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INTERACTION OF DICYCLOPENTADIENYLTITANIUM DICHLORIDE WITH BIS(TRIETHYLGERMYL)-CADMIUM AND -MERCURY

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Summary

The reaction of dicyclopentadienyltitanium dichloride with bis(triethylgermyl)mercury in benzene solution at 20° yields metallic mercury quantitatively, titanocene monochloride and triethylchlorogermane. The reaction of dicyclopentadienyltitanium dichloride with bis(triethylgermyl)cadmium leads to the formation of a complex of the following general composition: $[Cp_2TiCl_2 \cdot Cd(GeEt_3)_2]$. The reactivity of this complex has been studied: in toluene solution at 20° it decomposes slowly to yield metallic cadmium, triethylchlorogermane and $Cp_2TiCl(GeEt_3)$.

Introduction

Complexes of dicyclopentadienyltitanium dichloride with organic derivatives of metals of Groups I-III are of great interest since such systems are used for polymerization, fixation of molecular nitrogen and carbon dioxide, and other processes. In this respect compounds in which the carbon atom is substituted by another member of the Group (i.e. silicon, germanium or tin) are of some interest.

The general method of synthesis of such compounds is an exchange reaction of R_3ELi (E = Si,Ge,Sn) with the corresponding transition metal halides. This method gave a number of derivatives of general formula $Cp_2TiCl_n(ER_3)_{2-n}$ [1]. In some cases organomercurials $(R_3Si)_2Hg$ and $(R_3Ge)_2Hg$ are used since they sometimes simplify the synthesis. For instance they helped in the synthesis of organo-bielemental derivatives containing the bond Ge (or Si) — Fe (or Co,Ni,Pt) [2-5].

Results and discussion

The aim of this work is to study the reactions of the dicyclopentadienyltitanium halides Cp_2TiCl_2 and Cp_2TiCl with bis(triethylgermyl) mercury and -cadmium.

The reaction of Cp_2TiCl_2 with $(Et_3Ge)_2Hg$ (2/1) in benzene proceeds at room temperature to yield metallic mercury in quantitative amounts and to form triethylchlorogermane and dicyclopentadienyltitanium chloride. If the ratio of the starting compounds is altered to 1/1 half the bis(triethylgermyl)-mercury remains unreacted. The composition and yield of the products suggest the reaction pathway described in eqns. 1 and 2, followed by decomposition of the intermediate (eqn. 3).

$$(Et_3Ge)_2Hg + Cp_2TiCl_2 \rightarrow [Et_3GeHgTiCp_2Cl] + Et_3GeCl \quad (1)$$

$$[Et_3GeHgTiCp_2Cl] + Cp_2TiCl_2 \rightarrow Et_3GeCl + [(Cp_2TiCl)_2Hg] \quad (2)$$

$$[(Cp_2TiCl)_2Hg] \rightarrow Hg + 2Cp_2TiCl \quad (3)$$

Control experiments showed that under the conditions used (C_6H_6, THF, 20°) bis(triethylgermyl)mercury does not react with titanocene monochloride.

The reaction of dicyclopentadienyltitanium dichloride with bis(triethylgermyl)cadmium proceeds in a different manner. Unlike the reactions with bis(triethylgermyl)mercury which have been considered so far this process is not accompanied by reduction of the initial organotitanium compound. The influence of both the ratio of the starting compounds and the nature of the solvent seem to be significant.

The reaction of equimolar amounts of Cp_2TiCl_2 and $(Et_3Ge)_2Cd$ in tetrahydrofuran (20°, 72 h) did not lead to separation of metallic cadmium. Instead the main product was found to be a complex of $[Cp_2TiCl_2 \cdot Cd(GeEt_3)_2]$ (I) in 85% yield (eqn. 4).

$$Cp_2TiCl_2 + (Et_3Ge)_2Cd \rightarrow [Cp_2TiCl_2 \cdot Cd(GeEt_3)_2] \quad (4)$$

The reaction of bis(triethylgermyl)cadmium with 2 moles of dicyclopentadienyltitanium dichloride (toluene, 20°, 72 h) also proceeds according to eqn. 4, and in this case too no separation of metallic cadmium occurs. The yield of recrystallized complex is 72% and an equimolar excess of the initial Cp_2TiCl_2 is isolated unaltered from the reaction mixture.

Complex I is light green and crystalline, m.p. 94-96° (dec.), readily oxidizable in air, highly soluble in benzene, toluene and tetrahydrofuran, and insoluble in aliphatic hydrocarbons. In benzene complex I is monomeric. It is probably formed by coordination of the electron pairs on the chlorine atom with the empty *p*-orbitals of the cadmium atom. Solutions of the complex are stable at 0° for some months. It is also stable at 20° in tetrahydrofuran: only 5% of metallic cadmium was isolated after 9 days. In toluene at 20° slow decomposition is observed: 47% of Cd separated after 9 days, and 100% had separated after 20 days. In toluene at 100° quantitative yields of cadmium are produced in 6 hours.

It has been established that the complete decomposition of the complex in toluene at 20° proceeds according to eqn. 5.

$$\underset{(I)}{[Cp_2TiCl_2 \cdot Cd(GeEt_3)_2]} \rightarrow \underset{(II)}{Cp_2TiCl(GeEt_3)} + Cd + Et_3GeCl \qquad (5)$$

An asymmetric compound, dicyclopentadienyl(triethylgermyl)titanium chloride, which we have synthesized for the first time, may be obtained in almost quantitative amounts by the reaction of dicyclopentadienyltitanium chloride with bis(triethylgermyl)cadmium (eqn. 6).

$$2Cp_2TiCl + (Et_3Ge)_2Cd \xrightarrow[20^\circ]{\text{Toluene}} 2Cp_2TiCl(GeEt_3) + Cd \qquad (6)$$

On crystallization compound II gives glittering dark-green needles which are not oxidized on short contact with air.

Equimolar amounts of Cp_2TiCl_2 and $(Et_3Ge)_2Cd$ in toluene at 20° give after 240 hours, complex I (12%), $Cp_2TiCl(GeEt_3)$ (68%), metallic cadmium (70%), and triethylchlorogermane (65%). This is explained by simultaneous formation and decomposition of complex I (eqns. 4 and 5).

On heating I in toluene (100°, 6 h) reduction of the titanium atom occurs. In this case the products of the reaction are titanocene monochloride (75%), metallic cadmium (100%), triethylchlorogermane (50%) and triethylgermane (20%). Some experiments showed that the thermal decomposition of asymmetric $Cp_2TiCl(GeEt_3)$ (100°, 6 h, benzene or toluene) also yields Cp_2TiCl, Et_3GeCl and Et_3GeH. The primary stage of decomposition of I at 100° must therefore include formation of $Cp_2TiCl(GeEt_3)$ (II), which then decomposes into the products stated. Thus, the isolation of II points to the occurrence of exchange processes in complex I.

A study of the reactivity of complex I confirms its composition. The reaction of I with different halogen derivatives shows that the titanocene structure remains intact. When excess gaseous hydrogen chloride is passed for prolonged periods through a toluene solution of complex I cleavage of the metal—metal bonds is observed, with formation of dicyclopentadienyltitanium dichloride (85%), cadmium chloride (32%), triethylchlorogermane (77%), triethylgermane (14%) and hydrogen (70%) (eqn. 7).

$$[Cp_2TiCl_2 \cdot Cd(GeEt_3)_2] + 2HCl \rightarrow Cp_2TiCl_2 + CdCl_2 + 2Et_3GeH \qquad (7)$$

The presence of several equivalents of Et_3GeCl and H_2 is explained by reaction of the initially formed Et_3GeH with an excess of hydrogen chloride (eqn. 8).

$$Et_3GeH + HCl \rightarrow Et_3GeCl + H_2 \qquad (8)$$

Mercury(I) chloride readily undergoes a substitution reaction with complex I to yield dicyclopentadienyltitanium dichloride (88%), cadmium chloride (94%), mercury (92%) and triethylchlorogermane (88%) (eqns. 9 and 10).

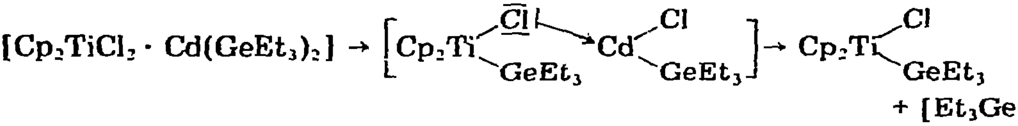
$$[Cp_2TiCl_2 \cdot Cd(GeEt_3)_2] + 2HgCl_2 \xrightarrow[80^\circ]{\text{Toluene}} Cp_2TiCl_2 + CdCl_2 + 2[Et_3GeHgCl] \qquad (9)$$

$$[Et_3GeHgCl] \rightarrow Et_3GeCl + Hg \qquad (10)$$

The influence of organohalogen compounds, especially 1,2-dibromoethane, on organo-bimetallic compounds has been studied in detail. Many experiments indicate that 1,2-dibromoethane cleaves the metal—metal bonds of the organo-bimetallic compound with formation of ethylene [6,7]. When complex I is treated with 1,2-dibromoethane in toluene solution at 80°, ethylene (77%), nearly quantitative amounts of cadmium and titanocene halides, and triethylbromogermane are produced.

The reaction of I with acetic acid in toluene at room temperature leads to decomposition of the starting compound, reduction of titanium to the trivalent state and isolation of dicyclopentadienyltitanium acetate. The fact that the acetate group is able to form a chelate complex with the metal and to stabilize its lower oxidation state is a determining factor of the formation of stable $Cp_2Ti(OCOCH_3)$ (79%) [8]. Aside from this acetate complex the other main products of the reaction are triethylgermane (72%) and cadmium chloride (72%).

Thus, all the reactions investigated support well the assumption made earlier concerning the structure of the complex in which exchange of triethylgermyl groups with chlorine occurred. In solution complex I probably dissociates according to eqn. 11.



$$[Cp_2TiCl_2 \cdot Cd(GeEt_3)_2] \rightarrow \left[Cp_2Ti\begin{matrix}\overline{Cl}\\GeEt_3\end{matrix}\rightarrow Cd\begin{matrix}Cl\\GeEt_3\end{matrix}\right] \rightarrow Cp_2Ti\begin{matrix}Cl\\GeEt_3\end{matrix} + [Et_3GeCdCl] \tag{11}$$

Electron-donor solvents such as tetrahydrofuran are known to stabilize asymmetric RCdX [9] and this indicates the greater stability of complex I in THF. In non-polar solvents decomposition occurs to form metallic cadmium.

Experimental

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

Reaction of dicyclopentadienyltitanium dichloride with bis(triethylgermyl)-cadmium (2/1)

A mixture of Cp_2TiCl_2 (9.31 g, 37.0 mmol) and $(Et_3Ge)_2Cd$ (8.00 g, 18.0 mmol) in toluene (25 ml), was kept at 20° for 72 h. The colour of the reaction solution changed from red to intense green with a sediment of unreacted Cp_2TiCl_2 (4.72 g, 18.9 mmol) remaining at the bottom of the ampoule. Et_3GeH (0.36 g, 2.2 mmol), Et_3GeCl (0.29 g, 1.5 mmol) and $(Et_3Ge)_2$ (0.12 g, 0.4 mmol) were isolated from the reaction mixture. Crystallization from toluene at −78° gave green crystals of $[Cp_2TiCl_2 \cdot Cd(GeEt_3)_2]$ (I) (10.60 g, 15.3 mmol), m.p. 94-96° (dec.). (Found: C, 38.29; H, 5.48; Cd, 16.20; Cl, 11.04; Ti, 7.11%; Mol. wt. (cryoscopy in benzene) 640. $C_{22}H_{40}Cl_2CdGe_2Ti$ calcd.: C, 38.81; H, 5.42; Cd, 16.55; Cl, 10.41; Ti, 7.05%; Mol. wt. 680.)

Reaction of dicyclopentadienyltitanium dichloride with bis(triethylgermyl)-cadmium (1/1) in tetrahydrofuran

A mixture of $(Et_3Ge)_2Cd$ (2.06 g, 4.8 mmol) and Cp_2TiCl_2 (1.20 g, 4.8 mmol) in THF (15 ml) was kept at 20° for 48 h after which time the colour of the solution had changed from red to intense green. The solvent was removed under vacuum and the residue was recrystallized from toluene/hexane. 2.72 g (4.0 mmol) of I, m.p. 94-96° (dec.), were isolated.

Reaction of dicyclopentadienyltitanium dichloride with bis(triethylgermyl)cadmium (1/1) in toluene

A mixture of Cp_2TiCl_2 (1.81 g, 7.2 mmol) and $(Et_3Ge)_2Cd$ (3.00 g, 7.0 mmol) in toluene (15 ml) was kept at 20° for 72 h. The reaction mixture turned bright-green and metallic cadmium separated out (0.54 g, 4.8 mmol). Et_3GeCl (0.86 g, 4.4 mmol), Et_3GeH (0.11 g, 0.7 mmol) and Et_6Ge_2 (0.06 g, 0.2 mmol) were found in the reaction solution. Most of the toluene was removed under vacuum; hexane (10 ml) was added to the residue and by fractional crystallization from toluene/hexane 0.17 g (0.2 mmol) of I, m.p. 94-96° and emerald green crystals of $Cp_2TiCl(GeEt_3)$ (II), (0.98 g, 2.3 mmol) m.p. 122-124° (dec.) were isolated. (Found: C, 51.68; H, 6.89; Cl, 9.37; Ge, 18.77; Ti, 12.38. $C_{16}H_{25}ClGeTi$ calcd.: C, 51.24; H, 6.75; Cl, 9.51; Ge, 19.49; Ti, 12.84%.)

Reaction of dicyclopentadienyltitanium monochloride with bis(triethylgermyl)cadmium (2/1)

A mixture of Cp_2TiCl (1.00 g, 4.6 mmol) and $Et_3Ge)_2Cd$ (1.00 g, 2.3 mmol) in toluene (20 ml) was kept at 20° for 48 h after which time metallic cadmium (0.24 g, 2.1 mmol) separated from the reaction mixture. The solvent was removed under vacuum and the residue was recrystallized from toluene/hexane mixture to yield 0.80 g (1.8 mmol) of $Cp_2TiCl(GeEt_3)$, m.p. 121-123°. (Found: Cl, 9.05; Ti, 13.00. $C_{16}H_{25}ClGeTi$ calcd.: Cl, 9.51; Ti, 12.84 %.)

Decomposition of I in toluene at 20°

Compound I (1.27 g, 1.8 mmol) was left standing in 10 ml toluene for 240 h. Metallic cadmium (0.20 g, 1.7 mmol) gradually separated out and Et_3GeCl (0.30 g, 1.8 mmol) was found in the reaction solution. $Cp_2TiCl(GeEt_3)$ (0.57 g, 1.6 mmol), m.p. 121° (dec.) was separated from toluene by recrystallization at −78°. (Found: Cl, 9.12; Ti, 12.55. $C_{16}H_{25}ClGeTi$ calcd.: Cl, 9.51; Ti, 12.84%.)

Decomposition of I in toluene at 100°

Complex I (3.60 g, 5.3 mmol) was heated at 100° for 6 h in toluene (or benzene) (45 ml), 0.55 g (4.9 mmol) of cadmium separated out after this time. Et_3GeCl (1.06 g, 5.1 mmol), Et_3GeH (0.31 g, 2.0 mmol) and Et_6Ge_2 (0.06 g, 0.2 mmol) were found in the reaction mixture. Cp_2TiCl (0.83 g, 3.9 mmol) was isolated from toluene by recrystallization. (Found: Cl, 17.08; Ti, 22.08. $C_{10}H_{10}ClTi$ calcd.: Cl, 16.66; Ti, 22.44%.)

Reaction of I with gaseous HCl

Dry gaseous HCl was passed through a mixture of I (0.95 g, 1.3 mmol) in toluene (30 ml) for 10 h at 20°. The colour of the reaction mixture turned from dark-green to red and a precipitate formed. The liquid was decanted, and the residue was extracted repeatedly with toluene and dried. $CdCl_2$ (0.22 g, 1.2 mmol) was isolated. Evaporation of the extract gave Cp_2TiCl_2 (0.27 g, 1.1 mmol), m.p. 280°. H_2 (0.7 mmol), Et_3GeCl (0.38 g, 2.0 mmol) and Et_3GeH (0.06 g, 0.4 mmol) were found in the gaseous phase and in the reaction solution.

Reaction of I with $HgCl_2$

Complex I (1.70 g, 2.5 mmol) and $HgCl_2$ (1.35 g, 5.0 mmol) were heated at 100° in toluene (45 ml) for 4 h. The colour of the reaction mixture turned from dark green to red and a pale grey precipitate formed at the bottom of the ampoule. Mercury (0.92 g, 4.5 mmol) and $CdCl_2$ (0.42 g, 2.3 mmol) were found in the precipitate, and Et_3GeCl (0.85 g, 4.4 mmol) was found in the reaction mixture. Recrystallization from toluene gave Cp_2TiCl_2 (0.55 g, 2.2 mmol), m.p. 281°.

Reaction of I with 1,2-dibromoethane

To a solution of I (1.40 g, 2.0 mmol) in toluene (15 ml) was added 1,2-dibromoethane (2.50 g, 13.0 mmol). The mixture was heated for 15 min at 100° during which time 1.54 mmol of C_2H_4 was evolved. The colour of the reaction solution turned to red and a precipitate formed. The same method as used in the preceding run revealed 1.6 mmol of CdX_2 and 1.6 mmol of Cp_2TiX_2 in the residue. Et_3GeBr (0.42 g, 1.8 mmol) was found in the reaction solution.

Reaction of I with CH_3COOH

A solution of I (2.30 g, 3.3 mmol) and CH_3COOH (5 ml) in toluene (30 ml) was kept at 20° for 48 h. The colour of the reaction mixture turned to blue and a pale yellow precipitate formed at the bottom of the ampoule. Et_3GeCl (0.23 g, 1.2 mmol) and Et_3GeH (0.83 g, 5.2 mmol) were found in the reaction mixture. The reaction solution was filtered and the residue washed with toluene and dried. $CdCl_2$ (0.50 g, 2.7 mmol) and $Cd(OCOCH_3)_2$ (0.14 g, 0.6 mmol) were isolated from the residue. After evaporation of the filtrate in vacuum and recrystallization from toluene/hexane $Cp_2Ti(COOCH_3)$ (0.63 g, 2.7 mmol), m.p. 110° was isolated. (Found: Ti, 20.05. $C_{12}H_{13}O_2Ti$ calcd.: Ti, 20.02%.) Ratio $Ti/OCOCH_3$ 1/1.

Reaction of dicyclopentadienyltitanium dichloride with bis(triethylgermyl)-mercury (2/1)

A mixture of Cp_2TiCl_2 (2.30 g, 9.2 mmol) and $(Et_3Ge)_2Hg$ (2.40 g, 4.6 mmol) was kept in benzene (40 ml) at 20° for 24 h. The colour of the reaction mixture turned from red to dark green. Metallic mercury (0.76 g, 3.8 mmol) was precipitated. Et_3GeCl (1.41 g, 7.3 mmol) was isolated from the reaction mixture. Recrystallization from benzene gave Cp_2TiCl (1.56 g, 7.4 mmol). (Found: C, 56.19; H, 4.82; Cl, 17.07; Ti, 22.38. $C_{10}H_{10}ClTi$ calcd.: C, 56.41; H, 4.61; Cl, 16.66; Ti, 22.44%.)

Reaction of dicyclopentadienyltitanium dichloride with bis(triethylgermyl)-mercury (1/1)

As in the preceding run the reaction of Cp_2TiCl_2 (0.63 g, 2.5 mmol) and $(Et_3Ge)_2Hg$ (1.30 g, 2.5 mmol) in benzene (30 ml) gave Hg (0.25 g, 1.2 mmol), Et_3GeCl (0.37 g, 1.9 mmol) and Cp_2TiCl (0.38 g, 1.9 mmol). Unreacted $(Et_3Ge)_2Hg$ (0.65 g, 1.2 mmol) was found in the reaction mixture.

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