Reaction of 1,3,5-Triazacyclohexanes with $TiCl_4$: Formation of Cationic Complexes

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Dedicated to Professor Herbert Schumann on the occasion of his 70th birthday

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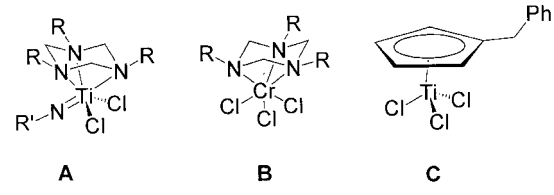
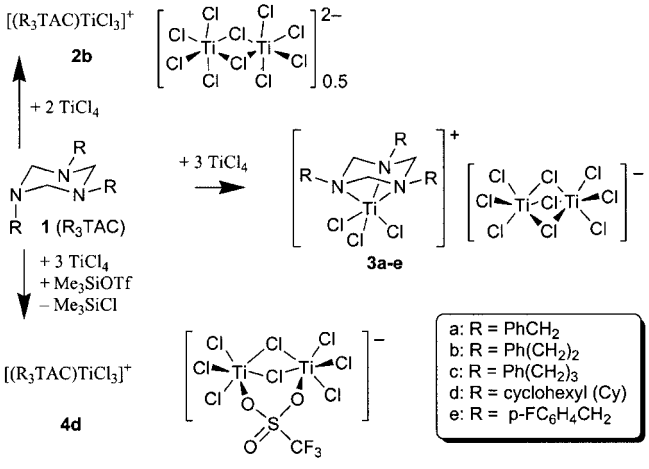
N-substituted 1,3,5-triazacyclohexanes [R_3TAC; R = cyclohexyl, *p*-fluorobenzyl or Ph$(CH_2)_n$ (*n* = 1, 2, 3)] react with excess $TiCl_4$ to give the corresponding cationic κ^3 complexes $[(R_3TAC)TiCl_3][Ti_2Cl_9]$. Attempts to prepare complexes with titanium-free anions at lower Ti:R_3TAC ratio or with added Me_3SiOTf lead to the same cations with $[Ti_2Cl_{10}]^{2-}$ and $[Ti_2Cl_8(OTf)]^-$ anions. Five complexes as well as (*p*-fluorobenzyl)$_3$TAC have been characterised by X-ray crystallography. The ring C–H bonds engage in hydrogen bonding interactions in the crystals and strongly solvent and anion dependent ^{1}H NMR signals are detected in solution.

Introduction

Many complexes containing triazacyclononane and larger macrocyclic amines are known.[1,2] They are used, for example, as bioinorganic model systems, reagents with high metal ion selectivity or as olefin polymerisation catalysts. The smaller *N*-substituted 1,3,5-triazacyclohexanes (R_3TAC) are much easier to prepare by the reaction of formaldehyde with primary amines allowing for a large variety of alkyl substituents. However, their coordination chemistry has mostly been explored only in the past ten years. A wide range of complexes with transition metals (like titanium complex **A**[3] in Scheme 1) and main group elements are well established. MAO activated chromium(III) complexes[4] (e.g. **B** in Scheme 1) are highly active homogeneous catalysts for the polymerisation and selective trimerisation of olefins.[5] Recently alternative catalysts for the selective trimerisation of ethylene based on aryl-substituted $CpTiCl_3$, **C**, have been discovered.[6] Since many features of the metal complexes containing R_3TAC, such as the ring centroid-metal distance, donor orbital orientation or positions of the ring substituents resemble those of analogous Cp rather than triazacyclononane complexes, we were interested in the preparation of analogous $[(R_3TAC)TiCl_3]^+$ complexes. The only previously described types of triazacyclohexane complexes of titanium are the neutral imido complexes **A** shown in Scheme 1.[3,7,8] In this paper we describe the synthesis of cationic 1,3,5-triazacyclohexane complexes by the reaction of the ligand with $TiCl_4$ (Scheme 2).



Scheme 1.



Scheme 2.

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Results and Discussion

Treatment of $TiCl_4$ with one equivalent of *N*-substituted triazacyclohexanes **1** gave complex mixtures of products. However, a few yellow crystals of **2b** grew from this mixture as in the case of R = $Ph(CH_2)_2$ (**1b**). X-ray crystallography revealed a cationic complex $[(R_3TAC)TiCl_3]^+$ with $[Ti_2Cl_{10}]^{2-}$ anions. Apparently, excess $TiCl_4$ can abstract chloride ions to produce cationic R_3TAC complexes. Indeed, reaction of excess $TiCl_4$ with **1** gave high yields of often crystalline orange compounds. The optimal ratio of $TiCl_4$ to R_3TAC for a clean reaction was found to be 3:1. The crystal structures of **3a**, **3b** and **3d** contain the same cations as in **2b** but with the relatively more titanium rich anions $[Ti_2Cl_9]^-$. Similar ionisation of $TiCl_4$ has previously been observed in the reaction of hexaalkylbenzene with three equivalents of $TiCl_4$ giving $[(arene)TiCl_3][Ti_2Cl_9]$[9] Contrary to these arene complexes, the formation of **3** is irreversible on dilution. Thus, triazacyclohexanes are much stronger ligands than the arenes. The similarity of this reaction and the structures of the products show that the coordination chemistry of triazacyclohexanes share many characteristics with cyclic π ligands in the orientation of the donor orbitals, the position of the substituents near the plane of the donor atoms as well as the steric requirements.

The well-defined complexes **3** show only limited solubility in most inert organic solvents. The isolated crystalline solids are poorly soluble even in chlorinated solvents. The concentrations of saturated solutions of **3a** and **3d** in CH_2Cl_2 were found to be 2×10^{-4} and 2×10^{-3} mol cm^{-3}, respectively, by ^{1}H NMR spectroscopy. We generally find low solubility of triazacyclohexane complexes, probably due to hydrogen bonding interactions between ring–CH and Cl of the anion (or the complex itself) found in many solid-state structures. Thus, long-chain *N*-substituents or strong donor solvents are usually required for sufficient solubility. The concentration of **3e** was high enough to obtain ^{1}H and ^{19}F NMR spectra in pure $CDCl_3$ (about 4×10^{-3} mol cm^{-3} by NMR spectroscopy). All complexes **3** dissolved well in a mixture of $CDCl_3$ and $SOCl_2$ without apparent decomposition. Solutions in this mixture remained stable for many days even when exposed to air. Comparison of the NMR spectra of **3e** in neat $CDCl_3$ and those in 1:1 $CDCl_3/SOCl_2$ showed little differences except for the chemical shift of the two doublets for the ring CH_2 signals (4.89 and 4.74 ppm in $CDCl_3$ vs. 4.98 and 4.48 ppm in $CDCl_3/SOCl_2$). The observation of these two doublets for the equatorial and axial hydrogen atoms in the ring is also the best evidence for κ^3-R_3TAC coordination to a metal as observed previously.[10] The chemical shift and shift difference appears to be highly dependent on the environment (solvent, anion), probably due to C–H···X hydrogen bonding interactions. The shift difference varies from 0.1–0.9 ppm and is significantly smaller than the difference found in the neutral imido complexes of type **A** (1–2 ppm).[3,7,8]

In an attempt to obtain analogous cationic titanium complexes with titanium free anions we added Me_3SiOTf to the reaction mixture. Me_3SiCl was formed, however, a crystal structure of the product, **4d**, revealed the same cation not with an isolated triflate anion but with the titanium containing anion $[Ti_2Cl_6(\mu\text{-}Cl)_2(\mu\text{-}OTf)]^-$. Elemental analysis of the bulk product indicates that a mixture of **4d** and **3d** was obtained.

Addition of one equivalent of $LiB(C_6F_5)_4$ to a $CDCl_3/SOCl_2$ solution of **3d** leads to a significant change in the chemical shift of the pair of ring CH_2 signals of the ^{1}H NMR spectrum without changing the rest of the spectrum (4.96 and 4.62 ppm vs. 4.97 and 4.77 ppm in **3d**) indicating an anion exchange. Preparative scale metathesis of **3** or $TiCl_4$/**1** with $LiB(C_6F_5)_4$ allows the isolation of analogous salts **5** with largely $B(C_6F_5)_4$ anions, although no pure samples could be obtained due to anion contamination. **5d** had an NMR spectrum identical to the NMR tube experiment mentioned above and the spectra for **5b** (4.91 and 4.30 ppm vs. 5.03 and 4.81 ppm in **3b**) and for **5c** (3.60 and 3.45 ppm vs. coinciding peaks at 4.83 for **3c**) showed an increasing effect of the anion exchange (up-field shift and larger separation) for decreasing bulk of the *N*-substituents. A mixture of **5b** and **3b** leads to NMR signals at average positions indicating fast anion exchange on the NMR time-scale.

The strong dependence of the ring CH_2 ^{1}H NMR signals on the anion and the solvent indicates significant interactions of these C–H bonds with the environment.

X-ray Crystal Structures

All structures contain the $[(R_3TAC)TiCl_3]^+$ cation with titanium containing anions. Except for one feature, structural differences between cations with different anions (**2b**, **3b** and **3d**, **4d**) as well as anions with different cations (**3a**, **3b**, **3d**) are small and allow a separate discussion of the anions and cations.

Structural parameters of the coordination environment around titanium in the cations $[(R_3TAC)TiCl_3]^+$ shown in Figure 1 are summarised in Table 1. The structures are very similar to the neutral $[(R_3TAC)CrCl_3]$ where the analogous structure for R = $PhCH_2CH_2$ is known.[5] However, the Ti–N bond (2.23 Å) is much longer than in the chromium complex (2.10 Å) whereas the Ti–Cl bonds (2.20 Å) are shorter than in the chromium complex (2.28 Å), despite nearly identical ionic radii for Cr^{III} and Ti^{IV}.[11] Thus the higher charge on titanium favours the chloride bonding over the amine bonding. As in other triazacyclohexane complexes the nitrogen lone pair cannot be directed towards the metal and results in a bent-bonding situation. However, the Ti–N bonding is improved by bending the N-substituent towards the N_3 plane and therefore the lone pair towards the metal as shown in Scheme 3.

This bending can be expressed by the Ti–N–C angle or better the distance Δ of the α-C of the N-substituent above (or below) the N_3 plane. This can also be compared to the free ligand; the published structure[12] of **1a** has severe temperature dependent disorder between axial and equatorial benzyl groups making it difficult to obtain reliable Δ values. We crystallised the known ligand **1e** (R = *p*-fluorobenzyl)

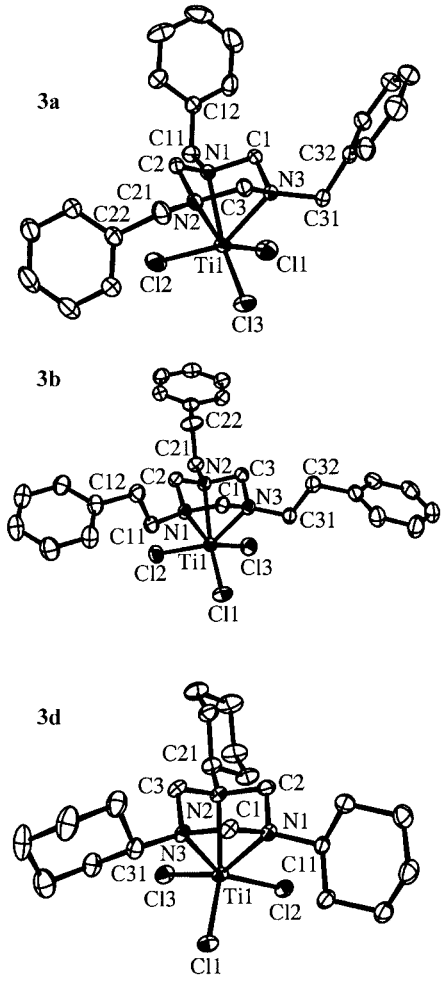
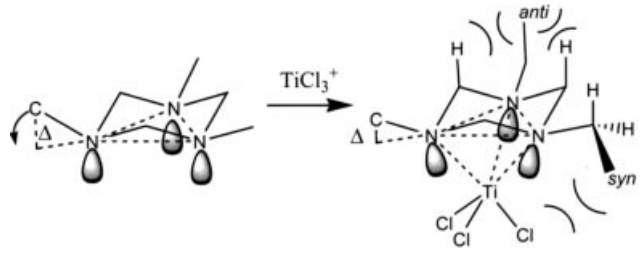


Figure 1. Structure of the cations in **3a**, **3b** and **3d**. The cations in **2b** and **4d** look nearly identical.



Scheme 3. Bent-bonding situation in triazacyclohexane complexes, definition of Δ, and the *syn* and *anti* conformation of the N-substituent.

and obtained a crystal structure without such disorder.[13] The structure of **1e** shows the most common conformation for free triazacyclohexanes with one axial and two equatorial N-substituents as shown in Figure 2. Δ for the two equatorial carbon atoms is +0.47 and +0.55 Å and close to the value of +0.49 Å expected for a ring with perfect tetrahedral angles and equal C–N bond lengths of 1.46 Å (average found in **1e**). The observed Δ values for the titanium complexes fall into three groups: +0.12 and +0.16 Å

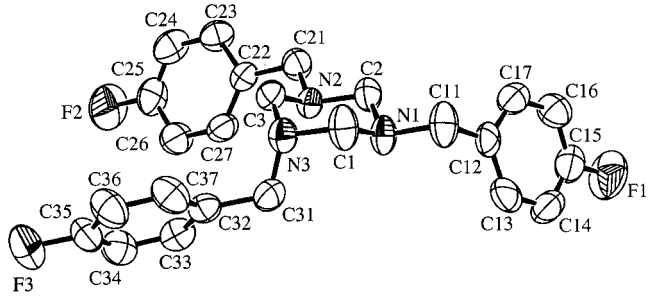


Figure 2. Structure of the complex **1e**.

Table 1. Selected averaged distances [Å] and angles [°] in $[(R_3TAC)TiCl_3]^+$ of **2**, **3** and **4**.

	R = $PhCH_2$ **3a**	R = $PhCH_2CH_2$ **2b** [**3b**]	R = cyclohexyl **3d** [**4d**]
Ti1–N1	2.221(1)[b]	2.205(2)[b] [2.236(2)[b]]	2.240(3) [2.236(2)]
Ti1–N2	2.254(1)[a]	2.218(2)[b] [2.230(2)[b]]	2.232(3) [2.239(2)]
Ti1–N3	2.228(1)[b]	2.227(2)[a] [2.223(2)[b]]	2.235(3) [2.227(2)]
av. Ti–N_{syn}	2.25	2.23 [–]	2.24 [2.23]
av. Ti–N_{anti}	2.22	2.21 [2.23]	
Ti1–Cl1	2.201(1)	2.208(1) [2.206(1)]	2.197(1) [2.204(1)]
Ti1–Cl2	2.191(1)	2.206(1) [2.196(1)]	2.213(1) [2.203(1)]
Ti1–Cl3	2.205(1)	2.199(1) [2.189(1)]	2.201(1) [2.212(1)]
av. Ti–Cl	2.20	2.20 [2.20]	2.20 [2.21]
Δ(C11)[c]	+0.02[b]	–0.01[b] [–0.02[b]]	+0.04 [+0.04]
Ti1–N1–C11	126.5(1)	125.7(2) [125.7(2)]	128.7(2) [128.2(1)]
Δ(C21)[c]	+0.16[a]	–0.01[b] [+0.03[b]]	+0.06 [+0.03]
Ti1–N2–C21	133.2(1)	126.1(2) [127.7(2)]	128.4(2) [127.8(1)]
Δ(C31)[c]	–0.02[b]	+0.12[a] [–0.07[b]]	+0.08 [+0.05]
Ti1–N3–C31	125.2(1)	131.5(2) [123.4(2)]	129.3(2) [128.2(1)]
av. Δ/Ti–*N*–C_{syn}	0.16/133	0.12/132 [–]	0.06/129 [0.04/128]
av. Δ/Ti–*N*–C_{anti}	0.00/126	–0.01/126 [–0.02/126]	
av. N–Ti–N	61.7	62.2 [61.9]	61.9 [62.1]
av. Cl–Ti–Cl	106	106 [106]	104 [104]
av. Ti–*N*–C–C_{syn}	54	75 [–]	55 [57]
av. Ti–*N*–C–C_{anti}	173	177 [177]	177 [176]

[a] *syn* conformation of R. [b] *anti* conformation of R. [c] Distance Δ above the N_3 plane (negative number on metal side).

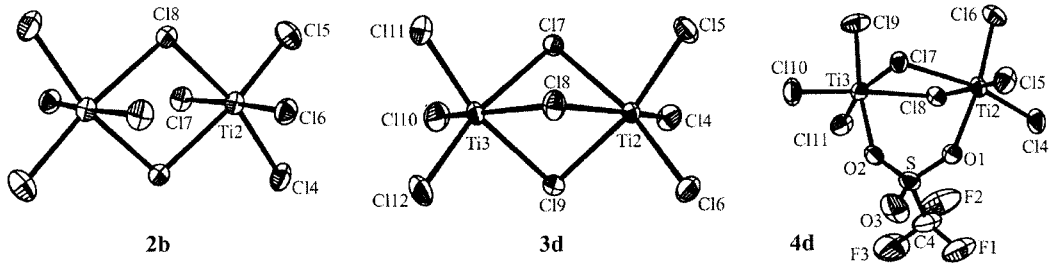


Figure 3. Structure of the anions in **2b**, **3d** and **4d**. The anions in **3a** and **3b** look nearly identical to that in **3d**.

for N-substituents in the *syn* conformation, –0.07 to +0.03 (av. –0.01) Å for the *anti* conformation and +0.03 to +0.08 (av. +0.05) Å for the cyclohexyl substituent (β-C in both *syn* and *anti* position). All values indicate a substantial bending of the N-substituent position towards the N_3 plane upon complexation in order to obtain better N-metal overlap. However, steric repulsion leads to less bending in the *syn* conformation (β-C···Cl) and increased bending in the *anti* conformation (β-C···axial ring C–H) with an intermediate case for cyclohexyl with repulsion at both β-C positions. The intermediate values for the cyclohexyl substituent show that both steric repulsions are important.

It is informative to compare the bonding parameters in these cationic $[(R_3TAC)TiCl_3]^+$ complexes with the neutral imido complexes **A**. The Ti–N bond lengths *trans* to Ti–Cl are nearly the same (2.23 Å) unless R is the bulky *t*Bu group (>2.30 Å) whereas the Ti–Cl bonds are substantially shorter in the cationic complexes (2.20 vs. 2.33–2.36 Å in **A**) but similar to those in the cationic arene complexes $[(arene)TiCl_3]^+$ (2.19 Å).[9] However, the Δ values for N-substituents *trans* to Cl in the imido complexes are much larger (+0.15 to 0.24 Å) than those found in the cationic complexes (–0.07 to +0.16 Å). Thus the tighter bonding of R_3TAC in cationic complexes is expressed as an improved nitrogen lone pair orientation (smaller Δ) rather than shorter Ti–N bonds.

All anions (Figure 3) contain two octahedrally coordinated titanium atoms. The two metals share one edge (two chloride bridges) in **2** or one face (three chloride bridges) in **3**. The anion in **4** contains a triflate bridge in addition to two chloride bridges and results in structural features intermediate between **2** and **3** as shown in Table 2. The anions in **2** and **3** have been observed before while the anion in **4** is new.[14]

The structures also allow us to look at the C–H···X interactions in the crystal and the effect of varying the N-substituents and anions. A CSD review of C–H···Cl interactions revealed H···Cl distances of 2.8–2.9 Å and C–H···Cl angles of 140–180° as the best parameters for this hydrogen bonding interaction when Cl is part of an anion.[15] The structures of all complexes in this work contain C–H···Cl contacts of this length or shorter and involve at least one ring C–H bond. Each anion has several contacts to neighbouring cations leading to an extended 3D network rationalising the poor solubility. However, there are noteworthy differences between the structures. The shortest contacts in **3** with the anion increase from **3b** (2.68 Å, R = $PhCH_2CH_2$) to **3a** (2.76 Å, R = $PhCH_2$) and **3d** (2.85 Å, R = cyclohexyl) as expected for increasing steric bulk exhibited by the substituent. In the latter case as well as in the similar **4d** (shortest C–H···Cl 2.78 Å + C–H···O(Tf) 2.51 Å) additional contacts of similar lengths with C–H groups of the substituents exist. The single short C–H···Cl contact in **3b** is replaced by two slightly longer contacts of 2.73 Å (ring CH) and 2.72 Å (α-CH_2 of R) reflecting the probably tighter binding of the Ti_2Cl_{10} dianion.

Table 2. Selected averaged distances [Å] and angles for the anions of **2**, **3** and **4**.

	$[Ti_2Cl_{10}]^{2-}$ **2b**	$[Ti_2Cl_9]^-$ **3a** [**3b**] {**3d**}	$[Ti_2Cl_8(OTf)]^-$ **4d**
Ti–(μ-Cl)	2.50	2.49 [2.49] {2.49}	2.48
Ti–Cl	2.27	2.22 [2.21] {2.21}	2.21
Ti–O			2.10
Ti···Ti	3.84	3.40 [3.43] {3.39}	3.75
Ti–(μ-Cl)–Ti	101°	86° [87°] {86°}	98°
(μ-Cl)–Ti–(μ-Cl)	79°	78° [78°] {79°}	80°
Cl–Ti–Cl	*cis*: 94°	98° [99°] {99°}	99°

The above study demonstrates that cationic triazacyclohexane complexes of titanium can be obtained by the reaction of the ligand with excess $TiCl_4$. The N-substituents are more bent towards the metal than in neutral complexes with improved metal–N bonding. The ring C–H bonds of the triazacyclohexanes interact with the environment through significant hydrogen-bonding interactions leading to surprisingly poor solubility of these 3D networks in chlorinated solvents.

Experimental Section

General Details: All manipulations of air- and moisture-sensitive compounds were carried out under nitrogen or argon using standard Schlenk-line or glove box techniques. Solvents were dried according to standard methods and collected by distillation. R_3TAC except for **1c** are known and have been prepared analogous to the method described for **1c**. **1a**,**b**,**d**,**e** were crystallised from petroleum ether. ^1H and ^{13}C NMR spectra were recorded with a Varian Mercury-400 or Bruker Avance-300 or 400 at 20 °C and assignments were confirmed by COSY spectra. Mr Alan Carver (University of

Bath) carried out the elemental analyses with an Exeter Analytical Instruments CE-440 Elemental Analyser.

Phenylpropyl$_3$TAC (1c): Phenylpropylamine (11.37 g, 84.22 mmol) and paraformaldehyde (2.53 g, 84.22 mmol) were dissolved in toluene (50 mL). The solution was heated to distil off the produced water as an azeotropic mixture with toluene. After 30 min the remaining solvent was removed by distillation under reduced pressure. The remaining pale yellow oil was dissolved in methanol (250 mL) and stored at 0 °C. The separated oil was washed with ethanol and dried under reduced pressure to give a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31–7.28 (6 H, C_6H_5–), 7.23 (9 H, C_6H_5–), 3.36 (br. s, 6 H, ring–CH_2), 2.69 (m, 6 H, –CH_2–Ph), 2.51 (m, 6 H, N–CH_2–), 1.83 (m, 6 H, Bz–CH_2–CH$_2$–N). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 142.1 (1-C_6H_5), 128.4 (3-C_6H_5), 128.2 (2-C_6H_5), 125.7 (4-C_6H_5), 74.5 (N–CH$_2$–N), 52.0 (PhEt–CH$_2$–N), 33.5 (Ph–CH$_2$–), 29.2 (Bz–CH$_2$–).

[(Benzyl$_3$TAC)TiCl$_3$]$^+$[Ti$_2$Cl$_9$]$^-$ (3a): I A solution of (PhCH$_2$)$_3$TAC (0.415 g, 1.16 mmol) in dichloromethane (25 mL) was added to a stirred solution of $TiCl_4$ (0.865 g, 4.56 mmol) in dichloromethane (25 mL) at room temperature under a stream of dinitrogen. After 5 h pale yellow platelets deposited. Washing with dichloromethane (10 mL) and drying in vacuo yielded clear yellow crystals. Yield: 0.56 g (52%). **II** A solution of (PhCH$_2$)$_3$TAC (1.24 g, 3.47 mmol) in toluene (25 mL) was added to a stirred solution of $TiCl_4$ (1.73 g, 9.12 mmol) in toluene (25 mL) at room temperature under a stream of dinitrogen. Dichloromethane (50 mL) was slowly added by condensation under reduced pressure. After 1 h of stirring, further $TiCl_4$ (1.73 g, 9.12 mmol) was added to give a dark orange solution. After another hour little orange crystals started to precipitate. These were dried under reduced pressure. Yield: 1.89 g (59%). ^{1}H NMR (300 MHz, $CDCl_3$/$SOCl_2$): δ = 7.48 m (9 H, C_6H_5–), 7.30 m (6 H, C_6H_5–), 5.06 and 4.14 (d, J = 9 Hz, 3 H, N–CH_2–N), 4.31 (s, 6 H, N–CH_2–Ph) ppm. ^{1}H NMR (400 MHz, saturated in CH_2Cl_2, 0.2 mM): δ = 7.5 (9 H, C_6H_5–), 7.3 (6 H, C_6H_5–), 4.75 and 4.25 (3 H, N–CH_2–N), 4.34 (s, 6 H, N–CH_2–Ph). ^{1}H NMR (400 MHz, saturated in CH_2Cl_2/$SOCl_2$, 1.0 mM): δ = 7.45 (9 H, C_6H_5–), 7.33 (6 H, C_6H_5–), 5.01 and 4.32 (d, 3 H, N–CH_2–N), 4.29 (s, 6 H, N–CH_2–Ph) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$/$SOCl_2$): δ = 130.7 (1-C_6H_5), 130.6 (3-C_6H_5), 129.9 (2-C_6H_5), 127.6 (4-C_6H_5), 76.5 (N–CH$_2$–N), 60.9 (Ph–CH$_2$–N). $C_{24}H_{27}N_3Ti_3Cl_{12}$ (926.58): calcd. C 31.11, H 2.94, N 4.54; found C 30.9, H 2.99, N 4.52 ppm.

[(Phenylethyl$_3$TAC)TiCl$_3$]$^+$[Ti$_2$Cl$_9$]$^-$ (3b): A solution of (PhC$_2$H$_4$)$_3$-TAC (1 g, 2.5 mmol) in dichloromethane (25 mL) was added slowly to a solution of $TiCl_4$ (1.330 g, 7.01 mmol) in dichloromethane (25 mL) at room temperature under a stream of dinitrogen to give a clear brown solution. The product was cautiously precipitated by slow addition of hexane (20 mL). After 48 h a brownish yellow precipitate was separated and dried under reduced pressure to give a brownish yellow powder. Yield: 2.17 g (96%). ^{1}H NMR (300 MHz, $CDCl_3$/$SOCl_2$): δ = 7.41–7.34 (9 H, C_6H_5–), 7.26–7.23 (6 H, C_6H_5–), 5.03 and 4.81 (d, J = 9.2 Hz, 3 H, N–CH_2–N), 3.55 (t, 6 H, Ph–CH_2–), 2.98 (t, 6 H, Bz–CH_2–N) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$/$SOCl_2$): δ = 135.3 (1-C_6H_5), 129.3 (3-C_6H_5), 128.5 (2-C_6H_5), 127.7 (4-C_6H_5), 77.9 (N–CH$_2$–N), 58.1 (Bz–CH$_2$–N), 30.5 (Ph–CH$_2$–) ppm. $C_{27}H_{33}N_3Ti_3Cl_{12}$ (968.66): calcd. C 33.48, H 3.43, N 4.34; found C 33.4, H 3.52, N 4.34.

[(Phenylpropyl$_3$TAC)TiCl$_3$]$^+$[Ti$_2$Cl$_9$]$^-$ (3c): A solution of (PhC$_3$H$_6$)$_3$-TAC (1 g, 2.26 mmol) in dichloromethane (25 mL) was added slowly to a solution of $TiCl_4$ (1.29 g, 6.80 mmol) in dichloromethane (25 mL) at room temperature under a stream of dinitrogen to give a clear dark brown solution. The product was cautiously precipitated by slow addition of hexane (20 mL). After 24 h a dark orange-brown precipitate was separated and dried under reduced pressure to give a brownish yellow crystal-like powder. Yield: 1.81 g (79%). ^{1}H NMR (300 MHz, $CDCl_3$/$SOCl_2$): δ = 7.34–7.27 (9 H, C_6H_5–), 7.24–7.18 (6 H, C_6H_5–), 4.85 and 4.81 (d, J = 9.6 Hz, 3 H, N–CH_2–N), 3.21 (m, 6 H, PhEt–CH_2–N) 2.68 (m, 6 H, Ph–CH_2), 1.98 (m, 6 H, PhCH$_2$–CH_2–) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$/$SOCl_2$): δ = 139.1 (1-C_6H_5), 128.7 (3-C_6H_5), 128.3 (2-C_6H_5), 126.6 (4-C_6H_5), 77.5 (N–CH$_2$–N), 56.2 (PhEt–CH$_2$–N), 32.4 (Ph–CH$_2$–), 25.1 (PhCH$_2$–CH$_2$) ppm. $C_{30}H_{39}N_3Ti_3Cl_{12}$ (1010.74): calcd. C 35.65, H 3.89, N 4.16; found C 36.0, H 3.76, N 4.24.

[(Cyclohexyl$_3$TAC)TiCl$_3$]$^+$[Ti$_2$Cl$_9$]$^-$ (3d): A solution of Cy$_3$TAC (1 g, 3.00 mmol) in dichloromethane (25 mL) was added slowly to a solution of $TiCl_4$ (1.71 g, 9.01 mmol) in dichloromethane (25 mL) at room temperature under a stream of dinitrogen to give a clear brown solution. A bright yellow solid began to precipitate from the dark solution. After 48 h in the refrigerator the precipitate was isolated, washed with dichloromethane (20 mL) and dried under reduced pressure to give bright yellow crystals. Yield: 2.03 g (75%). ^{1}H NMR (300 MHz, $CDCl_3$/$SOCl_2$): δ = 4.97 and 4.77 (d, J = 8.8, 3 H, N–CH_2–N), 3.22 [3 H, CH–N], 2.20 [6 H, eq. –CH_2–CHN)], 2.00 [6 H, eq. –CH_2–CH$_2$CHN], 1.72 (3 H, eq. –CH_2–CH$_2$CH$_2$CHN), 1.38 [12 H, ax. –CH_2–CH_2–CHN] 1.2 (3 H, ax. –CH_2–CH$_2$CH$_2$CHN) ppm. ^{1}H NMR (400 MHz, saturated in CH_2Cl_2, 2.3 mM): δ = 4.927 and 4.85 (d, J = 8.5, 3 H, N–CH_2–N), 3.2 [3 H, CH–N], 2.18 [6 H, eq. –CH_2–CHN)], 1.94 [6 H, eq. –CH_2–CH$_2$CHN], 1.70 (3 H, eq. –CH_2–CH$_2$CH$_2$CHN), 1.34 [12 H, ax. –CH_2–CH_2–CHN] 1.12 (3 H, ax. –CH_2–CH$_2$CH$_2$CHN) ppm. ^{1}H NMR (400 MHz, saturated in CH_2Cl_2/$SOCl_2$ (3:1), 2.8 mM): δ = 4.93 and 4.88 (3 H, N–CH_2–N), 3.2 [3 H, CH–N], 2.2 [6 H, eq. –CH_2–CHN)], 1.94 [6 H, eq. –CH_2–CH$_2$CHN], 1.70 (3 H, eq. –CH_2–CH$_2$CH$_2$CHN), 1.34 [12 H, ax. –CH_2–CH_2–CHN] 1.12 (3 H, ax. –CH_2–CH$_2$CH$_2$CHN) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$/$SOCl_2$): δ = 74.6 (N–CH$_2$–N), 66.6 (CH–N), 27.5 (CH$_2$–CHN), 25.2 (CH$_2$–CH$_2$CHN), 24.7 (CH$_2$–CH$_2$CH$_2$CHN) ppm. $C_{21}H_{39}N_3Ti_3Cl_{12}$ (902.64): calcd. C 27.94, H 4.36, N 4.66; found C 27.9, H 4.35, N 4.65.

[(Cyclohexyl$_3$TAC)TiCl$_3$]$^+$[[Ti$_2$Cl$_8$(OTf)]$^-$ (4d): Trimethylsilyl trifluoromethanesulfonate (0.67 mL, 3.7 mmol) was added to 5 mL of a 0.6 M solution of $TiCl_4$ in toluene (3 mmol) at 0 °C. The resulting deep red-brown solution was stirred for 30 min and then Cy$_3$TAC (1.0 g, 3.0 mmol) was added at 0 °C. After warming to ambient temperature and stirring for 1 h, hexane (30 mL) was added to give an orange precipitate. The solution was decanted and the residue dried under vacuum, washed with 50 mL of hexane and dried again under vacuum to give an orange-brown solid (2.6 g, 85%). Elemental analysis (CHN) of this product fits that of a mixture of complexes containing the cation with a 2:1 mixture of [Ti$_2$Cl$_8$(OTf)]$^-$ and [Ti$_2$Cl$_{10}$]$^{2-}$ anions. Crystals of **4d** were grown from a solution in $SOCl_2$/chloroform. ^{1}H NMR (300 MHz, $CDCl_3$/$SOCl_2$): δ = 4.92 and 4.87 (d, J = 9.4, 3 H, N–CH_2–N), 3.20 [3 H, CH–N], 2.19 [6 H, eq. –CH_2–CHN)], 1.98 [6 H, eq. –CH_2–CH$_2$CHN], 1.71 (3 H, eq. –CH_2–CH$_2$CH$_2$CHN), 1.4 [12 H, ax. –CH_2–CH_2–CHN] 1.2 (3 H, ax. –CH_2–CH$_2$CH$_2$CHN) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$/$SOCl_2$): δ = 77.9 (N–CH$_2$–N), 67.0 (CH–N), 27.3 (CH$_2$–CHN), 25.0 (CH$_2$–CH$_2$CHN), 24.6 (CH$_2$–CH$_2$CH$_2$CHN) ppm. $C_{22}H_{39}N_3Ti_3Cl_{11}SO_3F_3$ (1016.26): calcd. C 26.00, H 3.87, N 4.14. Calcd for the mixture $C_{22}H_{39}N_3Ti_{2.5}Cl_{9.5}S_{0.5}O_{1.5}F_{1.5}$: C 30.35, H 4.52, N 4.83; found C 30.1, H 4.65, N 4.48.

[(Fluorobenzyl$_3$TAC)TiCl$_3$]$^+$[Ti$_2$Cl$_9$]$^-$ (3e): A solution of (*p*-F–PhCH$_2$)$_3$TAC (0.163 g, 0.40 mmol) in dichloromethane (10 mL) was added to a stirred solution of $TiCl_4$ (0.16 mL, 0.28 g,

Table 3. Crystal data, data collection and refinement parameters for **2b, 3a, 3b, 3d and 4d**.

	2b·(toluene)	**3a**	**3b**	**3d**·(CH_2Cl_2)	**4d**
Empirical formula	$C_{41}H_{49}Cl_8N_3Ti_2$	$C_{24}H_{27}Cl_{12}N_3Ti_3$	$C_{27}H_{33}Cl_{12}N_3Ti_3$	$C_{22}H_{41}Cl_{14}N_3Ti_3$	$C_{22}H_{39}Cl_{11}F_3N_3O_3STi_3$
M [g mol^{-1}]	963.23	926.54	968.66	987.58	1016.27
Crystal colour	yellow	yellow	yellow	yellow	yellow
Crystal size [mm]	0.4 × 0.25 × 0.2	0.45 × 0.38 × 0.38	0.4 × 0.33 × 0.2	0.4 × 0.3 × 0.2	0.3 × 0.3 × 0.08
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	triclinic
Space group	$P2_1/a$ (no.14)	$P2_1/c$ (no.14)	$P\bar{1}$ (no.2)	$P2_1/c$ (no.14)	$P\bar{1}$ (no.2)
a [Å]	11.3330(2)	11.6700(1)	11.5000(4)	13.5980(2)	13.0210(2)
b [Å]	23.7790(4)	15.7590(1)	12.1700(5)	10.4900(2)	13.4030(2)
c [Å]	16.6530(4)	20.5150(2)	15.7990(7)	28.1290(4)	14.6230(2)
α [°]			69.985(2)		65.2640(8)
β [°]	96.9650(7)	103.2280(4)	83.7330(17)	94.8570(5)	68.9630(9)
γ [°]			69.130(2)		64.0170(8)
V [Å^3]	4454.66(15)	3672.76(5)	1941.09(14)	3998.00(11)	2034.78(5)
Z	4	4	2	4	2
D_c [g cm^{-3}]	1.436	1.676	1.657	1.641	1.659
μ(Mo-K_α) [mm^{-1}]	0.871	1.532	1.453	1.542	1.392
F(000)	1984	1848	972	1992	1024
$2\theta_{range}$ [°]	7–55	8–60	8–55	7–55	7–55
Collected data	71226	68831	21139	38570	35951
Unique data $I > 2\sigma(I)$	10005, R(int) = 0.087	10694, R(int) = 0.036	8525, R(int) = 0.049	8970, R(int) = 0.1625	9257, R(int) = 0.041
Refined parameter	487	379	407	379	415
min./max. density [e Å^{-3}]	–0.560/0.903	–0.891/0.778	–0.513/0.533	–1.028/0.758	–0.655/0.532
Extinction coeff.[a]			0.0033(6)		
R_1[b] [$I > 2\sigma(I)$]	0.0472	0.0297	0.0399	0.0626	0.0356
wR_2[c] [$I > 2\sigma(I)$]	0.0998	0.0700	0.0990	0.1454	0.0908
Gof[d]	1.038	1.047	1.059	1.046	1.049

[a] $F_c^* = kF_c[1 + 0.001F_c^2\lambda^3/\sin(2\theta)]^{-1/4}$. [b] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. [c] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^{2)2}]\}^{1/2}$. [d] Gof = $S = \{\Sigma[w(F_o^2 - F_c^2)^2]] / (n - p)\}^{1/2}$.

1.46 mmol) in dichloromethane (20 mL) at room temperature under a stream of dinitrogen. The solution was slowly concentrated to 2 mL and cooled to –20 °C. Yellow crystals grew overnight and were isolated by decanting the remaining solution, washing with two 1 ml portions of CH_2Cl_2 and drying in a stream of nitrogen. This results in about 1.5 or 2.5 remaining CH_2Cl_2 per **3e** according to elemental analysis and NMR spectroscopy, respectively. Yield: 0.29 g (74%). ^{1}H NMR (400 MHz, saturated solution in $CDCl_3$, 4 mM): δ = 7.40 (m, 6 H, C_6H_4F), 7.21 (6 H, C_6H_4F), 4.89 and 4.74 (d, J = 8.7 Hz, 3 H, N–CH_2–N), 4.26 (s, 6 H, N–CH_2–Ph) ppm. ^{1}H NMR (400 MHz, $CDCl_3$/$SOCl_2$): δ = 7.38 (m, 6 H, C_6H_4F), 7.18 (6 H, C_6H_4F), 4.98 and 4.48 (d, J = 8.9 Hz, 3 H, N–CH_2–N), 4.25 (s, 6 H, N–CH_2–Ph) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$/$SOCl_2$): 164.1 (d, 1-C_6H_4F, J = 252 Hz), 133.4 (d, 3-C_6H_4F, J = 8.8 Hz), 117.2 (d, 2-C_6H_4F, J = 21.6 Hz), 124.0 (d, 4-C_6H_4F, J = 3.3 Hz), 76.7 (N–CH$_2$–N), 59.9 (Ph–CH$_2$–N) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): –108.2 ppm. ^{19}F NMR (376 MHz, $CDCl_3$/$SOCl_2$): δ = –108.2 ppm. $C_{24}H_{24}F_3N_3Ti_3Cl_{12}$ (980.55): calcd. C 29.40, H 2.47, N 4.29, and for **3e**$(CH_2Cl_2)_{1.5}$ (1107.95): calcd. C 27.64, H 2.46, N 3.79; found C 27.7, H 2.58, N 3.89.

X-ray Crystallography: Intensity data for **1e**[13] were collected with a STOE STADI4 and for **2b**, **3a**, **3b**, **3d** and **4d** with a Nonius KappaCCD diffractometer. Details of the crystal structure determinations are shown in Table 3. Structure solution, followed by full-matrix least-squares refinement was performed using the WINGX-1.64 suite of programs throughout.[16]

CCDC-257783–257788 contain the crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information: Plots of the C–H···Cl contacts and NMR spectra (see also footnote on the first page of this article).

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[13] Crystallographic data for **1e**: $C_{24}H_{24}F_3N_3$, M = 411.46, monoclinic, space group $P2_1/n$, a = 9.977(2), b = 14.591(5), c = 15.490(4) Å, β = 107.30(3)°, V = 2152.9(10), Z = 4, D_c = 1.269 Mg m^{-3}, μ(Mo-K_α) = 0.094 mm^{-1}, T = 293 K, 6387 reflec-

tions collected, 3044 unique, (*R*int = 0.0304) final residuals $R_1[I > 2\sigma(I)] = 0.0463$, $wR_2 = 0.1068$.
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