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Titanium *tert*-Butoxyimido Compounds

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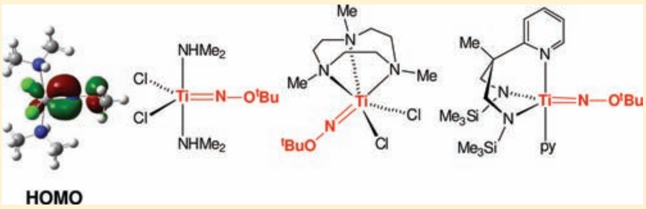
Supporting Information



ABSTRACT: The synthesis and molecular and electronic structures of the first *tert*-butoxyimido complexes of titanium ($TiNO^tBu$ functional group) are reported, featuring a variety of mono- or poly-dentate, neutral or anionic N-donor ligands. Reaction of $Ti(NMe_2)_2Cl_2$ with $^tBuONH_2$ gave good yields of $Ti(NO^tBu)Cl_2(NHMe_2)_2$ (**1**). Compound **1** serves as an excellent entry point into new *tert*-butoxyimido complexes by reaction with a variety of *fac*-N_3 donor ligands, namely, $Me_3[9]aneN_3$ (trimethyl-1,4,7-triazacyclononane), $HC(Me_2pz)_3$ (tris(3,5-dimethylpyrazolyl)methane), or $Me_3[6]aneN_3$ (trimethyl-1,3,5-triazacyclohexane) to give $Ti(NO^tBu)(Me_3[9]aneN_3)Cl_2$ (**2**), $Ti(NO^tBu)\{HC(Me_2pz)_3\}Cl_2$ (**3**), or $Ti(NO^tBu)(Me_3[6]aneN_3)Cl_2$ (**4**) in good yield. It was found that **4** could be converted into $Ti(NO^tBu)Cl_2(py)_3$ (**5**) in very good yield by reaction with an excess of pyridine. Compound **5** is effective in a range of salt metathesis reactions with lithiated amide or pyrrolide ligands, and reacts with $Li_2N_2N^{py}$, $Li_2N_2N^{Me}$, $LiN^{pyr}N^{Me_2}$, or $Li_2N_2{}^{pyr}N^{Me}$ to give $Ti(N_2N^{py})(NO^tBu)(py)$ (**6**), $Ti(N_2N^{Me})(NO^tBu)(py)$ (**7**), $Ti(N^{pyr}N^{Me_2})(NO^tBu)Cl(py)_2$ (**9**), or $Ti(N_2{}^{pyr}N^{Me})(NO^tBu)(py)_2$ (**10**) in moderate to good yields ($N_2N^{py} = (2\text{-}NC_5H_4)C(Me)(CH_2NSiMe_3)_2$; $N_2N^{Me} = MeN(CH_2CH_2NSiMe_3)_2$; $N^{pyr}N^{Me_2} = Me_2NCH_2(2\text{-}NC_4H_3)$; $N_2{}^{pyr}N^{Me} = MeN\{CH_2(2\text{-}NC_4H_3)\}_2$). Compounds **7**, **9**, and **10** reacted with 2,2′-bipyridyl by pyridine exchange reactions forming $Ti(N_2N^{Me})(NO^tBu)(bipy)$ (**8**), $Ti(N^{pyr}N^{Me_2})(NO^tBu)Cl(bipy)$ (**11**), and $Ti(N_2{}^{pyr}N^{Me})(NO^tBu)(bipy)$ (**12**). Ten *tert*-butoxyimido compounds, namely, **1–6**, **11**, and **12**, have been structurally characterized revealing approximately linear Ti–N–O^tBu linkages with Ti–N distances [range 1.686(2)–1.734(2) Å] that are generally intermediate between those in the homologous alkylimido and phenylimido analogues, and shorter than in the diphenylhydrazido counterparts. Density functional theory (DFT) studies on the model compounds $Ti(NR)Cl_2(NHMe_2)_2$ (**1_R**; R = OMe, Me, Ph, NMe_2) confirmed this trend and found that the destabilizing effect of the –OMe oxygen $2p_\pi$ lone pair on one of the Ti–N π-bonds in **1_OMe** is comparable to that of the occupied phenyl ring π orbitals in the phenylimido homologue **1_Ph** but much less than for the $-NMe_2$ nitrogen lone pair in **1_NMe$_2$**.

INTRODUCTION

Group 4 imido complexes of the type (L)MNR (R is almost exclusively alkyl or aryl) have been known for over 20 years. A large number of such complexes, which generally possess a formal metal–nitrogen triple bond ($\sigma^2\pi^4$ configuration), have been synthesized and studied in considerable detail with regard to their structures, bonding, and reactivity. They have been employed as both inert supporting ligands and as sites of reactivity in their own regard, as well as MOCVD precursors. This work has been summarized in a number of reviews.[1] Although the corresponding Group 4 terminal hydrazido(2-) complexes (L)MNNRR′ (R and/or R′ = H, alkyl, $SiMe_3$ or aryl) are as long-established as their imido counterparts,[2] their stoichiometric and catalytic reaction chemistry has only been significantly developed within the past 8–10 years. Unlike their Group 6 counterparts,[3] Group 4 hydrazido compounds, $(L)MNNR_2$, show a rich reaction chemistry of both the M–N_α and the N_α–N_β bonds, as well as alkylation,[4] protonation,[4b] or borane addition[5] at N_α or N_β. Reactions at the M–N_α bond are reminiscent of those of imido compounds and include cycloaddition, cycloaddition-insertion, cycloaddition–elimination, and NNR_2 group transfer with unsaturated substrates,[2c,5a,6] and also 1,2-addition of Si–H or Si–Cl bonds.[7] However, it is the facile substrate-induced N_α–N_β bond cleavage or insertion reactions of Group 4 hydrazides that set their chemistry apart from that of their imido analogues. For example, reaction of alkynes with $Cp_2Zr(NNPh_2)(py)$ or $Ti(N_2N^{Me})(NNPh_2)(py)$ ($N_2N^{Me} = MeN(CH_2CH_2NSiMe_3)_2$) give products of N_α–N_β bond cleavage or insertion.[2b,6d,f] Similar cleavage reactions occur with CO and isonitriles, as well as with other substrates.[2b,5a,8] Mechanistically, all of these N_α–N_β bond cleavage/insertion reactions proceed via initial attack at the M–N_α bond.[5a,6d,9]

As part of our ongoing research effort in this area we were interested in developing further new M–N–XR_n (X = heteroatom) functional group chemistry and its scope in new N–C and X–C bond-forming reactions. We noticed that the key step in the mechanism[6d] for alkyne insertion into the N_α–N_β of certain hydrazides is analogous to that proposed for the

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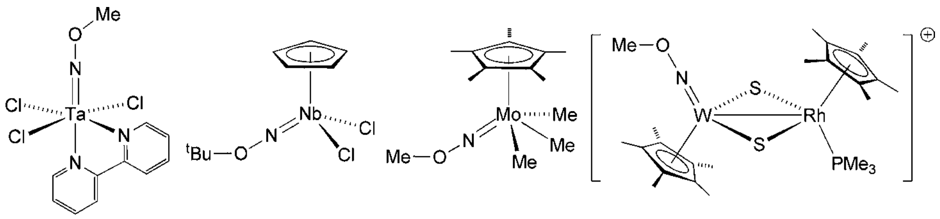
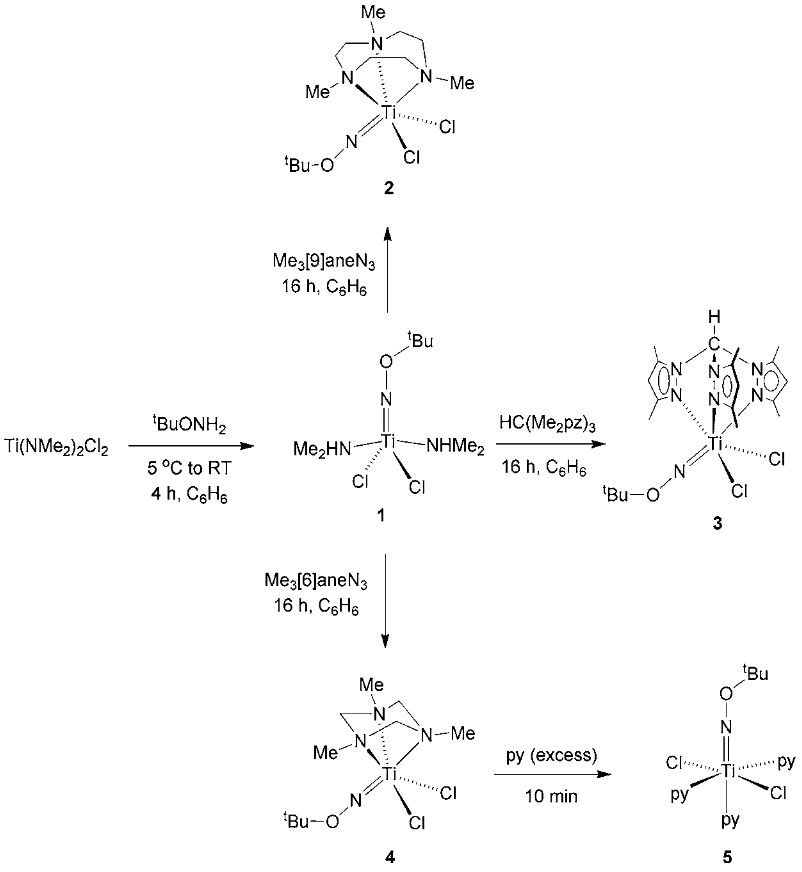


Figure 1. Examples of Group 5 and 6 alkoxyimido complexes.[13−15]

Scheme 1. Synthesis of $Ti(NO^tBu)Cl_2(NHMe_2)_2$ (1), Its Reactions with *fac*-N_3 Donor Ligands, and Synthesis of $Ti(NO^tBu)Cl_2(py)_3$ (5)



alkyl group insertion/reductive cleavage of the peroxide ligand O_α−O_β bond in $Cp^*_2Hf(R)(OO^tBu)$ (R = H or alkyl) to form $Cp^*_2Hf(OR)(O^tBu)$.[10] Indeed, Group 4 alkylperoxide complexes are in general rare with very few isolable examples having been reported.[10,11] We therefore speculated that alkoxyimido compounds of the type (L)TiNOR might allow access to ligand-induced N−O bond cleavage reactions analogous to those mentioned above by combining the reactivity features of terminal Ti−N multiple bonds (facile coupling with substrates) and peroxide ligand chemistry (facile O_α−O_β bond cleavage).

Surprisingly, despite nearly 20 years of metal-heteroatom multiple bond chemistry, no Group 4 alkoxyimido compounds have been reported previously.[12] Two structurally characterized examples have been reported for Group 5, namely, $Ta(NOMe)Cl_3(bipy)$[13] and $CpNb(NO^tBu)Cl_2$ (Figure 1),[14] which were prepared by Me_3SiCl or/and HCl elimination reactions starting from $MeON(SiMe_3)_2$ or $RONH_2$ and the appropriate halide precursors. The Group 6 species $Cp^*Mo(NOMe)Me_3$ and $[Cp^*W(NOMe)(\mu\text{-}S)_2RhCp^*(PMe_3)]^+$ were synthesized by alkylation of nitrosyl complexes, and the latter was structurally authenticated as its $[OTf]^-$ salt.[15] In addition, trinuclear Group 7 and 8 carbonyl clusters are also known in which the NOR group bridges between the three metal centers. These were also prepared by electrophilic attack on coordinated nitrosyl ligands.[16] To date no reactions of terminal (L)MNOR compounds have been reported, although under forcing thermolytic conditions the μ_3-bound NOR ligands in the trinuclear clusters can undergo N−O bond cleavage reaction to form bridging imido or nitrene ligands among product mixtures which require extensive purification.

In this contribution we report synthetic routes to a number of *tert*-butoxyimido complexes of titanium along with extensive structural characterization and density functional theory (DFT) comparisons of the bonding between alkoxyimido complexes and their imido and hydrazido analogues. Part of this work has been communicated.[17,18]

■ RESULTS AND DISCUSSION

In our previous work in titanium imido and hydrazido chemistry we have shown that readily prepared "synthons" of the type $Ti(NR)Cl_2(L)_n$ (R = ${}^tBu$, aryl, NPh_2; L = py, 4-$NC_5H_4{}^tBu$; n = 2 or 3)[19] and $Ti(NR)Cl_2(NHMe_2)_2$ (R = alkyl, aryl, or NPh_2)[20] are excellent entry points to new complexes and chemistry by substitution of the Cl or Lewis base ligands with neutral or anionic donors.[1b,f,h,6f,21] A further important route to new arylimido and hydrazido compounds has been through *tert*-butylimide-aniline or N,N-disubstituted hydrazine exchange, eliminating ${}^tBuNH_2$ and forming new TiNAr or $TiNNR_2$ functional groups.[6b,19,22] We therefore based our initial work in titanium alkoxyimido on these synthetic precedents, focusing on ${}^tBuONH_2$ as the alkoxyamine starting material because of its ready availability,[23] the above-mentioned synthetic precedents in Group 5 chemistry,[14] and the bulky *tert*-butyl substituent which we hoped would favor soluble, monomeric complexes.

Synthesis and Substitution Reactions of $Ti(NO^tBu)Cl_2(NHMe_2)_2$ (1). We have previously shown that reaction of $Ti(NMe_2)_2Cl_2$[24] with primary amines, anilines, or diphenylhydrazine allowed access to monomeric terminal imido and hydrazido compounds of the type $Ti(NR)Cl_2(NHMe_2)_2$ or $Ti(NNPh_2)Cl_2(NHMe_2)_2$.[20,25] The reaction between ${}^tBuONH_2$ and $Ti(NMe_2)_2Cl_2$ proceeds smoothly in benzene to give $Ti(NO^tBu)Cl_2(NHMe_2)_2$ (**1**, Scheme 1) as a green solid in 51% yield. The solid state structure (vide infra) of **1** confirms that shown in Scheme 1 and the solution ^1H NMR spectrum in C_6D_6 features resonances for a C_s symmetric species containing a NO^tBu and two $NHMe_2$ ligands. The solid state IR spectrum (Nujol mull) shows a broad band at 3247 cm^{-1} corresponding to ν(N−H) which lies within the range found for titanium imido and hydrazido species $Ti(NR)Cl_2(NHMe_2)_2$ (3220−3254 cm^{-1}). These exist as N−H···Cl hydrogen-bonded chains in the solid state, but as discrete monomers in CH_2Cl_2 with ν(N−H) values in the narrower range 3280−3288 cm^{-1}.[20] Compound **1** exhibits a very similar ν(N−H) band in CH_2Cl_2 (3289 cm^{-1}) so is also likely to be monomeric in solution.

It was not possible to cleanly substitute the $NHMe_2$ ligands with pyridine to synthesize $Ti(NO^tBu)Cl_2(py)_3$ (**5**) which would be the analogue of $Ti(NR)Cl_2(py)_3$ and $Ti(NNPh_2)Cl_2(py)_3$. Although at first sight surprising, analogous observations have been made for other titanium[20a] and vanadium[26] complexes of this type, even when the target pyridine complexes are known via other routes. In addition, reaction of $Ti(N^tBu)Cl_2(py)_3$ with ${}^tBuONH_2$ in an attempt to form **5** by an imide-amine exchange strategy we have used previously[19a,b,22b] for arylimido and hydrazido analogues of **5** also led to mixtures of products. Compound **5** was, however, eventually prepared via an alternative route as discussed below. We found that **1** slowly decomposes at room temperature in benzene or dichloromethane solution giving unknown products which appear to arise via the elimination of HCl since $[Me_2NH_2]Cl$ was observed among the mixtures. This process is accelerated upon addition of external base and helps to account for the unsuccessful reaction with pyridine.

Disappointing results were found in the reactions of Me_3SiONH_2 with either $Ti(NMe_2)_2Cl_2$ or $Ti(N^tBu)Cl_2(py)_3$ in an attempt to prepare siloxyimido analogues of **1** or **5**, giving complex mixtures in each case. Similar results have been found with the bulkier ${}^tBuMe_2SiONH_2$.[27] The origins of this different behavior are unclear.

Although clean substitution of the Me_2NH ligands in **1** by pyridine was not possible, macrocyclic and related neutral *fac*-N_3 donor ligands proved to be stable platforms as summarized in Scheme 1. Imido and hydrazido complexes supported by these and related *fac*-N_3 donor ligands are well-established and have an extensive stoichiometric and catalytic chemistry.[1g,21,25,28] The reactions of **1** with $Me_3[9]aneN_3$ (trimethyl-1,4,7-triazacyclononane), $HC(Me_2pz)_3$ (HMe_2pz = 3,5-dimethylpyrazole) and $Me_3[6]aneN_3$ (trimethyl-1,3,5-triazacyclohexane) proceeded smoothly in benzene solution at room temperature to give $Ti(NO^tBu)(Me_3[9]aneN_3)Cl_2$ (**2**), $Ti(NO^tBu)\{HC(Me_2pz)_3\}Cl_2$ (**3**), and $Ti(NO^tBu)(Me_3[6]aneN_3)Cl_2$ (**4**) in 72−82% isolated yield. When the reactions were followed in CD_2Cl_2 on the NMR tube scale, the yields were effectively quantitative and the expected $NHMe_2$ side product was observed. Compound **4** is obtained alongside small quantities of $[Me_2NH_2]Cl$ formed by HCl elimination, but this can be separated by extraction with CH_2Cl_2. The new compounds exist as six-coordinate monomeric compounds in the solid state according to X-ray crystallography (vide infra).

The solution ^1H NMR spectra of **2**−**4** feature characteristic resonances for C_s symmetrical species containing coordinated *fac*-N_3 donor ligands; in addition to these resonances a singlet at δ 1.23−1.42 is seen for the *tert*-butoxyimido group. The resonances for the *fac*-N_3 ligands are very similar to those found in the aforementioned imido and hydrazido complexes. In compounds **2** and **4**, for example, there are two sets of signals in a 2:1 ratio for the N-methyl groups cis or trans to the NO^tBu ligand, respectively. There are also characteristic "up" and "down" doublets assigned to the diasterotopic methylene hydrogens which, in the case of **4**, are slightly broadened, probably because of a fluxional process which exchanges the cis and trans positions via a trigonal twist of the $Me_3[6]aneN_3$ ligand as observed for the analogous imido and hydrazido complexes.[20c,28a]

As mentioned, $Ti(NO^tBu)Cl_2(py)_3$ (**5**), a potentially useful synthon, could not be prepared directly from **1**. However, mindful that the small ring size of $Me_3[6]aneN_3$ often makes its substitution by other ligands possible,[28a,29] we found that dissolving **4** in an excess of neat pyridine at room temperature followed by precipitation with hexanes gave the target tris(pyridine) complex **5** in 67% yield (Scheme 1). Compound **5** can also be efficiently prepared in a "one-pot" manner without the need to purify either **1** or **4** producing 4.6 g of **5** from 5 g of $Ti(NMe_2)_2Cl_2$ (41% overall yield). The solid state structure of **5** is discussed below and the ^1H and ^{13}C NMR spectra of **5** are also consistent with the six coordinate octahedral structure depicted in Scheme 1. The ^1H NMR spectrum features a singlet at δ 1.13 for the *tert*-butyl group and two sets of resonances (2:1 intensity ratio) for the pyridine ligands positioned cis and trans to the NO^tBu group. The broadened and upfield-shifted resonances for the pyridine trans to NO^tBu can be attributed to the strong trans influence of the *tert*-butoxyimido ligand as found for the corresponding imido and hydrazido complexes. These also show a tendency to lose this trans pyridine in vacuo.[19b,20c] Interestingly, **5** showed no evidence of pyridine loss even after extended periods under dynamic vacuum. Nonetheless, reaction of **5** with $Me_3[9]aneN_3$ or $HC(Me_2pz)_3$ on the NMR tube scale in CD_2Cl_2 quantitatively formed **2** or **3** and liberated pyridine, demonstrating that **5** is an effective synthon for pyridine exchange reactions in a analogous manner to the corresponding imido and hydrazido complexes, $Ti(NR)Cl_2(py)_3$ (R = ${}^tBu$, aryl or NPh_2).[19a,20c,28a]

Solid State Structures of $Ti(NO^tBu)Cl_2(NHMe_2)_2$ (1), $Ti(NO^tBu)(Me_3[9]aneN_3)Cl_2$ (2), $Ti(NO^tBu)\{HC(Me_2pz)_3\}Cl_2$

(3), Ti(NO^{t}Bu)(Me$_3$[6]aneN$_3$)Cl$_2$ (4), and Ti(NO^{t}Bu)Cl$_2$(py)$_3$ (5). The molecular structures of **1** and **5** are shown in Figure 2, the extended hydrogen-bonded motif for **1** is given in Figure 3, and selected bond lengths and angles are listed in Tables 1 and 2. The structures of **2**, **3**, and **4** are presented in Figure 4, and the corresponding distances and angles are compared in Table 3. These are the first X-ray structures of any Group 4 alkoxyimido complex, and we discuss the two sets of compounds in turn. As mentioned, only two structurally characterized examples from Group 5 and one from Group 6 have been reported previously.[13,14,15b]

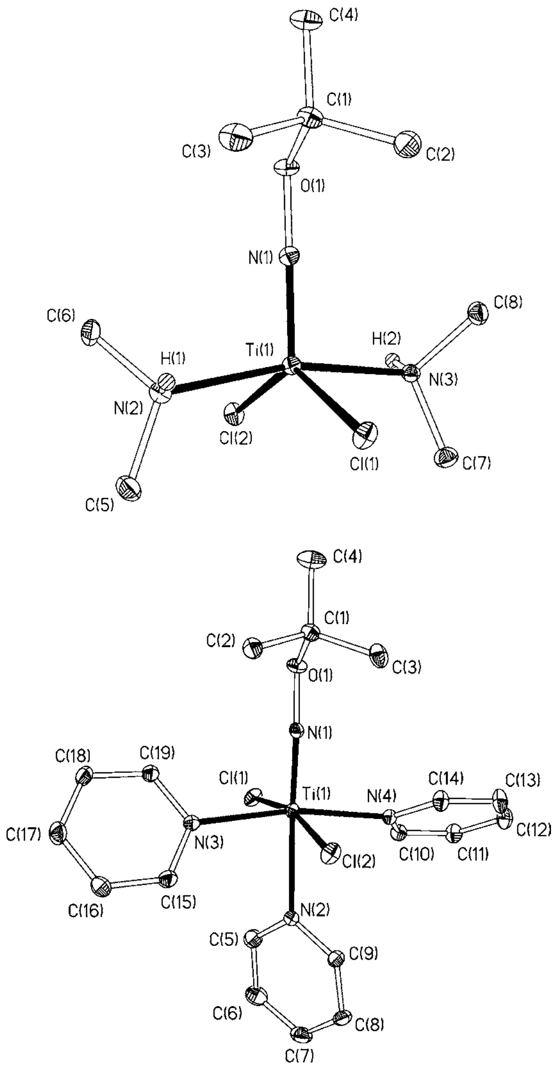


Figure 2. Displacement ellipsoid plot (20% probability) of Ti(NO^{t}Bu)Cl$_2$(NHMe$_2$)$_2$ (**1**) (top) and Ti(NO^{t}Bu)Cl$_2$(py)$_3$ (**5**) (bottom). C-bound H atoms are omitted for clarity. H(1) and H(2) are drawn as spheres of an arbitrary radius.

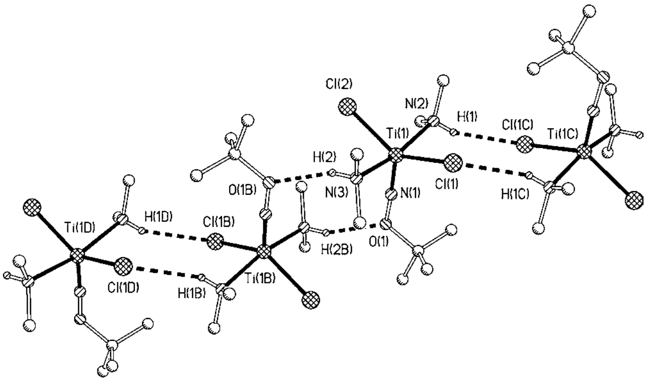


Figure 3. Partial packing diagram for Ti(NO^{t}Bu)Cl$_2$(NHMe$_2$)$_2$ (**1**) showing a portion of the infinite hydrogen-bonded chains. C-bound H atoms are omitted, and all atoms drawn as spheres of an arbitrary radius. Selected distances: O(1)···H(2B) = 2.16(4) A; Cl(1)···H(1C) = 2.65(3) A; Cl(2) forms no hydrogen bonds. Symmetry operators: B, [−1−*x*, −*y*, −*z*]; C, [−*x*, 1−*y*, −*z*]; D, [*x*−1, *y*−1, *z*].

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Ti(NO^{t}Bu)Cl$_2$(NHMe$_2$)$_2$ (1)^a

Ti(1)−N(1)	1.688(3) [1.691(3)]	Ti(1)−N(2)	2.214(3) [2.206(3)]
Ti(1)−N(3)	2.208(3) [2.221(3)]	Ti(1)−Cl(1)	2.358(1) [2.353(1)]
Ti(1)−Cl(2)	2.348(1) [2.346(1)]	N(1)−O(1)	1.368(3) [1.364(3)]
O(1)−C(1)	1.489(4) [1.481(4)]	N(2)−H(1)	0.81(4) [0.82(4)]
N(3)−H(2)	0.87(4) [0.81(1)]		
Ti(1)−N(1)−O(1)	177.0(2) [176.4(2)]	N(1)−O(1)−C(1)	114.2(2) [113.9(2)]
N(1)−Ti(1)−N(2)	96.7(1) [96.4(1)]	N(1)−Ti(1)−N(3)	97.1(1) [95.6(1)]
N(2)−Ti(1)−N(3)	166.1(1) [167.7(1)]	N(1)−Ti(1)−Cl(1)	110.5(1) [112.35(1)]
N(2)−Ti(1)−Cl(1)	87.27(8) [85.53(8)]	N(3)−Ti(1)−Cl(1)	88.98(8) [87.76(9)]
N(1)−Ti(1)−Cl(2)	114.6(1) [116.9(1)]	N(2)−Ti(1)−Cl(2)	87.75(8) [89.50(8)]
N(3)−Ti(1)−Cl(2)	88.98(8) [87.53(9)]	Cl(1)−Ti(1)−Cl(2)	134.88(4) [132.70(4)]

^{a}Values in brackets refer to the 2nd crystallographically independent molecule.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Ti(NO^{t}Bu)Cl$_2$(py)$_3$ (5)

Ti(1)−N(1)	1.7087(18)	Ti(1)−N(2)	2.4078(18)
Ti(1)−N(3)	2.2278(18)	Ti(1)−N(4)	2.2439(17)
Ti(1)−Cl(1)	2.4045(6)	Ti(1)−Cl(2)	2.4338(6)
N(1)−O(1)	1.350(2)	O(1)−C(1)	1.482(3)
Ti(1)−N(1)−O(1)	170.57(15)	N(1)−O(1)−C(1)	113.30(15)
N(1)−Ti(1)−N(2)	175.08(8)	N(1)−Ti(1)−N(3)	95.50(8)
N(2)−Ti(1)−N(3)	88.33(6)	N(1)−Ti(1)−N(4)	94.57(7)
N(2)−Ti(1)−N(4)	81.72(6)	N(3)−Ti(1)−N(4)	169.74(7)
N(1)−Ti(1)−Cl(1)	94.27(6)	N(2)−Ti(1)−Cl(1)	82.68(5)
N(3)−Ti(1)−Cl(1)	89.10(5)	N(4)−Ti(1)−Cl(1)	92.10(5)
N(1)−Ti(1)−Cl(2)	98.86(6)	N(2)−Ti(1)−Cl(2)	84.40(5)
N(3)−Ti(1)−Cl(2)	86.97(5)	N(4)−Ti(1)−Cl(2)	89.56(5)
Cl(1)−Ti(1)−Cl(2)	166.59(3)		

Five-coordinate Ti(NO^{t}Bu)Cl$_2$(NHMe$_2$)$_2$ (**1**) has an approximately trigonal bipyramidal geometry at Ti(1) with axial NHMe$_2$ groups and equatorially positioned Cl and NO^{t}Bu ligands. There are two crystallographically equivalent molecules of **1** in the asymmetric unit but no significant differences or interactions between them. Compound **1** can be compared with a number of structurally characterized Group 4[20a,30] and Group 5[26,31] imido complexes of the type M(NR)(NHMe$_2$)$_2$Cl$_2$ (M = Ti or V; R = alkyl or aryl) and has a broadly similar geometry.

Consistent with the solid state IR data (vide supra), molecules of **1** form extended hydrogen-bonded chains in the solid state,

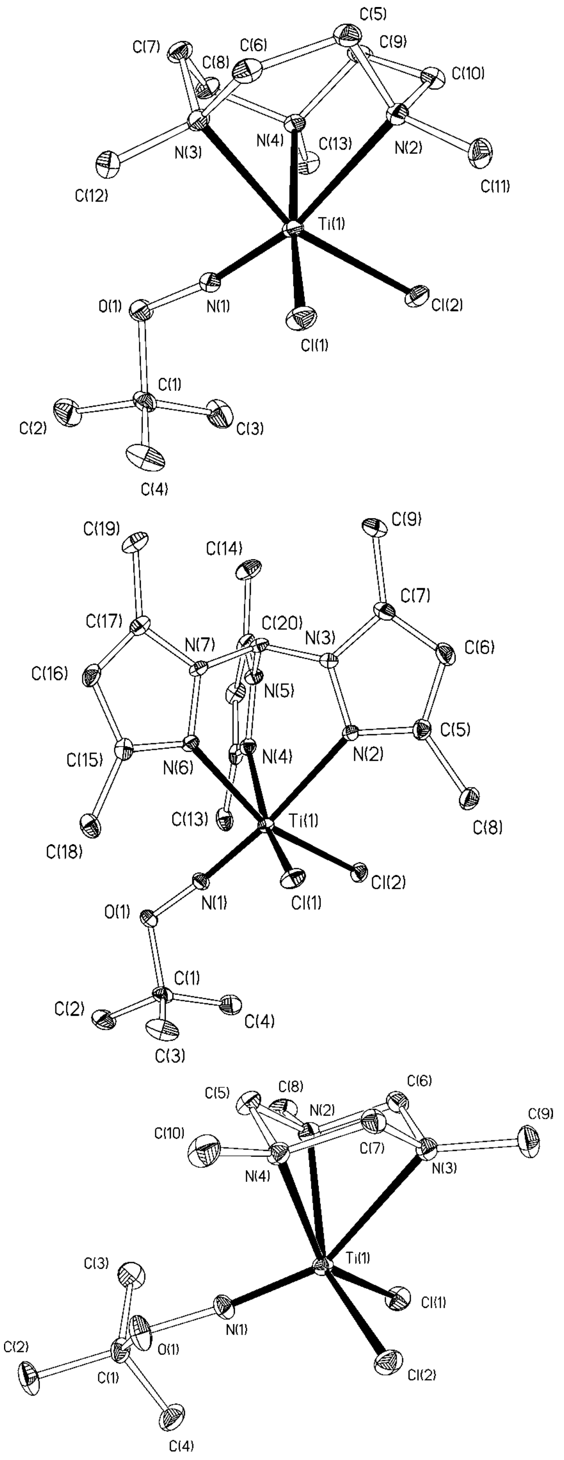


Figure 4. Displacement ellipsoid plots (20% probability) of $Ti(NO^tBu)(Me_3[9]aneN_3)Cl_2$ (**2**) (top), $Ti(NO^tBu)\{HC(Me_2pz)_3\}Cl_2$ (**3**) (middle), and $Ti(NO^tBu)(Me_3[6]aneN_3)Cl_2$ (**4**) (bottom). H atoms are omitted for clarity.

as illustrated in Figure 3, based on both N−H···O and N−H···Cl interactions which lie within the expected ranges.[32] While both $NHMe_2$ ligands act as H-bond donors, only Cl(1) acts as an acceptor, the other one being the alkoxyimido oxygen. This contrasts with the previously reported alkyl- or aryl-imido compounds $Ti(NR)Cl_2(NHMe_2)_2$ which generally form hydrogen-bonded chains in the solid state involving both Ti−Cl bonds of each Ti center.[20a]

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $Ti(NO^tBu)(Me_3[9]aneN_3)Cl_2$ (2), $Ti(NO^tBu)\{HC(Me_2pz)_3\}Cl_2$ (3), and $Ti(NO^tBu)(Me_3[6]aneN_3)Cl_2$ (4)[a]

	2	3	4
$Ti-N_{im}$	1.702(2)	1.703(2)	1.686(2)
$Ti-N_{trans}$	2.378(2)	2.353(2)	2.411(2)
$Ti-N_{cis}$	2.257(2)	2.223(2)	2.257(2)
$Ti-N_{cis}$	2.264(3)	2.230(2)	2.249(2)
Ti−Cl	2.400(1), 2.396(1)	2.391(1), 2.400(1)	2.360(1), 2.368(1)
$N_{im}-O$	1.370(3)	1.359(3)	1.374(3)
O−C	1.482(3)	1.476(4)	1.480(4)
$Ti-N_{im}-O$	171.0(2)	173.4(2)	169.5(2)
$N_{im}-O-C$	113.1(2)	113.2(2)	113.7(2)
Cl−Ti−Cl	95.6(1)	101.4(1)	104.1(1)
$N_{im}=Ti-N_{cis}$	94.1(1), 93.0(1)	94.8(1), 96.0(1)	102.6(1), 96.6(1)
$N_{cis}-Ti-N_{trans}$	75.5(1), 75.7(1)	78.7(1), 79.8(1)	59.3(1),59.6(1)
$N_{cis}-Ti-N_{cis}$	78.1(1)	77.0(1)	61.5(1)
$N_{im}=Ti-Cl$	100.7(1), 102.0(1)	101.0(1), 98.0(1)	105.5(1), 104.4(1)
$N_{trans}-Ti-Cl$	89.1(1), 87.1(1)	84.6(1), 85.1(1)	93.5(1), 87.2(1)
$N_{cis}-Ti-Cl$	90.4(1), 91.7(1)	87.8(1), 89.7(1)	93.7(1), 89.4(1)
$N_{cis}-Ti-Cl$	161.4(1), 162.8(1)	159.2(1), 161.5(1)	146.9(1), 145.1(1)

[a] N_{im} refers to the alkoxyimido nitrogen, and N_{trans} and N_{cis} to the *fac*-N_3 ligand nitrogen atoms *trans* and *cis* to N_{im}, respectively.

Six-coordinate $Ti(NO^tBu)Cl_2(py)_3$ (**5**) has an approximately octahedral titanium center with *mer*-coordinated pyridine ligands and mutually trans Cl atoms. Its geometry is analogous to previously structurally characterized Group 4 and 5 complexes of the type $M(NR)Cl_2(L)_3$ (M = Ti, R = alkyl, aryl, NPh_2, $P(S)Ph_2$ or $SiPh_3$; L = py or 4-$NC_5H_4{}^tBu$).[12,19b,22b,30,33] Ti(1) lies about 0.24 Å above the {Cl(1),Cl(2),N(3),N(4)} least-squares plane in **5**, presumably to enhance the multiple bonding in the Ti(1)−N(1) bond as described previously in d^0 metal-imido and -nitrido complexes.[34] The NO^tBu ligand in **5** exerts a strong trans influence of about 0.170(2) Å (av.)[35] on the N(2) pyridine ligand. This value lies between that generally found in imido complexes $Ti(NR)Cl_2(py)_3$ (e.g., R = ^tBu, Ph, Tol, $P(S)Ph_2$; range = 0.18−0.21 Å)[12,19b] and in the hydrazido complexes[19a] $Ti(NNPh_2)Cl_2(L)_3$ (L = py or 4-$NC_5H_4{}^tBu$; av. value ca. 0.160 Å). Experimental and computational studies have found that the trans influence in compounds of the type $Ti(NR)Cl_2(L)_3$ depends on a number of factors including the N-substituent and the Ti−N bond distance.[19b,34b] In both **1** and **5** the Ti−Cl distances are slightly shorter than those of their arylimido or hydrazido homologues, but longer than in the alkylimido ones. It is generally found that alkylimido ligands give a greater lengthening of other metal−ligand bonds than their arylimido or hydrazido counterparts.[36]

The main point of interest in **1** and **5** is the $TiNO^tBu$ group itself. The short Ti(1)−N(1) distances [range 1.688(3)−1.7087(18) Å] and near-linear Ti(1)−N(1)−O(1) linkages [range 170.57(15)−177.0(2)°, implying sp hybridization at N(1)] are consistent with titanium−nitrogen triple bonds ($\sigma^2\pi^4$ configuration), as supported by the DFT calculations presented later on. The longer Ti(1)−N(1) distance in **5** reflects the higher coordination number in this case. The N(1)−O(1) distances [1.350(2)−1.364(3) Å] are consistent

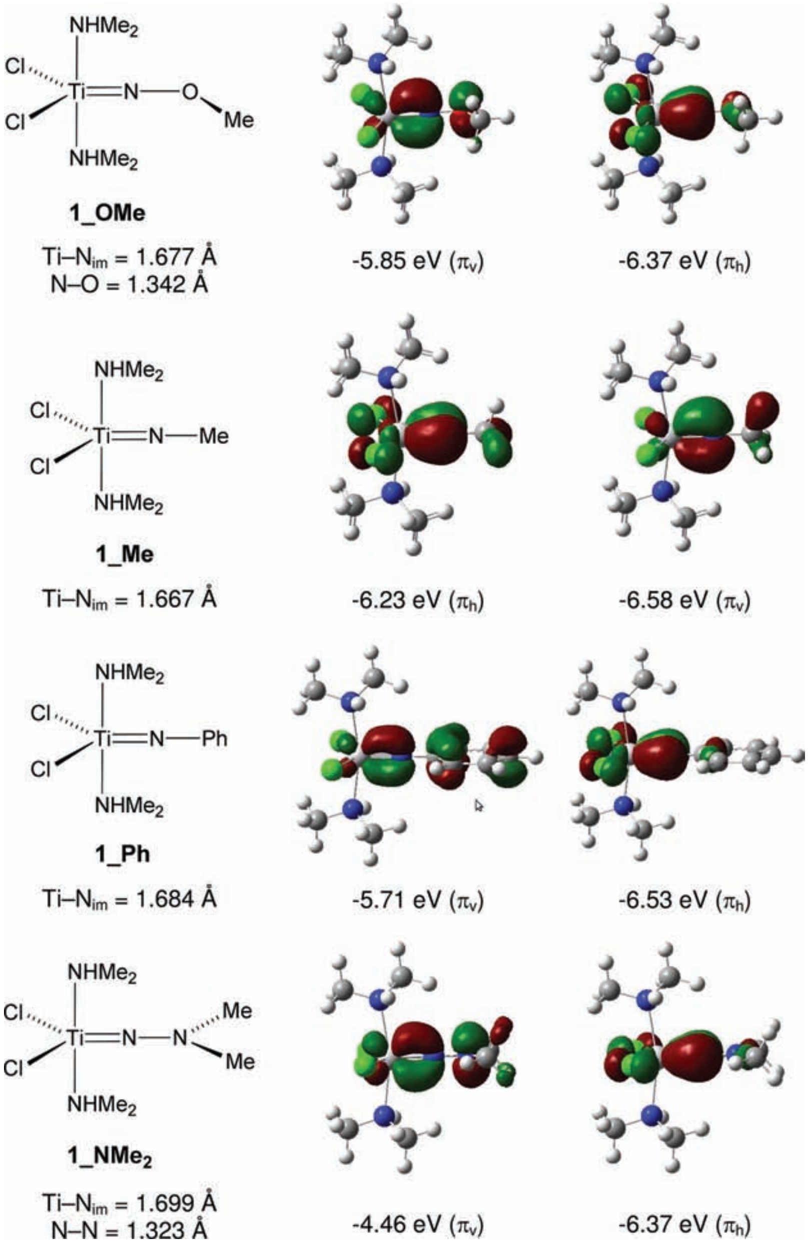


Figure 5. Model compounds $Ti(NR)Cl_2(NHMe_2)_2$ [R = OMe (**1_OMe**), Me (**1_Me**), Ph (**1_Ph**), or NMe_2 (**1_NMe$_2$**)] studied by DFT and selected bond distances (left); associated isosurfaces and energies of the HOMO (center) and HOMO-1 (right).

with single bonds but shorter than the usual values of about 1.40−1.46 for organic hydroxy- or alkoxy-amines or oximes (sp^3 or sp^2 hybridized N atoms),[32a,36] reflecting the sp hybridization of N(1). The N(1)−O(1) distances in **1** and **5** are comparable to those in the three Group 5 and 6 examples [Figure 1; range 1.342(5)−1.350(6) Å]. The N(1)−O(1)−C(1) angles of about 113−114° show sp^3 hybridization at O(1) as in the previous examples. In both titanium compounds N(1), O(1), and C(1) of the $TiNO^tBu$ moiety lie approximately in the plane defined by Ti(1), Cl(1), and Cl(2) as shown by the values of the dihedral angles Cl(1 or 2)−Ti(1)···O(1)−C(1) (ca. 170 and −10°). This feature is discussed later on in terms of the different Ti−N$_{im}$ π-bonding interactions in **1** (we use N$_{im}$ to represent the multiply bonded nitrogen in imido, hydrazido, and alkoxyimido compounds throughout this contribution).

It is typically found experimentally and computationally that Ti−N$_{im}$ bonds in alkylimido complexes are shorter than in their arylimido counterparts, and that hydrazido complexes have Ti−N$_{im}$ distances that are equal to or longer than in the homologous arylimides.[6b,19b,20c,34b,36] The structures of **1** and **5** and the others reported herein (vide infra) find that the Ti−N$_{im}$ bonds of alkoxyimido complexes are generally intermediate between those of alkyl- and aryl-imido complexes and shorter than in the hydrazido analogues. Thus the Ti(1)−N(1) bond lengths of 1.688(3) and 1.691(3) Å in **1** are longer than in the previously described alkylimido complex $Ti(N^iPr)Cl_2(NHMe_2)_2$ (1.672(2) Å) but generally shorter than in a series of eight arylimido complexes $Ti(NAr)Cl_2(NHMe_2)_2$ (av. Ti−N$_{im}$ = 1.703 Å, range 1.694(4)−1.708(2) Å).[20a,30] Likewise, the Ti(1)−N(1) distance of 1.7087(18) Å for **5** lies between that for Ti−N$_{im}$ in the alkylimides $Ti(N^tBu)Cl_2(py)_3$ (1.697(3) or 1.705(3) Å, two independent structure determinations)[19b,33] and $Ti\{NC(CCH)(c\text{-}C_5H_{10})\}Cl_2(py)_3$ (1.699(1) Å)[30] and a series of arylimido complexes $Ti(NAr)Cl_2(py)_3$ (av. Ti−N$_{im}$ =

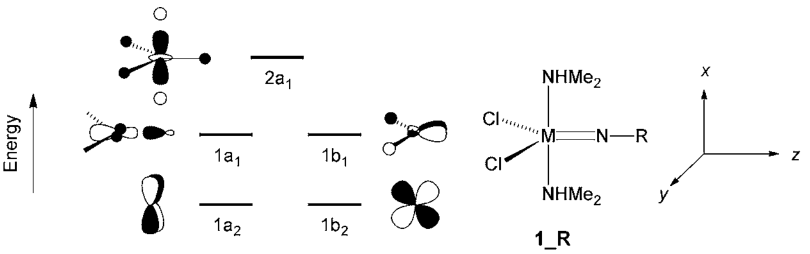


Figure 6. σ-Only frontier MOs (d orbitals only, arbitrary energies) for a hypothetical $Ti(NR)Cl_2(NHMe_2)_2$ compound **1_R** along with the coordinate system used in the text. Labels are for C_{2v} symmetry.[43]

1.718 Å, range 1.705(4)−1.730(2) Å for 6 examples), and is also shorter than $Ti-N_{im}$ for the diphenylhydrazido ligand in $Ti(NNPh_2)Cl_2(py)_3$ (1.727(2) Å).[19a]

We turn now to the structures of $Ti(NO^tBu)(Me_3[9]aneN_3)Cl_2$ (**2**), $Ti(NO^tBu)\{HC(Me_2pz)_3\}Cl_2$ (**3**), and $Ti(NO^tBu)(Me_3[6]aneN_3)Cl_2$ (**4**) (Figure 4 and Table 3). Each features an approximately octahedral titanium center ligated by the respective *fac*-coordinated N_3 donor ligand, two mutually cis chlorides and an approximately linear *tert*-butoxyimido group. The $Ti-N_{im}$ and $N_{im}-O$ distances are comparable to those in **1** and **5**, with the latter bond tending to be longer than in the Group 5 and 6 examples. All of the structures show evidence of a significant trans influence (ca. 0.12−0.16 Å) as expected.

The three $Ti(NO^tBu)(fac\text{-}N_3)Cl_2$ structures can be compared with previously structurally characterized *tert*-butylimido homologues for **2** ($Ti-N_{im}$ = 1.694(2) Å),[28c] **3** ($Ti-N_{im}$ = 1.703(2) Å),[37] and **4** ($Ti-N_{im}$ = 1.699(4) Å);[28a] four arylimido analogues for **2** (av. $Ti-N_{im}$ = 1.733, range 1.717(2)−1.7420(13) Å);[28c] and phenylimido analogues for **3** ($Ti-N_{im}$ = 1.719(2) Å)[38] and **4** ($Ti-N_{im}$ = 1.713(3) Å).[28c] The *fac*-coordinated N_3 donor ligands in **2**−**4** show similar geometric and structural parameters to those in their imido analogues.[28a,c,37,38] In general, the $Ti-N_{im}$ and Ti−Cl distances in **2**−**4** are somewhat more similar to those of their *tert*-butylimido analogues than the arylimido counterparts. The $Ti-N_{im}$ distance of 1.703(2) Å in **3** is significantly shorter than in its hydrazido analogue $Ti(NNPh_2)\{HC(Me_2pz)_3\}Cl_2$ ($Ti-NNPh_2$ = 1.718(2) Å).[20c]

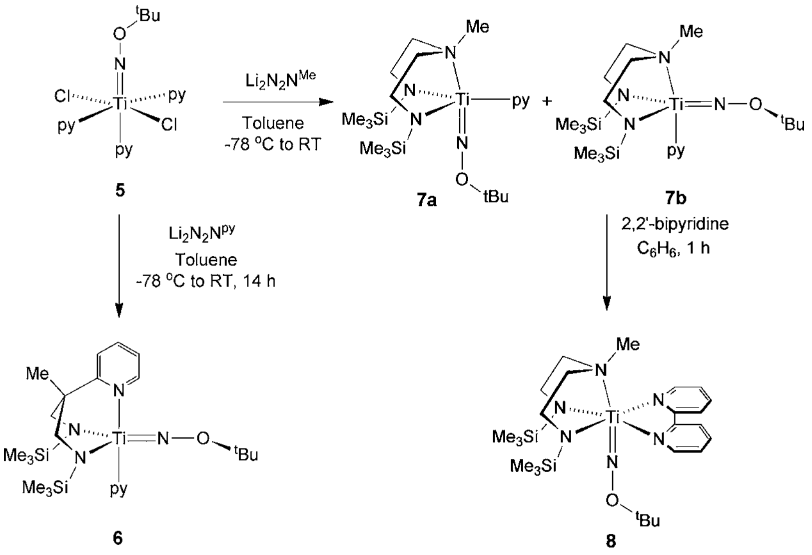
As expected from the previous studies, the $Me_3[6]aneN_3$ ligand in **4** is a poorer match for the titanium center than the $Me_3[9]aneN_3$ and $HC(Me_2pz)_3$ ligands in **2** and **3**. It has been previously noted that $Me_3[6]aneN_3$ is much less conformationally flexible than the corresponding $Me_3[9]aneN_3$ and $HC(Me_2pz)_3$ ligands because the smaller macrocycle is only able to deviate slightly from the ideal chair conformation,[39] which in turn gives a poorer overlap between the acceptor orbitals on titanium and the nitrogen lone pairs. This is evident from examination of the N_{trans}-Ti−N_{im} bond angles, which for ideal overlap would be 180°. In **2** and **3** the bond angles are 165.8(1) and 172.8(1)°, respectively, compared with 154.2(1)° for **4**. The poorer interaction of $Me_3[6]aneN_3$ with titanium in **4** is also evidenced by the significantly shorter $Ti-N_{im}$ and Ti−Cl distances in this compound compared to those in **2** and **3**, and helps explain the facile substitution reaction with pyridine to give **5**.

DFT Calculations for the Model Compounds $Ti(NR)Cl_2(NHMe_2)_2$ (R = OMe, Me, Ph, NMe_2). The solid state structures of **1**−**5** all show approximately linear Ti−N−O^tBu linkages and $Ti-N_{im}$ distances consistent with metal−nitrogen triple bonds ($\sigma^2\pi^4$ configuration) as is well-established for early transition metal imido and hydrazido complexes. As mentioned, The $Ti-N_{im}$ distances for the alkoxyimides (and also those discussed below) consistently lie between the values for the corresponding alkyl- and phenyl-imido congeners, and are shorter than in their hydrazido counterparts. The electronic structures of titanium imido compounds have been studied in detail,[1f,6b,28f,j,34b,40] and a number of DFT investigations of the bonding in hydrazides have also been reported.[4b,5b,6b,19a,20c,22a,41] There have also been two DFT reports comparing the molecular and electronic structures of model homologous imido and hydrazido complexes as a function of the NR group (R = Me, Ph, NPh_2, NMe_2),[6b,20c] but to date no quantum chemical comparisons between imido, hydrazido, and alkoxyimido complexes have been reported. To gain further insight into the bonding in the new alkoxyimido complexes a series of DFT calculations on model complexes were carried out at the B3PW91 level. The models used are $Ti(NR)Cl_2(NHMe_2)_2$ (R = OMe (**1_OMe**), Me (**1_Me**), Ph (**1_Ph**), or NMe_2 (**1_NMe₂**)). The geometries and selected bond distances, orbital representations, and associated energies are shown in Figure 5. Further details are provided in the Supporting Information.

Species **1_Me**, **1_Ph**, and **1_OMe** are models for the real compounds $Ti(N^iPr)Cl_2(NHMe_2)_2$,[20a] $Ti(NPh)Cl_2(NHMe_2)_2$,[20a] and $Ti(NO^tBu)Cl_2(NHMe_2)_2$ (**1**); **1_NMe₂** is a model for $Ti(NNPh_2)Cl_2(NHMe_2)_2$,[20c] but with the NPh_2 approximated to NMe_2 to avoid secondary electronic effects from mixing of the β-NR_2 lone pair with the phenyl substituents as discussed previously.[6b] Planarity at the NMe_2 nitrogen of **1_NMe₂** was maintained as this is invariably the case for aryl-substituted hydrazido complexes. The agreement between the calculated and the available experimental geometries is very good. For the imido and hydrazido complexes the expected trend in $Ti-N_{im}$ distance (i.e., $Ti-N_{alkyl}$ < $Ti-N_{aryl}$ < $Ti-NNR_2$ based on many crystallographic studies[1b,f,19b,c,36]) is observed (Figure 5). The $Ti-N_{im}$ distance of 1.677 Å for **1_OMe** lies between that of **1_Me** and **1_Ph** and is notably shorter than in **1_NMe₂** (1.699 Å), supporting the experimental trends. The −OMe substituent in **1_OMe** lies in the equatorial plane formed by Ti, N_{im} and the two Cl atoms, and the Cl−Ti···O−Me dihedral angles of 175.5 and −4.2° are close to the experimental values of about 170 and −10° in **1**. Likewise, the phenyl group of **1_Ph** and NMe_2 methyl groups of **1_NMe₂** also lie in the respective equatorial planes. The electronic origins of this systematic orientational preference in d^0 trigonal bipyramidal hydrazido complexes of the type $M(NNR_2)X_2(L)_2$ has been described by us previously and is discussed further below.[19a]

As anticipated, DFT finds that the NOMe ligand in **1_OMe** is a four-electron donor forming a metal−nitrogen triple bond through one σ- and two π-interactions. The highest occupied molecular orbital (HOMO) and HOMO-1 of **1_OMe**

Scheme 2. Reactions of $Ti(NO^tBu)Cl_2(py)_3$ (5) with $Li_2N_2N^{Me}$ and $Li_2N_2N^{py}$



correspond to the two $Ti{-}N_{im}$ $3d_\pi{-}2p_\pi$ bonding π MOs (Figure 5) denoted π_v and π_h, respectively, with respect to the equatorial plane containing Ti, 2 × Cl, and N_{im}. Although the formal net charge of NOMe is 2− (as is the case for imido and hydrazido ligands) the formal oxidation state of N_{im} is only −1 (compared to −3 or −2 in an imido or hydrazido ligand) owing to the electronegativity values of Ti, N, and O ($\chi_P(Ti) = 1.54$; $\chi_P(N) = 3.04$; $\chi_P(O) = 3.44$).[42] The main point of interest in **1_OMe**− **1_NMe$_2$** is the variation in energies of π_v and π_h with changing N_{im} substituent and the trends in Ti−N $_{im}$ bond distances. The MOs and their energies are depicted in Figure 5.

We consider first the imido and hydrazido complexes. For **1_Me** π_h and π_v are the HOMO and HOMO-1, respectively, of the complex with an energy separation of $\Delta = 0.35$ eV between them. This difference arises from the nature of the titanium π-acceptor orbitals of $Ti(NMe)Cl_2(NHMe_2)_2$ which combine with the $2p_\pi$ AOs of NMe to form π_h and π_v. The σ-only frontier orbitals for a hypothetical $Ti(NR)Cl_2(NHMe_2)_2$ compound **1_R** are shown in Figure 6.[43] The two metal-based orbitals $1b_1$ and $1b_2$ used to form π_h and π_v, respectively, have different energies because $1b_1$ is slightly metal−ligand σ^* antibonding. Therefore, although the $2p_x$ and $2p_y$ π-donor AOs of NMe are themselves isoenergetic, the resulting π_h MO lies above π_v and forms the HOMO of **1_Me**.

As expected from previous studies,[6b,20c,40d] the introduction of the Ph or NMe_2 substituents in **1_Ph** or **1_NMe$_2$** leads to a destabilization of one of the $2p_\pi$ AOs of NPh or NMe_2 because of an antibonding interaction between one of the filled π MOs of the phenyl group or, even more significantly, the β-NMe_2 lone pair. The destabilized $2p_\pi$ AO aligns with the best π-acceptor metal orbital, namely, $1b_2$, as this lies at lower energy than $1b_1$. This therefore explains the orientation of the phenyl and NMe_2 groups in **1_Ph** and **1_NMe$_2$** (i.e., in the equatorial plane as mentioned above) and why π_v is the HOMO in these complexes and is destabilized by 0.87 and 2.12 eV, respectively, relative to that in **1_Me**. As for **1_Ph** and **1_NMe$_2$**, π_v also represents the HOMO of **1_OMe**, and this can be attributed to the antibonding interaction with the $2p_x$ lone pair of the oxygen atom evident in Figure 5. However, this effect is smaller than in **1_Ph** and **1_NMe$_2$** and gives a 0.73 eV destabilization of π_v relative to **1_Me**. Therefore while the HOMO of **1_OMe** is less stable than that of **1_Me**, it is more stable than in either **1_Ph** or **1_NMe$_2$**. Nonetheless, the effect of the oxygen $2p_x$ lone pair is sufficient to orient the −OMe substituent of **1_OMe** (and likewise the $-O^tBu$ of **1**) in the same manner as for the hydrazido $Ti(NNR_2)X_2(L)_2$ counterparts.

As noted above, the $-O^tBu$ group in $Ti(NO^tBu)Cl_2(py)_3$ (**5**) is also oriented in the same way as the −OR groups in **1** and **1_OMe**. This may also have an electronic explanation. The HOMO of compounds of the type $Ti(N^tBu)Cl_2(L)_3$ is $Ti{-}N_{im}$ π-bonding but Ti−Cl π^* antibonding, and lies in the Cl−Ti−Cl plane.[34b] A similar Ti−Cl π^* interaction in **5** would lead to the $-O^tBu$ group being preferentially oriented in the Cl−Ti−Cl plane so as to place the O atom $2p_\pi$ lone pair perpendicular to this plane, thereby reducing additional destabilization of the $Ti{-}N_{im}$ π-bonding/Ti−Cl π^* antibonding orbital.

We turn finally to the effects of the different R-substituents on the Ti−NR distances in **1_R**. The longer Ti−NPh distance compared to Ti−NMe is attributed to partial donation of one of the $Ti{-}N_{im}$ π bond pairs into the phenyl ring π^* system.[6b] In contrast, the somewhat longer $Ti{-}NNMe_2$ distance originates from donation of the NMe_2 lone pair into one of the $Ti{-}N_{im}$ $3d_\pi{-}2p_\pi$ antibonding π^* MOs.[6b,19a] As noted, the Ti−NOR distances lie between those of alkyl- and aryl-imido counterparts in both the model and the experimental systems. Thus, the $Ti{-}N_{im}$ bond-lengthening effect of the β-NR_2 substituent lone pair previously established in hydrazide complexes is apparently present to some extent in alkoxyimido systems, but is much reduced owing to the higher electronegativity of O compared to N, and the more contracted 2p AOs. This interpretation is supported by an NBO second-order perturbation analysis[44] of the donor−acceptor interactions in **1_OMe** and **1_NMe$_2$** which are also consistent with metal−ligand triple bonds. Lone pair donation from NMe_2 into the π_v* NBO of **1_NMe$_2$** (41.6 kcal mol^{-1}) was significantly larger than from OMe into the corresponding orbital of **1_OMe** (14.1 kcal mol^{-1}). The weaker lone pair donation from OMe is consistent with the larger NBO population of 1.875 e in this case compared to 1.727 e for NMe_2. In addition the energy of the OMe lone pair NBO in **1_OMe** (−8.61 eV) is significantly lower than that for the NMe_2 lone pair NBO in **1_NMe$_2$** (−6.37 eV).

***tert*-Butoxyimido Complexes with Diamide-Amine and Bi- and Tridentate Pyrrolide Ligands.** Some of the more significant recent advances in stoichiometric and catalytic Group 4 hydrazido chemistry have been achieved using diamide-amine or pyrrolide-based supporting ligands. The former tend to promote $N_\alpha{-}N_\beta$ insertion/cleavage reactions,[5,6c−g,j,8,9,19a] whereas pyrrolide ligand-supported titanium complexes can be highly active catalysts for alkyne hydrohydrazination and related reactions.[1e,4a,6a,45] We were therefore interested to develop analogous *tert*-butoxyimido complexes as platforms for future reactivity studies. As mentioned above, complexes of the type Ti(NR)Cl$_2$(L)$_n$ (in particular for R = ^{t}Bu or NPh$_2$; L = py, n = 2 or 3) are extremely useful entry points for the synthesis of a wide range of imido and hydrazido complexes,[1b,c,f,h,6f,19a,46] and so our efforts focused on salt-elimination reactions starting from Ti(NO^{t}Bu)Cl$_2$(py)$_3$ (**5**). It was not possible to use Ti(NO^{t}Bu)Cl$_2$(NHMe$_2$)$_2$ (**1**) for the synthesis of the target complexes via salt elimination reactions with anionic reagents because of the relatively acidic protons on the NHMe$_2$ groups. Similar observations have been made for certain imido systems.[1f]

Diamide-Amine Ligands. On the basis of our previous experiences in the corresponding imido and hydrazido chemistry, we focused on the diamide-amine ligands N$_2$N^{py} [(2-NC$_5$H$_4$)C(Me)(CH$_2$NSiMe$_3$)$_2$] and N$_2$N^{Me} [MeN(CH$_2$CH$_2$NSiMe$_3$)$_2$]. The new chemistry is summarized in Scheme 2. Thus reaction of Li$_2$N$_2$N^{py} or Li$_2$N$_2$N^{Me} with **5** in toluene at −78 °C proceeds smoothly to give Ti(N$_2$N^{py})(NO^{t}Bu)(py) (**6**) or Ti(N$_2$N^{Me})(NO^{t}Bu)(py) (**7**) in 33% and 86% isolated yield, respectively. The disappointing isolated yield for **6** is attributed to its high solubility in hydrocarbon solvents.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **6** show the expected resonances for pyridine, NO^{t}Bu and κ^3-bound N$_2$N^{py} ligands, and that it exists as a single isomer in solution. This is assigned as the C_s-symmetric, 5-coordinate trigonal bipyramidal complex depicted in Scheme 2 with equatorial amido (N$_{am}$) donors and NO^{t}Bu ligands and mutually trans pyridine and pyridyl axial donors. Diffraction-quality crystals were grown from pentane, and the solid state structure (vide infra) confirms that shown in Scheme 2. Analogous geometries were found for Ti(N$_2$N^{py})(N^{t}Bu)(py)[43a] and Ti(N$_2$N^{py})(NNPh$_2$)(py).[19a]

In contrast, the ^{1}H NMR spectrum of **7** indicates that this compound exists as a mixture of two C_s-symmetric isomers (denoted **7a** and **7b**; ratio ca. 3:1 based on integration of the CMe$_3$ and SiMe$_3$ resonances) which we interpret in terms of the position of the NO^{t}Bu ligand being either trans (**7a**) or cis (**7b**) to the NMe donor. The ^{1}H NMR spectra are broad even at −80 °C (the ratio of the two isomers remaining ca. 3:1) preventing reliable nuclear Overhauser effect (NOE) measurements and therefore experimental determination of which is the major isomer was not possible. Diffraction-quality crystals were grown from a saturated hexanes solution at 4 °C, and these were shown to be the trans isomer **7a** (vide infra). Dissolving these crystals in C$_6$D$_6$ again gave the broad spectra showing a mixture of isomers which appear to be able to interconvert on the chemical and NMR time scales.

Addition of bipy (2,2′-bipyridyl) to a solution of **7** in C$_6$D$_6$ gave quantitative conversion to Ti(N$_2$N^{Me})(NO^{t}Bu)(bipy) (**8**) with the release of an equivalent of pyridine. Scaling up this reaction in benzene at room temperature afforded **8** in 82% isolated yield. Compound **8** exists as a single isomer, and its ^{1}H and ^{13}C NMR spectra are sharp and consistent with the C_s-symmetric, six-coordinate complex illustrated in Scheme 2 which was also confirmed by X-ray crystallography (vide infra). The related hydrazido compound Ti(N$_2$N^{Me})(NNPh$_2$)(bipy) (NNPh$_2$ trans to NMe) was formed in a similar way from Ti(N$_2$N^{Me})(NNPh$_2$)(py) in which the NNPh$_2$ is exclusively positioned cis to NMe in the equatorial plane.[6d] The positioning of the amide and alkoxyimide nitrogens cis to each other as in **8**, Ti(N$_2$N^{Me})(NNPh$_2$)(bipy) [and related complexes such as W(N$_2$N^{py})(NPh)Cl$_2$ and M(N$_2$N^{py})(NR)Cl(py) (M = Nb or Ta; R = ^{t}Bu or 2,6-C$_6$H$_3$^{i}Pr$_2$)[43b,47]] maximizes the M−N$_{am}$ and M−N$_{im}$ π-bonding interactions in these approximately octahedral complexes.[43b,47]

To help assign the two isomers of **7** and to determine their relative energies and structures, DFT (B3PW91) calculations were carried out using the reduced steric bulk model systems *trans*- and *cis*-Ti(N$_2$^{SiH3}N^{Me})(NOMe)(py) [**7a_q** and **7b_q**, respectively; N$_2$^{SiH3}N^{Me} = MeN(CH$_2$CH$_2$NSiH$_3$)$_2$] with OMe and SiH$_3$ groups in place of O^{t}Bu and SiMe$_3$. The electronic energy difference (ΔE) between these two isomers is 1.1 kcal mol^{-1} in favor of the trans isomer **7a_q** showing an electronic preference for the alkoxyimido ligand to be positioned in the axial coordination site. DFT calculations were also carried out on the full experimental systems *trans*- and *cis*-Ti(N$_2$N^{Me})(NO^{t}Bu)(py) (denoted **7a_Q** and **7b_Q**, respectively) with the trans isomer again being favored by 0.6 kcal mol^{-1}, consistent with the real species **7a** being the dominant isomer in solution. The relative Gibbs free energies of the isomers were also calculated including solvent (benzene or toluene) with the SMD approach[48] and confirmed the preferences indicated by the electronic energy differences (**7a_q** favored by ca. 1.2 kcal mol^{-1}; **7a_Q** favored by 0.6 kcal mol^{-1}). We have previously described in detail the various factors affecting the coordination site preferences of imido and hydrazido ligands in five-coordinate, diamide-amine supported complexes of the type [M(N$_2$N^L)(NR)(X)]^x (M = Group 4, 5, or 6 metal; N$_2$N^L = N$_2$N^{Me}, N$_2$N^{py} or related; X = Lewis base, Me or Cl; R = alkyl, Ph, or NNMe$_2$; x = 0 or +1).[19a,43b] The eventual outcome is governed by a balance of N$_2$N^R and NR group steric effects and π-donor characteristics, and we have not analyzed the detailed bonding position in Ti(N$_2$^{SiH3}N^{Me})(NOMe)(py) or Ti(N$_2$N^{Me})(NO^{t}Bu)(py).

The solid state structures of Ti(N$_2$N^{py})(NO^{t}Bu)(py) (**6**), Ti(N$_2$N^{Me})(NO^{t}Bu)(py) (**7a**), and Ti(N$_2$N^{Me})(NO^{t}Bu)(bipy) (**8**) are shown in Figure 7 and selected bond angles and distances are given in Table 4. As mentioned, compounds **6** and **7a** possess trigonal bipyramidal titanium centers with the diamide-amine ligand coordinating in a *fac*-manner. In **6** the alkoxyimide and amide donors occupy the equatorial positions as in Ti(N$_2$N^{py})(N^{t}Bu)(py) and Ti(N$_2$N^{py})(NNPh$_2$)(py).[19a,43a] In **7a** the two amide donors and the pyridine ligand occupy the equatorial positions with the alkoxyimide and NMe donor taking up the axial sites. In contrast, both Ti(N$_2$N^{Me})(NNPh$_2$)(py) and a related *tert*-butylimido complex Ti(N$_2$N^{SiMe_3})(N^{t}Bu)(py) [N$_2$N^{SiMe_3} = MeN(CH$_2$CH$_2$NSiMe$_3$)$_2$] have analogous structures to **6** with equatorially coordinated NNPh$_2$ or N^{t}Bu ligands.[19a,49] Compound **8** has an approximately octahedral titanium center with the amide nitrogens of N$_2$N^{Me} and those of the 2,2′-bipyridyl ligand lying in the equatorial plane as also found in Ti(N$_2$N^{Me})(NNPh$_2$)(bipy).[6d]

In general terms the Ti−N distances, geometries, and intraligand parameters associated with the N$_2$N^{py} and N$_2$N^{Me} ligands are comparable to those in previously described complexes (for example, shorter Ti−N$_{amide}$ and Ti−N$_{amine}$

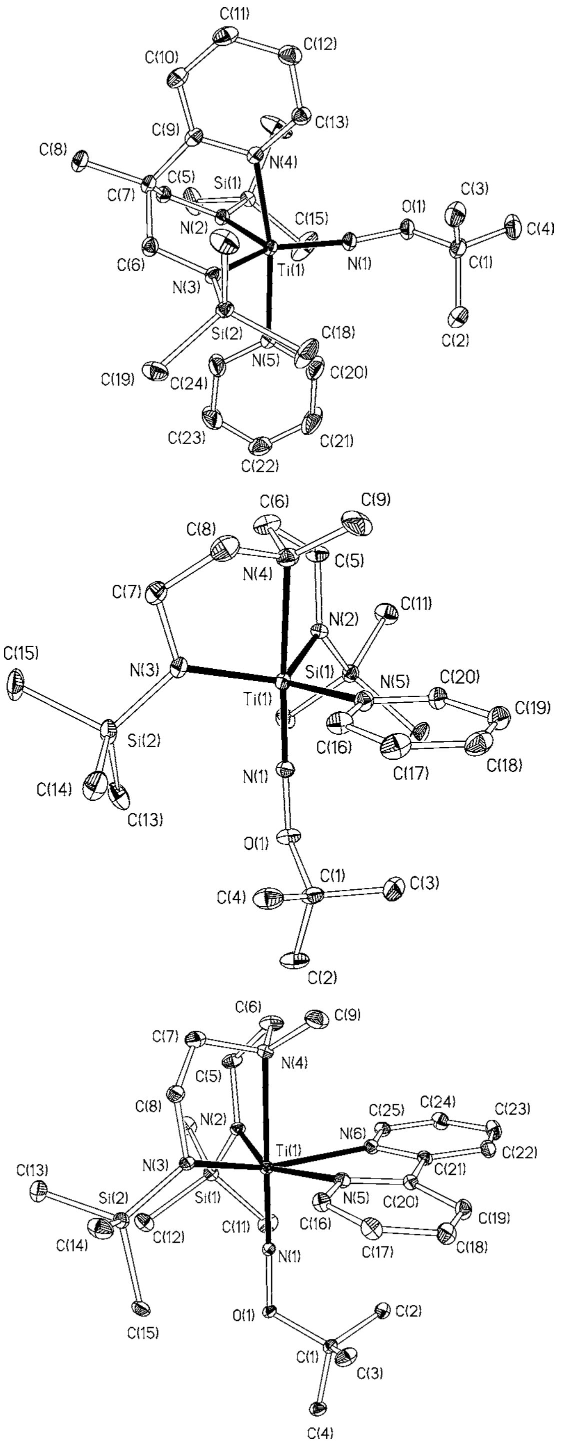


Figure 7. Displacement ellipsoid plot (20% probability) of $Ti(N_2N^{py})(NO^tBu)(py)$ (**6**) (top), $Ti(N_2N^{Me})(NO^tBu)(py)$ (**7a**) (middle), and $Ti(N_2N^{Me})(NO^tBu)(bipy)$ (**8**) (bottom). H atoms omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $Ti(N_2N^{py})(NO^tBu)(py)$ (6), $Ti(N_2N^{Me})(NO^tBu)(py)$ (7a), and $Ti(N_2N^{Me})(NO^tBu)(bipy)$ (8)

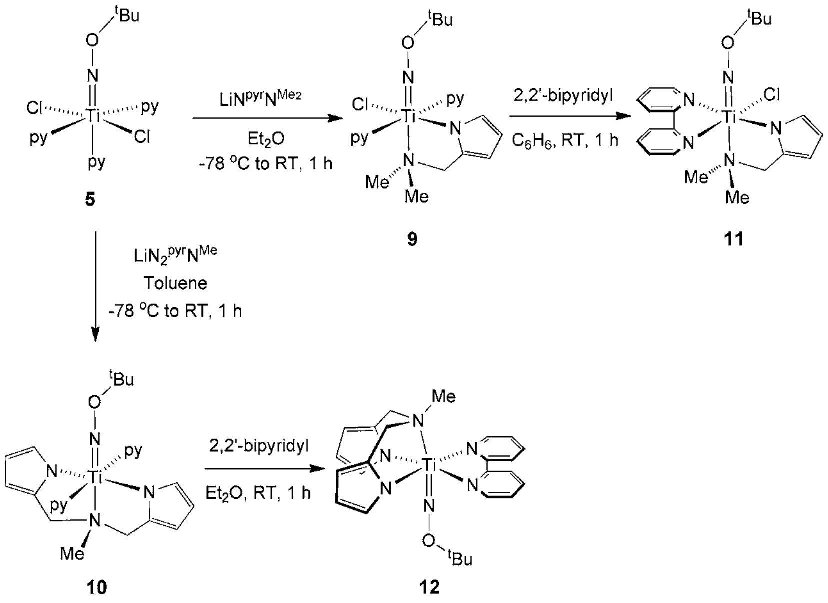
	6	7a	8
Ti(1)−N(1)	1.734(2)	1.721(2)	1.727(2)
Ti(1)−N(2)	1.966(2)	1.999(3)	2.037(2)
Ti(1)−N(3)	1.997(2)	2.019(2)	2.060(2)
Ti(1)−N(4)	2.200(2)	2.344(3)	2.362(2)
Ti(1)−N(5)	2.259(2)	2.199(2)	2.312(2)
Ti(1)−N(6)			2.308(2)
N(1)−O(1)	1.391(3)	1.385(3)	1.391(3)
O(1)−C(1)	1.457(3)	1.474(3)	1.466(3)
Ti(1)−N(1)−O(1)	162.9(2)	177.0(2)	177.2(2)
N(1)−Ti(1)−N(2)	121.0(1)	102.4(1)	100.7(1)
N(1)−Ti(1)−N(3)	129.5(1)	104.4(1)	103.4(1)
N(1)−Ti(1)−N(4)	94.8(1)	175.7(1)	177.4(1)
N(1)−Ti(1)−N(5)	94.9(1)	93.1(1)	95.0(1)
N(1)−Ti(1)−N(6)			94.7(1)
N(2)−Ti(1)−N(3)	108.9(1)	122.2(1)	109.0(1)
N(5)−Ti(1)−N(6)			69.4(1)

distances in **6** compared to those in **7** and **8**). These trends have been discussed in detail for the hydrazido complexes $Ti(N_2N^R)(NNPh_2)(py)$.[19a] Likewise the Ti−N distances for the py and bipy ligands are in the expected ranges.[6d,19a,36,43a,49] The slightly longer Ti−N distances to the N_2N^{Me} and NO^tBu ligands in **8** compared to **7a** reflect the higher coordination number in **8**.

The Ti(1)−N(1) distances for the *tert*-butoxyimido ligands lie in the range 1.721(2)−1.734(2) Å and, together with the approximately linear Ti(1)−N(1)−O(1) angles (162.9(2)−177.2(2)°) are consistent with substantial multiple bond character as expected from our previous bonding analyses of imido and hydrazido complexes of the type $M(N_2N^L)(NR)(py)$.[19a,43b] The $Ti-NO^tBu$ distance of 1.734(2) Å in **6** is closer to that for $Ti-N^tBu$ in $Ti(N_2N^{py})(N^tBu)(py)$ (1.724(2) Å)[43a] than for $Ti-NNPh_2$ in $Ti(N_2N^{py})(NNPh_2)(py)$ (1.759(2) Å);[19a] likewise the $Ti-NO^tBu$ distance of 1.727(2) Å in **6** is shorter than $Ti-NNPh_2$ in $Ti(N_2N^{Me})(NNPh_2)(bipy)$ (1.754(2) Å[6d]). These trends support those discussed above for $Ti(NO^tBu)Cl_2(NHMe_2)_2$ (**1**), $Ti(NO^tBu)(fac\text{-}N_3)Cl_2$ (**2−4**), and $Ti(NO^tBu)Cl_2(py)_3$ (**5**) in comparison with their imido and hydrazido homologues.

Both the $Ti-N_{im}$ and N−O bonds in **6−8** are significantly longer than in the five or six-coordinate dichloride complexes (ranges 1.686(2)−1.7087(18) Å and 1.350(2)−1.374(3) Å, respectively). This parallels the trends found for the corresponding imido and hydrazido compounds (the latter having particularly long $N_\alpha-N_\beta$ bonds in the presence of diamide-based ligands), and is due to the strongly σ- and π-donating amide nitrogens of the N_2N^{py} and N_2N^{Me} ligands which moderate the electron-deficiency of the metal center and compete with NO^tBu for the titanium $3d_\pi$ acceptor orbitals. We have discussed these effects in detail previously for the related imido and hydrazido complexes.[19a,43b] It is interesting to note that the $-O\,^tBu$ substituent in **6** is oriented in the equatorial plane (dihedral angles N(2)−Ti(1)···O(1)−C(1) = 179°, N(3)−Ti(1)···O(1)−C(1) = −9°) in the same way as is found for the phenyl substituents in $Ti(N_2N^L)(NNPh_2)(py)$ ($N_2N^L = N_2N^{py}$, N_2N^{Me}, and $N_2N^{SiMe_3}$), and described above for $Ti(NO^tBu)Cl_2(NHMe_2)_2$ (**1**) and the DFT model compound **1_OMe**. As discussed, positioning the $2p_\pi$ AO of the alkoxyimido oxygen atom perpendicular to the equatorial plane in trigonal bipyramidal complexes helps enhance the $Ti-N_{im}$ π-bonding interactions. The DFT models of **7b** [*cis*-$Ti(N_2^{SiH3}N^{Me})(NOMe)(py)$ (**7b_q**) and *cis*-$Ti(N_2N^{Me})(NO^tBu)(py)$ (**7b_Q**)] likewise find the −OMe or $-O^tBu$ substituents oriented in the equatorial planes in the energy-minimized geometries ($N_{am}-Ti\cdots O-C$ angles of 167 and −4°, and 156 and −13°, respectively).

Scheme 3. Synthesis of *tert*-Butoxyimido Complexes with Bi- and Tri-Dentate Pyrrolide Ligands



***tert*-Butoxyimido Complexes of Bi- and Tridentate Pyrrolide Ligands.** The reactions of the lithiated pyrrolides $\mathrm{LiN^{pyr}N^{Me_2}}$ and $\mathrm{Li_2N^{pyr}N^{Me}}$ with $\mathrm{Ti(NO^tBu)Cl_2(py)_3}$ (**5**) are summarized in Scheme 3 ($\mathrm{N^{pyr}N^{Me_2}} = \mathrm{Me_2NCH_2(2\text{-}NC_4H_3)}$; $\mathrm{N_2{}^{pyr}N^{Me}} = \mathrm{MeN\{CH_2(2\text{-}NC_4H_3)\}_2}$). As mentioned, these and related pyrrolide ligands have been used to good effect in stoichiometric and catalytic Group 4 hydrazido and imido chemistry in the past few years.[1e,4a,b,6a,45a,b,50]

Reaction of **5** with 1 equiv. of either $\mathrm{LiN^{pyr}N^{Me_2}}$ or $\mathrm{Li_2N^{pyr}N^{Me}}$ progresses smoothly in diethyl ether or toluene solution at −78 °C. After warming to room temperature and workup, $\mathrm{Ti(N^{pyr}N^{Me_2})(NO^tBu)Cl(py)_2}$ (**9**) and $\mathrm{Ti(N_2{}^{pyr}N^{Me})(NO^tBu)(py)_2}$ (**10**) were isolated in about 70% yield. Reaction of **5** with 2 equiv of $\mathrm{LiN^{pyr}N^{Me_2}}$ immediately gave $\mathrm{Ti(N^{pyr}N^{Me_2})(NO^tBu)Cl(py)_2}$ (**9**) and an equivalent of unreacted $\mathrm{LiN^{pyr}N^{Me_2}}$. Extended reaction times or elevated temperatures gave complex mixtures from which no single product could be isolated. The ^{1}H and ^{13}C NMR spectra of both **9** and **10** show resonances attributable to a *tert*-butoxyimido group and additional signals for a pyrrolide and two pyridine ligands. In **9** the $\mathrm{NMe_2}$ and $\mathrm{CH_2}$ groups appear as broad singlets at 3.00 and 1.89 ppm in the ^{1}H NMR spectra, and there is only one environment for the two pyridine ligands. The spectrum remains unchanged at −80 °C, and overall the data are consistent with the C_s-symmetric species depicted in Scheme 3 and found in the solid state for the related imido species $\mathrm{Ti(N^{pyr}N^{Me_2})(N^tBu)Cl(py)_2}$.[51] On the other hand, the NMR spectra of $\mathrm{Ti(N_2{}^{pyr}N^{Me})(NO^tBu)(py)_2}$ (**10**) reveal two chemically inequivalent pyridine ligands, and in the ^{1}H NMR spectrum the diastereotopic methylene hydrogens of $\mathrm{N_2{}^{pyr}N^{Me}}$ appear as a pair of mutually coupled doublets, consistent with *mer* coordination of the pyrrolide ligand as proposed in Scheme 3. Accordingly, only one of the pyridine ligands shows an NOE interaction to the $\mathrm{N_2{}^{pyr}N^{Me}}$ methyl group. The related crystallographically characterized phenylimido complex $\mathrm{Ti(N_2{}^{pyr}N^{Me})(NPh)(NHMe_2)_2}$ has an analogous geometry to that proposed for **10** with *mer* coordination of $\mathrm{N_2{}^{pyr}N^{Me}}$ and mutually trans coordination of the $\mathrm{NHMe_2}$ ligands.[4a]

Attempts to grow diffraction-quality crystals of **9** and **10** were unsuccessful. To improve their crystallinity the pyridine ligands were exchanged with 2,2′-bipyridyl in benzene or diethyl ether solution to give $\mathrm{Ti(N^{pyr}N^{Me_2})(NO^tBu)Cl(bipy)}$ (**11**) and $\mathrm{Ti(N_2{}^{pyr}N^{Me})(NO^tBu)(bipy)}$ (**12**), respectively. The isolated yields were very high yield, as expected, and when followed on the NMR tube scale the reactions were effectively quantitative. The solution ^{1}H and ^{13}C NMR spectra and other data are consistent with the solid state structures (vide infra) which confirm those illustrated in Scheme 3. For example the ^{1}H NMR spectrum of **11** shows eight inequivalent signals for the bipy ligand, and inequivalent $\mathrm{NMe_2}$ groups and methylene hydrogens of the $\mathrm{N^{pyr}N^{Me_2}}$ ligand. Compound **12** possesses C_s symmetry (four signals for the bipy ligand and equivalent pyrrolide rings); however, the appearance of the methylene groups as a pair of mutually coupled doublets is consistent with a change in $\mathrm{N_2{}^{pyr}N^{Me}}$ ligand coordination geometry from *mer* in **10** to *fac* in **12**.

The solid state structures of **11** and **12** are shown in Figure 8, and selected distances and angles are listed in Tables 5 and 6. Each possesses a six-coordinate, approximately octahedral titanium center with the $\mathrm{NO^tBu}$ ligand and either the $\mathrm{NMe_2}$ (for **11**) or NMe (for **12**) donor of the pyrrolide ligand defining the axial coordination sites. The bipy ligand, pyrrolide ring nitrogen(s), and (for **11**) chloride ligand are equatorially positioned. The Ti−N bond distances to the bipy, $\mathrm{N^{pyr}N^{Me_2}}$ and $\mathrm{N_2{}^{pyr}N^{Me}}$ ligands, as well as the Ti−Cl bond length, lie within previously reported ranges.[4a,b,6a,36,51] The Ti(1)−N(1) [1.7149(16) and 1.716(3) Å] and N(1)−O(1) distances [1.362(2) and 1.357(4) Å] are equivalent within error and, together with the approximately linear Ti(1)−N(1)−O(1) (av. ca. 172°) linkages, the data again suggest $\mathrm{Ti{\equiv}N_{im}}$ triple bonds.

The most relevant literature comparisons are with Odom's dipyrrolide-amine phenylimido and dimethyl- and phenylhydrazido complexes $\mathrm{Ti(N_2{}^{pyr}N^{Me})(NPh)(bipy^tBu_2)}$, $\mathrm{Ti(N_2{}^{pyr}N^{Me})(NNMe_2)(bipy^tBu_2)}$, and $\mathrm{Ti(N_2{}^{pyr}N^{Me})\{NN(H)Ph\}(bipy^tBu_2)}$ ($\mathrm{bipy^tBu_2}$ = 2,2′-4,4′-di-*tert*-butyl bipyridyl) complexes. These have $\mathrm{Ti{-}N_{im}}$ distances of 1.721(6), 1.708(3), and 1.712(4) Å, respectively,[4a,b] which are all equivalent within error to those in **12**. The $\mathrm{Ti{-}N_{im}}$ and N−O distances in the pyrrolide complexes lie between those in the dichloride complexes **1**−**5** (1.686(2)−1.7087(18) Å and

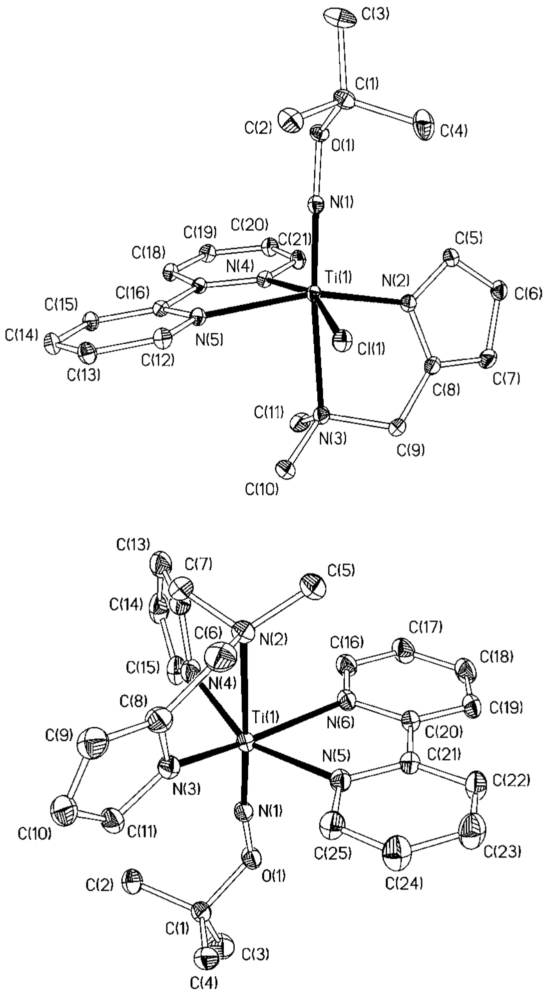


Figure 8. Displacement ellipsoid plots (20% probability) of Ti(N^{pyr}N^{Me_2})(NO^{t}Bu)Cl(bipy) (**11**) (top) and Ti(N$_2$^{pyr}N^{Me})(NO^{t}Bu)(bipy) (**12**) (bottom). H atoms and solvent of crystallization (toluene for **11** and THF for **12**) are omitted for clarity.

Table 5. Selected Bond lengths (Å) and Angles (deg) for Ti(N^{pyr}N^{Me2})(NO^{t}Bu)Cl(bipy) (11)

Ti(1)–N(1)	1.7149(16)	Ti(1)–N(2)	2.0541(15)
Ti(1)–N(3)	2.4855(16)	Ti(1)–N(4)	2.2307(15)
Ti(1)–N(5)	2.2543(15)	Ti(1)–Cl(1)	2.3898(5)
N(1)–O(1)	1.362(2)	O(1)–C(1)	1.475(2)
Ti(1)–N(1)–O(1)	173.98(12)	N(1)–O(1)–C(1)	113.45(13)
N(1)–Ti(1)–N(2)	98.10(7)	N(1)–Ti(1)–N(3)	172.06(6)
N(1)–Ti(1)–N(4)	91.82(6)	N(1)–Ti(1)–N(5)	101.47(6)
N(1)–Ti(1)–Cl(1)	100.70(5)	N(2)–Ti(1)–N(3)	74.96(6)
N(2)–Ti(1)–N(4)	92.63(6)	N(2)–Ti(1)–N(5)	155.23(6)
N(4)–Ti(1)–Cl(1)	161.34(4)	N(5)–Ti(1)–Cl(1)	91.99(4)
N(4)–Ti(1)–N(5)	71.83(5)		

1.350(2)–1.374(3) Å, respectively) and those in the diamide-amine complexes **6**–**8** (1.721(2)–1.734(2) Å and 1.385(3)–1.391(3) Å). These differences reflect the different σ- and π-donor abilities of the supporting ligand sets in each group of complexes, with pyrrolide-donors being intermediate between chloride and amide donors.

Table 6. Selected Bond lengths (Å) and Angles (deg) for Ti(N$_2$^{pyr}N^{Me})(NO^{t}Bu)(bipy) (12)

Ti(1)–N(1)	1.716(3)	Ti(1)–N(2)	2.422(3)
Ti(1)–N(3)	2.068(3)	Ti(1)–N(4)	2.067(3)
Ti(1)–N(5)	2.237(3)	Ti(1)–N(6)	2.248(3)
N(1)–O(1)	1.357(4)	O(1)–C(1)	1.473(4)
Ti(1)–N(1)–O(1)	170.0(2)	N(1)–O(1)–C(1)	115.6(2)
N(1)–Ti(1)–N(2)	177.27(13)	N(1)–Ti(1)–N(3)	104.89(13)
N(1)–Ti(1)–N(4)	100.85(14)	N(1)–Ti(1)–N(5)	97.34(12)
N(1)–Ti(1)–N(6)	94.51(12)	N(3)–Ti(1)–N(4)	101.93(13)
N(5)–Ti(1)–N(6)	71.64(10)		

■ CONCLUSIONS

We have reported the first examples of any Group 4 alkoxyimido complex and demonstrated that they can be readily prepared via protonolysis, Lewis base exchange, or salt elimination methodologies. Thus reaction of Ti(NMe$_2$)$_2$Cl$_2$ with ^{t}BuONH$_2$ gave Ti(NO^{t}Bu)Cl$_2$(NHMe$_2$)$_2$ (**1**) which was an effective starting material for Ti(NO^{t}Bu)(Me$_3$[9]aneN$_3$)Cl$_2$ (**2**), Ti(NO^{t}Bu){HC(Me$_2$pz)$_3$}Cl$_2$ (**3**), or Ti(NO^{t}Bu)(Me$_3$[6]-aneN$_3$)Cl$_2$ (**4**). The latter reacted with pyridine to give Ti(NO^{t}Bu)Cl$_2$(py)$_3$ (**5**) which could also be synthesized from Ti(NMe$_2$)$_2$Cl$_2$, ^{t}BuONH$_2$, and Me$_3$[6]aneN$_3$ without need to isolate or purify **1** or **4**. Ti(NO^{t}Bu)Cl$_2$(py)$_3$ (**5**) was effective in salt elimination reactions with a variety of lithiated ligands. In this manner Ti(N$_2$N^{py})(NO^{t}Bu)(py) (**6**), Ti(N$_2$N^{Me})(NO^{t}Bu)-(py) (**7**), Ti(N^{pyr}N^{Me_2})(NO^{t}Bu)Cl(py)$_2$ (**9**), and Ti-(N$_2$^{pyr}N^{Me})(NO^{t}Bu)(py)$_2$ (**10**) were synthesized along with certain 2,2′-bipyridyl derivatives. The X-ray structures of 10 *tert*-butoxyimido complexes were determined and, together with DFT calculations, showed the presence of Ti–N$_{im}$ triple bonds ($\sigma^2\pi^4$). In general, the Ti–NOR bonds lie between those of alkyl- and aryl-imides, and are shorter than in their diphenylhydrazido counterparts. The destabilizing effect of the N-bound oxygen 2p$_\pi$ is comparable to that of a phenyl ring π-system. As in the corresponding hydrazido chemistry, the longest Ti–N$_{im}$ and N–O bonds are found with strongly π-donating supporting diamide-amine ligands. The reactivity of these and related Group 4 alkoxyimido complexes is currently under investigation within our laboratory.

■ EXPERIMENTAL SECTION

General Methods and Instrumentation. All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon or dinitrogen. Solvents were degassed by sparging with dinitrogen and dried by passing through a column of the appropriate drying agent. Toluene was refluxed over sodium and distilled. Deuterated solvents were dried over sodium (C$_6$H$_6$) or P$_2$O$_5$ (CDCl$_3$ and CD$_2$Cl$_2$), distilled under reduced pressure and stored under dinitrogen in Teflon valve ampules. NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ^{1}H and ^{13}C-^{1}{H} NMR spectra were recorded on Varian Mercury-VX 300 and Varian Unity Plus 500 spectrometers at ambient temperature unless stated otherwise and referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances, and are reported relative to tetramethylsilane (δ = 0 ppm). Assignments were confirmed using two-dimensional ^{1}H–^{1}H and ^{13}C–^{1}H NMR correlation experiments. Chemical shifts are quoted in δ (ppm) and coupling constants in hertz (Hz). IR spectra were recorded on a Nicolet Magna 560 ESP FTIR spectrometer. Samples were prepared in a drybox as Nujol mulls between NaCl plates. Elemental analyses were carried out by the Elemental Analysis Service at the London Metropolitan University or Elemental Microanalysis Ltd., Devon.

Starting Materials. ^{t}BuONH$_2$,[23] Ti(NMe$_2$)$_2$Cl$_2$,[24] Me$_3$[9]aneN$_3$,[52] HC(Me$_2$pz)$_3$,[53] Me$_3$[6]aneN$_3$,[54] Li$_2$N$_2$N^{Me},[55] Li$_2$N$_2$N^{py},[56] Li$_2$N^{pyr}N^{Me_2},[57] and Li$_2$N$_2$^{pyr}N^{Me}[58] were synthesized according to literature procedures. Other reagents were purchased from Sigma-Aldrich and used without further purification.

Ti(NO^{t}Bu)Cl$_2$(NHMe$_2$)$_2$ (1). To Ti(NMe$_2$)$_2$Cl$_2$ (3.79 g, 18.4 mmol) in benzene (20 mL) cooled to 5 °C was added a solution of ^{t}BuONH$_2$ (2.00 mL, 18.4 mmol) in benzene (20 mL) dropwise. The dark brown mixture was then stirred for a further 4 h, after which time the slurry was filtered and washed with pentane (3 × 15 mL) to give **1** as a green solid. Yield: 1.45 g (51%). Diffraction-quality crystals were grown from a saturated toluene solution at room temperature (RT). ^{1}H NMR (C$_6$D$_6$, 299.9 MHz): 2.84 (2H, br. m, N$\underline{\mathrm{H}}$Me$_2$), 2.33 (12H, d, ^3J = 6.0 Hz, NH$\underline{\mathrm{Me_2}}$), 1.19 (9H, s, OCMe$_3$). ^{13}C{^{1}H} NMR (CD$_2Cl_2$, 75.4 MHz): 86.4 (O$\underline{\mathrm{C}}Me_3$), 41.0 (NHMe$_2$), 26.9 (OC$\underline{\mathrm{Me}}_3$). IR: 3247 (m, ν(N−H)), 1366 (s), 1261 (w), 1242 (w), 1157 (m) 1007 (m), 989 (m), 826 (m), 722 (m), 699 (w) cm^{-1}. IR (NaCl cell, CH$_2$Cl$_2$): 3289 (s, ν(N−H)) cm^{-1}. EI-MS: $[M - \mathrm{NMe_2}]^+$ 251 (20%). Anal. found (calcd. for C$_8$H$_{23}$Cl$_2$N$_3$OTi); C, 30.00 (32.45); H, 7.27 (7.83); N, 14.18 (14.19) %. Despite repeated attempts a more satisfactory elemental analysis could not be obtained.

Ti(NO^{t}Bu)(Me$_3$[9]aneN$_3$)Cl$_2$ (2). To a slurry of Ti(NO^{t}Bu)Cl$_2$(NHMe$_2$)$_2$ (**1**) (0.35 g, 1.2 mmol) in benzene (20 mL) was added a solution of Me$_3$[9]aneN$_3$ (0.20 g, 1.2 mmol) in benzene (20 mL) in one portion. A dark brown slurry formed after a mild exotherm. The mixture was then stirred for a further 16 h, after which time the slurry was concentrated (ca. 50%), filtered, and washed with pentane (3 × 15 mL) to give product as a green crystalline solid. Yield: 0.36 g (81%), Light green single crystals suitable for X-ray diffraction were obtained from a saturated dichloromethane solution layered with hexanes at RT. ^{1}H NMR (CD$_2$Cl$_2$, 499.9 MHz): δ 3.46 (4H, m, CH$_2$), 3.07 (4H, m, CH$_2$), 3.03 (6H, s, Me cis to NO^{t}Bu), 2.92 (2H, m, CH$_2$), 2.75 (2H, m, CH$_2$), 2.54 (2H, m, CH$_2$), 2.51 (3H, s, Me trans to NO^{t}Bu), 1.23 (9H, s, OCMe$_3$). ^{13}C{^{1}H} (CD$_2$Cl$_2$, 75.4 MHz): 85.5 (O$\underline{\mathrm{C}}$Me$_3$), 57.0 (CH$_2$), 56.3 (CH$_2$), 55.4 (NMe trans to Cl), 52.5 (NMe trans to NO^{t}Bu), 52.2 (CH$_2$), 49.1 (CH$_2$), 27.3 (OC$\underline{\mathrm{Me}}_3$). IR: 1294 (w), 1157 (s), 1064 (m), 1005 (s), 839 (w), 789 (w), 749 (w), 722 (s), 708 (m) cm^{-1}. Anal. found (calcd. for C$_{13}$H$_{30}$Cl$_2$N$_4$OTi.0.2(CH$_2$Cl$_2$)); C, 40.09 (40.22); H, 7.87 (7.77); N, 14.61 (14.21) %.

Ti(NO^{t}Bu){HC(Me$_2$pz)$_3$}Cl$_2$ (3). To a slurry of Ti(NO^{t}Bu)Cl$_2$(NHMe$_2$)$_2$ (**1**) (0.50 g, 1.7 mmol) in benzene (20 mL) was added a solution of HC(Me$_2$pz)$_3$ (0.50 g, 1.7 mmol) in benzene (20 mL) in one portion. A dark brown slurry formed after a mild exotherm. The mixture was then stirred for a further 16 h, after which time the slurry was concentrated (ca. 50%), filtered, and washed with pentane (3 × 15 mL) to give product as a green crystalline solid. Yield: 0.70 g (82%), Light green single crystals suitable for X-ray diffraction were obtained from a saturated dichloromethane solution layered with hexanes at RT. ^{1}H NMR (CD$_2$Cl$_2$, 299.9 MHz): 7.83 (1H, s, $\underline{\mathrm{H}}$C(Me$_2$pz)$_3$), 6.10 (2H, s, N$_2$C$_3$Me$_2$$\underline{\mathrm{H}}$ cis to NO^{t}Bu), 5.86 (1H, s, N$_2$C$_3$Me$_2$$\underline{\mathrm{H}}$ trans to NO^{t}Bu), 2.61 (6H, s, 3-N$_2$C$_3$Me$_2$H cis to NO^{t}Bu), 2.58 (3H, s, 3-N$_2$C$_3$Me$_2$$\underline{\mathrm{H}}$ trans to NO^{t}Bu), 2.54 (6H, s, 5-N$_2$C$_3$Me$_2$H trans to NO^{t}Bu), 2.46 (3H, s, 5-N$_2$C$_3$Me$_2$H trans to NO^{t}Bu), 1.42 (9H, s, OCMe$_3$). ^{13}C{^{1}H} (CD$_2$Cl$_2$, 75.4 MHz): 156.2 (3-N$_2$$\underline{\mathrm{C}}_3Me_2$H trans to Cl), 155.5 (3-N$_2$$\underline{\mathrm{C}}_3Me_2$H trans to NO^{t}Bu), 139.8 (5-N$_2$$\underline{\mathrm{C}}_3Me_2$H trans to Cl), 138.5 (5-N$_2$$\underline{\mathrm{C}}_3Me_2$H trans to NO^{t}Bu), 108.6 (4-N$_2$$\underline{\mathrm{C}}_3Me_2$H trans to NO^{t}Bu), 108.3 (4-N$_2$$\underline{\mathrm{C}}_3Me_2$H trans to Cl), 87.1 (O$\underline{\mathrm{C}}Me_3$), 67.9 (H$\underline{\mathrm{C}}$(Me$_2$pz)$_3$), 27.8 (OC$\underline{\mathrm{Me}}_3$), 15.2 (3-N$_2C_3$$\underline{\mathrm{Me}}_2$H trans to Cl), 14.8 (3-N$_2$C$_3$$\underline{\mathrm{Me}}_2$H trans to NO^{t}Bu), 11.3 (5-N$_2$C$_3$$\underline{\mathrm{Me}}_2$H trans to Cl), 10.9 (5-N$_2$C$_3$$\underline{\mathrm{Me}}_2$H trans to NO^{t}Bu). IR: 1569 (m), 1419 (w), 1310 (m), 1271 (m), 1156 (m), 112 (w), 1045 (m), 989 (w), 914 (m), 860 (m), 834 (m), 807 (w), 749 (w), 711 (m), 677 (w) cm^{-1}. Anal. found (calcd. for C$_{20}$H$_{31}$Cl$_2$N$_2$OTi); C, 47.41 (47.64); H, 6.39 (6.20); N, 19.15 (19.15) %.

Ti(NO^{t}Bu)(Me$_3$[6]aneN$_3$)Cl$_2$ (4). To a slurry of Ti(NO^{t}Bu)Cl$_2$(NHMe$_2$)$_2$ (**1**) (2.10 g, 3.40 mmol) in benzene (30 mL) cooled to 5 °C was added a solution of Me$_3$[6]aneN$_3$ (1.00 mL, 3.40 mmol) in benzene (20 mL) dropwise. The mixture was stirred for a further 16 h, after which time the slurry was concentrated (ca. 50%), filtered, and washed with cold (0 °C) dichloromethane (3 × 15 mL) to give **4** as a pink crystalline solid. Yield: 1.70 g (72%). Diffraction-quality crystals were grown from a saturated dichloromethane solution layered with hexanes. ^{1}H NMR (CD$_2$Cl$_2$, 299.9 MHz): 4.76 (1H, d, ^2J = 4.8 Hz, CH$_2$ trans to NO^{t}Bu), 4.26 (2H, d, ^2J = 4.5 Hz, CH$_2$ trans to Cl), 3.73 (1H, d, ^2J = 4.8 Hz, CH$_2$ trans to NO^{t}Bu), 3.36 (2H, d, ^2J = 4.5 Hz, CH$_2$ trans to Cl), 2.84 (6H, s, NMe trans to Cl), 2.16 (3H, s, NMe trans to NO^{t}Bu), 1.29 (9H, s, OCMe$_3$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 75.4 MHz): 86.0 ($\underline{\mathrm{C}}$Me$_3$), 78.3 (CH$_2$ trans to Cl), 76.8 (CH$_2$ trans to NO^{t}Bu), 41.3 (NMe trans to Cl), 37.0 (NMe trans to NO^{t}Bu), 27.0 (OC$\underline{\mathrm{Me}}_3$). IR: 1364 (w), 1358 (w), 1261 (m), 1178 (m), 1158 (s), 1120 (w), 1083 (w), 1011 (m), 937 (m), 836 (m), 748 (m), 721 (w), 703(m) cm^{-1}. Anal. found (calcd. for C$_{10}$H$_{24}$Cl$_2$N$_4$OTi); C, 35.91 (35.84); H, 7.03 (7.22); N, 16.39 (16.72) %.

Ti(NO^{t}Bu)Cl$_2$(py)$_3$ (5). Ti(NO^{t}Bu)(Me$_3$[6]aneN$_3$)Cl$_2$ (**4**) (1.00 g, 2.7 mmol) was dissolved in pyridine (10 mL) to form a dark purple solution. After 10 min hexanes (25 mL) were added and the resulting slurry filtered. The procedure was repeated, and the product was dried in vacuo to yield **5** as a dark purple crystalline powder. Yield: 0.80 g (67%), Diffraction-quality crystals were grown from a saturated solution in pyridine/hexanes (1:1 v/v) at 4 °C. ^{1}H NMR (CD$_2$Cl$_2$, 299.9 MHz, 253 K): 9.04 (4H, d, ^3J = 5.4 Hz, 2-py cis to NO^{t}Bu), 8.63 (2H, br. m, 2-py trans to NO^{t}Bu), 7.82 (2H, t, ^3J = 7.2 Hz, 4-py cis to NO^{t}Bu) 7.71 (1H, br. m, 4-py trans to NO^{t}Bu), 7.36 (4H, app. t, ^3J = 7.2 Hz, 3-py cis to NO^{t}Bu), 7.19 (2H, br. m, 3-py trans to NO^{t}Bu), 1.13 (9H, s, OCMe$_3$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 75.4 MHz, 253 K): 151.7 (2-py cis to NO^{t}Bu), 151.0 (2-py trans to NO^{t}Bu), 138.6 (4-py cis to NO^{t}Bu), 137.4 (4-py trans to NO^{t}Bu), 124.0 (3-py cis to NO^{t}Bu), 123.4 (4-py trans to NO^{t}Bu), 86.0 (O$\underline{\mathrm{C}}$Me$_3$), 26.8 (OC$\underline{\mathrm{Me}}_3$). IR: 1603 (s), 1597 (s), 1364 (m), 1227 (m), 1150 (m), 1068 (w), 1039 (m), 1004 (w), 832 (w), 768 (s), 760 (s), 702 (s), 632 (w) cm^{-1}. Anal. found (calcd. for C$_{19}$H$_{24}$Cl$_2$N$_4$OTi); C, 51.62 (51.49); H, 5.46 (5.37); N, 12.64 (12.38) %.

Alternative "One Pot" Synthesis of Ti(NO^{t}Bu)Cl$_2$(py)$_3$ (5). To a slurry of Ti(NMe$_2$)$_2$Cl$_2$ (5.00 g, 0.025 mol) in benzene (40 mL) at 5 °C was added dropwise a solution of ^{t}BuONH$_2$ (3.35 mL, 0.025 mol) in benzene (12 mL). The resulting dark red solution was stirred for 14 h, after which time the solution was cooled to 5 °C and Me$_3$[6]aneN$_3$ (3.55 mL, 0.025 mol) was added dropwise. A precipitate immediately formed, and the mixture was stirred for 14 h. The solid was filtered and washed with benzene (3 × 15 mL) at RT and dichloromethane (3 × 15 mL) at 0 °C. The light pink precipitate was dissolved in pyridine (10 mL), crystallized by addition of hexanes (50 mL), and filtered. This procedure was repeated twice. The product was then washed with pentane (3 × 15 mL) and dried in vacuo to give **5** as a purple crystalline powder. Yield: 4.63 g (41% based on Ti(NMe$_2$)$_2$Cl$_2$). The ^{1}H NMR spectrum was identical to that of a sample prepared from isolated **4** (see above).

NMR Tube Synthesis of Ti(NO^{t}Bu)(Me$_3$[9]aneN$_3$)Cl$_2$ (2) or Ti(NO^{t}Bu){HC(Me$_2$pz)$_3$}Cl$_2$ (3). To a solution of Ti(NO^{t}Bu)Cl$_2$(py)$_3$ (**5**) (0.05 mmol) in CD$_2$Cl$_2$ (0.5 mL) was added the appropriate *fac*-N$_3$ donor ligand (0.05 mmol). The ^{1}H NMR spectrum was identical to that of a sample of isolated **2** or **3**.

Ti(N$_2$N^{py})(NO^{t}Bu)(py) (6). A mixture of Ti(NO^{t}Bu)Cl$_2$(py)$_3$ (**5**) (0.78 g, 1.8 mmol) and Li$_2$ N$_2$^{TMS}N^{py} (0.56 g, 1.8 mmol) was cooled to −78 °C and toluene (20 mL) was added. The mixture was allowed to warm to room temperature and stirred for a further 14 h. The volatiles were removed under reduced pressure, and the solid residues extracted with diethyl ether (3 × 15 mL). The resulting solution was evaporated to dryness under reduced pressure, and the solid product washed with pentane (5 mL) to yield **6** as a dark red solid. Yield: 0.30 g (33%), ^{1}H NMR (C$_6$D$_6$, 299.8 MHz): δ 9.54 (1H, d, ^3J = 5.3 Hz, 2-NC$_5$H$_4$), 9.13 (2H, s, *o*-py), 7.22−7.06 (1H, m, 3-NC$_5$H$_4$), 6.92 (2H, d, ^3J = 8.0, overlapping 5-NC$_5$H$_4$ and *p*-py), 6.83−6.59 (3H, m, overlapping 4-NC$_5$H$_4$ and *m*-py), 3.75 (2H, d, ^2J = 12.0 Hz, CH$_2$), 3.33 (2H, d, ^2J = 12.0 Hz, CH$_2$), 1.46 (9H, s, OCMe$_3$), 1.16 (3H, s, Me), 0.12 (18H, s, SiMe$_3$). ^{13}C{^{1}H} (C$_6$D$_6$, 75.4 MHz): 161.21 (6-NC$_5$H$_4$), 151.72 (*o*-py), 150.39 (2-NC$_5$H$_4$), 149.12 (*p*-py), 137.47 (4-NC$_5$H$_4$), 123.52 (*m*-py), 120.47 (5-NC$_5$H$_4$), 119.80 (3-NC$_5$H$_4$), 79.93 (O$\underline{\mathrm{C}}$Me$_3$), 64.10

(CH$_2$), 46.25 ($\underline{C}$Me), 27.61 (OC$\underline{Me}_3$), 24.14 (C$\underline{Me}$), 1.09 (SiMe$_3$). IR: 1599 (m), 1244 (s), 1191 (m), 1158 (w), 1603 (m), 1038 (w), 957 (w), 982 (m), 837 (s), 754 (m), 698 (w), 668 (w) cm^{-1}. Anal. found (calcd. For **6** - 0.7(py), $C_{19}H_{38}N_4OSi_2Ti.0.3(NC_5H_5)$); C, 54.30 (54.16); H, 8.41 (8.32); N, 12.95 (13.20) %.

Ti(N$_2$N^{Me})(NO^{t}Bu)(py) (7). A mixture of Ti(NO^{t}Bu)Cl$_2$(py)$_3$ (**5**) (1.00 g, 2.26 mmol) and Li$_2$N$_2$N^{Me} (0.62 g, 2.26 mmol) was cooled to −78 °C, and cold toluene (15 mL) was added. The mixture was allowed to warm to RT and stirred for a further 60 min. The volatiles were removed under reduced pressure, and the solid residue extracted into diethyl ether (3 × 15 mL). The volatiles were again removed to afford **7** as a green solid which was dried in vacuo. Yield: 0.92 g (86%). Diffraction-quality crystals were grown from a saturated hexanes solution at 4 °C. Compound **7** exists as a mixture of isomers designated **7a** (NO^{t}Bu trans to NMe) and **7b** (NO^{t}Bu cis to NMe) (ratio **7a**:**7b** = ca. 3:1).

^{1}H NMR (C$_6$D$_6$, 299.9 MHz) for **7a**: 8.40 (2H, br. d, ^3J = 4.5 Hz, 2-py) 6.73 (1H, m, overlapping 4-py), 6.45 (2H, m, overlapping 3-py), 3.63 (4H, overlapping 2*m*, CH$_2$), 2.61 (2H, m, CH$_2$), 1.98 (2H, m, CH$_2$), 1.15 (3H, s, NMe), 1.04 (9H, s, OCMe$_3$), 0.50 (18H, s, SiMe$_3$) ppm. ^{1}H NMR (C$_6$D$_6$, 299.9 MHz) for **7b**: 8.71 (2H, br. d, ^3J = 5.4 Hz, 2-py), 6.73 (1H, m, overlapping 4-py), 6.45 (2H, m, overlapping 3-py), 3.40 (4H, 2 × overlapping m, CH$_2$), 2.81 (2H, m, CH$_2$), 2.45 (2H, m, CH$_2$), 1.41 (9H, br. s, OCMe$_3$), 0.16 (18H, s, SiMe$_3$) ppm. IR: 1357 (m), 1241 (m), 1190 (w), 1154 (w), 1092 (m), 1040 (m), 940 (s), 830 (s), 798 (m), 768 (m), 709 (w), 684 (w), 497 (s) cm^{-1}. Anal. found (calcd. for **7b** - 0.5(py), $C_{17.5}H_{40.5}N_{4.5}OSi_2Ti$); C, 48.76 (48.42); H, 9.46 (9.40); N, 14.20 (14.52) %.

Ti(N$_2$N^{Me})(NO^{t}Bu)(bipy) (8). To a mixture of Ti(N$_2^{TMS}$N^{Me})(NO^{t}Bu)(py) (7) (0.10 g, 0.21 mmol) and 2,2′-bipyridyl (0.33 g, 0.21 mmol) was added benzene (15 mL). The mixture was stirred for 1 h, then evaporated to dryness, and the dark brown crystalline product was washed with pentane (3 × 10 mL). Yield 0.96 g (82%). Dark brown single crystals suitable for X-ray diffraction were obtained from a saturated benzene solution. ^{1}H NMR (CD$_2$Cl$_2$, 299.9 MHz): 9.56 (2H, d, ^3J = 4.8 Hz, 2-bipy), 8.12 (2H, d, ^3J = 7.8 Hz, 5-bipy), 7.96 (2H, dt, ^3J = 7.2 Hz, ^3J = 1.5 Hz, 4-bipy), 7.47 (2H, app. t, 3-bipy), 3.41 (2H, m, C$\underline{H_2}$CH$_2$NMe), 3.29 (2H, m, C$\underline{H_2}$CH$_2$NMe), 2.49 (2H, m, C$\underline{H_2}$NMe), 2.02 (2H, m, C$\underline{H_2}$NMe), 1.23 (3H, s, NMe), 0.44 (9H, s, OCMe$_3$), 0.20 (18H, s, SiMe$_3$). ^{13}C{^{1}H} (CD$_2$Cl$_2$, 75.4 MHz): 154.7 (2-bipy), 153.2 (6-bipy), 138.7 (4-bipy), 125.1 (3-bipy), 120.7 (5-bipy), 80.3 (O$\underline{C}$Me$_3$), 60.3 ($\underline{C}$H$_2$NMe), 48.2 ($\underline{C}$H$_2$CH$_2$NMe), 43.9 (NMe), 26.9 (OC$\underline{Me}_3$), 3.0 (SiMe$_3$). IR: 1597 (m), 1571 (w), 1348 (w), 1300 (w), 1260 (m), 1231 (s), 1195 (w), 1167 (w), 1150 (m), 1102 (s), 1077 (s), 1151 (w), 1014 (s), 951 (s), 939 (s), 920 (m), 865 (m), 829 (s), 788 (w), 764 (s), 752 (m), 738 (w) cm^{-1}. Anal. found (calcd. for $C_{25}H_{46}N_6OSi_2Ti$); C, 54.31 (54.52); H, 8.63 (8.42); N, 15.05 (15.26) %.

Ti(N^{pyr}N^{Me_2})(NO^{t}Bu)Cl(py)$_2$ (9). A mixture of Ti(NO^{t}Bu)Cl$_2$(py)$_3$ (0.50 g, 1.13 mmol) and LiN^{pyr}N^{Me} (0.15 g, 1.13 mmol) was cooled to −78 °C, and diethyl ether (20 mL) was added. The mixture was allowed to warm to room temperature and was stirred for a further hour. The volatiles were removed under reduced pressure, and the solid residues extracted with diethyl ether (3 × 15 mL). The resulting solution was evaporated to dryness under reduced pressure, and the solid product washed with pentane (2 × 10 mL) to yield **9** as a dark brown solid. Yield: 0.37 g (72%). ^{1}H NMR (C$_6$D$_6$, 299.8 MHz): δ 9.11 (4H, d, ^3J = 4.6 Hz, *o*-py), 8.40 (1H, br. s, 2-pyr) 6.88 (1H, br. s, 3-pyr), 6.74 (2H, t, ^3J = 7.7, *p*-py), 6.50 (4H, br. t, ^3J = 6.4 Hz, *m*-py), 6.39 (1H, br. s, 4-pyr), 3.00 (2H, br. s, CH$_2$), 1.89 (6H, br. s, NMe$_2$), 1.11 (9H, s, ^{t}Bu). ^{13}C{^{1}H} (C$_6$D$_6$, 75.4 MHz): 152.05 (*o*-py), 150.65 (*o*-py), 137.20 (*p*-py), 135.80 (*p*-py), 130.85 (2-pyr), 124.01 (*m*-py), 123.54 (*m*-py), 109.59 (3-pyr), 103.72 (4-pyr), 84.25 (O$\underline{C}$Me$_3$), 61.51 (CH$_2$), 48.12 (NMe$_2$), 27.18 (OC$\underline{Me}_3$). IR: 1601 (m), 1419 (w), 1365 (s), 1348 (m), 1268 (w), 1219 (s), 1181 (w), 1150 (s), 1107 (w), 1070 (w), 1041 (m), 1031 (m), 1007 (w), 997 (w), 977 (m), 851 (w), 831 (w), 764 (m), 748 (w), 732 (m), 706 (m), 661 (w), 630 (w), 452 (w) cm^{-1}. A satisfactory elemental analysis could not be obtained.

Ti(N$_2^{pyr}$N^{Me})(NO^{t}Bu)(py)$_2$ (10). A mixture of Ti(NO^{t}Bu)Cl$_2$(py)$_3$ (1.00 g, 2.3 mmol) and Li$_2$N$_2^{pyr}$N^{Me} (0.45 g, 2.3 mmol) was cooled to −78 °C and toluene (20 mL) was added. The mixture was allowed to warm to room temperature and stirred for a further hour. The volatiles were removed under reduced pressure, and the solid residues extracted with diethyl ether (3 × 15 mL). The resulting solution was evaporated to dryness under reduced pressure, and the solid product washed with pentane (3 × 10 mL) to yield **10** as a dark brown solid. Yield: 0.75 g (69%), ^{1}H NMR (C$_6$D$_6$, 299.8 MHz): δ 8.44 (2H, d, ^3J = 4.6 Hz, *o*-py), 8.36 (2H, s, 2-pyr), 8.13 (2H, d, ^3J = 3.2 Hz, *o*-py), 6.97 (2H, m, 3-pyr), 6.64 (2H, m, overlapping *p*-py), 6.46 (2H, m, 4-pyr), 6.37 (4H, m, overlapping *m*-py), 3.38 (2H, d, ^2J = 13.7 Hz, CH$_2$), 3.18 (2H, d, ^2J = 13.7 Hz, CH$_2$), 1.69 (3H, s, Me), 1.01 (9H, s, ^{t}Bu). ^{13}C{^{1}H} (C$_6$D$_6$, 75.4 MHz): 151.50 (*o*-py), 150.65 (*o*-py), 138.98 (5-pyr), 137.1 (*p*-py), 136.87 (*p*-py), 129.10 (2-pyr), 124.41 (*m*-py), 124.16 (*m*-py), 109.65 (3-pyr), 104.16 (4-pyr), 81.91 (O$\underline{C}$Me$_3$), 60.43 (CH$_2$), 45.60 (NMe$_2$), 26.92 (OC$\underline{Me}_3$). IR: 1600 (s), 1419 (s), 1399 (s), 1360 (m), 1327 (w), 1289 (w), 1240 (w), 1215 (m), 1186 (m), 1154 (s), 1105 (w), 1094 (w), 1070 (w), 1040 (m), 1029 (s), 1006 (m), 969 (s), 867 (w), 841 (m), 761 (m), 731 (m), 726 (m), 704 (m), 666 (w), 630 (w), 622 (w) cm^{-1}. Anal. found (calcd. for $C_{25}H_{32}N_6OTi$); C, 62.35 (62.50); H, 6.90 (6.71); N, 17.31 (17.49) %.

Ti(N^{pyr}N^{Me_2})(NO^{t}Bu)Cl(bipy) (11). To a mixture of Ti(N^{pyr}N^{Me})(NO^{t}Bu)Cl(py)$_2$ (**9**) (0.10 g, 0.22 mmol) and 2,2′-bipyridyl (0.04 g, 0.27 mmol) was added benzene (5 mL) and stirred for 1 h. The volatiles were removed under reduced pressure, and the solid was washed with pentane (3 × 10 mL) to yield **11** as a dark brown solid. Yield: 0.08 g (81%). Single crystals suitable for X-ray diffraction studies were grown from a saturated benzene solution at room temperature. ^{1}H NMR (C$_6$D$_6$, 299.8 MHz): δ 9.96 (1H, d, ^3J = 4.7 Hz, 2-bipy), 8.30 (1H, d, ^3J = 4.9 Hz, 2-bipy), 8.23 (1H, d, ^3J = 8.1 Hz, 5-bipy), 8.17 (1H, d, ^3J = 8.2 Hz, 5-bipy), 8.08 (1H, td, ^3J = 8.0, ^4J = 1.6 Hz, 4-bipy), 7.93 (1H, td, ^3J = 8.0, ^4J = 1.6 Hz, 4-bipy), 7.61 (1H, m, 3-bipy), 7.53 (1H, s, 2-pyr), 7.31 (1H, m, 3-bipy), 6.10 (1H, m, 3-pyr), 5.79 (1H, m, 4-pyr), 3.94 (1H, d, ^2J = 12.9 Hz, CH$_2$), 2.69 (1H, d, ^2J = 12.9 Hz, CH$_2$), 1.78 (3H, s, NMe), 1.06 (3H, s, NMe), 0.93 (9H, s, ^{t}Bu). ^{13}C{^{1}H} (C$_6$D$_6$, 75.4 MHz): 153.2 (2-bipy), 152.9 (6-bipy), 152.0 (6-bipy), 151.5 (2-bipy), 140.9 (5-bipy), 140.2 (5-bipy), 137.4 (5-pyr), 130.1 (4-bipy), 126.6 (4-bipy), 126.6 (3-bipy), 122.5 (3-bipy), 108.1 (3-pyr), 103.1 (4-pyr), 89.1 (2-pyr), 85.1 (O$\underline{C}$Me$_3$), 61.1 (CH$_2$), 47.7 (NMe), 47.1 (NMe), 27.4 (OC$\underline{Me}_3$). IR: 1599 (s), 1419 (w), 1350 (m), 1316 (w), 1262 (m), 1220 (m), 1156 (s), 1105 (w), 1022 (s), 973 (m), 836 (m), 772 (m), 735 (s), 702 (w), 651 (m), 495 (s) cm^{-1}. Anal. found (calcd. for $C_{21}H_{28}ClN_5OTi$); C, 55.98 (56.07); H, 6.17 (6.27); N, 15.39 (15.37) %.

Ti(N$_2^{pyr}$N^{Me})(NO^{t}Bu)(bipy) (12). To a mixture of Ti(N$_2^{pyr}$N^{Me})(NO^{t}Bu)(py)$_2$ (**10**) (0.30 g, 0.62 mmol) and 2,2′-bipyridyl (0.11 g, 0.70 mmol) was added diethyl ether (10 mL), and the solution stirred for 1 h. The volatiles were removed under reduced pressure, and the solid product was washed with diethyl ether (3 × 10 mL). Yield: 0.27 g (90%). Single crystals suitable for X-ray diffraction studies were grown from a saturated tetrahydrofuran (THF) solution at 0 °C. ^{1}H NMR (CD$_2$Cl$_2$, 299.8 MHz): δ 8.16 (2H, d, ^3J = 8.0 Hz, 6-bipy), 7.99 (2H, t, ^3J = 7.8 Hz, 5-bipy), 7.60 (2H, d, ^3J = 5.3 Hz, 3-bipy), 7.55 (2H, s, 2-pyr), 7.41 (2H, ^3J = 5.3 Hz, 4-bipy), 6.20 (2H, s, 3-pyr), 5.90 (2H, s, 4-pyr), 3.62 (2H, d, ^3J = 13.6 Hz, CH$_2$), 3.03 (2H, d, ^3J = 13.6 Hz, CH$_2$), 1.38 (3H, s, NMe), 0.93 (9H, s, OCMe$_3$). ^{13}C{^{1}H} (C$_6$D$_6$, 75.4 MHz): 153.0 (2-bipy), 152.2 (5-bipy), 140.4 (6-bipy), 137.5 (5-pyr), 130.0 (2-pyr), 127.1 (4-bipy), 122.0 (3-bipy), 108.4 (3-pyr), 103.6 (4-pyr), 83.1 (O$\underline{C}$Me$_3$), 59.3 (CH$_2$), 45.2 (NMe), 27.3 (OC$\underline{Me}_3$). IR: 1603 (s), 1560 (w), 1402 (w), 1364 (m), 1339 (w), 1295 (w), 1261 (m), 1243 (m), 1211 (w), 1184 (m), 1174 (m), 1161 (s), 1126 (w), 1105 (m), 1162 (m), 1122 (s), 996 (m), 978 (w), 968 (s), 949 (w), 909 (w), 861 (m), 873 (w), 800 (w), 776 (s), 736 (s), 702 (m), 623 (m), 632 (w) cm^{-1}. Anal. found (calcd. for $C_{25}H_{30}N_6OTi$); C, 62.84 (62.76); H, 6.19 (6.32); N, 17.39 (17.57) %.

X-ray Structure Determinations. X-ray data collection and processing parameters are given in the Supporting Information. Crystals were mounted on MiTeGen MicroMounts using perfluoropolyether oil and cooled rapidly in a stream of cold N$_2$ using an Oxford Cryosystems Cryostream unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer. As appropriate, absorption and decay corrections were applied to the data and equivalent reflections merged.[59] The structures were solved with SIR92[60] or SHELXS-97[61] and further refinements and all other crystallographic calculations were performed using either the CRYSTALS program suite[62] or SHELXS-97.[61] Other details of the structure solution and refinements are given in the Supporting Information (CIF data). A full listing of atomic coordinates, bond lengths and angles and displacement parameters for all the structures have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Computational Details. All calculations were performed with the Gaussian03 package[63] of programs with the hybrid B3PW91 functional.[64] The Ti atom was represented by the relativistic effective core potential (RECP) from the Stuttgart group and the associated basis set.[65] The remaining atoms (C, H, N, O, Cl) were represented by a 6-31G(d,p) basis set.[66] The Si atom was represented by the RECP from the Stuttgart group and the associated basis set,[67] augmented by a d polarization function.[68] Full optimization of geometry was performed without any symmetry constraint, followed by analytical computation of the Hessian matrix to identify the nature of the located extrema as minima or transition states. Gibbs free energies in solution (toluene and benzene) were calculated by using the approximation reported by Maseras et al. ($\Delta G_{sol} = \Delta E_{sol} + (\Delta G - \Delta E)$).[48a,c] ΔE_{sol} was obtained by single point calculations using a 6-311++G(d,p) basis set for C, H, N, O and including solvent with the SMD approach.[48b] Natural Bonding Analysis was performed with the NBO 5.9 program interfaced with Gaussian.[44]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in CIF format and data collection and processing parameters for the X-ray structure determinations; further details of the DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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