DALTON

Synthesis and imido-group exchange reactions of *tert*-butylimidotitanium complexes †

Alexander J. Blake, Philip E. Collier, Simon C. Dunn, Wan-Sheung Li, Philip Mountford* and Oleg V. Shishkin

Department of Chemistry, The University of Nottingham, Nottingham NG7 2RD, UK

Treatment of $TiCl_4$ with Bu^tNH_2 (6 equivalents) followed by addition of bpy (2 equivalents, 4-*tert*-butylpyridine) or pyridine (py) (2 or 4 equivalents) afforded the five- or six-co-ordinate *tert*-butylimido complexes $[Ti(NBu^t)Cl_2(bpy)_2]$ or $[Ti(NBu^t)Cl_2(py)_n]$ ($n = 2$ or 3*) respectively in good yields. Reaction of $[Ti(NBu^t)Cl_2(py)_3]$ with RNH_2 gave the corresponding arylimido derivatives $[Ti(NR)Cl_2(py)_3]$ (R = Ph,* C_6H_4Me-4,* $C_6H_4NO_2$-4,* $C_6H_3Me_2$-2,6 or $C_6H_3Pr^i_2$-2,6). Addition of tmen or pmdien to $[Ti(NBu^t)Cl_2(py)_n]$ ($n = 2$ or 3 respectively) gave the corresponding bi- or tri-dentate amine complexes, $[Ti(NBu^t)Cl_2(tmen)]$ or $[Ti(NBu^t)Cl_2(pmdien)]$* (tmen = $Me_2NCH_2CH_2NMe_2$, pmdien = N,N,N',N'',N''-pentamethyldiethylenetriamine). Complexes labelled * have been crystallographically characterised.

The importance of imido complexes and their isolobal analogues in industrial processes, organic synthesis and catalysis is now very well established.[1–4] Terminal imido titanium complexes were only first fully characterised in 1990.[5,6] A number of such complexes have since been isolated, most requiring a different synthetic strategy for introducing the Ti=NR moiety.‡,[1] We have recently developed a very simple synthetic entry point to a range of imidotitanium complexes featuring a variety of supporting ancillary ligands.[7] The complexes are all prepared by generally high-yielding substitution reactions of $[Ti(NBu^t)Cl_2(bpy)_2]$[7] (bpy = 4-*tert*-butylpyridine) or its bis- or tris-(pyridine) homologue $[Ti(NBu^t)Cl_2(py)_n]$ ($n = 2$ or 3, see below) with the desired ancillary ligand(s) or their anion(s). The derivatives accessible *via* this straightforward metathetical route include tetraaza-macrocyclic, tris(pyrazolyl)borate, indenyl, cyclopentadienyl and bis(cyclopentadienyl) imidotitanium complexes.[7–11] In this contribution we describe the multigram syntheses of these versatile bis- and tris-(pyridine) *tert*-butylimidotitanium synthons, together with their ligand-exchange reactions with primary arylamines and bi- and tridentate tertiary amines. The crystal structures of five of the new complexes have been determined and allow a crystallographic evaluation of the relative structural and *trans* influences of the NBu^t, NPh, NC_6H_4Me-4 and $NC_6H_4NO_2$-4 ligands in a homologous series of d^0, six-co-ordinate complexes. Part of this work has been communicated.[12]

Results

The syntheses and proposed structures are summarised in Scheme 1. All the new compounds are air- and moisture-sensitive and have been fully characterised by spectroscopic methods, combustion microanalysis (C, H and N) and X-ray crystallography where possible. The characterising data are listed in the Experimental section.

Treatment of a cold (−50 °C) solution of $TiCl_4$ in dichloromethane solution with 6 equivalents of Bu^tNH_2 gave an orange precipitate as has been described previously.[13–15] Solvent extractions, treatment with *ca.* 2 equivalents of bpy and standard work-up afforded orange-red $[Ti(NBu^t)Cl_2(bpy)_2]$ **1** in 78% yield on a 12 g scale of product. By similar procedures the bis(pyridine) analogue $[Ti(NBu^t)Cl_2(py)_2]$ **2** may be prepared in 64% yield on a 7 g scale. In contrast to the preparation of **1**, the isolation of spectroscopically pure **2** was occasionally hampered by co-ordination of residual Bu^tNH_2 to the Ti as indicated by additional broad resonances at δ *ca.* 3.4 (NH_2) and 1.5 (Bu^tN) in the ^1H NMR spectrum[15] (relative intensities indicated that there was less than 1 equivalent of Bu^tNH_2 per $Ti{=}NBu^t$ unit). However, NMR-tube experiments in $CDCl_3$ established that addition of 2–3 equivalents of pyridine to samples of **2** contaminated in this way readily effected displacement of Bu^tNH_2.

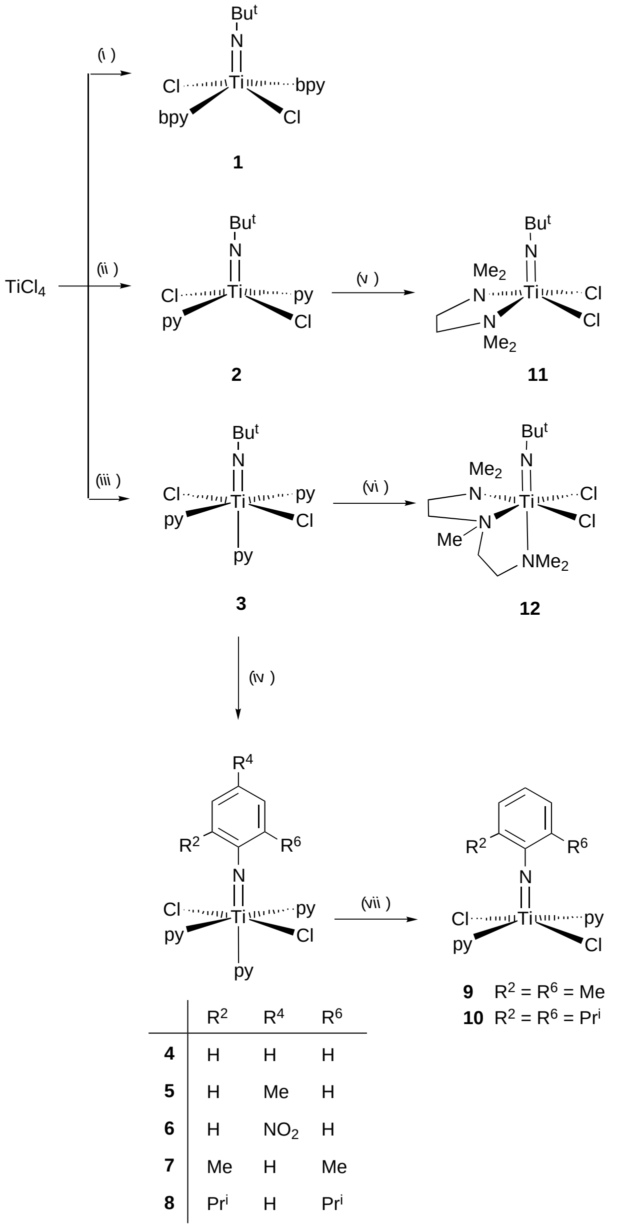
Owing to the difficulties associated with reproducibly achieving good yields of pure complex **2**, we modified the synthesis by adding 4 equivalents of py (per Ti) to the first-formed orange precipitate. This modification routinely allows near-quantitative isolation of the spectroscopically pure, tris(pyridine) complex $[Ti(NBu^t)Cl_2(py)_3]$ **3** on around a 35–40 g scale of product. Analytically pure, single crystals of **3** suitable for X-ray diffraction were obtained from a saturated pentane solution and important bond lengths and angles are listed in Table 1. Details of the structure determination and a thermal ellipsoid plot were given in a preliminary communication.[12]

The structure of complex **3** confirms the *trans* arrangement of the chloride and *mer* arrangement of the pyridine ligands shown in Scheme 1. A comparison of the bonding parameters with those of our other crystallographically characterised tris(pyridine) complexes is presented later. Consistent with the well known *trans* influence of multiply bonded ligands,[2,16–19] the pyridine ligand *trans* to the NBu^t group is less tightly bound compared to the *cis* pyridine ligands [differences between Ti−N (py) *cis* and *trans* bond lengths span 0.182(4) to 0.203(1) Å]. This *trans* labilisation is reflected in the solution NMR spectra of **3** which are consistent with the solid-state structure and show that the resonances for the *trans* pyridine occur at higher field and are somewhat broader than those of the *cis* pyridine ligands. The NMR line broadening is consistent with a dissociative equilibrium between **3** and (**2** + free pyridine). Indeed, ambient-temperature ^1H NMR spectra of **3** with 2–3 equivalents of additional pyridine show qualitatively that the *trans* and 'free' pyridine are in fast exchange on the NMR time-scale while the *cis* co-ordinated pyridine ligands do not show any

---

† *Non-SI unit employed:* D ≈ 3.33 × 10^{-30} C m.

‡ Although for ease of representation all titanium imido linkages are drawn 'Ti=NR', the formal titanium–imido nitrogen bond order in the complexes $[Ti(NR)Cl_2L_n]$ described herein is probably best thought of as three (pseudo-$\sigma^2\,\pi^4$, triple bond) rather than as two.[1]



	R^2	R^4	R^6
4	H	H	H
5	H	Me	H
6	H	NO$_2$	H
7	Me	H	Me
8	Pr^i	H	Pr^i

Scheme 1 Reagents and conditions: (*i*) Bu^{t}NH$_2$ (6 equivalents), CH$_2$Cl$_2$, −50 °C for 15 min then room temperature (r.t.) for 5 h, bpy (2.2 equivalents), yield 78%; (*ii*) Bu^{t}NH$_2$ (6.0 equivalents), CH$_2$Cl$_2$, −50 °C, 15 min then r.t. for 2 h, py (2.3 equivalents), 64%; (*iii*) Bu^{t}NH$_2$ (6.3 equivalents), −50 °C for 15 min then r.t. for 2 h, py (4.1 equivalents), 98%; (*iv*) aniline or substituted aniline (≈1 equivalent), CH$_2$Cl$_2$, r.t., 1–48 h, 36–86%; (*v*) tmen (1.02 equivalents), CH$_2$Cl$_2$, r.t. 16 h, >95%; (*vi*) pmdien (1 equivalent), Et$_2$O, r.t. 3 h, 55%; (*vii*) 65 °C, dynamic vacuum, 4–7 h, >95%

detectable broadening under these conditions. However, qualitative magnetisation-transfer (MT) experiments for the *cis* and *trans* py ligands in pure **3** show that exchange between these sites is significant on the MT time-scale at room temperature.

We also wished to prepare arylimido analogues of [Ti(NBu^t)Cl$_2$(py)$_3$] **3**. However, attempts to produce clean samples of such a complex by the addition of H$_2$NC$_6$H$_3$Me$_2$-2,6 to TiCl$_4$ in CH$_2$Cl$_2$ followed by treatment with pyridine (under conditions similar to those used for the synthesis of **3**) failed. The product mixtures appeared to contain an arylimido product (see below) but were always contaminated with free H$_2$NC$_6$H$_3$Me$_2$-2,6 which could neither be fully removed by recrystallisation nor by washing with hexane. However, the ready availability of **3** prompted us to investigate this complex as a potential starting material for the arylimido homologues.

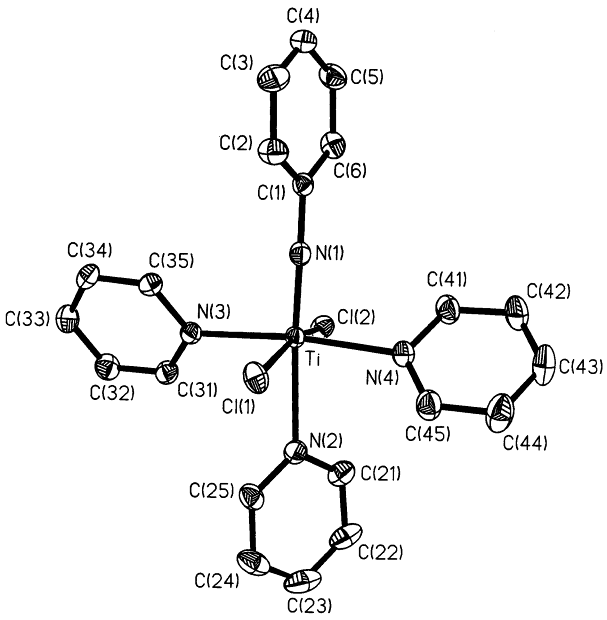


Fig. 1 Thermal ellipsoid plot (30% probability) of [Ti(NPh)Cl$_2$(py)$_3$] **4**. Hydrogen atoms and dichloromethane molecules of crystallisation omitted for clarity

As shown in Scheme 1, addition of *ca.* 1 equivalent of arylamine to a dichloromethane solution of complex **3** at ambient temperature affords generally good yields of the corresponding arylimido derivatives [Ti(NR)Cl$_2$(py)$_3$] (R = Ph **4**, C$_6$H$_4$Me-4 **5**, C$_6$H$_4$NO$_2$-4 **6**, C$_6$H$_3$Me$_2$-2,6 **7** or C$_6$H$_3$Pr$^i_2$-2,6 **8**). Some of the products can be obtained in spectroscopically pure form by simple removal of Bu^{t}NH$_2$ and dichloromethane. Analytically pure samples may be obtained by recrystallisation. The tris(pyridine) complexes **3**–**8** tend to lose the *trans* co-ordinated pyridine ligand on repeated washing or handling in solution. Indeed, prolonged exposure of **3** to a dynamic vacuum results in the near-quantitative formation of **2**. The bis(pyridine) arylimido homologues [Ti(NC$_6$H$_3$R′$_2$-2,6)Cl$_2$(py)$_2$] (R′ = Me **9** or Pr^i **10**) may similarly be obtained.

Single crystals of [Ti(NPh)Cl$_2$(py)$_3$] **4**, [Ti(NC$_6$H$_4$Me-4)Cl$_2$(py)$_3$] **5** and [Ti(NC$_6$H$_4$NO$_2$-4)Cl$_2$(py)$_3$] **6** suitable for X-ray diffraction studies were obtained from cold dichloromethane (**4**) or by layering a dichloromethane solution with pentane or hexane. A thermal ellipsoid plot of **4** is shown in Fig. 1. Important bond lengths are listed in Table 1 and data collection and processing parameters in Table 4. Details of the structure determinations of **5** and **6** were given previously.[12] The structures of **4**–**6** confirm the geometries shown in Scheme 1. A comparison of their bonding parameters with those of [Ti(NBu^t)Cl$_2$(py)$_3$] **3** is presented later.

The solution NMR spectra of complexes **4**–**8** are consistent with the solid-state geometries of **4**–**6** and suggest that the pyridine ligand bound *trans* to the arylimido group is more weakly bound than the *cis* co-ordinated pyridine ligands. This *trans* labilisation is illustrated by the structures of **4**–**6** where the difference between *cis*- and *trans*-Ti–N (py) bond lengths spans the range 0.181(4) to 0.201(4) Å. The 2,6-disubstituted arylimido complexes **7** and **8** are stable in solution under Ar or N$_2$ for at least several weeks. Solutions of the other arylimido derivatives **4**–**6** give rise to unknown decomposition products on standing at room temperature.

The bis- and tris-(pyridine) *tert*-butylimido complexes **2** and **3** allow access to bi- and tri-dentate tertiary amine adducts. Thus treatment of a dichloromethane solution of [Ti(NBu^t)Cl$_2$(py)$_2$] **2** with tmen (*N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine) gives essentially quantitative conversion to the previously described[15] yellow compound [Ti(NBu^t)Cl$_2$(tmen)] **11** after removal of pyridine and dichloromethane. Addition of 1 equivalent of the tridentate amine pmdien (*N*,*N*,*N*′,*N*″,*N*″-

Table 1 Comparison of selected bond lengths (Å) and angles (°) for the complexes $[Ti(NBu^t)Cl_2(py)_3]$ **3**, $[Ti(NPh)Cl_2(py)_3]$ **4**, $[Ti(NC_6H_4Me\text{-}4)Cl_2(py)_3]$ **5** and $[Ti(NC_6H_4NO_2\text{-}4)Cl_2(py)_3]$ **6** *

	$[Ti(NR)Cl_2(py)_3]$; R =			
	Bu^t (**3**)	Ph (**4**)	C_6H_4Me-4 (**5**)	$C_6H_4NO_2$-4(**6**)
Ti=N	1.705(3) 1.706(3)	1.714(2)	1.705(4)	1.722(3)
Ti–N (py *cis*)	2.247(3), 2.249(3) 2.255(3), 2.258(3)	2.225(3), 2.229(3)	2.227(2)	2.228(2)
Ti–N (py *trans*)	2.450(3) 2.440(3)	2.410(3)	2.428(4)	2.428(3)
Ti–Cl	2.432(1), 2.436(1) 2.431(1), 2.452(1)	2.413(1), 2.416(1)	2.394(1)	2.380(1)
=N–C	1.455(5) 1.446(5)	1.382(4)	1.378(6)	1.359(4)
N=Ti–N (py *cis*)	95.32(12), 97.55(13) 94.39(13), 99.18(13)	94.40(10), 92.68(10)	95.35(7)	97.66(2)
N=Ti–N (py *trans*)	176.23(14) 175.96(13)	176.26(10)	180	180
N=Ti–Cl	100.85(12), 94.84(12) 95.32(12), 98.32(12)	96.38(9), 97.57(9)	98.65(3)	95.33(5)
C–N=Ti	174.8(3) 171.7(3)	177.5(2)	180	180

* For compound **3** the two sets of figures (one below the other) correspond to the two crystallographically independent molecules; for **5** and **6** the molecules lie on a crystallographic two-fold axis passing through the C–N=Ti–N (py *trans*) vector and so there is only one value of Ti–Cl, Ti–N (py), *etc.* and N=Ti–N (py *trans*) must be 180°.

Table 2 Selected bond lengths (Å) and angles (°) for $[Ti(NBu^t)Cl_2(pmdien)]$ **12** with estimated standard deviations (e.s.d.s) in parentheses. The two values for each parameter correspond to the two independent molecules in the asymmetric unit

Ti(1)–N(1)	1.691(1)	1.696(3)
Ti(1)–N(2)	2.595(3)	2.588(4)
Ti(1)–N(3)	2.282(3)	2.274(3)
Ti(1)–N(4)	2.373(3)	2.409(3)
Ti(1)–Cl(1)	2.4261(11)	2.3888(12)
Ti(1)–Cl(2)	2.3608(12)	2.3798(11)
N(1)–C(1)	1.462(5)	1.455(5)
N(1)–Ti(1)–N(3)	98.36(4)	99.28(14)
N(1)–Ti(1)–N(4)	92.05(4)	93.26(14)
N(1)–Ti(1)–N(2)	168.99(14)	169.24(14)
N(1)–Ti(1)–Cl(1)	92.21(11)	91.84(12)
N(1)–Ti(1)–Cl(2)	103.47(12)	102.43(11)
N(3)–Ti(1)–N(4)	77.58(11)	76.92(12)
N(3)–Ti(1)–N(2)	74.22(12)	74.47(12)
N(3)–Ti(1)–Cl(1)	93.31(8)	93.92(9)
N(3)–Ti(1)–Cl(2)	155.03(10)	154.27(10)
N(4)–Ti(1)–Cl(1)	170.42(9)	170.12(9)
N(4)–Ti(1)–Cl(2)	89.56(9)	88.15(9)
N(4)–Ti(1)–N(2)	94.20(11)	93.79(12)
Cl(1)–Ti(1)–Cl(2)	97.78(4)	99.00(4)
Cl(1)–Ti(1)–N(2)	80.30(8)	80.03(9)
Cl(2)–Ti(1)–N(2)	85.65(9)	85.92(9)
C(1)–N(1)–Ti(1)	167.3(3)	164.8(3)

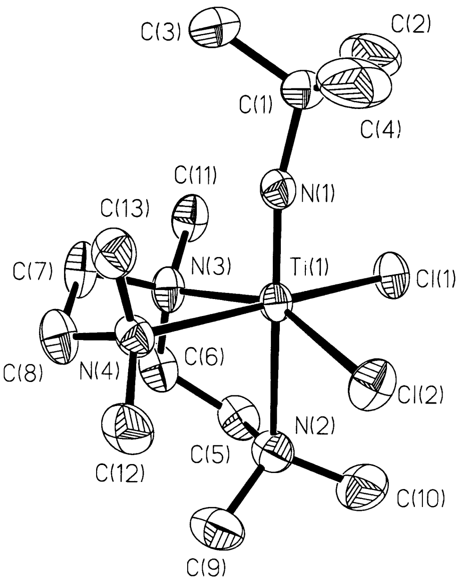


Fig. 2 Thermal ellipsoid plot (30% probability) of one of the two crystallographically independent molecules of $[Ti(NBu^t)Cl_2(pmdien)]$ **12**. Hydrogen atoms omitted for clarity

pentamethyldiethylenetriamine) to a diethyl ether solution of $[Ti(NBu^t)Cl_2(py)_3]$ **3** followed by cooling at −25 °C for 24 h afforded single crystals of orange $[Ti(NBu^t)Cl_2(pmdien)]$ **12** in 55% yield. A thermal ellipsoid plot of one of the two crystallographically independent molecules of **12** in the asymmetric unit is shown in Fig. 2, important bond lengths are listed in Table 2 and data collection and processing parameters are given in Table 4. The solid-state structure of **12** shows the pmdien ligand co-ordinated to the $Ti(NBu^t)Cl_2$ fragment in a *fac* mode with one of the terminal NMe_2 nitrogen atoms [N(2) in Fig. 2] bonded *trans* to the *tert*-butylimido group. Thus the structure does not contain a molecular mirror plane and all five pmdien methyl groups and all four methylene groups are chemically inequivalent.

The ambient-temperature ^1H and $^{13}C\text{-}\{^1H\}$ NMR solution spectra of complex **12** are not consistent with the solid-state structure. For example, the $^{13}C\text{-}\{^1H\}$ NMR spectrum shows only three types of methyl group carbon and two types of methylene group carbon for the co-ordinated pmdien. Together with the ^1H NMR spectrum, these solution data suggest: (*i*) that the molecule adopts a static solution structure with, for example, a *mer*- or a *fac*-pmdien ligand with the 'central' NMe nitrogen co-ordinated *trans* to the *tert*-butylimido group; or (*ii*) that the solid-state isomer is present in solution, but that rapid exchange of the *cis*- and *trans*-co-ordinated (with respect to the NBu^t ligand) NMe_2 groups takes place on the NMR time-scale at ambient temperature; or (*iii*) that a number of different solution-phase structures is present and that these all rapidly interconvert on the NMR time-scale. To address these possibilities low-temperature ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra of **12** were recorded. On cooling a CD_2Cl_2 solution to 213 K the spectra became very complicated and were consistent with the presence of several different compounds. The $^{13}C\text{-}\{^1H\}$ DEPT (distortionless enhancement by polarisation transfer) 135 NMR spectrum at 213 K showed nine different methylene group carbon resonances and twelve methyl group carbon resonances for pmdien ligands. We conclude that several different isomers of **12** are present in solution and rapidly interconvert at ambient temperature; the solid-state structure shown in Fig. 2 thus corresponds to only one of the solution isomers.

Discussion

Syntheses and spectroscopic data

The reaction of $TiCl_4$ with Bu^tNH_2 followed by treatment with bpy or py is an efficient and highly convenient route to multigram quantities of the *tert*-butylimidotitanium synthons $[Ti(NBu^t)Cl_2L_n]$ ($n = 2$, L = bpy **1** or py **2**; $n = 3$, L = py **3**). The reactions of $TiCl_4$ with primary amines were first described by Cowdell and Fowles[13] in 1960 but the identities of the various products obtained from the reaction with Bu^tNH_2 were only recently elucidated by Winter and co-workers.[15] Depending on the amount of Bu^tNH_2 available in the system three types of orange/orange-red titanium *tert*-butylimido species were obtained, namely mononuclear $[Ti(NBu^t)Cl_2(Bu^tNH_2)_3]$ (mixture of isomers), trinuclear $[\{Ti(\mu\text{-}NBu^t)Cl_2(Bu^tNH_2)_2\}_3]$ or hexanuclear $[\{Ti(\mu_3\text{-}NBu^t)Cl_2\}_6]$. Interconversion between the three complexes is achieved by addition or removal of Bu^tNH_2. We have not attempted to identify which (if any) of these species is formed under our reaction conditions and it is likely that any of them could react with bpy or py to give **1**–**3**. For example, Winter and co-workers[15] have shown that treatment of isolated trinuclear $[\{Ti(\mu\text{-}NBu^t)Cl_2(Bu^tNH_2)_2\}_3]$ with O-donor monodentate or N-donor bidentate compounds affords the five-co-ordinate complexes $[Ti(NBu^t)Cl_2L_2]$ ($L = OPPh_3$ or L_2 = tmen or *N*,*N*′-diisopropylethane-1,2-diamine).

The similarity of the IR and NMR spectra of the three *tert*-butylimido complexes **1**–**3** is consistent with monomeric, terminal *tert*-butylimido structures for **1** and **2** (as opposed to alternative, six-co-ordinate bi- or tri-nuclear formulations $[\{TiCl_2L_2(\mu\text{-}NBu^t)\}_x]$ where L = bpy or py and $x = 2$ or 3). We and others[15] have found that terminal *tert*-butylimidotitanium complexes show strong-to-medium intensity absorptions in the *ca.* 1200–1260 cm^{-1} region of their IR spectra. The identity of the vibrational mode(s) corresponding to such absorptions for terminal transition-metal imido complexes is the subject of ongoing debate.[20–22] Nonetheless, the presence of strong absorptions in this region for **1**–**3** is consistent with them all having terminal NBu^t groups. Additional strong bands in the 520–550 cm^{-1} region also appear to be associated with the $Ti{=}NBu^t$ functionality. Pyridine and bpy do not give rise to strong absorptions in the 1200–1260 and 520–550 cm^{-1} regions.[23] The ^1H NMR spectra of **1**–**3** in $CDCl_3$ show resonances for the NBu^t ligand at δ 0.99, 0.85 and 0.92 respectively, again consistent with this ligand having terminal co-ordination modes in all three complexes. In related studies we have found that bridging NBu^t groups appear at somewhat lower field compared to their terminal NBu^t counterparts in the ^1H NMR spectra of otherwise closely related complexes.[11,24] The ^{13}C NMR data for the NBu^t ligand in the three complexes are also comparable and consistent with terminal imido groups.

Mutually *trans* arrangements of the pyridine and chloride ligands in complexes **1** and **2** are assumed by comparison with the structure of $[Ti(NBu^t)Cl_2(OPPh_3)_2]$,[25] and the crystallographically characterised tris(pyridine) complexes described herein. The square-pyramidal (as opposed to trigonal-bipyramidal) limiting geometry depicted is expected by comparison with other structurally characterised, five-co-ordinate imidotitanium dichloride adducts of the type $[Ti(NR)Cl_2L_2]$.[15,25,26] The tris(pyridine) complex $[Ti(NBu^t)Cl_2(py)_3]$ **3** is analogous to $[Ti\{NP(S)R_2\}Cl_2(py)_3]$ (R = Ph or Pr^i),[6,27] but bis(pyridine) complexes $[Ti(NBu^t)Cl_2L_2]$ (L = bpy **1** or py **2**) are examples of the more usual five-co-ordinate imidotitanium derivatives of the type $[Ti(NR)X_2L_2]$.[1] We note that a 1963 report suggested that $[Ti(NSiMe_3)Cl_2(py)_2]$, obtained by treating $[Ti\{N(SiMe_3)_2\}Cl_3]$ with pyridine, has a proposed structure analogous to those suggested here for **1** and **2**.[28]

The reaction of $TiCl_4$ with $H_2NC_6H_3Me_2$-2,6 followed by addition of pyridine is not suitable for producing pure samples of complex **7**. We expect that attempts at preparing **4**–**6** and **8** using this route would also give disappointing outcomes. This failure is apparently due to difficulties in removal of the excess of aniline either by dynamic vacuum or recrystallisation. Indeed, Winter and co-workers[15] have previously shown that $H_2NC_6H_3Pr^i_2$-2,6 can react with $TiCl_4$ to give $[Ti(NC_6H_3Pr^i_2\text{-}2,6)Cl_2(H_2NC_6H_3Pr^i_2\text{-}2,6)_2]$. Similar difficulties in removing excess of disubstituted anilines have been encountered for related zirconium and hafnium arylimido systens.[29]

However, addition of 1 equivalent of RNH_2 to complex **3** does give generally good yields of $[Ti(NR)Cl_2(py)_3]$ (R = Ph **4**, C_6H_4Me-4 **5**, $C_6H_4NO_2$-4 **6**, $C_6H_3Me_2$-2,6 **7** or $C_6H_3Pr^i_2$-2,6 **8**). Although this arylamine/*tert*-butylimido exchange strategy has also recently found success in the synthesis of chromium,[30] molybdenum,[31,32] osmium[33] and iridium[34] arylimido derivatives, our examples are the first from Group 4. Mechanisms for the exchange reactions of the osmium and chromium systems have been proposed by Gibson[30] and Bergman[33] and co-workers. Factors contributing to the overall driving force for these exchange reactions presumably include the greater basicity of the imido nitrogen in the Bu^tN ligand compared to that in RN (R = aryl).

The complexes $[Ti(NR)Cl_2(py)_3]$ **4**–**8** are the first examples of six-co-ordinate titanium arylimido derivatives although the six-co-ordinate zirconium arylimido congener $[Zr(NC_6H_3Pr^i_2\text{-}2,6)Cl_2(py)_3]$ has recently been described.[29] The 2,6-disubstituted arylimido derivatives **7** and **8** are the most stable in solution and are also more soluble than the un- or 4-substituted arylimido homologues **4**–**6**. Moreover, since **7** and **8** are readily obtained in spectroscopically pure form and in good yield, they are potentially highly valuable synthons for the development of arylimidotitanium chemistry.

Substitution of the pyridine ligands in complexes **2** or **3** by the bi- or tri-dentate tertiary alkylamines tmen or pmdien to form **11** or **12** is straightforward, presumably with entropy factors helping to drive the reactions. The tmen derivative, $[Ti(NBu^t)Cl_2(tmen)]$ **11**, probably first prepared by Nielson[14] but formulated as a binuclear complex with $\mu\text{-}NBu^t$ ligands, has recently been structurally characterised as a mononuclear species.[15] The solution NMR behaviour of the pmdien derivative $[Ti(NBu^t)Cl_2(pmdien)]$ **12** is in contrast to that of the tris(pyridine) complexes $[Ti(NR)Cl_2(py)_3]$ (R = Bu^t or aryl). Its fluxional nature may reflect weaker binding of the pmdien aliphatic amine nitrogen atoms to the metal centre (see below for discussion of X-ray data). Indeed the tris(*tert*-butylamine) complex $[Ti(NBu^t)Cl_2(Bu^tNH_2)_3]$ also gives rise to complicated ^1H NMR spectra possibly indicative of a mixture of geometric isomers.[15]

Crystal structures

Thermal ellipsoid plots of complexes **4** and **12** are shown in Figs. 1 and 2 respectively; selected bond lengths and angles are presented in Tables 1 (**3**–**6**) and 2. In all five complexes the linear or near-linear Ti=N−R linkage implies that the NR ligand acts as a four-electron donor to titanium.[1–3]

A preliminary examination of the bond lengths and angles for these complexes immediately reveals that (*i*) the nitrogen atom bonded *trans* to the imido group is less tightly bound than those bonded *cis* and that (*ii*) the angles subtended at titanium between the imido nitrogen and the donor atoms of the ligands *cis* to it are all greater than 90°. These features are consequences of the *trans* influence frequently exerted by a multiply bonded ligand in a transition-metal complex. The likely origins (steric

Table 3 Comparison of metric data for pairs of homologous *tert*-butyl- and aryl-imido complexes

Homologous pair	M=N/Å	$\Delta_{M=N}$ [a]	Ref.
$[Ti(NBu^t)Cl_2(tmen)]$	1.662(4)		15
$[Ti(NPh)Cl_2(tmen)]$	1.702(4)	0.040(6)	26
$[Ti(omtaa)(NBu^t)]$ [b]	1.724(4)		7
$[Ti(tmtaa)(NC_6H_3Me_2\text{-}2,6)]$ [b]	1.720(4)	−0.004(6)	8
$[Ir(\eta\text{-}C_5Me_5)(NBu^t)]$	1.712(7)		34
$[Ir(\eta\text{-}C_5Me_5)(NC_6H_3Pr^i{}_2\text{-}2,6)]$	1.749(7)	0.037(10)	34
$[Ir(\eta\text{-}C_5Me_5NBu^t)]$	1.712(7)		34
$[Ir(\eta\text{-}C_5Me_5)(NC_6H_3Me_2\text{-}2,6)]$	1.729(7)	0.017(10)	34
$[W_2(NBu^t)_2Cl_6(\mu\text{-}Cl)_2]$	1.704(5)		44
$[W_2(NC_6H_4Me\text{-}4)_2Cl_6(\mu\text{-}Cl)_2]$	1.712(18)	0.008(18)	45
$[W_2(NBu^t)_2Cl_6(\mu\text{-}Cl)_2]$	1.704(5)		44
$[W_2(NC_6H_3Me_2\text{-}2,6)_2Cl_6(\mu\text{-}Cl)_2]$	1.712(7)	0.008(9)	46
$[Nb(\eta\text{-}C_5H_5)(NBu^t)Cl_2]$	1.752(3) and 1.744(3) [c]		47
$[Nb(\eta\text{-}C_5H_5)(NC_6H_3Pr^i{}_2\text{-}2,6)Cl_2]$	1.761(6)	0.017(7) and 0.009(7)	47
3 $[Ti(NBu^t)Cl_2(py)_3]$	1.705(3) and 1.706(3) [c]		This work
4 $[Ti(NPh)Cl_2(py)_3]$	1.714(2)	0.009(3) and 0.008(3)	This work
5 $[Ti(NC_6H_4Me\text{-}4)Cl_2(py)_3]$	1.705(4)	0.000(5) and −0.001(5)	This work

[a] Given by (M=N bond length for arylimido homologue) − (M=N bond length for *tert*-butylimido homologue). The e.s.d. of the difference of two values having individual e.s.d.s x and y is given by $\sqrt{(x^2 + y^2)}$.[48] Arylimido complexes with highly electron-withdrawing substituents on the ring (*e.g.* NO_2 or F) are excluded. [b] H_2tmtaa and H_2omtaa = tetra- and octa-methyldibenzotetraaza[14]annulene. [c] Two molecules in the asymmetric unit.

and/or electronic) of this phenomenon have been discussed in detail elsewhere.[2,16–19] More recently, density functional theory (DFT) calculations on the complex $[OsNCl_5]^{2-}$ showed that a stabilisation of the metal to (multiply bonded) ligand π interactions is the major force behind the *trans* influence, although the effects of steric repulsion between the multiply bonded atom and the ligands *cis* to it are also important.[35] Such calculations have also been used to study the bonding in six-co-ordinate molybdenum imido complexes.[36] For the purposes of discussion here we shall use the term '*trans* influence' to describe the lengthening of the bond *trans* to the imide ligand as compared to the equivalent bond *cis* to the imide ligand in the same complex.[2] We shall use the term 'structural influence' to describe the more general effects of the imide ligand on other groups co-ordinated.

It has been suggested that the overall order of *trans* influence between *different* multiply bonded ligands is nitrido > oxo > imido,[19] although exceptions to this general hierarchy exist.[37,38] The homologous series of tris(pyridine) d^0 derivatives **3**–**6** allows us the best crystallographic opportunity to date of comparing the structural and *trans* influences of an imide ligand within a simple six-co-ordinate complex as a function of the imide ligand N-substituent. Moreover, the absence of the usual aryl ring 2,6 substituents in **4**–**6** means that steric effects are minimised as far as possible. Not surprisingly, homologous series of imido complexes have been structurally characterised before. The series of d^2 18-electron complexes $[Re(NR)Cl_3(PEt_2Ph)_2]$ [R = Me, C_6H_4OMe-4 or $C_6H_4C(O)Me$-4][39,40] is the closest previous study of the possible different structural influence of different imido N-substituents in six-co-ordinate complexes. However, the X-ray data showed no apparent trends and both Nugent and Haymore[3] and Maatta and co-workers[41] have noted that the *trans* influence in these and certain related six-co-ordinate complexes can be negligible for d^2 18-electron complexes (and greatest for d^0 16-electron species). Lyne and Mingos[35,36] have very recently described the electronic origins of these empirical observations using DFT. The structures of the d^0 16-electron complexes $[W_2(NR)_2Cl_6(\mu\text{-}Cl)_2]$ (R = Et, Pr^i, Bu^t, C_6H_4Me-4 or $C_6H_3Pr^i{}_2$-2,6)[42–46] have been reported, but the binuclear nature of these complexes probably places non-quantifiable constraints on W−Cl bond lengths and RN=W−Cl angles *cis* and *trans* to the W=NR linkage which may perturb the intrinsic *trans* influence. The η-cyclopentadienyl and -pentamethylcyclopentadienyl derivatives $[Nb(\eta\text{-}C_5H_5)(NR)Cl_2]$ (R = Me, Bu^t or $C_6H_3Pr^i{}_2$-2,6) and $[Ir(\eta\text{-}C_5Me_5)(NR)]$ (R = Bu^t, $SiMe_2Bu^t$, $C_6H_3Me_2$-2,6 or $C_6H_3Pr^i{}_2$-2,6) have recently been described by Gibson[47] and Bergman and co-workers.[34] These last two series of homologous half-sandwich complexes allow some comparisons of the relative structural influences of *tert*-butyl- and aryl-imide ligands but do not allow an estimation of their formal *trans* influences.

Let us now examine the structural data in detail. The two crystallographically independent Ti=N bond lengths in $[Ti(NBu^t)Cl_2(py)_3]$ **3** are significantly shorter than the corresponding bonds in Roesky's $[Ti\{NP(S)R_2\}Cl_2(py)_3]$ [R = Ph, Ti=N 1.720(2); R = Pr^i, Ti=N 1.723(2) Å].[6,27] Furthermore, the Ti−Cl and Ti−N (py *cis* and *trans*) distances in **3** are generally significantly longer than in either of the $[Ti\{NP(S)R_2\}Cl_2(py)_3]$ analogues, indicating that the NBu^t ligand has a greater labilising structural influence than that of $N(S)PR_2$.

The Ti=N bond lengths in complex **3** and in the phenyl- and tolyl-imido homologues $[Ti(NC_6H_4R\text{-}4)Cl_2(py)_3]$ (R = H **4** or Me **5**) are equivalent within experimental error. A comparison of crystallographic data for a *collection* of homologous pairs of arylimido and *tert*-butylimido complexes (Table 3) shows that the transition metal to nitrogen bond lengths are generally longer for the arylimido complex. Indeed, one would expect that imido nitrogen electron density could be delocalised onto the phenyl ring of the arylimido complexes thus reducing the metal to nitrogen bond order. However, for *individual* homologous pairs of *tert*-butylimido and arylimido complexes (Table 3) the difference ($\Delta_{M=N}$) between the M=N bond lengths is significant only in a minority of cases.

Despite the experimentally identical Ti=N bond lengths in complexes **3**–**5**, the NBu^t and NC_6H_4R-4 (R = H or Me) ligands have significantly different structural influences on the $TiCl_2(py)_3$ fragment with the Ti−N (py) and Ti−Cl bond lengths for **3** being nearly all significantly longer than the corresponding ones in **4** and **5**. This ability of the NBu^t ligand to labilise other ligands present (as compared to arylimido homologues) generally appears also to exist in the literature compounds identified above, but the effects are not as straightforwardly traced as in **3**–**5**.

However, in the 4-nitrophenyl analogue $[Ti(NC_6H_4NO_2\text{-}4)$-

$Cl_2(py)_3]$ **6** there is a substantial effect of the imido N-substituent on the Ti=N bond length compared to **3** [$\Delta_{M=M}$ = 0.016(4) or 0.017(4)], **4** [0.008(4)] and **5** [0.017(5) Å]. Although some of these individual differences are not highly significant, the consistency of the direction of the difference is convincing. The imido nitrogen to *ipso*-carbon bond length in **6** is shorter by 0.023(6) and 0.019(7) Å than that in **4** and **5** respectively. This presumably indicates greater delocalisation of the imido nitrogen electron density onto the aromatic ring in **6**. Surprisingly, therefore, we find the Ti–N (py *cis* and *trans*) bond lengths in **4**–**6** are equivalent within error despite these implied differences in Ti=N bonding. In contrast the Ti–Cl bond length in **6** is significantly shorter than those in **4** and **5**. This might reflect enhanced π donation from the Cl ligands in **6** since any σ effects would presumably be reflected in the Ti–N (py) bond lengths.

Although there are no apparent structural effects of different electron-withdrawing or -donating groups in the imido aryl ring in the d^2 eighteen-electron complexes $[Re(NC_6H_4R\text{-}4)Cl_3(PEt_2Ph)_2]$ [R = OMe or C(O)Me],[40] solution dipole moments for a homologous series of these complexes have been reported.[49] The molecular dipole moments μ decrease in the order R = OMe (7.2) > Me (6.5) > H (5.9) > Br (5.2) > Cl (5.0) > F (4.6) > C(O)Me (4.5 D). These data are consistent with a through-ring, electron-withdrawing effect of the 4-nitro ring substituent on the imido nitrogen atom in **6**. We note that in the recently described $[Mo(NC_6F_5)(NC_{10}H_{15})Cl_2(dme)]$ ($C_{10}H_{15}$ = adamant-1-yl, dme = 1,2-dimethoxyethane)[31] the Mo=N (adamantyl) bond lengths [1.715(3) and 1.716(3) Å, two molecules in the asymmetric unit] are substantially shorter than the $Mo{=}NC_6F_5$ bond lengths [1.775(3) and 1.759(3) Å]. The Mo–O bonds *trans* to the adamantylimide ligands are longer [Mo–O (average) 2.370(2) Å] than those *trans* to NC_6F_5 [Mo–O (average) 2.346(2) Å].

Despite the different structural features of complexes **3**–**6** there is no difference in formal *trans* influence between them. For **4**–**6** the *trans* influence spans the range 0.181(4) to 0.201(4) Å while for **3** it lies between 0.182(4) and 0.203(1) Å. Interestingly, the *trans* influences of the imide ligands in $[Ti\{NP(S)R_2\}Cl_2(py)_3]$ [0.210(3) and 0.215(4) Å for R = Ph;[6] 0.178(4) and 0.192(4) Å for R = Pr^i [27]] span the values found for **3**–**6**. These results suggest that the *general* structural influence of the various imide ligands is not manifested as a *specific* experimentally significant perturbation of the *trans* ligand relative to the *cis* ligands. Finally we note that there are no apparent trends in the N=Ti–Cl or N=Ti–N (py, *cis*) angles for the complexes **3**–**6**.

Consider now the structure of $[Ti(NBu^t)Cl_2(pmdien)]$ **12**. The Ti–N (pmdien) bond lengths (Table 2) are all substantially longer than the corresponding Ti–N (py) bond lengths in **3**, consistent with the solution NMR fluxional behaviour of **12** and the good σ-donor ability of pyridine. The average $Ti{=}NBu^t$ bond length for the two crystallographically independent molecules of **12** is slightly shorter than that in **3**. This may reflect the different donor abilities of the ligand *trans* to the imido group. The average Ti–Cl bond length in **12** [2.389(1) Å] is substantially shorter than for **3** [2.438(1) Å]. It is also possible that this may reflect a greater *trans* influence of pyridine as compared to pmdien. Insufficient comparative structural data are available for early transition-metal d^0 complexes for a quantitative evaluation to be made at this time.

Although a search of the Cambridge Structural Database[50,51] showed that a number of complexes of the pmdien ligand have been structurally characterised for the later transition metals, $[Ti(NBu^t)Cl_2(pmdien)]$ **12** is the first example of an early transition-metal derivative. The *fac* co-ordination mode is unusual for pmdien, but this comparison is based on the apparent preferences of later transition-metal complexes which lack a multiply bonded ligand. Furthermore, the NMR data imply that different solution co-ordination modes are readily accessible. The closest Group 4 analogues of **12** are the macrocycle-supported, oxotitanium complexes $[Ti(O)X_2(Me_3[9]aneN_3)]$ (X = Cl or NCS) and $[Ti(O)X_2(Pr^i_3[9]aneN_3)]$ (X = NCO or NCS) which also have the two X ligands *cis* to the multiply bonded moiety ($R_3[9]aneN_3$ = 1,4,7-tri-R-1,4,7-triazacyclononane, R = Me or Pr^i).[52,53] The two $Me_3[9]aneN_3$ derivatives have been crystallographically characterised but no solution NMR data were reported. The *trans* influence of the oxide ligand in $[Ti(O)X_2(Me_3[9]aneN_3)]$ [0.172(8) and 0.182(7) Å for X = NCS; 0.157(6) and 0.149(5) Å for X = Cl] is somewhat smaller compared to that of the NBu^t ligand in **12**. This could as much imply a greater flexibility of the open-chain pmdien ligand compared to the cyclic $Me_3[9]aneN_3$ as it might a larger *trans* influence of the NBu^t ligand compared to oxo.[19] However, the average Ti–Cl bond length in **12** [2.389(1) Å] is slightly longer than that in $[Ti(O)Cl_2(Me_3[9]aneN_3)]$ [2.364(2) Å] and may imply that the NBu^t ligand has the better donor (or at least, *cis*-labilising) ability.[2]

Conclusion

We have described simple routes to synthetically useful quantities of pyridine-supported, *tert*-butylimidotitanium dichloride complexes. Straightforward arylamine/*tert*-butylimido exchange reactions give corresponding arylimidotitanium derivatives. The 2,6-disubstituted arylimido complexes are the most stable and soluble, and are readily obtained in a synthetically useful way. The bis- and tris-(pyridine) *tert*-butylimido complexes allow easy access to corresponding tmen and pmdien adducts and the solid-state structure and solution behaviour of the latter have been examined. The crystal structures of **3**–**6** suggest that there is no clear experimental relationship between Ti=NR bond length and the ability of the NR group to distort other Ti–py or –Cl bonds present. The formal *trans* influences of the NBu^t, NPh, $NC_6H_4Me\text{-}4$ and $NC_6H_4NO_2\text{-}4$ ligands are experimentally similar to each other and to those of $NP(S)Ph_2$ and $NP(S)Pr^i_2$ in the d^0, six-co-ordinate series $[Ti(NR)Cl_2(py)_3]$. Consistent with most previous studies, the NBu^t ligand has the greatest labilising effect on other ligands present in the metal co-ordination sphere.

Experimental

General methods and instrumentation

All manipulations were carried out under an atmosphere of dinitrogen or argon using either standard Schlenk-line or dry-box techniques. Solvents were predried over activated 4A molecular sieves and refluxed over sodium (toluene), sodium–potassium alloy (1 : 3 w/w) (pentane, diethyl ether), potassium (hexane), or calcium hydride (dichloromethane) under dinitrogen and collected by distillation; $CDCl_3$ and CD_2Cl_2 were dried over freshly ground calcium hydride, vacuum distilled and stored under dinitrogen in Teflon-valve ampoules. The NMR samples were prepared in a dry-box in Wilmad 505-PS tubes fitted with a J. Young NMR/5 valve. 4-Nitroaniline, 4-methylaniline and titanium tetrachloride (Aldrich) were used as received; 4-*tert*-butylpyridine was dried over activated 4A molecular sieves and used without further purification. Other reagents were dried over finely ground CaH_2 and either distilled at atmospheric pressure (Bu^tNH_2, pyridine) or under reduced pressure (aniline, $H_2NC_6H_3Me_2\text{-}2,6$ and $H_2NC_6H_3Pr^i_2\text{-}2,6$).

Proton and $^{13}C\text{-}\{^1H\}$ NMR spectra were recorded on either a Bruker WM 250, DPX 300 or AM 400 spectrometer. Where necessary ^{13}C assignments were confirmed by DEPT-135 and -90 $^{13}C\text{-}\{^1H\}$ experiments. The spectra were referenced internally to the residual protiosolvent (^1H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane (δ 0) at ambient probe temperature. Infrared spectra were recorded on a Nicolet 205 FTIR spectrometer as Nujol mulls between caesium bromide windows. Elemental analyses were carried out by the analysis department of this laboratory.

Syntheses

$[Ti(NBu^t)Cl_2(bpy)_2]$ 1. To a stirred solution of $TiCl_4$ (3.50 cm^3, 31.6 mmol) in dichloromethane (80 cm^3) at −50 °C was added Bu^tNH_2 (20.0 cm^3, 190 mol, 6.0 equivalents) over 15 min. An orange precipitate formed, the mixture was stirred at r.t. for 5 h and the volatiles were removed under reduced pressure. The residue was extracted into toluene (75 cm^3), filtered away from Bu^tNH_3Cl and the volatiles were removed under reduced pressure. These residues were re-extracted into dichloromethane (100 cm^3), treated with 4-*tert*-butylpyridine (10.1 cm^3, 68.0 mmol, 2.2 equivalents) and the resultant dark orange solution was stirred for 16 h. Volatiles were removed under reduced pressure and the residue extracted into toluene and filtered away from further residual Bu^tNH_3Cl. Subsequent evaporation of the volatiles under reduced pressure, washing with hexane (2 × 30 cm^3) and drying *in vacuo* gave complex **1** as an orange-red solid. Yield: 12.2 g (78%). It can be recrystallised from hexane if required. NMR ($CDCl_3$): ^{1}H (250 MHz), δ 9.17 (4 H, d, *J* = 6.7, *o*-H of $NC_5H_4Bu^t$), 7.46 (4 H, d, *J* = 6.7 Hz, *m*-H of $NC_5H_4\mathit{Bu}^t$), 1.36 (18 H, s, $NC_5H_4\mathit{Bu}^t$) and 0.99 (9 H, s, NBu^t); ^{13}C-{^{1}H} (62.9 MHz), δ 163.2 (*p*-C of $C_5H_4Bu^t$), 151.1 (*o*-C of $C_5H_4Bu^t$), 121.1 (*m*-C of $C_5H_4Bu^t$), 73.6 ($N\mathit{C}Me_3$), 35.1 ($C_5H_4\mathit{C}Me_3$), 30.5 ($NC\mathit{Me}_3$) and 30.2 ($C_5H_4CMe_3$). IR: 1614s, 1500m, 1419m, 1352w, 1275m, 1254m, 1235s, 1209m, 1071m, 1021m, 843m (sh), 832s, 571s and 547m cm^{-1} [Found (Calc. for $C_{22}H_{35}Cl_2N_3Ti$): C, 56.0 (57.4); H, 8.0 (7.7); N, 8.9 (9.1)%].

$[Ti(NBu^t)Cl_2(py)_2]$ 2. To a stirred solution of $TiCl_4$ (3.50 cm^3, 31.6 mmol) in dichloromethane (80 cm^3) at −50 °C was added Bu^tNH_2 (20.0 cm^3, 190 mol, 6.0 equivalents) over 15 min. An orange precipitate formed and the mixture was allowed to warm to r.t. and stirred for 2 h. It was filtered to give a clear orange solution to which was added pyridine (6.00 cm^3, 74.2 mmol, 2.3 equivalents). After 2 h the volatiles were removed from the orange-red mixture and the residue was extracted into toluene–dichloromethane (10 : 1, 50 cm^3). This solution was again filtered (to remove residual Bu^tNH_3Cl), evaporated to dryness under reduced pressure and the orange-red residue washed with hexane (2 × 20 cm^3) to give complex **2** after drying *in vacuo*. Yield: 7.0 g (64%). Samples thus prepared are sufficiently pure (according to ^{1}H NMR spectroscopy) to use in further reactivity studies and an analytically pure sample was obtained by slow cooling of a saturated hot toluene solution. NMR ($CDCl_3$): ^{1}H (250 MHz), δ 9.20 (4 H, d, *J* = 5.3, *o*-H of NC_5H_5), 7.78 (2 H, *J* = 7.5, *p*-H of NC_5H_5), 7.34 (4 H, apparent t, apparent *J* = 7.0 Hz, *m*-H of NC_5H_5) and 0.85 (9 H, s, NBu^t); ^{13}C-{^{1}H} (100.6 MHz), δ 151.7 (*o*-C of NC_5H_5), 138.5 (*p*-C of NC_5H_5), 123.9 (*m*-C of NC_5H_5), 73.1 ($N\mathit{C}Me_3$) and 30.3 ($NC\mathit{Me}_3$). IR: 1605s, 1483w, 1443s, 1361w, 1245s, 1215m, 1206w (sh), 1066m, 1043m, 1014w, 754m, 695s, 639m, 539m, 524m and 431m cm^{-1} [Found (Calc. for $C_{14}H_{19}Cl_2N_3Ti$): C, 48.2 (48.3); H, 5.4 (5.5); N, 12.5 (12.1)%].

$[Ti(NBu^t)Cl_2(py)_3]$ 3. To a stirred solution of $TiCl_4$ (10.0 cm^3, 0.091 mol) in dichloromethane (150 cm^3) at −50 °C was added Bu^tNH_2 (60 cm^3, 0.47 mol, 6.3 equivalents) over 15 min to give an orange-yellow precipitate. The mixture was stirred at r.t. for 2 h and pyridine (*ca.* 30 cm^3, 0.37 mol, 4.1 equivalents) was added to give a dark orange solution which was stirred at r.t. for 16 h. After filtration, the volatiles were removed under reduced pressure and the orange solid was washed with hexane (2 × 40 cm^3) to give complex **3** after drying *in vacuo.* Yield: 38.6 g (98%). Samples thus prepared are sufficiently pure (^{1}H NMR spectroscopy) to use in further reactivity studies. An analytically pure, X-ray-quality crystalline sample was obtained from a saturated pentane solution at r.t. NMR ($CDCl_3$): ^{1}H (250 MHz), δ 9.23 (4 H, d, *J* = 5.4, *o*-H of *cis*-NC_5H_5), 8.58 (2 H, br d, coupling not resolved, *o*-H of *trans*-NC_5H_5), 7.79 (2 H, t, *J* = 7.3, *p*-H of *cis*-NC_5H_5), 7.56 (1 H, br t, *J* = 7.3, *p*-H of *trans*-NC_5H_5), 7.35 (4 H, apparent t, apparent *J* = 7.0, *m*-H of *cis*-NC_5H_5), 7.10 (2 H, br, apparent t, apparent *J* = 7.0 Hz, *m*-H of *trans*-NC_5H_5) and 0.92 (9 H, s, NBu^t); ^{13}C-{^{1}H} (62.9 MHz), δ 151.9 (*o*-C of *cis*-NC_5H_5), 150.4 (*o*-C of *trans*-NC_5H_5), 139.3 (*p*-C of *cis*-NC_5H_5), 136.5 (*p*-C of *trans*-NC_5H_5), 123.7 (*m*-C of *cis*-NC_5H_5), 123.3 (*m*-C of *trans*-NC_5H_5), 71.5 ($N\mathit{C}Me_3$) and 30.0 ($NC\mathit{Me}_3$). IR: 1603s, 1484m, 1353m, 1247s, 1216s, 1071m, 1041m, 1012w, 756m, 701s, 636m, 541s and 429m cm^{-1} [Found (Calc. for $C_{19}H_{24}Cl_2N_4Ti$): C, 52.6 (53.4); H, 5.9 (5.7); N, 12.9 (13.1)%].

$[Ti(NPh)Cl_2(py)_3]$ 4. A solution of $[Ti(NBu^t)Cl_2(py)_3]$ **3** (773 mg, 1.80 mmol) in dichloromethane (30 cm^3) at r.t. was treated with aniline (0.17 cm^3, 1.80 mmol). After 1.5 h the volatiles were removed under reduced pressure to give a brown solid which was washed with hexane (2 × 10 cm^3) and dried *in vacuo*. Yield 800 mg (96%). This compound may be recrystallised at −25 °C from dichloromethane. Recrystallised yield 288 mg (36%). NMR ($CDCl_3$): ^{1}H (250 MHz), δ 9.11 (4 H, d, *J* = 4.9, *o*-H of *cis*-NC_5H_5), 8.71 (2 H, d, *J* = 4.3, *o*-H of *trans*-NC_5H_5), 7.81 (2 H, t, *J* = 7.6, *p*-H of *cis*-NC_5H_5), 7.63 (1 H, t, *J* = 7.6, *p*-H of *trans*-NC_5H_5), 7.36 (4 H, apparent t, apparent *J* = 6.9, *m*-H of *cis*-NC_5H_5), 7.25 (2 H, apparent t, apparent *J* = 6.6, *m*-H of *trans*-NC_5H_5), 7.03 (2 H, apparent t, *J* = 7.6, *m*-H of Ph), 6.94 (2 H, d, *J* = 7.04, *o*-H of Ph) and 6.76 (1 H, t, *J* = 7.2 Hz, *p*-H of Ph); ^{13}C-{^{1}H} (62.9 MHz), δ 159.7 (*ipso*-C of Ph), 151.6 (*o*-C of *cis*-NC_5H_5), 150.3 (*o*-C of *trans*-NC_5H_5), 138.6 (*p*-C of *cis*-NC_5H_5), 136.3 (*p*-C of *trans*-NC_5H_5), 128.1 (*o*-C of Ph), 124.1 (*m*-C of *cis*-NC_5H_5), 123.7 (*m*-C of *trans*-NC_5H_5), 122.2 (*p*-C of Ph), *m*-C of Ph obscured by py resonances [Found (Calc. for $C_{21}H_{20}Cl_2N_4Ti$): C, 57.5 (56.4); H, 4.7 (4.5); N, 13.0 (12.5)%].

$[Ti(NC_6H_4Me\text{-}4)Cl_2(py)_3]$ 5. A solution of complex **3** (483 mg, 1.13 mmol) in dichloromethane (30 cm^3) was added to a solution of 4-methylaniline (139 mg, 1.30 mmol) in dichloromethane (20 cm^3) at r.t. After 2 h volatiles were removed under reduced pressure to afford a brown solid which was dissolved in dichloromethane (20 cm^3). Careful layering of this solution with pentane (15 cm^3) at r.t. gave brown crystals of **5** suitable for X-ray diffraction after 16 h. These were washed with pentane (2 × 5 cm^3) and dried *in vacuo*. Yield: 224 mg (42%). NMR ($CDCl_3$): ^{1}H (250 MHz), δ 9.12 (4 H, d, *J* = 4.6, *o*-H of *cis*-NC_5H_5), 8.73 (2 H, br s, *o*-H of *trans*-NC_5H_5), 7.83 (2 H, t, *J* = 7.6, *p*-H of *cis*-NC_5H_5), 7.68 (1 H, t, *J* = 7.1, *p*-H of *trans*-NC_5H_5), 7.39 (4 H, apparent t, apparent *J* = 6.6 Hz, *m*-H of *cis*-NC_5H_5), 7.26 (2 H, br s, *m*-H of *trans*-NC_5H_5), 6.86 (4 H, apparent s, $C_6\mathit{H}_4Me$) and 2.23 (3 H, s, $C_6H_4\mathit{Me}$); ^{13}C-{^{1}H} (75.5 MHz), δ 151.5 (*o*-C of *cis*-NC_5H_5), 150.7 (*o*-C of *trans*-NC_5H_5), 138.7 (*p*-C of *cis*-NC_5H_5), 136.9 (*p*-C of *trans*-NC_5H_5), 128.6 (*o*-C of C_6H_4Me), 124.2, 123.8, 123.7 (*m*-C of *cis*- and *trans*-NC_5H_5 and of C_6H_4Me), 21.1 ($C_6H_4\mathit{Me}$), *ipso*-C for C_6H_4Me not observed [Found (Calc. for $C_{22}H_{22}Cl_2N_4Ti$): C, 57.1 (57.3); H, 5.0 (4.8); N, 12.2 (12.2)%].

$[Ti(NC_6H_4NO_2\text{-}4)Cl_2(py)_3]$ 6. A solution of complex **3** (443 mg, 1.04 mmol) in dichloromethane (15 cm^3) was added to a solution of 4-nitroaniline (143 mg, 1.04 mmol) in dichloromethane (30 cm^3) at r.t. After 48 h the volatiles were removed under reduced pressure and the red-brown solid was extracted into dichloromethane (15 cm^3). Careful layering of this solution with hexane (10 cm^3) at r.t. gave brown crystals of **6** suitable for X-ray diffraction after 16 h. These were washed with cold (−20 °C) hexane–dichloromethane (1 : 1, 2 × 15 cm^3) and dried *in vacuo*. Yield: 300 mg (59%). NMR ($CDCl_3$): ^{1}H (250 MHz), δ 9.07 (4 H, d, *J* = 4.9, *o*-H of *cis*-NC_5H_5), 8.76 (2 H, d, *J* = 4.2, *o*-H of *trans*-NC_5H_5), 7.96 (2 H, m, *m*-H of $C_6H_4NO_2$), 7.87 (2 H, t, $J = 7.7$, *p*-H of *cis*-NC_5H_5), 7.71 (1 H, t, $J = 7.5$, *p*-H of *trans*-NC_5H_5), 7.41 (4 H, apparent t, apparent $J = 7.0$, *m*-H of *cis*-NC_5H_5), 7.26 (2 H, apparent t, apparent $J = 6.8$ Hz, *m*-H of *trans*-NC_5H_5) and 6.86 (2 H, m, *o*-H of $C_6H_4NO_2$); $^{13}C\text{-}\{^1H\}$ (100.5 MHz), δ 151.3 (*o*-C of *cis*-NC_5H_5), 150.3 (*o*-C of *trans*-NC_5H_5), 138.9 (*p*-C of *cis*-NC_5H_5), 136.7 (*p*-C of *trans*-NC_5H_5), 124.6 (*m*-C of $C_6H_4NO_2$), 124.1 (*m*-C of *cis*-NC_5H_5), 123.6 (*m*-C of *trans*-NC_5H_5), 123.5 (*o*-C of $C_6H_4NO_2$), *ipso*-C for $C_6H_4NO_2$ not observed [Found (Calc. for $C_{21}H_{19}Cl_2N_5O_2Ti$): C, 50.7 (51.2); H, 3.9 (3.9); N, 14.3 (14.2)%].

$[Ti(NC_6H_3Me_2\text{-}2,6)Cl_2(py)_3]$ 7. A solution of complex **3** (485 mg, 1.13 mmol) in dichloromethane (30 cm^3) at r.t. was treated with 2,6-dimethylaniline (0.14 cm^3, 1.14 mmol). The initially orange solution became dark red over 2 h. Volatiles were removed under reduced pressure to afford **7** as a red-brown powder which was washed twice with pentane (2 × 15 cm^3) and dried *in vacuo*. Yield: 465 mg (86%). Samples thus prepared are normally >95% pure (^1H NMR spectroscopy). An analytically pure sample was obtained by careful layering of a dichloromethane solution of **7** (containing a small quantity of added pyridine) with hexane at r.t. NMR ($CDCl_3$): ^1H (250 MHz), δ 9.15 (4 H, d, $J = 6.4$, *o*-H of *cis*-NC_5H_5), 8.63 (2 H, br d, $J = 4.3$, *o*-H of *trans*-NC_5H_5), 7.87 (2 H, t, $J = 7.7$, *p*-H of *cis*-NC_5H_5), 7.66 (1 H, br t, $J = 7.6$, *p*-H of *trans*-NC_5H_5), 7.43 (4 H, d of d, $J = 6.4$ and 7.7, *m*-H of *cis*-NC_5H_5), 7.23 (2 H, br apparent t, apparent $J = 7.4$, *m*-H of *trans*-NC_5H_5), 6.77 (2 H, d, $J = 7.4$, *m*-H of $C_6H_3Me_2$), 6.58 (1 H, t, $J = 7.4$ Hz, *p*-H of $C_6H_3Me_2$) and 2.40 (6 H, s, $C_6H_3Me_2$); $^{13}C\text{-}\{^1H\}$ (62.9 MHz), δ 151.5 (*o*-C of *cis*-NC_5H_5), 150.4 (*o*-C of *trans*-NC_5H_5), 138.7 (*p*-C of *cis*-NC_5H_5), 136.3 (*p*-C of *trans*-NC_5H_5), 134.9 (*o*-C of $C_6H_3Me_2$), 126.8 (*m*-C of $C_6H_3Me_2$), 124.2 (*m*-C of *cis*-NC_5H_5), 123.5 (*m*-C of *trans*-NC_5H_5), 121.7 (*p*-C of $C_6H_3Me_2$), 18.9 ($C_6H_3Me_2$), *ipso*-C for $C_6H_3Me_2$ not observed [Found (Calc. for $C_{23}H_{24}Cl_2N_4Ti$): C, 58.5 (58.1); H, 5.2 (5.1); N, 12.1 (11.8)%].

$[Ti(NC_6H_3Pr^i_2\text{-}2,6)Cl_2(py)_3]$ 8. A solution of complex **3** (474 mg, 1.11 mmol) in dichloromethane (30 cm^3) at r.t. was treated with 2,6-diisopropylaniline (0.21 cm^3, 1.11 mmol). The orange solution became dark red over 3 h. Volatiles were removed under reduced pressure to afford **8** as a brown powder which was washed twice with hexane (2 × 15 cm^3) and dried *in vacuo*. Yield of the analytically pure product: 475 mg (84%). NMR ($CDCl_3$): ^1H (250 MHz), δ 9.17 (4 H, d, $J = 4.9$, *o*-H of *cis*-NC_5H_5), 8.66 (2 H, br s, *o*-H of *trans*-NC_5H_5), 7.90 (2 H, t, $J = 7.7$, *p*-H of *cis*-NC_5H_5), 7.68 (1 H, br s, *p*-H of *trans*-NC_5H_5), 7.48 (4 H, apparent t, apparent $J = 7.0$, *m*-H of *cis*-NC_5H_5), 7.25 (2 H, br s, *m*-H of *trans*-NC_5H_5), 6.92 (2 H, d, $J = 7.6$, *m*-H of $C_6H_3Pr^i_2$), 6.81 (1 H, t, $J = 7.6$, *p*-H of $C_6H_3Pr^i_2$), 4.33 (2 H, spt, $J = 6.9$, C*H*Me_2 of Pr^i) and 1.11 (12 H, d, $J = 6.9$ Hz, CH*Me*$_2$ of Pr^i); $^{13}C\text{-}\{^1H\}$ (62.9 MHz), δ 156.9 (*ipso*-C of $C_6H_3Pr^i_2$), 151.1 (*o*-C of *cis*-NC_5H_5), 150.3 (*o*-C of *trans*-NC_5H_5), 145.3 (*o*-C of $C_6H_3Pr^i_2$), 139.0 (*p*-C of *cis*-NC_5H_5), 136.3 (*p*-C of *trans*-NC_5H_5), 124.5 (*m*-C of *cis*-NC_5H_5), 123.6 (*p*-C of $C_6H_3Pr^i_2$), 123.0 (*m*-C of *trans*-NC_5H_5), 122.1 (*m*-C of $C_6H_3Pr^i_2$), 27.5 (*C*HMe_2 of Pr^i) and 23.9 (CH*Me*$_2$ of Pr^i) [Found (Calc. for $C_{27}H_{32}Cl_2N_4Ti$): C, 60.6 (61.0); H, 6.2 (6.1); N, 10.6 (10.5)%].

$[Ti(NC_6H_3Me_2\text{-}2,6)Cl_2(py)_2]$ 9. The complex $[Ti(NC_6H_3Me_2\text{-}2,6)Cl_2(py)_3]$ (457 mg, 1.01 mmol) was heated at 65 °C under a dynamic vacuum for 7 h. The resultant green powder was extracted into dichloromethane (20 cm^3) and filtered. Cooling to −25 °C and washing with cold hexane yielded **9** as a green powder. Yield: >95%. NMR ($CDCl_3$): ^1H (300 MHz), δ 9.16 (4 H, d, $J = 4.8$, *o*-H of NC_5H_5), 7.94 (2 H, t, $J = 7.7$, *p*-H of NC_5H_5), 7.53 (4 H, apparent t, apparent $J = 7.0$, *m*-H of NC_5H_5), 6.87 (2 H, d, $J = 7.9$, *m*-H of $C_6H_3Me_2$), 6.68 (1 H, t, $J = 7.5$ Hz, *p*-H of $C_6H_3Me_2$) and 2.56 (6 H, s, $C_6H_3Me_2$); $^{13}C\text{-}\{^1H\}$ (75.5 MHz), δ 151.0 (*o*-C of NC_5H_5), 139.0 (*p*-C of NC_5H_5), 134.5 (*o*-C of $C_6H_3Me_2$), 126.9 (*m*-C of $C_6H_3Me_2$), 124.6 (*m*-C of NC_5H_5), 122.5 (*p*-C of $C_6H_3Me_2$), 19.0 ($C_6H_3Me_2$), *ipso*-carbon resonance not observed [Found (Calc. for $C_{18}H_{19}Cl_2N_3Ti$): C, 54.3 (54.6); H, 5.2 (4.8); N, 10.8 (10.6)%].

$[Ti(NC_6H_3Pr^i_2\text{-}2,6)Cl_2(py)_2]$ 10. The complex $[Ti(NC_6H_3Pr^i_2\text{-}2,6)Cl_2(py)_3]$ (555 mg, 1.04 mmol) was heated at 65 °C under a dynamic vacuum for 4 h to give **10** as a green powder. Yield: >95%. NMR ($CDCl_3$): ^1H (300 MHz), δ 9.18 (4 H, d, $J = 4.9$, *o*-H of NC_5H_5), 7.94 (2 H, t, $J = 7.7$, *p*-H of NC_5H_5), 7.53 (4 H, apparent t, apparent $J = 7.0$, *m*-H of NC_5H_5), 6.96 (2 H, d, $J = 7.8$, *m*-H of $C_6H_3Pr^i_2$), 6.86 (1 H, t, $J = 7.6$, *p*-H of $C_6H_3Pr^i_2$), 4.34 (2 H, spt, $J = 6.9$, C*H*Me_2 of Pr^i) and 1.18 (12 H, d, $J = 6.9$ Hz, CH*Me*$_2$ of Pr^i); $^{13}C\text{-}\{^1H\}$ (75.5 MHz), δ 150.9 (*o*-C of NC_5H_5), 145.1 (*o*-C of $C_6H_3Pr^i_2$), 139.2 (*p*-C of NC_5H_5), 124.8 (*m*-C of NC_5H_5), 123.5 (*p*-C of $C_6H_3Pr^i_2$), 122.2 (*m*-C of $C_6H_3Pr^i_2$), 27.7 (*C*HMe_2 of Pr^i), 23.9 (CH*Me*$_2$ of Pr^i), *ipso*-carbon resonance not observed [Found (Calc. for $C_{22}H_{27}Cl_2N_3Ti$): C, 57.9 (58.4); H, 6.0 (6.0); N, 9.3 (9.3)%].

$[Ti(NBu^t)Cl_2(tmen)]$ 11. To a solution of $[Ti(NBu^t)Cl_2(py)_2]$ **1** (429 mg, 1.23 mmol) in dichloromethane (30 cm^3) was added tmen (0.19 cm^3, 1.26 mmol) giving a change from orange-red to yellow. After 16 h the volatiles were removed under reduced pressure to yield **11** as a spectroscopically pure yellow powder which was characterised by comparison of its ^1H NMR data with the literature values.[15] Yield: >95%.

$[Ti(NBu^t)Cl_2(pmdien)]$ 12. To a stirred suspension of $[Ti(NBu^t)Cl_2(py)_3]$ **3** (510 mg, 1.19 mmol) in diethyl ether (50 cm^3) was added pmdien (0.20 cm^3, 1.19 mmol). After 3 h the yellow solution was placed in a freezer at −25 °C to afford **12** as light orange, X-ray-quality crystals after 24 h. These were washed with the minimum volume of cold (−25 °C) diethyl ether and dried *in vacuo*. Yield: 238 mg (55%). NMR ($CDCl_3$): ^1H (250 MHz), δ 3.93 (2 H, apparent t, $J = 12.7$, CH_2), 3.01–2.90 (16 H, overlapping s and m, NMe_2 and CH_2), 2.32 [3 H, s, $CH_2N(Me)CH_2$], 1.87 (2 H, d, $J = 12.7$ Hz, CH_2) and 1.03 (NBu^t); $^{13}C\text{-}\{^1H\}$ (62.9 MHz), δ 61.8 (CH_2), 56.4 and 55.2 (NMe_2), 55.0 (CH_2), 44.5 [$CH_2N(Me)CH_2$], 30.8 ($NCMe_3$), CMe_3 quaternary carbon not observed [Found (Calc. for $C_{13}H_{32}Cl_2N_4Ti$): C, 43.2 (43.0); H, 9.2 (8.9); N, 15.5 (15.4)%].

Crystallography

For complex **4** a crystal was taken from under the dichloromethane mother-liquor, mounted on a glass fibre with RS3000 oil and transferred on a goniometer head to a Stoë Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device.[54] For **12** a crystal was sealed in a Lindemann glass capilliary under N_2 and transferred to a Siemens SMART CCD diffractometer. Data collection and processing parameters are listed in Table 4. The data were corrected for Lorentz-polarization and absorption effects, equivalent reflections were merged (for **12**) and systematically absent reflections rejected. The structures were solved by direct methods (**4**) or from a Patterson synthesis (**12**). Subsequent Fourier-difference syntheses revealed the positions of all other non-hydrogen atoms. The crystals of **4** contained 1.5 CH_2Cl_2 molecules of crystallisation per asymmetric unit. Non-hydrogen atoms were refined against F_o^2 with anisotropic displacement parameters by full-matrix least-squares procedures. Hydrogen atoms were located from Fourier-difference syntheses (**4**) or placed in estimated positions (**12**). Standard weighting schemes were applied. For **12** the data were corrected for isotropic extinction (not necessary for **4**). All crystallographic calculations were performed using SHELXS 86[55] and SHELXL 96.[56]

Table 4 Crystal data collection and processing parameters* for $[Ti(NPh)Cl_2(py)_3]\cdot 1.5CH_2Cl_2$ **4**$\cdot 1.5CH_2Cl_2$ and $[Ti(NBu^t)Cl_2(pmdien)]$ **12**

	4$\cdot 1.5CH_2Cl_2$	**12**
Molecular formula	$C_{21}H_{20}Cl_2N_4Ti\cdot 1.5CH_2Cl_2$	$C_{13}H_{32}Cl_2N_4Ti$
M	574.60	363.23
a/Å	30.493(8)	22.321(2)
b/Å	9.117(4)	19.535(2)
c/Å	18.980(4)	17.601(2)
β/°	95.14(2)	96.681(4)
U/Å^3	5255(3)	7622.7(13)
Z	8	16
D_c/Mg m^{-3}	1.452	1.266
μ/mm^{-1}	0.853	0.727
F(000)	2344	3104
Crystal size/mm	0.90 × 0.87 × 0.58	0.40 × 0.20 × 0.20
θ Range for data collection/°	2.54–25.05	1.74–26.05
Reflections collected	4633	15 775
Independent reflections	4633	6537
R_{int}	No reflections to be merged	0.0509
Reflections with $[I > 2\sigma(I)]$	3949	5502
Absorption correction	ψ Scans	Analytical
Maximum, minimum transmission	0.682, 0.600	0.775, 0.706
Decay correction (%)	9.1	None
Data, restraints, parameters	4633, 0, 386	6532, 0, 553
Final $R1$, $wR2$ $[I > 2\sigma(I)]$	0.0388, 0.0839	0.0581, 0.1198
(all data)	0.0512, 0.0949	0.0728, 0.1302
Goodness of fit on F^2	1.161	1.196
Final $(\Delta/\sigma)_{max}$	0.037	0.003
Largest residual peaks/e Å^{-3}	0.57, −0.66	0.44, −0.44

* Details in common: 150(2) K; Mo-Kα radiation (λ 0.710 73 Å); monoclinic, space group $C2/c$; $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$; goodness of fit $= [\Sigma w(F_o^2 - F_c^2)^2/(N_{obs} - N_{param})]^{\frac{1}{2}}$ (based on all data).

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/446.

Acknowledgements

We thank the University of Nottingham for a demonstratorship (to P. E. C.), the EPSRC for a studentship (to S. C. D.) and use of the X-Ray Crystallography Service (Cardiff), the Royal Society for an equipment grant and Professor J. A. K. Howard (Durham) for the use of X-ray crystallographic facilities. We also acknowledge the use of the EPSRC's Chemical Database Service at Daresbury.

References

1 D. E. Wigley, *Prog. Inorg. Chem.*, 1994, **42**, 239.
2 W. A. Nugent and J. M. Mayer, *Metal–Ligand Multiple Bonds*, Wiley-Interscience, New York, 1988.
3 W. A. Nugent and B. L. Haymore, *Coord. Chem. Rev.*, 1980, **31**, 123.
4 V. C. Gibson, *Adv. Mater.*, 1994, **6**, 37.
5 J. E. Hill, R. D. Profilet, P. E. Fanwick and I. P. Rothwell, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 664.
6 H. W. Roesky, H. Voelker, M. Witt and M. Noltemeyer, *Angew. Chem., Int. Eng. Engl.*, 1990, **29**, 669.
7 S. C. Dunn, A. S. Batsanov and P. Mountford, *J. Chem. Soc., Chem. Commun.*, 1994, 2007.
8 P. Mountford and D. Swallow, *J. Chem. Soc., Chem. Commun.*, 1995, 2357.
9 K. A. Butakoff, D. A. Lemenovskii, P. Mountford, L. G. Kuz'mina and A. V. Churakov, *Polyhedron*, 1996, **15**, 489.
10 S. C. Dunn, P. Mountford and O. V. Shishkin, *Inorg. Chem.*, 1996, **35**, 1006.
11 S. C. Dunn, P. Mountford and D. A. Robson, *J. Chem. Soc., Dalton Trans.*, 1997, 293.
12 P. E. Collier, S. C. Dunn, P. Mountford, O. V. Shishkin and D. Swallow, *J. Chem. Soc., Dalton Trans.*, 1995, 3743.
13 R. T. Cowdell and G. W. A. Fowles, *J. Chem. Soc.*, 1960, 2522.
14 A. J. Nielson, *Inorg. Chim. Acta*, 1988, **154**, 177.
15 T. S. Lewkebandara, P. H. Sheridan, M. J. Heeg, A. L. Rheingold and C. H. Winter, *Inorg. Chem.*, 1994, **33**, 5879.
16 R. Mason and A. D. C. Towl, *J. Chem. Soc. A*, 1970, 1601.
17 J. K. Burdett and T. A. Albright, *Inorg. Chem.*, 1979, **18**, 2112.
18 D. Bright and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 709.
19 E. M. Shustorovich, M. A. Porai-Koshits and Y. A. Buslaev, *Coord. Chem. Rev.*, 1975, **17**, 1.
20 K. Dehnicke and J. Strähle, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 413.
21 W. P. Griffith, A. J. Nielson and M. J. Taylor, *J. Chem. Soc., Dalton Trans.*, 1988, 647.
22 J. H. Osborne, A. L. Rheingold and W. C. Trogler, *J. Am. Chem. Soc.*, 1985, **107**, 7945.
23 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 4th edn., 1986.
24 P. E. Collier, A. J. Blake and P. Mountford, unpublished work.
25 C. H. Winter, P. H. Sheridan, T. S. Lewkebandara, M. J. Heeg and J. W. Proscia, *J. Am. Chem. Soc.*, 1992, **114**, 1095.
26 R. Duchateau, A. J. Williams, S. Gambarotta and M. Y. Chiang, *Inorg. Chem.*, 1991, **30**, 4863.
27 H. W. Roesky, T. Raubold, M. Witt, R. Bohra and M. Noltemeyer, *Chem. Ber.*, 1991, **124**, 1521.
28 H. Burger and U. Wannagat, *Monatsh. Chem.*, 1963, **94**, 761.
29 D. J. Arney, M. A. Bruck, S. R. Huber and D. E. Wigley, *Inorg. Chem.*, 1992, **31**, 3749.
30 M. P. Coles, C. I. Dalby, V. C. Gibson, W. Clegg and M. R. J. Elsegood, *Polyhedron*, 1995, **14**, 2455.
31 A. Bell, W. Clegg, P. W. Dyer, M. R. J. Elsegood, V. C. Gibson and E. L. Marshall, *J. Chem. Soc., Chem. Commun.*, 1994, 2247.
32 A. Bell, W. Clegg, P. W. Dyer, M. R. J. Elsegood, V. C. Gibson and E. L. Marshall, *J. Chem. Soc., Chem. Commun.*, 1994, 2547.
33 R. I. Michelman, R. G. Bergman and R. A. Andersen, *Organometallics*, 1993, **12**, 2741.
34 D. S. Glueck, J. Wu, F. J. Hollander and R. G. Bergman, *J. Am. Chem. Soc.*, 1991, **113**, 2041.
35 P. D. Lyne and D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1995, 1635.
36 P. D. Lyne and D. M. P. Mingos, *J. Organomet. Chem.*, 1994, **478**, 141.
37 R. C. B. Copley, P. W. Dyer, V. C. Gibson, J. A. K. Howard, E. L. Marshall, W. Wang and B. Whittle, *Polyhedron*, 1996, **15**, 3001.
38 W. Clegg, R. J. Errington, D. C. R. Hockless and C. Redshaw, *J. Chem. Soc., Dalton Trans.*, 1993, 1965.
39 D. Bright and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 703.
40 D. Bright and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 1099.

41 C. Y. Chou, J. C. Huffman and E. A. Maatta, *Inorg. Chem.*, 1986, **25**, 822.

42 D. C. Bradley, R. J. Errington, M. B. Hursthouse and R. L. Short, *J. Chem. Soc., Dalton Trans.*, 1990, 1043.

43 B. R. Ashcroft, G. R. Clark, A. J. Nielson and C. E. F. Rickard, *Polyhedron*, 1986, **5**, 2081.

44 W. Clegg and R. J. Errington, *Acta Crystallogr., Sect. C*, 1987, **43**, 2223.

45 K. Stahl, F. Weller, K. Dehnicke and P. Paetzold, *Z. Anorg. Allg. Chem.*, 1986, **534**, 93.

46 A. Bell, personal communication cited in ref. 1.

47 D. N. Williams, J. P. Mitchell, A. D. Poole, U. Siemeling, W. Clegg, D. C. R. Hockless, P. A. O'Neil and V. C. Gibson, *J. Chem. Soc., Dalton Trans.*, 1992, 739.

48 G. H. Stout and L. H. Jensen, *X-Ray Structure Determination*, Wiley, Toronto, 2nd edn., 1989.

49 J. Chatt, J. D. Garforth, N. P. Johnson and G. A. Rowe, *J. Chem. Soc.*, 1964, 1012.

50 F. H. Allen and O. Kennard, *Chem. Design Autom. News*, 1993, **8**, 1.

51 D. A. Fletcher, R. F. McMeeking and D. Parkin, *J. Chem. Inf. Comput. Sci.*, 1996, **36**, 746.

52 A. Bodner, P. Jeske, T. Weyhermüller, K. Wieghardt, E. Dubler, H. Schmalle and B. Nuber, *Inorg. Chem.*, 1992, **31**, 3737.

53 P. Jeske, G. Haselhorst, T. Weyhermüller, K. Wieghardt and B. Nuber, *Inorg. Chem.*, 1994, **33**, 2462.

54 J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105.

55 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.

56 G. M. Sheldrick, SHELXL 96, Institut für Anorganische Chemie der Universität Göttingen, 1996.

Received 14*th November* 1996; *Paper* 6/07735H