

Syntheses and properties of titanocene derivatives containing ferrocenecarboxylato ligands

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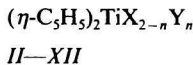
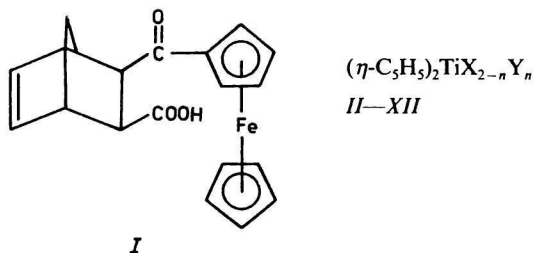
3-(Ferrocenylcarbonyl)bicyclo[2,2,1]hept-5-ene-2-carboxylic acid and eleven derivatives of titanium bis(cyclopentadienyl)ferrocenecarboxylate ($(\eta\text{-C}_5\text{H}_5)_2\text{TiX}_{2-n}\text{Y}_n$: X = Cl, $n = 1$ or 2, Y = ferrocenylcarbonyloxy, 2-ferrocenylacetoxo, 3-ferrocenyl-3-oxopropanoyloxy, 4-ferrocenyl-4-oxobutanoyloxy, 4-ferrocenylbutanoyloxy, and 3-(ferrocenylcarbonyl)bicyclo[2,2,1]hept-5-ene-2-carbonyloxy; X and Y = 4,4'-ferrocenyl-4,4'-dioxodibutanoyloxy) have been synthesized and their IR, ^1H NMR, and UV spectra are discussed. It is shown that these carboxyl groups are monodentate ligands in the mentioned titanium complexes.

Синтезированы 3-(ферроценилкарбонил)бицикло[2,2,1]гепт-5-ен-2-карбоновая кислота и одиннадцать производных бис(циклопентадиенил)ферроценкарбоксилата титана $(\eta\text{-C}_5\text{H}_5)_2\text{TiX}_{2-n}\text{Y}_n$: X = Cl, $n = 1$ или 2, Y = ферроценилкарбонилокси, 2-ферроценилацетокси, 3-ферроценил-3-оксопропаноилокси, 4-ферроценил-4-оксобутаноилокси, 4-ферроценилбутаноилокси и 3-(ферроценилкарбонил)бицикло[2,2,1]гепт-5-ен-2-карбонилокси; X и Y = 4,4'-ферроценил-4,4'-диоксодибутаноилокси, и обсуждаются их ИК-, ^1H ЯМР и УФ-спектры. Показано, что карбоксильные группы являются монодентатными лигандами в названных титановых комплексах.

In recent years, the chemistry of ferrocene and titanocene dichloride derivatives was extensively studied [1—8] due to their biological activity. But the organometallic complexes containing both iron and titanium were reported very little [9].

In this work, we synthesized 3-(ferrocenylcarbonyl)bicyclo[2,2,1]hept-5-ene-2-carboxylic acid (*I*) and eleven compounds of titanium bis(cyclopentadienyl)ferrocenecarboxylate (*II—XII*), which have not been reported so far

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where X = Cl, $n = 1$, Y = FcCOO (*II*), FcCH₂COO (*III*), FcCOCH₂COO (*IV*), FcCO(CH₂)₂COO (*V*), Fc(CH₂)₂COO (*VI*), FcCOC₇H₈COO (*VII*); $n = 2$, Y = FcCOO (*VIII*), FcCH₂COO (*IX*), FcCO(CH₂)₂COO (*X*), Fc(CH₂)₃COO (*XI*), and Fc = C₅H₅FeC₅H₄;
X and Y = Fe[C₅H₄CO(CH₂)₂COO]₂ (*XII*).

Experimental

Dichlorotitanocene [10], ferrocenecarboxylic acid [11], 2-ferrocenylacetic acid, and bis[(3-carboxy-1-oxopropionyl)cyclopentadienyl]iron [12], 4-oxo-4-ferrocenylbutyric acid [13], and 4-ferrocenylbutyric acid [14] are prepared by the methods described in literature.

Sodium ferrocenecarboxylate was prepared by reaction of the corresponding ferrocenecarboxylic acid and sodium ethoxide in ethanol, and the mixture was evaporated to dryness under vacuum. The sodium 3-oxo-3-ferrocenylpropanoate was prepared by the reaction of ethyl 3-oxo-3-ferrocenylpropanoate with a dilute solution of sodium hydroxide at 30°C.

IR spectra were obtained using KBr discs with a Nicolet FT-5DX spectrophotometer with sodium chloride optics. The measurement was carried out in the range of $\tilde{\nu} = 400\text{—}4000\text{ cm}^{-1}$. The ¹H NMR spectra were recorded on a PMX-60 or FT-80A spectrophotometer using deuteriochloroform as solvent and TMS as an internal standard. The UV spectra were measured with a DU-7B ultraviolet-visible spectrophotometer in the $\lambda = 200\text{—}500\text{ nm}$ region using 1,1'-dichloroethane as solvent.

All preparations should be carried out under nitrogen atmosphere. The elemental analyses and physical properties of compounds *I—XII* are shown in Table 1.

3-(Ferrocenylcarbonyl)bicyclo[2,2,1]hept-5-ene-2-carboxylic acid (I)

A solution of anhydrous aluminium chloride (7.5 g) in methylene dichloride (100 cm³) was added to a mixture of ferrocene (10 g) and bicyclo[2,2,1]hept-5-ene-2,3-dicarboxylic anhydride (4.4 g) in methylene chloride (150 cm³). Then the mixture was stirred for 3 h

Table 1

Characterization of compounds I—XII

Compound	Formula	$w_i(\text{calc.})/\%$ $w_i(\text{found})/\%$			Yield %	M.p. °C	Colour																																																																																																																				
		C	H	Cl																																																																																																																							
I	C ₁₉ H ₁₈ O ₃ Fe	65.14	5.18		93	174—175	Orange																																																																																																																				
		64.55	5.10					II	C ₂₁ H ₁₉ O ₂ ClFeTi	56.99	4.33	8.01	84	156 (decomposition)	Reddish brown	56.55	4.35	8.46	III	C ₂₂ H ₂₁ O ₂ ClFeTi	57.84	4.64	7.76	75	170 (decomposition)	Reddish orange	57.47	4.63	7.43	IV	C ₂₃ H ₂₁ O ₃ ClFeTi	57.00	4.37	7.32	65	130—132	Yellow	57.02	4.32	7.03	V	C ₂₄ H ₂₃ O ₃ ClFeTi	57.81	4.65	7.01	80	72—73	Orange	58.44	4.76	6.68	VI	C ₂₄ H ₂₅ O ₂ ClFeTi	59.48	5.20	7.32	75	195 (decomposition)	Yellow	59.05	5.18	7.53	VII	C ₂₉ H ₂₇ O ₃ ClFeTi	61.90	4.84	6.30	94	189 (decomposition)	Orange	62.01	4.85	5.93	VIII	C ₃₂ H ₂₈ O ₄ Fe ₂ Ti	60.42	4.44		78	184 (decomposition)	Yellow	60.24	4.34		IX	C ₃₄ H ₃₂ O ₄ Fe ₂ Ti	61.48	4.86		75	175 (decomposition)	Pale yellow	61.05	4.78		X	C ₃₈ H ₃₆ O ₆ Fe ₂ Ti	60.99	4.85		79	68—69	Yellow	60.42	4.83		XI	C ₃₈ H ₄₀ O ₄ Fe ₂ Ti	63.36	5.60		62	78—80	Reddish orange	63.01	5.53		XII	C ₂₈ H ₂₆ O ₆ FeTi	59.81	4.66		85
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at room temperature, and was introduced in a dilute hydrochloric acid with ice. The yellow precipitate produced was filtered. The methylene chloride layer was separated and a part of this solvent was removed under reduced pressure. Small amounts of precipitate were produced. They were combined, dissolved in aqueous solution of NaOH and the unreacted ferrocene was removed by filtering. The filtrate was acidified with dilute hydrochloric acid. The solid precipitate was collected on a filter and was recrystallized in aqueous acetic acid. The orange crystals were obtained, yield = 8.7 g (93 %).

Compounds II—XII

Sodium ferrocenecarboxylate (36 mg) was added to a solution of dichlorotitanocene (35.5 mg) in benzene (25 cm³) at 30 °C and reacted for 4.5 h. Sodium chloride produced

was removed by filtering and the filtrate was concentrated to 5 cm³ under vacuum. Hexane (10 cm³) was added to this solution, and immediately an orange precipitate was formed. The solid was recrystallized from chloroform-hexane and 53 mg of *II* was obtained. The preparation methods of compounds *III*–*XII* were similar to that used in case of *II*.

Table 2

¹H NMR spectra (δ /ppm) of compounds *I*–*XII*

Compound	C ₅ H ₅ FeC ₅ H ₄	(C ₅ H ₅) ₂ Ti	Other
<i>I</i>	4.30 (5H, s) 4.53 (2H, m) 4.84 (2H, m)		a 1.26–1.55 (m) b 2.99–3.38 (m) c 3.77 (m) d 4.55 (m) e 5.97–6.46 (m) f 11.7 (s)
<i>II</i>	4.27 (5H, s) 4.66 (2H, t) 4.77 (2H, t)	6.56 (10H, s)	
<i>III</i>	4.10 (9H, m)	6.40 (10H, s)	FcCH ₂ , 3.23 (2H, s)
<i>IV</i>	4.17 (5H, s) 4.50 (2H, t) 4.73 (2H, t)	6.43 (10H, s)	FcCOCH ₂ , 2.40 (2H, s)
<i>V</i>	4.20 (5H, s) 4.43 (2H, t) 4.76 (2H, t)	6.45 (10H, s)	FcCOCH ₂ ^b CH ₂ ^a , a 2.53 (2H, t) b 3.0 (2H, t)
<i>VI</i>	4.00 (9H, s)	6.23 (10H, s)	FcCH ₂ ^b CH ₂ ^a CH ₂ ^b , a 1.85 (2H, m) b 2.33 (4H, m)
<i>VII</i>	4.26 (5H, s) 4.65 (2H, m) 4.83 (2H, m)	6.26 (10H, s)	a 1.2–1.55 (m) b 2.95–3.4 (m) c 3.75 (m) d 4.45 (m) e 6.05–6.6 (m)
<i>VIII</i>	4.30 (10H, s) 4.36 (4H, t) 4.78 (4H, t)	6.57 (10H, s)	
<i>IX</i>	4.17 (18H, s)	6.30 (10H, s)	FcCH ₂ , 3.17 (4H, s)
<i>X</i>	4.19 (10H, s) 4.47 (4H, t) 4.78 (4H, t)	6.46 (10H, s)	FcCOCH ₂ ^b CH ₂ ^a , a 2.50 (4H, t) b 3.07 (4H, t)
<i>XI</i>	4.07 (18H, s)	6.40 (10H, s)	FcCH ₂ ^b CH ₂ ^a CH ₂ ^b , a 1.87 (4H, m) b 2.31 (8H, m)
<i>XII</i>	4.50 (4H, t) 4.83 (4H, t)	6.51 (10H, s)	FcCOCH ₂ ^b CH ₂ ^a , a 2.66 (4H, t) b 2.97 (4H, t)

s — singlet, t — triplet, m — multiplet.

Results and discussion

The elemental analyses show that the titanocene derivatives *II*—*XII* are produced by the reaction of Cp_2TiCl_2 with corresponding sodium ferrocene-carboxylate as follows



(Cp — cyclopentadienyl.) Diacyloxytitanocene compounds have not been obtained in case of reaction of Cp_2TiCl_2 with $\text{FcCOCH}_2\text{COONa}$ and $\text{FcCOC}_7\text{H}_8\text{COONa}$, because the former undergoes easily decarboxylation and yields acetylferrocene, the latter has more steric hindrance.

Compounds *II*—*XII* are unstable and sensitive to light and air. They are soluble in organic solvents such as benzene, acetone, methylene chloride, chloroform, and tetrahydrofuran, but insoluble in water, petroleum ether, hexane, and cyclohexane.

^1H NMR spectra of compounds *I*—*XII* are given in Table 2. It can be seen that five protons, which lie on the unsubstituted cyclopentadienyl ring in ferrocenyl group of compounds *I*, *II*, *IV*, *V*, *VII*, *VIII*, and *X* are equivalent protons and their signals appear at $\delta = 4.17$ — 4.30 ppm as a singlet. The proton signals of positions 3 and 4 on cyclopentadienyl ring substituted by carbonyl group appear at $\delta = 4.36$ — 4.66 ppm as a triplet, and those of positions 2 and 5 at $\delta = 4.77$ — 4.88 ppm as a triplet, because the presence of electronegative group reduces the shielding of cyclopentadienyl ring, so these proton signals shift downfield. But the proton signals in compounds *I* and *VII* are multiplet, it is possible that there is an effect of steric factor. In compound *XII*, since two cyclopentadienyl rings connect with carbonyl, the proton signals of positions 3,3',4,4' are exhibited at $\delta = 4.50$ ppm, and those of positions 2,2',5,5' at $\delta = 4.83$ ppm, all as triplets. The proton signals on substituted and unsubstituted cyclopentadienyl ring of ferrocenyl group in compounds *III*, *VI*, *IX*, and *XI* appear at $\delta = 4.0$ — 4.17 ppm as a multiplet and are resolved difficultly from each other, since these cyclopentadienyl rings are linked with the methylene group.

The proton signals of methylene connected directly with the cyclopentadienyl in compounds *III* and *IX* appear at $\delta = 3.17$ and 3.23 ppm, respectively, but in the compound *III*, the chemical shift of the proton on methylene is observed at $\delta = 2.4$ ppm as a singlet. The proton signals of two methylene groups appear at $\delta = 2.50$ — 2.66 ppm for H^a and at $\delta = 2.97$ — 3.07 ppm for H^b in compounds *V*, *X*, and *XII*, all as triplets.

The proton signals on cyclopentadienyl group of titanocene shift upfield ($\delta = 6.23$ — 6.50 ppm) as compared with that of the titanocene dichloride ($\delta = 6.55$ ppm), besides compounds *II* and *VIII*. It is possible that the cyclopentadienyl

tadienyl participates in d - p - π conjugate of d -orbital of titanium and p -orbital of oxygen in acyloxy group and leads to the decrease of circulating and deshielding effects of cyclopentadienyl ring.

The IR spectra of compounds *I*–*XII* are shown in Table 3. The cyclopentadienyl group in all compounds shows absorptions around $\tilde{\nu} = 3100 \text{ cm}^{-1}$ (C—H of ring stretching), 1450 and 1400 cm^{-1} (C—C of ring stretching), 1100 and 1020 cm^{-1} (C—H of ring deformation) and 820 cm^{-1} (C—H of ring out-of-plane bending). The characteristic stretching vibrations of carbonyl of ferrocenylformyl in *I*, *IV*, *V*, *VII*, *X*, and *XII* are identified by a very strong absorption at $\tilde{\nu} \approx 1665 \text{ cm}^{-1}$. The C=O stretching vibration of carboxyl in compound *I* exhibits a strong absorption at $\tilde{\nu} = 1696 \text{ cm}^{-1}$, its $\nu(\text{O—H})$ is identified by the strong and broad absorption at $\tilde{\nu} = 3409 \text{ cm}^{-1}$, but O—H...O out-of-plane bending is shown by broad absorption at $\tilde{\nu} = 910 \text{ cm}^{-1}$. The characteristic vibration of CH_2 (out-of-plane bending) in compounds *III*–*VII* and *IX*–*XII* appears at $\tilde{\nu} \approx 1250 \text{ cm}^{-1}$.

In compounds *II*–*XII*, the $\nu(\text{C=O})$ in carboxylato group is shown by a weak absorption at $\tilde{\nu} = 1700$ – 1728 cm^{-1} , but this absorption band was not observed in their sodium salts of the corresponding carboxylic acid. It is shown that the effect of metal ions on the $\nu(\text{O—C—O})$ is probably different. The carboxyl group in sodium salts exists in the form *A*, but in the carboxylato derivatives of titanocene in the form *B*



It is to be noted that the difference $\Delta\tilde{\nu}$ of $\nu_{\text{as}}(\text{O—C—O})$ and $\nu_{\text{s}}(\text{O—C—O})$ is of importance since these frequencies can be used for characterizing the type of bonding between metal and carboxyl. It can be seen from the difference $\Delta\tilde{\nu}$ for *II*–*XII* and the presence of $\nu(\text{C=O})$ at $\tilde{\nu} \approx 1714 \text{ cm}^{-1}$ that these carboxylato groups are monodentate ligands [5, 15, 16].

In addition, a new absorption band appears at $\tilde{\nu} \approx 660 \text{ cm}^{-1}$ which is characteristic of vibrations of Ti—O bond formed.

UV spectra of compound *I* show two bands at $\lambda = 245$ and 271 nm arising from π – π^* transition of cyclopentadienyl ring in ferrocenyl group and bands at $\lambda = 336$ and 455 nm attributed to charge-transfer transition between cyclopentadienyl ring and iron.

UV spectra of compounds *II*–*XII* are shown in Table 4. It can be seen that the band 1 at $\lambda = 247$ – 256 nm which belongs to strong absorption is K band due to π – π^* transition of cyclopentadienyl ring in titanocene, which undergoes a hypsochromic shift by 10–15 nm as compared with that of dichlo-

Table 3
IR spectra ($\tilde{\nu}/\text{cm}^{-1}$) of compounds I—XII

Compound	$\nu(\text{CH})$	$\nu(\text{C}=\text{O})^a$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}\cdots\text{C})$	$\pi(\text{CH}_2)^b$	$\delta(\text{CH})$	$\gamma(\text{CH})$	ν_{as}	ν_{s}	$\Delta\tilde{\nu}$	$\nu(\text{Ti}-\text{O})$			
I	3114 m	1696 s	1660 vs	1454 m		1157 w	818 m	$\nu(\text{O}-\text{H}),$ $\pi(\text{OH}\cdots\text{O})$	3409 br, s					
	2980 ms			1421 m		1103 w	844 w					910 br, w		
	2952 m					1054 w								
	2889 m													
II	3100 m	1706 w		1358 s		1100 w	819 s	1628 s	1358 s	270	674 w			
				1452 s		1018 m	792 m					(1546 vs) ^c	(1393 s)	(153)
III	3096 m	1723 w		1367 m	1232 m	1123 w	820 sh	1643 s	1305 s	338	662 m			
	2989 w			1442 m		1019 m						(1578 s)	(1392 s)	(186)
	2918 w													
IV	3107 w	1718 w	1665 s	1455 m	1238 m	1108 w	817 sh	1592 vs	1301 m	291	666 w			
	3053 w			1401 m		1003 w						(1606 vs)	(1411 m)	(195)
V	3132 w	1728 w	1663 vs	1452 m	1251 m	1169 w	822 sh	1630 s	1372 m	182	685 w			
	2959 w			1373 m		1023 w						(1596 vs)	(1414 s)	(150)
	2901 w													
VI	3163 w	1711 w		1440 m	1256 w	1105 w	800 sh	1630 s	1378 m	252	664 m			
	3086 w			1411 m		1019 w						(1562 vs)	(1412 s)	(175)
	2931 w													
VII	3114 m	1714 w	1664 s	1449 m	1236 s	1101 w	821 sh	1642 s	1351 s	291	657 w			
	2973 m			1411 w		1023 m						(1587 vs)	(1412 s)	(175)
	2896 w													
VIII	3093 m	1700 w		1453 s		1105 w	821 sh	1617 s	1324 s	293	660 w			
	2966 w			1377 m		1021 m						(1546 vs)	(1393 s)	(153)
IX	3093 m	1714 w		1412 sh	1239 w	1106 w	817 sh	1634 s	1328 m	306	664 m			
	2973 w					1022 w						(1578 s)	(1392 s)	(186)
	2966 w													
X	3093 w	1725 w	1664 vs	1451 s	1257 m	1083 w	824 sh	1644 m	1357 m	287	649 m			
	2973 w			1407 m		1025 w						(1596 vs)	(1414 s)	(182)
	2917 w													

Table 3 (Continued)

Compound	$\nu(\text{CH})$	$\nu(\text{C}=\text{O})^a$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}\cdots\text{C})$	$\pi(\text{CH}_2)^b$	$\delta(\text{CH})$	$\gamma(\text{CH})$	ν_{as}	ν_{s}	$\Delta\tilde{\nu}$	$\nu(\text{Ti}-\text{O})$
<i>XI</i>	3086 m	1707 w		1438 m	1252 m	1104 w	814 sh	1629 s	1371 m	258	654 s
	2931 m			1409 s		1018 w	(1562 vs)	(1412 s)	(150)		
	2861 w										
<i>XII</i>	3100 w	1725 w	1666 vs	1453 m	1257 s	1085 w	827 sh	1634 s	1340 s	294	650 m
	2915 w			1374 m		1021 w		(1576 vs)	(1414 s)	(162)	

a) Characteristic frequency of carbonyl in carboxylate group; *b*) methylene connected with carboxyl group; *c*) asymmetrical and symmetrical stretching vibration of sodium carboxylate, differences are given in parentheses.

vs — very strong, s — strong, w — weak, m — medium, sh — shoulder, br — broad.

Table 4

UV spectra (λ_{\max}/nm) of compounds II—XII

Compound	Characteristic absorption bands			
	1	2	3	4
II	252	223, 255	340, 435	377
III	253	223, 258	320, 441	380
IV	251	241, 266	327, 443	373
V	250	243, 263	335, 447	380
VI	249	227, 249	324, 424	379
VII	256	243, 268	330, 450	377
VIII	248	222, 270	343, 440	378
IX	249	224, 249	310, 427	374
X	250	249, 271	329, 457	373
XI	251	236, 261	335, 455	376
XII	247	231, 252	320, 434	375

rotitanocene (262 nm). The band 4 at $\lambda = 373\text{--}380$ nm which belongs to a weak absorption is attributed to charge-transfer transition between cyclopentadienyl ring and titanium [17], which exhibits a hypsochromic shift by 10—17 nm, too, as compared with the corresponding band of dichlorotitanocene (390 nm).

The band 2 at $\lambda = 222\text{--}249$ and 249—271 nm is of medium absorption and is attributed to $\pi\text{--}\pi^*$ transition of cyclopentadienyl ring in ferrocenyl group [17, 18]. The charge-transfer transition between the cyclopentadienyl ring and iron leads to band 4 at $\lambda = 310\text{--}340$ and 427—457 nm, the absorptions of which are weak, because the transition belongs to forbidden transitions.

It can be seen from the above-mentioned results that these ferrocenecarboxylato ligands coordinate to titanium in the monodentate form.

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