DOI: 10.1002/ejic.200600475

A General and Facile One-Step Synthesis of Imido–Titanium(IV) Complexes: Application to the Synthesis of Compounds Containing Functionalized or Chiral Imido Ligands and Bimetallic Diimido Architectures

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Keywords: Imido / N ligands / Multiple bonds / Titanium / Synthesis design

One-pot reactions of $Ti(NMe_2)_4$ with a wide range of primary alkyl, aryl, and silylamines RNH_2 in the presence of excess chlorotrimethylsilane produced the corresponding imido–titanium(IV) complexes $[Ti(=NR)Cl_2(NHMe_2)_2]$ (**1a–j**), in which R = *t*Bu, 1-adamantane, Ph_3C, Ph_3Si, Ph, 2,6-*i*Pr_2–C_6H_3, 2,6-Cl_2–C_6H_3, 2,6-Br_2–4-Me–C_6H_2, C_6F_5, and 3,5-$(F_3C)_2$–C_6H_3. This general synthesis, which starts from commercially available reagents, represents a simple and direct route to imido complexes. Reaction of complexes **1** with pyridine afforded the six-coordinate tris-pyridine adducts $[Ti(=NR)Cl_2(Py)_3]$ (**2**). Another advantage of this method is its tolerance to other functional groups; complexes that contain halides, ether, dialkylamino, cyano, ethynyl, olefin, and nitro substituents on the imido moiety have been prepared. The use of enantiomerically pure primary amines affords the first group of titanium complexes that contain chiral imido groups, and the use of diamines produces diimido complexes. Alternatively, CH_3I has been used as an alkylating agent to generate titanium–imido complexes of the type $[Ti(NR)I_2(THF)_2]_2$. All compounds were fully characterized by spectroscopic methods (IR, ^1H NMR, ^{13}C NMR) and elemental analysis. Some of the compounds were also analyzed by single-crystal X-ray diffraction studies.

Introduction

The last two decades have witnessed a strong interest in the coordination chemistry of transition-metal complexes that contain imido ligands $[NR]^{2-}$ (R = alkyl or aryl).[1] The dianionic π-donor terminal imido functional group is involved in many facets of chemistry that can be subdivided into two types: (1) reactions in which the imido group acts as a spectator ligand, the $[NR]^{2-}$ moiety is isolobal with $[C_5H_5]^-$[2] (e.g. in alkene metathesis[3] or olefin polymerization[1c,4–6]), (2) reactions in which the M = NR linkage itself is involved in stoichiometric or catalytic transformations such as metathesis reactions (with imines,[7] nitro- and nitrosoarenes,[8] or oxo–imido exchange[9]), C–H activation,[10] reactions with unsaturated C–C[11] or C–X bonds,[12] alkyne hydroaminations,[13,14] carboamination reactions,[15] and ring-opening reactions of strained heterocycles.[10d,16] Moreover, some imido derivatives have also found applications in material chemistry (OMCVD,[17] polyoxometalate[18]) and have been implicated in the ammoxidation of propene.[19]

As part of an ongoing study of vanadium complexes supported by various ligands,[20] we recently described the synthesis and molecular structure of the new terminal aryl–imido, and rare Cp-free, vanadium(IV)complex $[V(=N–2,6\text{-}iPr_2–C_6H_3)Cl_2(NHMe_2)_2]$.[5] We have further demonstrated that various aryl–imido groups could be very conveniently introduced by a one-pot synthesis from $V(NMe_2)_4$, the corresponding aniline, and chlorotrimethylsilane.[21] We have also studied the coordination chemistry of these new complexes with N- or P-donor neutral ligands,[21,22] and the results suggest that imido compounds of this type could lead to a large variety of vanadium coordination compounds. Furthermore, some of these imido–vanadium species have been shown to possess catalytic activities in olefin polymerization[5] and in alkyne hydroamination.[13a] Terminal imido–titanium complexes $[Ti(=N–t\text{Bu})Cl_2L_n]$ [L_n = $(NHMe_2)_2$, Py_2, Py_3, TMEDA] have proven to be very useful synthons for the preparation of many other imido derivatives through chloride and/or ligand base exchange metathesis; aryl– and silyl–imido derivatives are available by transimination reactions with the appropriate aryl and silylamine.[6a,13d,17c,23–26] Some of these imido–titanium complexes present potential activity in olefin polymerization,[6] alkyne hydroamination,[13] and have been used for the synthesis of TiN thin films,[17a–17c] which further justifies the quest for the cheapest and the most direct route for the preparation of such useful precursors.

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Two routes are commonly employed for the preparation of the now widely used synthon $[Ti(=N–R)Cl_2L_n]$ [L_n = $(NHMe_2)_2$, Py_3]. In the first method, $[Ti(=N–tBu)Cl_2Py_3]$ is prepared from $TiCl_4$, $tBuNH_2$, and pyridine.[23] Nevertheless, other analogues (i.e. aryl–imido) cannot be obtained this way, and their synthesis requires a second step that consists of an imido/amine exchange reaction (transimination) of $[Ti(=N–tBu)Cl_2Py_3]$ with the appropriate arylamine.[23] Moreover, the presence of pyridine renders these compounds somewhat insoluble, and pyridine ligands may be unwanted for certain applications. During the course of our studies, imido–titanium complexes $[Ti(=N–R)Cl_2(NHMe_2)_2]$ have been prepared by Mountford et al. with a procedure based on the reaction of $Ti(NMe_2)_2Cl_2$ with a primary alkyl- or arylamine.[26] Although this route appears more general than the one with $TiCl_4$, the precursor $Ti(NMe_2)_2Cl_2$ is not commercially available and needs to be prepared from $TiCl_4$ and $Ti(NMe_2)_4$.[27]

In this paper, and as an extension of our imido–vanadium method[21] to titanium, we report on a very convenient, one-pot synthesis of a series of alkyl–, aryl–, and silyl–imido derivatives of titanium(IV) complexes of the general formula $[Ti(=NR)Cl_2(NHMe_2)_2]$ (**1**), where R is an alkyl-, an aryl-, or a silyl group. Part of this work [synthesis of $Ti(=NPh)Cl_2(NHMe_2)_2$] has been previously communicated.[13a] Our method presents the advantage to afford the imido derivative in one single step with the use of a very simple one-pot synthesis from commercially available $Ti(NMe_2)_4$, the corresponding primary amine RNH_2, and an excess of chlorotrimethylsilane. Another important goal of this study was to explore the selectivity and the functional group tolerance of the reaction. Amines that contain additional functionality on their skeletons (e.g. ether, dialkylamino, cyano, ethynyl, olefin, or nitro substituents) were successfully used to generate original imido derivatives. In consequence, our procedure appears to be applicable to a wide range of primary amines including enantiomerically pure amines (to afford chiral imido functions) and diamines (to afford diimido complexes). Related complexes with pyridine ligands prepared by the substitution of the $NHMe_2$ ligands in $[Ti(=NR)Cl_2(NHMe_2)_2]$ by pyridine (Py) donors is also described. Finally, an alternative preparation for the related iodo analogue complex $[Ti(NAr)I_2(thf)_2]_2$ is also described; this method is based on the use of CH_3I instead of Me_3SiCl (Scheme 3).

Results and Discussion

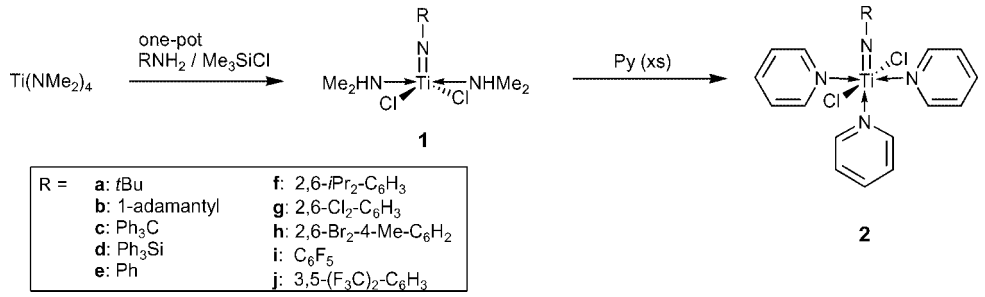
This work constitutes a systematic investigation of the synthetic and structural chemistry of imido–titanium(IV) complexes of the general formula $[Ti(=NR)Cl_2(NHMe_2)_2]$ that are prepared directly from a one-pot reaction of $Ti(NMe_2)_4$, RNH_2, and Me_3SiCl, as well as some related compounds. The synthesis and proposed structures of the imido complexes of titanium(IV) are summarized in Schemes 1–3. The structures of eleven complexes are set out in Figures 2–7, and Figures 9, 10, 12, and 14, selected metric data are collected in Tables 1 and 2.

1. General Synthesis of the Imido Complexes $[Ti(=NR)Cl_2(NHMe_2)_2]$ and $[Ti(=NR)Cl_2Py_3]$

In our previous study,[21] we described the synthesis of paramagnetic aryl–imido–vanadium complexes $[V(=NAr)Cl_2(NHMe_2)_2]$ from the reaction of an aniline with $V(NMe_2)_4$ in toluene followed by the addition of an excess of chlorotrimethylsilane. Inspired by this result, we attempted to use a similar one-pot synthesis for the production of related titanium–imido analogue complexes, and the scope of this method was first illustrated with a range of primary amines listed in Scheme 2.

$[Ti(=N–tBu)Cl_2(NHMe_2)_2]$	**1a**	$[Ti(=N–3\text{-}O_2N–6\text{-}Me–C_6H_3)Cl_2(NHMe_2)_2]$	**1q**
$[Ti(=N–1\text{-}adamantane)Cl_2(NHMe_2)_2]$	**1b**	$[Ti\{=N(C_6H_{10}C=CH)\}Cl_2(NHMe_2)_2]$	**1r**
$[Ti(=N–CPh_3)Cl_2(NHMe_2)_2]$	**1c**	$[Ti\{=N–[(S)\text{-}(–)\text{-}CHMePh]\}Cl_2(NHMe_2)_2]$	**1s***
$[Ti(=N–SiPh_3)Cl_2(NHMe_2)_2]$	**1d**	$[Ti\{=N–[(–)\text{-}cis\text{-}myrtanyl]\}Cl_2(NHMe_2)_2]$	**1t***
$[Ti(=N–Ph)Cl_2(NHMe_2)_2]$	**1e**	$[Ti(=N–SiPh_3)Cl_2(Py)_3]$	**2d**
$[Ti(=N–2,6\text{-}iPr_2–C_6H_3)Cl_2(NHMe_2)_2]$	**1f**	$[Ti(=N–4\text{-}NC–C_6H_4)Cl_2(Py)_3]$	**2l**
$[Ti(=N–2,6\text{-}Cl_2–C_6H_3)Cl_2(NHMe_2)_2]$	**1g**	$[Ti[=N(C_6H_{10}C=CH)]Cl_2(Py)_3]$	**2r**
$[Ti(=N–2,6\text{-}Br_2–4\text{-}Me–C_6H_2)Cl_2(NHMe_2)_2]$	**1h**	$[Ti\{=N–[(S)\text{-}(–)\text{-}CHMePh]\}Cl_2(Py)_3]$	**2s***
$[Ti(=N–C_6F_5)Cl_2(NHMe_2)_2]$	**1i**	$[Ti\{=N–[(–)\text{-}cis\text{-}myrtanyl]\}Cl_2(Py)_3]$	**2t***
$[Ti(=N–3,5\text{-}(F_3C)_2–C_6H_3)Cl_2(NHMe_2)_2]$	**1j**	$[Ti(N–2\text{-}EtO–C_6H_4)Cl_2(NHMe_2)_1]_2]$	**3**
$[Ti(=N–4\text{-}Et_2N–C_6H_4)Cl_2(NHMe_2)_2]$	**1k**	$[Ti[N–CH_2(CHO(CH_2)_3)]Cl_2(NHMe_2)_1]_2$	**4**
$[Ti(=N–4\text{-}NC–C_6H_4)Cl_2(NHMe_2)_2]$	**1l**	$[Ti[N–CH_2(CHO(CH_2)_3)]Cl_2(Py)_1]_2$	**5**
$[Ti(=N–2\text{-}NC–C_6H_4)Cl_2(NHMe_2)_2]$	**1m**	$[Ti\{=N–[(S)\text{-}(–)\text{-}CHMePh]\}Cl_2(NHMe_2)_1]_2$	**6***
$[Ti(=N–4\text{-}H_2C=CH–C_6H_4)Cl_2(NHMe_2)_2]$	**1n**	$[(Me_2HN)_2Cl_2Ti(=N–Me_2C_6H_2–C_6H_2Me_2–N=)TiCl_2(NHMe_2)_2]$	**7**
$[Ti(=N–2\text{-}MeC=CH_2–C_6H_4)Cl_2(NHMe_2)_2]$	**1o**	$[(Py)_3Cl_2Ti(=N–Me_2C_6H_2–C_6H_2Me_2–N=)TiCl_2(Py)_3]$	**8**
$[Ti(=N–3\text{-}HC=C–C_6H_4)Cl_2(NHMe_2)_2]$	**1p**	$[Ti(N–2,6\text{-}iPr_2–C_6H_3)I_2(thf)_2]_2$	**9**

Scheme 1. Designation of imido–titanium complexes described in this study.



R =		
	a: *t*Bu	**f**: 2,6-*i*Pr$_2$-C$_6$H$_3$
	b: 1-adamantyl	**g**: 2,6-Cl$_2$-C$_6$H$_3$
	c: Ph$_3$C	**h**: 2,6-Br$_2$-4-Me-C$_6$H$_2$
	d: Ph$_3$Si	**i**: C$_6$F$_5$
	e: Ph	**j**: 3,5-(F$_3$C)$_2$-C$_6$H$_3$

Scheme 2. General synthesis of imido–titanium(IV) complexes **1** and **2**.

When a toluene solution of $Ti(NMe_2)_4$ is reacted with one equiv. of RNH_2 [with R = *t*Bu, 1-adamantyl, Ph_3C, Ph_3Si, Ph, 2,6-*i*Pr$_2$–C$_6$H$_3$, 2,6-Cl$_2$–C$_6$H$_3$, 2,6-Br$_2$–4-Me–C$_6$H$_2$, C$_6$F$_5$, and 3,5-(F$_3$C)$_2$–C$_6$H$_3$] and an excess of chlorotrimethylsilane[28] (typically about 8 equiv.) at room temp. overnight, yellow–orange compounds $[Ti(=NR)Cl_2(NHMe_2)_2]$ [R = *t*Bu (**1a**), 1-adamantyl (**1b**), Ph_3C (**1c**), Ph_3Si (**1d**), Ph (**1e**), 2,6-*i*Pr$_2$–C$_6$H$_3$ (**1f**), 2,6-Cl$_2$–C$_6$H$_3$ (**1g**), 2,6-Br$_2$–4-Me–C$_6$H$_2$ (**1h**), C$_6$F$_5$ (**1i**), and 3,5-(F$_3$C)$_2$–C$_6$H$_3$ (**1j**)] are formed exclusively (Scheme 2). These complexes often separated by crystallization (while the reaction proceeds or upon the addition of pentane) as large, generally yellow–orange (for alkyl–imido) or red (for aryl–imido) needles or crystals with good yields (73–96%).

The detailed experimental protocols and full characterization are given in the Experimental Section. Compounds **1a**–**j** have been characterized by infrared spectroscopy (with strong ν_{NH} absorptions around 3250 cm^{-1}), multinuclear NMR spectroscopy, elemental analysis, and by X-ray structure determination for some (vide infra). The products are consistent with the proposed structure of a monomeric five-coordinate compound with 2 dimethylamine ligands that occupy the axes of the bipyramid. This one-pot synthesis cleanly affords a wide range of alkyl–, silyl–, and aryl–imido complexes $Ti(=NR)Cl_2(NHMe_2)_2$. It is important to note that titanium silyl–imido complexes remain comparatively rarer than their alkyl- or aryl analogues.[10b,12d,25,29]

When dissolved in pyridine, bis-dimethylamine adducts **1** are instantly and generally quantitatively converted into tris-pyridine complexes $[Ti(=NR)Cl_2(Py)_3]$ (**2**). In a few cases, it has been reported that the substitution of $NHMe_2$ ligands by pyridine is difficult or produces mixed $NHMe_2$–pyridine adducts.[21,26] Within this study, we have only experienced difficulties (vide infra) in the synthesis of one compound (namely **5** from **4**). We will not insist on this substitution reaction that has already been described by us on vanadium analogues,[21] and by Mountford on titanium complexes,[26] but these tris-pyridine complexes are generally obtained as large crystals with good X-ray quality that facilitates their structural characterization, vide infra (although they are sometimes poorly soluble in common organic solvents). In consequence, in this article we will refer to this substitution reaction only when a related tris-pyridine–imido compound was structurally characterized.

Single crystals of **2d** were grown from a CH_2Cl_2/pyridine solution of **2d** layered with pentane at room temp. and were analyzed by X-ray crystallography. A thermal ellipsoid plot is presented in Figure 1 along with selected bond lengths and angles in Table 1.

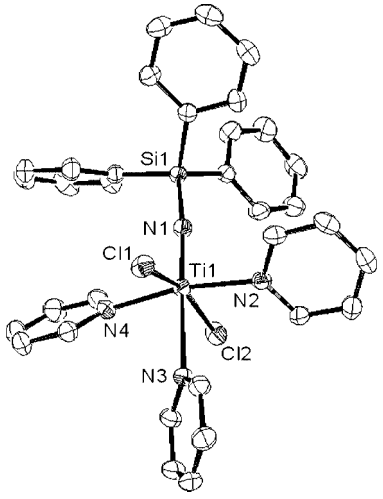


Figure 1. Molecular structure of **2d** with selected bond lengths [Å] and angles [°], which shows 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity.

Compound **2d** adopts a pseudooctahedral geometry around the metal center with mutually *trans* chloride and pyridine ligands. The third pyridine ligand is disposed *trans* to the imido group. Bond lengths and angles are unexceptional and were found to be very similar to those observed in titanium[23,25] and vanadium[21] analogues; the titanium–nitrogen bond lengths of the imido fragment is 1.7110(13) Å, with an almost linear Ti–N$_{imido}$–Si angle [171.12(9)°], and an average Ti–Cl ca. 2.39 Å. The *trans* Ti–N(Py) of 2.4742(14) Å is significantly longer than the average *cis* Ti–N(Py) bond lengths [2.224(2) Å], which reflects the *trans*-labilizing ability of the imido ligand.

2. Tolerance to Functional Groups on the Imido Moiety in $[Ti(=NR)Cl_2(NHMe_2)_2]$ and $[Ti(=NR)Cl_2Py_3]$ Complexes

Functionalized organoimido complexes of titanium, that is complexes that contain additional functional groups on the imido moiety, are extremely rare.[23,30] Since we have easy

Table 1. Comparison of the average interatomic distances [Å] and angles [°] in $Ti(=NR)Cl_2(NHMe_2)_2$ and $Ti(=NR)Cl_2(Py)_3$ complexes.

	1k	**1o**	**1p**	**1s***	**2d**	**2l**	**2r**
$Ti–N_{imido}$	1.6955(18)	1.7028(11)	1.700(2)	1.682(4)	1.7110(13)	1.726(2)	1.6988(12)
$N_{imido}–C_{ipso}$/Si	1.390(2)	1.3889(16)	1.384(4)	1.455(6)	1.7098(14)[a]	1.357(3)	1.4448(18)
Ti–Cl	2.3567(9)	2.3393(4)	2.3261(9)	2.3602(15)	2.3752(5)	2.3756(4)	2.4353(5)
	2.3553(11)	2.3509(4)	2.3301(9)	2.3393(17)	2.4037(5)		2.3999(5)
$Ti–N_{NHMe_2}$	2.2185(18)	2.2005(11)	2.207(3)	2.196(5)	–	–	–
	2.2186(17)	2.2119(11)	2.210(2)	2.214(5)			
$Ti–N_{Py}$(*trans*)	–	–	–	–	2.4742(14)	2.425(2)	2.4000(12)
$Ti–N_{Py}$(*cis*)	–	–	–	–	2.2140(14)	2.2201(13)	2.2433(12)
					2.2339(14)		2.2314(13)
$H_{NHMe_2}\cdots Cl$	2.516	2.391	2.708	2.563	–	–	–
	2.530						
$Ti–N_{imido}–C_{ipso}$/Si	178.21(15)	178.86(10)	169.4(2)	168.8(4)	171.12(9) [b]	180.0	174.31(10)
Cl–Ti–Cl	132.86(3)	131.357(16)	134.01(4)	140.12(6)	162.03(2)	164.59(3)	163.780(18)
$N_{NHMe_2}–Ti–N_{NHMe_2}$	167.27(6)	169.29(4)	168.35(10)	160.43(16)	–	–	–
$N_{N_{imido}}–Ti–N_{NHMe_2}$	96.39(8)	95.36(5)	93.64(11)	100.88(18)	–	–	–
	96.33(8)	95.31(5)	97.85(11)	98.65(19)			
N_{Py}(*cis*)–Ti–N_{Py}(*cis*)	–	–	–	–	169.87(5)	169.32(7)	168.24(4)
$N_{imido}–Ti–Cl$	113.97(7)	115.08(4)	115.41(10)	112.79(15)	91.44(4)	97.705(15)	98.77(4)
	113.17(6)	113.54(4)	110.45(10)	107.04(15)	99.15(5)		97.37(4)
$N_{imido}–Ti–N_{Py}$(*trans*)	–	–	–	–	178.09(6)	169.32(7)	179.23(5)
N–H···Cl	153.63	164.94	153.17	147.90	–	–	–
	151.20						
functional group	$N_{Et}–C_{Ar}$	C=C 1.338(2)	C≡C 1.183(5)	–	–	N≡C 1.144(4)	C≡C 1.187(2)
	1.386(3)						
			C–C≡C			N≡C–C	C–C≡C
			175.5(4)			180.0	178.93(18)

[a] N_{imido}–Si bond length. [b] Ti–N_{imido}–Si angle.

access to various Ti–imido complexes from readily available amines, it was of interest to probe the tolerance of our synthetic procedure towards the presence of functional groups on the alkyl/arylamine backbone, and also to learn the stability of the resulting functionalized imido compounds. The added functionality of the organoimido compounds may serve as an anchor to graft the complexes to a support, and their reactivity could be studied as well. We have already shown in the previous section that halides and CF_3-substituted anilines can be employed, and we have screened several other anilines and amines that contain ether, dialkylamine, cyano, alkyne, olefin, or nitro groups under the same conditions used above [$Ti(NMe_2)_4$, RNH_2, Me_3SiCl, toluene, room temp.]. These amines are depicted in Figure 2.

The general one-pot procedure proceeded as anticipated with anilines substituted with *p*-NEt_2, *p*-CN, *o*-CN, *p*-$HC=CH_2$, *o*-$MeC=CH_2$, *m*-C≡CH, and *m*-NO_2 groups with the formation of the expected corresponding bis-dimethylamine adducts $[Ti(=NAr)Cl_2(NHMe_2)_2]$ (**1k**–**q**) [with Ar = *p*-$Et_2N–C_6H_4$ (**1k**), *p*-$NC–C_6H_4$ (**1l**), *o*-$NC–C_6H_4$ (**1m**), *p*-$H_2C=CH–C_6H_4$ (**1n**), *o*-$MeC=CH_2–C_6H_4$ (**1o**), *m*-$HC≡C–C_6H_4$ (**1p**), and *m*-O_2N–*o*-$Me–C_6H_3$ (**1q**)]. Not surprisingly, some of these compounds have been easily converted into their tris-pyridine adducts $[Ti(=NAr)Cl_2(Py)_3]$ (**2**) by the addition of an excess of pyridine to the corresponding dimethylamine precursor. Only [Ti(=N–*p*-$NC–C_6H_4$)$Cl_2(Py)_3$] (**2l**) will be described later on as its molecular structure has been established (vide infra). These functional organoimido species have been characterized by means of spectroscopic methods (NMR, IR), and combustion analysis. The solution ^1H- and ^{13}C NMR spectroscopic data present features similar to those of their nonfunctional analogues – a single set of resonances for the coordinated $NHMe_2$ ligands (in **1**) or two different pyridine ligands in the ratio 2:1 (in **2**), and resonances attributable to the or-

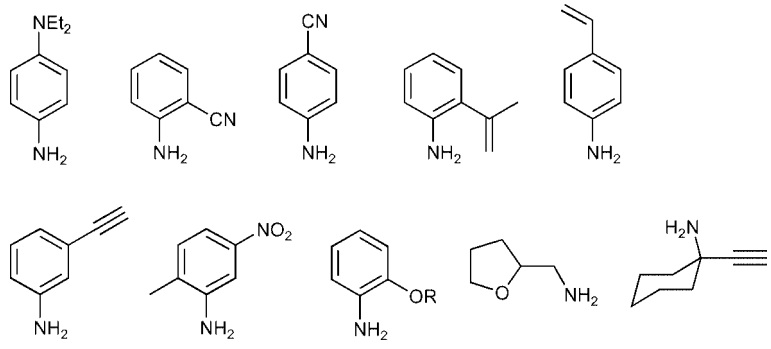


Figure 2. Functional amines used in this study.

ganoimido group. These data are consistent with the functional group that does not interact with the metal center. Indeed, according to the IR data, some of these functional groups are clearly observed in their normal regions ($\nu_{C\equiv N}$ 2243, 2242, and 2221 cm^{-1}, respectively, for **1l**, **1m**, and **2l**; $\nu_{C=C}$ 1624 and 1629 cm^{-1}, respectively, for **1n** and **2o**; $\nu_{C\equiv C}$ 2208 cm^{-1} for **1p**; ν_{NO_2} 1517 cm^{-1} for **1q**).

When reacted with $Ti(NMe_2)_4$ in the presence of chlorotrimethylsilane, 1-ethynylcyclohexylamine gave the imido complex $Ti[=N(C_6H_{10}C\equiv CH)]Cl_2(NHMe_2)_2$ (**1r**). Again, spectroscopic (^1H- and ^{13}C NMR) data suggest that the carbon–carbon triple bond does not coordinate to the titanium center. The corresponding pyridine analogue $[Ti[=N(C_6H_{10}C\equiv CH)]Cl_2(Py)_3]$ (**2r**), formed upon the addition of excess pyridine to **1r**, has been characterized by X-ray structure determination (vide infra) that clearly shows the free C≡C–H fragment.

Single-crystals suitable for X-ray diffraction studies were obtained for these functionalized organoimido compounds from room temp. toluene (**1k**, **1o**), cold toluene/pentane (**1p**), or pyridine-toluene/pentane (**2l**, **2r**) solutions. Thermal ellipsoid plots are presented in Figures 3, 4, 5, 6, 7; selected metric parameters are given in Table 1.

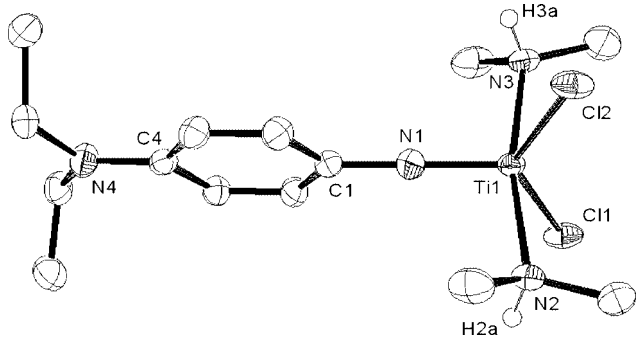


Figure 3. Molecular structure of **1k** with selected bond lengths [Å] and angles [°], which shows 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity.

In the solid state, the molecular structure of the three $NHMe_2$ adducts (**1k**, **1o**, **1p**) is best described as distorted trigonal bipyramid with axial dimethylamine ligands [τ = 0.58 (**1k**), 0.63 (**1o**), and 0.57 (**1p**)],[31] with N_{imido}–Ti–Cl angles in the range 110–115°, and N_{imido}–Ti–N_{NHMe_2} angles in the range 93–98°. The distances and angles associated with the titanium center and the ligands are comparable to those found in other $[M(=NR)Cl_2(NHMe_2)_2]$ complexes (M = Ti,[26] V[21]). Adducts **1k**, **1o**, and **1p** exhibit a short Ti–N_{imido} distance of 1.6955(18) Å for **1k**, 1.7028(11) Å for **1o**, and 1.700(2) Å for **1p**. The imido linkage is almost linear [Ti–N_{imido}–C_{ipso} angle = 178.21(15), 178.86(10), and 169.4(2)°, respectively, in **1k**, **1o**, and **1p**], and is consistent with the donation of the lone pair on nitrogen to an acceptor orbital on titanium (the imido Ti–N bond can be considered as a triple bond). The crystal structure determinations also unambiguously show noninteracting functional -NEt_2 (**1k**), -C(Me)=CH_2 (**1o**), and –C≡CH (**1p**) groups, with normal metric parameters that are listed in Table 1. Both of the chlorine atoms occupy equatorial sites

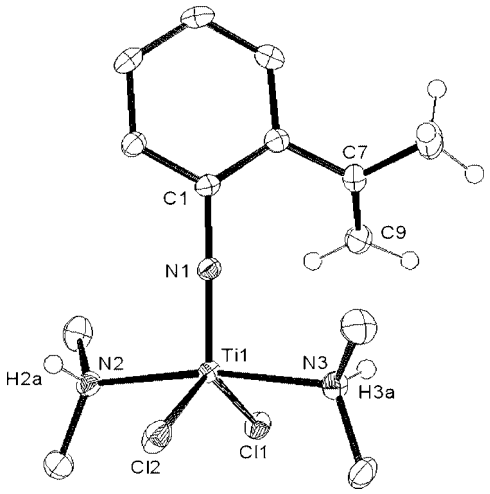


Figure 4. Molecular structure of **1o** with selected bond lengths [Å] and angles [°], which shows 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity.

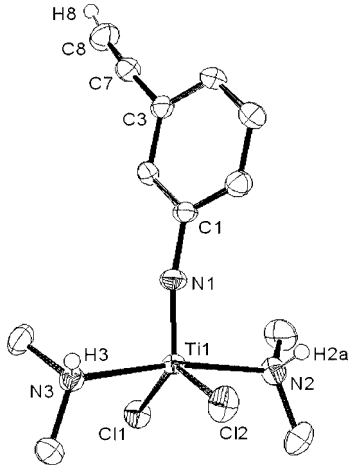


Figure 5. Molecular structure of **1p** with selected bond lengths [Å] and angles [°], which shows 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity.

in the trigonal bipyridine with a Cl1–Ti–Cl2 angle of 132.86(3)°, 131.357(16)°, and 134.01(4) Å for **1k**, **1o**, and **1p**, respectively, and mean Ti–Cl bond lengths of 2.36 Å, 2.34 Å, and 2.33 Å for **1k**, **1o**, and **1p**, respectively. The two *trans* dimethylamino ligands form the axis of the bipyramid, and have mean Ti–N_{NHMe_2} bonds of ca. 2.21 Å for the three compounds. The supramolecular structure is dominated by Me_2N–H···Cl hydrogen bonding (NH···Cl bond lengths are in the range 2.391 to 2.708 Å; associated N–H···Cl angles are 164.94 to 147.64°); features that they share with Mountford's related compounds.[26]

An ORTEP drawing of the molecular structure of **2l** and **2r** is shown in Figures 6 and 7, respectively. Crystals of **2r** contain one residual molecule of pyridine (not shown in Figure 6). In **2l**, the Ti–N_{imido} and C≡N vectors lie on a crystallographic two-fold rotation axis. The pendant functional cyano (**2l**) and ethynyl (**2r**) group on the imido moieties do not bind to the titanium center. Compounds **2l** and **2r** adopt a pseudooctahedral geometry around the titanium

center similar to the one described above for **2d** (with mutually *trans* chloride and pyridine ligands, the third pyridine ligand is disposed *trans* to the imido group). Bond lengths and angles are normal, and found to be very similar to those observed in titanium[23] and vanadium[21] analogues, as well as in previously described **2d** (Table 1). The titanium–nitrogen bond length of the imido fragments are 1.726(2) Å (**2l**) and 1.6988(12) Å (**2r**) with an angle Ti–N_{imido}–C_{ipso} of 180.0° (**2l**) and 174.31(10)° (**2r**), and Ti–Cl bond length of 2.3756(4) Å (**2l**) and 2.4353(5) and 2.3999(5) Å (**2r**).

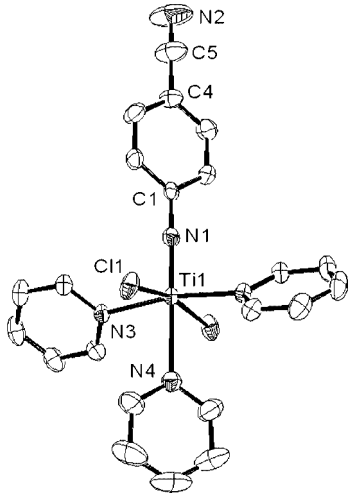


Figure 6. Molecular structure of **2l** with selected bond lengths [Å] and angles [°], which shows 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity.

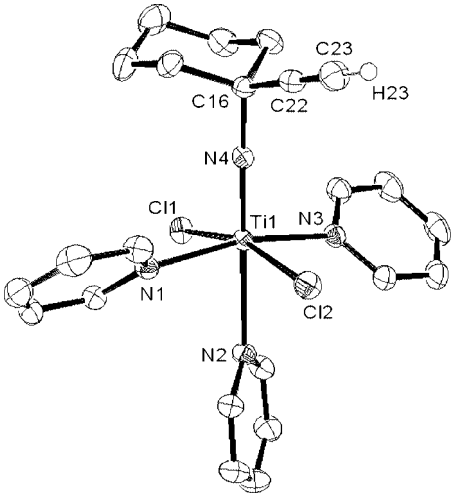


Figure 7. Molecular structure of **2r** with selected bond lengths [Å] and angles [°], which shows 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms and residual solvent (one molecule of pyridine) of crystallization are omitted for clarity.

Unlike the previous functional anilines, however, amines that contain an additional ether-function {i.e. 2-EtO–$C_6H_4NH_2$ and tetrahydrofurfurylamine [H_2NCH_2-$(CHO(CH_2)_3)$]} did not generate the bis-dimethylamine adduct, but rather reacted to afford the mono-dimethylamine adduct of the general formula [Ti(NR^o)Cl_2($NHMe_2$)] [with R^o = 2-EtO–C_6H_4 (**3**), and $CH_2(CHO(CH_2)_3)$ (**4**)] (Figure 8), as judged by spectroscopic ($NHMe_2$/NR^o, 1:1) and analytical data. The ^{1}H- and ^{13}C NMR spectra of **3** reveal diastereotopic methyl groups for the $NHMe_2$ ligand. Because of their poor solubility in common organic solvents, these compounds are probably imido-bridged dimers with the oxygen atom coordinated to the metal center.

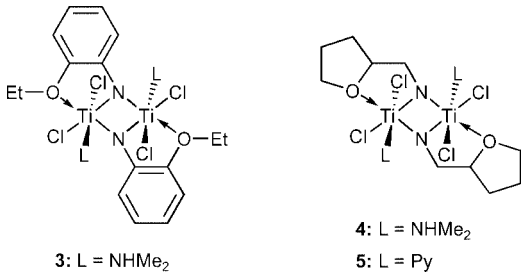


Figure 8. Proposed structure for complexes **3**–**5**.

Indeed, molecular structure determination (Figure 9) has unambiguously established that **3** is the centrosymmetric dimer [Ti[μ_2-[N]-η^1[O]-N–2-EtO–C_6H_4]Cl_2($NHMe_2$)]$_2$, with two aryl–imido ligands that bridge two (Me_2HN)Cl_2Ti moieties. The O atom of the ether function is coordinated *cis* to the N atom of its own ligand set, *trans* to the N atom of the other imido group, and the chlorine atoms are mutually *cis* to one another. The coordination geometry of titanium is distorted octahedral. The Ti_2N_2 core is planar (torsion angle 0°) and is characterized by a short Ti···Ti distance common in imido dimers[32] [Ti1···Ti1′ = 2.889(3) Å] with two Ti–N_{imido} bond lengths of 1.830(6) Å and 2.027(6) Å. The (Me_2HN)Cl_2Ti moiety is normal with the expected Ti–N_{amine} and Ti–Cl bond lengths and angles [Ti–N_{amine} 2.226(6) Å, Ti–Cl avg. 2.346 Å].

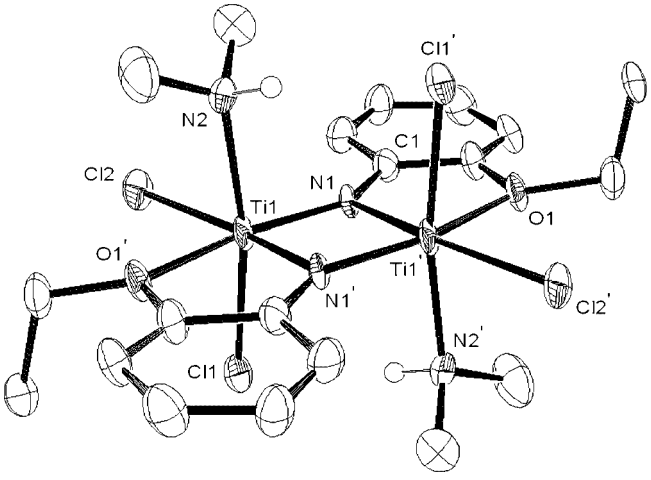


Figure 9. Molecular structure of **3** with selected bond lengths [Å] and angles [°], which shows 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity.

Addition of pyridine to **4** affords the pyridine complex [Ti(μ2-[N]-η^1[O]–NR^o)Cl_2(Py)]$_2$ (**5**) [R^o = $CH_2(CHO(CH_2)_3)$] and its molecular structure has also been assessed on the basis of X-ray structure determination. The ORTEP

drawing is shown in Figure 10, and selected bond lengths and angles are given in Table 2. Like **3**, compound **5** is dimeric in the solid state, and the overall geometry, distances, and angles are broadly comparable to those of **3**. Complex **5** is an imido-bridged dimer with two edge-sharing octahedral metal coordination spheres. Each distorted octahedron is completed by two mutually *cis* chlorine atoms [Ti–Cl avg. 2.367(2) Å, Cl–Ti–Cl 90.69(4)°], one pyridine ligand [Ti–N_{Py} 2.254(3) Å] and the O atom of the furan link [Ti–O 2.177(3) Å]. The Ti_2N_2 core is planar (torsion angle 0°) and is characterized by a short Ti···Ti distance [2.8502(13) Å]. The disymmetric imido bridges are characterized by two Ti–N_{imido} bond lengths of 1.821(3) Å and 2.013(3) Å, that are longer by ca. 0.1/0.3 Å than those generally observed in terminal imido complexes. The angle formed by the bridging nitrogen atoms with the two metal centers [Ti–N_{imido}–Ti′ = 95.92(14)°] deviates significantly from that expected for an sp^2 nitrogen atom. The (Py)Cl_2Ti moiety is normal with the expected Ti–N_{Py} and Ti–Cl bond lengths and angles [Ti–N_{Py} 2.254(3) Å, Ti–Cl avg. 2.367(2) Å].

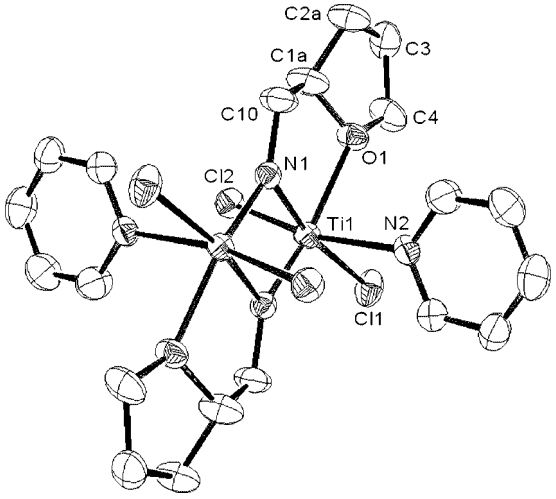


Figure 10. Molecular structure of **5** with selected bond lengths [Å] and angles [°], which shows 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity.

3. Application to the Synthesis of Diimido Complexes and Chiral Imido Complexes

In relation to the possible use of chiral imido complexes in catalysis for stereoselective olefin polymerization[33] and their involvement in alkyne/alkene hydroamination,[34] we have initiated the synthesis of chiral imido groups on titanium complexes from enantiomerically pure chiral amines.

Table 2. Comparison of the average interatomic distances [Å] and angles [°] in dimers **3**, **5**, **6***, and **8**.

	3	**5**	**6***	**8**
Ti–N_{imido}	Ti1–N1 1.830(6) Ti1–N1′ 2.027(6)	Ti1–N1 2.013(3) Ti1–N1′ 1.821(3)	Ti1–N1 1.821(4) Ti2–N1 1.965(4) Ti1–N2 1.840(4) Ti2–N2 1.971(4)	Ti1–N1 1.719(4) Ti2–N5 1.710(4)
N_{imido}–C_{ipso}	N1–C1 1.395(10)	N1–C10 1.452(5)	N1–C1 1.494(6) N2–C9 1.487(6)	N1–C16 1.374(6) N5–C27 1.378(6)
Ti–Cl	Ti1–Cl1 2.360(2) Ti1–Cl2 2.333(2)	Ti1–Cl1 2.3592(12) Ti1–Cl2 2.3755(11)	Ti1–Cl1 2.2542(17) Ti1–Cl2 2.2482(16) Ti2–Cl3 2.3500(16) Ti2–Cl4 2.3588(16)	Ti1–Cl1 2.4075(16) Ti1–Cl2 2.4059(18) Ti2–Cl3 2.4185(17) Ti2–Cl4 2.3893(16)
Ti–N_{NHMe_2} or Ti–N_{Py}	2.226(6)	Ti1–N1 2.254(3)	Ti2–N3 2.215(4) Ti2–N4 2.233(4)	Ti1–N2 2.249(5) Ti1–N3 2.386(4) Ti1–N4 2.235(5) Ti2–N6 2.223(4) Ti2–N7 2.406(4) Ti2–N8 2.236(5)
Ti–O	Ti1–O1′ 2.240(5)	Ti1–O1 2.177(3)	–	–
H_{NHMe_2}···Cl	–	–	2.638	–
Ti···Ti	2.889(3)	2.8502(13)	2.8239(14)	13.33
Ti–N_{imido}–C_{ipso}	Ti1–N1–C1 143.9(5) Ti1′–N1–C1 119.2(5)	Ti1–N1–C10 118.1(3) Ti1′–N1–C10 145.6(3)	C1–N1–Ti1 130.2(3) C1–N1–Ti2 133.0(3) C9–N2–Ti1 132.4(3) C9–N2–Ti2 132.0(3)	Ti1–N1–C16 174.6(4) Ti2–N5–C27 178.1(4)
Cl–Ti–Cl	90.34(9)	90.69(4)	Cl1–Ti1–Cl2 114.10(7) Cl3–Ti2–Cl4 95.91(6)	Cl1–Ti1–Cl2 163.93(7) Cl3–Ti2–Cl4 166.35(6)
N_{imido}–Ti–Cl	N1–Ti–Cl1 98.3(2) N1–Ti–Cl2 109.7(2)	N1–Ti–Cl1 169.36(11) N1–Ti–Cl2 94.52(9)		N1–Ti1–Cl1 98.51(15) N1–Ti1–Cl2 97.32(15) N5–Ti1–Cl3 95.76(16) N5–Ti2–Cl4 97.89(16)
misc.	N1–Ti1–O1′ 157.7(2) N1–Ti1′–O1 74.8(2) Ti1–N1–Ti1′ 96.9(3) N1–Ti1–N1′ 83.1(3)	N1–Ti1–O1 76.25(12) N1′–Ti1–O1 159.71(12) Ti1–N1–Ti1′ 95.92(14) N1–Ti1–N1′ 84.08(14)	N–H···Cl 147.64 N3–Ti2–N4 163.95(16) Ti1–N1–Ti2 96.41(19) Ti1–N2–Ti2 95.57(19) N1–Ti1–N2 87.56(18) N1–Ti2–N2 80.10(17)	N1–Ti1–N3 177.00(19) N5–Ti2–N7 178.20(18) N2–Ti1–N4 166.03(17) N6–Ti2–N8 165.37(16)

Following our one-pot procedure, the chiral amine (*S*)-(–)-α-methylbenzylamine was treated with $Ti(NMe_2)_4$ in the presence of excess Me_3SiCl, and the resulting yellow complex $[Ti\{=N\text{-}[(S)\text{-}(-)\text{-}CHMePh]\}Cl_2(NHMe_2)_2]$ (**1s***) was obtained in good yields (74%) (Figure 11). By the treatment with pyridine, **1s*** was transformed into the tris-pyridine adduct $[Ti\{=N\text{-}[(S)\text{-}(-)\text{-}CHMePh]\}Cl_2(Py)_3]$ (**2s***). These complexes represent the first examples of a chiral imido group on titanium complexes.[35]

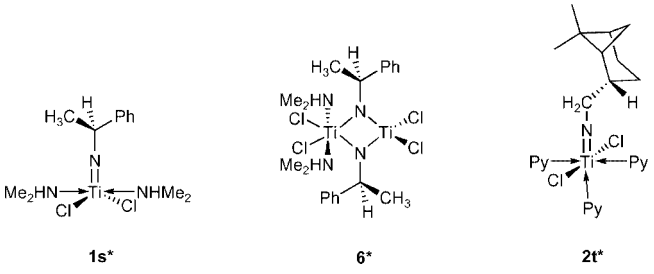


Figure 11. Chiral imido–titanium(IV) complexes.

Single-crystals of **1s*** (yellow blocks) were obtained from a toluene/pentane solution at room temp., and the crystal structure was determined. Complex **1s*** crystallized in the monoclinic space group $P2_1$.[36] A thermal ellipsoid plot is presented in Figure 12 along with selected bond lengths and angles in Table 1. In the solid state, the molecular structure of **1s*** resembles that of other five-coordinate $M(=NR)\text{-}Cl_2(NHMe_2)_2$ complexes described in this article and by others (M = Ti,[26] V[21]), and the metric parameters are comparable [avg. N_{imido}–Ti–Cl 109.9°, avg. N_{imido}–Ti–N_{NHMe_2} 99.8, Ti–N_{imido} distance of 1.682(4) Å, Ti–N_{imido}–C1 angle = 168.8(4)°, Cl–Ti–Cl angle of 140.12(6)°, mean Ti–Cl bond lengths of 2.350 Å, Ti–N_{amine} bond lengths of avg. 2.205 Å]. In this case, the geometry around the metal center is closer to square planar (τ = 0.34).

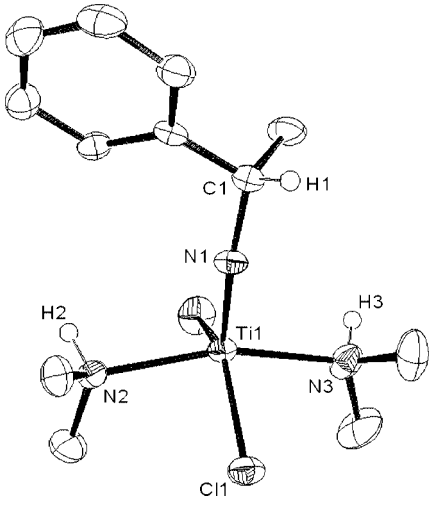


Figure 12. Molecular structure of **1s*** with selected bond lengths [Å] and angles [°], which shows 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity.

Note that when less than 1 equiv. of chiral benzylic amine is used, we have observed by ^1H NMR spectroscopy the concomitant formation of another imido species **6*** as a minor side product. The lower solubility of **6*** allowed us to selectively obtain a few crystals and to determine its solid-state structure. **6s*** crystallized in the tetragonal space group $P4_2$. The molecular structure is presented in Figure 13 and selected distances and angles are summarized in Table 2. Compound **6*** is an imido-bridged dimer formulated as $[Cl_2Ti\{\mu\text{-}N\text{-}[(S)\text{-}(-)\text{-}CHMePh]\}_2TiCl_2(NHMe_2)_2]$ that consists of one four- and one six-coordinate titanium center.[37] Molecules of **6*** possess approximately tetrahedral (Ti1) and octahedral (Ti2) metals linked by bridging aryl–imido ligands. The Ti–Cl [average Ti1–Cl 2.25 Å, average Ti2–Cl 2.35 Å] and Ti–N_{imido} [Ti1–N1 1.821(4) Å, Ti1–N2 1.840(4) Å, Ti2–N1 1.965(4) Å, Ti2–N2 1.971(4) Å] distances for Ti2 are longer than those for Ti1 by ca. 0.1 Å (Ti–Cl) and ca. 0.13 Å (Ti–N_{imido}), which is consistent with the higher coordination number of Ti2. The torsion angle Ti1–N1–Ti2–N2 of the Ti_2N_2 core is 4.5(2)°.

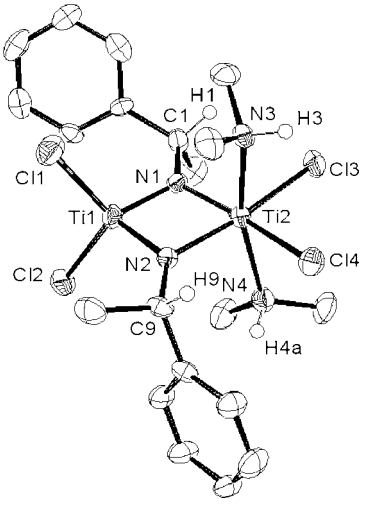
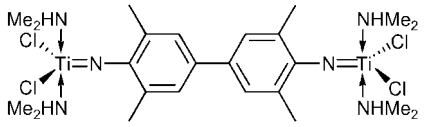


Figure 13. Molecular structure of **6*** with selected bond lengths [Å] and angles [°], which shows 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity.

Similarly, we have attempted the synthesis of the related imido complex $[Ti\{=N\text{-}[(-)\text{-}cis\text{-myrtanyl}]\}Cl_2(NHMe_2)_2]$ (**1t***) that has a *cis*-myrtanyl function (Figure 11). However, we have not been able to isolate **1t*** in a pure form – the resulting orange material probably contains a mixture of imido compounds with a lower number of dimethylamine coligands as judged by its poor solubility and by the low *N*-content determined by combustion analysis (unfortunately the ^1H NMR spectrum was extremely broad and a full assignment of the signals was not possible). Nevertheless, a subsequent addition of pyridine afforded the desired pyridine complex $[Ti\{=N\text{-}[(-)\text{-}cis\text{-myrtanyl}]\}Cl_2(Py)_3]$ (**2t***) as the unique product.[38]

Interestingly, as an extension, our procedure may be used to generate multimetallic architectures held together by imido functions.[39] For instance, diimido complexes have been obtained directly from diamines. The reaction of

3,3′,5,5′-tetramethyl[1,1′-biphenyl]-4,4′-diamine (H_2N–*BP*–NH_2) with 2 equiv. of $Ti(NMe_2)_4$ in the presence of an excess of Me_3SiCl afforded the binuclear derivative $[(Me_2HN)_2Cl_2Ti(=N–BP–N=)TiCl_2(NHMe_2)_2]$ (**7**, Figure 14). Replacement of the dimethylamine ligands was prompted by the addition of pyridine to **7** and afforded the pyridine analogue $[(Py)_3Cl_2Ti(=N–BP–N=)TiCl_2(Py)_3]$ (**8**). An X-ray structure determination of a crystal of **8** (Figure 15 and Table 2) reveals a binuclear titanium complex with a bridging spacer composed of the diimido unit. The two titanium centers have an octahedral geometry with structure, bond lengths, and angles similar to the monometallic species. The titanium–nitrogen bond length of the imido fragments are 1.719(4) Å and 1.710(4) Å, the imido fragment were found to be almost linear [Ti–N_{imido}–C_{ipso} 174.6(4)° and 178.1(4)°], and Ti–Cl bond lengths are in the range 2.39–2.42 Å. The dihedral angle between the planes of the two benzene rings of the biphenyl unit is 14.0(2)°.

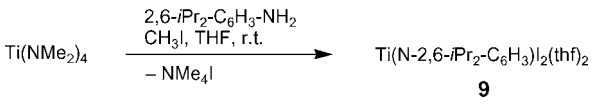


7

Figure 14. Diimido-titanium(IV) complex **7**.

4. Alternative Synthesis of Imido–Titanium Species

The reaction of $Ti(NMe_2)_4$ with 2,6-*i*Pr_2–$C_6H_3NH_2$ in THF with an excess of CH_3I in place of chlorotrimethylsilane can be used to generate an aryl–imido complex. This reaction proceeds at room temperature (Scheme 3), with alkylation of the four dimethylamido groups.[40] After filtration of the insoluble Me_4NI salt, the imido complex formulated as $[Ti(NAr)I_2(thf)_2]$ (**9**) (Ar = 2,6-*i*Pr_2–C_6H_3), as judged by ^1H NMR spectroscopy and combustion analysis, is obtained in 79% yield. This compound is most probably a dimer with bridging iodides as in the structurally established phenylimido analogue $[Ti(=NPh)Cl(\mu\text{-}Cl)(thf)_2]_2$.[4c] This new synthesis could be important as an alternative method for the preparation of imido complexes when N-donor coligands ($NHMe_2$) are not wanted. The scope of this synthesis will be developed elsewhere.



Scheme 3. Alternative synthesis of imido–titanium(IV) compounds.

Conclusions

We have reported a direct and efficient method to generate titanium(IV) complexes of the type $Ti(=NR)Cl_2(NHMe_2)_2$ from commercially available $Ti(NMe_2)_4$ and a wide range of primary amines under simple and mild conditions. We have also demonstrated the functional group tolerance of this reaction, and it has been applied to the synthesis of titanium complexes that have an additional functionality on the imido moiety. The reactivity of these functionalized imido groups can now be ascertained and the added functionality may also serve as an anchor to graft this species onto a support. Also of great interest, we have been able to prepare complexes with diimido ligands, as well as the first Ti compounds that contain chiral imido supporting ligands. As an alternative method, we have reported some preliminary results on the synthesis of imido–titanium complexes of the type $[Ti(NAr)I_2(thf)_2]_2$ that use CH_3I as a reagent.

Experimental Section

General Methods and Instrumentation: All manipulations were carried out with a standard Schlenk line or dry box techniques under an atmosphere of argon. Solvents were refluxed and dried with the appropriate drying agents under an atmosphere of argon, and collected by distillation. NMR spectra were recorded with a Bruker AM200, AM250, ARX250, DPX300, or Avance500 spectrometers, referenced internally to residual protio-solvent (^1H) resonances, and are reported relative to tetramethylsilane (δ = 0 ppm). ^{19}F NMR spectra were recorded with a Bruker AM200 spectrometer (reference CF_3CO_2H). ^{29}Si NMR spectra were recorded with a Bruker Avance500 spectrometer. Infrared spectra were prepared under an argon atmosphere in a glove box and were recorded with

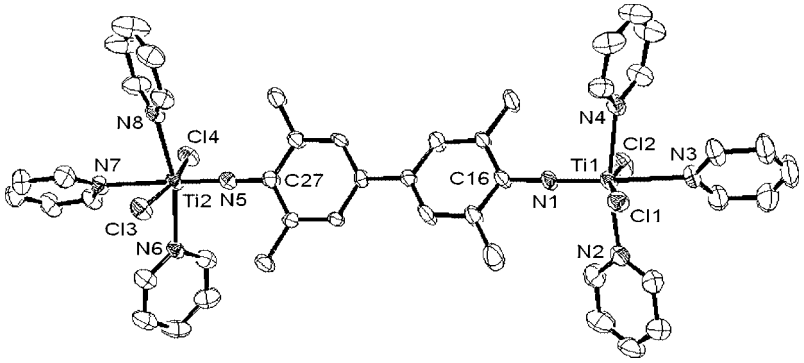


Figure 15. Molecular structure of **8** with selected bond lengths [Å] and angles [°], which shows 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity.

a Perkin–Elmer Spectrum GX FT-IR spectrometer. Elemental analyses were performed at the Laboratoire de Chimie de Coordination (Toulouse, France) (C, H, N) or by the Service Central de Microanalyses du CNRS at Vernaison (France) (C, H, N, Cl).

The $Ti(NMe_2)_4$ used in this study was prepared by a modification of a literature procedure,[41] or purchased from commercial sources (Aldrich, Acros). Liquid anilines and amines were dried with KOH or CaH_2, refluxed, distilled, and stored over 4 Å molecular sieves under an argon atmosphere before use. Trimethylchlorosilane was distilled and stored over 4 Å molecular sieves under an argon atmosphere before use. The optical purity of the enantiomerically pure chiral amines used in this study [(*S*)-(–)-α-methylbenzylamine and (–)-*cis*-myrtanylamine] was 98% (Aldrich).

Crystal Structure Determination: Crystals of **1k** (dark-green blocks), **1o** (orange plates), **1p** (orange plates), **1s*** (yellow blocks), **2d** (yellow blocks), **2l** (orange plates), **2r** (orange parallelepipeds), **3** (dark-red blocks), **5** (orange blocks), **6*** (green plates), and **8** (orange blocks) were obtained. Crystal data collection and processing parameters are given in Table 3 and Table 4. The selected crystals, sensitive to air and moisture, were mounted on a glass fiber with perfluoropolyether oil and cooled rapidly to 180 K in a stream of cold N_2. Data were collected at low temperature (T = 180 K) with a Stoe Imaging Plate Diffraction System (IPDS) equipped with an Oxford Cryosystems Cryostream Cooler Device or an Oxford Diffraction Kappa CCD Excalibur diffractometer equipped with an Oxford Instrument cryojet, with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Final unit cell parameters were obtained by means of a least-squares refinement of a set of 8000 well-measured reflections, and crystal decay was monitored during data collection by the measurement of 200 reflections by image; no significant fluctuation of intensities has been observed. Structures have been solved by means of Direct Methods with the program SIR92,[42] and subsequent difference Fourier maps. Models were refined by least-squares procedures on a F^2 with SHELXL-97[43] integrated in the package WINGX version 1.64;[44] empirical absorption corrections were applied on the data.[45] All hydrogen atoms have been located on differences Fourier maps, and introduced into the refinement as fixed contributors with a riding model with an isotropic thermal parameter fixed at 20% higher than those of the Csp^2 atoms and 50% for the Csp^3 atoms to which they were connected. The methyl groups were refined with the torsion angle as a free variable. Some exceptions for a few specific hydrogen atoms were made, which have been isotropically refined (like nitrogen bound hydrogens). For the seven structures all non-hydrogen atoms were anisotropically refined, and in the last cycles of the refinement weighting schemes were used, where weights are calculated from the following formula: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. The poor quality of the structure determination of **3** is due to the small size of the crystal, and was not sufficient to give precise bond lengths and angles. For **8** it was not possible to resolve diffuse electron-density residuals (enclosed solvent molecules). Treatment with the SQUEEZE facility from PLATON,[46] with a localized void of about 1730 $Å^3$ and 75 recovered electrons, resulted in a smooth refinement. Since a few low-order reflections are missing from the data set, the electron count will be underestimated. Thus, the values given for D_{calc}, $F(000)$ and the molecular weight are only valid for the ordered part of the structure. For **1s***, the Flack parameter[47] was refined to a value of 0.11(7). Although, the standard deviation on this parameter is rather high, inversion of the configuration gave a value of 0.89, and so the absolute configuration could be determined and it agrees with the synthetic pathway [in addition, the Flack parameter for complex **6***, which is derived from **1s***, was refined to a satisfying value of 0.04(3)]. The deviation of the Flack parameter from 0 is probably due to the weak anomalous diffusion of Ti and Cl atoms. CCDC-608174 to -608184 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 3. Crystallographic data, data collection and refinement parameters for compounds **1k**, **1p**, **1o**, **1s***, **2d**, and **2l**.

	1k	**1o**	**1p**	**1s***[a]	**2d**	**2l**
Chemical formula	$C_{14}H_{28}Cl_2N_4Ti$	$C_{13}H_{23}Cl_2N_3Ti$	$C_{12}H_{19}Cl_2N_3Ti$	$C_{12}H_{23}Cl_2N_3Ti$	$C_{33}H_{30}Cl_2N_4SiTi$	$C_{22}H_{19}Cl_2N_5Ti$
Formula weight	371.20	340.14	324.10	328.10	629.50	472.22
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/a$	$P2_1$	$P2_1/c$	$C2/c$
a [Å]	9.182(5)	13.9252(7)	8.9189(7)	9.0267(9)	10.8267(5)	8.2536(6)
b [Å]	9.694(5)	10.2394(5)	20.246(2)	10.5665(18)	11.2667(5)	23.3710(11)
c [Å]	12.436(5)	12.1777(6)	9.1104(8)	9.0580(12)	26.8863(14)	12.5545(6)
α [°]	107.181(5)	90.0	90.0	90.0	90.0	90.0
β [°]	109.035(5)	89.897(4)	98.747(10)	103.210(10)	107.819(4)	105.544(5)
γ [°]	94.289(5)	90.0	90.0	90.0	90.0	90.0
V([Å]^3)	981.6(8)	1736.36(15)	1626.0(2)	841.1(2)	3122.3(3)	2333.1(2)
Z	2	4	4	2	4	4
D_{calc} (g cm^{-3})	1.256	1.301	1.324	1.296	1.339	1.344
μ (Mo-K_α) [mm^{-1}]	0.708	0.792	0.842	0.815	0.513	0.614
F(000)	392	712	672	344	1304	968
θ range [°]	3.51–32.06	3.54–32.15	2.48–25.68	2.87–32.04	2.96–32.26	3.49–25.68
Measured reflections	10407	17009	12282	8603	26117	7813
Unique reflections/Rint	6192/0.0223	5707/0.0277	3070/0.0549	3962/0.0746	10210/0.0209	2215/0.0242
Parameters/restraints	196/0	183/3	166/1	169/1	370/0	140/0
Final *R* indices [$I>\sigma 2(I)$]	R_1 = 0.0424	R_1 = 0.0338	R_1 = 0.0509	R_1 = 0.0552	R_1 = 0.0452	R_1 = 00.0304
	wR_2 = 0.1131	wR_2 = 0.0819	wR_2 = 0.1082	wR_2 = 0.1067	wR_2 = 0.1080	wR_2 = 0.0703
Final *R* indices all data	R_1 = 0.0516	R_1 = 0.0497	R_1 = 0.0583	R_1 = 0.1065	R_1 = 0.0578	R_1 = 0.0346
	wR_2 = 0.1170	wR_2 = 0.0873	wR_2 = 0.1106	wR_2 = 0.1383	wR_2 = 0.01157	wR_2 = 0.0731
Goodness of fit	1.077	1.067	1.167	0.841	1.070	1.051
$\Delta\rho$max and $\Delta\rho$min	0.905 and –0.514	0.531 and –0.311	0.349 and –0.305	0.360 and –0.407	0.462 and –0.529	0.264 and –0.210

[a] Absolute structure parameter: 0.11(7).

Table 4. Crystallographic data, data collection and refinement parameters for compounds **2r**, **3**, **5**, **6***, and **8**.

	2r	**3**	**5**	**6***[a]	**8**
Chemical formula	$C_{23}H_{26}Cl_2N_4Ti$, C_5H_5N	$C_{20}H_{32}Cl_4N_4O_2Ti_2$	$C_{20}H_{28}Cl_4N_4O_2Ti_2$	$C_{20}H_{32}Cl_4N_4Ti_2$	$C_{46}H_{46}Cl_4N_8Ti_2$
Formula weight	556.38	598.04	594.06	566.10	948.51
Crystal system	monoclinic	monoclinic	monoclinic	tetragonal	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P4_2$	$P2_1/n$
a [Å]	9.1233(9)	9.868(2)	10.1969(15)	13.043(2)	15.7668(12)
b [Å]	10.3422(11)	7.9255(16)	11.9115(13)	13.043(2)	17.2900(12)
c [Å]	15.5338(13)	16.575(3)	11.0227(15)	15.073(3)	21.7813(19)
α [°]	76.531(8)	90.0	90.0	90.0	90.0
β [°]	80.338(8)	90.77(3)	112.931(15)	90.0	96.202(7)
γ [°]	87.611(9)	90.0	90.0	90.0	90.0
V([Å]^3)	1405.2(2)	1296.2(4)	1233.0(3)	2564.2(8)	5903.0(8)
Z	2	2	2	4	4
D_{calc} (g cm^{-3})	1.315	1.532	1.600	1.466	1.067
μ (Mo-K_α) [mm^{-1}]	0.520	1.053	1.107	1.055	0.484
F(000)	580	616	608	1168	1960
θ range [°]	2.73–32.05	3.30–23.25	2.64–25.68	3.12–24.69	3.02–26.37
Measured reflections	14916	7332	9348	17232	41980
Unique reflections/Rint	8919/0.0312	1854/0.1297	2332/0.1180	4373/0.1019	12047/0.1418
Parameters/restraints	325/0	148/0	145/0	277/1	545/0
Final R indices [I>σ2(I)]	R_1 = 0.0372 wR_2 = 0.0923	R_1 = 0.0996 wR_2 = 0.2462	R_1 = 0.0432 wR_2 = 0.0951	R_1 = 0.0431 wR_2 = 0.0549	R_1 = 0.0950 wR_2 = 0.2361
Final R indices all data	R_1 = 0.0544 wR_2 = 0.1045	R_1 = 0.1203 wR_2 = 0.2684	R_1 = 0.0853 wR_2 = 0.1051	R_1 = 0.0765 wR_2 = 0.0622	R_1 = 0.1510 wR_2 = 0.2649
Goodness of fit	0.958	1.058	0.851	0.784	0.993
$\Delta\rho$max and $\Delta\rho$min	0.488 and –0.586	1.322 and –1.089	0.308 and –0.321	0.274 and –0.254	0.634 and –0.792

[a] Absolute structure parameter 0.04(3).

[Ti(=NR)Cl$_2$(NHMe$_2$)$_2$] (1a–t). General Synthetic Procedure: To a toluene solution (5 mL) of Ti(NMe$_2$)$_4$ (250 mg, 1.115 mmol), amine RNH$_2$ (1 equiv. 1.115 mmol) was added at room temperature. To this solution Me$_3$SiCl (1.00 g) was slowly added at room temperature. The resulting solution was stirred overnight at room temp. (or at 60 °C for **1a**, for the other compounds we did not notice significant changes in yields when the reaction was performed at 60 °C). Depending on the amine RNH$_2$ used, the product separates from the solution as a crystalline compound (without or upon the addition of pentane), or the volatiles were removed under reduced pressure. The yellow–orange microcrystalline solid was then washed with pentane (2×10 mL), and dried under vacuum to afford the analytically and spectroscopically pure material. Pure **1** was obtained by recrystallization from toluene/pentane. Yields are calculated on the basis of 250-mg scale reaction of Ti(NMe$_2$)$_4$. Some of these compounds have been prepared with up to 2 g of Ti(NMe$_2$)$_4$ with similar yields.

[Ti(=N–*t*Bu)Cl$_2$(NHMe$_2$)$_2$] (1a): Yield 260 mg (93%) (yellow). ^{1}H NMR (250 MHz, CD$_2$Cl$_2$): δ = 3.46 (br. m, 2 H, N*H*), 2.71 (d, ^3J = 6.2 Hz, 12 H, NH*Me$_2$*), 1.05 (s, 9 H, *t*Bu) ppm. ^{13}C{^{1}H} NMR (62.90 MHz, CD$_2$Cl$_2$): δ = 73.6 (*C*Me$_3$), 41.1 (NH*Me$_2$*), 31.5 (C*Me$_3$*) ppm. IR (KBr): $\tilde{\nu}$ = 3234 (s, NH), 2973 (s), 1517 (m), 1363 (w), 1244 (m), 1184 (m), 1090 (m), 1015 (s), 975 (s), 901 (m), 810 (w), 557 (m), 498 (w) cm^{-1}. C$_8$H$_{23}$Cl$_2$N$_3$Ti (280.06): calcd. C 34.31, H 8.28, N 15.00; found C 34.33, H 8.35, N 14.86.

[Ti(=N–1-Adamantane)Cl$_2$(NHMe$_2$)$_2$] (1b): Yield 320 mg (80%) (yellow). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ = 3.48 (br. m, 2 H, N*H*), 2.71 (d, ^3J = 6.0 Hz, 12 H, NH*Me$_2$*), 1.89 (br. s, 3 H, C*H*$_{ada}$), 1.66 (br. s, 6 H, C*H*$_{2ada}$), 1.48 (br. s, 6 H, C*H*$_{2ada}$) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, CD$_2$Cl$_2$): δ = 75.4 (*C*$_q$), 45.4 (*C*$_q$), 41.2 (NH*Me$_2$*), 36.5 (*C*$_{ada}$), 30.1 (*C*$_{ada}$) ppm. IR (KBr): $\tilde{\nu}$ = 3233 (w, NH), 2921 (vs), 1465 (m), 1365 (m), 1237 (s), 1097 (m), 1016 (m), 894 (s), 499 (w) cm^{-1}. C$_{14}$H$_{29}$Cl$_2$N$_3$Ti (358.17): calcd. C 46.95, H 8.16, N 11.73; found C 47.05, H 8.19, N 11.60.

[Ti(=N–CPh$_3$)Cl$_2$(NHMe$_2$)$_2$] (1c): Yield 475 mg (91%) (yellow). ^{1}H NMR (250 MHz, CD$_2$Cl$_2$): δ = 7.21–7.38 (m, 15 H, C$_6$*H*$_5$), 3.27 (br. sept, 2 H, N*H*), 2.44 (d, ^3J = 6.1 Hz, 12 H, NH*Me$_2$*) ppm. ^{13}C{^{1}H} NMR (62.90 MHz, CD$_2$Cl$_2$): δ = 147.7, 129.0, 128.0, 126.9 (*C*$_6$H$_5$, one signal not observed), 40.7 (NH*Me$_2$*) ppm. IR (KBr): $\tilde{\nu}$ = 3233 (m, NH), 2929 (m), 2780 (m), 1596 (m), 1467 (m), 1443 (m), 1209 (m), 1020 (m), 991 (w), 893 (m), 755 (m), 699 (s), 636 (m), 420 (m) cm^{-1}. C$_{23}$H$_{29}$Cl$_2$N$_3$Ti (466.27): calcd. C 59.25, H 6.27, N 9.01; found: C 59.07, H 6.24, N 8.87.

[Ti(=N–SiPh$_3$)Cl$_2$(NHMe$_2$)$_2$] (1d): Yield 490 mg (91%) (yellow). ^{1}H NMR (250 MHz, CD$_2$Cl$_2$): δ = 7.72 (m, 6 H, C$_6$*H*$_5$), 7.38 (m, 9 H, C$_6$*H*$_5$), 3.39 (br. sept, 2 H, N*H*), 2.55 (d, ^3J = 6.2 Hz, 12 H, NH*Me$_2$*) ppm. ^{13}C{^{1}H} NMR (125.81 MHz, CD$_2$Cl$_2$): δ = 136.9, 135.5, 130.6, 129.7 (*C*$_6$H$_5$), 41.2 (NH*Me$_2$*) ppm. ^{29}Si NMR (99.40 MHz, CD$_2$Cl$_2$): δ = –43 ppm. IR (KBr): $\tilde{\nu}$ = 3242 (s, NH), 1465 (m), 1427 (m), 1111 (vs), 893 (w), 703 (s), 507 (s) cm^{-1}. C$_{22}$H$_{29}$Cl$_2$N$_3$SiTi (482.34): calcd. C 54.78, H 6.06, N 8.71; found C 54.66, H 6.07, N 8.66.

[Ti(=N–Ph)Cl$_2$(NHMe$_2$)$_2$] (1e): Yield 273 mg (81%) (red–orange). ^{1}H NMR (250 MHz, CD$_2$Cl$_2$): δ = 7.07 (t, 2 H, C$_6$*H*$_5$), 6.82 (m, 3 H, C$_6$*H*$_5$), 3.56 (br. sept, 2 H, N*H*), 2.76 (d, ^3J = 6.2 Hz, 12 H, NH*Me$_2$*) ppm. C$_{10}$H$_{19}$Cl$_2$N$_3$Ti (300.05): calcd. C 40.03, H 6.38, N 14.00; found C 39.86, H 6.41, N 13.92.

[Ti(=N–2,6-*i*Pr$_2$–C$_6$H$_3$)Cl$_2$(NHMe$_2$)$_2$] (1f): Yield 410 mg (96%) (orange). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 6.99 (d, ^3J = 7.5 Hz, 2 H, C$_6$*H*$_3$), 6.85 (t, ^3J = 7.6 Hz, 1 H, C$_6$*H*$_3$), 4.67 (sept, ^3J = 6.7 Hz, 2 H, C*H*Me$_2$), 2.91 (br. m, 2 H, N*H*), 2.27 (d, ^3J = 6.3 Hz, 12 H, NH*Me$_2$*), 1.44 (d, ^3J = 6.9 Hz, 12 H, CH*Me$_2$*) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, C$_6$D$_6$): δ = 157.8, 144.7, 123.8, 122.7 (*C*$_6$H$_3$), 40.8 (NH*Me$_2$*), 28.0 (*C*HMe$_2$), 24.6 (CH*Me$_2$*) ppm. IR (KBr): $\tilde{\nu}$ = 3255 (w, NH), 2961 (m), 1465 (s), 1334 (s), 1288 (s), 1021 (m), 896 (m), 753 (s), 668 (vs) cm^{-1}. C$_{16}$H$_{31}$Cl$_2$N$_3$Ti (384.21): calcd. C 50.02, H 8.13, N 10.94; found C 49.93, H 8.20, N 10.81.

[Ti(=N–2,6-Cl_2–C_6H_3)Cl_2($NHMe_2$)$_2$] (1g): Yield 300 mg (73%) (orange). ^{1}H NMR (250 MHz, C_6D_6): δ = 6.90 (d, ^3J = 8.0 Hz, 2 H, C_6H_3), 6.13 (t, ^3J = 7.9 Hz, 1 H, C_6H_3), 2.97 (br. m, 2 H, N*H*), 2.28 (d, ^3J = 6.2 Hz, 12 H, NHMe_2) ppm. ^{13}C{^{1}H} NMR (62.90 MHz, C_6D_6): δ = 158.0, 130.6, 122.2 (C_6H_3, one signal not observed, probably obscured under C_6D_6), 41.2 (NHMe_2) ppm. IR (KBr): $\tilde{\nu}$ = 3251 (s, NH), 2977 (m), 2931 (m), 2783 (m), 1610 (w), 1468 (m), 1434 (vs), 1397 (m), 1332 (s), 1258 (w), 1192 (w), 1071 (w), 1011 (s), 983 (m), 894 (s), 788 (s), 759 (m), 718 (m), 568 (m), 458 (w), 425 (w) cm^{-1}. $C_{10}H_{17}Cl_4N_3Ti$ (368.94): calcd. C 32.55, H 4.64, N 11.39; found C 32.53, H 4.60, N 11.25.

[Ti(=N–2,6-Br_2–4-Me–C_6H_2)Cl_2($NHMe_2$)$_2$] (1h): Yield 451 mg (96%) (orange). ^{1}H NMR (250 MHz, C_6D_6): δ = 6.97 (d, 2 H, C_6H_2), 3.17 (br. m, 2 H, N*H*), 2.36 (d, ^3J = 6.1 Hz, 12 H, NHMe_2), 1.69 (s, 3 H, Me_{Ar}) ppm. ^{13}C{^{1}H} NMR (62.90 MHz, C_6D_6): δ = 152.7, 133.7, 132.4, 120.5 (C_6H_2), 41.4 (NHMe_2), 20.2 (Me_{Ar}) ppm. IR (KBr): $\tilde{\nu}$ = 3248 (s, NH), 3008 (w), 2975 (w), 2937 (w), 2781 (w), 1465 (m), 1442 (s), 1332 (s), 1255 (w), 1011 (s), 896 (s), 850 (m), 741 (s), 713 (m), 581 (m), 568 (m), 459 (w), 423 (w) cm^{-1}. $C_{11}H_{19}Br_2Cl_2N_3Ti$ (471.87): calcd. C 28.00, H 4.06, N 8.91; found C 28.05, H 4.08, N 8.89.

[Ti(=N–C_6F_5)Cl_2($NHMe_2$)$_2$] (1i): Yield 405 mg (93%) (orange). ^{1}H NMR (250 MHz, C_6D_6): δ = 2.70 (br. m, 2 H, N*H*), 2.21 (d, ^3J = 6.1 Hz, 12 H, NHMe_2) ppm. ^{19}F NMR (C_6D_6, 188.3 MHz): δ = –78.8 (d, 2F, *o*-C_6F_5), –89.5 (t, 2F, *m*-C_6F_5), –90.3 (t, 1F, *p*-C_6F_5) ppm. $C_{10}H_{14}Cl_2F_5N_3Ti$ (390.00): calcd. C 30.80, H 3.62, N 10.77; found C 30.75, H 3.57, N 10.70.

[Ti[=N–3,5-(F_3C)$_2$–C_6H_3]Cl_2($NHMe_2$)$_2$] (1j): Yield 380 mg (87%) (red–orange). ^{1}H NMR (250 MHz, C_6D_6): δ = 7.36 (br. s, 3 H, C_6H_3), 2.36 (br. m, 2 H, N*H*), 2.11 (d, ^3J = 6.0 Hz, 12 H, NHMe_2) ppm. ^{13}C{^{1}H} NMR (62.90 MHz, C_6D_6): δ = 159.1, 132.7, 124.3, 123.7 (C_6H_3), 115.4 (CF_3), 41.0 (NHMe_2) ppm. ^{19}F NMR (188.3 MHz, C_6D_6): δ = 13.31 ppm. IR (KBr): $\tilde{\nu}$ = 3229 (m, NH), 3008 (w), 2982 (w), 1598 (w), 1466 (m), 1460 (m), 1387 (s), 1278 (vs), 1177 (s), 1132 (vs), 1040 (s), 1022 (m), 894 (m), 876 (m), 682 (m), 426 (w) cm^{-1}. $C_{12}H_{17}Cl_2F_6N_3Ti$ (436.05): calcd. C 33.05, H 3.93, N 9.64; found C 33.03, H 3.94, N 9.51.

[Ti(=N–4-Et_2N–C_6H_4)Cl_2($NHMe_2$)$_2$] (1k): Yield 345 mg (93%) (green). ^{1}H NMR (250 MHz, C_6D_6): δ = 7.11 (d, ^3J = 8.9 Hz, 2 H, C_6H_4), 6.40 (d, ^3J = 9.0 Hz, 2 H, C_6H_4), 2.94 [q, ^3J = 7.0 Hz, 4 H, N(CH_2CH_3)$_2$], 2.80 (br. m, 2 H, N*H*), 2.36 (d, ^3J = 6.1 Hz, 12 H, NHMe_2), 0.86 [t, ^3J = 7.0 Hz, 6 H, N(CH_2CH_3)$_2$] ppm. ^{13}C{^{1}H} NMR (250 MHz, C_6D_6): δ = 156.2, 144.2, 125.9, 112.7 (C_6H_4), 45.2 [N(CH_2CH_3)$_2$], 41.2 (NHMe_2), 13.4 [N(CH_2CH_3)$_2$] ppm. IR (KBr): $\tilde{\nu}$ = 3249 (s, NH), 2973 (s), 1597 (m), 1499 (vs), 1465 (m), 1320 (m), 1265 (vs), 1005 (m), 896 (m), 815 (s), 458 (w) cm^{-1}. $C_{14}H_{28}Cl_2N_4Ti$ (371.17): calcd. C 45.30, H 7.60, N 15.09; found C 45.12, H 7.74, N 14.99.

[Ti(=N–4-NC–C_6H_4)Cl_2($NHMe_2$)$_2$] (1l): Yield 280 mg (77%) (orange). ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 7.39 (d, ^3J = 8.6 Hz, 2 H, C_6H_4), 6.85 (d, ^3J = 8.5 Hz, 2 H, C_6H_4), 3.54 (br. m, 2 H, N*H*), 2.75 (d, ^3J = 6.3 Hz, 12 H, NHMe_2) ppm. The low solubility of **1l** precluded its ^{13}C{^{1}H} NMR analysis. IR (KBr): $\tilde{\nu}$ = 3214 (m, NH), 2978 (w), 2923 (w), 2243 (s, CN), 1586 (s), 1487 (s), 1441 (s), 1168 (m), 1021 (m), 961 (w), 897 (m), 836 (m), 773 (w), 551 (w) cm^{-1}. $C_{11}H_{18}Cl_2N_4Ti$ (325.06): calcd. C 40.64, H 5.58, N 17.24; found C 40.54, H 5.52, N 17.12.

[Ti(=N–2-NC–C_6H_4)Cl_2($NHMe_2$)$_2$] (1m): Yield 350 mg (96%) (orange). ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 7.31 (app. t, app. ^3J = 8.6 Hz, 2 H, C_6H_4), 6.85 (app. t, app. ^3J = 7.3 Hz, 2 H, C_6H_4), 3.82 (br. m, 2 H, N*H*), 2.78 (d, ^3J = 5.6 Hz, 12 H, NHMe_2) ppm. ^{13}C{^{1}H} NMR (62.90 MHz, CD_2Cl_2): δ = 160.5, 133.3, 131.9, 129.2, 128.3, 123.8, 122.0, 41.3 (NHMe_2) ppm. IR (KBr): $\tilde{\nu}$ = 3228 (m, NH), 2971 (w), 2934 (w), 2242 (s, CN), 1570 (s), 1462 (s), 1446 (s), 1350 (s), 1262 (m), 1018 (m), 995 (m), 973 (w), 898 (m), 765 (s) cm^{-1}. $C_{11}H_{18}Cl_2N_4Ti$ (325.06): calcd. C 40.64, H 5.58, N 17.24; found C 40.37, H 5.44, N 17.06.

[Ti(=N–4-H_2C=CH–C_6H_4)Cl_2($NHMe_2$)$_2$] (1n): Yield 240 mg (74%) (red). ^{1}H NMR (250 MHz, C_6D_6): δ = 7.15 (d, ^3J = 8.3 Hz, 2 H, C_6H_4), 6.96 (d, ^3J = 8.3 Hz, 2 H, C_6H_4), 5.57 (dd, J = 17.6 and 11.8 Hz, 1 H, =C*H*), 5.53 (d, ^3J = 18.5 Hz, 1 H, =C*H*), 5.02 (d, ^3J = 12.0 Hz, 1 H, =C*H*), 2.62 (m, 2 H, N*H*), 2.25 (d, ^3J = 6.1 Hz, 12 H, NHMe_2) ppm. ^{13}C{^{1}H} NMR (62.90 MHz, C_6D_6): δ = 161.5 (C_6H_4), 137.2 (=*C*H), 132.6, 127.0, 124.5 (C_6H_4), 112.7 (=*C*H$_2$), 41.0 (NHMe_2) ppm. IR (KBr): $\tilde{\nu}$ = 3266 (m, NH), 3237 (m, NH), 2973 (m), 2935 (m), 1624 (w, C=C), 1588 (w), 1491 (s), 1466 (s), 1400 (w), 1326 (s), 1264 (m), 1114 (m), 1018 (s), 893 (s), 842 (s), 609 (w) cm^{-1}. $C_{12}H_{21}Cl_2N_3Ti$ (326.09): calcd. C 44.20, H 6.49, N 12.89; found C 44.10, H 6.50, N 12.54.

[Ti(=N–2-MeC=CH_2–C_6H_4)Cl_2($NHMe_2$)$_2$] (1o): Yield 250 mg (73%) (red). ^{1}H NMR (250 MHz, C_6D_6): δ = 7.31 (dd, ^3J = 9.0 Hz, 1 H, C_6H_4), 7.07 (dd, ^3J = 7.6 Hz, 1 H, C_6H_4), 7.00 (td, ^3J = 9.6 Hz, 1 H, C_6H_4), 6.74 (t, ^3J = 7.4 Hz, 1 H, C_6H_4), 5.26 (app d, app. J = 12.9 Hz, 2 H, CH_2), 2.77 (br. m, 2 H, N*H*), 2.52 (s, 3 H, CH_3), 2.26 (d, ^3J = 6.3 Hz, 12 H, NHMe_2) ppm. ^{13}C{^{1}H} NMR (62.90 MHz, C_6D_6): δ = 158.8, 147.2, 136.0 (C_6H_4, 1 peak obscured under C_6D_6), 123.2 (*C*=CH$_2$), 115.2 (C=*C*H$_2$), 41.0 (NHMe_2), 25.0 (*C*H$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3226 (m, NH), 2973 (w), 2934 (w), 1629 (w, C=C), 1517 (w), 1466 (s), 1430 (s), 1322 (s), 1115 (w), 1094 (w), 1020 (m), 997 (w), 973 (w), 982 (w), 894 (m), 750 (m), 573 (w), 472 (w) cm^{-1}. $C_{13}H_{23}Cl_2N_3Ti$ (340.11): calcd. C 45.91, H 6.82, N 12.35; found C 45.83, H 6.98, N 11.91.

[Ti(=N–3-HC≡C–C_6H_4)Cl_2($NHMe_2$)$_2$] (1p): Yield 260 mg (72%) (red). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 7.07 (t, ^3J = 8.0 Hz, 1 H, C_6H_4), 6.99 (s, 1 H, C_6H_4), 6.98 (d, ^3J = 8.5 Hz, 1 H, C_6H_4), 6.85 (d, ^3J = 8.6 Hz, 1 H, C_6H_4), 3.60 (br. m, 2 H, N*H*), 3.11 (s, 1 H, ≡C*H*), 2.78 (d, ^3J = 6.1 Hz, 12 H, NHMe_2) ppm. ^{13}C{^{1}H} NMR (125.81 MHz, CD_2Cl_2): δ = 159.6, 128.4, 126.7, 126.0, 123.8, 121.9 (C_6H_4), 83.3 (*C*≡CH), 76.7 (≡*C*H), 40.8 (NHMe_2) ppm. IR (KBr): $\tilde{\nu}$ = 3270 (m, NH), 3255 (m, NH), 2977 (m), 2208 (w, C≡C), 1577 (w), 1467 (s), 1407 (m), 1329 (s), 1261 (m), 1099 (m), 1025 (s), 993 (s), 794 (s), 676 (m) cm^{-1}. $C_{12}H_{19}Cl_2N_3Ti$ (324.07): calcd. C 44.47, H 5.91, N 12.97; found C 45.94, H 6.53, N 11.91. We were unable to obtain satisfactory elemental analysis for this compound even on a recrystallized sample (from cold toluene/pentane solutions). A ^{1}H NMR spectrum is provided in the supporting information.

[Ti(=N–3-O_2N–6-Me–C_6H_3)Cl_2($NHMe_2$)$_2$] (1q): Yield 270 mg (67%) (brown). ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 7.70 (s, 1 H, *o*-C_6H_3), 7.54 (d, ^3J = 8.3 Hz, 1 H, *p*-C_6H_3), 7.12 (d, ^3J = 8.3 Hz, 1 H, *m*-C_6H_3), 3.57 (br. m, 2 H, N*H*), 2.78 (d, ^3J = 5.6 Hz, 12 H, NHMe_2), 2.56 (s, 3 H, C_6H_3Me) ppm. ^{13}C{^{1}H} NMR (125.81 MHz, CD_2Cl_2): δ = 130.0 (C_6H_3), 40.9 (NHMe_2), 35.4 (C_6H_3Me) ppm (because of poor solubility, not all C_6H_3 resonances are observed). IR (KBr): $\tilde{\nu}$ = 3281 (s, NH), 2976 (w), 2934 (w), 2776 (w), 1517 (vs, NO_2), 1468 (s), 1400 (m), 1353 (vs), 1313 (m), 1250 (w), 1099 (w), 1020 (m), 1002 (m), 894 (s), 844 (m), 740 (m), 640 (w), 420 (w) cm^{-1}. $C_{12}H_{20}Cl_2N_4O_2Ti$ (359.07): calcd. C 36.79, H 5.61, N 15.60; found C 36.58, H 5.48, N 15.38.

[Ti{=N(C_6H_{10}C≡CH)}Cl_2($NHMe_2$)$_2$] (1r): Yield 220 mg (60%) (yellow). ^{1}H NMR (500 MHz, C_6D_6): δ = 2.78 (m, 2 H, N*H*), 2.36 (d, ^3J = 6.0 Hz, 12 H, NHMe_2), 2.10 (s, 1 H, ≡C*H*), 1.91 (br. m, 2 H, CH_2), 1.62 (br. m, 2 H, CH_2), 1.54 (br. m, 4 H, CH_2), 1.41 (br. m, 1 H, CH_aH$_b$), 1.07 (br. m, 1 H, CH$_a$H$_b$) ppm. ^{13}C{^{1}H}

NMR (125.81 MHz, C_6D_6): δ = 88.0 (*C*≡CH), 73.0 (*C*N), 71.0 (C≡*C*H), 41.7 (*C*H$_2$), 41.5 (NH*Me$_2$*), 26.1 (*C*H$_2$), 23.7 (*C*H$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3278 (s, ≡CH), 3263, 3248 (m, NH), 2935 (s), 1466 (m), 1342 (m), 1266 (s), 1198 (s), 1005 (s), 895 (s), 668 (m), 655 (m), 600 (w), 537 (w), 487 (w), 419 (w) cm^{-1}. $C_{12}H_{25}Cl_2N_3Ti$ (330.12): calcd. C 43.66, H 7.63, N 12.73; found C 43.50, H 7.72, N 12.34.

[Ti{=N–[(*S*)-(–)-CHMePh]}Cl$_2$(NHMe$_2$)$_2$] (1s*): Yield 270 mg (74%) (yellow). ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 7.45 (d, ^3J = 8.4 Hz, 2 H, *o*-C$_6$*H*$_5$), 7.31 (app t, app. *J* = 7.8 Hz, 2 H, *m*-C$_6$*H*$_5$), 7.20 (t, ^3J = 7.3 Hz, 1 H, *p*-C$_6$*H*$_5$), 4.41 (q, ^3J = 6.5 Hz, 1 H, C*H*Me), 3.38 (br. m, 2 H, N*H*), 2.61 (d, ^3J = 6.3 Hz, 12 H, NH*Me$_2$*), 1.31 (d, ^3J = 6.7 Hz, 3 H, CH*Me*) ppm. ^{13}C{^{1}H} NMR (62.90 MHz, CD_2Cl_2): δ = 146.0, 128.5, 126.6, 126.1 (*C*$_6$H$_5$), 77.4 (*C*HMe), 40.8 (NH*Me$_a$*Me$_b$), 40.7 (NHMe$_a$*Me$_b$*), 25.7 (CH*Me*) ppm. IR (KBr): $\tilde{\nu}$ = 3203 (s, NH), 3013 (w), 2979 (w), 2790 (w), 1465 (m), 1452 (m), 1261 (w), 1112 (w), 1070 (w), 1051 (w), 1015 (m), 933 (m), 893 (s), 766 (m), 706 (m), 659 (m), 581 (m), 458 (m) cm^{-1}. $C_{12}H_{23}Cl_2N_3Ti$ (328.10): calcd. C 43.93, H 7.07, N 12.81; found C 43.74, H 7.12, N 12.66.

[Ti(=N–SiPh$_3$)Cl$_2$(Py)$_3$] (2d): Complex **1d** (180 mg) was dissolved in dichloromethane (2 mL) and pyridine (1 mL) was added. The resulting solution stood overnight and was then layered with toluene (ca. 1 mL) and pentane (20 mL) to afford **2d** as a crystalline sample. The crystals were collected and washed with pentane (3 × 5 mL) and dried under vacuum. Yield 220 mg (93%) (yellow). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 9.01 (d, ^3J = 5.5 Hz, 4 H, *cis*-Py), 8.61 (br. s, 2 H, *trans*-Py), 7.81 (t, ^3J = 7.5 Hz, 2 H, *cis*-Py), 7.64 (d, ^3J = 8.3 Hz, 6 H, C$_6$*H*$_5$), 7.38 (s, 1 H, *trans*-Py), 7.35 (d, ^3J = 7.5 Hz, 3 H, C$_6$*H*$_5$), 7.30–7.25 (m, 12 H, *cis*-Py, *trans*-Py, C$_6$*H*$_5$) ppm. ^{13}C{^{1}H} NMR (75.81 MHz, CD_2Cl_2): δ = 151.6 (Py), 150.3 (Py), 139.2 (Py), 136.4 (*C*$_6$H$_5$), 135.5 (*C*$_6$H$_5$), 129.5 (*C*$_6$H$_5$), 127.8 (*C*$_6$H$_5$), 127.8 (Py), 124.4 (Py), 123.8 (Py) ppm. ^{29}Si NMR (99.40 MHz, CD_2Cl_2): δ = –43 ppm. IR (KBr): $\tilde{\nu}$ = 3050 (w), 1603 (m), 1595 (m), 1485 (m), 1442 (m), 1425 (m), 1217 (m), 1109 (vs), 1068 (m), 755 (w), 693 (s), 511 (s) cm^{-1}. $C_{33}H_{30}Cl_2N_3SiTi$ (629.48): calcd. C 62.97, H 4.80, N 8.90; found C 62.90, H 4.70, N 8.81.

[Ti(=N–4-NC–C$_6$H$_4$)Cl$_2$(Py)$_3$] (2l): This compound was obtained from **1l** (100 mg) with a procedure similar to the one described for **2d**. Yield 145 mg (99%) (orange). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 9.07 (br. d, 4 H, *cis*-Py), 8.65 (br. s, *trans*-Py), 7.93 (br. t, 2 H, *cis*-Py), 7.73 (br. s, *trans*-Py), 7.46 (br. t, 4 H, *cis*-Py), 7.37 (d, ^3J = 8.3 Hz, 2 H, C$_6$*H*$_4$), 7.32 (br. s, *trans*-Py), 6.84 (d, ^3J = 8.5 Hz, 2 H, C$_6$*H*$_4$) ppm (integration of the *trans*-Py signals is not given because of the poor solubility and partial decomposition of **2l** in CD_2Cl_2, which makes the integration of the *trans*-Py obscured by free pyridine signals). ^{1}H NMR (250 MHz, [D$_5$]Pyridine): δ = 7.40 (d, 2 H, C$_6$*H*$_4$), 7.14 (d, 2 H, C$_6$*H*$_4$) ppm. The low solubility and partial decomposition of **2l** in CD_2Cl_2 precluded its ^{13}C NMR analysis. IR (KBr): $\tilde{\nu}$ = 2221 (s, CN), 1603 (s), 1587 (s), 1484 (s), 1442 (s), 1347 (s), 1212 (m), 1160 (m), 1043 (m), 966 (m), 841 (s), 759 (m), 700 (s), 680 (m), 638 (m), 549 (m). $C_{22}H_{19}Cl_2N_5Ti$ (472.19): calcd. C 55.96, H 4.06, N 14.83; found C 55.64, H 3.96, N 14.63.

[Ti[=N(C$_6$H$_{10}$C≡CH)]Cl$_2$(Py)$_3$] (2r): This compound was obtained from **1r** (100 mg) with a procedure similar to the one described for **2d**. Yield 100 mg (69%) (ochre). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 9.20 (d, ^3J = 5.0 Hz, 4 H, *cis*-Py), 8.65 (br. s, 2 H, *trans*-Py), 7.85 (t, ^3J = 7.6 Hz, 2 H, *cis*-Py), 7.66 (br. s, 1 H, *trans*-Py), 7.40 (t, ^3J = 6.6 Hz, 4 H, *cis*-Py), 7.18 (br. s, 2 H, *trans*-Py), 2.36 (s, 1 H, ≡C*H*), 1.64–1.48 (m, 6 H, C*H*$_2$), 1.33–1.22 (br. m, 3 H, C*H*$_2$, C*H$_a$*H$_b$), 1.13 (m, 1 H, CH$_a$*H$_b$*) ppm. ^{13}C{^{1}H} NMR (125.81 MHz, CD_2Cl_2): δ = 152.6 (*cis*-Py), 152.0 (*trans*-Py), 138.7 (*cis*-Py), 136.7 (*trans*-Py), 123.9 (*cis*-Py), 123.5 (*trans*-Py), 87.1 (*C*≡CH), 71.1 (*C*N), 69.9 (C≡*C*H), 39.5 (*C*H$_2$), 25.3 (*C*H$_2$), 22.6 (*C*H$_2$) ppm. $C_{23}H_{26}Cl_2N_4Ti$ (477.25): calcd. C 57.88, H 5.49, N 11.74; found C 57.86, H 5.44, N 11.78.

[Ti{=N–[(*S*)-(–)-CHMePh]}Cl$_2$(Py)$_3$] (2s*): This compound was obtained from **1s*** (250 mg) with a procedure similar to the one described for **2d**. Yield 160 mg (44%) (orange needles). ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 9.04 (d, ^3J = 4.9 Hz, 4 H, Py), 8.64 (s, 2 H, Py), 7.85 (t, ^3J = 7.5 Hz, 2 H, Py), 7.69 (s, 1 H, Py), 7.38 (app. t, app. *J* = 7.0 Hz, 6 H, Py, C$_6$*H*$_5$), 7.13–7.24 (m, 4 H, Py, C$_6$*H*$_5$), 4.49 (q, ^3J = 6.7 Hz, 1 H, C*H*Me), 1.26 (d, ^3J = 6.7 Hz, 3 H, CH*Me*) ppm. ^{13}C{^{1}H} NMR (62.90 MHz, CD_2Cl_2): δ = 146.0, 128.5, 126.6, 126.1 (*C*$_6$H$_5$), 77.4 (*C*HMe), 40.8 (NH*Me$_a$*Me$_b$), 40.7 (NHMe$_a$*Me$_b$*), 25.7 (CH*Me*) ppm. $C_{23}H_{24}Cl_2N_4Ti$ (475.24): calcd. C 58.13, H 5.09, N 11.79; found C 57.96, H 4.97, N 11.56.

[Ti{=N–[(–)-*cis*-myrtanyl]}Cl$_2$(Py)$_3$] (2t*): This compound was prepared from unisolated **1t*** [prepared from Ti(NMe$_2$)$_4$ and (–)-*cis*-myrtanylamine/Me$_3$SiCl as described above for **1a**] with a procedure similar to the one described for **2d**. Yield 250 mg [44% based on starting Ti(NMe$_2$)$_4$] (orange). ^{1}H NMR (250 MHz, C_6D_6): δ = 9.45 (br. s, 3 H, Py), 8.81 (br. s, 3 H, Py), 6.85 (br. t, 3 H, Py), 6.58 (br. d, 6 H, Py), 4.00 (s, 1 H, C*H*), 3.58 (dd, ^3J = 7.5 Hz, 2 H, C*H*$_2$N), 2.52 (m, 1 H, C*H*), 2.28 (br. s, 2 H, C*H*$_2$), 1.95 (br. m, 1 H, C*H*), 1.83–1.74 (br. s, 3 H, C*H*, C*H*$_2$), 1.35 (m, 1 H, C*H*), 1.11 (s, 3 H, C*H*$_3$), 0.87 (s, 3 H, C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (125.81 MHz, C_6D_6): δ = 152.2, 151.5, 138.3, 136.8, 124.1, 76.4, 55.1, 44.9, 42.2, 39.1, 34.1, 28.6, 27.1, 23.9, 20.1 ppm. $C_{25}H_{32}Cl_2N_4Ti$ (507.32): calcd. C 59.19, H 6.36, N 11.04; found C 59.04, H 6.35, N 10.91.

[Ti(N–2-EtO–C$_6$H$_4$)Cl$_2$(NHMe$_2$)$_1$]$_2$ (3): This compound was obtained from a procedure similar to the one described for **1a**–**t**. Pure **3** was obtained after recrystallization from a THF/toluene solution layered with pentane. Yield 235 mg (70%) (dark red). ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 7.58 (dd, ^3J = 7.8 Hz, 2 H, C$_6$*H*$_4$), 7.05 (m, 4 H, C$_6$*H*$_4$), 6.91 (dd, ^3J = 8.1 Hz, 2 H, C$_6$*H*$_4$), 5.37 (m, 2 H, N*H*), 5.02 (qd, ^3J = 7.1 Hz, 4 H, OC*H*$_2$CH$_3$), 2.48 (d, ^3J = 5.8 Hz, 6 H, NH*Me$_a$*Me$_b$), 2.35 (d, ^3J = 6.1 Hz, 6 H, NHMe$_a$*Me$_b$*), 1.62 (t, ^3J = 7.0 Hz, 6 H, OCH$_2$C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (125.81 MHz, CD_2Cl_2): δ = 144.2, 142.3, 128.2, 126.7, 124.7, 111.4 (*C*$_6$H$_4$), 71.7 (O*C*H$_2$CH$_3$), 42.5 (NH*Me$_a$*Me$_b$), 40.0 (NHMe$_a$*Me$_b$*), 13.40 (OCH$_2$*C*H$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3149 (w, NH), 2978 (m), 1473 (s), 1254 (s, CO), 1191 (m), 1112 (m), 1041 (m), 1002 (m), 922 (m), 896 (m), 751 (m), 652 (w), 419 (w) cm^{-1}. $C_{20}H_{32}Cl_4N_4O_2Ti_2$ (598.04): calcd. C 40.17, H 5.39, N 9.37; found C 40.20, H 5.41, N 9.39.

[Ti[N–CH$_2$(CH(OCH$_2$)$_3$)]Cl$_2$(NHMe$_2$)$_1$]$_2$ (4): This compound was obtained from a procedure similar to the one described for **1a**–**t**. Yield 260 mg (89%) (orange). The very poor solubility of **4** in CD_2Cl_2 and in [D$_8$]THF precluded its ^{1}H and ^{13}C NMR analysis. In [D$_5$]Py the HNMe$_2$ ligands are displaced by [D$_5$]Py ligands. ^{1}H NMR (250 MHz, [D$_5$]Py): δ = 4.13 (br., 2 H), 3.90–3.25 (br., app t), 1.96 (br., 4 H), 1.75–1.56 (br., 4 H) ppm. IR (KBr): $\tilde{\nu}$ = 3215 (w, NH), 2983 (m), 2917 (s), 2773 (s), 1459 (m), 1257 (w, CO), 1126 (s), 1043 (s), 1029 (s), 981 (m), 893 (m), 821 (m), 699 (m), 463 (m) cm^{-1}. $C_{14}H_{32}Cl_4N_4O_2Ti_2$ (525.98): calcd. C 31.97, H 6.13, N 10.65; found C 32.07, H 6.09, N 10.66.

[Ti[N–CH$_2$(CHO(CH$_2$)$_3$)]Cl$_2$(Py)$_1$]$_2$ (5): This compound was only obtained as a few red crystals by the crystallization of **4** in pyridine/toluene solutions. Attempted large scale synthesis (even in hot pyridine) gave only insoluble materials (precluding NMR analysis), and with an elemental analysis close to that of **4** which proves that

the substitution of $NHMe_2$ in **4** by Py is difficult (vide infra). In consequence, **5** was only characterized by X-ray analysis.

[Ti{=N–[(*S*)-(–)-CHMePh]}$Cl_2(NHMe_2)_1]_2$ (6*): This compound was observed in the synthesis of **1s*** when only 0.8 equiv. of the chiral amine was treated with $Ti(NMe_2)_4$ (1 equiv.) and Me_3SiCl (10 equiv.). ^1H NMR (250 MHz, CD_2Cl_2): δ = 7.70 (d, ^3J = 8.3 Hz, 4 H, C_6H_5), 7.40 (m, 6 H, C_6H_5), 5.62 (q, ^3J = 6.8 Hz, 2 H, C*H*Me), 3.00 (br. m, 4 H, N*H*), 2.59 (d, ^3J = 6.1 Hz, 6 H, NHMe_2), 2.45 (d, ^3J = 5.9 Hz, 6 H, NHMe_2), 1.80 (d, ^3J = 6.8 Hz, 6 H, CH*Me*) ppm.

[$(Me_2HN)_2Cl_2Ti$(=N–$Me_2C_6H_2$–$C_6H_2Me_2$–N=)$TiCl_2(NHMe_2)_2$] (7): This compound was obtained from a procedure similar to the one described for **1a**–**t**. Yield 280 mg (77%) (yellow). ^1H NMR (250 MHz, CD_2Cl_2): δ = 6.98 (s, 4 H, C_6H_2), 3.59 (m, ^3J = 6.1 Hz, 4 H, N*H*), 2.75 (d, ^3J = 6.2 Hz, 24 H, NHMe_2), 2.56 (s, 12 H, $C_6H_2Me_2$) ppm. $^{13}C\{^1H\}$ NMR (125.81 MHz, CD_2Cl_2): δ = 159.4, 134.2, 133.9, 124.9 (C_6H_2), 41.0 (NHMe_2), 19.0 ($C_6H_2Me_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3251 (s, NH), 2972 (m), 2936 (m), 1465 (m), 1459 (m), 1311 (s), 1117 (w), 1093 (w), 1020 (m), 1006 (m), 894 (m), 859 (m), 803 (w), 758 (w), 735 (w), 462 (w), 415 (w) cm^{-1}. $C_{24}H_{44}Cl_4N_6Ti_2$ (654.19): calcd. C 44.06, H 6.78, N 12.85; found C 43.93, H 6.84 N 12.62.

[$(Py)_3Cl_2Ti$(=N–$Me_2C_6H_2$–$C_6H_2Me_2$–N=)$TiCl_2(Py)_3$] (8): This compound was obtained from **7** (100 mg) with a procedure similar to the one described for **2d**. Yield 137 mg (94%) (orange). ^1H NMR (250 MHz, [D_5]Py): δ = 7.31 (s, 4 H, C_6H_2), 2.79 (s, 12 H, Me) ppm. The very poor solubility in CD_2Cl_2 precluded its ^{13}C NMR analysis. IR (KBr): $\tilde{\nu}$ = 1604 (s), 1444 (vs), 1299 (s), 1217, 1069, 1012 (m), 681 (w), 754 (m), 695 (vs), 637, 429 (m) cm^{-1}. $C_{46}H_{46}Cl_4N_8Ti_2$ (948.46): calcd. C 58.25, H 4.89, N 11.81; found C 57.99, H 4.71, N 11.55.

[$Ti(N$–2,6-iPr_2–$C_6H_3)I_2(thf)_2]_2$ (9): A THF solution (5 mL) of $Ti(NMe_2)_4$ (250 mg, 1.115 mmol) was treated with 2,6-iPr_2–$C_6H_3NH_2$ (1 equiv., 1.115 mmol) at room temperature. To this solution, MeI (1.58 g) was slowly and carefully added. The resulting solution was stirred at room temp. for 1 d. Toluene (5 mL) were added and the white precipitate of Me_4NI was filtered and washed with toluene(2 × 3 mL). The volatiles were removed under vacuum, and the resulting sticky solid was washed with pentane (2 × 10 mL) and dried under vacuum to afford the product. Yield 550 mg (79%) (orange). ^1H NMR (250 MHz, C_6D_6): δ = 6.96 (d, ^3J = 7.7 Hz, 2 H, C_6H_3), 6.82 (t, ^3J = 7.6 Hz, 1 H, C_6H_3), 4.89 (sept, ^3J = 6.8 Hz, 2 H, C*H*Me_2), 4.32 (br. t, 8 H, OCH_2), 1.45 (d, ^3J = 6.8 Hz, 12 H, CHMe_2), 1.24 (br. t, 8 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (62.90 MHz, C_6D_6): δ = 160.0, 144.3, 125.0, 122.8 (C_6H_3), 77.1 (OCH_2), 28.6 (*C*HMe_2), 25.2 (CH_2), 24.8 (CHMe_2) ppm. IR (KBr): $\tilde{\nu}$ = 2954 (vs), 1459 (s), 1326 (s), 1279 (s), 1175 (w), 1037 (w), 1011 (s), 921 (m), 853 (vs), 751 (s), 686 (w), 544 (w) cm^{-1}. $C_{20}H_{33}I_2NO_2Ti$ (621.16): calcd. C 38.67, H 5.35, N 2.25; found C 35.99, H 4.96, N 2.05 (the elemental analysis always gave low C and N content).

Supporting Information (see footnote on the first page of this article): ^1H NMR spectra of complexes **1p** and **9**.

Acknowledgments

We are grateful to the CNRS for financial support.

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[37] Overall, complex **6s*** only differs from **1s*** by the loss of one $NHMe_2$ ligand/Ti center. To explain its formation, we suspect the concomitant formation [when $Ti(NMe_2)_4/R^*NH_2$ ratio > 1] of a small amount of $[TiCl_3(NMe_2)(HNMe_2)]_2$ that would trap some of the $HNMe_2$ ligand needed to form **1s*** and thus **6s*** is formed. These studies, that are related to the mechanism of the general reaction $Ti(NMe_2)_4/RNH_2/Me_3SiCl$, are under current investigations and will be reported in due course.

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Received: May 22, 2006
Published Online: August 7, 2006

