Benzylzirconium Compounds

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Summary Tetrabenzylzirconium, prepared by reaction of benzylmagnesium chloride with $ZrCl_4$, reacts with HCl gas to give benzylzirconium chlorides; the benzylzirconium compounds show catalytic activity in the polymerization of α-olefins.

WE described[1] the synthesis and characterization of some benzyl derivatives of titanium with unusual thermal stability and interesting catalytic properties in the polymerization of olefins. Since carbon–zirconium bonds are usually more stable than titanium–carbon bonds,[2] we have now prepared some benzyl derivatives of zirconium and studied their reactivity.

From the reaction of $ClMgCH_2Ph$ with $ZrCl_4$ in diethyl ether at $-15°$ a crystalline yellow product was obtained, m.p. 133—134° (diethyl ether, pentane, toluene). The analytical data and the molecular weight (*M* 438) determined by cryoscopy in benzene are consistent with the formula $Zr(CH_2Ph)_4$ (I).

Compound (I) is stable for a long time if kept in the solid state at or in solution in the dark 0°, and decomposes slowly in hydrocarbon solution at 110° to yield toluene (2·6 moles per g. atom of Zr) and low-valency zirconium compounds, which are being now characterized. The reaction of CH_3OD with (I) in benzene solution gives 4 moles of $PhCH_2D$ per g. atom of zirconium. Compound (I) also reacts with oxygen, absorbing two moles of it per g. atom of zirconium; hydrolysis of the oxidized product gives benzyl alcohol, although not in a quantitative yield (50% with respect to the benzyl groups present in the compound).

Unlike the related titanium compound, $Zr(CH_2Ph)_4$ reacts with hydrogen at 50° and atmospheric pressure, forming toluene. In this connection, it was observed that reduction products of $Zr(CH_2Ph)_4$ also behave as hydrogenation catalysts for the aromatic rings at 50°. Moreover, $Zr(CH_2Ph)_4$ reacts with CO_2 much more rapidly than does $Ti(CH_2Ph)_4$ (2 moles per g. atom of zirconium). The different reactivity of the benzyl derivatives of zirconium and titanium is probably due to the higher polarity of the Zr–C bond, as may be expected from the lower electronegativity of Zr as compared with Ti. As already observed for the titanium derivative, $Zr(CH_2Ph)_4$ was found to be a good catalyst for α-olefin isomerizations and hydrogenations even at atmospheric pressure and at 0°, at which temperature (I) does not react with hydrogen in the absence of olefins.

The n.m.r. spectrum of (I) in deuteriated benzene at 30° shows a sharp singlet at τ 8·47 corresponding to the methylene protons, and two multiplets at τ 3·62 and 2·94 assigned, respectively, to 2-H and 6-H; and 3-, 4-, and 5-H in the phenyl group. The n.m.r. spectrum at room temperature is virtually the same as that at −60° in deuteriated toluene. These data, coupled with the results obtained from the reaction with CH_3OD, provied evidence for the σ nature of the bonds between the benzyl groups and the metal; however, a considerable shift of the signal due to the *ortho*-hydrogens of the aromatic ring was observed, which indicates a strong interaction with the metal atom.

Compound (I) reacts with 1 or 2 moles of HCl gas in aromatic solvents, the expected amounts of toluene and $(PhCH_2)_3ZrCl$ (II) (m.p. 89°), or $(PhCH_2)_2ZrCl_2$ (III) (decomposes above 100°) are formed. Compounds (II) and (III) are soluble in aromatic and chlorinated solvents and are monomers on the basis of crysocopic measurements on their benzene solutions. Halogenated derivatives are thermally less stable than $Zr(PhCH_2)_4$. All benzyl derivatives of zirconium show catalytic activity in the polymerization of ethylene and of α-olefins.

We thank Prof. Piero Pino (Technisch-chemisches Laboratorium der ETH, Zürich) for helpful discussions.

(*Received, July 31st,* 1969; *Com.* 1173.)

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