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SYMMETRICALLY DISUBSTITUTED FERROCENES

IV. THE PREPARATION AND SPECTRAL STUDIES OF SOME [3]FERROCENOPHANES

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Summary

A series of 1,3-dithia[3]ferrocenophanes of C, Si, Ge, and Sn have been prepared from ferrocene-1,1′-dithiol. The fluxional behavior and limiting conformations of these molecules together with the related molecules 1,2,3-trithial-[3]ferrocenophane and 1,2,3-trithia[3]cobalticiniumophane hexafluorophosphate have been elucidated by variable temperature proton magnetic resonance.

Introduction

The efficient preparation of 1,1′-disubstituted ferrocenes [1] $(\eta^5\text{-}C_5H_4L)_2Fe$, where L = AsR_2, PR_2, SH, followed the discovery that ferrocene could be readily dimetallated [1,2]. The coordination complexes [3] of these ferrocene chelates can be viewed as [3]ferrocenophanes which contain the donor atoms in the 1- and 3-positions and the metal in the 2-position of the bridge. The isolation of 1,2,3-trithia[3]ferrocenophanes [4] and its quantitative conversion to ferrocene-1,1′-dithiol provided a potential bidentate chelating dithiolate. However, tractable complexes of this ligand system have not been obtained with transition metals. In marked contrast, however, a series of 1,3-dithia[3]ferrocenophanes containing carbon, silicon, germanium and tin can be readily prepared. These compounds are fluxional molecules. This work describes the synthesis and variable temperature proton magnetic resonance spectra of these molecules and the fluxional behavior of the closely related 1,2,3-trithia[3]-ferrocenophane and 1,2,3-trithia[3]cobalticiniumophane. The lowest energy conformations and fluxional behavior are discussed in terms of the stereochemical requirements of the atoms in the bridge.

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Experimental

General data and starting materials

Microanalyses were performed by Alfred Bernhardt, Mikroanalytisches Laboratorium, Mülheim (Ruhr), West Germany and Scandinavian Microanalytical Laboratory, Herlev, Denmark. All melting points are corrected and were determined using a Thomas Hoover "Unimelt" melting point apparatus on samples sealed in capillaries, under nitrogen or vacuum. Infrared spectra were recorded on Perkin—Elmer 337 and 521 spectrophotometers as Kel-F and Nujol mulls and are reported in cm^{-1}. Routine PMR spectra were recorded on a Varian Associates T-60 spectrometer, and variable temperature PMR spectra and decoupling experiments were obtained from Varian Associates HA-100 and Hitachi—Perkin—Elmer R-20B spectrometers. Chemical shifts are reported with respect to tetramethylsilane as an internal reference. Mass spectra were recorded on a Hitachi Perkin—Elmer RMU-6D mass spectrometer.

Reagent grade solvents were distilled prior to use and stored under nitrogen. The compounds ferrocene-1,1′-dithiol and 1,2,3-trithia[3]ferrocenophane were prepared as previously described [1]. The preparation of the isoelectronic 1,2,3-trithia[3]cobalticiniumophane will be reported elsewhere [5]. All other chemicals were of commercial reagent grade and were used without further purification.

Dreiding ferrocene models were supplied by W. Büchi, Glasapparatefabrik, Flawil, Switzerland.

1,3-Dithia-2,2-dimethylsilyl[3]ferrocenophane

A solution of 0.232 g (0.425 mmol) of ferrocene-1,1′-dithiol in 15 ml anhydrous benzene in a 25 ml Erlenmeyer flask was flushed with nitrogen and capped with a rubber septum. Dichlorodimethylsilane (0.150 g, 1.15 mmol) was added via syringe, followed by the slow addition of 0.30 ml (2.14 mmol) of triethylamine. Triethylammonium chloride precipitated immediately and the reaction was allowed to stand for ten minutes, filtered, and the solvent was removed in vacuo to yield yellow crystals. Further purification by vacuum sublimation (100° C 0.3 mmHg) yielded 0.280 g (91%) of the complex. An analytical sample was prepared by recrystallization from benzene/heptane, followed by vacuum sublimation, m.p. 183—184° C.

Anal.: Found: C, 47.06; H, 4.60; S, 18.23. Calcd. for $C_{12}H_{14}FeS_2Si$: C, 47.05; H, 4.61; S, 20.94%. PMR ($DCCl_3$): δ (ppm) 0.88 (6 H, s), 3.07 (4 H, t, J 2 Hz), 4.24 (4 H, t, J 2 Hz). IR: 3095(sh), 3080w, 1405m, 1380m, 1360w, 1357w, 1242m, 1163m, 1027s, 1020(sh), 891m, 880w, 837, 815m, 802m, 776m, 671m, 522s, 497m, 484w, 475w.

1,3-Dithia-2,2-dimethylgermyl[3]ferrocenophane

This compound was prepared similarly, from dichlorodimethylgermane. However, the reaction mixture was heated to 50° C. It was sublimed at 125° C/ 0.3 mmHg and obtained as orange crystals, m.p. 187—188° C, yield 75%.

Anal.: Found: C, 41.85; H, 4.13; S, 17.99. $C_{12}H_{14}FeGeS_2$ calcd.: C, 41.09; H, 4.02; S, 18.28%. PMR ($DCCl_3$): δ (ppm) 1.05 (6 H, s) 3.99 (4 H, t, J 2 Hz) 4.20 (4 H, t, J 2 Hz). IR: 3075w, 1415m, 1380w, 1365m, 1230m, 1166m, 1162m, 1127s, 1122(sh), 892s, 843s, doublet, 815s, doublet, 804s, 746w, 720w, 615m, 610w, 583m, 522s, 487s, 480m.

1,3-Dithia-2,2-dimethylstannyl[3]ferrocenophane

A procedure similar to that described above gave orange crystals from dichlorodimethylstannene, m.p. 163—165° C, yield 94%.

Anal.: Found: C, 36.18; H, 3.55; S, 16.59. Calcd. for $C_{12}H_{14}FeS_2Sn$: C, 36.31; H, 3.56; S, 16.16% PMR ($DCCl_3$): δ (ppm) 0.89 (6 H, s), 3.98 (4 H, t, J 2 Hz), 4.13 (4 H, t, J 2 Hz). IR: 3105w, 1415m, 1390w, 1360w, 1193, 1186m, 1162s, 1155s, 1047w, 1040w, 1030m, 1022s, 890s, 888w, 843w, 835w.

1,3-Dithia[3]ferrocenophane

This complex was obtained from diiodomethane, in 80% yield, after 6 h of reflux as yellow crystals, m.p. 183—184° C (sealed tube); the material sublimes at 148° C in a sealed tube.

Anal.: Found: C, 50.37; H, 3.85; S, 23.95. Calcd. for $C_{11}H_{10}FeS_2$: C, 50.39; H, 3.85; S, 24.46%. PMR (CS_2): δ (ppm) 3.94 (4 H, t, J 2 Hz), 4.05 (2 H, s), 4.20 (4 H, t, J 2 Hz). IR: 3080w, 3060w, 2975m, 2915w, 1395m, 1365m, 1340m, 1205w, 1202w, 1190m, 1167s, 1160(sh), 1144w, 1053w, 1046w, 1035w, 1025(sh), 1019s, 1015s, 895s, 862m, 853m, 839m, doublet, 824s, 734(sh), 720w (br), 693s, 645w, 618m, 583w, 521s, doublet, 510s, 497s, 425w.

1,3-Dithia-2,2-dimethyl[3]ferrocenophane

To a 50 ml round-bottomed flask equipped with a vacuum jacketed Vigreux column and distillation head, was added 0.155 g (0.62 mmol) ferrocene-1,1'-dithiol, 0.5 ml reagent acetone, 30 ml anhydrous benzene and a few crystals of *p*-toluene sulfonic acid monohydrate. The solution was heated slowly to reflux, and the water and excess acetone were removed by distillation until a total volume of ca. 10 ml was removed. The remaining solvent was removed in vacuo, and the residue sublimed (130°C/0.3 mmHg) to yield 0.46 g (74%) of orange product. An analytical sample was prepared by recrystallization from hexane/benzene, m.p. 154—156° C.

Anal.: Found: C, 53.67; H, 5.01; S, 21.91. Calcd. for $C_{13}H_{14}FeS_2$: C, 53.80; H, 4.86; S, 22.09%. PMR ($DCCl_3$): δ (ppm) 1.95 (6 H, s), 4.06 (4 H, t, J 2 Hz), 4.34 (4 H, t, J 2 Hz). IR: 3070w, 1400w, 1380w, 1355w, 1200w, 1170s, 1147s, 1104m, 1028s, 1020(sh), 890s, 882m, 853w, 842s, doublet, 828w, 813s (br), 717m, 652w, 610m, 543m, 520m, 502s (br), 485w, 452m, 415w.

1,3-Dithia-2,2-diphenyl[3]ferrocenophane

The yellow-orange crystals (230—245° C dec.) of this complex were obtained in 56% yield from benzophenone. It did not sublime and was recrystallized from toluene/heptane (×2; 2/1, v/v).

Anal.: Found: C, 66.87; H, 4.36; S, 15.65. Calcd. for $C_{23}H_{18}FeS_2$: C, 66.67; H, 4.38; S, 15.48%. PMR ($DCCl_3$): δ (ppm) 3.83 (4 H, t, J 2 Hz), 4.23 (4 H, t, J 2 Hz), 7.37 (6 H, multiplet), 7.70 (4 H, multiplet). IR: 3090(sh), 3070w, 3050m, 3030(sh), 3000(sh), 1480m, 1470(sh), 1440s, 1400m, 1380m, 1350w, 1318m, 1188w, 1180w, 1167m, 1158m, 1142w, 1076m, 1056w, 1032s, 1023m, 1003w, 987w, 925w, 893m, 882m, 863w, 852w, 835m, 832(sh), 825m, 816s, 812(sh), 746s, 725s, 704s, 694s, 677w, 643m, 630m, 618w, 612w, 602w, 532s, 512s, 503s, 494s, 476m, 442m.

1,3-Dithia-2-phenyl[3]ferrocenophane

This complex was obtained as yellow crystals (63%) that decomposed on melting (210° C dec.). They could not be sublimed and were purified by crystallization from benzene/hexane.

Anal.: Found: C, 60.28; H, 4.14; S, 18.84. Calcd. for $C_{17}H_{14}FeS_2$: C, 60.36; H, 4.17; S, 18.96%. PMR ($DCCl_3$): δ (ppm) 3.88 (2 H, m), 4.32 (4 H, m), 5.18 (1 H, s), 7.37 (5 H, m). IR: 3100w, 3080w, 3050w, 3015w, 1490m, 1445m, 1405m, 1380m, 1175w, 1168w, 1162w, 1072w, 1062w, 1050w, 1030w, 1018w, 890m, 850m, 843w, 820m, 810s, 697s, 615m, 520m, 501m, 495w, 473w, 444w.

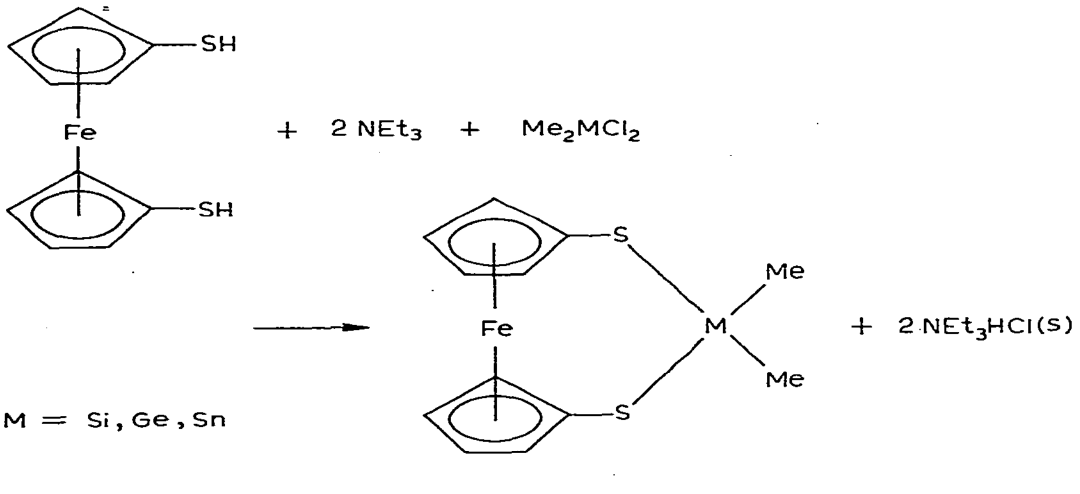
Bis(ferrocene-1,1'-dithiolato)tin(IV)

To a solution of 0.372 g (1.49 mmol) of ferrocene-1,1'-dithiol in 25 ml anhydrous ethanol in a 50 ml beaker, was added 0.336 g (1.49 mmol) $SnCl_2(H_2O)_2$. The solution turned from yellow to red and slowly deposited golden crystals with a bright metallic reflex. This suspension was heated to approximately 50° C for thirty minutes, and the ethanol removed in vacuo. The remaining yellow material was extracted with hot benzene (4 X 20 ml) to yield a red solution. The volume was reduced to ca. 20 ml by boiling on a hot plate, and gave, on cooling, 0.214 g (55%) of red crystals with a gold reflex. An analytical sample was prepared by recrystallization from toluene, dec. 250° C. The identical product was obtained by the reaction of ferrocene-1,1'-dithiol with $SnCl_4$ in benzene in the presence of triethylamine.

Anal.: Found: C, 40.17; H, 2.71; S, 20.61. Calcd. for $C_{20}H_{16}Fe_2S_4Sn$: C, 39.06; H, 2.62; S, 20.85%. IR: 3095w, 3080w, 3065w, 3050w, 1405m, 1385m, 1355w, 1160s, 1155(sh), 1050m, 1042w, 1025s, 1020s, 1012m, 890(sh), 885m, 870(sh), 855w, 842m, 825w, 815s, 805s, 512s, 494s, 482m, 478w.

Results and discussion

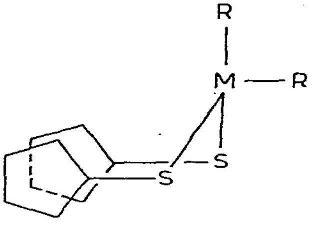
The reaction of ferrocene-1,1'-dithiol in benzene with dimethylsilicon, germanium and tin dihalides in the presence of two equivalents of triethylamine gave good yields of the [3]ferrocenophanes.



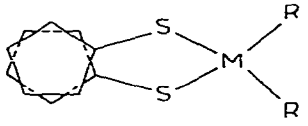
They are air stable yellow-orange crystalline solids which are sublimable in vacuo. A similar reaction with diiodomethane in refluxing benzene, for six hours, gave 1,3-dithia[3]ferrocenophane. Acid catalyzed condensation reactions with aldehydes and ketones were used to prepare the 2-phenyl, 2,2-diphenyl and 2,2-dimethyl derivatives.

The room temperature PMR spectra are deceptively simple, and characteristically have a closely spaced pair of triplets for the cyclopentadienyl protons in the range δ = 3.8—4.4 ppm, similar to those found in symmetrically disubstituted ferrocenes (*AA'BB'* spectra with J_{AB} and $J_{A'B}$ or $J_{B'A}$ approximately equal) and smaller than the chemical shift difference ($\delta_A - \delta_B$). Rosenblum first observed that the parent [3] and [4]ferrocenophanes [6] were fluxional molecules and their relatively simple 40° C spectra were the result of a dynamic process which was fast on the NMR time scale. The dimethyl compounds exhibited a sharp singlet for the time averaged methyl resonances.

A series of variable temperature (VT) PMR studies were undertaken to determine qualitatively how the various structural features of this group of [3]ferrocenophanes influenced their fluxional behavior. The low temperature limiting spectra obtained for the 2,2-disubstituted-1,3-dithia[3]ferrocenophanes allowed an unambiguous assignment between the two possible limiting conformations (I and II). While an ABCD pattern would be expected for the ring protons in both conformations, the substituents on the 2-atom in the eclipsed conformation (I) would lie in the mirror plane and be magnetically non-equivalent and in the staggered conformation (II), they would be related by a two-fold rotation axis and be magnetically equivalent.



(I)



(II)

M = C

R = H or Me

The VT spectra of 1,3-dithia[3]ferrocenophane are shown in Fig. 1. The high temperature limiting spectrum consists of a symmetrical pair of triplets for the ring protons and sharp methylene singlet. On lowering the temperature from 20 to —20° C the following features are readily apparent. All of the resonances show a chemical shift temperature dependence. This is most marked for the methylene resonance with shifts to higher fields and simultaneously broadens. In this interval the triplet at higher field broadens markedly while the triplet at lower field remains relatively sharp. At —40° C only the broad methylene resonances and the slightly broadened lower field triplet are apparent. By —60° C, the spectrum is largely collapsed. At —80° C the ring protons exhibited an *ABCD* pattern, and the methylene protons appear as an *AB* pattern in which

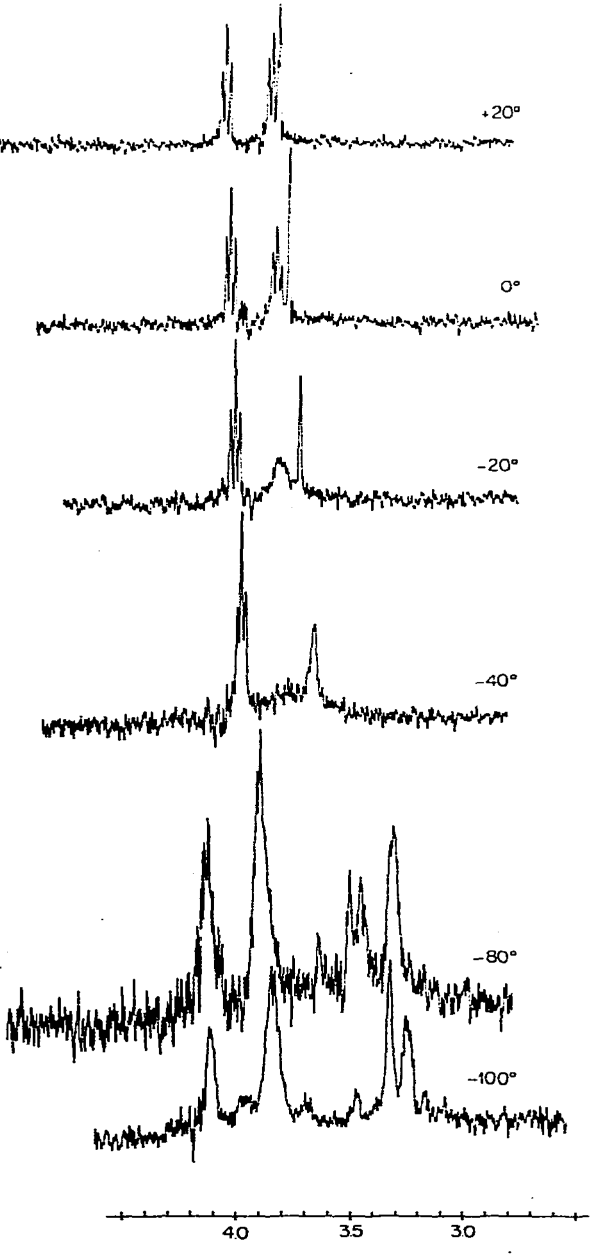


Fig. 1. The variable temperature 60 MHz PMR spectra of 1,3-dithia[3]ferrocenophane in dueterotoluene/carbondisulfide, 1/1, v/v.

J_{AB} is comparable to the chemical shift difference ($\delta_A - \delta_B$). The change in the spectrum between —80° C and —100° C can be attributed to the variation in the chemical shift difference of the magnetically non-equivalent methylene resonances as a function of temperature. This lowers $\delta_A - \delta_B$ and produces the three line pattern observed at —100° C.

Similar spectral changes shown in Fig. 2 occurred for 1,3-dithia-2,2-dimethyl-

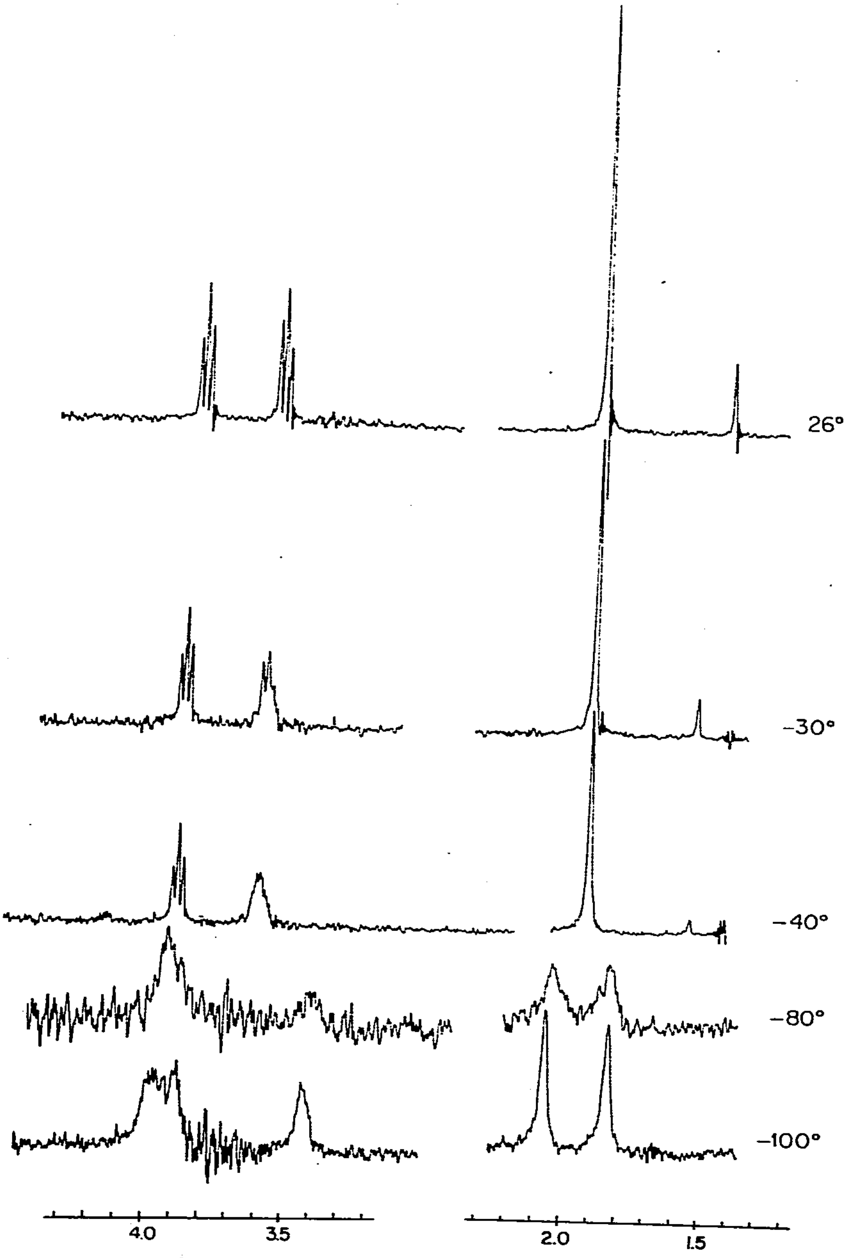


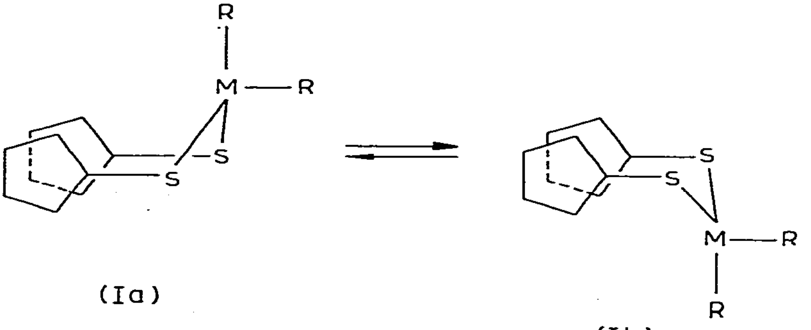
Fig. 2. The variable temperature 60 MHz PMR spectra of 1,3-dithia-2,2-dimethyl[3]ferrocenophane in fluorodichloromethane/chlorodifluoromethane, 3/1, v/v. The resonance at δ 1.45 ppm is an impurity.

[3]ferrocenophane. At —30° C the higher field triplet and methyl singlet show marked broadening and by —70° C the spectrum is largely collapsed. Between —80 and —100° C two methyl resonances are apparent and the ring protons display an emerging *ABCD* pattern. Low solubility of this derivative precluded spectral studies at lower temperatures, but it is clear from these spectra that the

eclipsed conformation (I) is the limiting one for the dihydro and dimethyl substituted carbon derivatives.

The PMR spectra of the dimethylsilicon and germanium derivatives at —115 and —130° C, respectively, closely resembled the features of the dimethylcarbon analogue at —40° C. In both cases there was marked broadening of the methyl resonances which clearly indicated that the eclipsed limiting conformation (I, M = Si, Ge; R = Me) was still favored for both molecules. The low solubility of these complexes prevented further studies at lower temperatures. The tin derivative was even less soluble and spectra below —50° C were not obtained. At this temperature, however, none of the spectral changes evident in the germanium and silicon derivatives were observed.

All of the spectral changes described above were concentration independent and were completely reversible with temperature. Studies on 1,3-dithia[3]-ferrocenophanes in a number of solvents showed that chemical shifts in the high and low temperature limiting spectra were both solvent and temperature dependent. It is thus clear that for 1,3-dithia[3]ferrocenophane and the 2,2-dimethyl derivatives of carbon, silicon and germanium the fluxional process is one which takes the molecule from conformation Ia to Ib. This process will quite clearly interchange the magnetically non-equivalent R groups and simultaneously interchange pairs of protons at the 2,5 and 3,4 positions of the rings in accord with the observed spectral changes. This process can most easily be envisaged as occurring by mutual rotation and tilting of the rings to give an intermediate configuration similar to II. However, it is not possible to say whether this configuration is a high temperature intermediate or just a transition state.



(Ia) (Ib)

It is apparent from a qualitative comparison of the spectra that the barrier to the fluxional process of these [3]ferrocenophanes is lowered as the bridge size increases from carbon to tin. If the eclipsed configuration is maintained throughout this series, Dreiding molecular models indicate that the rings will be tilted outward at the bridge head carbons for the germanium and tin derivatives. This distortion could be relieved by rotating the rings to a staggered conformation. It appears that as the staggered conformation becomes less distorted, and perhaps even favored, that the energy difference between the two conformations I and II, and the barrier to fluxional motion from one through the other is lowered.

An example of the effect of substituents on the stereochemistry in this sys-

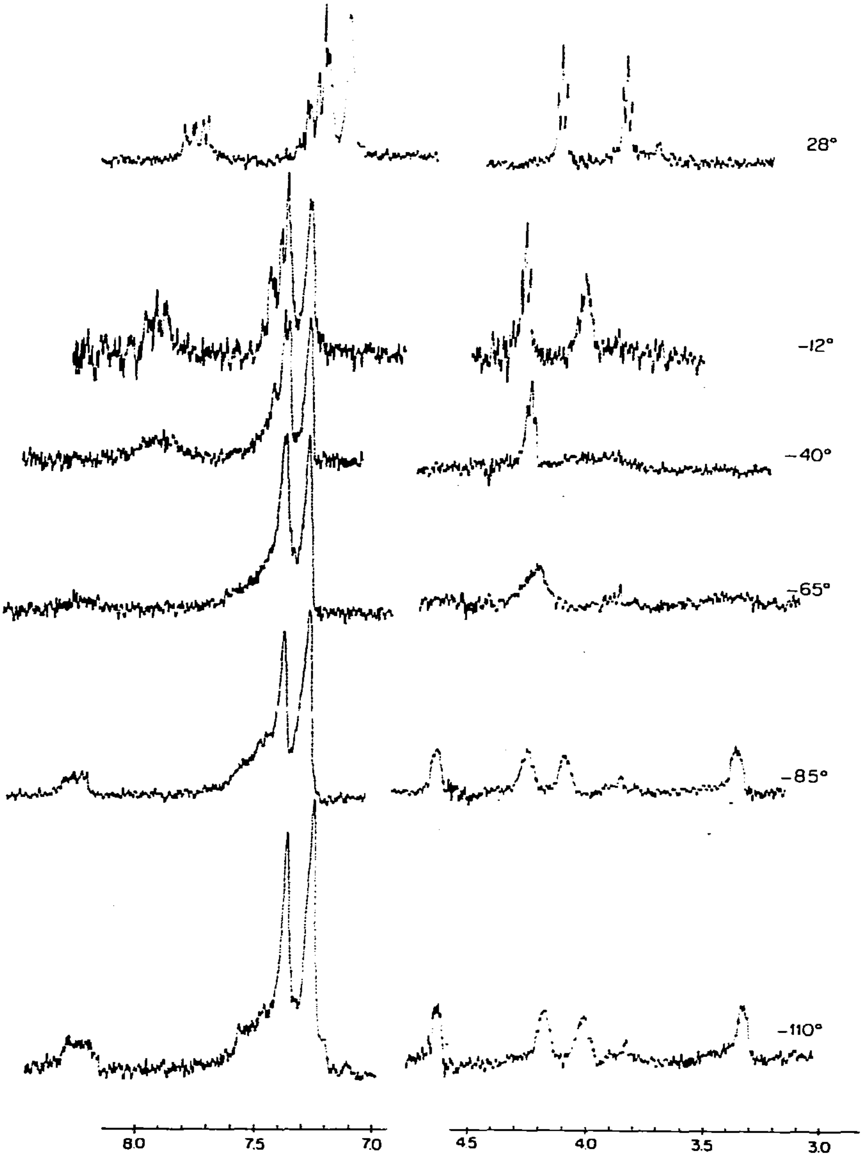


Fig. 3. The variable temperature PMR spectra of 1,3-dithia-2,2-diphenyl[3]ferrocenophane in deuterotoluene/carbondisulfide, 1/1, v/v. (The marked chemical shift variation as a function of temperature is clearly seen on the low field triplet in the 28 to —65° C spectra.)

tem has also been found. Variable temperature PMR spectra in Fig. 3 of 1,3-dithia-2,2-diphenyl[3]ferrocenophane showed changes similar to the methyl and unsubstituted analogue, but with some distinct differences. The *ABCD* pattern of the low temperature limiting spectrum exhibits a marked increase in the chemical shift differences between the four areas of resonance. More significantly, there are virtually no changes in the absorbances of the phenyl protons throughout the temperature range.

Molecular models of the eclipsed configuration indicated a severe crowding of the *ortho* protons of the *endo* phenyl group with the ring protons adjacent to the bridge. This interaction could be effectively relieved by rotating the rings to the staggered conformation. While this conformation requires a moderate

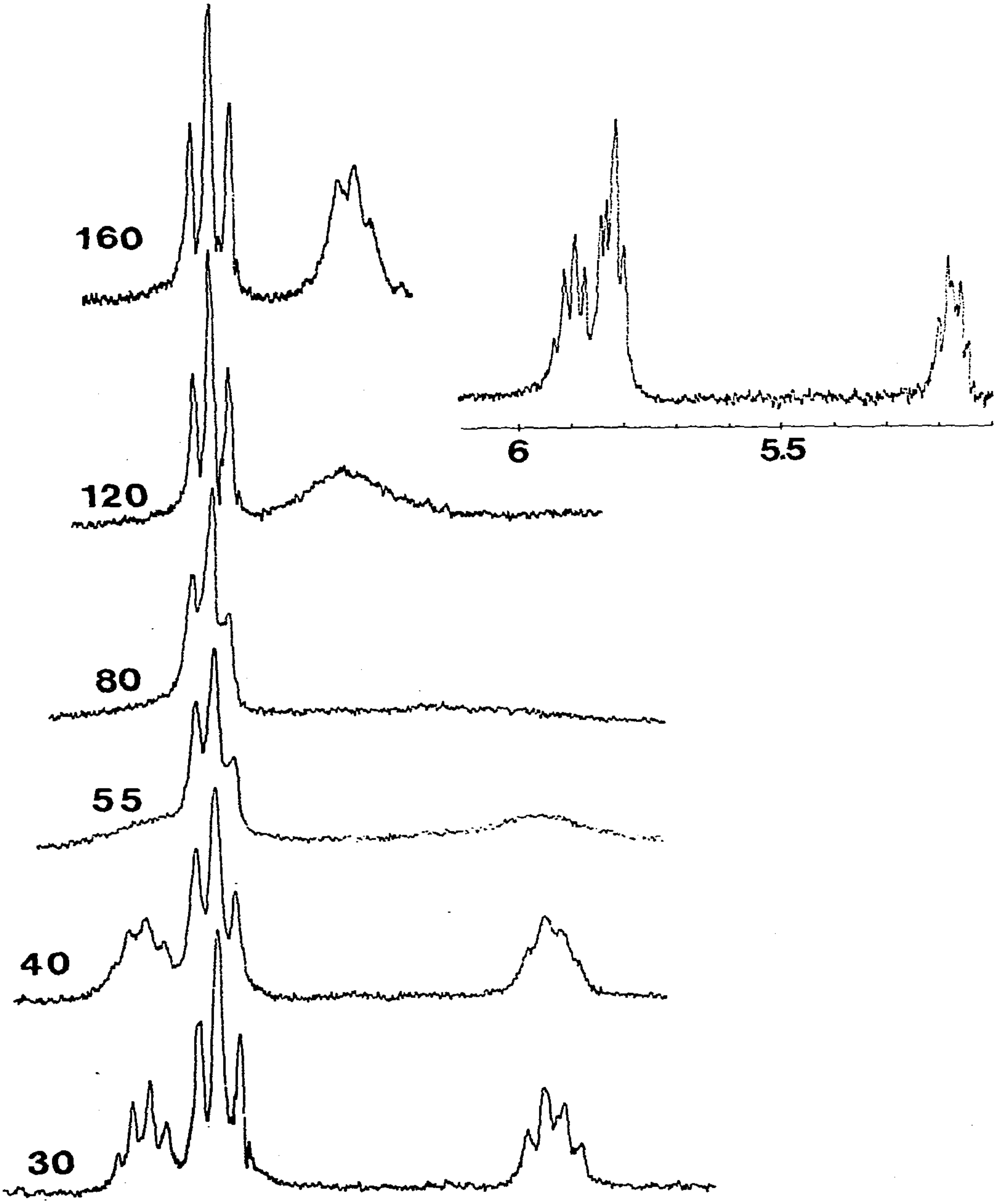


Fig. 4. The variable temperature PMR spectra of 1,2,3-trithia[3]cobalticiniumophane hexafluorophosphate in dimethylsulfoxide from a Hitachi—Perkin—Elmer 60 MHz spectrometer. The prominent peaks in each of the three regions in the 30°C spectrum are at δ 5.42, δ 6.08, δ 6.17 ppm. The insert is the —10°C spectrum in acetonitrile-d_3 at 100 MHz.

amount of inward ring tilt at the bridge head carbons, it appears to be less than that in [2]ferrocenophanes [7].

Thus, it appears that the steric requirements of the phenyl groups in 1,3-dithia-2,2-diphenyl[3]ferrocenophane, cause the molecule to adopt the chiral low temperature limiting conformation II in preference to the eclipsed conformation I. The fluxional process in this molecule is, in essence, an intramolecular racemization.

The monosubstituted 1,3-dithia-2-phenyl[3]ferrocenophane displayed an *ABCD* pattern at room temperature. This pattern resembled that found in the low temperature limiting spectra of the unsubstituted derivative and was distinctly different from the 2,2-diphenyl derivative. Variable temperature PMR spectra from —63 to 110° C showed virtually no changes other than changes in the chemical shift of the 2-hydrogen and there was no evidence for some detectable concentration of another isomer. Clearly this compound has an eclipsed conformation of the rings with the phenyl group in the sterically less hindered *exo* position.

The known iron and cobalt 1,2,3-trithia[3]metallocenophane complexes [1,5], were found to be fluxional molecules. The 100 MHz PMR spectrum of $[(\eta^5\text{-}C_5H_4)S_3Co]PF_6$ at —10° C in CH_3CN and the 60 MHz variable temperature studies in DMSO-d_6 in the range 20—180° C are shown in Fig. 4. The 100 MHz PMR spectrum $[(\eta^5\text{-}C_5H_4)_2S_3Fe]$ at 26° C in CS_2 is well resolved and is shown in Fig. 5. The variable temperature PMR spectrum of the iron derivative in a number of solvents is similar to that for the cobalt compound. The onset of spectral changes is about 50° C higher and the highest temperature spectra at 170° C resembled the cobalt 120° C case. It is clear that these isoelectronic complexes have similar structures in the low temperature limit. The iron complex displays its low temperature limiting spectrum below 50° C. The PMR spectrum of

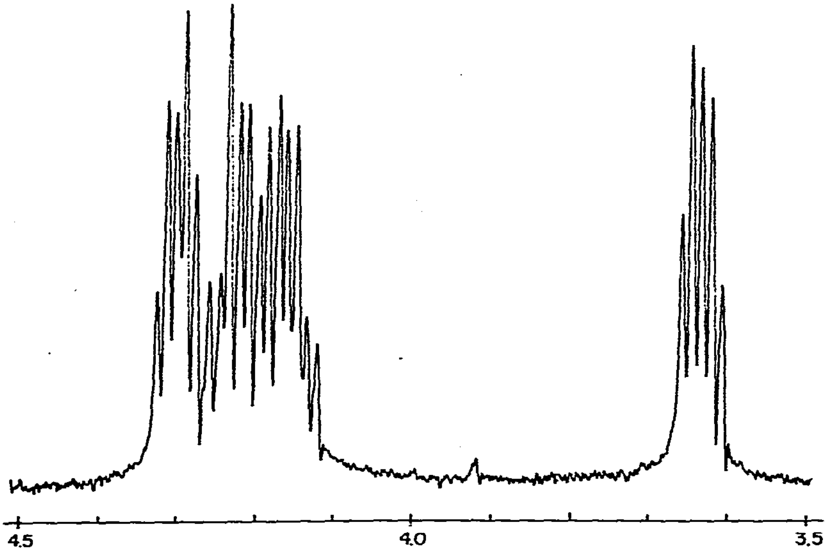
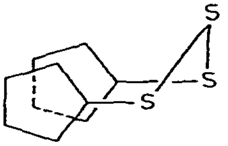
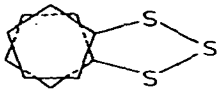


Fig. 5. The 100 MHz PMR spectrum of 1,2,3-trithia[3]ferrocenophane in carbon disulfide at 26°C.

$[(\eta^5\text{-}C_5H_5)S_3Fe]$ is quite complex and markedly solvent dependent. A symmetrical four multiplet pattern is observed in benzene. Homonuclear spin decoupling confirmed that the protons associated with each multiplet were mutually coupled and the spectrum was of the type *ABCD*. The complete range of low temperature to high temperature limiting spectra for both molecules was not achieved due to decomposition in solvents at temperatures greater than ca, 160° C. However, the main features are apparent in the observed spectra. In the range 20—40° C for the cobalt complex (50—80° C for the iron case), the outer multiplets broaden and lose fine structure while the inner multiplets average to a well resolved triplet, which undergoes no further change with increasing temperature. As the temperature is raised the outer multiplets first collapse and then emerge a single feature at ca. 60° C for the cobalt complex (ca. 110° C for iron). This feature continues to sharpen and a poorly resolved triplet structure is seen at ca. 120° C (170° C for iron). By 180° C this is a well resolved triplet, but the line widths are larger than those of the low field one. At temperatures above 180° C rapid decomposition occurred. For the iron complex a number of substituted arenes were tried as solvents for temperature greater than ca. 170° C without success. Although the high temperature limiting spectrum could not be reached it is quite clear that it is approaching the *AA'*, *BB'* pattern of a symmetrical pair of triplets for the ring protons that was observed for the other [3]ferrocenophanes of this study. A static eclipsed conformation has generally been assumed [8] for [3]ferrocenophanes. This conformation (III) was favored for 1,2,3-trithia[3]ferrocenophane from the examination of Dreiding ferrocene models. This was confirmed by an X-ray crystallographic determination in which Bernal [9] found almost perfectly eclipsed cyclopentadienyl rings that had a slight inward tilt at the bridge head carbons (dihedral angle ca. 2.85°). The sulfur—sulfur bond distances and bond angles of the bridge were close to those found in other systems. The eclipsed conformation III has a mirror plane C_s symmetry and clearly has four non equivalent hydrogens on each ring. Any mutual rotation of the rings destroys the mirror plane. If this rotation is continued until the rings are staggered to give the C_2 configuration (IV) there is considerable inward tilting of the rings. In this conformation and all of the intermediate conformations between III and IV there are four non-equivalent hydrogens on each ring. The fluxional process for the iron and cobalt compounds must clearly be similar to that described previously for the other eclipsed [3]ferrocenophanes.



(III)



(IV)

A complete analysis of the *ABCD* spectra of the [3]metallocenophanes discussed in this paper was not performed. A detailed line shape analysis including the effects of spin—spin splitting would be required to provide accurate values of the activation parameters. This could not be obtained because the complete spectral range from the high to the low temperature limiting spectra was only achieved in 1,3-dithia[3]ferrocenophane and 1,3-dithia-2,2-diphenyl[3]ferrocenophane. In addition, both of these complexes exhibited a marked temperature dependence of their chemical shifts in both the high and low temperature regions of the spectrum, which would make a comparison of the computed and observed spectra somewhat imprecise.

The qualitative features of the fluxional process and the limiting structures are non-the-less clear. The 1,2,3-trithia[3]metallocenophanes of iron and cobalt have eclipsed conformations and their activation energies must be quite high. The 2,2'-disubstituted [3]ferrocenophanes have much lower activation energies, by probably at least 8—10 kcal/mol. In the dimethyl disubstituted derivatives from carbon through tin, it is qualitatively obvious that the energy barrier to the fluxional process decreases and with the possible exception of tin, that the eclipsed limiting conformation is favored. The 2,2'-diphenyl derivative has a barrier to its fluxional process comparable to the other 1,3-dithia[3]ferrocenophanes, but it is felt to have a limiting structure of C_2 virtual symmetry.

The observation that the limiting structures of the sterically uncrowded [3]ferrocenophanes deduced in this study and that found crystallographically for 1,2,3-trithia[3]ferrocenophane [9] have idealized C_s symmetry is in accord with a "gauche effect".

A "gauche effect" has been defined by Wolfe [10] as "a tendency (of a molecule) to adopt that structure which has the maximum number of gauche interactions between adjacent electron pairs and/or polar bonds".

The eclipsed metallocenophanes with C_s symmetry have gauche conformations of the atoms in the bridge. 1,3-dithia-2,2-diphenyl[3]ferrocenophanes has a C_2 limiting structure, so quite clearly the steric requirements of the phenyl groups must override the "gauche effect".

In the 1,2,3-trithia[3]metallocenophanes, the fluxional process will take the atoms of the bridge from their preferred gauche—gauche configuration, through a total of four electron pair eclipsing interactions. In the intermediate C_2 conformation both sulfur—sulfur bonds will be rotated halfway between gauche and eclipsed, to the *syn*-periplanar configuration. In these molecules the barrier to fluxional behavior will depend upon a number of complex factors such as the energies required to rotate the cyclopentadenyl rings, the barrier to tilt of the rings from their limiting configuration and the barriers to rotation about the bonds which comprise the bridging groups and steric interaction from large substituents. The mutual interplay of these effects determines the energy difference between the limiting and intermediate conformations of the molecule throughout the fluxional process and there is little point in treating these effects separately from the data available.

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