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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.

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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 molecules have been characterized by X-ray crystallographic analysis and structural characteristics are discussed.

1. 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 been 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 mild reaction conditions for the reduction of amides to aldehydes [9], with up to 90% isolated yields. However, further analysis showed the product to be a mixture of the aldehyde and carbinol products. 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 beyond 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 reported ruthenium, rhodium and iridium picolinamide complexes in the development of anti-cancer drugs, with high cytotoxicities against a range of tumours [17–19]. We have also reported the use of aluminium picolinamides for the ring-opening polymerization of *rac*-lactide in the preparation of colored polymeric materials [20] and picolinamide ligands as effective ligands for copper-catalyzed aryl ether formation [21]. Herein, we report the reactions of picolinamide ligands with titanium(IV) precursors and discuss their structural properties. 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 species. The products obtained are analytically pure and fully characterized by NMR, mass spectrometry and elemental analysis, and their structures have been confirmed by X-ray crystallographic analysis.

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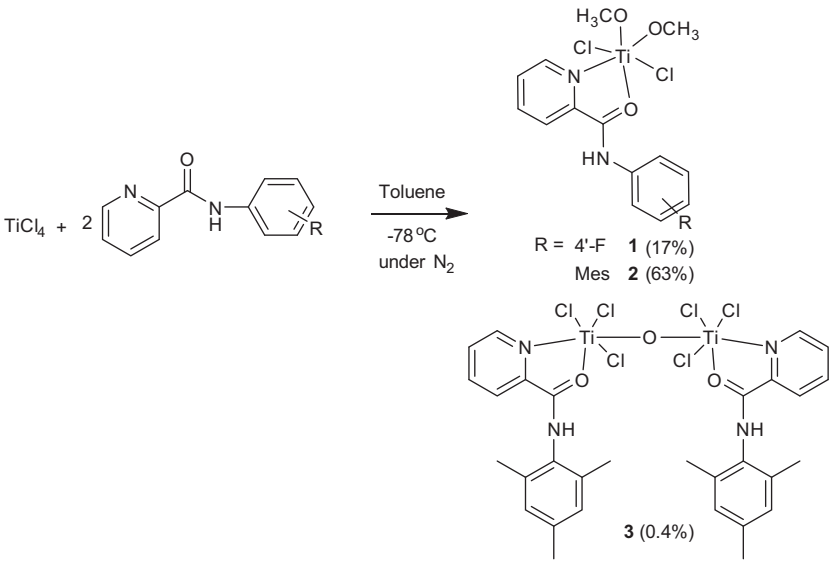
2. Results and discussion

In attempts to synthesis titanium complexes of the type TiL_2X_2, two equivalents of L (picolinamide ligand) were reacted with one equivalent of a titanium salt. Reactions were carried out with $TiCl_4$ and addition of either (i) an electron-withdrawing ligand, picolinyl-(4′-fluorophenyl)amide, or (ii) an 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 h, the suspension filtered and the product 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.

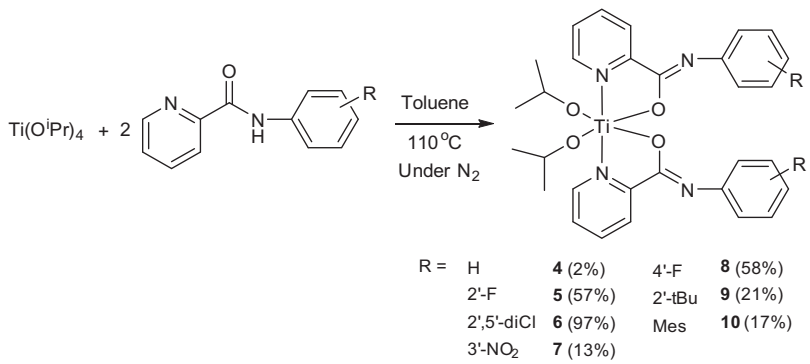
Upon analysis of the ^{1}H NMR spectra for complexes **1** and **2**, a single resonance was observed in the range of 3.35–3.28 ppm. This corresponds to the methoxy groups, which were later confirmed by X-ray crystallographic analysis. The complexes were recrystallized from methanol and due to the titanium having a higher affinity for oxygen, the chloride ligands are hydrolyzed by methanol and substituted for methoxy ligands. It is postulated that a dimer similar to complex **3** is formed before recrystallization; however, there was insufficient data 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. The crystal data for complexes **2**–**3** were not fully resolved, but the bond lengths showed the double bond character of the carbonyl C═O (1.255 (2)–1.264(4) Å) and the single bond character of the *ipso* C—N (1.316(5)–1.319(3) Å). This evidence suggests that these ligands bind to the titanium centre as the protonated amide, and is one of the possible binding modes observed for these ligands. Other metal picolinamide complexes show the ligand bound as either *N*,*O* or *N*,*N*, in which the nitrogen is deprotonated [17–19].

Further reactions were carried out according to Scheme 2, in which two equivalents of a functionalized picolinamide ligand in toluene were added to $Ti(OiPr)_4$ in toluene. After reflux for 16 h and addition of petroleum ether, the solutions were stored at −20 °C, yielding analytically pure products in yields ranging from 2% to 97%. The ^{1}H NMR spectra of complexes **4**–**10** show no broad NH resonance in the region of 10.5–10.0 ppm and the iminolate binding mode of the ligand is observed, this was confirmed by X-ray crystallographic analysis.

Single crystals were obtained for complexes **6** and **9**; the molecular structures are shown in Fig. 1 and selected bond lengths are stated in Table 1. Complex **6** crystallized in a monoclinic cell with structural solution performed in the $P2_1/c$ space group, whilst



Scheme 1. Synthetic route to mononuclear and dinuclear titanium picolinamide complexes **1**–**3**.



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