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1,1′-Ferrocenediyl Bis(dialkyldithiocarbamate) and Ferrocenyl Dialkyldithiocarbamate Derivatives

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A series of (dialkyldithiocarbamato)ferrocene complexes, 1,1′-ferrocenediyl bis(dialkyldithiocarbamate) and ferrocenyl dialkyldithiocarbamate, $Fe(C_5H_4SCSNR_2)_2$ and $Fe(C_5H_5)(C_5H_4SCSNR_2)$ (R = Me, Et, and *i*-Pr), have been prepared by reaction of lithioferrocene with tetraalkylthiuram disulfide. The complexes were characterized by ^1H NMR, ^{13}C NMR, IR, and ultraviolet and visible spectroscopic techniques. Rotation around the C–N carbamate bond was studied by ^1H NMR, and for the methyl and ethyl derivatives **1**, **2**, **4**, and **5**, approximate barriers to rotation are ca. 16 kcal/mol. In the isopropyl complexes **3** and **6** however, rotation around the isopropyl–nitrogen bond predominates.

Introduction

The dithiocarbamate ligand has played a major role in the chemistry of transition-metal sulfide complexes.[1,2] In this paper we report the preparation of a series of mono- and bis(dialkyldithiocarbamato)ferrocene derivatives where the dithiocarbamate is attached to ferrocene through a thio ester linkage.

Tetraalkylthiuram disulfides undergo nucleophilic attack at the disulfide linkage by cyanide ions, amines, and Grignard reagents.[3] Recently Cava[4] reported that aryllithium derivatives react with tetraisopropylthiuram disulfide to give dithiocarbamate esters that were precursors to aromatic thiols.

We have prepared the (dialkyldithiocarbamato)ferrocenes to serve as ligands for forming complexes with other metals and to test such complexes as catalysts in organic syntheses.

Experimental Section

Air-sensitive reagents were manipulated in a prepurified argon or nitrogen atmosphere by using Schlenck techniques. Hexane was freshly distilled from calcium hydride.

Infrared spectra were obtained by use of a Perkin-Elmer 457 grating spectrophotometer or a Perkin-Elmer 239B spectrophotometer by using Nujol or Fluorolube mulls between CsBr plates. Ultraviolet and visible spectra were recorded by use of a Cary 17 spectrophotometer and acetonitrile solutions. Mass spectra were obtained by means of a Finnigan 4000 instrument with an Incos data system at 70 eV. All melting points were determined by using a Thomas-Hoover melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Proton NMR spectra were obtained by use of a Bruker WM-250 spectrometer at 250 MHz. Unless otherwise noted, all NMR spectra were recorded in chloroform-d_1 solutions with chemical shifts reported in parts per million downfield from a tetramethylsilane internal standard.

Carbon-13 NMR (broad-band proton decoupled and gated decoupled) were obtained by use of a Bruker WM-250 spectrometer at 62.9 MHz. Carbon-13 NMR spectra were recorded in methylene chloride with deuterium oxide as an external lock and chemical shifts, referenced to methylene chloride, and are uncorrected for volume susceptibilities.

1,1′-Bis(dimethyldithiocarbamato)ferrocene (1). Ferrocene (10 g, 53.7 mmol) was added to a solution of *N,N,N′,N′*-tetramethylethylenediamine (16.85 mL, 112 mmol) and 1.6 M *n*-butyllithium in hexane (68 mL, 112 mmol) in oxygen-free hexane (200 mL) in a 1-L round-bottom flask, equipped with a side arm and serum cap, under nitrogen. The solution was stirred at least 3 h or until bright orange, and then tetramethylthiuram disulfide (26.5 g, 110 mmol) in 500 mL of benzene was added slowly via cannula to the solution which was at −40 °C. The solution was allowed to reach room temperature and was stirred overnight to give a black/gray solution. Water (90 mL) was added, and the solution was filtered. The gray precipitate was washed with water and then chromatographed on alumina. The yellow band, eluted with CH_2Cl_2, was evaporated to dryness to yield 16 g of **1** (70% yield). The filtrate was separated from the aqueous layer, dried, and chromatographed. The first band, eluted with hexane, contained 0.95 g of ferrocene whereas the second band eluted with CH_2Cl_2 contained **1** and traces of the disulfide. The thiuram disulfide is removed by washing with benzene. Total yield was 18.2 g (80% yield). Compound **1** was recrystallized from CH_2Cl_2/hexane to give yellow crystals, mp 170–173 °C; mass spectrum, *m/e* (relative intensity) 424 (100, M^+), 328 (53), 240 (42), 88 (65). Anal. Calcd for $C_{16}H_{20}S_4N_2Fe$: C, 45.28; H, 4.75; N, 6.60; S, 30.22. Found: C, 45.29; H, 4.81; N, 6.57; S, 30.30.

1,1′-Bis(diethyldithiocarbamato)ferrocene (2). Tetraethylthiuram disulfide (32.68 g, 110 mmol) in 500 mL of toluene was added slowly via cannula to 1,1′-dilithioferrocene (54 mmol) at −78 °C. The solution was allowed to reach room temperature and was stirred overnight to give a blackish solution. Water (100 mL) was added, and the solution was filtered. The gray precipitate was washed with water and then chromatographed on alumina. The yellow band eluted with CH_2Cl_2 gave 13 g of **2**, 50% yield. The brown filtrate, which contains ferrocene, thiuram disulfide and **2**, was chromatographed to yield 4.5 g of **2**, total yield 68%. Recrystallization from CH_2Cl_2/hexane gave yellow crystals that decomposed at 160–163 °C and melted at 181 °C: mass spectrum, *m/e* (relative intensity) 480 (54, M^+), 384 (51)°, 268 (69), 116 (100), 85 (96), 60 (72). Anal. Calcd for $C_20H_{28}N_2S_4Fe$: C, 49.99; H, 5.87; N, 5.83; S, 26.69. Found: C, 49.90% H, 5.80; N, 5.75; S, 26.90.

1,1′-Bis(diisopropyldithiocarbamato)ferrocene (3). Tetraisopropylthiuram disulfide (25 g, 71 mmol) in 250 mL of toluene was added slowly via cannula to 1,1′-dilithioferrocene (35 mmol) at −78 °C. The solution was allowed to reach room temperature and was stirred overnight to give a black solution. Water (100 mL) was added, and the solution was filtered. The green precipitate was washed with water (to remove ferricenium salts) and then chromatographed to give 15 g of **3**, 79% yield. Complex **3** was recrystallized from CH_2Cl_2/hexane to give yellow crystals that decompose at 180 °C and melt at 225–226 °C: mass spectrum, *m/e* (relative intensity) 536 (8, M^+), 440 (8), 296 (14), 144 (31), 102 (100), 60 (56), 43 (92). Anal. Calcd for $C_{24}H_{36}N_2S_4Fe$: C, 53.77; H, 6.76. Found: C, 53.77; H, 6.90.

(Dimethyldithiocarbamato)ferrocene (4). Ferrocene (6.14 g, 33 mmol) was added to a solution of TMEDA (5.1 mL, 33 mmol) and *n*-butyllithium (20.1 mL, 33 mmol) in 150 mL of hexane, and the solution was stirred for 3 h. Tetramethylthiuram disulfide (7.92 g, 33 mmol) in 120 mL of benzene was added via cannula to the bright orange solution that had been cooled to −78 °C. The solution was allowed to reach room temperature and was stirred

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Table I. ^{1}H NMR Data for $Fe(C_5H_4SCSNR_2)_2$ and $FeCp(C_5H_4SCSNR_2)$ Complexes

		δ					
compd	*T*, °C	$C_{2,5}$	$C_{3,4}$	Cp	CH	CH_2	CH_3
$Fe(C_5H_4SCSNMe_2)_2$	22	4.50 (t)	4.38 (t)				3.48 (s)
							3.43 (s)
$Fe(C_5H_4SCSNEt_2)_2$	22	4.52 (t)	4.42 (t)			3.99 (q, *J* = 7 Hz)	1.39 (t, *J* = 7 Hz)
						3.85 (q, *J* = 7 Hz)	1.26 (t, *J* = 7 Hz)
$Fe(C_5H_4SCSN\text{-}i\text{-}Pr_2)_2$	71	4.46 (t)	4.38 (t)		4.78 (m, *J* = 6.5 Hz)		1.47 (d, *J* = 6.5 Hz)
$FeCp(C_5H_4SCSNMe_2)$	22	4.44 (t)	4.34 (t)	4.24 (s)			3.51 (s)
							3.45 (s)
$FeCp(C_5H_4SCSNEt_2)$	22	4.42 (t)	4.34 (t)	4.22 (s)		3.69 (q, *J* = 7 Hz)	1.37 (t, *J* = 7 Hz)
						3.82 (q, *J* = 7 Hz)	1.23 (t, *J* = 7 Hz)
$FeCp(C_5H_4SCSN\text{-}i\text{-}Pr_2)$	59	4.40 (t)	4.33 (t)	4.20 (s)	4.76 (m, *J* = 6.5 Hz)		1.48 (d, *J* = 6.6 Hz)

overnight, and then 50 mL of water was added to the brownish black solution. The solution was filtered, and the sticky black precipitate was chromatographed on alumina. The first band, eluted with hexane, yielded 2.9 g of ferrocene. The second yellow band, which was eluted with benzene, gave 300 mg of an unidentified product: ^{1}H NMR δ 4.28 (t), 4.19 (s), 4.15 (t); mass spectrum, *m/e* 402 (base peak). The third band, eluted with benzene, yielded 470 mg of 4 (9% yield based on the ferrocene reacted). Numerous additional bands were eluted with benzene and methylchloroform, but the products were not isolated. Compound 4 was recrystallized from CH_2Cl_2/hexane to give yellow crystals that decompose at 180–184 °C: mass spectrum, *m/e* (relative intensity) 305 (87, M^+), 240 (22, $M^+ - Cp$), 217 (20), 209 (61), 121 (21) 88 (100, $CSNMe_2$). Anal. Calcd for $C_{13}H_{15}FeNS_2$: C, 51.15; H, 4.95. Found: C, 51.36; H, 4.92.

(Diethyldithiocarbamato)ferrocene (5). Bromoferrocene, prepared according to Rosenblum's[5] procedure, was dried in vacuo before use. Butyllithium (7.47 mL, 11.8 mmol) was added slowly via syringe to a solution of bromoferrocene (2.64 g, 10.0 mmol) in 70 mL of dry diethyl ether that was cooled to −40 °C. After the solution was stirred at room temperature for 20 min, tetraethylthiuram disulfide (3.27 g, 11.0 mmol) in 40 mL of toluene was added slowly via cannula to the bright yellow solution, which had been cooled to −78 °C. The solution was stirred for 12–18 h at room temperature to give a brown solution. Water (20 mL) was added, and the organic layer was separated, dried, and chromatographed on alumina. The first yellow band, eluted with hexane, contained bromoferrocene and a small amount of ferrocene whereas the second yellow band, eluted with methylene chloride, yielded 2 g of 5, 60% yield. Complex 5 was recrystallized from CH_2Cl_2/hexane to give yellow crystals that melt at 127.5–128.5 °C. Mass spectrum, *m/e* (relative intensity) 333 (18, M^+), 237 (8), 217 (6), 116 (100, $CSNEt_2$), 88 (87), 60 (61). Anal. Calcd for $C_{15}H_{19}NS_2Fe$: C, 54.06; H, 5.75; N, 4.20. Found: C, 53.95; H, 5.76; N, 4.29.

(Diisopropyldithiocarbamato)ferrocene (6). Butllithium (4.9 mL, 7.8 mmol) was slowly added via syringe to a solution of bromoferrocene (1.73 g, 6.5 mmol) in 100 mL of dry diethyl ether. After the solution was stirred at room temperature for 20 min, tetraisopropylthiuram disulfide (2.41 g, 6.8 mmol) in 80 mL of hexane was added slowly via cannula to the bright orange solution that had been cooled to −78 °C. The solution was stirred at room temperature for 18 h to give a light brown reaction mixture. Water (30 mL) was added, and then the organic layer was separated, dried, and evaporated to dryness to give a brown oil that was chromatographed on alumina. The first yellow band, eluted with hexane, contained a small amount of bromoferrocene and 340 mg of ferrocene. The second yellow band, eluted with methylene chloride, was concentrated, and then the crystalline mass was washed briefly with benzene (to remove the disulfide). Yellow needles, recrystallized from methylene chloride/hexane, were obtained in 84% yield based on the bromoferrocene reacted: mp 189–190 °C dec; mass spectrum, *m/e* (relative intensity) 361 (100, M^+), 218 (99), 217 (41), 144 (30), 121 (6), 102 (32). Anal. Calcd for $C_{17}H_{23}NS_2Fe$: C, 56.51; H, 6.42. Found: C, 56.69; H, 6.61.

Results

Reaction of dilithioferrocene with a series of tetraalkylthiuram disulfides gave rise to bis(dialkyldithiocarbamato)ferrocene derivatives in high yield. A solution of the tetraalkylthiuram disulfide was added slowly to a hexane slurry of dilithioferrocene that had been cooled to −78 °C (see Scheme I).

In contrast to results obtained by Cava only the desired product and no thioamide derivative was observed. The thioamide species arises from competing nucleophilic attack at the thione carbon rather than at the sulfur–sulfur bond in the tetraalkylthiuram disulfide.

A series of monosubstituted (dialkyldithiocarbamato)ferrocene derivatives was also prepared by reaction of tetraalkylthiuram disulfide with lithioferrocene. When lithioferrocene was prepared from ferrocene and a mixture of butyllithium and tetramethylethylenediamine, (dimethyldithiocarbamato)ferrocene was isolated in 9% yield. Monosubstituted (dialkyldithiocarbamato)ferrocene derivatives were, however, obtained in 60–80% yield by lithiation of bromoferrocene (see Scheme II).

In these reactions, the lithium containing was not recovered but may have been LiS_2CNR_2.

^{1}H NMR data for the (dialkyldithiocarbamato)ferrocene derivatives 1–6 are given in Table I. The two apparent "triplets" observed for the cyclopentadienyl protons are characteristic of 1,1′-disubstituted ferrocene and are consistent with an AA′BB′ spin system where J_{AB} and $J_{A'B}$ (or $J_{AB'}$) are equal and smaller than the chemical shift between A and B.[6] The "triplets" are slightly deshielded as expected for the electron-withdrawing dithiocarbamate substituent. Two separate signals are observed for the dialkyl protons at room temperature.

The ^{13}C NMR data for the (dialkyldithiocarbamato)ferrocene complexes is presented in Table II. In the cyclopentadienyl region the signal around 76 ppm has been tentatively assigned to the nuclei in the $C_{2,5}$ positions that are primarily influenced by the inductive effect and the magnetic anisotropy of the dialkyldithiocarbamate substituent.[7] The $C_{3,4}$ resonance is found further upfield at around 70 ppm. As in the ^{1}H NMR the alkyl groups exhibit two separate signals at room temperature.

Table III contains the absorption spectra of the (dialkyldithiocarbamato)ferrocene derivatives. The absorption maxima are identical for the corresponding mono- and bissubstituted ferrocene complexes except that the extinction coefficents for the bands centered at 270 and 240 nm are significantly lower for the monosubstituted species as shown in Table III.

Tentative assignments of the absorption maxima have been made. The band centered around 430 nm (ε 350 M^{-1} cm^{-1}) is slightly blue shifted relative to the d–d transition observed at 440 nm in ferrocene. Two well-defined max-

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(6) Bishop, J. J.; Davison, A. *Inorg. Chem.* **1971**, *10*, 832–837.

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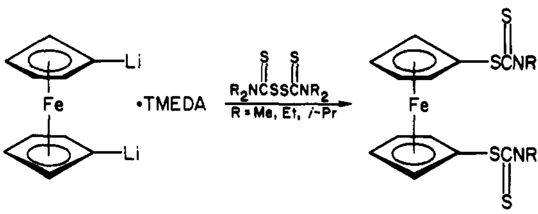
Table II. ^{13}C NMR Data for $Fe(C_5H_4SCSNR_2)_2$ and $FeCp(C_5H_4SCSNR_2)$

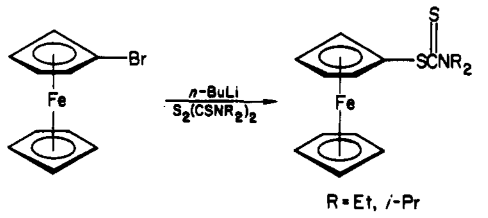
compd	δ C=S	C_1	$C_{2,5}$	$C_{3,4}$	Cp	CH	CH_2	CH_3
$Fe(C_5H_4SCSNMe_2)_2$	199.7 (s)	76.7 (s)	77.4 (d)	72.0 (d)				45.3 (q) 41.7 (q)
$Fe(C_5H_4SCSNEt_2)_2$	197.5 (s)	76.1 (s)	77.2 (d, J = 175 Hz)	71.6 (d, J = 177 Hz)			49.4 (t) 46.9 (t, J = 134 Hz)	12.5 (q) 11.2 (q, J = 126 Hz)
$Fe(C_5H_4SCSN\text{-}i\text{-}Pr_2)_2$[a]	198.0 (s)	76.1 (s)	77.1 (d, J = 183 Hz)	71.3 (d, J = 178 Hz)		53.3 (d, J = 137 Hz)		19.7 (q, J = 127 Hz)
$FeCp(C_5H_4SCSNMe_2)$	199.9 (s)	75.0 (s)	75.7 (d)	70.3 (d)	69.4 (d)			45.2 (q) 41.5 (q)
$FeCp(C_5H_4SCSNEt_2)$	198.7 (s)	75.2 (s)	76.0 (d)	70.4 (d)	69.5 (d)		49.6 (t) 47.2 (t)	12.6 (q) 11.5 (q)
$FeCp(C_5H_4SCSN\text{-}i\text{-}Pr_2)$[b]	198.0 (s)	75.2 (s)	76.0 (d)	70.2 (d)	69.4 (d)	54.1		19.9 (q)

[a] Measured at 45 °C. [b] Measured at 47 °C.

Scheme I

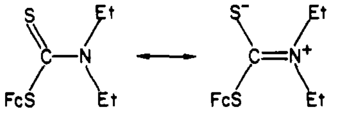


Scheme II



ima at 270 and 240 nm are characteristic of dithiocarbamates and have been assigned as intraligand transitions.[8] The band at 272–279 nm (η ~10^4) could be assigned to an n → σ* transition whereas the band at 239–248 nm (ε ~10^4) could be a π → π* transition. The high-energy band located at 210 nm (ε ~30000) is probably a ligand-to-metal charge-transfer band associated with the ferrocene.[9]

Dynamic NMR Studies. Two possible resonance forms for the (dialkyldithiocarbamato)ferrocene complexes are shown.



The second resonance form introduces a degree of double-bond character into the carbon–nitrogen bond that prevents free rotation around the C–N bond.

In the ^1H NMR and ^{13}C NMR data two separate signals are observed for the *N,N*-dialkyl protons in the (methylcarbamato)- and (ethyldithiocarbamato)ferrocene derivatives **1**, **2**, **4**, and **5** at room temperature. When the temperature is raised, the two *N,N*-dialkyl signals coalesce, and as the fast exchange limit is approached they sharpen to a single peak. The protons on the cyclopentadienyl rings show no variation with temperature.

The behavior of the alkyl protons is due to the restricted rotation around the carbamate C–N bond and a rough approximation of the barrier to rotation about this bond has been determined.[10]

NMR parameters, rate constants, and an approximate value of the barrier to rotation in compounds **1**, **2**, **4**, and **5** are given in Table IV). The values of the rotational barriers lie in a fairly narrow range from 15.75 to 16.15 ±

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(9) Sohn, Y. S.; Hendrickson, D. N.; Gray, H. B. *J. Am. Chem. Soc.* **1971**, *93*, 3603–3612.

(10) The rate constant, k_c, at the coalescence temperature, T_c, was determined from the peak separation, $\delta\nu$, at slow exchange using equation $k_c = \pi\delta\nu/(2)^{1/2}$ or $k_c = \pi[\delta\nu^2 + 6J^2]^{1/2}/(2)^{1/2}$ for coupled systems.[11] An approximate rotational free energy barrier was obtained from the Eyring equation: $\Delta G^* = 2.3RT[10.3 - \log(k_c/T_c)]$.

(11) Gunther, H. "NMR Spectroscopy-An Introduction"; Wiley: New York, **1980**. Sutherlane, I. O. *Annu. Rep. NMR Spectrosc.* **1971**, *4*, 71–225.

Table III. Electronic Absorption Spectra of $Fe(C_5H_4SCSNR_2)_2$ and $Fe(C_5H_5)(C_5H_4SCSNR_2)$ (R = Me, Et, *i*-Pr) at 24 °C in MeCN Solution at Approximate Concentration of 8.0×10^{-5} M

	$Fe(C_5H_4SCSNR_2)_2$		$Fe(C_5H_5)$-$(C_5H_4SCSNR_2)$	
R	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	λ_{max}, nm	ϵ, M^{-1} cm^{-1}
Me	430	360	437	410
	273	17 400	272	12 900
	241	24 100	239 sh	17 000
	220	30 000	210	30 000
Et	435	380	435	300
	276	17 200	274	12 800
	245	25 500	245	16 900
	223 (sh)	29 700		
	205 (sh)	32 400	210	30 000
i-Pr	437	370	437	310
	279	13 500	274	12 800
	248	22 100	247	14 300
	227	25 600		
	205	31 600	210	30 000

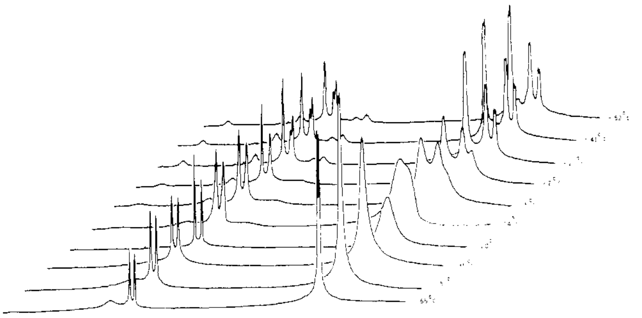

Figure 1. Variable-temperature ^1H NMR spectra of $Fe(C_5H_4SCSN\text{-}i\text{-}Pr_2)_2$.

0.3 kcal/mol and appear to be independent of the nature of the alkyl group.

Hollaway[12] has determined rotational barriers about the carbamate C–N bond in a series of *N*,*N*-dialkyldithiocarbamate esters. Activation energies of 10–12 kcal/mol suggested that an appreciable amount of C–N double-bond character was present. Hollaway was able to correlate the C–N double-bond character with the "thioureide" band between 1489 and 1498 cm^{-1} in the infrared region. The "thioureide" band that has been assigned to the partial double character in the carbon–nitrogen bond was observed at 1480 cm^{-1} in the (dialkyldithiocarbamato)ferrocene derivatives as shown in Table IV.

The variable temperature ^1H NMR spectra for the isopropyl derivatives, (3) and (6), are considerably more complex and are shown in Figures 1 and 2, respectively. The NMR spectra for the mono- and bis(diisopropyldithiocarbamato)ferrocene derivatives are very similar, which suggests that in the bissubstituted species the dithiocarbamate groups are on opposite sides and act independently of each other.

Various groups have studied methyl *N*,*N*-diisopropyldithiocarbamate, $MeSCSN\text{-}i\text{-}Pr_2$,[13-16] and have concluded that hindered rotation occurs around the carbamate C–N bond and the isopropyl–nitrogen bonds. Similar processes seem to occur in the ferrocene derivative. Figures 1 and 2 indicate that at high temperature the ^1H NMR spectrum consists of a septet for the methine protons, a doublet for the isopropyl methyl groups, and the signals associated with the ring protons. This spectrum is consistent with rapid rotation around the carbamate C–N and isopropyl–nitrogen bonds. As the temperature is lowered, the signals broaden, and at the slow-exchange limit there are four methine septets and at least three methyl doublets are clearly visible.

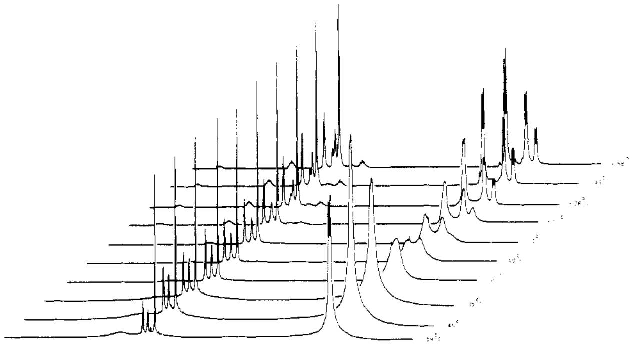

Figure 2. Variable-temperature ^1H NMR spectra of $Fe(C_5H_5)(C_5H_4SCSN\text{-}i\text{-}Pr_2)$.

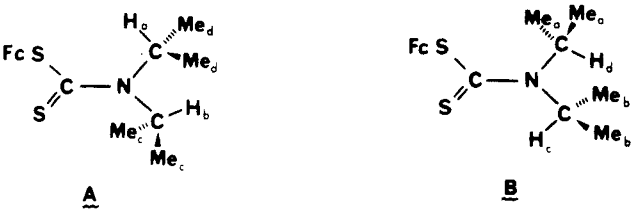

Figure 3. Two conformers A and B of $Fe(C_5H_5)(C_5H_4SCSN\text{-}i\text{-}Pr_2)$.

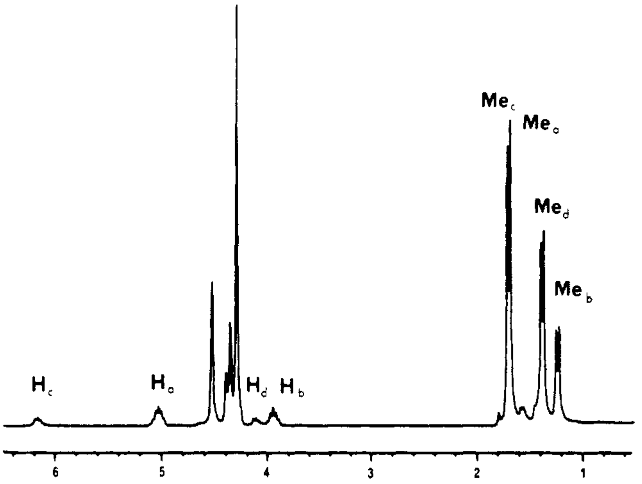

Figure 4. ^1H NMR spectrum and peak assignments for $Fe(C_5H_5)(C_5H_4SCSN\text{-}i\text{-}Pr_2)$ at −58 °C.

The low-temperature spectrum can be interpreted in terms of a mixture of the two conformer A and B, shown in Figure 3, which exist in different relative populations. Conformer A is the preferred conformer as in conformer B there is significant interaction between the isopropyl methyl groups and the bulky ferrocene. Integration of the methine septets suggest that conformer A and conformer B are present in a 2.1:1 ratio.

Tentative assignments, based on the magnetic aniso-

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Table IV. NMR Parameters, Kinetics, and Infrared Data for $Fe(C_5H_4SCSNR_2)_2$ and $Fe(C_5H_5)(C_5H_4SCSNR_2)$ Where R = Me and Et

	$\delta\nu$, Hz	k_c, s^{-1}	T_c, K	$\Delta G^\ddagger \pm 0.3$, kcal/mol	IR, cm^{-1}
$Fe(C_5H_4SCSNMe_2)_2$	16.48	36.61	314	16.15	1480
$Fe(C_5H_4SCSNEt_2)_2$	43.95	104.24	319	15.75	1480
$Fe(C_5H_5)(C_5H_4SCSNMe_2)$	17.70	39.32	312	16.00	1475
$Fe(C_5H_5)(C_5H_4SCSNEt_2)$	31.74	79.40	320	15.98	1480

tropy of the thiocarbonyl group, are shown in Figure 4. The lowest field septet is assigned to H_c—the proton adjacent to the thiocarbonyl. The next lowest field septet is attributed to H_a that is adjacent to the C–SFc bond. The high field septets are assigned to H_d and H_b. The methyl groups are assigned as shown where Me_a and Me_c appear to be accidentally degenerate. A resolution enhanced spectrum of the isopropyl methyl region suggests that a third conformer is present in low concentration as has been observed in the MeSCSN-*i*-Pr_2 complex.[12,15]

The dynamic NMR studies suggest that in the (methyldithiocarbamato)- and (ethyldithiocarbamato)ferrocene derivatives carbamate C–N bond rotation is observed whereas in the isopropyl analogues isopropyl–nitrogen bond rotation predominates.

The (dialkyldithiocarbamato)ferrocene derivatives 1–6 are very similar to the dithiocarbamate ligands except that the ferrocene species is neutral.

A preliminary investigation of the coordination of $Fe(C_5H_5)(C_5H_4SCSNEt_2)$ with palladium chloride suggests that both sulfur atoms chelate the palladium atom.[17]

Registry No. 1, 91711-53-4; 2, 91687-04-6; 3, 91687-05-7; 4, 91687-06-8; 5, 91687-07-9; 6, 91687-08-0; ferrocene, 102-54-5; 1,1′-dilithioferrocene, 33272-09-2; bromoferrocene, 1273-73-0; tetramethylthiuram disulfide, 137-26-8; tetraethylthiuram disulfide, 97-77-8; tetraisopropylthiuram disulfide, 4136-91-8.

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(17) Infrared data indicate that the "thioureide" vibration at 1480 cm^{-1} in $Fe(C_5H_5)(C_5H_4SCSNEt_2)$ shifts to 1550 cm^{-1} in the palladium complex. This shift to higher frequencies can be correlated with an increase in the double-bond character of the carbamate C–N bond.