

# Reactions of titanium imido complexes with $\alpha$ -diimines: complexation *versus* Ti=N/C=N bond metathesis

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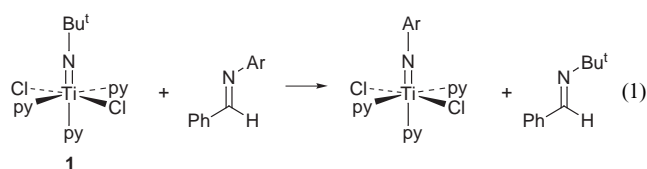
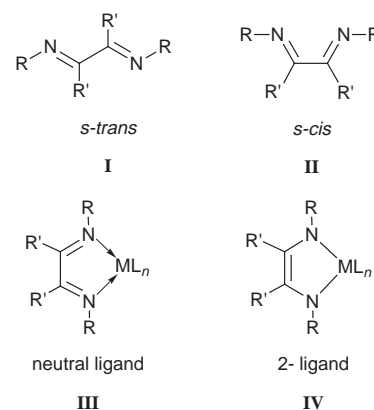
The reactions of the titanium imido complexes  $[\text{Ti}(\text{NR})\text{Cl}_2(\text{py})_3]$  ( $\text{R} = \text{Bu}^t$  **1**,  $\text{C}_6\text{H}_3\text{Me}_2$ -2,6 **2** or  $\text{C}_6\text{H}_3\text{Pr}^i$ -2,6 **3**) with  $\alpha$ -diimines (1,4-diaza-1,3-butadienes) of the type  $\text{ArNC}(\text{R}')\text{C}(\text{R}')\text{NAr}$  ( $\text{Ar} = \text{phenyl}$  or substituted phenyl,  $\text{R}' = \text{H}$  or methyl) are reported. The reaction products and metal complex stability are critically dependent on the nature of both the imido N- and diimine N- and backbone C-substituents. Reaction of **3** with  $\text{PhNC}(\text{Me})\text{C}(\text{Me})\text{NPh}$  gave the crystallographically characterised adduct  $[\text{Ti}(\text{NC}_6\text{H}_3\text{Pr}^i\text{-2,6})\text{Cl}_2\{\eta^2\text{-PhNC}(\text{Me})\text{C}(\text{Me})\text{NPh}\}(\text{py})]$  **4** which possesses mutually *trans* Cl ligands and has one diimine nitrogen atom *cis* and one *trans* to the arylimido group. The compound **4** is the first crystallographically characterised titanium complex to have a formally neutral (*i.e.* non-reduced)  $\alpha$ -diimine ligand and decomposes fairly quickly in solution at room temperature.  $^1\text{H}$  NMR evidence only is presented for the formation of the *tert*-butyl- and 2,6-dimethylphenyl-imido homologues of **4**, namely  $[\text{Ti}(\text{NR})\text{Cl}_2\{\eta^2\text{-ArNC}(\text{Me})\text{C}(\text{Me})\text{NAr}\}(\text{py})]$  ( $\text{R} = \text{Bu}^t$  or  $\text{C}_6\text{H}_3\text{Me}_2$ -2,6;  $\text{Ar} = \text{Ph}$  or tolyl, Tol): these compounds are considerably less stable in solution, rapidly decomposing to a number of products including the corresponding amines  $\text{RNH}_2$  and  $[\text{Ti}(\text{NR})\text{Cl}_2(\text{py})_n]$  ( $n = 2$  or  $3$ ). Reaction of **1** with  $\alpha$ -diimines of the type  $\text{ArNC}(\text{H})\text{C}(\text{H})\text{NAr}$  ( $\text{Ar} = \text{Tol}$  or 2,6- $\text{C}_6\text{H}_3\text{Me}_2$ ), *i.e.* without methyl substituents in the backbone, do not give detectable adducts analogous to **4**. In these cases titanium imide/organic imine metathesis occurs to form  $[\text{Ti}(\text{NAr})\text{Cl}_2(\text{py})_n]$  ( $n = 2$  or  $3$ ) and  $\text{Bu}^t\text{NC}(\text{H})\text{C}(\text{H})\text{NAr}$  and/or  $\text{Bu}^t\text{NC}(\text{H})\text{C}(\text{H})\text{NBu}^t$ .

## Introduction

The  $\alpha$ -diimines (also commonly known as 1,4-diaza-1,3-butadienes) of the type  $\text{RNC}(\text{R}')\text{C}(\text{R}')\text{NR}$  (**I** and **II** where typically  $\text{R} = \text{alkyl}$ , phenyl or substituted phenyl,  $\text{R}' = \text{H}$ , phenyl or methyl) represent a class of ligand that has received sustained and extensive attention synthetically, theoretically and spectroscopically for a range of main group-, transition-, lanthanide- and actinide-metal complexes.<sup>1–11</sup>  $\alpha$ -Diimines are typically prepared by condensation reactions of amines or anilines,  $\text{RNH}_2$ , with glyoxal or the corresponding  $\alpha$ -diketone  $\text{R}'\text{C}(\text{O})\text{C}(\text{O})\text{R}'$ ,<sup>12</sup> and adopt the *s-trans* conformation **I** in preference to the *s-cis* alternative **II** in the absence of bulky R- and/or R'-substituents.<sup>12</sup>  $\alpha$ -Diimines may coordinate as neutral bidentate ligands (as in **III**), but most commonly act as formally mono- or di-anionic (**IV**) moieties owing to their ability to accept electron density into the  $\pi_3$  lowest unoccupied molecular orbital,<sup>4,8</sup> which results in a shortening of the diimine C–C and lengthening of the C–N bonds in comparison to those of the free ligand.<sup>1,2</sup>

As part of an ongoing study of early transition metal imido chemistry<sup>13–19</sup> we recently reported the stoichiometric imide/imine metathesis reactions of  $[\text{Ti}(\text{NBu}^t)\text{Cl}_2(\text{py})_3]$  **1**<sup>20</sup> with monoimines of the type  $\text{PhC}(\text{NAr})\text{H}$  [ $\text{Ar} = \text{C}_6\text{H}_3\text{Me}_2$ -2,6 or tolyl, Tol, eqn. (1)].<sup>21</sup>

Such imide/imine metathesis reactions are very uncommon transformations in transition metal chemistry,<sup>22–24</sup> even though the corresponding carbene(alkylidene)/alkene metathesis reaction is very well established and widely applied.<sup>25</sup> In the context of these previous studies we were therefore interested to study the reactions of  $\alpha$ -diimines with the previously described titanium imido complexes  $[\text{Ti}(\text{NR})\text{Cl}_2(\text{py})_3]$  ( $\text{R} = \text{Bu}^t$  **1**,  $\text{C}_6\text{H}_3\text{Me}_2$ -2,6 **2** and  $\text{C}_6\text{H}_3\text{Pr}^i$ -2,6 **3**).<sup>‡,20</sup>



## Experimental

### General methods and instrumentation

Manipulations were carried out under an atmosphere of dinitrogen or argon using either standard Schlenk-line or dry-box techniques. Solvents were pre-dried over molecular sieves and refluxed over potassium (hexane), sodium (toluene), sodium–potassium alloy (pentane) or calcium hydride

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<sup>‡</sup> Although for ease of representation all titanium–imido linkages are drawn “Ti=NR”, the formal Ti–N bond order in the complexes  $[\text{Ti}(\text{NR})\text{Cl}_2\{\eta^2\text{-RNC}(\text{R}')\text{C}(\text{R}')\text{NR}\}(\text{py})]$  is generally best thought of as three (pseudo- $\sigma^2\pi^4$  triple bond) rather than as two.<sup>35</sup>

(dichloromethane) under an atmosphere of dinitrogen and collected by distillation.  $C_6D_6$  was dried over molten potassium and  $CDCl_3$  and  $CD_2Cl_2$  were dried over calcium hydride at room temperature (r.t.). All NMR solvents were distilled under reduced pressure and stored under  $N_2$  in Young's ampoules in a dry-box. NMR samples were prepared in a dry-box in Teflon valve (Young's) 5 mm tubes.

$^1H$  and  $^{13}C$  NMR spectra were recorded on a Bruker DPX 300 spectrometer at ambient temperature unless stated otherwise. The spectra were referenced internally to residual protio-solvent ( $^1H$ ) or solvent ( $^{13}C$ ) resonances and are reported relative to tetramethylsilane ( $\delta = 0$  ppm). Chemical shifts are quoted in  $\delta$  (ppm) and coupling constants in Hz. Assignments were supported by DEPT-135 and DEPT-90, homo- and hetero-nuclear and one- and two-dimensional experiments as appropriate. Elemental analysis was carried out by the analysis laboratory of this department.

### Literature preparations

The titanium imido complexes  $[Ti(NR)Cl_2(py)_3]$  ( $R = Bu^t$ ,  $C_6H_3Me_2-2,6$ ,  $C_6H_3Pr^i_2-2,6$ ) were prepared according to literature methods.<sup>20</sup>  $\alpha$ -Diimines  $RNC(R')C(R')NR$  were prepared by condensation reactions<sup>12</sup> of the corresponding  $\alpha$ -dicarbonyl compounds ( $R' = H$  or  $Me$ ) and amines ( $R = Bu^t$ ,  $Ph$ ,  $Tol$ ,  $C_6H_3Me_2-2,6$  or  $C_6H_3Pr^i_2-2,6$ ) according to literature procedures and purified either by distillation or recrystallisation from appropriate solvents.<sup>26-29</sup>

### Syntheses

**$[Ti(NC_6H_3Pr^i_2-2,6)Cl_2\{\eta^2-PhNC(Me)C(Me)NPh\}(py)]$  4.** To a solution of  $[Ti(NC_6H_3Pr^i_2-2,6)Cl_2(py)_3]$  (0.31 g, 0.58 mmol) in  $CH_2Cl_2$  (5 ml) was added a solution of  $PhNC(Me)C(Me)NPh$  (0.16 g, 0.68 mmol) in  $CH_2Cl_2$  (5 ml). The solution immediately turned deep green. After 10 minutes hexane (20 ml) was added to afford a green powder which was washed with hexane ( $2 \times 5$  ml) and dried *in vacuo*. Yield: 0.30 g (75%, for  $[Ti(NC_6H_3Pr^i_2-2,6)Cl_2\{\eta^2-PhNC(Me)C(Me)NPh\}(py)] \cdot 0.8CH_2Cl_2$ ). The product contained *ca.* 0.8 equivalent of residual  $CH_2Cl_2$  (by  $^1H$  NMR and elemental analysis). Diffraction quality crystals of  $4 \cdot CH_2Cl_2$  were grown at  $-25^\circ C$  by layering a saturated dichloromethane solution with hexane.  $^1H$  NMR ( $CD_2Cl_2$ , 300.1 MHz, 298 K):  $\delta$  8.79 (d, 2 H,  $J = 5.0$ , *ortho*- $NC_5H_5$ ), 7.57 (tt, 1 H,  $J = 7.6$ ,  $J = 1.6$ , *para*- $NC_5H_5$ ), 7.37 (d, 2 H,  $J = 8.4$ , *ortho*- $C_6H_5$ ), 7.24 (t, 2 H,  $J = 8.4$ , *meta*- $C_6H_5$ ), 7.13–7.00 (m, 2 H, *meta*- $NC_5H_5$ ), 2 H *ortho*- $C_6H_5$ ; 2 H, *ortho*- $C_6H_5$ ;  $2 \times 1$  H,  $2 \times$  *para*- $C_6H_5$ ), 6.55 (d, 2 H,  $J = 7.3$ , *meta*- $C_6H_3Pr^i_2$ ), 6.45 (t, 1 H,  $J = 7.3$ , *para*- $C_6H_3Pr^i$ ), 4.36 (septet, 2 H,  $J = 6.8$ , *CHMe*<sub>2</sub>), 2.28 (s, 3 H, *NC(Me)C(Me)N*), 2.15 (s, 3 H, *NC(Me)C(Me)N*), 0.87 (d, 12 H,  $J = 6.8$ , *CHMe*<sub>2</sub>).  $^{13}C$ - $\{^1H\}$  NMR ( $CD_2Cl_2$ , 62.5 MHz, 258 K):  $\delta$  165.7 (*C(Me)NPh*), 154.7 (*ipso*- $C_6H_3Pr^i_2$ ), 151.0, 146.3 ( $2 \times$  *ipso*- $C_6H_5$ ), 151.0 (*ortho*- $NC_5H_5$ ), 146.8 (*ortho*- $C_6H_3Pr^i_2$ ), 138.2, (*para*- $NC_5H_5$ ), 128.8 (*meta*- $C_6H_5$ ), 128.7 (*meta*- $C_6H_5$ ), 120.6, 121.1 ( $2 \times$  *ortho*- $C_6H_5$ ), 126.0 (*para*- $C_6H_5$ ), 123.5 (*meta*- $NC_5H_5$ ), 121.4 (*ortho*- $C_6H_5$ ), 121.3 (*meta*- $C_6H_3Pr^i_2$ ), 121.2, (*para*- $C_6H_3Pr^i_2$ ), 26.7 (*CHMe*<sub>2</sub>), 24.3 (*CHMe*<sub>2</sub>), 20.2 (*NC(Me)C(Me)N*), 19.7 (*NC(Me)C(Me)N*) [Found (calc. for  $C_{33}H_{38}Cl_2N_4Ti \cdot 0.8CH_2Cl_2$ ): C, 59.5 (59.9); H, 5.7 (5.9); N, 8.0 (8.3)%].

**NMR tube scale syntheses of  $[Ti(NC_6H_3Pr^i_2-2,6)Cl_2\{\eta^2-TolNC(Me)C(Me)NTol\}(py)]$  5,  $[Ti(NC_6H_3Me_2-2,6)Cl_2\{\eta^2-PhNC(Me)C(Me)NPh\}(py)]$  6 and  $[Ti(NBu^t)Cl_2\{\eta^2-TolNC(Me)C(Me)NTol\}(py)]$  7.** Because of their instability (especially for 6 and 7) these compounds were prepared and characterised only by  $^1H$  NMR according to the following general procedure.  $CDCl_3$  solutions of  $[Ti(NR)Cl_2(py)_3]$  ( $R = C_6H_3Pr^i_2-2,6$ ,  $C_6H_3Me_2-2,6$  or  $Bu^t$ , *ca.* 0.07 mmol in 0.5 ml) and either  $PhNC(Me)C(Me)NPh$  **A** or  $TolNC(Me)C(Me)NTol$  **B** (*ca.* 0.07 mmol in 0.5 ml) were mixed in the dry-box to give green solu-

tions, and the  $^1H$  NMR spectra were recorded immediately. Solutions of **5**, **6** and **7** showed extensive decomposition after less than *ca.* 4 hours, 1 hour and 10 minutes at r.t., respectively.  $^1H$  NMR ( $CDCl_3$ , 300.1 MHz, 298 K) data for **5**:  $\delta$  8.89 (m, 2 H, *ortho*- $NC_5H_5$ ), 7.66 (m, 1 H, *para*- $NC_5H_5$ ), 7.39–6.97 (overlapping m, 12 H, *ortho*- and *meta*- $C_6H_4Me$ , *meta*- $NC_5H_5$ ), 6.71 (strongly second order d, 2 H, *meta*- $C_6H_3Pr^i_2$ ), 6.62 (strongly second order t, 1 H, *para*- $C_6H_3Pr^i_2$ ), 4.40 (septet, 2 H,  $J = 6.8$ , *CHMe*<sub>2</sub>), 2.35 (s, 3 H, *NC(Me)C(Me)N*), 2.30, 2.24 ( $2 \times$  s,  $2 \times$  3 H, *para*- $C_6H_4Me$ ), 2.14 (s, 3 H, *NC(Me)C(Me)N*), 0.97 (d, 12 H,  $J = 6.8$ , *CHMe*<sub>2</sub>); for **6**:  $\delta$  8.85 (m, 2 H, *ortho*- $NC_5H_5$ ), 7.52 (m, 1 H, *para*- $NC_5H_5$ ), 7.23–6.95 (overlapping m, 14 H,  $C_6H_5$  and *meta*- $NC_5H_5$ ), 6.47 (d, 2 H,  $J = 7.3$ , *meta*- $C_6H_3Me_2$ ), 6.31 (t, 1 H,  $J = 7.3$ , *para*- $C_6H_3Me_2$ ), 2.34 (s, 3 H, *NC(Me)C(Me)N*), 2.29 (s, 6 H,  $C_6H_3Me_2$ ), 2.34 (s, 3 H, *NC(Me)C(Me)N*); for **7**:  $\delta$  9.08 (m, 2 H, *ortho*- $NC_5H_5$ ), 7.64 (m, 1 H, *para*- $NC_5H_5$ ), 7.40–7.20 (overlapping m, 4 H,  $C_6H_4Me$ ), 7.02 (m, 2 H, *meta*- $NC_5H_5$ ), 6.80–6.70 (overlapping m, 4 H,  $C_6H_4Me$ ), 2.38 (s, 3 H, *NC(Me)C(Me)N*), 2.18, 2.11 ( $2 \times$  s,  $2 \times$  3 H,  $2 \times$   $C_6H_4Me$ ), 2.07 (s, 3 H, *NC(Me)C(Me)N*), 0.35 (s, 9 H,  $Bu^t$ ).

**Preparative scale reaction of  $[Ti(NBu^t)Cl_2(py)_3]$  1 with  $ArNC(H)C(H)NAr$  ( $Ar = C_6H_3Me_2-2,6$ ).** A solution of  $[Ti(NBu^t)Cl_2(py)_3]$  (0.60 g, 1.40 mmol) and  $ArNC(H)C(H)NAr$  (0.40 g, 1.5 mmol, *ca.* 1.1 equivalents) in toluene (20 ml) was heated at  $100^\circ C$  for 7 days. The volatiles were removed under reduced pressure to give spectroscopically pure  $[Ti(NC_6H_3Me_2-2,6)Cl_2(py)_2]$  **2'** as a green powder after washing with pentane and drying *in vacuo*. Yield of **2'** *ca.* 100%. The compound **2'** was characterised by comparison with an authentic sample.<sup>20</sup>

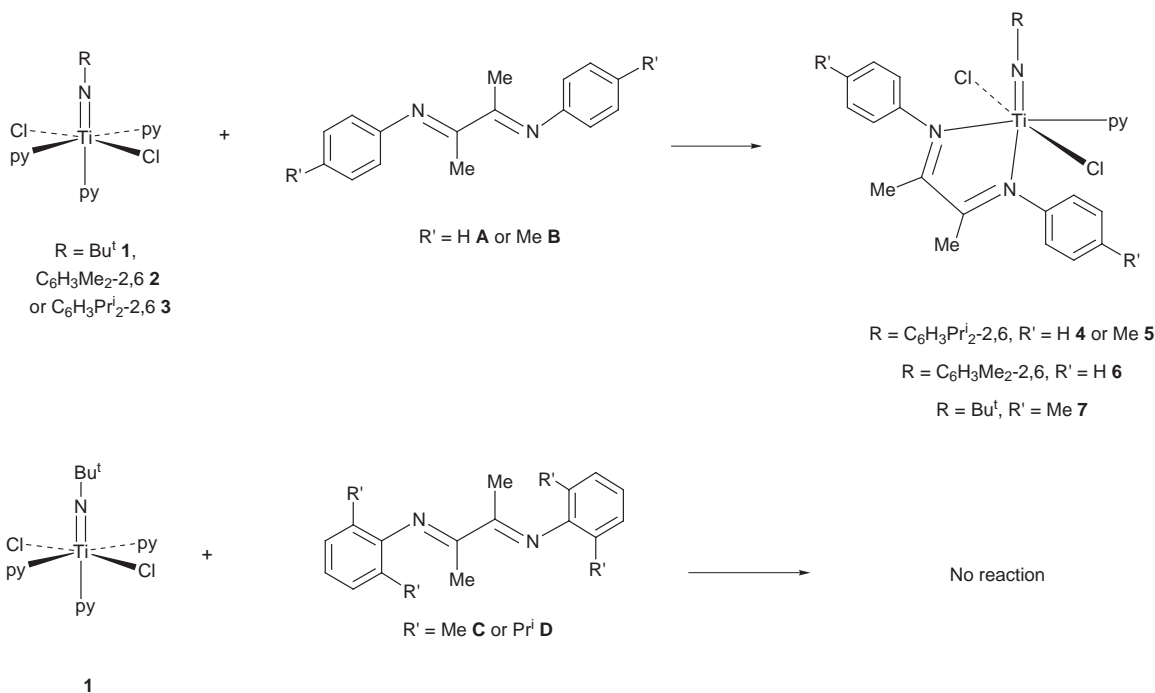
**NMR tube scale reactions of  $[Ti(NBu^t)Cl_2(py)_3]$  1 with  $ArNC(H)C(H)NAr$  ( $Ar = C_6H_3Me_2-2,6$ ).** (i) A mixture of  $[Ti(NBu^t)Cl_2(py)_3]$  (12 mg, 0.028 mmol) and  $ArNC(H)C(H)NAr$  (8 mg, 0.03 mmol, *ca.* 1.1 equivalents) in  $CDCl_3$  (1 ml) was heated for 6 days at  $60^\circ C$ . The resultant  $^1H$  NMR spectra showed the formation of  $[Ti(NC_6H_3Me_2-2,6)Cl_2(py)_2]$  **2'**,  $ArNC(H)C(H)NBu^t$  **G**, and  $Bu^tNC(H)C(H)NBu^t$  **F** in the ratio 1:0.21:0.40, along with 0.63 equivalent of unchanged  $ArNC(H)C(H)NAr$  **E**. The diimine **F** and  $[Ti(NC_6H_3Me_2-2,6)Cl_2(py)_2]$  **2'** were characterised by comparison with authentic samples.<sup>20,27</sup> The mixed diimine **G** was characterised by  $^1H$  NMR spectroscopy *in situ*.  $^1H$  NMR ( $CDCl_3$ , 300.1 MHz, 298 K) data for **G**:  $\delta$  7.1–6.9 [m, 3 H,  $C_6H_3Me_2$  (partially obscured)], 2.15 (s, 6 H,  $C_6H_3Me_2$ ), 1.34 (s, 9 H,  $Bu^t$ ). *NC(H)C(H)N* resonances obscured.

(ii) When the above reaction was carried out with a *ca.* 2:1 ratio of  $[Ti(NBu^t)Cl_2(py)_3]$  to  $ArNC(H)C(H)NAr$  only the diimine  $Bu^tNC(H)C(H)NBu^t$  **F** and  $[Ti(NC_6H_3Me_2-2,6)Cl_2(py)_2]$  **2'** were observed.

**NMR tube scale reaction of  $[Ti(NBu^t)Cl_2(py)_3]$  1 with  $TolNC(H)C(H)NTol$  E.** A mixture of  $[Ti(NBu^t)Cl_2(py)_3]$  (34 mg, 0.08 mmol) and  $TolNC(H)C(H)NTol$  (9 mg, 0.04 mmol, *ca.* 0.5 equivalent) in  $CDCl_3$  (1 ml) was allowed to stand at r.t. for 24 hours.  $^1H$  NMR examination of the reaction mixture showed quantitative conversion to  $[Ti(NTol)Cl_2(py)_3]$  and  $Bu^tNC(H)C(H)NBu^t$  **F** which were characterised by comparison with authentic samples.<sup>20,27</sup>

### Crystal structure determination of $[Ti(NC_6H_3Pr^i_2-2,6)Cl_2\{\eta^2-PhNC(Me)C(Me)NPh\}(py)] \cdot CH_2Cl_2$ (**4**· $CH_2Cl_2$ )

Crystal data collection and processing parameters are given in Table 1. An orange-brown block was mounted in a film of RS3000 perfluoropolyether oil (Hoechst) on a glass fibre and transferred to a Stoë Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device.<sup>30</sup> Data were collected at 150 K using  $\omega$ - $\theta$  scans with Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) and an absorption correction



**Scheme 1** Reactions of titanium imido complexes with  $\alpha$ -diimine ligands containing methyl groups in their backbone.

**Table 1** X-Ray data collection and processing parameters for  $[\text{Ti}(\text{NC}_6\text{H}_3\text{Pr}^i\text{-2,6})\text{Cl}_2\{\eta^2\text{-PhNC}(\text{Me})\text{C}(\text{Me})\text{NPh}\}(\text{py})] \cdot \text{CH}_2\text{Cl}_2$  **4**  $\cdot \text{CH}_2\text{Cl}_2$

Formula	$\text{C}_{33}\text{H}_{38}\text{Cl}_2\text{N}_4\text{Ti} \cdot \text{CH}_2\text{Cl}_2$
$M$	694.43
System, space group	Triclinic, $P\bar{1}$
$a/\text{\AA}$	11.093(3)
$b/\text{\AA}$	12.533(5)
$c/\text{\AA}$	12.687(5)
$\alpha/^\circ$	82.49(3)
$\beta/^\circ$	85.22(2)
$\gamma/^\circ$	85.28(3)
$U/\text{\AA}^3$	1738.1(8)
$Z$	2
$\mu/\text{mm}^{-1}$	0.58
Reflections collected	6159
Total independent, $R_{\text{int}}$	5722, 0.040
Final $R$ , <sup>a</sup> $R_w$ , <sup>b</sup>	0.080, 0.089 for 4220 data with $I > 2\sigma(I)$

<sup>a</sup>  $R = \Sigma |F_o| - |F_c| / \Sigma |F_o|$ . <sup>b</sup>  $R_w = \{\Sigma w(|F_o| - F_c)^2 / \Sigma w F_o^2\}^{1/2}$ .

was applied to the data. Equivalent reflections were merged and the structures were solved by direct methods (SIR92<sup>31</sup>). Subsequent Fourier-difference syntheses revealed the positions of all other non-hydrogen atoms. Residual electron density was modelled as a full-occupancy dichloromethane molecule solvent (in a general position). All non-H atoms were refined anisotropically and hydrogen atoms were placed geometrically: these were refined in a riding model with fixed isotropic displacement parameters. A Chebychev weighting scheme<sup>32</sup> was applied towards the end of the refinements. Examination of the refined secondary extinction parameter<sup>33</sup> and an agreement analysis suggested that no extinction correction was required. Crystallographic calculations were performed using SIR92<sup>31</sup> and CRYSTALS-PC.<sup>34</sup>

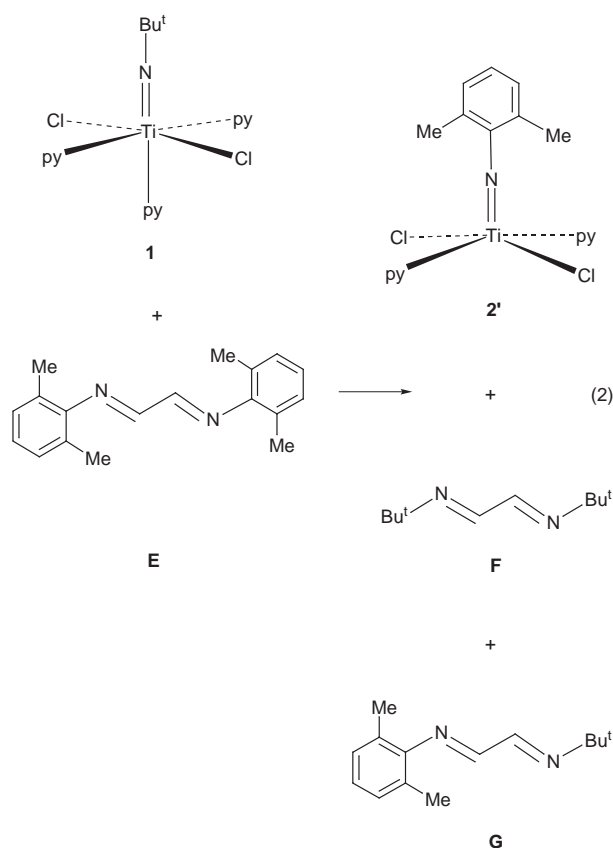
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See <http://www.rsc.org/suppdata/dt/1998/3623/> for crystallographic files in .cif format.

## Results and discussion

The reactions of  $[\text{Ti}(\text{NR})\text{Cl}_2(\text{py})_3]$  ( $R = \text{Bu}^t$  **1**,  $\text{C}_6\text{H}_3\text{Me}_2$ -2,6 **2** and  $\text{C}_6\text{H}_3\text{Pr}^i$ -2,6 **3**) with  $\alpha$ -diimines divide into two types.  $\alpha$ -Diimines with methyl substituents in the backbone give rise to coordination complexes (Scheme 1), while those with only

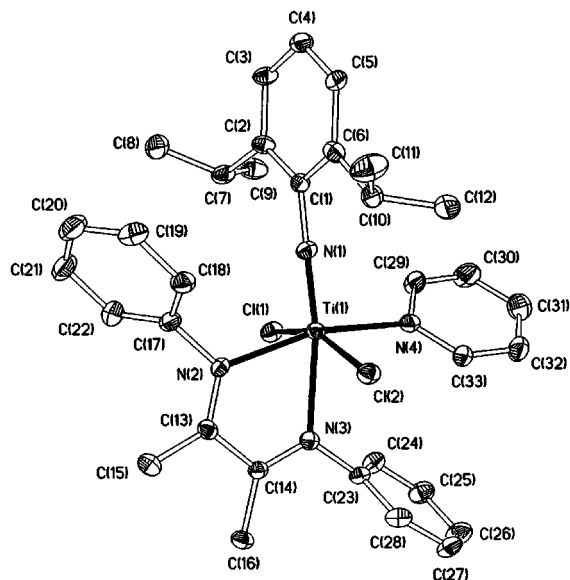
H atom substituents result in imide/imine metathesis with no detectable new complex being formed [eqn. (2) and (3)].



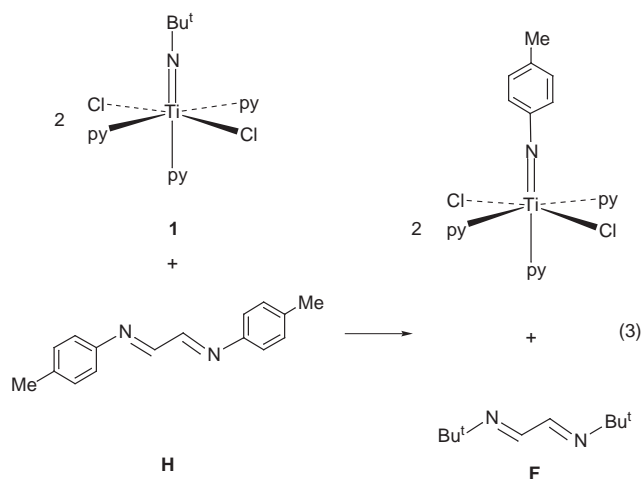
As shown in Scheme 1, reaction of  $\text{PhNC}(\text{Me})\text{C}(\text{Me})\text{NPh}$  **A** or  $\text{ToIN}(\text{C}(\text{Me})\text{C}(\text{Me})\text{NTol}$  **B** with  $[\text{Ti}(\text{NR})\text{Cl}_2(\text{py})_3]$  gives immediate formation of the new complexes  $[\text{Ti}(\text{NR})\text{Cl}_2\{\eta^2\text{-ArNC}(\text{Me})\text{C}(\text{Me})\text{NAr}\}(\text{py})]$  ( $R = \text{C}_6\text{H}_3\text{Pr}^i$ -2,6,  $\text{Ar} = \text{Ph}$  **4** or  $\text{Tol}$  **5**;  $R = \text{C}_6\text{H}_3\text{Me}_2$ -2,6,  $\text{Ar} = \text{Ph}$  **6**;  $R = \text{Bu}^t$ ,  $\text{Ar} = \text{Tol}$  **7**). Compound **4** was fully characterised by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, elemental analysis and X-ray crystallography (see below). Although stable in the solid state and in solution at

**Table 2** Selected bond distances (Å) and angles (°) for [Ti(NC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub>-2,6)Cl<sub>2</sub>{η<sup>2</sup>-PhNC(Me)C(Me)NPh}(py)] **4**

Ti(1)–N(1)	1.729(4)	N(2)–C(13)	1.290(7)
Ti(1)–N(2)	2.200(5)	N(2)–C(17)	1.457(8)
Ti(1)–N(3)	2.317(4)	N(3)–C(14)	1.268(7)
Ti(1)–N(4)	2.222(5)	N(3)–C(23)	1.434(8)
Ti(1)–Cl(1)	2.399(2)	C(13)–C(14)	1.509(8)
Ti(1)–Cl(2)	2.391(2)	C(13)–C(15)	1.487(8)
		C(14)–C(16)	1.513(7)
N(1)–Ti(1)–N(2)	98.3(2)	Cl(1)–Ti(1)–Cl(2)	158.94(6)
N(1)–Ti(1)–N(3)	169.1(2)	Ti(1)–N(1)–C(1)	179.0(4)
N(2)–Ti(1)–N(3)	70.8(2)	Ti(1)–N(2)–C(13)	120.6(4)
N(1)–Ti(1)–N(4)	97.0(2)	Ti(1)–N(2)–C(17)	120.4(3)
N(2)–Ti(1)–N(4)	164.6(2)	C(13)–N(2)–C(17)	118.9(5)
N(3)–Ti(1)–N(4)	93.8(2)	Ti(1)–N(3)–C(14)	116.7(4)
N(1)–Ti(1)–Cl(1)	100.6(2)	Ti(1)–N(3)–C(23)	122.9(3)
N(2)–Ti(1)–Cl(1)	88.2(1)	C(14)–N(3)–C(23)	120.3(5)
N(3)–Ti(1)–Cl(1)	80.5(1)	N(2)–C(13)–C(14)	114.9(5)
N(4)–Ti(1)–Cl(1)	88.3(1)	N(2)–C(13)–C(15)	125.9(6)
N(1)–Ti(1)–Cl(2)	100.7(2)	C(14)–C(13)–C(15)	119.2(5)
N(2)–Ti(1)–Cl(2)	88.4(1)	N(3)–C(14)–C(13)	116.2(5)
N(3)–Ti(1)–Cl(2)	78.7(1)	N(3)–C(14)–C(16)	125.0(5)
N(4)–Ti(1)–Cl(2)	89.4(1)	C(13)–C(14)–C(16)	118.8(5)



**Fig. 1** Displacement ellipsoid (35%) plot of [Ti(NC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub>-2,6)Cl<sub>2</sub>{η<sup>2</sup>-PhNC(Me)C(Me)NPh}(py)] **4**. Hydrogen atoms and dichloromethane molecule of crystallisation are omitted.



–25 °C, room temperature solutions of pure **4** decompose substantially over *ca.* 4 hours (also in CDCl<sub>3</sub>, C<sub>6</sub>D<sub>6</sub> or CD<sub>2</sub>Cl<sub>2</sub> in sealed NMR tubes) to complex mixtures containing [Ti(NC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub>-2,6)Cl<sub>2</sub>(py)<sub>2</sub>] **3'** and free aniline H<sub>2</sub>NC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub>-2,6. The fate of the  $\alpha$ -diimine ligand is unknown but the simultaneous appearance of a fairly viscous, oily material points towards  $\alpha$ -diimine oligomer and/or polymer formation. The compounds **6** and **7** were substantially less stable in solution, NMR tube scale reactions showing extensive decomposition of the first-formed diimine complexes after *ca.* 1 hour and 10 minutes, respectively. Although these compounds and **5** were therefore characterised by <sup>1</sup>H NMR spectroscopy only, the close similarity of these spectra (exhibiting, for example, two different ArNC(Me)C(Me)NAr methyl group resonances) to those for the fully-characterised **4** lends confidence to the structures proposed in Scheme 1. Single crystals of [Ti(NC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub>-2,6)Cl<sub>2</sub>{η<sup>2</sup>-PhNC(Me)C(Me)NPh}(py)]·CH<sub>2</sub>Cl<sub>2</sub> were grown at –25 °C by layering a saturated dichloromethane solution of **4** with hexane. A view of the molecular structure of **4** is shown in Fig. 1 and selected bond lengths and angles are given in Table 2.

Molecules of **4** contain a six-coordinate Ti centre ligated by a 2,6-diisopropylphenylimido group with one pyridine and two mutually *trans* Cl ligands *cis* to it. The coordination sphere is completed by an η<sup>2</sup>-coordinated PhNC(Me)C(Me)NPh ligand with one nitrogen *cis* and one *trans* to the imido group. The titanium–imido nitrogen, –pyridine nitrogen and –chloride distances are unexceptional for this type of six-coordinate imido

complex.<sup>13,35</sup> The *trans* (with respect to the imido group) bond from titanium to nitrogen of the  $\alpha$ -diimine [Ti(1)–N(3) = 2.317(4) Å] is significantly longer than that to the *cis* nitrogen [Ti(1)–N(2) = 2.200(5) Å], consistent with the well-known *trans* influence of the imido group.<sup>20,36,37</sup> The [Ti(1)N(2)C(13)C(14)–N(3)] ring is effectively planar (maximum deviation from the best fit plane is 0.054 Å) and the PhNC(Me)C(Me)NPh ligand adopts an *s-cis* conformation as required for bidentate coordination. The internal C=N [N(2)–C(13) = 1.290(7), N(3)–C(14) = 1.268(7) Å] and C–C [C(13)–C(14) = 1.509(8) Å] distances are indicative of double and single bonds respectively, being comparable to those of free  $\alpha$ -diimines [average C=N = 1.28(2) and C–C = 1.52(4) Å for four crystallographically-characterised examples].<sup>38</sup> These data therefore show that the diimine is coordinated as a neutral  $\sigma$ -donor ligand as in **III** above, as expected since the Ti(IV) centre in the {Ti(NC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub>-2,6)Cl<sub>2</sub>(py)} moiety has no d-electrons available for back-donation to the diimine ligand.

[Ti(NC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub>-2,6)Cl<sub>2</sub>{η<sup>2</sup>-PhNC(Me)C(Me)NPh}(py)] **4** is the first structurally characterised example of a titanium complex with a neutral  $\alpha$ -diimine ligand, and only the third for Group 4.<sup>6,7</sup> It is interesting to compare the Ti–N(diimine), diimine C=N and backbone C–C distances for **1** with those of nine previously described  $\alpha$ -diimine complexes of titanium in which the ligand may be assigned a formal negative charge between –1 and –2.<sup>38</sup> For these reduced diimine complexes substantially shorter Ti–N(diimine) [average 1.96(8) Å] and diimine C–C [average 1.39(2) Å] distances, and longer diimine C=N [average 1.37(2) Å] distances are found, consistent with a significant contribution from resonance form **IV** above.

The solution <sup>1</sup>H and <sup>13</sup>C NMR (recorded at 258 K owing to its limited solution stability) data for **4** are consistent with the solid state structure. In particular the <sup>13</sup>C resonances for the PhN=C imino carbons appear at  $\delta$  165.7, very close to the corresponding signals for free diimines ArNC(Me)C(Me)NAr, and not substantially upfield (*i.e.* more olefinic) as would be expected for a reduced diimine as in **IV**.<sup>39</sup> The <sup>1</sup>H NMR data for the less stable compounds **5**, **6** and **7** are very similar to those of **1** and so also consistent with the structures illustrated in Scheme 1.

As shown in Scheme 1, attempts to synthesise complexes using the aryl ring-substituted  $\alpha$ -diimines ArNC(Me)C(Me)NAr (Ar = C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6 **C** or C<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub>-2,6 **D**) were unsuccessful and led to no reaction. However, heating a toluene solution of *tert*-butylimido complex [Ti(NBu<sup>t</sup>)Cl<sub>2</sub>(py)<sub>3</sub>] **1** with *ca.* 1.1

equivalents of ArNC(H)C(H)CNAr (Ar = C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6 **E**, *i.e.* with no methyl groups in the backbone) at 100 °C for 1 week followed by subsequent workup afforded the previously described<sup>20</sup> arylimido bis(pyridine) complex [Ti(NC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6)Cl<sub>2</sub>(py)<sub>2</sub>] **2'** as the only metal-containing product [eqn. (2)].

When the reaction was monitored on an NMR tube scale (ratio of **1**:**E** again *ca.* 1.0:1.1) at 60 °C in CDCl<sub>3</sub>, resonances for [Ti(NC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6)Cl<sub>2</sub>(py)<sub>2</sub>] **2'** grew in over 6 days until all of the starting complex **1** was converted to **2'**. The NMR tube experiment also revealed the organic side products of the reaction to be Bu<sup>t</sup>NC(H)C(H)NBu<sup>t</sup> **F** and ArNC(H)C(H)NBu<sup>t</sup> (Ar = C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6 **G**). The ratio of **2**:**G**:**F**:unchanged starting diimine **E** was *ca.* 1.0:0.21:0.40:0.63. No resonances for  $\alpha$ -diimine complexes of either the starting or product diimines were observed at any time. When the NMR tube reaction of **1** and **E** was carried out on a *ca.* 2:1 scale (*i.e.* a 1:1 ratio of Ti=NBu<sup>t</sup> to C=NAr functional group) negligible quantities of the mixed aryl-*tert*-butyl diimine **G** were formed, the major observed products being imido complex **2'** and diimine **F**.

In order to make a better comparison with the complex formation reactions of the methyl-substituted diimines (Scheme 1) and the imide/imine metathesis reaction in eqn. (2) the reaction of the di-*p*-tolyl- $\alpha$ -diimine **H** with **1** was followed by <sup>1</sup>H NMR [eqn. (3)]. The reaction of **1** with **H** (ratio of **1**:**H** *ca.* 2:1, *i.e.* a 1:1 ratio of Ti=NBu<sup>t</sup> to C=NTol functional group) proceeds smoothly and cleanly at room temperature to give quantitative formation of the previously described [Ti(NTol)Cl<sub>2</sub>(py)<sub>3</sub>]<sup>20</sup> and Bu<sup>t</sup>NC(H)C(H)NBu<sup>t</sup> **F** after 24 hours. Examination of the reaction at intervals showed no evidence for formation of a complex such as [Ti(NBu<sup>t</sup>)Cl<sub>2</sub>{ $\eta^2$ -TolNC(H)C(H)NTol}(py)] that would be analogous to **4** (Scheme 1), although signals attributable to the expected intermediate mixed  $\alpha$ -diimine TolNC(H)C(H)NBu<sup>t</sup> were observed at intermediate stages of the reaction.

The imide/ $\alpha$ -diimine reactions of [Ti(NBu<sup>t</sup>)Cl<sub>2</sub>(py)<sub>3</sub>] **1** in eqn. (2) and (3) are analogous to those with *N*-aryl monoimines shown in eqn. (1).<sup>21</sup> As with the diimine reactions above, the bulkier (ring-substituted) mono-imine PhC(NC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6)H requires elevated temperatures and longer reaction times compared with the tolyl monoimine PhC(NTol)H which proceeded at room temperature. That the *ca.* 1:1 reaction of **1** with aryl  $\alpha$ -diimine **E** [eqn. (2)] gave mainly symmetric Bu<sup>t</sup>NC(H)C(H)NBu<sup>t</sup> **F** as the product diimine, and not proportionally more of the asymmetric, mono-substituted diimine ArNC(H)C(H)NBu<sup>t</sup> **G**, implies that there is negligible selectivity in these particular reactions and they are therefore probably not suitable for the practical synthesis of mixed  $\alpha$ -diimines.

It is intriguing that the two types of  $\alpha$ -diimine studied here (*i.e.* with and without methyl backbone substituents) should show such different reactivity towards the titanium imido complexes **1**–**3**. One factor contributing to this differing behaviour might be as follows. Although the *s-trans* form (**I** above) of the free  $\alpha$ -diimines is usually the more stable conformation, introduction of methyl or other R' groups into the backbone can help favour (in order to reduce N lone pair...R' interactions) the *s-cis* conformer **II** which is the arrangement required for metal complex formation.<sup>1,2</sup> The introduction of bulkier aryl groups in the diimines **C** and **D** inhibits complexation (Scheme 1): this may simply be due to steric crowding at the metal centre in the desired product complexes and/or attributable to the destabilisation of the *s-cis* conformer as the diimine N-substituents are made bulkier.<sup>1,2</sup>

Although we have good evidence that the non-methyl-substituted diimines **E**–**H** do not form significant equilibrium concentrations of metal complex, we cannot rule out such species as reactive intermediates in the overall imide/imine metathesis reactions of eqn. (2) and (3).<sup>40</sup> Our observations that the methyl-substituted  $\alpha$ -diimines do not give metathesis products could suggest that the increased steric crowding of the imino C=NAr carbon inhibits this type of reaction, but it is

most likely that the process of complex formation in these cases makes accessible facile diimine oligomerisation and/or polymerisation routes not otherwise available (under analogous conditions in the absence of metal imide complex the  $\alpha$ -diimines **A** and **B** are stable in solution). Thus although there might be a pathway for imide/imine metathesis reactions of **A** and **B** it presumably cannot compete with the rapid  $\alpha$ -diimine complex formation and subsequent degradation.

## Conclusions

We have described the first metal imide/ $\alpha$ -diimine metathesis reactions together with a rare example of a structurally-characterised, neutral  $\alpha$ -diimine metal complex (the first such derivative for titanium). The transition metal and organic products obtained are highly dependent on the nature of the imido N-group and the  $\alpha$ -diimine N- and backbone C-substituents.

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- 40 Kinetic studies have shown that the intimate mechanism of the titanium imide complex reactions with mono-imines [eqn. (1)] is unclear (see ref. 21) and so we do not wish to speculate on the details of the imide/ $\alpha$ -diimine mechanism here.

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