

Short communication

Titanium complexes based on pyridine containing dialcohols: Effect of a ligand



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ABSTRACT

Substituted 2,6-bis(hydroxyalkyl)pyridines, **H₂L**, **1–3** (2,6-Py(CH₂(X)OH)(CH₂(Y)OH), X = Y = cyclo-C₆H₁₀, **1**; X = Y = 1-Ad, **2**; X = CPh₂, Y = CH₂CPh₂, **3**), were used as ligands for the synthesis of titanium(IV) complexes, (i-PrO)₂Ti(L), **1a–3a**. On the contrary, application of related dialcohol based on 2,2'-bipyridine, **H₂L'**, **5** (2,2'-bipy-6,6'-(CH₂Ph₂OH)₂), resulted in titanyl complex, (L')Ti=O, **6**. The molecular structure of **6** was investigated by X-ray analysis. Compounds **1a** and **3a** were tested as initiators in ring-opening polymerization of L-lactide and ε-caprolactone showing moderate activity.

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Nowadays titanium complexes based on polydentate ligands, such as amino alcohols, find wide application in chemistry, for example, as precursors for ceramic materials using sol–gel [1] or MOCVD techniques [2], catalysts for organic reactions [3], cytotoxic compounds [4], in synthesis of oligomeric complexes [5] or initiators in polymerization of lactones [6] or polymerization of alkenes [7]. Therefore, an investigation of these compounds may be regarded as an actual scientific subject.

General approach for the synthesis of titanium(IV) oxo-alkoxides consists in partial hydrolysis followed by dehydration and dealkoxylation of intermediate Ti alkoxides [8]. However, this method does not allow predicting the structure of oxo-alkoxide product. It was found for secondary Ti alkoxides that sometimes the oxo-fragment may be formed in water-free conditions at high temperature evolving ethers [9], chloroalkanes or ketones [10], alkene [11]. In this case, the product structure strongly depends on ligand structure. The mechanism of this transformation has not been fully understood yet, but the initial skepticism about oxo-fragment formation under stringently anhydrous conditions has gradually been dispelled.

Pyridine containing dialcohols were used earlier as ligands for the synthesis of titanium complexes [12] and stabilized germynes and stannylenes [13]. In this work three pyridine dialcohols with

voluminous substituents, **1** [14], **2** [15], and **3** [16] were used for the synthesis of titanium(IV) complexes (Scheme 1).

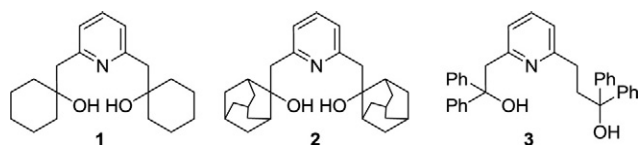
Our goal was to investigate how switching from pyridine to 2,2'-bipyridine fragment will influence the structure and reactivity of titanium complexes. From structural viewpoint the additional nitrogen donor atom can lead to more effective stabilization of complexes in the monomeric form which is essential for ring-opening polymerization (ROP) catalysis in accordance with the “single-site catalyst” concept. For the synthesis of **5** we used a method which is similar for the synthesis of known compounds **1** and **2**. The method somewhat differed from that used for the synthesis of **4** and **5** by Kellogg and co-workers [17]. Our approach includes two-step synthesis with isolation of intermediate product **4** and the application of *n*-BuLi as lithiating agent instead of LDA (Scheme 2). Isolation of monosubstituted product **4** is useful for subsequent modifications.

Compounds **4** and **5** were isolated as white solids in moderate yields. The structure of tetradentate ligand **5** in the solid state was investigated by X-ray analysis. This molecule exists in transoid conformation with strong intramolecular hydrogen bonds (Fig. 1; Supporting Information, Table S1).

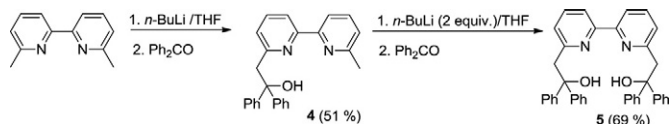
Transesterification reaction [3a,12,18] was carried out between corresponding ligands **1–3** and Ti(O-*i*-Pr)₄ in toluene at room temperature to synthesize complexes **1a–3a** (Scheme 3). These compounds were obtained in analytically pure form without admixtures of the corresponding bis-ligated species due to more rigid structure of the ligands.

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Scheme 1. Structures of ligands 1–3.



Scheme 2. The synthesis of ligand 5.

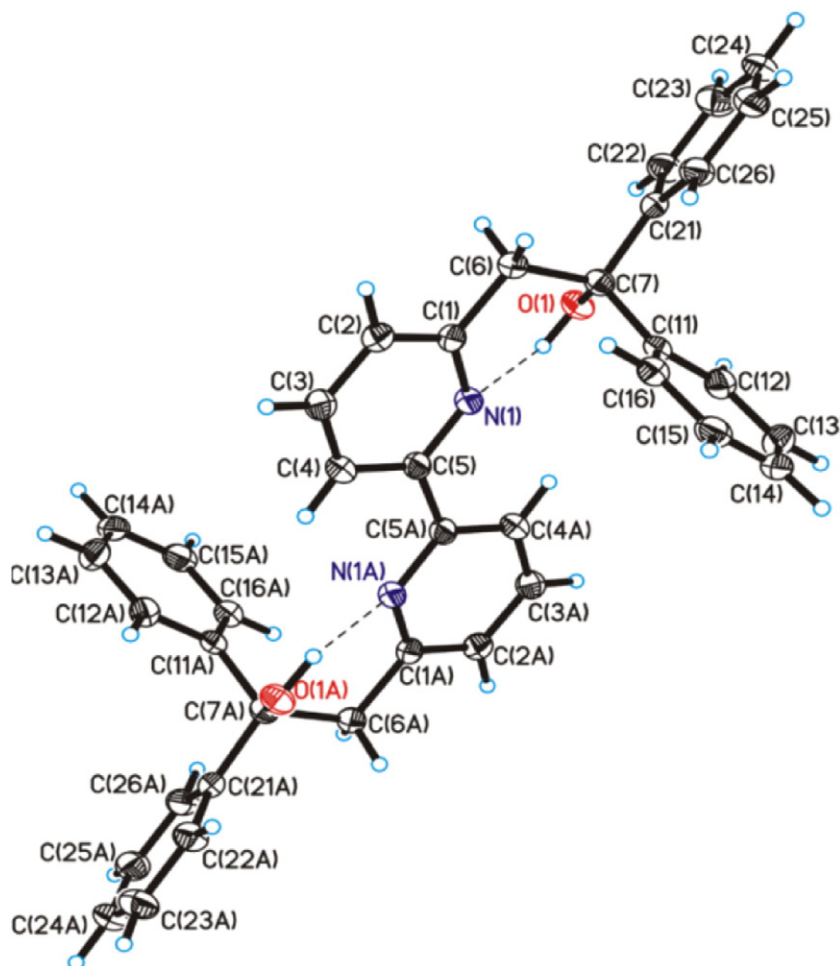
Compounds **1a–3a** were obtained in a good yield as air- and moisture sensitive compounds.

The structures of complexes **1a–3a** were established on the basis of NMR spectroscopy. The ^1H and ^{13}C NMR spectra of these compounds contain one set of ligand signals which is typical for such compounds; the protons of CH_2 groups appear as singlets. This situation is common for monomeric structures with trigonal bipyramidal Ti atom with C_{2v} (**1a**, **2a**) or C_s (**3a**) molecular symmetry structure (or in fast exchange between different possible geometries). Only in the case of **3a** the methyl groups are diastereotopic due to nonsymmetrical ligand nature (two signals of Me groups in ^{13}C NMR).

In contrast to the synthesis of **1a–3a**, the reaction between of $\text{Ti}(\text{O-}i\text{-Pr})_4$ and bipyridine ligand **5** under similar conditions (room temperature, toluene or dichloromethane) resulted in a mixture of several compounds (according to NMR), including the expected di-isopropoxy complex **5a** and another bipyridine containing species (approximate ratio 2:1). The attempts to recrystallize this mixture in absolutely anhydrous conditions from toluene resulted in decreasing the quantity of **5a**. The final product in this reaction is titanyl derivative **6** (Scheme 4). The formation of complex **5a** can be clearly observed, but the attempts to obtain it in analytically pure form were unsuccessful. Furthermore, compound **6** may be obtained in moderate yield under prolonged reflux of the reaction mixture.

The formation of compound **6** may be explained by thermal decomposition of intermediate product **5a** which is caused by the ligand structure. The appearance of additional oxygen atom under anhydrous conditions in titanium complexes based on polydentate ligands [1] has been observed earlier [19]. In the case of complex **6** the elimination of propene was detected by gas chromatography–mass spectrometry which is similar to known reaction [11].

According to the literature, titanyl complexes are not sufficiently studied [20]. In the precedent works $\text{Ti}=\text{O}$ fragment is also stabilized by organic ligands of porphyrin or phthalocyanine types, though there are some examples of $\text{Ti}=\text{O}$ fragments in the presence of cyclopentadienyl organic framework [21]. Synthesis of titanyl complexes based on phthalocyanines can be carried out by the reaction of ligands with TiCl_3 , TiCl_4 , $\text{Ti}(\text{O-}n\text{-Bu})_4$ or $\text{Ti}(\text{O-}i\text{-Pr})_4$ in high boiling solvents in the presence of urea [22] or without solvent [23].

Fig. 1. Molecular structure of ligand 5. Selected bond length (Å): $d(\text{O}\cdots\text{N}) = 2.738(2)$ Å.

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