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Structural Studies of Titanium(IV) Picolinamide Alkoxide and Oxide Derivatives

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Dedicated to Prof. M. L. H. Green, a fearless innovator.

Abstract

Reactions have been carried out using the titanium(IV) precursors, $TiCl_4$ and $Ti(OiPr)_4$, with addition of two equivalents of a functionalized picolinamide ligand. The reactions with $TiCl_4$ led to the formation of either a mononuclear titanium species, $[Ti(N,O)Cl_2X_2]$ or a dinuclear titanium species $[Ti(N,O)X_3]_2[\mu\text{-}O]$ (X = OMe or Cl), with incorporation of one picolinamide ligand. The ligand is bound to the titanium centre as the protonated amide. The reactions with $Ti(OiPr)_4$ resulted in the formation of mononuclear titanium *bis*-picolinamide species $[Ti(N,O)_2(OiPr)_2]$, and also dinuclear and trinuclear products, $[(N,O)Ti(OiPr)_2][\mu\text{-}OiPr]_2$ and $[(N,O)Ti(OiPr)_2]_2[\mu\text{-}OiPr]_2[(OiPr)_2Ti]$ $[\mu_3\text{-}O]$ respectively. In these cases the picolinamide ligand was found to be deprotonated and bound to the titanium as the iminolate. These possible intermediates have been characterized by X-ray crystallographic analysis and structural characteristics are discussed.

Keywords: Titanium; Amides; Iminolates; Isopropoxide; Catalysis

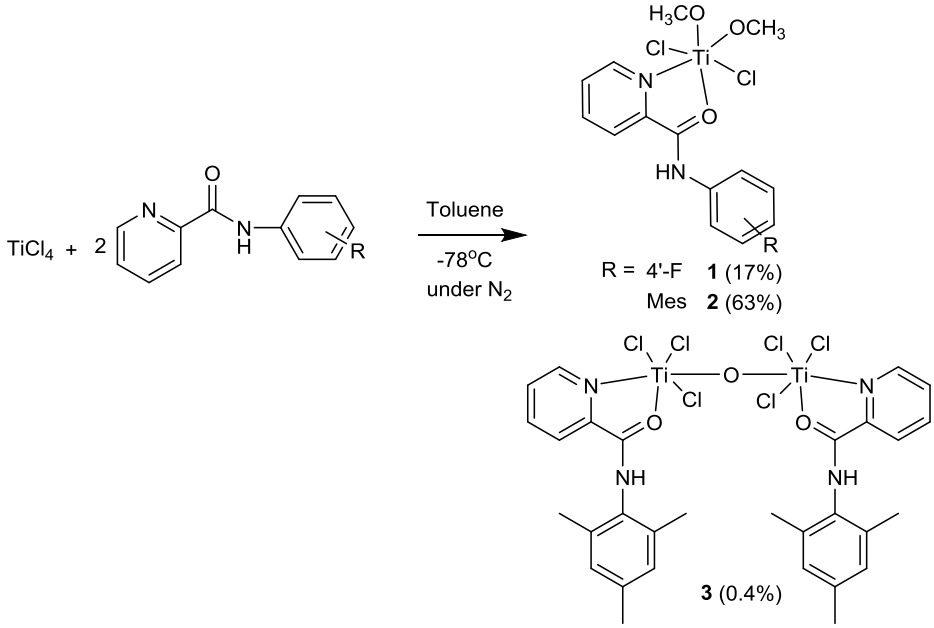
Introduction

The cost-effectiveness and biocompatibility of titanium means it has been widely used in many applications, including medicine,[1] nuclear waste storage[2,3] and as effective catalysts.[4-8] More importantly for this research, titanium salts have shown to be effective catalysts in the reduction of amides, showing high conversions to either the aldehyde, carbinol or the amine.[9] Lemaire *et al.* have developed and reported the use of 1,1,3,3-tetramethyldisiloxane (TMDS) activated by titanium(IV) isopropoxide for the reduction of phosphine oxides to phosphines,[10-12] nitriles to amines[13] and the reduction of aromatic and aliphatic tertiary amides.[9] They report the use of these mild condition reactions for the reduction of amides to aldehydes,[9] with up to 90% isolated yields. However, after screening one of the compounds, it was found that both the aldehyde and carbinol products were present. More recently, Luo *et al.* have shown low-valent titanium, prepared *in situ* from $TiCl_4$/Mg, is effective in the reduction of amides to amines, with up to 93% isolated yield of the amine.[14] A study by Iversen in 1970, explored the possible electrochemical reduction of picolinamide and isonicotinamide to the corresponding aldehydes.[15] However, there was no attempt to investigate the utility of this reaction past the aldehyde stage. Toomey, Jr. published a patent in 1987 on the electrochemical reduction of pyridine carboxamide bases,[16] and found that in the absence of a titanium salt the reduction gives high yields of the carbinol. In contrast, the addition of a titanium salt gave high isolated yields of the amine, suggesting a titanium complex intermediate is present in this conversion.

Our research has been aimed at both early and late transition metal organometallic and coordination complexes incorporating picolinamide ligands. We have previously shown ruthenium, rhodium and iridium picolinamides complexes in the development of anti-cancer drugs, with high cytotoxicities against a range of tumours.[17-19] We have also reported the uses of aluminium picolinamides for the ring-opening polymerisation of *rac*-lactide for use in the preparation of coloured polymeric materials[20] and picolinamide ligands as effective ligands for copper-catalysed aryl ether formation.[21] Herein, we report the reactions of picolinamide ligands with titanium(IV) precursors and discuss the structural properties of the potential intermediates. The reactions give titanium complexes with the ligand bound as either the amide or iminolate, in which the ligand is exclusively bound *N,O*. The intermediates are not easily predicted and give either mononuclear, dinuclear or trinuclear titanium metal complexes. The products obtained are analytically pure and fully characterized by NMR, mass spectroscopy and elemental analysis where possible, and their structures have been confirmed by X-ray crystallographic analysis.

Results and Discussion

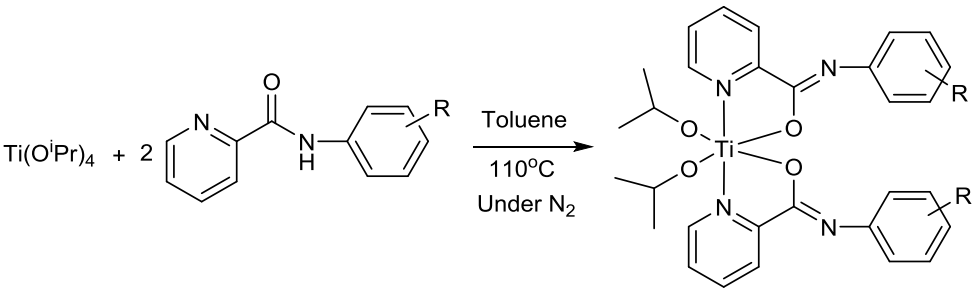
A preliminary mechanistic investigation using two equivalents of picolinamide ligand and copper proved to be affective for copper-catalysed aryl ether coupling.[21] Therefore, following the same synthetic procedure, reactions were carried out with $TiCl_4$ and addition of either i) an electron-withdrawing ligand, picolinyl-(4'-fluorophenyl)amide, or ii) electron donating ligand, (picolinyl-(Mes-trimethylphenyl)amide). Two equivalents of ligand in toluene were added to a solution of $TiCl_4$ in toluene at -78 °C (**Scheme 1**).The mixtures were warmed to room temperature and stirred for 16 hours, the suspension was filtered and recrystallized from methanol. Single crystals of complexes **1** and **2** were obtained in low to moderate yields from a concentrated methanol solution at -20 °C. The X-ray crystallographic data proves the connectivity of these structures; however, the data could not be solved to a publishable quality. The dimeric product **3** was obtained when the crude product of complex **2** was recrystallized from acetonitrile at -20 °C and only obtained in trace amounts.



Scheme 1 *Synthetic route of mononuclear and dinuclear titanium picolinamide complexes* ***1-3***

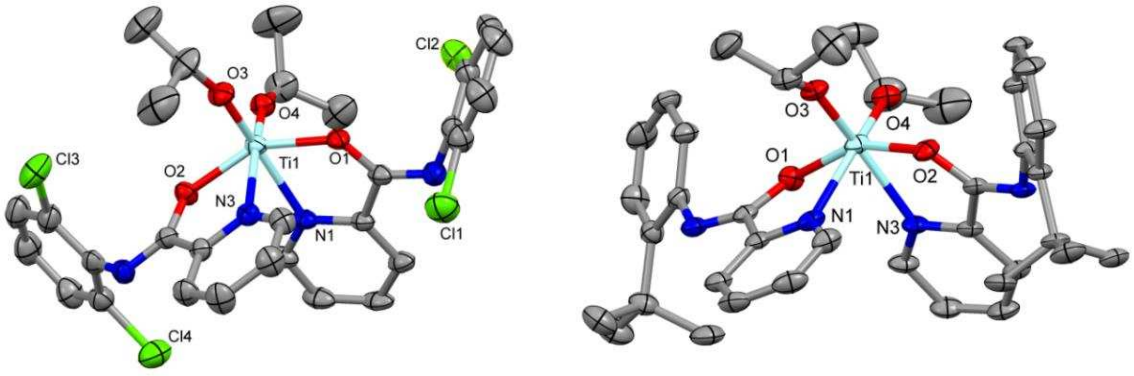
Upon analysis of the ^{1}H NMR spectra for complexes **1** and **2**, a single resonance was observed in the range of 3.35-3.28 ppm. This corresponds to the methoxy groups, which were later confirmed by X-ray crystallographic analysis. The complexes were recrystallized from methanol and due to the titanium having a higher affinity for oxygen, the chloride ligands are hydrolysed by methanol and substituted for methoxy ligands. It is postulated that a dimer similar to complex **3** is formed before recrystallization; however, the data was not sufficient enough to confirm this product. A broad resonance for complexes **1**-**3** is observed in the region of 10.2-10.0 ppm, which was assigned to that of the amide NH proton. Even though the crystal data was not fully resolved, the bond lengths showed the double bond character of the carbonyl C=O and the single bond character of the *ipso* C-N. This evidence suggests that these complexes bind to the titanium centre as the protonated amide, and is the usual binding mode previously observed for these ligands.[17-19]

Further reactions were carried out according to **Scheme 2**, in which two equivalents of a functionalised picolinamide ligand in toluene were added to Ti(O*i*Pr)$_4$ in toluene. After reflux for 16 hours and addition of petroleum ether, the solutions were stored at -20 °C, yielding analytically pure products in trace amounts to good yields. The ^{1}H NMR spectra of complexes **4**-**10** have no broad NH resonance in the region of 10.5-10.0 ppm and show the less common iminolate form of the ligand, which was confirmed by X-ray crystallographic analysis.



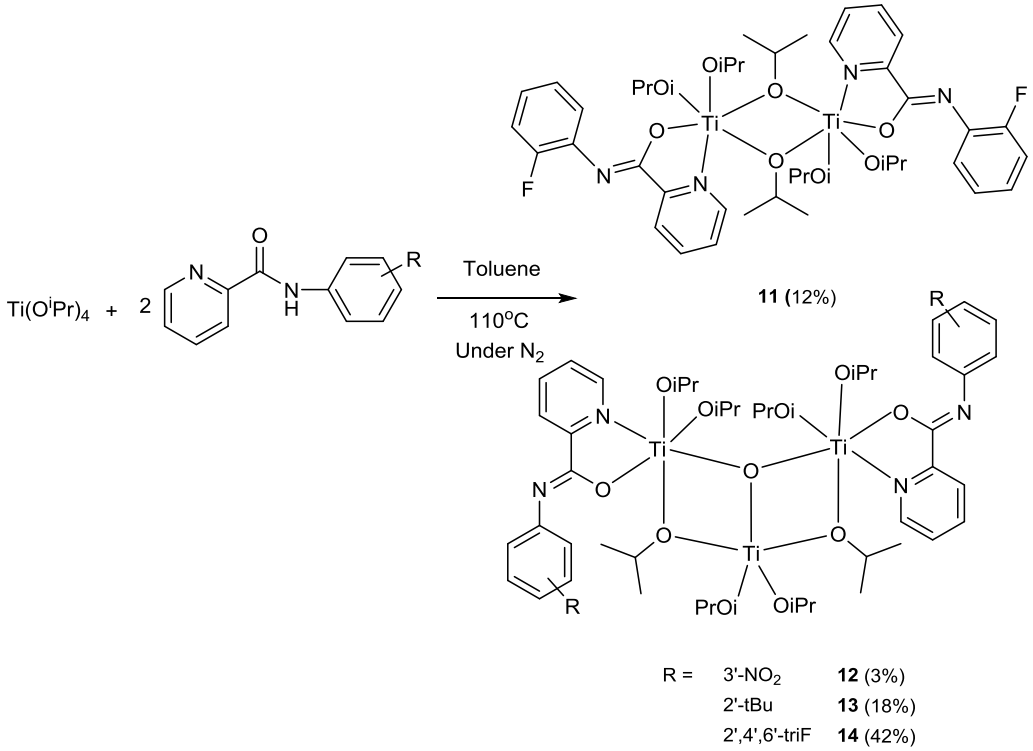
Scheme 2 *Synthetic pathway for the formation of titanium bis-picoliniminolate isopropoxide complexes* ***4***-***10***

Single crystals were obtained for complexes **6** and **9**, the molecular structures are shown in **Figure 1** and selected bond lengths are stated in **Table 1**. Complex **6** crystallised in a monoclinic cell and structural solution was performed in the $P2_1/c$ space group. The asymmetric unit contains one molecule and the titanium centre has a distorted *cis*-*cis*-*trans* octahedral arrangement. Complex **9** crystallised in a triclinic cell and structural solution was performed in the $P\bar{1}$ space group. The asymmetric unit contained one molecule and titanium centre is also a distorted *cis*-*cis*-*trans* octahedral arrangement.



6 **9**

Figure 1 *Molecular structures of complexes **6** and **9**, hydrogen atoms are omitted for clarity and ellipsoids are at the 50% probability level.*



Scheme 3 *Synthetic pathway for the synthesis of dinuclear titanium picoliniminolate complex **11** and trinuclear titanium picoliniminolate complexes **12**-**14***

The reactions with picolinyl-(2'-fluorophenyl)amide and Ti(O*i*Pr)$_4$, yielded yellow single crystals of complex **11**, which were obtained after recrystallisation from toluene (**Scheme 4**). The molecular structure is shown in **Figure 2** and selected bond lengths are stated in **Table 1**. Complex **11** crystallised in a monoclinic cell and structural solution was performed in the *P*2$_1$/*c* space group, with half a molecule in the asymmetric unit.

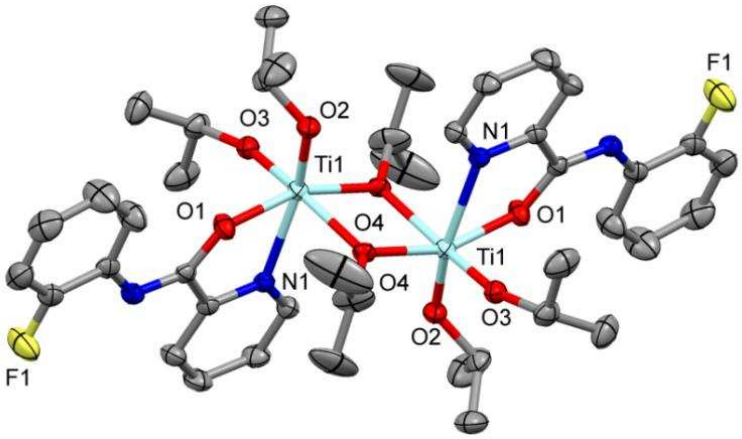


Figure 2 *Molecular structure of complex **11**. Hydrogen atoms are omitted for clarity and ellipsoids are at the 50% probability level.*

There are very few analogous complexes of this type and no crystal data to allow comparisons to be made.[22-25] The complex that closest resembles **11** is that of the dimeric methoxyethyl titanium structure $Ti_2(OCH_2CH_2OCH_3)_8$.[22] However, this structure was proposed based only on mass spectrometry data. It was synthesised as part of an investigation of solution routes to perovskite-phase mixed-metal oxides, in which bimetallic cluster complexes are a common product.[23-25]

Colourless single crystals were obtained from the reactions of Ti(O*i*Pr)$_4$ with picolinyl-(3-nitrophenyl)amide and picolinyl-(2-*t*butylphenyl)amide ligands (**Scheme 3**). These were recrystallised from either petroleum ether at -20 °C or from toluene, yielding complexes **12** and **13** respectively. Complex **14** was synthesised according to **Scheme 4** and recrystallised from petroleum ether at -20 °C. These complexes all yield trinuclear titanium complexes, with one triply bridging μ-O and two doubly bridging μ-O*i*Pr groups. Two of the metal centres are bound to one picoliniminolate ligand each, whereas the third centre only binds two O*i*Pr substituents.

Complex **12** is a trinuclear titanium complex, with a triply bridged μ-O and two doubly bridged μ-O*i*Pr. Two of the metal centres are bound to one picoliniminolate ligand each, whereas the third centre is bound to two O*i*Pr substituents. Complex **12** crystallised in a triclinic cell and structural solution was performed in the $P\ \bar{1}$ space group. The asymmetric unit contained two molecules and the molecular structure is shown in **Figure 3** and selected bond lengths are stated in **Table 1**. This structure also contained a molecule of ethyl acetate in the unit cell, which was present from the recrystallization of the picolinyl-(3'-nitrophenyl)amide ligand.

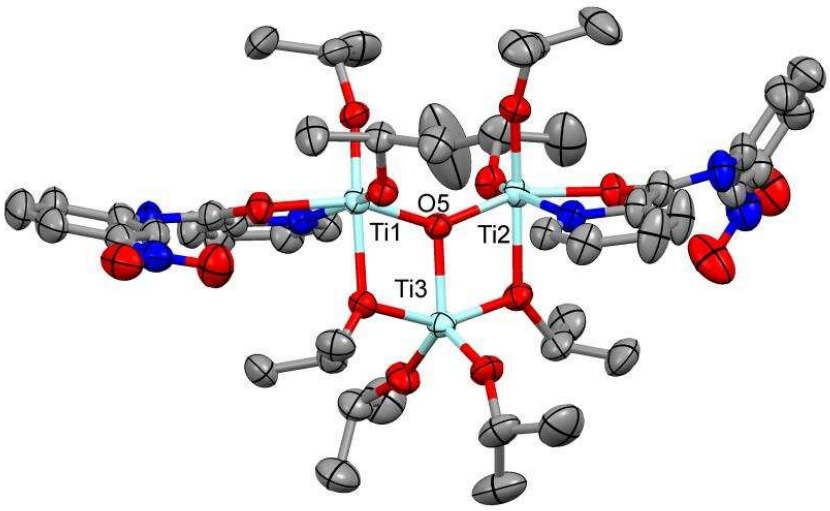


Figure 3 *Molecular structure of complex* ***12****, hydrogen atoms are omitted for clarity and ellipsoids are at the 50% probability level.*

Multi-centre titanium alkoxide compounds have shown to have applications in catalysis and supramolecular chemistry, for example, in the sol-gel process of preparing ceramic materials, where the hydrolysis and condensation of titanium(IV) alkoxides produces titanium(IV)-oxides.[26,27] Henry *et al.* have characterised various trinuclear titanium compounds using different alkyl and aryl ligands in a range of stoichiometries.[28,29] It was deduced from the studies that a co-solvent was required in order to produce crystals containing ligand. The ^{1}H NMR spectra of complex **12** suggests multiple picoliniminolate ligand environments, as seen between 9.87-6.24 ppm, but only one septet present for the O*i*Pr groups. However, the solid state crystal structure confirms a possibility of three environments for these O*i*Pr groups. Variable temperature NMR was recorded in order to calculate the coalescence rate of the methyl groups (OCH(C$\underline{H}_3$)$_2$). At 223 K the protons are observable as two separate resonances at 1.23 and 1.16 ppm. Upon warming to 323 K, the methyl groups now appear as a broad doublet; and raising the temperature further to 333 K shows the methyl groups as one broad single, this is the temperature of coalescence. The NMRs and calculations for exchange rate and Gibbs energy are shown in the *Supplementary Information* (**Figure S2**).

Complex **14** has a trinuclear structure and is isostructural with complex **12**. Complex **14** crystallised in a triclinic cell and structural solution was performed in the $P\ \bar{1}$ space group. The asymmetric unit contained two molecules and the molecular structure is shown in **Figure 4** and selected bond lengths are stated in **Table 1**. It was seen in the X-ray crystal structures and also by the absence of the amide proton in the ^{1}H NMR spectrum that the ligand binds to the metal as the tautomeric iminolate.

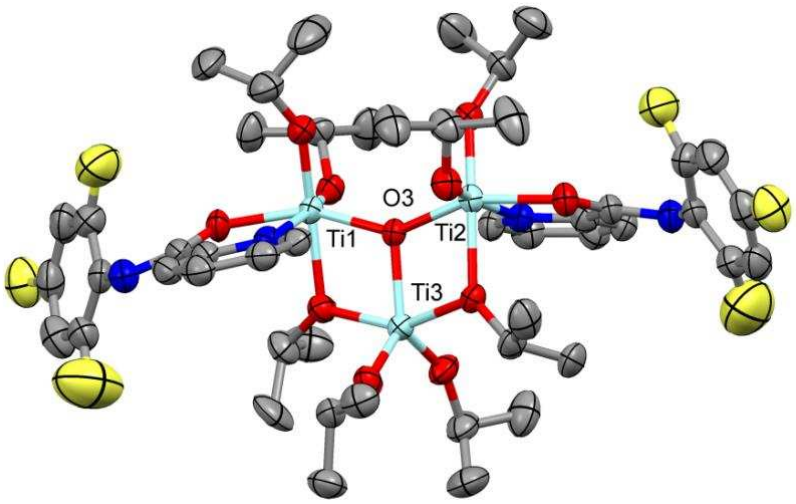


Figure 4 *Molecular structure of complex* ***14****, hydrogen atoms are omitted for clarity and ellipsoids are at the 50% probability level.*

Comparison of the dinuclear complex **11** and trinuclear titanium complexes **12** and **14**, with the mononuclear titanium complexes **6** and **9**, shows similar bond lengths of the Ti-O bond of the picoliniminolate ligands, but a slightly longer Ti-N bond length is observed for complexes **11**, **12** and **14**. Comparing the free picolinamide ligand to these titanium complexes shows that the free ligand has a C=O bond length of 1.21 Å, resulting from its double bond character. This bond is significantly elongated upon complexation, showing a C-O bond length ranging from 1.300(4)-1.343(3) Å. Consequently the *ipso* C-N bond length of 1.36 Å in the free ligand is shortened upon complexation to an *ipso* C=N bond length ranging from 1.287(4)-1.355(3) Å. This iminolate binding is for the first time observed for the picolinamide ligands, showing the Ti(O*i*Pr)$_4$ is a strong enough base to remove the acidic amide NH proton. Previously we have shown that the picolinamide ligands bind to the metal centre *via* an oxygen dative bond and are amides; here we see that these structures show the iminolate tautomer to bind upon metallation.

Table 1 *Selected bond lengths for complexes* ***6, 9, 11, 12*** *and* ***14***

	Mononuclear		**Dinuclear**	**Trinuclear**	
Bond Length	**6**	**9**	**11**	**12**	**14**
Ti-O(lig)	2.001(3)/ 1.992(3)	1.988(2)/ 1.963(2)	2.006(2)	2.0854(19)/ 1.995(2)	1.984(6)/ 1.985(5)
Ti-N(lig)	2.253(3)/ 2.268(3)	2.283(3)/ 2.281(2)	2.316(2)	2.290(2)/ 2.291(2)	2.298(6)/ 2.306(6)
Ti-O*i*Pr	1.791(3)/ 1.795(3)	1.805(2)/ 1.813(2)	1.829(2)/ 1.795(2)	1.772(2)/ 1.812(2) 1.772(2)/ 1.809(2) 1.771(2)/ 1.781(2)	1.809(5)/ 1.792(5) 1.789(5)/ 1.805(5) 1.761(5)/ 1.772(5)
Ti-μ-O*i*Pr	-	-	1.9986(19)	2.0854(19)/ 1.964(2) 2.087(2)/ 1.964(2)	2.088(5)/ 1.974(5) 2.082(5)/ 1.969(5)
Ti-μ-O	-	-	-	1.9612(19)/ 1.9515(19)/ 1.9715(19)	1.943(5)/ 1.968(5)/ 1.948(5)
C-O	1.317(4)/ 1.323(4)	1.339(3)/ 1.343(3)	1.324(3)	1.310(4)/ 1.300(4)	1.318(9)/ 1.306(9)
C-N	1.287(5)/ 1.298(5)	1.355(3)/ 1.292(3)	1.302(4)	1.287(4)/ 1.291(4)	1.292(10)/ 1.292(11)

Table 2 *Crystallographic data for complexes* ***6, 9, 11, 12*** *and* ***14***

Complex	**6**	**9**	**11**	**12**	**14**
Formula	$C_{30}H_{28}Cl_4N_4O_4Ti$	$C_{38}H_{48}N_4O_4Ti$	$C_{42}H_{58}F_2N_4O_8Ti_2$	$C_{48}H_{72}N_6O_{15}Ti_3 \cdot 0.1(C_4H_8O_2)$	$C_{48}H_{69}F_6N_4O_{11}Ti_3$
formula wt	698.26	672.7	880.72	1125.54	1135.77
cryst syst	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	9.8745(9)	8.3863(9)	12.7797(10)	12.4280(10)	13.3630(2)
b (Å)	24.040(2)	12.9525(14)	17.8904(16)	22.1490(2)	13.6320(2)
c (Å)	15.6525(13)	18.555(2)	10.1188(7)	23.3800(2)	17.5730(3)
α (°)	90.00	74.020(6)	90.00	72.7058(9)	70.3320(10)
β (°)	97.229(5)	80.440(6)	96.728(5)	78.2739(7)	68.4840(10)
γ (°)	90.00	81.490(6)	90.00	89.9250(6)	70.7310(10)
V (Å³)	3686.0(6)	1899.6(4)	2297.6(3)	6004.36(9)	2725.28(8)
Z	4	2	2	4	2
density (mg/m³)	1.489	1.176	1.724	1.245	1.384
absorp coeff (mm⁻¹)	0.558	0.267	0.441	0.453	0.508
λ[Mo−Kα] (Å)	0.71073	0.71073	0.71073	071073	0.71073
T (K)	123(2)	150(2)	273(2)	173(2)	150(2)
reflns collected	92516	11910	21087	27453	11513
independent reflns	9612	5953	3609	20384	8546
R_1	0.0660	0.0839	0.0438	0.0538	0.1118
wR_2	0.2450	0.2305	0.1191	0.1699	0.3286
GOOF	1.049	1.031	1.032	1.043	1.337

Summary

This work reports new titanium picolinamide complexes from the reactions of picolinamide ligands with the titanium precursors, TiX_4 and $Ti(OiPr)_4$. X-ray crystallographic analysis has been obtained for mononuclear (**6**, **9**), dinuclear (**11**) and trinuclear (**12**, **14**) titanium picolinamide isopropoxide complexes. The provide insight into the possible intermediates formed in the reduction of amides using titanium precursors. Results show these reactions give multiple products, with variable control over the structural properties of the products obtained. The reactions with TiX_4 yield titanium complex in which the picolinamide ligand carbonyl group is bound datively to the metal centre. When using the basic $Ti(OiPr)_4$, the picolinamide NH proton is removed and the ligand binds in a cationic fashion, which is the first time this has been observed for this ligand. These modes of binding have been confirmed by ^1H NMR and X-ray crystallographic analysis, in which no NH is observed and the bond lengths of the carbonyl C-O and *ispo* C-N can be seen to lengthen and shorten respectively. Research is been undertaken to optimise the conditions for these reactions, in order to provide higher yields and allow catalytic reactions to be studied.

Experimental

Materials

All ligand preparation were conducted using standard air-stable techniques, whilst all complex preparations were conducted using standard Schlenk line techniques under an inert atmosphere of dry N_2 using a dual vacuum/N_2 line or in a Braun Labmaster 100 glove box. Dry N_2 was obtained by passing N_2 gas through a double column of self-indicating phosphorus pentoxide and activated 4 Å molecular sieves. Solvents were pre-dried over the appropriate drying agent and distilled under an inert atmosphere of dry N_2. Chemicals were obtained from Sigma-Aldrich Chemical Co., Lancaster Synthesis Ltd., Acros Organics, Strem Chemical Co., BOC gases and the Department of Chemistry Breached Bottle Store. Unless otherwise stated these were used as received. Deuterated NMR solvents were purchased from GOSS Scientific Ltd. or Apollo Scientific Ltd. and were used as purchased or dried using the appropriate drying agent.

Analysis

All NMR spectra were recorded on a Bruker ARX 250 spectrometer, a Bruker DPX 300 spectrometer, a Bruker DRX 500 spectrometer or a Bruker DRX 500 spectrometer. Microanalyses were recorded at the University of Leeds Microanalytical Service. Mass Spectra were recorded on a Micromass ZMD spectrometer with electrospray ionisation and photoiodide array analyser at the University of Leeds Mass Spectrometry Service.

X-ray Crystallography

A suitable single crystal was selected and immersed in an inert oil. The crystal was then mounted on a glass capillary or nylon loop and attached to a goniometer head on a Nonius KappaCCD area detector diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073Å), using 1.0° ϕ-rotation frames. The crystal was cooled to between 123(2)-273(2) K by an Oxford Cryostream low temperature device.[30] The full data sets were recorded and the images processed using DENZO and SCALEPACK programs[31] or CrysAlis Pro software.[32]

Structure solution by direct methods was achieved through the use of SHELXS programs,[33] and the structural model refined by full matrix least squares on F^2 using SHELX97 Unless otherwise stated, hydrogen atoms were placed using idealised geometric positions (with free rotation for methyl groups), allowed to move in a "riding model" along with the atoms to which they were attached, and refined isotropically. Molecular graphics were plotted using Mercury[34] and Olex2.[35] Editing of CIFs and construction of tables of bond lengths and angles were achieved using PLATON.

Synthesis of $Ti(C_{12}H_9N_2OF)Cl_2(OCH_3)_2$ (1). To $TiCl_4$ (0.10 mL, 0.91 mmol) in toluene at -78°C was added picolinyl-(4-fluorophenyl)amide (0.45 g, 2.09 mmol) in toluene drop-wise. The mixture was warmed to room temperature and stirred for 16 hours. The suspension was filtered and the orange solid dried *in vacuo* and recrystallised from dry methanol at -20°C. **Yield:** 60.0 mg, 0.15 mmol, 17%. **ES MS (+):** m/z 354.9 $[M\text{-}2OMe+Na]^+$. **Anal. Found:** C 42.4; H 3.6; N 7.2%. **Anal. Calculated for $C_{14}H_{15}Cl_2FN_2O_3Ti$:** C 42.4; H 3.8; N 7.0%. **^{1}H NMR** (MeOD, 300.13 MHz, 300K) δ 8.86 [s, 1H], 8.47 [d, 1H, $^3J(^1H\text{-}^1H)$ = 7.8 Hz], 8.35 [m, 1H], 7.86 [m, 3H], 7.18 [m, 2H], 3.35 [m, 6H]. **$^{13}C\{^1H\}$ NMR** (MeOD, 75.48 MHz, 300K) δ 163.3 [Q, d, $^2J(^{13}C\text{-}^{19}F)$ = 18.1 Hz], 160.0 [Q], 148.8 [CH], 142.0 [CH], 135.6 [Q], 129.2 [CH], 124.6 [CH], 124.3 [CH], 124.1 [CH], 117.1 [CH], 116.8 [CH].

Synthesis of 2 and 3. To $TiCl_4$ (1.00 mL, 9.12 mmol) in toluene at -78°C was added picolinyl-(2',4',6'-trimethylphenyl)amide (4.35 g, 18.4 mmol) in toluene drop-wise. The mixture was warmed to room temperature and stirred for 16 hours. The suspension was filtered and the yellow solid dried *in vacuo* and recrystallised from dry methanol. Pale blue crystals of **2** were obtained from vapour diffusion with ether and methanol at -20°C. The crude product was recrystallised from acetonitrile at -20°C yielding yellow crystals of the dimeric complex **3**.

$Ti(C_{15}H_{16}N_2O)Cl_2(OCH_3)_2$ (2). Yield: 2.58 g, 5.73 mmol, 63%. **ES MS (+):** m/z 375.1 $[M^{2+}\text{-}2Cl^-+Na]^+$, 381.1 $[M^{2+}\text{-}2OMe+Na]^+$. **Anal. Found:** C 48.3; H 5.0; N 6.8%. **Anal. Calculated for $C_{17}H_{22}Cl_2N_2O_3Ti$:** C 48.5; H 5.3; N 6.7%. **^{1}H NMR** (MeOD, 300.13 MHz, 300K) δ 8.75 [br. s, 1H], 8.28 [d, 1H, $^3J(^1H\text{-}^1H)$ = 7.5 Hz], 8.18 [d, 1H, $^3J(^1H\text{-}^1H)$ = 6.9 Hz], 7.74 [m, 1H], 6.96 [m, 2H], 3.35-3.28 [m, 6H, OCH_3], 2.23 [d, 9H, $^2J(^1H\text{-}^1H)$ = 23.1 Hz, $CH(CH_3)_3$]. **$^{13}C\{^1H\}$ NMR** (MeOD, 75.48 MHz, 300K) δ 164.2 [Q, C-O], 149.7 [Q], 148.8 [CH], 140.9 [CH], 138.4 [Q], 131.4 [Q], 130.2 [CH], 129.8 [CH], 128.5 [CH], 123.9 [CH], 49.9 [OCH_3], 21.0 [$CH(CH_3)_3$], 18.3 [$CH(CH_3)_3$].

$[Ti(C_{15}H_{16}Cl_3N_2O)]_2[\mu\text{-}O]$ (3). Yield: 16.3 mg, 0.02 mmol, 0.4%. **ES MS (+):** m/z 805.0 $[MH]^+$. **Anal. Found:** C 45.7; H 4.1; N 6.2%. **Anal. Calculated for $C_{30}H_{32}Cl_6N_4O_3Ti_2$:** C 44.8; H 4.0; N 6.7%. **^{1}H NMR** (d^6-DMSO, 300.13MHz, 300K) δ 10.12 [s, 2H, NH], 8.74[m, 2H], 8.21 [m, 2H], 8.00 [m, 2H], 7.61 [m, 2H], 6.92 [s, 4H], 2.26 [d, 6H, $^3J(^1H\text{-}^1H)$ = 3.6 Hz, $CH(CH_3)_3$], 2.19 [d, 6H, $^3J(^1H\text{-}^1H)$ = 3.6 Hz, $CH(CH_3)_3$]. **$^{13}C\{^1H\}$ NMR** (d^6-DMSO, 75.48MHz, 300K) δ 173.3 [Q, C-O], 148.1 [CH], 137.4 [CH], 126.2 [CH], 121.9 [$CH(CH_3)_3$], 20.1 [$CH(CH_3)_3$], 17.7 [$CH(CH_3)_3$].

Syntheis of $Ti(C_{12}H_9N_2O)_2(OC_3H_7)_2$ (4). To $Ti(^iOPr)_4$ (0.37 mL, 1.25 mmol) in toluene was added picolinyl-phenyl amide (0.5 g, 2.52 mmol) in toluene drop-wise. The mixture was heated under reflux for 16 hours and the solvent removed *in vacuo*. Petroleum ether was added and the mixture heated, cooled and then filtered. The resulting crude product was recrystallised from acetonitrile and stored at -20°C to yield colourless crystals of complex **4**.

Yield: 15.0 mg, 0.03 mmol, 2%. **ES MS (+):** m/z 561.2 $[MH]^+$. **Anal. Found:** C 64.3; H 5.2; N 11.1%. **Anal. Calculated for $C_{30}H_{32}N_4O_4Ti$:** C 64.3; H 5.8; N 10.2%. **^{1}H NMR** (C_6D_6, 300.13 MHz, 300K) δ 8.47 [m, 2H], 8.34 [m, 4H], 7.58 [m, 4H], 7.25 [m, 4H], 6.79 [m, 2H], 6.28 [m, 2H], 4.78 [m, 2H, C<u>H</u>$(CH_3)_2$], 1.36 [s, 6H, CH$(C\underline{H}_3)_3$], 1.29 [s, 6H, CH$(C\underline{H}_3)_3$]. **^{13}C{^{1}H} NMR** (C_6D_6, 125.76 MHz, 300K) δ 161.4 [Q, <u>C</u>-O], 155.7 [Q], 145.6 [<u>C</u>H], 138.5 [<u>C</u>H], 137.2 [<u>C</u>H], 129.1 [<u>C</u>H], 128.8 [<u>C</u>H], 127.7 [<u>C</u>H], 126.3 [<u>C</u>H], 126.2 [<u>C</u>H], 125.9 [<u>C</u>H], 124.4 [<u>C</u>H], 123.8 [<u>C</u>H], 119.5 [<u>C</u>H], 79.5 [<u>C</u>H$(CH_3)_2$], 25.3 [CH$(\underline{C}H_3)_2$].

Synthesis of 5 and 11. To Ti(^{i}OPr)$_4$ (0.34 mL, 1.15 mmol) in toluene was added picolinyl-(2-fluorophenyl)amide (0.50 g, 2.31 mmol) in toluene drop-wise. The mixture was heated under reflux for 16 hours and the solvent removed *in vacuo*. Petroleum ether was added and the mixture heated, cooled and then filtered. The crude product was recrystallised from acetonitrile and stored -20°C to give yellow crystalline product of complex **5**. The remaining residue was recrystallised from toluene to give colourless crystals of complex **11**.

Ti($C_{12}H_8FN_2O)_2(OC_3H_7)_2$ (5). **Yield:** 390 mg, 0.65 mmol, 57%. **ES MS (+):** m/z 597.16 $[MH^+]$. **Anal. Found:** C 61.3; H 4.5; N 11.1%. **Anal. Calculated for $C_{30}H_{30}F_2N_4O_4Ti\cdot(C_2H_3N)$:** C 60.7; H 5.3; N 10.8%. **^{1}H NMR** (C_6D_6, 300.13 MHz, 300K) δ 10.66 [br. s, 1H] 9.16 [m, 1H], 8.65 [d, 1H, $^3J(^1H\text{-}^1H)$ = 6.0 Hz], 8.30 [m, 2H], 8.17 [m, 1H], 8.06 [m, 1H], 7.18 [m, 1H], 7.09 [m, 1H], 7.03-6.69 [m, 5H], 6.67 [m, 1H], 6.45 [m, 1H], 4.68 [m, 2H, C<u>H</u>$(CH_3)_2$], 1.23 [d, 6H, $^3J(^1H\text{-}^1H)$ = 6.1 Hz, CH$(C\underline{H}_3)_2$], 1.19 [d, 6H, $^3J(^1H\text{-}^1H)$ = 6.1 Hz, CH$(C\underline{H}_3)_2$]. **^{13}C{^{1}H} NMR** (C_6D_6, 125.76 MHz, 300K) δ 162.0 [Q, <u>C</u>-O], 160.5 [Q], 156.5 [Q, <u>C</u>-F, d, $^1J(^{13}C\text{-}^{19}F)$ = 175.9 Hz], 155.1 [Q], 153.2 [Q, <u>C</u>-F, d, $^1J(^{13}C\text{-}^{19}F)$ = 238.8 Hz], 150.2 [<u>C</u>H], 148.1 [<u>C</u>H], 138.9 [<u>C</u>H], 137.3 [<u>C</u>H], 126.3 [<u>C</u>H], 125.7 [<u>C</u>H], 125.0 [<u>C</u>H], 124.2 [<u>C</u>H], 122.4 [<u>C</u>H], 121.4 [<u>C</u>H], 116.2 [<u>C</u>H, d, $^2J(^{13}C\text{-}^{19}F)$ = 18.8 Hz], 114.9 [<u>C</u>H, d, $^2J(^{13}C\text{-}^{19}F)$ = 18.9 Hz], 80.0 [<u>C</u>H$(CH_3)_2$], 25.2 [CH$(\underline{C}H_3)_2$]

[$(C_{12}H_9FN_2O)Ti(OC_3H_7)_2]_2[\mu\text{-}OC_3H_7]_2$ (11). **Yield:** 60.7 mg, 0.07 mmol, 12%. **ES MS (+):** 883.34 m/z $[MH^+]$. **Anal. Found:** C 57.0; H 6.8; N 6.5%. **Anal. Calculated for $C_{42}H_{60}F_2N_4O_8Ti$:** C 57.2; H 6.9; N 6.4%. **^{1}H NMR** (C_6D_6, 300.13 MHz, 300K) δ 8.39 [d, 2H, $^3J(^1H\text{-}^1H)$ = 6.0Hz] 8.23 [m, 6H], 7.21 [m, 2H], 6.82 [m, 2H], 6.28 [m, 2H], 4.74 [m, 2H, C<u>H</u>$(CH_3)_2$], 1.31 [d, 6H, $^3J(^1H\text{-}^1H)$ = 6.0 Hz, CH$(C\underline{H}_3)_2$], 1.22 [d, 6H, $^3J(^1H\text{-}^1H)$ = 6.0 Hz, CH$(C\underline{H}_3)_2$]. **^{13}C{^{1}H} NMR** (C_6D_6, 75.47 MHz, 300K) δ 160.3 [Q, <u>C</u>-O], 155.9 [Q], 146.0 [<u>C</u>H], 139.1 [<u>C</u>H], 125.7 [<u>C</u>H], 124.0 [<u>C</u>H], 115.8 [<u>C</u>H, d, $^2J(^{13}C\text{-}^{19}F)$ = 15.1 Hz], 80.1 [<u>C</u>H$(CH_3)_2$], 25.8 [CH$(\underline{C}H_3)_2$]

Synthesis of Ti($C_{12}H_7Cl_2N_2O)_2(OC_3H_7)_2$ (6). To Ti(^{i}OPr)$_4$ (0.11 mL, 0.37 mmol) in toluene was added picolinyl-(2',5'-dichlorophenyl)amide (0.20 g, 0.75 mmol) in toluene drop-wise. The mixture was heated under reflux for 16 hours and the solvent removed *in vacuo*. Petroleum ether was added and the mixture heated, cooled and then filtered. The resulting petroleum ether mixture was stored at -20°C to give crystals suitable for X-ray crystallography. **Yield:** 251 mg, 0.36 mmol, 97%. **ES MS (+):** m/z 698.05 $[MH]^+$. **Anal. Found:** C 51.6; H 4.8; N 7.8%. **Anal. Calculated for $C_{30}H_{28}Cl_4N_4O_4Ti$:** C 51.6; H 4.1; N 8.0%. **^{1}H NMR** (C_6D_6, 300.13 MHz, 300K) δ 8.87 [d, 2H, $^3J(^1H\text{-}^1H)$ = 6.0 Hz] 8.32 [d, 2H, $^3J(^1H\text{-}^1H)$ = 6.0 Hz], 7.35 [d, 4H, $^3J(^1H\text{-}^1H)$ = 9.0 Hz], 6.81 [m, 2H], 6.68-6.58 [m, 4H], 4.53 [m, 2H, C<u>H</u>$(CH_3)_2$], 1.12 [d, 12H, $^3J(^1H\text{-}^1H)$ = 6.1 Hz, CH$(C\underline{H}_3)_2$]. **^{13}C{^{1}H} NMR** (C_6D_6, 125.76 MHz, 300K) δ 161.6 [Q, <u>C</u>-O] 153.5 [Q], 146.5 [<u>C</u>H], 146.1 [<u>C</u>H], 139.3 [<u>C</u>H], 137.3 [Q], 127.6 [<u>C</u>H$(CH_3)_2$], 126.3 [<u>C</u>H], 124.3 [<u>C</u>H], 123.6 [<u>C</u>H], 122.9 [<u>C</u>H], 80.4 [<u>C</u>H], 22.8 [CH$(\underline{C}H_3)_2$]

Synthesis of 7 and 12. To Ti(^{i}OPr)$_4$ (0.31 mL, 1.05 mmol) in toluene was added picolinyl-(3'-nitrophenyl)amide (0.50 g, 2.06 mmol) in toluene drop-wise. The mixture was heated under reflux for 16 hours and the solvent removed *in vacuo*. Petroleum ether was added and the mixture heated, cooled and then filtered. The resulting petroleum ether mixture was stored at -20°C to give yellow crystals of complex **7**. The remaining residue was recrystallised from toluene to give a colourless crystals of complex **12**.

Ti($C_{12}H_8N_3O_3$)$_2$(OC_3H_7)$_2$ (7). **Yield:** 92.0 mg, 0.14 mmol, 13%. **Anal. Found:** C 54.3; H 4.5; N 13.0%. **Anal. Calculated $C_{30}H_{30}N_6O_8Ti$:** C 55.4; H 4.7; N 12.9%. **^{1}H NMR** (C_6D_6, 300.13 MHz, 300K) δ 9.29 [d, 2H, ^3J(^{1}H-^{1}H) = 2.1 Hz] 8.39 [d, 2H, ^3J(^{1}H-^{1}H) = 5.2 Hz], 8.23 [d, 2H, ^3J(^{1}H-^{1}H) = 7.9 Hz], 8.09 [m, 2H], 7.91 [m, 2H], 7.20 [m, 2H], 6.79 [m, 2H], 6.33 [m, 2H], 4.81 [m, 2H, C<u>H</u>(CH$_3$)$_2$], 1.32 [d, 6H, ^3J(^{1}H-^{1}H) = 6.1 Hz, CH(C<u>H</u>$_3$)$_2$], 1.24 [d, 6H, ^3J(^{1}H-^{1}H) = 6.1 Hz, CH(C<u>H</u>$_3$)$_2$]. **^{13}C{^{1}H} NMR** (C_6D_6, 125.76 MHz, 300K) δ 161.8 [Q, <u>C</u>-O], 154.8 [C Q], 149.7 [Q], 145.7 [<u>C</u>H], 139.1 [<u>C</u>H], 132.2 [<u>C</u>H], 129.2 [<u>C</u>H], 127.6 [<u>C</u>H], 126.0 [<u>C</u>H], 120.4 [<u>C</u>H], 119.0 [<u>C</u>H], 80.9 [<u>C</u>H(CH$_3$)$_2$], 25.3 [CH(<u>C</u>H$_3$)$_2$]

[($C_{12}H_8N_3O_3$)Ti(OC_3H_7)]$_2$[OC_3H_7]$_2$[(OC_3H_7)$_2$Ti][μ-O] (12). **Yield:** 10.6 mg, 0.01 mmol, 3%. **ES MS (+):** m/z 1069.4 [MH]$^+$. **Anal. Found:** C 55.2; H 6.9; N 7.5%. **Anal. Calculated for $C_{48}H_{72}N_6O_{11}Ti_3$:** C 54.8; H 6.9; N 8.0%. **^{1}H NMR** (C_6D_6, 500.13 MHz, 300K) δ 9.21 [m, 1H] 8.39 [m, 1H], 8.01 [m, 1H], 7.84 [m, 1H], 7.57 [m, 3H], 6.24 [m, 1H], 4.72 [m, 1H, C<u>H</u>(CH$_3$)$_2$], 1.23 [d, 3H, ^3J(^{1}H-^{1}H) = 6.1 Hz, CH(C<u>H</u>$_3$)$_2$], 1.16 [d, 3H, ^3J(^{1}H-^{1}H) = 6.1 Hz, CH(C<u>H</u>$_3$)$_2$]. **^{13}C{^{1}H} NMR** (C_6D_6, 125.76 MHz, 300K) δ 162.6 [Q, <u>C</u>-O], 155.9 [Q], 149.6 [Q], 146.2 [<u>C</u>H], 132.7 [<u>C</u>H], 127.0 [<u>C</u>H], 125.2 [<u>C</u>H], 123.3 [<u>C</u>H], 119.1 [<u>C</u>H], 81.4 [<u>C</u>H(CH$_3$)$_2$], 25.9 [CH(<u>C</u>H$_3$)$_2$].

Synthesis of Ti($C_{12}H_8FN_2O$)$_2$(OC_3H_7)$_2$ (8). To Ti(^{i}OPr)$_4$ (0.34 mL, 1.15 mmol) in toluene was added picolinyl-(4-fluorophenyl)amide (0.5 g, 2.31 mmol) in toluene drop-wise. The mixture was heated under reflux for 16 hours and the solvent removed *in vacuo* and petroleum ether added. The mixture was heated until dissolution, cooled and then filtered. The resulting petroleum ether mixture was stored at -20°C to give only ligand. The residue was recrystallised from toluene at -20°C to yield complex **8**. **Yield:** 398 mg, 0.67 mmol, 58%. **ES MS (+):** 597.17m/z [MH$^+$]. **Anal. Found:** C 59.9; H 4.8; N 9.5%. **Anal. Calculated for $C_{30}H_{30}F_2N_4O_4Ti$:** C 60.4; H 5.1; N 9.4%. **^{1}H NMR** (C_6D_6, 300.13MHz, 300K) δ 8.38 [d, 2H, ^{3}J(^{1}H-^{1}H) = 6.0Hz, CH of C$_5$<u>H</u>$_4$N] 8.24 [m, 6H, CH of C$_6$<u>H</u>$_4$F & C$_5$<u>H</u>$_4$N], 7.21 [t of d, CH of C$_6$<u>H</u>$_4$F], 6.82 [t of d, 2H, CH of C$_5$<u>H</u>$_4$N], 6.28 [t of d, 2H, CH of C$_5$<u>H</u>$_4$N], 4.74 [sept., 2H, CH of OC<u>H</u>(CH$_3$)$_2$], 1.31 [d, 6H, ^{2}J(^{1}H-^{1}H) = 6.0Hz, CH of OCH(C<u>H</u>$_3$)$_2$], 1.22 [d, 6H, ^{2}J(^{1}H-^{1}H) = 6.0Hz, CH of OCH(C<u>H</u>$_3$)$_2$]. **^{13}C NMR** (C_6D_6, 75.47MHz, 300K) δ 160.3 [C of <u>C</u>ON], 155.9 [C of <u>C</u>$_5$H$_4$N], 146.0 [CH of <u>C</u>$_5$H$_4$N], 139.1 [CH of <u>C</u>$_6$H$_4$F], 125.7 [CH of <u>C</u>$_5$H$_4$N], 124.0 [CH of <u>C</u>$_5$H$_4$N], 115.9-115.7 [d, ^{2}J(^{13}C-^{19}F) = 15.1Hz, CH of <u>C</u>$_6$H$_4$F], 80.1 [CH of O<u>C</u>H(CH$_3$)$_2$], 25.8 [CH of OCH(<u>C</u>H$_3$)$_2$]

Synthesis of 9 and 13. To Ti(^{i}OPr)$_4$ (0.29 mL, 0.98 mmol) in toluene was added picolinyl-(2-tbutylphenyl)amide (0.50 g, 1.97 mol) in toluene drop-wise. The mixture heated under reflux for 16 hours under nitrogen and the solvent removed *in vacuo*. The crude product was recrystallised from acetonitrile and stored at -20°C to yield colourless crystals of complex **9**. The filtrate of these crystals also yielded colourless crystals of complex **13**.

$Ti(C_{16}H_{17}N_2O)_2(OC_3H_7)_2$ (9). Yield: 138 mg, 0.21 mmol, 21%. **ES MS (+):** m/z 673.3 $[MH]^+$. **Anal. Found:** C 65.7; H 6.7; N 9.5%. **Anal. Calculated for $C_{32}H_{48}N_4O_4Ti·0.5(C_2H_3N)$:** C 65.2; H 7.7; N 9.8%. **^{1}H NMR** (C_6D_6, 300.13 MHz, 300K) δ 8.56 [d, 2H, $^3J(^1H\text{-}^1H)$ = 5.1 Hz], 8.23 [m, 4H], 7.69 [m, 2H], 7.48 [m, 2H], 7.26 [m, 2H], 6.86 [m, 2H], 6.45 [m., 2H], 4.71 [m, 2H, C<u>H</u>$(CH_3)_2$], 1.86 [s, 18H, CH(C<u>H</u>$_3)_3$], 1.30 [d, 6H, $^3J(^1H\text{-}^1H)$ = 6.0 Hz, CH(C<u>H</u>$_3)_2$], 1.20 [d, 6H, $^3J(^1H\text{-}^1H)$ = 6.0 Hz, CH(C<u>H</u>$_3)_2$]. **$^{13}C\{^1H\}$ NMR** (C_6D_6, 125.76 MHz, 300K) δ 158.6 [Q, <u>C</u>-O], 156.0 [Q], 147.5 [<u>C</u>H], 146.4 [Q], 143.7 [<u>C</u>H], 139.3 [Q], 126.8 [<u>C</u>H], 126.3 [<u>C</u>H], 125.4 [<u>C</u>H], 124.4 [<u>C</u>H], 123.8 [<u>C</u>H], 79.9 [<u>C</u>H$(CH_3)_2$], 36.4 [Q, <u>C</u>$(CH_3)_3$)], 31.1 [C(<u>C</u>$H_3)_3$], 25.7 [<u>C</u>H$(CH_3)_2$].

$[(C_{16}H_{17}N_2O)Ti(OC_3H_7)_2]_2[\mu\text{-}OC_3H_7]_2[(OC_3H_7)_2Ti][\mu\text{-}O)$ (13). Yield: 66.6 mg, 0.06 mmol, 18%. **ES MS (+):** m/z 1138.5 $[MH]^+$. **Anal. Found:** C 58.7; H 6.7; N 6.7%. **Anal. Calculated for $C_{44}H_{62}N_4O_{11}Ti_3$:** C 58.5; H 6.9; N 6.2%. **^{1}H NMR** (C_6D_6, 500.13 MHz, 300K) δ 8.93 [m, 1H], 8.57 [m, 1H], 8.44 [m, 1H], 8.25 [m, 3H], 7.69 [m, 1H] 7.45 [m, 2H], 7.30 [m, 2H], 7.13 [m, 2H], 6.85 [m, 1H], 6.70 [m, 1H], 6.44 [m, 1H], 4.71 [m, 2H, C<u>H</u>$(CH_3)_2$], 1.86 [s, 9H, C(C<u>H</u>$_3)_3$], 1.55 [s, 9H, C(C<u>H</u>$_3)_3$], 1.30 [d, 6H, $^3J(^1H\text{-}^1H)$ = 6.0 Hz, CH(C<u>H</u>$_3)_2$], 1.21 [d, 6H, $^3J(^1H\text{-}^1H)$ = 6.0 Hz, CH(C<u>H</u>$_3)_2$]. **$^{13}C\{^1H\}$ NMR** (C_6D_6, 125.76 MHz, 300K) δ 147.7 [<u>C</u>H], 137.2 [<u>C</u>H], 127.0 [<u>C</u>H], 126.3 [<u>C</u>H], 125..6 [<u>C</u>H], 124.8 [<u>C</u>H], 122.5 [<u>C</u>H], 63.6 [<u>C</u>H$(CH_3)_2$], 30.3 [Q, <u>C</u>$(CH_3)_3$], 25.2 [C(<u>C</u>$H_3)_3$].

Synthesis of $Ti(C_{15}H_{15}N_2O)_2(OC_3H_7)_2$ (10). To $Ti(^iOPr)_4$ (0.31 mL, 1.04 mmol) in toluene was added picolinyl-(2',4',6'-trimethylphenyl)amide (0.50 g, 2.08 mmol) in toluene drop-wise. The mixture was heated under reflux for 16 hours and the solvent removed *in vacuo*. Petroleum ether was added and the mixture heated, cooled and then filtered. The resulting petroleum ether mixture was stored at -20°C to yield complex **13**. **Yield:** 115 mg, 0.18 mmol, 17%. **ES MS (+):** m/z 668.3 [M+Na]. **Anal. Found:** C 68.7; H 5.9; N 8.3%. **Anal. Calculated for $C_{36}H_{44}N_4O_4Ti·0.2(C_7H_8)$:** C 67.8; H 6.9; N 8.5%. **^{1}H NMR** (C_6D_6, 500.13 MHz, 300K) δ 9.33 [br. s, 2H], 8.32 [d, 2H, $^3J(^1H\text{-}^1H)$ = 4.7 Hz], 8.27 [m, 2H], 7.03 [m, 2H], 6.78 [m, 4H], 3.66 [m, 2H, C<u>H</u>$(CH_3)_2$], 2.23 [s, 12H, C(C<u>H</u>$_3)_3$], 2.13 [s, 6H, C(C<u>H</u>$_3)_3$], 0.95 [d, 12H, $^4J(^1H\text{-}^1H)$ = 3.7 Hz, CH(C<u>H</u>$_3)_3$]. **$^{13}C\{^1H\}$ NMR** (C_6D_6, 125.76MHz, 300K) δ 147.7 [<u>C</u>H], 137.0 [<u>C</u>H], 128.9 [<u>C</u>H], 127.6 [<u>C</u>H], 125.6 [<u>C</u>H], 122.4 [<u>C</u>H], 63.6 [<u>C</u>H$(CH_3)_2$], 25.2 [CH(<u>C</u>$H_3)_2$], 20.7 [C(<u>C</u>$H_3)_3$], 18.4 [C(<u>C</u>$H_3)_3$].

Synthesis $[(C_{12}H_6F_3N_2O)Ti(OC_3H_7)_2]_2[\mu\text{-}OC_3H_7]_2[(OC_3H_7)_2Ti][\mu\text{-}O]$ (14). To $Ti(^iOPr)_4$ (0.32 mL, 1.08 mmol) in toluene was added picolinyl-(2',4',6'-trifluorophenyl)amide (0.50 g, 2.10 mmol) in toluene drop-wise and the mixture heated under reflux for 16 hours and the solvent removed *in vacuo*. Petroleum ether was added and the mixture heated, cooled and then filtered. The resulting petrol mixture was stored at -20°C to give yellow crystals of complex **14** (This complex was too unstable to obtain good EA data). **Yield:** 133 mg, 0.15 mmol, 42%. **ES MS (+):** m/z 1098.3 $[M+2H]^{+\cdot}$ **^{1}H NMR** (C_6D_6, 300.13MHz, 300K) δ 8.55 [d, 1H, $^3J(^1H\text{-}^1H)$ = 5.4 Hz] 8.30 [d, 1H, $^3J(^1H\text{-}^1H)$ = 7.8 Hz], 8.04 [m, 1H], 7.02-6.81 [m, 3H], 6.78 [m, 1H], 4.67 [m, 1H, C<u>H</u>$(CH_3)_2$], 1.19 [d, 6H, $^3J(^1H\text{-}^1H)$ = 6.1 Hz, CH(C<u>H</u>$_3)_2$]. **$^{13}C\{^1H\}$ NMR** (C_6D_6, 125.76 MHz, 300K) δ 161.4 [Q, <u>C</u>-O], 160.5 [Q], 156.7 [Q, <u>C</u>-F, d, $^1J(^{13}C\text{-}^{19}F)$ = 260.3 Hz], 154.6 [Q], 150.0 [<u>C</u>H], 145.8 [<u>C</u>H], 139.0 [<u>C</u>H], 133.7 [<u>C</u>H, d, $^3J(^{13}C\text{-}^{19}F)$ = 3.7 Hz], 126.7 [<u>C</u>H], 126.2 [<u>C</u>H], 125.7 [<u>C</u>H], 124.1 [<u>C</u>H], 122.4 [<u>C</u>H], 111.2 [<u>C</u>H, d, $^2J(^{13}C\text{-}^{19}F)$ = 90.5 Hz], 104.3 [<u>C</u>H], 80.1 [<u>C</u>H$(CH_3)_2$], 25.2 [CH(<u>C</u>$H_3)_2$].

Appendix A. Supplementary data

CCDC 1455809-1455812 and 1455814 contains the supplementary crystallographic data for complexes **6**, **9**, **11**, **12** and **14**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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