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A CRYSTALLIZABLE ORGANOMETALLIC COMPLEX CONTAINING TITANIUM AND ALUMINUM

Sir:

Following our previous researches[1] concerning the nature of the catalytic agent promoting the α-olefins polymerization, we have isolated a crystallizable compound containing titanium, aluminum and organometallic bonds, which causes the polymerization of ethylene.

By treating 0.01 mole of bis-(cyclopentadienyl)-titanium dichloride[2] suspended in 50 ml. of *n*-heptane with 0.025 mole of triethylaluminum at 70°, in the absence of air and of moisture, a slow gas evolution takes place, the titanium compound is dissolved and the solution becomes dark blue. By cooling the solution at −50°, a blue crystalline solid has been obtained in good yield.

The macroscopic blue needles of the compound, recrystallized four times from *n*-heptane, melt at 126–130° without appreciable decomposition.

The blue compound contains titanium, aluminum, chlorine and organic groups; from the elementary quantitative analysis a ratio Ti:Al:Cl = 1:1:2 has been found.

The values 331 and 339 have been calculated for the molecular weight of the blue compound from two different cryoscopic measurements in benzene.

By treating the blue product with 2-ethylhexanol, ethane is evolved; a quantitative gas volumetric determination shows that two moles of ethane are evolved per mole of compound.

By treating the product with anhydrous hydrochloric acid in ether solution bis-(cyclopentadienyl)-titanium dichloride is formed in almost quantitative yield (more than 90%).

The analytical data and the chemical behavior agree very well with a formula $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$, as shown in the table for $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$

	Calcd.	Found	
Cl, %	21.22	21.02[3]	20.78[4]
Al, %	8.073	7.92	7.90[3]
Ti, %	14.33	14.34	14.55[3]
$-C_2H_5$, %	17.40	16.07	17.67[5]
Mol. weight	334	331	339[6]

It seems probable that, in the complex, both C_5H_5- groups are bound to the titanium atom and that both C_2H_5- groups are bound to the aluminum atom.

By polymerizing ethylene in heptane solution in the presence of 0.6 g. of the Ti–Al complex at 40 atm. and 95° after a reaction time of 20 hours, 8.4 g. of white polymer has been obtained, which has been fractionated by boiling solvent extraction (acetone extractable fraction 10.1%; ether extractable fraction 1.8%, carbon tetrachloride extractable fraction 17.20%, residue 70.9% having intrinsic viscosity in tetralin at 135° = 1.55 × 100 ml./g.).

As it is reported in the next table, $(C_5H_5)_2TiCl_2$ alone is completely inactive for the ethylene polymerization; $Al(C_2H_5)_3$, accordingly with previously published data,[7] does not give solid polyethylene in the reaction conditions, but only low molecular weight oily polymers. Comparative experiments were carried out at 95° and 40 atm.

Soluble catalyst Type	Moles	Solvent Type	Cc.	Reaction time, hours	Crystalline polyethylene, g.	Oily polymers, g.
$(C_5H_5)_2TiCl_2$	0.005	Benzene	100	20	0	0
$Al(C_2H_5)_3$	.05	*n*-Heptane	300	8	0	11.07[a]
$(C_5H_5)_2TiCl_2$-$Al(C_2H_5)_2$	.003	*n*-Heptane	40	8	7	0.4

[a] 66% of the product consists of hydrocarbons lower than decane.

Although the complex is a catalyst for the ethylene polymerization, less active than the catalyst prepared from $TiCl_4$ and $Al(C_2H_5)_3$, the composition of the complex strongly supports the hypothesis that the Ziegler type catalysts[8] for the polymerization of ethylene are, generally, bimetallic complexes containing organometallic bonds.

(1) G. Natta, P. Pino, E. Mantica, F. Danusso, G. Mazzanti and M. Peraldo, *La Chimica e l'Industria*, 38, 124 (1956); G. Natta, P. Pino, G. Mazzanti, U. Giannini, E. Mantica and M. Peraldo, *ibid.*, 39, 19 (1957).

(2) G. Wilkinson and G. M. Birmigam, This Journal, 76, 4281 (1954).

(3) Decomposition of the complex by H_2SO_4 5%; titanium has been determined as titanium cupferrate, aluminum as 8-oxyquinolinate, chlorine by gravimetric determination (I. Ubaldini and F. Capizzi, *Chimica e Industria*, 37, 779 (1955)).

(4 Decomposition of the complex by Na_2O_2; chlorine has been determined by the Volhard titration.

(5) By gas volumetric determination.

(6) By cryoscopic determination in benzene solution.

(7) G. Natta, P. Pino, and M. Farina, *Supplemento Ric. Scient.*, 25, 120 (1955).

(8) K. Ziegler, Belgian Patent 533,362; K. Ziegler, E. Holzkamp, H. Breil and H. Martin, *Angew. Chem.*, 67, 541 (1955).

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