once with -78 °C petroleum ether (5 mL) to yield 31.7% (25 mg) of product based on I_2. The product contained traces of impurities. MS showed parent ion at m/e 690. 400.1-MHz ^1H NMR (99.5% cyclohexane-d_{12}): δ 2.16 (s, 15 H, Cp*), 2.14, 2.19 (both s, both 6 H, $C_5Me_4CH_2I$), 4.01 (s, 2 H, $C_5Me_4CH_2I$), 7.22-6.87 (m, 5 H, C_6H_5).

Photolysis of 1a under a Nitrogen Atmosphere. In an NMR tube attached to a Teflon needle valve via a ground-glass joint was placed $Cp^*_2Zr(H)CH_2CH(CH_3)_2$ (25 mg) and 0.5 mL of benzene-d_6. One atmosphere of N_2 (excess) was placed over the solution, the needle valve closed, and the sample photolyzed (blacklight) for 24 h. The sample was then cooled to -196 °C, the tube was torch sealed under slightly reduced pressure, and the contents were analyzed by NMR.

H_2 (D_2) and 3. One atmosphere of H_2 (D_2) was placed over a petroleum ether (10 mL) solution of **3** (40 mg) contained in a 50-mL flask. Conversion to $Cp^*_2Zr(C_6H_5)H$ was complete in 15 min (D_2 complete in 30-40 min).

HCl and 3. One atmosphere of anhydrous HCl (excess) was placed over a solution of **3** (60 mg) in 10 mL of benzene. Within minutes the reaction was complete and $Cp^*_2ZrCl_2$ was recovered upon removal of the solvent.

PMe_3 and 3. In an NMR tube attached to a needle valve was placed benzene-d_6 and **3**. A sixfold excess of PMe_3 was then condensed into the sample at -196 °C and the tube sealed. An NMR spectrum recorded after 6 days showed no sign of reaction.

CO and 3. One atmosphere of CO was placed over a benzene (10 mL) solution of **3** (30 mg). After 24 h an NMR revealed a profusion of products.

MeI and 3. Excess MeI was condensed at -78 °C into 15 mL of benzene containing **3** (40 mg). After 24 h, the volatiles were removed and an NMR revealed that no reaction had occurred.

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Registry No. **1a**, 67108-86-5; **1b**, 112532-21-5; **1c**, 112532-22-6; **2**, 112532-20-4; **3**, 105501-02-8; **4**, 112532-25-9; $Cp^*_2ZrMe_2$, 67108-80-9; $Cp^*_2ZrCl_2$, 54039-38-2; $Cp^*_2ZrH_2$, 61396-34-7; $Cp^*_2Zr(D)CH_2CD(CH_3)_2$, 67108-87-6; $Cp^*Zr(C_6H_5)I$, 112532-23-7; $Cp^*_2Zr(C_6D_5)D$, 112532-24-8; ethene, 74-85-1; propene, 115-07-1; isobutene, 115-11-7; benzene, 71-43-2.

Chiral 1-[1-(Dimethylamino)ethyl]-2-[(dialkylthiocarbamoyl)thio]ferrocene and 1-[(Dimethylamino)methyl]-2-[(dialkylthiocarbamoyl)thio]-ferrocene Derivatives

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A series of chiral 1-[1-(dimethylamino)ethyl]-2-[(dialkylthiocarbamoyl)thio]ferrocene and 1-[(dimethylamino)methyl]-2-[(dialkylthiocarbamoyl)thio]ferrocene derivatives, (*R,S*)-$C_5H_5FeC_5H_3(CHMeNMe_2)(SCSNR_2)$ and $C_2H_5FeC_5H_3(CH_2NMe_2)(SCSNR_2)$ (R = Me, Et), have been prepared by reaction of (*R,R*)-1-[1-(dimethylamino)ethyl]-2-lithioferrocene and 1-[(dimethylamino)methyl]-2-lithioferrocene, respectively, with tetraalkylthiuram disulfide. The derivatives were characterized by ^1H NMR, ^{13}C NMR, IR, and MS techniques. Rotation around the C-N carbamate bond was studied by dynamic ^1H NMR, and the approximate barriers to rotation for the methyl and ethyl derivatives **1**, **2**, **4**, and **5** are 15.83, 16.18, 15,36, and 15.81 kcal/mol, respectively, and are correlated with the "thioureide" band in the infrared.

Introduction

The dithiocarbamate ligand has played a major role in the chemistry of transition-metal sulfide complexes.[1,2] In the bid to introduce chirality to these dithiocarbamate ligands, we have prepared a series of chiral 1-[1-(dimethylamino)ethyl]-2-[(dialkylthiocarbamoyl)thio]-ferrocene and 1-[(dimethylamino)methyl]-2-[(dialkylthiocarbamoyl)thio]ferrocene derivatives, where the dithiocarbamate is attached to the ferrocene through a thioester linkage at the 2-position. The former contains both planar and central elements of chirality while the latter contains only a chiral plane.

Tetraalkylthiuram disulfides undergo nucleophilic attack at the disulfide linkage by cyanide ions, amines, and Grignard reagents.[3] Cava also reported that aryllithium derivatives react with tetraisopropylthiuram disulfide to give dithiocarbamate esters that were precursors to aromatic thiols.[4] Recently, a series of mono- and bis[(dialkylthiocarbamoyl)thio]ferrocene derivatives was synthesized in our laboratory.[5]

Experimental Section

Air-sensitive reagents were manipulated in a prepurified argon or nitrogen atmosphere by using Schlenck techniques or in a glovebox. Solvents were dried and distilled by standard methods.[6]

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Infrared spectra were obtained by use of a Perkin-Elmer Model 457 grating spectrophotometer by using KBr pellets. Mass spectra were obtained by use of a Finnigan Model 4021 instrument with an INCOS data system at 70 eV. All melting points were determined by using a Thomas-Hoover capillary melting point apparatus and were corrected before use. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Orbital rotations were determined by use of a Perkin-Elmer Model 141 polarimeter.

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 TMS internal standard.

^{13}C NMR spectra (broad-band proton decoupled and off-resonance decoupled) were obtained by use of the Bruker WM 250 spectrometer at 62.9 MHz. ^{13}C NMR spectra were recorded in methylene-d_2 chloride, chloroform-d_1, or acetone-d_6 with chemical shifts reported in parts per million downfield from a TMS internal standard. [(Dimethylamino)methyl]ferrocene and tetraalkylthiuram disulfides were purchased from Aldrich Chemical Co.

1-[(Dimethylamino)methyl]-2-[(dimethylthiocarbamoyl)thio]ferrocene (1). A 2.7 M solution of *n*-BuLi in hexane (4.1 mL, 11.1 mmol) was added over a half-hour period to a solution of [(dimethylamino)methyl]ferrocene (2.4 g, 8.7 mmol) in 50 mL of dry ether under Ar in a 250-mL round-bottomed Schlenk flask equipped with a magnetic stirring bar at −78 °C. The suspension was stirred for 20 h at room temperature under argon, and then 6.0 g (25.0 mmol) of tetramethylthiuram disulfide in 100 mL of dry benzene was added via cannula at −78 °C. One hour later, the reaction mixture was warmed to room temperature and stirred 30 h to give a black/gray solution. The mixture was slowly added to aqueous $NaHCO_3$ and was cooled in an ice bath, and the cloudy solution was filtered. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with ice water, dried over anhydrous sodium sulfate, and concentrated in vacuo to afford a dark gray solid that was dissolved in methylene chloride and was chromatographed on a silica gel column by gradient elution (hexane/ether/methylene chloride). The yield was 75.3%. The compound was recrystallized from hot hexane to give yellowish brown single crystals: mp 133–134 °C; IR (KBr pellet) 474, 512, 542, 826, 972, 998, 1033, 1100, 1172, 1250, 1378, 1452, 1498, 2780, 2830, 2860, 2940 cm^{-1}; MS, *m/e* (relative intensity) 44 (12, NMe_2), 45 (6, $HNMe_2$), 56 (19, Fe), 58 (14, CH_2NMe_2), 65 (4, C_5H_5), 88 (100, $CSNMe_2$), 120 (15, $SCSNMe_2$), 121 (37, C_5H_5Fe), 209 (18, $M^+ - CSNMe_2 - C_5H_5$), 241 (50, $M^+ - C_5H_5Fe$), 242 (32, $M^+ - SCSNMe_2$), 274 (2, $M^+ - CSNMe_2$), 297 (4, $M^+ - C_5H_5$), 362 (57, M^+). Anal. Calcd for $C_{16}H_{22}FeN_2S_2$: C, 53.03; H, 6.08. Found: C, 52.56; H, 6.25.

1-[(Dimethylamino)methyl]-2-[(diethylthiocarbamoyl)thio]ferrocene (2). The 1-[(dimethylamino)methyl]-2-lithioferrocene was made as with **1** by using 2.4 g (8.7 mmol) of [(dimethylamino)methyl]ferrocene, 50 mL of dry ether, and 4.0 mL (10.8 mmol) of a 2.7 M solution of *n*-BuLi in hexane at −78 °C. The suspension was stirred for 24 h at room temperature under Ar, and then 5.2 g (17.4 mmol) of tetraethylthiuram disulfide in 250 mL of dry ether was added via cannula at −78 °C. One hour later, the reaction mixture was warmed to room temperature and stirred 30 h to give a gray solution. The mixture was slowly added to aqueous $NaHCO_3$ and was cooled in an ice bath, and the cloudy solution was filtered. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with ice water, dried over anhydrous sodium sulfate, and concentrated in vacuo to afford a dark gray solid that was dissolved in methylene chloride and was chromatographed on a silica gel column by gradient elution (hexane/ether/methylene chloride). The product was obtained as a yellowish brown solid after the solvent was removed; yield 59.3%. The compound was recrystallized from hot hexane to give yellowish brown crystals: mp 89–90 °C; IR (KBr pellet) 471, 503, 826, 978, 1033, 1103, 1203, 1270, 1354, 1379, 1418, 1455, 1487, 2880, 2940, 2980, 3080 cm^{-1}; MS, *m/e* (relative intensity) 44 (42, NMe_2), 45 (13, $HNMe_2$), 56 (16, Fe), 58 (14, CH_2NMe_2), 65 (10, C_5H_5), 66 (10, C_5H_6), 72 (5, NEt_2), 73 (6, $HNEt_2$), 76 (6, CS_2), 116 (100, $CSNEt_2$), 121 (32, C_5H_5Fe, $M^+ - C_5H_5Fe - SCSNEt_2$), 149 (20, $HSCSNEt_2$), 242 (21, $M^+ - SCSNEt_2$), 269 (24, $M^+ - C_5H_5Fe$), 324 (5, $M^+ - C_5H_6$), 390 (4, M^+). Anal. Calcd for $C_{18}H_{26}FeN_2S_2$: C, 55.38; H, 6.67. Found: C, 55.58; H, 6.97.

(*R*)-1-[(Dimethylamino)ethyl]ferrocene [(*R*)-3]. The amine (*R*)-**3** was prepared and resolved by using (+)-tartaric acid as described by Ugi.[8] The amine was recrystallized twice to give a dark brown oil that partly solidified on cooling: ^1H NMR δ 1.44 (d, 3 H, CH_3), 2.09 (s, 6 H, NMe_2), 3.60 (q, 1 H, CH), 4.11 (s, 5 H, C_5H_5), 4.12 (m, 4 H, C_5H_4); $[\alpha]^{25}_D$ −14.0° (lit.[8] $[\alpha]^{25}_D$ −14.1°).

(*R*,*S*)-1-[1-(Dimethylamino)ethyl]-2-[(diethylthiocarbamoyl)thio]ferrocene (4). A 2.7 M solution *n*-BuLi in hexane (1.6 mL, 4.3 mmol) was slowly added via a syringe to a solution of (*R*)-1-[1-(dimethylamino)ethyl]ferrocene (1.0 g, 3.9 mmol) in 50 mL of dry diethyl ether at −78 °C. The solution was allowed to reach room temperature and stirred for an additional 12 h under N_2. Etramethylthiuram disulfide (0.94 g, 3.9 mmol) in 60 mL of benzene was added via cannula to the orange solution that had been cooled to −78 °C. The solution was allowed to reach room temperature and was stirred overnight, and 40 mL of saturated aqueous $NaHCO_3$ was added to the dark brown solution. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with cold water, and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave a dark brown product mixture that was chromatographed on a silica gel column (hexane/benzene/ether/methanol). The product was recrystallized from CH_2Cl_2/hexane to give yellowish orange crystals: yield 82.2%; mp 102–105 °C; MS, *m/e* (relative intensity) 376 (61, M^+), 311 (33, $M^+ - Cp$), 287 (20), 256 (100, $M^+ - SCSNMe_2$), 255 (19, $M^+ - FeCp$), 241 (93, $M^+ - SCSNMe_2 - Me$), 121 (3, FeCp), 88 (52, $CSNMe_2$), 255 (11, $CHMeNMe_2$); IR (KBr pellet) 2980, 2940, 2780, 1495 cm^{-1}; ^1H NMR (at 22 °C) δ 4.63 (dd, 1 H, H_3, H_5), 4.46 (t, 1 H, H_4), 4.40 (dd, 1 H, H_3, H_4), 4.15 (s, 5 H, Cp), 3.71 (q, J = 7.0 Hz, 1 H, NC*H*Me), 3.50 (s, 6 H, NMe_2), 2.10 (s, 6 H, NMe_2), 1.52 (d, J = 7.0 Hz, 3 H, $NCHCH_3$); ^{13}C NMR (at 27 °C) δ 198.9 (s, CS), 91.7 (s, C_1), 76.2 (d, C_3, C_4, C_5), 74.9 (s, C_2), 69.9 (s, Cp), 69.9 (d, C_3, C_4, C_5), 68.6 (d), 68.4 (s), 55.6 (t, NCHMe), 4.08 (q, NMe_2), 18.0 (q, $NCHCH_3$). Anal. Calcd for $C_{17}H_{24}FeN_2S_2$: C, 54.25; H, 6.38. Found: C, 54.27; H, 6.49.

(*R*,*S*)-1-[1-(Dimethylamino)ethyl]-2-[(diethylthiocarbamoyl)thio]ferrocene (5). A 2.5 M solution *n*-BuLi in hexane (1.0 mL, 2.57 mmol) was slowly added via a syringe to a solution of (*R*)-1-[1-(dimethylamino)ethyl]ferrocene (0.65 g, 2.57 mmol) in 30 mL of dry diethyl ether at −78 °C. The solution was allowed to reach room temperature and stirred for an additional 12 h under N_2. The solution was then cooled to −78 °C, and tetraethylthiuram disulfide (0.8 g, 2.7 mmol) in 35 mL of toluene was added. The solution was stirred overnight at room temperature and 30 mL of saturated aqueous $NaHCO_3$ added. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with cold water, and dried. Evaporation of the solvent gave a brown product mixture that was chromatographed on a silica gel column (hexane/benzene/ether/methanol). The product was recrystallized from CH_2Cl_2/hexane to give brown crystals: mp 82–85 °C; MS, *m/e* (relative intensity) 404 (2, M^+) 297 (16), 213 (11), 148, (12, $SCSNEt_2$), 116 (100, $CSNEt_2$), 72 (2, NEt_2); IR (KBr, Nujol) 1498 cm^{-1}; ^1H NMR (at 27 °C) δ 4.60 (dd, 1 H, H_3, H_5), 4.48 (t, 1 H, H_4), 4.40 (dd, 1 H, H_3, H_5), 4.12 (s, 5 H, Cp), 3.96 (q, J = 7.0 Hz, 2 H, CH_2CH_3), 3.82 (q, J = 7.0 Hz, 2 H, CH_2CH_3), 3.63 (q, J = 7.0 Hz, 1 H, NC*H*Me), 2.15 (s, 6 H, NMe_2), 1.46 (d, 3 H, $NCHCH_3$), 1.3–1.42 (tt, 6 H, carbamate CH_3); ^{13}C NMR δ 197.3 (s, CS), 86.6 (s, C_1), 86.5, 77.5, 76.5, 68.6 (d, Cp), 67.8 (C_3, C_4, C_5), 67.4 (d, NCHMe), 66.6, 66.4, 57.9, 51.0 (t, NCH_2), 46.8 (t, carbamate CH_2), 39.9, 15.2 (q, $NCHCH_3$), 12.9 (q, carbamate CH_3), 10.0 (q, carbamate CH_3). Anal. Calcd for $C_{19}H_{28}FeN_2S_2$: C, 56.44; H, 6.93. Found: C, 56.91; H, 6.98.

Results

Reaction of 1-[(dimethylamino)methyl]-2-lithioferrocene

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Table I. ^{1}H NMR Data for (*R*)-3, (*R,S*)-$C_5H_5FeC_5H_3(CHMeNMe_2)$(R) [R = $SCSNMe_2$ (4), $SCSNEt_2$ (5)], $C_5H_5Fe(C_5H_3$-1-CH_2NMe_2-2-R) [R = $SCSNMe_2$ (1), $SCSNEt_2$ (2)], and $C_5H_5FeC_5H_4R$ (R = $SCSNMe_2$, $SCSNEt_2$) (δ)

compd	*T*, °C	substituted ring	C_5H_5	NCH	NMe_2	CH_2	CH_3
$C_5H_5Fe(C_5H_3$-1-CH_2NMe_2-2-$SCSNMe_2$) (1)	27	4.43 t					
		4.45 dd		3.40 d			
		4.62 dd	4.16 s	3.18 d	2.21 s		3.50 s
$C_5H_5Fe(C_5H_3$-1-CH_2NMe_2-2-$SCSNEt_2$) (2)	27	4.42 t					
		4.49 dd		3.19 d		3.85 q	1.22 t
		4.59 dd	4.14 s	3.48 d	2.18 s	3.98 q	1.39 t
(*R*)-3	25	4.11	4.08 s	3.60 d	2.09 s		1.46 d
(*R,S*)-$C_5H_5FeC_5H_3(CHMeNMe_2)$	22	4.63 dd			3.50 s		
($SCSNMe_2$) (4)		4.46 t	4.15 s	3.71 q	2.10 s		1.52 d
		4.40 dd					
(*R,S*)-$C_5H_5FeC_5H_3(CHMeNMe_2)$	27	4.60 dd					
($SCSNEt_2$) (5)		4.48 t				3.96 q	1.46 d
		4.40 dd	4.12 s	3.63 q	2.15 s	3.82 q	1.3–1.42 tt
$C_5H_5Fe(C_5H_4SCSNMe_2)$[a]	22	4.44 t					
		4.34 t	4.24 s				3.51 s
$C_5H_5Fe(C_5H_4SCSNEt_2)$[a]	22	4.42 t				3.82 q	1.23 t
		4.34 t	4.22			3.96 q	1.37 t

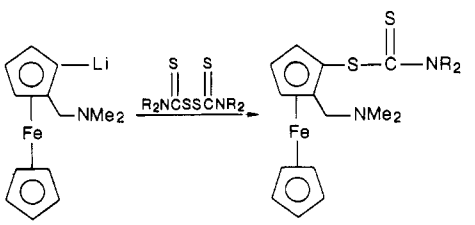
[a] Reference 5.

Table II. ^{13}C NMR Data for (*R*)-3, (*R,S*)-$C_5H_5FeC_5H_3(CHMeNMe_2)$(R), $C_5H_5Fe(C_5H_3$-1-CH_2NMe_2-2-R), and $C_5H_5FeC_5H_4R$ (R = $SCSNMe_2$ and $SCSNEt_2$) (δ)

compound	C=S	substituted ring C_1, C_2, C_3, C_4, C_5	C_5H_5	NCH	NMe_2	CH_2	CH_3
$C_5H_5Fe(C_5H_3$-1-CH_2NMe_2-2-$SCSNMe_2$) (1)	199.3	88.1, 75.0, 69.4, 71.3, 76.3	70.2	56.8	45.5		41.7
$C_5H_5Fe(C_5H_3$-1-CH_2NMe_2-2-$SCSNEt_2$) (2)	197.4	87.7, 75.2, 69.2, 71.2, 76.7	70.0	56.6	45.2	46.8	11.4
(*R*)-3							
(*R,S*)$C_5H_5FeC_5H_3(CHMeNMe_2)(SCSNMe_2)$ (4)	198.9	91.7, 74.9, 68.6, 69.6, 76.2	69.9	55.6	40.8		18
(*R,S*)$C_5H_5FeC_5H_3(CHMeNMe_2)(SCSNEt_2)$ (5)	197.3	86.6, 86.5, 67.8, 68.6, 77.5	68.6	51.0	39.9	46.8	12.9
$C_5H_5Fe(C_5H_4SCSNMe_2)$[a]	199.9	70.3, 75.7, 75.0	69.4				41.5
							45.2
$C_5H_5Fe(C_5H_4SCSNEt_2)$[a]	198.7	70.4, 76.0, 75.2	69.5			47.2	11.5
						49.6	12.6

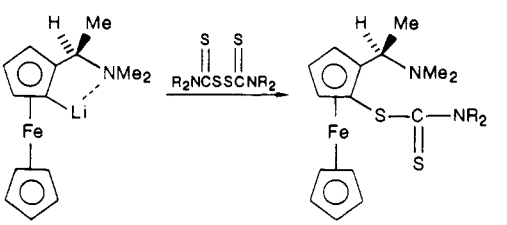
[a] Reference 5.

Scheme I



1, R=Me
2, R=Et

Scheme II



4, R=Me
5, R=Et

with tetramethylthiuram disulfide and tetraethylthiuram disulfide gave a high yield of 1-[(dimethylamino)-methyl]-2-[(dimethylthiocarbamoyl)thio]ferrocene (1) and 1-[(dimethylamino)methyl]-2-[diethylthiocarbamoyl)-thio]ferrocene (2), respectively (see Scheme I).

These derivatives contain a chiral plane that is absent in bis[(dialkylthiocarbamoyl)thio]ferrocene derivatives and [(dialkylthiocarbamoyl)thio]ferrocene derivatives.[5]

Reaction of (*R,R*)-1-[1-(dimethylamino)ethyl]-2-lithioferrocene with tetramethylthiuram disulfide and tetraethylthiuram disulfide gave a high yield of (*R,S*)-1-[1-(dimethylamino)ethyl]-2-[(dimethylthiocarbamoyl)thio]-ferrocene (4) and (*R,S*)-1-[1-(dimethylamino)ethyl]-2-[(diethylthiocarbamoyl)thio]ferrocene (5), respectively (Scheme II).

These new compounds contain a chiral plane that is absent in bis[(dialkylthiocarbamoyl)thio]ferrocene and [(dialkylthiocarbamoyl)thio]ferrocene derivatives.[5] They also contain a chiral center that is absent in 1-[(dimethylamino)methyl]-2-[(dialkylthiocarbamoyl)thio]-ferrocene derivatives, 1 and 2. In contrast to the results obtained by Cava, only the desired product and no thio amide derivative was obtained.

The thio amide species arise from competing nucleophilic attack at the thione carbon rather than at the sulfur–sulfur bond in the tetraalkylthiuram disulfide.

The 250-MHz ^{1}H NMR data for the 1-[(dimethylamino)methyl]-2-[(dialkylthiocarbamoyl)thio]ferrocene derivatives, 1 and 2, is given in Table I. The chemical shift difference ($\Delta\delta$) between the two diastereotopic protons of the aminomethylene group is dependent on the steric crowding of the substituent at the 2-position of the disubstituted ring. The electron-withdrawing effect of a $SCSNR_2$ group leads to pronounced differences in chemical shifts between the 2,5- and 3,4-protons of the monosubstituted ferrocene ring, and the inductive effect shifts the substituted ring protons to lower field especially at the 2,5-position of the ring.[7,9] Two separated signals are ob-

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Table III. NMR Parameters, Kinetics, and Infrared Data for (R,S)-$C_5H_5FeC_5H_3(CHMeNMe_2)(R)$, $C_5H_5Fe(C_5H_3$-1-$(CH_2NMe_2$-2-R), and $C_5H_5FeC_5H_4R$ (R = $SCSNMe_2$, $SCSNEt_2$)

compound	$\Delta\nu$, Hz	K_c, s^{-1}	T_c, K	ΔG^*, kcal/mol	IR ν, cm^{-1}
$C_5H_5Fe(C_5H_3$-1-CH_2NMe_2-2-$SCSNMe_2)$	5.28 ± 0.13	11.73	296	15.83 ± 0.3	1498
$C_5H_5Fe(C_5H_3$-1-CH_2NMe_2-2-$SCSNEt_2)$	43.87 ± 0.13	104.62	328	16.18 ± 0.3	1487
(R,S)-$C_5H_5FeC_5H_3(CHMeNMe_2)(SCSNMe_2)$	4.15 ± 0.13	9.22	285	15.36 ± 0.3	1495
(R,S)-$C_5H_5FeC_5H_3(CHMeNMe_2)(SCSNEt_2)$	41.25 ± 0.13	91.63	319	15.81 ± 0.3	1498
$C_5H_5Fe(C_5H_4SCSNMe_2)$[a]	17.70 ± 0.13	39.32	312	16.00 ± 0.3	1475
$C_5H_5Fe(C_5H_4SCSNEt_2)$[a]	31.74 ± 0.13	79.40	320	15.98 ± 0.3	1480

[a] Reference 5.

served for the N,N-diethyl protons due to restricted rotation around the carbamate C–N bond, but one broad signal is observed for the N,N-dimethyl protons at 27 °C due to incompletely restricted rotation around the carbamate C–N bond at this temperature.

The ^{13}C NMR data for the 1-[(dimethylamino)methyl]-2-[(dialkylthiocarbamoyl)thio]ferrocene derivatives, **1** and **2**, is presented in Table II. Compare the assignments of the substituted cyclopentadienyl ring carbons, the chemical shifts of the $C_{2,5}$ carbons increase in a series of OMe[10] < NH_2[11] < di-SMe[12] < SeMe[13] < di-SeMe[13] because the resonance effect (shielding to upfield) of these electron-donating substituents is more sensitive at the 2,5-position.[10,11] The $C_{3,4}$ carbons are downfield relative to the $C_{2,5}$ carbons when the substituents on the ferrocene are OMe, NH_2, SMe, and SeMe and are upfield if the substituents are CH_2NMe_2 and Me because the inductive effect (shielding to upfield) of these substituents on the ferrocene is more sensitive at the 3,4-position. It is reasonable to assign $\delta(C_{3,4}) > \delta(C_{2,5})$ in the [(dialkylthiocarbamoyl)thio]ferrocene and bis[(dialkylthiocarbamoyl)thio]ferrocene derivatives because the $SCSNR_2$ group is an electron-donating substituent and its resonance and inductive effects to the ferrocene are close to those of SeR groups. The assignments of $\delta(C_2)$ 75.0 and 75.2 for compounds **1** and **2**, respectively, are compared with $\delta(C_1)$ 75.0 and 75.2 for [(dialkylthiocarbamoyl)thio]ferrocene derivatives and is made with the help of the off-resonance-decoupled spectrum. The assignments of $\delta(C_3) < \delta(C_4) < \delta(C_5)$ are based on the conclusion that has been used for 1-[(dimethylamino)methyl]-2-(alkylthio)ferrocene derivatives.[14] As in the ^1H NMR the ethyl group exhibits two separate signals at room temperature but not the methyl group.

Dynamic NMR Studies. Two possible resonance forms for the [(dialkylthiocarbamoyl)thio]ferrocene complexes are shown.

Fc = ferrocenyl backbone

The second resonance form introduces a degree of double-bond character into the carbon–nitrogen bond that hinders 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 group of the [(dimethylthiocarbamoyl)thio]ferrocene derivatives, **2** and **5**, at room temperature, but the two ^1H NMR signals for the [(diethylthiocarbamoyl)thio]ferrocene derivatives, **1** and **4**, are observed only at low temperature. When the temperature is raised, the two N,N-dialkyl signals coalesce, and as the fact rotation limit is approached, they sharpen to a single peak. The protons on the cyclopentadienyl rings show no variation with temperature.

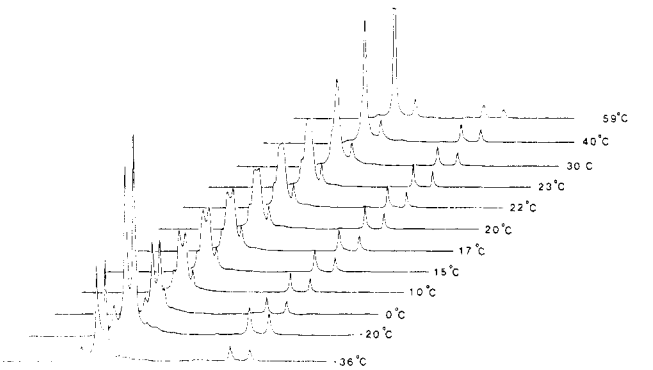

Figure 1. Variable-temperature ^1H NMR spectra of $C_5H_5Fe(C_5H_3$-1-CH_2NMe_2-2-$SCSNMe_2)$ (**1**).

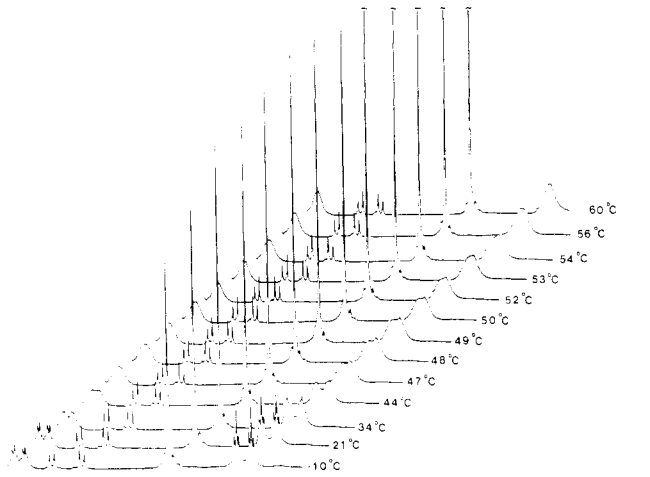

Figure 2. Variable-temperature ^1H NMR spectra of $C_5H_5Fe(C_5H_3$-1-CH_2NMe_2-2-$SCSNEt_2)$ (**2**).

The behavior of the alkyl protons is due to the restricted rotation around the carbamate C–N bond, and an approximation of the barrier to rotation about this bond has been determined.

The chemical shift change of the carbamate methyl group is temperature dependent, shown in Figures 1–3. This linear relationship ($\delta\nu$ vs T) observed in the absence of exchange permits the true chemical shift, $\delta\nu$, to be obtained at the coalescence temperature. For **1**, the least-squares line observed over the temperature range −50 to −10 °C is

$$\Delta\nu = (-0.0077 \pm 0.0015)T + 5.460 \pm 0.037$$

For **2**, the least-squares line observed over the temperature range −50 to 0 °C is

$$\Delta\nu = (-0.0066 \pm 0.0012) + 44.232 \pm 0.038$$

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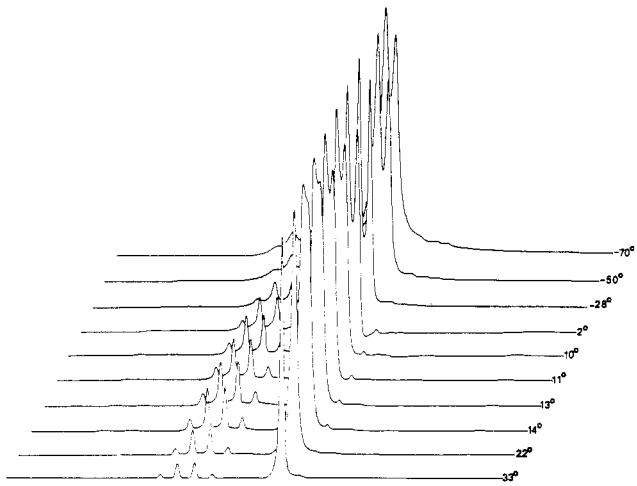

Figure 3. Variable-temperature ^1H NMR spectra of $C_5H_5FeC_5H_3(CHMeNMe_2)(SCSNMe_2)$ (**4**).

NMR parameters, rate constants, and an approximate value of the barrier to rotation in compounds **1**, **2**, **4**, and **5** are given in Table III. The rate constant, k_c, at the coalescence temperature, T_c, was determined from the peak separation, $\Delta\nu$, at slow exchange by using the 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.[15] An approximate rotational free energy barrier was obtained from the Eyring equation: $\Delta G^{\ddagger} = 2.3RT[10.3 - \log(k_c/T_c)]$. The values of the rotational barriers are 15.8 ± 0.3, 16.2 ± 0.3, 15.4 ± 0.3, and 15.8 ± 0.3 kcal/mol, for **1**, **2**, **4**, and **5**, respectively. The rotational barrier of $SCSNEt_2$ in **2** and **5** is higher than that of $SCSNMe_2$ in **1** and **4** because the diethylamino group has higher steric hindrance than the dimethylamino group in a 1,2-disubstituted cyclopentadienyl ring.

Hollaway[16] 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-bond character in carbon–nitrogen bond was observed at 1498 and 1487 cm^{-1} for the dimethyldithiocarbamate derivative **1** and the diethyldithiocarbamate derivative **2**, respectively, and at 1495 and 1498 cm^{-1} for derivatives **4** and **5**, respectively.

The variable-temperature ^1H NMR spectra for the dialkyldithiocarbamate derivatives **1**, **2**, and **4** are shown in Figures 1, 2, and 3, respectively. At low temperature, the ^1H NMR spectrum consists of two singlets for two methyl groups of **1** and of two triplets and two quartets for two methyl and two methylene groups of **2**. As the temperature is raised, the signals broaden, and at fast rotation all of the signals become singlets.

The infrared region, between 970 and 1010 cm^{-1}, is associated with the $\bar{\nu}$(CSS) vibrations and has been used to differentiate between monodentate and bidentate dithiocarbamate ligands. The compounds $C_5H_5Fe(C_5H_3\text{-}1\text{-}CH_2NMe_2\text{-}2\text{-}SCSNR_2)$ (R = Me, Et) exhibit two bands at 972, 998 and 978, 1003 cm^{-1}, respectively. On the basis of work by Bonati and Ugo,[17] the strong band at 972 and 978 cm^{-1} can be assigned to an uncomplexed C=S stretch. Caution must be observed as absorption from the ferrocene moiety is found in this region around 1000 cm^{-1}. Many studies have supported the use of the bands in 950–1050 cm^{-1} region to ascertain whether the dithiocarbamate ligand is monodentate or bidentate.[18]

Registry No. **1**, 112532-16-8; **2**, 112532-18-0; (*R*)-**3**, 31886-58-5; **4**, 112532-17-9; **5**, 112532-19-1; [(dimethylamino)methyl]ferrocene, 1271-86-9; tetramethylthiuram disulfide, 137-26-8; tetraethylthiuram disulfide, 97-77-8.

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Theoretical Study of the Conformation of *cis*-Bis(carbene) Complexes

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The conformation of transition-metal *cis*-bis(carbene) complexes has been studied by means of extended Hückel calculations. To understand the preferred conformations of the complexes, back-donation and the interaction between a σ M–L (L = CR_2) bond and an empty p_C orbital situated on the adjacent cis carbene group, which will be referred to as an M–L/ligand interaction, must be considered. Back-donation favors the edge-to-edge (E,E) conformation while the M–L/ligand interaction favors the face-to-face (F,F) conformation. The relative importance of the two effects depends on the nature of the metal, ancillary ligands, and substituents on the carbenes. In the complexes with high-lying d orbitals and no deactivated carbenes, the back-donation predominates while in the complexes with low-lying d orbitals and deactivated carbenes, the M–L/ligand interaction is dominant. The conformation of single faced π-acceptor ligands such as carbene and olefin (see also ref 8a of this work) can thus be fully analyzed with these two factors.

Transition-metal carbene complexes are key intermediates in numerous organometallic reactions[1] especially for the transformations of conjugated systems such as olefin metathesis and polymerization and the formation of small

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