

CYCLOPENTADIENYLTRIMETHYLTITANIUM

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METALLOORGANIC compounds of tetravalent titanium in which all the valences are saturated by organic groups have been isolated in the pure state only when two of the organic groups are cyclopentadienyl<sup>1,2</sup> or substituted cyclopentadienyl.<sup>2</sup>

The presence of the two cyclopentadienyl nuclei gives a particular stability to this class of metallorganic compounds. Thus, for instance, dicyclopentadienyldiphenyltitanium and dicyclopentadienyldimethyltitanium are not decomposed by water or by alcohols and are not oxidized when exposed to air.<sup>1,2</sup>

We have now prepared and isolated in the pure state a monocyclopentadienyl compound of tetravalent titanium in which all the valences are saturated by organic groups, corresponding to the formula  $(C_5H_5)Ti(CH_3)_3$ .

Reaction under nitrogen at  $-30^\circ C$  of cyclopentadienyltitanium-trichloride\* (4 g, 18.2 millimoles) suspended in anhydrous diethylether (100 mls.) with lithium methyl (1.32 g, 60 millimoles) dissolved in

\*  $(C_5H_5)TiCl_3$  prepared by us according to R. D. Gorsich<sup>3</sup> showed, after crystallization from xylene, m.p.  $210-213^\circ C$ , contrary to previous indications.<sup>3,4</sup>

- 1 L. Summers, R. H. Uloth, A. Holmes, J. Amer. Chem. Soc. 77, 3604 (1955)
- 2 D.P. 1,037,443, 28/8/1958, Farbwerke Hoechst.
- 3 R. D. Gorsich, J. Amer. Chem. Soc. 80, 4744 (1958)
- 4 O. L. Sloan, W. A. Barber, J. Amer. Chem. Soc. 81, 1364 (1959)

80 ml of ether is accompanied by dissolution of the titanium compound to a yellow solution and precipitation of lithium chloride.

After about 2 hours the solvent is removed by evaporation and then the reaction product is sublimed at the room temperature/0.5 mm, and collected on a tube wall cooled to  $-70^{\circ}\text{C}$ .

1.1 g of intensely yellow needle crystals\* are thus isolated (Found: Ti, 30.4; Me, (o) 28.6; M, (oo) 165.4.  $(\text{C}_5\text{H}_5)\text{Ti}(\text{CH}_3)_3$  requires Ti, 30.3; Me, 28.53%; M, 158.09).

(o) determined by measuring the volume of methane evolved on reaction with 2-ethylhexanol.

(oo) Cryoscopic in benzene.

A further purification of the product may be accomplished by recrystallization from pentane solutions at about  $-70^{\circ}\text{C}$ .

Cyclopentadienyltrimethyltitanium kept under an inert atmosphere decomposes very slowly at temperatures near  $0^{\circ}\text{C}$ , and rapidly at temperatures higher than  $40^{\circ}\text{C}$ . It may be kept for a long time without significant decomposition when it is maintained at about  $-70^{\circ}\text{C}$ .

Unlike  $(\text{C}_5\text{H}_5)_2\text{Ti}(\text{CH}_3)_2$  and  $(\text{C}_5\text{H}_5)_2\text{Ti}(\text{C}_6\text{H}_5)_2$ , cyclopentadienyltrimethyltitanium quickly reacts with water and alcohols, with formation of methane, and is rapidly oxidized by air. Therefore this compound shows a reactivity similar to that of methyltitaniumtrichloride.<sup>5</sup> From this behaviour it is possible to deduce that, when only one cyclopentadienyl group is present in the molecule, the methyl groups are bound to titanium by means of bonds having a limited stability and a high reactivity, contrary to what happens in the case of dicyclopentadienyl derivatives.

<sup>5</sup> D.B.P. 1,023,766, 16/12/1955, Farbwerke Hoechst; C. Beerman, H. Bestian, Ang. Chem. 71, 618 (1959).

\* In which chlorine is absent.