Bis(ferrocenecarbothioyl) Sulfide. Synthesis and Characterization

Shinzi KATO,* Tetsuaki FUKUSHIMA, Hideharu ISHIHARA, and Toshiaki MURAI
Department of Chemistry, Faculty of Engineering, Gifu University, 1-1 Yanagido, Gifu 501-11
(Received August 21, 1989)

Synopsis. Bis(ferrocenecarbothioyl) sulfide **1** was synthesized and characterized. The sulfide **1** was found to serve as an efficient ferrocenecarbothioylating reagent for amines, alcoholates, thiolates, and selenolates.

Since the discovery of ferrocene, a number of ferrocene derivatives have been prepared.[1] However, the preparation of ferrocenecarbothioyl chloride and bis(ferrocenecarbothioyl) sulfide which are expected to serve as ferrocenecarbothioylating reagent has been still remained, because of the difficulty in synthesis. In the earlier studies concerning thio- and dithiocarboxylic acid derivatives, we have developed the preparation of ammonium ferrocenecarbothioates[2] and -dithioates[3] and bis(acyl)-[4] and bis(thioacyl) sulfides.[5] We now report the first isolation and characterization of bis(ferrocenecarbothioyl) sulfide **1** and its some thioacylating reactions.[6]

Bis(ferrocenecarbothioyl) sulfide **1** was found to be isolated from the reaction of piperidinium ferrocenecarbodithioate with 2-chloro-1-methylpyridinium iodide (Eq. 1).

A typical procedure is as follows. A methanol solution of piperidinium ferrocenecarbodithioate (1 mmol) was added to a suspension of 2-chloro-1-methylpyridinium iodide (0.5 mmol) in methanol at −20 °C and stirred for 1 h at that temperature. Filtration of the precipitates and washing with cold methanol afforded 76% of chemically pure bis(ferrocenecarbothioyl) sulfide as dark blue crystals.

Bis(Ferrocenecarbothioyl) sulfide is relatively stable thermally and towards oxygen and water. It can be stored in refrigerator (−20 °C) for over one year and did not change at 20 °C for 5 h. The sulfide **1** readily reacted with primary and secondary amines, sodium alcoholates, thiolates, and selenolates at room temperature to give the corresponding ferrocenecarbothioamides **2**, carbothioic *O*-esters **3**, carbodithioic esters **4**, and carboselenothioic *Se*-esters **5** in moderate to good yields, respectively (Eq. 2 and Table 1).

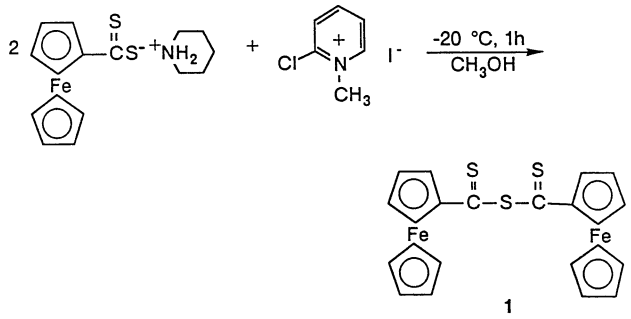
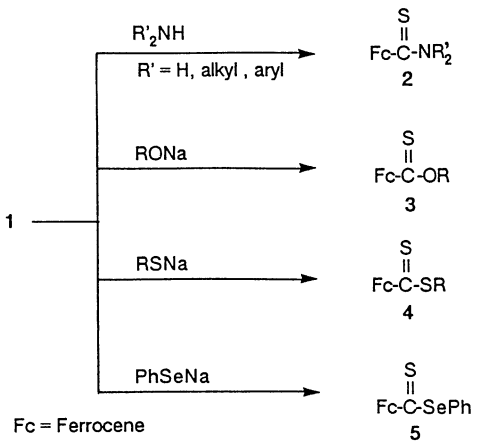


Table 1. Yields and Spectral Data of Ferrocenecarbothioamides **2**, *O*-Alkyl and *O*-Aryl Ferrocenecarbothioates **3**, Phenyl Ferrocenecarbodithioate **4**, and *Se*-Phenyl Ferrocenecarboselenothioate **5**

No.	FcCS-E E	Yield[a] %	Mp °C	IR (KBr) νC=S/cm^{-1}	^{1}H NMR[b] δ	^{13}C NMR[b] δ	UV/Vis/nm[c] λ_{max}(log ε)	Exact MS[d] m/z
2a		83	79—81		1.6—1.9 (m, 6H, CH_2) 3.8—4.1 (m, 4H, CH_2) 4.1—4.6 (m, 9H, Cp)	24.4, 52.9, 69.0 71.2, 71.7, 88.1 198.8 (C=S)	280 (4.22) 463 (2.78)	Found 313.05816 Calcd 313.05865 for $C_{16}H_{19}NSFe$
2b	C_6H_5NH[e]	45	128—129		4.2—5.0 (m, 9H, Cp) 7.2—7.7 (m, 5H, Ar) 8.79 (s, 1H, NH)	69.1, 70.9, 71.2 71.6, 84.9, 124.1 126.5, 129.0 138.8, 199.3 (C=S)	287 (4.15) 334sh 475 (3.00)	Found 321.04223 Calcd 321.02737 for $C_{17}H_{15}NSFe$
3a	CH_3O[f]	38	69—71	1239	4.16 (s, 3H, CH_3) 4.5—5.0 (m, 9H, Cp)	58.2 (CH_3O) 70.7, 70.9, 72.3 82.3, 217.3 (C=S)	255 (3.09) 304 (4.04) 364 (3.28) 483 (3.76)	Found 259.99333 Calcd 259.99756 for $C_{12}H_{12}OSFe$
3b	C_6H_5O[f]	68	121—124	1216	4.2—5.2 (m, 9H, Cp) 7.0—7.5 (m,5H, Ar)	71.2, 73.0, 81.9 122.4, 126.2, 129.5, 154.4 216.1 (C=S)	255 (4.51) 310 (4.58) 370 (3.81) 498 (3.76)	Found 322.01429 Calcd 322.01140 for $C_{17}H_{14}OSFe$
4	C_6H_5S[f]	71	139—141	1273	4.2—5.3 (m, 9H, Cp) 7.48 (s, 5H, Ar)	70.2, 72.1, 73.3 88.0, 127.5, 129.4, 130.0, 135.9, 227.9 (C=S)	251sh 316 (4.15) 539 (3.32)	Found 337.98859 Calcd 337.98855 for $C_{17}H_{14}S_2Fe$
5	C_6H_5Se[f]	46	104—105	1275	4.2—5.2 (m, 9H, Cp) 7.4—7.6 (m, 5H, Ar)	69.4, 70.3, 72.3 73.6, 90.3, 129.3 129.5, 137.2, 229.2 (C=S)	269 (4.27) 344 (4.11) 543 (3.36)	Found 385.93036 Calcd 385.93299 for $C_{17}H_{14}SSeFe$

a) Isolated Yields. b) $CDCl_3$/TMS. c) CH_2Cl_2. d) 70 eV. e) Bis(ferrocenecarbothioyl) disulfide was obtained in 43% yields as a by-product. f) Sodium ferrocenecarbodithioate was obtained as a by-product.



Experimental

The melting points were obtained by using a Yanagimoto micro melting point apparatus and are uncorrected. The IR spectra were measured on a JASCO grating IR spectrophotometer (IR-G and A-302). The UV/Vis spectra were taken from a Hitachi 124 and 330 spectrometer. The ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-GX-270 (270 MHz) with tetramethylsilane as an internal standard. The mass spectra were taken from a Hitachi RMU-6M mass spectrometer. High resolution mass spectroscopy was taken by a Shimadzu high-resolution mass spectrometer (GCMS 9020-DF/PAC-1100). Elemental analyses were performed by the Elemental Analyses Center of Kyoto University.

Materials. Piperidinium ferrocenecarbodithioate[2] and diphenyl diselenide[7] were prepared according to literatures. Sodium alcoholates and thiolates were prepared from the reaction of the corresponding alcohols or thiols with sodium metal. Solvents were dried with sodium metal.

Bis(ferrocenecarbothioyl) Sulfide (1). To a suspension of 2-chloro-1-methylpyridinium iodide (256 mg, 1.0 mmol) in methanol (10 ml), a solution of piperidinium ferrocenecarbodithioate (694 mg, 2 mmol) in methanol (40 ml) was added dropwise at −20 °C and the mixture was stirred for 1 h at that temperature. Filtration of the resulting precipitates and washing with cold methanol (5 ml) afford 392 mg (76%) of **1** as dark blue microfine crystals. Mp 101—102 °C. MS (70 eV) *m/z* (relative intensity): 490 (M^+, 8), 326 (22), 262 (71), 229 (100), 154 (50); UV/Vis (CH_2Cl_2) λ_{max} (log ε): 263 (4.10), 324 (4.19), 590 (3.62) nm; ^1H NMR ($CDCl_3$): δ=4.31 (s, 10H), 4.81 (t, 4H), 5.15 (t, 4H); ^{13}C NMR ($CDCl_3$): δ=71.1, 72.3, 74.8, 91.1, 221.0 (C=S); IR (KBr): 1436, 1422, 1405, 1395, 1372, 1244, 1315, 1292, 1206, 1195, 1071, 1061, 1050, 1004, 995, 920, 909, 880, 860, 814, 764, 642, 570, 525, 490 cm^{-1}. Found: C, 53.59; H, 3.45%. Calcd for $C_{22}H_{18}S_3Fe_2$: C, 53.89; H, 3.70%.

Typical thioacylating procedures are described below. The spectral data were collected in Table 1. All reactions were carried out under nitrogen atmosphere.

***N*-(Ferrocenylcarbothioyl)piperidine (2a):** An ether solution (10 ml) of piperidine (170 mg, 2.0 mmol) was added at 15 °C to a solution of bis(ferrocenecarbothioyl) sulfide **1** (180 mg, 0.36 mmol) in ether (20 ml), and the mixture was stirred for 5 h at that temperature. Filtration of the resulting precipitates gave 84 mg (67%) of piperidinium ferrocenecarbodithioate. Ether (40 ml) and water (40 ml) were added to the filtrate. The organic layer was washed with water (40 ml) and dried with anhydrous sodium sulfate. The ether was evaporated by rotary evaporator. The residue was chromatographed on silica-gel column [CH_2Cl_2/hexane (1 : 1), R_f=0.25] to yield 96 mg (83%) of **2a** as brown microfine crystals.

***O*-Methyl Ferrocenecarbothioate (3a):** A mixture of sodium methanolate (136 mg, 2.5 mmol) and bis(ferrocenecarbothioyl) sulfide **1** (246 mg, 0.5 mmol) in methanol (50 ml) was stirred at 20 °C for 20 h. The mixture was concentrated to ca. 3 ml under reduced pressure. Ether (60 ml) was added, washed with water (3×50 mL). The organic layer was dried with anhydrous sodium sulfate. The solvent was removed by rotary evaporator. The residue was chromatographed on silica-gel column [CH_2Cl_2/hexane (1:4), R_f= 0.37] to give 50 mg (38%) of **3a** as orange crystals. Mp 66—68 °C.

***O*-Phenyl Ferrocenecarbothioate (3b):** A mixture of sodium phenolate (290 mg, 2.5 mmol) and bis(ferrocenecarbothioyl) sulfide **1** (123 mg, 0.25 mmol) in tetrahydrofuran (THF, 20 ml) was stirred at 0 °C for 5 h. The solvent was removed by rotary evaporator. Ether (40 ml) was added and washed with water (2×20 ml). The organic layer was dried with sodium sulfate. The solvent was evaporated in vacuo and the residue was chromatographed on silica-gel column [CH_2Cl_2/hexane (1 : 4), R_f=0.30] to give 55 mg (68% of **3b** as red crystals. Mp 121—124 °C.

Phenyl Ferrocenecarbodithioate 4: A mixture of sodium benzenethiolate (212 mg, 1.6 mmol) and bis(ferrocenecarbothioyl) sulfide **1** (160 mg, 0.32 mmol) in THF (40 ml) was stirred at 17 °C for 5 h. The solvent was removed by rotary evaporator. Ether (40 ml) was added and washed with water (2×20 ml) and then dried with anhydrous sodium sulfate. The ether was distilled in vacuo and the residue was chromatographed on silica-gel column [CH_2Cl_2/hexane (1 : 4), R_f=0.36] to give 80 mg (71%) of **4** as dark red crystals. Mp 139—141 °C.

***Se*-Phenyl Ferrocenecarboselenothioate 5:** A solution of bis(ferrocenecarbothioyl) sulfide **1** (246 mg, 0.5 mmol) in ether (40 ml) was added dropwise to sodium benzeneselenolate (0.5 mmol) at −20 °C, freshly prepared by treatment of diphenyl diselenide (78 mg, 0.25 mmol) with sodium borohydride (0.5 mmol) in a mixed solvent (12 mL) of methanol and ether (1 : 5). The mixture was stirred at 0 °C for 1 h. Ether (40 ml) was added and washed with water (3×40 ml). The organic layer was dried with anhydrous sodium sulfate. The solvent was distilled in vacuo and the residue was chromatographed on silica-gel column [CH_2Cl_2/hexane (1 : 1), R_f=0.49] to give 88 mg (46%) of **5** as purple crystals. Mp 104—105 °C.

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