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Coordination compounds of titanium (IV) and 2-hydroxymethylphenol derivatives: Their synthesis, structure and catalytic activity in ethylene and 1-hexene polymerization

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A series of titanium complexes $LTiCl_2 \cdot (^iPrOH)_2$ **12-18** and heterobimetallic complex $L_2Ti \cdot {}^iPrOLi \cdot THF$ **19** bearing saligenin-type $[O,O]^{2-}$ ligands **6-11** were synthesized in high yields from $Cl_2Ti(O^iPr)_2$ or $LiTi(O^iPr)_5$. X-ray structure analyses for **15** and **19** revealed that these complexes adopt a distorted octahedron or distorted tetragonal pyramid geometry. When activated by binary activator $\{3Et_2AlCl + Bu_2Mg\}$, complexes **12-19** exhibited moderate to high activities toward ethylene and 1-hexene polymerization, giving high molecular weight polymers with broad molecular weight distributions. The results of this study show the unique ability of Li and Mg chlorides to improve the catalytic ability of post-metallocene pre-catalysts.

1. Introduction

Achievements in post-metallocene catalysis were summarized in several recent reviews [1–5]. It is generally recognized that the most efficient post-metallocene catalysts are the group 4 metals coordination compounds stabilized by phenoxide ligands. Usually, those ligands contain additional donor atoms, such as imine or amine nitrogen [6] (O,N ligands), or sulfur [7] (O,S ligands). There are substantially fewer examples of metal complexes with OO-type ligands used as precatalysts for the olefin polymerization catalysis. And among those saligenin-based complexes (where ligand structure contain both phenol and alcohol hydroxyls) are indeed unique [8,9].

The purpose of present work was to synthesize the Ti (IV) complexes with a variety of saligenin ligands, and to evaluate their structure and catalytic activity in ethylene and 1-hexene polymerization reactions upon activation by different co-catalysts, as well as the impact of non-transition metals salts (Li, Mg) in catalytic activity.

2. Results and discussion

2.1. Ligands and complexes synthesis

When choosing the saligenin benzylic carbon substituents, we have originally favored the fluorine-containing moieties. We expected them to be similar to the phenoxyimines [6,10,11] and TADDOLs complexes [12–14] where introduction of fluorine moiety in ligand structure results in increase of Ti atom acidity and thus improving the catalytic activity of resulting complex.

Ligands **6-9** were synthesized by reacting the 1-(3,5-di-*tert*-butyl-2-hydroxyphenyl)-2,2,2-trifluoroethanone with respective metal-organic derivatives (Scheme 1). Ligands without fluorine moieties **10-11** were synthesized by lithiation of 2,4-di-*tert*-butyl-6-bromo-phenol, with subsequent treatment of lithium derivative with respective carbonyl compound.

Titanium complexes **12-18** were synthesized by direct interaction of ligands **6-11** with one equivalent of $TiCl_2(O\text{-}^iPr)_2$ in toluene (Scheme 2, path a). The X-ray structure of representative complex **15** is presented on Fig. 1. In **15** titanium atom has a distorted octahedron coordination formed by chlorine atoms, oxygens of original ligand and isopropanol oxygens of leaving isopropoxy groups.

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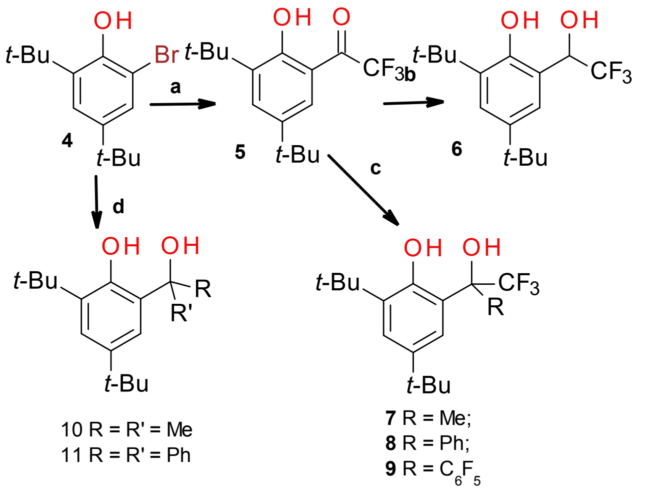
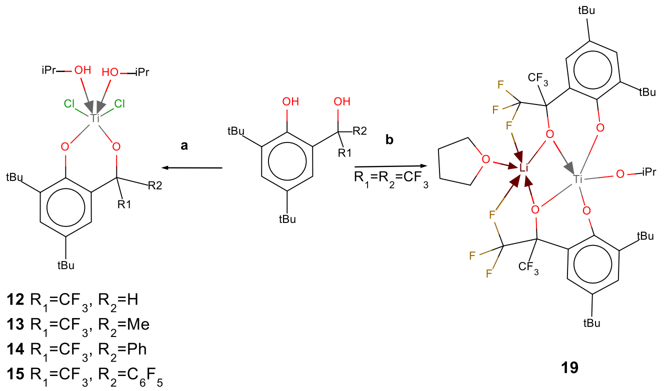


a BuLi, CF_3CO_2Me; **b** $NaBH_4$, MeOH; **c** RLi or RMgHal; **d** BuLi, R_2CO

Scheme 1. Synthesis of ligands **6-11**.



12 $R_1=CF_3$, $R_2=H$
13 $R_1=CF_3$, $R_2=Me$
14 $R_1=CF_3$, $R_2=Ph$
15 $R_1=CF_3$, $R_2=C_6F_5$
16 $R_1=R_2=Ph$
17 $R_1=R_2=Me$
18 $R_1=R_2=H$

a) $Cl_2Ti(O^iPr)_2$, toluene; **b**) $LiTi(O^iPr)_5$, THF

Scheme 2. Synthesis of Ti (IV) complexes with saligenines.

In our previous reports [9,12,13,15–17] we have associated a relatively high catalytic activity of OO- or ONO-type ligands Ti complexes to the Li or Mg compounds involved in formation of secondary complexes through ligands oxygens. To evaluate the possibility of such scenario we have studied the interaction of saligenin-type ligand 6-(1,1,1,3,3,3-hexofluoro-2-hydroxypropane-2-yl)-4,6-di-tert-butylphenol with $LiTi(O^iPr)_5$. The structure of synthesized heterometallic complex $L_2Ti{\cdot}{}^iPrOLi{\cdot}TGF$ (**19**) was resolved by X-ray crystallography (Fig. 1, on the right).

Compound **19** co-crystallizes with a solvate methylene chloride molecule. Ti atom coordination polyhedron is a distorted tetragonal pyramid, where foundation is formed by ligands' oxygens, and the top is formed by an isopropyl fragment oxygen. Lithium coordination polyhedron is a significantly distorted tetragonal pyramid, where foundation is formed by alcohol oxygens O(2) and O(4) as well as fluorine atoms of trifluoromethyl groups F(1) and F(7), and the top is formed by O(1T) - a coordinated tetrahydrofuran oxygen.

Considering the synthetic method, complex **19** structure and composition, serve as a proof of secondary complexation resulting in a molecular heterometallic complex.

2.2. Catalytic activity and polymer properties

Catalytic properties of synthesized compounds in the reaction of ethylene and 1-hexene polymerization are summarized in Tables 1 and 2. All compounds listed in Table 1 cannot be activated by such common co-catalysts as methylalumoxide, trimethylaluminum or diethylalumochloride (MAO, Me_3Al or Et_2AlCl, ratio of Ti/Al ≤ 1:500). However, they demonstrate moderate activity in presence of {$3Et_2AlCl/MgBu_2$} binary co-catalyst [18,19].

For example, complex **3** containing two CF_3 groups [9], demonstrates the highest catalytic activity at [Al]/[Ti] ratio equal to 500 (Table 1, runs 1–2). Substitution of one CF_3 group for hydrogen, methyl, phenyl or pentafluorophenyl groups (compounds **12, 13, 14, 15**) leads to the notable increase of catalytic activity that does not change significantly upon the decrease of [Al]/[Ti] ratio to 300.

The increase of catalytic activity in complexes with a single CF_3 group compared to **3** was unexpected, as we anticipated a contrary effect. Even more surprising was the high catalytic activity displayed by complexes lacking the CF_3 groups altogether. Complex **16** containing two phenyl moieties in benzyl position has catalytic activity that is twice of that for the **3** (Table 1, runs 1 and 13). This difference decreases upon Al/Ti ratio increase to about 500 (Table 1, run 16); and at ratio equal to 1000, the overall system catalytic activity is notably decreased. The kinetics of ethylene catalytic polymerization in presence of this catalyst is stable and the whole system is reasonably thermostable. It is active at both 50 and 80 °C, albeit the increase of temperature results in 2 fold decrease of catalytic activity and increase of the polydispersity index (runs 14 and 15).

The most active compounds of the series were **17** with two methyl groups in benzyl position and **18** that is based on 2,4-di-

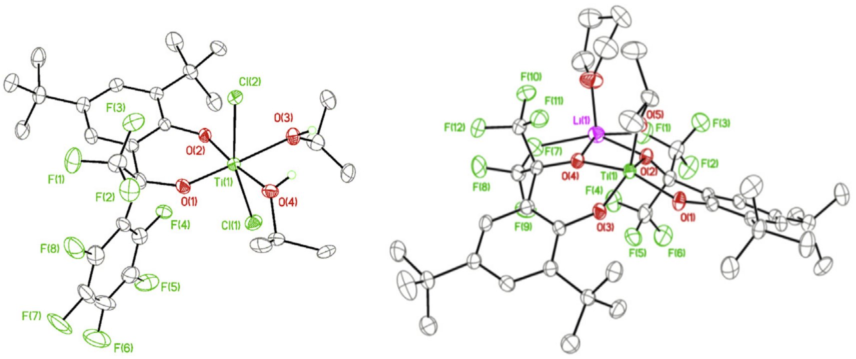


Fig. 1. General view of **15** (on the left; only the major component of dis-ordered molecule is shown) and **19** (on the right) in thermal ellipsoid representation (p = 50%). Hydrogen atoms except those of coordinated isopropyl moieties are omitted for clarity.