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Cyclopentadienyl, indenyl and bis(cyclopentadienyl) titanium imido compounds†

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The titanium *tert*-butyl imido compounds $[Ti(NBu^t)Cl_2(NC_5H_4R\text{-}4)_n]$ (R = H, n = 2 or 3; R = Bu^t, n = 2) have been found to be entry points to the half-sandwich η^5-cyclopentadienyl derivatives $[Ti(\eta^5\text{-}C_5R'_4R'')(NBu^t)Cl(NC_5H_4R\text{-}4)]$ (R = Bu^t, R′ = R″ = H or Me; R = H, R′ = H, R″ = H, Me or Pr^i; R = H, R′ = Me, R″ = Me, Et or C_4H_7), the η^5-1,2,3-trimethylindenyl species $[Ti(\eta^5\text{-}C_9H_4Me_3)(NBu^t)Cl(NC_5H_4Bu^t\text{-}4)]$ and the bis(η^5-cyclopentadienyl) compound $[Ti(\eta^5\text{-}C_5H_5)_2(NBu^t)(NC_5H_5)]$, the crystal structure of which has been determined. The complex $[Ti(\eta^5\text{-}C_5H_5)(NBu^t)Cl(NC_5H_5)]$ readily loses pyridine under vacuum in the solid state to form the binuclear complex $[Ti_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}NBu^t)_2Cl_2]$. Treatment of $[Ti(\eta^5\text{-}C_5Me_4R)(NBu^t)Cl(NC_5H_5)]$ (R = Me or Et) with $Na[C_5H_5]$ gives the corresponding mixed-ring sandwich derivatives $[Ti(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_4R)(NBu^t)Cl(NC_5H_5)]$. Addition of $Li[C_9H_7]$ to $[Ti(\eta^5\text{-}C_5H_5)(NBu^t)Cl(NC_5H_5)]$ gave the η^5-cyclopentadienyl, η^3-indenyl mixed-ring analogue $[Ti(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_9H_7)(NBu^t)(NC_5H_5)]$. The complex $[Ti(\eta^5\text{-}C_5H_5)_2(NBu^t)(NC_5H_5)]$ undergoes a room-temperature cyclopentadienyl ligand-redistribution reaction with $[Ti(NBu^t)Cl_2(NC_5H_5)_2]$ forming $[Ti(\eta^5\text{-}C_5H_5)(NBu^t)Cl(NC_5H_5)]$ in quantitative yield. Variable-temperature NMR spectra for the half-sandwich complexes show that the co-ordinated pyridine exchanges with free pyridine *via* an associative mechanism. The compound $[Ti(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_4Et)(NBu^t)(NC_5H_5)]$ is also fluxional and exhibits reversible pyridine dissociation at higher temperatures and restricted rotation about the Ti–N (pyridine) bond at lower temperatures.

Transition-metal imido chemistry in general has undergone an impressive expansion during recent years,[1–3] particularly for Group 4. Terminal zirconium imido complexes were only first reported in 1988[4,5] and terminal titanium imido complexes were first structurally characterised in 1990.‡[,7,8] Group 4 compounds containing bridging imide ligands are also very well known,[9–18] but it is only the terminal M=NR (M = Group 4 metal, R = organic fragment) linkage§ which is able to demonstrate extremely high chemical reactivity such as C–H bond activation[4,5,19–22] and N–C bond-forming reactions with unsaturated substrates.[4,23–28]

This paper describes the synthesis and characterisation of a range of monomeric sandwich and half-sandwich terminal titanium imido complexes. Half-sandwich terminal zirconium and hafnium imido complexes have been described recently,[16,29] and Bergman and co-workers[20,25,30–32] have achieved considerable success in exploiting the bis(η^5-cyclopentadienyl) fragment as a coligand environment in zirconium imido chemistry. Two monomeric half-sandwich terminal titanium imido complexes $[Ti(\eta^5\text{-}C_5R_n)(NBu^t)Cl(NC_5H_5)]$ ($C_5R_n = C_5H_4SiMe_3$ or C_5Me_5) have recently been prepared by dehydrohalogenation of primary amido dichloride precursors in the presence of pyridine.[33] Bis(η^5-cyclopentadienyl)titanium vinyl imido derivatives of the type $[Ti(\eta^5\text{-}C_5H_5)_2\{=NC(R)=CH_2\}L]$ (R = Bu^t or adamantyl; L = N- or P-atom donor Lewis base) have been prepared by treating titanocene methylidene sources (such as Tebbe's reagent) with nitriles.[26,27]

As part of our continuing studies of Group 4 imido chemistry,[28,34–40] we have demonstrated that the readily available titanium *tert*-butylimido complexes $[Ti(NBu^t)Cl_2(NC_5H_4Bu^t\text{-}4)_2]$[34] and $[Ti(NBu^t)Cl_2(NC_5H_5)_n]$ (n = 2 or 3)[39] are valuable entry points to new classes of titanium imido complex through simple metathetical reactions.[34,36,37] We now report a unified synthetic approach to η^5-cyclopentadienyl, η^5-indenyl, bis(η^5-cyclopentadienyl), mixed-ring bis(η^5-cyclopentadienyl) and η^5-cyclopentadienyl, η^3-indenyl terminal titanium imido complexes. Part of this work has been communicated.§[,34]

Results and Discussion

Synthesis of half-sandwich η^5-cyclopentadienyl and η^5-1,2,3-trimethylindenyl titanium imido compounds

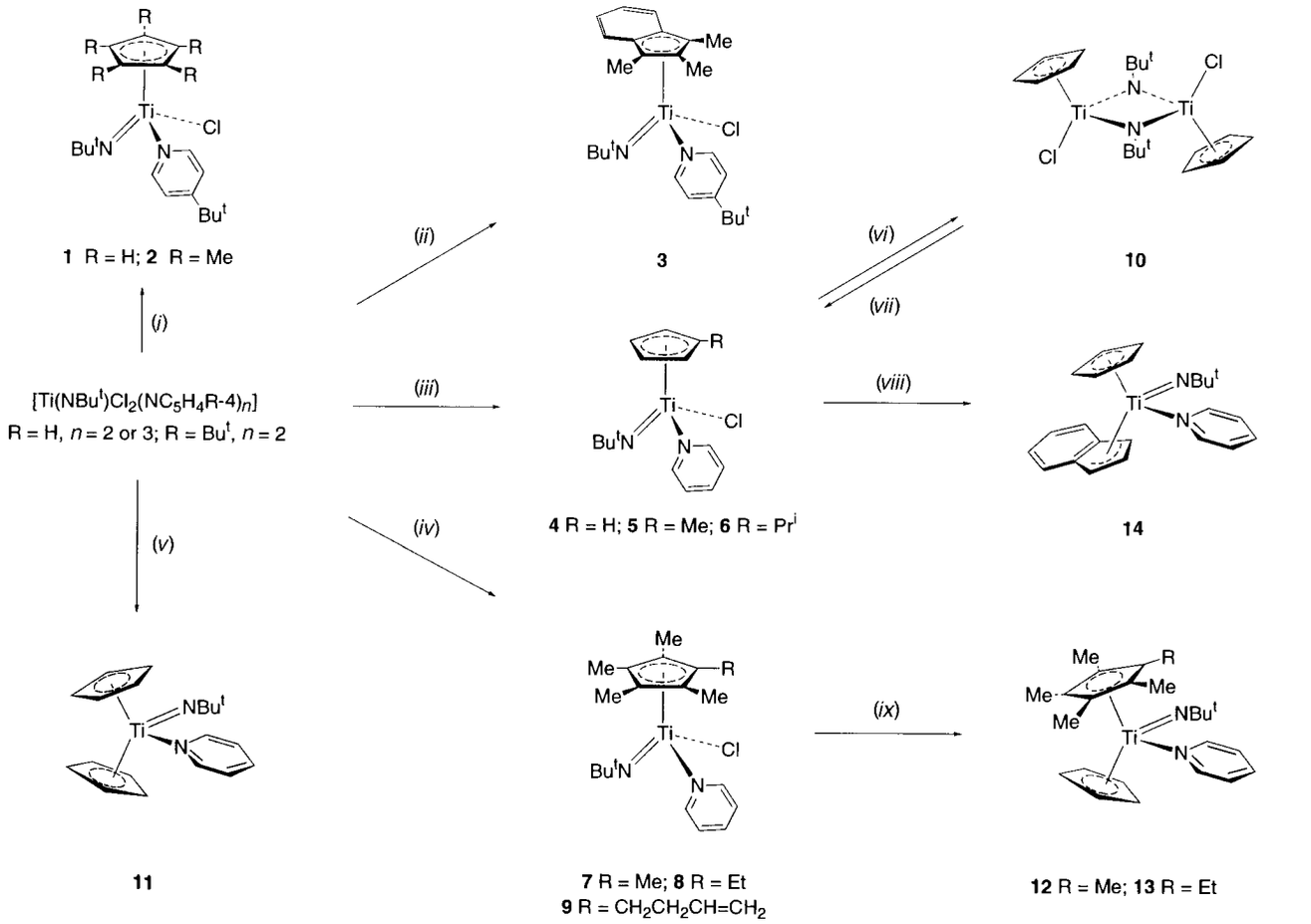
Treatment of $[Ti(NBu^t)Cl_2(NC_5H_4Bu^t\text{-}4)_2]$[34] with 1 equivalent of $Na[C_5H_5]$ or $Li[C_5Me_5]$ in tetrahydrofuran (thf) followed by recrystallisation from alkane solutions at −25 °C afforded the new compounds $[Ti(\eta^5\text{-}C_5R_5)(NBu^t)Cl(NC_5H_4\text{-}Bu^t\text{-}4)]$ (R = H **1** or Me **2**) in *ca.* 50% isolated yield. The structures proposed for all the complexes prepared in this study are shown in Scheme 1 and their characterising data are given in the Experimental section. The red, air- and moisture-sensitive compounds **1** and **2** are very soluble in pentane and hexane. They are assigned monomeric structures by analogy with the structurally characterised[33] pyridine-substituted homologue $[Ti(\eta^5\text{-}C_5Me_5)(NBu^t)Cl(NC_5H_5)]$ **7** (independently prepared in this study, see below), and by comparison of the NMR and IR spectra of **1** and **2** with those of **7**. For example, the IR spectra of **1**, **2** and **7** all show strong bands in the 1230–1260 cm^{-1} region. We have found such absorptions to be empirically diagnostic of terminal Ti=NBu^t linkages. The assignment of these bands to either ν(Ti=N) or ν(N–C), or to a combination of the two modes, is not clear and there is continuing literature debate concerning the assignment of metal–imido group vibrational spectra.[41–43]

We also wished to prepare a half-sandwich indenyltitanium imido derivative. Thus treatment of $[Ti(NBu^t)Cl_2(NC_5H_4\text{-}Bu^t\text{-}4)_2]$ with $Li[C_9H_4Me_3]$[44] ($C_9H_4Me_3$ = 1,2,3-trimethyl-

† *Non-SI unit employed*: bar = 10^5 Pa.

‡ It is possible that the compound $[Ti(NSiMe_3)Cl_2(NC_5H_5)_2]$ described in 1963 contained the first terminal Ti=NSiMe$_3$ linkage.[6]

§ Although for ease of representation all titanium–imido linkages are drawn 'Ti=NR', the formal Ti–N bond order in the complexes $[Ti(NBu^t)Cl_2(NC_5H_4R\text{-}4)_n]$ and $[Ti(\eta\text{-ring})(NBu^t)Cl(NC_5H_4R\text{-}4)]$ is generally best thought of as three (pseudo-$\sigma^2\,\pi^4$ triple bond) rather than as two.[3] The difficulties associated with assigning a formal bond order to the imido linkage in the bis(η^5-cyclopentadienyl) complexes are addressed later.



Scheme 1 Synthesis of cyclopentadienyl and indenyl sandwich and half-sandwich titanium imido complexes. Reagents and conditions: (*i*) for **1**, $Na[C_5H_5]$, thf, room temperature (r.t.), 4 h, yield 48%; for **2**, $Li[C_5Me_5]$, thf, −45 °C then r.t., 10 h, 46%; (*ii*) $Li[C_9H_4Me_3]$, thf, −50 °C then r.t., 19 h, 37%; (*iii*) for **4**, $Na[C_5H_5]$, thf, 3 h, 75%; for **5**, $Li[C_5H_4Me]$, thf, −45 °C then r.t., 12 h, 32%; for **6**, $Li[C_5H_4Pr^i]$, thf, −45 °C then r.t., 12 h, 56%; (*iv*) for **7**, $Li[C_5Me_5]$, thf, −45 °C then r.t., 12 h, 70%; for **8**, $Li[C_5Me_4Et]$, thf, −45 °C then r.t., 12 h, 37%; for **9**, $Li[C_5Me_4(C_4H_7)]$, thf, −50 °C then r.t., 14 h, >95%; (*v*) 2 $Na[C_5H_5]$, thf, r.t., 5 h, 41%; (*vi*) 1×10^{-2} mbar, 85 °C, 14 h, *ca.* 100%; (*vii*) NC_5H_5 (3 equivalents), $CDCl_3$, 7 d, >95%; (*viii*) $Li[C_9H_7]$, thf, −45 °C then r.t., 12 h, 47%; (*ix*) $Na[C_5H_5]$, thf, r.t., 12 h, 11 (**12**) and 16% (**13**)

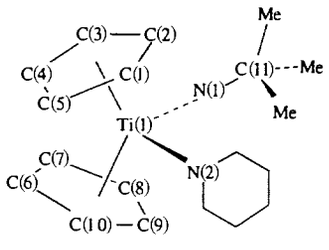
indenyl) gave the compound $[Ti(\eta^5\text{-}C_9H_4Me_3)(NBu^t)Cl(NC_5H_4Bu^t\text{-}4)]$ **3** in 37% yield. Compound **3** is the first example of a monomeric Group 4 indenyl–imido complex. A binuclear, base-free species $[Ti_2(\eta^5\text{-}C_9H_7)_2(\mu\text{-}NMe)_2Cl_2]$ (C_9H_7 = indenyl) has very recently been described.[45] Our attempts to synthesize a ring non-methylated analogue of **3** were unsuccessful. In accordance with the proposed structure, the three diastereotopic Me groups and four ring H atoms of the prochiral $\eta^5\text{-}C_9H_4Me_3$ ligand in **3** each give rise to individual resonances in the ^{1}H NMR spectrum. For mid to late transition-metal complexes, low-field chemical shifts (*i.e.* downfield of *ca.* 130 ppm) of the bridgehead quaternary carbon atoms of an indenyl ligand are indicative of a trihapto co-ordination mode,[46–51] and their chemical shift may give an indication of the degree of folding of the indenyl ligand.[52,53] Unfortunately, there are relatively few published ^{13}C NMR data for Group 4 transition-metal indenyl complexes. However, those data that are available for crystallographically characterised examples suggest that the chemical shifts of bridgehead carbon atoms in pentahapto-co-ordinated indenyl and ring-methylated indenyl ligands usually appear in the δ 127–136 region.[54–56] For **3** the bridgehead ^{13}C chemical shifts are δ 130.7 and/or 126.1. While these values could, in principal, be equally consistent with either a tri- or penta-hapto co-ordination mode, we favour the latter by analogy with the η^5-cyclopentadienyl complexes and the resultant 16-valence-electron count.

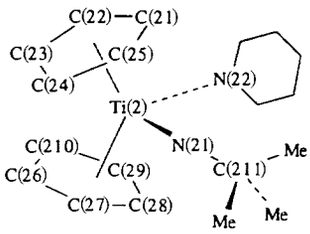
The high solubility of the cyclopentadienyl complexes **1**–**3** and occasional difficulties in removing the poorly volatile $NC_5H_4Bu^t$-4 ligand from reaction product mixtures prompted us to prepare the unsubstituted pyridine homologues. Suitable starting materials are the bis- and tris-(pyridine) titanium imido dichlorides, $[Ti(NBu^t)Cl_2(NC_5H_5)_n]$ ($n = 2$ or 3), readily available in multigram quantities.[39] Simple treatment of thf solutions of these complexes with sodium or lithium cyclopenpentadienides afforded $[Ti(\eta^5\text{-}C_5R_4R')(NBu^t)Cl(NC_5H_5)]$ (R = H, R′ = H **4**, Me **5** or Pr^i **6**; R = Me, R′ = Me **7**, Et **8** or C_4H_7 **9**) in 32 to >95% yield. Complex **7** has been described previously.[33]

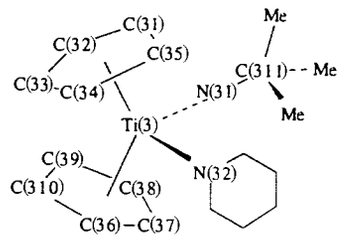
The half-sandwich derivatives **1**–**9** are isoelectronic with the hydrotris(pyrazolyl)borate complexes $[TiL(NBu^t)Cl(NC_5H_4Bu^t\text{-}4)]$ [L = tris(3,5-dimethylpyrazolyl)hydroborate, hydrotris(3-isopropylpyrazolyl)borate or tris(4-bromo-3-isopropylpyrazolyl)hydroborate] which are fluxional on the ^{1}H and ^{13}C NMR time-scales, the spectra indicating restricted rotation about the Ti–N (pyridine) bond.[37] The 213 K ^{1}H NMR spectrum of $[Ti(\eta^5\text{-}C_5Me_5)(NBu^t)Cl(NC_5H_4Bu^t\text{-}4)]$ **2** in CD_2Cl_2, however, showed no evidence for restricted rotation, an observation consistent with the lesser steric demands of the $\eta^5\text{-}C_5Me_5$ ligand as compared with the hydrotris(pyrazolyl)borates.[57,58]

The cyclopentadienyl ring mono- or non-substituted complexes **4**–**6** tend to lose pyridine to give binuclear products. For example, heating a sample of **4** at 85 °C for 14 h under a dynamic vacuum gave quantitative conversion into the base-free dimer $[Ti_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}NBu^t)_2Cl_2]$ **10**[11] to which we assign the *trans* geometry shown in Scheme 1 by analogy with the crystallographically characterised analogue $[Ti_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}NPh)_2Cl_2]$.[11] The IR spectrum of **10** does not show a band in the 1230–1260 cm^{-1} region consistent (see below) with the

Table 1 Selected bond lengths (Å) and angles (°) for $[Ti(\eta^5\text{-}C_5H_5)_2(NBu^t)(NC_5H_5)]$ **11**. The line drawings indicate the respective numbering schemes for the three crystallographically independent molecules. See text for further details







Ti(1)–N(1)	1.71(1)	Ti(2)–N(21)	1.73(1)	Ti(3)–N(31)	1.730(9)
Ti(1)–N(2)	2.22(2)	Ti(2)–N(22)	2.22(2)	Ti(3)–N(32)	2.32(2)
Ti(1)–C(1)	2.71(2)	Ti(2)–C(21)	2.52(3)	Ti(3)–C(31)	2.44(2)
Ti(1)–C(2)	2.67(2)	Ti(2)–C(22)	2.76(3)	Ti(3)–C(32)	2.51(2)
Ti(1)–C(3)	2.65(2)	Ti(2)–C(23)	2.86(3)	Ti(3)–C(33)	2.55(2)
Ti(1)–C(4)	2.67(2)	Ti(2)–C(24)	2.69(3)	Ti(3)–C(34)	2.52(2)
Ti(1)–C(5)	2.71(2)	Ti(2)–C(25)	2.49(3)	Ti(3)–C(35)	2.44(2)
Ti(1)–C(6)	2.72(2)	Ti(2)–C(26)	2.42(3)	Ti(3)–C(36)	2.47(2)
Ti(1)–C(7)	2.66(2)	Ti(2)–C(27)	2.32(3)	Ti(3)–C(37)	2.32(2)
Ti(1)–C(8)	2.48(2)	Ti(2)–C(28)	2.46(3)	Ti(3)–C(38)	2.31(2)
Ti(1)–C(9)	2.42(2)	Ti(2)–C(29)	2.64(3)	Ti(3)–C(39)	2.45(2)
Ti(1)–C(10)	2.58(2)	Ti(2)–C(210)	2.62(3)	Ti(3)–C(310)	2.55(2)
N(1)–C(11)	1.43(1)	N(21)–C(211)	1.46(1)	N(31)–C(311)	1.45(1)
Ti(1)–Cp(1)*	2.37	Ti(3)–Cp(21)*	2.34	Ti(3)–Cp(31)*	2.16
Ti(1)–Cp(2)*	2.24	Ti(3)–Cp(22)*	2.15	Ti(3)–Cp(32)*	2.06
N(1)–Ti(1)–N(2)	93.6(12)	N(21)–Ti(2)–N(22)	102.5(13)	N(31)–Ti(3)–N(32)	92.0(10)
Ti(1)–N(1)–C(11)	161.6(21)	Ti(2)–N(21)–C(211)	167.6(21)	Ti(3)–N(31)–C(311)	165.3(4)
Cp(1)–Ti(1)–Cp(2)	133.7	Cp(21)–Ti(22)–Cp(22)	108.3	Cp(31)–Ti(3)–Cp(32)	122.0

* Cp(1), Cp(2), Cp(21), Cp(22), Cp(31) and Cp(32) refer to the computed centroids for the ring carbons C(1)–C(5), C(6)–C(10), C(21)–C(25), C(26) to C(210), C(31)–C(35) and C(36) to C(310) respectively.

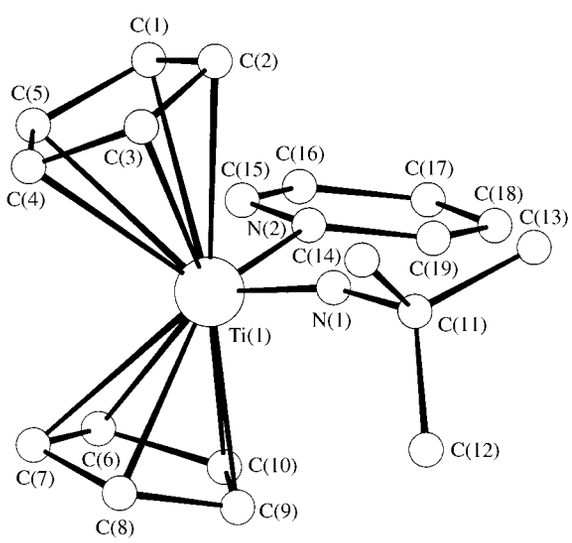


Fig. 1 A CAMERON[59] plot of one of the three crystallographically independent molecules of $[Ti(\eta\text{-}C_5H_5)_2(NBu^t)(NC_5H_5)]$ **11**. Hydrogen atoms omitted for clarity

absence of a terminal Ti=NBu^t moiety. The NMR tube experiments show that pyridine loss also occurs slowly in solution but that the dimerisation process is reversible. Thus addition of 5 equivalents of pyridine to pure **10** in $CDCl_3$ at room temperature gave quantitative conversion into mononuclear **4** after 1 week. Attempts to prepare a binuclear η^5-pentamethylcyclopentadienyl analogue $[Ti_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}NBu^t)_2Cl_2]$ from **7** were unsuccessful. Roesky and co-workers[18] recently suggested that the reaction of $[Ti_2(\eta^5\text{-}C_5H_4Me)_2(\mu\text{-}NPh)_2Cl_2]$ with $SnMe_3F$ to form $[Ti_2(\eta^5\text{-}C_5H_4Me)_2(\mu\text{-}NPh)_2F_2]$ is catalysed by pyridine, presumably *via in situ* generation of monomeric $[Ti(\eta^5\text{-}C_5H_4Me)(NPh)Cl(NC_5H_5)]$.

Syntheses of sandwich bis(η^5-cyclopentadienyl), mixed-ring bis(η^5-cyclopentadienyl) and η^5-cyclopentadienyl, η^3-indenyl titanium imido compounds

Treatment of $[Ti(NBu^t)Cl_2(NC_5H_5)_3]$ with 2 equivalents of $Na[C_5H_5]$ afforded red crystals of $[Ti(\eta^5\text{-}C_5H_5)_2(NBu^t)(NC_5H_5)]$ **11** in 41% isolated yield after standard work-up. The crystal structure has been determined and the crystals contain three independent molecules of **11** in the asymmetric unit. The molecular structure of one of them is shown in Fig. 1, and selected bond lengths and angles are listed in Table 1 together with line drawings describing the numbering schemes.

Owing to pseudo-translational symmetry in the crystals of complex **11** the data were relatively weak and a satisfactory refinement was only possible through the use of 'rigid-body' approximations for the $\eta^5\text{-}C_5H_5$ ligands and similarity restraints on the bond lengths and angles of the {Ti=N–Bu^t} units (see the Experimental section for further details). The $\eta^5\text{-}C_5H_5$ rings were, however, allowed to move freely during refinement and so the principal features of the Ti–($\eta^5\text{-}C_5H_5$) interactions can be assessed. While the necessary use of restraints will mean that individual bond lengths and angles associated with the three {Ti=N–Bu^t} moieties may tend to be 'smoothed out' over the three independent molecules, the ranges for these values will be meaningful.

The crystal structure of $[Ti(\eta^5\text{-}C_5H_5)_2(NBu^t)(NC_5H_5)]$ **11** confirms that proposed in Scheme 1. In two of the molecules the cyclopentadienyl rings are best described as mutually eclipsed, in the third they are approximately staggered. The average angle subtended at the imido nitrogen atom is *ca.* 165° consistent with the NBu^t ligand being able to act as a four-electron donor according to hybridisation theory.[3] The Ti=N bond length (average *ca.* 1.723 Å over the three molecules) lies at the long end of the range of Ti=NBu^t bond lengths [1.662(4)–1.722(4) Å for a wide variety of ancilliary ligand environments].[3,34,36,37,60] The cyclopentadienyl ligand carbon to

titanium distances approximately *trans* to the NBu^t ligand in all three molecules are substantially lengthened compared to the other Ti–C distances within the same ring, consistent with the well known *trans* influence of the imide ligand.[2,36,61] A search of the Cambridge Structural Database (using the QUEST program[62]) showed that for **11** the average Ti–C bond length (*ca.* 2.56 Å over the three molecules), titanium–ring centroid distance (average *ca.* 2.22 Å) and ring centroid–titanium–ring centroid angle (average *ca.* 121°) are substantially different to those usually found in titanium(IV) pseudo-four-co-ordinate bis(η^5-cyclopentadienyl) derivatives of the type [Ti(η^5-C_5H_5)$_2$X$_2$] (*e.g.* X = Cl, SR or OR)[63–66] where the ranges of average values are Ti–C 2.36–2.40 Å, titanium–ring centroid 2.03–2.08 Å and ring-centroid to Ti to ring-centroid angle 128–133°. Relatively long Ti–C distances have also been found in the isoelectronic oxo complex [Ti(η^5-C_5Me_5)$_2$O{NC_5H_4(C_5H_6)-4}].[67]

The ^{1}H and ^{13}C NMR spectra of complex **11** are consistent with the solid-state structure assuming a negligible activation energy barrier to rotation about the Ti–N (pyridine) bond. The ^{1}H NMR spectrum at −70 °C showed no evidence for inequivalence of the η-C_5H_5 ligands or pyridine *o*- and *m*-protons. The isoelectronic vanadium complexes [V(η^5-C_5H_5)(η^1-C_5H_5)(NBu^t)X] (X = NHBu^t or OBu^t)[68,69] are fluxional in solution at room temperature and the latter shows a time-averaged bis(η^5-cyclopentadienyl) structure at high temperature.[68]

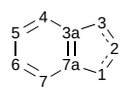
Compound **11** is, at first sight, a twenty-valence-electron complex. In principle, the two η^5-C_5H_5 rings (each providing one σ and two π donor orbitals) may contribute ten electrons, the approximately linear, sp-hybridised NBu^t (providing one σ and two π donor orbitals) may donate four electrons, and pyridine donates two electrons. It is likely that the relatively long Ti=NBu^t bond and somewhat distorted titanium–cyclopentadienyl ligand interactions are a consequence of the excess of ligand π-donor orbitals (six in total) compared with the available metal π-acceptor orbitals (five in total). Analogous bonding conflicts have been well studied by crystallographic, theoretical and spectroscopic techniques in a number of imido- and oxo-bis(η-cyclopentadienyl)[70–74] and tris(imido) 'π-loaded',[75–77] as well as for binuclear homoleptic imido[77] and imido–(η-cyclopentadienyl)[78] complexes. A general group-theoretical analysis of metal–ligand multiply bonded complexes has recently been reported.[79]

Consider the tris(imido) complexes [Re(NR)$_3$X] (R = Bu^t or aryl, X = one-electron donor).[3] These are not genuine twenty-valence-electron complexes because (by symmetry) the a_2 π-donor symmetry-adapted linear combination of the {NR}$_3$ fragment has no match among the metal orbitals and thus forms a ligand-based, non-bonding lone pair in the resultant complex.[79] The formal Re=NR bond order in these complexes is therefore 2.67. The complex [Ti(η^5-C_5H_5)$_2$(NBu^t)(NC_5H_5)] **11** is isoelectronic and isolobal[80,81] with [Re(NR)$_3$X] but symmetry does not tell us the relative donor abilities (and hence bond orders to Ti) of the η^5-C_5H_5 and NBu^t ligands. We must therefore use crystallographic and chemical reactivity studies to interpret the relative significance of these groups' interactions with the Ti. From the studies described here we propose that the Ti=NBu^t bond order in **11** lies between two and three as suggested for other imido- and oxo-bis(η-cyclopentadienyl) metal complexes.[70–74]

We have also prepared mixed-ring bis(η^5-cyclopentadienyl) analogues of complex **11**. Thus treatment of the half-sandwich complexes [Ti(η^5-C_5Me_4R)(NBu^t)Cl(NC_5H_5)] (R = Me **7** or Et **8**) with Na[C_5H_5] afforded modest isolated yields of the corresponding sandwich products [Ti(η^5-C_5H_5)(η^5-C_5Me_4R)(NBu^t)(NC_5H_5)] (R = Me **12** or Et **13**). The ^{1}H and ^{13}C NMR spectra of **12** and **13** are consistent with structures analogous to that of **11**; the variable-temperature ^{1}H NMR spectra for **13** are described below. Attempts to prepare the complexes **12** or **13** by treating the ring non-substituted half-sandwich complex [Ti(η^5-C_5H_5)(NBu^t)Cl(NC_5H_5)] **4** with Li[C_5Me_4R] (R = Me or Et) were unsuccessful and only unidentified paramagnetic complexes were produced. Similarly, attempts to prepare a bis(η^5-C_5Me_5) titanium imido complex from **7** and Li[C_5Me_5] at low temperature gave only green solutions indicative of reduction from Ti^{IV} to Ti^{III}.

Mixed-ring analogues of titanocene dichloride have been known for some time.[82,83] Interestingly, some of these preparations {from the corresponding half-sandwich compounds [Ti(η^5-C_5R_5)Cl$_3$] and an anionic ring-transfer reagent} give rise to ring-scrambled mixtures. We have not encountered analogous problems in our preparations of mixed-ring titanium imido complexes.

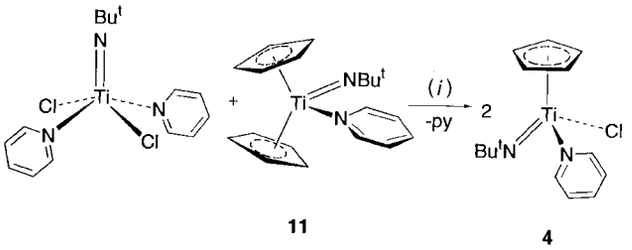
Treatment of cold thf solutions of [Ti(η-C_5H_5)(NBu^t)-Cl(NC_5H_5)] **4** with 1 equivalent of Li[C_9H_7] gave the mixed-ring η^5-cyclopentadienyl, η^3-indenyl titanium imido species [Ti(η^5-C_5H_5)(η^3-C_9H_7)(NBu^t)(NC_5H_5)] **14** in 47% isolated yield. Attempts to synthesize η^3-allyl analogues were unsuccessful. The structure of **14** was assigned from its ^{1}H, ^{13}C and ^{1}H–^{13}C correlation NMR spectra. The indenyl ligand numbering scheme is shown below. The NC_5H_5, η^5-C_5H_5 and NBu^t ligands



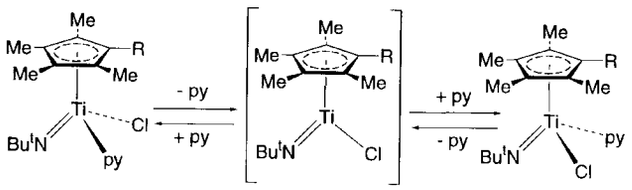
in **14** give rise to the expected NMR resonances with chemical shifts and coupling constants comparable to those of other titanium imido complexes described herein. The prochiral indenyl ligand gives rise to seven individual resonances in the ^{1}H NMR spectrum and to eight resonances (two signals overlapping) in the ^{13}C NMR spectrum, as would be expected from the proposed structure of **14** which does not contain a mirror plane. Significantly, the resonance for the ring proton in the indenyl ligand 2 position (*i.e.* H^2) appears to low field (δ 7.95–7.85) of the 4- to 7-protons, while H^1 and H^3 appear to high field (δ 6.05 and 5.51). These features are diagnostic of trihapto co-ordinated indenyl ligands[47–50] and may be contrasted with the ^{1}H NMR literature data for [Ti(η^5-C_5H_5)(η^5-C_9H_7)Cl$_2$][82] and [Ti(η^5-C_9H_7)Cl$_2$X] (X = Cl, OMe or Me, all crystallographically characterised)[54,55,84] in which all of the three resonances H^1, H^2 and H^3 appear to higher field of H^4–H^7. In the ^{13}C NMR spectrum of **14** the C^2 (δ 124.5) and C^1 and C^3 (δ 102.1 and 90.3) resonances are well separated as is found for other η^3-C_9H_7 derivatives. We note also that the bridghead (C^{3a} and C^{7a}) resonances appear to somewhat lower field (δ 140.5 and 135.4) of the corresponding signals in the η^5-indenyltitanium complexes [Ti(η^5-C_9H_7)Cl$_2$X] (X = Cl, OMe or Me).[54,55] Taken together, these ^{1}H and ^{13}C NMR features are highly supportive of a 'ring-slipped' η^3-indenyl ligand in **14**.

The trihapto co-ordination of the indenyl ligand in complex **14** is consistent with the strong π-donor ability of the NBu^t ligand which presumably forms a full triple bond to Ti in this complex. A related η^5-cyclopentadienyl, η^3-indenyl molybdenum imido complex has recently been described.[47] Mixed-ring complexes containing an η^3-indenyl moiety have recently been crystallographically characterised.[85–87]

The sandwich complexes **11**–**14** are considerably more sensitive to air and moisture than their half-sandwich analogues. Furthermore, whereas the half-sandwich complexes are stable in $CDCl_3$ solution for several days, **11**–**14** readily decompose. For example, a solution of [Ti(η^5-C_5H_5)$_2$(NBu^t)(NC_5H_5)] **11** in $CDCl_3$ gives *ca.* 50% conversion into the half-sandwich complex **4** after 3 h. The fate of the organic residues in this reaction is unknown. Complex **11** also undergoes a facile cyclopentadienyl ligand-redistribution reaction with [Ti(NBu^t)Cl$_2$(NC_5H_5)$_2$] in C_6D_6 (Scheme 2) to form **4** in quantitative yield at room temperature after 12 h. This reaction is analogous to that between [Ti(η^5-C_5H_5)$_2$Cl$_2$] and $TiCl_4$ in hot (115–120 °C) *p*-xylene to form [Ti(η^5-C_5H_5)Cl$_3$] after 24 h.[88] However, for the imido-supported system the required conditions are consider-



Scheme 2 (*i*) C_6D_6, r.t., 12 h



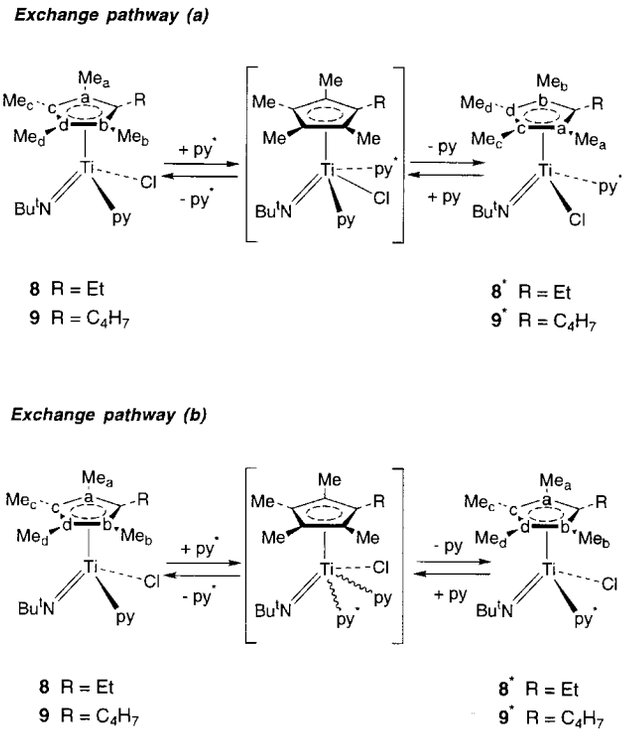
Scheme 3 R = C_4H_7 or Et

ably milder, again consistent with the apparent labilisation of the η-cyclopentadienyl rings in **11** by the π-donor NBu^t ligand.

Variable-temperature NMR studies of the half-sandwich and sandwich complexes

The pyridine ligands in the half-sandwich complexes **1**–**9** undergo facile exchange with free pyridine at room temperature on the NMR time-scale. For example, the ^{1}H NMR spectra of pure [Ti(η^5-C_5Me_4R)(NBu^t)Cl(NC_5H_5)] (R = Et **8** or C_4H_7 **9**) show sharp resonances (*i.e.* coupling resolved) for the pyridine *o*-, *m*- and *p*-hydrogen atoms, and the four diastereotopic ring Me groups give rise to individual resonances. Addition of free pyridine (*ca.* 0.5–2 equivalents) to NMR samples of **8** or **9** causes broadening and/or coalescence of the resonances of co-ordinated and free pyridine suggestive of an exchange process. Furthermore, the changed appearance of the ring Me resonances to two signals implies an apparent molecular mirror plane on the NMR time-scale at room temperature. Analogous features were seen in the ^{13}C NMR spectra. For **8**, ^{1}H magnetisation-transfer experiments on the NC_5H_5 resonances confirmed exchange between free and co-ordinated pyridine on the NMR time-scale. At low (213 K) temperatures distinct resonances for free pyridine and **8** or **9** were observed showing that the exchange process(es) may be easily 'frozen out'. No evidence was found in either the ^{1}H or ^{13}C NMR low-temperature spectra for significant equilibrium concentrations of the eighteen-electron, bis(pyridine) adducts [Ti(η^5-C_5Me_4R)(NBu^t)Cl(NC_5H_5)$_2$] in these mixtures.

Since no dynamic NMR behaviour is observed in the absence of added pyridine, a dissociative exchange mechanism (on the NMR time-scale) of the type described in Scheme 3 may be discounted. The NMR experiments are thus consistent with an associative-exchange mechanism. The extent of line broadening of the resonances of η^5-C_5Me_4R and co-ordinated NC_5H_5 depends on the concentration of added pyridine, also consistent with a bimolecular exchange process. Any proposed mechanism must account both for the pyridine-exchange process (implied by coalescence of the resonances of free and co-ordinated pyridine) and the interconversion of the enantiomers of [Ti(η^5-C_5Me_4R)(NBu^t)Cl(NC_5H_5)] (implied by collapse of the diastereotopy of the η^5-C_5Me_4R ligand resonances). Scheme 4(*a*) shows a likely exchange mechanism in which a postulated C_s symmetric bis(pyridine) intermediate may either lose initially free pyridine (labelled py*) to reform **8** or **9**, or may lose initially co-ordinated pyridine (labelled py) to form the opposite enantiomers (labelled **8*** or **9***). It is possible that pyridine exchange



Scheme 4 Two possible associative pathways for enantiomer interconversion and/or exchange of co-ordinated and free pyridine in the complexes [Ti(η^5-C_5Me_4R)(NBu^t)Cl(NC_5H_5)] (R = Et **8** or C_4H_7 **9**); py and py* refer to initially co-ordinated and free pyridine respectively, '**8***' and '**9***' indicate the opposite enantiomeric configuration for the metal complexes

could also occur *via* a second mechanism as shown in Scheme 4(*b*). In this alternative pathway the exchange of py and py* is not accompanied by enantiomer interconversion. Therefore, although the exchange pathway in Scheme 4(*a*) is needed to account for enantiomer interconversion (and also allows py ⟷ py* exchange), the second pathway [Scheme 4(*b*)] might nevertheless be available for py ⟷ py* exchange alone. *A priori* one cannot exclude the possibility that both exchange mechanisms are in operation in these half-sandwich complexes.

In order to establish the relative contributions of these two mechanisms we have carried out variable-temperature ^{13}C-{^{1}H} NMR experiments on the highly soluble [Ti{η^5-C_5Me_4-(C_4H_7)}(NBu^t)Cl(NC_5H_5)] **9** in CD_2Cl_2 in the presence of added pyridine. If the rate of exchange of co-ordinated and free pyridine is approximately the same as that for enantiomer interconversion then only the exchange pathway in Scheme 4(*a*) can be in operation, and that shown in Scheme 4(*b*) makes at best a minor contribution. Note that in earlier studies we[38] and others[89] have shown that the $CH_2CH_2CH{=}CH_2$ side chain does not interact with the d^0 metal centre in Group 4 complexes comparable to **9**. The results are summarised in Table 2. The values of k_{obs} (at 262 K) obtained for py ⟶ py* (33.6 and 38.3 s^{-1}) are in excellent agreement with those obtained for **9** ⟶ **9*** (33.0 and 36.0 s^{-1}). The values of $\Delta G^{\ddagger}$(262 K) for **9** ⟶ **9*** (51.1 and 51.3 kJ mol^{-1}) also compare very well with the values of $\Delta G^{\ddagger}$(262 K) for py ⟶ py* (51.2 and 51.3 kJ mol^{-1}) calculated from the $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ values. It is apparent therefore that only the exchange mechanism shown in Scheme 4(*a*) operates to any significant extent. The substantially negative activation entropy ($\Delta S^{\ddagger}$ = −117 and −116 J K^{-1} mol^{-1}) is consistent with the proposed associative mechanism. The structure of the proposed bis(pyridine) intermediate is analogous to that found in the crystal structure of the C_s-symmetric zirconium complex [Zr(η^5-C_5Me_5)($NC_6H_3Pr^i_2$-2,6)Cl(NC_5H_5)$_2$].[29] Presumably the larger Zr is able to accommodate more easily the two pyridine ligands making the bis(pyridine) structure the more stable in this instance.

Table 2 Rate constants and activation parameters for pyridine exchange and enantiomer interconversion in [Ti{η^5-$C_5Me_4(C_4H_7)$}(NBu^t)Cl(NC_5H_5)] **9**; *ortho*, *meta*, C_a/C_b and C_c/C_d are used in parentheses to denote the parameters derived from these resonances. See the text and Scheme 4 for other details

(*a*) Pyridine exchange†

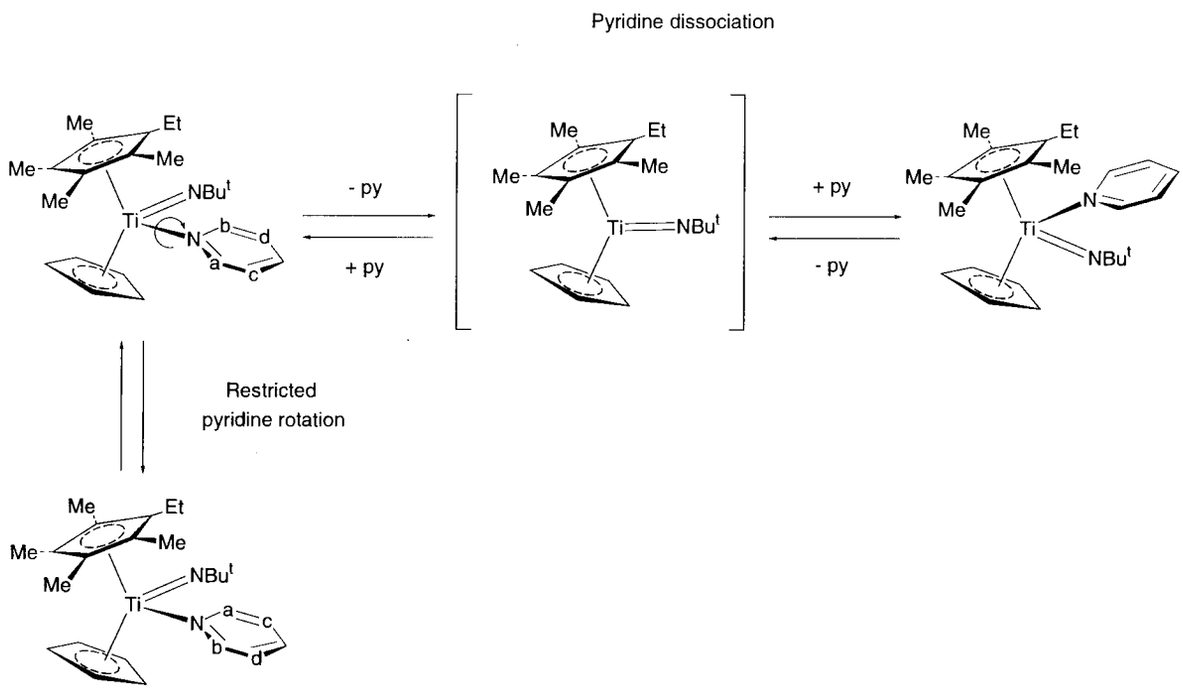
T/K	k_{obs} (*ortho*)/s^{-1}	k_{obs} (*meta*)/s^{-1}	k_2 (*ortho*)/$dm^3\ mol^{-1}\ s^{-1}$	k_2 (*meta*)/$dm^3\ mol^{-1}\ s^{-1}$
246	18.2	18.5	182	185
250	19.5	23.3	195	233
254	24.8	25.5	248	255
258	31.1	30.2	311	301
262	33.6	38.3	336	383

$\Delta H^{\ddagger}$ = 20.6 (*ortho*) and 20.8 (*meta*) kJ mol^{-1}, $\Delta S^{\ddagger}$ = −117 (*ortho*) and −116 (*meta*) J K^{-1} mol^{-1}, $\Delta G^{\ddagger}$(262 K) = 51.3 (*ortho*) and 51.2 (*meta*) kJ mol^{-1}

(*b*) Enantiomer interconversion†

k_{obs} = 36.0 (C_a/C_b) and 33.0 (C_c/C_d) s^{-1} at 262 K, k_2 = 360 (C_a/C_b) and 330 (C_c/C_d) $dm^3\ mol^{-1}\ s^{-1}$ at 262 K, $\Delta G^{\ddagger}$(262 K) = 51.1 (C_a/C_b) and 51.3 (C_c/C_d) kJ mol^{-1}

† Note that the rate constants quoted here are for the processes py ⟶ py* and **9** ⟶ **9***. Strictly speaking, rates for exchange/interconversion (*i.e.* py ⟷ py* and **9** ⟷ **9***) are twice these values for equally populated sites.[90]



Scheme 5 Fluxional processes in [Ti(η^5-C_5H_5)(η^5-C_5Me_4Et)(NBu^t)(NC_5H_5)] **13**

The mixed-ring bis(η^5-cyclopentadienyl) complex [Ti(η^5-C_5H_5)(η^5-C_5Me_4Et)(NBu^t)(NC_5H_5)] **13** also shows fluxional behaviour in its variable-temperature ^{1}H NMR spectra. The spectrum of pure **13** at 313 K shows the ring Me resonances as two sharp singlets and the ethyl group CH_2 linkage as a binomial quartet. Cooling the sample to 273 K caused the diastereotopic ring Me groups to appear as four singlets and the diastereotopic CH_2 linkage gives rise to two broad quartets. On further cooling to 213 K the *o*-H resonances of NC_5H_5 separate into two broad multiplets while the *m*-hydrogen atoms still appear as a single broad signal. Magnetisation-transfer experiments on the *o*-hydrogen resonances confirmed exchange between these two sites even at 213 K.

The NMR data are consistent with the dynamic processes shown in Scheme 5 and the structure proposed for **13** in Scheme 1. In the absence of added pyridine the collapse of the diastereotopy of the η^5-C_5Me_4Et ligand must be attributable to pyridine dissociation to give transient C_s-symmetric [Ti(η^5-C_5H_5)(η^5-C_5Me_4Et)(NBu^t)]. For the more sterically crowded bis(pentamethylcyclopentadienyl) ligand set the pyridine-free species [Ti(η^5-$C_5Me_5)_2$(NR)] (R = aryl) may be isolated.[91] At lower temperatures restricted rotation about the Ti–N (pyridine) bond in **13** accounts for the inequivalence of the *o*-hydrogen atoms. There are two possible orientations of the NC_5H_5 ligand that would give inequivalent *o*-hydrogens, namely with the pyridine ligand lying in or out of the {TiN_2} plane. We favour the former by analogy with the orientation of the pyridine ligand in the crystallographically characterised [Ti(η^5-$C_5H_5)_2$(NBu^t)(NC_5H_5)] **11** and the isoelectronic titanium oxo species [Ti(η^5-$C_5Me_5)_2$O(NC_5H_4Ph-4)].[67]

Conclusion

We have found a general route to an interesting class of sandwich and half-sandwich titanium imido derivatives and have characterised the various fluxional processes in both types of complex. The η-indenyl and mixed-ring species are the first such examples for Group 4 imido complexes. Complex **11** is the first crystallographically characterised titanocene imido complex. Without doubt the bis(η^5-cyclopentadienyl) complexes will produce a rich and exciting reaction chemistry as has already been established for isoelectronic zirconium imido and titanium oxo analogues.

Experimental

General methods and instrumentation

Manipulations were carried out under an atmosphere of dinitrogen or argon using either standard Schlenk-line or dry-box techniques. Solvents were pre-dried over molecular sieves and refluxed over potassium (tetrahydrofuran, hexane), sodium–potassium alloy (pentane, diethyl ether) or calcium hydride (dichloromethane) under an atmosphere of dinitrogen and collected by distillation; C_6D_6 and $C_6D_5CD_3$ were dried over molten potassium and sodium respectively, $CDCl_3$ and CD_2Cl_2 over calcium hydride at r.t. Deuteriated solvents were distilled under reduced pressure and stored under N_2 in Young's ampoules in a dry-box. The NMR samples were prepared in a dry-box in Teflon-valve (Young's) 5 mm tubes.

Proton and ^{13}C NMR spectra were recorded on either a Bruker WM 250 or AM 400 spectrometer at 298 K unless stated otherwise, referenced internally to residual protio-solvent (^1H) or solvent (^{13}C) resonances and reported relative to tetramethylsilane (δ 0). Chemical shifts are quoted in δ (ppm). Assignments were supported by distortionless enhancements of polarisation transfer (DEPT)-135 and -90, homo- and hetero-nuclear, one- and two-dimensional experiments as appropriate. Infrared spectra were recorded on a Nicolet 205 FTIR spectrometer in the range 4000–400 cm^{-1}. Samples were prepared in the dry-box as Nujol mulls between CsBr plates. Elemental analyses were carried out by the analysis department of this laboratory.

Starting materials

Cyclopentadiene dimer and methylcyclopentadiene dimer were obtained from Aldrich and freshly 'cracked' to produce C_5H_6 and C_5H_5Me before use. Sodium hydride (60% dispersion in mineral oil) was obtained from Aldrich and washed thoroughly with hexanes before use. Pyridine was obtained from Aldrich and distilled from calcium hydride under dinitrogen. Indene (98%) and *n*-butyllithium (1.6 mol dm^{-3} in hexanes) were obtained from Aldrich and used as received. The compounds C_5Me_5H,[92] $Li[C_5H_4Pr^i]$,[93] $Li[C_5Me_4(C_4H_7)]$,[94] $Li[C_9H_4Me_3]$,[44] $[Ti(NBu^t)Cl_2(NC_5H_4Bu^t\text{-}4)_2]$[34] and $[Ti(NBu^t)Cl_2(py)_n]$ ($n = 2$ or 3)[39] were prepared according to literature methods; C_5Me_4EtH was prepared in an analogous manner to C_5Me_5H but using MgEtBr in place of MgMeI in the final alkylation step. The compound $Na[C_5H_5]\cdot x$thf (amount of thf determined by ^1H NMR spectroscopy) was prepared from C_5H_6 and NaH in cold thf; $Li[C_5H_4Me]$, $Li[C_9H_7]$, $Li[C_5Me_5]$ and $Li[C_5Me_4Et]$ were prepared by treating the corresponding organic precursor with *n*-butyllithium in cold hexanes.

Preparations

$[Ti(\eta^5\text{-}C_5H_5)(NBu^t)Cl(NC_5H_4Bu^t\text{-}4)]$ 1. To a stirred solution of $[Ti(NBu^t)Cl_2(NC_5H_4Bu^t\text{-}4)_2]$ (0.5 g, 1.09 mmol) in thf (20 cm^3) was added a solution of $Na[C_5H_5]\cdot$0.4thf (0.121 g, 1.03 mmol) in thf (20 cm^3). The solution instantly changed from orange to red, and over 10 min a fine precipitate of NaCl formed. Stirring was continued for 4 h, after which the volatiles were removed under reduced pressure. The resultant light red residue was extracted into hexane (60 cm^3) and filtered through a filter cannula fitted with a glass-fibre disc. The volume was concentrated to 30 cm^3 and cooled to −25 °C. After 2 d small red crystals of complex **1** formed which were washed with cold hexane (2 × 20 cm^3) and dried *in vacuo*. Yield: 0.175 g (48%). NMR ($CDCl_3$): ^1H (250 MHz), δ 8.63, 7.42 (2 × 2 H, 2 × d, 2 × *J* 6.7 Hz, *o*- and *m*-H of $NC_5H_4Bu^t$ respectively), 6.34 (5 H, s, C_5H_5), 1.35 (9 H, s, $NC_5H_4Bu^t$) and 1.08 (9 H, s, NBu^t); $^{13}C\text{-}\{^1H\}$ (62.5 MHz), δ 163.9, 151.4, 121.6 (*p*-, *o*- and *m*-C of $NC_5H_4Bu^t$ respectively), 110.9 (C_5H_5), 69.0 ($NCMe_3$), 35.3 ($NC_5H_4CMe_3$), 31.5 ($NCMe_3$) and 30.2 ($NC_5H_4CMe_3$). IR: 1615s, 1447s, 1417s, 1352m, 1275w, 1233s, 1221m, 1210m, 1108m, 1066s, 1030s, 1014m, 841m, 792s, 729w and 575s cm^{-1} (Found: C, 59.7; H, 7.8; N, 7.9. Calc. for $C_{18}H_{27}ClN_2Ti$: C, 60.9; H, 7.7; N, 7.4%).

$[Ti(\eta^5\text{-}C_5Me_5)(NBu^t)Cl(NC_5H_4Bu^t\text{-}4)]$ 2. The complex $[Ti(NBu^t)Cl_2(NC_5H_4Bu^t\text{-}4)_2]$ (1.00 g, 2.17 mmol) was dissolved in thf (20 cm^3) and cooled to −45 °C. To this was added a cold (−45 °C) suspension of $Li[C_5Me_5]$ (0.309 g, 2.17 mmol) in thf (40 cm^3) with vigorous stirring. The mixture was allowed to warm to r.t., and stirred for 10 h, after which it had turned light brown and LiCl had formed. The volatiles were removed under reduced pressure and the residue was extracted into pentane (70 cm^3), filtered and concentrated to 40 cm^3. Cooling this solution to −25 °C afforded red crystals of complex **2** which were washed with cold pentane (2 × 20 cm^3) and dried *in vacuo*. Yield: 0.56 g (46%). NMR ($CDCl_3$): ^1H (250 MHz), δ 8.48, 7.43 (2 × 2 H, 2 × d, 2 × *J* 6.7 Hz, *o*- and *m*-H of $NC_5H_4Bu^t$ respectively), 1.97 (15 H, s, C_5Me_5), 1.35 (9 H, s, $NC_5H_4Bu^t$) and 1.03 (9 H, s, NBu^t) (*p*-H of $NC_5H_4Bu^t$ not observed); $^{13}C\text{-}\{^1H\}$ (62.5 MHz), 150.9, 121.1 (*o*- and *m*-C of $NC_5H_4Bu^t$ respectively), 120.1 (C_5Me_5), 68.9 ($NCMe_3$), 35.6 ($NC_5H_4CMe_3$), 32.2 ($NCMe_3$), 30.5 ($NC_5H_4CMe_3$) and 12.1 (C_5Me_5). IR: 1614s, 1419s, 1349m, 1271w, 1239s, 1223m, 1205m, 1117w, 1069s, 1029s, 839s, 801w, 728w, 575m and 535w cm^{-1} (Found: C, 64.3; H, 9.2; N, 6.2. Calc. for $C_{23}H_{37}ClN_2Ti$: C, 65.0; H, 8.8; N, 6.6%).

$[Ti(\eta^5\text{-}C_9H_4Me_3)(NBu^t)Cl(NC_5H_4Bu^t\text{-}4)]$ 3. The complex $[Ti(NBu^t)Cl_2(NC_5H_4Bu^t\text{-}4)_2]$ (1.00 g, 2.17 mmol) and $Li[C_9H_4Me_3]$ (0.357 g, 2.17 mmol) were each dissolved in thf (2 × 20 cm^3) and cooled to −50 °C. The solutions were combined over a period of 10 min giving a change from orange to deep dichroic red-green. The solution was allowed to warm to r.t. and stirred for 19 h. The volatiles were then removed under reduced pressure and the residue extracted into pentane (25 cm^3), filtered and cooled to −25 °C. After 2 weeks a dark red powder had formed, which was washed with cold pentane (2 × 15 cm^3) and dried *in vacuo* to give complex **3**. Yield: 0.434 g (37%). NMR ($CDCl_3$): ^1H (250 MHz), δ 7.93 (2 H, d, *J* 6.7, *o*-H of $NC_5H_4Bu^t$), 7.43 (1 H, d, *J* 8.3, H^4 or H^7 of $C_9H_4Me_3$), 7.27 (2 H, d, *J* 6.7, *m*-H of $NC_5H_4Bu^t$), 6.96 (1 H, apparent t, apparent *J* 8.0, H^5 or H^6 of $C_9H_4Me_3$), 6.76 (1 H, apparent t, apparent *J* 8.0, H^5 or H^6 of $C_9H_4Me_3$), 6.69 (1 H, d *J* 8.3 Hz, H^4 or H^7 of $C_9H_4Me_3$), 2.79 (3 H, s, 2-Me of $C_9H_4Me_3$), 2.49, 2.35 (2 × 3 H, 2 × s, 1- and 3-Me of $C_9H_4Me_3$), 1.32 (9 H, s, $NC_5H_4Bu^t$) and 1.04 (9 H, s, NBu^t); $^{13}C\text{-}\{^1H\}$ (62.5 MHz), δ 163.8, 150.5 (*p*- and *o*-C of $NC_5H_4Bu^t$ respectively), 130.7, 126.1 (two signals overlapping), C^2, C^{3a} and C^{7a} of $C_9H_4Me_3$), 122.8, 121.9 (two of $C^{4\text{–}7}$ of $C_9H_4Me_3$), 120.8 (two signals overlapping, *m*-C of $NC_5H_4Bu^t$ and one of $C^{4\text{–}7}$ of $C_9H_4Me_3$), 119.9 (two of $C^{4\text{–}7}$ of $C_9H_4Me_3$), 111.8, 107.7 (C^1 and C^3 of $C_9H_4Me_3$), 70.1 ($NCMe_3$), 35.1 ($NC_5H_4CMe_3$), 31.5 ($NCMe_3$), 30.1 ($NC_5H_4CMe_3$), 14.1 (2-Me of $C_9H_4Me_3$) and 11.6 (two signals overlapping, 1- and 3-Me of $C_9H_4Me_3$). IR: 1613s, 1421m, 1346m, 1274w, 1238s, 1227m, 1208m, 1171w, 1070m, 1028s, 834m, 804w, 742s and 572m cm^{-1} (Found: C, 65.6; H, 8.1; N, 6.3. Calc. for $C_{25}H_{35}ClN_2Ti$: C, 67.2; H, 7.9; N, 6.3%).

$[Ti(\eta^5\text{-}C_5H_5)(NBu^t)Cl(NC_5H_5)]$ 4. To a stirred solution of $[Ti(NBu^t)Cl_2(NC_5H_5)_3]$ (3.5 g, 8.19 mmol) in thf (40 cm^3) was added a solution of $Na[C_5H_5]\cdot$0.4thf (0.958 g, 8.19 mmol). The solution became red and after 10 min a precipitate of NaCl had formed. The solution was stirred for 3 h, the volatiles were removed under reduced pressure and the residue was extracted into Et_2O (30 cm^3) and filtered. Cooling this solution to −25 °C gave complex **4** as a red powder which was washed with cold Et_2O (2 × 20 cm^3) and dried *in vacuo*. Yield of first crop: 1.51 g. Concentration of the washings and mother-liquors produced 0.343 g of **4**. Total yield: 1.853 g (75%). NMR ($CDCl_3$): ^1H (250 MHz), δ 8.73 (2 H, d, *J* 5.0, *o*-H of NC_5H_5), 7.88 (1 H, t, *J* 7.5, *p*-H of NC_5H_5), 7.45 (2 H, d of d, *J* 5.0 and 7.5 Hz, *m*-H of

NC_5H_5), 6.32 (5 H, s, C_5H_5) and 1.05 (9 H, s, NBu^t); ^{13}C-{^1H} (62.5 MHz), δ 151.8, 139.1, 124.8 (*o*-, *p*- and *m*-C of NC_5H_5 respectively), 111.4 (C_5H_5), 69.4 ($NCMe_3$) and 31.8 ($NCMe_3$). IR: 1443s, 1352m, 1236s, 1210s, 1064m, 1043m, 1014s, 798m, 761m, 697m, 641w and 541m cm^{-1} (Found: C, 56.6; H, 6.6; N, 9.4. Calc. for $C_{14}H_{19}ClN_2Ti$: C, 56.3; H, 6.4; N, 9.4%).

[Ti(η^5-C_5H_4Me)(NBu^t)Cl(NC_5H_5)] 5. To a stirred solution of [Ti(NBu^t)Cl_2(NC_5H_5)$_2$] (0.75 g, 2.15 mmol) in thf (20 cm^3) at −45 °C was added a cold (−45 °C) suspension of Li[C_5H_4Me] (0.185 g, 2.15 mmol) in thf (20 cm^3). The solution darkened, was allowed to warm to r.t. and stirred for 12 h. The volatiles were removed under reduced pressure and the resultant oil was extracted into pentane (30 cm^3) and filtered. Concentration of the solution and cooling to −25 °C produced oily orange crystals of complex **5** which were washed with cold pentane (2 × 10 cm^3) and dried *in vacuo*. Yield: 0.216 g (32%). NMR (CD_2Cl_2): ^1H (400 MHz), δ 8.73 (2 H, d, *J* 4.7, *o*-H of NC_5H_5), 7.88 (1 H, t, *J* 7.7, *p*-H of NC_5H_5), 7.45 (2 H, apparent t, apparent *J* 6.8 Hz, *m*-H of NC_5H_5), 6.41, 5.99 (2 × 2 H, 2 × br s, H^2 and H^5, H^3 and H^4 of C_5H_4Me), 1.91 (3 H, s, C_5H_4Me) and 1.07 (9 H, s, NBu^t); ^{13}C-{^1H} (100.6 MHz), δ 151.9, 139.5 (*o*- and *p*-C of NC_5H_5 respectively), 125.8 (C^1 of C_5H_4Me), 125.2 (*m*-C of NC_5H_5), 112.2, 110.3 (C^2 and C^5, C^3 and C^4 of C_5H_4Me), 69.2 ($NCMe_3$), 32.0 ($NCMe_3$) and 15.2 (C_5H_4Me). Satisfactory analysis was not obtained, possibly due to difficulties in removing residual pyridine. This would also account for the appearance of the diastereotopic η^5-C_5H_4Me ring CH groups as broad signals in the ^1H and ^{13}C NMR spectra.

[Ti(η^5-$C_5H_4Pr^i$)(NBu^t)Cl(NC_5H_5)] 6. To a stirred solution of [Ti(NBu^t)Cl_2(NC_5H_5)$_2$] (1.00 g, 2.87 mmol) in thf (20 cm^3) at −45 °C was added a cold (−45 °C) suspension of Li[$C_5H_4Pr^i$] (0.33 g, 2.87 mmol) in thf (30 cm^3). The solution darkened and was allowed to warm to r.t. then stirred for 12 h. The volatiles were removed under reduced pressure and the resultant brown solid was extracted into pentane (30 cm^3) and filtered. Concentration of the solution and cooling to −25 °C produced orange-brown crystals of complex **6** which were washed with cold pentane (2 × 15 cm^3) and dried *in vacuo*. Yield: 0.55 g (56%). NMR (CD_2Cl_2, 193 K): ^1H (400 MHz), δ 8.55, 7.91, 7.47 (2 H, 1 H, 2 H, 3 × br m, *o*-, *p*- and *m*-H of NC_5H_5 respectively), 6.64, 6.43, 5.88 (two signals overlapping, 1 H, 1 H and 2 H, 3 × br m, $H^{2–5}$ of $C_5H_4Pr^i$), 2.53 (1 H, br m, $CHMe_2$) and 1.2–1.0 (15 H, overlapping br s, $CHMe_2$ and NBu^t); ^{13}C-{^1H} (100.6 MHz), δ 152.2, 140.6 (*o*- and *p*-C of NC_5H_5 respectively), 138.5 (C^1 of $C_5H_4Pr^i$), 125.8 (*m*-C of NC_5H_5), 112.1, 110.5, 109.5, 107.7 ($C^{2–5}$ of C_5H_4Me), 69.5 ($NCMe_3$), 32.1 ($NCMe_3$), 29.2 ($CHMe_2$), 24.6, 23.6 (2 × $CHMe_2$). IR: 1602m, 1444s, 1349w, 1260w, 1237m, 1208w, 1098m, 1069m, 1044m, 1013m, 792s, 761w and 697w cm^{-1} (Found: C, 58.7; H, 7.4; N, 8.7. Calc. for $C_{17}H_{25}ClN_2Ti$: C, 59.9; H, 7.4; N, 8.2%).

[Ti(η^5-C_5Me_5)(NBu^t)Cl(NC_5H_5)] 7. To a stirred solution of [Ti(NBu^t)Cl_2(NC_5H_5)$_3$] (2.50 g, 5.85 mmol) in thf (20 cm^3) at −45 °C was added a cold (−45 °C) suspension of Li[C_5Me_5] (0.832 g, 5.85 mmol) in thf (50 cm^3). The solution darkened, was allowed to warm to r.t. and then stirred for 12 h. After removal of the volatiles under reduced pressure the residue was extracted into Et_2O (30 cm^3) and filtered. This solution was evaporated to dryness under reduced pressure and the resultant light brown solid washed with hexane (2 × 20 cm^3) to give complex **7**. Yield: 1.51 g (70%). Samples prepared by this route are sufficiently pure (by ^1H NMR spectroscopy) to use in further reactivity studies. The compound was characterised by comparison of its ^1H NMR spectrum with literature values.[33] The literature ^1H NMR data for **7** are given for C_6D_6 solvent and so for comparison with our other complexes we report the corresponding values in $CDCl_3$. In addition, ^{13}C-{^1H} NMR data for **7** have not been previously reported and so we also give these data here for completeness, together with our IR data. NMR ($CDCl_3$): ^1H (250 MHz), δ 8.62 (2 H, d, *J* 5.0, *o*-H of NC_5H_5), 7.89 (1 H, t, *J* 7.5, *p*-H of NC_5H_5), 7.48 (2 H, d of d, *J* 5.0 and 7.5 Hz, *m*-H of NC_5H_5), 1.97 (5 H, s, C_5Me_5) and 1.03 (9 H, s, NBu^t); ^{13}C-{^1H} (62.5 MHz), δ 151.2, 139.1, 124.8 (*o*-, *p*- and *m*-C of NC_5H_5 respectively), 120.3 (C_5Me_5), 69.0 ($NCMe_3$), 32.1 ($NCMe_3$) and 12.1 (C_5Me_5). IR: 1603m, 1446s, 1348s, 1240s, 1207s, 1117m, 1071m, 1043m, 792m, 761s, 699s and 540m cm^{-1}.

[Ti(η^5-C_5Me_4Et)(NBu^t)Cl(NC_5H_5)] 8. To a stirred solution of [Ti(NBu^t)Cl_2(NC_5H_5)$_2$] (1.00 g, 2.87 mmol) in thf (20 cm^3) at −45 °C was added a cold (−45 °C) suspension of Li[C_5Me_4Et] (0.449 g, 2.87 mmol) in thf (30 cm^3). The solution darkened, was allowed to warm to r.t. and then stirred for 12 h. The volatiles were removed under reduced pressure and the resultant red oil was extracted into hexane (30 cm^3) and filtered. Concentration of the solution and cooling to −25 °C produced **8** as a red powder which was washed with cold hexane (2 × 10 cm^3) and dried *in vacuo*. Yield: 0.422 g (37%). NMR: ^1H (C_6D_6, 250 MHz), δ 8.59 (2 H, d, *J* 4.8, *o*-H of NC_5H_5), 6.82 (1 H, t, *J* 7.5, *p*-H of NC_5H_5), 6.52 (2 H, d of d, *J* 4.8 and 7.5, *m*-H of NC_5H_5), 2.43, 2.42 (2 × 1 H, overlapping 2 × d of q, ^2J 6.1 and ^3J 7.5, 2 CH_2Me), 2.29, 2.20, 2.14, 2.08 (4 × 3 H, 4 × s, 2- to 5-Me of C_5Me_4Et), 1.07 (9 H, s, NBu^t) and 1.20 (3 H, t, *J* 7.5 Hz, CH_2Me); ^{13}C-{^1H} ($CDCl_3$, 100.6 MHz), δ 150.9, 138.8 (*o*- and *p*-C of NC_5H_5 respectively), 125.7 (C^1 of C_5Me_4Et), 124.4 (*m*-C of NC_5H_5), 120.2, 120.1, 119.4, 119.2 ($C^{2–5}$ of C_5Me_4Et), 68.7 ($NCMe_3$), 31.8 ($NCMe_3$), 20.3 (CH_2Me), 15.1 (CH_2Me) and 11.8–11.6 (overlapping 4 $C^{2–5}$ of C_5Me_4Et). IR: 1604m, 1445s, 1350m, 1260w, 1242s, 1211m, 1066m, 1044m, 1022m, 792s, 757m, 697s and 542w cm^{-1} (Found: C, 61.7; H, 8.3; N, 7.1. Calc. for $C_{20}H_{31}ClN_2Ti$: C, 62.7; H, 8.2; N, 7.3%).

[Ti{η^5-$C_5Me_4(C_4H_7)$}(NBu^t)Cl(NC_5H_5)] 9. To a cold (−50 °C) solution of [Ti(NBu^t)Cl_2(NC_5H_5)$_2$] (0.653 g, 1.88 mmol) in thf (15 cm^3) was added a solution of Li[$C_5Me_4(C_4H_7)$] (0.363 g, 1.99 mmol) in cold thf (15 cm^3) over 25 min. The dark red solution was stirred for 3 h at −50 °C and then at r.t. for 14 h. Volatiles were removed under reduced pressure and the residue was extracted into CH_2Cl_2 (25 cm^3) and filtered to give a clear red solution. The volatiles were removed under reduced pressure and the red oily product was dried *in vacuo* (80 °C, 2 × 10^{-2} mbar) for 14 h. Attempts to obtain solid samples of complex **9** either by vacuum sublimation (decomp.) or by crystallisation were unsuccessful. Yield: 0.770 g (>95%). NMR: ^1H (C_6D_6, 250 MHz), δ 8.49 (2 H, d, *J* 5.0, *o*-H of NC_5H_5), 6.88 (1 H, t, *J* 7.4, *p*-H of NC_5H_5), 6.55 (2 H, apparent t, apparent *J* 6.9, *m*-H of NC_5H_5), 5.90 (1 H, m, =$CHCH_2$), 5.10 (1 H, br d, *J* 15.0, *Z*-=CH_2), 5.02 (1 H, br d, *J* 10.0 Hz, *E*-=CH_2), 2.80–2.70 (2 × 1 H, overlapping 2 × m, $C_5Me_4CH_2$), 2.28 (2 H, m, =$CHCH_2$), 2.16, 2.08, 2.02, 1.96 (4 × 3 H, 4 × s, 2- to 5-Me of $C_5Me_4C_4H_7$) and 1.28 (9 H, s, NBu^t); ^{13}C-{^1H} ($CDCl_3$, 62.5 MHz), δ 151.0 (*o*-C of NC_5H_5), 138.9, 138.4 (*p*-C of NC_5H_5 and =$CHCH_2$), 124.2 (*m*-C of NC_5H_5), 125.7 (C^1 of $C_5Me_4C_4H_7$), 120.4, 120.2, 119.7, 119.4 ($C^{2–5}$ of $C_5Me_4C_4H_7$), 114.6 (=CH_2), 68.6 ($NCMe_3$), 35.5 (=$CHCH_2$), 32.3 ($NCMe_3$), 27.5 ($C_5Me_4CH_2$), 12.3, 12.1 (two signals overlapping) and 11.9 ($C^{2–5}$ of $C_5Me_4C_4H_7$) (Found: C, 63.1; H, 8.0; N, 6.4. Calc. for $C_{22}H_{33}ClN_2Ti$: C, 64.6; H, 8.1; N, 6.8%).

[Ti_2(η^5-C_5H_5)$_2$(μ-NBu^t)$_2Cl_2$] 10. The complex [Ti(η^5-C_5H_5)(NBu^t)Cl(NC_5H_5)] (0.50 g, 1.67 mmol) was heated to 85 °C under vacuum (1 × 10^{-2} mbar) for 14 h. During this time the solid changed from red to brown to give complex **10** in quantitative yield. It was characterised by comparison of its ^1H and ^{13}C-{^1H} NMR spectra with the available literature values.[11] Since the literature gives ranges for only the η-C_5H_5 shifts, we report full ^1H and ^{13}C-{^1H} NMR data here for completeness, together with our IR data. NMR ($CDCl_3$): ^1H (250 MHz), δ 6.66

(10 H, s, C_5H_5) and 1.21 (18 H, s, NBu^t); ^{13}C-{^1H} (62.5 MHz), δ 116.6 (C_5H_5) and 34.5 ($NCMe_3$) ($NCMe_3$ not observed, possibly obscured by $CDCl_3$). IR: 1363s, 1165m, 1039w, 1021m, 945m, 835m, 809s, 620m, 603m and 512w cm^{-1}.

[Ti(η^5-C_5H_5)$_2$(NBu^t)(NC_5H_5)] 11. To a stirred solution of [Ti(NBu^t)Cl_2(py)$_3$] (3.46 g, 8.10 mmol) in thf (40 cm^3) was added, over 10 min, a solution of Na[C_5H_5]·0.4thf (2.08 g, 17.8 mmol) in thf (40 cm^3). The solution became dark red and cloudy very rapidly, and stirring was continued for 5 h. The volatiles were then removed under reduced pressure and the residue extracted into Et_2O (30 cm^3), filtered and cooled to −25 °C. After 12 h dark red X-ray-quality crystals had formed. These were washed with cold Et_2O (2 × 20 cm^3) and dried *in vacuo*. A second crop was obtained by combination of the washings and mother-liquors, concentration and cooling at −25 °C. Yield: 1.09 g (41%). NMR: ^1H (C_6D_6, 250 MHz), δ 8.80 (2 H, d, *J* 7.5, *o*-H of NC_5H_5), 6.93 (1 H, t, *J* 7.5, *p*-H of NC_5H_5), 6.56 (2 H, apparent t, apparent *J* 7.5 Hz, *m*-H of NC_5H_5), 6.15 (10 H, s, C_5H_5) and 1.30 (9 H, s, NBu^t); ^{13}C-{^1H} ($CDCl_3$, 100.1 MHz), δ 154.8, 137.6, 123.9 (*o*-, *p*- and *m*-C of NC_5H_5 respectively), 109.7 (C_5H_5), 69.3 ($NCMe_3$) and 31.9 ($NCMe_3$). IR: 1598m, 1440s, 1348s, 1234s, 1210m, 1150w, 1105m, 1066m, 1040m, 780s, 758s, 701s, 690w and 522m cm^{-1} (Found: C, 68.7; H, 7.5; N, 8.4. Calc. for $C_{19}H_{24}N_2Ti$: C, 69.5; H, 7.4; N, 8.5%).

[Ti(η^5-C_5H_5)(η^5-C_5Me_5)(NBu^t)(NC_5H_5)] 12. To a stirred, dark red solution of [Ti(η^5-C_5Me_5)(NBu^t)Cl(NC_5H_5)] **7** (0.500 g, 1.36 mmol) in thf (20 cm^3) was added a solution of Na[C_5H_5]·0.4thf (0.159 g, 1.36 mmol) in thf (20 cm^3). The solution darkened, and a fine precipitate of NaCl separated. After stirring for 12 h the volatiles were removed under reduced pressure and the residue was extracted into pentane (20 cm^3) and filtered. Cooling the solution to −25 °C produced complex **12** as dark red crystals. These were washed with cold pentane (2 × 10 cm^3) and dried *in vacuo*. Yield: 0.059 g (11%). NMR (C_6D_6): ^1H (250 MHz), δ 8.75 (2 H, br m, *o*-H of NC_5H_5), 6.94 (1 H, br m, *p*-H of NC_5H_5), 6.63 (2 H, br m, *m*-H of NC_5H_5), 6.20 (5 H, s, C_5H_5), 2.00 (15 H, s, C_5Me_5) and 1.37 (9 H, s, NBu^t); ^{13}C-{^1H} (62.5 MHz), δ 155.1, 136.6, 123.3 (*o*-, *p*- and *m*-C of NC_5H_5 respectively), 117.1 (C_5Me_5), 108.0 (C_5H_5), 68.7 ($NCMe_3$), 32.9 ($NCMe_3$) and 12.9 (C_5Me_5). Satisfactory elemental analysis was not obtained.

[Ti(η^5-C_5H_5)(η^5-C_5Me_4Et)(NBu^t)(NC_5H_5)] 13. To a stirred, dark red solution of [Ti(η^5-C_5Me_4Et)(NBu^t)Cl(NC_5H_5)] **8** (0.286 g, 0.75 mmol) in thf (20 cm^3) was added a solution of Na[C_5H_5]·0.4thf (0.087 g, 0.75 mmol) in thf (15 cm^3). The solution darkened and a fine precipitate of NaCl separated. After stirring for 12 h the volatiles were removed under reduced pressure and the residue was extracted into pentane (10 cm^3) and filtered. Cooling the solution to −25 °C produced **13** as a dark red powder which was washed with cold pentane (2 × 10 cm^3) and dried *in vacuo*. Yield: 0.050 g (16%). NMR: ^1H ($C_6D_5CD_3$, 250 MHz, 223 K), δ 9.40 (1 H, br m, *o*-H of NC_5H_5), 8.16 (1 H, br m, *o*-H of NC_5H_5), 6.88 (1 H, br m, *p*-H of NC_5H_5), 6.56 (2 H, br m, *m*-H of NC_5H_5), 6.28 (5 H, s, C_5H_5), 2.43–2.38 (2 H, overlapping br m, CH_2Me), 2.27, 2.16, 2.07, 2.04 (4 × 3 H, 4 × s, 2- to 5-Me of C_5Me_4Et), 1.52 (9 H, s, NBu^t) and 1.32 (3 H, br t, *J ca.* 7 Hz, CH_2Me); ^{13}C-{^1H} (CD_2Cl_2, 100.1 MHz, 213 K), δ 156.9, 152.4, 137.0, 123.8, 123.4 (2 × *o*-, *p*- and 2 × *m*-C of NC_5H_5 respectively), 121.2 (1-C_5Me_4Et), 121.2, 115.8, 115.4 (two signals overlapping, C^{2-5} of C_5Me_4Et), 106.9 (C_5H_5), 68.4 ($NCMe_3$), 31.9 ($NCMe_3$), 20.5 (CH_2Me), 15.1 (CH_2Me), 12.4, 12.3, 11.9 and 11.6 (C^{2-5} of C_5Me_4Et) (Found: C, 71.8; H, 8.9; N, 6.4. Calc. for $C_{25}H_{36}N_2Ti$: C, 72.8; H, 8.8; N, 6.8%).

[Ti(η^5-C_5H_5)(η^3-C_9H_7)(NBu^t)(NC_5H_5)] 14. To a stirred solution of [Ti(η^5-C_5H_5)(NBu^t)Cl(NC_5H_5)] **4** (0.500 g, 1.67 mmol) in thf (30 cm^3) at −45 °C was added a cold (−45 °C) solution of Li[C_9H_7] (0.204 g, 1.67 mmol) in thf (30 cm^3). The resulting solution was allowed to warm to r.t. and stirred for 12 h, after which it had become dark red-green. The volatiles were removed under reduced pressure and the resultant oil was extracted into hexane–Et_2O (20:1, 40 cm^3). After filtering and concentrating to 25 cm^3 the solution was placed at −25 °C. After 2 d large brown crystals precipitated and were washed with cold hexane–Et_2O (20:1, 2 × 20 cm^3). Drying *in vacuo* produced complex **14** as a tan powder. Yield: 0.302 g (47%). NMR (CD_2Cl_2): ^1H (250 MHz), δ 8.21 (2 H, d, *J* 4.9, *o*-H of NC_5H_5), 7.95–7.85 (2 H, overlapping 2 × m, 2-C_9H_7 and *p*-H of NC_5H_5), 7.46 (1 H, d, *J* 7.7, H^4 or H^7 of C_9H_7), 7.37 (2 H, d of d, apparent *J* 4.9 and 7.0, *m*-H of NC_5H_5), 7.17 (1 H, d, *J* 7.7, H^7 or H^4 of C_9H_7), 6.95, 6.87 (2 × 1 H, 2 × apparent t, apparent *J* 7.5 and 7.3, H^5 and H^6 of C_9H_7), 6.05, 5.51 (2 × 1 H, 2 × apparent t, apparent *J* 2.1 and 2.2, H^1 and H^3 of C_9H_7), 5.41 (5 H, s, C_5H_5) and 1.16 (9 H, s, NBu^t); ^{13}C-{^1H} (62.5 MHz), δ 154.9 (*o*-C of NC_5H_5), 140.5 (C^{3a} or C^{7a} of C_9H_7), 139.5 (*p*-C of NC_5H_5), 135.4 (C^{3a} or C^{7a} of C_9H_7), 125.2 (*m*-C of NC_5H_5), 124.5 (C^2 of C_9H_7), 122.1 (C^5 or C^6 of C_9H_7), 121.1 (overlapping C^4 or C^7 of C_9H_7 and C^6 or C^5 of C_9H_7), 120.8 (C^7 or C^4 of C_9H_7), 110.1 (C_5H_5), 102.1, 90.3 (C^1 and C^3 of C_9H_7), 70.2 ($NCMe_3$) and 33.3 ($NCMe_3$) (Found: C, 72.3; H, 7.3; N, 7.2. Calc. for $C_{23}H_{26}N_2Ti$: C, 73.0; H, 6.9; N, 7.4%).

NMR tube reactions

[Ti(η^5-C_5H_5)$_2$(NBu^t)(NC_5H_5)] with [Ti(NBu^t)Cl_2(NC_5H_5)$_2$]. A solution containing [Ti(η^5-C_5H_5)$_2$(NBu^t)(NC_5H_5)] **11** (20 mg, 0.061 mmol) and [Ti(NBu^t)Cl_2(NC_5H_5)$_2$] (21 mg, 0.061 mmol) in C_6D_6 (0.75 cm^3) was allowed to stand at r.t. for 12 h. The ^1H NMR spectrum showed quantitative formation of [Ti(η^5-C_5H_5)(NBu^t)Cl(NC_5H_5)] **4**.

[Ti$_2$(η^5-C_5H_5)$_2$(μ-NBu^t)$_2Cl_2$] with an excess of NC_5H_5. A mixture of [Ti$_2$(η^5-C_5H_5)$_2$(μ-NBu^t)$_2Cl_2$] (20 mg, 0.065 mmol) and pyridine (26 μl, 0.33 mmol) in $CDCl_3$ (0.5 cm^3) was allowed to stand at r.t. for 7 d. The ^1H NMR spectrum showed quantitative formation of complex **4**.

Variable-temperature NMR experiments for [Ti{η^5-C_5Me_4-(C_4H_7)}(NBu^t)Cl(NC_5H_5)] 9

Kinetic parameters for the py ⟶ py* process were obtained from five ^{13}C-{^1H} NMR spectra of complex **9** in the range 246 ⩽ T ⩽ 262 K in the slow-exchange regime. Lorentzian curve fitting of the pyridine *o*- and *m*-carbon resonances afforded $\nu_{\frac{1}{2}}$ (bandwidth at half-height) values from which were subtracted the estimated natural linewidths (at 213 K) to give corrected $\nu_{\frac{1}{2}}$ values. Pseudo-first-order rate constants (k_{obs}, Table 2) were calculated according to the expression $k_{obs} = \pi\nu_{\frac{1}{2}}$.[90] Owing to signal overlaps in both the ^1H and ^{13}C NMR spectra of **9**, it was not possible to carry out a full lineshape analysis for any resonances of the η^5-$C_5Me_4(C_4H_7)$ ligand. It was possible, however, to measure the coalescence temperature (262 K) of the C_a/C_b and C_c/C_d quaternary carbon resonances (see Scheme 4 for labelling) and thus to find the pseudo-first-order rate constants (k_{obs}) for **9** ⟶ **9*** at coalescence (Table 2) from the expression $k_{obs} = \pi(\delta\nu)(\sqrt{2})^{-1}$ where δν = frequency separation of C_a and C_b and of C_c and C_d in the slow-exchange limit.[90]

Applying the steady-state approximation to standard kinetic expressions describing the mechanism shown in Scheme 4(*a*) gives equation (1) where k_2, the second-order rate constant, is

$$\text{Rate } \mathbf{9} \longrightarrow \mathbf{9}^* = \text{Rate py} \longrightarrow \text{py}^* = \tfrac{1}{2}k_2\,[\mathbf{9}][\text{py}^*] \quad (1)$$

related to k_{obs} according to the expression $k_2 = 2[\text{py}^*]^{-1}\,k_{obs}$. The derived k_2 values afforded the activation parameters for py ⟶ py* (Table 2) from Eyring plots and the coalescence $\Delta G^{\ddagger}$(262 K) for **9** ⟶ **9*** (Table 2) according to standard procedures.[95]

Table 3 Crystal data for $[Ti(\eta^5\text{-}C_5H_5)_2(NBu^t)(NC_5H_5)]$ **11**

Empirical formula	$C_{19}H_{24}N_2Ti$
M	328.31
Crystal colour	Red
Crystal size/mm	0.29 × 0.12 × 0.12
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	13.455(1)
b/Å	14.200(5)
c/Å	27.469(3)
U/Å^3	5248
Z	12 (3 independent molecules per asymmetric unit)
D_c/g cm^{-3}	1.246
μ/cm^{-1}	4.810
hkl Index ranges	−14 to 14, −12 to 16, −29 to 24
θ range (minimum, maximum)/°	2.06, 25.05
Reflections collected	16626 (approximately one hemisphere of reciprocal space)
Independent reflections	4452
No. observations [$I > 2\sigma(I)$]	1367
Absorption correction	DIFABS
Minimum/maximum correction	0.91,0.99
F(000)	2088
R_{merge}	0.068
Refinement method	Full-matrix least squares
No. variables	146
Weighting scheme	Chebychev
Largest difference peak and hole/e Å^{-3}	+0.88, −0.58
Flack parameter for given hand	0.259(137)
R,[a] R' [b]	0.096, 0.093

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$.

Crystallography

Crystallographic parameters of $[Ti(\eta^5\text{-}C_5H_5)_2(NBu^t)(NC_5H_5)]$ **11** are given in Table 3. All crystallographic and data-collection measurements were made at 120 K using a Delft FAST TV area-detector diffractometer and Mo-Kα radiation (λ 0.710 69 Å) following previously described procedures.[96] Examination of the systematic absences suggested the space group $P2_12_12_1$. Equivalent reflections were merged and systematically absent reflections rejected.

The locations of most non-hydrogen atoms of the three crystallographically independent molecules of complex **11** in the asymmetric unit were revealed by direct methods (SIR92[97]). Analysis of the normalised structure factors supported the choice of a non-centrosymmetric space group. The SIR92 output also indicated significant three-fold pseudo-translational symmetry effects in the l group of reflections. Examination of the distribution of intensities among the 1367 observed [$I > 2\sigma(I)$] reflections showed that 1059 had $l = 3n$ (n = integer) with an $|F_o| = 90.8$, while only 308 had $l \neq 3n$ with an average $|F_o| = 38.5$. A search for possible transformations (using MISSYM[98]) to higher symmetry was unfruitful. Further Fourier-difference syntheses revealed the positions of all non-hydrogen atoms. Static rotational disorder was found for one of the *tert*-butyl groups with *ca.* 50% relative site-occupancy factors as estimated by refinement of the two disordered Me_3 group site-occupancy factors with fixed isotropic thermal parameters.

Owing to the lack of observed data (due to the non-centrosymmetric space group and pseudo-translational absences) it was necessary to refine the fractional atomic coordinates and isotropic thermal parameters of the cyclopentadienyl, pyridine and Me_3 groups using rigid-body approximations. The net translational/rotational motions of these groups was not restrained, however. The positional parameters of the Ti, imido N and *tert*-butyl quaternary carbon atoms were refined independently subject to 'soft' similarity restraints[99] on the three sets of Ti=N−C and =N−C−Me angles, and Ti=N, N−C and C−Me distances. An empirical absorption correction (DIFABS[100]) based on the fully isotropic model was applied. Only the Ti atoms could finally be refined in the anisotropic approximation. Other non-H atoms were refined isotropically. Hydrogen atoms were (re)placed in estimated [C−H 0.96 Å, $U_{iso}(H) = 1.3U_{iso}(C)$] positions between successive cycles of least-squares refinement and a Chebychev[101] weighting scheme was applied. Examination of the refined Flack parameter[102] confirmed the correct choice of polarity of the asymmetric unit and the data were corrected for the effects of anomalous dispersion in the final cycles of refinement. Examination of a refined overall extinction parameter[103] and comparison of $|F_o|$ and $|F_c|$ for the strongest reflections showed the absence of any significant extinction effects. There were no unexpected large correlations between the least-square shifts of parameters for the crystallographically independent molecules.

We propose that the final agreement factor ($R = 0.096$) is adequate for the purposes of confirming the overall connectivity and principal structural features of complex **11**. Interestingly, the $l = 3n$ sub-group of reflections had an associated average $R = 0.067$ while for the $l \neq 3n$ sub-group the average R value was 0.340, underlining the drastic effects of pseudo-translational effects in these (weak) data. An alternative attempted refinement of the structure against F_o^2 using all independent data did not lead to an improved model [as judged by stability to anisotropic refinement, errors on bond parameters, or the $I > 2\sigma(I)$ conventional R factor]. All crystallographic calculations were performed using SIR92[97] and CRYSTALS-PC.[104]

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 186/311.

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