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THE PREPARATION OF FERROCENEDITHIOCARBOXYLIC ACID DERIVATIVES AND THEIR SPECTRAL PROPERTIES

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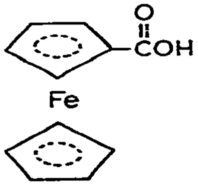
Summary

Ferrocenedithiocarboxylic acid and various derivatives have been prepared and characterized. The molecular extinction coefficients for the $n \rightarrow \pi^*$ transition of the thiocarbonyl group in the visible spectra of these derivatives are 10—15 fold greater than expected for aromatic dithio acids.

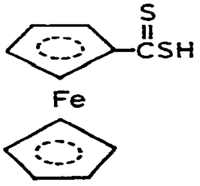
Introduction

Although the preparation of ferrocenecarboxylic acid (I) has been reported [1—3], ferrocenedithiocarboxylic acid (II) and its derivatives have not yet been described. It is well known that dithio acids are unstable; their sodium and potassium salts are oily substances containing small amounts of water, while their crystalline heavy metal salts (Zn, Pb, etc.) do not react with ordinary electrophilic reagents such as alkyl bromides and iodides. Recently, however, it was found that the crystalline ammonium salts of dithio acids are anhydrous. They react readily with electrophiles, and are very suitable for the purification of the acids [4—5].

In this paper we describe the preparation of a variety of ferrocenedithiocarboxylic acid derivatives and report their spectral data.



(I)



(II)

Results and discussion

Preparation

Ferrocenedithiocarboxylic acid and its ammonium salts were prepared by the reaction sequence shown in eqn. 1. The preparation of ferrocenylmagnesium bromide is according to the previously reported method of Shechter and Helling [6] *, except that we used diethyl ether as the solvent and 1,2-dibromoethane as

$$\mathrm{FcBr}\xrightarrow[\text{Ether}\ (\mathrm{CH_2})_2\mathrm{Br_2}]{\mathrm{Mg}}\mathrm{FcMgBr}\xrightarrow[\mathrm{THF}]{\mathrm{CS_2}}\mathrm{FcCs_2MgBr}\xrightarrow{\mathrm{HCl}}\xrightarrow{\mathrm{NaOH}}\xrightarrow{\mathrm{HCl}}\xrightarrow{\text{amines (X)}}$$

$$\mathrm{Fc\overset{-}{C}S_2\overset{+}{X}H}\xrightarrow{\mathrm{HCl}}\underset{(\mathrm{II})}{\mathrm{FcCS_2H}} \tag{1}$$

initiator in order to keep the reaction temperature below 35°. In addition, we found it essential to use tetrahydrofuran as solvent in the carbon disulfide insertion reaction, and to extract the dithio acid with sodium hydroxide solution in order to remove the by-products (ferrocene, diferrocenyl) and excess carbon disulfide. These modifications repeatedly gave over 50% yields of ferrocenedithiocarboxylic acid ammonium salts, confirmed by elemental analysis and spectra data (see Tables 1, 3 and 4).

The ammonium salts obtained were fairly stable and remained unchanged on being left in the atmosphere for five days. However, when the salts were heated to above their melting point, IIIa decomposed to give reddish brown ferrocenethiocarboxypiperidide (m.p. 83—84°) in 56% yield with the evolution of hydrogen sulfide, while IIIc decomposed to ferrocenedithiocarboxylic acid and trimethylamine. The salts were relatively soluble in chloroform, acetone, and ethanol, and readily reacted with a variety of usual electrophilic reagents (alkyl bromides, and chlorides having an electron-withdrawing group in the α-position, etc.) to give the corresponding esters in excellent yields. In addition, they readily underwent salt exchange reaction in water with various heavy metal halides or acetates, except mercuric acetate and chloride, to give the corresponding salts in quantitative yields (see Tables 2—4). Moreover, usual acidolysis of the salts (IIIa) with concentrated hydrochloric acid gave ferrocenedithiocarboxylic acid (II) (98% yield) as blackish granular crystals having a definite melting point of 75—76°**. The solid dithio acid is relatively stable and did not change over 10 days on storage at 0—5°. However, it decomposed in solution ($\mathrm{CDCl_3}$) and the absorption due to the SH proton at δ 5.45 ppm disappeared completely after 3 days. Interestingly, although the $\mathrm{p}K_a$ value (ca. 6.2) of ferrocenedithiocarboxylic acid is the same as that (6.20) [7] of the oxygen analogue ($\mathrm{FcCO_2H}$), the dithio acid readily reacted with phenyl isocyanate to give crystalline phenylcarbamoyl ferrocenedithiocarboxylate (VI) in good yield***.

Spectral data

IR spectra. Ferrocenedithiocarboxylic acid and its salts (amine and metal) obtained have two characteristic, intense absorption bands near 1270 and 1000 cm^{-1}. The latter band may be assigned to the dithiocarboxylate group ($\mathrm{CS_2^-}$), since various salts of aromatic and aliphatic dithio acids without exception show

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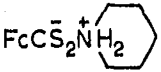
* Shechter and Helling investigated in detail the preparation of ferrocenyl Grignard reagents in tetrahydrofuran. In our laboratory, however, the preparation of ferrocenylmagnesium bromide according to their method repeatedly gave yields of below 20%.

** To our knowledge, this is the first example of a dithio acid having a melting point over 30°.

*** Reaction of ferrocenecarboxylic acid with phenyl isocyanate did not afford the corresponding carbamoyl ester [$\mathrm{FcCO_2C(O)NHPh}$].

TABLE 1

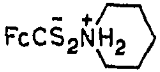
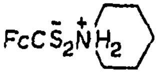
YIELDS AND NMR SPECTRA OF FERROCENEDITHIOCARBOXYLIC ACID AND ITS AMINE SALTS

No.	Compound	M.p. (°C)	Yield (%)	Color [a]	NMR ($CDCl_3$), δ (ppm)		
					SH or NH	Cp-ring	Amine
II	$FcCS_2H$	75– 76	57	BB	5.45 (SH, s, 1H)	5.02 (2,5-CH, t, 2H) 4.68 (3,4-CH, t, 2H) 4.24 (1-CH, s, 1H)	
IIIa		125–126	59	RP	8.47 (NH, s, 2H)	5.26 (2,5-CH, t, 2H) 4.48 (3,4-CH, t, 2H) 4.12 (1-CH, s, 1H)	3.24 (ring 2,6-CH, m, 4H) 2.00–1.40 (ring 3,4,5-CH, m, 6H)
IIIb	$FcC\overset{-}{S}_2\overset{+}{N}Et_2H_2$	113–115	53	RP	6.86 (NH, s, 2H)	5.22 (2,5-CH, t, 2H) 4.44 (3,4-CH, t, 2H) 4.12 (1-CH, s, 1H)	3.06 (CH_2, m, 4H) 1.35 (CH_3, t, 6H)
IIIc	$FcC\overset{-}{S}_2\overset{+}{N}Me_3H$		56	DP	8.00 (NH, s, 1H)	5.24 (2,5-CH, t, 2H) 4.44 (3,4-CH, t, 2H) 4.13 (1-CH, s, 1H)	2.81 (CH_3, s, 9H)

[a] BB: blue black, RP: reddish purple, DP: dark purple.

TABLE 2

REACTIONS OF FERROCENEDITHIOCARBOXYLIC ACID OR ITS AMINE SALTS WITH ELECTROPHILES (at room temperature)

Dithio acid (II) or amine salt (III)	Reactant (R)	Mol ratio R/2 or 3	Solvent	Time (h)	Products	M.p. (°C)	Yield (%)	Color [a]
	p-BrPhCOCH$_2$Br	1/1	MeOH	5	FcCS$_2$CH$_2$COPhBr-p (IVa)	149–150	87	RP
	ClCH$_2$CO$_2$H	5/1	CH$_2$Cl$_2$	1	FcCS$_2$CH$_2$CO$_2$H (IVb)	100–101	16	DP
	PhCH$_2$Cl	1/1	CH$_2$Cl$_2$	5	FcCS$_2$CH$_2$Ph (IVc)	67– 68	10	DP
$Fc\overset{-}{C}S_2\overset{+}{N}Et_2H_2$	Ph$_3$SnCl	1/1	CH$_2$Cl$_2$	3½	FcCS$_2$SnPh$_3$ (IVd)	146–147	61	DP
	Ph$_2$SnCl$_2$	1/2	CH$_2$Cl$_2$	10	(FcCS$_2$)$_2$SnPh$_2$ (IVe)	155–157	64	DP
	PhSO$_2$Cl	[b]	Et$_2$O	1	(FcCS$_2$)$_2$ (IVf)	155–157	84	DP
	n-BuCl	5/1	THF	48	no reaction			
	MnCl$_2$	5/1	H$_2$O	96	(FcCS$_2$)$_2$Mn (Va)	160–168	93	DP
	FeCl$_2$				(FcCS$_2$)$_2$Fe (Vb)	125–129	93	DP
	CoCl$_2$				(FcCS$_2$)$_2$Co (Vc)	118–122	86	RP
	NiCl$_2$				(FcCS$_2$)$_2$Ni (Vd)	>300	99	DP
	CuCl$_2$				(FcCS$_2$)$_2$Cu (Ve)	>300	98	DP
	ZnCl$_2$				(FcCS$_2$)$_2$Zn (Vf)	>300	97	BB
	Zr(O$_2$CCH$_3$)$_2$				(FcCS$_2$)$_2$Zr (Vg)	103–110	95	RP
$Fc\overset{-}{C}S_2\overset{+}{N}H_2Et_2$	PdCl$_2$	5/1	H$_2$O	96	(FcCS$_2$)$_2$Pd (Vh)	>300	99	DP
	Cd(O$_2$CCH$_3$)$_2$				(FcCS$_2$)$_2$Cd (Vi)	~210 (dec.)	96	DP
	BaCl$_2$				(FcCS$_2$)$_2$Ba (Vj)	>300	88	DP
	Ce(O$_2$CCH$_3$)$_2$				(FcCS$_2$)$_3$Ce (Vk)	>300	98	DP
	Pb(O$_2$CCH$_3$)$_2$				(FcCS$_2$)$_2$Pb (Vl)	~200 (dec.)	97	RP
FcCS$_2$H	PhNCO	1/1	Et$_2$O	2	FcCS$_2$CONHPh (VI)	101–103	84	BB

[a] RP: reddish black, DP: dark purple, BB: blue black. [b] Four drops.

TABLE 3

ELEMENTAL ANALYSES

Compound	Empirical formula	Analysis found (calcd.) (%)				
		C	H	N	S	Br
II	$C_{16}H_{21}S_2Fe$	50.50 (50.40)	3.92 (3.84)		24.56 (24.46)	
IIIa	$C_{16}H_{21}NS_2Fe$	55.30 (55.33)	6.03 (6.10)	4.09 (4.03)	18.33 (18.46)	
IIIb	$C_{16}H_{21}NS_2Fe$	53.82 (53.73)	6.44 (6.31)	4.11 (4.18)	19.36 (19.12)	
IIIc	$C_{14}H_{19}NS_2Fe$	52.51 (52.34)	5.90 (5.96)	4.03 (4.18)	20.03 (19.96)	
IVa	$C_{19}H_{15}OS_2BrFe$	50.01 (49.71)	3.31 (3.29)		14.02 (13.96)	17.52 (17.40)
IVb	$C_{13}H_{12}O_2S_2Fe$	48.99 (48.77)	3.85 (3.77)		20.43 (20.03)	
IVc	$C_{18}H_{16}S_2Fe$	61.32 (61.57)	4.44 (4.55)		18.26 (18.11)	
IVd	$C_{29}H_{24}S_2FeSn$	56.93 (56.99)	4.01 (3.96)		10.52 (10.49)	
IVe	$C_{34}H_{28}S_4Fe_2Sn$	51.47 (51.35)	3.61 (3.55)		16.51 (16.13)	
IVf	$C_{22}H_{18}S_4Fe_2$	50.63 (50.59)	3.51 (3.47)		24.59 (24.55)	
Va	$C_{22}H_{18}S_4Fe_2Mn$	45.83 (45.77)	3.09 (3.14)		22.46 (22.22)	
Vb	$C_{22}H_{18}S_4Fe_3$	50.73 (50.59)	3.50 (3.47)		24.83 (24.55)	
Vc	$C_{22}H_{18}S_4FeCo$	45.63 (45.46)	3.08 (3.12)		22.21 (22.06)	
Vd	$C_{22}H_{18}S_4Fe_2Ni$	45.53 (45.49)	3.06 (3.12)		22.11 (22.07)	
Ve	$C_{22}H_{18}S_4Fe_2Cu$	45.32 (45.10)	3.06 (3.10)		21.77 (21.89)	
Vf	$C_{22}H_{18}S_4Fe_2Zn$	45.12 (44.95)	3.13 (3.09)		21.36 (21.82)	
Vg	$C_{22}H_{18}S_4Fe_2Zr$	43.21 (43.07)	3.06 (2.96)		20.68 (20.90)	
Vh	$C_{22}H_{18}S_4Fe_2Pd$	42.34 (42.02)	2.86 (2.89)		20.51 (20.40)	
Vi	$C_{22}H_{18}S_4Fe_2Cd$	41.77 (41.63)	2.83 (2.86)		20.64 (20.20)	
Vj	$C_{22}H_{18}S_4Fe_2Ba$	40.22 (40.06)	2.76 (2.75)		19.73 (19.44)	
Vk	$C_{22}H_{18}S_4Fe_2Pb$	36.19 (36.22)	2.44 (2.49)		17.36 (17.58)	
Vl	$C_{33}H_{27}S_6Fe_3Ce$	43.06 (42.91)	2.87 (2.95)		20.52 (20.83)	
VI	$C_{18}H_{15}NOS_2Fe$	56.78 (56.69)	4.03 (3.97)	3.75 (3.67)	16.91 (16.82)	

absorption in the 1120—950 cm^{-1} region [4]. Bak et al. [8] have shown by a simplified force-constant calculation that the C=S frequency should be in the vicinity of 1200 and the C—S frequency at about 700 cm^{-1}, and in a series of 21 carboxymethyl dithioesters, the values of ν(C=S) were found to lie between 1190 1240 cm^{-1}. Our esters (IVa—IVf) all showed a relatively intense band in the 1300—1250 cm^{-1} reigon, which can be attributed to ν(C=S). The thiocarbonyl stretching bands of thioacyloxytrimethylsilanes [RC(S)OSiMe$_3$, R = alkyl] were observed in the same region [9].

UV and visible spectra. The absorption maxima (λ_{max}) are listed in Table 4. Ferrocenedithiocarboxylic acid and its derivatives have three or four character-

TABLE 4

SPECTRAL DATA OF FERROCENEDITHIOCARBOXYLIC ACIDS AND THE DERIVATIVES

Compound	IR (KBr) (cm^{-1})				UV (CHCl$_3$)			
	ν(SH) or ν(NH)	ν(C=O)	ν(C=S)	ν(C–S)	λ_{max} (nm) (ϵ_{max})			
II	2400 (SH)		1278	656	250 (6340)	300 (8120)	337 (8070)	549 (1930)
IIIa	3000–2500 (NH)		986	669	260 (7200)	310 (10300)	335 [a] (9500)	533 (1910)
IIIb	3000–2500 (NH)		990	668	260 (7200)	308 (10300)	335 [a] (9000)	533 (1900)
IIIc	3000–2500 (NH)		1010	652	260 (7400)	315 (9280)	330 [a] (9000)	550 (1920)
IVa		1687	1274	658	263 (21000)	315.5 (15700)	390 [a] (1880)	546 (2530)
IVb		1700	1270	650	256 (17000)	311 (21600)	330 [a] (19200)	550 (2780)
IVc			1270	654	250 (15600)	316 (11000)		550 (2850)
IVd			1267	659	257 (13100)	321 (18500)		550 (2940)
IVe			1270	663	257 (16600)	330 (27200)		560 (5750)
IVf			1278	650	264 (13700)	320 (23600)	395 [a] (3480)	559 (5440)
Va			1010	652	260 [b]	323 [b]		567 [b]
Vb			1009	655	260 [b]	320 [b]		585 [b]
Vc			984	658	260 [b]	323 [b]		549 [b]
Vd			956	658	270 [b]	343 [b]		586 [b] 620 [a,b]
Ve			998	652	260 [b]	338 [b] 378 [b]		587 [b]
Vf			992	665	264 [b]	332 [b]		587 [b]
Vg			1010	654	260 (13500)	320 (20200)		550 (4460)
Vh			1008	654	262 [b]	324 [b]		562 [b]
Vi			989	664	275 [b]	339 [b] 375 [b]		559 [b]
Vj			1000	656	275 [b]	322 [b]		590 [b]
Vk			981	666	266 [b]	329 [b] 375 [b]		550 [b]
Vl			1010	650	260 [b]	320 [b]		560 [b]
VI		1691	1274	655	244 (15600)	336 (13300)		578 (3000)
FeCO$_2$H [c,d]							342 (361)	445 (223)
FeCOCH$_3$ [c,e]					225 (14000)	268 (5400)	335 (1120)	445 (420)
PhCS$_2$H [f]						297 (14000)		533 (93)
PhCS$_2$NHMe$_3$ [c,g]						286 (9000)	362 (7600)	491 (152)
C$_{10}$H$_7$CS$_2$CH$_3$ [f,h]					221 (6300)	274 (5400)	306 (10500)	494 (130)

[a] Shoulder. [b] The molecular extinction coefficients could not be exactly measured due to their very slight solubility in CHCl$_3$. [c] Ethanol (solvent). [d] See refs. [11–12]. [e] See ref. [12]. [f] Cyclohexane (solvent). [g] See ref. [5]. [h] See ref. [10].

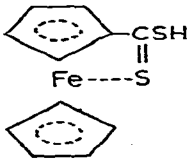


Fig. 1.

istic maxima at 240—260 (ϵ 6000—20000), 305—340 (ϵ 6000—20000), 335—380 (ϵ 8000—20000) and 530—580 (ϵ 1900—3000), respectively. The former two or three bands can be ascribed to the $\pi \rightarrow \pi^*$ and the third to the $n \rightarrow \pi^*$ transition of the thiocarbonyl group. Interestingly, the molecular extinction coefficients for the $n \rightarrow \pi^*$ transition of thiocarbonyl group are without exception 10—15 times greater than expected either for an aromatic dithio acid and its derivatives [4, 10] or for ferrocenecarboxylic acid [11] and its derivatives [11, 12] as is seen in Table 4. These enhanced extinction coefficients can be interpreted either in terms of through space interaction between the iron and thiocarbonyl sulfur atoms (Fig. 1), or by a conjugative effect of the ferrocenyl moiety through the bond to the thiocarbonyl group. In a later paper we will present X-ray data, which we hope will shed some light on the unusually high molecular coefficient of the thiocarbonyl group in these ferrocenedithiocarboxylic acid derivatives.

Experimental

IR spectra were measured on a Jasco Grating IR spectrophotometer IR-G. UV spectra were recorded on a Hitachi 124 spectrophotometer. NMR spectra were recorded on a Hitachi R-22 (90 MHz) instrument, with tetramethylsilane as internal standard. Analyses were carried out by the Elemental Analysis Center of Kyoto University. The acid constant was measured in 20 volume % of methanol/water (1/1) in dioxane, essentially according to the method described by Roberts [13] using a Horiba F-7DE pH meter.

Materials

Ferrocene [14], bromoferrocene [15] and dichlorodiphenylstannane and chlorotriphenylstannane [16] were prepared according to procedures described in the literature. The other reagents used were commercial materials. The solvents were rigorously dried. Some typical procedures are given below. The new compounds were identified by their elemental analyses and spectral data. The data are summarized in Tables 1—4.

Preparation of piperidinium ferrocenedithiocarboxylate (IIIa)

An ethereal solution of ferrocenyl bromide (20 mmol) was added dropwise to a suspension of 20 mmol of magnesium metal and 10 mmol of 1,2-dibromoethane in anhydrous ether (20 ml) at 25°. Reaction commenced immediately and the mixture was stirred for 3 h. To the resulting ferrocenylmagnesium bromide solution carbon disulfide (20 mmol) in anhydrous THF (20 ml) was slowly added at 0°. After about 15 h at room temperature, this reaction mixture was poured into 20 ml of 15% HCl at 5°; then 300 ml of ether was added and the mixture was shaken. The ether layer was separated and extracted with 100 ml of 15% NaOH solution. The dark purple aqueous layer was acidified with 200 ml of 15% HCl, then extracted three times with 300 ml of ether at 5°. The combined ether extract was washed with water, then dried over anhydrous magnesium sulfate and treated with 16 mmol of piperidine. Filtration of the resulting precipitate gave a 54% yield of dark reddish needles (IIIa) having a definite melting point (125—126°).

Preparation of ferrocenedithiocarboxylic acid (II)

Concentrated HCl (30 ml) was added to a suspension of piperidinium ferrocenedithiocarboxylate (IIIa) [0.20 g, 0.63 mmol] in ether (100 ml) and the mixture was shaken vigorously. The ether layer was separated, washed with water, then dried over anhydrous $MgSO_4$. Removal of the solvent in vacuo gave 0.16 g (98%) of pure ferrocenedithiocarboxylic acid as blackish granular crystals, m.p. 75—76°.

Thermolysis of the ammonium salts (III)

Piperidinium ferrocenedithiocarboxylate (IIIa). The salt IIIa [0.20 g, 0.6 mmol] was heated at 150° for 5 h in a glass ampoule filled with nitrogen. When the ampoule was opened, the presence of hydrogen sulfide was confirmed by the colorization of lead acetate paper. The decomposition products were extracted with ether using a Soxhlet extractor. Concentration of the extract and filtration of the resulting precipitate gave 0.10 g (56%) of pure ferrocenethiocarboxypiperidide as dark brown crystals, which was identified by elemental analysis and spectral data, m.p. 83—84°. (Found: C, 61.48; H, 6.29; N, 4.53; S, 10.41. $C_{16}H_{19}NSFe$ calcd.: C, 61.36; H, 6.11; N, 4.47; S, 10.23%. IR spectrum (KBr) 3160 ν(CH) s, 2940 and 2850 $\nu(CH_2)$ s, 1563 s, 1440 s, 1240 ν(C=S) s, 1105 m, 1000 s, 810 $\nu(\pi\text{-}C_5H_5)$ s, 480 s cm^{-1}. The ether insoluble residue was a blackish solid, having a melting point over 300°. The IR spectrum was analogous to that of bis(thiocarboxyferrocenyl) disulfide.

Reaction of piperidinium ferrocenedithiocarboxylate (IIIa) with p-bromophenacyl bromide

The mixture of the piperidinium salt (IIIa) [0.2 g, 0.58 mmol] and *p*-bromophenacyl bromide (0.17 g, 0.61 mmol) in methanol (10 ml) was stirred for 5 h at room temperature. Filtration of the resulting precipitate, then washing with water and methanol, gave 0.23 g (87%) of pure *p*-bromophenacyl ferrocenedithiocarboxylate (IVa).

Reaction of the piperidinium salt (IIIa) with n-butyl chloride

An equimolar amount of the salt (IIIa) [0.20 g, 0.6 mmol] and n-butyl chloride (0.056 g, 0.6 mmol) was stirred for 48 h at 50°. After removal of the solvent in vacuo, washing of the residue (crystals) with small portions of ether gave 0.19 g (95%) of the starting salt (IIIa).

Reaction of diethylammonium ferrocenedithiocarboxylate (IIIb) with chlorotriphenylstannane

The mixture of the diethylammonium salt IIIb [0.2 g, 0.6 mmol] and chlorotriphenylstannane (0.23 g, 0.6 mmol) was stirred in dichloromethane (10 ml) for 3.5 h at room temperature. After removal of the solvent in vacuo, the residue was extracted with petroleum ether (b.p. $< 40°$) using a Soxhlet extractor. Vacuum evaporation of the extract, then recrystallization of the solid from ether/petroleum ether, gave 0.22 g (61%) of triphenylstannyl ferrocenedithiocarboxylate (IVd).

Reaction of piperidinium ferrocenedithiocarboxylate (IIIa) with benzenesulfonyl chloride

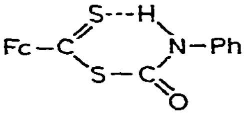
To a suspension of the piperidinium salt IIIa [0.35 g, 1 mmol] in ethanol (5 ml) was added four drops of benzenesulfonyl chloride, and the mixture was stirred for 1 h at room temperature. Filtration of the insoluble crystals, then washing with water and ethanol, gave 0.22 g (84%) of pure bis(ferrocenethiocarboxyl) disulfide (IVf). The melting point and IR spectra exactly coincided with those of an authentic sample prepared by treatment of the piperidinium salt (IIIa) with iodine.

Reaction of diethylammonium ferrocenedithiocarboxylate (IIIb) with zinc chloride

The mixture of the diethylammonium salt IIIb [0.20 g, 0.6 mmol] and zinc chloride (0.20 g, 3 mmol) in water (10 ml) was vigorously stirred for 5 days at room temperature. Filtration of the crystalline solid, then washing with water and methanol, gave 0.15 g (84%) of zinc ferrocenedithiocarboxylate (Vf).

Reaction of ferrocenedithiocarboxylic acid (II) with phenyl isocyanate

Phenyl isocyanate (0.06 g, 0.5 mmol) was added dropwise to ferrocenedithiocarboxylic acid (0.13 g, 0.5 mmol) in anhydrous ether (40 ml) and the mixture was stirred for 2 h at room temperature. After concentrating the reaction mixture in vacuo, filtration of the resulting crystalline precipitate, washing with small portions of ether/petroleum ether (1/1) gave 0.16 g (84%) of phenylcarbamoyl ferrocenedithiocarboxylate (VI). The IR spectrum of VI showed no N—H stretching absorption band in the expected range (3100—3400 cm^{-1}); instead, we observed a new band near 2900 cm^{-1}, considered to be due to the N—H stretch. Such an unusual shift in ν(N—H) suggests a structure containing an intramolecular hydrogen bond between sulfur and hydrogen. The NMR spectrum (NH, δ 11.7 ppm) further supported structure VI.



(VI)

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