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New binuclear alkyl and half-sandwich cyclopentadienyl imido titanium complexes containing acetamidinate and benzamidinate supporting ligands

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Abstract

Chloride metathesis reactions of the binuclear titanium *N*,*N*′-bis(cyclohexyl)acetamidinato-μ-imido compound $[Ti_2(\mu\text{-}NBu^t)_2\{MeC(NC_6H_{11})_2\}_2Cl_2]$ (**1**) and the mononuclear *N*,*N*′-bis(trimethylsilyl)benzamidinato-imido analogue $[Ti(NBu^t)\{PhC(NSiMe_3)_2\}Cl(py)_2]$ (**2**) are described. Thus, reaction of **1** or **2** with LiC_5R_5 ($R = H$ or Me) gave the half-sandwich compounds $[Ti(NBu^t)\{MeC(NC_6H_{11})_2\}(\eta\text{-}C_5H_5)]$ and $[Ti(NBu^t)\{PhC(NSiMe_3)_2\}(\eta\text{-}C_5Me_5)]$, respectively. These compounds are also accessible from $[Ti(NBu^t)(\eta\text{-}C_5R_5)Cl(L)]$ ($R = H$ or Me; $L = py$ or $4\text{-}NC_5H_4Bu^t$) and the appropriate lithium amidinate. Treatment of **1** with MeLi gave the binuclear 12-electron methyl derivative $[Ti_2(\mu\text{-}NBu^t)_2\{MeC(NC_6H_{11})_2\}_2(Me)_2]$ which has been crystallographically characterised. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Titanium; Imide; Benzamidinate; Acetamidinate; Cyclopentadienyl; X-ray diffraction

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1. Introduction

As part of an ongoing study of titanium imido chemistry [1] we recently described the synthesis and structures of $[Ti_2(\mu\text{-}NR)_2\{MeC(NC_6H_{11})_2\}_2Cl_2]$ (**1**) and $[Ti(NBu^t)\{PhC(NSiMe_3)_2\}Cl(py)_2]$ ($R = Bu^t$ **2** or aryl) [2]. These compounds contain the unusual amidinate-imide ligand set. This is a very recently reported ligand combination [2–6], and has not yet been exploited to any significant extent as a supporting environment for new transition metal chemistry. We thought this surprising since the chemistry of compounds containing either the imide (NR, where typically R is alkyl or aryl) or amidinate ($RC(NR')_2$ where usually R is H, alkyl or aryl and R′ is alkyl, aryl or trimethylsilyl) ligand are very well-established [7–10]. Furthermore, since there is much current interest in developing non-metallocene early transition metal chemistry [11–15], we were interested to explore the potential of the amidinate-imide ligand set for supporting new organometallic complexes of titanium. The trianionic net charge for the $\{[RC(NR)_2](NR)\}$ moiety is an alternative to the well-known dianionic bis(cyclopentadienyl), tetraazamacrocyclic, Schiff-base, diamide, and cyclopentadienyl-amide moeties [11–17]. Here we describe new amidinato-imido chemistry of titanium which thus far has been largely dominated by compounds with one or two cyclopentadienyl co-ligands [18].

2. Results and discussion

The starting compounds $[Ti_2(\mu\text{-}NBu^t)_2\{MeC(NC_6H_{11})_2\}_2Cl_2]$ (**1**) and $[Ti(NBu^t)\{PhC(NSiMe_3)_2\}Cl(py)_2]$

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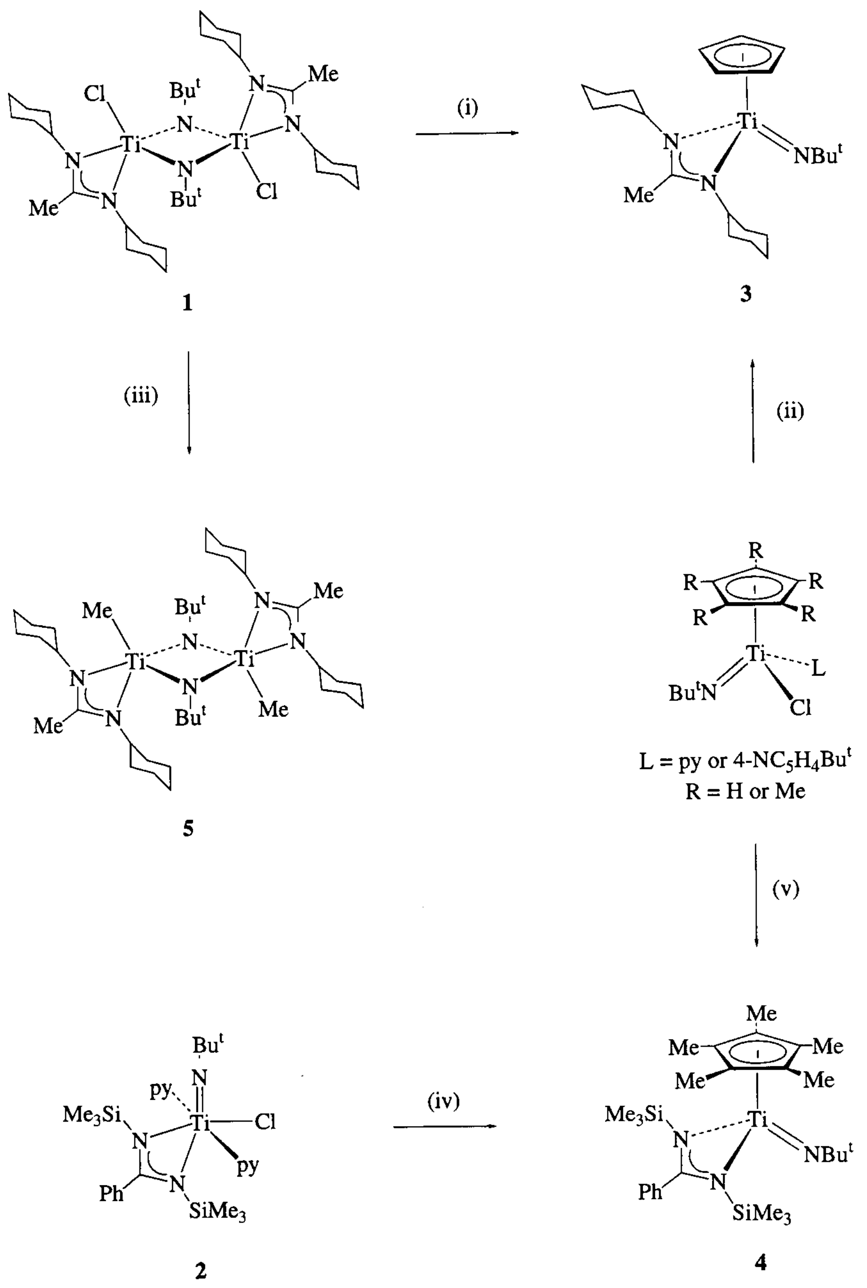

Scheme 1. Reagents and conditions: (i) LiC_5H_5, C_6D_6, r.t. then 60°C, 6 days, > 95%; (ii) $LiMeC(NC_6H_{11})_2$, toluene, − 50°C then r.t., 18 h, 97%; (iii) MeLi, Et_2O/THF, − 60°C then r.t., 2 h, 67%; (iv) LiC_5Me_5, toluene, 90°C, 66 h, 79%; (v) $LiPhC(NSiMe_3)_2$, C_6D_6, r.t., 23 h, > 95%.

(**2**, Scheme 1) were prepared as recently reported [2] by treatment of $[Ti(NBu^t)Cl_2(py)_3]$ [19] with $LiMeC(NC_6H_{11})_2$ [20] or $LiPhC(NSiMe_3)_2$ [21,22], respectively. The half-sandwich complexes $[Ti(NBu^t)(\eta\text{-}C_5R_5)Cl(L)]$ (R = H or Me; L = py or $4\text{-}NC_5H_4Bu^t$) were prepared from the appropriate LiC_5R_5 and $[Ti(NBu^t)Cl_2(4\text{-}NC_5H_4Bu^t)_2]$ or $[Ti(NBu^t)Cl_2(py)_3]$ [23].

The new half-sandwich *N*,*N*′-bis(cyclohexyl)acetamidinate-imido complex $[Ti(NBu^t)\{MeC(NC_6H_{11})_2\}(\eta\text{-}C_5H_5)]$ (**3** in Scheme 1) was obtained as a spectroscopically pure red oil in 97% yield via reaction of $LiMeC(NC_6H_{11})_2$ with $[Ti(NBu^t)(\eta\text{-}C_5H_5)Cl(py)]$ [23]. Unfortunately all attempts to crystallise **3** were unsuccessful. An NMR scale reaction demonstrated that compound **3** could also be obtained by treatment of $[Ti_2(\mu\text{-}NBu^t)_2\{MeC(NC_6H_{11})_2\}_2Cl_2]$ (**1**) with two equivalents of LiC_5H_5 in C_6D_6.

In order to obtain a solid sample of this new class of complex we prepared a benzamidinate analogue of **3**. Thus reaction of one equivalent of LiC_5Me_5 with $[Ti(NBu^t)\{PhC(NSiMe_3)_2\}Cl(py)_2]$ **2** in toluene at 90°C gave the pentamethylcyclopentadienyl derivative $[Ti(NBu^t)\{PhC(NSiMe_3)_2\}(\eta\text{-}C_5Me_5)]$ (**4**) as a red, waxy solid in 79% yield after high vacuum sublimation (120–

160°C, 2×10^{-5} mbar). An NMR scale reaction showed that **4** was also accessible by reaction of one equivalent of $LiPhC(NSiMe_3)_2$ with $[Ti(NBu^t)(\eta\text{-}C_5Me_5)Cl(4\text{-}NC_5H_4Bu^t)]$ in C_6D_6. This reaction proceeds slowly, probably due to the steric bulk of the ligands involved and the limited solubility of LiC_5Me_5 in C_6D_6.

The new half-sandwich compounds are proposed to possess the 16-electron, monomeric structures illustrated in Scheme 1 and, to the best of our knowledge, are the first examples of this particular combination of ligand sets. The compounds **3** and **4** may be compared with the bis(cyclopentadienyl) complexes $[Ti(\eta\text{-}C_5H_5)(\eta\text{-}C_5R_5)(NBu^t)(L)]$ (R = H or Me, L = py or $NC_5H_4Bu^t$) and the cyclopentadienyl-indenyl complex $[Ti(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)(NBu^t)(py)]$, all of which exist as pyridine adducts [23]. It appears therefore that the amidinate ligand in **3** and **4** has greater steric demands than those of the η-cyclopentadienyl or -indenyl ligands; this is consistent with previous work [24]. Other (non-imido) group 4 compounds containing the cyclopentadienyl-amidinate ligand set have been described previously [25].

We were also interested to prepare alkyl complexes supported by amidinate-imide ligands. Accordingly, reaction of $[Ti_2(\mu\text{-}NBu^t)_2\{MeC(NC_6H_{11})_2\}_2Cl_2]$ (**1**), with MeLi in Et_2O/THF at −60°C gave, after standard workup and recrystallisation from hexane, orange-red diffraction-quality crystals of the binuclear, 12-electron dimer $[Ti_2(\mu\text{-}NBu^t)_2\{MeC(NC_6H_{11})_2\}_2(Me)_2]$ (**5**) in 67% yield. Details of data collection and processing are given in Table 1. Attempts to prepare titanium methyl complexes with benzamidinate supporting ligands were unsuccessful.

A view of the molecular structure of $[Ti_2(\mu\text{-}NBu^t)_2\{MeC(NC_6H_{11})_2\}_2(Me)_2]$ (**5**) is shown in Fig. 1 and important bond lengths and angles are listed in Table 2. Compound **5** possesses a crystallographically centrosymmetric, binuclear geometry which is very similar to that of $[Ti_2(\mu\text{-}NBu^t)_2\{MeC(NC_6H_{11})_2\}_2Cl_2]$ (**1**) [2]. There is disordered hexane of crystallisation in the lattice of $\mathbf{5\cdot C_6H_{14}}$ and this was satisfactorily modelled. The Ti...Ti separation of 2.803(2) Å in **5** is comparable to that of **1**, but the difference between the two Ti–μ-N(imido) bond lengths (0.109(7) Å for **5**) is less (0.162(4) Å for **1**). The titanium–N(amidinate) bonds (2.160(5) and 2.105(5) Å) in **5** are longer than those of **1** (2.112(3) and 2.076(3) Å), possibly because the methyl ligand is a better and less electronegative donor than chloride. A 14-electron, binuclear analogue of **5**, namely the cyclopentadienyl μ-imido-alkyl compound $[Ti_2(\mu\text{-}NPh)_2(\eta\text{-}C_5H_5)_2(Me)_2]$ was reported by Teuben some time ago [26] but was not crystallographically characterised.

The H atoms of the methyl ligand were located from Fourier difference syntheses and were positionally refined in an isotropic model. The titanium to methyl hydrogen distances (2.55(8), 2.59(8), 2.59(8) Å) are normal (i.e. not indicative of an α-agostic interaction with Ti [27,28]) and also equivalent within one standard deviation. The Ti(1)–C(19)–H angles are also equivalent and have normal values. Furthermore, the Ti–C(methyl) bond length of 2.160(6) Å is slightly longer than average for a such bonds (average 2.143 Å for 53 examples) [29,30], and not the relatively shortened distance that might be expected if there were α-agostic interactions in this 12-electron compound [27].

The r.t. ^{1}H-NMR spectrum of $[Ti_2(\mu\text{-}NBu^t)_2\{MeC(NC_6H_{11})_2\}_2(Me)_2]$ in benzene-d_6 shows several broad cyclohexyl resonances; the methyl group attached to titanium appears as a singlet at 1.35 ppm. The equivalence of the cyclohexyl methine resonances indicates that this complex is fluxional at r.t. since the two rings are inequivalent in the solid state (see Fig. 1). The limited solubility of **5** in non-halogenated solvents

Table 1
X-ray data collection and processing parameters for $[Ti_2(\mu\text{-}NBu^t)_2\{MeC(NC_6H_{11})_2\}_2(Me)_2]\cdot C_6H_{14}$ ($\mathbf{5\cdot C_6H_{14}}$)

Molecular formula	$C_{38}H_{74}N_6Ti_2\cdot C_6H_{14}$
Formula weight	797.00
Temperature (K)	220(2)
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
Unit cell dimensions	
a (Å)	10.359(2)
b (Å)	10.5974(9)
c (Å)	11.097(1)
α (°)	93.404(9)
β (°)	100.12(1)
γ (°)	87.84(1)
Volume (Å^3)	1196.7(3)
Z	1
Density (calculated) (mg m^{-3})	1.11
Absorption coefficient (mm^{-1})	0.36
$F(000)$	438
Crystal description and size (mm)	Red plate, $0.34\times0.19\times0.06$
Theta range for data collection (°)	2.61–23.51
Scan type	ω-θ
Index ranges	$-11\le h\le 11$, $-11\le k\le 11$, $-8\le l\le 12$
Independent reflections	3541
Observed reflections [$I>2\sigma(I)$]	2577
Absorption correction	None
Variation in standard reflections	Random $\pm$ 3.8%
Data/restraints/parameters	2577/10/253
Refinement method	Blocked-matrix least squares on F
Weighting scheme	Unit weights
Final R indices[a] [$I>2\sigma(I)$]	$R=0.0798$, $R_w=0.0873$
Goodness-of-fit	1.545
Final $(\Delta/\sigma)_{max}$	0.05
Largest residual peaks (e Å^{-3})	0.46 and −0.48

[a] $R=R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$; $R_w=\sqrt{\{\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2\}}$.

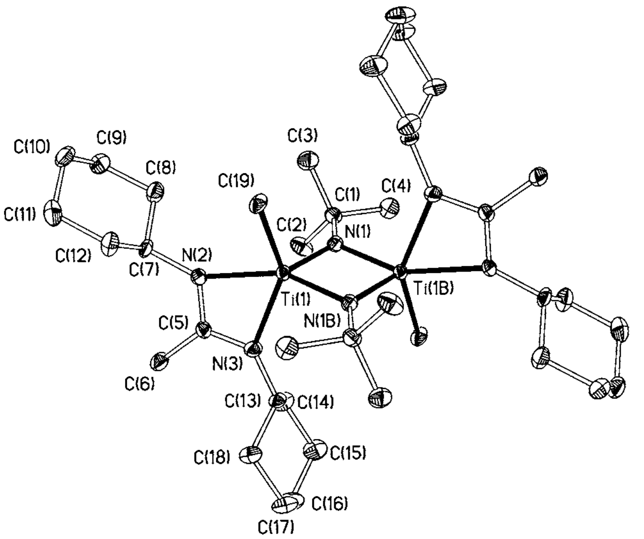

Fig. 1. Displacement ellipsoid (30%) plot of $[Ti_2(\mu\text{-}NBu^t)_2\{MeC(NC_6H_{11})_2\}_2(Me)_2]$ (**5**). Hydrogen atoms and the hexane molecule of crystallisation are omitted. Atoms carrying the suffix 'B' are related to their non-suffixed counterparts by the symmetry operator $[1-x,\ -y,\ 2-z]$.

hindered attempts to record low temperature spectra. Interestingly, the gated decoupled ^{13}C-NMR spectrum at 25°C shows a binomial quartet for the titanium-bound methyl carbon at $\delta = 41.9$ ppm with an averaged $^1J_{CH}$ coupling constant of ca. 120 Hz which in the range previously suggested to be consistent with agostic interactions [27]. However, the absence of a low ν(C–H) absorption in the IR spectrum of **5** and of a close C_α–H–Ti contact in the solid state structure militates against a significant α-agostic interaction of the methyl group with titanium. Moreover, the lowering of $^1J_{CH}$ values for carbons bound to electropositive metals compared to those of their non-metallated counterparts is well known.

Table 2
Selected bond lengths (Å) and angles (°) for $[Ti_2(\mu\text{-}NBu^t)_2\{MeC(NC_6H_{11})_2\}_2(Me)_2]$ (**5**). Atoms carrying the suffix 'B' are related to their counterparts by the symmetry operator $[1-x,\ -y,\ 2-z]$

Ti(1)...Ti(1B)	2.803(2)	Ti(1)–C(19)	2.160(6)
Ti(1)–N(1)	1.860(5)	N(1)–C(1)	1.481(8)
Ti(1)–N(1B)	1.969(5)	Ti(1)...H(191)	2.55(8)
Ti(1)–N(2)	2.160(5)	Ti(1)...H(192)	2.59(8)
Ti(1)–N(3)	2.105(5)	Ti(1)...H(193)	2.59(8)
Ti(1B)...Ti(1)–N(1)	44.5(2)	Ti(1)...Ti(1B)–C(19)	106.6(2)
Ti(1B)...Ti(1)–N(1B)	41.4(2)	N(1)–Ti(1)–C(19)	105.5(3)
N(1)–Ti(1)–N(1B)	85.9(2)	N(1B)–Ti(1)–C(19)	98.8(2)
Ti(1B)...Ti(1)–N(2)	157.7(2)	N(2)–Ti(1)–C(19)	89.6(2)
N(1)–Ti(1)–N(2)	117.0(2)	N(3)–Ti(1)–C(19)	139.8(2)
N(1B)–Ti(1)–N(2)	152.6(2)	Ti(1)–N(1)–Ti(1B)	94.1(2)
Ti(1B)...Ti(1)–N(3)	109.6(2)	Ti(1)–C(19)–H(191)	105(5)
N(1)–Ti(1)–N(3)	112.4(2)	Ti(1)–C(19)–H(192)	112(6)
N(1B)–Ti(1)–N(3)	96.7(2)	Ti(1)–C(19)–H(193)	107(5)
N(2)–Ti(1)–N(3)	61.8(2)		

3. Experimental section

All manipulations were carried out under an atmosphere of dinitrogen or argon using standard Schlenk-line or dry-box techniques. All protio-solvents and commercially-available reagents were pre-dried over activated molecular sieves and refluxed over an appropriate drying agent under an atmosphere of dinitrogen and collected by distillation. $CDCl_3$ was dried over freshly ground calcium hydride at r.t. and C_6D_6 was dried over molten potassium. All NMR solvents were distilled under reduced pressure and stored under N_2 in a J. Young ampoule. NMR samples were prepared in the dry-box in 5 mm Wilmad tubes equipped with a Young's Teflon valve.

^1H and ^{13}C spectra were recorded on a Bruker DPX 300 spectrometer and referenced internally to residual protio-solvent (^1H) or solvent (^{13}C) resonances. Chemical shifts are reported relative to tetramethylsilane ($\delta = 0$ ppm) in δ (ppm) and coupling constants in Hz. Assignments were supported by DEPT-135 and DEPT-90, homo- and hetero-nuclear, one- and two-dimensional experiments as appropriate. IR spectra were recorded on a Nicolet 205 FTIR spectrometer in the range 400–4000 cm^{-1}. Samples were prepared in the dry-box between KBr or CsBr plates as Nujol mulls or as thin films and data are quoted in wavenumbers (ν, cm^{-1}). Elemental analyses were carried out by the analysis laboratory of this department.

$Li[PhC(NSiMe_3)_2]$ [21,22], $Li[MeC(NC_6H_{11})_2]$ [20], $[Ti_2(\mu\text{-}NBu^t)_2\{MeC(NC_6H_{11})_2\}_2Cl_2]$ (**1**) [2], $[Ti(NBu^t)\{PhC(NSiMe_3)_2\}Cl(py)_2]$ (**2**) [2], and $[Ti(NBu^t)(\eta^5\text{-}C_5R_5)Cl(L)]$ (R = H or Bu^t; L = py or $4\text{-}NC_5H_4Bu^t$) [23] were prepared according to literature methods. LiC_5R_5 (R = H or Me) was prepared from *n*-butyllithium and C_5R_5H in cold hexanes.

3.1. $[Ti(NBu^t)\{MeC(NC_6H_{11})_2\}(\eta\text{-}C_5H_5)]$ (3)

Cold (– 50°C) toluene (25 ml) was added slowly to a mixture of $[Ti(NBu^t)(\eta\text{-}C_5H_5)Cl(py)]$ (0.585 g, 1.96 mmol) and $LiMeC(NC_6H_{11})_2$ (0.568 g, 1.96 mmol). The resulting red solution was allowed to warm to r.t., stirred for 18 h then filtered. Volatiles were removed under reduced pressure to yield **3** as a red oil which could not be crystallised. Yield: 0.77 g (97%).

^1H-NMR ($CDCl_3$, 300.1 MHz, 25°C): 6.35 (s, 5H, $C_5\mathit{H}_5$), 3.31 (t of t, $J = 10.6$ and 3.7 Hz, 2H, $NC\mathit{H}C_5H_{10}$), 2.01 (s, 3H, $\mathit{Me}CN_2$), 1.80 to 0.92 (series of multiplets, 20H, $NCHC_5\mathit{H}_{10}$), 0.94 (s, 9H, $N\mathit{Bu}^t$). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 75.5 MHz, 25°C): 158.8 ($Me\mathit{C}N_2$), 110.1 (C_5H_5), 66.8 ($N\mathit{C}Me_3$), 56.6

($\mathrm{N}\mathit{C}\mathrm{HC_5H_{10}}$), 36.6, 36.1 ($2\times\mathrm{NCH}\mathit{C}_5\mathrm{H_{10}}$), 32.4 ($\mathrm{NC}\mathit{Me}_3$), 26.0, 25.7, 25.5 ($3\times\mathrm{NCH}\mathit{C}_5\mathrm{H_{10}}$), 10.9 ($\mathit{Me}\mathrm{CN_2}$). IR (KBr plates, thin film): 3102 (w), 2959 (s), 2926 (vs), 2851 (s), 2666 (w), 1763 (w), 1664 (w), 1491 (s), 1449 (s), 1418 (m), 1360 (s), 1348 (s), 1307 (w), 1244 (s), 1211 (s), 1182 (w), 1141 (w), 1120 (w), 1093 (m), 1050 (w), 1013 (m), 953 (w), 922 (w), 887 (w), 861 (w), 843 (w), 826 (w), 788 (s), 777 (s), 673 (w), 616 (w), 595 (w), 537 (m), 507 (w) $\mathrm{cm^{-1}}$. Satisfactory elemental analysis was not obtained for this compound, which was an oil.

3.2. NMR tube synthesis of **3** from $[\mathrm{Ti_2(\mu\text{-}NBu^t)_2\{MeC(NC_6H_{11})_2\}_2Cl_2}]$ and $\mathrm{LiC_5H_5}$

A solution of $[\mathrm{Ti_2(\mu\text{-}NBu^t)_2\{MeC(NC_6H_{11})_2\}_2Cl_2}]$ (**1**) (5.1 mg, 0.007 mmol) and $\mathrm{LiC_5H_5}$ (1 mg, 0.014 mmol) in $\mathrm{C_6D_6}$ (0.6 ml) was transfered to a 5 mm J. Young NMR tube. The ^{1}H-NMR spectra over 5 days showed slow formation (15% complete) of $[\mathrm{Ti(NBu^t)\{MeC(NC_6H_{11})_2\}(\eta^5\text{-}C_5H_5)}]$ (**3**). The reaction went to completion when the solution was heated at 60°C for 24 h.

3.3. $[\mathrm{Ti(NBu^t)\{PhC(NSiMe_3)_2\}(\eta\text{-}C_5Me_5)}]$ (**4**)

An orange solution of $\mathrm{LiC_5Me_5}$ (0.053 g, 0.37 mmol) and $[\mathrm{Ti(NBu^t)\{PhC(NSiMe_3)_2\}Cl(py)_2}]$ (0.214 g, 0.37 mmol) in toluene (40 ml) was refluxed at 90°C under reduced pressure in a J. Young ampoule for 66 h. After cooling, the resulting red solution was filtered and volatiles were removed under reduced pressure to leave **4** as a red oil. Sublimation at 120–160°C, 2×10^{-5} mbar onto a cold finger at -78°C gave **4** as a red waxy solid. Yield: 0.152 g (79%).

^{1}H-NMR ($\mathrm{CDCl_3}$, 300.1 MHz, 25°C): 7.38, (m, 3H, *ortho*- and *para*-$\mathrm{C_6}\mathit{H}_5$), 7.28, (m, 2H, *meta*-$\mathrm{C_6}\mathit{H}_5$), 2.14 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$), 1.00 (s, 9 H, $\mathrm{N}\mathit{Bu}^t$), -0.10 (s, 18H, $\mathrm{Si}\mathit{Me}_3$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$-NMR ($\mathrm{CDCl_3}$, 75.5 MHz, 25°C): 173.1 ($\mathrm{C_6H_5}\mathit{C}\mathrm{N_2}$), 139.5 (*ipso*-$\mathrm{C_6H_5}$), 128.3, 128.2, 127.6 (*ortho*-, *meta*- and *para*-$\mathrm{C_6H_5}$), 119.4 ($\mathit{C}_5\mathrm{Me_5}$), 67.1 ($\mathrm{N}\mathit{C}\mathrm{Me_3}$), 32.5 ($\mathrm{NC}\mathit{Me}_3$), 12.4 ($\mathrm{C_5}\mathit{Me}_5$), 3.0 ($\mathrm{Si}\mathit{Me}_3$). IR (CsBr plates, Nujol mull): 1654 (w), 1246 (s), 1206 (w), 1004 (m), 994 (m), 841 (vs), 762 (m), 722 (w), 702 (w), 541 (w), 506 (w), 412 (w) $\mathrm{cm^{-1}}$. Anal. Found (calculated for $\mathrm{C_{27}H_{47}N_3Si_2Ti}$): C, 61.0 (62.6); H, 9.2 (9.2); N, 7.6 (8.1)%. The low %C and %N found for this compound may be attributed to poor combustion and titanium carbide and/or nitride formation.

3.4. NMR tube synthesis of **4** from $[\mathrm{Ti(NBu^t)(\eta\text{-}C_5Me_5)Cl(4\text{-}NC_5H_4Bu^t)}]$ and $\mathrm{LiPhC(NSiMe_3)_2}$

A solution of $[\mathrm{Ti(NBu^t)(\eta\text{-}C_5Me_5)Cl(4\text{-}NC_5H_4Bu^t)}]$ (16.9 mg, 0.040 mmol) and $\mathrm{LiPhC(NSiMe_3)_2}$ (11.2 mg, 0.041 mmol) in $\mathrm{C_6D_6}$ (0.6 ml) was transfered to a 5 mm J. Young NMR tube. The ^{1}H-NMR spectrum after 23 h at r.t. showed quantitative formation of $[\mathrm{Ti(NBu^t)\{PhC(NSiMe_3)_2\}(\eta\text{-}C_5Me_5)}]$ (**5**) together with new resonances attributable to free $4\text{-}\mathrm{NC_5H_4Bu^t}$.

3.5. $[\mathrm{Ti_2(\mu\text{-}NBu^t)_2\{MeC(NC_6H_{11})_2\}_2(Me)_2}]$ (**5**)

MeLi (0.19 ml of 1.4 M solution in $\mathrm{Et_2O}$, 0.27 mmol) was added to a stirred solution of $[\mathrm{Ti_2(\mu\text{-}NBu^t)_2\{MeC(NC_6H_{11})_2\}_2Cl_2}]$ (0.096 g, 0.13 mmol) in THF (20 ml) at -60°C. The resulting red solution was allowed to warm to r.t. then stirred for a further 2 h. The volatiles were removed under reduced pressure and the solid residue was redissolved in warm hexane (30 ml, 50°C) and filtered. Concentration to 20 ml then cooling to r.t. afforded **5** as orange-red crystals overnight. These were washed with cold hexane (2×5 ml) and dried in vacuo. Yield: 0.061 g (67%).

^{1}H-NMR ($\mathrm{C_6D_6}$, 300.1 MHz, 25°C): 3.57 (m, 4H, $\mathrm{NC}\mathit{H}\mathrm{C_5H_{10}}$), 1.82 (s, 6H. $\mathit{Me}\mathrm{CN_2}$), 2.1 to 1.0 (40H, series of multiplets corresponding to $\mathrm{NCHC_5}\mathit{H}_{10}$ of two pairs of inequivalent cyclohexyl rings), 1.53 (s, 18H, $\mathrm{N}\mathit{Bu}^t$), 1.35 (s, 6H, Ti–*Me*). $^{13}\mathrm{C}\{^1\mathrm{H}\}$-NMR ($\mathrm{C_6D_6}$, 75.5 MHz, 25°C): 178.6 ($\mathrm{Me}\mathit{C}\mathrm{N_2}$), 69.7 ($\mathrm{N}\mathit{C}\mathrm{Me_3}$), 58.8 ($\mathrm{N}\mathit{C}\mathrm{HC_5H_{10}}$), 41.9 (q, $^1J_{\mathrm{CH}}=120$ Hz, Ti–*Me*), 35.4 ($2\times\mathrm{NCH}\mathit{C}_5\mathrm{H_{10}}$), 32.6 ($\mathrm{NC}\mathit{Me}_3$), 26.9 (overlapping $2\times\mathrm{NCH}\mathit{C}_5\mathrm{H_{10}}$), 26.3 ($1\times\mathrm{NCH}\mathit{C}_5\mathrm{H_{10}}$), 14.1 ($\mathit{Me}\mathrm{CN_2}$); note: ^1J for the $\delta=41.9$ Ti–Me resonance was obtained from a gated-coupled ^{13}C-NMR spectrum of **5** in the same solvent and at the same temperature. IR (KBr plates, Nujol mull): 1716 (w), 1652 (m), 1491 (m), 1356 (s), 1313 (w), 1257 (m), 1192 (s), 1181 (s), 1138 (w), 1094 (m), 1078 (m), 1027 (m), 1002 (m), 890 (w), 800 (m), 766 (w), 744 (w), 722 (w), 700 (w), 668 (w), 648 (vs), 607 (w), 590 (w), 557 (w), 549 (w), 542 (w) $\mathrm{cm^{-1}}$. Anal. Found (calculated for $\mathrm{C_{38}H_{74}N_6Ti_2}$: C, 63.3 (64.2); H, 10.5 (10.5); N, 11.6 (11.8)%. The low %C found for this compound may be attributed to poor combustion and titanium carbide formation.

3.6. Crystal structure determination of $[\mathrm{Ti_2(\mu\text{-}NBu^t)_2\{MeC(NC_6H_{11})_2\}_2(Me)_2}]\cdot\mathrm{C_6H_{14}}$ (**5·C₆H₁₄**)

Crystal data collection and processing parameters are given in Table 1. A crystal 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 [31]. Data were collected using Mo–K_α radiation ($\lambda=0.71073$ Å). No absorption correction was applied to the data. Equivalent reflections were merged and the structure was solved by direct methods using SIR92 [32]. Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms. Non-H atoms of $[Ti_2(\mu\text{-}NBu^t)_2\{MeC(NC_6H_{11})_2\}_2(Me)_2]$ were refined anisotropically. Residual electron density was modelled as a hexane molecule (there is one hexane molecule per $[Ti_2(\mu\text{-}NBu^t)_2\{MeC(NC_6H_{11})_2\}_2(Me)_2]$ dimer) disordered across a crystallographic inversion centre. The non-H atoms of this solvate were refined isotropically with similarity restraints applied to C–C distances and C–C–C angles. Hydrogen atoms for $[Ti_2(\mu\text{-}NBu^t)_2\{MeC(NC_6H_{11})_2\}_2(Me)_2]$ were located from Fourier difference syntheses. Those for the hexane molecule of crystallisation were placed geometrically. All H atoms were refined in a riding model, except for those of the titanium–methyl carbon [C(19)] which were positionally refined with a common U_{iso} value. The H atoms for the *tert*-butyl methyl groups, the amidinate methyl group, the two cyclohexyl rings were assigned common U_{iso} values which were refined. Data were collected to only $\theta_{max} = 23.5°$ since there were no detectable diffraction peaks beyond this point. Attempted F^2 refinement on all data gave unstable results and so this structure was refined on F with data selected above the $I > 2\sigma(I)$ threshold. Examination of the refined extinction parameter and an agreement analysis suggested that no extinction correction was required. All crystallographic calculations were performed using SIR92 and CRYSTALS-PC [33].

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