Letter

Titanium imido complexes with 1,3,5-triazacyclohexane ligands: syntheses, solution dynamics and solid state structures

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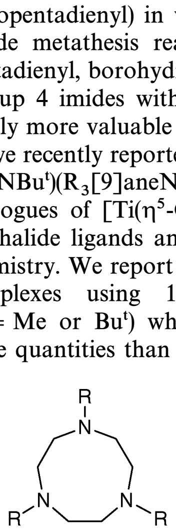
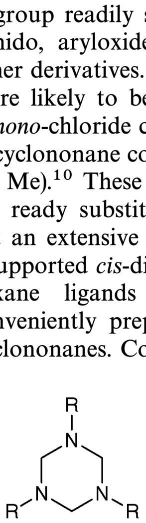
The multi-gram scale syntheses of the first 1,3,5-triazacyclohexane imido complexes [Ti(NR)(R$'_3$tach)Cl$_2$] (R = Bu^t, C$_6$H$_3$Pr$^i_2$-2,6; R′ = Me, Bu^t) are described together with the X-ray structures of [Ti(NBu^t)(Me$_3$tach)Cl$_2$] and [Ti(NBu^t)(Bu$^t_3$tach)Cl$_2$]; the complexes of Me$_3$tach exhibit dynamic NMR behaviour *via* an unusual trigonal twist of the facially coordinated Me$_3$tach ligand (Me$_3$tach and Bu$^t_3$tach = 1,3,5-trimethyl- and tri-*tert*-butyl-1,3,5-triazacyclohexane, respectively).

There is a great deal of interest in the development of new early transition metal complexes for synthetic and catalytic purposes.[1] Of particular importance are compounds of the type [M(L$_n$)X$_2$] (M = d^0 metal centre; L$_n$ = supporting ligand set; X = halide or hydrocarbyl) in which the *cis*-MX$_2$ fragment is a well recognised structural pre-requisite for the stoichiometric or catalytic transformation of organic substrates, including alkene polymerisation. A wide range of L$_n$ supporting ligand sets have been employed, including bis(η^5-cyclopentadienyl), cyclopentadienyl-amido and -amino, bis(amido), bis(alkoxide), Schiff-base and tetraazamacrocyclic moieties.[2,3] Of relevance to this contribution are recently reported group 5 and 6 *cis*-MX$_2$ compounds that feature one or two imido (NR where R = alkyl or aryl) groups in the L$_n$ supporting ligand set.[4,5]

Although now well established, the reaction chemistry of Group 4 imido complexes has focused almost exclusively on transformations involving the M$=$NR linkage, rather than employing the imido group simply as an ancilliary ligand.[6,7] Very recently, however, we reported two classes of mono-chloride complexes [Ti(NR)(L)Cl(py)$_n$] (L = amidinato or cyclopentadienyl) in which the imido group readily supports halide metathesis reactions giving amido, aryloxide, cyclopentadienyl, borohydride, alkyl and other derivatives.[8,9] Since Group 4 imides with *cis*-MX$_2$ units are likely to be significantly more valuable targets than the *mono*-chloride complexes, we recently reported the 1,4,7-triazacyclononane complexes [Ti(NBu^t)(R$_3$[9]aneN$_3$)Cl$_2$] (R = H or Me).[10] These isolobal analogues of [Ti(η^5-C$_5$H$_5$)$_2$Cl$_2$] allow ready substitution of the halide ligands and already suggest an extensive reaction chemistry. We report here new imido-supported *cis*-dichloride complexes using 1,3,5-triazacyclohexane ligands R$_3$tach (R = Me or Bu^t) which are more conveniently prepared in large quantities than the 1,4,7-triazacyclononanes. Complexes of these ligands have recently been reported for middle to late transition metals and some p-block metals,[11–16] but complexes of Group 4 or any with metal imido fragments have not been described previously.



R$_3$[9]aneN$_3$

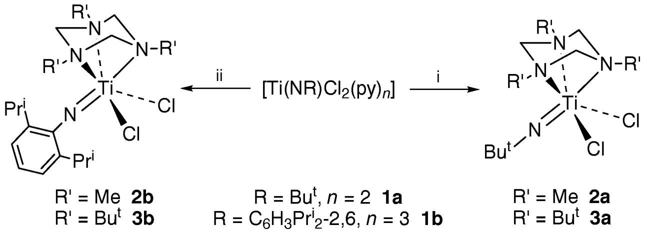


R$_3$tach (R = Me or Bu^t)

The synthesis and proposed structures of the new compounds are shown in Scheme 1. The starting titanium imido compounds [Ti(NR)Cl$_2$(py)$_n$] (n = 2, R = Bu^t **1a**; n = 3, R = C$_6$H$_3$Pr$^i_2$-2,6 **1b**)[17] and the 1,3,5-triazacyclohexane ligands R$_3$tach (R = Me or Bu^t)[18,19] can all be readily prepared in 'one-pot' reactions on large scales. Addition of Me$_3$tach to a solution of **1a** or **1b** in CH$_2$Cl$_2$ gives quantitative formation of spectroscopically pure [Ti(NR)(Me$_3$tach)Cl$_2$] (R = Bu^t **2a** or C$_6$H$_3$Pr$^i_2$-2,6 **2b**) within hours at room temperature.[‡] Reactions of the bulkier ligand Bu$^t_3$tach with **1a** and **1b** are somewhat slower as might be expected, and give the analogous products [Ti(NR)(Bu$^t_3$tach)Cl$_2$] (R = Bu^t **3a** or C$_6$H$_3$Pr$^i_2$-2,6 **3b**) in high yields (*ca.* 86%). Analytically pure samples were obtained by recrystallisation from CH$_2$Cl$_2$–hexane mixtures.

The new compounds **2a**–**3b** can all be prepared on a multi-gram scale. In a typical preparation, reaction of 2.55 g of Bu$^t_3$tach and 3.48 g of **1a** affords 4.58 g of recrystallised **3a** (86%). Diffraction-quality crystals of the *tert*-butylimido complexes [Ti(NBu^t)(Me$_3$tach)Cl$_2$] **2a** and [Ti(NBu^t)(Bu$^t_3$tach)Cl$_2$] **3a** were obtained by layering a solution of **2a** in dichloromethane with hexane or by cooling a saturated solution of **3a** in toluene.[§] The molecular structure of **3a** is shown in Fig. 1; that of **2a** is broadly analogous. Selected bond distances and angles for both complexes are given in the caption of Fig. 1.

The structures of **2a** and **3a** comprise pseudo-octahedral titanium centres with *fac*-R$_3$tach (R = Me or Bu^t) rings and mutually *cis tert*-butylimido and chloride ligands. The respective Ti–N$_{\text{imide}}$ and Ti–Cl distances for the two compounds are identical within error, whereas the Ti–N$_{\text{ring}}$ distances are significantly longer (by *ca.* 0.05–0.09 Å) for **3a**, presumably reflecting the increased steric demands of Bu$^t_3$tach. The Ti–N$_{\text{ring}}$ distances in [Ti(NBu^t)(Me$_3$[9]aneN$_3$)Cl$_2$][10] are intermediate between those of **2a** and **3a**. The Ti–Cl distances for the Me$_3$[9]aneN$_3$ derivative (av. 2.393 Å) are somewhat longer than for **2a** and **3a** whereas the Ti–N$_{\text{imide}}$ distance [1.694(2) Å] is comparable. The Cl–Ti–Cl angle of 95.75(4)° in [Ti(NBu^t)(Me$_3$[9]aneN$_3$)Cl$_2$] is smaller than for either R$_3$tach



Scheme 1 *Reagents and conditions*: i, Me$_3$tach, CH$_2$Cl$_2$, r.t., 14 h, 94% for **2a**, Bu$^t_3$tach, CH$_2$Cl$_2$, r.t., 7 d, 86% for **3a**; ii, Me$_3$tach, CH$_2$Cl$_2$, r.t., 14 h, 89% for **2b**; Bu$^t_3$tach, CH$_2$Cl$_2$, r.t., 7 d, 86% for **3b**.

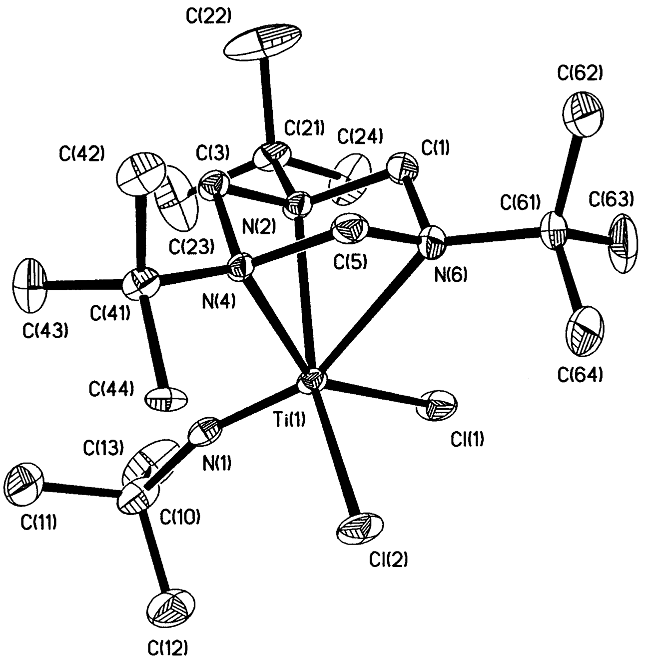


Fig. 1 Displacement ellipsoid (25% probability) plot for $[Ti(NBu^t)(Bu^t_3tach)Cl_2]$ **3a** with hydrogen atoms omitted. Selected bond lengths (Å) and angles (°) for **3a** with the corresponding values for $[Ti(NBu^t)(Me_3tach)Cl_2]$ **2a** in single brackets: Ti(1)–N(1) 1.692(4) [1.699(4)], Ti(1)–N(2) 2.292(4) [2.241(5)], Ti(1)–N(4) 2.290(4) [2.247(5)], Ti(1)–N(6) 2.513(4) [2.424(4)], Ti(1)–Cl(1) 2.351(2) [2.356(2)], Ti(1)–Cl(2) 2.351(1) [2.363(2)]; N(2)–Ti(1)–N(4) 61.2(1) [61.4(2)], N(2)–Ti(1)–N(6) 58.5(1) [59.0(2)], N(4)–Ti(1)–N(6) 58.4(1) [58.9(2)], Cl(1)–Ti(1)–Cl(2) 99.44(7) [102.72(6)], Ti(1)–N(1)–C(10) 164.0(4) [176.3(4)], N(1)–Ti(1)–Cl(1) 101.6(2) [106.3(2)], N(1)–Ti(1)–Cl(2) 100.7(1) [106.2(2)].

derivative, with that in **3a** being slightly smaller than in **2a**. The geometries of the R_3tach ligands are similar in each complex and comparable to those found in previous examples.[11–15]

The solution ^1H and ^{13}C NMR spectroscopic data for the Bu^t_3tach complexes **3a** and **3b** are fully consistent with the solid state structures and show sharp resonances for the imido N-substituents along with two types of ring NBu^t substituents and diastereotopic methylene protons on the triazacyclohexane ring. In contrast, the resonances for the Me_3tach ligand in $[Ti(NR)(Me_3tach)Cl_2]$ ($R = Bu^t$ **2a** or $C_6H_3Pr^i_2$-2,6 **2b**) are very broad at room temperature, whereas those for the imido N-substituents are sharp and temperature independent. Detailed variable temperature NMR spectroscopic experiments [including spin saturation transfer (SST) and ^1H lineshape (rate constant) analysis] were used to characterise the dynamic process.

The NMR spectra for **2a** and **2b** are consistent with an in-place trigonal twist of the Me_3tach ligand. In the slow exchange limit (268 K) the ^1H NMR spectra for both 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 transformations being half of those for *trans*-Me → *cis*-Me, as expected.[20] In addition, SST ^1H NMR experiments confirm exchange between the two types of 'down' methylene hydrogens of Me_3tach, and also between the two types of 'up' hydrogens. Significantly, there was no exchange between the 'down' and 'up' hydrogens indicating that the dynamic process does not involve dissociation of the triazacyclohexane ring. Analysis of the methyl group exchange rate constants (using standard Eyring plots[21]) for **2a** affords: $\Delta H\ddagger = 65.7 \pm 0.5$ kJ mol^{-1}; $\Delta S\ddagger = 9.6 \pm 2$ J mol^{-1} K^{-1}; $\Delta G\ddagger = 62.9 \pm 0.5$ kJ mol^{-1} at 292 K. The effectively zero value for $\Delta S\ddagger$ lends further support to a non-dissociative mechanism for the exchange process. Previous studies of fluxional processes for a range of bis(acetylacetonato)titanium complexes proposed to undergo trigonal twists found negative $\Delta S\ddagger$ values in the range *ca.* −55 to −90 J mol^{-1} K^{-1}.[22] The more positive $\Delta S\ddagger$ for **2a** indicates a less-ordered transition state compared to those for the previously studied titanium systems.

The trigonal twist mechanism has long been established for bis(bidentate ligand) chelate complexes of titanium(IV),[22,23] but to our knowledge the fluxional processes for **2a** and **2b** are the first such examples for any triazacycloalkane ligand. That the complexes **2a** and **2b** are fluxional whereas **3a** and **3b** and those of the larger $R_3[9]aneN_3$ rings (R = H or Me)[10] 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.[22,24]

The proposed mechanism presumably proceeds *via* a trigonal prismatic transition state (or intermediate). Ground state trigonal prismatic six-coordinate transition metal complexes ML_6 are well established and their structures have been rationalised theoretically.[25] It is now 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 weakly π-donating) ligand. For ML_6 complexes where the ligand set contains effective π-donors the octahedral geometry is preferred.[26] This consideration of electronic effects appears to account for the ground-state pseudo-octahedral geometries found for **2** and **3** which feature strongly π-donating organoimido ligands. However, it appears that the trigonal prismatic alternatives are accessible on the NMR timescale for the less sterically crowded Me_3tach homologues **2**.

In summary we have firmly established the first 1,3,5-triazacyclohexane complexes both for Group 4 metal and for any metal imido fragment. The complexes **2a**–**3b** are new isolobal analogues of metallocene dihalides and can be readily prepared in synthetically useful quantities. Both ring and imido substituents can be varied, and the new compounds therefore promise a rich and diverse reaction chemistry. The fluxional complexes **2a** and **2b** represent the first examples of a trigonal twist mechanism for any pseudo-octahedral triazacycloalkane complex. Synthetic and catalytic investigations of all the new compounds and their homologues are currently underway in our laboratories.

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Notes and references

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‡ Satisfactory spectroscopic and analytical data have been obtained for the new compounds.

§ *Crystal data* for **2a** and **3a**: crystals were mounted in a film of RS3000 perfluoropolyether oil (Hoechst) on a glass fibre and transferred to a Stoë Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device.[27] Data were collected at 150(2) K using graphite-monochromated Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å) and ω–θ scans in the range $2.5 \leqslant \theta \leqslant 25°$, and semi-empirical absorption corrections based on ψ-scans were applied. Crystallographic calculations were performed using SIR92[28] and CRYSTALS-PC;[29] $R = \Sigma \| F_o| - |F_c \| / \Sigma |F_o|$, $R_w = \{\Sigma w(F_o - F_c)^2 / \Sigma w(F_o)^2\}^{1/2}$.

2a: $C_{10}H_{24}Cl_2N_4Ti$, $M = 319.14$, orthorhombic, space group $P2_12_12_1$, $a = 7.053(2)$, $b = 13.818(5)$, $c = 16.452(5)$ Å, $U = 1603.4(7)$ Å^3, $Z = 4$, $\mu = 0.85$ mm^{-1}, pale yellow rod of dimensions $0.40 \times 0.16 \times 0.13$ mm, 1435 independent observed $[I > 2\sigma(I)]$ reflections ($R_{\text{merge}} = 0.02$) used in refinement, no. of parameters refined 154, full-matrix least squares on F with Chebychev polynomial weighting scheme, $R = 0.0455$, $R_w = 0.0475$, GOF = 1.119, absolute structure parameter 0.09(9), final $(\Delta/\sigma)_{\max} = 0.003$, largest residual peaks 0.36 and -0.63 e Å^{-3}.

3a: $C_{19}H_{42}Cl_2N_4Ti$, $M = 445.27$, monoclinic, space group $P2_1/n$, $a = 9.871(5)$, $b = 16.677(11)$, $c = 15.020(11)$ Å, $\beta = 103.51(5)°$, $U = 2404(2)$ Å^3, $Z = 4$, $\mu = 0.59$ mm^{-1}, yellow block of dimensions $0.35 \times 0.27 \times 0.26$ mm, 3079 independent observed $[I > 2\sigma(I)]$ reflections used in refinement, no. of parameters refined 262, full-matrix least squares on F with unit weights, $R = 0.068$, $R_w = 0.067$, GOF = 0.938, final $(\Delta/\sigma)_{\max}$ 0.003, largest residual peaks 0.41 and -0.63 e Å^{-3}.

CCDC reference number 440/083. See http://www.rsc.org/suppdata/nj/1999/271/for crystallographic files in cif format.

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Letter 8/07985D