

SOME REACTIONS OF *BIS*(CYCLOPENTADIENYL)DIFERROCENYL TITAN¹

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Reaction of *bis*(cyclopentadienyl)diferrocenyltitanium Cp_2TiFc_2 (**1**) with iodine (toluene, 20 °C, 24 h) proceeds with formation of *bis*(cyclopentadienyl)titanium diiodide Cp_2TiI_2 (**2**) and diferrocenyl Fc-Fc (**3**); a byproduct of the reaction is the salt Fc-Fc·I₃ (**4**). Interaction of **1** with carbon monoxide (100 bar, benzene, 50 °C, 3 h) leads to the synthesis of diferrocenylketone (**5**) and *bis*(cyclopentadienyl) titanium dicarbonyl (**6**).

Keywords: *bis*(cyclopentadienyl)diferrocenyltitanium, reaction, iodine, carbonyl carbon.

Introduction

It is known that alkyl and aryl compounds of titanium are especially labile complexes, sensitive to heating and action of oxygen and atmospheric moisture [1]. Introduction of the ligands, stabilizing σ -bonds C–Ti, into the coordination sphere of titanium makes it possible to increase the stability of titanium complexes [2,3]. The most thermally stable of this series is *bis*(cyclopentadienyl)-diferrocenyltitanium Cp_2TiFc_2 (**1**), its decomposition temperature reaches 156 °C [3].

Note that complex **1** is one of only a few titanium compounds, for which high-temperature pyrolysis leads to formation of metallic titanium films [4], hence the investigation of complex **1** reactivity is undeniably urgent.

Experimental

Reaction of 1 with iodine. To the solution of 0.65 g (1.20 mmol) complex **1** in 50 mL toluene at 20 °C 0.30 g (1.20 mmol) iodine in 20 mL toluene was added. In 24 h the solvent was removed, the residue was sequentially extracted by hexane and benzene. From benzene solution 0.31 g (0.60 mmol) complex **1** and 0.22 g (0.51 mmol) *bis*(cyclopentadienyl)titanium (**2**, decomposition temperature 314 °C) were isolated by fractional crystallization. Found, %: C 27.11, H 2.38, I 57.86. Calculated for $\text{C}_{10}\text{H}_{10}\text{I}_2\text{Ti}$, %: C 27.77, H 2.31, I 58.79. After evaporation of hexane extracts diferrocenyl was isolated (**3**, m.p. 231 °C). Found, %: C 64.90, H 4.79, Fe 29.55. Calculated for $\text{C}_{20}\text{H}_{18}\text{Fe}_2$, %: C 64.86, H 4.86, Fe 30.28. The residue, insoluble in benzene (0.07 g) constituted a black crystal substance with decomposition temperature 172 °C. Found, %: C 32.69, H 2.75, I 49.89. Calculated for $\text{C}_{20}\text{H}_{18}\text{Fe}_2\text{I}_3$, %: C 31.98, H 2.27, I 50.73.

Reaction of 1 with carbon monoxide. The sample 0.65 g (1.20 mmol) complex **1** in 15 mL benzene was placed into 50 mL autoclave. The pressure of carbon monoxide was increased up to 100 atm, the temperature was 50 °C. After agitation of the reaction mixture during 3 h it was cooled, the pressure was released, 0.15 g (1.20 mmol) iodine was added in order to confirm the formation of *bis*(cyclopentadienyl)titanium dicarbonyl. Liberation of 45 mL (2.00 mol) carbon monoxide was observed. The reaction mixture was sequentially extracted by benzene and chloroform. After evaporation of benzene 0.35 g (0.88 mmol) diferrocenylketone was obtained (**3**, m.p. 210 °C). Found, %: C 63.02, H 4.73, Fe 28.07. Calculated for $\text{C}_{21}\text{H}_{18}\text{Fe}_2\text{O}$, %: C 63.29, H 4.52, Fe 28.14. Chloroform extracts were used to isolate 0.46 g (1.06 mmol) complex **2**.

Results and Discussion

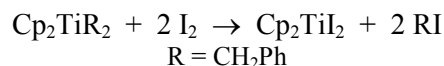
Synthesizing a number of ferrocenyl compounds of transition metals has revealed the research objects in chemistry of metallocenes containing metal-ferrocenyl σ -bonds [4]. Studying the peculiarities of their structure has helped to determine the character of the abovementioned bond that is of π -character to

¹ The research was carried out by V.V. Sharutin under supervision of academician G.A. Razuvaev in 1982.

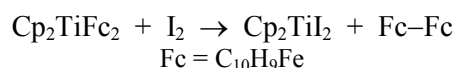
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some extent [4,5], so it is important to study reactivity of ferrocenyl compounds on the example of *bis*(cyclopentadienyl)diferrocenylytitanium (**1**) reactions with iodine and carbon monoxide.

It is known that the action of halogenes (Hal_2) on many organometallic compounds containing M-R σ -bonds leads to bond-breaking with formation of RHal and metal halogenides, *e.g.* in the reaction of Cp_2TiR_2 with iodine [6]:

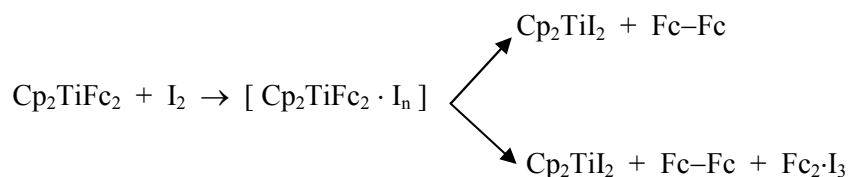


The interaction of **1** with iodine, studied by us, proceeds in somewhat different way, which obviously points at the reaction direction being governed by the kind of σ -bonded ligand at the titanium atom. Thus, apart from the initial complex **1** isolated from the reaction mixture, titanocene diiodide and diferrocenyl have been identified:



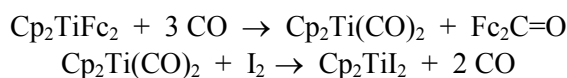
Besides, a minor amount of diferricinium salt $\text{Fc}_2\cdot\text{I}_3$ has been separated from the reaction mixture. Its presence among the reaction products suggests the direct participation of the oxidized form of ferrocenyl ligand in the process course, as it was earlier shown that at the same conditions iodine and diferrocenyl, when taken separately, did not react with each other [4].

Increase of percent yield for diferricinium salt $\text{Fc}_2\cdot\text{I}_3$ at excess amount of iodine in this reaction, as well as the familiar property of ferrocene treated with iodine to produce compounds $\text{FcH}\cdot\text{I}_n$ ($n = 3-10$), speaks for intermediate complex of *bis*(cyclopentadienyl)diferrocenylytitanium with iodine, which decomposes next, according to the scheme:



As far as is known, the interaction of *bis*(cyclopentadienyl)diphenyltitanium with carbon dioxide (toluene, 80°C , 1 atm) is accompanied by elimination of benzene and formation of titanocyclic compound [7,8], therefore it is of interest to investigate how such a titanium complex with σ -bonded ferrocenyl ligands reacts with carbon dioxide.

We have found that at the abovementioned conditions complex **1** does not react with carbon dioxide. Increase of reaction temperature up to 160°C is accompanied by removal of σ -bonded ferrocenyl ligands in the form of ferrocene and by breakdown of the initial biscyclopentadienyl structure into titanium-containing remainder with the empirical formula « $\text{C}_{10}\text{H}_8\text{Ti}$ ». At the same time the interaction of *bis*(cyclopentadienyl)diferrocenylytitanium with carbon monoxide (benzene, 100 atm, 50°C , 3 h) leads to the synthesis of diferrocenylketone and titanocene dicarbonyl, the presence of which has been proved by chemical method:



Conclusions

Thus, the nature of the ligands, σ -bonded with the central atom in titanium complexes of the general formula Cp_2TiR_2 ($\text{R}=\text{Fc}$, Ph), determines the scheme of their interaction with iodine and carbon oxides.

References

1. Nesmeyanov A.N. *Metody elementoorganicheskoy khimii. Podgruppy medi, skandiya, titana, vanadiya, khroma, margantsa* [Methods of Organoelemental Chemistry. Copper, Scandium, Titanium, Vanadium, Chromium, Manganese Groups]. Moscow, Nauka Publ., 1974. 470 p. (in Russ.)
2. Burger H., Kluess C. Titan-stickstoff-verbindungen. XVII. σ -(Ferrocenyl)-titan-dialkylamide. *J. Organometal. Chem.*, 1973, vol. 56, pp. 269–277. doi:10.1016/S0022-328X(00)89975-1
3. Razuvaev G.A., Domrachev G.A., Sharutin V.V., Suvorova O.N. Ferrocenyl Derivatives of Dicyclopentadienyltitanium, -Zirconium and -Hafnium. *J. Organometal. Chem.*, 1977, vol. 141, pp. 313–317. DOI: doi:10.1016/S0022-328X(00)90854-4
4. Sharutin V.V. *Ferrotsenil'nye i tsimantrenil'nye soedineniya metallov IV-V grupp*: Diss. kand. khim. nauk [Ferrocenyl and Cymantrenyl Compounds of Metals of Groups IV-V. Cand. Sci. Diss.]. Gorky, 1982. 112 p.
5. Zakharov L.N., Struchkov Yu.T., Sharutin V.V., Suvorova O.N. Diferrocenyltitanocene, $C_{30}H_{28}Fe_2Ti$. *Cryst. Struct. Comm.*, 1979, vol. 8, pp. 439–444.
6. Razuvaev G.A., Latyaeva V.N., Vyshinskaya L.I. [Benzyl Derivative of Titanocene]. *Dokl. AN SSSR* [Proceedings of the USSR Academy of Sciences], 1969, vol. 189, pp. 103–104. (in Russ.)
7. Kolomnikov I.S., Lobeeva T.S., Gorbachevskaya V.V., Aleksandrov G.G., Struchkov Yu.T., Vol'pin M.E. Reaction of Carbon Dioxide with Diphenyltitanocene and X-ray Crystal Structure of the Product. *J. Chem. Soc. D*, 1971, pp. 972–973. DOI: 10.1039/C29710000972
8. Sharutin V.V., Senchurin V.S. *Imennye reaktsii v khimii elementoorganicheskikh soedineniy* [Name Reactions in Chemistry of Organoelemental Compounds]. Chelyabinsk, South Ural St. Univ. Publ., 2011. 426 p. (in Russ.)

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НЕКОТОРЫЕ РЕАКЦИИ БИС(ЦИКЛОПЕНТАДИЕНИЛ)ДИФЕРОЦЕНИЛТИТАНА¹

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Взаимодействие бис(циклопентадиенил)диферроценилтитана Cr_2TiFe_2 (1) с иодом (толуол, 20 °С, 24 ч) протекает с образованием диодида бис(циклопентадиенил)титана Cr_2TiI_2 (2) и диферроценила $Fe-Fe$ (3); побочным продуктом реакции является соль $Fe-Fe-I_3$ (4). Взаимодействие 1 с оксидом углерода (100 атм, бензол, 50 °С, 3 ч) приводит к синтезу диферроценилкетона (5) и дикарбонила бис(циклопентадиенил)титана (6).

Ключевые слова: бис(циклопентадиенил)диферроценилтитан, реакция, иод, карбонил углерода.

Литература

1. Несмеянов, А.Н. Методы элементоорганической химии. Подгруппы меди, скандия, титана, ванадия, хрома, марганца / А.Н. Несмеянов. – М.: Наука, 1974. – 470 с.
2. Burger, H. Titan-stickstoff-verbindungen. XVII. σ -(Ferrocenyl)-titan-dialkylamide / H. Burger, C. Kluess // *J. Organometal. Chem.* – 1973. – V. 56, № 2. – P. 269–277.

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Organometallic chemistry

3. Ferrocenyl derivatives of dicyclopentadienyltitanium, -zirconium and -hafnium / G.A. Razuvaev, G.A. Domrachev, V.V. Sharutin, O.N. Suvorova // *J. Organometal. Chem.* – 1977. – V. 141, № 3. – P. 313–317.
4. Шарутин, В.В. Ферроценильные и цимантренильные соединения металлов IV-V групп: дисс. ... канд. хим. наук / В.В. Шарутин. – Горький, 1982. – 112 с.
5. Diferrocenyltitanocene, $C_{30}H_{28}Fe_2Ti$ / L.N. Zakharov, Yu.T. Struchkov, V.V. Sharutin, O.N. Suvorova // *Cryst. Struct. Comm.* – 1979. – V. 8. – P. 439–444.
6. Разуваев, Г.А. Бензильное производное титаноцена / Г.А. Разуваев, В.Н. Латяева, Л.И. Вышинская // *Докл. АН СССР.* – 1969. – Т. 189, № 1. – С. 103–104.
7. Reaction of carbon dioxide with diphenyltitanocene and X-ray crystal structure of the product / I.S. Kolomnikov, T.S. Lobeeva, V.V. Gorbachevskaya et al // *Chem. Comm.* – 1971. – № 16. – P. 972–973.
8. Шарутин, В.В. Именные реакции в химии элементоорганических соединений / В.В. Шарутин, В.С. Сенчурин. – Челябинск: Издательский центр ЮУрГУ, 2011. – 426 с.

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ОБРАЗЕЦ ЦИТИРОВАНИЯ

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