

Synthesis and structural characterization of new organo-diimido and organo-imido niobium and titanium complexes

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The organo-diimido complexes $[\{\text{Nb}(\text{L}_2)\text{Cl}_3\}_2(\mu\text{-}1,4\text{-NC}_6\text{H}_4\text{N})]$, $\text{L} = \text{CH}_3\text{CN}$ **1a** or 4-'Bupy **2a**, $[\{\text{Nb}(\text{L}_2)\text{Cl}_3\}_2(\mu\text{-}1,3\text{-NC}_6\text{H}_4\text{N})]$, $\text{L} = \text{CH}_3\text{CN}$ **1b** or 4-'Bupy **2b**, and $[\{\text{Nb}(\text{L}_2)\text{Cl}_3\}_2(\mu\text{-}1,2\text{-NC}_6\text{H}_4\text{N})]$, $\text{L} = \text{CH}_3\text{CN}$ **1c** or 4-'Bupy **2c** were isolated by treating NbCl_5 in the presence of CH_3CN or 4-'Bupy with the appropriate amount of the corresponding aniline *N,N,N',N'*-tetrakis(trimethylsilyl)-1,4-, -1,3-, or -1,2-phenylenediamine, respectively. Compound **1a** reacts with appropriate alkylating reagents to give the corresponding alkyl complexes, namely $[\{\text{NbLR}_3\}_2(\mu\text{-}1,4\text{-NC}_6\text{H}_4\text{N})]$, $\text{L} = \text{CH}_3\text{CN}$, $\text{R} = \text{CH}_2\text{SiMe}_3$ **3a**; or CH_2CMe_3 **3b**; $\text{L} = \text{THF}$, $\text{R} = \text{CH}_2\text{SiMe}_3$ **4a** or CH_2CMe_3 **4b**. The crystal structure determination of **3a** was carried out. Reaction of $[\text{Ti}(\text{py})_3\text{Cl}_2(\text{N}'\text{Bu})]$ with *N,N,N',N'*-tetramethyl-1,4-phenylenediamine, in 2:1 or 1:1 stoichiometric ratio, afforded the organo-imido complexes $[\text{Ti}(\text{py})_n\text{Cl}_2(1,4\text{-NC}_6\text{Me}_4\text{NH}_2)]$, $n = 3$ (**5a**) or 2 (**5b**), while analogous reactions with 1,4- or 1,3-phenylenediamine give intractable mixtures of products. Organo-imido and organo-diimido titanium complexes were easily prepared by treating TiCl_4 with the appropriate *N,N,N',N'*-tetrakis(trimethylsilyl)phenylenediamines in CH_2Cl_2 in 1:1 and 2:1 molar ratios in the presence of 4-*tert*-butylpyridine or *N,N,N',N'*-tetramethylethylenediamine (TMEDA). The compounds prepared in this way are $[\text{Ti}(4\text{'Bupy})_2\text{Cl}_2\{1,4\text{-NC}_6\text{H}_4\text{N}(\text{SiMe}_3)_2\}]$ **6a**, $[\text{Ti}(\text{TMEDA})\text{Cl}_2\{1,4\text{-NC}_6\text{H}_4\text{N}(\text{SiMe}_3)_2\}]$ **6b**, $[\text{Ti}(\text{TMEDA})\text{Cl}_2\{1,3\text{-NC}_6\text{H}_4\text{N}(\text{SiMe}_3)_2\}]$ **7b**, $[\{\text{Ti}(4\text{'Bupy})_2\text{Cl}_2\}_2(\mu\text{-}1,4\text{-NC}_6\text{H}_4\text{N})]$ **8a**, $[\{\text{Ti}(\text{TMEDA})\text{Cl}_2\}_2(\mu\text{-}1,4\text{-NC}_6\text{H}_4\text{N})]$ **8b**, $[\{\text{Ti}(4\text{'Bupy})_2\text{Cl}_2\}_2(\mu\text{-}1,3\text{-NC}_6\text{H}_4\text{N})]$ **9a** and $[\{\text{Ti}(\text{TMEDA})\text{Cl}_2\}_2(\mu\text{-}1,3\text{-NC}_6\text{H}_4\text{N})]$ **9b**. Finally, the same reaction with *N,N,N',N'*-tetrakis(trimethylsilyl)-1,2-phenylenediamine, in the presence of 4-'Bupy or TMEDA, gives the diamido complexes $[\text{Ti}(4\text{'Bupy})_2\text{Cl}_2\{1,2\text{-C}_6\text{H}_4(\text{NH})_2\}]$ **10a** and $[\text{Ti}(\text{TMEDA})\text{Cl}_2\{1,2\text{-C}_6\text{H}_4(\text{NH})_2\}]$ **10b**. The structures of the different families of complexes were determined by spectroscopic methods.

Introduction

Metal imido complexes of Groups 5 and 6 early transition metals have widely been studied and, in particular, a great number of well established imido functional groups of d^0 niobium and tantalum are known.¹ In contrast, the first titanium imido species to be structurally well characterized were described in 1990 and these were the six-co-ordinate $[\text{Ti}(\text{py})_3\text{Cl}_2(\text{NP}(\text{S})\text{Ph}_2)]$ and the five-co-ordinate $[\text{Ti}(\text{py})_2(\text{OC}_6\text{H}_3\text{Pr}_2\text{-}2,6)_2(\text{NPh})]$ ($\text{py}' = 4\text{-pyrrolidinopyridine}$) complexes.^{2,3} Since then, however, a significant number of titanium complexes containing the $\text{Ti}=\text{NR}$ functional group have been described and such systems are mainly prepared by a straightforward metathetical route from the complexes $[\text{Ti}(\text{L})_n\text{Cl}_2(\text{NR})]$ ($\text{L} = \text{py}$ or $\text{NC}_5\text{H}_4\text{'Bu-}4$; $n = 2$ or 3; $\text{R} = \text{'Bu}$ or aryl) with different ancillary ligands.⁴

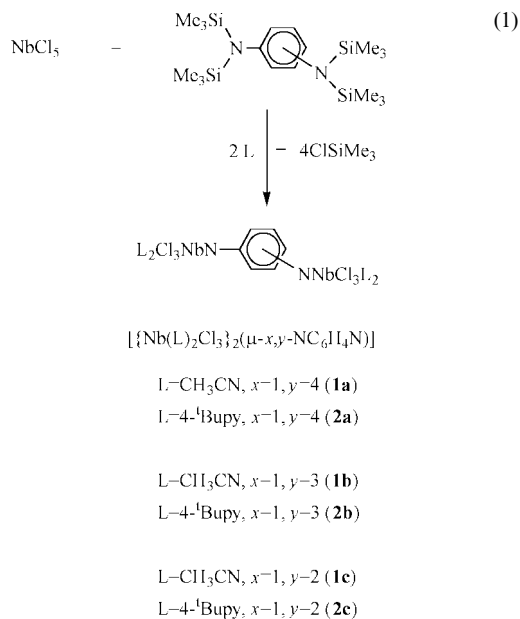
In addition, transition metal complexes in which the metal centres are linked by a bridging ligand possessing a delocalized π system are well known and have been the subject of intense research due to their potential applications in the design of low-dimensional, polymeric materials with novel electrical and/or magnetic properties. In this respect, several complexes that incorporate aryldiimido bridges have been described.⁵

We recently reported⁶ the preparation of niobocene organo-diimido complexes, namely $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}\}_2(\mu\text{-N}_2\text{C}_6\text{H}_4)]$, from the reaction of $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}\}_2]$ with the appropriate amount of the corresponding aniline, 1,4- or 1,3-phenylenediamine. As a continuation of our research in this field we examined the reactivity of NbCl_5 and TiCl_4 towards different phenylenediamines in the presence of different ancillary ligands in order to synthesize new types of binuclear organo-diimido niobium and titanium complexes with both centres linked by conjugated π systems.

Results and discussion

First, the preparation of organo-diimido niobium complexes was considered. In fact, NbCl_5 reacts with the appropriate *N,N,N',N'*-tetrakis(trimethylsilyl)-1,4-, -1,3-, or -1,2-phenylenediamine in the presence of acetonitrile or 4-'Bupy to afford the corresponding organo-diimido complexes $[\{\text{Nb}(\text{L}_2)\text{Cl}_3\}_2(\mu\text{-}x,y\text{-NC}_6\text{H}_4\text{N})]$ **1** and **2** and SiMe_3Cl , eqn. (1).

Previously we described⁶ the formation of analogous niobocene complexes by the reaction of $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{-SiMe}_3)\text{Cl}\}_2]$ with the appropriate aniline. In this case it was



proposed that an initial oxidative addition of the amine gave rise to an amido intermediate, which underwent subsequent thermolytic expulsion of H₂.⁷ In our reactions a selective elimination of SiMe₃Cl by interaction of the tetrakis(trimethylsilyl)diamine with NbCl₅ takes place. The reactions were carried out under mild experimental conditions and complete substitution of the four trimethylsilyl groups was achieved to give the appropriate organo-diimido species in high yields.

The reactions can be carried out by two alternative experimental methods. The first involves initial formation of the corresponding NbCl₅·L adduct, L = acetonitrile or 4-tBupy, followed by addition of the appropriate phenylenediamine. The second method consists of the initial formation of the corresponding organo-diimido species and subsequent addition of the ligand. These methods can be used in all cases except for complex **2c**, where the first experimental method failed. Steric factors could explain this behaviour since the initial coordination of the bulky 4-tBupy ligand to the niobium centre could hinder the subsequent interaction with 1,2-phenylenediamine, where the functional groups are adjacent in the 1 and 2 positions. Alternatively, complex **2** can be prepared from a solution of **1** by simple addition of 4-tBupy because the ligand displaces the more labile acetonitrile.

The method described above constitutes a very easy and selective route to prepare imido complexes because the formation of the volatile SiMe₃Cl by-product facilitates the isolation of the corresponding imido complex. This method was subsequently employed to prepare analogous titanium species (see below). In addition, non-reductive processes of the niobium(v) or titanium(IV) centres were implied in the processes. The organo-diimido niobium complexes, as well as the other complexes described in this work, were characterized by ¹H, ¹³C NMR and IR spectroscopy (see Experimental section).

It is noteworthy that, on the basis of both spectroscopic and analytical data, two acetonitrile or tBupy ligands are present in the proposed octahedral environment. Thus, ¹H NMR resonances of two non-equivalent tBupy units appear for complexes **2**. The spectra for complexes **1** in CD₃CN each show a signal corresponding to free CH₃CN, which is removed by the deuterated solvent. In order to confirm the presence of two coordinated acetonitrile ligands in this type of complex, the spectrum of **1a** was obtained in CD₃NO₂. In this case a broad signal was observed that was shifted to low field with respect to free acetonitrile and corresponds to the two ligands (see Experimental section).

Given the data described above, octahedral structures for these complexes can be proposed. Although we have been

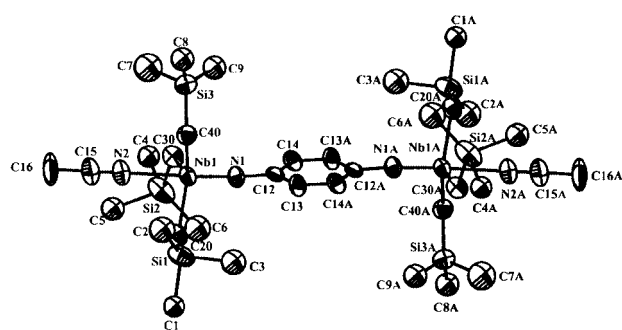
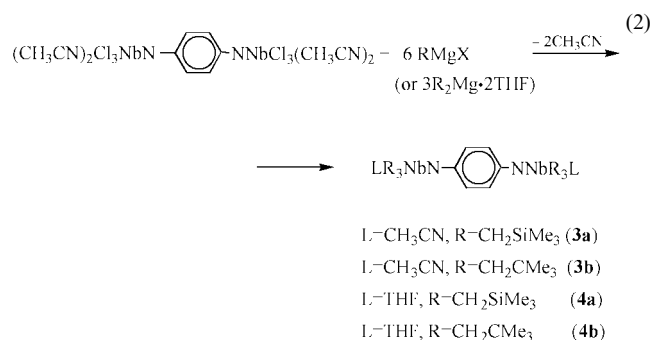


Fig. 1 Crystal structure of complex **3a**.

unable to isolate crystals suitable for X-ray diffraction studies, by analogy with the structures described for the niobocene organo-diimido complexes mentioned above,⁶ it appears reasonable that a diimidophenylene group bridges two niobium atoms, which are probably located in the plane formed by this ligand.

In addition, we propose that both nitrogen atoms are sp hybridized with the following two limiting descriptions Nb≡N-R and Nb=N-N-R, that are an accurate representation of the bonding situation.⁸

Complex **1a** was alkylated using the appropriate Grignard reagent in a 1:6 molar ratio and the reaction afforded the corresponding alkyl complexes [NbL(R)₃]₂(μ-1,4-NC₆H₄N)] (L = CH₃CN, R = CH₂SiMe₃ **3a** or CH₂CMe₃ **3b**; L = THF, R = CH₂SiMe₃ **4a** or CH₂CMe₃ **4b**) in good yields (80–90%), eqn. (2). Alternatively, these complexes can be prepared in similar



yields by treating **1a** with dialkylmagnesium reagents MgR₂·(THF)₂ (see, as illustrative examples, the preparation of **3b** and **4b** in the Experimental section). Complexes **3** were isolated when the alkylation reactions were carried out in diethyl ether, but when THF was employed as the solvent the acetonitrile was replaced by THF to give **4**. Moreover, these complexes can be obtained from **3** by simple addition of THF. The different alkyl complexes were isolated as air-sensitive yellow crystalline solids after the appropriate work-up and all are sparingly soluble in alkanes and soluble in Et₂O or THF. The structural characterization of the alkyl complexes was carried out by spectroscopic and X-ray diffraction studies. The ¹H and ¹³C NMR spectra for complexes **3a,3b** and **4a,4b** show the characteristic resonances of alkyl groups bound to a niobium atom (see Experimental section). When the co-ordinated acetonitrile was replaced by THF the ¹H and the ¹³C resonances were shifted slightly. The ¹³C NMR spectra of these complexes exhibit a broad signal between δ 60 and 93 for the methylene group bound to the niobium atom.

In order unequivocally to establish the structural disposition of these alkyl complexes an X-ray molecular structural analysis of **3a** was carried out. The molecular structure and atomic numbering scheme are shown in Fig. 1 and selected bond distances and angles are given in Table 1.

Complex **3a** crystallizes in the monoclinic space group C2/c and the asymmetric unit contains half an independent

Table 1 Selected bond lengths (Å) and angles (°) for complex **3a**

Nb(1)–N(1)	1.762(7)	N(1)–Nb(1)–C(30)	98.7(3)
Nb(1)–N(2)	2.402(8)	N(1)–Nb(1)–C(20)	99.3(3)
Nb(1)–C(20)	2.170(9)	C(30)–Nb(1)–C(20)	116.5(3)
Nb(1)–C(30)	2.149(9)	N(1)–Nb(1)–C(40)	96.1(3)
Nb(1)–C(40)	2.198(9)	C(30)–Nb(1)–C(40)	118.1(4)
N(1)–C(12)	1.402(10)	C(20)–Nb(1)–C(40)	119.6(3)
N(2)–C(15)	1.120(11)	N(1)–Nb(1)–N(2)	177.2(3)
C(12)–C(13)	1.363(10)	C(30)–Nb(1)–N(2)	82.8(3)
C(12)–C(14)	1.375(11)	C(20)–Nb(1)–N(2)	82.0(3)
C(13)–C(14)	1.380(11)	C(40)–Nb(1)–N(2)	81.1(3)
C(15)–C(16)	1.454(14)	C(12)–N(1)–Nb(1)	174.4(6)
		C(15)–N(2)–Nb(1)	178.3(10)
		Si(1)–C(20)–Nb(1)	124.2(4)
		Si(2)–C(30)–Nb(1)	121.3(5)
		Si(3)–C(40)–Nb(1)	121.6(5)

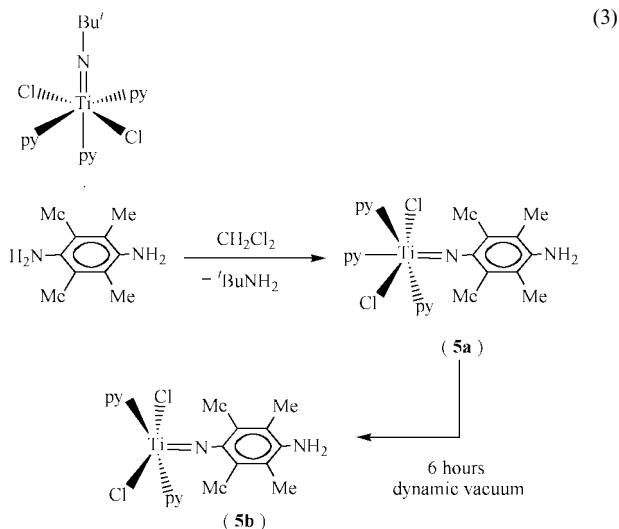
Symmetry transformation: $i - x + \frac{3}{2}, -y + \frac{1}{2}, -z$.

molecule. The structure shows a binuclear arrangement. Each Nb atom has trigonal bipyramidal geometry with an acetonitrile ligand and an imido ligand in apical positions, and three CH_2SiMe_3 groups in equatorial positions. The Nb–N1 distance is 1.762(7) Å and the angle at the imido nitrogen atom is in the range normally associated with linear imido ligands [Nb–N1–C12 174.4(6)°]. The Nb–N2 distance of 2.402(8) Å is within the typical range. The three CH_2SiMe_3 groups at each niobium centre are staggered with regard to the corresponding groups of the other niobium atom centre, as indicated by the value of the torsion angle C20–Nb1–Nb1A–C30A of 60.2°.

On the basis of the molecular structure for complex **3a**, a trigonal bipyramidal disposition for each niobium centre in a binuclear situation, in which the acetonitrile ligand is located in a *trans* disposition to the imido ligand, can be proposed for the different alkyl niobium species. This structural disposition, where a labile ligand such as acetonitrile or pyridine is located in a co-ordination site *trans* to the imido ligand, has been found in several imido-containing early transition metal complexes.⁹

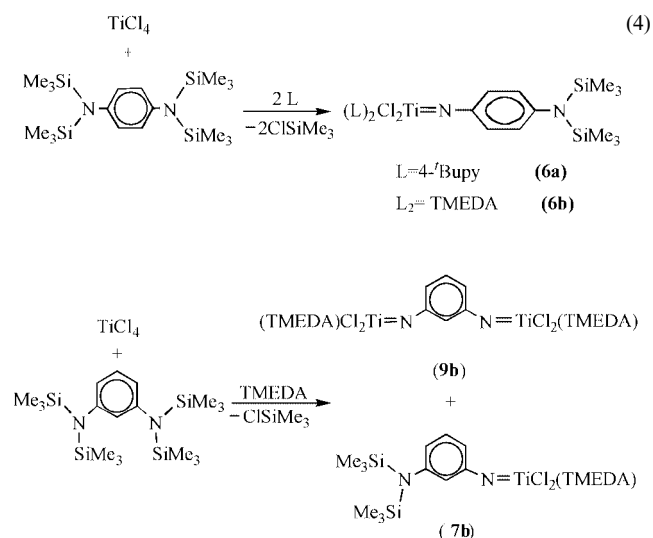
In the second part of this work we undertook a study into the synthesis and characterization of organo-imido and organo-diimido titanium complexes. First, we employed the metathetical reaction of $[\text{Ti}(\text{py})_3\text{Cl}_2(\text{N}^i\text{Bu})]$ with 1,4- or 1,3-phenylenediamine⁹ in order to prepare the corresponding organo-diimido complexes, but the reactions in different molar ratios (1:1 or 1:2) gave rise to intractable mixtures of products. However, when the same reaction was carried out using tetramethyl-1,4-phenylenediamine, in 1:1 or 2:1 molar ratios, the organo-imido complex $[\text{Ti}(\text{py})_3\text{Cl}_2(1,4\text{-NC}_6\text{Me}_4\text{NH}_2)]$ **5a** was isolated as the only organometallic species, eqn. (3).

Attempts to prepare the corresponding organo-diimido species $[\{\text{Ti}(\text{py})_3\text{Cl}_2\}_2(1,4\text{-NC}_6\text{Me}_4\text{N})]$, even when a large excess



of the titanium complex was used, were unsuccessful. Terminal titanium imido complex **5a**, which has a proposed pseudo-octahedral disposition, was isolated as an air-sensitive solid that tends to lose the *trans*-co-ordinated pyridine ligand to give **5b**, which is proposed to have a square-pyramidal structure. Similar behaviour has previously been found in analogous complexes.⁹

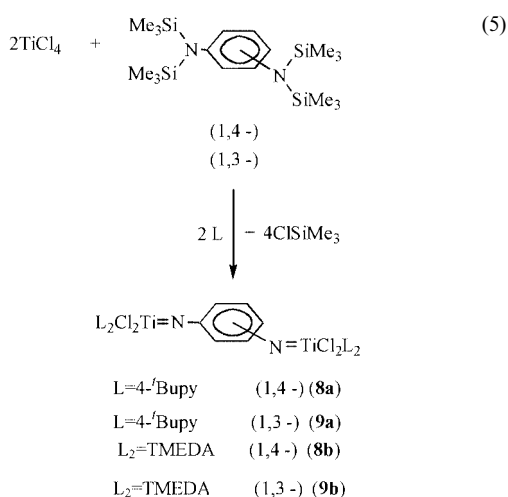
As stated above, the reactivity of silylated phenylenediamines towards early transition metal halides has been confirmed as a useful synthetic route to prepare organo-imido and organo-diimido species of these metals in high yields. This method functions well due to the ease of removal of the SiMe_3Cl that is formed as a by-product. Thus, the reaction of TiCl_4 with the appropriate *N,N,N',N'*-tetrakis(trimethylsilyl)phenylenediamine in a 1:1 molar ratio in the presence of 4-*tert*-butylpyridine or *N,N,N',N'*-tetramethylethylenediamine (TMEDA) as an ancillary ligand gives the corresponding terminal imido complexes $[\text{Ti}(4\text{-}^t\text{Bupy})_2\text{Cl}_2\{1,4\text{-NC}_6\text{H}_4\text{N}(\text{SiMe}_3)_2\}]$ **6a**, $[\text{Ti}(\text{TMEDA})\text{Cl}_2\{1,4\text{-NC}_6\text{H}_4\text{N}(\text{SiMe}_3)_2\}]$ **6b** and $[\text{Ti}(\text{TMEDA})\text{Cl}_2\{1,3\text{-NC}_6\text{H}_4\text{N}(\text{SiMe}_3)_2\}]$ **7b**, eqn. (4).



When *N,N,N',N'*-tetrakis(trimethylsilyl)-1,4-phenylenediamine was used the corresponding complexes **6a** and **6b** were obtained in high yields as the only products. However, when the same reaction was carried out using *N,N,N',N'*-tetrakis(trimethylsilyl)-1,3-phenylenediamine a mixture of the corresponding mononuclear compound **7** and the binuclear compound **9** (see below) was obtained. When TMEDA was the ancillary ligand the mixture could be resolved since the mononuclear complex **7b** is soluble in chloroform while the binuclear complex **9b** is completely insoluble. This behaviour can tentatively be explained in terms of the possibility of deactivation of the second SiMe_3 group in the *para* position when one equivalent of titanium is co-ordinated to the *N,N,N',N'*-tetrakis(trimethylsilyl)-1,4-phenylenediamine. This fact would make attack of a second TiCl_4 molecule on unchanged *N,N,N',N'*-tetrakis(trimethylsilyl)-1,4-phenylenediamine much more favourable kinetically than the corresponding reaction with the $\text{N}(\text{SiMe}_3)_2$ moiety of the mononuclear product.

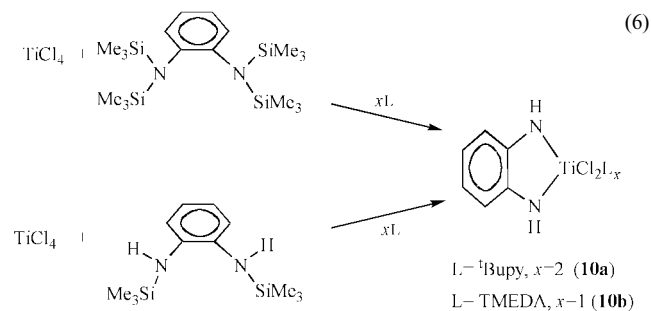
The choice of dichloromethane as solvent was a crucial factor in the success of the reaction, as well as in the subsequent processes described below for the preparation of organo-diimido species. In fact, when other solvents (such as toluene, THF or acetonitrile) were used, a mixture of products was obtained that exhibits several SiMe_3 signals in the ^1H NMR spectrum. This indicates that a partial desilylation of the diamine has taken place, probably because the co-ordination ability of the solvent diminishes the acidity of the metal centre. Complexes **6a**, **6b** and **7b** were isolated as air-sensitive solids. Complex **6a** is soluble in toluene, dichloromethane, THF,

diethyl ether and chloroform, while **6b** and **7b** are only soluble in chloroform. When the reaction of TiCl_4 and the appropriate silylated phenylenediamine was carried out in a 2:1 molar ratio, the organo-diimido binuclear complexes $[\{\text{Ti}(\text{L}_2)\text{Cl}_2\}_2(\mu-x,y\text{-NC}_6\text{H}_4\text{N})]$ ($\text{L} = 4\text{'Bupy}$, $x = 1$, $y = 4$ **8a**; $\text{L}_2 = \text{TMEDA}$, $x = 1$, $y = 4$ **8b**; $\text{L} = 4\text{'Bupy}$, $x = 1$, $y = 3$ **9a**; $\text{L}_2 = \text{TMEDA}$, $x = 1$, $y = 3$ **9b**) were isolated, eqn. (5). These compounds were



isolated in high yields as air-sensitive solids after the appropriate work-up. Complexes **8a** and **9a** are soluble in toluene, dichloromethane, THF and diethyl ether, while **8b** and **9b** are insoluble in these solvents. It is noteworthy that under our experimental conditions a selective desilylation process takes place to give cleanly the organo-diimido species.

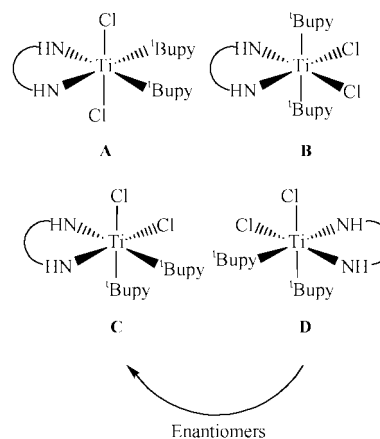
The mononuclear and binuclear imido titanium complexes were spectroscopically characterized by ^1H , ^{13}C NMR and IR spectroscopy (see Experimental section). The similarity between the spectra of the mononuclear titanium compounds **6**, **7** and the analogous complexes previously described^{3,9} suggests that monomeric terminal imido square-pyramidal structures could be proposed. In addition, a diimidophenylene group that bridges two titanium atoms, which are probably located in the plane formed by this ligand, can also be considered for **8**, **9** as a possibility in a similar way to the previously discussed niobium complexes. Finally, the reaction of TiCl_4 with N,N,N',N' -tetrakis(trimethylsilyl)-1,2-phenylenediamine in 1:1 or 2:1 molar ratios, in the presence of 4-'Bupy or TMEDA as ancillary ligand, gave the diamido complexes $[\text{Ti}(4\text{'Bupy})_2\text{Cl}_2\{1,2\text{-C}_6\text{H}_4(\text{NH})_2\}]$ **10a** and $[\text{Ti}(\text{TMEDA})\text{Cl}_2\{1,2\text{-C}_6\text{H}_4(\text{NH})_2\}]$ **10b**, eqn. (6), as the only organometallic species isolated.



The reaction was carried out under extremely anhydrous conditions and there is no clear explanation for the source of the protonation process on the nitrogen of the proposed initially formed imido ligand. We have subsequently confirmed the formation of **10a** and **10b** by the direct reaction of TiCl_4 with N,N' -bis(trimethylsilyl)-1,2-phenylenediamine in the presence of 4-'Bupy or TMEDA, eqn. (6). Complexes **10a** and **10b**

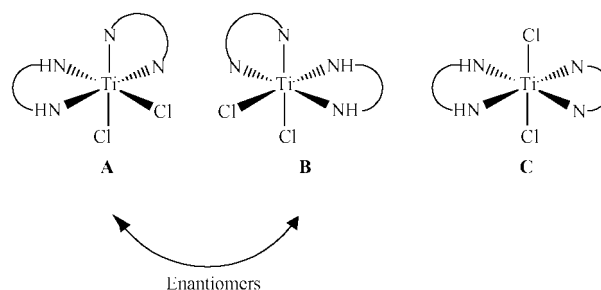
were isolated as air-sensitive solids after the appropriate work-up; **10a** is soluble in toluene, dichloromethane, THF and diethyl ether and **10b** in dichloromethane, THF and diethyl ether. Both compounds were characterized spectroscopically (see Experimental section). The ^1H NMR spectrum of **10a** shows a broad signal at δ 11.14 for the amido protons, two pseudodoublets at *ca.* δ 9.13 and 7.50 for the pyridine protons, and a singlet at δ 1.35 for the *tert*-butyl groups, indicating that in a proposed octahedral geometry the two amido groups as well as both 4-'Bupy ligands are occupying equivalent co-ordination sites.

Scheme 1 shows the different possible structural dispositions



Scheme 1

for complex **10a** and, on the basis of the aforementioned ^1H NMR as well as the ^{13}C NMR data, the structures **C** and **D**, in which the titanium atom is a chiral centre, must be ruled out. Structure **B** could be seen as more favourable on the basis of steric arguments, although **A** cannot be ruled out. In contrast, the ^1H NMR spectrum of **10b** shows two signals at δ 11.79 and 9.55 for the amido protons and four signals at δ 3.22, 3.20, 3.00 and 2.32 for the methyl groups of the TMEDA ligand. These signals indicate that an asymmetric disposition in a proposed octahedral geometry must be considered. The three possible structural dispositions are depicted in Scheme 2 and, on the basis of the spectroscopic data, structure **C** can be discarded.



Scheme 2

In conclusion, we have reported a straightforward method to prepare organo-imido and organo-diimido complexes with metals of Groups 4 and 5 by reaction of the corresponding halide with silylated phenylenediamines. The new species were isolated in high yields and from selective processes due to the formation of the volatile SiMe_3Cl by-product. New efforts to assess the scope of the method and to study the reactivity of the imido-containing complexes are in progress.

Experimental

General methods and instrumentation

All manipulations were carried out under an argon atmosphere using either standard Schlenk techniques or an MBraun glove-

Table 2 Crystal data and structure refinement for complex **3a**

Empirical formula	C ₃₄ H ₇₆ N ₄ Nb ₂ Si ₆
Formula weight	895.34
<i>T</i> /K	293(2)
<i>λ</i> /Å	0.71070
Crystal system, space group	Monoclinic, <i>C2/c</i>
<i>a</i> /Å	19.306(8)
<i>b</i> /Å	16.0717(7)
<i>c</i> /Å	19.428(4)
<i>β</i> /°	117.19(2)
<i>V</i> /Å ³	5362(2)
<i>Z</i>	4
<i>μ</i> /cm ⁻¹	5.85
Reflections collected/unique	6471/6471
Data/restraints/parameters	6471/34/196
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0800, <i>wR</i> 2 = 0.1545
Largest diff. peak and hole/e Å ⁻³	0.666 and -0.529

box. Solvents were dried and distilled under argon: tetrahydrofuran and diethyl ether from sodium–benzophenone, hexane and pentane from sodium and potassium alloy, acetonitrile and CDCl₃ from finely ground calcium hydride.

Titanium tetrachloride was distilled under argon from copper; 4-*tert*-butylpyridine was dried over activated 4 Å molecular sieves and used without further purification; pyridine, aniline and *N,N,N',N'*-tetramethylethylenediamine were dried over finely ground calcium hydride and distilled under argon; 2,3,5,6-tetramethyl-1,4-phenylenediamine was sublimed prior to use and stored under argon. Other reagents were obtained from commercial sources and used as received or prepared as reported elsewhere: *N,N,N',N'*-tetrakis(trimethylsilyl)phenylenediamine.¹⁰

IR spectra were recorded in Nujol mulls between CsI pellets over the range 4000–370 cm⁻¹ on a Perkin-Elmer model 883 and IR-FT 2000 spectrophotometer; ¹H and ¹³C NMR spectra on a Gemini-200 and/or UNITY-300 (Varian) spectrometers. Chemical shifts (*δ* ppm) were measured relative to residual ¹H and ¹³C resonances for acetonitrile-*d*₃, chloroform-*d*₁ and benzene-*d*₆ as solvents. C, H and N analyses were carried out with a Perkin-Elmer 240-13, 240 C and/or Heraeus-CHN-O-Rapid microanalyser.

Crystallographic study of complex **3a**

A single crystal of approximate dimensions 0.3 × 0.2 × 0.2 mm was mounted in a glass capillary. Intensity data were collected on a NONIUS-MACH3 diffractometer, equipped with graphite monochromated Mo-K α radiation source, using an ω -2 θ scan technique to a maximum value of 56°. Data were corrected in the usual fashion for Lorentz and polarization effects and empirical absorption correction was not necessary. The structure was solved using direct methods (SHELXS).¹¹ Refinement of *F*² was carried out by full-matrix least-squares techniques.¹¹ The SiMe₃ groups showed rotational disorder with an occupation factor of 0.5 and were refined isotropically. All the other non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in their calculated positions and refined isotropically. Crystal data are given in Table 2.

CCDC reference number 186/2013.

See <http://www.rsc.org/suppdata/dt/b0/b002743j/> for crystallographic files in .cif format.

Preparations

[{Nb(CH₃CN)₂Cl₃}₂(μ -1,4-NC₆H₄N)] **1a**, [{Nb(CH₃CN)₂Cl₃}₂(μ -1,3-NC₆H₄N)] **1b**, and [{Nb(CH₃CN)₂Cl₃}₂(μ -1,2-NC₆H₄N)] **1c**. To a solution of NbCl₅ in acetonitrile was added dropwise, at room temperature during 45 min, a solution of the corresponding *N,N,N',N'*-tetrakis(trimethylsilyl)phenylenediamine in CH₂Cl₂ in a molar ratio of 2:1. Vigorous stirring

was required during the addition. The initial yellow solution changed to deep red for **1a** and **1c**, and to pale red for complex **1b**. The mixture was vigorously stirred overnight at room temperature. The solvent was removed under vacuum and the residual solids were washed several times with hexane and identified as **1a**, **1b** and **1c**, respectively.

Complex **1a**: from NbCl₅ (1.93 g, 7.14 mmol) and 1,4-((Me₃Si)₂N)₂C₆H₄ (1.42 g, 3.57 mmol), 2.1 g of a green solid were obtained (yield 88%). ¹H NMR (300 MHz): (CD₃CN) δ 1.95 (s, 12 H, free CH₃CN) and 7.21 (s, 4 H, phenylene ring); (CD₃NO₂) δ 2.90 (broad signal, 12 H, CH₃CN) and 7.79 (s, 4 H, phenylene ring). ¹³C-¹H} NMR (CD₃CN, 75 MHz): δ 1.7 (CH₃CN), 126.3 (phenylene ring), 127.2 (CH₃CN) and 153.4 (*C*_{ipso} of phenylene ring). IR: 2313m, 2282m, 1479s, 1408w, 1366m, 1321m, 1007m, 942w, 846m, 832m, 529m, 425m and 376m cm⁻¹ [Found (Calc. for C₇H₈Cl₃N₃Nb): C, 25.3 (25.2); H, 2.4 (2.4); N, 12.0 (12.6)%].

Complex **1b**: from NbCl₅ (1.79 g, 6.64 mmol) and 1,3-((Me₃Si)₂N)₂C₆H₄ (1.32 g, 3.32 mmol), 2.0 g of a pink solid were obtained (yield 90%). ¹H NMR (CD₃CN, 300 MHz): δ 1.95 (s, 12 H, free CH₃CN), 7.00 (part A₂ of an A₂MX spin system, 2 H, phenylene ring), 7.1 (part M of an A₂MX spin system, 1 H, phenylene ring) and 7.34 (part X of an A₂MX, 1 H, phenylene ring). ¹³C-¹H} NMR (CD₃CN, 75 MHz): δ 1.7 (CH₃CN), 121.7, 124.6, 129.8 (phenylene ring), 129.5 (CH₃CN) and 154.4 (*C*_{ipso} of phenylene ring). IR: 2314m, 2285m, 1567m, 1554m, 1417m, 1365m, 1346m, 1312s, 1244m, 1029s, 977w, 943m, 879m, 790s, 678m, 578w, 512m, 488m and 388s cm⁻¹ [Found (Calc. for C₇H₈Cl₃N₃Nb): C, 24.9 (25.2); H, 2.5 (2.4); N, 11.6 (12.6)%].

Complex **1c**: from NbCl₅ (1.63 g, 6.04 mmol) and 1,2-((Me₃Si)₂N)₂C₆H₄ (1.20 g, 3.02 mmol), 1.8 g of a dark brown solid were obtained (yield 89%). ¹H NMR (CD₃CN, 300 MHz): δ 1.95 (s, 12 H, CH₃CN), 7.13 (part AA' of an AA'XX' spin system, 2 H, phenylene ring) and 7.51 (part XX' of an AA'XX' spin system, 2 H, phenylene ring). ¹³C-¹H} NMR (CD₃CN, 75 MHz): δ 1.7 (CH₃CN), 128.0, 129.9 (phenylene ring), 129.1 (CH₃CN) and 148.2 (*C*_{ipso} of phenylene ring). IR: 2317s, 2287s, 1399w, 1339w, 1261w, 1152w, 1115w, 1025m, 993w, 975w, 949m, 848m, 806m, 760m, 668w, 592w, 522w and 379m cm⁻¹ [Found (Calc. for C₇H₈Cl₃N₃Nb): C, 25.1 (25.2); H, 2.6 (2.4); N, 11.7 (12.6)%].

[{Nb(*t*Bupy)₂Cl₃}₂(μ -1,4-NC₆H₄N)] **2a** and [{Nb(*t*Bupy)₂Cl₃}₂(μ -1,3-NC₆H₄N)] **2b**. To a vigorously stirred suspension of NbCl₅ in CH₂Cl₂ was added *t*Bupy in molar ratio 1:2. The initial yellow suspension changed to a yellow solution. To this was added dropwise, during 45 min, a solution of the corresponding *N,N,N',N'*-tetrakis(trimethylsilyl)phenylenediamine in CH₂Cl₂ at room temperature. Vigorous stirring was required during the addition. The initial yellow solution changed to dark red for complex **2a** and pale red for **2b**. The mixture was vigorously stirred for 2 h at room temperature. The solvent was removed under vacuum and the solids were washed several times with hexane and identified as **2a** and **2b**.

Complex **2a**: from NbCl₅ (1.04 g, 3.83 mmol), 1,4-((Me₃Si)₂N)₂C₆H₄ (0.76 g, 1.92 mmol) and 4-*tert*-butylpyridine (1.13 ml, 7.68 mmol), 2.0 g of a pink solid were obtained (yield 90%). ¹H NMR (CDCl₃, 300 MHz): δ 1.30 (s, 18 H, NC₅H₄^tBu), 1.34 (s, 18 H, NC₅H₄^tBu), 7.32 (s, 4 H, phenylene ring), 7.33 (AA' part of an AA'XX' spin system, 4 *m*-H of NC₅H₄^tBu), 7.41 (AA' part of an AA'XX' spin system, 4 *m*-H of NC₅H₄^tBu), 8.57 (XX' part of an AA'XX' spin system, 4 *o*-H of NC₅H₄^tBu) and 9.0 (XX' part of an AA'XX' spin system, 4 *o*-H of NC₅H₄^tBu). ¹³C-¹H} NMR (CDCl₃, 75 MHz): δ 29.8 [NC₅H₄C(CH₃)₃], 30.0 [NC₅H₄C(CH₃)₃], 34.9 [NC₅H₄C(CH₃)₃], 35.1 [NC₅H₄C(CH₃)₃], 121.0 (*m*-C, NC₅H₄^tBu), 121.4 (*m*-C, NC₅H₄^tBu), 125.5 (phenylene ring), 150.9 (*o*-C, NC₅H₄^tBu), 151.1 (*o*-C, NC₅H₄^tBu), 152.3 (*C*_{ipso} of phenylene ring), 163.1 (*C*_{ipso} of NC₅H₄^tBu) and 164.7 (*C*_{ipso} of NC₅H₄^tBu). IR: 1635w,

1617s, 1543w, 1501m, 1421s, 1320s, 1276m, 1235m, 1203w, 1093w, 1067s, 1019s, 1006m, 993s, 842s, 572s, 531m, 421m and 377m cm^{-1} [Found (Calc. for $\text{C}_{21}\text{H}_{28}\text{Cl}_3\text{N}_3\text{Nb}$): C, 48.4 (48.3); H, 5.7 (5.4); N, 7.5 (8.0)%].

Complex **2b**: from NbCl_5 (0.86 g, 3.18 mmol), 1,3- $\{(\text{Me}_3\text{Si})_2\text{N}\}_2\text{C}_6\text{H}_4$ (0.63 g, 1.59 mmol) and 4-*tert*-butylpyridine (0.94 ml, 6.36 mmol), 1.5 g of a pink solid were obtained (yield 90%). ^1H NMR (CDCl_3 , 300 MHz): δ 1.29 (s, 18 H, $\text{NC}_5\text{H}_4\text{Bu}$), 1.33 (s, 18 H, $\text{NC}_5\text{H}_4\text{Bu}$), 7.21 (m, 3 H, phenylene ring), 7.35 (m, 1 H, phenylene ring), 7.36 (AA' part of an AA'XX' spin system, 4 *m*-H of $\text{NC}_5\text{H}_4\text{Bu}$), 7.41 (AA' part of an AA'XX' spin system, 4 *m*-H of $\text{NC}_5\text{H}_4\text{Bu}$), 8.61 (XX' part of an AA'XX' spin system, 4 *o*-H of $\text{NC}_5\text{H}_4\text{Bu}$) and 9.01 (XX' part of an AA'XX' spin system, 4 *o*-H of $\text{NC}_5\text{H}_4\text{Bu}$); ^{13}C - $\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz): δ 30.1 [$\text{NC}_5\text{H}_4\text{C}(\text{CH}_3)_3$], 30.2 [$\text{NC}_5\text{H}_4\text{C}(\text{CH}_3)_3$], 35.1 [$\text{NC}_5\text{H}_4\text{C}(\text{CH}_3)_3$], 35.4 [$\text{NC}_5\text{H}_4\text{C}(\text{CH}_3)_3$], 121.3 (*m*-C, $\text{NC}_5\text{H}_4\text{Bu}$), 121.8 (*m*-C, $\text{NC}_5\text{H}_4\text{Bu}$), 121.0, 124.9, 128.2 (phenylene ring), 151.1 (*o*-C, $\text{NC}_5\text{H}_4\text{Bu}$), 151.4 (*o*-C, $\text{NC}_5\text{H}_4\text{Bu}$), 153.4 (C_{ipso} of phenylene ring), 163.3 (C_{ipso} of $\text{NC}_5\text{H}_4\text{Bu}$) and 165.0 (C_{ipso} of $\text{NC}_5\text{H}_4\text{Bu}$). IR: 1636w, 1616s, 1567m, 1553m, 1501m, 1420s, 1342w, 1310w, 1293w, 1275m, 1233m, 1202w, 1068s, 1015s, 972w, 876w, 830s, 788m, 679m, 571s, 542m, 513m, 489w and 464w cm^{-1} [Found (Calc. for $\text{C}_{21}\text{H}_{28}\text{Cl}_3\text{N}_3\text{Nb}$): C, 47.9 (48.3); H, 5.8 (5.4); N, 7.9 (8.0)%].

$[\{\text{Nb}(\text{Bupy})_2\text{Cl}_3\}_2(\mu\text{-}1,2\text{-NC}_6\text{H}_4\text{N})]$ **2c**. To a vigorously stirred suspension of NbCl_5 (0.527 g, 1.95 mmol) in CH_2Cl_2 (30 ml) was added dropwise a solution of 1,2- $\{(\text{Me}_3\text{Si})_2\text{N}\}_2\text{C}_6\text{H}_4$ (0.39 g, 0.97 mmol) in CH_2Cl_2 (30 ml). The initial yellow suspension became green. The mixture was stirred for 3 h and 4-*tert*-butylpyridine (0.576 ml, 3.90 mmol) was added. The suspension changed to a deep red solution. After 90 min the solvent was removed under vacuum, the solid washed several times with hexane and the resulting dark brown solid identified as complex **2c** (0.9 g, 0.86 mmol) (yield 88%). ^1H NMR (CDCl_3 , 300 MHz): δ 1.24 (s, 18 H, $\text{NC}_5\text{H}_4\text{Bu}$), 1.33 (s, 18 H, $\text{NC}_5\text{H}_4\text{Bu}$), 7.08 (AA' part of an AA'XX' spin system, 2 H, phenylene ring), 7.36 (AA' part of an AA'XX' spin system, 4 *m*-H of $\text{NC}_5\text{H}_4\text{Bu}$), 7.38 (AA' part of an AA'XX' spin system, 4 *m*-H of $\text{NC}_5\text{H}_4\text{Bu}$), 7.87 (XX' part of an AA'XX' spin system, 2 H, phenylene ring), 8.9 (XX' part of an AA'XX' spin system, *o*-H of $\text{NC}_5\text{H}_4\text{Bu}$) and 9.02 (XX' part of an AA'XX' spin system, *o*-H of $\text{NC}_5\text{H}_4\text{Bu}$); ^{13}C - $\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz): δ 30.0 [$\text{NC}_5\text{H}_4\text{C}(\text{CH}_3)_3$], 30.2 [$\text{NC}_5\text{H}_4\text{C}(\text{CH}_3)_3$], 35.1 [$\text{NC}_5\text{H}_4\text{C}(\text{CH}_3)_3$], 35.3 [$\text{NC}_5\text{H}_4\text{C}(\text{CH}_3)_3$], 121.1 (*m*-C, $\text{NC}_5\text{H}_4\text{Bu}$), 121.8 (*m*-C, $\text{NC}_5\text{H}_4\text{Bu}$), 126.9, 130.8 (phenylene ring), 147.7 (C_{ipso} of phenylene ring), 151.3 (*o*-C, $\text{NC}_5\text{H}_4\text{Bu}$), 152.1 (*o*-C, $\text{NC}_5\text{H}_4\text{Bu}$), 163.1 (C_{ipso} of $\text{NC}_5\text{H}_4\text{Bu}$) and 164.5 (C_{ipso} of $\text{NC}_5\text{H}_4\text{Bu}$). IR: 1615s, 1542w, 1502m, 1421s, 1325m, 1275m, 1233m, 1113w, 1068m, 1016m, 987w, 965w, 831m, 756m, 572m and 392w cm^{-1} [Found (Calc. for $\text{C}_{21}\text{H}_{28}\text{Cl}_3\text{N}_3\text{Nb}$): C, 48.8 (48.3); H, 5.6 (5.4); N, 7.2 (8.0)%].

Complexes **1a-1c** and **2a,2b** could alternatively be prepared by a similar procedure to that described for **2c**, although the latter complex could not be prepared by the first method described for these complexes.

$[\{\text{Nb}(\text{CH}_3\text{CN})(\text{CH}_2\text{SiMe}_3)_3\}_2(\mu\text{-}1,4\text{-NC}_6\text{H}_4\text{N})]$ **3a**. To a suspension of complex **1a** (1.346 g, 2.02 mmol) in Et_2O (40 ml) was added dropwise a 1.0 M solution of $\text{Me}_3\text{SiCH}_2\text{MgCl}$ (12.1 ml, 12.1 mmol) diluted in Et_2O (40 ml) at -78°C . The mixture was stirred overnight at room temperature. The initial green suspension became yellow. The solid was filtered off and afterwards extracted with Et_2O (4 portions of 15 ml). From the combined solutions the solvent was removed *in vacuo* to give a yellow solid, which was identified as **3a** (1.6 g, 1.78 mmol) (yield 88%). ^1H NMR (C_6D_6 , 300 MHz): δ 0.27 [s, 54 H, $\text{Si}(\text{CH}_3)_3\text{CH}_2$], 0.59 (s, 6 H, CH_3CN), 1.18 (s, 12 H, $\text{Si}(\text{CH}_3)_3\text{CH}_2$) and 7.74 (s, 4 H, phenylene ring). ^{13}C - $\{^1\text{H}\}$ NMR (C_6D_6 , 75 MHz): δ 0.2 (CH_3CN), 2.93 [$\text{Si}(\text{CH}_3)_3\text{CH}_2$], 63.0 ($\text{Si}(\text{CH}_3)_3\text{CH}_2$), 121.7

(CH_3CN), 125.4 (phenylene ring) and 154.3 (C_{ipso} of phenylene ring). IR: 2309w, 2280w, 1488m, 1327s, 1242, 992w, 900s, 847s, 741m, 699m, 668m, 609w, 577w, 504w, 484w, 465w and 451w cm^{-1} [Found (Calc. for $\text{C}_{17}\text{H}_{38}\text{N}_2\text{NbSi}_3$): C, 45.7 (45.6); H, 8.3 (8.6); N, 6.5 (6.3)%].

$[\{\text{Nb}(\text{CH}_3\text{CN})(\text{CH}_2\text{CMe}_3)_3\}_2(\mu\text{-}1,4\text{-NC}_6\text{H}_4\text{N})]$ **3b**. To a suspension of complex **1a** (0.635 g, 0.95 mmol) in Et_2O (40 ml) was added dropwise a solution of $\text{MgNp}_2 \cdot 2\text{THF}$ [$\text{Np} = (\text{CH}_3)_3\text{CCH}_2$] (0.88 g, 2.85 mmol) in Et_2O (40 ml) at -78°C . The mixture was stirred overnight at room temperature. The initial green suspension became yellow. The solid was filtered off and afterwards extracted with Et_2O (4 portions of 15 ml). The solvent was removed *in vacuo* to give a yellow solid, which was identified as **3b** (0.6 g, 0.75 mmol) (yield 79%). ^1H NMR (C_6D_6 , 300 MHz): δ 0.50 (s, 6 H, CH_3CN), 1.28 [s, 54 H, $(\text{CH}_3)_3\text{CCH}_2$], 1.36 (s, 12 H, $(\text{CH}_3)_3\text{CCH}_2$) and 7.89 (s, 4 H, $\text{NC}_6\text{H}_4\text{N}$); ^{13}C - $\{^1\text{H}\}$ NMR (C_6D_6 , 75 MHz): δ 1.37 (CH_3CN), 34.5 [$(\text{CH}_3)_3\text{CCH}_2$], 35.8 [$(\text{CH}_3)_3\text{CCH}_2$], 91.2 (Me_3CCH_2), 119.3 (CH_3CN), 126.2 ($\text{NC}_6\text{H}_4\text{N}$) and 154.5 (C_{ipso} of phenylene ring). IR: 2308w, 2275w, 1497m, 1358m, 1315s, 1230m, 988m, 880w, 843m, 770w, 744w, 668w, 552w, 504w and 405w cm^{-1} [Found (Calc. for $\text{C}_{20}\text{H}_{38}\text{N}_2\text{Nb}$): C, 60.4 (60.3); H, 9.3 (9.5); N, 7.1 (7.0)%].

$[\{\text{Nb}(\text{THF})(\text{CH}_2\text{SiMe}_3)_3\}_2(\mu\text{-}1,4\text{-NC}_6\text{H}_4\text{N})]$ **4a**. To a suspension of complex **1a** (1.423 g, 2.13 mmol) in THF (40 ml) was added dropwise a 1.0 M solution of $\text{Me}_3\text{SiCH}_2\text{MgCl}$ (12.8 ml, 12.8 mmol) diluted in THF (40 ml) at -78°C . The mixture was stirred overnight at room temperature. The initial green suspension became yellow. The solvent was removed and the residue extracted with Et_2O (4 portions of 20 ml). The solvent was removed *in vacuo* to give a yellow solid, which was identified as **4a** (1.8 g, 1.77 mmol) (yield 85%). ^1H NMR (C_6D_6 , 300 MHz): δ 0.20 [s, 54 H, $\text{Si}(\text{CH}_3)_3\text{CH}_2$], 0.80 (s, 12 H, SiMe_3CH_2), 3.91 (m, 8 H, $\text{C}_4\text{H}_8\text{O}$), 1.43 (m, 8 H, $\text{C}_4\text{H}_8\text{O}$) and 7.64 (s, 4 H, phenylene ring). ^{13}C - $\{^1\text{H}\}$ NMR (C_6D_6 , 75 MHz): δ 3.0 [$\text{Si}(\text{CH}_3)_3\text{CH}_2$], 25.5 ($\text{C}_4\text{H}_8\text{O}$), 60.9 (SiMe_3CH_2), 70.4 ($\text{C}_4\text{H}_8\text{O}$), 125.4 ($\text{NC}_6\text{H}_4\text{N}$) and 154.2 (C_{ipso} of phenylene ring). IR: 1487s, 1407w, 1322s, 1245s, 922w, 877m, 846s, 742w, 694m, 604w and 530w cm^{-1} [Found (Calc. for $\text{C}_{19}\text{H}_{43}\text{NNbOSi}_3$): C, 47.7 (47.7); H, 9.0 (9.0); N, 3.4 (2.9)%].

$[\{\text{Nb}(\text{THF})(\text{CH}_2\text{CMe}_3)_3\}_2(\mu\text{-}1,4\text{-NC}_6\text{H}_4\text{N})]$ **4b**. To a suspension of complex **1a** (0.872 g, 1.31 mmol) in THF (40 ml) was added dropwise a solution of $\text{MgNp}_2 \cdot 2\text{THF}$ (1.22 g, 3.92 mmol) in THF (40 ml) at -78°C . The mixture was stirred overnight at room temperature. The initial green suspension changed to yellow. The solvent was removed and the residue extracted with Et_2O (4 portions of 20 ml). The solvent was removed *in vacuo* to give a yellow solid, which was identified as **4b** (0.9 g, 1.04 mmol) (yield 80%). ^1H NMR (C_6D_6 , 300 MHz): δ 1.19 [s, 54 H, $(\text{CH}_3)_3\text{CCH}_2$], 1.21 (s, 12 H, Me_3CCH_2), 1.37 (m, 8 H, $\text{C}_4\text{H}_8\text{O}$), 3.67 (m, 8 H, $\text{C}_4\text{H}_8\text{O}$) and 7.74 (s, 4 H, $\text{NC}_6\text{H}_4\text{N}$). ^{13}C - $\{^1\text{H}\}$ NMR (C_6D_6 , 75 MHz): δ 25.7 ($\text{C}_4\text{H}_8\text{O}$), 34.4 [$(\text{CH}_3)_3\text{CCH}_2$], 35.7 [$(\text{CH}_3)_3\text{CCH}_2$], 69.47 ($\text{C}_4\text{H}_8\text{O}$), 92.7 (Me_3CCH_2), 125.9 (phenylene ring) and 154.9 (C_{ipso} of phenylene ring). IR: 1581w, 1315s, 1231m, 990w, 914w, 874m, 837m, 722m, 668w, 554w and 500 cm^{-1} [Found (Calc. for $\text{C}_{22}\text{H}_{43}\text{NNbO}$): C, 61.2 (61.4); H, 10.1 (9.9); N, 3.2 (3.2)%].

$[\text{Ti}(\text{py})_3\text{Cl}_2(1,4\text{-NC}_6\text{Me}_4\text{NH}_2)]$ **5a**. To a solution of $[\text{Ti}(\text{py})_3\text{Cl}_2(\text{N}^t\text{Bu})]$ (0.5 g, 1.17 mmol) in CH_2Cl_2 (25 ml) was added dropwise a solution of 2,3,5,6-tetramethyl-1,4-phenylenediamine (0.19 g, 1.17 mmol) in CH_2Cl_2 . The mixture was stirred for 2 h at room temperature and the volatile materials were removed under reduced pressure to give complex **5a** (0.59 g, 1.07 mmol) as a dark yellow solid. An analytically pure sample was obtained by careful layering of a dichloromethane solution of the compound with hexane at room temperature. The

product contained *ca.* 0.4 equivalent of residual CH₂Cl₂ (by ¹H NMR spectroscopy and elemental analysis). Yield for C₂₅H₂₉Cl₂N₅Ti·0.4CH₂Cl₂: 91%. ¹H NMR (CDCl₃, 300 MHz): δ 1.94 and 2.49 (s, 12 H, Me of amine), 3.47 (s br, 2 H, NH₂), 7.23 (m, 2 H, *m*-H of *trans* NC₅H₅), 7.44 (m, 4 H, *m*-H of *cis* NC₅H₅), 7.65 (m, 1 H, *p*-H of *trans* NC₅H₅), 7.86 (m, 2 H, *p*-H of *cis* NC₅H₅), 8.60 (m, 2 H, *o*-H of *trans* NC₅H₅) and 9.11 (m, 4 H, *o*-H of *cis* NC₅H₅). ¹³C-¹H NMR (CDCl₃, 75 MHz): δ 13.4 and 15.3 (Me of amine), 116.6 and 131.6 (*o*- and *m*-C of phenylene ring), 123.6 and 124.3 (*m*-C of *cis* and *trans* NC₅H₅), 136.1 and 138.7 (*p*-C of *cis* and *trans* NC₅H₅), 150.1 and 151.2 (*o*-C of *cis* and *trans* NC₅H₅), 155.6 (C_{ipso} of phenylene ring) and 151.5 (*p*-C of phenylene ring). IR: 3451m, 3363m, 1626m, 1602s, 1570m, 1484s, 1445s, 1216m, 1070s, 1041s, 1012s, 760s, 734s, 697s, 637m, 484m and 464m cm⁻¹ [Found (Calc. for C₂₅H₂₉Cl₂N₅Ti·0.4CH₂Cl₂): C, 55.4 (55.2); H, 5.7 (5.4); N, 12.9 (12.7)%].

[Ti(py)₂Cl₂(1,4-NC₆Me₄NH₂)] 5b. The complex [TiCl₂(py)₃-(1,4-NC₆Me₄NH₂)] (0.5 g, 0.91 mmol) was heated at 65 °C under a dynamic vacuum for 6 h to give **5b** (0.38 g, 0.86 mmol) as a green-yellow powder (yield 95%). ¹H NMR (CDCl₃, 300 MHz): δ 1.98 and 2.59 (s, 12 H, Me of amine), 3.51 (s br, 2 H, NH₂), 7.48 (m, 4 H, *m*-H of NC₅H₅), 7.89 (m, 2 H, *p*-H of NC₅H₅) and 9.11 (m, 4 H, *o*-H of NC₅H₅). ¹³C-¹H NMR (CDCl₃, 75 MHz): δ 13.5 and 15.4 (Me of amine), 116.6 and 131.5 (*o*- and *m*-C of phenylene ring), 124.6 (*m*-C of NC₅H₅), 138.9 (*p*-C of NC₅H₅), 150.9 (*o*-C of NC₅H₅), C_{ipso} of phenylene ring not observed. IR: 3467m, 3371m, 1626m, 1603s, 1487m, 1444s, 1218m, 1154m, 1043s, 1012s, 760s, 698s, 635m and 457m cm⁻¹ [Found (Calc. for C₂₀H₂₄Cl₂N₄Ti): C, 55.2 (54.7); H, 5.9 (5.5); N, 12.9 (12.8)%].

[Ti(4'-Bupy)₂Cl₂{1,4-NC₆H₄N(SiMe₃)₂}] 6a, [{Ti(4'-Bupy)₂Cl₂}(μ-1,4-NC₆H₄N)] 8a and [{Ti(Bupy)₂Cl₂}(μ-1,3-NC₆H₄N)] 9a. To a solution of the corresponding *N,N,N',N'*-tetrakis(trimethylsilyl)phenylenediamine in CH₂Cl₂ (50 ml) was added dropwise at 0 °C a solution of TiCl₄ in CH₂Cl₂ (50 ml). After stirring the mixture for 16 h at room temperature the solvent was evaporated to dryness to give a black solid, which was washed with toluene (2 × 15 ml) and hexane (3 × 15 ml). The resulting black powder was added to toluene (40 ml) and the suspension obtained treated with 4-*tert*-butylpyridine to give a red solution. After 6 h the solvent was evaporated to dryness to yield a solid, which was washed with hexane (2 × 20 ml), dried *in vacuo* and identified as complex **6a**, **8a** or **9a**.

Complex 6a: from 1,4-[(Me₃Si)₂N]₂C₆H₄ (1.0 g, 2.52 mmol), TiCl₄ (0.25 ml, 2.27 mmol) and 4-*tert*-butylpyridine (0.68 ml, 4.56 mmol), 1.2 g of a green solid were obtained (yield 85%). ¹H NMR (CDCl₃, 300 MHz): δ -0.01 (s, 18 H, SiMe₃), 1.33 (s, 18 H, NC₅H₄CMe₃), 6.53 and 6.72 (AA' and BB' part of an AA'BB' spin system, 4 H, phenylene ring), 7.45 (XX' part of an AA'XX' spin system, 4 H, *m*-H of NC₅H₄'Bu) and 9.03 (AA' part of an AA'XX' spin system, 4 H, *o*-H of NC₅H₄'Bu). ¹³C-¹H NMR (CDCl₃, 50 MHz): δ 2.0 (SiMe₃), 30.2 (NC₅H₄-CMe₃), 35.2 (NC₅H₄CMe₃), 121.5 (*m*-C of NC₅H₄'Bu), 123.4 and 129.4 (*o*- and *m*-C of phenylene ring), 142.7 (*p*-C of phenylene ring), 150.4 (*o*-C of NC₅H₄'Bu), 158.4 (C_{ipso} of phenylene ring) and 163.3 (*p*-C of NC₅H₄'Bu). IR: 1615s, 1490m, 1417m, 1320m, 1258s, 1211s, 1067m, 1023m, 978s, 904s, 837s, 827s, 755m, 729m, 572s and 441s cm⁻¹ [Found (Calc. for C₃₀H₄₈Cl₂N₄Si₂Ti): C, 55.7 (56.3); H, 7.6 (7.6); N, 8.8 (8.8)%].

Complex 8a: from 1,4-[(Me₃Si)₂N]₂C₆H₄ (3.0 g, 7.56 mmol), TiCl₄ (1.66 ml, 15.1 mmol) and 4-*tert*-butylpyridine (4.4 ml, 30 mmol), 5.1 g of a green solid were obtained (yield 76%). ¹H NMR (CDCl₃, 300 MHz): δ 1.33 (s, 36 H, NC₅H₄CMe₃), 6.64 (s, 4 H, phenylene ring), 7.43 (XX' part of an AA'XX' spin system, 8 H, *m*-H of NC₅H₄'Bu) and 8.99 (AA' part of an AA'XX' spin system, 8 H, *o*-H of NC₅H₄'Bu). ¹³C-¹H NMR (CDCl₃, 50 MHz): δ 30.3 (NC₅H₄CMe₃), 35.2 (NC₅H₄CMe₃),

121.4 (*m*-C of NC₅H₄'Bu), 123.7 (phenylene ring), 150.6 (*o*-C of NC₅H₄'Bu), 157.0 (C_{ipso} of phenylene ring) and 163.4 (*p*-C of NC₅H₄'Bu). IR: 1613s, 1543m, 1419m, 1274s, 1229s, 1203s, 1071s, 1022s, 989m, 833s, 572s, 399s and 209m cm⁻¹ [Found (Calc. for C₂₁H₂₈Cl₂N₃Ti): C, 57.0 (57.2); H, 6.3 (6.4); N, 9.4 (9.5)%].

Complex 9a: from 1,3-[(Me₃Si)₂N]₂C₆H₄ (3.0 g, 7.56 mmol), TiCl₄ (1.66 ml, 15.1 mmol) and 4-*tert*-butylpyridine (4.4 ml, 30 mmol), 5.8 g of a red solid were obtained (yield 85%). ¹H NMR (CDCl₃, 300 MHz): δ 1.29 (s, 36 H, NC₅H₄CMe₃), 6.40 and 6.71 (M and X parts of A₂MX spin system, 2 H, phenylene ring), 6.46 (A₂ part of A₂MX spin system, 2 H, phenylene ring), 7.33 (XX' part of an AA'XX' spin system, 8 H, *m*-H of NC₅H₄'Bu) and 8.97 (AA' part of an AA'XX' spin system, 8 H, *o*-H of NC₅H₄'Bu). ¹³C-¹H NMR (CDCl₃, 75 MHz): δ 30.2 (NC₅H₄-CMe₃), 35.2 (NC₅H₄CMe₃), 116.5, 119.3, 127.5 (phenylene ring), 121.5 (*m*-C of NC₅H₄'Bu), 150.5 (*o*-C of NC₅H₄'Bu), 160.4 (C_{ipso} of phenylene ring) and 163.5 (*p*-C of NC₅H₄'Bu). IR: 1613s, 1555s, 1498m, 1419s, 1329m, 1300s, 1276s, 1230s, 1201m, 1151m, 1068s, 1025s, 870m, 834s, 782s, 571s, 390s and 251m cm⁻¹ [Found (Calc. for C₂₁H₂₈Cl₂N₃Ti): C, 57.1 (57.2); H, 6.5 (6.4); N, 9.3 (9.5)%].

[Ti(TMEDA)Cl₂{1,4-NC₆H₄N(SiMe₃)₂}] 6b, [{Ti(TMEDA)Cl₂}(μ-1,4-NC₆H₄N)] 8b and [{Ti(TMEDA)Cl₂}(μ-1,3-NC₆H₄N)] 9b. To a solution of *N,N,N',N'*-tetrakis(trimethylsilyl)-1,4-phenylenediamine in CH₂Cl₂ (30 ml) was added dropwise at 0 °C a solution of TiCl₄ in CH₂Cl₂ (30 ml). After stirring the mixture for 16 h at room temperature the solvent was evaporated to dryness to give a black solid, which was washed with toluene (2 × 10 ml) and hexane (3 × 10 ml). The resulting black powder was added to hexane (30 ml) and the suspension treated with *N,N,N',N'*-tetramethylethylenediamine to give, after 24 h, a suspension. The solid was filtered off and washed with hexane (2 × 10 ml), dried *in vacuo* and identified as complex **6b**, **8b** or **9b**.

Complex 6b: from 1,4-[(Me₃Si)₂N]₂C₆H₄ (1.0 g, 2.52 mmol), TiCl₄ (0.25 ml, 2.27 mmol) and *N,N,N',N'*-tetramethylethylenediamine (0.34 ml, 2.27 mmol), 0.92 g of a yellow solid was obtained (yield 84%). ¹H NMR (CDCl₃, 300 MHz): δ 0.03 (s, 18 H, SiMe₃), 2.94 (s, 12 H, Me of TMEDA), 3.16 (s br, 4 H, CH₂ of TMEDA), 6.50 and 6.68 (AA' and BB' part of an AA'BB' spin system, 4 H, phenylene ring). ¹³C-¹H NMR (CDCl₃, 75 MHz): δ 2.1 (SiMe₃), 51.3 (Me of TMEDA), 58.9 (CH₂ of TMEDA), 122.6 and 129.4 (*o*- and *m*-C of phenylene ring), 142.6 (*p*-C of phenylene ring) and 158.7 (C_{ipso} of phenylene ring). IR: 1593m, 1313s, 1250s, 1213s, 1093m, 1067m, 971s, 928s, 901s, 842s, 804s, 518m and 451m cm⁻¹ [Found (Calc. for C₁₈H₃₈Cl₂N₄Si₂Ti): C, 44.2 (44.5); H, 7.6 (7.9); N, 12.1 (11.5)%].

Complex 8b: from 1,4-[(Me₃Si)₂N]₂C₆H₄ (0.37 g, 0.94 mmol), TiCl₄ (0.21 ml, 1.88 mmol) and *N,N,N',N'*-tetramethylethylenediamine (0.29 ml, 1.88 mmol), 0.41 g of a green solid was obtained (yield 76%). ¹H NMR (DMSO, 300 MHz): δ 2.16 (s, 24 H, Me of TMEDA), 2.36 (s, 4 H, CH₂ of TMEDA) and 6.50 (s br, 4 H, phenylene ring). ¹³C-¹H NMR (CDCl₃, 75 MHz): δ 45.4 (Me of TMEDA), 56.9 (CH₂ of TMEDA), 123.1 (phenylene ring) and 153.7 (C_{ipso} of phenylene ring). IR: 1515m, 1316s, 1211m, 1011m, 982m, 948s, 849s, 803s, 510s and 472m cm⁻¹ [Found (Calc. for C₉H₁₉Cl₂N₃Ti): C, 37.5 (37.5); H, 6.1 (6.6); N, 13.8 (14.6)%].

Complex 9b: from 1,3-[(Me₃Si)₂N]₂C₆H₄ (0.37 g, 0.94 mmol), TiCl₄ (0.21 ml, 1.88 mmol) and *N,N,N',N'*-tetramethylethylenediamine (0.29 ml, 1.88 mmol), 0.41 g of a red solid was obtained (yield 72%). ¹H NMR (DMSO, 300 MHz): δ 2.16 (s, 24 H, Me of TMEDA), 2.36 (s, 4 H, CH₂ of TMEDA), 6.15, 6.56, 6.66 (m br, 4 H, phenylene ring). ¹³C-¹H NMR (CDCl₃, 75 MHz): δ 45.4 (Me of TMEDA), 56.9 (CH₂ of TMEDA), 116.1, 119.1, 128.2 (phenylene ring) and 158.7 (C_{ipso} of phenylene ring). IR: 1555s, 1542m, 1398m, 1337s, 1299s, 1285s, 1233s,

1146m, 1068m, 1021m, 995m, 945s, 881m, 803s, 790m, 501m, 461m and 399m cm^{-1} [Found (Calc. for $\text{C}_9\text{H}_{19}\text{Cl}_2\text{N}_3\text{Ti}$): C, 37.3 (37.5); H, 6.3 (6.6); N, 14.0 (14.6)%].

[Ti(TMEDA)Cl₂{1,3-NC₆H₄N(SiMe₃)₂}] 7b. To a solution of *N,N,N',N'*-tetrakis(trimethylsilyl)-1,3-phenylenediamine (2.0 g, 5.04 mmol) in CH_2Cl_2 (40 ml) was added dropwise at 0 °C a solution of TiCl_4 (0.5 ml, 4.56 mmol) in CH_2Cl_2 (50 ml). After stirring the mixture for 16 h at room temperature the solvent was evaporated to dryness to give a black solid, which was washed with toluene (2 × 10 ml) and hexane (3 × 10 ml). The resulting black powder was added to hexane (40 ml) and the suspension obtained treated with *N,N,N',N'*-tetramethylethylenediamine (0.68 ml, 4.56 mmol) to give, after 24 h, a red suspension. The solid was filtered off, washed with hexane (2 × 10 ml) and extracted with chloroform (5 × 15 ml). The resulting red solution was evaporated to dryness to give complex **7b** (1.08 g, 2.22 mmol) as a red solid (yield 44%). ¹H NMR (CDCl_3 , 300 MHz): δ 0.00 (s, 18 H, SiMe₃), 2.92 (s, 12 H, Me of TMEDA), 3.13 (s, 4 H, CH₂ of TMEDA), 6.35, 6.40, 6.53, 6.83 (m, 4 H, phenylene ring). ¹³C-¹H NMR (CDCl_3 , 75 MHz): δ 2.0 (SiMe₃), 51.3 (Me of TMEDA), 58.9 (CH₂ of TMEDA), 117.5, 123.9, 125.2 and 127.6 (phenylene ring), 142.6 (*p*-C of phenylene ring) and 161.4 (*C*_{ipso} of phenylene ring). IR: 1569s, 1407m, 1320m, 1249s, 1186s, 1521m, 1019m, 967s, 910s, 841s, 801m, 697m, 632m, 445m and 387m [Found (Calc. for $\text{C}_{18}\text{H}_{38}\text{Cl}_2\text{N}_4\text{Si}_2\text{Ti}$): C, 44.1 (44.5); H, 7.6 (7.9); N, 11.9 (11.5)%].

[Ti(4-'Bupy)₂Cl₂{1,2-C₆H₄(NH)₂}] 10a. *Method A.* To a solution of *N,N'*-bis(trimethylsilyl)-1,2-phenylenediamine (0.68 g, 2.69 mmol) in CH_2Cl_2 (30 ml) was added dropwise, at 0 °C, a solution of TiCl_4 (0.30 ml, 2.69 mmol) in CH_2Cl_2 (30 ml). After stirring the mixture for 16 h at room temperature the solvent was evaporated to dryness to give a brown solid, which was washed with toluene (2 × 10 ml) and hexane (3 × 10 ml). The resulting brown powder was added to CH_2Cl_2 (40 ml) and the suspension obtained treated with 4-*tert*-butylpyridine (0.68 ml, 4.56 mmol) to give a red solution. After 2 h the solvent was removed and the resulting red solid washed with hexane (2 × 20 ml) and dried *in vacuo* to give complex **10a** (1.22 g, 2.47 mmol) as a red solid (yield 92%).

Method B. To a solution of *N,N,N',N'*-tetrakis(trimethylsilyl)-1,2-phenylenediamine (2.00 g, 5.04 mmol) in CH_2Cl_2 (30 ml) was added dropwise, at 0 °C, a solution of TiCl_4 (1.10 ml, 10.1 mmol) in CH_2Cl_2 (30 ml). After stirring the mixture for 16 h at room temperature the solvent was evaporated to dryness to give a brown solid, which was washed with toluene (2 × 15 ml) and hexane (3 × 15 ml). The resulting black powder was added to toluene (40 ml) and the suspension obtained treated with 4-*tert*-butylpyridine (2.9 ml, 20 mmol) to give a red solution. After 2 h the solution was cooled to -40 °C for 10 h and the red solid obtained filtered off, washed with hexane (2 × 10 ml) and dried *in vacuo* to give complex **10a** (1.20 g, 2.42 mmol) (yield 48%). ¹H NMR (CDCl_3 , 300 MHz): δ 1.35 (s, 18 H, NC₅H₄CMe₃), 5.69, 6.34 (AA' and XX' part of an AA'XX' spin system, 4 H, phenylene ring), 7.50 (XX' part of an AA'XX' spin system, 4 H, *m*-H of NC₅H₄'Bu), 9.13 (AA' part of an AA'XX' spin system, 4 H, *o*-H of NC₅H₄'Bu) and 11.14 (s br, 2 H, NH). ¹³C-¹H NMR (CDCl_3 , 50 MHz): δ 30.2 (NC₅H₄CMe₃), 35.2 (NC₅H₄CMe₃), 110.7 and 123.0 (phenylene ring), 121.4 (*m*-C of NC₅H₄'Bu), 144.7 (*C*_{ipso} of phenylene ring), 149.2 (*o*-C of NC₅H₄'Bu) and 163.7 (*p*-C of NC₅H₄'Bu). IR 3299s, 1612s, 1271s, 1191m, 1069m, 1021m, 834s, 748s, 627m, 568m and 395m cm^{-1} [Found (Calc. for $\text{C}_{24}\text{H}_{32}\text{Cl}_2\text{N}_4\text{Ti}$): C, 57.6 (58.2); H, 6.6 (6.5); N, 11.0 (11.3)%].

[Ti(TMEDA)Cl₂{1,2-C₆H₄(NH)₂}] 10b. *Method A.* To a solution of *N,N'*-bis(trimethylsilyl)-1,2-phenylenediamine (1.0 g, 3.96 mmol) in CH_2Cl_2 (40 ml) was added dropwise, at 0 °C, a

solution of TiCl_4 (0.44 ml, 3.96 mmol) in CH_2Cl_2 (40 ml). After stirring the mixture for 16 h at room temperature the solvent was evaporated to dryness to give a brown solid, which was washed with toluene (2 × 10 ml) and hexane (3 × 10 ml). The resulting brown powder was added to CH_2Cl_2 (75 ml) and the suspension obtained treated with TMEDA (0.59 ml, 3.96 mmol) to give a red solution. After 2 h the solvent was removed and the resulting dark red solid recrystallized from acetonitrile and dried *in vacuo* to give complex **10b** (1.1 g, 3.22 mmol) as a dark red solid (yield 82%).

Method B. To a solution of *N,N,N',N'*-tetrakis(trimethylsilyl)-1,2-phenylenediamine (1.00 g, 2.52 mmol) in CH_2Cl_2 (40 ml) was added dropwise, at 0 °C, a solution of TiCl_4 (0.55 ml, 5.05 mmol) in CH_2Cl_2 (40 ml). After stirring the mixture for 16 h at room temperature the solvent was evaporated to dryness to give a brown solid, which was washed with toluene (2 × 15 ml) and hexane (3 × 15 ml). The resulting black powder was added to hexane (40 ml) and the suspension obtained treated with TMEDA (0.76 ml, 5.05 mmol) to give a dark red suspension after 2 h. The solid was filtered off and washed with cold (-40 °C) dichloromethane, purified by recrystallization from acetonitrile and identified as complex **10b** (0.38 g, 1.33 mmol) (yield 45%). ¹H NMR (CDCl_3 , 300 MHz): δ 2.32 (s, 3 H, Me of TMEDA), 2.47 (m, 4 H, CH₂ of TMEDA), 3.00, 3.20, 3.22 (s, 9 H, Me of TMEDA), 5.59 and 6.26 (m, 4 H, phenylene ring), 9.55, 11.79 (s br, 2 H, NH). ¹³C-¹H NMR (CDCl_3 , 75 MHz): δ 49.7, 51.4, 51.5, 54.4, 57.9 and 58.4 (CH₂ and CH₃ of TMEDA), 110.1, 111.3, 122.7, 123.6 (phenylene ring), 153.0, 155.2 (*C*_{ipso} of phenylene ring). IR: 3344m, 3283s, 1576m, 1276m, 1191m, 1064m, 1013m, 949m, 801s, 752s, 745s, 662s, 629m, 449m and 392m cm^{-1} [Found (Calc. for $\text{C}_{14}\text{H}_{22}\text{Cl}_2\text{N}_4\text{Ti}$): C, 41.6 (42.3); H, 6.6 (6.5); N, 16.3 (16.4)%].

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