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SYNTHESIS AND PROPERTIES OF SOME TITANIUM AND ZIRCONIUM BENZYL DERIVATIVES

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SUMMARY

Syntheses of $Ti(CH_2C_6H_5)_4$ (I), $Zr(CH_2C_6H_5)_4$ (IX) and their halogen and alkoxy derivatives are described. Their physical properties and reactivity with H_2, O_2, CO_2 and olefins has been investigated. Spectroscopic and chemical data are consistent with the σ-nature of the metal–carbon bond.

(I) and (IX) react in a different way with $Al(CH_2C_6H_5)_3$ to form polynuclear complexes.

INTRODUCTION

Preparation of benzyl derivatives of titanium(IV) and of zirconium(IV) has been recently described[1-5]. Since these compounds exhibit unusual thermal stability with respect to other organometallic compounds of the same metals containing M–C bonds of the σ-type[6-8], it has been possible to examine their physical properties and to study their reactivity towards organometallic compounds of other metals.

RESULTS

A. Synthesis of benzyl derivatives of titanium and zirconium

$Ti(CH_2Ph)_4$ (I) and $Zr(CH_2Ph)_4$ (IX) were prepared by reaction at −20° of ether solutions of the respective tetrachlorides with benzylmagnesium chloride. After filtration and solvent evaporation, compound (I) or (IX) were isolated in the pure state by crystallization from aliphatic or aromatic hydrocarbons.

Solutions of (IX) were carefully shielded from light in order to avoid photochemical transformation.

Dibenzyltitanium diethoxide (VIII) was prepared by reaction of (I) with a stoichiometric amount of ethyl alcohol. Attempts to isolate the monoethoxide derivative were unsuccessful, since this compound disproportionates into (I) and dialkoxide derivative.

(I) and (IX) react at low temperature (−20°) in toluene with anhydrous hydrogen halides to form the corresponding halogenated derivatives (III), (IV) and (V). Dibenzyltitanium dibromide (VII) was also prepared from equimolecular amounts of (I) and titanium tetrabromide at −20°.

Tribenzyltitanium fluoride was obtained by reaction of (I) with BF_3 in toluene solution at −20°.

Owing to the marked instability of these halogenated derivatives in solution, long reaction times should be avoided and the compounds should be isolated as solids as soon as possible.

Attempts to prepare dibenzyltitanium dichloride by reaction of (I) with anhydrous HCl or $TiCl_4$ were not successful: the isolated product always contained large amounts of trivalent titanium compounds.

Tribenzylmethyltitanium (VI) was prepared by reaction between $Ti(CH_2Ph)_3$-Cl and CH_3MgI.

B. Physical Properties

Table 1 lists melting (or decomposition) points and molecular weights (determined by cryoscopy in benzene), of the obtained products. Except for $Ti(CH_2Ph)_3F$ and $Ti(CH_2Ph)_2(OEt)_2$, all the compounds were found to be monomers; $Ti(CH_2Ph)_3$-F is partially associated, the degree of association being larger for higher concentrations (Fig. 1), while $Ti(CH_2Ph)_2(OEt)_2$ is a dimer.

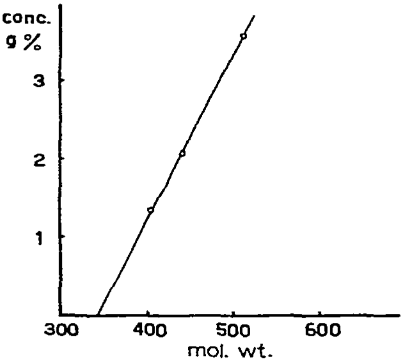
All the examined benzyl derivatives are soluble in aromatic solvents and ethers

TABLE 1

SYNTHESIS OF BENZYL COMPOUNDS[a]

No.	Compound	Yield (%)	Colour	M.p. (°C)	Analyses, found (calcd.) (%)				Mol. wt.[b] Found (calcd.)
					C	H	Hal	Ti or Zr	
(I)	$Ti(CH_2Ph)_4$	40	dark red	70–71	80.50 (81.54)	6.73 (6.84)		11.51 (11.61)	412 (412)
(II)	$Ti(CH_2Ph)_3F$	40	red-brown	100–102[d]			5.42 (5.58)	13.86 (14.08)	[e] (340)
(III)	$Ti(CH_2Ph)_3Cl$	86	red-brown	100[d]			9.92 (9.94)	13.10 (13.44)	330 (357)
(IV)	$Ti(CH_2Ph)_3Br$	89	red	100–103[d]			19.63 (19.62)	11.99 (11.94)	388 (401)
(V)	$Ti(CH_2Ph)_3I$	10	dark-red				27.94 (28.33)	11.57 (10.69)	 (448)
(VI)	$Ti(CH_2Ph)_3CH_3$[c]	25	dark-red	63–64[d]				14.47 (14.24)	330 (336)
(VII)	$Ti(CH_2Ph)_2Br_2$	60	red	80			39.20 (40.98)	12.18 (12.28)	 (390)
(VIII)	$Ti(CH_2Ph)_2(OC_2H_5)_2$	70	orange-red	102–103	66.83 (67.50)	7.57 (7.55)		14.71 (14.96)	600 (320)
(IX)	$Zr(CH_2Ph)_4$	30	yellow	133–134	72.82 (73.79)	6.16 (6.19)		19.91 (20.03)	437 (456)
(X)	$Zr(CH_2Ph)_3Cl$	80	yellow	89			8.55 (8.86)	21.62 (22.80)	386 (400)
(XI)	$Zr(CH_2Ph)_2Cl_2$	60	orange-yellow	60[f]			20.54 (20.59)	26.04 (26.49)	 (344)

[a] Decomposition of these compounds with ethanol gave quantitative yields of toluene identified by gas-chromatography and mass spectrometry. [b] By cryoscopy in benzene. [c] CH_4 identified by gas-chromatography after-hydrolysis: found 4.2; calcd. 4.47 %. [d] Melting with decomposition visible at this temperature. [e] See Fig. 1. [f] Does not melt, decomposition over this temperature.



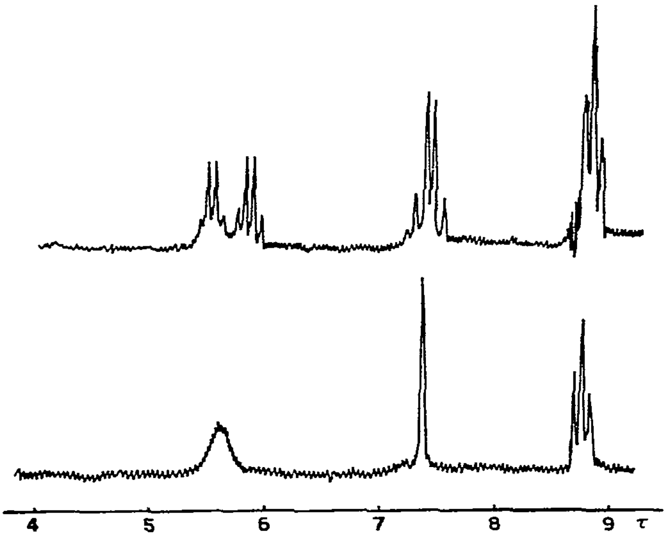


Fig. 1. Dependence of molecular weight of $Ti(CH_2Ph)_3F$ on the concentration in benzene solution (by cryoscopy).

Fig. 2. Proton NMR spectra of $Ti(CH_2Ph)_2(OC_2H_5)_2$ in $C_6D_5CD_3$ at temperatures of +30° (above) and +80° (below).

and slightly soluble in aliphatic hydrocarbons, from which most of them are crystallisable.

The IR spectra of (I) and (IX) do not differ much from that of $Sn(CH_2Ph)_4$ and

TABLE 2

NMR SPECTRA OF SOME BENZYL COMPOUNDS

Compound	Solvent	Temp. (°C)	Methylene protons (τ)[a]	Ring protons (τ)[b]	
				Ortho	*Meta, para*
$Ti(CH_2Ph)_4$	$C_6D_5CD_3$	+30	7.21[c]	3.39[c]	2.9[c]
		−70	7.74	3.64	3.0
	$CFCl_3$	+10	7.37	3.49	3.0
		−98	8.12	3.71	2.8
$Ti(CH_2Ph)_3F$	$C_6D_5CD_3$	−50	7.64		
$Ti(CH_2Ph)_3Cl$	$C_6D_5CD_3$	−50	7.01		
$Ti(CH_2Ph)_3Br$	$C_6D_5CD_3$	+30	6.91	3.48	2.9
		−50	7.14		
$Zr(CH_2Ph)_4$	$C_6D_5CD_3$	+30	8.56	3.64	3.0
		−60	8.70	3.84	
$Zr(CH_2Ph)_3Cl$	C_6D_6	+30	8.53	3.66	3.0
$Al(CH_2Ph)_3$	$C_6D_5CD_3$	+30	8.56	3.24	3.0
$B(CH_2Ph)_3$	C_6D_6	+30	7.50	3.20	3.0
$Sn(CH_2Ph)_4$	C_6D_6	+30	7.85	3.34	3.0

[a] Sharp singlet; [b] Multiplet centered about this frequency; [c] These are the right values instead of the previously reported[2].

show the characteristic absorptions of a monosubstituted aromatic ring. Most of the obtained compounds were also examined by NMR spectroscopy; Table 2 lists the τ values of aromatic and methylenic protons measured at 100 MHz with various solvents and temperatures. For comparison τ values of some benzyl derivatives of non-transition metals are also listed. For all the compounds two multiplets, respectively assigned to *o* and *m*, *p* protons, are present in the region of aromatic protons.

The attribution of the resonances of *o* and *m*, *p* protons is based on the relative integrated intensities (2/3) of the signals and on earlier measurements on benzyltin derivatives[9]. The resonance of the methylenic protons is a singlet even at low temperature.

The NMR spectrum of $Ti(CH_2Ph)_2(OEt)_2$ at room temperature is consistent with the dimeric form of the compound (Fig. 2); in fact two quartets are found centered at τ 5.58 and 5.91 assigned to the CH_2 protons of the ethoxide groups; probably two ethoxide groups, namely those corresponding to the signal centered at τ 5.58, bridge the two titanium atoms in the dimeric molecule. The resonance of CH_2 protons of the benzyl groups centered at τ 7.49 is of the *AB* type, *i.e.* characteristic of two geminal non-equivalent protons; as the temperature is raised to 80° this resonance simplifies to a singlet.

C. Chemical properties

(a). Reaction with protonic acids O_2, H_2, CO_2 and olefins. In accordance with the high electropositivity of the metals, the benzyl derivatives of Ti and of Zr all react with stoichiometric amounts of proton active substances, such as hydrogen halides or ethyl alcohol, with formation of toluene and the compounds listed in Table 1.

$$M(CH_2Ph)_4 + HX \rightarrow M(CH_2Ph)_3X + CH_3Ph$$
$$(X = F, Cl, Br, I \text{ or } OC_2H_5)$$

Similarly, treatment of (I) and (IX) with CH_3OD gives the stoichiometric amounts of $PhCH_2D$. Both (I) and (IX) react with two moles of oxygen per g.atom of metal; by hydrolysis of the reaction product, benzyl alcohol is obtained, although not in quantitative yield (ca. 50% with respect to the benzyl groups present). (I) and (IX) show different reactivity with respect to hydrogen; in fact at atmospheric pressure, (I) does not react up to 50°, whereas (IX) at 50° undergoes hydrogenolysis of the M–C bond with formation of toluene. In a competitive reaction, catalysed by the reduction products of (IX), the formed toluene is reduced to methylcyclohexane.

Both (I) and (IX) are able to catalyse the hydrogenation of olefins also at 0° and at atmopsheric pressure, under which conditions, none of the two compounds reacts with hydrogen. Unlike the other organometallic compounds of transition metals containing M–C bonds[10], (I) and (IX) react with carbon dioxide, absorbing two moles of CO_2 per mole of compound even at room pressure and temperature, the reaction being much faster for (IX) than for (I). After hydrolysis of the reaction product phenylacetic acid and tribenzylcarbinol were isolated in almost equimolar amounts. Tertiary alcohols are frequently formed in addition to carboxylic acids in the reaction between CO_2 and organometallic compounds of non-transition metals, such as Al[11] and Mg[12]. The higher reactivity of (IX) with regard to (I) may be related to the lower electronegativity of Zr with respect to Ti and therefore the higher polarity of the Zr–C bond.

All the benzyl compounds of titanium and zirconium behave as catalysts in the polymerization of ethylene and olefins[4]. Both (I) and (IX) can promote isomerization of olefins (Table 3); however, the solutions of (IX) are active only after light exposure. A hydride derivative, formed by photochemical decompostion of (IX) (see section *Cb*), is thought to be the actual isomerization catalyst.

TABLE 3

ISOMERIZATION OF 1-HEXENE WITH $Zr(CH_2Ph)_4$[a] AND $Ti(CH_2Ph)_4$[a]

Benzyl compound	Isomer distribution in hexene recovered/after hydrolysis[b] (%)		
	1-Hexene	*cis*-2-Hexene	*trans*-2-Hexene
$Ti(CH_2Ph)_4$	66.0	5.2	28.8
$Zr(CH_2Ph)_4$	58.0	5.2	36.8

[a] Solution of the benzyl compound (1 mmole) and 1-hexene (16 mmoles) in toluene (15 ml) aged for five days at 25° in the light. [b] Determined by gas-chromatographic analysis.

(*b*). *Stability to heat and to light.* Unlike the previously known tetraorgano compounds of Ti and Zr, tetrabenzyl derivatives show good thermal stability. If stored in the solid state at 0°, (I) is stable for years, and (IX) is stable even at room temperature. However, these compounds are unstable in solution: toluene and low valence insoluble titanium and zirconium compounds are formed, the decomposition rate increasing with the temperature. Taking the amount of Ti^{III} formed as a measure of the degree of decomposition, the thermal stabilities of some benzyl derivatives of Ti at different temperatures were compared (Table 4). The stability is markedly decreased by replacing benzyl groups with halogen atoms; the higher the electronegativity of the halogen, the lower the stability of halogenated benzyl compound; on the contrary, stability is increased by the introduction of alkoxide groups.

TABLE 4

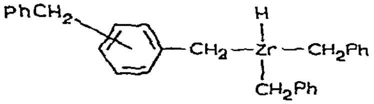
Ti^{III} PERCENTAGE AFTER THERMAL AGEING[a]

Compound	At 25°	At 60°
$Ti(CH_2Ph)_4$	1.7	41.5
$Ti(CH_2Ph)_2(OC_2H_5)_2$	1.2	1.6
$Ti(CH_2Ph)_3Br$	11.5	
$Ti(CH_2Ph)_2Br_2$	13.0	
$Ti(CH_2Ph)_3Cl$	20.6	
$Ti(CH_2Ph)_3F$	61.1	

[a] Toluene solutions aged for 8 h.

Tetrabenzylzirconium is more stable than (I) even when in solution, but it can be photochemically decomposed. Light changes the colour of its solutions from yellow to brown even at temperatures at which no thermal decomposition occurs.

The reaction of the irradiated solution with CH_3OD causes release of HD, which indicates the presence of a Zr–H bond. Photolysis of (IX) is faster in ethers or aromatic hydrocarbons than in aliphatic hydrocarbons. After irradiation at −70° of a toluene solution of (IX) a brown solid product was precipitated by n-heptane addition. This compound which could not be further purified because of its instability even at 0°, is soluble in aromatic solvents and diamagnetic. Analytical data suggest that it mainly consists of a zirconium hydride with formula:



Consistently, hydrolysis yields hydrogen, toluene and a mixture of 2- and 4-methyldiphenylmethane in 1/1 ratio; and more than 90% of the gas obtained by reaction with CH_3OD is HD. The presence of the Zr–H bond could, however, not be confirmed by IR or NMR spectroscopy.

By irradiation of toluene solutions of (I) at −78°, nearly 50% of the titanium is reduced to trivalent state; we could not ascertain whether such a reduction occurs through a hydride intermediate analogous to that isolated by irradiation of (IX).

(c). *Reaction with other organometallic compounds.* Tetrabenzyltitanium reacts rapidly with $Al(C_2H_5)_3$, in hydrocarbon solution giving ethane (80%), ethylene (20%) and an insoluble precipitate which contains titanium (mainly in the trivalent state) and aluminium in variable ratios on varying the starting Al/Ti ratios. Exchange of organic groups between the two metals is thought to take place, with formation of unstable compounds containing $Ti{-}C_2H_5$ bonds, which decompose with consequent reduction of titanium. On the contrary, when (I) is treated with nearly stoichiometric amounts of tribenzylaluminium, no precipitate is formed, and the valence of titanium remains almost unchanged for short reaction times (2–3 h). NMR spectra of the reaction mixture show an initial decrease of intensity of the resonance of the methylenic protons of $Al(CH_2Ph)_3$ and the simultaneous appearance of the signal of toluene methyl protons. Toluene formation was confirmed by gas-chromatographic analysis on liquid products obtained by distillation of the reaction mixture under vacuum at 0°. The amount of toluene formed increases with increasing reaction time or $Al(CH_2Ph)_3$ to (I) ratio (Tables 5 and 6).

Decomposition of the reaction mixture with CH_3OD yields, besides non-

TABLE 5

FORMATION OF TOLUENE IN THE REACTION BETWEEN $Ti(CH_2Ph)_4$ AND $Al(CH_2Ph)_3$[a]

Ageing time (min)	Toluene[b] (mmoles)
6	1.60
30	2.68
120	4.15
180	4.27

[a] Reaction conditions: $Ti(CH_2Ph)_4$ 3.32 mmoles; $Al(CH_2Ph)_3$ 3.32 mmoles; xylene 52 ml; temperature 25°.
[b] Detected by GLC.

TABLE 6

MASS-SPECTROMETRIC ANALYSIS[a]

Reactants[b]	Ti/Al molar ratio	Moles (%)			
		C_7H_8	C_7H_7D	$C_7H_6D_2$	$C_7H_5D_3$
$Ti(CH_2Ph)_4/Al(CH_2Ph)_3$	0.5	32.6	52.4	8.7	6.3
$Ti(CH_2Ph)_4/Al(CH_2Ph)_3$	1	23.8	66.0	6.1	4.1
$Ti(CH_2Ph)_4/Al(CH_2Ph)_3$	2	15.9	76.5	3.9	3.7
$Ti(CH_2Ph)_3Cl/Al(CH_2Ph)_3$	1	26.9	68.3	2.2	2.5

[a] After decomposition with CH_3OD. [b] Reaction for 2 h at 25° in C_6H_6 solution; concentration of $Al(CH_2Ph)_3$ 11 mmole·l^{-1}.

deuterated toluene, the compounds C_7H_7D, $C_7H_6D_2$ and $C_7H_5D_3$ (Table 6). By precipitation with aliphatic hydrocarbons from benzene reaction solutions, it is also possible to isolate solid products containing different ratios of Ti and Al, depending on the reaction conditions; decomposition of these products with CH_3OD yields C_7H_7D, $C_7H_6D_2$ and $C_7H_5D_3$. Similar reaction also takes place between $Al(CH_2Ph)_3$ and $Ti(CH_2Ph)_3X$ (X = Cl or Br), but with partial reduction of titanium to trivalent state; however the degree of reduction is the same as that found for the titanium compound, under the same conditions of temperature, concentration and ageing in the absence of $Al(CH_2Ph)_3$ (Table 7). On the other hand, when tetrabenzyltitanium is treated with dibenzylaluminium monochloride or monobromide, a rapid reduction of titanium to trivalent state is observed; the reduction is certainly not only due to the formation of compounds of the type $Ti(CH_2Ph)_{4-n}X_n$, through an exchange reaction, because under the same conditions, the rate of decomposition of these compounds is much slower (compare Tables 4 and 7).

In the reaction of equimolecular amounts of $Al(CH_2Ph)_3$ and of (IX) in an aromatic hydrocarbon at room temperature, a crystalline slightly soluble, red product is formed, which melts at 114–115°. As previously reported[4], the analytical data agree with formula $AlZr(CH_2Ph)_7$ (XII), whereas cryoscopic measurements show that the compound is partially dissociated in benzene solution. Dissociation seems to be of the

$$AlZr(CH_2Ph)_7 \rightleftharpoons Al(CH_2Ph)_3 + Zr(CH_2Ph)_4$$

type, since conductivity measurements do not indicate the presence of ionic species in solution. Ethyl ether decomposes the complex into (IX) and tribenzylaluminium

TABLE 7

REDUCING ACTION OF BENZYLALUMINIUM COMPOUNDS ON THE BENZYLTITANIUM DERIVATIVES[a]

Benzyl-titanium compound	Benzyl-aluminium compound	Ti^{III} (%)	Ageing time (h)
$Ti(CH_2Ph)_4$	$Al(CH_2Ph)_3$	< 1	2
$Ti(CH_2Ph)_3Cl$	$Al(CH_2Ph)_3$	20	5
$Ti(CH_2Ph)_4$	$Al(CH_2Ph)_2Br$	52	2
$Ti(CH_2Ph)_4$	$Al(CH_2Ph)_2Cl$	50	2

[a] Reactions carried out in aromatic solvents at 0°; molar ratio Ti/Al 1.

etherate, which indicates that in the complex, (IX) and $Al(CH_2Ph)_3$ are bound by not very strong coordination bonds. In order to establish the nature of such bonds, we carried out NMR analysis. Table 8 lists the values of the resonances of both aromatic and methylenic protons of $AlZr(CH_2Ph)_7$ measured at 100 MHz in deuterated benzene at 30° ; the values for the mixtures $AlZr(CH_2Ph)_7 + Al(CH_2Ph)_3$ and $AlZr(CH_2Ph)_7 + Zr(CH_2Ph)_4$ are listed also. Because of the partial overlap with the signal of the protons of non-completely deuterated benzene, the values corresponding to the aromatic protons of the benzyl groups bound to aluminium are omitted. Examination of the resonance arising from the organic entity bound in the complex (XII) to the zirconium atom, shows that in comparison with (IX), there is no shift of the sharp singlet assigned to CH_2 protons ; on the other hand, large and similar shifts to higher fields occur, with the two multiplets attributed to the *o* and *m*, *p* aromatic protons. With the benzyl groups bound to the Al atom, a shift to lower fields of the sharp singlet attributed to methylene protons is observed compared with the values found for $Al(CH_2Ph)_3$. For the mixture $AlZr(CH_2Ph)_7 + Zr(CH_2Ph)_4$, the number of resonances remains unchanged but the intensity of the signals of the protons of the benzyl groups bound to Zr increases. Moreover, a shift is observed of the signal of the aromatic protons toward the characteristic position of them in (IX). Analogously for the $AlZr(CH_2Ph)_7 + Al(CH_2Ph)_3$ mixture an upfield shift occurs in the signal from the CH_2 protons bound to the Al atom.

From these results we draw the following conclusions:

(1). No exchange is observed of the benzyl group between Al and Zr at least on the NMR time scale, while, at least at room temperature, the benzyl groups bound to a given metal, are equivalent.

(2). The variations found in the NMR spectra of the mixtures between the complex and (IX) or $Al(CH_2Ph)_3$ may be easily interpreted by assuming that the equilibrium

$$AlBr(CH_2Ph)_7 \rightleftharpoons Al(CH_2Ph)_3 + Zr(CH_2Ph)_4\,.$$

exists in benzene solution.

Because of this equilibrium, (IX) and $Al(CH_2Ph)_3$ can exchange with the corresponding compound associated in the complex and therefore the chemical shifts

TABLE 8

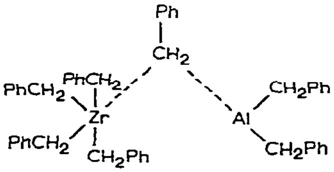
NMR SPECTRA OF $ZrAl(CH_2Ph)_7$ IN DEUTEROBENZENE[a]

Compound	Methylene protons (τ)		Ring protons (τ)[b]	
	[c]	[d]	*Meta, para*	*Ortho*
$ZrAl(CH_2Ph)_7$	8.14	8.58	3.4	4.01
$ZrAl(CH_2Ph)_7 + Zr(CH_2Ph)_4$[e]	8.11	8.57	3.2	3.80
$ZrAl(CH_2Ph)_7 + Al(CH_2Ph)_3$[e]	8.38	8.58	3.5	4.08

[a] Recorded at 30° and 100 MHz on a Varian HA-100 spectrometer. [b] These absorptions, which we ascribe to the ring protons of benzyl groups directly bounded to the zirconium atom, are not well resolved but are centered about this frequency. [c] Protons of the CH_2 groups (sharp singlet) directly bound to the aluminium atom. [d] Protons of the CH_2 groups (sharp singlet) directly bound to the zirconium atom. [e] Molar ratio between the two compounds 1/1.

observed in the mixtures are average values of the chemical shifts of the protons in the complex and in the isolated compounds.

(3). The shifts of the protons resonances of the benzyl groups bound to Zr and Al in the complex (XII), with respect to those in (IX) and $Al(CH_2Ph)_3$ may be interpreted by postulating a shift of electrons from the Al compound to the Zr one through a three center and two electrons bond, such as:



DISCUSSION

(*a*). *Structure*

The contrast between the stabilities of the tetrabenzyl derivatives of Ti and Zr, and those of the corresponding methyl and phenyl compounds might suggest the presence of π bonds between the metal and the benzyl groups. In the case of the compound $(\pi\text{-}C_5H_5)MoCH_2C_6H_5(CO)_2$ (where the benzyl group is π-bonded to the metal) the methylenic protons are not equivalent and their resonance, which is a singlet at high temperature, becomes a doublet at $-30°$ [13]. The resonance of the CH_2 protons of (I) is, by contrast, a singlet even in the low-temperature spectrum ($-98°$), and thus we conclude that the benzyl groups are bound to the metal only by σ-bonds*. The absence of deuterium in the ring of toluene obtained in the reaction between (I) or (IX) and CH_3OD, is consistent with the presence of σ-bonds, but is not a good proof of the structure proposed because methanol is a strong Lewis base and it might be complexed with the metal and cause a transformation of the π-bond into a σ-bond before the protonolysis of the bond itself. For the same reason, the positive response of (I) and (IX) to the Gilman colour test no. 1 is not a certain proof of the σ-nature of the M–C bond. The NMR spectra of the benzyl derivatives reveal some interesting peculiarities, even if it does not supply further information for structure determination. For all the compounds, a strong upfield shift of the *ortho* aromatic proton resonance is observed with respect to the aromatic protons of toluene; on the other hand, only negligible variations are observed for *meta*- and *para*-proton resonances. Such a shift is also found for the benzyl derivatives of B, Al and Sn, and varies in a nearly regular way with the ionic radius of the element. In the case of tetrabenzyltin, it was attributed to an interaction between the metal and the π-electronic system of the aromatic ring[9]. The chemical shift of methylenic protons of tetrabenzyltitanium is very surprising, for it is at much lower field than those of the benzyl derivatives of metals with similar or higher electronegativity. It is known for $(\pi\text{-}C_5H_5)_2TiClR$, with R = benzyl, phenylethyl and neopentyl, that the protons of the CH_2 group bound to Ti are deshielded[14].

The downfield shift of the resonance of the CH_2 protons observed on replacing a benzyl group with a halogen atom is in agreement with the inductive effect of the

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* Preliminary X-ray investigations carried out by Prof. Bassi on $Ti(CH_2Ph)_4$ confirm that all the Ti–C bonds are of the σ-type.

halogen. Among all the benzyltitanium halides, the position of the methylenic resonance of $Ti(CH_2Ph)_3F$ is at the highest field, in spite of the higher electronegativity of the fluorine. This discrepancy may be due either to a lower neighbour-anisotropy effect of the Ti–F bond or to the existence in solution of the equilibrium between the monomer and dimer forms revealed by cryoscopic measurements.

(b). Stability and mechanism of decomposition

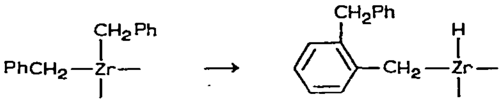
Benzylzirconium compounds show thermal stabilities higher than those of the corresponding titanium compounds. This is in conflict with some previous theoretical predictions[15] according to which the M–C bond should become weaker as the atomic weight of the transition metal increases.

Replacement of benzyl groups by halogen atoms causes a decrease of stability; the opposite effect is brought about by introducing alkoxide groups. These results are in agreement with the observations of Nelson[16] on the phenyltitanium compounds and of Beerman and Klauss on methyltitanium derivatives[6,17]. The fact that halogen atoms and alkoxide groups, both electronegative substituents, are in opposite may be due either to the lower ligand field strength of the alkoxide group [18] or to the relatively lower decrease of electron density on the metal in the dimer $[Ti(CH_2Ph)_2(OC_2H_5)_2]_2$. Indeed, in (VIII) the electron donor action of the two bridge-bound oxygen atoms, opposes the withdrawing action of the alkoxide groups.

Several hypotheses have been advanced for the mechanism of decomposition of organotitanium compounds. According to Nelson[16], the decomposition takes place by homolytic cleavage of the M–C bond, and the formed radicals rearrange by coupling or dismutation or reaction with the solvent. On the other hand De Vries[19], on the basis of his studies with deuteriated methyltitanium compounds, ruled out the formation of free radicals and suggested that decomposition takes place by bimolecular dismutation. Bürger and Neese[20] studied the decomposition of tris(dialkylamino)alkyltitaniums; they did not observe reduction of the metal but only formation of the hydrocarbon corresponding to the alkyl group bound to titanium; and hence they proposed a heterolytic cleavage of the Ti–C bond followed by an attack of the alkyl anion on the amidic hydrogen atoms. In studies of the decomposition of $Cr(CH_2Ph)_3 \cdot 3THF$ in ethers, Zeiss[21] did not detect the presence of free radicals, but he did not exclude the possibility that decomposition takes place by homolytic cleavage of the Cr–C bond. He suggested that the benzyl radicals formed might remain within the confines of the organochromium complex and subsequently react with the other benzyl groups bound to the metal or with the coordinated solvent.

In the thermal decomposition of the benzyl derivatives of titanium and zirconium in hydrocarbon or ether solvents, toluene but no coupling products (dibenzyl) are formed. If decomposition is carried out in deuteriated solvents, no deuteriated toluene is produced, thus excluding the possibility of a reaction between benzyl radicals and solvent. Hence if benzyl radicals are formed, they react with the other benzyl groups bound to titanium. On the basis of the largest amount of toluene formed during decomposition (2.66 moles per mole of compound), it may be assumed that hydrogen atoms of the methylenic groups participate in toluene formation; in fact 2.66 is the largest amount of toluene that could be formed starting from one mole of (I) or (IX) using only the methylenic hydrogen atoms for toluene formation. The number of moles of toluene formed during decomposition is higher than the number of equivalents of trivalent titanium produced, and thus the formation of toluene takes place, at least in part, by a process which seems to be independent of the titanium reduction. According to Bürger and Neese, the formation of toluene probably occurs by intra- or intermolecular metallation of the methylenic groups. It is significant that bi- and trideuteriated toluene are obtained in the reaction between CH_3OD and the products of partial decomposition of (I).

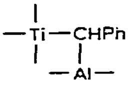
The photochemical decomposition of $Zr(CH_2Ph)_4$, probably occurs through a mechanism similar to that proposed by Zeiss[21] to account for the formation of 2-methyldiphenylmethane in the thermal decomposition of $Cr(CH_2Ph)_3 \cdot 3THF$:



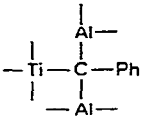
Eisch and Considine[22] suggested that an analogous compound was produced during the photolysis of $AlPh_3$, but in this case a benzyne intermediate was thought to be formed.

(c). *Interaction with organometallic compounds of aluminium*

The reaction between (I) and $Al(CH_2Ph)_3$ may be interpreted by postulating a condensation reaction between the two organometallic compounds with elimination of toluene. Such a reaction is similar to that known to occur between $(\pi\text{-}C_5H_5)_2TiClCH_3$ and $Al(CH_3)_3$[23]; methane is released in this case, the metal valence remaining unchanged and Ti–CH_2–Al bonds are formed. Also in the reaction between (I) and $Al(CH_2Ph)_3$, which may be regarded as a metallation reaction, compounds are probably formed in which two or three metal atoms are bound to the same carbon atom, as in one of the two compounds (A) or (B):



(A)



(B)

As followed by NMR spectroscopy in the reaction between equimolecular amounts of (I) and $Al(CH_2Ph)_3$ the intensity of the methylenic protons resonance of $Al(CH_2Ph)_3$ decreases more rapidly than that of the corresponding signal from $Ti(CH_2Ph)_4$. This can be explained by assuming that Ti–$CH_2C_6H_5$ bonds are formed again by an exchange reaction between the (A) or (B) compounds and $Al(CH_2Ph)_3$.

In contrast with the reaction between (I) and $Al(CH_2Ph)_3$, and in that between $(\pi\text{-}C_5H_5)_2ZrClC_2H_5$ and $Al(C_2H_5)_3$, investigated by Sinn[24], in which bonds of the Zr–CH(Al)–CH_2–Al type are formed, in the reaction between (IX) and $Al(CH_2C_6H_5)_3$ no condensation of the two organometallic compounds takes place, and the addition compound $AlZr(CH_2Ph)_7$ is formed.

EXPERIMENTAL

All experiments were carried out in an atmosphere of oxygen-free dry nitrogen. Solvents were purified by conventional methods, dried and then distilled from sodium ribbon or $LiAlH_4$ under nitrogen. All the starting materials were of reagent grade and were dried and then distilled under nitrogen before use. $ZrCl_4$ (received from Schuchardt) was sublimed. $TiCl_4$ was used as received from Carlo Erba. CH_3OD was of 95% isotopic purity.

$Al(CH_2Ph)_3$ was prepared by the literature method[25]. This compound is monomeric in benzene. $Al(CH_2Ph)_2Cl$ and $Al(CH_2Ph)_2Br$ were obtained by treating $Al(CH_2Ph)_3$ with stoichiometric quantities of $AlCl_3$ or $AlBr_3$. The compounds $Sn(CH_2Ph)_4$ and $B(CH_2Ph)_3$ were made by established methods[26,27].

The oxidation state of titanium was measured as previously described[28] after decomposition of the cooled aromatic hydrocarbon solution of the titanium compound with methanol and aqueous HCl.

Gas-chromatographic analyses were performed by means of a Perkin–Elmer model 116 gas chromatograph. Mass spectra were recorded on a Hitachi–Perkin–Elmer model RMU/6E mass spectrometer. IR spectra were recorded with a Perkin–Elmer model 125 spectrophotometer on nujol mulls, oxygen and moisture being strictly excluded. NMR spectra were measured with Perkin–Elmer RM 10, Varian HA 100 and JEOL 4H 100 S instruments. All the samples were measured as solutions in sealed tubes under nitrogen with a concentration of less than 25 mmole percent. In order to avoid possible reactions between TMS and the benzyl derivatives, we used a commercial sample (Sogesil) of silicone as internal standard (0.22 ppm in benzene, 0.24 ppm in toluene, 0.09 ppm in $CFCl_3$ downfield from TMS). The values in ppm are referred to TMS = 10.

*Tetrabenzyltitanium**

A solution of $(PhCH_2)MgCl$ (0.8461 moles) in 850 ml of ether was placed in a 1500 ml, three necked flask equipped with stirrer and an addition funnel with equalizing arm. A solution of 0.2110 moles of $TiCl_4$ in 215 ml of n-heptane was added dropwise at −15° during 2 h. The red-brown reaction mixture was stirred for a further 3 h at the same temperature; the cooled solution was filtered and the residue extracted with ether (1500 ml). The solvent was removed in vacuo and the red residue extracted with n-heptane at room temperature. By slow cooling the hydrocarbon solution at −20°, 34.60 g (40%) of $Ti(CH_2Ph)_4$ were obtained as dark red crystals.

Tetrabenzylzirconium

To a stirred solution of 1.0801 moles of $(PhCH_2)MgCl$ in 1480 ml of ether, $ZrCl_4$ (60 g, 0.2561 moles) was added in portions at −15°. After 15 h the yellow-brown mixture was filtered at 0° and the residue washed with ether (500 ml).

Evaporation of the solvent in vacuo and crystallization of the residue from toluene gave 35 g (30%) of $Zr(CH_2Ph)_4$ as yellow plates. Further purification was achieved by recrystallisation from the same solvent. In order to avoid photochemical decomposition, all operations were conducted in the absence of light.

Dibenzyltitanium diethoxide

To a stirred benzene solution (36 ml) containing $Ti(CH_2Ph)_4$ (4.79 g, 0.0115

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* The analytical data, melting points and the cryoscopic molecular weight determinations of all the isolated compounds are given in Table 1.

moles), 0.0231 moles of anhydrous and deaerated ethyl alcohol in benzene (25 ml) were added dropwise, at 5°. After 14 h, the solvent was removed in *vacuo* and the red-orange residue washed with n-heptane and then crystallized from concentrated toluene solution by slowly adding n-heptane. Red-orange $Ti(CH_2Ph)_2(OC_2H_5)_2$, 2.6 g (70%) was thus obtained.

Tribenzyltitanium chloride

512.2 ml (0.0230 moles) of anhydrous HCl were slowly (2 h) introduced at −10° in an evacuated 250 ml three-necked flask equipped with stirrer and thermometer and containing a solution of $Ti(CH_2Ph)_4$ (9.55 g, 0.0231 moles) in 150 ml of toluene. The solution became red-brown and some brown precipitate was formed. The mixture was filtered at −10° and the residue extracted 3 times with 200 ml of toluene. By pouring the toluene solution into 1000 ml of n-heptane cooled at −78°, 6.75 g (86%) of red-brown crystalline $Ti(CH_2Ph)_3Cl$ was obtained.

Tribenzyltitanium bromide, tribenzyltitanium iodide and tribenzylzirconium chloride

By the procedure described above, and using $Ti(CH_2Ph)_4$ or $Zr(CH_2Ph)_4$ and the appropriate hydrogen halide, the following compounds were obtained: $Ti(CH_2Ph)_3Br$, $Ti(CH_2Ph)_3I$, $Zr(CH_2Ph)_3Cl$ (yield: 89%, 10% and 80%, resp.).

Tribenzyltitanium fluoride

97.53 ml (0.0048 moles) of gaseous BF_3 were slowly (2 h) introduced at −10° in a flask containing a solution of $Ti(CH_2Ph)_4$ (5.53 g, 0.0144 moles) in 80 ml of toluene. A red-brown crystalline precipitate of $Ti(CH_2Ph)_3F$ was formed (1.96 g, 40%).

Dibenzylzirconium dichloride

441 ml (0.0184 moles) of anhydrous HCl were slowly (100 minutes) introduced at −10° in an evacuated 250 ml three-necked flask equipped with stirrer and thermometer and containing a solution of $Zr(CH_2Ph)_4$ (4.220 g, 0.0092 moles) in 50 ml of toluene. When the introduction of HCl was complete an orange solid precipitated. The reaction mixture was stirred for a further 2 h. The orange $Zr(CH_2Ph)_2Cl_2$ 1.8 g (60%) was filtered, washed with n-heptane and dried in vacuo at −10°.

Dibenzyltitanium dibromide

To a stirred solution of $Ti(CH_2Ph)_4$ (1.31 g, 0.0032 moles) in 30 ml of toluene cooled to −10° was slowly (30 min) added a solution of $TiBr_4$ (1.16 g, 0.0032 moles) in 7 ml of toluene. After filtration the solution was evaporated to dryness in vacuo at −10°, to give $Ti(CH_2Ph)_2Br_2$ 1.48 g (60%), a red solid.

Tribenzylmethyltitanium

To a stirred solution of $Ti(CH_2Ph)_3Cl$ (10.11 g, 0.0283 moles) in diethyl ether (120 ml), 26 ml of a 1.1 *M* ether solution of CH_3MgI were slowly added at −20°. After 4 h the red mixture was filtered at −20° and the residue washed with ether. Evaporation in vacuo at −20° of the filtrate left a residue which was extracted with n-heptane and filtered at the same temperature; cooling to −78°, gave 2.38 g (25%) of deep-red crystals of $Ti(CH_2Ph)_3CH_3$.

Compound isolated from reaction of $Zr(CH_2Ph)_4$ *with* $Al(CH_2Ph)_3$

$Al(CH_2Ph)_3$ (1.315 g, 0.0044 moles) and $Zr(CH_2Ph)_4$ (2.011 g, 0.0044 moles) were dissolved in xylene (42 ml) and the solution was stirred for 2 h at room temperature.

The colour of the reaction mixture turned from orange to deep-red and a red microcrystalline precipitate was formed. This was filtered off and crystallized from toluene to give 2.65 g (79.5%) of red crystals of $ZrAl(CH_2Ph)_7$, m.p. 114–115°. (Found: C, 77.03; H, 6.54; Al, 3.77; Zr, 12.17; mol. wt. cryoscopic in benzene, 650. $C_{49}H_{49}AlZr$ calcd.: C, 77.83; H, 6.53; Al, 3.57; Zr, 12.16%; mol. wt., 756.) After hydrolysis with methyl alcohol the calculated amount of toluene was found by GLC analysis.

Reaction of $ZrAl(CH_2Ph)_7$ *with ethyl ether*

As soon as $ZrAl(CH_2Ph)_7$ (0.93 g, 0.0012 moles) was dissolved at room temperature in 5 ml of ether, a yellow crystalline solid deposited. After cooling to 0° this solid was filtered off, washed with additional ether and dried in vacuum; yield 0.31 g (55%) of $Zr(CH_2Ph)_4$, m.p. 133–134°. (Found: Zr, 19.46. $C_{28}H_{28}Zr$ calcd.: Zr, 20.03%.) The ether layer was evaporated and the oily residue extracted at −10° with n-heptane to leave 0.060 g (10.7%) of yellow crystals insoluble in n-heptane. These were also identified as $Zr(CH_2Ph)_4$.

Evaporation of the n-heptane solution afforded an oily product identified by GLC and IR as $Al(CH_2Ph)_3\cdot(C_2H_5)_2O$.

Reaction of $Ti(CH_2Ph)_4$ *with* $Al(CH_2Ph)_3$

200 ml benzene solution containing 7.04 g (0.0117 moles) of $Ti(CH_2Ph)_4$ and 3.95 g (0.0131 moles) of $Al(CH_2Ph)_3$ were stirred for 3 h at room temperature. After filtration of the dark brown reaction mixture the filtrate was evaporated in vacuum at −10° to leave a brown solid, which was washed with cold n-heptane and then dried in vacuum (4 g). (Found: Al, 6.31; Ti, 7.25%. Toluene by GLC, after alcoholysis, 86.44%.) Analysis by mass-spectrometry after reaction with CH_3OD: C_7H_8, 5.1; C_7H_7D, 72.3; $C_7H_6D_2$, 10.4; $C_7H_5D_3$, 12.2%.

Reaction of $Zr(CH_2Ph)_4$ *with* O_2

A flask equipped with magnetic stirrer, cooled to 15° and containing $Zr(CH_2Ph)_4$ (0.255 g, 0.00056 moles) dissolved in 8 ml of xylene, was evacuated and then connected with a graduated buret containing O_2. In 20 minutes 25.8 mol (0.00115 moles) of O_2 (s.t.p.) were absorbed. Benzyl alcohol (0.0012 moles) was found by GLC in the reaction mixture after hydrolysis with butyl alcohol and HCl.

Reaction of $Zr(CH_2Ph)_4$ *with* CO_2

A 100 ml stainless steel autoclave was charged with a solution of $Zr(CH_2Ph)_4$ (4.61 g, 0.0101 moles) in toluene (50 ml) and carbon dioxide was introduced (13 atm). In 20 h at room temperature 0.0202 moles of CO_2 were absorbed. The reaction mixture was then hydrolysed with 10% aqueous hydrochloric acid and the organic layer chromatographed on an alumina column. Elution with benzene gave a fraction which after evaporation to dryness and crystallisation from petroleum ether gave white crystals m.p. 114.5°; mixed m.p. with tribenzylcarbinol 114.5°; the IR and NMR spectra were also in agreement. Further elution with methyl alcohol and then with 5% aqueous NaOH, gave a fraction which was acidified with aqueous HCl and extracted with ethyl ether. The ether layer was dried over $MgSO_4$, filtered and evaporated to dryness; after crystallization of the residue from petroleum ether white needles, m.p. 76–77°, were obtained; mixed m.p. with phenylacetic acid, 76–77°.

Irradiation of $Zr(CH_2Ph)_4$

A solution of $Zr(CH_2Ph)_4$ (15.25 g) in 180 ml of toluene was irradiated in a quartz apparatus, at −60°, for 17 h with Hanovia 450 W medium pressure lamp. After irradiation, the dark-brown solution was poured into 1000 ml of n-heptane cooled at −78°. The separated precipitate was filtered, washed repeatedly with n-pentane, and dried in high vacuum at −30°. The obtained brown product (6 g) decomposes above 0°. (Found: Zr, 22.3%. Toluene by GLC, after alcoholysis, 49.2; H_2, 0.3; 2- and 4-methyldiphenylmethane, 30.2%).

Thermal decomposition of $Ti(CH_2Ph)_4$

A solution of $Ti(CH_2Ph)_4$ (0.46 g, 0.0011 moles) in 60 ml of n-heptane was refluxed for 24 h. The red solution rapidly changed to deep-brown and then a black precipitate separated out. After filtration the colourless solution was analysed by GLC and only toluene (0.259 g, 0.0028 moles) was found along with n-heptane. The black solid amounted to 0.13 g (29%). (Found: Ti, 24.63%.)

Thermal decomposition of $Zr(CH_2Ph)_4$

A solution of $Zr(CH_2Ph)_4$ (0.3917 g, 0.00086 moles) in 82 ml of n-octane was heated for 5 days at 100° in the absence of light. The yellow colour of the solution changed slowly to dark green and than a black precipitate 0.1047 g (26.8%) separated out. (Found: Zr, 37.26%.)

After filtration the colourless solution was analysed by GLC and only toluene (0.204 g, 0.0022 moles) was found.

Isomerization of 1-hexene with $Zr(CH_2Ph)_4$

To a 15 ml toluene solution containing 0.41 g of $Zr(CH_2Ph)_4$ were added 2 ml of 1-hexene. After standing for five days in the light, at room temperature (the solution became more and more dark brown but was not observed any precipitate) the solution was decomposed with water and the organic layer analysed by GLC (see Table 3).

Isomerization of 1-hexene with $Ti(CH_2Ph)_4$

Employing the procedure above, the results in Table 3 were obtained.

Hydrogenation of 1-hexene with tetrabenzylzirconium

A vessel containing a solution of $Zr(CH_2Ph)_4$ (0.201 g) in 10 ml of toluene and equipped with a magnetic stirrer was evacuated and 3 ml of 1-hexene were added. The vessel was then connected with a graduated buret containing dried H_2. In 7 h 328 ml of H_2 were adsorbed. After hydrolysis was found, by GLC: hexane, 53.2; 1-hexene, 40.1; *trans*-2-hexene, 4.31; *cis*-2-hexene, 1.6; *trans*-3-hexene, 0.3%.

Hydrogenation of 1-hexene with tetrabenzyltitanium

Employing the procedure above the following results were obtained after 100 h: hexane, 46.8; *trans*-2-hexene 32.9; *cis*-2-hexene, 17.95; *trans*-3-hexene, 2.35%.

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