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REACTION OF DICYCLOPENTADIENYLDIPHENYLTITANIUM WITH PHENYLLITHIUM

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SUMMARY

The reaction of dicyclopentadienyldiphenyltitanium with phenyllithium in ether solution takes place with reduction of titanium(IV) to titanium(III) and then to titanium(II). The reaction products in the presence of excess phenyllithium are diphenyltitanium, cyclopentadienyllithium, benzene, metallic lithium and small amounts of diphenyl and triphenylene. Titanium compounds were found to catalyse the decomposition of phenyllithium to benzene and lithium.

Summers and Uloth[1], the first to obtain dicyclopentadienyldiphenyltitanium (Cp_2TiPh_2), found that this compound can dissolve in an excess of an ethereal solution of phenyllithium; They explained this by the formation of an anion complex:

$$Cp_2TiPh_2 + PhLi \rightleftarrows (Cp_2TiPh_3)^- Li^+$$

On further study of this reaction, they found[2] that in the presence of a twofold excess of PhLi, the initial Cp_2TiPh_2 was eventually destroyed and that PhLi disappeared but they did not, however, ascertain the nature of the processes occurring in this case.

The present work reports on a detailed study of the reaction of diphenyltitanocene with PhLi. All experiments were carried out in absolute diethyl ether at room temperature, in an atmosphere of dry argon.

When the solution of Cp_2TiPh_2 was mixed with excess PhLi in a ratio of 1:3, the colour change from yellow to blackish-green was found to be related to the reduction processes occurring in the reaction mixture. As soon as the initial reagents were mixed, a signal of a titanium(III) compound with a g-factor, 1.986 ± 0.001, appeared in the electronic paramagnetic resonance spectrum of the mixture, with a width of ~ 4 ersteds. The intensity of the signal increased rapidly and in 70–80 min reached its maximum after which it began to diminish. Measurements of the intensity have shown that between 60 and 180 min after the beginning of the reaction, a great bulk of organo-titanic molecules are paramagnetic. Later, along with the decrease in the intensity of the initial signal (a day after the beginning of the reaction, it is about 10% of the initial concentration of the organotitanium compound), the spectrum becomes more complex: the initial spectrum broadens and new weak signals appear ($g = 1.979$ and 1.959).

The resultant data show that in the course of the reaction of Cp_2TiPh_2 with excess PhLi, the initial titanium(IV)-compound is reduced, passing through the titanium(III) stage. A similar picture was observed previously when studying the thermal decomposition of compounds of type Cp_2TiR_2[3].

An investigation of the products of the reaction of Cp_2TiPh_2 with excess PhLi (molar ratio Cp_2TiPh_2 : PhLi = 1 : 3) (see Tables 1 and 2), show that the reduction of Cp_2TiPh_2 is accompanied by the disappearance of PhLi and the formation of benzene and small amounts of diphenyl. A day after the beginning of the reaction, carboxylation of the reaction mixture no longer produces benzoic acid, indicating that the solution does not contain PhLi. According to infrared spectral data the amount of benzene in the mixture at this time is 3 moles*.

TABLE 1

YIELD OF C_6H_6 IN THE REACTION OF Cp_2TiPh_2 WITH PhLi AT 20°

Cp_2TiPh_2 : PhLi	Reaction time (h)	C_6H_6 (mole/mole Cp_2TiPh_2)
1 : 1	24	0.97
1 : 1	36	1.00
1 : 1	96	0.97
1 : 1	264	1.10
1 : 3	1.5	1.40
1 : 3	4.0	2.10
1 : 3	24	2.97
1 : 3	264	3.06
1 : 10	24	3.00
1 : 10	48	4.00
1 : 10	264	8.55

TABLE 2

REACTION OF DICYCLOPENTADIENYLDIPHENYLTITANIUM WITH PHENYLLITHIUM

Molar ratio ($Cp_2TiPh_2^a$: PhLi)	Reaction time (h)	Reaction products (mole/mole Cp_2TiPh_2)							
		Benzene		Diphenyl	Tri-phenylene	CpLi	Li metal	After treatment by CCl_4+HCl	
		Before hydro-lysis	After hydro-lysis					Cp_2TiCl_2	$CpTiCl_3$
1 : 1	24.0	0.97	1.97			1.0 (0.7)	None		
1 : 3	1.5	1.40						0.66	0.15
1 : 3	4.0	2.10						0.31	0.02
1 : 3	24.0	2.87	1.86	0.11	0.073	1.8	1.04	None	None
1 : 10	264.0	8.55					5.90	None	None

[a] Initial concentration of Cp_2TiPh_2, 0.03 mole/l.

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* Throughout this paper the yields of all products are given in moles/mole of initial Cp_2TiPh_2.

With a tenfold excess of PhLi, nearly all the PhLi also enters gradually into the reaction; after 11 days about 9 moles of PhLi have reacted and about 9 moles of benzene have formed.

Parallel with the disappearance of PhLi and benzene formation, the sandwich structure of the initial Cp_2TiPh_2 is destroyed. This process was followed by treating the reaction mixture at certain time intervals with carbon tetrachloride saturated with HCl when, as shown earlier[4], di- and monocyclopentadienyl derivatives of titanium can be transformed into Cp_2TiCl_2 and $CpTiCl_3$, respectively. It can be seen from Table 2 that 90 min after the beginning of the reaction, most of the titanium-containing compounds are still in the form of dicyclopentadienyl derivatives, although there appears to be some monocyclopentadienyl compounds. During the reaction, the number of titanium compounds still retaining the sandwich structure diminishes and a day later the initial sandwich titanium compound has practically decomposed.

The destruction of the cenic structure is accompanied by the formation of cyclopentadienyllithium detected by reaction with ferrous chloride to give ferrocene. Sandwich compounds of titanium do not yield ferrocene under these conditions[3]. When alcohol acts on the reaction mixture, cyclopentadiene is separated, and is identified as cyclopentadienylthallium. The amount of PhLi a day after the beginning of the reaction was about 2 moles/mole of Cp_2TiPh_2, which indicates the complete destruction of the initial "cenic" structure.

Diphenyltitanium, $(C_6H_5)_2Ti$, proved to be the final product of the reaction of Cp_2TiPh_2 with excess PhLi. Its formation was verified as follows. If a day after the beginning of the reaction the mixture is treated with absolute methanol, about an additional 2 moles of benzene are formed. Alcoholysis of the mixture with deuteroethanol, C_2H_5OD, produces the appropriate amount of monodeuterobenzene. Treatment of the reaction mixture with HCl gives benzene, hydrogen and titanium trichloride, *i.e.*, products typical of the reaction of diphenyltitanium with HCl. Finally, it was possible to isolate diphenyltitanium from the reaction mixture as the etherate, $(C_6H_5)_2Ti\cdot(C_2H_5)_2O$. When heated this compound decomposes with production of metallic titanium, benzene and diphenyl.

In the process of alcoholysis or hydrolysis of the reaction mixture, there is evolution of molecular hydrogen which seemed to be due to the presence of metallic lithium in the mixture and which was isolated as an amalgam with mercury. The amount of lithium was determined by hydrolysis of the amalgam with excess 0.1 *N* HCl, (evolution of H_2) and subsequent back-titration of the remaining acid. The amount of lithium formed as a result of the reaction of Cp_2TiPh_2 with PhLi (molar ratio, $Cp_2TiPh_2 : PhLi = 1:3$) was 1 g-atom.

It was concluded that the reaction of Cp_2TiPh_2 with PhLi (1:3) proceeds mainly according to the following scheme:

$$Cp_2TiPh_2 + 3\ PhLi \rightarrow TiPh_2 + 2\ CpLi + 3\ [Ph^\cdot] + Li \qquad (1)$$

Phenyl radicals forming as a result of the reaction split off the hydrogen atom from ether to give benzene. The reaction of Cp_2TiPh_2 with 1 mole of PhLi was also investigated. In this case, also, when the reagents are mixed, a signal of a titanium-(III) compound appears in the electronic paramagnetic resonance spectrum, and is preserved for a considerably longer time (11 days or more) than in the experiments with a large amount of PhLi. The reduction is therefore discontinued at the titanium(III) stage. Chemical examination of the reaction products in this case (Table 1) indicates that when a mole of PhLi acts on Cp_2TiPh_2, 1 mole of benzene is formed (the amount is not increased subsequently), as well as 1 mole of cyclopentadienyllithium and of a trivalent titanium(III) compound, apparently $CpTiPh_2$. This is proved by the formation of $CpTiCl_3$* when HCl acts on the reaction mixture, and by the formation of an additional 2 moles of benzene upon alcoholysis of this mixture with methanol.

DISCUSSION OF RESULTS

The experimental data obtained suggest the following scheme for the processes taking place in the reaction between Cp_2TiPh_2 and PhLi.

According to Summers and Uloth[1], the formation of an anion complex is the initial stage of the reaction:

$$Cp_2TiPh_2 + PhLi \rightleftarrows (Cp_2TiPh_3)^-Li^+$$

However, this complex is unstable and decomposes with a homolytic break of the Ti–Ph bond and separation of the C_5H_5-groups as C_5H_5Li. These processes can proceed with a different sequence, *e.g.*:

$$(Cp_2TiPh_3)^-Li^+ \rightarrow (Cp_2TiPh_2)^-Li^+ + [Ph^\bullet]$$

$$(Cp_2TiPh_2)^-Li^+ \rightarrow CpTiPh_2 + CpLi$$

The resultant phenyl radicals split off the hydrogen atoms from the solvent (ether), yielding benzene.

The excess PhLi causes further decomposition of the resultant titanium(III) compounds, diphenyltitanium being the final product of the reaction:

$$CpTiPh_2 + PhLi \rightleftarrows (CpTiPh_3)^-Li^+ \rightarrow TiPh_2 + CpLi + [Ph^\bullet]$$

Thus, the transformation of Cp_2TiPh_2 into $TiPh_2$ consumes 2 moles of PhLi:

$$Cp_2TiPh_2 + 2\ PhLi \rightarrow TiPh_2 + 2\ CpLi + 2\ [Ph^\bullet]$$

If 3 moles of PhLi are added to the reaction, the third mole is the source of metallic lithium and of 1 benzene molecule. It may be assumed that the formation of lithium results from the reaction of the excess of PhLi with diphenyltitanium according to the scheme:

$$TiPh_2 + PhLi \rightleftarrows (TiPh_3)^-Li^+ \xrightarrow{-[Ph\cdot]} (TiPh_2)^-Li^+ \rightarrow TiPh_2 + Li$$

It could be shown that a prepared sample of diphenyltitanium (obtained from tetraphenyltitanium[5]) can react with PhLi, to produce benzene and metallic lithium. As evident from scheme (2), the process of decomposition of PhLi is accompanied by regeneration of diphenyltitanium. This means that the decomposition of PhLi upon interaction with diphenyltitanium and consequently with Cp_2TiPh_2 should be of a catalytic nature. Indeed, when a tenfold excess of PhLi is added to diphenyltitanium, the amount of lithium increases and after 96 h is already 4 g-atoms/mole of Ph_2Ti. An equivalent amount of benzene is also formed. A similar catalytic

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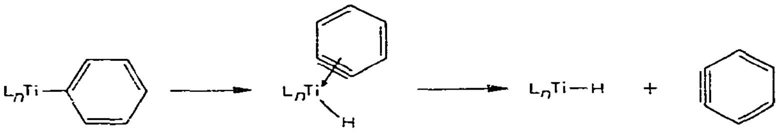
* Some Cp_2TiCl_2 is also formed, indicating that a compound with Cp_2Ti-fragments is present in the reaction mixture.

process is also observed in the reaction of PhLi with Cp_2TiPh_2. In this case, when the ratio, Cp_2TiPh_2 : PhLi is 1 : 10, 4 g-atoms of lithium/mole of Cp_2TiPh_2 are obtained after 48 h.

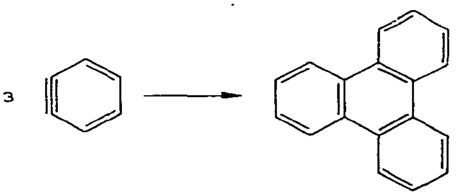
Scheme (1) shows that the reduction of Cp_2TiPh_2 to diphenyltitanium primarily results from the homolytic decomposition of Ti–Ph bonds, accompanied by the formation of phenyl radicals. The splitting of Ti–Ph bonds in the process of reduction may also take place in another way, although to a smaller extent.

In addition to benzene and diphenyl, small amounts of triphenylene are present in the reaction mixture, which suggests the intermediate formation of dehydrobenzene at one stage of the reduction. Dehydrobenzene formation may occur either through the stage of *ortho*-metallization of the phenyl ring connected with the titanium atom or by intramolecular transfer of the hydrogen *ortho*-atom to titanium.



(L = C_5H_5 or C_6H_5)

The dehydrobenzene obtained as a result of the reaction is further subjected to cyclic trimerization, yielding triphenylene:



Hence, interaction between Cp_2TiPh_2 and PhLi leads to the reduction of Cp_2TiPh_2, accompanied by the formation of diphenyltitanium, cyclopentadienyllithium and benzene, and of small amounts of diphenyl and triphenylene. In this case, an excess of PhLi disintegrates catalytically to metallic lithium.

EXPERIMENTAL

Reaction of dicyclopentadienyldiphenyltitanium with phenyllithium (1 : 1)

A 1 *N* ethereal solution of PhLi (6.0 ml, 0.006 mole) was added, with stirring in a stream of argon, to 2.00 g (0.006 mole) of Cp_2TiPh_2 in 200 ml of diethyl ether at room temperature. The colour of the solution changed gradually from yellow to blackish-green. A day later, the mixture no longer contained PhLi (carboxylation with gaseous CO_2 at −5° produced no benzoic acid). Benzene (0.46 g, 0.0058 mole) was found in the solution (from infrared spectra). After alcoholysis with absolute methanol, the total amount of benzene was 1.40 g (0.018 mole). The cyclopentadiene formed during the hydrolysis of cyclopentadienyllithium was identified by means of a thallium reagent as cyclopentadienylthallium; yield, 1.61 g (0.006 mole). Cyclopentadienyllithium was also determined by transformation to ferrocene by adding a suspension of ferrous chloride in tetrahydrofuran to the reaction mixture in a stream of argon and heating 4 h; the solvent was then distilled from the solution. The residue was treated with steam. Ferrocene (0.74 g, 0.004 mole) was isolated from the distillate and then purified by sublimation *in vacuo*, m.p. 72°. Mixed m.p. with ferrocene produces no depression.

In a parallel experiment, 50 ml of carbon tetrachloride saturated with hydroggen chloride was added to the reaction mixture 24 h after the beginning of the reaction and the mixture heated for 4 h. The precipitate was filtered off and the filtrate evaporated to dryness *in vacuo*. The two solids were dissolved in dichloroethane and the solution was analysed by paper chromatography for the content of dicyclopentadienyltitaniumdichloride (0.96 mmole) and monocyclopentadienyltitanium trichloride (0.78 mmole).

Reaction of dicyclopentadienyldiphenyltitanium with phenyllithium (1 : 3)

A 1 *N* ethereal solution of PhLi (18.0 ml, 0.018 mole) was added in a stream of argon, while stirring, to 2.0 g (0.006 mole) of Cp_2TiPh_2 in 200 ml of diethyl ether at 20°.

After 1.5 h the solution contained 0.66 g (0.0084 mole) of benzene, after 4 h 0.98 g (0.0126 mole), and after 24 h 1.34 g (0.0172 mole). The reaction products contained 0.10 g (0.00065 mole) of diphenyl. The solution contained no PhLi 24 h after the beginning of the reaction. Absolute methanol (50 ml) was added to this solution in a stream of argon and hydrogen was evolved (0.002 mole). The solvents were distilled over thallium reagent[6] and the precipitate of C_5H_5Tl (1.69 g, 0.0063 mole) was separated. The distillate contained 2.22 g (0.0284 mole) of benzene.

In a separate experiment, the reaction mixture was successively treated with methyl alcohol and 20% H_2SO_4. The aqueous layer was extracted with ether, and the extract dried with $MgSO_4$ and then carefully evaporated. The residue was recrystallized from n-hexane, and 0.10 g (0.00044 mole) of triphenylene was separated m.p. 196–197° (mixed m.p. 198°). (Found: C, 94.67, 94.69; H, 5.30, 5.39. C_8H_{12} calcd.: C, 94.70; H, 5.30%.)

Cyclopentadienyllithium was determined as in the preceding experiment. After the action of $FeCl_2$, 1.00 g (0.0054 mole) of ferrocene was separated.

In a parallel experiment, 5 ml of metallic mercury was added a day after the reactants had been mixed. The ethereal solution was stirred for 20 h at room temperature and then decanted from the mercury. The resultant mercury amalgam was washed with dry ether until the ether extracts no longer produced an alkaline reaction upon hydrolysis. The amalgam was decomposed with excess 1 *N* HCl solution (100 ml) when 80.6 ml (0.0036 mole) of hydrogen was evolved. Titration of the excess HCl showed that 0.0062 g-atom of metallic lithium had been produced.

In a separate experiment, diphenyltitanium etherate, $(C_6H_5)_2Ti \cdot (C_2H_5)_2O$, was isolated from the reaction mixture according to the method described earlier[5]. (Found: Ti, 17.44. $C_{16}H_{20}OTi$ calcd.: Ti, 17.36%.) The isolated diphenyltitanium etherate (0.47 g, 0.0017 mole) was heated for 20 h at 200° in a sealed double-horned vacuumed ampoule. The liquid products of thermal decomposition were frozen out in the other bend of the ampoule and were found to contain 0.12 g (0.0015 mole) of benzene. In addition, 0.12 g (0.0008 mole) of diphenyl was separated.

Reaction of dicyclopentadienyldiphenyltitanium with phenyllithium (1 : 10)

A 1 *N* ethereal solution of PhLi (60 ml; 0.060 mole) was added with stirring in a stream of argon to 2.00 g (0.006 mole) of Cp_2TiPh_2 in 200 ml of ether at 20°.

As a result of carboxylation with solid CO_2, 5.12 g (0.042 mole) of benzoic acid were separated 24 h after the beginning of the reaction; 48 h after carboxylation, 4.15 g (0.034 mole) of benzoic acid were obtained. The solution was determined spectrometrically to contain 1.40 g (0.018 mole) of benzene, and after 48 h, 1.87 g (0.024 mole) of benzene. After 11 days, the amount of benzene reached 4.01 g (0.0513 mole).

The method for determining metallic lithium is similar to that already described. The amount of lithium 264 h after the beginning of the reaction was 0.0354 g-atom.

Reaction of diphenyltitanium with phenyllithium

A 1 *N* solution of PhLi (90 ml, 0.09 mole) was added with stirring in a stream of argon at 20°, to an ethereal solution of 0.009 mole of Ph_2Ti obtained by thermal decomposition of tetraphenyltitanium in ether[5]. A spectrometrical determination showed that after 48 h the reaction mixture contained 0.70 g (0.009 mole) of benzene; after 96 h, 2.46 g (0.0315 mole), and after 168 h, 3.23 g (0.0414 mole) of benzene.

After 96 h, 7 ml of metallic mercury was added to the reaction mixture. The resultant mercury amalgam was washed with dry ether until the ether extract no longer produced an alkaline reaction upon hydrolysis. The amalgam was destroyed by 100 ml of 1 *N* HCl. The amount of LiOH corresponding to metallic lithium, was 0.0315 mole.

In a separate experiment, the solvents from the reaction mixture were distilled, and the residue treated with steam. The residue was not steam distilled but was filtered and dried. The presence of triphenylene was proved by the method of thin-layer chromatography.

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