

Organometallic and related imidotitanium compounds containing a pendant arm functionalised benzamidinate ligand

A. Charis R. Croft, Catherine L. Boyd, Andrew R. Cowley, Philip Mountford*

Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, UK

Received 27 March 2003; received in revised form 5 May 2003; accepted 5 May 2003

Abstract

Chloride ligand substitution reactions of *tert*-butyl- and aryimido-titanium complexes supported by the pendant arm functionalised *N*-trimethylsilyl benzamidinate ligand $\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2$ are described. Reaction of previously-described $[\text{Ti}(\text{N}^t\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**1**) with PhLi afforded thermally sensitive $[\text{Ti}(\text{N}^t\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Ph}]$ (**2**). The corresponding reaction of **1** with MeLi afforded $[\text{Ti}(\text{N}^t\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Me}]$ (**3**) detected by $^1\text{H-NMR}$ spectroscopy but this compound could not be isolated. Reaction of **1** with $\text{LiCH}_2\text{SiMe}_3$ gave a complex mixture, but with $\text{LiN}(\text{SiMe}_3)_2$ and $\text{LiO-2,6-C}_6\text{H}_3\text{Me}_2$ the compounds $[\text{Ti}(\text{N}^t\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{X}]$ ($\text{X} = \text{N}(\text{SiMe}_3)_2$ (**4**) or $\text{O-2,6-C}_6\text{H}_3\text{Me}_2$ (**5**)) were isolated. The X-ray structure of **5** was determined. Reaction of the homologous compound $[\text{Ti}(\text{N}^t\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**6**) (containing a 2-carbon atom chain in the pendant arm) with MeLi or PhLi were unsuccessful although the aryloxy compound $[\text{Ti}(\text{N}^t\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2\}\{\text{O-2,6-C}_6\text{H}_3\text{Me}_2\}]$ (**7**) could be isolated from the reaction of **6** with $\text{LiO-2,6-C}_6\text{H}_3\text{Me}_2$. Reaction of the 3-carbon pendant arm aryimido compound $[\text{Ti}(\text{N-2,6-C}_6\text{H}_3\text{Me}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**8**) with MeLi afforded thermally sensitive $[\text{Ti}(\text{N-2,6-C}_6\text{H}_3\text{Me}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Me}]$ (**9**), and although the analogous phenyl homologue was elusive, the aryloxy derivative $[\text{Ti}(\text{N-2,6-C}_6\text{H}_3\text{Me}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\{\text{O-2,6-C}_6\text{H}_3\text{Me}_2\}]$ (**10**) was successfully isolated and structurally characterised. Comparison of the X-ray structures of **5** and **10** show unexpectedly large differences between the Ti=NR and Ti-OAr bond lengths in the two compounds.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Titanium; Imido; Benzamidate ligands; Amide; Aryloxy; Methyl; Phenyl

1. Introduction

Transition metal imido compounds provide a wealth of molecular reactivity, this occurring either at the $\text{M} = \text{NR}$ linkage itself (i.e. imido ligand as a reactive site) or at some other point in the $\text{L}_n\text{M}(\text{NR})$ coordination sphere (imido ligand acting as a supporting group) [1,2a,b]. Both types of reactivity are well-established, and in recent years we have been interested to exploit the chemistry of imidotitanium compounds in both of these regards [2]. Clearly the type of reactivity exhibited by an imido compound depends on the nature of the substrate(s) involved and the identity of the ancillary

ligand(s). In some cases there might well be ambiguity in regard to the actual site of reactivity.

An interesting question concerning reaction site selectivity has been raised recently by Jensen and Børve [3] in calculations on Gibson's olefin polymerisation catalysts $[\text{Cr}(\text{NR}')_2\text{R}_2]$ ($\text{R}' = ^t\text{Bu}$ or aryl; $\text{R} = \text{Me}$ or CH_2Ph) [4]. At first sight, one would probably envisage that these would give rise to cationic active species $[\text{Cr}(\text{NR}')_2\text{R}]^+$ ($\text{R} =$ initiating alkyl group or growing polymer chain) with monomer enchainment proceeding through migratory insertion reactions of the Cr–R bond. However, for chemically realistic model systems $[\text{Cr}(\text{NR}')_2\text{R}]^+$ it appears that [3] ethylene cycloaddition to the Cr = NR' bond can compete with insertion into the Cr–R bond, in turn leading (after further modification) to a reduced Cr (IV) species which may in fact be the resting state for this catalytic system. In very recent

* Corresponding author. Fax: +44-186-527-2690.

E-mail address: philip.mountford@chem.ox.ac.uk (P. Mountford).

work, we ourselves reported that the cationic imido-tungsten methyl compound $[W\{MeC(2-C_5H_4N)-(CH_2NSiMe_3)_2\}(NPh)Me]^+$ (anion = $[MeB(C_6F_5)_3]^-$) reacts with CO_2 or isocyanates appear to undergo cycloaddition reactions at the $W=NPh$ bond and not insertion into the $W-Me$ bond [5,6]. This is despite the latter product being the most thermodynamically favourable according to DFT calculations, and insertion reactions of CO_2 into W -alkyl bonds being extremely well preceded in the literature. With these and other observations in mind we have been interested to prepare new imido complexes containing potentially reactive $M=NR$ linkages, and which additionally contain metal-hydrocarbyl σ -bonds.

We have previously reported amidinate [5–7] supported imidotitanium complexes [8] $[Ti(NR)\{PhC(NSiMe_3)_2\}Cl(py)_n]$ ($n = 2$ (**I**) or 1 (**II**); $R = tBu$ or aryl—see Chart 1) and $[Ti_2(\mu-NtBu)_2\{MeC(NC_6H_{11})_2\}_2Cl_2]$. Chloride ligand metathesis reactions of **I/II** (which exist in a dynamic, temperature-dependent equilibrium) yield alkyl, borohydride, amide, aryloxy and cyclopentadienyl derivatives [9]. Some of the latter family of complexes, namely $[Ti(NAr)(\eta-C_5Me_5)\{MeC(N^iPr)_2\}]$ (**III**, $Ar =$ substituted phenyl group), react with CO_2 (via an initial cycloaddition reaction) to form $[Ti(\eta-C_5Me_5)\{MeC(N^iPr)_2\}\{O(CO)N(Ar)(CO)O\}]$; the double CO_2 activation reaction leading to these compounds was the first example for any transition metal imide [10]. To develop this promising line of study, we more recently [11] reported complexes of the type $[Ti(NR)\{Me_3SiNC(Ph)N(CH_2)_nNMe_2\}Cl]$ ($n = 2$ or 3, $R = tBu$ or aryl, **IV**) containing pendant amino donor groups. These form better defined compounds in solu-

tion (i.e. do not engage in temperature-dependent dynamic equilibria) as compared with **I/II**. Furthermore, the pendant NMe_2 donor group of the $Me_3SiNC(Ph)N(CH_2)_nNMe_2$ ancillary ligands in **IV** might, in principle, dissociate in solution (or during the course of a reaction) to form a more reactive, lower coordination number metal centre (an approach we have used with considerable success in other N -donor ligand supported imidotitanium systems **2b**). We therefore anticipated that replacement of the chloride ligand in certain of the compounds $[Ti(NR)\{Me_3SiNC(Ph)N(CH_2)_nNMe_2\}Cl]$ (**IV**) would provide interesting and well-defined metal complexes for the further study of imidotitanium chemistry. An investigation of this possibility is the subject of our present contribution [12].

2. Results and discussion

2.1. Syntheses

The starting compounds $[Ti(NR)\{Me_3SiNC(Ph)NCH_2CH_2CH_2NMe_2\}Cl]$ ($R = tBu$ **1** or 2,6- $C_6H_3Me_2$ (**8**)) and $[Ti(N^iBu)\{Me_3SiNC(Ph)NCH_2CH_2NMe_2\}Cl]$ (**6**) were prepared as previously-described [11] by reaction of $[Ti(NR)Cl_2(py)_3]$ [13] with the corresponding lithiated amidinates $Li\{Me_3SiNC(Ph)NCH_2CH_2CH_2NMe_2\}$ [14] and $Li\{Me_3SiNC(Ph)NCH_2CH_2NMe_2\}$ [15]. We have focussed most of our efforts on the 3-carbon pendant arm systems **1** and **8** since previous studies [11] showed these are the most easily handled and give rise to fewer unwanted side-reactions.

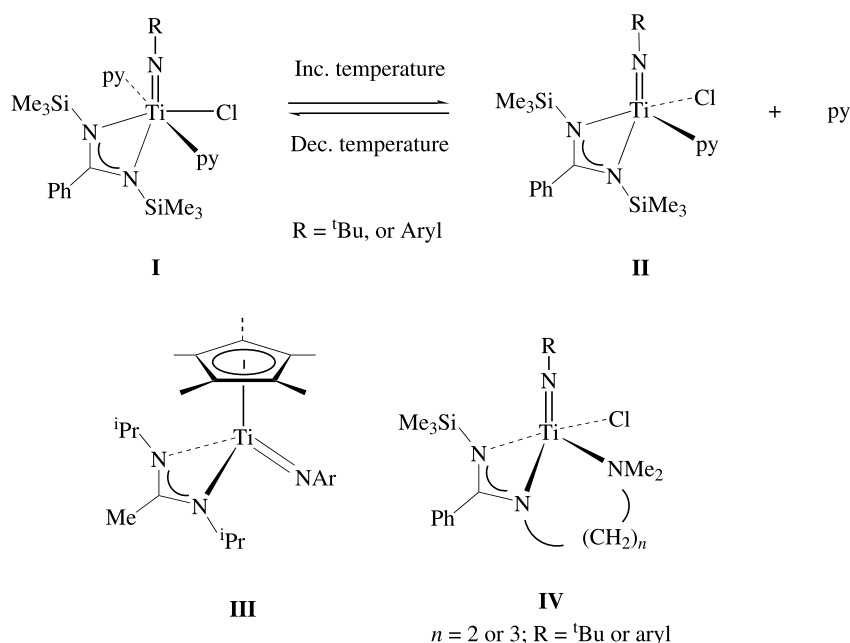


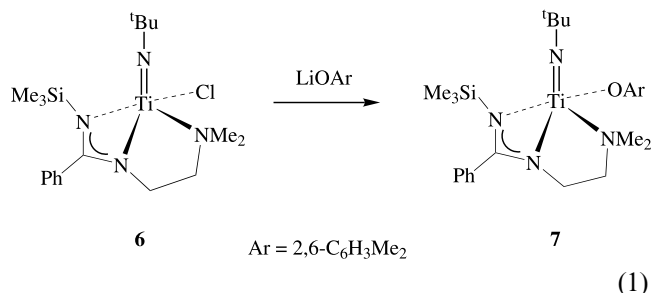
Chart 1.

MeLi in C_6D_6 on an NMR tube scale gave clean conversion to the methyl derivative $[Ti(N^tBu)\{Me_3SiNC(Ph)NCH_2CH_2CH_2NMe_2\}Me]$ (**3**) as judged by 1H -NMR spectroscopy. In addition to resonances for the *tert*-butyl and $Me_3SiNC(Ph)NCH_2CH_2CH_2NMe_2$ groups a further singlet at 0.79 (relative integral 3H) was reproducibly observed. The compound did not appear to be especially light- or temperature-sensitive in solution, but attempts to scale up the reaction on a preparative scale were unsuccessful (see, however, the successful synthesis of the arylimido homologue **9** below). Reaction of **1** with $LiCH_2SiMe_3$ in C_6D_6 gave a complex mixture. This was particularly disappointing since we had previously found **8a** that the analogous reaction of $[Ti(N^tBu)\{PhC(NSiMe_3)_2\}Cl(py)_2]$ gave reasonable yields of crystallographically characterised $[Ti(N^tBu)\{PhC(NSiMe_3)_2\}(CH_2SiMe_3)(py)]$.

Reaction of **1** with $LiN(SiMe_3)_2$ gave $[Ti(N^tBu)\{Me_3SiNC(Ph)NCH_2CH_2CH_2NMe_2\}\{N(SiMe_3)_2\}]$ (**4**) as a highly soluble, yellow crystalline solid. It was not wholly possible to recrystallise **4** away from impurities which evidently possess similar solubility characteristics. However, resonances for the *tert*-butyl and amidinate moieties in **4** were similar to those found for **2** and **3**. The bulky $N(SiMe_3)_2$ substituent appeared as two singlets (relative intensity 9H each) in the 1H -NMR spectrum, consistent with restricted rotation about the Ti–N bond.

To establish structurally that Cl-substitution products of **1** possess the geometries proposed in Scheme 1, the comparatively stable aryloxy derivative $[Ti(N^tBu)\{Me_3SiNC(Ph)NCH_2CH_2CH_2NMe_2\}(O-2,6-C_6H_3Me_2)]$ (**5**) was prepared. Thus reaction of **1** with $LiO-2,6-C_6H_3Me_2$ in toluene followed by recrystallisation from hexanes afforded yellow crystalline **5** in 63% isolated yield. The compound **5** has been crystallographically characterised (see below) and this confirmed the structure proposed in Scheme 1. The NMR data for the $\{Ti(N^tBu)(Me_3SiNC(Ph)NCH_2CH_2CH_2NMe_2)\}$ moiety of **5** are analogous to those of the organometallic homologues **2** and **3**. Additional resonances for a 2,6- $C_6H_3Me_2$ moiety are also observed, the methyl and *meta* ring protons of which appear as four individual signals. This evidence of restricted rotation about the Ti–O bond on the NMR timescale indicates that the coordination environment around titanium in **5** (as also found in **4** above) is in fact quite crowded. The corresponding benzamidinate compound without a pendant arm, namely $[Ti(N^tBu)\{PhC(NSiMe_3)_2\}(O-2,6-C_6H_3Me_2)(py)]$ **8a**, did not exhibit evidence for an analogous restricted rotation at room temperature (although the 2,6-di-*tert*-butyl homologue $[Ti(N^tBu)\{PhC(NSiMe_3)_2\}(O-2,6-C_6H_3^tBu_2)(py)]$ did) (Eq. (1)).

Speculating that the greater steric crowding associated with the $Me_3SiNC(Ph)NCH_2CH_2CH_2NMe_2$ ligand might be contributing to the instability of some of the



products we investigated certain chloride substitution reactions of the corresponding 2-carbon pendant arm system $[Ti(N^tBu)\{Me_3SiNC(Ph)NCH_2CH_2NMe_2\}Cl]$ (**6**) [11]. Reaction of **6** with $LiO-2,6-C_6H_3Me_2$ (Eq. (1)) gave $[Ti(N^tBu)\{Me_3SiNC(Ph)NCH_2CH_2NMe_2\}(O-2,6-C_6H_3Me_2)]$ (**7**) as a yellow crystalline material in 25% recrystallised yield. The NMR resonances for the $Ti(N^tBu)\{Me_3SiNC(Ph)NCH_2CH_2NMe_2\}$ moiety in **7** are comparable to those of **6**. The *ortho* methyl groups in the room temperature 1H and ^{13}C spectra of **7** appear as a single resonances (the *meta* ring protons and carbons could not be clearly assigned due to overlap with resonances from the amidinate phenyl group). Thus restricted rotation about the Ti–O bond of **7** at room temperature (at the same spectrometer field as for **5**) is not observed, possibly implying that the coordination environment about titanium in **7** is not as crowded as that in **5**. Unfortunately, reaction of **6** with MeLi or PhLi both failed to give rise to isolable products, although the NMR tube scale reaction with MeLi looked fairly promising (just as for **1**).

Certain comparative reactions of the arylimido compound $[Ti(N-2,6-C_6H_3Me_2)\{Me_3SiNC(Ph)NCH_2CH_2CH_2NMe_2\}Cl]$ (**8**) [11] were investigated (Scheme 1). NMR tube scale reactions with PhLi in C_6D_6 gave complex mixtures, but with MeLi in cold Et_2O the methyl derivative $[Ti(N-2,6-C_6H_3Me_2)\{Me_3SiNC(Ph)NCH_2CH_2CH_2NMe_2\}Me]$ (**9**) was obtained as brown, thermally sensitive solid in 50% isolated yield. The NMR spectra for **9** are consistent with the structure proposed in Scheme 1. Notably, the titanium-bound methyl group appears at 0.95 ppm in the 1H -NMR spectrum (38.20 in the ^{13}C spectrum) which is comparable to that for $[Ti(N^tBu)\{Me_3SiNC(Ph)NCH_2CH_2CH_2NMe_2\}Me]$ (**3**), i.e. 0.79 ppm.

For comparative purposes the reaction of **8** with $LiO-2,6-C_6H_3Me_2$ was carried out. This afforded $[Ti(N-2,6-C_6H_3Me_2)\{Me_3SiNC(Ph)NCH_2CH_2CH_2NMe_2\}(O-2,6-C_6H_3Me_2)]$ (**10**) as an orange solid in 63% yield. The solid state structure has been determined (see below) and confirms that illustrated in Scheme 1. As for **7** (and in contrast to that found for **5**) there is no evidence for

restricted rotation about the Ti–O bond on the NMR timescale at room temperature.

2.2. X-ray structures

The molecular structures of $[\text{Ti}(\text{N}^t\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\{\text{O}-2,6\text{-C}_6\text{H}_3\text{Me}_2\}]$ (**5**) and $[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3\text{Me}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\{\text{O}-2,6\text{-C}_6\text{H}_3\text{Me}_2\}]$ (**10**) are shown in Figs. 1 and 2, and selected bond distances and angles are presented in Table 1. For comparison, corresponding values for $[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3\text{Me}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**8**) [11] are also listed.

Molecules of **5** and **10** possess monomeric, five-coordinate structures in the solid state. All three nitrogens of the $\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2$ ligands are firmly coordinated to titanium with similar Ti–N distances to those found previously in the chloride analogues $[\text{Ti}(\text{N}-2,6\text{-C}_6\text{H}_3\text{R}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (R = Me **8** or ^tPr) [11]. The N(3) and N(4) atoms are approximately sp^2 hybridised as indicated by their approximately trigonal planar geometry (the sums of the angles subtended at the N(3) and N(4) atoms lie in the range $353.8(4)$ – $358.7(5)^\circ$). The Ti–N distances to the amidinate ligand are significantly longer for **5** than for **10** as expected based on the better donor ability of *tert*-butylimido ligands compared to their arylimido homologues [16,12b,13].

While the geometry at Ti(1) in **5** and **10** may be reasonably well described as distorted square base pyramidal (with N(1) occupying the axial position), that of **10** is somewhat closer to trigonal bipyramidal

with N(1), O(1) and N(3) formally occupying the equatorial positions. Clearly both structures are constrained by the chelating amidinate ligand and inherently small bite angle of the N_2CPh moiety. Four five-coordinate, crystallographically characterised arylimido-titanium compounds containing two monodentate aryloxy ligands and two Lewis base donor atoms have been described previously [17–19]. Two of these [18,19] feature bidentate Lewis base donors and are thus somewhat constrained. The other two are of the type $[\text{Ti}(\text{NAr})(\text{OAr})_2(\text{L})_2]$ (Ar = phenyl or 2,6-disubstituted phenyl; L = pyridine or substituted pyridine) and possess well-defined trigonal bipyramidal geometries with $\text{ArN}=\text{Ti}-\text{O}$ angles of ca. 113 – 114° and $\text{ArN}=\text{Ti}-\text{L}$ angles of ca. 96 – 99° . The compounds **5** and **10** are the first structurally characterised imidotitanium compounds featuring only one aryloxy ancillary ligand.

Turning now to the Ti = NR and Ti–OAr units, it is interesting to note the significant differences between the two Ti = NR distances for R = ^tBu (1.6991(15) Å) and R = 2,6- $\text{C}_6\text{H}_3\text{Me}_2$ (1.756(2) Å), and the two Ti–OAr distances (1.8887(13) Å for **5**; 1.828(2) Å for **10**). The previously established ranges are as follows [16]: for terminal Ti = N ^tBu linkages the mean value is 1.702(18) Å with a range of 1.656(9)–1.738(4) Å; for terminal Ti = N-2,6- $\text{C}_6\text{H}_3\text{Me}_2$ linkages the mean value is 1.725(16) Å with a range of 1.695(8)–1.752(8) Å; for Ti–OAr linkages with two *ortho*-methyl (or sterically similar) substituents the mean value is 1.825(46) Å with a range of 1.735(7)–1.952(4) Å. For the four arylimido-titanium compounds containing two monodentate aryloxy ligands and two Lewis base donor atoms mentioned

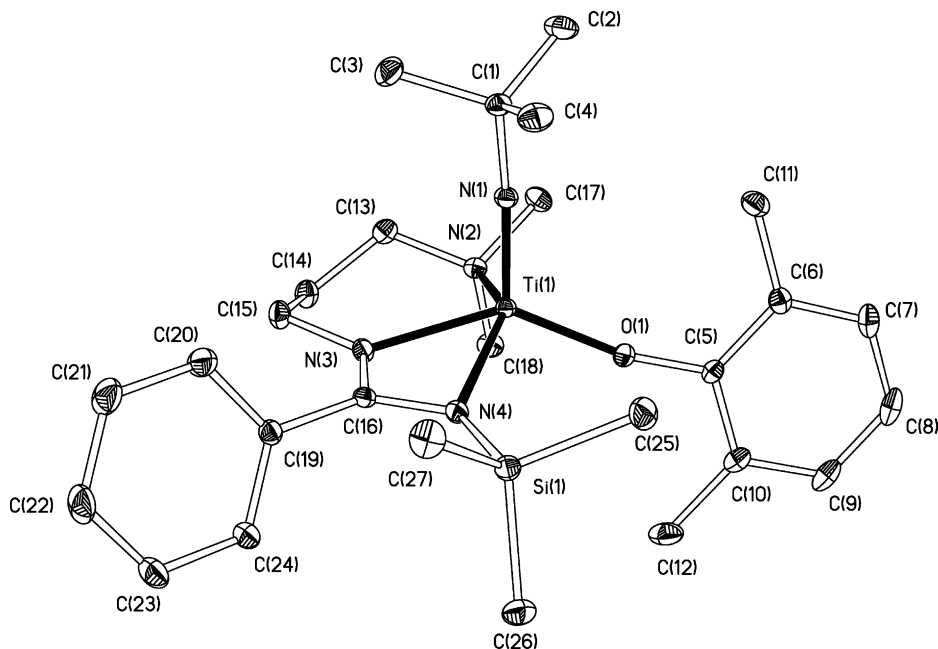


Fig. 1. Molecular structure of $[\text{Ti}(\text{N}^t\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\{\text{O}-2,6\text{-C}_6\text{H}_3\text{Me}_2\}]$ (**5**). Displacement ellipsoids are drawn at the 20% probability level. H atoms omitted for clarity.

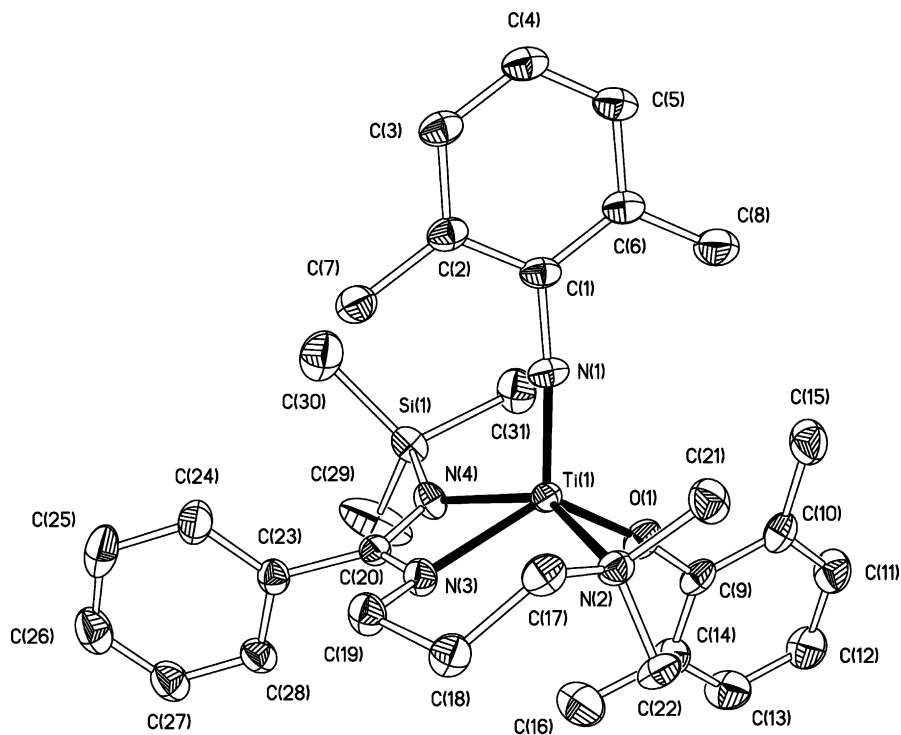


Fig. 2. Molecular structure of $[\text{Ti}(N\text{-}2,6\text{-C}_6\text{H}_3\text{Me}_2)\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\{\text{O-}2,6\text{-C}_6\text{H}_3\text{Me}_2\}]$ (**10**). Displacement ellipsoids are drawn at the 20% probability level. H atoms and hexane molecule of crystallisation omitted for clarity.

above the average $\text{Ti}=\text{NAr}$ distance is 1.721(4) (range 1.709(5)–1.734(4) Å) and the average $\text{Ti}-\text{OAr}$ distance is 1.882(9) (range 1.853(4)–1.932(3) Å). The angles subtended at N(1) and O(1) are approximately linear for these four compounds and for **5** and **10**, indicating that in all instances these atoms are effectively *sp* hybridised and the imido and aryloxo groups can, in principle, donate four or five electrons respectively to titanium [12b,20], subject to orbital availability. While the actual $\text{Ti}=\text{NR}$ and $\text{Ti}-\text{OAr}$ distances in **5** and **10** lie (within error) within the previously determined general ranges of values, there is an unexpectedly large difference between the $\text{Ti}=\text{NR}$ and $\text{Ti}-\text{OAr}$ distances between the two molecules. Furthermore, when specifically comparing the data for **10** with those for the previous four arylimidotitanium compounds containing two monodentate aryloxo ligands, the $\text{Ti}=\text{NAr}$ distance appears to be surprisingly long and $\text{Ti}-\text{OAr}$ rather short. Although it is perhaps not surprising that a longer $\text{Ti}=\text{NR}$ distance might be correlated with a shorter $\text{Ti}-\text{OAr}$ (since both NR and OAr groups are π -donors and potentially in competition for available d_π acceptor orbitals), it is not clear *why* the $\text{Ti}=\text{NAr}$ distance is so comparatively long and $\text{Ti}-\text{OAr}$ so short in **10**, especially since most other features of **10** are comparable with those of **5** and **8**. There appear to be no adverse intra- or inter-molecular contacts.

3. Experimental

3.1. Literature preparations

The compounds $[\text{Ti}(\text{NR})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ ($\text{R} = \text{tBu}$ **1** or 2,6- $\text{C}_6\text{H}_3\text{Me}_2$ **8**) and $[\text{Ti}(\text{N}^t\text{Bu})\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2\}\text{Cl}]$ (**6**) were prepared as reported previously [11].

3.2. General methods and instrumentation

All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon or of dinitrogen. Solvents were predried over activated 4 Å molecular sieves and were refluxed over appropriate drying agents under a dinitrogen atmosphere and collected by distillation. Deuterated solvents were dried over appropriate drying agents, distilled under reduced pressure, and stored under dinitrogen in Teflon valve ampoules. NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ^1H -, $^{13}\text{C}\{^1\text{H}\}$ -, and ^{13}C -spectra were recorded on Varian Unity Plus 500 and Varian Mercury spectrometers. ^1H and ^{13}C assignments were confirmed when necessary with the use of nOe, DEPT-135, DEPT-90, DEPT-45, and two-dimensional ^1H - ^1H and ^{13}C - ^1H -NMR experiments. All spectra were

Table 1

Comparison of selected bond distances (Å) and angles (°) for [Ti(N^tBu){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}(O-2,6-C₆H₃Me₂)] (**5**) and [Ti(N-2,6-C₆H₃Me₂){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}(O-2,6-C₆H₃Me₂)] (**10**)

	5	10	[8]
<i>Bond lengths</i> ^a			
Ti(1)–N(1)	1.6991(15)	1.756(2)	[1.713(1)]
Ti(1)–N(2)	2.2548(15)	2.235(2)	[2.223(1)]
Ti(1)–N(3)	2.1081(15)	2.084(2)	[2.080(1)]
Ti(1)–N(4)	2.1531(15)	2.119(2)	[2.124(1)]
Ti(1)–O(1)	1.8887(13)	1.828(2)	[–]
N(4)–CPh	1.336(2)	1.319(3)	[1.337(2)]
N(1)–C(1)	1.446(2)	1.383(3)	[1.377(2)]
O(1)–CAr	1.337(2)	1.352(3)	[–]
N(4)–Si(1)	1.7294(15)	1.730(2)	[1.734(1)]
N(3)–CPh	1.320(2)	1.320(3)	[1.316(2)]
<i>Bond angles</i> ^a			
N(1)–Ti(1)–O(1)	115.90(7)	118.75(12)	[–]
N(1)–Ti(1)–N(2)	100.81(7)	96.78(9)	[98.13(4)]
N(1)–Ti(1)–N(3)	105.61(7)	113.99(11)	[110.09(5)]
N(1)–Ti(1)–N(4)	105.36(7)	103.5(1)	[104.53(4)]
N(2)–Ti(1)–N(3)	81.55(6)	82.65(8)	[83.16(4)]
N(2)–Ti(1)–N(4)	140.02(6)	144.82(8)	[144.58(4)]
N(3)–Ti(1)–O(1)	138.45(6)	127.17(11)	[–]
N(3)–Ti(1)–N(4)	62.69(6)	62.94(9)	[63.71(4)]
Ti(1)–N(1)–C(1)	171.93(13)	174.5(2)	[178.58(9)]
Ti(1)–O(1)–CAr	167.84(12)	170.3(2)	[–]
Ti(1)–N(3)–CH ₂	136.65(12)	140.8(5)	[138.75(8)]
Ti(1)–N(3)–CPh	92.16(11)	92.88(16)	[92.26(7)]
CPh–N(3)–CH ₂	124.95(16)	124.3(2)	[125.4(1)]
Ti(1)–N(4)–CPh	89.8(1)	91.35(16)	[89.77(7)]
Ti(1)–N(4)–Si(1)	135.11(8)	134.03(12)	[129.04(6)]
Si(1)–N(4)–CAr	132.13(13)	133.3(2)	[131.58(8)]
N(4)–CPh–N(3)	113.22(15)	112.6(2)	[113.5(1)]

For comparison, the corresponding values for previously reported [**11**] [Ti(N-2,6-C₆H₃Me₂){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Cl] (**8**) are given in brackets.

^a For **5** the generic labels CPh, CAr and CH₂ refer to C(16), C(5) and C(15), respectively in Fig. 1. For **10** CPh, CAr and CH₂ refer to C(20), C(9) and C(19), respectively in Fig. 2.

referenced internally to residual protio-solvent (¹H) or solvent (¹³C) resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm). Chemical shifts are quoted in δ (ppm) and coupling constants in hertz. Infrared spectra were prepared as Nujol mulls between NaCl plates and were recorded on Perkin–Elmer 1600 and 1700 series spectrometers. Infrared data are quoted in wavenumbers (cm⁻¹). Mass spectra were recorded by the mass spectrometry service of the University of Oxford's Inorganic Chemistry Laboratory. Combustion analyses were recorded by the analytical services of the University of Oxford's Inorganic Chemistry Laboratory. Despite repeated recrystallisations, several of the compounds gave consistently low elemental analyses for %N and/or %C, consistent with incomplete combustion (nitride/carbide formation) [21].

3.3. [Ti(N^tBu){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}-Ph] (**2**)

To a stirred solution of [Ti(N^tBu){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Cl] (0.41 g, 9.50 × 10⁻⁴ mol) in Et₂O (15 ml) at -80 °C was added a solution of PhLi (0.10 g, 1.20 × 10⁻³ mol) in Et₂O (15 ml) dropwise over 15 min. The resulting yellow solution was stirred at room temperature (r.t.) for 30 min. Volatiles were removed under reduced pressure and the resulting black solid was extracted into benzene (20 ml). The black/brown product was triturated with pentane (30 ml) and dried in vacuo. Yield: 0.29 g, (68%).

¹H-NMR (C₆D₆, 300.1 MHz, 293 K): 8.31 (2H, d, ³J = 6.5 Hz, *o*-TiPh), 7.46 (1H, t, ³J = 7.6 Hz, *p*-TiPh), 7.33 (2H, m, *m*-TiPh), 7.42–7.06 (5H, overlapping m, PhCN₂), 3.05–2.82 (3H, overlapping m, 2 × CN₂CH₂, CH₂NMe₂), 2.65 (3H, s, NMe), 1.82 (1H, m, CH₂NMe₂), 1.68 (3H, s, NMe), 1.41 (9H, s, CMe₃), 1.34 (1H, m, CH₂CH₂CH₂), 1.02 (1H, m, CH₂CH₂CH₂), -0.11 (s, 9H, SiMe₃). ¹³C{¹H}-NMR (C₆D₆, 75.0 MHz, 293 K): 187.10 (CN₂), 175.20 (*ipso*-TiPh), 137.05 (*o*-TiPh), 136.77 (*ipso*-PhCN₂), 128.59, 128.50, 128.43, 127.76, 126.91, 126.53, 126.31 (9C, partially obscured by solvent, TiPh, PhCN₂), 69.23 (CMe₃), 61.79 (CH₂NMe₂), 52.04 (NMe), 47.02 (CN₂CH₂), 43.71 (NMe), 33.59 (CMe₃), 25.82 (CH₂CH₂CH₂), 2.21 (SiMe₃). IR (Nujol mull, NaCl plates): 2726 (w), 1944(w), 1578 (w), 1506 (w), 1344 (s), 1299 (m), 1248 (s), 1206 (m), 1153 (w), 1130 (w), 1104 (m), 1061 (m), 1017 (m), 979 (s), 946 (m), 918 (s), 898 (m), 857 (w), 838 (m), 820 (w), 783 (m), 766 (w), 722 (w), 702 (m), 648 (s). Accurate mass EI-MS for [Ti(N^tBu){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Ph]⁺. Found: (Calc. for C₂₅H₄₀N₄TiSi): *m/z* = 472.2508 (472.2502). Anal. Found: (Calc. for C₂₅H₄₀N₄TiSi): C 60.4 (63.5), H 9.1 (8.5), N 11.7 (11.9)%

3.4. [Ti(N^tBu){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}-Me] (**3**; NMR tube scale synthesis)

A solution of [Ti(N^tBu){Me₃SiNC(Ph)NCH₂CH₂CH₂NMe₂}Cl] (6.0 mg, 1.40 × 10⁻⁵ mol) in C₆D₆ (0.5 ml) in a 5 mm NMR tube was treated with ca. one equivalent of 1.6 M solution of MeLi in Et₂O. The ¹H-NMR spectrum showed formation of **3** as the dominant product.

¹H-NMR (C₆D₆, 300.2 MHz, 293 K) 7.21–7.02 (5H, overlapping m, PhCN₂), 3.03–2.80 (3H, overlapping m, 2 × CN₂CH₂, CH₂NMe₂), 2.66 (3H, s, NMe), 2.04–1.91 (3H, overlapping m, CH₂NMe₂, 2 × CH₂CH₂CH₂), 1.39 (9H, s, CMe₃), 0.79 (3H, s, TiMe), 0.22 (9H, s, SiMe₃).

3.5. $[Ti(N^tBu)\{Me_3SiNC(Ph)NCH_2CH_2CH_2NMe_2\}-\{N(SiMe_3)_2\}]$ (4)

To a stirred solution of $[Ti(N^tBu)\{Me_3SiNC(Ph)NCH_2CH_2CH_2NMe_2\}Cl]$ (0.34 g, 7.87×10^{-4} mol) in benzene (20 ml), was added a solution of $LiN(SiMe_3)_2$ (0.13 g, 7.87×10^{-4} mol) in benzene (20 ml) dropwise over 20 min. The yellow solution was heated at 50 °C for 30 h. Volatiles were removed under reduced pressure and the yellow solid was extracted into benzene (15 ml). The dark yellow solid was recrystallised from hexane (30 ml) at -80 °C and washed with 3×10 ml cold hexane yielding an orange solid which was dried in vacuo. Yield: 0.13 g (30%).

1H -NMR (C_6D_6 , 300.1 MHz, 293 K): 7.56–7.01 (5H, overlapping m, $PhCN_2$), 2.97–2.79 (3H, overlapping m, $2 \times CN_2CH_2$, CH_2NMe_2), 2.72 (3H, s, NMe), 2.03 (3H, s, NMe), 1.82 (1H, m, CH_2NMe_2), 1.31 (9H, s, CMe_3), 1.31–1.22 (2H, overlapping m, $CH_2CH_2CH_2$), 0.78 (9H, s, $N(SiMe_3)_2$), 0.35 (9H, s, $N(SiMe_3)_2$), 0.29 (9H, s, $PhCNSiMe_3$). $^{13}C\{^1H\}$ -NMR (C_6D_6 , 75.0 MHz, 293 K): 176.36 (CN_2), 137.13 (*ipso-PhCN*), 129.4, 128.32, 127.67, 126.61 ($PhCN_2$), 69.73 (CMe_3), 63.57 (CN_2CH_2), 54.66 (NMe), 48.01 (CH_2NMe_2), 47.11 (NMe), 33.21 (CMe_3), 25.52 ($CH_2CH_2CH_2$), 8.22 ($N(SiMe_3)_2$), 1.36 (overlapping $N(SiMe_3)_2$ and $PhCNSiMe_3$). IR (Nujol mull, NaCl plates): 4331 (m), 4257 (m), 3061 (m), 2786 (s), 2765 (m), 2723 (m), 2680 (m), 2361 (w), 2342 (w), 2206 (w), 2132 (w), 2092 (w), 1947 (w), 1884 (w), 1808 (w), 1636 (m), 1603 (m), 1577 (s), 1509 (s), 1485 (s), 1456 (s), 1365 (s), 1347 (m), 1311 (s), 1300 (m), 1260 (m), 1245 (s), 1205 (s), 1153 (s), 1099 (w), 1062 (w), 1017 (m), 983 (m), 932 (s), 920 (m), 901 (s), 868 (s), 839 (s), 803 (s), 785 (s), 760 (m), 722 (s), 672 (m). Anal. Found: (Calc. for $C_{25}H_{53}N_5TiSi_3$): C 49.2 (54.0), H 8.9 (9.6), N 10.0 (12.6)%.

3.6. $[Ti(N^tBu)\{Me_3SiNC(Ph)NCH_2CH_2CH_2NMe_2\}-\{O-2,6-C_6H_3Me_2\}]$ (5)

To a stirred solution of $[Ti(N^tBu)\{Me_3SiNC(Ph)NCH_2CH_2CH_2NMe_2\}Cl]$ (0.55 g, 1.29×10^{-3} mol) in toluene (20 ml), was added a solution of $LiO-2,6-C_6H_3Me_2$ (0.16 g, 1.29×10^{-3} mol) in toluene (40 ml) dropwise over 15 min. The resulting yellow solution was stirred at r.t. for 2 h. Volatiles were removed under reduced pressure, and the resultant yellow solid was extracted into hexane (50 ml). The yellow solid was recrystallised from hexane (20 ml) at -80 °C, washed with 5×10 -ml cold hexane and dried in vacuo. Yield: 0.41 g (63%).

1H -NMR (CD_2Cl_2 , 500.0 MHz, 233 K): 7.50–7.29 (5H, overlapping m, $PhCN_2$), 7.03 (1H, d, $J = 7.08$ Hz, *m-C* $_6H_3Me_2$), 6.93 (1H, d, $^2J = 6.51$ Hz, *m-C* $_6H_3Me_2$), 6.57 (1H, m, *p-C* $_6H_3Me_2$), 3.63 (1H, m, CH_2NMe_2), 3.38–3.24 (2H, overlapping m, CN_2CH_2), 2.87 (3H, s,

NMe), 2.68 (3H, s, $C_6H_3Me_2$), 2.55 (1H, m, CH_2NMe_2), 2.13 (3H, s, $C_6H_3Me_2$), 1.94 (3H, s, NMe), 1.89 (1H, m, $CH_2CH_2CH_2$), 1.59 (1H, m, $CH_2CH_2CH_2$), 1.00 (9H, s, CMe_3), -0.38 (9H, s, $SiMe_3$). $^{13}C\{^1H\}$ -NMR (CD_2Cl_2 , 125.0, MHz, 233 K): 173.87 (CN_2), 160.72 (*ipso-C* $_6H_3Me_2$), 135.93 (*ipso-PhCN*), 128.28, 128.19, 127.91, 127.81, 127.50, 127.08, 126.14, 126.08, 125.51 (9C $PhCN_2$ and $C_6H_3Me_2$), 116.43 (*p-C* $_6H_3Me_2$), 68.06 (CMe_3), 62.69 (CH_2NMe_2), 51.65 (NMe), 47.07 (CN_2CH_2), 43.74 (NMe), 32.59 (CMe_3), 25.49 ($CH_2CH_2CH_2$), 18.21 ($C_6H_3Me_2$), 17.09 ($C_6H_3Me_2$), 0.81 ($SiMe_3$). IR (Nujol mull, NaCl plates): 2726 (m), 2684 (w), 2588 (w), 2360 (m), 2342 (m), 2250 (w), 2098 (w), 1942 (w), 1892 (w), 1832 (w), 1804 (w), 1590 (s), 1576 (m), 1506 (s), 1364 (m), 1348 (s), 1294 (s), 1250 (s), 1236 (s), 1208 (m), 1178 (w), 1150 (w), 1128 (w), 1110 (m), 1090 (m), 1062 (m), 1016 (m), 980 (m), 948 (m), 918 (m), 908 (s), 902 (s), 860 (m), 838 (s), 820 (m), 806 (w), 782 (m), 760 (s), 742 (w), 718 (m), 698 (s), 628 (w), 596 (w). Anal. Found: (Calc. for $C_{27}H_{44}N_4OTiSi$): C 62.1 (62.8), H 8.7 (8.6), N 10.4 (10.8)%.

3.7. $[Ti(N^tBu)\{Me_3SiNC(Ph)NCH_2CH_2NMe_2\}-\{O-2,6-C_6H_3Me_2\}]$ (7)

To a stirred solution of $[Ti(N^tBu)\{Me_3SiNC(Ph)NCH_2CH_2NMe_2\}Cl]$ (0.41 g, 8.8×10^{-4} mol) in toluene (15 ml) was added a solution of $LiO-2,6-C_6H_3Me_2$ (0.14 g, 8.8×10^{-4} mol) in toluene (30 ml) dropwise over 15 min. The yellow solution was stirred at r.t. for 16 h. Volatiles were removed under reduced pressure, and the resulting orange–brown solid was extracted into benzene (30 ml). The yellow solid was recrystallised from hexane (25 ml) at -80 °C and washed with 5×10 ml cold hexane. Yield: 0.11 g (25%).

1H -NMR (C_6D_6 , 500.0 MHz, 293 K): 7.23–7.19 (4H, overlapping m, $PhCN_2$ and *m-C* $_6H_3Me_2$), 7.04–7.03 (3H, overlapping m, $PhCN_2$ and *m-C* $_6H_3Me_2$), 6.88 (1H, t, $^2J = 7.3$ Hz, *p-C* $_6H_3Me_2$), 3.25 (1H, overlapping m, CN_2CH_2), 2.70 (1H, overlapping m, CN_2CH_2), 2.62 (3H, s, NMe), 2.61 (6H, s, $C_6H_3Me_2$), 2.12 (1H, m, CH_2NMe_2), 1.80 (3H, s, NMe), 1.77 (1H, m, CH_2NMe_2), 1.32 (s, 9H, CMe_3), 0.14 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ -NMR (C_6D_6 , 125.0 MHz, 293 K): 174.06 (CN_2), 161.70 (*ipso-C* $_6H_3Me_2$), 136.03 (*ipso-PhCN*), 129.68, 128.52, 125.50, 127.68, 126.54 ($PhCN_2$ and $C_6H_3Me_2$), 118.25 (*p-C* $_6H_3Me_2$), 68.39 (CMe_3), 63.11 (CN_2CH_2), 49.49 (NMe), 46.88 (CH_2NMe_2), 45.20 (NMe), 33.57 (CMe_3), 18.50 ($C_6H_3Me_2$), 2.32 ($SiMe_3$). IR (Nujol mull, NaCl plates): 4331 (m), 4258 (m), 4065 (w), 2727 (m), 2361 (m), 2342 (w), 1950 (w), 1889 (w), 1828 (w), 1771 (w), 1592 (m), 1505 (m), 1405 (m), 1349 (s), 1330 (m), 1290 (m), 1262 (m), 1249 (s), 1232 (s), 1207 (m), 1159 (w), 1126 (m), 1090 (s), 1063 (w), 1025 (s), 947 (m), 934 (m), 919 (m), 892 (s), 868 (s), 840 (s), 820 (m), 805 (m), 759 (s), 740 (w), 723 (m), 703 (m), 669 (w), 629

(w). Anal. Found: (Calc. for $C_{26}H_{45}N_4TiOSi$): C 58.2 (61.8), H 8.4 (9.0), N 9.6 (11.1)%.

3.8. $[Ti(N-2,6-C_6H_3Me_2)\{Me_3SiNC(Ph)NCH_2CH_2CH_2NMe_2\}Me]$ (**9**)

To a stirred solution of $[Ti(N-2,6-C_6H_3Me_2)\{Me_3SiN(Ph)NCH_2CH_2CH_2NMe_2\}Cl]$ (0.36 g, 7.57×10^{-4} mol) in Et_2O (40 ml) at $-80^\circ C$ was added 1.6M MeLi/ Et_2O solution (0.47 ml, 7.57×10^{-4} mol) over 15 min. The resulting orange solution was stirred at $-80^\circ C$ for 15 min before being allowed to warm to r.t. over 20 min. Volatiles were removed under reduced pressure, and the resulting brown solid extracted into benzene (25 ml). The resulting solid was triturated with pentane (25 ml) to give a brown solid. Yield: 0.17 g (50%).

1H -NMR (C_6D_6 , 300.0 MHz, 293 K): 7.21–7.06 (7H, overlapping m, $C_6H_3Me_2$, $PhCN_2$), 6.80 (1H, t, $^2J = 7.32$ Hz, $p-C_6H_3Me_2$), 2.87 (6H, s, $C_6H_3Me_2$), 2.85–2.73 (2H, overlapping m, $2 \times CN_2CH_2$), 2.33 (3H, s, NMe), 2.32 (1H, m, CH_2NMe_2), 2.01 (3H, s, NMe), 1.82 (1H, m, CH_2NMe_2), 1.31–1.09 (2H, overlapping m, $2 \times CH_2CH_2CH_2$), 0.95 (3H, s, $TiMe$), 0.11 (9H, s, $SiMe_3$). ^{13}C -NMR (C_6D_6 , 75.0, MHz, 293 K): 177.55 (CN_2), 159.66 (*ipso*- $C_6H_3Me_2$), 136.25 (*ipso*- $PhCN_2$), 132.09 ($C_6H_3Me_2$), 129.01, 128.63, 128.29, 127.80 ($PhCN_2$), 127.47 ($C_6H_3Me_2$), 119.14 ($p-C_6H_3Me_2$), 61.18 (CH_2NMe_2), 50.54 (NMe), 46.88 (NMe), 45.76 (CN_2CH_2), 38.20 ($TiMe$), 20.20 ($C_6H_3Me_2$), 1.96 ($SiMe_3$). IR (Nujol mull, NaCl plates): 4330 (m), 4257 (m), 2726 (m), 1588 (m), 1505 (m), 1345 (m), 1316 (s), 1262 (m), 1247 (m), 1226 (w), 1205 (w), 1173 (m), 1153 (m), 1093 (s), 1063 (s), 1016 (m), 981 (w), 949 (w), 918 (m), 897 (s), 839 (m), 820 (s), 785 (m), 756 (s), 741 (w), 723 (m), 701 (m). Anal. Found: (Calc. for $C_{24}H_{38}N_4TiSi$): C 61.3 (62.8), H 8.9 (8.4), 11.9 (12.2)%.

3.9. $[Ti(N-2,6-C_6H_3Me_2)\{Me_3SiNC(Ph)NCH_2CH_2CH_2NMe_2\}(O-2,6-C_6H_3Me_2)]$ (**10**)

To a stirred solution of $[Ti(N-2,6-C_6H_3Me_2)\{Me_3SiN(Ph)NCH_2CH_2CH_2NMe_2\}Cl]$ (0.56 g, 1.17×10^{-3} mol) in toluene (30 ml) was added a solution of LiO-2,6- $C_6H_3Me_2$ (0.15 g, 1.17×10^{-3} mol) in toluene (30 ml) dropwise over 15 min. The red brown solution became orange in colour and was stirred at r.t. for 16 h. Volatiles were removed under reduced pressure, and the resulting orange–brown solid was extracted into hexane (50 ml). The orange solid was recrystallised from hexane (15 ml) at $-80^\circ C$ and washed with 4×10 ml cold hexane. Yield: 0.10 g (63%).

1H -NMR (C_6D_6 , 500.0 MHz, 293 K): 7.26–7.05 (9H, overlapping m, $m-N-2,6-C_6H_3Me_2$, $m-O-2,6-C_6H_3Me_2$, $PhCN_2$), 6.86 (1H, t, $^2J = 7.32$ Hz, $p-N-2,6-C_6H_3Me_2$),

6.74 (1H, t, $^2J = 7.32$ Hz, $p-O-2,6-C_6H_3Me_2$), 3.12 (1H, m, CN_2CH_2), 2.95 (1H, m, CN_2CH_2), 2.86 (1H, m, CH_2NMe_2), 2.80 (6H, s, $N-2,6-C_6H_3Me_2$), 2.51 (6H, s, $O-2,6-C_6H_3Me_2$), 2.50 (3H, s, NMe), 1.76 (3H, s, NMe), 1.71 (1H, m, CH_2NMe_2), 1.25 (1H, m, $CH_2CH_2CH_2$), 1.04 (1H, m, $CH_2CH_2CH_2$), -0.08 (9H, s, $SiMe_3$). $^{13}C\{^1H\}$ -NMR (C_6D_6 , 125.0 MHz, 293 K): 175.93 (CN_2), 162.37 (*ipso* $N-2,6-C_6H_3Me_2$), 159.83 (*ipso* $O-2,6-C_6H_3Me_2$), 135.96 (*ipso* $PhCN_2$), 132.24 (*o*- $O-2,6-C_6H_3Me_2$), 129.10, 128.75, 128.61, 128.53, 127.48, 126.76, 126.41 (overlapping $m-O-2,6-C_6H_3Me_2$, $m-N-2,6-C_6H_3Me_2$, *o*- $N-2,6-C_6H_3Me_2$, $PhCN_2$), 119.56 (*p*- $O-2,6-C_6H_3Me_2$), 119.03 (*p*- $N-2,6-C_6H_3Me_2$), 61.97 (CH_2NMe_2), 52.06 (NMe), 45.89 (CH_2CN_2), 45.74 (NMe), 25.40 ($CH_2CH_2CH_2$), 20.44 ($N-2,6-C_6H_3Me_2$), 18.13 ($O-2,6-C_6H_3Me_2$), 1.68 ($SiMe_3$). IR (Nujol mull, NaCl plates) 2722 (w), 2678 (w), 2356 (w), 2340 (w), 1888 (w), 1732 (w), 1590 (m), 1344 (m), 1312 (m), 1276 (s), 1236 (s), 1208 (m), 1178 (w), 1152 (w), 1110 (m), 1092 (s), 1060 (m), 1026 (w), 1012 (m), 980 (s), 948 (w), 896 (s), 854 (m), 838 (m), 818 (w), 784 (m), 756 (s), 740

Table 2

X-ray data collection and processing parameters for $[Ti(N^iBu)\{Me_3SiNC(Ph)NCH_2CH_2CH_2NMe_2\}(O-2,6-C_6H_3Me_2)]$ (**5**) and $[Ti(N-2,6-C_6H_3Me_2)\{Me_3SiNC(Ph)NCH_2CH_2CH_2NMe_2\}(O-2,6-C_6H_3Me_2)] \cdot 0.5(C_6H_{14})$ (**10**· $0.5(C_6H_{14})$)

	5	10 · $0.5(C_6H_{14})$
Molecular formula	$C_{27}H_{44}N_4O_2SiTi$	$C_{31}H_{44}N_4O_2SiTi \cdot 0.5(C_6H_{14})$
Formula weight	516.66	607.80
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
Unit cell dimensions		
<i>a</i> (Å)	10.4590(2)	12.7710(2)
<i>b</i> (Å)	15.8439(3)	19.5990(3)
<i>c</i> (Å)	18.0981(4)	14.4818(3)
α (°)	97.3378(7)	99.2435(7)
<i>V</i> (Å ³)	2974.5	3577.7
<i>Z</i>	4	4
Absorption coefficient (mm ⁻¹)	0.352	0.302
Crystal description	Pale yellow block	Orange fragment
Crystal size (mm)	0.20 × 0.28 × 0.32	0.06 × 0.12 × 0.34
Reflections collected	26442	41144
Unique reflections	7024	8147
<i>R</i> _{int}	0.048	0.043
Observed reflections	4606	4733 [<i>I</i> > 3σ(<i>I</i>)]
Absorption correction	Semi-empirical	Semi-empirical
<i>T</i> _{min} , <i>T</i> _{max}	0.89, 0.93	0.90, 0.98
Number of parameters refined	307	388
Final <i>R</i> indices ^a	<i>R</i> ₁ = 0.0364 <i>wR</i> = 0.0407	<i>R</i> ₁ = 0.0507 <i>wR</i> = 0.0645
Largest residual Δ _p features (e Å ⁻³)	−0.27, 0.31	−0.30 and 0.43

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

(m), 722 (m), 626 (w), 566 (m). Anal. Found: (Calc. for $C_{31}H_{44}N_4OTiSi$): C 63.6 (65.9), H 8.2 (7.8), N 9.5 (9.9)%.

3.10. *Crystal structure determination of*
 $[Ti(N^tBu)\{Me_3SiNC(Ph)NCH_2CH_2CH_2NMe_2\}(O-2,6-C_6H_3Me_2)]$ (**5**) and $[Ti(N-2,6-C_6H_3Me_2)\{Me_3SiNC(Ph)NCH_2CH_2CH_2NMe_2\}(O-2,6-C_6H_3Me_2)] \cdot 0.5(C_6H_{14})$ (**10**·0.5(C_6H_{14}))

Crystal data collection and processing parameters are given in Table 2. Crystals were mounted on a glass fibre using perfluoropolyether oil and cooled rapidly to 150 K in a stream of cold N_2 using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using an Enraf–Nonius KappaCCD diffractometer (graphite–monochromated $Mo-K_{\alpha}$ radiation, $\lambda = 0.71073$ Å). Intensity data were processed using the DENZO-SMN package [22]. The structures were solved using SIR-92 [23], which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite [24]. Coordinates and anisotropic thermal parameters of most non-hydrogen atoms were refined (see below for treatment of **10**·0.5(C_6H_{14})). Hydrogen atoms were positioned geometrically after each cycle of refinement. Chebychev polynomial weighting schemes were applied.

Molecules of **10** were partially disordered: examination of difference Fourier maps after refinement of the preliminary non-H atom structure showed a number of relatively large peaks of electron density. Some of these were assigned as a hexane molecule disordered over two orientations related by a crystallographic centre of inversion; other peaks were assigned as the C atoms of a second orientation of the $NCH_2CH_2CH_2NMe_2$ group, related to the major orientation by reflection in the N_2Ti plane. Coordinates and isotropic thermal parameters were refined for the hexane, with C–C bond lengths restrained to 1.54(2) Å and C–C–C bond angles restrained to 112(2)°. Coordinates, site occupancies and anisotropic thermal parameters were refined for the major positions of the disordered ligand C atoms, whereas coordinates, site occupancies and isotropic thermal parameters were refined for the minor positions. Geometric similarity restraints were applied to the disordered fragment: bond lengths related by reflection in the N_2Ti plane were restrained to be within 0.01 Å of their common mean; related bond angles were restrained to be within 1° of their common mean.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC, No. 206510 for compound **5** and

No. 206511 for compound **10**. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

Acknowledgements

We thank the EPSRC for support.

References

- [1] For recent reviews and leading references see: (a) W.A. Nugent, J.M. Mayer, *Metal–Ligand Multiple Bonds*, New York, Wiley-Interscience, 1988; (b) D.E. Wigley, *Prog. Inorg. Chem.* 42 (1994) 239; (c) R.R. Schrock, *Acc. Chem. Res.* 23 (1990) 158; (d) P.R. Sharp, *Dalton Trans.* (2000) 2647; (e) V.C. Gibson, *Adv. Materials* 6 (1994) 37; (f) Special Theme Issue ‘Organometallic Chemistry with N and O π -donor ligands’ Guest Editor P. Mountford; *J. Organomet. Chem.* 591 (1999) 2–213.
- [2] See the following and references therein: (a) P. Mountford, *Chem. Commun.* (1997) 2127 (Feature Article); (b) L.H. Gade, P. Mountford, *Coord. Chem. Rev.* 216–217 (2001) 65; (c) D.J.M. Trösch, P.E. Collier, A. Bashall, L.H. Gade, M. McPartlin, P. Mountford, S. Radojevic, *Organometallics* 20 (2001) 3308; (d) S.A. Lawrence, M.E.G. Skinner, J.C. Green, P. Mountford, *Chem. Commun.* (2001) 705; (e) N. Adams, A.R. Cowley, S.R. Dubberley, A.J. Sealey, M.E.G. Skinner, P. Mountford, *Chem. Commun.* (2001) 2738; (f) A.J. Blake, P.E. Collier, L.H. Gade, J. Lloyd, P. Mountford, S.M. Pugh, M. Schubart, M.E.G. Skinner, D.J.M. Trösch, *Inorg. Chem.* 40 (2001) 870.
- [3] (a) V.R. Jensen, K.J. Børve, *Chem. Commun.* (2002) 543; (b) V.R. Jensen, K.J. Børve, *Organometallics* 20 (2001) 616.
- [4] M.P. Coles, C.I. Dalby, V.C. Gibson, I.R. Little, E.L. Marshall, M.H. Ribeiro da Costa, S. Mastroianni, *J. Organomet. Chem.* 591 (1999) 78.
- [5] B.D. Ward, E. Clot, S.R. Dubberley, L.H. Gade, P. Mountford, *Chem. Commun.* (2002) 2618.
- [6] For reviews of amidinate chemistry see: J. Barker, M. Kilner, *Coord. Chem. Rev.* 133 (1994) 219; F.T. Edelman, *Coord. Chem. Rev.* 137 (1994) 403.
- [7] For recent work with Group 4, non-imido amidinate systems see the following and references therein: (a) R.J. Keaton, L.A. Koterwas, J.C. Fettinger, L.R. Sita, *J. Am. Chem. Soc.* 124 (2002) 5932; (b) J.R. Hagadorn, J. Arnold, *Organometallics* 17 (1998) 1355; (c) R. Gómez, R. Duchateau, A.N. Chernega, A. Meetsma, F.T. Edelman, J.H. Teuben, M.L.H. Green, *J. Chem. Soc. Dalton Trans.* (1995) 217.
- [8] P.J. Stewart, A.J. Blake, P. Mountford, *Inorg. Chem.* 36 (1997) 3616.
- [9] (a) P.J. Stewart, A.J. Blake, P. Mountford, *Organometallics* 17 (1998) 3271; (b) P.J. Stewart, A.J. Blake, P. Mountford, *J. Organomet. Chem.* 564 (1998) 209.
- [10] A.E. Guiducci, A.R. Cowley, M.E.G. Skinner, P. Mountford, *J. Chem. Soc. Dalton Trans.* (2001) 1392.
- [11] C.L. Boyd, A.E. Guiducci, S.R. Dubberley, B.R. Tyrrell, P. Mountford, *J. Chem. Soc. Dalton Trans.* (2002) 4175.
- [12] (a) Although for ease of representation all titanium imido linkages are drawn ‘Ti=NR’, the formal titanium–imido nitrogen bond order in the complexes described herein is probably best thought of as closer to three (pseudo- $\sigma^2 \pi^4$; triple bond) rather than as

- two: (b) T.R. Cundari, Chem. Rev. 100 (2000) 807; N. Kaltsoyannis and P. Mountford, J. Chem. Soc. Dalton Trans. (1999) 781, and references therein.
- [13] A.J. Blake, P.E. Collier, S.C. Dunn, W.-S. Li, P. Mountford, O.V. Shishkin, J. Chem. Soc. Dalton Trans. (1997) 1549.
- [14] D. Doyle, Y.K. Gun'ko, P.B. Hitchcock, M.F. Lappert, J. Chem. Soc. Dalton Trans. (2000) 4093.
- [15] (a) M.J.R. Brandsma, E.A.C. Brussee, A. Meetsma, B. Hessen, J.H. Teuben, Eur. J. Inorg. Chem. (1998) 1867; (b) S. Bambirra, A. Meetsma, B. Hessen, J.H. Teuben, Organometallics 19 (2000) 3197.
- [16] (a) F.H. Allen, O. Kennard, Chemical Design Automation News 8 (1993) 1 and 31. (b) The United Kingdom Chemical Database Service, D.A. Fletcher, R.F. McMeeking, D.J. Parkin, Chem. Inf. Comput. Sci. 36 (1996) 746.
- [17] J.E. Hill, P.E. Fanwick, I.P. Rothwell, Inorg. Chem. 30 (1991) 1143.
- [18] C.H. Zambrano, R.D. Profilet, J.E. Hill, P.E. Fanwick, I.P. Rothwell, Polyhedron 12 (1993) 689.
- [19] P.E. Collier, A.J. Blake, P. Mountford, J. Chem. Soc. Dalton Trans. (1997) 2911.
- [20] M.R. Russo, N. Kaltsoyannis, A. Sella, Chem. Commun. (2002) 2458.
- [21] C.J. Carmalt, A. Newport, I.P. Parkin, P. Mountford, A.J. Sealey, S.R. Dubberley, J. Mater. Chem. 13 (2003) 84.
- [22] Z. Otwinowski, W. Minor, in: C.W. Carter and R.M. Sweet (Eds.), Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods Enzymol., 276 (1997), Academic Press.
- [23] A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, J. Appl. Cryst. 27 (1994) 435.
- [24] D.J. Watkin, C.K. Prout, J.R. Carruthers, P.W. Betteridge, R.I. Cooper, CRYSTALS issue 11, Chemical Crystallography Laboratory, Oxford, UK, 2001.