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New titanium imido chemistry

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A general entry point to new titanium imido chemistry is gained *via* the readily prepared synthons [Ti(NR)$Cl_2(py)_3$] (R = Bu^t or aryl) and their homologues, from which straightforward metathesis reactions afford a wide range of derivatives. The structures, solution dynamics and reactivity of these new compounds are reviewed.

Introduction

Transition metal imido chemistry is one of the growth areas of inorganic research and has been reviewed up to the end of 1993.[1–4] The dianionic terminal imido ligand in complexes of the general formula $[M(NR)_n(L)_m]$ [R = alkyl or aryl usually; $(L)_m$ = ancilliary ligand set] can act as a four-electron donor that is capable of forming a strong triple bond to the metal centre.† As such the M=NR linkage is valence isoelectronic with the terminal oxo group M=O, and the $\{NR\}^{2-}$ moiety is isolobal with $\{C_5R_5\}^-$.[5,6] The π-donor imido functional group gives rise to chemistry that is generally dominated by medium to high metal oxidation states; this contrasts with the familiar low to medium oxidation state chemistry that is characteristic of transition metal complexes supported by the neutral, π-acceptor carbonyl ligands.

While there has clearly been a strong curiosity-driven element to the development of transition metal imido chemistry, the importance of imido compounds and of their isolobal analogues in industrial processes, organic synthesis and catalysis is now very well recognised.[3,4,7] Generally speaking, by the end of the 1980s the chemistry of terminal imido compounds of Group 5–8 transition metals was firmly (although by no means comprehensively) established. By way of contrast, well defined derivatives for Groups 4 and 9 did not appear until about this time.[4] The primary objective of this article is to highlight the more recent advances in titanium imido chemistry. However, it will be helpful to begin by summarising some of the early developments in order to set the later work in context.

Structurally characterised terminal titanium imido complexes were only first described in 1990. These were the five-coordinate $[Ti(NPh)(OC_6H_3Pr^i_2\text{-}2,6)_2(py')_2]$ (py′ = 4-pyrrolidinopyridine) and six-coordinate $[Ti\{NP(S)Ph_2\}Cl_2(py)_3]$, prepared by Rothwell and coworkers[8] and Roesky *et al.*[9] respectively [Fig. 1(*a*) and (*b*)]. In 1991 Wolczanski and coworkers described the preparation and chemistry of the highly reactive transient species $[Ti(NSiBu^t_3)(NHSiBu^t_3)_2]$ [Fig. 1(*c*)] which can activate benzene C–H bonds.[10] Other reactive transient titanium imido species were also described around this time.[11] By 1993 a number of five- and six-coordinate complexes analogous to those shown in Fig. 1(*a*) and (*b*) had been reported,[4] but the range of titanium imido reaction chemistry appeared to be very polarised. In other words, it looked as though titanium imido compounds could either be isolated but were (apparently) unreactive, or could be generated *in situ* and were extremely reactive. In 1994 we started work in titanium imido chemistry by identifying a synthetic strategy that we hoped would allow us to extend significantly the range of ancilliary ligand environments for the Ti=NR functional group, and hence to find new reaction chemistry.[12] The remainder of this article describes this general entry to new titanium imido chemistry, an overview of the scope and range of new compounds that can be prepared, and some aspects of their structures, solution dynamics and reactivity.

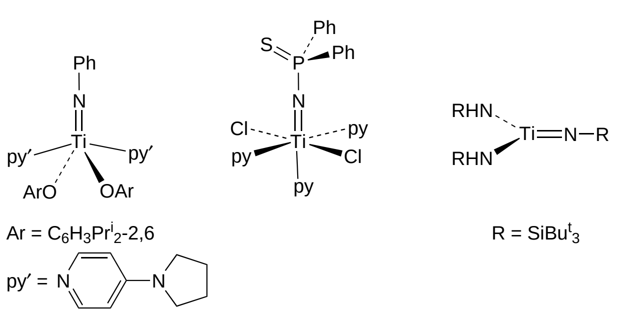


Fig. 1 The first crystallographically characterised (*a*) five-[8] and (*b*) six-coordinate[9] titanium imido complexes, and (*c*) a highly reactive transient species[10]

A convenient entry point to new titanium imido chemistry

Syntheses

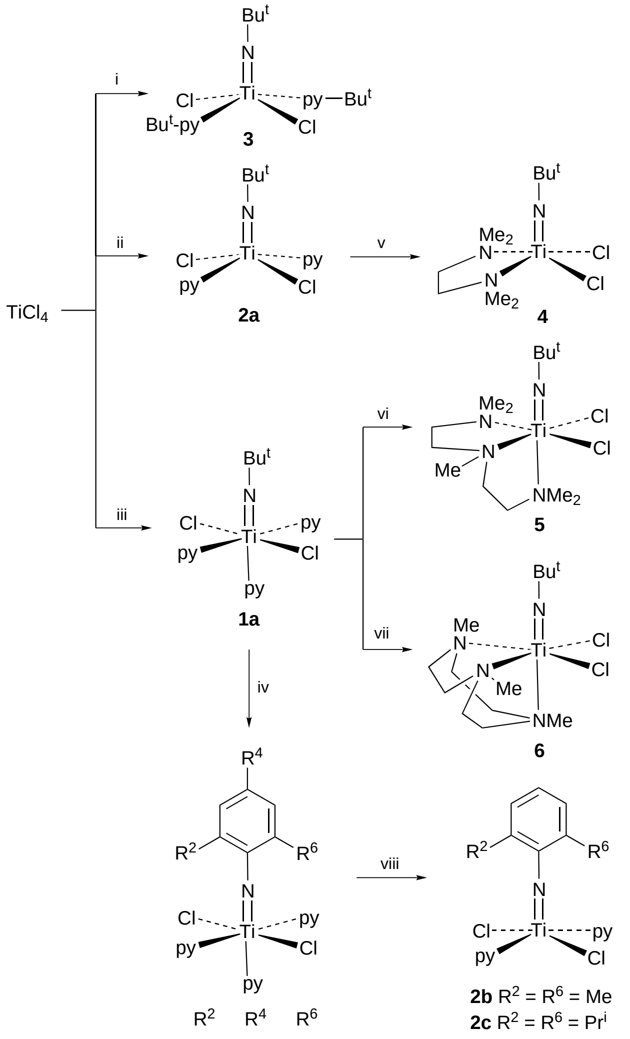
Being aware of the fairly facile reduction of Ti^{IV} to Ti^{III} in much of the element's chemistry, we decided to introduce the titanium imido group first, and any desired ancilliary ligands last. We have found that the compounds $[Ti(NR)Cl_2(L)_n]$ (R = Bu^t or aryl; L = py or $NC_5H_4Bu^t$-4; n = 2 or 3; see Fig. 2) are excellent synthons in this regard.[12,13] The success of these complexes as entry points to new titanium imido derivatives (*vide infra*) may partly be attributed to the π-donor imido ligand's ability to stabilise higher oxidation states. Hence almost none of the anion metathesis reactions described herein are complicated by reduction of the Ti^{IV} centre.

The *tert*-butyl imido complexes $[Ti(NBu^t)Cl_2(L)_n]$ (**1a** L = py, n = 3; **2a** L = py, n = 2; **3** L = $NC_5H_4Bu^t$-4, n = 2) are readily and efficiently obtained from $TiCl_4$, Bu^tNH_2 and the appropriate L (Fig. 2).‡ Compound **1a** in particular is available on a 35–40 g scale in near-quantitative yield.[12,13] Analogous aryl imido pyridine derivatives cannot be obtained directly from $ArNH_2$ and $TiCl_4$, but arylamine/*tert*-butyl imide exchange reactions of $[Ti(NBu^t)Cl_2(py)_3]$ **1a** readily afford the desired $[Ti(NAr)Cl_2(py)_3]$ (Ar = $C_6H_3Me_2$-2,6 **1b**; $C_6H_3Pr^i_2$-2,6 **1c**; C_6H_5 **1d**; C_6H_4Me-4 **1e**; $C_6H_4NO_2$-4 **1f**).[13,14] These were the first such exchange reactions for Group 4 imido compounds. The 2,6-disubstituted aryl derivatives **1b** and **1c** are by far the most stable and readily prepared; compounds **1a** and **1d**–**1f** have been crystallographically characterised. Five-coordinate bis(pyridine) derivatives $[Ti(NAr)Cl_2(py)_2]$ (Ar = $C_6H_3Me_2$-2,6 **2b**; $C_6H_3Pr^i_2$-2,6 **2c**) are also easily obtained, reflecting the *trans*-labilising ability of the imido group.

The homologous series $[Ti(NR)Cl_2(py)_3]$ (R = Bu^t **1a**, Ph **1d**, C_6H_4Me-4 **1e** or $C_6H_4NO_2$-4 **1f**) provided the first opportunity to use crystallographic results to compare the general structural and *trans* influence [the average difference between the *cis*-Ti–N(py) and *trans*-Ti–N(py) bond lengths] of different imido ligands within a series of simple six-coordinate, d^0 complexes as a function of the imido N-substituent. The absence of aryl ring 2,6-substituents in **1d–f** meant that steric effects were minimised as far as possible. Interestingly, despite the significantly different nitrogen substituents in **1a** and **1d–f**, there is no experimental difference in *trans* influence between them.[13,14]

Bi- and tri-dentate amine adducts

Early transition metal, d^0 complexes with *cis*-dichloride ligands are potential precursors to alkene polymerisation catalysts.[15,16] As shown in Fig. 2, the bis- and tris-pyridine adducts **2a** and **1a** afford fourteen- and sixteen-electron, bi- and tri-dentate amine adducts $[Ti(NBu^t)Cl_2(tmeda)]$ (**4**; tmeda = tetramethylethylenediamine),[17] $[Ti(NBu^t)Cl_2(pmdeta)]$ (**5**; pmdeta = pentamethyldiethylenetriamine) and $[Ti(NBu^t)Cl_2(Me_3[9]aneN_3)]$ (**6**; $Me_3[9]aneN_3$ = 1,4,7-trimethyl-1,4,7-triazacyclononane) in good yields.[13,18] The crystallographically characterised compounds **5** and **6** are isolobal analogues of $[Ti(\eta^5\text{-}C_5H_5)_2Cl_2]$. The open-chain triamine adduct $[Ti(NBu^t)Cl_2(pmdeta)]$ **5** is highly labile in solution whereas the cyclic triamine analogue $[Ti(NBu^t)Cl_2(Me_3[9]aneN_3)]$ **6** is rigid on the NMR timescale and generally more easily handled. Compound **6** is the first structurally characterised, triazacyclonane-supported transition metal imido complex. Studies of the substitution chemistry and polymerisation activity of **4–6** and their heavier Group 4 and Group 5 analogues are currently in progress.



	R^2	R^4	R^6
1b	Me	H	Me
1c	Pr^i	H	Pr^i
1d	H	H	H
1e	H	Me	H
1f	H	NO_2	H

Fig. 2 Versatile synthons for new titanium imido compounds and some pyridine substitution reactions.[13,18] *Reagents and conditions*: (i) Bu^tNH_2 (6 equiv.), py-Bu^t (2.2 equiv.); (ii) Bu^tNH_2 (6.0 equiv.), py (2.3 equiv.); (iii) Bu^tNH_2 (6.3 equiv.), py (4.1 equiv.); (iv) aniline or substituted aniline; (v) tmeda; (vi) pmdeta; (vii) $Me_3[9]aneN_3$; (viii) 65 °C, dynamic vacuum. py-Bu^t = $NC_5H_4Bu^t$-4.

Cyclopentadienyl and indenyl derivatives

Half-sandwich compounds

Straightforward metathesis reactions of $[Ti(NBu^t)Cl_2(NC_5H_4R\text{-}4)_n]$ (**1a**, **2a** or **3**) with sodium or lithium cyclopentadienides gives the range of half-sandwich derivatives $[Ti(\eta^5\text{-}C_5R'_5)(NBu^t)Cl(NC_5H_4R\text{-}4)]$ (**7–14**, Fig. 3).[12,19,20] Similarly, treatment of **3** with lithium trimethylindenide afforded the first Group 4 indenyl imido derivative $[Ti(\eta^5\text{-}C_9H_4Me_3)(NBu^t)Cl(NC_5H_4\text{-}Bu^t\text{-}4)]$ **15** for which a pentahapto coordination of the indenyl ligand was inferred from ^{13}C NMR data. Compound **15** is relatively labile and ring non-substituted indenyl analogues could not be isolated. The structurally characterised compound $[Ti(\eta^5\text{-}C_5Me_5)(NBu^t)Cl(py)]$ **12** was first obtained *via* dehydrohalogenation of $[Ti(\eta^5\text{-}C_5Me_5)(NHBu^t)Cl_2]$ in the presence of pyridine.[21] The ring non- or mono-substituted compounds **9** and **10** lose pyridine in solution or the solid state forming μ-imido bridged dimers. However, the ring penta-substituted homologues **12–14** are stable to pyridine loss under comparable conditions.

Bis(pyridine), half-sandwich titanium imides analogous to those of zirconium and hafnium[22] were not isolated, but variable temperature NMR measurements identified C_s-symmetric complexes $[Ti(\eta^5\text{-}C_5Me_4R)(NBu^t)Cl(py)_2]$ as intermediates in the free/coordinated pyridine exchange reactions of **7–14**; ^{13}C NMR lineshape and coalescence measurements for $[Ti(\eta^5\text{-}C_5Me_4C_4H_7)(NBu^t)Cl(py)]$ **14** yielded activation parameters for this process.

Sandwich compounds

The Bergman group has developed an extensive reaction chemistry of zirconocene imido derivatives.[23,24] We were thus interested to find an entry point to analogous titanium imido systems.§

Syntheses: Fig. 3 shows that addition of two equivalents of sodium cyclopentadienide to $[Ti(NBu^t)Cl_2(py)_3]$ **1a** gave reasonable yields of $[Ti(\eta^5\text{-}C_5H_5)_2(NBu^t)(py)]$ **17**. Mixed ring analogues $[Ti(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_4R)(NBu^t)(py)]$ (R = Me **18** or Et **19**) were prepared from $Na[C_5H_5]$ and **12** or **13**. Attempts to prepare bis(pentamethylcyclopentadienyl)titanium imides from **12** and $Li[C_5Me_5]$ were unsuccessful and appeared to result in reduction to Ti^{III}.¶ The X-ray structure of **17** confirmed the pentahapto coordination of the cyclopentadienyl rings in the solid state and revealed a near-linear $Ti{=}NBu^t$ linkage. The sandwich titanium imido compounds are considerably more air- and moisture-sensitive than their half-sandwich analogues.

At first sight, the titanocene imido complexes **17–19** are twenty valence electron species. However, it appears that in these and related metallocene imido and oxo compounds[25,26] two of the 'excess' electrons are located in a ligand-based, non-bonding orbital having both C_5H_5 carbon and NBu^t nitrogen character. Thus the actual $Ti{=}NBu^t$ bond order in compounds **17–19** is probably somewhere between two and three, with the titanium–cyclopentadienyl interactions presumably also somewhat weakened relative to 'normal' sixteen- and eighteen-electron titanocene derivatives. The $Ti\text{–}Cp_{cent}$ distances and $Cp_{cent}\text{–}Ti\text{–}Cp_{cent}$ angles (Cp_{cent} = computed C_5H_5 centroid) for **17** are consistent with this hypothesis. Furthermore, reaction of lithium indenide with $[Ti(\eta^5\text{-}C_5H_5)(NBu^t)Cl(py)]$ **9** afforded the eighteen-electron, ring-slipped derivative $[Ti(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_9H_7)(NBu^t)(py)]$ **20**. Moreover, an equimolar mixture of $[Ti(NBu^t)Cl_2(py)_2]$ **2a** and $[Ti(\eta^5\text{-}C_5H_5)_2(NBu^t)(py)]$ **17** in C_6D_6 underwent a very facile, room temperature redistribution reaction in C_6D_6 to give **9** quantitatively, again indicative of C_5H_5 ligand labilisation in the bis(cyclopentadienyl) com-

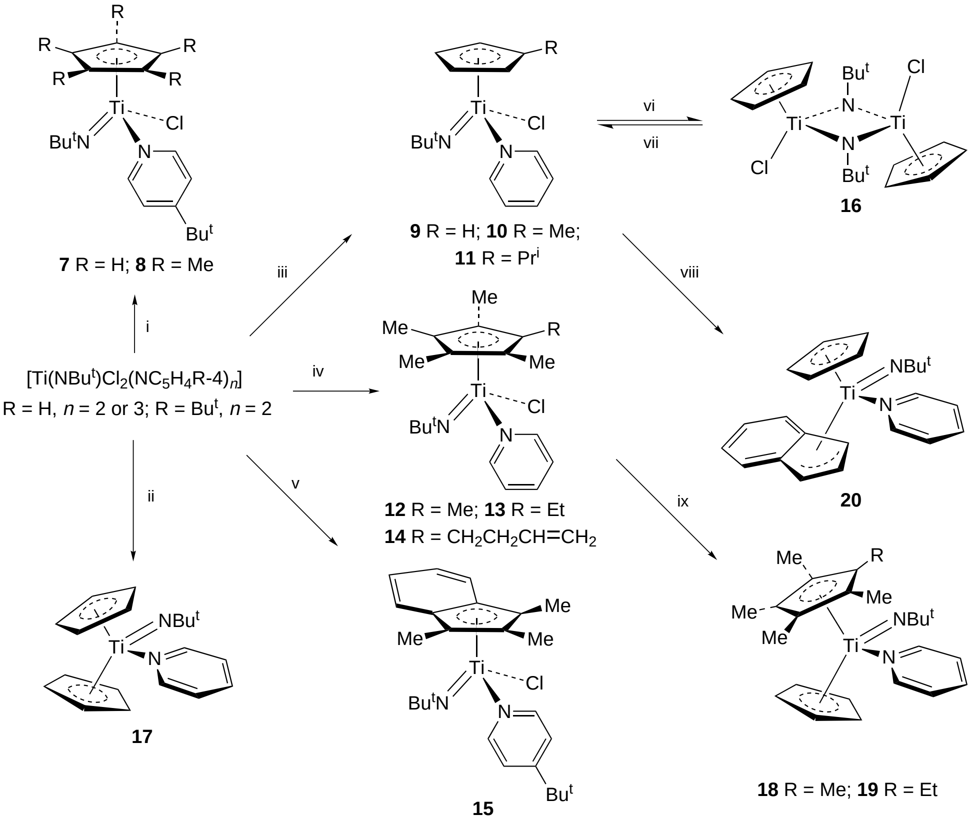


Fig. 3 Sandwich and half-sandwich titanium imido derivatives.[20] *Reagents and conditions*: (i) for **7**: Na[C_5H_5], for **8**: Li[C_5Me_5]; (ii) Na[C_5H_5] (2 equiv.); (iii) for **9**: Na[C_5H_5], for **10**: Li[C_5H_4Me], for **11**: Li[$C_5H_4Pr^i$], (iv) for **12**: Li[C_5Me_5], for **13**: Li[C_5Me_4Et], for **14**: Li[$C_5Me_4C_4H_7$]; (v) Li[$C_9H_4Me_3$]; (vi) 1×10^{-2} mbar, 85 °C; (vii) py (3 equiv.); (viii) Li[C_9H_7]; (ix) Na[C_5H_5].

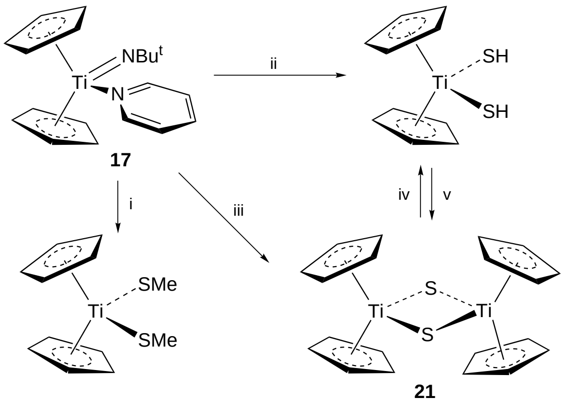


Fig. 4 Reactions of $[Ti(\eta^5-C_5H_5)_2(NBu^t)(py)]$ **17** with S–H bonds.[28] *Reagents*: (i) MeSH (excess); (ii) H_2S (excess); (iii) H_2S (1 equiv.); (iv) H_2S (excess); (v) **17** (1 equiv.).

plexes. By way of comparison, the analogous C_5H_5 ring redistribution reaction between $[Ti(\eta^5-C_5H_5)_2Cl_2]$ and $TiCl_4$ required elevated temperatures and longer reaction times.[27]

Reactions with S–H bonds: Tetraazamacrocycle-supported titanium *tert*-butyl imido derivatives (*vide infra*) undergo facile exchange of Ti=NBu^t for terminal Ti=E (E = O, S, NAr or $NNPh_2$) groups on treatment with H_2E. We have investigated possible analogous routes to titanocene mono(sulfide) complexes (Fig. 4).[28] Not surprisingly, reaction of $[Ti(\eta^5-C_5H_5)_2(NBu^t)(py)]$ **17** with an excess of MeSH affords the previously described $[Ti(\eta^5-C_5H_5)_2(SMe)_2]$. An intermediate species formulated as $[Ti(\eta^5-C_5H_5)_2(NHBu^t)(SMe)]$ was observed by ^1H NMR spectroscopy but was not isolated. With an excess of H_2S, **17** gives high yields of $[Ti(\eta^5-C_5H_5)_2(SH)_2]$, but with one equivalent of H_2S the new bis(μ-sulfide) $[Ti_2(\eta^5-C_5H_5)_4(\mu-S)_2]$ **21** was obtained. Compound **21** may also be prepared by reaction of **17** with $[Ti(\eta^5-C_5H_5)_2(SH)_2]$. In neither of these reactions was evidence for a titanocene terminal sulfido derivative found.¶ The thermally labile compound **21** is a possible intermediate in the formation of $[Ti(\eta^5-C_5H_5)_2(SH)_2]$ since treatment of **21** with an excess of H_2S gave a quantitative yield of $[Ti(\eta^5-C_5H_5)_2(SH)_2]$.

These reactions comprised the first reports of S–H bond ‘activation’ for Group 4 metal imido complexes. Furthermore, the complex $[Ti_2(\eta^5-C_5H_5)_4(\mu-S)_2]$ **21** represents a kind of ‘missing link’ both in the titano- and zircono-cene bis(μ-chalcogenido) series $[M_2(\eta-C_5R_5)_4(\mu-E)_2]$ (M = Ti or Zr; E = S or Se) and in the bis(titanocene) μ-(poly)sulfido series $[Ti_2(\eta-C_5H_4R)_4(\mu-S_x)_2]$ (x = 1, 2 or 3), which have been the subject of considerable research activity.

Mono- and bi-nuclear derivatives with aryloxide ligands: fine control by *ortho*-substituents

As mentioned, five-coordinate aryloxide-supported derivatives were among the first terminal titanium imido compounds to be structurally characterised.[8,29] The transient imido complex $[Ti(NSiBu^t)(OSiBu^t)_2]$ has been proposed as a reactive intermediate.[30] We were interested in extending these studies by exploring in detail the dependence of the structures, nuclearity and metal coordination number of aryloxide-supported titanium imides upon the steric demands of the ligand O- and N-substituents.[31]

The reaction products of $[Ti(NBu^t)Cl_2(py)_3]$ **1a** with lithium aryloxides (Fig. 5) show the relationship between the product nuclearity and coordination number and the steric bulk of the aryloxide ligand *ortho*-substituents. The structure of $[Ti_2(\mu-NBu^t)_2(OC_6H_3Me_2-2,6)_4]$ **22** was confirmed by X-ray crystallography and $[Ti(NBu^t)(OC_6H_3Bu^t_2-2,6)_2(py)]$ **24** was established as a monomer by solution molecular mass determinations. The {Ti(μ-NBu^t)$_2$Ti} core in compound **22** can be cleaved by an excess of pyridine to form mononuclear $[Ti(NBu^t)(OC_6H_3Me_2\text{-}2,6)_2(py)_2]$ **25a**. Although the *tert*-butyl imido compound **25a** slowly dimerises to **22** over time, the aryl imido homologues $[Ti(NC_6H_3R_2\text{-}2,6)(OC_6H_3Me_2\text{-}2,6)_2(py)_2]$ [R = Me **25b** (X-ray structure) or Pr^i **25c**] are stable.

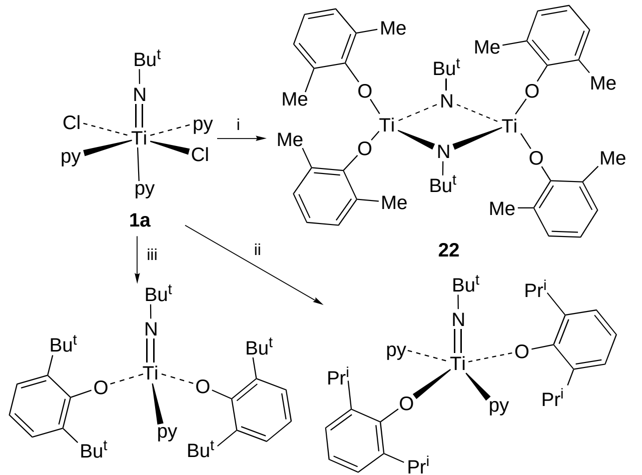
We have analysed the bonding in $[Ti_2(\mu\text{-}NBu^t)_2(OC_6H_3Me_2\text{-}2,6)_4]$ **22** using extended Hückel molecular orbital (EHMO) calculations and reached two important conclusions.[31] First, symmetry constraints mean that the Ti centres in **22** can only ever achieve a valence electron count of sixteen, even though the formal hybridisation of the imido N- and terminal aryloxide O-atoms suggests that metal electron counts of eighteen are apparently possible. Second, the deviation of the μ-imido Bu^t substituents from coplanarity with the Ti_2N_2 unit in both **22** and related species such as $[Ti_2(\mu\text{-}NBu^t)_2(NMe_2)_4]$ can be attributed to a second-order Jahn–Teller distortion which arises because of competition between the terminal and bridging π-donor ligands for metal d_π-acceptor orbitals.

Amidinate derivatives

In contrast to other areas of main group and transition metal chemistry, amidinate ligands[32,33] have been little used in metal imido systems.[34–38] We have recently reported new niobium imido (and oxo) benzamidinate derivatives,[39] and this work is complemented by the titanium imido amidinate chemistry summarised below.

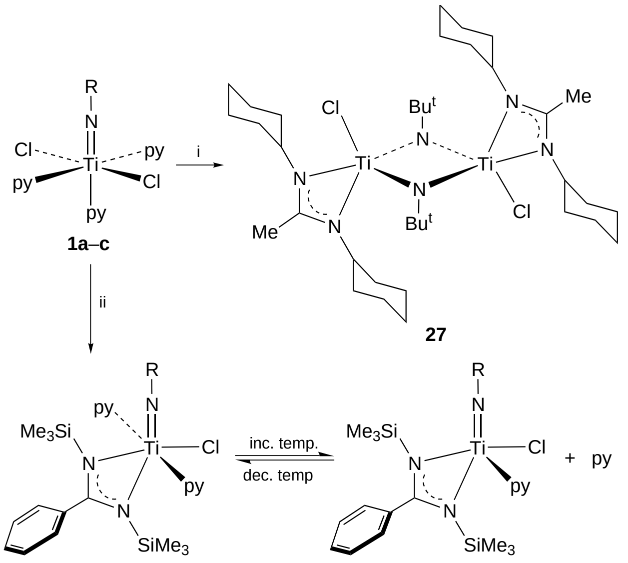
The steric and solubility properties of amidinate ligands $R'C(NR)_2$ may be modified by changing the R′ and R groups. We have compared (Fig. 6) the reactions of lithium *N*,*N*′-bis(trimethysilyl)benzamidinate and lithium *N*,*N*′-bis(cyclohexyl)acetamidinate with $[Ti(NR)Cl_2(py)_3]$ (R = Bu^t **1a**, $C_6H_3Me_2$-2,6 **1b** and $C_6H_3Pr^i_2$-2,6 **1c**).[40] Reaction of $Li[PhC(NSiMe_3)_2]$ with **1a–1c** afforded the corresponding mononuclear compounds $[Ti(NR)\{PhC(NSiMe_3)_2C\}l(py)_2]$ **26a–c** as confirmed by X-ray crystallography for **26b**. In contrast, reaction of $Li[MeC(NC_6H_{11})_2]$ with **1a** led to the structurally characterised binuclear derivative $[Ti_2(\mu\text{-}NBu^t)_2\text{-}\{MeC(NC_6H_{11})_2\}_2Cl_2]$ **27** which contains no pyridine coligands. Attempts to prepare aryl imido analogues of **26** or **27** from $Li[MeC(NC_6H_{11})_2]$ and $[Ti(NC_6H_3Me_2\text{-}2,6)Cl_2(py)_3]$ **1b** were unsuccessful.

All three compounds **26a–c** form six-coordinate bis(pyridine) adducts in the solid state, but in solution they exist in temperature-dependent dynamic equilibrium with the fourteen valence electron, mono(pyridine) homologues **26a′–c′** (Fig. 6). Thermodynamic parameters (Table 1) associated with these equilibria have been determined by NMR spectroscopy and reveal the underlying effects of the different imido N-substituents. Activation parameters for the forward (*i.e.* **26a** or **26b** → **26a′** or **26b′** + py) and reverse (**26a′** or **26b′** + py → **26a** or **26b**) processes have also been measured. The differences between the derived $\Delta G^{\ddagger}_{258\,K}$ values for the forward and reverse steps compare very well with the equilibrium thermodynamic $\Delta G_{258\,K}$ values which show that all three equilibria are effectively thermochemically neutral. The large positive ΔS values are consistent with the dissociative equilibria as written and nearly compensate for the endothermic ΔH term at higher temperatures.



1a **22** **24** **23**

Fig. 5 Reactions of $[Ti(NBu^t)Cl_2(py)_3]$ **1a** with $Li[OC_6H_3R_2\text{-}2,6]$: fine control by *ortho*-substituents.[31] *Reagents*: (i) $Li[OC_6H_3Me_2\text{-}2,6]$ (2 equiv.); (ii) $Li[OC_6H_3Pr^i_2\text{-}2,6]$ (2 equiv.); (iii) $Li[OC_6H_3Bu^t_2\text{-}2,6]$ (2 equiv.).



1a–c **27**

26a R = Bu^t
26b R = $C_6H_3Me_2$-2,6
26c R = $C_6H_3Pr^i_2$-2,6

26a' R = Bu^t
26b' R = $C_6H_3Me_2$-2,6
26c' R = $C_6H_3Pr^i_2$-2,6

Fig. 6 Mono- and bi-nuclear titanium imido complexes with amidinate ligands.[40] *Reagents*: (i) $Li[MeC(NC_6H_{11})_2]$; (ii) $Li[PhC(NSiMe_3)_2]$.

Very recent results for $[Ti(NBu^t)\{PhC(NSiMe_3)_2C\}l(py)_2]$ **26a** promise an extensive reaction chemistry for the amidinate-supported titanium imido compounds.[18] Straightforward metathesis reactions afford a range of organometallic and inorganic derivatives in good to excellent yields (Fig. 7). The half-sandwich compound **29** can also be prepared from $Li[PhC(NSiMe_3)_2]$ and $[Ti(\eta^5\text{-}C_5Me_5)(NBu^t)Cl(NC_5H_4Bu^t\text{-}4)]$ **8**.[18]

Tris(pyrazolyl)hydroborate derivatives

Fig. 8 summarises the synthesis of sixteen valence electron tris(pyrazolyl)hydroborate derivatives $[Ti(L)(NBu^t)\text{-}Cl(NC_5H_4Bu^t\text{-}4)]$ (L = Tp^{Me2} **34**, Tp^{Pr^i} **35** or $Tp^{Pr^i,Br}$ **36**) *via* reaction of $[Ti(NBu^t)Cl_2(NC_5H_4Bu^t\text{-}4)_2]$ **3** with one equivalent of $K[Tp^{Me2}]$, $K[Tp^{Pr^i}]$ or $K[Tp^{Pr^i,Br}]$ [Tp^{Me2} = tris(3,5-dimethylpyrazolyl)hydroborate; Tp^{Pr^i} = tris(3-isopropylpyrazolyl)hydroborate; $Tp^{Pr^i,Br}$ = tris(3-isopropyl-4-bromopyrazolyl)hydroborate] respectively.[41] Compounds **34–36** are the first Group 4 tris(pyrazolyl)hydroborate-supported imido complexes and are isolobal analogues of the half-sandwich

Table 1 Thermodynamic parameters for the dissociative equilibria of $[Ti(NR)\{PhC(NSiMe_3)_2\}Cl(py)_2]$ [R = Bu^t **26a**, $C_6H_3Me_2$-2,6 **26b** or $C_6H_3Pr^i_2$-2,6 **26c**][40]

R	ΔH/ kJ mol^{-1}	ΔS/ J mol^{-1} K^{-1}	$\Delta G_{258\,K}$/ kJ mol^{-1}
Bu^t **26a**	38.7 ± 1.5	108 ± 5	10.8 ± 2.8
$C_6H_3Me_2$-2,6 **26b**	47.3 ± 1.9	142 ± 5	10.7 ± 3.2
$C_6H_3Pr^i_2$-2,6 **26c**	45.7 ± 2.0	172 ± 5	1.2 ± 3.3

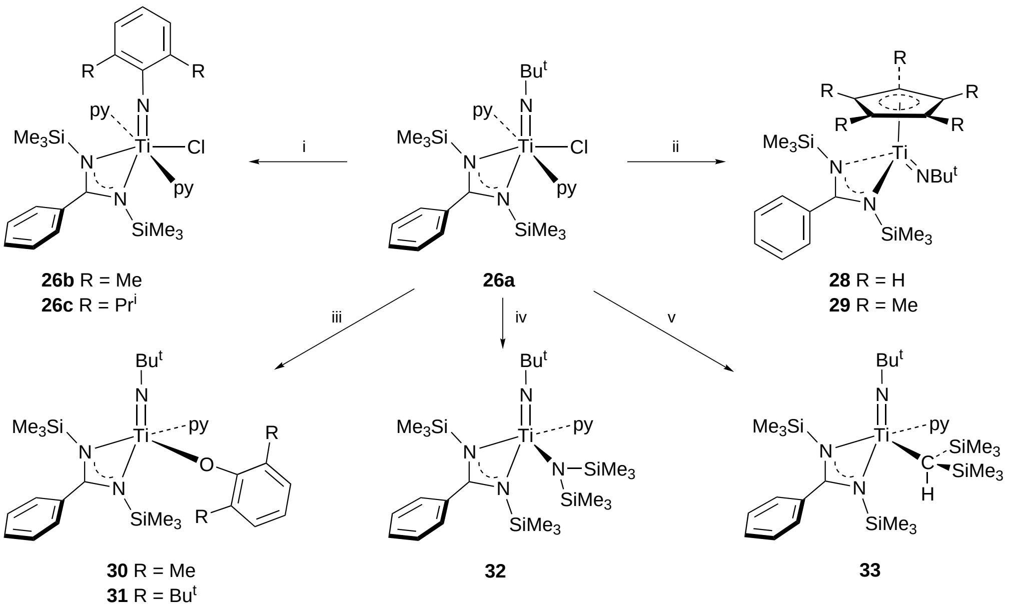
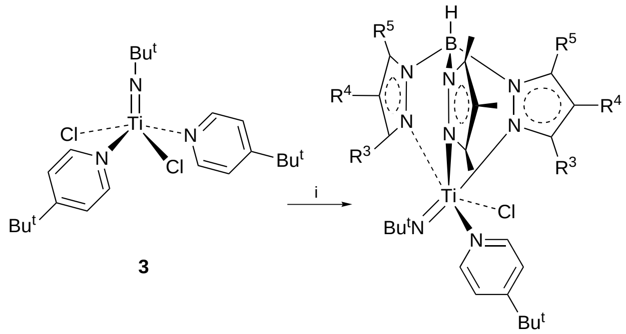


Fig. 7 Substitution reactions of $[Ti(NBu^t)\{PhC(NSiMe_3)_2\}Cl(py)_2]$ **26a**.[18] *Reagents*: (i) $H_2NC_6H_3R_2$-2,6 where for **26b**: R = Me, for **26c**: R = Pr^i; (ii) for **28**: $Na[C_5H_5]$, for **29**: $Li[C_5Me_5]$; (iii) $Li[OC_6H_3R_2$-2,6] where for **30**: R = Me, for **31**: R = Bu^t; (iv) $Li[N(SiMe_3)_2]\cdot Et_2O$; (v) $Li[CH(SiMe_3)_2]$.



	R^3	R^4	R^5
34 Tp^{Me_2}	Me	H	Me
35 Tp$^{Pr^i}$	Pr^i	H	H
36 Tp$^{Pr^i,Br}$	Pr^i	Br	H

Fig. 8 Titanium imido complexes with tris(pyrazolyl)hydroborate ligands.[41] *Reagents*: (i) for **34**: K[Tp^{Me_2}], for **35**: K[Tp$^{Pr^i}$], for **36**: K[Tp$^{Pr^i,Br}$].

complexes $[Ti(\eta^5\text{-}C_5R'_5)(NBu^t)Cl(NC_5H_4R\text{-}4)]$ (**7**–**14**). Unlike the cyclopentadienyl compounds, however, the tris(pyrazolyl)hydroborate species are fluxional on the ^1H and ^{13}C NMR timescales, the spectra indicating restricted rotation about the Ti–($NC_5H_4Bu^t$-4) bond. Activation parameters were determined for **34** and the barrier to pyridine rotation obtained from coalescence measurements ($\Delta G^{\ddagger}_{267\,K}$ = 51.1 kJ mol^{-1}) compared very well with that calculated (51.4 kJ mol^{-1}) from the $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ values using lineshape analysis.

Diamidoamine and diamidopyridine derivatives

The tetradentate, triamidoamine (tren) ligands $[(RNCH_2CH_2)_3N]^{3-}$ have been used with spectacular success for developing the metal–ligand multiple bond chemistry of groups 5–7.[42] We have started to explore the potential of tridentate diamidoamine[43] and diamidopyridine[44] ligands in Group 4 imido chemistry. While being related to the triamidoamines, the dianionic diamidoamine and diamidopyridine ligands have a dative nitrogen donor ‘arm’ which can in principle readily detach from the metal centre to open up reversibly a more reactive site. Furthermore, they require only two d electrons for metal–ligand bonding, thus enabling neutral imido derivatives for the Group 4 metals. Although our work in this area is at a very early stage, some important results have already been obtained (Fig. 9).[18,45]

Reaction of $Li_2[Me_3SiN(CH_2CH_2NSiMe_3)_2]$ with $[Ti(NBu^t)Cl_2(py)_3]$ **1a** gave the crystallographically characterised derivative $[Ti(NBu^t)\{Me_3SiN(CH_2CH_2NSiMe_3)_2\}py)]$ **37** in good yield. Similarly, addition of $[Li_2\{MeC(C_5H_4N\text{-}2)(CH_2NSiMe_3)_2\}]_2$ to **1a** in benzene gave $[Ti(NBu^t)\{MeC(C_5H_4N\text{-}2)(CH_2NSiMe_3)_2\}(py)]$ **38** which has also been crystallographically characterised. Compounds **37** and **38** are the first fully characterised examples of terminal titanium imides supported by amido ligands, although the complex $[Ti(NSiBu^t_3)(NHSiBu^t_3)_2]$ has been proposed as a reactive transient in C–H bond activation reactions.[10] Fig. 9 shows the product of the remarkable reaction between **38** and methyl isocyanide, namely $[Ti\{MeC(C_5H_4N\text{-}2)(CH_2NSiMe_3)_2\}\{N(Me)N(Bu^t)\text{-}1,2\text{-}(C_4H_3N_2Me\text{-}3)\}]$ **39**, which has been structurally characterised. The Ti=NBu^t linkage of **1a** has clearly undergone a C–N and C–C coupling reaction (with concomitant C–H bond migration) with three molecules of MeNC to form a coordinated 3-methyl-5,6-diamino-2,3-dihydropyrimidine derivative. The type of reaction giving rise to **39** is unprecendented in Group 4 imido chemistry. It is also highly selective with **39** being the only new species formed when the reaction was

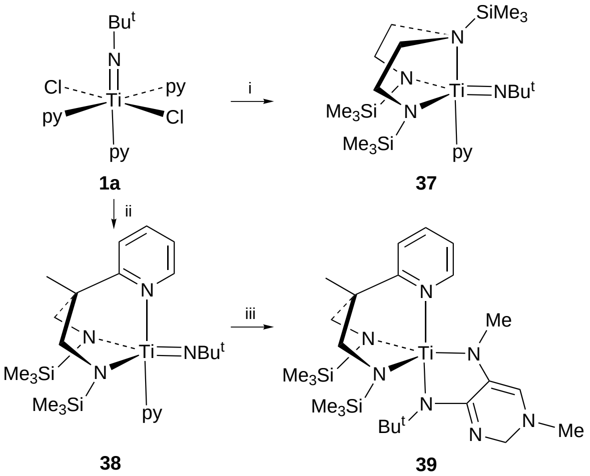
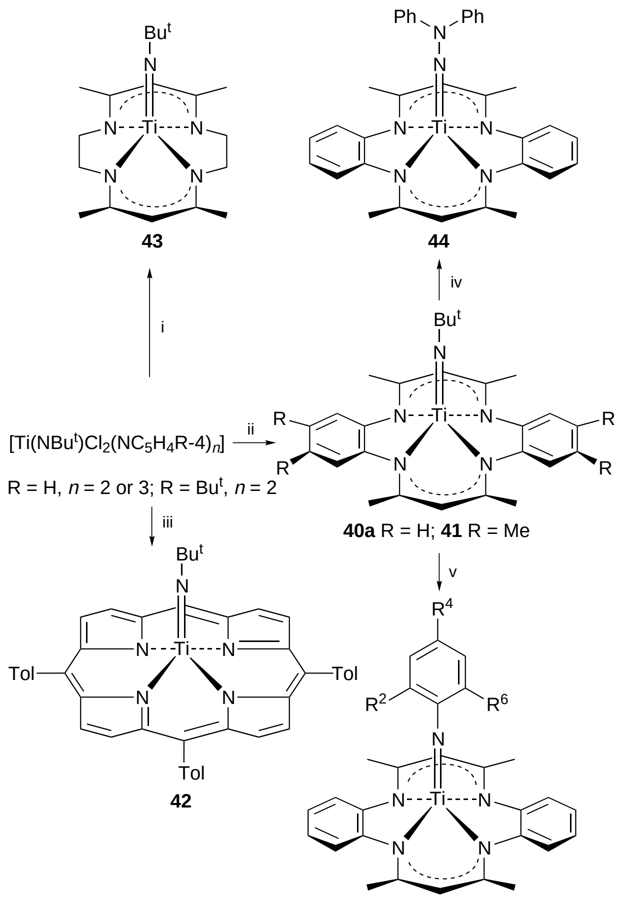


Fig. 9 Titanium imido complexes with diamidoamine and diamidopyridine ligands.[18,45] *Reagents*: (i) $Li_2[Me_3SiN(CH_2CH_2NSiMe_3)_2]$; (ii) $[Li_2\{MeC(C_5H_4N\text{-}2)(CH_2NSiMe_3)_2\}]_2$; (iii) MeNC (3 equiv.).



	R^2	R^4	R^6
40b	Me	H	Me
40c	Pr^i	H	Pr^i
40d	H	H	H
40e	H	Me	H
40f	H	NO_2	H
40g	H	NMe_2	H

Fig. 10 Titanium imido complexes with dibenzotetraaza[14]annulene and some other tetraazamacrocyclic ligands.[12,18,52] *Reagents*: (i) $Li_2[Me_4taen]$; (ii) for **40a**: $Li_2[Me_4taa]$, for **41**: $Li_2[Me_8taa]$; (iii) $Li_2[ttp]$; (iv) Ph_2NNH_2; (v) aniline or substituted aniline.

followed by ^1H NMR spectroscopy. The $Ti{=}NBu^t$ functional group in **38** also reacts with a range of other unsaturated organic substrates and work is in progress to determine the scope of this chemistry.

Tetraazamacrocycle-supported derivatives

Syntheses

Prompted by reports that the Ti=O linkage in the tetraazamacrocycle-supported compound $[Ti(O)(Me_4taa)]$[46] (H_2Me_4taa = tetramethyldibenzotetraaza[14]annulene) is reactive towards a range of organic and inorganic substrates,[47] we prepared (Fig. 10) the titanium *tert*-butyl imido analogues $[Ti(NBu^t)(Me_n taa)]$ (n = 4 **40a** or 8 **41**; H_2Me_8taa = octamethyldibenzotetraaza[14]annulene) from $[Ti(NBu^t)Cl_2(L)_n]$ and $Li_2[Me_n taa]$.[12,48] Compounds **40a** and **41** were the first reported macrocycle-supported Group 4 imido compounds. Woo and coworkers subsequently reported the synthesis of [Ti(NR)(ttp)] (R = Bu^t **42**, Ph, C_6H_4Me-4 or C_6H_{11}; H_2ttp = tetratolylporphyrin) from $[Ti(ttp)Cl_2]$.[49] We have shown that **42** can also be obtained in good yield by treating $[Ti(NBu^t)Cl_2(py)_3]$ **1a** with $Li_2[ttp]$.[18] In related studies (Fig. 10) we found that reactions of $Li_2[Me_4taen]$ (H_2Me_4taen = 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene) with **1a** gives $[Ti(NBu^t)(Me_4taen)]$ **43**. We have also recently prepared related Me_4taa-supported zirconium imido and amido complexes.[50,51]

Exchange reactions (Fig. 10) of $[Ti(NBu^t)(Me_4taa)]$ **40a** with a range of anilines or *N*,*N*-diphenylhydrazine afforded the homologues $[Ti(NAr)(Me_4taa)]$ (Ar = $C_6H_3Me_2$-2,6 **40b**, $C_6H_3Pr^i{}_2$-2,6 **40c**, Ph **40d**, C_6H_4Me-4 **40e**, $C_6H_4NO_2$-4 **40f** or $C_6H_4NMe_2$-4 **40g**) and $[Ti(NNPh_2)(Me_4taa)]$ **44** respectively.[18,52] Although most of these reactions were quantitative by ^1H NMR spectroscopy, they were noticeably slower than those of $[Ti(NBu^t)Cl_2(py)_3]$ **1a** (Fig. 2). Indeed, the 2,6-diisopropylphenyl imido derivative **40c** was only obtained in trace quantities after long reaction times. The X-ray structures of **40b**[52] and **41**[12] have been determined. No bis(amide) intermediates were observed when the reactions of $[Ti(NBu^t)(Me_4taa)]$ **40a** with anilines were followed by ^1H NMR spectroscopy and no evidence was found for equilibrium concentrations of $[Ti(NHR)_2(Me_4taa)]$ in solutions containing $[Ti(NR)(Me_4taa)]$ and H_2NR (R = Bu^t or $C_6H_3Me_2$-2,6). In contrast, the zirconium aryl imido homologue (which is obtained as a pyridine adduct) $[Zr(NC_6H_3Pr^i{}_2\text{-}2,6)(py)(Me_4taa)]$ reacts immediately and irreversibly with $H_2NC_6H_3Pr^i{}_2$-2,6 to form the bis(anilide) $[Zr(HNC_6H_3Pr^i{}_2\text{-}2,6)_2(Me_4taa)]$.[50] Interestingly, we note that $[Ti(NBu^t)(ttp)]$ **43** does not undergo exchange reactions with anilines.[49] This underlines the importance of the choice of macrocyclic ligands.

Reactions of [Ti(NBu^t)(Me₄taa)] **40a** *with O–H and S–H bonds*

Treatment of **40a** with H_2E (E = O or S) gave the previously described[46] $[Ti(E)(Me_n taa)]$ in quantitative yield (Fig. 11). Compound **40a** also undergoes protonolysis with aryl and alkyl alcohols and diols to form $[Ti(OR)_2(Me_4taa)]$ (R = Me **45** or $OC_6H_3Me_2$-2,6 **46**; $(OR)_2$ = $O_2C_2Me_4$ **47** or $O_2C_6H_4$ **48**[46]), and with MeSH to form $[Ti(SMe)_2(Me_4taa)]$ **49** by ^1H NMR spectroscopy. Reaction of **49** with H_2S forms $[Ti(S)(Me_4taa)]$ and MeSH. By analogy with the *tert*-butyl imide/aniline exchange processes (Fig. 10), when reactions of $[Ti(NBu^t)(Me_4taa)]$ **40a** with $HOC_6H_3Me_2$-2,6, MeSH or H_2S were followed by ^1H NMR spectroscopy, no six-coordinate intermediates $[Ti(ER)(NHBu^t)(Me_4taa)]$ (ER = $OC_6H_3Me_2$-2,6, SMe or SH) were observed. Furthermore, reaction of **40a** with one equivalent of $HOC_6H_3Me_2$-2,6 gave a *ca.* 50% yield of $[Ti(OC_6H_3Me_2\text{-}2,6)_2(Me_4taa)]$ and unreacted **40a**.

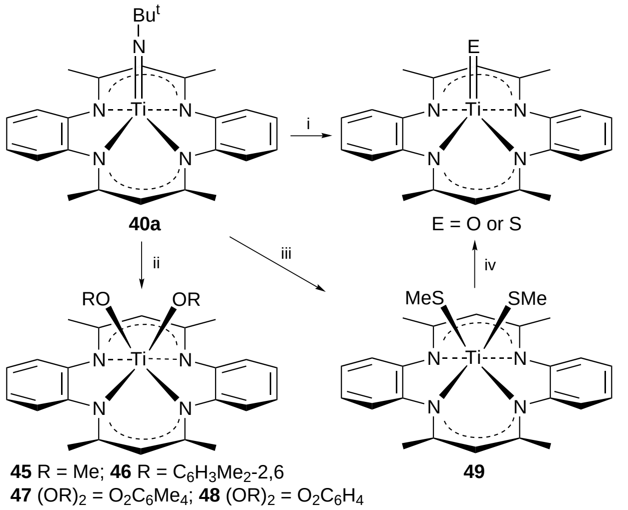


Fig. 11 Reactions of $[Ti(NBu^t)(Me_4taa)]$ **40a** with O–H and S–H bonds.[12,18] *Reagents*: (i) H_2E (E = O or S); (ii) ROH (2 equiv. of OH functional group); (iii) MeSH (2 equiv.); (iv) for $[Ti(S)(Me_4taa)]$: H_2S (excess).

Reactions of [Ti(NAr)(Me_4taa)] (Ar = Ph **40d** *or Tol* **40e***) with isocyanates, CO_2 and carbodiimides*

We have studied the cycloaddition and metathesis reactions of the compounds [Ti(NR)(Me_4taa)] **40** with a range of organic substrates.[18,50] Fig. 12 summarises some of the reactions of [Ti(NAr)(Me_4taa)] (Ar = Ph **40d** or Tol **40e**), along with some new, comparative reactions of [Ti(O)(Me_4taa)].

Reaction of **40d** or **40e** with isocyanates PhNCO or TolNCO gave the *N,N′*-bonded ureates [Ti{N(Ar)C(O)N(Ar)}(Me_4taa)] (Ar = Ph **50** or Tol **51**, respectively) in good yields.[50] The mixed N-aryl substituent ureate [Ti{N(Ph)C(O)N(Tol)}(Me_4taa)] **52** was prepared similarly from **40e** and PhNCO. In related studies, [Zr(N-$C_6H_3Pr^i{}_2$-2,6)(py)(Me_4taa)] reacted with Bu^{t}NCO to give the crystallographically characterised *N,N′*-bound ureate [Zr{N($C_6H_3Pr^i{}_2$-2,6)C(O)N(Bu^t)}(Me_4taa)].[50] The titanium congener **52** exhibits novel reactivity such that treatment with an excess of PhNCO gave [Ti{N(Ph)C(O)N(Ph)}(Me_4taa)] **50** with extrusion of TolNCO from the ureate ligand. ^{1}H NMR crossover experiments eliminated [Ti(NPh)(Me_4taa)] **40d** as an intermediate, thus suggesting that the PhNCO–TolNCO exchange involves an unusual associative mechanism proceeding *via* a biuret-type species, [Ti{N(Ph)C(O)N(Ph)C(O)N(Tol)}(Me_4taa)]. The exchange reaction of **52** was the first example of the reversible insertion of an isocyanate into the metal–N bond of a ureate ligand.

Reaction of [Ti(NTol)(Me_4taa)] **40e** with di-*p*-tolylcarbodiimide gave [Ti{N(Tol)C(NTol)N(Tol)}(Me_4taa)] **53** which is a rare example of a triazatrimethylene methane metal complex.[53] Reaction of **40e** with CO_2 gave the *O,O′*-bonded carbamate species [Ti{OC(NTol)O}(Me_4taa)] **54**. Compound **54** is presumably a thermodynamic (as opposed to kinetic) product since the expected first-formed product would be the *N,O*-bonded linkage isomer [Ti{N(Tol)C(O)O}(Me_4taa)]. In comparative studies, we found that treatment of [Ti(O)(Me_4taa)] with TolNCO also formed **54** exclusively. This is again consistent with compound **54** being the thermodynamically favoured isomer. Thus rearrangements of the macrocycle-supported titanium-imido and -oxo cycloaddition products appears to be facile, as emphasised by the reaction of [Ti(O)(Me_4taa)] with di-*p*-tolylcarbodiimide (Fig. 12). This gave the *N,N′*-bound ureate **51** (also obtained from **40e** and TolNCO) rather than the *N,O*-bonded linkage isomer [Ti{OC(NTol)N(Tol)}(Me_4taa)] which would presumably form as a first intermediate in a Ti=O + TolN=C=NTol [2 + 2] cycloaddition reaction. Furthermore, even if the reactions in Fig. 12 proceed *via* nucleophilic attack of the imido N- or oxo O-atom at the central cumulene carbon E=C=E′ (*i.e.*, instead of going *via* direct cycloaddition), the formation of **54** from **40e**, and of **51** from [Ti(O)(Me_4taa)], still require rearrangement processes involving Ti–N and Ti–O bond cleavage respectively.

Titanium imides with other dianionic ligands

Ongoing work in our group with other dianionic ligands has established further new classes of organometallic and coordination titanium imido compounds. As with the syntheses of the tetraazamacrocyle-supported derivatives [Ti(NBu^t)(Me_4taa)] **40a**, [Ti(NBu^t)(ttp)] **42** and [Ti(NBu^t)(Me_4taen)] **43**, straighforward reactions of disodium or dilithium salts $Li_2[C_8H_6(SiMe_3)_2]$, $[Na_2(L)]_2$ (LH_2 = 1,3-dimethyl ether *p-tert*-butylcalix[4]arene) or Na_2[Bu$^t{}_4$salen] [H_2Bu$^t{}_4$salen = tetrakis(*tert*-butyl)salen] with [Ti(NBu^t)Cl_2(py)$_3$] gave good yields of the corresponding new imido complexes [Ti(NBu^t){η^8-$C_8H_6(SiMe_3)_2$}] **55**, [Ti(NBu^t)(L)] **56** or [Ti(NBu^t)(Bu$^t{}_4$salen)] **57** repectively.[18,48,54] Studies of these and related systems are currently underway.

Concluding remarks

Over the last three years we have shown that many new types of titanium and other Group 4 metal imido complex can be readily accessed through high-yielding, straightforward synthetic methods. A variety of both new and familiar reaction types have already been found for the new compounds. It is very likely that the next phase of Group 4 imido chemistry will focus much more on developing new reactions towards organic substrates and catalytic processes.

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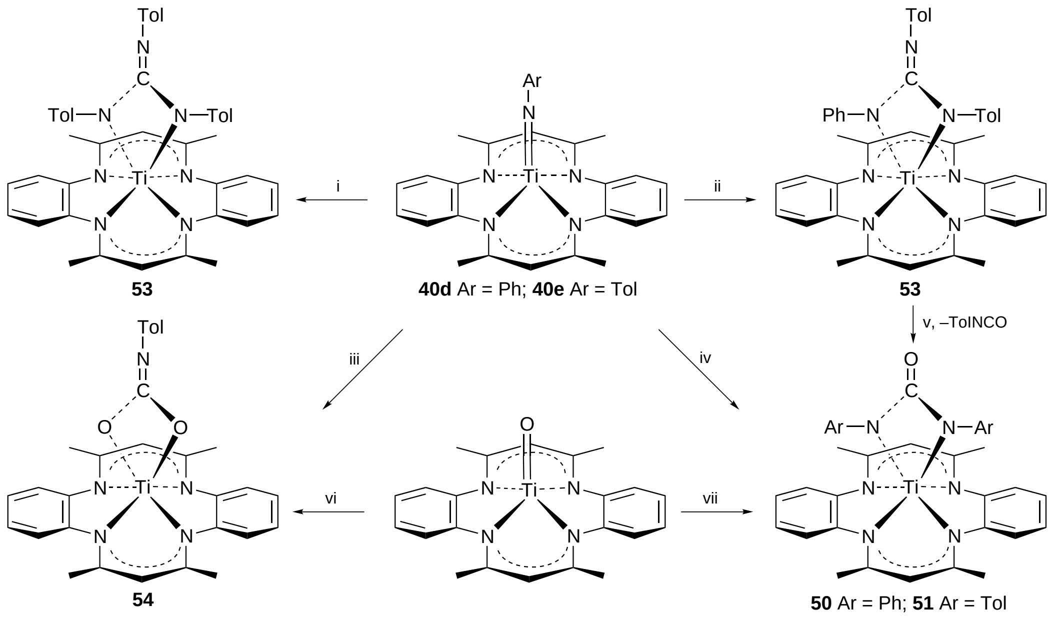

Fig. 12 Selected reactions of [Ti(NAr)(Me_4taa)] and [Ti(O)(Me_4taa)] with cumulenes.[18,50] *Reagents*: (i) from **40e**: TolN=C=NTol; (ii) from **40e**: PhNCO; (iii) from **40e**: CO_2; (iv) from **40d**: PhNCO, from **40e**: TolNCO; (v) for **50**: PhNCO (5 equiv.); (vi) TolNCO; (vii) for **51**: TolN=C=NTol.

Philip Mountford (b. 1962) gained a BSc (Hons) degree at Hatfield Polytechnic (1982–1986) and a DPhil degree at the University of Oxford (1986–1989) under the supervision of Professor M. L. H. Green. He remained at Oxford as a Junior Research Fellow at Wolfson College (1989–1992), Departmental Demonstrator at the Inorganic Chemistry Laboratory (1990–1992), and College Lecturer at Keble College (1990–1992). In 1992 he was appointed to a lectureship at the University of Nottingham. His research interests centre around studies of the synthesis, structure, bonding and reactivity of organometallic and coordination compounds and he is author or coauthor of over 75 publications in this area.

Footnotes and References

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† Although for ease of representation all metal–imido or –oxo linkages are drawn M=NR or M=O, the formal metal–ligand multiple bond order in the Group 4 imido compounds described herein is probably best thought of as three (pseudo-σ^2 π^4; triple bond) rather than as two.[4] Formal bond orders for the imido linkage in the bis(η^5-cyclopentadienyl)titanium imido and related compounds have been addressed.[4,20] General bond order assignments in a number of poly(imido) transition metal compounds have been proposed.[55]

‡ Throughout this review the suffixes **a**, **b** and **c** for homologous series of imido compounds $[Ti(NR)(L)_n]_m$ refer to those with R = Bu^t, $C_6H_3Me_2$-2,6 and $C_6H_3Pr^i_2$-2,6, respectively.

§ Vinylimido titanocene derivatives have been described but their reactions invariably involve [4 + 2] cycloadditions. Hence the reactivity of the non-conjugated Ti=NR functional group cannot be studied in these systems.[56]

¶ Although bis(pentamethylcyclopentadienyl) derivatives cannot be obtained *via* our route, Andersen and co-workers have recently found that reaction of $[Ti(\eta\text{-}C_5Me_5)_2(\eta^2\text{-}C_2H_4)]$ with ArN_3 or with S_8 and pyridine affords $[Ti(\eta\text{-}C_5Me_5)_2(NAr)]$[57] and $[Ti(\eta\text{-}C_5Me_5)_2(S)(py)]$ respectively.[58]

This ChemComm is also available in enhanced multi-media format *via* the World Wide Web: http://chemistry.rsc.org/rsc/ccenha.htm which contains more details of the bonding in the dibenzotetraaza[14]annulene systems

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