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PREPARATION AND PROPERTIES OF DIMETHYLTITANIUM 2-METHYL-2,4-PENTANEDIOLATE*

HIROZO SUGAHARA AND YASUSUKE SHUTO
Research Institute of Idemitsu Kosan Co., Ltd., Tokuyama, Yamaguchi (Japan)

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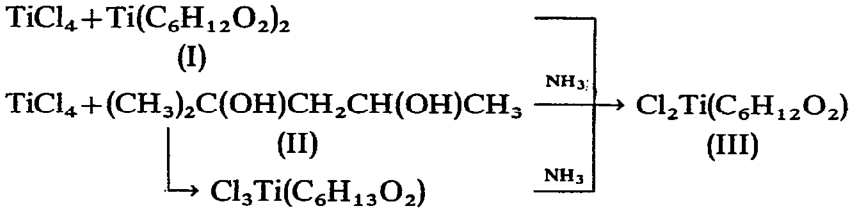
SUMMARY

The preparation of dimethyltitanium 2-methyl-2,4-pentanediolate $(CH_3)_2$-$Ti(C_6H_{12}O_2)$ and its homologs is described and its molecular structure is discussed.

INTRODUCTION

Although methyltitanium compounds, such as methyltitanium trichloride, dimethyltitanium diisopropoxide, tetramethyltitanium and di-π-cyclopentadienyldimethyltitanium, have been prepared, physical properties of most of these compounds have not been known well because of their thermal instability. In a study of the polymerization of olefins with some methyltitanium compounds, we found that dimethyltitanium 2-methyl-2,4-pentanediolate was thermally quite stable and the catalysts consisting of this compound and titanium halides had fairly high activities in the polymerization of ethylene and propylene. The present paper deals with the synthesis and properties of dimethyltitanium 2-methyl-2,4-pentanediolate and its homologs.

Bertrand[1] and Yamamoto *et al.*[2] reported the preparation of dialkoxytitanium 2-methyl-2,4-pentanediolate and titanium bis(2-methyl-2,4-pentanediolate) (I) from titanium tetraalkoxide and 2-methyl-2,4-pentanediol (II). Dichlorotitanium 2-methyl-2,4-pentanediolate (III) is easily prepared by the disproportionation reaction between titanium tetrachloride and (I). (III) is also prepared from the reaction of titanium tetrachloride with (II) and a base such as ammonia.



$$TiCl_4 + \underset{(I)}{Ti(C_6H_{12}O_2)_2}$$

$$TiCl_4 + \underset{(II)}{(CH_3)_2C(OH)CH_2CH(OH)CH_3} \xrightarrow{NH_3} \underset{(III)}{Cl_2Ti(C_6H_{12}O_2)}$$

$$\rightarrow Cl_3Ti(C_6H_{13}O_2) \xrightarrow{NH_3}$$

Dimethyltitanium 2-methyl-2,4-pentanediolate (IV) is obtained in good yield

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from the reaction of (III) with the methyl Grignard reagent.

$$Cl_2Ti(C_6H_{12}O_2)+2CH_3MgX \rightarrow \underset{\text{(IV)}}{(CH_3)_2Ti(C_6H_{12}O_2)}+2\,MgXCl$$

EXPERIMENTAL

Preparation of dichlorotitanium 2-methyl-2,4-pentanediolate

Titanium tetrachloride (0.397 mole) in 200 ml of benzene was added dropwise to 0.397 mole of $Ti(C_6H_{12}O_2)_2$ in 1500 ml of 2/1 benzene/pentane with vigorous stirring at room temperature. White crystals separated; these were washed with pentane and dried under reduced pressure. Yield 92.5%; the crystals become slightly brown at 90°, black-brown at 150° and do not melt at 300° or above. They are soluble in THF, temporarily soluble in ether forming an adduct which is insoluble in ether and poorly soluble in hydrocarbons (Found: Cl, 30.51; Ti, 20.65. $C_6H_{12}Cl_2O_2Ti$ calcd.: Cl, 30.18; Ti, 20.39%.)

Preparation of dimethyltitanium 2-methyl-2,4-pentanediolate

Methylmagnesium iodide (0.257 mole) in ether was added dropwise to 0.128 mole of $Cl_2Ti(C_6H_{12}O_2)$ in 1 l of anhydrous THF with vigorous stirring at −10° during three or four hours. One-half l of cooled heptane was added to the reaction mixture and the resulting white precipitate was separated by filtration. Solvents were removed at −10° under reduced pressure, and the dark yellow residue was dried at 30° under high vacuum for two hours. The residue was extracted with 600 ml of cooled pentane at −10°, and extracts were kept for one day at −78° to form pale yellow crystals of $(CH_3)_2Ti(C_6H_{12}O_2)$. The yellow crystals were separated, washed twice with 10 ml of cooled pentane and dried under reduced pressure at −10°; yield 55–70%.

When ether is used as a solvent instead of THF, the reaction does not proceed smoothly and gives reddish-orange tar. In a similar reaction in which CH_3MgCl is used instead of CH_3MgI, either THF or ether can be used as solvents.

Some properties of dimethyltitanium 2-methyl-2,4-pentanediolate

Although crystals of $(CH_3)_2Ti(C_6H_{12}O_2)$ are considerably stable at room temperature, compared to $(CH_3)_2Ti(O\text{-}i\text{-}Pr)_2$, their surface becomes slightly black after several days of storage in the dark. The compound melts and turns black at 93°, and decomposes at 98°. It is somewhat less stable in solution than in the crystalline state, and its pale yellow solutions turn slightly brown after several hours at room temperature. Below 10° the compound is fairly stable even in solution and can be stored longer than one month without any change.

The compound also is sensitive to oxygen and moisture in the air, and decomposes immediately on such exposure, similar to $(CH_3)_2Ti(O\text{-}i\text{-}Pr)_2$. (Found: Ti, 24.11. $C_8H_{18}O_2Ti$ calcd.: Ti, 24.69%.) Magnesium and halogens were not detected. Hydrogen and carbon were not analyzed because of its sensitivity to air as mentioned above. Alcoholysis with 2-ethylhexanol yields 92% of the calculated amount of methane.

Molecular weight

Mean 388 (calculated for the dimer, 388); standard deviation 20. No concentration dependency was observed. Poor reproducibility, especially at low concentrations, is due to the high sensitivity of the compound to impurities in the solvent used (benzene, cyclohexane and dioxane).

Chemical properties

(*i*). Reaction with alcohols, water and hydrogen chloride: $(CH_3)_2Ti(C_6H_{12}O_2)$ reacts immediately with stoichiometric amounts of ROH, H_2O and HCl to produce CH_4 and $(RO)_2$-, $(HO)_2$- and $Cl_2Ti(C_6H_{12}O_2)$, respectively.

(*ii*). Olefin polymerization: Propylene was polymerized with the catalyst consisting of $(CH_3)_2Ti(C_6H_{12}O_2)$ and $TiCl_3$ and gave a highly crystalline polymer[4]. A typical result was as follows; 200 ml autoclave, propylene (67 g), $TiCl_3$ (0.5 mmole), $(CH_3)_2Ti(C_6H_{12}O_2)/TiCl_3$ 2/1, 70°, 1 h. Catalytic activities 250–400 g of polymer/g of $TiCl_3$. Molecular weight 150×10^4. Heptane insoluble portion: 80–84%. The molecular weight can be controlled by using hydrogen and/or $(C_2H_5)_2Zn$ as modifiers. Ethylene is also polymerized with the catalyst consisting of $(CH_3)_2Ti(C_6H_{12}O_2)$ and $TiCl_4$ and gives a crystalline polymer[3]. The molecular weight can be controlled by using hydrogen. The catalytic activity reaches 800 g of polymer/g of $TiCl_4$/h.

Butadiene is polymerized slowly in the presence of $(CH_3)_2Ti(C_6H_{12}O_2)$ in hydrocarbons at room temperature and gives a rubber-like polymer.

DISCUSSION

The results of the measurements of the molecular weight of $(CH_3)_2Ti(C_6H_{12}O_2)$ suggests strongly the occurrence of a dimeric structure. Yoshino and Iidaka[5] now have determined the molecular and crystal structure of this compound, and the molecular structure is shown in Fig. 1. The details of the X-ray studies will be published soon.

The NMR spectrum of $(CH_3)_2Ti(C_6H_{12}O_2)$ is shown in Fig. 2.

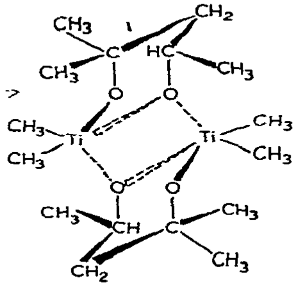

Fig. 1. Molecular structure of dimethyltitanium 2-methyl-2,4-pentanediolate.

An inexplicable peak at τ 8.68 which appears always even in a 100 MHz spectrum must be due to some impurity.

According to the conclusions of Herman and Nelson[6] on the stability of organotitanium compounds R_nTiX_m, a sufficiently high electronegative field is required around the titanium to stabilize it. The stability of the compounds increases in the following order: butyl < methyl < ethynyl < *p*-anisyl < phenyl < α-naphthyl

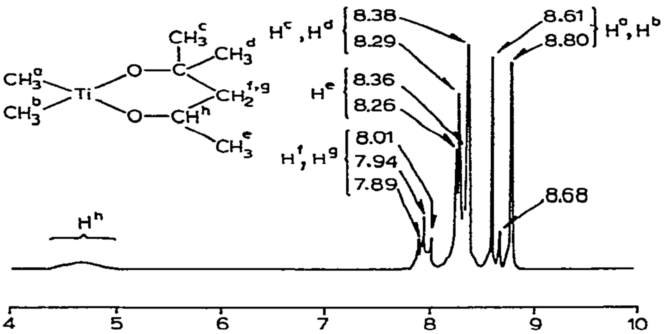

Fig. 2. NMR spectrum of dimethyltitanium 2-methyl-2,4-pentanediolate in benzene. $J(H^e-H^h) = 6$ Hz.

$<$ indenyl. The stability is greatest when $n=1$ and decreases markedly with $n=2$ or more. Though stabilizing effects of the X group are not so clear, the stability is decreased with increasing electronegativity of the X as follows: butoxy $>$ methoxy; chloro $>$ fluoro. Thus, most dimethyltitanium compounds (except dicyclopentadienyldimethyltitanium) are rather unstable.

Alkyl-substituted trimethylenedioxy groups—OCR^{1}R^{2}CR^{3}R^{4}CR^{5}R^{6}O— which form a rigid six-membered ring including a titanium atom were found to increase the stability of the organometallic bond. A trimethylenedioxy group which has more alkyl substituents, such as the 2-methyl-2,4-pentanedioxy = 1,1,3-trimethyltrimethylenedioxy group, gave better results. Subsequently, Ogawa[7] prepared dimethyltitanium 2,2-dimethyltrimethylenediolate and 2-methyl-1-propyltrimethylenediolate which also were fairly stable. Attempts to prepare dimethyltitanium trimethylenediolate and 1-methyltrimethylenediolate have been unsuccessful.

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