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Titanocene Aminocylates

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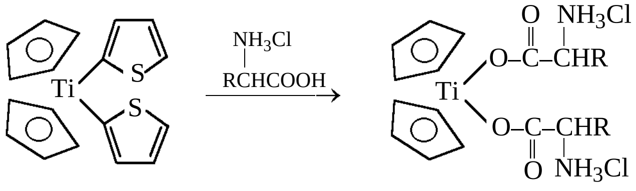
Abstract—Dicyclopentadienyldithienyltitanium $(C_5H_5)_2Ti(C_4H_3S)_2$ was reacted with valine, leucine, and isoleucine hydrochlorides to obtain the corresponding titanocene aminoacylates $(C_5H_5)_2Ti[OCOCH(NH_3Cl)R]_2$.

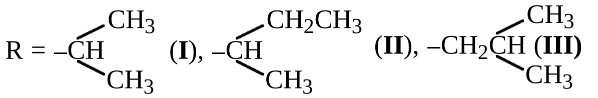
Earlier we showed that the cleavage of titanium–carbon σ bonds in dicyclopentadienyldithienyltitanium $(\pi\text{-}C_5H_5)_2Ti(\alpha\text{-}C_4H_3S)_2$ and dicyclopentadienylthienyltitanium chloride $(\pi\text{-}C_5H_5)_2TiCl(\alpha\text{-}C_4H_3S)$ under the action of carboxylic acids, phenols, or β-diketones provides a convenient synthetic route to titanocene and chlorotitanocene acylates and phenolates $(C_5H_5)_2Ti(OCOR)_2$ [1], $(C_5H_5)_2TiCl(OCOR)$ [2], $(C_5H_5)_2Ti(OAr)_2$, and $(C_5H_5)_2TiCl(OAr)$ [3], as well as chlorotitanocene β-diketonates $(C_5H_5)_2TiCl\cdot(RCOCHCOR')$ [4]. In the present work we studied utility of this approach for synthesis of titanocene aminoacylates.

It was found that dicyclopentadienyldithienyltitanium fails to react with valine, leucine, and isoleucine. Even after 40-h stirring in benzene at 40–50°C the reaction mixtures still contained intact starting materials. When dicyclopentadienyldithienyltitanium was reacted with valine, leucine, and isoleucine hydrochlorides, we observed cleavage of titanium–carbon σ bonds to give the corresponding titanocene aminoacylates. The reactions could be brought to completion by 5–6-stirring in benzene at 40–55°C.

Compounds **I**–**III** are solid colored substances soluble in polar organic solvents. Their structures were proved by the ^1H NMR and IR spectra and the elemental analyses. Some physicochemical characteristics of the products are listed in Table 1 and their ^1H NMR spectra, in Table 2.



I–**III**



$R = -CH(CH_3)_2$ (**I**), $-CH(CH_3)CH_2CH_3$ (**II**), $-CH_2CH(CH_3)_2$ (**III**)

Compounds **I** and **II** were studied by mass spectrometry. The mass spectra lack molecular ion peaks. The highest *m/e* peaks belong to $[M - HCl]^+$ ions. Further fragmentation involves loss by the metal atom of its ligand environment. The mass spectra also show peaks due to ions formed by CO_2 expulsion. Principal peaks and their relative intensities are listed in Table 3.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrophotometer for KBr pellets. The ^1H NMR spectra were obtained on a Tesla BS-567A spectrometer for $CDCl_3$ solutions, reference TMS. The mass spectra were measured on an MKh-1320 instrument at 35 eV. All operations were performed under argon in dry solvents.

Table 1. Physicochemical characteristics of titanocene aminoacylates **I**–**III**

Comp. no.	Yield, %	mp, °C	ν(CO), cm^{-1}	Found, %				Formula	Calculated, %			
				C	H	Cl	N		C	H	Cl	N
I	75	183–186	1660, 1305	53.01	7.26	15.60	6.09	$C_{20}H_{32}Cl_2N_2O_4Ti$	53.23	7.15	15.71	6.21
II	77	165–168	1670, 1300	55.32	7.71	14.55	5.62	$C_{22}H_{36}Cl_2N_2O_4Ti$	55.13	7.57	14.79	5.84
III	71	170–172	1665, 1310	55.41	7.63	14.50	5.69	$C_{22}H_{36}Cl_2N_2O_4Ti$	55.13	7.57	14.79	5.84

Table 2. ^{1}H NMR spectra of titanocene aminoacylates **I–III**, δ, ppm

Comp. no.	C_5H_5	NH_3	CH_3	CH	CH_2
I	6.70 s (10H)	8.80 s (6H)	1.20 d (6H) 1.34 d (6H)	2.64 m (2H) 3.75 m (2H)	–
II	6.71 s (10H)	8.79 s (6H)	1.05 t (6H) 1.30 d (6H)	2.27 m (2H) 3.84 m (2H)	1.58 m (4H)
III	6.70 s (10H)	8.82 s (6H)	1.04 d (12H)	2.18 m (2H) 3.85 m (2H)	1.93 d.d (4H)

Table 3. Mass spectra of compounds **I** and **II**

Ion	*m*/*e*	I_{rel}, %	Ion	*m*/*e*	I_{rel}, %
$(C_5H_5)_2Ti[OCOCH(NH_3Cl)CH(CH_3)_2]_2$ (**I**)					
$C_{20}H_{31}ClN_2O_4Ti^+$	446	5	$C_9H_{22}Cl_2N_2O_2Ti^+$	308	40
$C_{15}H_{27}Cl_2N_2O_4Ti^+$	417	2	$C_{14}H_{25}N_2O_2Ti^+$	301	21
$C_{20}H_{30}N_2O_4Ti^+$	410	23	$C_{15}H_{20}NO_2Ti^+$	294	70
$C_{19}H_{31}ClN_2O_2Ti^+$	402	8	$C_{10}H_{20}N_2O_4Ti^+$	280	12
$C_{15}H_{26}ClN_2O_4Ti^+$	381	40	$C_9H_{21}ClN_2O_2Ti^+$	272	44
$C_{10}H_{22}Cl_2N_2O_4Ti^+$	352	16	$C_{14}H_{20}NTi^+$	250	51
$C_{15}H_{25}N_2O_4Ti^+$	345	2	$C_{10}H_{10}Ti^+$	178	100
$C_{14}H_{26}ClN_2O_2Ti^+$	337	21	$C_5H_{10}NO_2Ti^+$	164	25
$C_{15}H_{21}ClNO_2Ti^+$	330	7	$C_5H_{11}ClNO_2^+$	152	41
$C_{10}H_{21}ClN_2O_4Ti^+$	316	3	$C_5H_5Ti^+$	113	62
$(C_5H_5)_2Ti[OCOCH(NH_3Cl)CH(CH_3)CH_2CH_3]_2$ (**II**)					
$C_{22}H_{35}ClN_2O_4Ti^+$	474	3	$C_{11}H_{26}Cl_2N_2O_2Ti^+$	336	28
$C_{17}H_{31}Cl_2N_2O_4Ti^+$	445	2	$C_{16}H_{29}N_2O_2Ti^+$	329	17
$C_{22}H_{34}N_2O_4Ti^+$	438	19	$C_{16}H_{22}NO_2Ti^+$		
$C_{21}H_{35}ClN_2O_2Ti^+$	430	6	$C_{12}H_{24}N_2O_4Ti^+$	308	51
$C_{17}H_{30}ClN_2O_4Ti^+$	409	37	$C_{11}H_{25}ClN_2O_2Ti^+$	300	35
$C_{12}H_{26}Cl_2N_2O_4Ti^+$	380	14	$C_{15}H_{22}NTi^+$	264	48
$C_{17}H_{29}N_2O_4Ti^+$	373	1	$C_{10}H_{10}Ti^+$	178	100
$C_{16}H_{30}ClN_2O_2Ti^+$	365	18	$C_6H_{12}NO_2Ti^+$		
$C_{16}H_{23}ClNO_2Ti^+$			$C_6H_{13}ClNO_2^+$	166	40
$C_{12}H_{25}ClN_2O_4Ti^+$	344	4	$C_5H_5Ti^+$	113	70

Titanocene aminoacylates. To a solution of 1 mmol of dicyclopentadienyldithienyltitanium in 75 ml of benzene we added 2.1 mmol of correponding amino acid hydrochloride. The reaction mixture was stirred at 50°C for 6 h and filtered. The filtrate was reduced in a vacuum to 20 ml and treated with 70 ml of hexane. The precipitate that formed was separated, washed with ether and pentane, and vacuum-dried. The products were purified by reprecipitation from benzene. The yields and melting points of titanocene aminoacylates are listed in Table 1.

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