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INTERACTION OF DIPHENYLZINC WITH "TITANOCENE" AND ITS DERIVATIVES

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Summary

The reaction of dicyclopentadienyldiphenyltitanium with diphenylzinc proceeds at 60°C in diethyl ether, THF or toluene solutions with the elimination of 4 mol of benzene and the formation of a complex, containing titanium and zinc. Based upon a study of the chemical properties, the structure of the complex has been proposed. The interaction of diphenylzinc with different forms of "titanocene" has been investigated.

Introduction

On reaction with organometallic compounds of nontransition elements organotitanium compounds tend to form different complexes. Earlier we studied the interaction of Cp_2TiPh_2 with diphenylzinc (molar ratio 2/1) in diethyl ether [1]. The reaction was accompanied by the elimination of 4 mol of benzene and the formation of a titanium- and zinc-containing complex (I). It was necessary to study the properties of complex I and to make some conclusions concerning its structure.

Results and discussions

To specify the general formula of complex I, we have studied the reaction of Cp_2TiPh_2 and diphenylzinc (molar ratio 2/1) in toluene or THF. The reaction results in the formation of 4 mol of benzene and of complex I, in all solvents.

In every case the complex formation occurs at 60°C, i.e. during the decomposition of the starting Cp_2TiPh_2. It is known that the thermolysis of Cp_2TiPh_2 in various solvents proceeds with the homolytic cleavage of the titanium—phenyl bond. Benzene is formed mainly by intramolecular hydrogen abstraction from the π-coordinated cyclopentadienyl rings. Thus it may be concluded that the donors of the hydrogen atoms for benzene formation in the 2 Cp_2TiPh_2 + Ph_2Zn

reactions are also the cyclopentadienyl ligands. So the final product should have four hydrogen atoms less and be of the following general formula: ($C_{20}H_{16}Ti_2Ph_2Zn$).

A similar complex is formed in the 2 Cp_2TiMe_2 + Ph_2Zn and 2 Cp_2TiPh_2 + Me_2Zn systems under the same conditions (60° C, 10 h, diethyl ether). Three mol of CH_4 and 1 mol of C_6H_6 are eliminated in the first system, and 3 mol of C_6H_6 and 1 mol of CH_4 in the second one. Complexes of identical composition [$C_{20}H_{16}TiPh(Me)Zn$] (II) are formed in both systems.

It is known that the Cp_2Ti fragment in the starting Cp_2TiPh_2 is an angular sandwich. If it is preserved in I then the action of hydrogen chloride in the presence of oxygen will convert I to Cp_2TiCl_2, which has been readily isolated and identified by UV spectroscopy [3]. Complex I was treated with hydrogen chloride in toluene solution at room temperature. Cp_2TiCl_2 was not found in the reaction products, either in the solution or in the residue. This indicates that the Cp_2Ti-fragment is not preserved in complex I.

The reaction of I with hydrogen chloride results in the elimination of 1 mol of benzene and 1 mol of H_2 *. The elimination of hydrogen points to the presence of the hydrogen ligand in the complex. This is also confirmed by the reaction of the complex with DCl. The evolved gas consists mainly of HD (HD/D_2/H_2 24/6/1), which is formed from the reaction of the hydride substituent with DCl. Methane (0.5 mol) evolved according to the Tserevitinov—Chugaev reaction, indicates that there is one hydrogen atom per two titanium atoms. As mentioned above, the general formula of complex I involves two phenyl groups. An exchange reaction with mercuric chloride was employed to determine the number of σ-bonded phenyl groups. Complex I reacts with excess mercuric chloride in THF at room temperature to give 0.92 mol of PhHgCl and 0.92 mol of mercurous chloride. The amount of phenylmercuric chloride shows that the two phenyl groups in complex I are not identical, and only one is σ-bonded to a metal. The formation of mercurous chloride indicates that an oxidation—reduction reaction also occurs: $Ti^{3+} + Hg^{2+} \rightarrow Ti^{4+} + Hg^{1+}$. The evolution of 0.92 mol of mercurous chloride suggests that almost the total titanium is tervalent in the starting complex I.

Thus, in the complex we have found no Cp_2Ti fragment, but there are one hydrogen atom and one phenyl group bonded to a metal.

To determine completely the components of the complex, reactions with compounds having a labile hydrogen atom, for example CH_3COOH, H_2O and C_2H_5OH, have been investigated.

Complex I reacts with acetic acid in toluene at room temperature to provide H_2 (0.86 mol), C_6H_6 (0.98 mol), cyclopentadiene (0.75 mol) and phenylcyclopentadiene (0.60 mol). The last compound was identical with that synthesized from cyclopentanone and phenyllithium [4]. The zinc-containing product was isolated as zinc diacetate (0.95 mol).

The reaction mixture, obtained upon reaction of complex I with CH_3COOH, gave an ESR signal, characteristic for Ti^{3+}. Green crystals of $CpTi(OCOCH_3)_2$ have been isolated from the reaction solution. However, we failed to obtain this

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* Here and further the yield is expressed in units per 1 mol of the starting complex I.

substance in an analytically pure state on sublimation in vacuo. A disproportionation reaction has been shown to occur on heating $CpTi(OCOCH_3)_2$ [5]:

$$2\,CpTi(OCOCH_3)_2 \xrightarrow{T\,(^\circ C)} Cp_2Ti(OCOCH_3) + Ti(OCOCH_3)_3$$

Therefore dark blue crystals of $Cp_2Ti(OCOCH_3)$ (m.p. 110° C) are sublimed instead of $CpTi(OCOCH_3)_2$ [6].

Reaction of a dioxane solution of complex I with water or ethyl alcohol at 20° C produced H_2 (1.00 mol), C_6H_6 (1.01 mol), cyclopentadiene (0.84 mol) and phenylcyclopentadiene (0.50 mol).

The data suggest that the decomposition of the complex results in the formation of an extraordinary compound, phenylcyclopentadiene. It is extremely reactive and readily polymerises at room temperature, either as a solid or a solution. Therefore quantitative data are usually underestimated. To determine the amount of phenylcyclopentadiene in complex I, the latter was oxidized by alkaline potassium permanganate. Then $C_6H_5C_5H_5$ was estimated from the amount of C_6H_5COOH, the main product of oxidation. Benzoic acid (0.65 mol) was isolated. The elimination of phenylcyclopentadiene suggests that the formation of the complex involves migration of a phenyl group from titanium to the cyclopentadienyl ring. At present there is a great number of examples of such migrations in the literature. It has been particularly well investigated for cyclopentadienyl derivatives of vanadium and molybdenum [7,8].

The total amount of C_5H_6 and $C_6H_5C_5H_5$ (2 mol) shows that two of the four dehydrogenated cyclopentadienyl ligands in the complex may be combined into a fulvalene fragment, and which cannot give rise to cyclopentadiene.

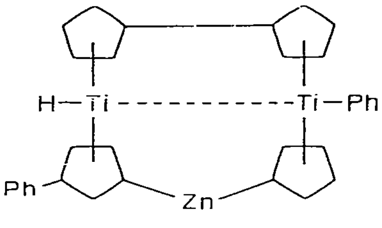
Unfortunately the low volatility and poor solubility of complex I prevent the obtainment of useful mass and NMR spectra. Therefore, the information on bonding in the complex can be obtained only from IR spectral and magnetic susceptibility data. The magnetic susceptibility data showed the complex to be diagmagnetic, even though it contains Ti^{3+}. Consequently, metal—metal interaction is suggested to be present in the complex.

Its IR spectrum shows absorption bands at 710, 740 cm^{-1}, characteristic of phenyl groups and at 820 cm^{-1}, characteristic of a η^5-cyclopentadienyl group. No absorption band is observed at 1230 cm^{-1} indicating that there is no $\mathrm{Ti}{<}^{H}_{H}{>}\mathrm{Ti}$ group in molecule I. The IR spectrum of the product from reactions of the complex with HCl is similar to that of the chloride $(C_{10}H_9TiCl)_2$ obtained on treatment of the hydride form of "titanocene" $(C_{10}H_9TiH)_2$ with HCl [9].

On the basis of the experimental data some conclusions on the components of complex I may be drawn. There is one phenyl ligand, σ-bonded to a metal atom, one hydride unit bonded to titanium; one cyclopentadienyl, one phenylcyclopentadienyl and a fulvalene ligands in the complex. Thus structures IA and IB may be proposed.

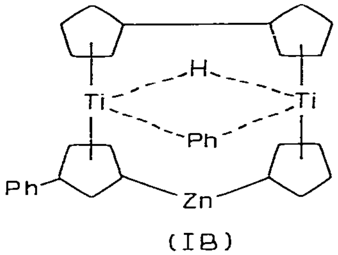
Precise information on the structure of the complex can be obtained only by X-ray diffraction anlysis. However, all the attempts to grow suitable crystals failed. The proposed structure is consistent with the other properties of complex I.

For example, the reaction of I with iodine occurs in toluene solution at room temperature and is accompanied by the formation of 0.70 mol of ben-



(IA)

or

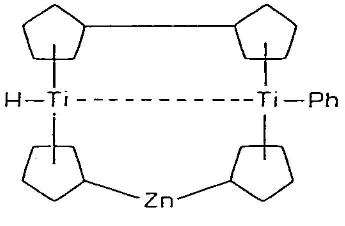


(IB)

zene and a dark-green precipitate, containing Ti/Zn/I in a ratio 2/1/4.

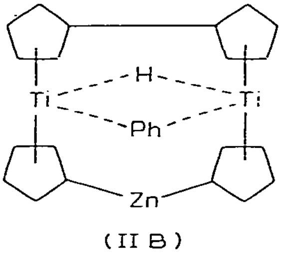
We have studied thermal properties of complex I both in the solid state and in toluene or xylene solution. By the DTA method it has been found that complex I decomposes with maximum exothermic effect at 238° C. Benzene (0.50 mol) and metallic zinc (0.90 mol) are found to be the main products under all decomposition conditions. No hydrogen was liberated during the decomposition which might be explained by the intramolecular formation of benzene. Diphenylzinc was not observed among the decomposition products and hence a zinc-phenyl fragment is not present in I.

The formation of a similar complex might be expected on reaction of diphenylzinc with various forms of "titanocene". Cp_2Ti synthesized by hydrogen reduction of Cp_2TiMe_2 interacts with Ph_2Zn (2/1 molar ratio) in toluene at 20° C. Reaction products are benzene (0.98 mol) and a violet complex. Elemental analysis, IR spectra and the products of reaction with gaseous HCl suggest that a complex (II), similar to complex I, is obtained and can be represented as IIA and IIB. Recently the preparation of a new form of titanocene-$\mu(\eta^1 : \eta^5$-cyclopentadienyl)tris(η^5-cyclopentadienyl)dititanium(III) has been reported.



(IIA)

or



(II B)

It was obtained by the low-temperature reduction of Cp_2TiCl_2 with potassium naphthalene [11]. The reaction of III with diphenylzinc does not result in the formation of complex II, but instead the decomposition of Ph_2Zn (up to 10%) takes place. This is due to reactions the impurity with $(C_{10}H_9TiH)_2$ (5—10%) in III.

Complete decomposition of Ph_2Zn to metallic zinc and an equivalent amount of benzene is observed upon reaction of diphenylzinc and the hydride form of "titanocene" obtained by sodium-amalgam or -naphthalene reduction of Cp_2TiCl [9,12]. The literature cites one more example of the decomposition of an organozinc compound, diethylzinc, by action of $(C_{10}H_9TiH)_2$ [13].

On reaction with $(C_{10}H_9TiH)_2$, diphenylmercury (an analog of diphenylzinc) decomposes under mild conditions (20° C) to form metallic mercury and benzene.

Experimental

All reactions were carried out in vacuum sealed ampoules or under argon. Melting points were measured in vacuum capillaries. Liquid and gaseous products were analyzed by GLC.

Reaction of dicyclopentadienyldiphenyltitanium with diphenylzinc (2/1)

A mixture of Ph_2Zn (1.28 g, 5.8 mmol) and Cp_2TiPh_2 (3.85 g, 11.6 mmol) was heated at 60°C for 10 h in diethyl ether, THF, or toluene (80 ml). The colour of the reaction solution changed from orange to violet. Benzene (1.81 g, 23.2 mmol) was found in the reaction mixture as well as a dark violet precipitate which was recrystallized from benzene (2.28 g, 4.0 mmol). It was very sensitive to moisture and oxygen. $(C_{20}H_{15})Ph_2(H)Ti_2Zn$ (I), m.p. 238°C. (Found C, 66.98; H, 4.91; Ti, 16.50; Zn, 11.49. $C_{32}H_{26}Ti_2Zn$ Calcd.: C, 67.25; H, 4.55; Ti, 16.80; Zn, 11.38%.

Reaction of I with gaseous HCl

To a solution of I (0.45 g, 0.8 mmol) in toluene (20 ml) an excess of HCl in toluene was added at 20°C. H_2 (18 ml, 0.8 mmol) and C_6H_6 (0.06 g, 0.8 mmol) were isolated from the reaction mixture. The colour of the reaction solution changed from violet to dark and a grey-green precipitate, containing Ti (18.50%) and Zn (10.80%), was formed.

Reaction of I with mercuric chloride

$HgCl_2$ (1.95 g, 7.0 mmol) was added in small portions to a solution of I (0.80 g, 1.4 mmol) in THF (30 ml) at 20°C with stirring. The colour of the reaction mixture changed from violet to red-brown and a grey-green precipitate was formed.

$ZnCl_2$ (0.16 g, 12 mmol), PhHgCl (0.41 g, 1.3 mmol) and Hg_2Cl_2 (0.63 g, 1.3 mmol) were found in the residue.

Reaction of I with CH_3COOH

A mixture of I (0.46 g, 0.8 mmol) and acetic acid (2 ml) in toluene (20 ml) was kept at 20°C for 24 h. H_2 (18 ml, 0.8 mmol) was isolated. C_6H_6 (0.06 g, 0.8 mmol), C_5H_6 (0.04 g, 0.6 mmol) and $C_6H_5C_5H_5$ (0.07 g, 0.5 mmol) were found in the reaction mixture. The colour of the reaction solution changed to green and a pale-green precipitate appeared. The reaction solution was filtered and the remaining residue was washed with toluene and dried. It was found to contain $Zn(OCOCH_3)_2$ (0.14 g, 0.8 mmol). On evaporating the filtrate and subliming the residue in vacuo, we obtained a small quantity of blue crystalline $Cp_2Ti(OCOCH_3)$, m.p. 110°C. On mixing it with analytically pure $Cp_2Ti(OCOCH_3)$, no depression of the melting point was observed.

Oxidation of I with alkaline $KMnO_4$

Complex I (0.80 g, 1.4 mmol) was hydrolyzed with distilled water under argon. The colour of the reaction mixture changed from violet to blue. Alkaline $KMnO_4$ was added to the resulting solution. The mixture was boiled for 3 h and the cooled solution was acidified. Extraction with diethyl ether gave benzoic acid C_6H_5COOH (0.11 g, 0.9 mmol), m.p. 121°C.

Reaction of I with iodine

I_2 (2.8 mmol) in toluene solution (20 ml) was added to I (0.43 g, 0.7 mmol). The colour of the reaction solution changed from violet to brown and a dark residue separated out. C_6H_6 (0.04 g, 0.5 mmol) was found in the reaction mixture. The reaction solution was filtered and the residue was recrystallized from toluene to give $(C_{20}H_{15})(C_6H_5)Ti_2I_2ZnI_2$ Found: I, 49.84; Ti, 8.98; Zn, 6.05. Calcd.: I, 50.74; Ti, 9.53; Zn, 6.45%.

Decomposition of I in toluene at 110°C

Complex I (0.61 g, 1.0 mmol) was heated at 110°C for 6 h in toluene (10 ml). This resulted in the formation of a mirrow of metallic zinc (0.06 g, 0.9 mmol) on the walls of the ampoule. The colour of the reaction solution changed to brown-green. C_6H_6 (0.04 g, 0.5 mmol) was found in the reaction mixture. The residue (C, 76.70; Ti, 16.50; H, 8.58%) was isolated from the toluene solution.

Reaction of Cp_2Ti, obtained by hydrogen reduction of Cp_2TiMe_2, with Ph_2Zn (2/1).

A mixture of Cp_2Ti (0.53 g, 3.0 mmol) and Ph_2Zn (0.34 g, 1.5 mmol) in toluene (70 ml) was stored at 20°C for 24 h. The colour of the reaction solution changed from green to violet. C_6H_6 (0.23 g, 3.0 mmol) was found in the reaction mixture.

The dark-violet fine-crystalline substance (0.49 g, 1.0 mmol) was recrystallized from toluene. $(C_{10}H_8)(H)(C_6H_5)Ti_2(C_5H_4)_2Zn$: Found: C, 62.71; H, 4.42; Ti, 19.90; Zn, 13.59. Calcd: C, 63.03; H, 4.44; Ti, 19.39; Zn, 13.13%.

References

1 G.A. Razuvaev, V.N. Latyaeva, L.I. Vishinskaya, T.P. Denisova and Y.A. Gorelov, Dokl. Akad. Nauk SSSR, 202 (1972) 1090.

2 V. Kokman and J.G. Bucklidge, Chem. Commun., (1971) 1340.

3 V.N. Latyaeva, L.I. Vishinskaya and N.N. Vishinskiy, Use of molecular spectroscopy in chemistry, Science Publ., Moscow, 1966.

4 R. Reimschnerider and R. Nerin, Monatsh. Chem., 91 (1960) 829.

5 R.S.P. Coutts, R.L. Martin and P.C. Wailes, Austr. J. Chem., 20 (1967) 1579.

6 R.S.P. Coutts and P.C. Wailes, Austr. J. Chem., 26 (1973) 941.

7 A.N. Nesmeyanov, Y.A. Chapovskiy, B.V. Lokshin, V.A. Kisin and L.G. Makarova, Dokl. Akad. Nauk SSSR, 171 (1966) 637.

8 G. Fachinetti and G. Floriani, Chem. Commun., (1974) 516.

9 H.H. Brintzinger and J.E. Bercaw, J. Amer. Chem. Soc., 92 (1970) 6182.

10 J.E. Bercaw, R.H. Marvich, L.G. Bell and H.H. Brintzinger, J. Amer. Chem. Soc., 94 (1972) 1219.

11 G.P. Pez, J. Amer. Chem. Soc., 98 (1976) 8072.

12 G.W. Watt and F.O. Drummond, J. Amer. Chem. Soc., 92 (1970) 826.

13 K. Shikata, K. Nishino and K. Azuma, J. Chem. Soc. Japan., 68 (1965) 1251.