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New transition metal imido chemistry with diamido-donor ligands

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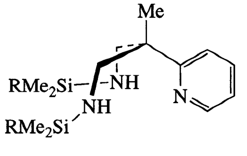
Abstract

This short review presents an account of the synthesis and chemistry to date of new Groups 4, 5 and 6 imido complexes derived from the diamido–pyridine or diamido–amine ligand precursors $MeC(2\text{-}C_5H_4N)(CH_2NHSiMe_2R)_2$ (abbreviated as $H_2N_2N_{py}$ for R = Me or $H_2N_2N^*_{py}$ for R = Bu^t) and $Me_3SiN(CH_2CH_2NHSiMe_3)_2$ (abbreviated as $H_2N_2N_{am}$). Reaction of the dilithium salts $Li_2N_2N_{py}$, $Li_2N_2N^*_{py}$ or $Li_2N_2N_{am}$with metal imido synthons of the general type $[M(NR)_xCl_y(L_B)_z]$ (M = Groups 4–6 transition metals; R = alkyl or aryl substituents; L_B = Lewis base) gives a diverse range of products among which are the following complexes: $[Ti(NR)(N_2N_{py})]$, $[M(NR)(L_{N2N})(L_B)]$ (M = Ti or Zr; L_{N2N} = a general diamido-donor ligand), $[M(NR)(N_2N_{py})Cl(py)]$ (M = Nb or Ta), $[Nb(\mu\text{-}NBu^t)(N_2N_{am})(\mu\text{-}Cl)]_2$, $[W(NR)(L_{N2N})Cl_2]$ ($L_{N2N} = N_2N_{py}$ or N_2N_{am}), $[Mo(NR)_2(L_{N2N})]$ ($L_{N2N} = N_2N_{py}$ or N_2N_{am}). The diamido–pyridine supported titanium imido complexes $[Ti(NR)(N_2N_{py})]$ and $[Ti(NR)(N_2N_{py})(py)]$ in particular have reactive Ti = NR linkages and these undergo a wide range of coupling reactions with the following unsaturated organic substrates: RNC, MeCN, Bu^{t}CP, ArNCO, RC_2Me, and $RCHCCH_2$. Many of these transformations are the first, or among the first, of their type in transition metal imido chemistry. The combined diamido–pyridine–imido donor set also forms a useful supporting ligand environment for new chemistry at Groups 5 and 6 metal centres, especially in the Group 5 complexes $[M(NR)(N_2N_{py})Cl(py)]$ (M = Nb or Ta) in which the chloride can be substituted by a range of N-, O- and C-donor ligands.

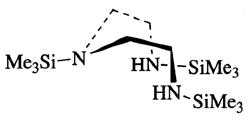
Keywords: Imido; Amido; Polydentate ligands; Transition metals; Cycloaddition; C–H bond activation

1. Introduction

Transition metal imido compounds of the general formula $[M(NR)_n(L)_m]$ (R typically = alkyl or aryl; L_m is an ancilliary ligand set) have been a focus of considerable activity, particularly over the last 15 years [1,2]. This activity has spanned several fields of interest including unusual molecular and electronic structures, fundamental reactivity, and potential applications in industrially relevant areas such as alkene polymerization and metathesis catalysis [3]. This short review presents an account of the synthesis and chemistry to date of new Groups 4, 5 and 6 imido complexes derived from the diamido–pyridine or diamido–amine ligands $MeC(2\text{-}C_5H_4N)(CH_2NHSiMe_2R)_2$ (abbreviated as $H_2N_2N_{py}$ for R = Me or $H_2N_2N^*_{py}$ for R = Bu^t) [4a] and $Me_3SiN(CH_2CH_2NHSiMe_3)_2$ (abbreviated as $H_2N_2N_{am}$) [4c] shown below. A number of dianionic diamido-donor ligands of these types have been developed over the last 5–10 years and their chemistry and applications outside of the area of imido chemistry have very recently been reviewed [5].



R = Me ($H_2N_2N_{py}$)
or Bu^t $H_2N_2N_{py}{}^*$



$H_2N_2N_{am}$

The chemistry of imido complexes is, unsurprisingly, governed in part by the nature of the supporting ligand set, and a wide range of supporting ligand environments have been explored [1,2]. One approach to the controlled design of reactive imido complexes has been to use chelating N- and/or O- donor ligands, and a number of imido compounds supported by di- and trianionic, fairly rigid di-, tri- and tetradentate ligands of this type have been described [6–11]. However, an attraction of the $H_2N_2N_{py}$ and $H_2N_2N_{am}$ diamido-donor type of ligands is the potential flexibility they offer in terms of coordination number and geometry of the polydentate ligand. This aspect is elaborated on in Section 4 below.

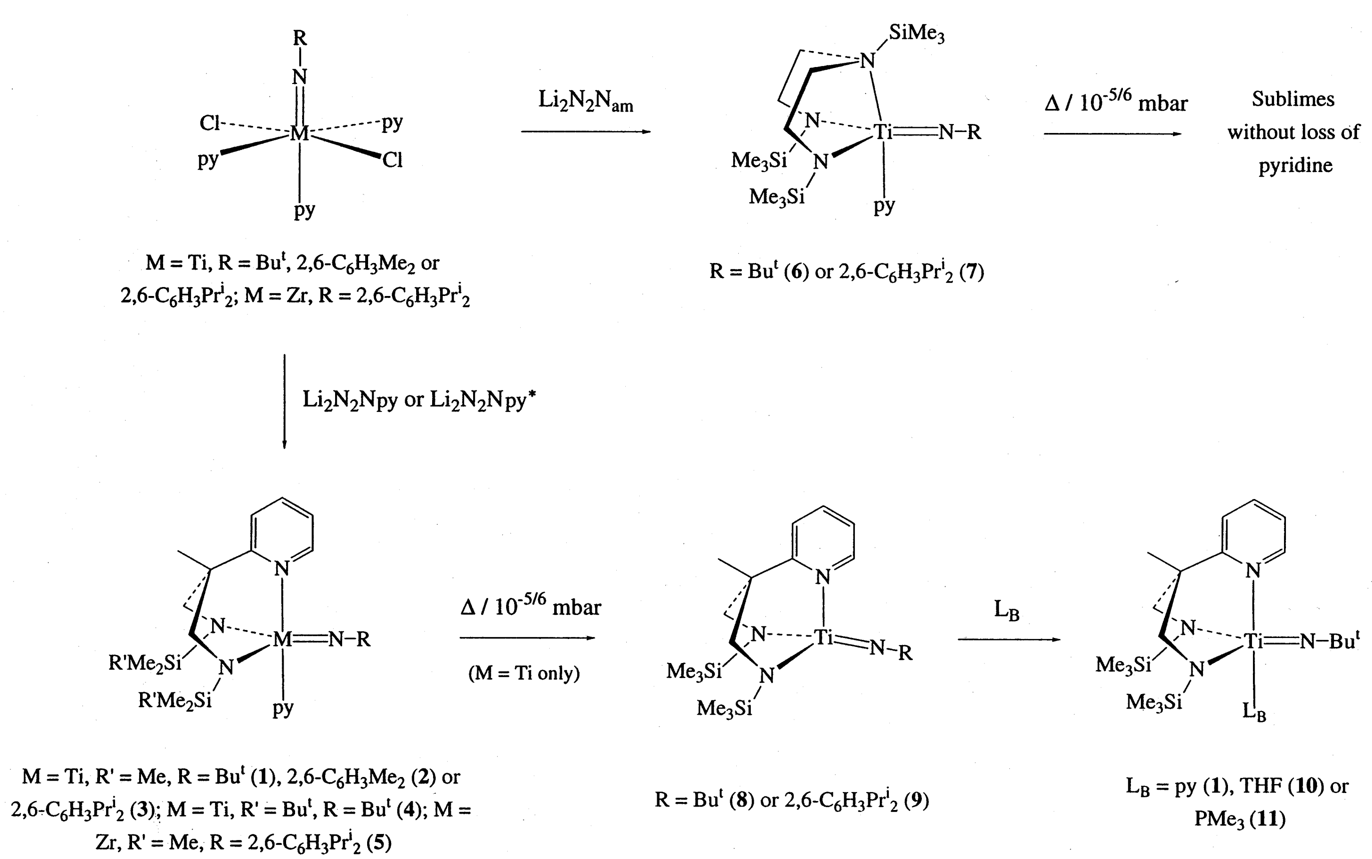
The remainder of this review surveys the synthesis, structures and reactivity of Groups 4–6 transition metal imido complexes of diamido-donor ligands.

2. Synthesis of transition metal imido complexes of diamido-donor ligands

2.1. Group 4 complexes

Reaction of $Li_2N_2N_{py}$, $Li_2N_2N^*_{py}$ or $Li_2N_2N_{am}$ with the titanium or zirconium imido complexes $[M(NR)Cl_2(py)_3]$ ($M = Ti$, $R = Bu^t$, 2,6-$C_6H_3Me_2$ or 2,6-$C_6H_3Pr^i_2$; $M = Zr$, $R = 2,6\text{-}C_6H_3Pr^i_2$) affords the corresponding diamido-donor supported imido complexes $[M(NR)(L_{N2N})(py)]$ (**1**–**7**) in fair to good yield (Scheme 1) [12,13a]. Attempts to form zirconium imido complexes of the N_2N_{am} ligand were unsuccessful, as was the reaction of $Li_2N_2N_{py}$ with the bis(THF) complex $[Zr(N–2,6\text{-}C_6H_3Pr^i_2)Cl_2(THF)_2]$, the aim of which was to make $[Zr(N–2,6\text{-}C_6H_3Pr^i_2)(N_2N_{py})(THF)]$, the THF analogue of **5**. The five-coordinate trigonal bipyramidal structures shown in Scheme 1 have been confirmed by X-ray crystallography for $[Ti(NBu^t)(N_2N_{py})(py)]$ (**1**), $[Zr(N–2,6\text{-}C_6H_3Pr^i_2)(N_2N_{py})(py)]$ (**5**) and $[Ti(NBu^t)(N_2N_{am})(py)]$ (**6**). The solid state structures of **1** and **6** are shown in Fig. 1(a) and (b), respectively. In addition to the X-ray structures, further evidence of coordination of the pyridyl moiety of the diamido–pyridine ligand in **1**–**5** can be obtained from the ^{1}H-NMR chemical shift of the pyridyl *ortho* hydrogen atom which moves, usually very significantly, downfield when the pyridyl group is metal-bound [4a].

The solid state structures of **1** and **6** show that while the Ti–N(imido) and Ti–N(amido) bond lengths in the two complexes are mutually comparable, the Ti–N(pyridine) distance of 2.278(2) Å in **1** is significantly longer than that of 2.228(3) Å in **6**. This apparently reflects both the nature and orientation (with respect to the *trans* pyridine ligand) of the Lewis base N-donor function of the N_2N_{py} (neutral N-donor = pyridyl) or N_2N_{am} (neutral N-donor = trimethylsilylamine) in the two complexes. This apparent difference in Ti–pyridine bonding is reflected in the different labilities of the pyridine ligands. While the diamido–amine derivative **6** sublimes cleanly at 75°C in high vacuum without loss of pyridine, heating samples of $[Ti(NR)(N_2N_{py})(py)]$ ($R = Bu^t$ (**1**) or 2,6-$C_6H_3Pr^i_2$ (**3**)) to 125–155°C in vacuo gave quantitative conversion to the corresponding four-coordinate



Scheme 1. Synthesis of Group 4 imido complexes of diamido donor ligands.

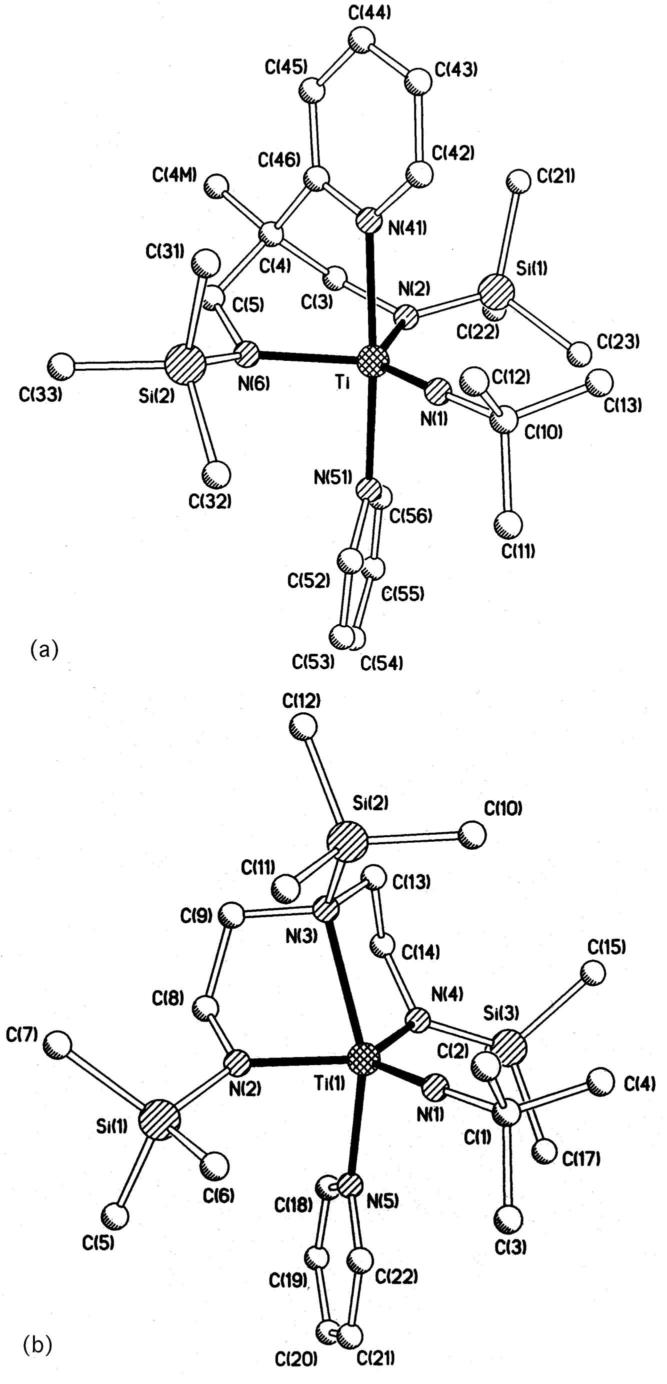


Fig. 1. The molecular structures of (a) [Ti(NBu^t)(N_2N_{py})(py)] (**1**), (b) [Ti(NBu^t)(N_2N_{am})(py)] (**6**) and (c) [Ti(NBu^t)(N_2N_{py})] (**8**).

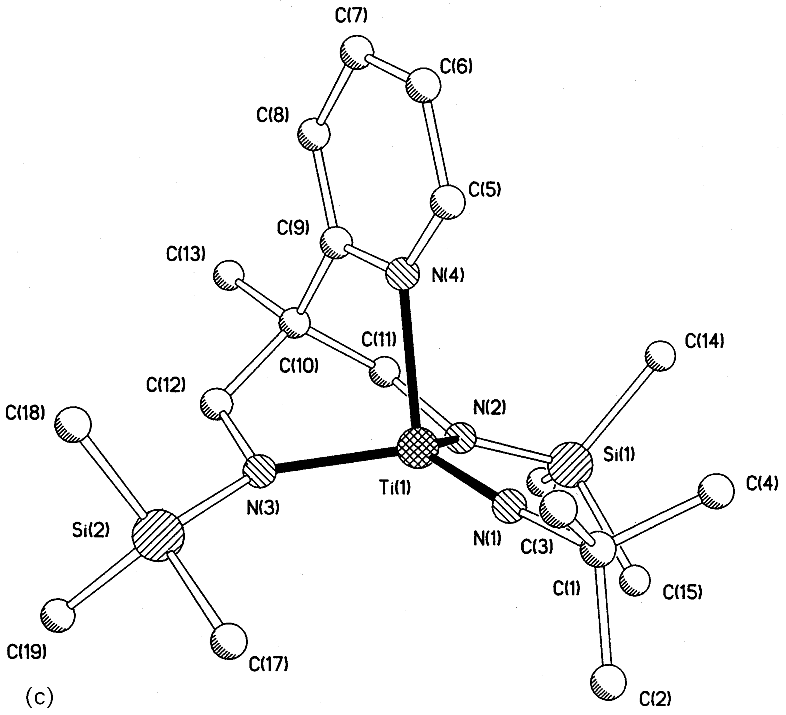
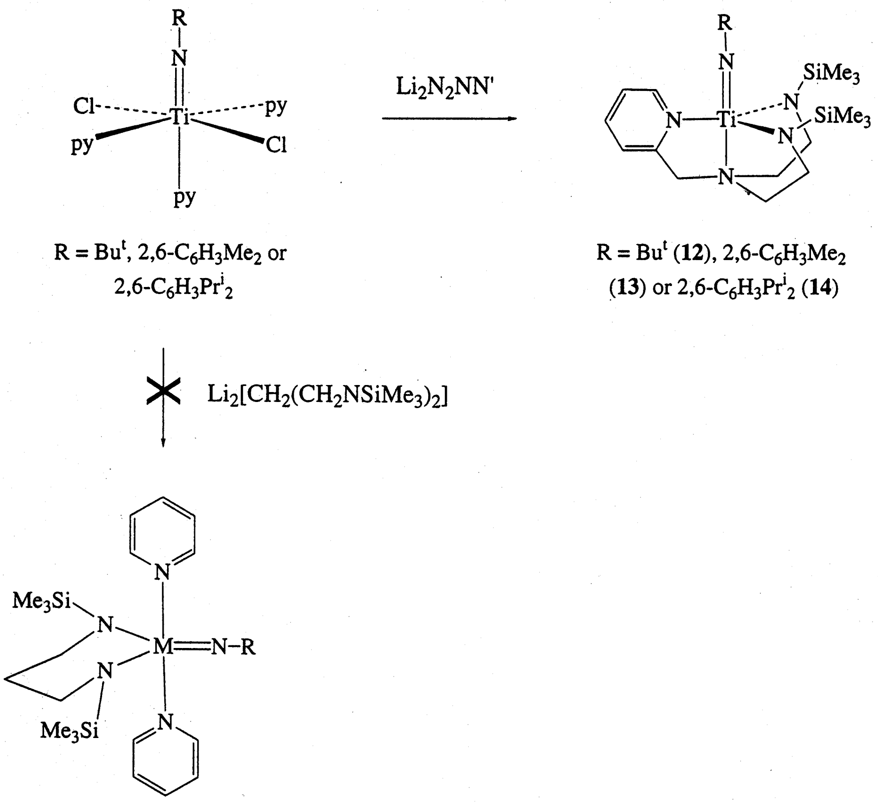


Fig. 1. (*Continued*)

species [Ti(NR)(N_2N_{py})] (R = Bu^t (**8**) or 2,6-$C_6H_3Pr^i_2$ (**9**)) as shown in Scheme 1. Both of the compounds **8** (see Fig. 1(c)) and **9** have been characterized structurally and possess unusual pseudo-trigonal base pyramidal geometries with the titanium displaced by only ca. 0.3 Å from the plane formed by the amido and imido ligand N atoms [13a]. When compared to the five-coordinate precursor **1**, all of the Ti–N bond lengths in **8** are shortened significantly in keeping with the reduction in valence electron count and coordination number. Scheme 1 shows that **8** readily adds pyridine or other Lewis bases to (re)form [Ti(NBu^t)(N_2N_{py})(L_B)] (L_B = py (**1**), THF (**10**) or PMe_3 (**11**)).

It is of interest to consider the formal valence electron counts of the metal centres in the five- and four-coordinate complexes **1**–**7** and **8**–**9**, respectively. The solid state structures of all these complexes reveal near-trigonal planar (i.e. sp^2-hydbridized) N_2N_{py} or N_2N_{am} amido donor nitrogens and so each of these can in principle donate three electrons to the metal centre [5]. In each compound the Ti=N(imido)–R bond angles lie in the range ca. 170–180° and so the imido ligands can in, principle, donate four electrons to the metal [1]. At first sight the complexes **1**–**7** and **8**–**9** therefore possess metal valence electron counts of 18 and 16, respectively. However, a qualitative orbital analysis [13a] of the $M_{d\pi}$–$N_{p\pi}$ bonding interaction in all of these complexes reveals that one of the imido $N_{p\pi}$ donor



Scheme 2. Reactions of $[Ti(NR)Cl_2(py)_3]$ with Li_2N_2NN' or $Li_2[CH_2(CH_2NSiMe_3)_2]$.

orbitals competes with one of the amido $N_{p\pi}$ linear combinations for the same metal d_π acceptor orbital, reducing the real valence electron count of the metal in the five- and four-coordinate complexes to only 16 and 14, respectively. Similar conflicts between π-donor ligands for available metal π-acceptor orbitals have been described previously [1,14]. Furthermore, since the M=N(imido) bond lengths are generally 0.25–0.30 Å shorter than the M–N(amido) bond lengths it is probably best to think of the imido ligand in the complexes **1**–**7** and **8**–**9** as net four-electron donors and each amido nitrogen as a net two-electron donor.

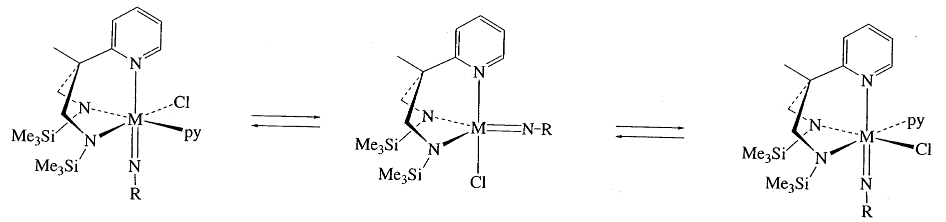
Scheme 2 summarizes reactions of $[Ti(NR)Cl_2(py)_3]$ with diamido-type ligands that are related to the N_2N_{py}, $N_2N^*_{py}$ and N_2N_{am} systems in Scheme 1. To gain an insight into the importance of the pyridyl donor arm of N_2N_{py} and $N_2N^*_{py}$ reactions with the lithium salt of the previously reported chelating diamido ligand $CH_2(CH_2NSiMe_3)_2$ have been studied [15]. Reaction of $Li_2[CH_2(CH_2NSiMe_3)_2]$ with the aim of forming $[Ti(NR)\{CH_2(CH_2NSiMe_3)_2\}(py)_2]$ gave instead very complex mixtures of products. This indicates that at least one chelating N-donor function needs to be incorporated into a diamido-donor ligand to obtain kinetically stable complexes. In contrast, reaction of $[Ti(NR)Cl_2(py)_3]$ with Li_2N_2NN', where

N_2NN' = the tetradentate diamido-bis(donor) ligand $(2\text{-}NC_5H_4)CH_2N(CH_2CH_2\text{-}NSiMe_3)_2$, gives the stable, five-coordinate compounds $[Ti(NR)(N_2NN')]$ (R = Bu^t (**12**), 2,6-$C_6H_3Me_2$ (**13**) or 2,6-$C_6H_3Pr^i_2$ (**14**)) in good yields [10]. The compounds **12**–**14** are analogues of **1**–**7** and compound **14** has been characterized structurally to confirm the pseudo-trigonal bipyramidal geometry shown in Scheme 2. However, presumably because of the geometric contraints of the N_2NN' ligand itself, the imido ligand in **12**–**14** occupies a coordination site *cis* to the amido donor functions (in other words the axial position of a trigonal bipyramid as opposed to the equatorial position found in **1**–**7**). Very recent work has shown that zirconium analogues of the compounds **12**–**14** can also be prepared [10b].

2.2. Group 5 complexes

Syntheses of the new niobium and tantalum imido complexes derived from diamido-donor ligands are summarized in Scheme 3. Reaction of $Li_2N_2N_{py}$ with $[M(NR)Cl_3(py)_2]$ (M = Nb, R = Bu^t; M = Ta, R = Bu^t or 2,6-$C_6H_3Pr^i_2$) gives fair to reasonable yields of $[M(NR)(N_2N_{py})Cl(py)]$ (M = Nb, R = Bu^t (**15**); M = Ta, R = Bu^t (**16**) or 2,6-$C_6H_3Pr^i_2$ (**17**)) [16]. All three complexes have been crystallographically characterized and the data support the octahedral structures shown in Scheme 3. The amido and imido N-donors adopt mutually *cis* coordination sites in **15**–**17** and solution NMR data show that these structures, although fluxional, are maintained in solution.

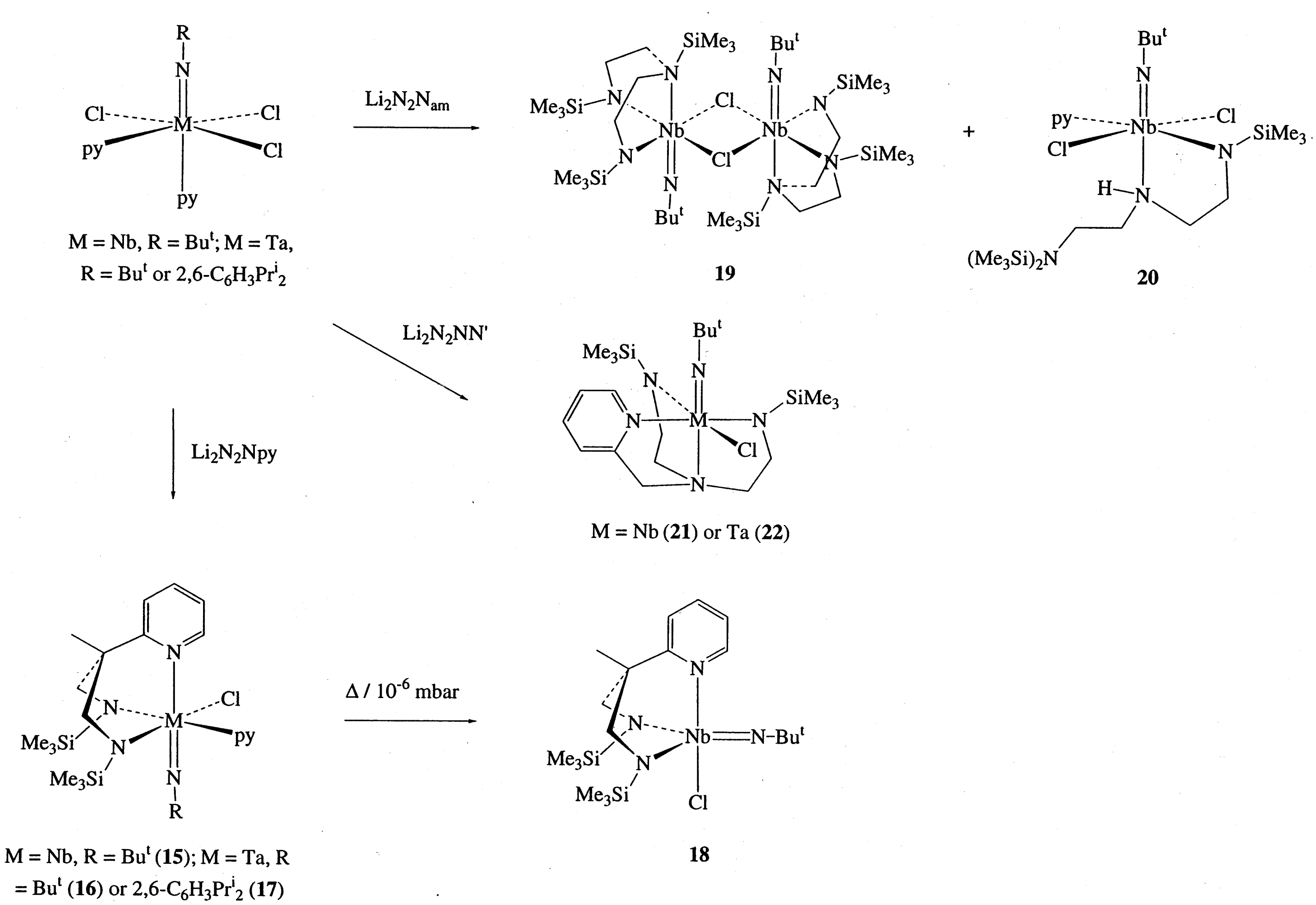
The proposed fluxional process in the compounds **15**–**17** involves interconversion of the two enantiomeric forms of **15**–**17** via the corresponding trigonal bipyramidal, five-coordinate intermediates $[M(NR)(N_2N_{py})Cl]$ as shown in Eq. (1). Activation parameters for the fluxional processes extracted from variable temperature NMR data support this mechanism. The activation enthalpy, $\Delta H^{\ddagger}$, for the niobium complex **15** is 80.2 ± 2.5 kJ mol^{-1} whereas that for the tantalum congener **16** is 87.6 ± 2.3 kJ mol^{-1}. The larger $\Delta H^{\ddagger}$ value for **16** presumably reflects the increasing metal–ligand bond strengths typically observed on descending a transition metal triad [17].



M = Nb, R = Bu^t (**15**); M = Ta, R = Bu^t (**16**) or 2,6-$C_6H_3Pr^i_2$ (**17**)

(1)

Although the NMR spectra of **15**–**17** do not show observable equilibrium concentrations of the pyridine-free complexes $[M(NR)(N_2N_{py})Cl]$, evidence for their existence comes from the the high vacuum thermolysis of **15** (Scheme 3) which



M = Nb, R = Bu^t; M = Ta, R = Bu^t or 2,6-C$_6$H$_3$Pr$^i_2$

19

20

M = Nb (**21**) or Ta (**22**)

M = Nb, R = Bu^t (**15**); M = Ta, R = Bu^t (**16**) or 2,6-C$_6$H$_3$Pr$^i_2$ (**17**)

18

Scheme 3. Niobium and tantalum imido complexes derived from N$_2$N$_{py}$ and N$_2$N$_{am}$ ligands.

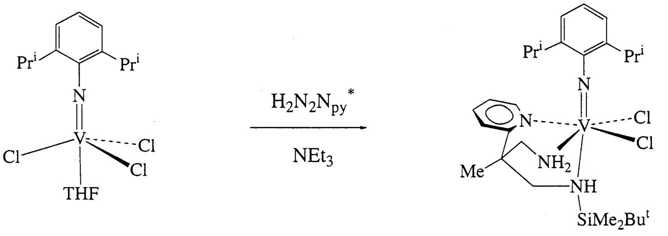
affords pyridine-free [Nb(NR)(N_2N_{py})Cl] (**18**). The compound **18** decomposes slowly in hydrocarbon solvents over ca. 1 day under an inert atmosphere, but nuclear Overhauser effect (nOe) NMR spectra of freshly prepared samples support the geometry shown in Scheme 3 in which the amido and imido ligands occupy the equatorial sites of a trigonal bipyramid. This structure is analogous to those of the valence isolectronic Group 4 complexes [M(NR)(L_{N2N})(py)] (**1**–**7**) and the tantalum(V) ethyl compound [Ta{$N(CH_2CH_2N)(CH_2CH_2NSiMe_3)_2$}Et] which contains a chelating diamido–imido–amine ligand [18].

The preferred isomer of **15**–**17**, i.e. with the imido ligand *trans* to the pyridyl group, can be accounted for by consideration of the π-donor requirements of the amido and imido groups [16]. If the metal–ligand σ bonds are defined as lying along Cartesian axes, and if the M=N(imido) vector lies along the z-axis, then imido to metal $p_\pi \rightarrow d_\pi$ donation takes place into the metal d_{yz} and d_{xz} orbitals. The geometry at the amido nitrogens is effectively trigonal planar, but the amido groups are twisted so that the amido lone pair $2p_\pi$ orbital is better aligned with with the remaining metal d_π acceptor orbital (i.e. d_{xy}). Only one of the two linear combinations of amido π-donor orbitals can therefore find a match with metal acceptor orbitals and hence the valence electron count of the complexes [M(NR)(N_2N_{py})-Cl(py)] (**15**–**17**) is 18.

In contrast to the reactions of $Li_2N_2N_{py}$ with [M(NR)$Cl_3(py)_2$], the reactions of $Li_2N_2N_{am}$ are less well-behaved (Scheme 3) [13b]. Thus reaction of $Li_2N_2N_{am}$ with [Nb(NBu^t)$Cl_3(py)_2$] leads reproducibly to two different products, namely [Nb(μ-NBu^t)(N_2N_{am})(μ-Cl)]$_2$ (**19**, major) and [Nb(NBu^t)Cl_2{$Me_3SiN(CH_2)_2NH(CH_2)_2N(SiMe_3)_2$}(py)] (**20**). The compound **19** is an oil and although there is no direct evidence for it being a binuclear species, a μ-chloride bridged six-coordinate structure is assigned on the basis of the apparent high Lewis base affinity of five-coordinate [Nb(NBu^t)(N_2N_{py})Cl] for pyridine which is also present in reaction mixtures leading to **19**. Since the compound **19** does not contain pyridine it is thought that the sixth coordination site must be occupied by a bridging Cl ligand. The minor product **20** has been characterized structurally. It is clearly a niobium(V) imido complex but in this compound the N_2N_{am} ligand has undergone a transformation to a monoamido–diamine ligand in which the $SiMe_3$ group of the N_2N_{am} central amino nitrogen has effectively migrated to one of the terminal nitrogens; in addition the central amino nitrogen has apparently abstracted an H atom (or proton). It is thought that competing redox side-reactions are responsible for the reproducible formation of **20** in these reactions [13b].

The reactions of [M(NBu^t)$Cl_3(py)_2$] with Li_2N_2NN' have also been studied recently and give rise to the complexes [M(NBu^t)(N_2NN')Cl] (M = Nb (**21**) or Ta (**22**)) as shown in Scheme 3 [10]. These are analogues of the N_2N_{py}-supported derivatives **15**–**17** but are not fluxional on the NMR timescale indicating that the pyridyl donor of N_2NN' is more tightly bound than the pyridine ligand in the compounds **15**–**17**. The additional benefits of the ‘extra’ pyridyl donor arm in the N_2NN' ligand set can be appreciated in the following way. Both the N_2N_{am} and N_2NN' ligands may be viewed as derivatives of the parent system $RN(CH_2CH_2NSiMe_3)_2$ where R = $SiMe_3$ for N_2N_{am} and $CH_2(2\text{-}NC_5H_4)$ for

N_2NN'. Hence while for compound **19** 'free' pyridine is apparently unable to prevent dimerization, the chelating pyridyl arm in **21** helps enforce a mononuclear species.



23

(2)

Competing redox-type processes are clearly involved in the low-yield formation of the vanadium(IV) compound $[V(N\text{-}2,6\text{-}C_6H_3Pr^i_2)Cl_2\{MeC(2\text{-}C_5H_4N)(CH_2NH_2)(CH_2NSiHMe_2Bu^t)\}]$ (**23**) from the vanadium(V) imido complex $[V(N\text{–}2,6\text{-}C_6H_3Pr^i_2)Cl_3(THF)]$ and the ligand precursor $H_2N_2N^*_{py}$ in the presence of Et_3N (Eq. (2)) [16]. The compound **23** has been characterized structurally (Fig. 2) and in the solid state exists as a Cl···H–N hydrogen bond bridged binuclear complex.

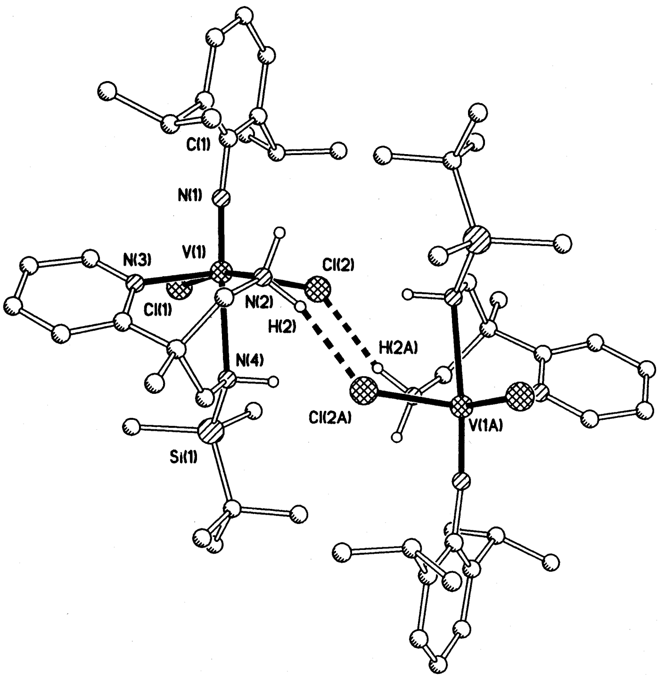
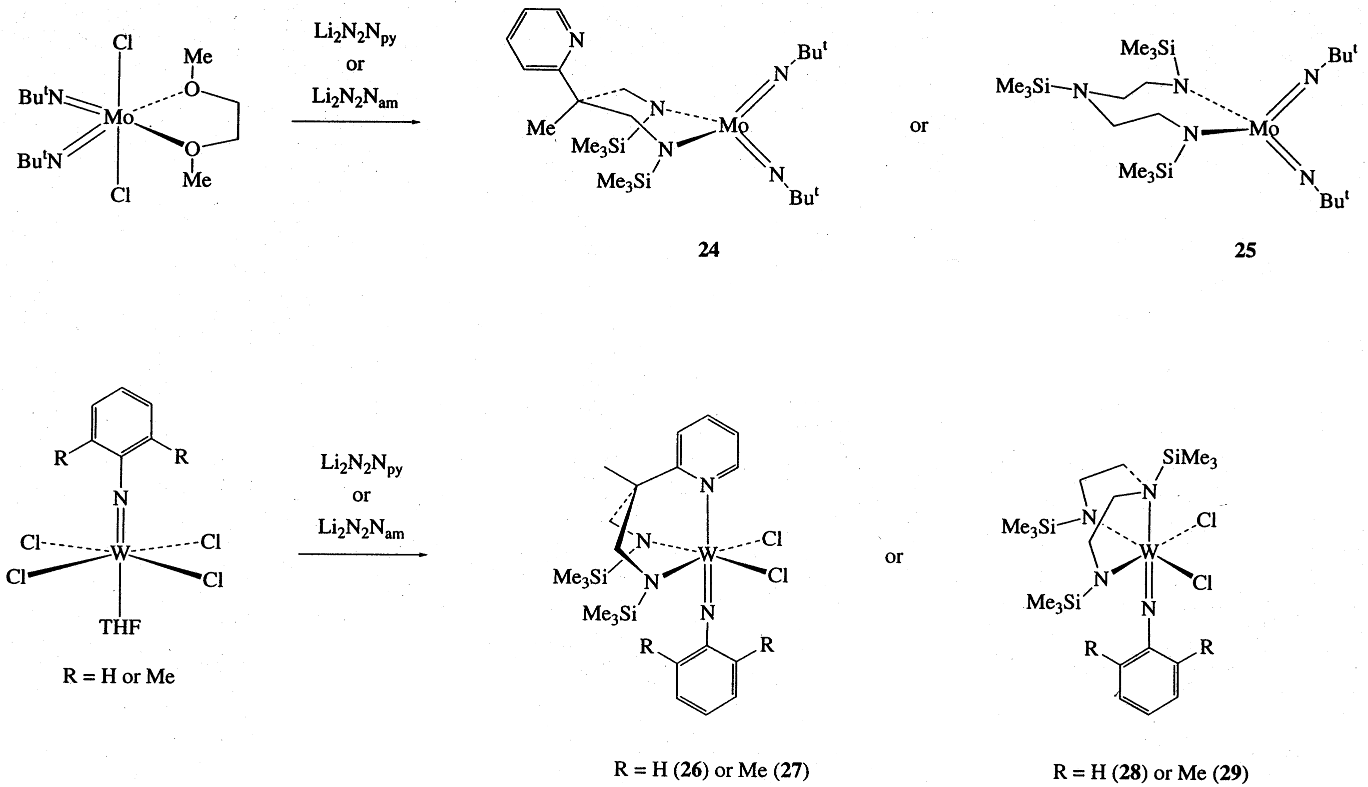


Fig. 2. The dimeric, hydrogen bond bridged molecular structure of $[V(N\text{–}2,6\text{-}C_6H_3Pr^i_2)Cl_2\{MeC(2\text{-}C_5H_4N)(CH_2NH_2)(CH_2NSiHMe_2Bu^t)\}]$ (**23**).



24

25

R = H (**26**) or Me (**27**)

R = H (**28**) or Me (**29**)

Scheme 4. Molybdenum bis(imido) and tungsten mono(imido) complexes of N_2N_{py} and N_2N_{am} ligands.

It is not known whether this binuclear structure persists in solution. The $H_2N_2N^*_{py}$ ligand has clearly undergone a degradation process in the formation of **23** by loss of $SiMe_2Bu^t$ (in the form of $ClSiMe_2Bu^t$ as determined by NMR) from one of the terminal amino nitrogens which has also gained a H atom (or proton). Overall the $MeC(2\text{-}C_5H_4N)(CH_2NH_2)(CH_2NSiHMe_2Bu^t)$ ligand in **23** acts as a neutral *fac*-N_3 donor. Further supporting evidence for a vanadium(IV) centre in **23** comes from a room temperature EPR spectrum in THF that reveals an eight line pattern with $g = 1.982$ and $A = 90.9$ G.

2.3. Group 6 complexes

To date only N_2N_{py} and N_2N_{am} supported bis(*tert*-butylimido)molybdenum and mono(arylimido)–tungsten complexes have been prepared successfully [19]. The syntheses and structures of these Group 6 compounds are summarized in Scheme 4.

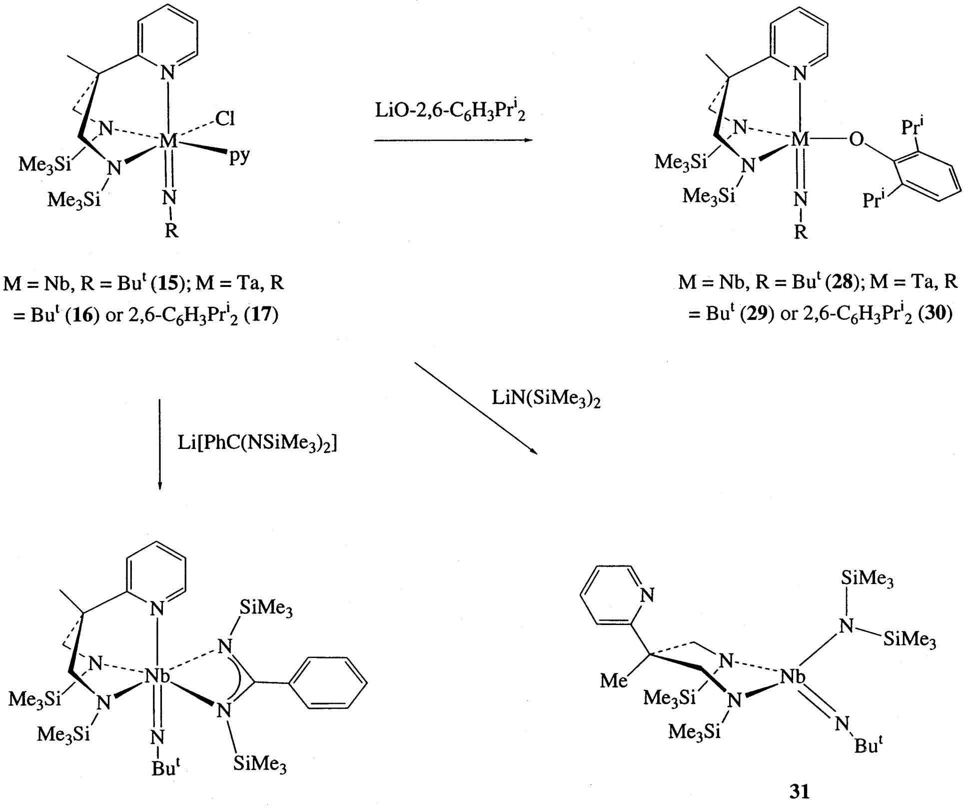
Reaction of $[Mo(NBu^t)_2Cl_2(DME)]$ with $Li_2N_2N_{py}$ or $Li_2N_2N_{am}$ affords the monomeric, four-coordinate complexes $[Mo(NBu^t)_2(N_2N_{py})]$ (**24**) and $[Mo(NBu^t)_2(N_2N_{am})]$ (**25**), respectively. [19] The κ^2 coordination mode for the N_2N_{py} ligand in **24** is inferred from the ^1H chemical shift of the pyridyl group *ortho*-hydrogen and given the similar steric effects at the metal centre of the N_2N_{am} ligand the compound **25** is thought to have an analogous structure. While a wide number of monomeric, four-coordinate bis(*tert*-butylimido)molybdenum have been reported previously [1], the structures proposed for **24** and **25** contrast with that reported by Boncella for binuclear, five-coordinate $[Mo(NPh)(\mu\text{-}NPh)\{o\text{-}C_6H_4(NSiMe_3)_2\}]_2$ which contains a chelating diamido ligand [6a]. Attempts to prepare a bis(phenylimido) molybdenum analogue of **24** by reaction of $Li_2N_2N_{py}$ with $[Mo(NPh)_2Cl_2(DME)]$ gave mixtures of products including the ligand precursor $H_2N_2N_{py}$, indicative of competing redox side-reactions.

Although Boncella et al. could obtain mono(imido) molybdenum(VI) complexes of the type $[Mo(NPh)\{o\text{-}C_6H_4(NSiMe_3)_2\}Cl_2(L)]$ ($L = PhNH_2$, THF or PMe_3) by protonolysis of an imido group of $[Mo(NPh)_2Cl_2(DME)]$ by reaction with $o\text{-}C_6H_4(NHSiMe_3)_2$ [6a], attempts to prepare mono(imido) molybdenum complexes in this way from $H_2N_2N_{py}$ and $[Mo(NBu^t)_2Cl_2(DME)]$ were unsuccessful [19]. However, as shown in Scheme 4, N_2N_{py} and N_2N_{am} supported mono(arylimido) complexes of tungsten(VI) are readily obtained from the reaction of either $Li_2N_2N_{py}$ or $Li_2N_2N_{am}$ with $[W(N\text{–}2,6\text{-}C_6H_3R_2)Cl_4(THF)]$ (R = H or Me) [19]. The geometries proposed for $[W(N\text{–}2,6\text{-}C_6H_3R_2)(N_2N_{py})Cl_2]$ (R = H (**26**) or Me (**27**)) and $[W(N\text{–}2,6\text{-}C_6H_3R_2)(N_2N_{am})Cl_2]$ (R = H (**28**) or Me (**29**)) are based on those of the valence isoelectronic, six-coordinate Group 5 complexes $[M(NR)(N_2N_{py})Cl(py)]$ (**15**–**17**). The diamido-donor supported complexes **26**–**29** are relatives of Boncella's chelating diamido complexes $[M(NPh)\{o\text{-}C_6H_4(NSiMe_3)_2\}Cl_2(L)]$ (M = Mo or W; L = Lewis base donor) [6]. A tungsten(IV) complex loosely related to **26**–**29** (in that it contains a chelating diamido–imido–amine ligand) was reported by Schrock [20].

3. Reactions in which the diamido-donor–imido set acts as a supporting/ancillary ligand environment

In general the syntheses of diamido–pyridine (N_2N_{py}) supported imido complexes proved to be more successful than those of diamido–amine (N_2N_{am}) analogues. Reactivity studies have therefore been limited to the former systems.

One feature of amido and imido ligands in general is their ability to act as 'spectator' or 'ancilliary' ligands, forming a protective mask of part of a metal centre while new reaction chemistry occurs elsewhere in the complex [1,5]. The diamido-donor–imido ligand set Group 5 complexes $[M(NR)(N_2N_{py})Cl(py)]$ (**15**–**17**) and the tungsten analogues $[W(NR)(N_2N_{py})Cl_2]$ (**26** or **27**) can be viewed as a tetradentate, tetra-anionic, 10-electron donor supporting ligand set and as such is an unusual supporting environment in organometallic and coordination chemistry. This Section describes reactions of **15**–**17** and **26**–**27** where the diamido-donor–imido set acts as a supporting ligand environment for substitution chemistry at the metal centres.



M = Nb, R = Bu^t (**15**); M = Ta, R = Bu^t (**16**) or 2,6-$C_6H_3Pr^i_2$ (**17**)

M = Nb, R = Bu^t (**28**); M = Ta, R = Bu^t (**29**) or 2,6-$C_6H_3Pr^i_2$ (**30**)

31

32

Scheme 5. Group 5 aryloxide, amido and amidinate complexes supported by the N_2N_{py}–imido ligand set.

3.1. Group 5 derivatives

3.1.1. Aryloxide, amido and amidinate complexes

The synthesis and structures of Group 5 aryloxide, amido and amidinate complexes supported by the N_2N_{py}–imido ligand set are shown in Scheme 5 [16]. Studies have, on the whole, focussed on the niobium *tert*-butylimido system **15** because of its ease of preparation (relative to that of **16** and **17**) and the observation that the chemistry of **15** does not significantly differ from that of **16** and **17** where such comparisons have been made (but see also Section 3.1.2).

Reaction of **15**–**17** with LiOAr ($Ar = 2,6\text{-}C_6H_3Pr^i_2$) gives the corresponding five-coordinate aryloxide complexes $[M(NR)(N_2N_{py})(OAr)]$ (M = Nb, R = Bu^t (**28**); M = Ta, R = Bu^t (**29**) or $2,6\text{-}C_6H_3Pr^i_2$ (**30**)) in which the OAr ligand has replaced both the Cl and py ligands of **15**–**17**. The solid state structures of **28** (see Fig. 3) and **30** have been determined and confirm the geometry shown in Scheme 5. The M–O–Ar linkages in **28** and **30** are non-linear ($M\text{–}O\text{–}C_{ipso} = 135.8(2)$ and 158.5(2)°, respectively), particularly so for the less sterically crowded **28**, and the M–O bond lengths are significantly longer than those normally found for Group 5 aryloxide complexes [21]. Such features could, in principle, be attributed to crystal packing forces. Alternatively, they could, together with the relative coordination site positions of the NR and OAr groups (i.e. in the axial and equatorial sites of a trigonal bipyramid, respectively) be attributed to the competition between the π-donor ligands in the three complexes [16].

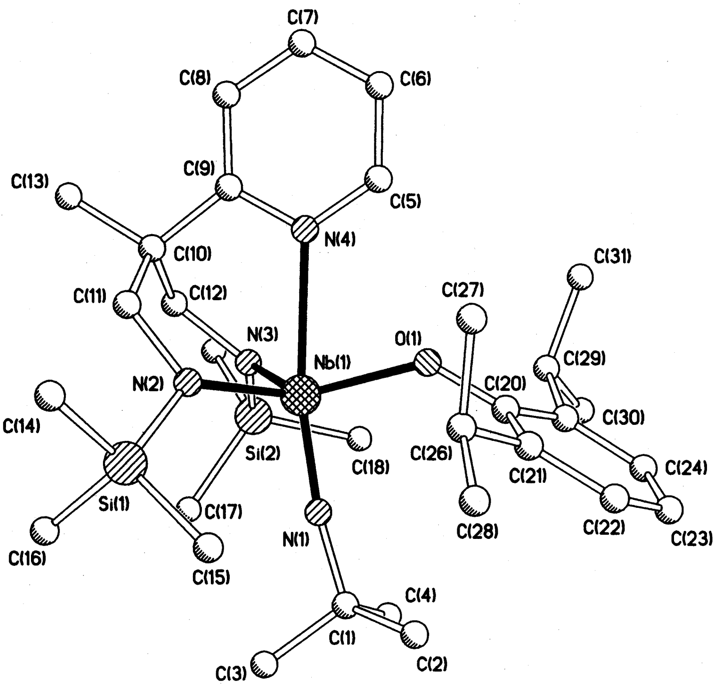


Fig. 3. The molecular structure of $[Nb(NBu^t)(N_2N_{py})(O\text{–}2,6\text{-}C_6H_3Pr^i_2)]$ (**28**).

Despite the steric crowding at the metal centres in **28**–**30** the pyridyl moiety of N_2N_{py} remains coordinated in both the solid state and solution. However, on reaction of **15** with the bulky lithiated amide, $LiN(SiMe_3)_2$, four-coordinate $[Nb(NBu^t)(N_2N_{py})\{N(SiMe_3)_2\}]$ (**31**) is formed. The ^{1}H-NMR shift of the *ortho*-pyridyl proton reveals that this group is now pendant. Perhaps surprisingly, given the four-coordinate nature of **31**, reaction of **15** with $Li[PhC(NSiMe_3)_2]$ gives the benzamidinate derivative $[Nb(NBu^t)(N_2N_{py})\{PhC(NSiMe_3)_2\}]$ (**32**) which possesses a five-coordinate niobium centre. The coordination of the pyridyl group is indicated by the *ortho*-pyridyl proton chemical shift and an observed nOe interaction between this hydrogen atom and the hydrogens of the benzamidinate $SiMe_3$ groups.

3.1.2. Alkyl, allyl and cyclopentadienyl complexes

The synthesis and structures of Group 5 alkyl, allyl and cyclopentadienyl complexes supported by the N_2N_{py}–imido ligand set are shown in Scheme 6 [16]. As for the chemistry reported in Section 3.1.1, studies have been largely focussed on **15**.

Reaction of **15** with $PhCH_2MgCl$ gives the relatively unstable, six-coordinate benzyl complex $[Nb(NBu^t)(N_2N_{py})(CH_2Ph)(py)]$ (**33**) which, by NMR spectroscopy, has the geometry shown in Scheme 6. With $[M(Bu^t)(N_2N_{py})Cl(py)]$ (M = Nb (**15**) or Ta (**16**)) and the bulkier lithiated alkyl reagent, $LiCH(SiMe_3)_2$, the considerably more stable and synthetically reproducible complexes $[M(NBu^t)(N_2N_{py})\{CH(SiMe_3)_2\}]$ (M = Nb (**34**) or Ta (**35**)) are obtained. The solid state structure of **34** is shown in Fig. 4 and features a four-coordinate, pseudo-tetrahedral geometry at Nb

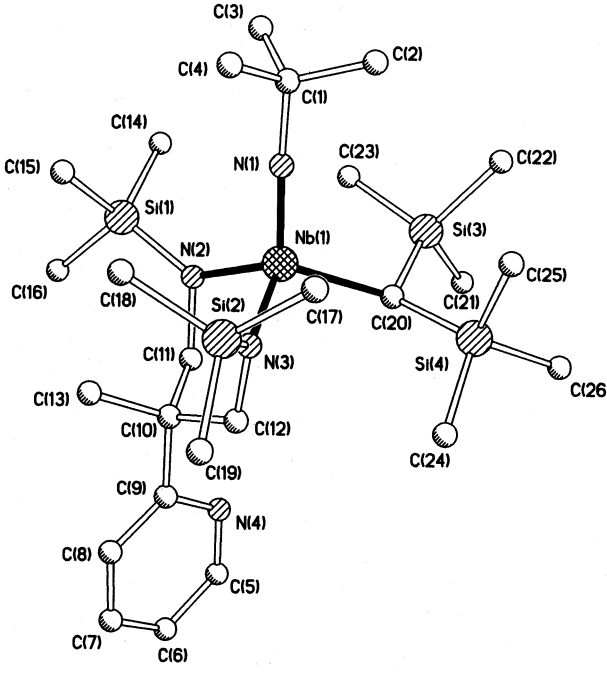
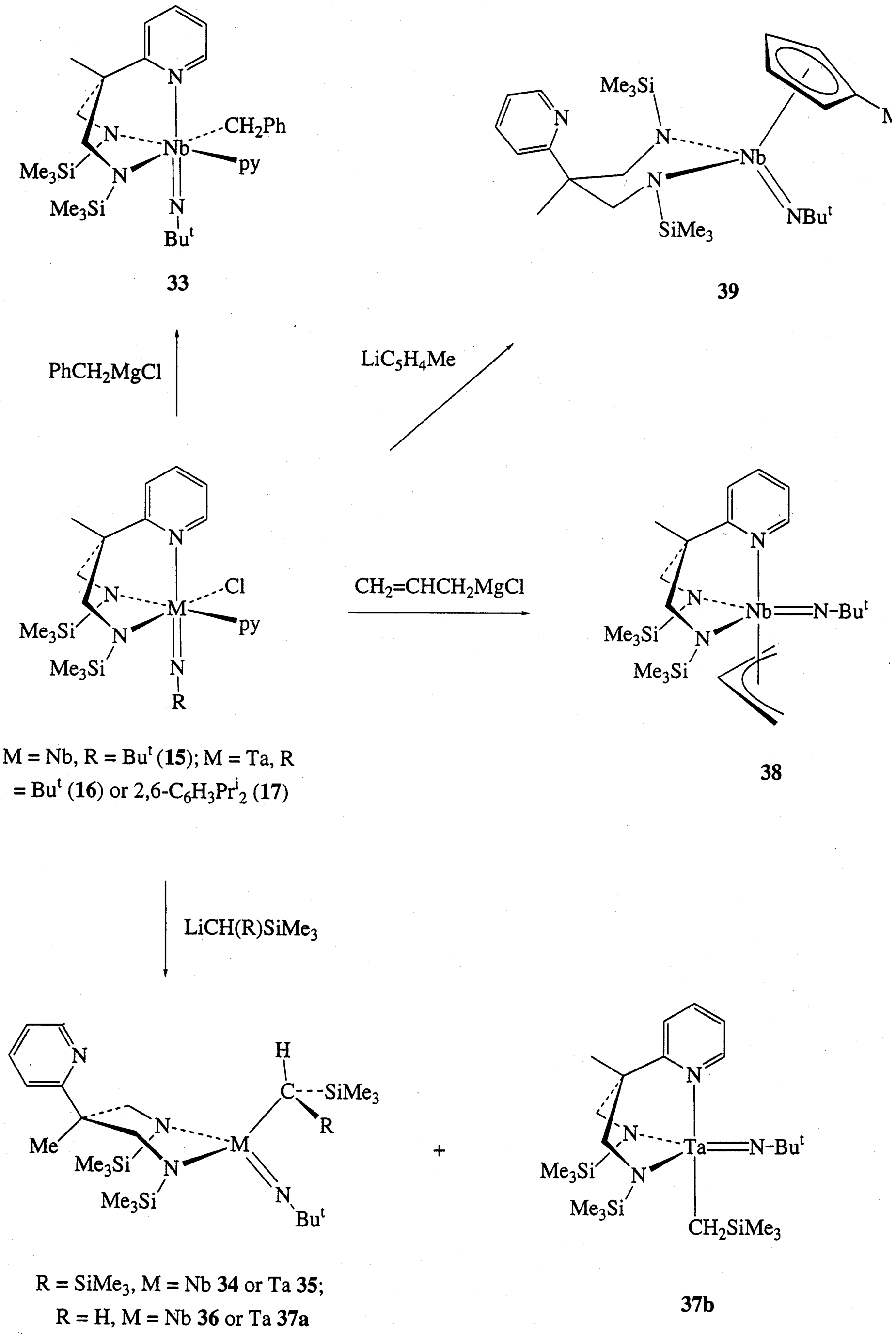


Fig. 4. The molecular structure of $[Nb(NBu^t)(N_2N_{py})\{CH(SiMe_3)_2\}]$ (**34**).



Scheme 6. Group 5 organometallic complexes supported by the N_2N_{py}–imido ligand set.

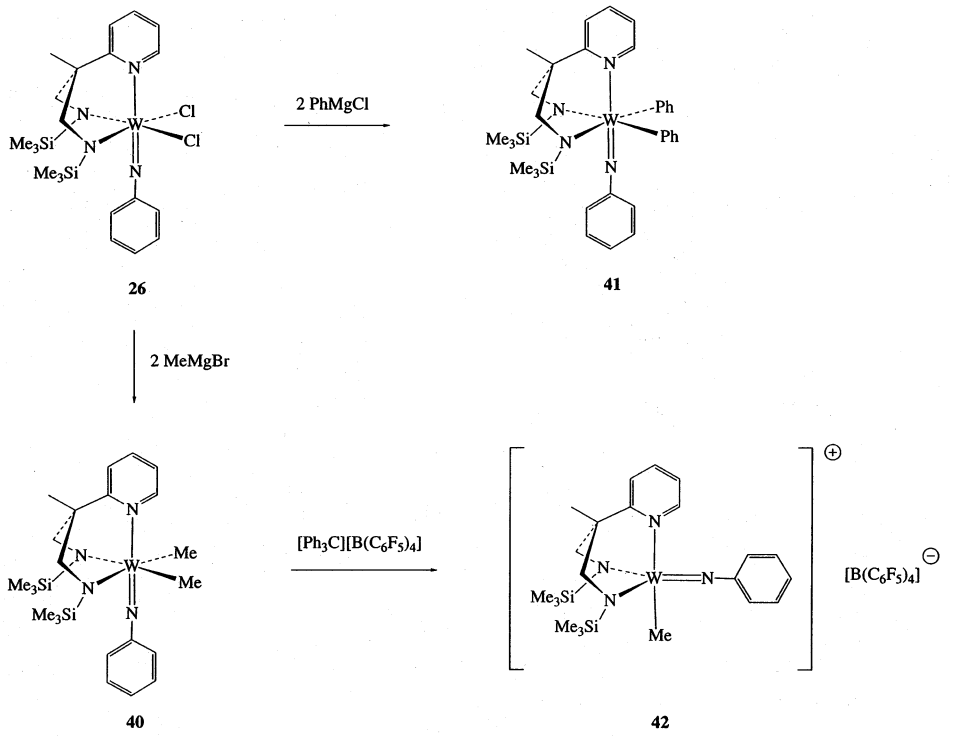
with the pyridyl group of the N_2N_{py} ligand pendant. Although the compounds **34** and **35** have relatively low coordination numbers and a maximum possible valence electron count of 16, there is no evidence (as is also the case with the compounds **36** and **37** discussed below) for agostic interactions between the metal centre and the α-H of the alkyl group in either the solid or solution state. The structural authentication of **34** provides further supporting evidence for the four-coordinate geometry proposed for the bis(trimethylsilylamido) complex **31**.

The reaction of the compounds **15** or **16** with the somewhat less bulky lithiated alkyl $LiCH_2SiMe_3$ gives one or two types of isomeric product depending on the identity of the metal (Scheme 6). Reaction of $LiCH_2SiMe_3$ and the niobium compound **15** gives the four-coordinate alkyl $[Nb(NBu^t)(N_2N_{py})(CH_2SiMe_3)]$ (**36**) as the only isomer formed. With the tantalum congener **16**, however, two products are obtained as an inseparable mixture, namely the four- (**37a**, major) and five- (**37b**, minor) coordinate isomers of $[Ta(NBu^t)(N_2N_{py})(CH_2SiMe_3)]$. The two isomers were distinguished using nOe and other NMR spectroscopic methods; spin saturation transfer experiments showed that there is no detectable interconversion between **37a** and **37b** at room temperature. Since the atomic radii of Nb and Ta are effectively identical [22], the tendency for the Ta homologue of $[M(NBu^t)(N_2N_{py})(CH_2SiMe_3)]$ to achieve a higher coordination number has been attributed to the general increase in metal–ligand bond strengths as a transition metal triad is descended [17].

While the organometallic derivatives **33**–**37** all contain η^1-bound alkyl ligands, complexes containing a higher hapticity hydrocarbyl group can also be prepared [16]. Reaction of **15** with CH_2CHCH_2MgCl gives the fluxional η^3-allyl derivative $[Nb(NBu^t)(N_2N_{py})(\eta^3\text{-}C_3H_5)]$ (**38**). The overall geometry of **38**, i.e. with the imido group *cis* to pyridyl (which in turn is still coordinated to the metal centre), has been deduced by spectroscopic techniques. At room temperature the ^{1}H-NMR resonances for the allyl ligand appear as a mutually coupled quintet (1H) and doublet (4H) suggesting a rapid dynamic equilibrium between $\eta^3 \leftrightarrow \eta^1 \leftrightarrow \eta^3$ coordination modes. Even at 176 K this process cannot be fully ‘frozen out’ on the NMR timescale. Reaction of **15** with LiC_5H_4Me gives the half-sandwich complex $[Nb(NBu^t)(N_2N_{py})(\eta\text{-}C_5H_4Me)]$ (**39**), whereas with LiC_5Me_5 a mixture of unidentified products are formed, presumably due to steric hinderence. The compound **39** does not have the pyridyl donor of N_2N_{py} bound to the metal centre and is isolobal with the molybdenum bis(imido) complexes $[Mo(NBu^t)_2(N_2N_{py})]$ (**24**) and $[Mo(NBu^t)_2(N_2N_{am})]$ (**25**).

3.2. Group 6 derivatives

Chloride ligand substitution reactions of the Group 6 diamido-donor complexes $[W(NR)(L_{N2N})Cl_2]$ ($L_{N2N} = N_2N_{am}$ or N_2N_{py}; $R = Ph$ or 2,6-$C_6H_3Me_2$ (**26**–**29**)) have so far focused on alkyl and aryl derivatives of **26** since this is the homologue that is most readily prepared in synthetically useful quantities. The new chemistry is summarized in Scheme 7 [19].



Scheme 7. Neutral and cationic organometallic tungsten complexes.

A range of alkylation reactions of **26** have been attempted with organolithium and Grignard reagents, but the only ones that gave isolable products were with MeMgBr to form [W(NPh)(N_2N_{py})Me_2] (**40**) and with PhMgCl to form [W(NPh)(N_2N_{py})$(Ph)_2$] (**41**). This contrasts with Boncella's extensive chemistry of related tungsten imido systems with chelating diamido ligands [6b]. By NMR spectroscopy the compounds are thought to possess the geometries shown with the phenylimido ligand *trans* to the pyridyl donor. Reaction of **40** with [Ph_3C][B$(C_6F_5)_4$] gives the cationic derivative [W(NPh)(N_2N_{py})Me][B$(C_6F_5)_4$] via a methyl group abstraction process. Further reactions of [W(NPh)(N_2N_{py})Cl_2] (**26**) and of the new organometallic compounds **40**–**42** are currently underway.

4. Reactions at the Ti=NR linkage of the compounds [Ti(NR)(N_2N_{py})(py)]

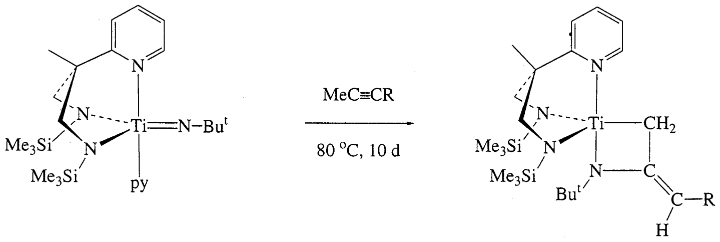
The imido group is a widely employed ancillary ligand in the high oxidation state coordination chemistry of Group 5 and 6 metals due to its relative chemical inertness [1]. This is in contrast to the reactivity observed in Group 4 imido compounds [1,2]. The most remarkable reactive behaviour has been reported by Wolczanski et al. for low-coordinate, transiently-generated imido titanium species which undergo C–H bond activation reactions with saturated and unsaturated hydrocarbons [23–26]. This potential reactivity of low-coordinate titanium imido complexes was an important consideration in the design of complex $[Ti(NBu^t)(N_2N_{py})(py)]$ (**1**) [12]. The polydentate ligand conferred considerable thermal stability on this species which allows its facile isolation and manipulation. However, it was also envisaged that since this type of imido complex possess labile pyridine and pyridyl ligands, under appropriate reaction conditions they could dissociate to yield unsaturated and highly reactive species of the type investigated by Wolczanski via irreversible thermolysis of the respective precursor molecules (Scheme 8).

In fact, sublimation of compound 1 in high vacuum has yielded the four-coordinate complex $[Ti(NR)(N_2N_{py})]$ (**8**) already mentioned in Section 2.1 [13a]. However, there has been no evidence for the postulated highly unsaturated, three-coordinate species A to date.

The high and intrinsic reactivity of Group 4 imido complexes is due to the combination of the high $M=NR$ bond polarity and the unsaturated nature of this structural element. While the former renders it highly reactive towards polar organic substrates, the latter situation enables the fomation of covalent bonds between the substrate and the $M=NR$ unit while leaving the nitrogen atom covalently bound to the metal centre. This is expected to allow a wide range of C–N or heteroatom-N coupling reactions which were the focus of the investigation into the reactivity of **1** and its homologues.

4.1. Reactions of $[Ti(NR)(N_2N_{py})(py)]$ with alkynes and allenes

Heating compound **1** dissolved in neat 2-butyne or 1-phenylpropyne at 80°C for 10 days in a sealed tube led to its complete conversion to the novel complexes $[Ti(N_2N_{py})\{CH_2C(=CHR)NBu^t\}]$ (R = H (**43**) or Ph (**44**)) (Eq. (3)), respectively, which were isolated by direct crystallization from the reaction mixture [27].

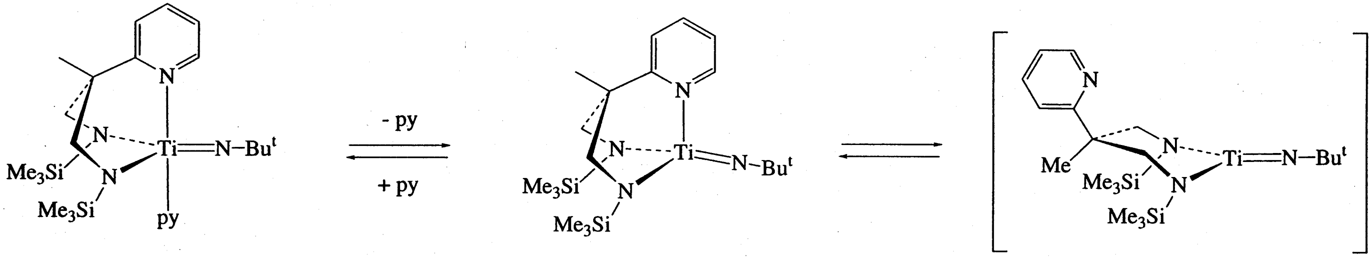


(3)

1

R = H (**43**) or Ph (**44**)

The identity of both compounds was established by their analytical and spectroscopic data as well as by X-ray diffraction studies. The molecular structure of **43** is depicted in Fig. 5. The coordination geometry of the molecule is distorted trigonal



1 **8** **A**

Scheme 8. Stabilization and ‘masking’ of low-coordinate titanium imido complexes.

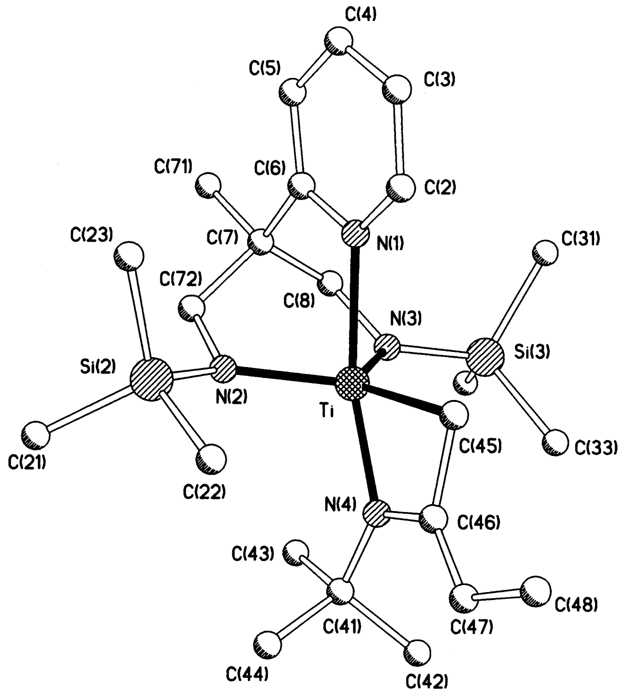
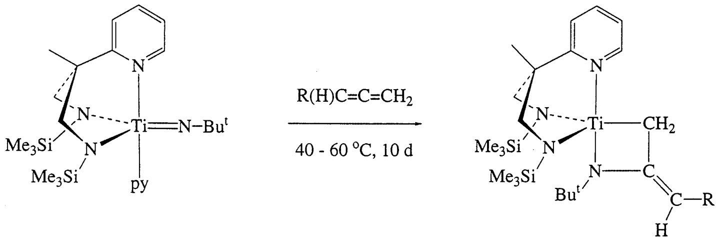


Fig. 5. The molecular structure of [Ti(N_2N_{py}){$CH_2C(=CH_2)NBu^t$}] (**43**).

bipyramidal. The two amido functions of the tripodal ligand as well as the alkyl C–atom C(45) occupy the equatorial sites, while the pyridyl N-atom and the amido-N atom derived from the imido ligand represent the axial ligating atoms. The bond lengths and interbond angles within the C–N-coupled organic fragment clearly support its interpretation as a metallated enamine with C(45)–C(46) = 1.515(9) and C(46)–N(4) = 1.404(8) Å representing single bonds and C(46)–C(47) = 1.338(9) Å being consistent with a C–C-double bond.

For this unusual combined C–H bond activation and C–N coupling reaction the mechanism displayed in Scheme 9 has been proposed. In a first reaction step (formation of intermediate B) the CH_3-group of the methyl acetylene adds across the Ti=NR bond generating an R(H)N–amido ligand and a Ti–alkyl unit. Such C–H bond activation reactions of transiently generated imido compounds have been studied extensively by Wolczanski [23–26]. In a proposed second step H atom transfer to an acetylene C-atom leads to the re-formation of the imido unit and an η^2-bonded allene ligand (C). These fragments couple in the third and final step to give the four-membered azatitanacycle present in **43** and **44**. Supporting evidence for this third step was obtained independently by the reaction of compound **1** with 1-methyl allene and 1-phenyl allene, respectively. In both cases the same reaction products (i.e. **43** and **44**, respectively) as those described above were obtained (Eq. (4)). Alternatively, intermediate B may also be converted to the metallacycle directly via a concerted ring closure step.

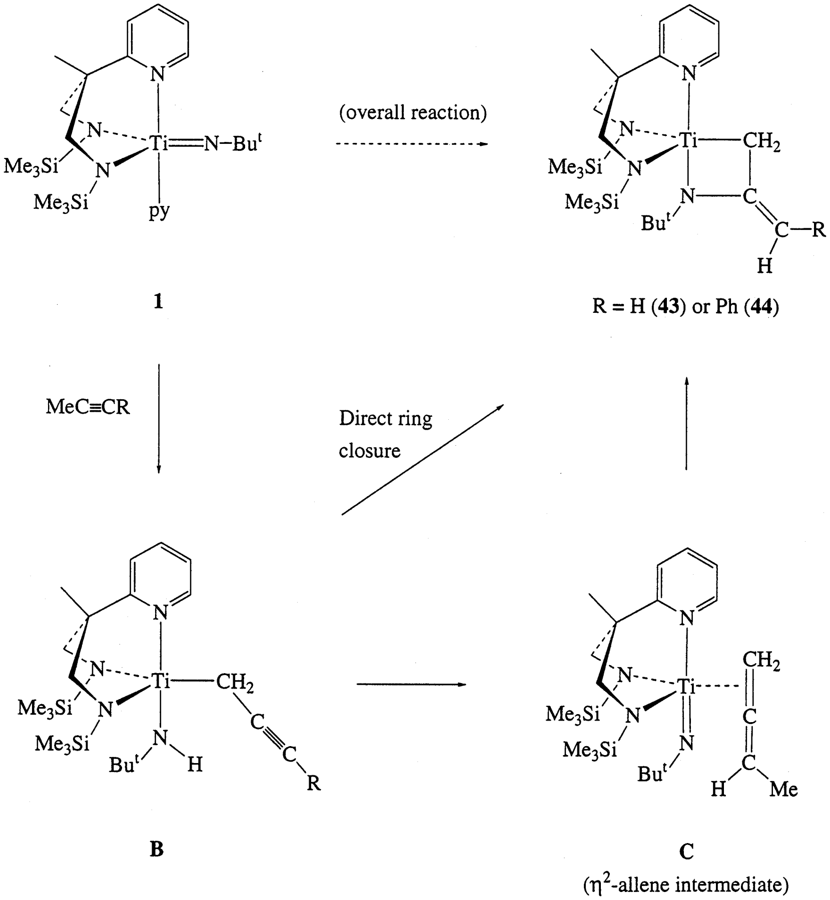


1

R = H (**43**) or Ph (**44**)

(4)

The reactions of **1** with $CH_3C{\equiv}CR$ and $CH_2{=}C{=}CHR$ to form **43** and **44** are the first examples of such transformations in transition metal chemistry. Although reactions of imido complexes with internal alkynes to form metallacycles



Scheme 9. Possible mechanisms for the formation of $[Ti(N_2N_{py})\{CH_2C(=CHR)NBu^t\}]$ (R = H (**43**) or Ph (**44**)).

[M(L$_n$){N(R′)C(R)=CR}] are known [28], no examples of the activation of sp^3 C–H bonds in apparent preference to forming the simple cyclization products have been described. The reaction of **1** with allenes to form a metalla-azetidine is the first fully-characterized example of this type for imido complexes. Very recently the reaction of [Zr(ebthi)(NBu^t)] with allene to form [Zr(ebthi){N(Bu^t)C(=CH$_2$)CH$_2$}] (ebthi=bis(tetrahydroindenyl)ethane) was described by Bergman and coworkers [29].

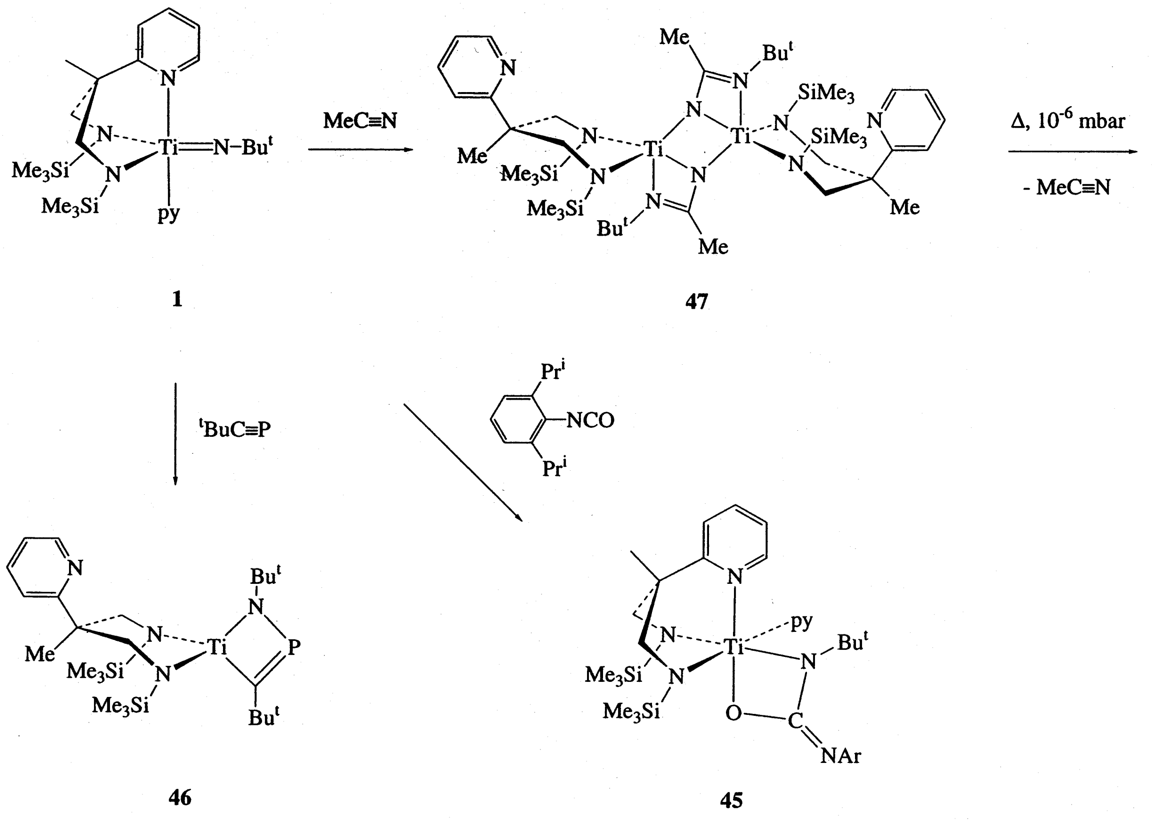
*4.2. Reactions of [Ti(NR)(N$_2$N$_{py}$)(py)] (**1**) with RNCO, RCN and RCP*

As already discussed above, the high degree of polarity of the Ti=NR unit in these imido complexes renders it particularly reactive towards polar unsaturated organic substrates. Imidotitanium complexes stabilized by polydentate ligands have been previously shown to undergo formal [2 + 2] cycloadditions with isocyanides, carbidiimides, CO$_2$ and phosphaalkynes [7a,30]. Similar reactivity has also been established for **1** and the reactions studied are summarized in Scheme 10 [31].

Reaction of **1** with ArNCO (Ar = 2,6-C$_6$H$_3$Pr$^i_2$) gives the [2 + 2] cycloaddition product [Ti(N$_2$N$_{py}$){OC(=NAr)NBu^t}(py)] (**45**) which contains an N,O-bound ureate ligand [31a]. The structure of **45** was assigned on the basis of nOe measurements and other NMR spectroscopic data and, apart from the coordinated pyridine ligand, is related to those of the alkyl–allene coupling products **43** or **44** (Eq. (4)). The reaction of other titanium imido complexes with isocyanates has exclusively yielded *N,N*-bound ureate ligands [7a]; the reasons for the differing mode of coordination of the ureate ligand in **45** are not clear but may in part be attributed to the bulky aryl group. The use of a sterically demanding isocyanate N-substituent is critical in this reaction since reaction of **1** with PhNCO or Bu^{t}NCO gave only intractable mixtures [31a], as was also the case when **1** was reacted with CO$_2$.

Particularly notable in Scheme 10 are the reactions with acetonitrile and Bu^{t}CP to give the compounds [Ti(N$_2$N$_{py}$){N(Bu^t)PC(Bu^t)}] (**46**) and [Ti(N$_2$N$_{py}$){μ-NC(Me)NBu^t}]$_2$ (**47**) [31b]. Thus, whereas the cycloaddition reaction with the phosphaalkyne generated a mononuclear product **46**, the reaction with the nitrile yielded the dimer **47**. Both in the solid state and in solution the neutral pyridyl function remains pendant. The different polarity pattern of the RC≡P relative to the RC≡N triple bond induces a different regioselectivity of the cycloaddition generating metallacycles containing NPC and NCN units, respectively. Whereas the reaction with MeCN is without precedent, the phosphaalkyne cycloaddition is analogous to the one found very recently for transient [ZrCp$_2$(NR)] (R = Bu^t or 2,6-C$_6$H$_3$Pr$^i_2$) with Bu^{t}CP [30]. Furthermore, it was found that certain titanium imido complexes such as [Ti(NBu^t)Cl$_2$(py)$_3$] and [Ti(NBu^t)(η^8-C$_8$H$_8$)] react with two equivalents of Bu^{t}CP to form 1:2 (Ti:Bu^{t}CP) addition products containing an η^5-Bu^{t}NP(CBu^t)$_2$P ligand which possesses a P$_2$C$_2$ ring. However, such a product of a second CP-cycloaddition was not observed for **46**.

Attempted high vacuum sublimation of **47** led to the virtually quantitative formation of the pyridine-free complex [Ti(NBu^t)(N$_2$N$_{py}$)] (**8**). In a separate experiment **47** was heated under a dynamic vacuum and in-line monitoring of the volatiles by mass spectrometry confirmed the formation of MeCN. This cyclorever-



Scheme 10. Reactions of [Ti(NBu^t)(N$_2$N$_{py}$)(py)] (**1**) with MeCN, Bu^{t}CP and ArNCO.

sion has no precedent in organonitrile chemistry although it may be related to the observed reversibility of cycloadditions of other unsaturated substrates, such as alkenes, alkynes and imines to imidozirconium complexes as reported by Bergman and coworkers.

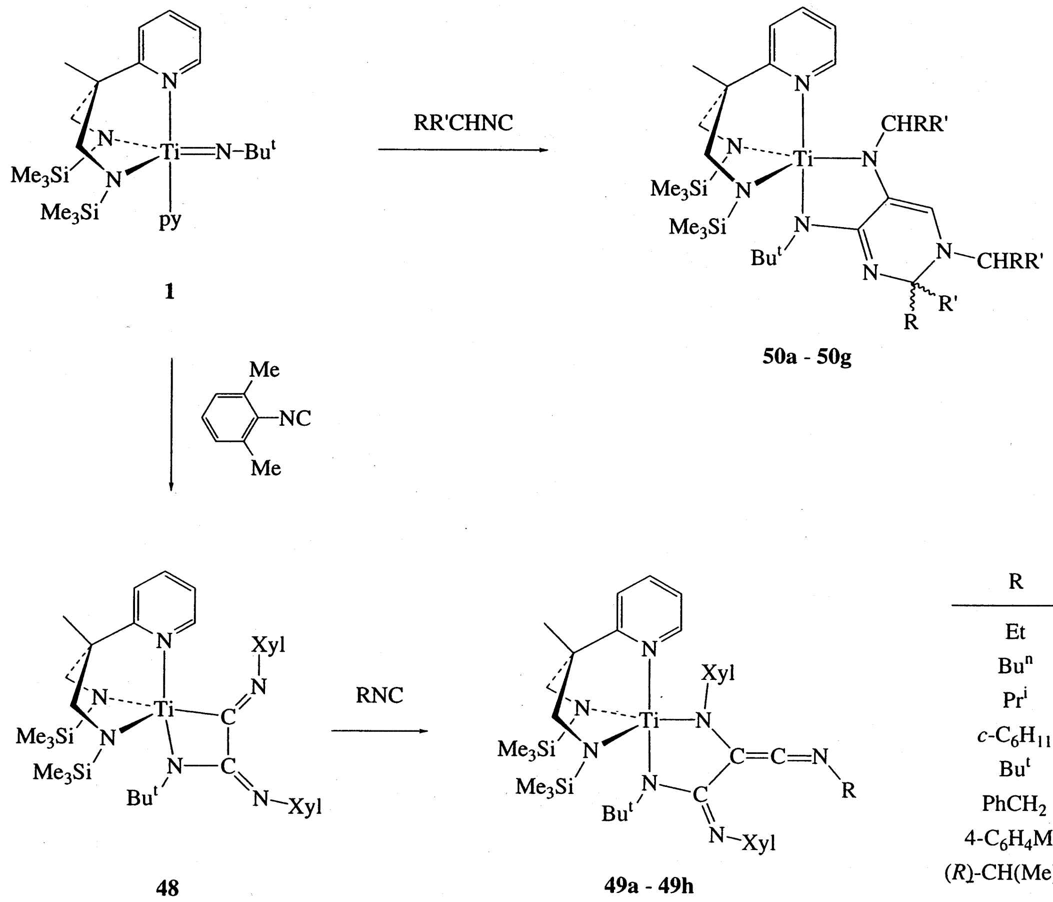
[2 + 2] Cycloadditions are also thought to occur in C=N bond metatheses of imines with imidotitanium and zirconium complexes [32,33]. In such reactions the imido complex may act as a catalyst to effect C=N bond redistribution similar to the C=C bond cleavages and reformations observed in olefin metathesis [3a,b,34]. This type of reactivity was not observed for **1**, possibly due to the efficient steric shielding of the imido unit by the polydentate amido-donor ligand.

4.3. The multifaceted reactivity of [Ti(NR)(N_2N_{py})(py)] towards isocyanides

Bergman and coworkers reported the C–N coupling of an imido ligand in the transient species [ZrCp$^*_2$(NBu^t)] and *tert*-butyl isocyanide [28b]. The result is a zirconium complex containing an η^2-coordinated carbodiimide ligand. The reaction of the imido titanium compound **1** with 2,6-xylylisocyanide was thus carried out with the aim of obtaining the product of a similar C–N coupling reaction, namely a metal-bonded carbodiimide. While *tert*-butyl isocyanide proved to be unreactive towards **1**, a whole range of alkyl- and aryl-isocyanides reacted immediately [12,35]. However, no product of a single C–N coupling reaction could be isolated with any of the substrates. The most straightforward reaction was that of **1** with xylylisocyanide which cleanly gave the product of a double insertion into the Ti=NBu^t bond, namely [Ti(N_2N_{py}){N(Bu^t)C(N-2,6-$C_6H_3Me_2$)C(N–2,6-$C_6H_3Me_2$)}] (**48**) (Scheme 11) which has been characterized structurally [35].

The clean reaction of **1** with xylylisocyanide to give complex **48** is probably a consequence of the steric demand of the 2,6-xylyl groups which suppresses further reaction with excess xylylisocyanide. Another factor may be the low solubility of the reaction product in benzene which leads to immediate precipitation upon its formation. That the metallacycle **48** is by no means an unreactive species is apparent from its interaction with isocyanides other than the bulky 2,6-xylylisocyanide or 2,6-diisopropylphenylisocyanide. Thus, reaction of **48** with a large series of isocyanides RNC [R = Et, Bu^n, Pr^i, C_6H_{11}, Bu^t, PhCH$_2$, 4-C_6H_4Me, (R)-CH(CH_3)Ph] led to the selective conversion to the complexes [Ti(N_2N_{py}){N(2,6-$C_6H_3Me_2$)C(CNR)C(N–2,6-$C_6H_3Me_2$)N(Bu^t)}] (**49a**–**h**), respectively, which contain an imidoylketimine unit coordinated to the metal centre and that are the products of a triple isocyanide cross-coupling reaction (Scheme 11).

The structures of compounds **49d**, **49f** and **49g** were established by X-ray diffraction and are the first structurally characterized complexes in which an iminoketene group and an imino group have a mutual *Z*-configuration; that of **49d** is shown in Fig. 6. The fragments are not located in the same plane due to steric interactions between the iminoketene unit and the neighbouring xylyl groups. There are two examples of complexes in the literature in which an imino group and an iminoketene unit adopt an *E*-configuration. Gerlach and Arnold reported the crystal structure analysis of [V{N(SiMe$_3$)$_2$}$_2${Bu^{t}N=C(Me)C(C=C=NBu^t)NBu^t}] [36]



R, R'	
H, H	**50a**
H, Me	**50b**
H, Pr^n	**50c**
H, Ph	**50d**
Me, Me	**50e**
Me, Ph	**50f**
c-C_5H_{10}	**50g**

R	
Et	**49a**
Bu^n	**49b**
Pr^i	**49c**
c-C_6H_{11}	**49d**
Bu^t	**49e**
$PhCH_2$	**49f**
4-C_6H_4Me	**49g**
(R)-CH(Me)Ph	**49h**

Scheme 11. Reactions of [Ti(NBu^t)(N_2N_{py})(py)] (**1**) with isocyanides.

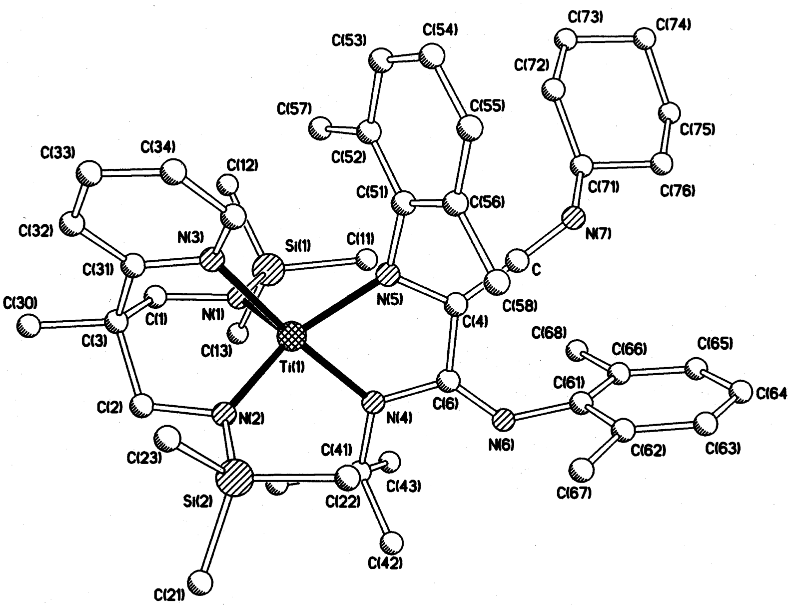


Fig. 6. The molecular structure of $[Ti(N_2N_{py})\{N(2,6\text{-}C_6H_3Me_2)C(CNC_6H_{11})C(N\text{-}2,6\text{-}C_6H_3Me_2)\text{-}N(Bu^t)\}]$ (**49d**).

and Rothwell et al. synthesized $[Ta(O\text{-}2,6\text{-}C_6H_3Pr^i_2)_2Cl_2\{Bu^tN{=}CHC(C{=}CNBu^t)\text{-}NBu^t)\}]$ [37].

The reaction of methyl isocyanide with **1** occurred spontaneously and highly selectively at ambient temperature [12,35]. The conversion to a single product **50a** was complete after addition of three molar equivalents of the isocyanide as was confirmed by NMR monitoring of the reaction. Even if small quantities of the substrate were titrated to the solution of the imido complex, at 200 K in toluene-d_8, no intermediates could be detected in the ^{1}H-NMR spectra which were recorded during the procedure. The ^{1}H- and ^{13}C-NMR spectra of the reaction product were consistent with the formation of a metal-bound diaminodihydropyrimidine as shown in Scheme 11.

The molecular structure of the reaction product **50a** was established by a single crystal X-ray structure analysis and is shown in Fig. 7. The compound **50a** contains a five-coordinate Ti atom with a distorted trigonal-bipyramidal arrangement of the N-donor atoms. The Ti=NBu^t unit of **1** has undergone C–N and C–C coupling (with concomitant C–H bond migration) with three molecules of MeNC to form a coordinated 3-methyl-5,6-diamino-2,3-dihydropyrimidine derivative. In the ^{1}H-NMR spectrum of **50a** the signal of the methylene protons in the heterocycle is observed at δ 4.86 while that of the CH-group appears at 5.45 ppm.

In order to establish the generality of this reaction, the analogous conversion was carried out using EtNC, Bu^{n}NC and PhCH$_2$NC which yielded the cyclization products **50b**–**d**. It was also possible to generate quaternary carbon centres in the

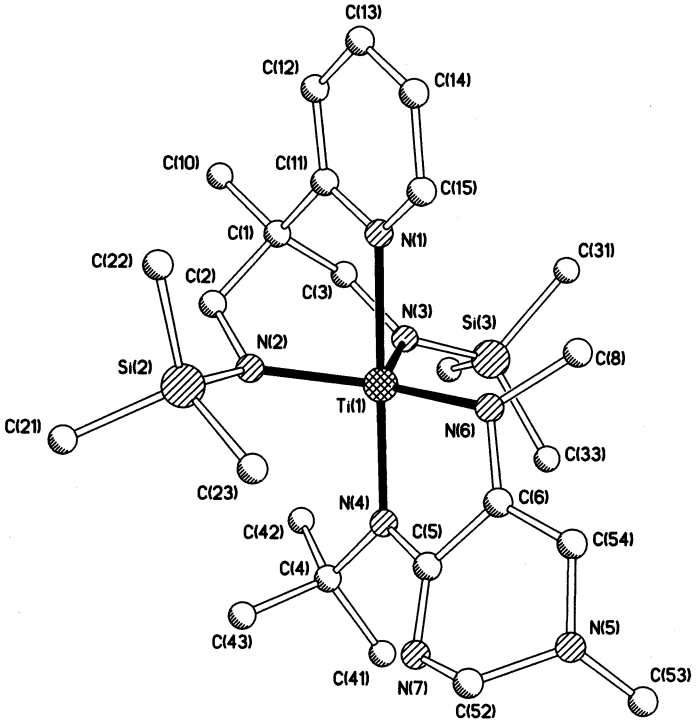
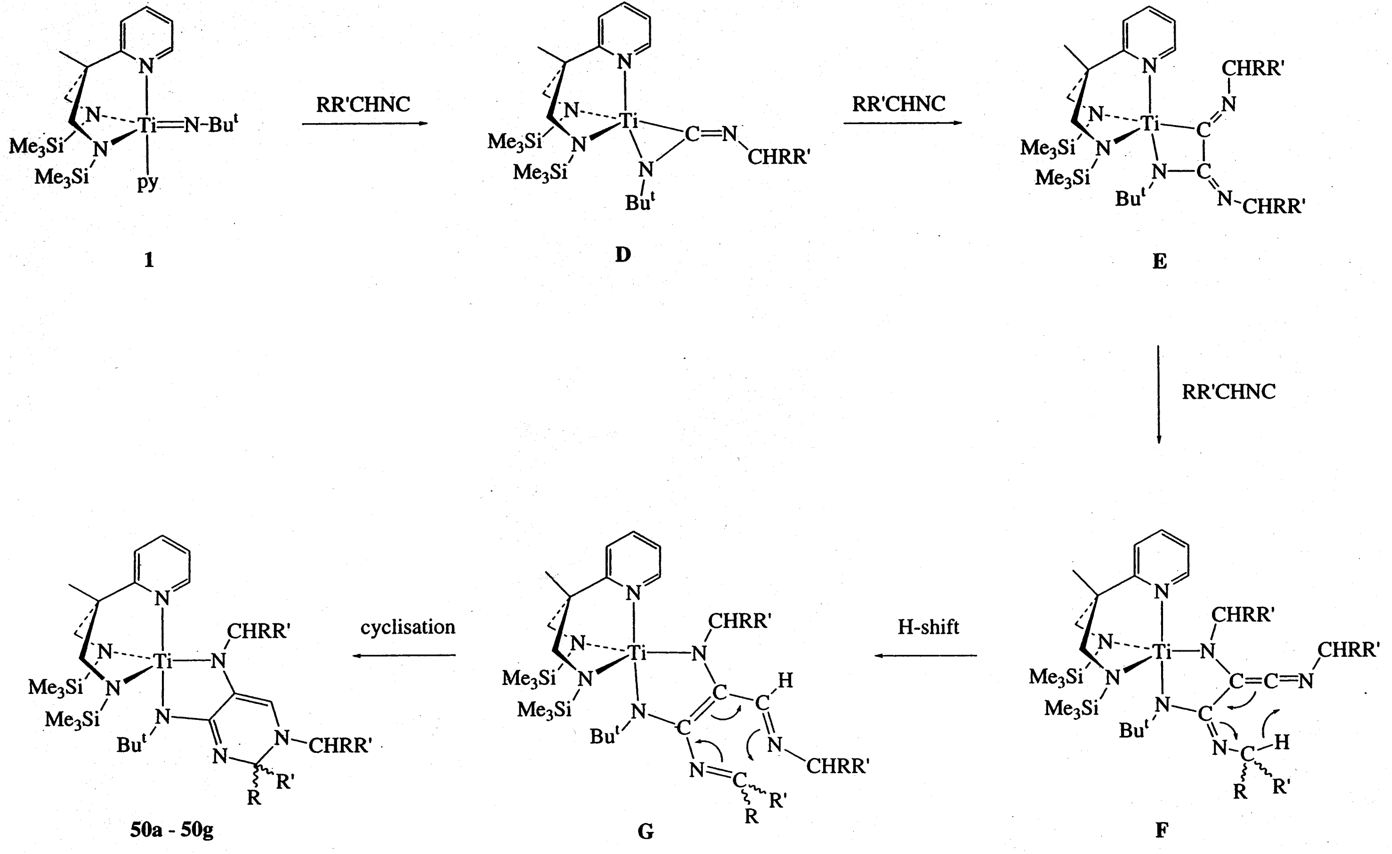


Fig. 7. The molecular structure of [Ti(N_2N_{py}){N(Me)N(Bu^t)($C_4H_3N_2Me$)}] (**50a**).

N-heterocyclic ring by reaction of the imido complex **1** with the secondary alkyl isocyanides Pr^iNC, (R)-Ph(Me)CHNC and c-C_6H_{11}NC thus forming **50e**–**g** (Scheme 11). In all three cases an immediate conversion to the titanium complexes bearing the N-heterocycles was observed (Scheme 11).

As mentioned above, the reaction of the imido complex **1** with alkyl isocyanides to give the N-heterocyclic fragments coordinated to titanium occurs without detectable intermediates which implies that the first reaction step is the rate determining step in this conversion. This is the situation even if the pyridine-free imidotitanium complex [Ti(NBu^t)(N_2N_{py})] (**8**) [13a] is employed in these reactions. The first C–N coupling reaction is therefore assumed to be the slow reaction step rather than the displacement of pyridine. Unfortunately, the extreme rapidity of this conversion to the cyclized species even at low temperatures renders the system unsuitable for a kinetic study using conventional methods. The proposed mechanism displayed in Scheme 12 is thus based on the evidence obtained in the reactions described above and by analogy with known reactions of isocyanides.

The first step is thought to be the insertion of an isocyanide group into the imidotitanium unit to give the metal bonded carbodiimido of the type **D**. Although no model compound derived from **1** of this first postulated intermediate could be characterized, the existence of such species has been established by Bergman and coworkers in their studies of the reactivity of zirconium and iridium imido



Scheme 12. Proposed mechanism for the isocyanide coupling reactions of $[Ti(NBu^t)(N_2N_{py})(py)]$ (**1**).

complexes towards isocyanides [28b,38]. A rapid successive step is therefore thought to be a second insertion of an isocyanide to give four-membered titanacycle **E**. This proposed intermediate is structurally analogous to complex **48** discussed above. The facile conversion of **48** to give the iminoketene derivatives **49a**–**h** (Scheme 11) leads us to consider a similar transformation in the reaction cascade presented in Scheme 12 (giving **F**). This reaction could possibly occur via a short lived carbene intermediate, for which we were unable to obtain direct evidence. However, in view of the well established chemistry of Arduengo's carbenes [39] as well as the known reaction of carbenes and carbenoids with isocyanides to give iminoketenes [40], this appears to us to be a reasonable suggestion.

The isolation of the iminoketene compounds **49a**–**h** (Scheme 11) was achieved probably due to the absence of an N-bonded α-CH unit at the imino-group. In the presence of a hydrogen atom in this position, however, a sigmatropic H-shift occurs generating a metal bound 1,5-diazahexatriene **G** which undergoes ring closure to give finally the N-heterocyclic structures **50a**–**g**. The proposed intermediate **G**, in which one of the tetrahedral α-carbon centres of an isocyanide is planarized also explains the observation of a mixture of diastereomers in the reaction of **1** with (R)-Ph(Me)CHNC to give **50f**. The latter rearrangement of in situ generated imidoylketimines to dihydropyrimidines is a known conversion which may be used in the synthesis of certain dihydropyrimidine derivatives [41].

The cascade of reactions discussed here is an example of the complicated but selective conversions which isocyanides may undergo with early transition metal imido complexes. A notable example from the literature of an imido–isocyanide coupling sequence leading to a metal-bonded N-heterocyclic system was reported by Wilkinson and coworkers who studied the reactivity of in-situ generated $[CrCp^*(N{-}2,6\text{-}C_6H_3Pr^i_2)]$ towards isocyanides resulting in a coordinated amino-functionalized dihydroquinoline [42].

5. Concluding remarks

We have shown how the diamido–pyridine and diamido–amine ligands can be used to support new transition metal imido chemistry. In Group 4 in particular the hemi-labile nature of the neutral N-donor functional group allows access to a rich seam of chemistry and hitherto undiscovered transformations of organic substrates.

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