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Novel bi- and hexanuclear titanium (IV) complexes: Synthesis, structure and catalytic activities in oligo- and polymerization of 1-hexene

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ABSTRACT

Novel bi- and hexanuclear titanium (IV) complexes with 2,2′-bis-(hydroxymethyl)-1,1′-biphenole derivative were synthesized. Structure of complexes **4**–**5** were established by X-ray diffraction. Resulting catalytic systems obtained by pre-catalysts activation by diethylaluminum chloride or ethyl aluminum sesquichloride were active in the 1-hexene oligomerization. Replacement of alkylaluminumchlorides by a {$3Et_2AlCl + Bu_2Mg$} binary system results in formation of predominantly isotactic, high molecular weight poly-1-hexene (content of isotactic pentad mmmm 70%). Systems treated with "traditional" activators – MAO and AlR_3 were not active.

1. Introduction

Hydrogenated oligomers of linear α-olefins are used as base oils in the synthetic lubricants production [1], while high molecular weight poly-α-olefins can be used as viscosity reducing additives for oil transportation through pipelines [2–4]. Due to the applied significance of these substances, the search for more active and selective catalysts for their synthesis is ongoing [5]. In recent years, most attention is paid to non-metallocene catalyst based on coordination compounds of nickel [6] and chromium [7–9], and to a lesser extent – with Group IV metal [9,10].

Group IV metal complexes with ligands containing only oxygen donor atoms are less studied. There are a few examples of such catalytic systems – biphenoxide and binaphtoxide chelate complexes of titanium, activated with MAO (Fig. 1, structures **A**–**C**). They demonstrate a relatively high activity, and depending on the structure of the catalyst, form low molecular weight atactic poly-1-hexene or oligomeric products [11].

Previously, we proposed a new group of Ti complexes with 2-hydroxymethylphenol derivatives (Fig. 1, structures **D**) [12] which showed relatively high activity and stability in the oligomerization and polymerization of α-olefins [13–15].

In this work we further study the abovementioned area, concentrating on the synthesis of the tetradentat $[OOOO]^{4-}$-type ligands, and bi- and hexa-nuclear titanium (IV) complexes based on those ligands, as well as the evaluation of their structure and catalytic activity in the 1-hexene oligomerization and polymerization.

2. Results and discussion

The precursor to the present ligand **3**, 2,2′-dihydroxy-3,3′-dibromo-5,5′di-*tert*-butyl-diphenyl **2** was synthesized according to the literature procedure. Lithiation of dibromo-derivative followed by treatment with benzophenone yielded ligand **3** (Scheme 1). Direct interaction of ligand **3** with dichloro(diisopropoxy)titanium ($TiCl_2(O^iPr)_2$) or $Ti(O^iPr)_4$ in toluene resulted in chloride complex **4** and alkoxo-complex **5** (Scheme 1). The ligand and complexes were characterized by IR, ^1H and ^{13}C NMR measurements as well as by elemental analysis.

Structures of compounds **4**–**5** were resolved by a standard set of physical and chemical methods and X-ray diffraction (Figs. 2–3).

In the crystal structure of **4** (Fig. 2) both Ti atoms adopt a

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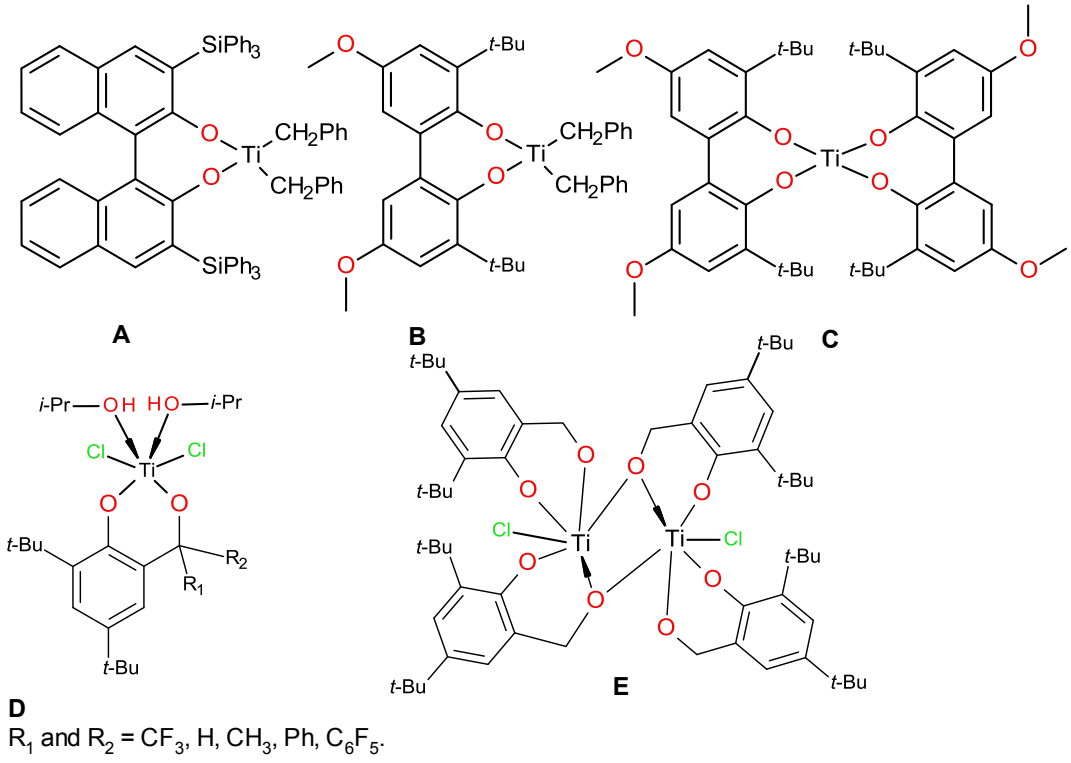
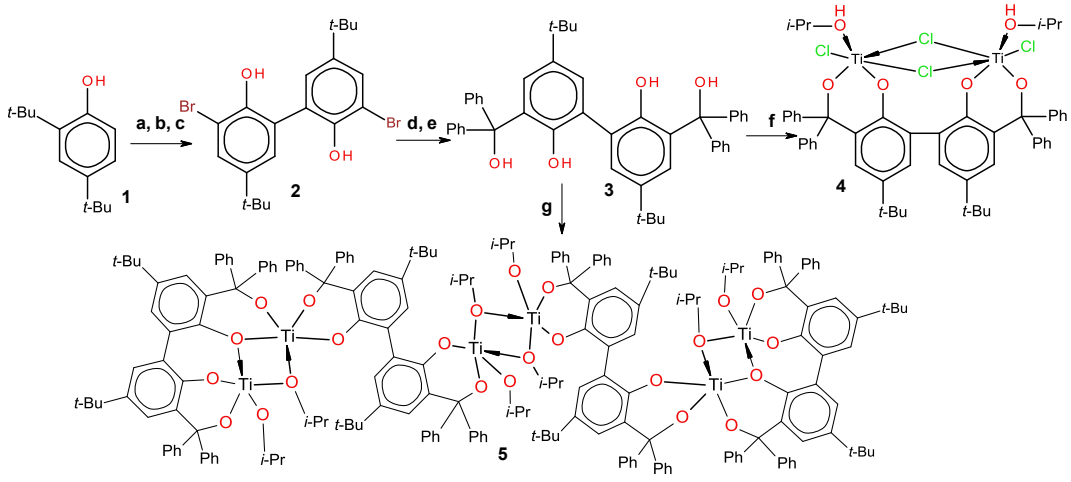


Fig. 1. Examples of titanium (IV) complexes with oxygen-containing ligands, catalytically active in oligo- and polymerization of 1-hexene.



a $CuCl_2$, TMEDA, MeOH, air; **b** $AlCl_3$, $C_6H_5NO_2$, toluene; **c** Br_2, AcOH; **d** BuLi, THF, -78°C; **e** Ph_2CO, THF, -78°C - r.t.
f $Cl_2Ti(O^iPr)_2$, toluene; **g** $Ti(O^iPr)_4$, toluene

Scheme 1. Synthesis of ligand **3**, binuclear **4** and hexanuclear **5** titanium (IV) complexes.

distorted *mer* octahedral geometry formed by μ2 chlorine, terminal chlorine and oxygen atoms of the ligands and ^{i}PrOH moiety. The central Ti_2Cl_2 fragment is not planar with the Ti(1)Cl(2)Cl(3)Ti(2) torsion angle equal to 151.76(4)°, that is not typical for such type of cyclic moiety. Such non-planarity is most probably caused by steric effects of the ligand, which coordinates both metal atoms.

Three of Ti–Cl bonds in cyclic moiety have similar lengths: (Ti(1)–Cl(2) 2.5381(9), Ti(1)–Cl(3) 2.5435(9), Ti(2)–Cl(2) 2.5675(9) Å), while the fourth bond Ti(2)–Cl(3) is considerably shorter (2.4560(9) Å). The distances Ti(1)–Cl(1) and Ti(2)–Cl(4) also differ significantly (2.2554(9) and 2.3097(9) Å). Both Ti bonds with oxygen atoms of the biphenolate fragment are by ca. 0.03 Å longer than those for other two ligand atoms. That may be indicative of steric effects in coordination environment. The 55.58(14)° angle between the average planes of the phenyl rings in biphenolate fragment of is typical for coordination compounds. In crystal the hydrogen atoms of the coordinated isopropanol fragments participate in rather weak hydrogen bonds with chlorine atoms of the neighboring molecules.

The structure of **5** (Fig. 3) is the first example of a complex