperature, after which the solvent was removed in vacuo. 20 mL of fresh toluene was added to the residue which was dissolved by warming. The clear solution was then filtered, by cannula, in to a clean Schlenk and the solution left to cool to room temperature, yielding a crop of colourless crystals. The product was isolated by filtration, and washed with 5 mL of cold hexane and dried in vacuo; yield 3.14 g 84%. $\mathrm{C_{10}H_{21}F_3O_6S_1Ti_1}$ (374.23): calcd. C 32.10, H 5.66; found C 32.51, H 8.86. ^{1}H NMR (300 MHz, 23 °C, $\mathrm{CDCl_3}$): δ = 1.34 [br. m, 18 H, $\mathrm{OCH(C}H_3)_2$], 4.91 [br. m, 3 H, $\mathrm{OC}H(\mathrm{CH_3})_2$] ppm. ^{13}C{^{1}H} NMR (75.5 MHz, 23 °C, $\mathrm{CDCl_3}$): δ = 26.4, 76.3 ppm. ^{19}F NMR (376 MHz, 23 °C): δ = –77.4 ppm.

The titanium complexes **3a**–**e** and **4** were prepared using standard procedures for both the direct and in-situ synthesis, examples of both procedures are given below.

[{HC(Pz)$_3$}Ti(O*i*Pr)$_3$][OTf] (3a): In-situ method; neat trimethylsilyl triflate (0.22 g, 1 mmol) was added to a solution of tris(pyrazolyl)methane (0.21 g, 1 mmol) and [Ti(O*i*Pr)$_4$] (0.31 mL, 1 mmol) in 10 mL of toluene. The mixture was stirred for 20 min at room temperature, after which the solvent was removed in vacuo. Fresh toluene (15 mL) was then added to the residue. Warming resulted in dissolution of the residue and formation of a clear solution, which was filtered by cannula into a clean Schlenk. Cooling the solution at –15 °C resulted in the formation of a crop of colourless crystals, which were isolated by filtration and washed with 5 mL of cold hexane and dried in vacuo; yield 0.41 g, 70%. $\mathrm{C_{20}H_{31}F_3N_6O_3STi}$ (540.46): calcd. C 40.82, H 5.31, N 14.28; found C 40.32, H 5.29, N 14.13. ^{1}H NMR (300 MHz, 23 °C, $\mathrm{CDCl_3}$): δ = 1.20 [d (^3J = 12 Hz), 6 H, $\mathrm{OCH(C}H_3)_2$], 4.73 [sept (^3J = 6 Hz), 3 H, $\mathrm{OC}H(\mathrm{CH_3})_2$], 6.34 [dd, ($^3J$ = 1.8 Hz, ^3J = 2.6 Hz), 3 H, C*H*], 7.82, [d (^3J = 1.6 Hz), 3 H, C*H*], 8.38 [d (^3J = 2.6 Hz), 3 H, C*H*], 9.97 (s, 1 H, $\mathrm{N_3C}H$) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, 23 °C, $\mathrm{CDCl_3}$): δ = 26.1, 74.7, 79.8, 107.48, 132.8, 143.4 ppm. ^{19}F NMR (376 MHz, 23 °C): δ = –76.1 ppm.

Direct Method: To a solution of **2** (0.37 g, 1 mmol) in 10 mL of toluene, a toluene solution (2 mL) of tris(pyrazolyl)methane (0.21 g, 1 mmol) was added. The reaction was stirred for 20 min. The solvent was then removed in vacuo and fresh toluene added to the solid residue. The solid was dissolved with warning followed by cannula filtration into a clean Schlenk. Cooling of the clear solution to –15 °C resulted in the formation of a crop of colourless crystals, which were isolated by filtration and washed with 5 mL of cold hexane and dried in vacuo; yield 0.42 g (71%). Analysis showed the product to be identical to that prepared by the in-situ method.

[{Et$_3$-TAC}Ti(O*i*Pr)$_3$][OTf] (3b): In-situ method; yield 0.33 g (60%) [(direct); yield 0.40 g (73%)]. $\mathrm{C_{19}H_{42}F_3N_3O_6S_1Ti_1}$ (545.51): calcd. C 41.84, H 7.76, N 7.70; found C 41.76, H 7.99, N 7.59. ^{1}H NMR (300 MHz, 23 °C, $\mathrm{CDCl_3}$): δ = 1.19 [t (^3J = 9 Hz), 9 H, $\mathrm{TAC\text{-}CH_2C}H_3$] 1.25 [d ($^3J$ = 7 Hz), 18 H, $\mathrm{OCH(C}H_3)_2$], 2.84 [q (^3J = 9 Hz), 6 H, $\mathrm{TAC\text{-}C}H_2\mathrm{CH_3}$], 4.03 [m, 6 H, $\mathrm{(NCH_2)_3}$], 4.52 [sept (^3J = 7 Hz), 3 H, $\mathrm{OC}H(\mathrm{CH_3})_2$] ppm. ^{13}C{^{1}H} NMR (75.5 MHz, 23 °C, $\mathrm{CDCl_3}$): δ = 10.6, 26.7, 48.1, 73.2, 79.9 ppm. ^{19}F NMR (376 MHz, 23 °C): δ = –76.5 ppm.

[{Bz$_3$-TAC}Ti(O*i*Pr)$_3$][OTf] (3c): In-situ method; yield 0.48 g (66%) [(direct); yield 0.45 g (61%)]. $\mathrm{C_{34}H_{48}F_3NN_3O_6STi}$ (745.73): calcd. C 55.81, H 6.61, N 5.74; found C 55.98, H 6.74, N 5.72. ^{1}H NMR (300 MHz, 23 °C), $\mathrm{CDCl_3}$: δ = 1.15 [d (^3J = 6 Hz), 18 H, $\mathrm{OCH(C}H_3)_2$], 3.48 [d (^3J = 9 Hz), 3 H ($\mathrm{C}H_a\mathrm{H_bN}$)] 3.85 (s, 6 H, $\mathrm{TAC\text{-}C}H_2$-Ph), 4.21 [d (^3J = 9 Hz), 3 H ($\mathrm{CH_a}H_b\mathrm{N}$)], 4.54 [sept ($^3J$ = 6 Hz), 3 H, $\mathrm{OC}H(\mathrm{CH_3})_2$], 7.18–7.27 (m, 15 H, CH) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, 23 °C, $\mathrm{CDCl_3}$): δ = 26.9, 58.2, 73.5, 80.6, 128.8, 129.4, 130.9, 131.5 ppm. ^{19}F NMR (376 MHz, 23 °C): δ = –76.2 ppm.

[{*p*-FBz$_3$-TAC}Ti(O*i*Pr)$_3$][OTf] (3d): In-situ method; yield 0.64 g (81%) [(direct) Yield 0.57 g (72%)]; yield 0.44 g 72%. $\mathrm{C_{34}H_{45}F_6N_3O_6S_1Ti_1}$ (785.69): calcd. C 51.98, H 5.77, N 5.33; found C 52.04, H 5.81, N 5.29. ^{1}H NMR (300 MHz, 23 °C), $\mathrm{CDCl_3}$: δ = 1.18 [d (^3J = 7 Hz), 18 H, $\mathrm{OCH(CH_3)_2}$], 3.49 [d (^3J = 9 Hz), 3 H, ($\mathrm{C}H_a\mathrm{H_bN}$)], 3.86 (s, 6 H, $\mathrm{TAC\text{-}C}H_2\mathrm{\text{-}C_6H_4F}$), 4.21 [d ($^3J$ = 9 Hz), 3 H, ($\mathrm{CH_a}H_b\mathrm{N}$)], 4.57 [sept ($^3J$ = 7 Hz), 3 H, $\mathrm{OC}H(\mathrm{CH_3})_2$] 6.91–7.04 (m, 6 H, CH), 7.21–7.32 (m, 6 H, CH) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, 23 °C $\mathrm{CDCl_3}$): δ = 26.9, 57.3, 73.3, 80.7, 116.4 (d, ^2J = 21.9 Hz), 127.4 (d, ^4J = 3.0 Hz), 132.8 (^3J = 8.3 Hz), 163.5 (^1J = 249.2 Hz) ppm. ^{19}F NMR (376 MHz, 23 °C): δ = –74.8 ppm.

[{*s*-(PhC(Me)H)$_3$-TAC}Ti(O*i*Pr)$_3$][OTf] (3e): In-situ method; yield 0.46 g (60%) [(direct) yield 0.48 g (62%)]. $\mathrm{C_{37}H_{54}F_3N_3O_6S_1Ti_1}$ (773.80): calcd. C 57.43, H 7.03, N 5.43; found C 57.28, H 7.16, N 5.40. ^{1}H NMR (300 MHz, 23 °C), $\mathrm{CDCl_3}$: δ = 1.34 [d (^3J = 8 Hz), 18 H, $\mathrm{OCH(CH_3)_2}$], 1.74 [d (^3J = 6 Hz), 9 H, TAC-CH(*Me*)Ph], 2.56 [d (^3J = 9 Hz), 3 H, ($\mathrm{C}H_a\mathrm{H_bN}$)], 4.09 [q ($^3J$ = 6 Hz), 3 H, TAC-C*H*(Me)Ph], 4.87 [sept (^3J = 8 Hz), 3 H, $\mathrm{OCH(CH_3)_2}$], 7.09–7.29 (m, 15 H, CH) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, 23 °C $\mathrm{CDCl_3}$): δ = 17.9, 26.9, 63.0, 71.1, 80.9, 126.2, 128.4, 129.4, 135.2 ppm. ^{19}F NMR (376 MHz, 23 °C): δ = –76.6 ppm.

[Ti(O*i*Pr)$_2$(OTf)$_2${κ^1-(C$_6$H$_4$)NC(H)N(Ph)CH$_2$}$_2$] (4): In-situ method; yield 0.26 g (30% based on Ti) [(direct) yield 0.21 g (24% based on Ti)]. $\mathrm{C_{36}H_{38}F_6N_4O_8S_2Ti_1{\cdot}C_7H_8}$: calcd. C 53.09, H 4.77, N 5.76; found C 52.9, H 4.70, N 5.81. ^{1}H NMR (400 MHz, 23 °C, $\mathrm{CDCl_3}$): δ = 1.82 [d (3*J* = 7 Hz), 12 H, $\mathrm{OCH(C}H_3)_2$], 4.46 (br. m, 4 H, $\mathrm{CH_2N}$), 5.34 [sept (^3J = 7 Hz), 2 H, $\mathrm{OC}H(\mathrm{CH_3})_2$], 6.7–7.2 (m, 16 H, CH), 8.42 [d (^3J = 12 Hz), 2 H, CH], 8.62 (s, 2 H, N–C*H*–N) ppm.

X-ray Crystallographic Study: Crystallographic data for compounds **3a**, **3b**, **3c**, and **4** are summarised in Table 3. All data collections were implemented on a Nonius–Kappa CCD diffractometer. Structure solution and refinement was performed using SHELX86[24] and SHELX97[25] software, respectively. Full matrix anisotropic refinement was implemented in the final least-squares cycles throughout. All data were corrected for Lorentz and polarisation and, with for extinction. Hydrogen atoms were included at calculated positions throughout.

In **3a** two of the three isopropyl groups within the cationic fragment based on O(1) and O(3), are disordered over two positions. For both isopropyl groups the disordered atoms were modelled anisotropically in 70:30 occupancy ratios. The ASU of **3b** consist of 1/3 of the complex, with the Ti atom of the cation and the carbon and sulfur atoms of the triflate anion residing on special 3-forl rotational axis.

In addition the isopropyl group within the ASU exhibits disorder centred about the CH group of the isopropyl unit, C(11). Accordingly the methyl groups are modelled anisotropically of over two positions, C(12) & C(13) vs. C(12A) & C(13A) in a 50:50 ratio.

In complex **3c** the two isopropyl groups based on O(1) and O(2) exhibit significant disorder, and as such have been modelled isotropically over 2 positions, in a 70:30 occupancy ratio. Additional disorder is present in the anion component of **3c** with the fluorine and oxygen atoms of the triflate unit showing rotational disorder about the C–S axis. The disorder could not be well defined and as such the disordered atoms are modelled isotropically in single positions.

The ASU of **4** consists of two molecules of the titanium complex and two half-molecules of disordered toluene [C(1s)–C(7s) and C(11s)–C(17s), respectively]. Both half molecules of toluene reside on special positions between adjacent asymmetric unit cells and

Table 3. Crystal data and structure refinement for compounds **3a**, **3b**, **3c**, and **4**.

	3a	**3b**	**3e**	**4**
Formula	$C_{20}H_{31}F_3N_6O_6S_1Ti_1$	$C_{19}H_{42}F_3N_3O_6S_1Ti_1$	$C_{34}H_{48}F_3N_3O_6S_1Ti_1$	$C_{36}H_{38}F_6N_4O_8S_2Ti_1\cdot0.5C_7H_8$
Formula weight	588.47	545.52	731.71	962.78
T /K	150(2)	150(2)	150(2)	150(2)
Crystal system	monoclinic	cubic	orthorhombic	triclinic
Space group	$P2_1/c$	$P2_13$	$Pc2_1b$	$P\bar{1}$
a /Å	11.9370(2)		9.41900(10)	10.5520(2)
b /Å	14.9290(2)	13.9840(2)	16.4870(2)	20.1980(3)
c /Å	16.4330(3)		24.1100(3)	20.3100(4)
α /°				88.2430(10)
β /°	103.6660(10)			89.8210(10)
γ /°				80.7170(10)
U /Å^3	2845.58(8)	2734.60(7)	3744.07(8)	4269.95(13)
Z	4	4	4	4
D_c /g cm^{-3}	1.374	1.325	1.298	1.442
μ /mm^{-1}	0.437	0.445	0.344	0.380
F(000)	1224	1160	1544	1916
Crystal size /mm	$0.32\times0.25\times0.13$	$0.32\times0.25\times0.22$	$0.15\times0.12\times0.08$	$0.30\times0.28\times0.17$
Theta range /°	3.69 to 27.52	4.37 to 27.45	3.55 to 26.38	8.52 to 25.93
Reflections collected	36116	53932	72363	39104
Independent reflections	6499 [$R_{(\mathrm{int})}$ = 0.0430]	2094 [$R_{(\mathrm{int})}$ = 0.0547]	7647 [$R_{(\mathrm{int})}$ = 0.0626]	15810 [$R_{(\mathrm{int})}$ = 0.0386]
Reflections [$I > 2\sigma(I)$]				
Data/restraints/parameters	6499/0/399	2094/0/124	7647/1/410	15810/6/1069
Goodness-of-fit on F^2	1.032	1.112	1.045	1.118
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0481, 0.1254	0.0261, 0.0622	0.0820, 0.2257	0.0704, 0.1589
Final $R1$, $wR2$ (all data)	0.0649, 0.1383	0.0318, 0.0652	0.0949, 0.2405	0.0842, 0.1659
Max., min. diff./ e Å^{-3}	0.427, –0.404	0.178, –0.169	1.404, –0.746	1.292, –0.594
Absolute structure parameter	–	–0.02(3)	0.00(5)	–

have been refined at 50% occupancy. The toluene rings are refined as ridged hexagons, with the disordered methyl groups constrained by DFIX commands.

CCDC-837014 (for **3a**), -837015 (for **3b**), -837016 (for **3e**), -837017 (for **4**) contains the supplementary crystallographic data for this paper. 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: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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