



Synthesis and catalytic activity of dinuclear imido titanium complexes: the molecular structure of $[\text{Ti}(\text{NPh})\text{Cl}(\mu\text{-Cl})(\text{THF})_2]_2$

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Abstract

Reaction of TiCl_4 with the reagents $\text{RN}(\text{SiMe}_3)_2$ in dichloromethane precipitates red to black powders ($\text{R} = 1\text{-adamantyl}$, phenyl, pentafluorophenyl, 3,5-bis(trifluoromethyl)phenyl), which on treatment with tetrahydrofuran gives the new THF adducts $[\text{Ti}(\text{NR})\text{Cl}(\mu\text{-Cl})(\text{THF})_2]_2$. The complexes are dimeric in the solid state with bridging chloride and terminal imido ligands. Activation with MAO (methylaluminoxane) gives ethene polymerisation catalysts with productivities of up to 31 kg PE $[\text{mol complex h bar}]^{-1}$.

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1. Introduction

Metal imido complexes are known to adopt a number of structural motifs [1]. For example, titanium forms complexes in which imido ligands adopt either bridging (for example **I**, Chart 1) [2] or terminal (**II**) [3] bonding modes [4]. We recently reported the synthesis and structure of $[\text{Ti}(\mu\text{-NAr}^P)\text{Me}_2(\text{THF})_2]$ (**III**) ($\text{Ar}^P = m\text{-C}_6\text{H}_4\text{P}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_2$) in which the imido ligand is bridging [5]. This result contrasts with Nielson's 2-*tert*-butyl- (**IV**) and 2-phenyl-phenylimido complexes which form chloride-bridged dimers [6] and Carmalt's exclusively chloride-bridged tetramer (**V**) [7]. In the absence of basic co-ligands structures with even higher nuclearity have been observed [8–10]. We continue to be interested in the factors dictating whether the imido ligand adopts a bridging or terminal bonding mode and the implica-

tions for alkene polymerisation catalysis using titanium imido precatalysts [6,11]. We report here the synthesis, structure and polymerisation activity of compounds of the type $[\text{Ti}(\text{NR})\text{Cl}_2(\text{THF})_2]$.

2. Results and discussion

Most commonly imidotitanium complexes are prepared through an imido exchange reaction between $[\text{Ti}(\text{NBu}^t)\text{Cl}_2(\text{L})_x]$ and the corresponding primary amine [6]. We chose to employ an alternative dehalosilylation methodology in order to access the base-free compounds [12]. The ligand precursors $\text{RN}(\text{SiMe}_3)_2$ (**1a–g**) were readily prepared by the step-wise deprotonation of the parent amine and reaction with trimethylsilylchloride (Scheme 1). Treating TiCl_4 with **1a–d** in dichloromethane solution led to the precipitation of sparingly soluble red to black solids (Scheme 2). Unfortunately the poor solubility of these crude materials in non-basic

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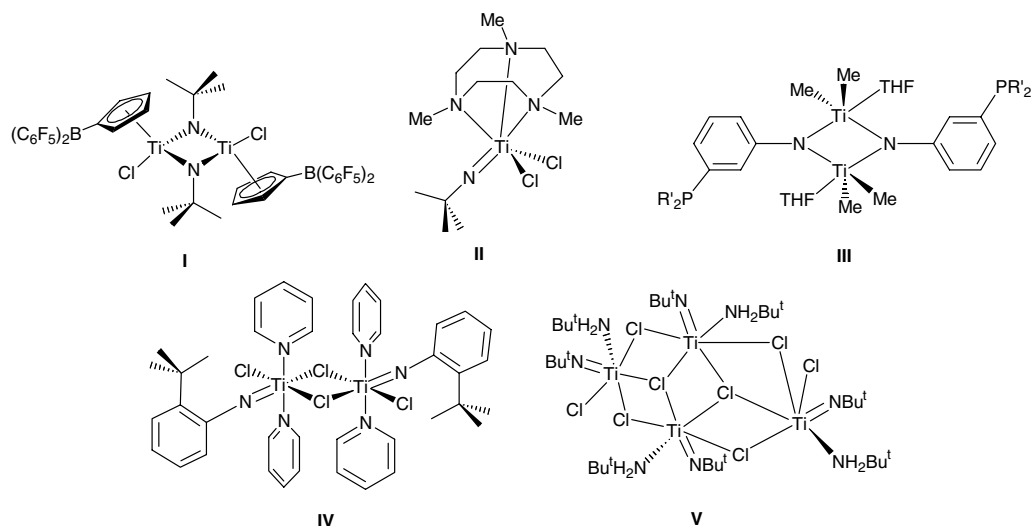


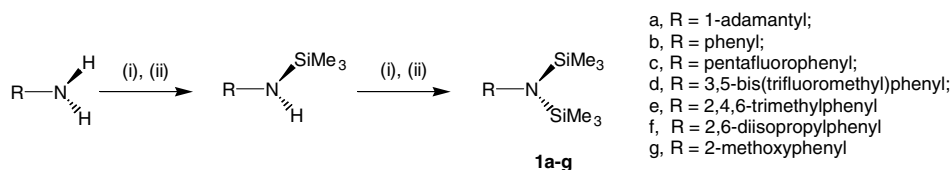
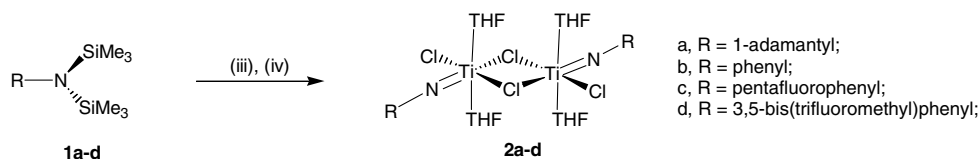
Chart 1.

solvents, which presumably reflects high nuclearity, precluded spectroscopic characterisation or attempts to obtain X-ray quality crystals. However, the solids reacted exothermically on dissolution in tetrahydrofuran and could be isolated as THF adducts **2a–d** on crystallisation from THF/light petroleum mixtures. ^1H NMR spectroscopy of **2a–d** confirmed that quantitative dehalosilylation had taken place and indicated a ligand RN:THF ratio of 1:2, which was supported by the elemental analysis. This composition differs from that observed for $[\text{Ti}(\mu\text{-NAr}^P)\text{Cl}_2(\text{THF})_2]$ where the ligand RN:THF ratio is 1:1 [5], but is consistent with a formulation analogous to complex **IV**, which has a chloride-bridged structure with terminal imido ligands. While the dehalosilylation route is effective for the introduction of *meta*-substituted aryl imido ligands, the *ortho* disubstituted reagents **1e** and **1f** failed to react with TiCl_4 , even after refluxing in toluene, presumably as a consequence of steric encumbrance. However, the mononuclear complex $[\text{Ti}(\text{NAr}^R)\text{Cl}_2(\text{py})_3]$ ($\text{Ar}^R = 2,6\text{-diisopropylphenyl}$, $\text{py} =$

pyridine) is accessible through an imido exchange reaction [3c]. The *o*-OMe compound **1g** reacted with TiCl_4 but the resulting product was intractable and could not be isolated even after treatment with THF.

The structure of **2b** (Fig. 1) was determined by X-ray crystallography and confirmed as a chloride-bridged dimer with two edge-sharing octahedral metal coordination spheres. Each distorted octahedron is completed by terminal chloride and imido ligands opposite the bridging chlorides and two mutually *trans* THF ligands. The geometry resembles the 2-*tert*-butylphenyl imido complex **IV**, which has *trans* pyridine ligands.

Selected bond lengths and angles for complex **2b** are shown in Table 1. While the terminal imido bond length is insensitive to the differences between **2b**, **IV** and the mononuclear complex $[\text{Ti}(\text{NC}_6\text{H}_5)\text{Cl}_2(\text{py})_3]$ at 1.710(2), 1.702(2) and 1.714(2) Å, respectively, the Cl–N1–Ti1 angle decreases from the almost linear, 177.5(2)°, in $[\text{Ti}(\text{NC}_6\text{H}_5)\text{Cl}_2(\text{py})_3]$ to 167.5(2)° in **2b** and 165.9(2)° in **IV**, which reflects the increase in steric crowding.

Scheme 1. Reagents and conditions: (i) *n*-BuLi, THF, -78°C to room temperature; (ii) SiClMe_3 , THF, -78°C to room temperature.Scheme 2. Reagents and conditions: (iii) TiCl_4 , CH_2Cl_2 , room temperature; (iv) tetrahydrofuran, room temperature.

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