Benzyltitanium Compounds

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No tetra-alkyl or tetra-aryl compounds of titanium reasonably stable at room temperature have been described. Interest in these compounds arises from the need for a better understanding of the catalytic activity of organometallic titanium compounds in the polymerization of olefins. We have thus investigated some benzyl derivatives of titanium.

Solutions of $Ti(CH_2Ph)_4$ in ethyl ether have been prepared[1] by the reaction of $ClMg{\cdot}CH_2Ph$ with $TiCl_4$ but apparently no attempt to isolate the pure compound was made.

By evaporating such solutions a red product (I) was obtained, m.p. 70—71° (pentane); the molecular weight of (I), obtained by cryoscopy in benzene (412), is consistent with the formula $Ti(CH_2Ph)_4$ at the concentrations used (40·5 g./1000 g.), as are the analytical data.

The n.m.r. spectrum of (I) in deuteriated toluene at 30° shows a sharp singlet at τ 7·43 corresponding to the methylene protons, and two multiplets at τ 3·58 and 3·19, assigned respectively to the protons at 2 and 6 and 3, 4 and 5 in the phenyl group. Only a slight shift in the signals, but no change of their shape, was observed in the spectrum obtained at −70°. The i.r. spectrum confirms the presence of monosubstituted phenyl groups. Compound (I) is stable for months if stored at about 0° but is decomposed in a few hours at 100° in boiling heptane to yield toluene (about 2·4 moles per g.atom of Ti) and low valency titanium compounds. It readily reacts at room temperature with alcohols and acids yielding four moles of toluene per g.atom of titanium in benzene solution, while under the same conditions it absorbs two moles of oxygen per g.atom of titanium; however, hydrogen does not react with (I) at room pressure and temperature even if catalysts like colloidal palladium or nickel are present.

Accordingly we assign the structural formula $(PhCH_2)_4Ti$ to compound (I), the benzyl groups being bound to titanium by σ-bonds.

The reaction of (I) with two equivalents of ethanol gives crystals of compound (II), stable at room temperature in the absence of air and moisture (m.p. 102—103°); the molecular weight, 590, determined by cryoscopy in benzene, is consistent with the formula $[(EtO)_2Ti(CH_2Ph)_2]_2$. The reaction of (I), dissolved in toluene, with one equivalent of hydrogen chloride gave red crystals of compound (III), m.p. 100° (decomp.), to which we assign the formula $(PhCH_2)_3TiCl$ (M = 330).

All three benzyl derivatives of titanium slowly polymerize ethylene with a rate increasing in the order (III) > (I) > (II); furthermore, while (III) and (I) yield only high polymers (II) yields a mixture of high polymers, but-1-ene, and oligomers; only (III) polymerizes propene at a reasonable rate.

These results confirm that titanium catalysts, in the absence of any other metals or organometallic compounds can polymerize ethylene and α-olefins.[2]

The authors are grateful to Professor P. Pino (University of Pisa) for helpful discussions.

(*Received, June 5th,* 1968; *Com.* 731.)

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