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SYNTHESIS AND CHEMICAL PROPERTIES OF BENZYLTITANIUM HALIDES ($RTiX_2$ AND R_2TiX)

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Summary

Benzyltitanium chlorides and iodides were prepared by interaction of tribenzyltitanium with HCl and iodine in aromatic hydrocarbon media. The compounds are stable at temperatures below −30°C. Heating to room temperature induces quantitative disproportionation into an equimolecular mixture of Ti^{II} and Ti^{IV} compounds. The composition of the disproportionation products was studied. Small amounts of dienes or organoaluminium compounds were found to completely suppress the process of disproportionation; complex formation of organotitanium compounds with organoaluminium ones was investigated. A direct synthesis of TiR_3 compounds from $TiCl_3$ and the corresponding alkyllithiums was performed at low temperatures.

Only few results on the methods of synthesis and chemical properties of organotitanium(III) halides have been reported in the literature. The information available only concerns the synthesis of $PhTiCl_2 \cdot 3Py$ [1] and $Ph_2TiCl \cdot 3Et_2O$ [2], stable at 6–30°C and −20°C respectively.

As it was found in our laboratory in 1976 [3], the reaction of $TiCl_3$ with Me_3SiCH_2Li at room temperature does not result in TiR_3, but forms an equimolecular mixture of TiR_4 and TiR_2. The absence of TiR_3 in the reaction products was attributed to the instability of the intermediate alkyltitanium halides R_nTiCl_{3-n} and their disproportionation into equimolecular amounts of Ti^{IV} and Ti^{II} compounds. Later, it was shown that TiR_3 ($R = CH_2C_6H_5$ and CH_2SiMe_3) may be obtained in high yields from the corresponding TiR_4 and C_2H_5Li [4]:

$$R_4Ti + C_2H_5Li \rightarrow [(R_4TiC_2H_5)Li] \rightarrow R_3Ti + 0.5C_2H_4 + 0.5C_2H_6$$

The present study deals with the synthesis and chemical properties of benzyltitanium halides $(PhCH_2)_{3-n}TiX_n$ ($X = Cl, I$; $n = 1,2$). These compounds were prepared from tribenzyltitanium synthesized as reported [4].

We have found that a quantitative reaction of tribenzyltitanium and molecular iodine occurs rapidly in aromatic hydrocarbons at low temperatures:

$$(PhCH_2)_3Ti + nI_2 \rightarrow (PhCH_2)_{3-n}TiI_n + nPhCH_2I \ (n = 1\text{–}3) \qquad (1)$$

With excess iodine reaction 1 may be used for quantitative determination of the Ti–C bond content. With an equimolecular ratio of the reagents at −35 to 40°C the reaction between $(PhCH_2)_3Ti$ and I_2 proceeds in two stages:

$$(PhCH_2)_3Ti + I_2 \rightarrow (PhCH_2)_2TiI + PhCH_2I \qquad (2)$$

$$(PhCH_2)_2TiI + PhCH_2I \rightarrow PhCH_2TiI_2 + PhCH_2CH_2Ph \qquad (3)$$

The first stage (reaction 1) proceeds at a high rate and is complete in 5–10 minutes. Under the same conditions the interaction between benzyl iodide and organotitanium compounds is slow. For instance, reaction 3 at −35°C takes about 20 hours (Table 1), while the interaction between benzyl iodide and tribenzyltitanium about 10 hours. The reactions are characterized by iodide being present in the products of hydrolysis of the reaction mixtures with aqueous sulfuric acid. In both cases the yield of dibenzyl, determined by GLC with an internal standard, was quantitative. Therefore, 1 mole of tribenzyltitanium reacts with 1 mole of iodine to give benzyltitanium diiodide and with 0.5 mole of iodine to afford dibenzyltitanium iodide:

$$(PhCH_2)_3Ti + I_2 \rightarrow PhCH_2TiI_2 + PhCH_2CH_2Ph$$

$$(PhCH_2)_3Ti + 0.5I_2 \rightarrow (PhCH_2)_2TiI + 0.5PhCH_2CH_2Ph$$

Benzyltitanium chlorides (R_2TiCl and $RTiCl_2$) were prepared by interaction of tribenzyltitanium in ethylbenzene solution and a calculated amount of dry hydrogen chloride (reaction time 1 hour at −35°C):

$$(PhCH_2)_3Ti + nHCl \rightarrow (PhCH_2)_{3-n}TiCl_n + nPhCH_3 \ (n = 1,2)$$

The reaction was followed by the amount of toluene formed during the process. Toluene was determined by GLC in an aliquot of the reaction mixture treated with an excess of iodine solution in n-decane (this treatment converts the benzyl groups of the organotitanium compounds into benzyl iodide so that they do not disturb the analysis).

The content of Ti–C bonds in the benzyltitanium halides was determined by two

TABLE 1

INTERACTION OF TRIBENZYLTITANIUM (R_3Ti) WITH IODINE AT −35°C [a]

Reaction time, hours	Found after hydrolysis, mol/mol	
	I^-/Ti	R–R/Ti
0.1	0.97	
1	0.98	
5	1.06	
10	1.20	
20	1.98	1.02
40	1.98	0.98

[a] $C(R_3Ti) = 0.040$ mole/l, $C(I_2) = 0.040$ mole/l, toluene + benzene (3 : 1)

TABLE 2

ANALYTICAL DATA FOR BENZYLTITANIUM HALIDES

R_nTiX_{3-n}	Consumption of I_2, (mol/mol)	Found after hydrolysis (mol/mol)	
		X^-/Ti^{III}	RH/Ti^{III}
$RTiCl_2$	1.02±0.02	2.00±0.03	0.96±0.03
R_2TiCl	1.98±0.04	0.98±0.02	1.98±0.02
$RTiI_2$	1.02±0.02	1.98±0.03	0.96±0.03
R_2TiI	2.01±0.04	0.98±0.02	0.03±0.02

independent methods: (1) iodometrically by the consumption of molecular iodine (benzene solution) and (2) chromatographically by the amount of toluene resulting from the hydrolysis of titanium–benzyl bonds with 0.2–0.4 *M* oxygen-free aqueous sulfuric acid. The content of halide-ions was also determined (argentometrically) as was that of Ti^{II} and Ti^{III}. Bivalent titanium was absent and the proportion of the trivalent metal corresponded to the theoretical prediction to within the experimental error (±2%). The yields of benzyltitanium halides were practically quantitative. Table 2 presents the analytical data.

Benzyltitanium halides are well soluble in aromatic hydrocarbons and stable at temperatures below −30°C (Table 3). As the temperature is raised to 20°C, all these compounds undergo quantitative disproportionation into an equimolecular mixture of Ti^{II} and Ti^{IV} compounds:

$$2\,Ti^{III} \rightarrow Ti^{II} + Ti^{IV} \qquad (4)$$

TABLE 3

YIELD OF HYDROGEN BY ACIDOLYSIS OF BENZYLTITANIUM HALIDE SOLUTIONS AND THEIR MIXTURES WITH BUTADIENE AND ORGANOALUMINIUM COMPOUNDS

No.	Ti compound	Additive, A	A/Ti (mol)	Storage conditions		Yield of H_2(% of theory) [a]
				T(°C)	Time(h)	
1	R_2TiI	–	–	−78	500	0
2	R_2TiI	–	–	−15	15	0
3	R_2TiI	–	–	20	2	98
4	R_2TiI	C_4H_6	10	20	5	0
5	R_2TiI	$(i\text{-}C_4H_9)_3Al$	1	20	5	0
6	R_2TiI	$(i\text{-}C_4H_9)_2AlCl$	1	20	5	0
7	R_2TiI	$(i\text{-}C_4H_9)_2AlI$	1	20	5	0
8	R_2TiCl	–	–	−30	5	0
9	R_2TiCl	–	–	20	5	100
10	$RTiCl_2$	–	–	−30	5	0
11	$RTiCl_2$	–	–	20	5	100
12	$RTiI_2$	–	–	−30	5	0
13	$RTiI_2$	–	–	20	5	100

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[a] According to eq 4 and 5, acidolysis carried out after the disproportionation is completed should lead to evolution of 0.25 mol of H_2 per mol of the starting $R_{3-n}TiX_n$.

Reaction 4 was followed as the bivalent titanium compounds formed, which were determined by the amount of hydrogen evolved as the reaction mixture was hydrolyzed with 0.5 *M* degassed aqueous sulfuric acid:

$$\mathrm{Ti^{II} + H^+ \rightarrow Ti^{III} + 0.5\ H_2} \qquad (5)$$

Table 3 presents data on the yield of hydrogen by the acidolysis of benzyltitanium halides solutions stored under different conditions.

Products of the disproportionation of dibenzyltitanium halides were investigated. It was found that a solution of dibenzyltitanium chloride stored at room temperature yields almost quantitatively a precipitate identified as $TiCl_2$. The hydrocarbon solution separated from the precipitate contains only tetrabenzyltitanium. A dibenzyltitanium iodide solution stored at room temperature gives no precipitate, although the disproportionation, as already mentioned, does occur. The composition of the products was determined by the extraction technique. The solvent was evaporated from dibenzyltitanium iodide solution at room temperature. The solid residue was extracted with n-pentane and then with *o*-xylene. The pentane solution was found to contain tribenzyltitanium iodide, and the *o*-xylene solution proved to contain a quantitative amount of benzyltitanium(II) iodide. Thus, disproportionation of dibenzyltitanium halides proceeds according to the following equations:

$$\mathrm{2\ (PhCH_2)_2TiCl \rightarrow TiCl_2 + (PhCH_2)_4Ti}$$

$$\mathrm{2\ (PhCH_2)_2TiI \rightarrow PhCH_2TiI + (PhCH_2)_3TiI}$$

Disproportionation of benzyltitanium halides at room temperature is suppressed completely by small amounts of butadiene or organoaluminium compounds (see, e.g. runs 4–7 in Table 3). Indeed, no hydrogen is present in the products of acidolysis of reaction mixtures of benzyltitanium halides with these species after 5–10 h of storage at 20°C. An IR spectroscopic investigation * of the products of the interaction of dibenzyltitanium iodide with butadiene (C_4H_6 : Ti=20 : 1) shows in particular, that organotitanium compounds of η^3-allyl type are formed. The IR spectrum of the sample contained a complete set of absorption bands typical of an η^3-allyl ligand, i.e. 460 cm^{-1}(ν_{as}(Ti–C)), 540 ($\delta_{\|}$(C–C–C)), 970,1020,1220–1240 ($\delta_{\perp}$ (C–C–H)), 1500 cm^{-1} (ν(C=C)). The spectrum also exhibits absorption bands characteristic of the benzyl group, i.e. 700, 750, 1040, 1500 and 1610 cm^{-1}. The 910, 970, 1315 and 1650 cm^{-1} bands are due to vibrations of bonds and angles in the isolated double bond of the polybutadiene chain formed.

The disproportionation reaction is also suppressed completely by trialkylaluminium and dialkylaluminium halides. Using the $(PhCH_2)_2TiI + i\text{-}Bu_2AlCl$ (Al : Cl=1 : 1) system as an example, it was shown by high-resolution PMR spectroscopy ** that complex formation between the organometallic compounds involves transalkylation, so that i-C_4H_9 groups are transferred to titanium and benzyl groups to aluminium (see next formula). This process is evidenced by the absence of PMR signals of benzyl groups bounded to titanium (no signals of methylene protons at δ 2.21 ppm). The signal at δ 1.25 ppm belongs to the methylene protons of the benzyl

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* IR spectra were recorded on a Karl Zeiss UR-20 spectrometer. The authors wish to thank Dr. G.N. Bondarenko for recording and interpreting the spectra.

** PMR spectra were recorded on a Bruker-270 spectrometer. The authors are indebted to Dr. L.S. Bresler for recording and interpretation.

groups attached to aluminium, and that at δ 1.70 ppm is due to the methylene protons of the isobutyl group bonded to titanium.

Evidence for transalkylation is also provided by our data on the consumption of benzyl groups during butadiene polymerization in the presence of dibenzyltitanium iodide and its complex with diisobutylaluminium chloride (Fig. 1). Figure 1 shows that in the case of R_2TiI, at a monomer conversion about 40% the products of acidolysis of the reaction mixture contain no toluene, while with the R_2TiI + i-Bu_2AlCl system benzyl groups do not participate in polymerization initiation at all. It is well known that polymerization of dienes by such systems involves Ti–C bonds. Thus the presence of toluene in the hydrolysis products in the case of the R_2TiI + i-Bu_2AlCl system testifies to the fact that the first molecule of the monomer inserts into the titanium–isobutyl bond.

Remarkable results were obtained in the study of the interaction of tribenzyltitanium and dibenzyltitanium iodide with $(i\text{-}C_4H_9)_2AlH$. It was found that a mixture of hydrocarbon solutions of these compounds (Al : Ti = 1 : 1) at −35°C yields 0.5 mol hydrogen per mol of R_2AlH. Acidolysis after the reaction was complete resulted in the same amount of hydrogen. These data indicate that during an exchange reaction the hydride ion of the organoaluminium compounds is transferred to titanium. The resulting unstable titanium hydride decomposes to form hydrogen and bivalent titanium:

$$(PhCH_2)_2TiX + R_2AlH \rightarrow \left[\rangle Ti\text{-}H\right] \rightarrow 0.5H_2 + Ti^{II} \xrightarrow{H^+} 0.5H_2$$

$$X = CH_2Ph \text{ or } I$$

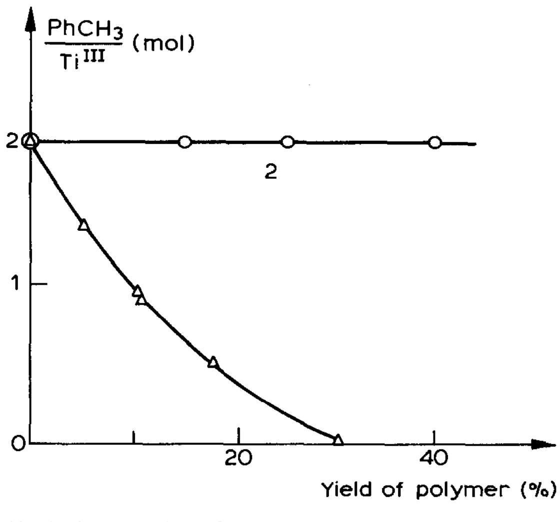

Fig. 1. Consumption of benzyl groups during butadiene polymerization under the action of dibenzyltitanium iodide (curve 1) and the dibenzyltitanium iodide-diisobutylaluminium chloride system (Al : Ti = 1 : 1). Solvent ethylbenzene, $C_{cat.} = 0.003$, $C_{mon.} = 5.00$ mol/l, 20°C.

On the other hand, a reaction between diisobutylaluminium hydride and the organotitanium compounds in the presence of butadiene gives neither hydrogen nor Ti^{II}. Under these conditions butadiene apparently adds to the Ti–H bond to afford stable derivatives of trivalent titanium.

Direct synthesis of TiR_3 from $TiCl_3$ and alkyllithium compounds

Since benzyltitanium halides proved reasonably stable at temperatures below −30°C, it became possible to carry out a direct synthesis of TiR_3 from β-$TiCl_3$ and the corresponding organolithium compounds containing no hydrogen in β-position to the metal. Thus we have prepared $(PhCH_2)_3Ti$ in a 50% yield from β-$TiCl_3$ and $PhCH_2Li$ in a 1 : 2 ratio at −30°C in diethyl ether:

$$3PhCH_2Li + TiCl_3 \rightarrow (PhCH_2)_3Ti + 3LiCl$$

Likewise, β-$TiCl_3$ and $(CH_3)_3SiCH_2Li$ (Li : Ti=2 : 1) in toluene at −40°C gave tris-trimethylsilylmethyltitanium in a 60% yield:

$$3Me_3SiCH_2Li + TiCl_3 \rightarrow (Me_3SiCH_2)_3Ti + 3LiCl$$

Experimental section

All the experiments were performed in glassware in an atomsphere of pure dry argon (the contents of oxygen and water did not exceed 5 ppm). Prior to filling the glass equipment with argon it was heated and evacuated to a residual pressure of 10^{-2}–5×10^{-3} Torr. All solvents were purified to eliminate traces of oxygen and water according to the common techniques for active organometallic compounds and stored in argon over sodium wire. The solutions of organotitanium compounds were stored in glass vessels with metal valves at −78°C.

Synthesis of tribenzyltitanium

(a) Interaction of TiR_4 and C_2H_5Li. A three-necked flask was equipped with an efficient stirrer, a dropping funnel and outlets for connection to a vacuum line and for introducing the solution of $(PhCH_2)_4Ti$. Under an argon atmosphere was placed tetrabenzyltitanium into the flask (100 ml, 0.130 M in toluene, 0.013 mol) and into the funnel was placed ethyllithium (24 ml, 0.560 M in benzene, 0.013 mol). Upon cooling the flask to 0°C the ethyllithium solution was added to the vigorously stirred solution of tetrabenzyltitanium during 30–40 min in a vacuum. The reaction mixture gradually became dark brown. When all the ethyllithium had been added, the mixture was stirred for 15 minutes, then cooled to −78°C, and gaseous CO_2 (0.025–0.026 mol) purified by repeated vacuum sublimation was added under vigorous stirring. After 10–12 min the reaction mixture was evacuated at −78°C and then the temperature was raised to 0°C in order to remove completely the excess of CO_2. The solution obtained of tribenzyltitanium was filtered, the residue was extracted with toluene and the extract (two portions, 40–50 ml each) united with the filtrate.

The yield of tribenzyltitanium in the solution was about 93%.

(b) Interaction of β-$TiCl_3$ with $PhCH_2Li$. The reaction between β-$TiCl_3$ and benzyllithium obtained from tribenzylantimony [5] was performed in diethyl ether at −30°C at a mole ratio Li : Ti = 2 : 1. As the reaction was completed, the ether was

evaporated in a vacuum at a temperature below 0°C. To the dry residue were added 50 ml n-pentane which was also evaporated to remove traces of ether. The dry residue was extracted with *o*-xylene. The yield of tribenzyltitanium in the solution was 50%. According to the analytical data the consumption of iodine was 2.96 mol per mol titanium; hydrolysis led to 3.00 mol toluene per mol titanium, while no Li^+ or Cl^- were present in the solution.

Synthesis of tris(trimethylsilyl)titanium

Tris(trimethylsilylmethyl)titanium was prepared from β-$TiCl_3$ and Me_3SiCH_2Li in toluene at −40°C at a mole ratio of Li : Ti = 2 : 1. After 3 h the solution was filtered from the precipitate and analyzed. Li^+ and Cl^- ions were absent and the RH : Ti ratio after hydrolysis was 3.01 : 1. To purify the final product the solvent was condensed in liquid nitrogen and the residue distilled below 50°C in a high vacuum. The yield of $[(CH_3)_3SiCH_2]_3Ti$ (pale yellow viscous liquid) was 60%.

Analysis of benzyltitanium derivatives

(a) The content of Ti^{II} was determined from the amount of hydrogen evolved in the decomposition of the organotitanium compound by a degassed aqueous solution of sulfuric acid. This method is based on the ability of Ti^{II} compounds to evolve hydrogen from acidic aqueous solutions [6]. The hydrocarbon layer was completely decolorized in 20–30 min at room temperature. The volumetrical analysis was carried out to within ±3%.

(b) The content of Ti^{III} was determined by a reaction with Fe^{III} as reported [7].

(c) The total content of Ti was determined trilonometrically. An aliquot of the solution of the organotitanium compound was first decomposed with aqueous KOH (3–5 ml of a 10% solution), then the pH was brought to 2–3 with 6 *M* HNO_3. In the aliquote of the aqueous solution thus obtained Ti^{IV} was determined using Trilon B by back-titration with lead(II) nitrate in the presence of hexamine and xylenol orange as indicator.

(d) Halide ions were determined argentometrically as reported [8].

(e) Lithium ions were determined by atomic absorption.

(f) The number of $Ti{-}CH_2Ph$ bonds in benzyl derivatives of Ti^{III} was determined by two independent techniques, i.e. (1) iodometrically, as it was found that all the benzyl derivatives of titanium react quantitatively with iodine, 2 equivalents of iodine being consumed for every Ti–C bond, and (2) chromatographically by the amount of toluene resulting from acidolysis of $Ti{-}CH_2Ph$ bonds with oxygen-free 0.1–0.2 *M* aqueous sulfuric acid.

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