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FULL PAPER

Reactions of titanium imido complexes with α-diimines: complexation *versus* Ti=N/C=N bond metathesis

Jacqueline M. McInnes, Alexander J. Blake and Philip Mountford *†

School of Chemistry, University of Nottingham, Nottingham, UK NG7 2RD

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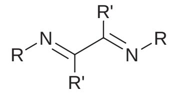
The reactions of the titanium imido complexes [Ti(NR)Cl$_2$(py)$_3$] (R = Bu^t **1**, C$_6$H$_3$Me$_2$-2,6 **2** or C$_6$H$_3$Pr$^i_2$-2,6 **3**) with α-diimines (1,4-diaza-1,3-butadienes) of the type ArNC(R′)C(R′)NAr (Ar = phenyl or substituted phenyl, R′ = H or methyl) are reported. The reaction products 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 PhNC(Me)C(Me)NPh gave the crystallographically characterised adduct [Ti(NC$_6$H$_3$Pr$^i_2$-2,6)Cl$_2${η^2-PhNC(Me)C(Me)NPh}(py)] **4** which posseses 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) α-diimine ligand and decomposes fairly quickly in solution at room temperature. ^{1}H NMR evidence only is presented for the formation of the *tert*-butyl- and 2,6-dimethylphenyl-imido homologues of **4**, namely [Ti(NR)Cl$_2${η^2-ArNC(Me)C(Me)NAr}(py)] (R = Bu^t or C$_6$H$_3$Me$_2$-2,6; Ar = Ph or tolyl, Tol): these compounds are considerably less stable in solution, rapidly decomposing to a number of products including the corresponding amines RNH$_2$ and [Ti(NR)Cl$_2$(py)$_n$] (n = 2 or 3). Reaction of **1** with α-diimines of the type ArNC(H)C(H)NAr (Ar = Tol or 2,6-C$_6$H$_3$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 [Ti(NAr)Cl$_2$(py)$_n$] (n = 2 or 3) and Bu^{t}NC(H)C(H)NAr and/or Bu^{t}NC(H)C(H)NBu^t.

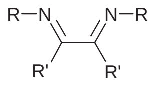
Introduction

The α-diimines (also commonly known as 1,4-diaza-1,3-butadienes) of the type RNC(R′)C(R′)NR (**I** and **II** where typically R = alkyl, phenyl or substituted phenyl, R′ = 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.[1–11] α-Diimines are typically prepared by condensation reactions of amines or anilines, RNH$_2$, with glyoxal or the correpsonding α-diketone R′C(O)-C(O)R′,[12] 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.[1,2] α-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 π$_3$ lowest unoccupied molecular orbital,[4,8] 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.[1,2]



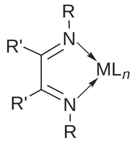
s-trans

I



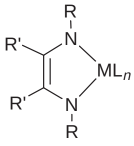
s-cis

II



neutral ligand

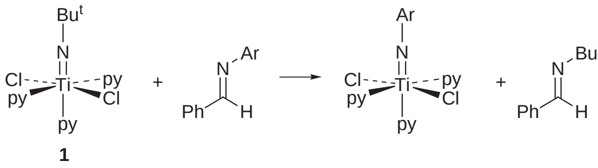
III



2- ligand

IV

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



1

(1)

Such imide/imine metathesis reactions are very uncommon transformations in transition metal chemistry,[22–24] even though the corresponding carbene(alkylidene)/alkene metathesis reaction is very well established and widely applied.[25] In the context of these previous studies we were therefore interested to study the reactions of α-diimines with the previously described titanium imido complexes [Ti(NR)Cl$_2$(py)$_3$] (R = Bu^t **1**, C$_6$H$_3$-Me$_2$-2,6 **2** and C$_6$H$_3$Pr$^i_2$-2,6 **3**).‡,[20]

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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† *Present address*: Inorganic Chemistry Laboratory, South Parks Road, Oxford, UK OX1 3QR. E-mail: philip.mountford@chemistry.oxford.ac.uk

‡ Although for ease of representation all titanium–imido linkages are drawn "Ti=NR", the formal Ti–N bond order in the complexes [Ti(NR)Cl$_2${η^2-RNC(R′)C(R′)NR}(py)] is generally best thought of as three (pseudo-σ^{2}π^4 triple bond) rather than as two.[35]

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

^{1}H 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 (^{1}H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm). Chemical shifts are quoted in δ (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 $[\mathrm{Ti(NR)Cl_2(py)_3}]$ (R = Bu^t, $\mathrm{C_6H_3Me_2}$-2,6, $\mathrm{C_6H_3Pr^i_2}$-2,6) were prepared according to literature methods.[20] α-Diimines RNC(R′)C(R′)NR were prepared by condensation reactions[12] of the corresponding α-dicarbonyl compounds (R′ = H or Me) and amines (R = Bu^t, Ph, Tol, $\mathrm{C_6H_3Me_2}$-2,6 or $\mathrm{C_6H_3Pr^i_2}$-2,6) according to literature procedures and purified either by distillation or recrystallisation from appropriate solvents.[26–29]

Syntheses

$[\mathrm{Ti(NC_6H_3Pr^i_2\text{-}2,6)Cl_2\{\eta^2\text{-}PhNC(Me)C(Me)NPh\}(py)}]$ 4. To a solution of $[\mathrm{Ti(NC_6H_3Pr^i_2\text{-}2,6)Cl_2(py)_3}]$ (0.31 g, 0.58 mmol) in $\mathrm{CH_2Cl_2}$ (5 ml) was added a solution of PhNC(Me)C(Me)NPh (0.16 g, 0.68 mmol) in $\mathrm{CH_2Cl_2}$ (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 × 5 ml) and dried *in vacuo*. Yield: 0.30 g (75%, for $[\mathrm{Ti(NC_6H_3\text{-}Pr^i_2\text{-}2,6)Cl_2\{\eta^2\text{-}PhNC(Me)C(Me)NPh\}(py)]\cdot 0.8CH_2Cl_2}$). The product contained *ca.* 0.8 equivalent of residual $\mathrm{CH_2Cl_2}$ (by ^{1}H NMR and elemental analysis). Diffraction quality crystals of **4**·$\mathrm{CH_2Cl_2}$ were grown at −25 °C by layering a saturated dichloromethane solution with hexane. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 300.1 MHz, 298 K): δ 8.79 (d, 2 H, $J = 5.0$, *ortho*-$\mathrm{NC_5H_5}$), 7.57 (tt, 1 H, $J = 7.6$, $J = 1.6$, *para*-$\mathrm{NC_5H_5}$), 7.37 (d, 2 H, $J = 8.4$, *ortho*-$\mathrm{C_6H_5}$), 7.24 (t, 2 H, $J = 8.4$, *meta*-$\mathrm{C_6H_5}$), 7.13–7.00 (m, 2 H, *meta*-$\mathrm{NC_5H_5}$; 2 H *meta*-$\mathrm{C_6H_5}$; 2 H, *ortho*-$\mathrm{C_6H_5}$; 2 × 1 H, 2 × *para*-$\mathrm{C_6H_5}$), 6.55 (d, 2 H, $J = 7.3$, *meta*-$\mathrm{C_6H_3Pr^i_2}$), 6.45 (t, 1 H, $J = 7.3$, *para*-$\mathrm{C_6H_3Pr^i}$), 4.36 (septet, 2 H, $J = 6.8$, C*H*$\mathrm{Me_2}$), 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, $J = 6.8$, CH*Me*$_2$). ^{13}C-{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 62.5 MHz, 258 K): δ 165.7 (*C*(Me)NPh), 154.7 (*ipso*-$\mathrm{C_6H_3Pr^i_2}$), 151.0, 146.3 (2 × *ipso*-$\mathrm{C_6H_5}$), 151.0 (*ortho*-$\mathrm{NC_5H_5}$), 146.8 (*ortho*-$\mathrm{C_6H_3Pr^i_2}$), 138.2, (*para*-$\mathrm{NC_5H_5}$), 128.8 (*meta*-$\mathrm{C_6H_5}$), 128.7 (*meta*-$\mathrm{C_6H_5}$), 120.6, 121.1 (2 × *ortho*-$\mathrm{C_6H_5}$), 126.0 (*para*-$\mathrm{C_6H_5}$), 123.5 (*meta*-$\mathrm{NC_5H_5}$), 121.4 (*ortho*-$\mathrm{C_6H_5}$), 121.3 (*meta*-$\mathrm{C_6H_3\text{-}Pr^i_2}$), 121.2, (*para*-$\mathrm{C_6H_3Pr^i_2}$), 26.7 (C*H*$\mathrm{Me_2}$), 24.3 (CH*Me*$_2$), 20.2 (NC(*Me*)C(Me)N), 19.7 (NC(Me)C(*Me*)N) [Found (calc. for $\mathrm{C_{33}H_{38}Cl_2N_4Ti\cdot 0.8CH_2Cl_2}$): C, 59.5 (59.9); H, 5.7 (5.9); N, 8.0 (8.3)%].

NMR tube scale syntheses of $[\mathrm{Ti(NC_6H_3Pr^i_2\text{-}2,6)Cl_2\{\eta^2\text{-}TolNC(Me)C(Me)NTol\}(py)}]$ 5, $[\mathrm{Ti(NC_6H_3Me_2\text{-}2,6)Cl_2\{\eta^2\text{-}PhNC(Me)C(Me)NPh\}(py)}]$ 6 and $[\mathrm{Ti(NBu^t)Cl_2\{\eta^2\text{-}TolNC(Me)C(Me)NTol\}(py)}]$ 7. Because of their instability (especially for **6** and **7**) these compounds were prepared and characterised only by ^{1}H NMR according to the following general procedure. $\mathrm{CDCl_3}$ solutions of $[\mathrm{Ti(NR)Cl_2(py)_3}]$ (R = $\mathrm{C_6H_3Pr^i_2}$-2,6, $\mathrm{C_6H_3Me_2}$-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 solutions, and the ^{1}H 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. ^{1}H NMR ($\mathrm{CDCl_3}$, 300.1 MHz, 298 K) data for **5**: δ 8.89 (m, 2 H, *ortho*-$\mathrm{NC_5H_5}$), 7.66 (m, 1 H, *para*-$\mathrm{NC_5H_5}$), 7.39–6.97 (overlapping m, 12 H, *ortho*- and *meta*-$\mathrm{C_6H_4Me}$, *meta*-$\mathrm{NC_5H_5}$), 6.71 (strongly second order d, 2 H, *meta*-$\mathrm{C_6H_3Pr^i_2}$), 6.62 (strongly second order t, 1 H, *para*-$\mathrm{C_6H_3Pr^i_2}$), 4.40 (septet, 2 H, $J = 6.8$, C*H*$\mathrm{Me_2}$), 2.35 (s, 3 H, NC(*Me*)C(Me)N), 2.30, 2.24 (2 × s, 2 × 3 H, *para*-$\mathrm{C_6H_4Me}$), 2.14 (s, 3 H, NC(Me)C(*Me*)N), 0.97 (d, 12 H, $J = 6.8$, CH*Me*$_2$); for **6**: δ 8.85 (m, 2 H, *ortho*-$\mathrm{NC_5H_5}$), 7.52 (m, 1 H, *para*-$\mathrm{NC_5H_5}$), 7.23–6.95 (overlapping m, 14 H, $\mathrm{C_6H_5}$ and *meta*-$\mathrm{NC_5H_5}$), 6.47 (d, 2 H, $J = 7.3$, *meta*-$\mathrm{C_6H_3Me_2}$), 6.31 (t, 1 H, $J = 7.3$, *para*-$\mathrm{C_6H_3Me_2}$), 2.34 (s, 3 H, NC(*Me*)C(Me)N), 2.29 (s, 6 H, $\mathrm{C_6H_3}$*Me*$_2$), 2.34 (s, 3 H, NC(Me)C(*Me*)N); for **7**: δ 9.08 (m, 2 H, *ortho*-$\mathrm{NC_5H_5}$), 7.64 (m, 1 H, *para*-$\mathrm{NC_5H_5}$), 7.40–7.20 (overlapping m, 4 H, $\mathrm{C_6}$*H*$_4$Me), 7.02 (m, 2 H, *meta*-$\mathrm{NC_5H_5}$), 6.80–6.70 (overlapping m, 4 H, $\mathrm{C_6}$*H*$_4$Me), 2.38 (s, 3 H, NC(*Me*)C(Me)N), 2.18, 2.11 (2 × s, 2 × 3 H, 2 × $\mathrm{C_6H_4}$*Me*), 2.07 (s, 3 H, NC(*Me*)C(Me)N), 0.35 (s, 9 H, Bu^t).

Preparative scale reaction of $[\mathrm{Ti(NBu^t)Cl_2(py)_3}]$ 1 with ArNC(H)C(H)NAr (Ar = $\mathrm{C_6H_3Me_2}$-2,6). A solution of $[\mathrm{Ti(NBu^t)Cl_2(py)_3}]$ (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 °C for 7 days. The volatiles were removed under reduced pressure to give spectroscopically pure $[\mathrm{Ti(NC_6H_3Me_2\text{-}2,6)Cl_2(py)_2}]$ **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.[20]

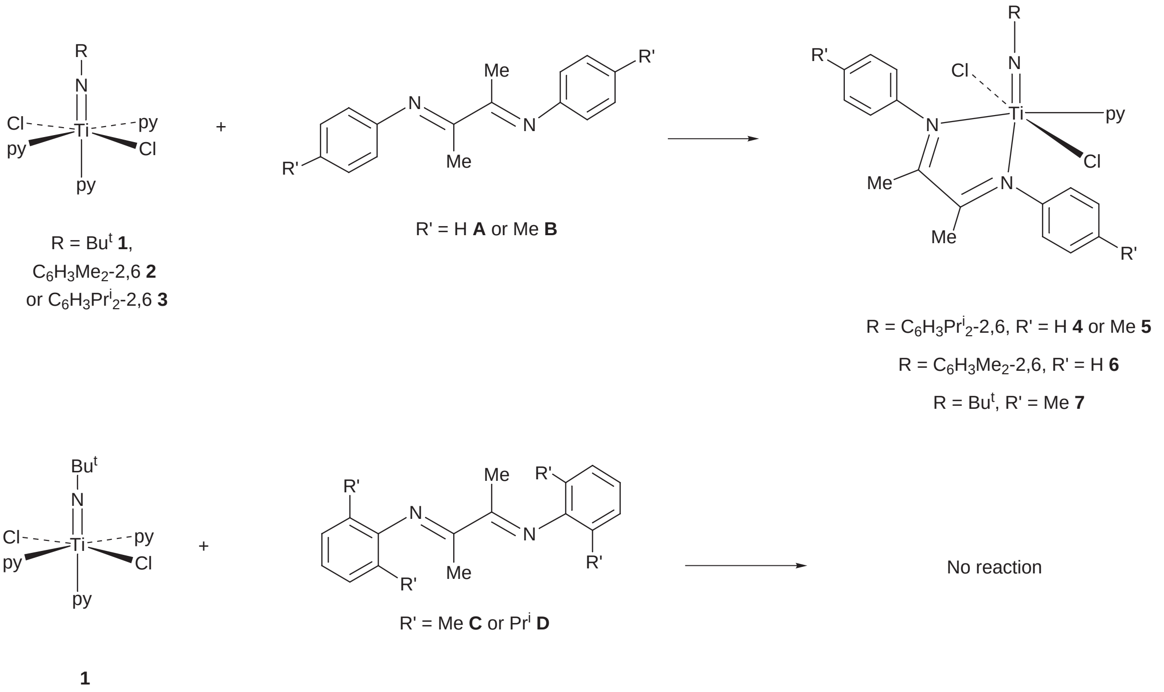
NMR tube scale reactions of $[\mathrm{Ti(NBu^t)Cl_2(py)_3}]$ 1 with ArNC(H)C(H)NAr (Ar = $\mathrm{C_6H_3Me_2}$-2,6). (i) A mixture of $[\mathrm{Ti(NBu^t)Cl_2(py)_3}]$ (12 mg, 0.028 mmol) and ArNC(H)C(H)NAr (8 mg, 0.03 mmol, *ca.* 1.1 equivalents) in $\mathrm{CDCl_3}$ (1 ml) was heated for 6 days at 60 °C. The resultant ^{1}H NMR spectra showed the formation of $[\mathrm{Ti(NC_6H_3Me_2\text{-}2,6)Cl_2(py)_2}]$ **2′**, ArNC(H)C(H)NBu^t **G**, and Bu^{t}NC(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 $[\mathrm{Ti(NC_6H_3Me_2\text{-}2,6)Cl_2(py)_2}]$ **2′** were characterised by comparison with authentic samples.[20,27] The mixed diimine **G** was characterised by ^{1}H NMR spectroscopy *in situ*. ^{1}H NMR ($\mathrm{CDCl_3}$, 300.1 MHz, 298 K) data for **G**: δ 7.1–6.9 [m, 3 H, $\mathrm{C_6}$*H*$_3$$\mathrm{Me_2}$ (partially obscured)], 2.15 (s, 6 H, $\mathrm{C_6H_3}$*Me*$_2$), 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 $[\mathrm{Ti(NBu^t)Cl_2(py)_3}]$ to ArNC(H)C(H)NAr only the diimine Bu^{t}NC(H)C(H)NBu^t **F** and $[\mathrm{Ti(NC_6H_3Me_2\text{-}2,6)Cl_2(py)_2}]$ **2′** were observed.

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

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

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.[30] Data were collected at 150 K using *ω*–*θ* scans with Mo-Kα radiation ($\lambda = 0.71073$ Å) and an absorption correction



Scheme 1 Reactions of titanium imido complexes with α-diimine ligands containing methyl groups in their backbone.

Table 1 X-Ray data collection and processing parameters for [Ti(NC$_6$H$_3$Pr$^i_2$-2,6)Cl$_2${η^2-PhNC(Me)C(Me)NPh}(py)]·CH$_2$Cl$_2$ **4**·CH$_2$Cl$_2$

Formula	$C_{33}H_{38}Cl_2N_4Ti{\cdot}CH_2Cl_2$
M	694.43
System, space group	Triclinc, $P\bar{1}$
a/Å	11.093(3)
b/Å	12.533(5)
c/Å	12.687(5)
α/°	82.49(3)
β/°	85.22(2)
γ/°	85.28(3)
U/Å^3	1738.1(8)
Z	2
μ/mm^{-1}	0.58
Reflections collected	6159
Total independent, R_{int}	5722, 0.040
Final *R*,[a] R_w[b]	0.080, 0.089 for 4220 data with $I > 2\sigma(I)$

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

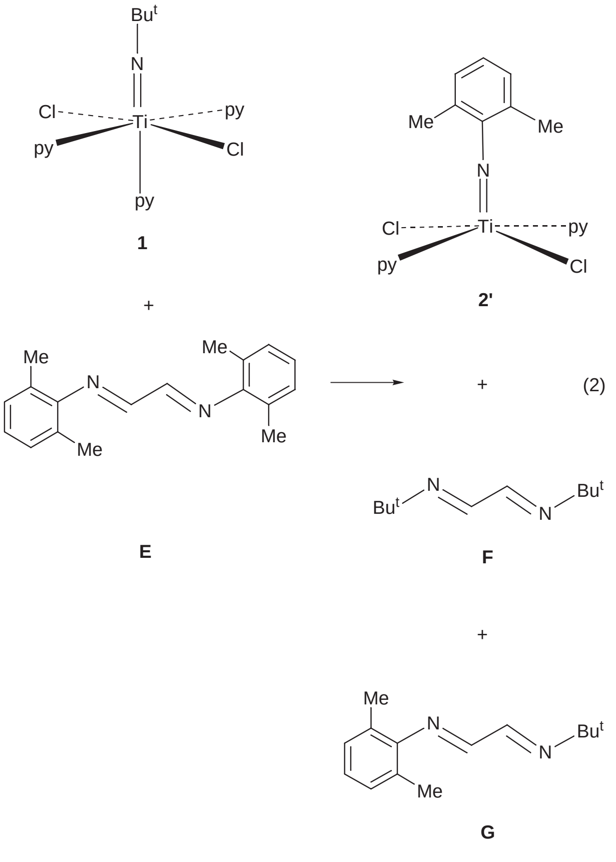
was applied to the data. Equivalent reflections were merged and the structures were solved by direct methods (SIR92[31]). Subsequent Fourier-difference syntheses revealed the positions of all other non-hydrogen atoms. Residual electron density was modelled as a full-occupancy dichloromethane molecule 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[32] was applied towards the end of the refinements. Examination of the refined secondary extinction parameter[33] and an agreement analysis suggested that no extinction correction was required. Crystallographic calculations were performed using SIR92[31] and CRYSTALS-PC.[34]

CCDC number 186/1162.

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

Results and discussion

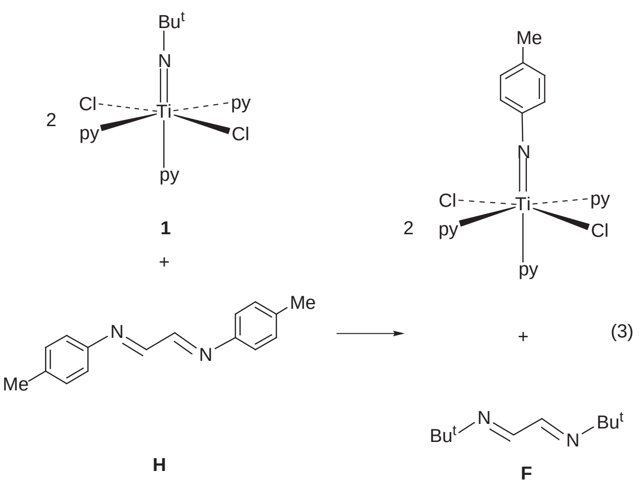
The reactions of [Ti(NR)Cl$_2$(py)$_3$] (R = Bu^t **1**, C$_6$H$_3$Me$_2$-2,6 **2** and C$_6$H$_3$Pr$^i_2$-2,6 **3**) with α-diimines divide into two types. α-Diimines with methyl substituents in the backbone give rise to coordination complexes (Scheme 1), while those with only H atom substituents result in imide/imine metathesis with no detectable new complex being formed [eqn. (2) and (3)].



As shown in Scheme 1, reaction of PhNC(Me)C(Me)NPh **A** or TolNC(Me)C(Me)NTol **B** with [Ti(NR)Cl$_2$(py)$_3$] gives immediate formation of the new complexes [Ti(NR)Cl$_2${η^2-ArNC(Me)C(Me)NAr}(py)] (R = C$_6$H$_3$Pr$^i_2$-2,6, Ar = Ph **4** or Tol **5**; R = C$_6$H$_3$Me$_2$-2,6, Ar = Ph **6**; R = Bu^t, Ar = Tol **7**). Compound **4** was fully characterised by ^{1}H and ^{13}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$_6$H$_3$Pr$^i_2$-2,6)Cl$_2${η^2-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)



(3)

−25 °C, room temperature solutions of pure **4** decompose substantially over *ca.* 4 hours (also in CDCl$_3$, C$_6$D$_6$ or CD$_2$Cl$_2$ in sealed NMR tubes) to complex mixtures containing [Ti(NC$_6$H$_3$Pr$^i_2$-2,6)Cl$_2$(py)$_2$] **3′** and free aniline H$_2$NC$_6$H$_3$Pr$^i_2$-2,6. The fate of the α-diimine ligand is unknown but the simultaneous appearance of a fairly viscous, oily material points towards α-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 ^{1}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$_6$H$_3$Pr$^i_2$-2,6)Cl$_2${η^2-PhNC(Me)C(Me)NPh}(py)]·CH$_2$Cl$_2$ 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^2-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.[13,35] The *trans* (with respect to the imido group) bond from titanium to nitrogen of the α-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.[20,36,37] 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 α-diimines [average C=N = 1.28(2) and C–C = 1.52(4) Å for four crystallographically-characterised examples].[38] These data therefore show that the diimine is coordinated as a neutral σ-donor ligand as in **III** above, as expected since the Ti(IV) centre in the {Ti(NC$_6$H$_3$Pr$^i_2$-2,6)Cl$_2$(py)} moiety has no d-electrons available for back-donation to the diimine ligand.

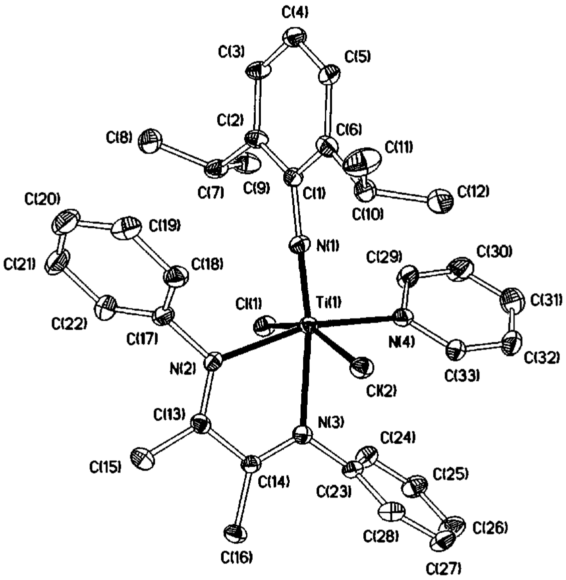


Fig. 1 Displacement ellipsoid (35%) plot of [Ti(NC$_6$H$_3$Pr$^i_2$-2,6)Cl$_2$-{η^2-PhNC(Me)C(Me)NPh}(py)] **4**. Hydrogen atoms and dichloromethane molecule of crystallisation are omitted.

[Ti(NC$_6$H$_3$Pr$^i_2$-2,6)Cl$_2${η^2-PhNC(Me)C(Me)NPh}(py)] **4** is the first structurally characterised example of a titanium complex with a neutral α-diimine ligand, and only the third for Group 4.[6,7] 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 α-diimine complexes of titanium in which the ligand may be assigned a formal negative charge between −1 and −2.[38] 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 ^{1}H and ^{13}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 ^{13}C resonances for the PhN=*C* imino carbons appear at δ 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**.[39] The ^{1}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 α-diimines ArNC(Me)C(Me)-NAr (Ar = C$_6$H$_3$Me$_2$-2,6 **C** or C$_6$H$_3$Pr$^i_2$-2,6 **D**) were unsuccessful and led to no reaction. However, heating a toluene solution of *tert*-butylimido complex [Ti(NBu^t)Cl$_2$(py)$_3$] **1** with *ca.* 1.1

equivalents of ArNC(H)C(H)CNAr (Ar = $C_6H_3Me_2$-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[20] arylimido bis(pyridine) complex [Ti($NC_6H_3Me_2$-2,6)Cl_2(py)$_2$] **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 $CDCl_3$, resonances for [Ti($NC_6H_3Me_2$-2,6)Cl_2(py)$_2$] **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^tNC(H)C(H)NBu^t **F** and ArNC(H)C(H)NBu^t (Ar = $C_6H_3Me_2$-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 α-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^t 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-α-diimine **H** with **1** was followed by ^{1}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^t to C=NTol functional group) proceeds smoothly and cleanly at room temperature to give quantitative formation of the previously described [Ti(NTol)Cl_2(py)$_3$][20] and Bu^tNC(H)C(H)NBu^t **F** after 24 hours. Examination of the reaction at intervals showed no evidence for formation of a complex such as [Ti(NBu^t)Cl_2{η^2-TolNC(H)C(H)NTol}(py)] that would be analogous to **4** (Scheme 1), although signals attributable to the expected intermediate mixed α-diimine TolNC(H)C(H)NBu^t were observed at intermediate stages of the reaction.

The imide/α-diimine reactions of [Ti(NBu^t)Cl_2(py)$_3$] **1** in eqn. (2) and (3) are analogous to those with *N*-aryl monoimines shown in eqn. (1).[21] As with the diimine reactions above, the bulkier (ring-substituted) mono-imine PhC($NC_6H_3Me_2$-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 α-diimine **E** [eqn. (2)] gave mainly symmetric Bu^tNC(H)C(H)NBu^t **F** as the product diimine, and not proportionally more of the asymmetric, mono-substituted diimine ArNC(H)C(H)NBu^t **G**, implies that there is negligible selectivity in these particular reactions and they are therefore probably not suitable for the practical synthesis of mixed α-diimines.

It is intriguing that the two types of α-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 α-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.[1,2] 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.[1,2]

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).[40] Our observations that the methyl-substituted α-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 α-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 α-diimine complex formation and subsequent degradation.

Conclusions

We have described the first metal imide/α-diimine metathesis reactions together with a rare example of a structurally-characterised, neutral α-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 α-diimine N- and backbone C-substituents.

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References

1 G. van Koten and K. Vrieze, *Adv. Organomet. Chem.*, 1982, **21**, 151.
2 K. Vrieze and G. van Koten, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon Press, Oxford, 1987; vol. 2, p. 206.
3 F. G. N. Cloke, H. C. de Lemos and A. A. Sameh, *J. Chem. Soc., Chem. Commun.*, 1986, 1344.
4 F. G. N. Cloke, C. I. Dalby, P. J. Daff and J. C. Green, *J. Chem. Soc., Dalton Trans.*, 1991, 181.
5 P. Scott and P. B. Hitchcock, *J. Chem. Soc., Chem. Commun.*, 1995, 579.
6 Structural characterisation of [$ZrCl_4${η^2-ArNC(Ph)C(Ph)NAr}] (Ar = C_6H_4OMe-4): B. Richter, J. Scholz, B. Neumüller, R. Weimann and H. Schumann, *Z. Anorg. Allg. Chem.*, 1995, **621**, 365.
7 Structural characterisation of 2,2′-bi-2-thiazine or 2,2′-bi-2-thiazoline complexes of $ZrCl_4$ or Zr$(NCS)_4$: R. A. Johnson, R. B. Von Dreele and T. M. Brown, *Inorg. Chem.*, 1984, **23**, 4302.
8 N. Kaltsoyannis, *J. Chem. Soc., Dalton Trans.*, 1996, 1583.
9 M. G. Gardiner, G. R. Hanson, M. J. Henderson, F. C. Lee and C. L. Raston, *Inorg. Chem.*, 1994, **33**, 2456.
10 J. Feldman, S. J. McLain, A. Parthasarathy, W. J. Marshall, J. C. Calabrese and S. D. Arthur, *Organometallics*, 1997, **16**, 1514.
11 C. M. Killian, D. J. Tempel, L. K. Johnson and M. Brookhart, *J. Am. Chem. Soc.*, 1996, **118**, 11664.
12 J. March, *Advanced Organic Chemistry*, Wiley-Interscience, New York, 4th edn., 1992, pp. 896–897 and refs. therein.
13 P. Mountford, *Chem. Commun.*, 1997, 2127.
14 A. J. Blake, P. E. Collier, L. H. Gade, P. Mountford, M. Schubart and I. J. Scowen, *Chem. Commun.*, 1997, 1555.
15 A. J. Blake, S. C. Dunn, J. C. Green, N. M. Jones, A. G. Moody and P. Mountford, *Chem. Commun.*, 1998, 1235.
16 G. I. Nikonov, A. J. Blake and P. Mountford, *Inorg. Chem.*, 1997, **36**, 1107.
17 P. J. Wilson, A. J. Blake, P. Mountford and M. Schröder, *Chem. Commun.*, 1998, 1007.
18 P. J. Stewart, A. J. Blake and P. Mountford, *Inorg. Chem.*, 1997, **36**, 1982.
19 P. J. Stewart, A. J. Blake and P. Mountford, *Organometallics*, 1998, **17**, 3271.
20 A. J. Blake, P. E. Collier, S. C. Dunn, W.-S. Li, P. Mountford and O. V. Shishkin, *J. Chem. Soc., Dalton Trans.*, 1997, 1549.
21 J. M. McInnes and P. Mountford, *Chem. Commun.*, 1998, 1669.
22 K. E. Meyer, P. J. Walsh and R. G. Bergman, *J. Am. Chem. Soc.*, 1995, **117**, 974.

23 G. K. Cantrell and T. Y. Meyer, *Organometallics*, 1997, **16**, 5381; *Chem. Commun.*, 1997, 1551.

24 G. K. Cantrell and T. Y. Meyer, *J. Am. Chem. Soc.*, 1998, **120**, 8035.

25 For a recent review and leading references see: R. H. Grubbs and S. Chang, *Tetrahedron*, 1998, **54**, 4413.

26 J. Alcázar, M. Begtrup and A. de la Hoz, *J. Chem. Soc.*, *Perkin Trans. 1*, 1995, 2467.

27 H. tom Dieck and I. W. Renk, *Chem. Ber.*, 1971, **104**, 92.

28 H. tom Dieck, M. Svoboda and T. Greiser, *Z. Naturforsch.*, *Teil B*, 1981, **36**, 823.

29 L. N. Ferguson and T. C. Goodwin, *J. Am. Chem. Soc.*, 1949, **71**, 633.

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

31 A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435.

32 J. R. Carruthers and D. J. Watkin, *Acta Crystallogr.*, *Sect. A*, 1979, **35**, 698.

33 A. C. Larson, *Acta Crystallogr.*, 1967, **23**, 664.

34 D. J. Watkin, C. K. Prout, J. R. Carruthers and P. W. Betteridge, CRYSTALS Issue 10, Chemical Crystallography Laboratory, University of Oxford, 1996.

35 D. E. Wigley, *Prog. Inorg. Chem.*, 1994, **42**, 239.

36 E. M. Shustorovich, M. A. Porai-Koshits and Y. A. Buslaev, *Coord. Chem. Rev.*, 1975, **17**, 1.

37 W. A. Nugent and J. M. Mayer, *Metal-Ligand Multiple Bonds*, Wiley-Interscience, New York, 1988.

38 The United Kingdom Chemical Database Service: D. A. Fletcher, R. F. McMeeking and D. Parkin, *J. Chem. Inf. Comput. Sci.*, 1996, **36**, 746.

39 K.-H. Thiele, B. Richter and B. Neumüller, *Z. Anorg. Allg. Chem.*, 1994, **620**, 1627.

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/α-diimine mechanism here.

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