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Titanium imido complexes containing 1,3,5-triazacyclohexane ligands

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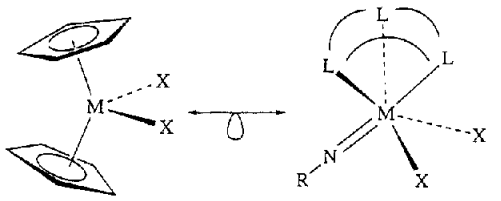
Abstract

The syntheses of the 1,3,5-trimethyl- and tri-*tert*-butyl-1,3,5-triazacyclohexane-supported imido complexes $[M(NR)(R'_3tach)Cl_2]$ (M = Ti or Zr (NMR only); R = Bu^t or 2,6-$C_6H_3Pr^i_2$; R′ = Me or Bu^t) are reported, along with that of the thermally robust dibenzyl derivative $[Ti(NBu^t)(Me_3tach)(CH_2Ph)_2]$. The *tert*-butylimido ligand in $[Ti(NBu^t)(Me_3tach)Cl_2]$ undergoes exchange with $ArNH_2$ (Ar = 4-C_6H_4Me or 2,6-$C_6H_3Pr^i_2$) to form the corresponding arylimides $[Ti(NAr)(Me_3tach)Cl_2]$. The Me_3tach ring in $[Ti(NR)(Me_3tach)Cl_2]$ undergoes slow exchange with Bu^t_3tach or Me_3tacn (1,4,7-trimethyl-1,4,7-triazacyclononane) to give the ring-exchanged products $[Ti(NR)(Bu^t_3tach)Cl_2]$ and $[Ti(NR)(Me_3tacn)Cl_2]$, respectively. The complexes $[Ti(NR)(Me_3tach)X_2]$ (R = Bu^t or 2,6-$C_6H_3Pr^i_2$; X = Cl or CH_2Ph) exhibit room-temperature dynamic NMR behaviour via an unusual trigonal twist of the facially coordinated Me_3tach ligand, and the activation parameters for these processes have been measured and are discussed. The X-ray structures of $[Ti(NR)(Bu^t_3tach)Cl_2]$ (R = Bu^t or 2,6-$C_6H_3Pr^i_2$) and $[Ti(NBu^t)(Me_3tach)(X)_2]$ (X = Cl or CH_2Ph) are reported. Me_3tach and Bu^t_3tach = 1,3,5-trimethyl- and tri-*tert*-butyl-1,3,5-triazacyclohexane, respectively.

Keywords: Titanium; Zirconium; Imide; Triazacyclohexane; X-ray diffraction; Fluxional; Benzyl

1. Introduction

As part of an ongoing research programme in transition-metal imido chemistry [1], we have been interested in developing the chemistry of Group 4 complexes of the general type $[M(NR)(fac\text{-}L_3)X_2]$ (R = alkyl or aryl; R = halide or alkyl), where the *fac*-L_3 ligand represents a *N*-peralkylated triazacycle such as a 1,4,7-triazacyclononane (R_3tacn) or a 1,3,5-triazacyclohexane (R_3tach) derivative [2,3]. Our interest in such complexes stems from the isolobal relationships between the six-electron-donor ligands *fac*-L_3 (neutral), cyclopentadienide (formally monanionic) and imide (RN^{2-}, formally dianionic) [4]. Complexes of the type $[M(NR)(fac\text{-}L_3)X_2]$ are therefore isolobal analogues of corresponding metallocenes $[M(\eta\text{-}C_5H_5)_2X_2]$, which form a very important class of compound in contemporary fundamental and catalytic organotransition metal chemistry [5][3].



M = Group 4 metal; X = halide or alkyl; *fac*-L_3 = R_3tach or R_3tacn (R = alkyl)

As part of this programme we recently described the synthesis and X-ray structures of the 1,4,7-triazacyclononane-supported imido titanium complexes

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[3] Note that although for ease of representation all titanium–imido linkages are drawn 'Ti=NR', the formal $Ti\text{–}N_{imide}$ bond order in the complexes described herein is generally best thought of as three (pseudo-σ^2-π^4 triple bond) rather than as two [1c,4a,23].

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$[Ti(NBu^t)(R_3tacn)Cl_2]$ (R = H or Me) [2a]. These isolobal analogues of $[Ti(\eta\text{-}C_5H_5)_2Cl_2]$ allow ready substitution of the chloride ligands and already suggest an extensive reaction chemistry [2b]. We report here parallel studies of the synthesis, structures and reaction dynamics of Group 4 imido complexes of the 1,3,5-trialkyl-1,3,5-triazacyclohexane ligands, R_3tach (R = Me or Bu^t). In general, complexes of R_3tach ligands have mostly been reported for middle to late transition metals [6]. Part of the work described below has been communicated [3]. During the course of our studies, imido titanium complexes of Bu^t_3tach and Et_3tach were independently reported by Baker et al. [7].

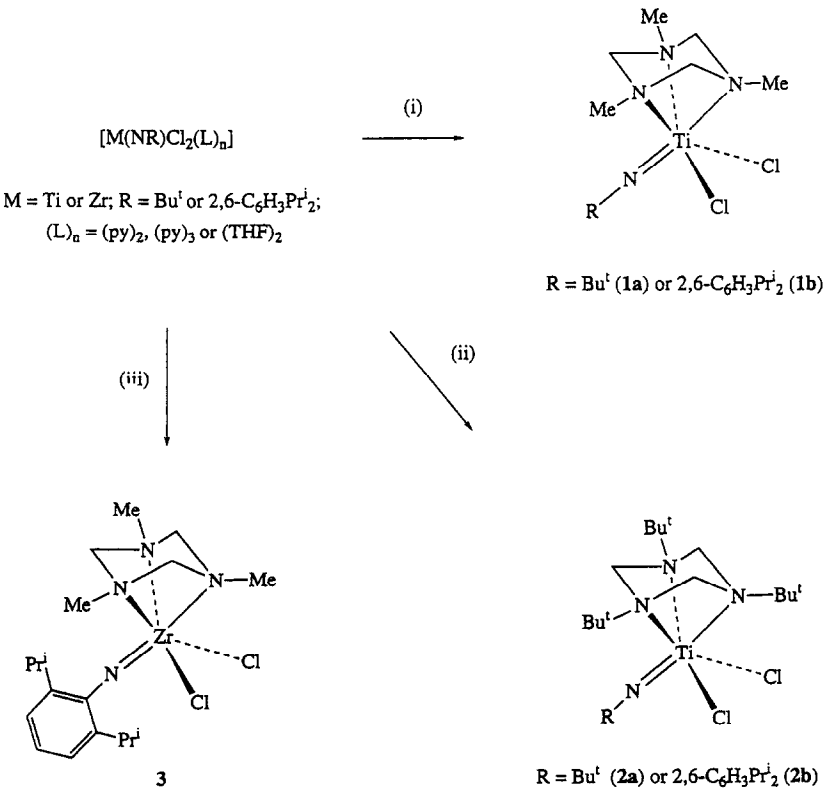
2. Results and discussion

2.1. Syntheses

In previous studies, we found that the complexes $[Ti(NR)Cl_2(py)_n]$ (R = Bu^t or aryl, $n = 2$ or 3) are useful entry points to new imido titanium chemistry [1,8]. The compounds $[Ti(NBu^t)Cl_2(py)_2]$ and $[Ti(N\text{-}2,6\text{-}C_6H_3Pr^i_2)Cl_2(py)_3]$ in particular are readily prepared in multi-gram quantites, and form the starting point for the syntheses described herein. A wide number of 1,3,5-trisubstituted 1,3,5-triazacyclohexanes, R_3tach, have been described [9]. We focused our studies on the trimethyl and tri-*t*-butyl homologues Me_3tach [9a] and Bu^t_3tach [9d] as representative examples of their class in terms of steric and solubility factors.

Reaction of one equivalent of Me_3tach with $[Ti(NBu^t)Cl_2(py)_2]$ in dichloromethane at room temperature immediately afforded a bright yellow solution. Within minutes, a mass of microcrystalline yellow needles formed leaving a pale yellow supernatant. After concentration of the supernatant, collection of the crystalline product afforded $[Ti(NBu^t)(Me_3tach)Cl_2]$ (**1a**) as a yellow powder in 94% yield. The corresponding reaction of one equivalent of Me_3tach with the arylimido complex $[Ti(N\text{-}2,6\text{-}C_6H_3Pr^i_2)Cl_2(py)_3]$ in dichloromethane at room temperature for 16 h, followed by removal of the volatiles and recrystallisation from dichloromethane–hexane mixtures, afforded $[Ti(N\text{-}2,6\text{-}C_6H_3Pr^i_2)(Me_3tach)Cl_2]$ (**1b**) as a pale brown powder in 89% yield. The syntheses of all of the new compounds $[M(NR)(R'_3tach)Cl_2]$ are summarised in Scheme 1.

The corresponding imidotitanium complexes of Bu^t_3tach were prepared in an analogous manner. Thus reaction of one equivalent of Bu^t_3tach with $[Ti(NBu^t)Cl_2(py)_2]$ for 7 days gave $[Ti(NBu^t)(Bu^t_3tach)Cl_2]$ (**2a**) as a mustard yellow powder in 86% yield. An analogous



Scheme 1. Reagents and conditions: (i) Me_3tach, CH_2Cl_2, 1 or 14 h, 94 or 89%; (ii) Bu^t_3tach, CH_2Cl_2, 7 days, 86%; (iii) Me_3tach, CD_2Cl_2, 15 min, 100% (NMR).

reaction of one equivalent of Bu^t_3tach with [Ti(*N*-2,6-$C_6H_3Pr^i_2$)Cl_2(py)$_3$] afforded [Ti(*N*-2,6-$C_6H_3Pr^i_2$)(Bu^t_3tach)Cl_2] (**2b**) as a red–brown powder, also in 86% yield (Scheme 1). The complexes **2a** and **2b** exhibit higher solubilities than **1a** and **1b**, respectively, as might be expected from the presence of the three ring *tert*-butyl substituents in **2a** and **2b**.

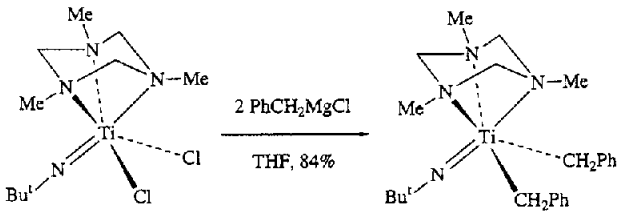
The room temperature NMR data for [Ti(NR)(Bu^t_3tach)Cl_2] (R = Bu^t **2a** or 2,6-$C_6H_3Pr^i_2$ **2b**) and the low-temperature (slow exchange) NMR data for [Ti(NR)(Me_3tach)Cl_2] (R = Bu^t **1a** or 2,6-$C_6H_3Pr^i_2$ **1b**) are consistent with the structures proposed in Scheme 1. These NMR spectra reveal resonances assignable to a *tert*-butyl or 2,6-$C_6H_3Pr^i_2$ group, and to a coordinated R_3tach ligand (Me or Bu^t). The R_3tach sub-spectra feature different chemical shifts for the R groups *cis* or *trans* to Ti=NR, and resonances for two pairs of chemically inequivalent diastereotopic methylene linkages. The room temperature spectra for **1a** and **1b** are broad and indicative of a fluxional process. The single-crystal X-ray structures of **1a**, **2a** and **2b**, along with the solution dynamic NMR behaviour of **1a** and **1b**, are described in detail below.

We were also interested to prepare zirconium analogues of compounds **1** or **2**. An NMR tube-scale reaction of one equivalent of Me_3tach with [Zr(*N*-2,6-$C_6H_3Pr^i_2$)Cl_2(THF)$_2$] [10] in CD_2Cl_2 at room temperature afforded the complex [Zr(*N*-2,6-$C_6H_3Pr^i_2$)(Me_3tach)Cl_2] (**3**) in near-quantitative yield, as determined by ^{1}H- and ^{13}C{^{1}H}-NMR spectroscopy. Unfortunately, this compound could not be isolated on a preparative scale, possibly due to weak binding of the Me_3tach ligand to the larger metal. Compound **3** was therefore characterised by NMR methods alone. The NMR data for **3** are analogous to those for the fully characterised titanium congener **1b**, and are thus consistent with the structure proposed in Scheme 1.

2.2. Ligand substitution chemistry

The triazacyclohexane ligand in [Ti(NR)(Me_3tach)Cl_2] (**1a**, **1b**) and the *tert*-butylimide and chloride groups in [Ti(NBu^t)(Me_3tach)Cl_2] (**1a**) can all be substituted. The reactions are discussed in turn.

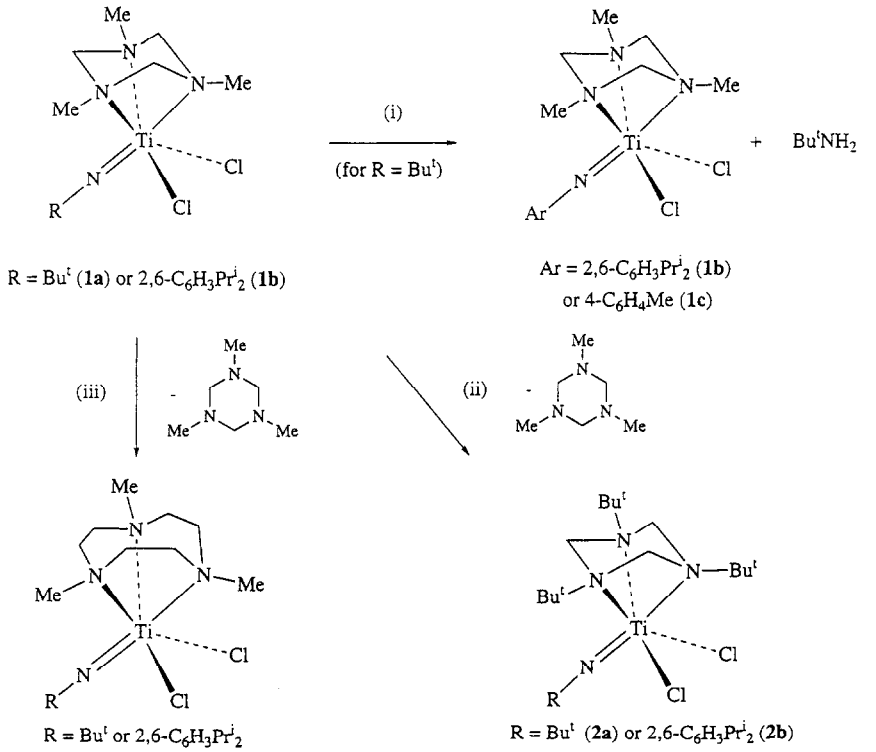
A few metal alkyl complexes containing facially coordinated triazacyclohexane rings have been reported previously [6c–d,f–g]. For example, Köhn and co-workers have described the di- and trialkyl complexes [Cr(Pr^i_3tach)(CH_2SiMe_3)$_2$Cl] and [Cr(R_3tach)(CH_2Ph)$_3$] (R = CH_2Ph, cyclohexyl) [6c]. Thus, reaction of two equivalents of benzylmagnesium chloride with [Ti(NBu^t)(Me_3tach)Cl_2] (**1a**) in THF at −50°C gave a bright yellow solution. Stirring at room temperature overnight, followed by the addition of 1,4-dioxane, filtration and removal of the volatiles afforded a pale yellow solid, which was recrystallised from toluene–hexane to give [Ti(NBu^t)(Me_3tach)(CH_2Ph)$_2$] (**4**) as a semi-crystalline, yellow powder in 84% yield. The X-ray structure and dynamic NMR behaviour of **4** are discussed below and support the structure proposed in Eq. (1). The low-temperature NMR spectra of **4** are comparable to those of the dichloride precursor **1a**, but feature additional resonances for two η^1-coordinated benzyl ligands. The diasterotopic H atoms of the methylene groups of the chemically equivalent benzyl ligands appear as a pair of mutually-coupled doublets (^2J = 8.9 Hz) at 3.37 and 2.39 ppm. Attempted preparation of [Ti(NBu^t)(Bu^t_3tach)(CH_2Ph)$_2$] from **2a** and benzylmagnesium chloride yielded intractable mixtures.



1a **4** (1)

Scheme 2 summarises the imido and triazacyclic ligand exchange reactions of the Me_3tach complexes **1a** and **1b**. Reaction of one equivalent of 4-methylaniline with [Ti(NBu^t)(Me_3tach)Cl_2] (**1a**) in dichloromethane at room temperature, followed by subsequent heating to 50°C for 2 days gave the arylimido complex [Ti(*N*-4-C_6H_4Me)(Me_3tach)Cl_2] (**1c**) as an orange powder in 93% yield. The ^{1}H- and ^{13}C{^{1}H}-NMR spectra of **1c** are similar to those of the complexes **1a** and **1b**, and analogous fluxional behaviour (see below) is observed at room temperature. In order to establish the scope of the imido group exchange reactions for **1a**, [Ti(*N*-2,6-$C_6H_3Pr^i_2$)(Me_3tach)Cl_2] (**1b**) was synthesised in an analogous manner on an NMR scale. Thus reaction of **1a** with one equivalent of 2,6-diisopropylaniline in $CDCl_3$ heated at 75°C for 3 days afforded quantitative yields of **1b** and *tert*-butylamine. While compound **1a** undergoes *tert*-butylimide/arylamine exchange reactions in an NMR tube-scale reaction, the sterically more crowded homologue [Ti(NBu^t)(Bu^t_3tach)Cl_2] (**2a**) showed no reactivity towards 4-methylaniline even after 14 days at 75°C in $CDCl_3$. Although *tert*-butylimide/arylamine exchange reactions are generally well established in imido titanium chemistry [1a,8], it is interesting that [Ti(NBu^t)(Me_3tach)Cl_2] (**1a**) undergoes such reactions since the triazacyclononane analogue [Ti(NBu^t)(Me_3tacn)Cl_2] does not [2].

Based on an analysis of the relative stabilities of free and complexed R_3tach ligands, Baker and co-workers have suggested that the stability order of homologous triazacyclohexane complexes [M(R_3tach)L_n] is R = Bu^t > Et > Me [6h–j]. To establish whether this se-



Scheme 2. Reagents and conditions: (i) $ArNH_2$, CH_2Cl_2 or $CDCl_3$, 50–75°C, 2–3 days, 93–100 (NMR) %; (ii) Bu^t_3tach, $CDCl_3$, 6–11 days, r.t. −75°C, 35% (NMR); (iii) Me_3tacn, $CDCl_3$, 7–8 days, r.t. −75°C, 100% (NMR).

quence applies to the complexes $[Ti(NR)(R'_3tach)Cl_2]$ (**1a,b** and **2a,b**), NMR tube-scale reactions were performed in which one equivalent of Bu^t_3tach was added to a solution of $[Ti(NR)(Me_3tach)Cl_2]$ (**1a,b**) in $CDCl_3$ (Scheme 2). After 6 days at room temperature, 20% conversion of **1a** to $[Ti(NBu^t)(Bu^t_3tach)Cl_2]$ (**2a**) and Me_3tach had occurred. Similar results were obtained for the conversion of $[Ti(N\text{-}2,6\text{-}C_6H_3Pr^i_2)(Me_3tach)Cl_2]$ (**1b**) to $[Ti(N\text{-}2,6\text{-}C_6H_3Pr^i_2)(Bu^t_3tach)Cl_2]$ (**2b**). Heating the samples to 75°C for a further 5 days drove the reactions only to ca. 35% conversion in both cases (giving K_{eq} ca. 0.3 for **1a,b** → **2a,b**). Further reaction times (up to 14 days) had negligible effects on the extent of conversion. The Me_3tach ligands in **1a** and **1b** are therefore labile towards displacement by Bu^t_3tach, but the reactions are slow and the differences in complex stability are relatively small (exchange $\Delta G_{348} <$ ca. 4 kJ mol^{-1}) and favour **1a,b** and free Bu^t_3tach over **2a,b** and free Me_3tach in these titanium imido systems.

Baker and co-workers have also proposed that the triazacyclohexane complexes $[M(Me_3tach)(CO)_3]$ (M = Cr, Mo, W; R = Me, Et, Bu^t) are less stable than their triazacyclononane analogues [6h]. In parallel studies we have prepared the triazacyclononane analogues of **1a** and **1b**, namely $[Ti(NR)(Me_3tacn)Cl_2]$ (R = Bu^t or 2,6-$C_6H_3Pr^i_2$) [2]. We have thus been able to establish the relative stabilities of the Me_3tach and Me_3tacn imido titanium complexes by triazacycle exchange NMR tube scale reactions. Reaction of one equivalent of Me_3tacn with $[Ti(NR)(Me_3tach)Cl_2]$ (**1a,b**) in $CDCl_3$ (Scheme 2) gave ca. 50% conversion to the corresponding $[Ti(NR)(Me_3tacn)Cl_2]$ and free Me_3tach after 7 days at r.t. Heating the samples at 75°C for a further 24 h forced the reactions to completion. In contrast, the *tert*-butyl-substituted triazacyclohexane complexes $[Ti(NR)(Bu^t_3tach)Cl_2]$ (**2a,b**) showed no reaction with Me_3tacn at room temperature over 14 days, and subsequent heating of the samples to 75°C for similar periods gave rise to only traces of $[Ti(NR)(Me_3tacn)Cl_2]$ and free Bu^t_3tach. No reaction occurred between complexes $[Ti(NR)(Me_3tacn)Cl_2]$ and Bu^t_3tach under similar conditions.

The Me_3tacn-supported imido titanium complexes are thus considerably more stable than their corresponding Me_3tach counterparts, **1a,b**. However, the triazacycle exchange reactions are slow, indicating that there is a significant activation barrier to these processes. The lack of reactivity observed for the Bu^t_3tach complexes is not unexpected on steric grounds, and suggests that the complexes **2a,b** are kinetically more stable than the Me_3tach analogues, **1a,b**.

Taken all together, the reactions summarised in Scheme 2 reveal the thermodynamic stability order: $[Ti(NAr)(R_3tach)Cl_2] + Bu^tNH_2 \gg [Ti(NBu^t)(R_3tach)Cl_2] + ArNH_2$; $[Ti(NBu^t)(Me_3tacn)Cl_2] + R_3tach \gg [Ti(NBu^t)(R_3tach)Cl_2] + Me_3tacn$; $[Ti(NBu^t)(Me_3tach)Cl_2] + Bu^t_3tach > [Ti(NBu^t)(Bu^t_3tach)Cl_2] + Me_3tach$.

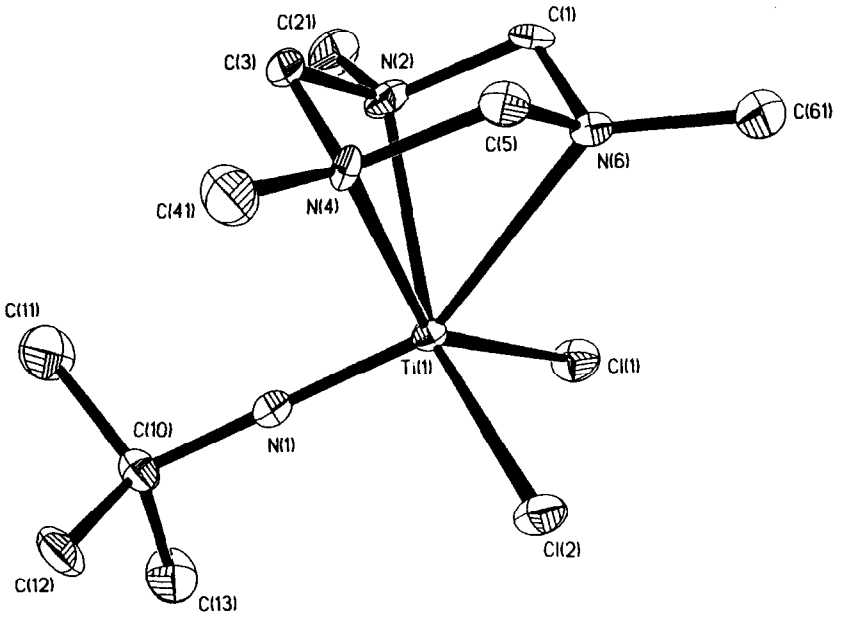


Fig. 1. Displacement ellipsoid plot of [Ti(NBu^t)(Me$_3$tach)Cl$_2$] (**1a**). Ellipsoid boundaries are drawn at the 40% probability level and H atoms are omitted.

2.3. Solid-state structures

The X-ray structures of the *cis*-dichloride complexes [Ti(*N*-Bu^t)(Me$_3$tach)Cl$_2$] (**1a**), [Ti(*N*-Bu^t)(Bu$^t_3$tach)Cl$_2$] (**2a**) and [Ti(*N*-2,6-C$_6$H$_3$Pr$^i_2$)(Bu$^t_3$tach)Cl$_2$] (**2b**), and of the dibenzyl species [Ti(NBu^t)(Me$_3$tach)(CH$_2$Ph)$_2$] (**4**) have been determined. Displacement ellipsoid plots are shown in Figs. 1–4, data collection and processing parameters are listed in Table 1, and selected bond lengths and angles are presented in Table 2.

All four complexes feature a six-coordinate, pseudo-octahedral titanium centre with a facially coordinated R$_3$tach ring, an organoimido ligand and two mutually *cis* chloride (**1a**, **2a** or **2b**) or benzyl (**4**) ligands. The bond lengths and angles within the R$_3$tach moieties, imide N-substituents and η^1-benzyl ligands are comparable with previously reported examples [6,11]. The Ti=N$_{imide}$ bond distances and Ti=N$_{imide}$–R angles are within the normal ranges [1], and are consistent with the imido groups in these complexes forming a triple bond to titanium. The Ti=N$_{imide}$ distance of 1.732(6) Å for the arylimido species **2b** is significantly longer than those for the two *tert*-butylimido derivatives (**1a**, **2a**) with *cis*-chloride ligands, for which values of 1.699(4) and 1.692(5) Å are found. This is consistent with the known tendency of arylimido complexes to feature longer M=N$_{imide}$ bond lengths than their alkylimido homologues [11], which may be attributed to the delocalisation of nitrogen π-electron density onto the aryl ring [1a,c]. The increased Ti=N$_{imide}$ distance in **4** compared with that in **1a** most likely reflects the better σ-donor ability of benzyl ligands as compared with chloride.

The Ti–N$_{tach}$ distances in all of the four complexes are consistent with single, dative bonds. The Ti–N$_{tach}$ bond distances *trans* to the imido ligand in all of the complexes are consistently longer than those that are *cis*, this reflecting the well-known *trans* influence of multiply bonded ligands such as imide [1c,12]. The average *trans* influences for the three dichloride complexes vary in the sequence **1a** (avg. 0.180 Å) < **2a** (avg. 0.222 Å) > **2b** (avg. 0.142 Å). The electronic origins of the typically larger *trans* influence in six-coordinate *tert*-butylimido complexes (such as **1a** and **2a**) com-

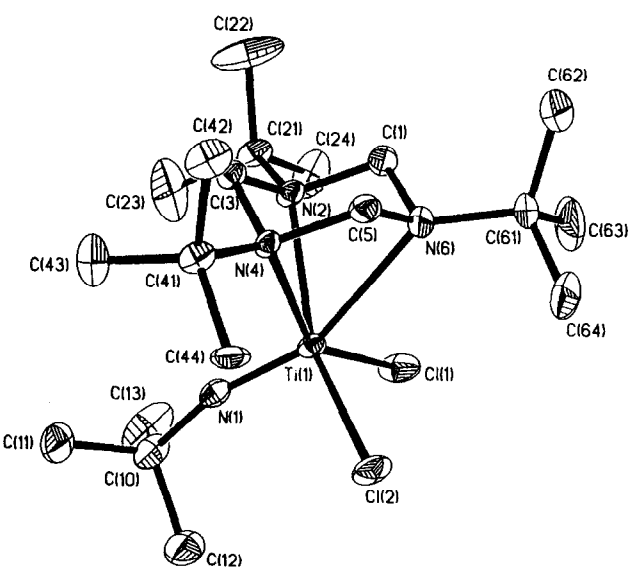


Fig. 2. Displacement ellipsoid plot of [Ti(NBu^t)(Bu$^t_3$tach)Cl$_2$] (**2a**). Ellipsoid boundaries are drawn at the 40% probability level and H atoms are omitted.

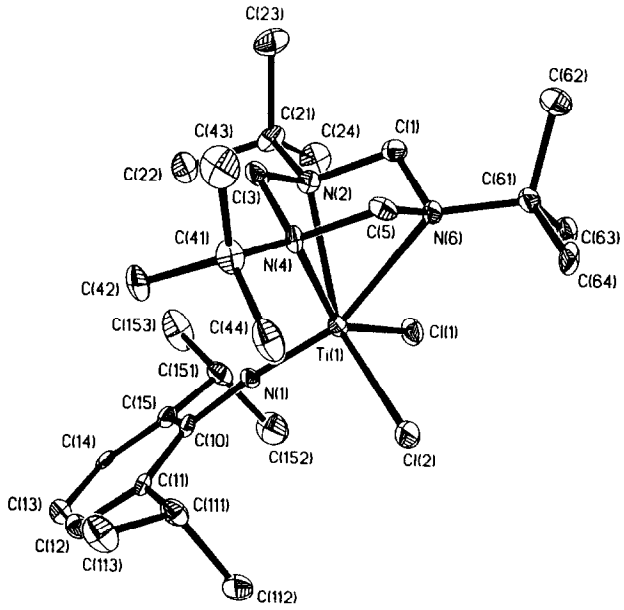


Fig. 3. Displacement ellipsoid plot of [Ti(*N*-2,6-$C_6H_3Pr^i_2$)(Bu^t_3tach)Cl_2] (**2b**). Ellipsoid boundaries are drawn at the 40% probability level and H atoms are omitted.

pared with their arylimido homologues (e.g. **2b**) have been explained by us elsewhere [1c]. The longer Ti–N_{tach} distances in the Bu^t_3tach complexes **2a** and **2b** as compared with those in [Ti(NBu^t)(Me_3tach)Cl_2] (**1a**) is presumably a consequence of the increased steric bulk of the Bu^t_3tach ligand compared with Me_3tach. The Ti–N_{tach} distances in **4** are all longer than those in **1a**, again reflecting the good σ-donor ability of the benzyl ligands in **4**.

The Ti–Cl distances in all three complexes **1a**, **2a** and **2b** are unexceptional in comparison with other titanium(IV) complexes [1,11], but those for **2b** are significantly shorter than in **1a** and **2a**. This probably reflects the longer Ti–N_{tach} distances (avg. 2.334 Å) *trans* to the chloride ligands in this latter complex compared with the other two (avg. 2.244 for **1a** and 2.291 Å for **2a**). In [Ti(NBu^t)(Me_3tach)(CH_2Ph)$_2$] (**4**) the Ti–C bond lengths of 2.213(4) and 2.214(4) Å and the Ti–C–Ph bond angles of 119.0(2) and 114.9(2)° are normal for titanium-bound η^1-benzyl ligands [11]. The C–H bond distances of 0.96(5), 0.91(4), 0.94(5) and 0.99(4) Å and associated Ti–C–H angles for the benzyl methylene group hydrogen atoms (which were located from Fourier maps and isotropically refined) confirm the absence of α-agostic Ti···H interactions in the solid state. Furthermore, the interatomic Ti···H distances (range 2.52(4)–2.67(4) Å) are too long to suggest agostic interactions. The classical benzyl group coordination is, however, not surprising since the six-coordinate, titanium(IV) centre of **4** has a 16-valence-electron count and so one would not necessarily expect to find agostic interactions in a titanium complex of this type [13].

It is interesting to compare the structural data for [Ti(NR)(R^t_3tach)Cl_2] with those of the previously reported triazacyclonane complexes [Ti(NBu^t)(R_3tacn)Cl_2] (R = H or Me) [2a]. The Ti=N_{imide} distances in the R_3tacn complexes are comparable with those in **1a**, **2a** and **2b**, whereas the Ti–Cl distances (avg. 2.405 and 2.374 Å for R = H and Me, respectively) are longer. The Cl–Ti–Cl angles for the R_3tacn complexes [97.23(4) and 95.75(4)° for R = H and Me, respectively] are both smaller (consistent with the longer Ti–Cl distances) than in any of the R_3tach complexes described here. Not surprisingly, the N_{tacn}–Ti–N_{tacn} angles (avg. 74.7 and 75.6° for R = H and Me, respectively) are all substantially larger than N_{tach}–Ti–N_{tach} for any of the four R_3tach complexes **1a**, **2a**, **2b** or **4** (range 58.0(1) to 61.4(2)°), reflecting the different triazacycle ring sizes.

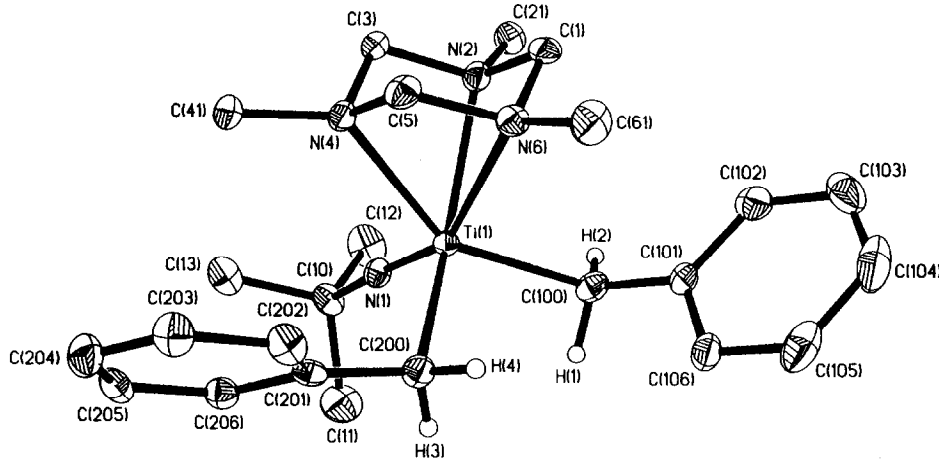


Fig. 4. Displacement ellipsoid plot of [Ti(NBu^t)(Me_3tach)(CH_2Ph)$_2$] (**4**). Non-H atom ellipsoid boundaries are drawn at the 40% probability level. H atoms are omitted except for those of the benzylic methylene linkages: these are shown as spheres of an arbitary radius.

Table 1
X-ray data collection and processing parameters for [Ti(NBu^t)(Me$_3$tach)Cl$_2$] (**1a**), [Ti(NBu^t)(Bu$^t_3$tach)Cl$_2$] (**2a**), [Ti(*N*-2,6-C$_6$H$_3$Pr$^i_2$)(Bu$^t_3$tach)Cl$_2$] (**2b**), and [Ti(NBu^t)(Me$_3$tach)(CH$_2$Ph)$_2$] (**4**)

	1a	**2a**	**2b**	**4**
Molecular formula	$C_{10}H_{24}Cl_2N_4Ti$	$C_{19}H_{42}Cl_2N_4Ti$	$C_{27}H_{50}Cl_2N_4Ti$	$C_{24}H_{38}N_4Ti$
Formula weight	319.14	445.38	549.53	430.50
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/n$	$P2_1/n$	$P2_1/c$
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Unit cell dimensions				
a (Å)	7.053(2)	9.871(5)	8.852(3)	16.804(4)
b (Å)	13.818(5)	16.677(11)	18.905(5)	11.226(3)
c (Å)	16.452(6)	15.020(11)	17.937(5)	13.603(3)
β (°)		103.51(5)	91.36(3)	103.91(3)
Volume (Å^3)	1603.4(7)	2404(2)	3000.9(2)	2490.8(9)
Z	4	4	4	4
Absorption coefficient (mm^{-1})	0.85	0.59	0.48	0.35
Crystal description	Pale yellow rod	Yellow block	Orange plate	Yellow plate
Crystal size (mm)	0.40 × 0.16 × 0.13	0.35 × 0.27 × 0.26	0.35 × 0.15 × 0.05	0.65 × 0.45 × 0.20
Theta range for data collection (°)	2.88–25.06	2.56–24.99	2.51–22.54	2.5–25.0
Scan type	ω–θ	ω–θ	ω–θ	ω–θ
Reflections collected	1803	4131	6460	6994
Independent reflections	1659	4131	3927	4366
R_{merge}	0.02	0 (no reflections to be merged)	0.07	0.02
Observed reflections	1435 [$I>2\sigma(I)$]	3079 [$I>2\sigma(I)$]	2453 [$I>2\sigma(I)$]	3264 [$I>2\sigma(I)$]
Absorption correction	ψ-scans	ψ-scans	Integration	ψ-scans
T_{min}, T_{max}	0.904, 0.998	0.772, 0.883	0.926, 0.973	0.771, 0.889
No. of data used in refinement	1435	3079	2453	3264
Number of restraints applied	0	6	0	0
Number of parameters refined	154	262	307	278
Refinement method		Full-matrix least-squares		
Extinction parameter		None required		
Absolute structure parameter	0.09(9)	–	–	–
Weighting scheme	Chebychev polynomial	Unit weights	Unit weights	Unit weights
Final R indices [a]	$R_1 = 0.045$, $R_w = 0.047$ [$I>2\sigma(I)$]	$R_1 = 0.068$, $R_w = 0.067$ [$I>2(I)$]	$R_1 = 0.085$, $R_w = 0.070$ [$I>2(I)$]	$R_1 = 0.04$, $R_w = 0.05$ [$I>2(I)$]
Goodness-of-fit	1.119	0.938	1.097	0.999
Final $(\Delta/\sigma)_{max}$	0.003	0.003	0.001	0.03
Largest residual $\Delta\rho$ features (e Å^{-3})	0.36 and −0.63	0.41 and −0.63	0.70 and −0.73	0.30 and −0.32

[a] $R = R_1 = \Sigma\|F_o|-|F_c\|/\Sigma|F_o|$; $R_w = \sqrt{\{\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2\}}$.

2.4. Dynamic NMR behaviour of [Ti(NR)(Me$_3$tach)X$_2$]

The solution ^{1}H- and ^{13}C-NMR spectroscopic data for the Bu$^t_3$tach complexes **2a** and **2b** are fully consistent with the solid-state structures and show sharp resonances for the imido N-substituents along with two types of ring N-Bu^t substituents and diastereotopic methylene protons of the triazacyclohexane ring. In contrast, the resonances for the Me$_3$tach ligand in [Ti(NR)(Me$_3$tach)Cl$_2$] (R = Bu^t **1a** or 2,6-C$_6$H$_3$Pr$^i_2$ **1b**) and [Ti(NBu^t)(Me$_3$tach)(CH$_2$Ph)$_2$] (**4**) are broad at room temperature. However, the resonances for the imido N-substituents (and also the benzyl ligands in **4**) are sharp and their linewidths are temperature-independent. The Me$_3$tach sub-spectra of **1a**, **1b** and **4** are temperature dependent and, on cooling of the samples, sharpen to become analogous to those of the Bu$^t_3$tach complexes, fully consistent with the solid-state structures described above. Standard variable-temperature NMR spectroscopic experiments including spin saturation transfer (SST) and ^{1}H lineshape (rate constant) analyses were used to characterise the dynamic processes [14].

The dynamic NMR spectra for **1a**, **1b** and **3** are consistent with an in-place trigonal twist of the Me$_3$tach ligand, as discussed further below. In the slow exchange limit (268 K for **1a** and **1b** and 243 K for **3**) the ^{1}H-NMR spectra for all three complexes show two sharp resonances in a ratio 3H:6H for the methyl groups *trans* and *cis* to the imido ligand, respectively. On increasing the probe temperature, these groups undergo site exchange (confirmed by SST) with the rate constants for the *cis*-Me → *trans*-Me jumps being half of those for *trans*-Me → *cis*-Me, as expected from mass-balance requirements [14b]. In addition, SST ^{1}H-NMR experiments confirm exchange between the two types of

'down' (*endo*, with respect to Ti) methylene hydrogens of Me_3tach, and also between the two types of 'up' (*exo*) hydrogens. Significantly, there was no exchange between the 'down' and 'up' hydrogens, indicating that the dynamic process does not involve complete dissociation of the triazacyclohexane ring. In additional NMR experiments we found no evidence for SST between the methyl groups of the coordinated Me_3tach in [Ti(NBu^t)(Me_3tach)Cl_2] and added free Me_3tach at temperatures approaching the fast (intramolecular) exchange limit.

Table 2
Selected bond distances (Å) and angles (°) for [Ti(NBu^t)(Me_3tach)Cl_2] (**1a**), [Ti(NBu^t)(Bu^t_3tach)Cl_2] (**2a**), [Ti(*N*-2,6-$C_6H_3Pr^i_2$)(Bu^t_3tach)Cl_2] (**2b**), and [Ti(NBu^t)(Me_3tach)(CH_2Ph)$_2$] (**4**)

	1a	**2a**	**2b**	**4**
Bond distances				
Ti(1)–N(1)	1.699(4)	1.692(5)	1.732(6)	1.713(3)
Ti(1)–N(2)	2.241(5)	2.292(4)	2.335(6)	2.290(3)
Ti(1)–N(4)	2.247(5)	2.290(4)	2.332(6)	2.306(3)
Ti(1)–N(6)	2.424(4)	2.513(5)	2.476(6)	2.480(3)
Ti(1)–Cl(1) or C(100)	2.356(2)	2.351(2)	2.324(2)	2.213(4)
Ti(1)–Cl(2) or C(200)	2.363(2)	2.351(2)	2.337(2)	2.214(4)
Bond angles				
Ti(1)–N(1)–C(10)	176.3(4)	164.1(4)	173.2(5)	176.8(3)
N(2)–Ti(1)–N(4)	61.4(2)	61.2(1)	59.8(2)	60.2(1)
N(2)–Ti(1)–N(6)	59.0(2)	58.5(1)	58.9(2)	58.0(1)
N(4)–Ti(1)–N(6)	58.9(2)	58.4(1)	58.6(2)	58.0(1)
Cl(1)–Ti(1)–Cl(2) or C(100)–Ti(1)–C(200)	102.72(6)	99.44(8)	100.69(9)	100.0(1)
Ti(1)–C(100)–C(101)				119.0(2)
Ti(1)–C(200)–C(201)				114.9(2)

Table 3
Activation parameters for the Me_3tach ligand N-methyl group exchange for [Ti(NR)(Me_3tach)X_2] (X = Cl, R = Bu^t **1a** or 2,6-$C_6H_3Pr^i_2$ **1b**; X = CH_2Ph, R = Bu^t **4**) [a]

Compound	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})	$\Delta G^{\ddagger}_{292}$ (kJ mol^{-1})
1a	65.3 ± 1.0	7.9 ± 3.5	63.0 ± 1.4
	66.2 ± 1.3	11.3 ± 4.7	62.9 ± 1.9
1b	58.4 ± 1.5	−5.8 ± 5.5	60.1 ± 2.2
	59.9 ± 1.2	−0.3 ± 4.3	60.0 ± 1.7
4	49.9 ± 3.0	−27.3 ± 11.9	57.8 ± 4.6
	46.7 ± 3.3	−39.9 ± 12.7	58.3 ± 5.0

[a] The two values for each activation parameter for each compound correspond to the two independent measurements of each one, namely by lineshape analysis of the *cis* or *trans* (with respect to imide) methyl resonances (see text for details). All NMR measurements were made in CD_2Cl_2 at 4 K intervals in the range 268–308 K (**1a**), 260–288 K (**1b**) or 244–264 K (**4**).

Lineshape analyses of the methyl group resonances yielded exchange rate constants for all three Me_3tach imido titanium complexes, and activation parameters (Table 3) were extracted using standard Eyring plots [14a]. An example of one of the Eyring plots is given in Fig. 5 for the *cis* to *trans* and *trans* to *cis* Me_3tach ligand N-methyl group exchanges for [Ti(NBu^t)(Me_3tach)Cl_2] (**1a**).

The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ (and therefore $\Delta G^{\ddagger}$) values decrease in the order **1a** > **1b** > **4**. Muetterties and Guggenberger have suggested that ligand bite angle and steric factors influence greatly the activation energies for octahedral → trigonal prismatic → octahedral twists [15]. Larger bite angles necessitate more reorganisation and therefore produce higher activation barriers. From the X-ray structures of **1a** and **4** it was found that the Ti–N_{tach} distances for **1a** (avg. 2.304 Å) are shorter than those for **4** (avg. 2.359 Å), and the N_{tach}–Ti–N_{tach} bite angles are larger for **1a** (avg. 59.8°) than for **4** (avg. 58.7°). The lower $\Delta H^{\ddagger}$ for **4** as compared with **1a** is therefore consistent with these solid-state structural features. We do not have structural data for compound **1b** for direct comparison with **1a**, but we can compare the Ti–N_{tach} distances for the Bu^t_3tach homologues, **2a** and **2b** (average Ti–N_{tach} = 2.356 and 2.381 Å for **2a** and **2b**, respectively) and triazacycle bite angles (average N_{tach}–Ti–N_{tach} = 59.4 and 59.1° for **2a** and **2b**, respectively). While the differences between the distances and bite angles for **2a** and **2b** are not as substantial as between **1a** and **4**, they are nonetheless consistent with the lower $\Delta H^{\ddagger}$ for **1b** as compared with **1a**, assuming that the solid-state structures of the Me_3tach complexes show the same trends as the Bu^t_3tach homologues.

The effectively zero (or slightly negative) values for $\Delta S^{\ddagger}$ lend further support to a non-dissociative (e.g. trigonal-twist) mechanism for the exchange processes in **1a**, **1b** and **4**. Previous studies of fluxional processes for a range of octahedral, bis(acetylacetonato)titanium complexes that undergo trigonal-twist rearrangements yielded somewhat more negative $\Delta S^{\ddagger}$ values (in the range ca. −55 to −90 J mol K^{-1}) [16a]. The more positive $\Delta S^{\ddagger}$ values for **1a**, **1b** and **4** indicate a less-ordered transition state compared with those for the previously studied titanium systems.

While an in-place trigonal-twist mechanism fully accounts for the dynamic NMR and activation parameter data, we note that five-coordinate systems often readily isomerise via Berry pseudorotations, or by the so called 'turnstile' mechanism [17]. In the six-coordinate complexes under consideration here, one donor atom (presumably the Me_3tach nitrogen *trans* to imide) would first have to dissociate in order to allow this form of rearrangement. Although it is possible that the *trans* triazacyclic nitrogen could dissociate in such a manner, detailed inspection of molecular models and the experimentally measured activation energies (in par-

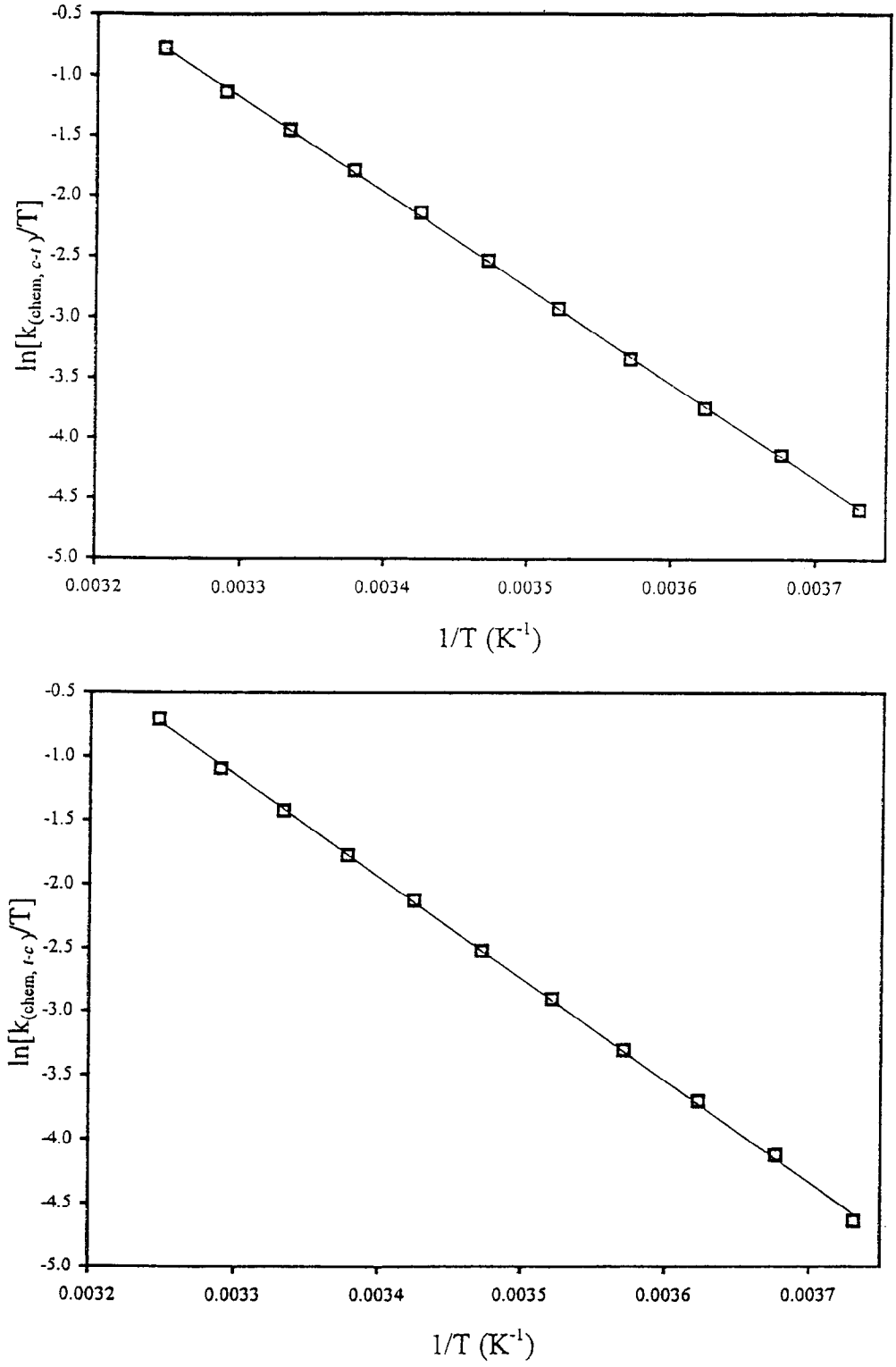


Fig. 5. Eyring plots for the *cis* to *trans* (top) and *trans* to *cis* Me_3tach ligand N-methyl group exchange for [Ti(NBu^t)(Me_3tach)Cl_2] (**1a**).

ticular, the values of $\Delta S^{\ddagger}$ which might be expected to be larger and more positive than those observed) favour a trigonal-twist mechanism.

The trigonal-twist mechanism has long been established for bis(bidentate ligand) chelate complexes of titanium(IV) [16], but, to our knowledge, the fluxional processes for **1a**, **1b** and **4** are the first such examples for any triazacyclic ligand. The fact that the complexes **1a** and **1b** are fluxional, whereas **2a** and **2b** and those of the larger R_3tacn rings (R = H or Me) [2] are not, is

consistent with previous reports concerning the importance of steric factors and ligand bite angle on the energies of activation for such processes [15,16a]. Ground-state trigonal prismatic six-coordinate transition metal complexes ML_6 are well established and their structures have been rationalised theoretically, and it is generally accepted that a trigonal prismatic geometry can be favoured over the octahedral alternative for d^0 complexes, where L is a σ-only (or is only a weakly π-donating) ligand [18]. For ML_6 complexes where the ligand set contains effective π-donors, the octahedral geometry is preferred [19]. This consideration of electronic effects appears to account for the ground-state pseudo-octahedral geometries found for the R_3tach and R_3tacn complexes since they feature strongly π-donating imido ligands. However, it appears that the trigonal prismatic alternatives are accessible on the NMR timescale for the less sterically crowded Me_3tach homologues with small bite angles.

3. Summary and conclusions

We have described a series of metallocene analogues based on triazacyclohexane-supported Group 4 imido complexes. Depending on the identity of the R_3tach N-substituents, the Me_3tach, *tert*-butylimide and chloride ligands in the new complexes can be substituted. Competitive ring-exchange reactions allowed the relative stabilities of imido titanium complexes of different R_3tach and R_3tacn triazacycles to be determined. The fluxional processes in a series of Me_3tach imido titanium complexes has been investigated and activation parameters have been measured. These processes are classified as octahedral → trigonal prism → octahedron trigonal twists, analogous to bis(chelate) titanium complexes described previously. The X-ray crystal structures of four of the new complexes allow the effects of varying the R-, R′- and X-substituents in [Ti(NR)-(R'_3tach)X_2] to be analysed.

4. Experimental

4.1. General

All manipulations of air- and/or moisture-sensitive compounds were carried out under an atmosphere of dinitrogen or argon using standard Schlenk-line or dry-box techniques. All protio-solvents were pre-dried over activated molecular sieves and refluxed over an appropriate drying agent under an atmosphere of dinitrogen and collected by distillation. NMR solvents for air- and/or moisture-sensitive compounds were dried over freshly ground calcium hydride at room temperature (r.t.) (CD_2Cl_2, $CDCl_3$) or molten potassium (C_6D_6), distilled under reduced pressure and stored under N_2 in Young ampoules. NMR samples of air- and moisture-sensitive compounds were prepared in the dry-box in 5 mm Wilmad tubes, generally equipped with a Young's Teflon valve.

^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker DPX 300 spectrometer and referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances. Chemical shifts are reported relative to TMS ($\delta = 0$ ppm) in δ (ppm) and coupling constants in Hertz. Assignments were supported by DEPT-135 and DEPT-90, homo- and heteronuclear, one- and two-dimensional experiments as appropriate. Elemental analyses were carried out by the analysis laboratory of The School of Chemistry, Nottingham. In the NMR assignments given below the '*cis*' and '*trans*' notations are defined as being with respect to the imido ligand.

[Ti(NR)Cl_2(py)$_n$] (R = Bu^t or 2,6-$C_6H_3Pr^i_2$; $n = 2$ or 3) [8], [Zr(*N*-2,6-$C_6H_3Pr^i_2$)Cl_2(THF)$_2$] [10] and R_3tach (R = Me or Bu^t) [6a,d] were prepared according to literature methods.

4.2. [Ti(NBu^t)(Me_3tach)Cl_2] (1a)

A solution of Me_3tach (1.292 g, 10.00 mmol) in dichloromethane (5 ml) was added to a solution of [Ti(NBu^t)Cl_2(py)$_2$] (3.481 g, 10.00 mmol) in dichloromethane (30 ml) at r.t. Within minutes a crop of bright yellow needle crystals formed. After the mixture was stirred for 60 min the volume was decreased under reduced pressure to approximately 6 ml. The resulting crystalline yellow precipitate was filtered off, washed with cold dichloromethane (5 ml, −20°C), hexane (5 ml), pentane (5 ml) and then dried under reduced pressure to give **1b** as a bright yellow powder. Yield: 3.00 g (94%).

^{1}H-NMR ($CDCl_3$, 300.1 MHz, 298 K): 4.82 [br d, 1H, *endo*-C*H*$_2$(*cis*-NMe)$_2$], 4.15 [br d, 2H, *endo*-(*trans*-NMe)C*H*$_2$(*cis*-NMe)], 3.77 [br d, 1H, *exo*-C*H*$_2$(*cis*-NMe)$_2$], 3.29 [br d, 2H, *exo*-(*trans*-NMe)C*H*$_2$(*cis*-NMe)], 2.89 (br s, 6H, *cis*-NMe), 2.13 (br s, 3H, *trans*-NMe), 1.06 (s, 9H, Bu^t). ^{13}C{^{1}H}-NMR ($CDCl_3$, 75.5 MHz, 298 K): 77.4 [(*trans*-NMe)*C*H$_2$(*cis*-NMe)], 76.8 [*C*H$_2$(*cis*-NMe)$_2$], 70.7 (*C*Me$_3$), 41.5 (*cis*-NMe), 36.8 (*trans*-NMe), 31.4 (C*Me*$_3$). Anal. Found: C, 37.5; H, 7.9; N, 17.4. Calc. for $C_{10}H_{24}Cl_2N_4Ti$: C, 37.6; H, 7.6; N, 17.6%.

4.3. [Ti(*N*-2,6-$C_6H_3Pr^i_2$)(Me_3tach)Cl_2] (1b)

A solution of Me_3tach (0.646 g, 5.00 mmol) in dichloromethane (5 ml) was added to a stirred solution of [Ti(*N*-2,6-$C_6H_3Pr^i_2$)Cl_2(py)$_3$] (2.657 g, 5.00 mmol) in dichloromethane (20 ml) at r.t. The resulting dark brown solution was stirred for 14 h and then the volatiles were removed under reduced pressure. The

product was extracted into dichloromethane (15 ml) and then cautiously precipitated by the slow addition of hexane (40 ml) with vigorous stirring. The resulting brown precipitate was filtered off, washed with hexane (5 ml) and then dried under reduced pressure to give **1b** as a pale brown powder. Yield: 1.88 g (89%).

^{1}H-NMR ($CDCl_3$, 300.1 MHz, 298 K): 6.86 (d, J = 7.5 Hz, 2H, 3-$C_6H_3Pr^i_2$), 6.72 (t, J = 7.5 Hz, 1H, 4-$C_6H_3Pr^i_2$), 4.51 [br s, 1H, *endo*-CH_2(*cis*-NMe)$_2$], 4.30 (sept, J = 6.9 Hz, 2H, $CHPr^i_2$), 4.27 [br s, 2H, *endo*-(*trans*-NMe)CH_2(*cis*-NMe)], 3.83 [br s, 1H, *exo*-CH_2(*cis*-NMe)$_2$], 3.55 [br s, 2H, *exo*-(*trans*-NMe)-CH_2(*cis*-NMe)], 2.76 (br s, 6H, *cis*-NMe), 2.24 (br s, 3H, *trans*-NMe), 1.25 (d, J = 6.9 Hz, 12H, $CHMe_2$). ^{13}C{^{1}H}-NMR ($CDCl_3$, 75.5 MHz, 298 K): 156.3 (1-$C_6H_3Pr^i_2$), 144.1 (2-$C_6H_3Pr^i_2$), 122.0 (3-$C_6H_3Pr^i_2$), 121.8 (4-$C_6H_3Pr^i_2$), 77.5 [(*trans*-NMe)CH_2(*cis*-NMe)], 77.1 [CH_2(*cis*-NMe)$_2$], 41.0 (*cis*-NMe), 36.8 (*trans*-NMe), 27.4 ($CHMe_2$), 24.5 ($CHMe_2$). Anal. Found: C, 50.8; H, 7.7; N, 13.3. Calc. for $C_{18}H_{32}Cl_2N_4Ti$: C, 51.1; H, 7.6; N, 13.2%.

4.4. [Ti(N-4-C_6H_4Me)(Me_3tach)Cl_2] (1c)

A solution of 4-methylaniline (0.027 g, 0.25 mmol) in dichloromethane (2 ml) was added to a stirred solution of [Ti(NBu^t)(Me_3tach)Cl_2] (**1c**, 0.080 g, 0.25 mmol) in dichloromethane (4 ml) in a Young's ampoule. The stirred solution was then heated to 50°C for 48 h after which the volatiles were removed under reduced pressure to leave an orange solid. The product was extracted into dichloromethane (5 ml) and then cautiously precipitated by the slow addition of hexane (3 ml) with vigorous stirring. The resulting orange precipitate was filtered off, washed with hexane (4 ml) and dried under reduced pressure to give **1c** as an orange powder. Yield: 0.082 g (93%). Satisfactory elemental analysis was not obtained for this compound.

^{1}H-NMR (CD_2Cl_2, 300.1 MHz, 298 K): 6.89 (d, J = 8.0 Hz, 2H, 3-C_6H_4Me), 6.74 (d, J = 8.0 Hz, 2H, 2-C_6H_4Me), 4.62 [br d, 1H, *endo*-CH_2(*cis*-NMe)$_2$], 4.27 [br d, 2H, *endo*-(*trans*-NMe)CH_2(*cis*-NMe)], 3.83 [br d, 1H, *exo*-CH_2(*cis*-NMe)$_2$], 3.51 [br d, 2H, exo-(*trans*-NMe)CH_2(*cis*-NMe)], 2.82 (br s, 6H, *cis*-NMe), 2.26 (br s, 3H, *trans*-NMe), 225 (s, 3H, C_6H_4Me). ^{13}C{^{1}H}-NMR (CD_2Cl_2, 75.5 MHz, 298 K): 158.5 (1-C_6H_4Me), 131.6 (4-C_6H_4Me), 129.0 (3-C_6H_4Me), 123.2 (2-C_6H_4-Me), 78.2 [(*trans*-NMe)CH_2(*cis*-NMe)], 77.1 [CH_2(*cis*-NMe)$_2$], 41.3 (*cis*-NMe), 37.3 (*trans*-NMe), 21.0 (C_6H_4Me).

4.5. [Ti(NBu^t)(Bu$^t_3$tach)Cl_2] (2a)

A solution of Bu$^t_3$tach (2.554 g, 10.00 mmol) in dichloromethane (5 ml) was added to a stirred solution of [Ti(NBu^t)Cl_2(py)$_2$] (3.481 g, 10.00 mmol) in dichloromethane (40 ml). The resulting dark red solution was stirred for 7 days and then the volatiles were removed under reduced pressure to leave a yellow–brown solid. The product was extracted into dichloromethane (20 ml) and then cautiously precipitated by the slow addition of hexane (50 ml) with vigorous stirring. The resulting yellow precipitate was filtered off, washed with hexane (2 × 10 ml) and then dried under reduced pressure to give **2a** as a mustard yellow powder. Yield: 3.83 g (86%).

^{1}H-NMR ($CDCl_3$, 300.1 MHz, 298 K): 5.18 [d, J = 7.9 Hz, 1H, *endo*-CH_2(*cis*-NMe)$_2$], 4.61 [d, J = 7.1 Hz, 2H, *endo*-(*trans*-NMe)CH_2(*cis*-NMe)], 3.43 [d, J = 8.0 Hz, 1H, *exo*-CH_2(*cis*-NMe)$_2$], 3.18 [d, J = 8.2 Hz, 2H, *exo*-(*trans*-NMe)CH_2(*cis*-NMe)], 1.77 (s, 18H, *cis*-NBu^t), 1.69 (s, 9H, *trans*-NBu^t), 1.56 (s, 9H, TiNBu^t). ^{13}C{^{1}H}-NMR ($CDCl_3$, 75.5 MHz, 298 K): 71.1 (TiNCMe_3), 67.0 (*cis*-NCMe_3), 66.6 (*trans*-NCMe_3), 57.6 [(*trans*-NMe)CH_2(*cis*-NMe)], 56.6 [CH_2(*cis*-NMe)$_2$], 30.8 (TiNCMe_3), 26.7 (*cis*-NCMe_3), 26.2 (*trans*-NCMe_3). Anal. Found: C, 51.0; H, 9.7; N, 12.5. Calc. for $C_{19}H_{42}Cl_2N_4Ti$: C, 51.2; H, 9.5, N, 12.6%.

4.6. [Ti(N-2,6-$C_6H_3Pr^i_2$)(Bu$^t_3$tach)Cl_2] (2b)

A solution of Bu$^t_3$tach (1.277 g, 5.00 mmol) in dichloromethane (5 ml) was added to a stirred solution of [Ti(*N*-2,6-$C_6H_3Pr^i_2$)Cl_2(py)$_3$] (2.657 g, 5.00 mmol) in dichloromethane (20 ml) at r.t. The resulting dark brown solution was stirred for 7 days and then the volatiles were removed under reduced pressure to leave a dark brown solid. The product was extracted into dichloromethane (15 ml) and then cautiously precipitated by the slow addition of hexane (35 ml) with vigorous stirring. The resulting brown precipitate was filtered off, washed with hexane (2 × 5 ml) and then dried under reduced pressure to give **2b** as a red–brown powder. Yield: 2.36 g (86%).

^{1}H-NMR ($CDCl_3$, 300.1 MHz, 298 K): 6.88 (d, J = 7.5 Hz, 2H, 3-$C_6H_3Pr^i_2$), 6.73 (t, J = 7.5 Hz, 1H, 4-$C_6H_3Pr^i_2$), 5.15 [d, J = 7.8 Hz, 1H, *endo*-CH_2(*cis*-NMe)$_2$], 4.77 [d, J = 7.5 Hz, 2H, *endo*-(*trans*-NMe)CH_2(*cis*-NMe)], 4.45 (sept, J = 6.8 Hz, 2H, $CHPr^i_2$), 3.49 [d, J = 8.0 Hz, 1H, CH_2(*cis*-NMe)$_2$], 3.28 [d, J = 7.9 Hz, 2H, *exo*-(*trans*-NMe)CH_2(*cis*-NMe)], 1.51 (s, 18H, *cis*-NBu^t), 1.28 (s, 9H, *trans*-NBu^t), 1.25 (d, J = 6.8 Hz, 12H, $CHMe_2$). ^{13}C{^{1}H}-NMR ($CDCl_3$, 75.5 MHz, 298 K): 156.5 (1-$C_6H_3Pr^i_2$), 144.7 (2-$C_6H_3Pr^i_2$), 122.3 (3-$C_6H_3Pr^i_2$), 121.7 (4-$C_6H_3Pr^i_2$), 67.6 (*cis*-NCMe_3), 66.3 (*trans*-NCMe_3), 57.4 [(*trans*-NMe)CH_2(*cis*-NMe)], 56.6 [CH_2(*cis*-NMe)$_2$], 27.7 ($CHMe_2$), 26.3 (*cis*-NCMe_3), 26.2 (*trans*-NCMe_3), 25.4 ($CHMe_2$). Anal. Found: C, 58.8; H, 9.1; N, 10.2. Calc. for $C_{27}H_{50}Cl_2N_4Ti$: C, 59.0; H, 9.2; N, 10.2%.

4.7. [Zr(N-2,6-$C_6H_3Pr^i_2$)(Me_3tach)Cl_2] (3)

This compound could only be prepared on an NMR tube scale. A solution of Me_3tach (5.2 mg, 0.040 mmol) and Zr(*N*-2,6-$C_6H_3Pr^i_2$)Cl_2(THF)$_2$] (19.2 g, 0.040 mmol) in CD_2Cl_2 (0.6 ml) were mixed together in a sealed NMR tube. The ^{1}H- and ^{13}C{^{1}H}-NMR spectrum of the mixture after 15 min showed quantitative formation of **3**, together with two equivalents of free THF.

^{1}H-NMR (CD_2Cl_2, 300.1 MHz, 298 K): 6.85 (d, $J = 7.5$ Hz, 2H, 3-$C_6H_3Pr^i_2$), 6.56 (t, $J = 7.5$ Hz, 1H, 4-$C_6H_3Pr^i_2$), 4.51 (d, $J = 7.9$ Hz, 3H, *endo*-NCH_2N), 4.13 (sept, $J = 6.9$ Hz, 2H, C*H*Pr^i_2), 3.35 (d, $J = 8.2$ Hz, 3H, *exo*-NCH_2N), 2.56 (s, 9H, *cis* and *trans*-NMe), 1.19 (d, $J = 6.9$ Hz, 12H, CH*Me*$_2$). ^{13}C{^{1}H}-NMR (CD_2Cl_2, 75.5 MHz, 298 K): 152.5 (1-$C_6H_3Pr^i_2$), 142.0 (2-$C_6H_3Pr^i_2$), 122.1 (3-$C_6H_3Pr^i_2$), 118.5 (4-$C_6H_3Pr^i_2$), 78.1 (NCH_2N), 39.7 (*cis*- and *trans*-NMe), 28.2 (*C*HMe$_2$), 24.2 (CH*Me*$_2$).

4.8. [Ti(NBu^t)(Me_3tach)(CH_2Ph)$_2$] (4)

Benzylmagnesium chloride (2.00 ml, 1.0 M in Et_2O, 2.00 mmol) was added to a stirred solution of [Ti(NBu^t)(Me_3tach)Cl_2] (**1a**) (0.319 g, 1.00 mmol) in THF (60 ml) at −50°C and in the absence of light. The resulting bright yellow solution was allowed to slowly warm to r.t. and then stirred for a further 18 h. 1,4-Dioxane (0.5 ml, 5.9 mmol) was added to the solution with stirring, resulting in a slight cloudiness. The volatiles were removed under reduced pressure to give a pale yellow solid. The product was extracted into toluene (80 ml) and the solution then filtered and the volume reduced to approximately 20 ml. The product was then cautiously precipitated by the slow addition of hexane (40 ml) with vigorous stirring. The resulting yellow microcrystalline precipitate was filtered off, washed with hexane (2 × 5 ml) and dried under reduced pressure to give **4** as a bright yellow powder. Yield: 0.362 g (84%).

^{1}H-NMR (C_6D_6, 300.1 MHz, 298 K): 7.20 (m, 8H, overlapping 2- and 3-C_6H_5), 6.80 (m, 2H, 4-C_6H_5), 3.40 (br s, 3H, *endo*-N*C*H_2N), 3.37 and 2.39 (2 × d, 2 × J = 8.9 Hz, 2 × 2H, 2 × CH_2Ph), 1.75 (br s, 3H, *exo*-N*C*H_2N), 1.51 (br s, 6H, *cis*-NMe), 1.41 (NBu^t), 1.34 (br s, 3 H, *trans*-NMe). ^{13}C{^{1}H}-NMR (C_6D_6, 75.5 MHz, 298 K): 155.2 (1-C_6H_5), 128.1 (3-C_6H_5), 126.1 (2-C_6H_5), 118.1 (4-C_6H_5), 76.4 (NCH_2N), 67.3 (N*C*Me$_3$), 59.9 (*C*H_2Ph), 39.2 (*cis*- and *trans*-NMe), 33.5 (NC*Me*$_3$). Anal. Found: C, 64.1; H, 8.8; N, 12.9. Calc. for $C_{10}H_{24}Cl_2N_4Ti$: C, 67.0; H, 8.9; N, 13.0%. The consistently low %C is possibly indicative of incomplete combustion due to carbide formation.

4.9. Crystal structure determinations of [Ti(NBu^t)(Me_3tach)Cl_2] (1a), [Ti(NBu^t)(Bu$^t_3$tach)Cl_2] (2a), [Ti(N-2,6-$C_6H_3Pr^i_2$)(Bu$^t_3$tach)Cl_2] (2b), and [Ti(NBu^t)(Me_3tach)(CH_2Ph)$_2$] (4)

Crystal data collection and processing parameters are given in Table 1. The crystals were coated in a film of perfluoropolyether oil on a glass fibre and transferred to a Stoë Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device [20]. Data were collected at 150(2) K using Mo–K_α radiation. Corrections for Lorentz, polarisation and absorption effects were performed and the structures were solved by direct methods using SIR92 [21]. Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms. Hydrogen atoms for all structures were placed geometrically and their positions allowed to vary using a riding model, with the exception of the benzyl ligand methylene H atoms of **4**: these were located from Fourier difference maps and refined isotropically. For **2a** one of the *tert*-butyl substituents for the Bu$^t_3$tach ligand was disordered. Two orientations for the methyl substituents were refined anisotropically [C(42), C(43), C(44) and C(421), C(431) and C(441)] with site occupancy factors of 0.38 and 0.62, subject to similarity restraints on the C(quat)–C(methyl) distances. Weighting schemes and other corrections were applied as required in the final stages of refinement. All crystallographic calculations were performed using SIR92 and CRYSTALS-PC [22].

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 440/083 (compounds **1a** and **2a**), 135523 (compound **2b**), and 135524 (compound **4**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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