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Synthesis and characterization of 1-ferrocenecarboxysilatranes and crystal structures of $FcC(CH_3)=CHCOOSi(OCH_2CH_2)_3N$ and *p*-$FcC_6H_4COOSi(OCH_2CH_2)_3N$

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Abstract

A series of novel silatranes containing ferrocenyl carboxylate were obtained by the reaction of 1-ethoxysilatrane with ferrocenyl carboxylic acids, and characterized by elemental analysis, IR and ^{1}H-NMR. The crystal structure of $FcC(CH_3)=CHCOOSi(OCH_2CH_2)_3N$ and *p*-$FcC_6H_4COOSi(OCH_2CH_2)_3N$ was determined by X-ray diffraction. The Si–N distances of the two compounds are 2.065 and 2.052 Å, respectively. Both the bond distances are shorter than that of 1-alkyl or 1-alkoxysilatranes and close to that of 1-halosilatranes. The antibacterial activity of *p*-$FcC_6H_4COOSi(OCH_2CH_2)_3N$ was determined.

Keywords: Silatranes; Crystal structure; Ferrocene; Ferrocenyl carboxylate

1. Introduction

For many years, much interest has focused on ferrocenyl derivatives for their antitumor [1] and insecticidal activities [2]. Recently, Zakaria et al. [3] and Chohan and Praveen [4] reported, respectively, antimicrobial and antibacterial ferrocene derivatives. Introducing ferrocenyl group into heterocyclic ring molecule also exhibit good activities [5,6]. In addition, ferrocene is ideal for use in drug design because of the low toxicity of the molecule containing a ferrocenyl moiety.

Silatranes are a class of cage compounds that contain a hypervalent silicon atom with a transannular bond to nitrogen (bond length of 2.0–2.4 Å) [7–10]. In the past decades, many silatrane derivatives have been synthesized for their high toxic [11], potential pharmacological [12], plant growth regulator [13] and so on. For example, 1-ethoxysilatrane and 1-chloromethylsilatrane are able to heal burn and wound [14,15], but 4-chlorophenylsilatrane is a new organic silicon raticide. Recently, Lin and Wang [16] reported that the silatrane derivatives exhibit biological activity against k562 oncocytes of erythroleukemia. Ferrocenylsilatranes and ferrocenylethylsilatranes were also reported as potential materials for applications in nonlinear optics (NLOs).

Since we reported 1-alkylacyloxysilatranes which were low or medium toxicities and exhibited good curative effects on Ehrlich cancer in 1987 [17], our research group has engaged in the synthesis, structure and bioactivity studies of group IVA metallatranes [18]. The aim of this work was to replace the alkylacyloxy moiety by ferrocenecarboxyl in silatranes. This replacement was expected to induce great changes in molecular properties, such as the hydrophobicity, toxicity and bioactivities. We present herein the synthesis and characterization of some ferrocenecarboxyl silatranes.

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2. Result and discussion

2.1. Preparations

The general reaction scheme is shown as follows:

$$\mathrm{FcRCOOH+EtOSi(OCH_2CH_2)_3N \xrightarrow[\text{reflux}]{\text{chlorobenzene}} FcRCOOSi(OCH_2CH_2)_3N}$$

For compounds: R = –C(CH$_3$)=CH– (**I**), *p*-C$_6$H$_4$ (**II**), –CH=CH– (**III**), –COCH$_2$CH$_2$– (**IV**), –CH$_2$– (**V**).

All compounds are prepared under mild condition in nitrogen atmosphere. The reactions of ferrocenyl carboxylic acids with 1-ethoxysilatranes represent a satisfactory method of synthesis of the products. Because of the greater polarity of β-ferrocenyl propionic acids, its solubility is lower in chlorobenzene than that of the other acids. When this method is used to prepare compound **IV**, the yield is lower. Upon heating, the solvent molecule of compound **I** is lost at 101 °C while the melting point is 202–203 °C.

All compounds are color crystals. They are unstable under ordinary conditions and easy to decompose, and so they should be reserved in dryer. The compounds are easily soluble in organic solvents such as chloroform and dichloromethane, but not soluble in *n*-hexane and petroleum ether.

2.2. IR

The IR spectra of these compounds have been recorded in the range 4000–400 cm^{-1}. The absorption bands can be assigned on the basis of earlier publications and the important data are listed in Table 1.

The IR spectroscopic data provide further support for the molecular constitution of the title compounds. The broaden absorption of region 2500–3200 cm^{-1} of O–H in the corresponding acids disappear. The absorptions of interest are those of carbonyl C=O, Si–O and Si–N bonds. In the spectra, medium to weak bands in the region 2800–3100 cm^{-1} are assigned to C–H [8]. A moderately intense band assigned to stretching vibrations of the coordinate Si–N bond is observed in the 578–592 cm^{-1} region. The medium absorption in the region 1088–1096 cm^{-1} is assigned to Si–O bonds. From Table 1, we find that the asymmetric absorption vibration frequencies (v_{asym}) of carbonyl groups of compounds **I**–**III** are lower than that of compound **V**, the most probable reason is that there are conjugations of C=C and C=O in compounds **I**–**III**.

The differences of the asymmetric absorption frequencies and the symmetric absorption vibration frequencies [$\Delta v(CO_2)$] are 283–380 cm^{-1} which shows that the carbonyl groups are monodentate ligand and there are no interactions between the silicon atom and the carbonyl oxygen atoms of the carboxyl groups (see Section 2.4).

2.3. ^{1}H-NMR

The ^{1}H-NMR data of the title compounds are listed in Table 2. Comparing ^{1}H-NMR spectra of the title compounds with those of usual 1-alkyl or 1-alkoxysilatranes, we find a downfield shift for the proton with Si(OCH$_2$CH$_2$)$_3$N moiety and the peak changing from triplet to singlet [8]. This change indicates the electron withdrawing effect of the carbonyl of carboxyl groups. So we can assume that the bond length of Si–N of the title compounds is stronger than that of 1-alkyl or 1-alkoxysilatranes.

From Table 2, we find the chemical shifts of proton of R groups in the silatranes are lower than those in the corresponding acids. This shows that Si(OCH$_2$CH$_2$)$_3$N is a large volume donor group in the molecule. The conclusion is in agreement with the work done by others [8].

All protons in the compounds have been identified and the total number of protons calculated from the integration curve tallies with what is expected from the molecular formula.

2.4. Crystal structure

A red-needle crystal of compound **I** and an orange-flake crystal of compound **II** were recrystallized from chloroform and *n*-hexane, respectively. Fig. 1 shows the molecular structure of compound **I** and gives the atom-numbering scheme. The molecular structure of compound **II** with the atom-numbering scheme is depicted in Fig. 2. The selected bond distances and angles of the two compounds are listed in Tables 3 and 4, respectively. The two compounds possess the usual skeleton contain-

Table 1
IR data of the compounds (cm^{-1})

No.	v_{Fc}	$v_{asym}(CO_2)$	$v_{sym}(CO_2)$	$\Delta v(CO_2)$	v_{Si-O}	v_{Si-N}
I	1122, 1028	1676	1318	358	1094	578
II	1121, 1023	1682	1318	365	1088	588
III	1121, 1022	1668	1316	353	1092	584
IV	1120, 1022	1660	1377	283	1096	592
V	1115, 1024	1714	1334	380	1085	583

Table 2
^{1}H-NMR data of the compounds

No.	C_5H_5	C_5H_4	OCH_2	NCH_2	R [protons of corresponding acids]
I	4.07(5H,s)	4.27(2H,s), 4.47(2H,s)	3.95(6H,s)	2.97(6H,s)	2.48(3H,s), 6.14(1H,s) [2.50(3H,s), 6.18(1H,s)]
II	4.05(5H,s)	4.40(2H,s), 4.74(2H,s)	3.98(6H,s)	3.00(6H,s)	7.35–7.38(2H,d), 7.95–7.98(2H,d) [7.62–7.66(2H,d), 7.91–7.95(2H,d)]
III	4.08(5H,s)	4.27(2H,s), 4.41(2H,s)	3.95(6H,s)	2.96(6H,s)	6.04–6.12(1H,d), 7.42–7.50(1H,d) [5.98–6.06(1H,d), 7.64–7.72(1H,d)]
IV	4.18(5H,s)	4.44(2H,s), 4.78(2H,s)	3.95(6H,s)	3.04(6H,s)	2.75(2H,m), 3.00(2H,s) [2.75(2H,s), 3.03(2H,s)]
V $EtOSi(OCH_2CH_2)_3N$	4.24(5H,s)	4.24(4H,s)	3.90(6H,s) 3.80–3.86(6H,t)	2.95(6H,s) 2.81–2.87(6H, t)	3.19(2H,s) [3.34(2H,s)]

ing a five-coordinate silicon atom. The N(1)–Si(1)–O(1) angle of compounds **I** and **II** are 175.7° and 177.7°, respectively. The Si atoms of compounds **I** and **II** are displaced 0.395 and 0.1047 Å, respectively, from the center of the plane defined by O(1), O(2) and O(3) to O(4). The stereochemistry of silicon is distorted trigonal-bipyramidal. The Si–N lengths of the two compounds are 2.065 and 2.052 Å, respectively. Both the bond distances are shorter than that of 1-alkyl or 1-alkoxysilatranes [8] and close to that of 1-halosilatranes. This proves the Si–N bonds of compounds **I** and **II** are stronger than that in 1-alkyl or 1-alkoxysilatranes and agree with the conclusion of ^{1}H-NMR.

Comparing compound **I** with its corresponding acid, we find that the C(7)–O(4) distance becomes longer (from 1.285 to 1.354 Å) and the C(7)–O(5) distance becomes shorter (from 1.238 to 1.209 Å) [21], the angles of O(4)–C(7)–O(5) and C(8)–C(7)–O(5) are changed from 122.3° and 123.9° to 123.1° and 126.5°, respectively, but the C(8)–C(7)–O(4) angle of compound **I** is 3.4° smaller than that of its corresponding acid (from 113.8° to 110.4°). These numbers prove when silicon atom makes bond with oxygen of carboxyl group, the $Si(OCH_2CH_2)_3N$ group acts as an electron-donor which makes C(7)–O(4) bond weaker and C(7)–O(5) bond stronger. All these agree with ^{1}H-NMR. On the other hand, the configuration of compound **I** is *trans*-isomer.

Table 3
Selected bond lengths of compounds **I** and **II**

	Bond lengths (Å)	
	I	**II**
N(1)–Si(1)	2.065(5)	2.052(3)
Si(1)–O(1)	1.635(5)	1.648(2)
Si(1)–O(2)	1.651(5)	1.646(2)
Si(1)–O(3)	1.641(5)	1.653(2)
Si(1)–O(4)	1.706(4)	1.732(2)
N(1)–C(2)	1.411(8)	1.478(4)
N(1)–C(4)	1.478(9)	1.471(4)
N(1)–C(6)	1.470(8)	1.481(4)
O(4)–C(7)	1.354(8)	1.329(4)
O(5)–C(7)	1.209(7)	1.208(4)

2.5. Biological evaluation

The antibacterial activity of compound **II** (50 ppm) was determined in vitro against *Gibberella saubinetii*, *Cladosporium fulvum*, *Bremia lactucae*, *Alternaria mali* and *Isariopsis clavispora*. The relative inhibitory ratios (%) were 25, 25, 0, 0 and 23.5, respectively. The data indicated that compound **II** shows weak antibacterial activity. The other biological activities such as insecticide and antitumor were tested at the moment and the result will be presented in the future.

3. Experimental

3.1. Instruments

Elemental analyses were determined on a Yanaca CHN Corder MT-3 elemental analyzer. IR spectra were

Table 4
Selected bond angles of compounds **I** and **II**

	Bond angles (°)	
	I	**II**
N(1)–Si(1)–O(4)	175.9(3)	177.7(2)
O(1)–Si(1)–O(2)	120.0(3)	119.6(2)
O(1)–Si(1)–O(3)	119.1(3)	118.0(2)
O(2)–Si(1)–O(3)	118.7(3)	121.2(2)
O(1)–Si(1)–O(4)	97.2(2)	91.3(2)
O(2)–Si(1)–O(4)	90.2(2)	95.7(2)
O(3)–Si(1)–O(4)	97.2(2)	93.7(2)
O(1)–Si(1)–N(1)	84.7(2)	86.8(2)
O(2)–Si(1)–N(1)	85.7(2)	86.4(2)
O(3)–Si(1)–N(1)	85.0(2)	85.9(2)
C(7)–O(4)–Si(1)	128.5(4)	125.2(2)
O(4)–C(7)–C(8)	110.4(6)	113.3(3)
O(5)–C(7)–C(8)	126.5(7)	121.1(4)
O(5)–C(7)–O(4)	123.1(6)	125.6(3)

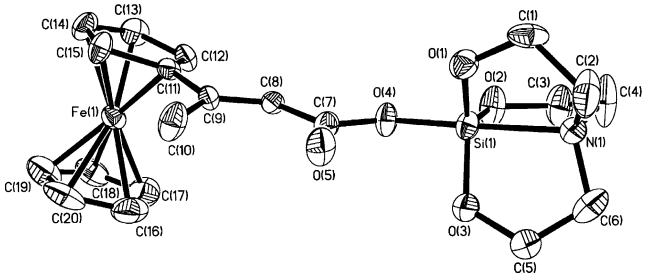

Fig. 1. The molecular structure of $FcC(CH_3)=CHCOO-Si(OCH_2CH_2)_3N$.

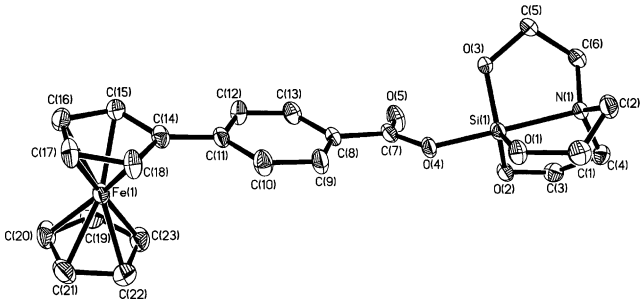

Fig. 2. The molecular structure of p-$FcC_6H_4COOSi(OCH_2CH_2)_3N$.

recorded on a Bruker Equinox 55 spectrometer in KBr discs. ^{1}H-NMR spectra were measured on a Bruker AC-200 spectrometer in $CDCl_3$ solution with TMS as internal standard.

3.2. Reagents

Solvents were dried by standard methods and distilled prior to use. β-Ferrocenylacrylic acid, β-ferrocenyl butenic acid, p-ferrocenyl benzoic acid, ferrocenylacetic acid and β-ferrocenyl propionic acid were synthesized by the method of literatures [19–22]. 1-Ethoxysilatrane was obtained by reaction of tetraethoxysiloxane with triethanolamine [23] and the solid product was recrystallized from toluene–petroleum ether.

3.3. Synthesis of the title compounds

A mixture of corresponding ferrocenyl carboxylic acids (5 mmol), 1.1 g 1-ethoxysiltrane (5 mmol) and 50 ml chlorobenzene was heated to reflux for 3 h under nitrogen. Then ethanol was removed by azeotropic distillation with approximately 35 ml chlorobenzene for 1.5 h. The reaction mixture was filtered and recrystallized from $CHCl_3$/n-hexane or CH_2Cl_2/n-hexane system. The yield, melting points and elemental analysis of the prepared compounds are given in Table 5.

3.4. X-ray crystallography

Crystals of compounds **I** and **II** were obtained from chloroform and n-hexane solutions. Diffraction measurements of compounds **I** and **II** were carried out on a Bruker SMART 1000CCD diffractometer operating at 50 kV and 20 mA using Mo–K_α radiation ($\lambda = 0.71073$ Å). Data collection at 293 K and reduction were performed using the SMART and SAINT software [24]. An empirical absorption correction (SADABS) was applied to the raw intensities [25]. The crystal structures were determined by direct methods and refined by full-matrix least-squares using the SHELXTL-PC program package [26]. Non-hydrogen atoms were subjected to anisotropic refinement. All hydrogen atoms were generated geometrically (C–H lengths fixed at 0.96 Å), assigned appropriate isotropic thermal parameters, and included in structure factor calculations in the final stage of F^2 refinement. A summary of the crystal data is given in Table 6.

4. Supplementary material

Crystallographic data for the structures of compounds **I** and **II** have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 208203 and 208204, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK

Table 5
Yields and elemental analyses of the compounds

Compound	Formula for calc.	State	Yield (%)	m.p. (°C)	Elemental analysis (%, calc.)		
					C	H	N
I	$C_{21}H_{26}Cl_3FeNO_5Si$	red needles	65.7	202–203	44.86 (44.82)	4.52 (4.66)	2.63 (2.49)
II	$C_{23}H_{25}FeNO_5Si$	orange flakes	79.2	245 (dec)	57.43 (57.63)	5.26 (5.26)	3.00 (2.92)
III	$C_{20}H_{24}Cl_3FeNO_5Si$	red needles	67.2	236 (dec)	43.76 (43.78)	4.52 (4.41)	2.47 (2.55)
IV	$C_{20}H_{25}FeNO_6Si$	yellow needles	34.5	195–196	52.46 (52.30)	5.48 (5.49)	3.07 (3.05)
V	$C_{18}H_{23}FeNO_5Si$	yellow needles	82.3	213–214	51.76 (51.81)	5.62 (5.55)	3.30 (3.36)

Table 6
Crystallographic data for compounds **I** and **II**

	I	**II**
Empirical formula	$C_{21}H_{26}Cl_3FeNO_5Si$	$C_{23}H_{25}FeNO_5Si$
Crystal system	orthorhombic	monoclinic
Space group	$P2(1)2(1)2(1)$	$P2(1)/c$
Unit cell dimensions		
a (Å)	7.3689(18)	15.158(3)
b (Å)	12.929(3)	11.121(3)
c (Å)	25.802(7)	12.832(3)
α (°)	90	90
β (°)	90	96.283(4)
γ (°)	90	90
V (Å^3)	2458.3(11)	2150.2(8)
Z	4	4
D_{calc} (mg mm^{-3})	1.520	1.481
Absorption coefficient (mm^{-1})	1.021	0.793
$F(0\,0\,0)$	1160	1000
Crystal size (mm^3)	$0.15 \times 0.10 \times 0.05$	$0.30 \times 0.25 \times 0.20$
Theta range for data collection (°)	2.23–25.02	2.28–25.02
Limiting indices	$-8 \le h \le 5$, $-9 \le k \le 15$, $-30 \le l \le 30$	$-12 \le h \le 18$, $-11 \le k \le 13$, $-15 \le l \le 15$
Reflections collected	8768	8763
Independent reflections	4260 ($R_{int} = 0.0725$)	3792 ($R_{int} = 0.0681$)
Completeness to $\theta = 25.02°$	98.5%	99.9%
Goodness-of-fit	1.041	0.952
Final R indices [$I > 2s(I)$]	$R_1 = 0.0583$, $wR_2 = 0.0922$	$R_1 = 0.0465$, $wR_2 = 0.0716$
R indices (all data)	$R_1 = 0.1220$, $wR_2 = 0.1055$	$R_1 = 0.0988$, $wR_2 = 0.0837$
Large difference peak and hole (e Å^{-3})	0.381 and −0.400	0.258 and −0.342

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