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Titanium–Manganese Compound with a Chiral Mn_3Ti Center

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We have shown here for the first time a facile route to the molecular compound $[Mn_3Ti(\mu_3\text{-}OCH_2CH_2OCH_3)_2(\mu\text{-}OCH_2CH_2OCH_3)_3(\mu\text{-}Cl)Cl_2(O^iPr)_2]$ with a Mn_3Ti motif, where the Ti atom is in the chiral position and the Mn atoms occupy nonchiral sites.

Although more than 50 years have passed since its "discovery", Ziegler−Natta (Z−N) catalysis remains one of the most important and profitable processes.[1] Despite its long history, it is also the fastest growing segment of the polymer industry.[2] Several generations of Z−N catalysts have been developed.[3,4] Each generation contributed with a higher productivity of the process and quite often significant improvement of the stereospecificity of the α-olefin polymerization.[5] The use of $MgCl_2$ to make catalysts with $TiCl_4$ became known through a patent issued to Kashiwa and his colleagues at Mitsui Petrochemical Industries.[4h] Remarkably, these catalysts display 2 orders of magnitude greater activities for olefin polymerization than Ziegler's original $TiCl_4$/alkylaluminum catalysts and have revolutionized the polyolefin manufacturing industry.[6] Note that $[Mg_2(\mu\text{-}Cl)_3(THF)_6][TiCl_5(THF)]$ (THF = tetrahydrofuran) supported on SiO_2 together with an organometallic cocatalyst is used as a commercial ethylene polymerization catalyst.[7,8] Giannini and a group at Montedison invented catalysts in which $MgCl_2$ or $MnCl_2$ was combined with a transition-metal halide and an ''electron donor" such as an ester, alcohol, ether, and amine.[4c] Comprehensive contributions to this topic have been provided by Hlatky,[5a] Gibson and Spitzmesser,[5b] and Chen and Marks.[5c]

The high-activity industrial isotactic propylene polymerization catalysts are formed from a procatalyst, which typically contains magnesium and titanium chlorides or alkoxides. The stoichiometry of an alkoxide procatalyst is complex and could be illustrated by the formula $Mg_3Ti(OR)_8X_2$ (X = *o*-cresol, OEt),[9] but its structure is unknown. The present paper is our contribution to the better understanding of the nature of the $Mg_3Ti(OR)_8X_2$ adduct, which takes an active part in the stereoregular polymerization process of propylene units in a regular head-to-tail manner.[10] We can now report that a synthetic route has been developed into this area of inorganic chemistry. In the course of our investigations, as the starting material we have used Mn species because they have properties similar to those of Mg compounds but they are more soluble in hydrocarbons and

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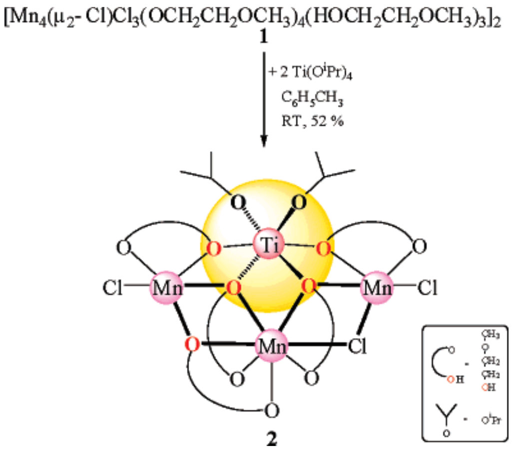
Scheme 1. Synthesis of **2**



THF.[11] Various reactions between Ti and Mn species were explored. $[Mn_4(\mu\text{-Cl})Cl_3(OCH_2CH_2OCH_3)_4(HOCH_2CH_2OCH_3)_3]_2$ (**1**)[12] and $Ti(O^iPr)_4$ have been found to be useful precursors for $[Mn_3Ti(\mu_3\text{-}OCH_2CH_2OCH_3)_2(\mu\text{-}OCH_2CH_2OCH_3)_3(\mu\text{-Cl})Cl_2(O^iPr)_2]$ (**2**) compound formation.

As shown in Scheme 1, treatment of **1** with $Ti(O^iPr)_4$ in toluene at room temperature gave a dark-brown solution from which after workup colorless crystals of **2** in 52% yield were obtained. Compound **2** is soluble in a wide range of common aromatic organic solvents and sensitive toward moisture but as a solid can be stored at room temperature under N_2 for weeks. It was characterized by X-ray diffraction, microanalysis, as well as magnetic and spectroscopic methods as described in the Supporting Information. Magnetic measurements indicate the presence of weak antiferromagnetic interactions. The effective magnetic moment decreases from 9.88 μ_B at 300 K to 5.35 μ_B at 1.9 K. The room temperature μ_{eff} value is a little smaller than the expected value for three uncoupled Mn^{II} ions (10.25 μ_B).

Compound **2** crystallizes in the monoclinic space group $P2_1/c$. The molecular structure is shown in Figure 1. Compound **2** contains the rhombohedral Mn_3Ti core, a structural pattern common for many tetranuclear alkoxide aggregates.[13] The metal ions are held together by two μ_3-O(alkoxo), three μ-O(alkoxo) oxygen atoms, and one μ-Cl ion. The geometry around the Mn2 and Mn3 atoms is a distorted square pyramid with O_4Cl and O_3Cl_2 donor sets, respectively. Instead, the Mn1 atom is seven-coordinate by O_6Cl atoms set with a coordination polyhedron described as a distorted capped trigonal prism. Because of the presence of four bridging O atoms of alkoxo chelating agents and two terminal, mutually *cis*-O^iPr groups, the geometry around the Ti atom is chiral, and the molecule as a whole possesses C_2 symmetry. The Ti and Mn atoms are linked by μ-O and μ_3-O atoms and form an almost coplanar TiO_2Mn moiety with geometrical parameters comparable to those found in $[\{Ti_2(OC_2H_5)_8Cl\}_2Mg_2(\mu\text{-Cl})_2]$[14] and $[Mg_2Ti_2(acac)_4(OMe)_8]$[15] compounds with TiO_2Mg units. The Ti−O and Mn−O distances of nonbridging and bridging alkoxide ligands are in the expected range for Ti^{IV} [16−19] and Mn^{II} [20,21] complexes. The Mn···Mn nonbonded distances in **2** are 3.270(1), 3.350(1), and 5.620(2) Å.

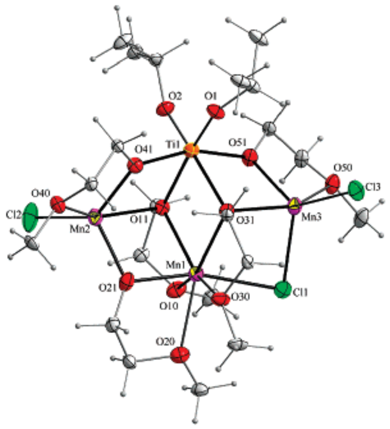


Figure 1. Molecular structure of **2** (ORTEP plot; thermal ellipsoids set at 50%). Selected interatomic contacts [Å]: Mn1···Mn2 3.270(1), Mn1···Mn3 3.350(1), Mn2···Mn3 5.620(2), Ti1···Mn1 3.489(1), Ti1···Mn2 3.310(1), Ti1···Mn3 3.303(1).

Preliminary tests of the catalytic properties of the **2**/methylaluminoxane (MAO) system for propylene polymerization have shown no activity. However, the results of an ethylene polymerization test at 50 °C on **2**/$AlEt_2Cl$ and **2**/MAO give ca. 720 and 104 g of polyethylene (g of Ti per h)$^{-1}$, respectively ($[Ti]_0 = 0.03$ mmol dm^{-3}, $[AlEt_2Cl] = 8$ mmol dm^{-3}, and $[MAO] = 15$ mmol dm^{-3}). These results are in agreement with the earlier observations. Gambarotta and co-workers[22a] have recently reported an approach to Mn^{II} complexes and compared their performance in olefin polymerization with that of Fe^{II} and Ni^{II} catalysts. In this approach, they showed that the compound $[MnCl_2L_2]$ (L = $[2,6\text{-}(^iPr)PhN{=}C(Me)]_2(C_3H_5N)$), in contrast to its Fe and Co analogues, does not exhibit ethylene polymerization activity upon activation with MAO. Also, the complexes $[Mn(acac)_3]$, $[Cp_2Mn]$, and [Mn(salen)Cl] in combination with MAO yielded only trace amounts of polymers.[22b] Generally, several orders of magnitude lower activities are observed for Mn^{II} species bearing ligands that give highly active catalysts with other late transition metals.

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In summary, we report for the first time a facile route to the molecular compound **2** with a Mn_3Ti motif, in which the Ti atom is in the chiral position and the Mn atoms occupy nonchiral sites. This compound possesses a formula similar to that proposed by Job for an industrial α-olefin polymerization catalyst $Mg_3Ti(OR)_8X_2$ precursor[9] and is expected to be a model for the orientation of the incoming molecules and isotactic propagation of the polymer chain.[10] An obvious next goal is to synthesize the Mn_3Ti-type compound with new specific ligands capable of creating a more active Ti site.

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Supporting Information Available: General procedures and materials, additional experimental details (synthesis of **2** and SQUID magnetometry data), and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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