Interaction of bis(trimethylsilyl)acetylene complex of titanocene with mercury trifluoroacetate

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The reaction of the bis(trimethylsilyl)acetylene complex of titanocene $Cp_2Ti(Me_3SiC_2SiMe_3)$ with mercury trifluoroacetate $(CF_3COO)_2Hg$ at 20 °C in a THF medium affords titanocene bis(trifluoroacetate) $Cp_2Ti(OCOCF_3)_2$ and metallic mercury. The structure of $Cp_2Ti(OCOCF_3)_2$ was established by the analytical and spectroscopic methods and X-ray diffraction analysis.

Key words: acetylene complexes of titanocene, mercury trifluoroacetate, trifluoroacetate complexes, X-ray diffraction analysis.

We have recently reported the first example of the electrophilic substitution of the H atom in the Cp ring for titanium η^5-cyclopentadienyl derivatives.[1,2] It was found that the reaction of the bis(trimethylsilyl)acetylene complexes of titanocene $Cp_2Ti(Me_3SiC_2SiMe_3)$ (**1**) with tris(pentafluorophenyl)borane $B(C_6F_5)_3$ in toluene at 20 °C affords an unusual zwitterionic complex of trivalent titanium $Cp[\eta^5\text{-}C_5H_4B(C_6F_5)_3]Ti$ containing the $B(C_6F_5)_3$ group in the Cp ligand. The reaction is accompanied by H_2 evolution. Bis(trimethylsilyl)acetylene and 1,2-bis(trimethylsilyl)ethane were found among the organic products of the reaction. Taking into account these data, we decided to study the reaction of complex **1** with mercury trifluoroacetate $(CF_3COO)_2Hg$, assuming that in this case the electrophilic mercuration of the Cp ring in molecule **1** to form the $Cp[\eta^5\text{-}C_5H_4Hg(OCOCF_3)]Ti(OCOCF_3)$ complex would take place. However, the process unexpectedly occurred in another direction. In the present work, we report the results of studying this reaction.

Results and Discussion

Experiments were carried out in a THF solution at room temperature in an argon atmosphere. Under these conditions, the interaction of complex **1** with an equimolar amount of $(CF_3COO)_2Hg$ results in the fast reduction of the starting mercury salt to metallic mercury and in the formation of titanocene bis(trifluoroacetate) $Cp_2Ti(OCOCF_3)_2$ (**2**) (Scheme 1). The reaction is completed within 15 min, and the yield of compound **2** is 93%.

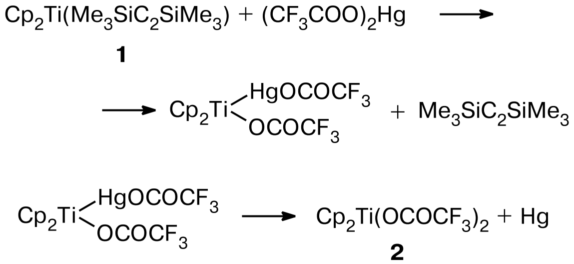
Scheme 1

$$\underset{\mathbf{1}}{Cp_2Ti(Me_3SiC_2SiMe_3)} + (CF_3COO)_2Hg \longrightarrow$$

$$\longrightarrow Cp_2Ti(OCOCF_3)_2 + Hg + Me_3SiC_2SiMe_3$$

The mechanism of this process includes, apparently, the step of oxidative addition of $(CF_3COO)_2Hg$ to titanocene Cp_2Ti, which is generated from the starting acetylene complex, followed by the elimination of the Hg atom from the unstable intermediate containing the Ti—Hg bond (Scheme 2).

Scheme 2



$$\underset{\mathbf{1}}{Cp_2Ti(Me_3SiC_2SiMe_3)} + (CF_3COO)_2Hg \longrightarrow$$

$$\longrightarrow Cp_2Ti\begin{cases}HgOCOCF_3\\OCOCF_3\end{cases} + Me_3SiC_2SiMe_3$$

$$Cp_2Ti\begin{cases}HgOCOCF_3\\OCOCF_3\end{cases} \longrightarrow \underset{\mathbf{2}}{Cp_2Ti(OCOCF_3)_2} + Hg$$

Isolated complex **2** is a red-orange crystalline substance stable in air. The structure of complex **2** was established by the analytical and spectroscopic methods and confirmed by X-ray diffraction analysis. The ^1H NMR spectrum of compound **2** in $CDCl_3$ contains a singlet of the η^5-cyclopentadienyl protons (δ 6.63), and its ^{19}F NMR

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spectrum contains a singlet of the F atoms of the CF_3 group (δ 2.45 relatively to $CFCl_3$). The $^{13}C\{^1H\}$ NMR spectrum of this complex in $CDCl_3$ is characterized by a singlet of the carbon atoms of the Cp ligands (δ 120.04), a quartet (1 : 3 : 3 : 1) of the C atom of the CF_3 group (δ 115.33; $^1J_{F,C} = 288.9$ Hz), and a quartet (1 : 3 : 3 : 1) of the C atom of the COO group (δ 161.45; $^2J_{F,C} = 39.7$ Hz). The IR spectrum of compound **2** exhibits (in addition to other absorption bands) bands of stretching vibrations of the C—H bonds of the Cp rings (at 3120 cm^{-1}) and the monodentate trifluoromethylcarboxylate group (at 1710 cm^{-1}). The electronic spectrum of the complex in a $CHCl_3$ solution is characterized by absorption bands with maxima at 393 and 520 nm. According to the elemental analysis data, the composition of the compound corresponds to the formula $Cp_2Ti(OCOCF_3)_2$.

Table 1. Selected bond lengths (*d*) and bond angles (φ) in complex **2**

Bond	*d*/Å	Angle	φ/deg
Ti(1)—O(1)	1.976(2)	O(1)—Ti(1)—O(3)	90.14(7)
Ti(1)—O(3)	1.990(2)	Cp(1)—Ti(1)—Cp(2)	132.0(1)
C(11)—O(1)	1.267(3)	C(11)—O(1)—Ti(1)	142.2(2)
C(11)—O(2)	1.200(3)	C(13)—O(3)—Ti(1)	139.9(2)
C(13)—O(3)	1.270(3)	O(2)—C(11)—O(1)	128.8(3)
C(13)—O(4)	1.210(3)	O(2)—C(11)—C(12)	118.9(3)
Ti(1)—Cp(1)	2.043(3)	O(1)—C(11)—C(12)	112.3(2)
Ti(1)—Cp(2)	2.034(3)	O(4)—C(13)—O(3)	129.8(3)
		O(4)—C(13)—C(14)	119.4(2)
		O(3)—C(13)—C(14)	110.8(2)

The structure of complex **2** is shown in Fig. 1, and the selected bond lengths and angles in its molecule are presented in Table 1. As can be seen, the complex has the structure of titanocene bis(trifluoroacetate) in which each trifluoroacetate ligand is bound to the Ti atom through a single O atom. The Ti(1)—O(1) and Ti(1)—O(3) distances in molecule **2** are 1.976(2) and 1.990(2) Å, respectively. The C(11)—O(1) (1.267(3) Å) and C(13)—O(3) (1.270(3) Å) bonds coordinated to the Ti atom are considerably longer than the noncoordinated C(11)—O(2) (1.200(3) Å) and C(13)—O(4) (1.210(3) Å) bonds. The wedge-shaped sandwich in molecule **2** has a usual geometry. The planes of the η^5-Cp rings form the dihedral angle of 49.7°. The Ti atom and the O(1) and O(3) atoms coordinated to Ti are arranged approximately in the bisector plane of this dihedral angle (the O(1)—Ti(1)—O(3) bond angle is 90.14(7)°). The Ti(1)—Cp(1) and Ti(1)—Cp(2) distances are 2.043(3) and 2.034(3) Å (Cp(1) and Cp(2) are centroids of the η^5-C_5H_5 rings C(1)—C(5) and C(6)—C(10), respectively). The C—C bond lengths in the Cp ligands vary in the 1.379(4)—1.414(5) Å range, and the Ti—C(Cp) distance ranges from 2.345(3) to 2.378(3) Å.

Complex **2** has first been synthesized[3] by the reaction of Cp_2TiCl_2 with CF_3COOAg or CF_3COOK in benzene or acetone. The orange-red compound isolated was characterized by elemental analysis, melting point (177—178.5 °C, from toluene), and UV spectrum in a $CHCl_3$ solution (λ_{max} 245 nm, ε = 29492). The synthe-

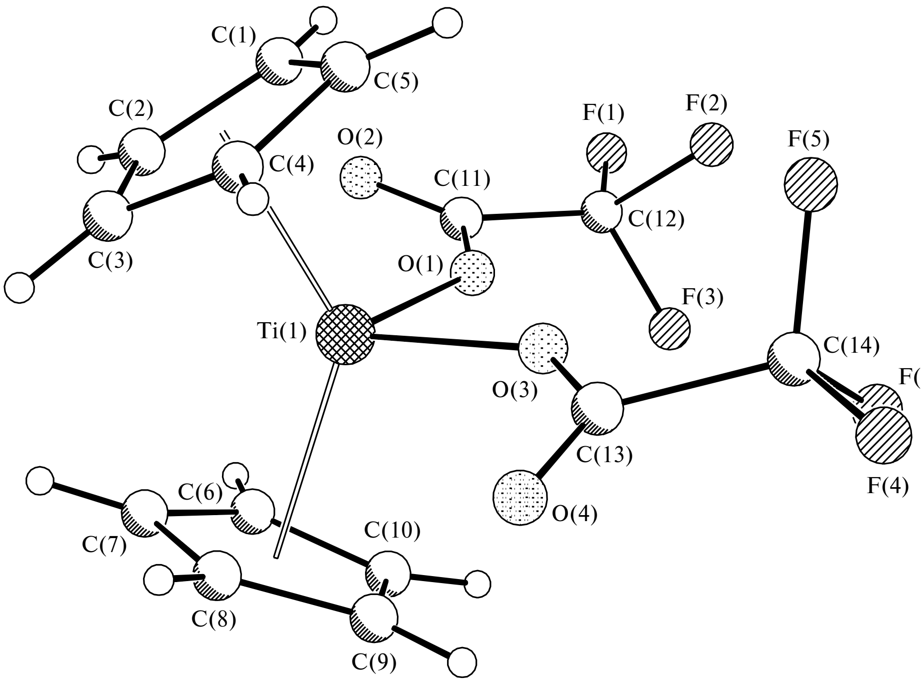

Fig. 1. Molecular structure of complex **2**. Another orientation of the disordered trifluoromethyl groups is not shown.

sis of compound **2** by the reaction of Cp_2TiCl_2 with CF_3COOAg in CH_2Cl_2 has been described later.[4] The compound was purified by recrystallization from a CH_2Cl_2—hexane mixture followed by sublimation at 110—120 °C *in vacuo* (0.01 Torr). The IR spectra, as well as ^1H and ^{19}F NMR spectra, were used to prove the structure of the product. However, the compound described by the authors of this paper[4] differed strongly by the melting point (130 °C, with decomp.) from the sample obtained in the earlier work[3] (m.p. 177—178.5 °C). Our samples of complex **2** have m.p. 175—176 °C (with decomp.), which virtually coincides with the value presented in this work,[3] the melting point remaining unchanged regardless of its measuring in a sealed capillary in argon or in air. In addition, compound **2** isolated by us, unlike that in the work,[4] is not sublimed at 110—120 °C *in vacuo* even at residual pressures <0.01 Torr. At the same time, the spectroscopic characteristics of complex **2** obtained by us and the authors of the paper[4] are close to each other, on the whole, despite some distinctions. Thus, compound **2** described in the work[4] is also probably titanocene bis(trifluoroacetate) but contaminated, most likely, with admixtures. In this connection, note that, according to the data of this work,[4] the IR spectrum of compound **2** contains absorption bands at 882 (m), 1000 (w), 1318 (w), and 1446 (w) cm^{-1}, which are absent from the spectrum of the compound isolated in our study (see Experimental).

Complex **2** was also synthesized[5] by the reaction of the σ-alkenyl derivatives of titanocene monotrifluoroacetate $Cp_2Ti(CR=CHR)(OCOCF_3)$ (R = H, Me) with CF_3COOH. Unfortunately, the melting point and spectroscopic characteristics of the complex obtained are not presented in this paper but its structure was reliably proved[5] by the X-ray diffraction data, which revealed the monodentate coordination of both trifluoroacetate groups with the Ti atom as well. However, since in this work the X-ray experiment was carried out at 298 K, the accuracy of structure **2** was not high ($R = 0.092$) because of the strong libration of the CF_3 groups. In our experiment, X-ray diffraction measurements were carried out at 110 K, which made it possible to "freeze out" the libration motion of the CF_3 ligands and to obtain more exact values of the bond lengths and bond angles for molecule **2**.

Thus, the results obtained show that the interaction of complex **1** with $(CF_3COO)_2Hg$ in THF at 20 °C results in the elimination of the bis(trimethylsilyl)acetylene ligand from the Ti atom, and the generated titanocene Cp_2Ti reacts further with the starting mercury salt to form complex **2**. This result in combination with the previous data on the reactions of complex **1** with tolan,[6,7] acetone,[7] benzophenone,[7] fullerene C_{60},[8] and others indicates that compound **1** can be used as a convenient source of unstable titanocene having the carbenoid properties, which is of great interest for the organometallic synthesis and catalysis.

Experimental

All procedures were carried out in an argon atmosphere with careful exclusion of air and moisture. Complex **1** was synthesized according to a previously described method.[6,7] Mercury trifluoroacetate was prepared by the reaction of red mercury oxide with a small excess of aqueous CF_3COOH. Solvents (THF, toluene, hexane) were purified by conventional methods and were distilled over sodium under Ar before use. IR spectra were recorded on a Magna-IR-750 instrument in KBr pellets. Electronic spectra were obtained on a Specord M-40 spectrophotometer in a $CHCl_3$ solution. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker ARX-400 instrument in $CDCl_3$. ^{19}F NMR spectra were recorded on a Bruker WP-200 SY instrument using $CFCl_3$ as external standard.

Synthesis of complex 2. A solution of $(CF_3COO)_2Hg$ (0.50 g, 1.17 mmol) in THF (5 mL) was added to a solution of complex **1** (0.41 g, 1.17 mmol) in THF (5 mL) under argon, and the resulting mixture was stirred at ~20 °C. During the reaction the color of the mixture changed rapidly from greenish-brown to orange-red, and metallic mercury (0.21 g, 1.05 mmol) precipitated from the solution in 90% yield. After 15 min, the orange-red solution was decanted and evaporated at 20 °C *in vacuo* to dryness. The resulting red-orange complex **2** was recrystallized from toluene, washed with hexane on a filter, and dried *in vacuo*. The yield of the complex is 0.40 g (93%), m.p. 175—176 °C (with decomp., in sealed capillary, Ar), *cf.* Ref. 3: m.p. 177—178.5 °C. Found (%): C, 41.68; H, 2.53. $C_{14}H_{10}F_6O_4Ti$. Calculated (%): C, 41.61; H, 2.49. ^1H NMR, δ: 6.63 (s, η^5-C_5H_5). ^{19}F NMR, δ: 2.45 (s, CF_3). $^{13}C\{^1H\}$ NMR, δ: 115.33 (q, CF_3, $^1J_{F,C} = 288.9$ Hz), 120.04 (s, η^5-C_5H_5), 161.45 (q, COO, $^2J_{F,C} = 39.7$ Hz). IR, ν/cm^{-1}: 3120 (w), 1710 (s), 1562 (w), 1406 (s), 1145 (s), 1025 (w), 1016 (w), 832 (m, sh), 782 (m), 721 (m). UV—Vis (λ_{max}/nm): 393 ($\varepsilon = 2133$), 526 ($\varepsilon = 209$).

X-ray diffraction analysis of complex 2. Crystals **2** were grown from toluene. They are monoclinic, space group $P2_1/c$, at 110 K $a = 10.257(2)$, $b = 10.733(2)$, $c = 14.694(4)$ Å, $\beta = 104.153(5)°$, $V = 15686(6)$ Å^3, $Z = 4$, $d_{calc} = 1.711$ g cm^{-3}, $\mu = 6.29$ cm^{-1}. Intensities of 10443 reflections were measured on a SMART CCD-1000 automated diffractometer (graphite monochromator, λ(Mo-Kα) = 0.71073 Å, ω scan mode, $\theta_{max} = 27.5°$). The structure was solved by the direct method and refined by the full-matrix least-squares method against F^2_{hkl} with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were revealed from the difference synthesis and included into refinement in the anisotropic approximation. Analysis of the difference Fourier syntheses showed disordering of the F atoms of both CF_3 groups, whose positions were refined anisotropically with equal population. The final divergence factors were $R_1 = 0.0424$ (against F^2 for 2171 observed reflections with $I > 2\sigma(I)$), $wR_2 = 0.1030$, GOOF = 0.912, and the number of refined parameters was 320. The coordinates of atoms are deposited with the Cambridge Structural Data Base. Calculations were performed on a personal computer using the SHELXTL PLUS programs.

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