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NEW CHIRAL FERROCENYLAMINE THIOETHER LIGANDS

AND THEIR APPLICATIONS TO CATALYSIS

presented by

Michael Onyekachi Okoroafor

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

Carl H. Brubaker Jr.
Major professor

Date November 14, 1985

NEW CHIRAL FERROCENYLAMINE THIOETHER LIGANDS AND THEIR APPLICATIONS TO CATALYSIS

By

Michael Onyekachi Okoroafor

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ABSTRACT

NEW CHIRAL FERROCENYLAMINE THIOETHER LIGANDS AND THEIR APPLICATIONS TO CATALYSIS

By

Michael Onyekachi Okoroafor

New chiral ferrocenylamine thioether ligands of the type, (R,S)-$C_5H_5FeC_5H_3[CHMeNMe_2][SR]$, R = Me, Et, i-Pr, n-Bu, i-Bu, t-Bu, i-Pentyl, Ph, CH_2Ph, p-tolyl, 4-chlorophenyl, have been prepared by lithiation of optically active N,N-dimethyl-1-ferrocenylethylamine followed by reaction with the appropriate disulfide. These compounds are air-stable and were characterized by use of spectroscopic techniques such as ^1H and ^{13}C NMR, infrared (IR) and mass spectroscopy as well as elemental analysis. These chiral ferrocenylamine thioethers readily chelate platinum and palladium chloride to form the chiral heterobimetallic complexes, (R,S)-$C_5H_5FeC_5H_3[CHMeNMe_2][SR]/MCl_2$, (R = Me, i-Pr, n-Pr, i-Bu, Ph, p-tolyl, 4-chlorophenyl; M = Pd, Pt). ^1H NMR, IR, MS and elemental analysis data were obtained for the chiral complexes. An X-ray crystal structure of (R,S)-$C_5H_5C_5H_3[CHMeNMe_2][SMe]/PdCl_2$ was determined.

The catalytic applications of the chiral complexes were examined. The chiral palladium thioether complexes are effective asymmetric Grignard cross-coupling catalysts. The enantiomeric excess (e.e.) of the asymmetric

cross-coupling product was determined by ^1H NMR spectroscopy in the presence of a chiral shift reagent, Tris(d,d-dicampholylmethanato)europium(III), [Eu(dcm)$_3$]. A possible mechanism of Grignard cross-coupling is proposed.

The complexes are also highly effective as selective hydrogenation catalysts, converting dienes to monoenes at room temperature.

The chiral dialkyldithiocarbamate derivatives, (R,S)-$C_5H_5FeC_5H_3$[CHMe-NMe_2][$SCSNR_2$], R = Me and Et, were prepared by reaction of (R,R)-N,N-dimethyl-lithioferrocenylethylamine with tetraalkylthiuramdisulfide. ^1H and ^{13}C NMR, IR, MS and elemental analysis data were obtained. Dynamic NMR studies indicate that restricted rotation occurs around the carbamate carbon—nitrogen bond in these derivatives and two conformers are present at low temperature. Approximate rotational free energy barriers were determined and were correlated with the "thioureide" band in the infrared.

All things are possible with

those who trust in God.

DEDICATION

In Memory of Our Daughter, Ogechukwu.

ACKNOWLEDGEMENTS

I sincerely appreciate the constant guidance, inspiration and encouragement of Professor Carl H. Brubaker, Jr., throughout this work.

In addition, I would like to thank Dr. C.K. Chang and Dr. W.H. Reusch for many helpful discussions and Dr. L.D. Le, for technical expertise in obtaining NMR spectra. My gratitude also to Dr. D. Ward for his assistance in obtaining the X-ray structures.

I would also like to thank Dr. Beth McCulloch, Dr. Robert V. Honeychuck, Dr. Lie-Hang Shen and all the members of the group for their help and friendship.

To our friends, especially Lewe Okereke, Ike and Chi Ononye, and our God-daughter Katrina, I will always remain indebted.

Finally, my deepest gratitude goes to my wife, Ngozi, and her profound love, unrivalled understanding, great patience, professional assistance in interpreting some of my results and prayers throughout this work, and to my mother and her love.

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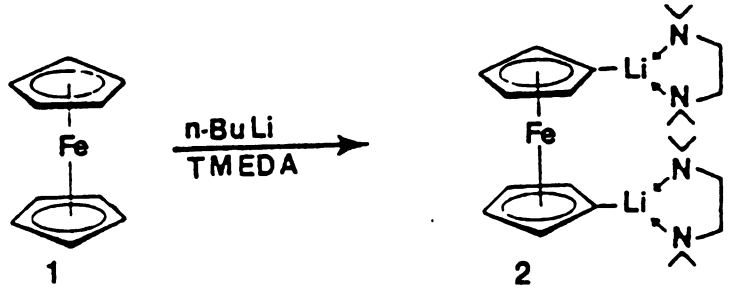
I. INTRODUCTION

INTRODUCTION

Ferrocene chemistry has generated much interest since its discovery in 1951,[1] primarily due to stability and unusual reactivity. It readily undergoes a variety of aromatic substitution reactions such as acylation, alkylation, formylation, mercuration and sulfonation.[2] Most of these substitution reactions are electrophilic and are limited to electrophiles which do not oxidize the iron atom or destroy the cyclopentadienyl ring-metal bond.

Metallation reaction complements electrophilic substitution in that it provides an alternate route to introducing reactive functional groups on ferrocene.

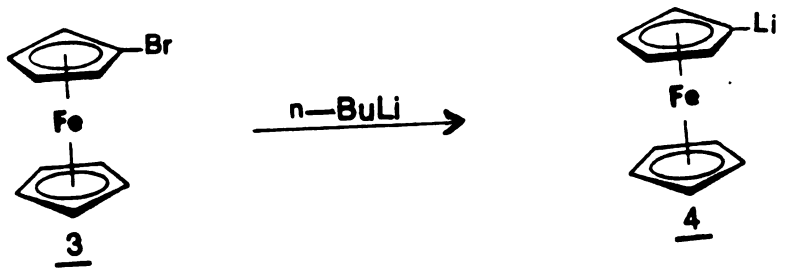
Metallation may be achieved by the reaction of ferrocene with n-butylithium, amylsodium or phenylsodium.[3] Ferrocene is dilithiated in over 90% yield by a mixture of n-butyllithium and tetramethylethylenediamine (TMEDA).[4] The dimetallated species could be isolated as a pyrophoric red-orange crystals where TMEDA chelates the dilithium reagent. Application of the lithium reagent isolated as a pure solid, rather than the in situ slurry, results in higher yields in the subsequent reaction with electrophiles.



1 2

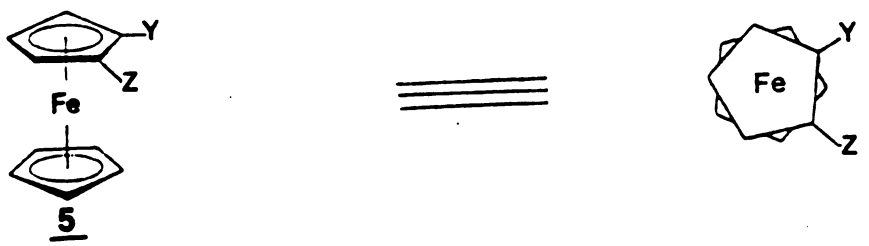
In contrast to the dilithioferrocene, synthesis of monolithioferrocene by addition of stoichiometric amounts of n-butyllithium/TMEDA to ferrocene results in

a mixture of monolithiated and dilithiated species.[5] Another route to lithioferrocene where alkyllithium is added to chloromercuriferrocene produces a reactive dialkylmercury compound that forms undesirable side products.[6] High yields of lithioferrocene, with no concurrent dilithiation, is however obtained by reaction of n-butyllithium and bromoferrocene.[7]



3 4

Although the chemistry of ferrocene derivatives resembles that of benzene derivatives, important differences between them arise, when the stereochemistry of these systems is considered. The stereochemistry of metallocene derivatives has generated much interest in the past.[8-12] This interest is due, in part, to the recognition that ferrocene derivatives are chiral if one ring carries two different substituents (5).[11] Optical activity, however, arises because there is no S_n axis.[11,13] Both the central and planar elements of chirality could be manifested in such disubstituted ferrocene



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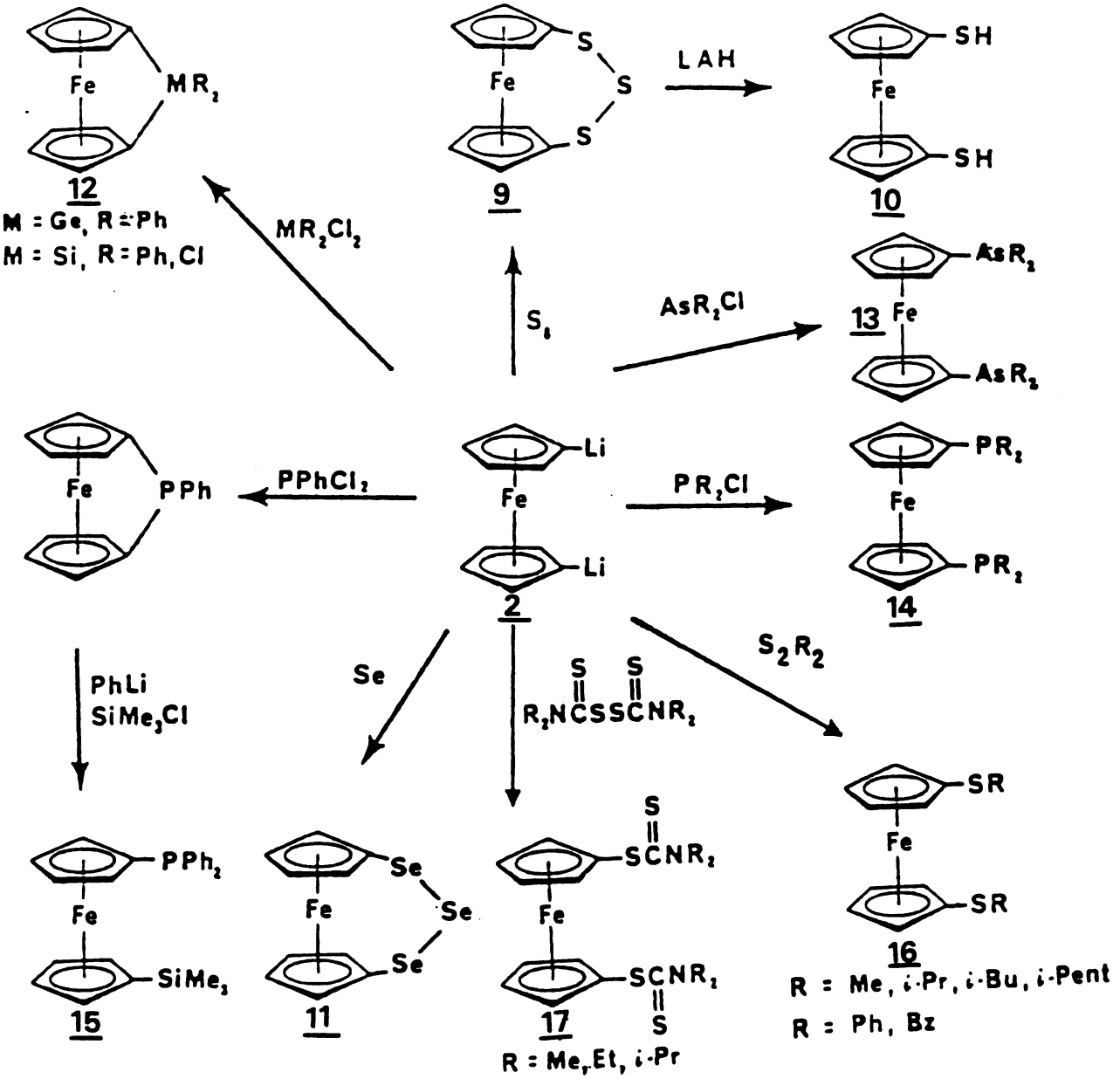
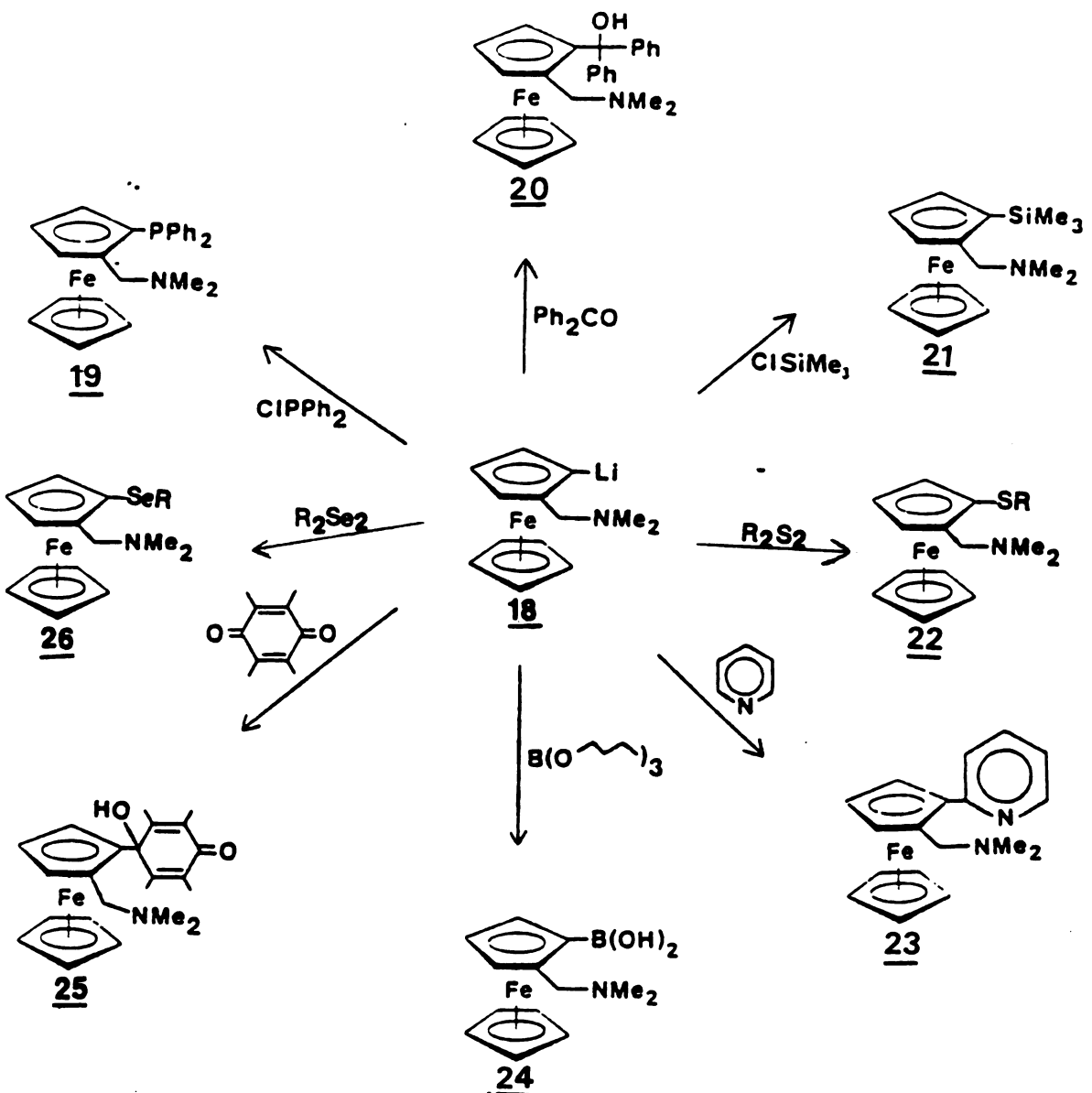
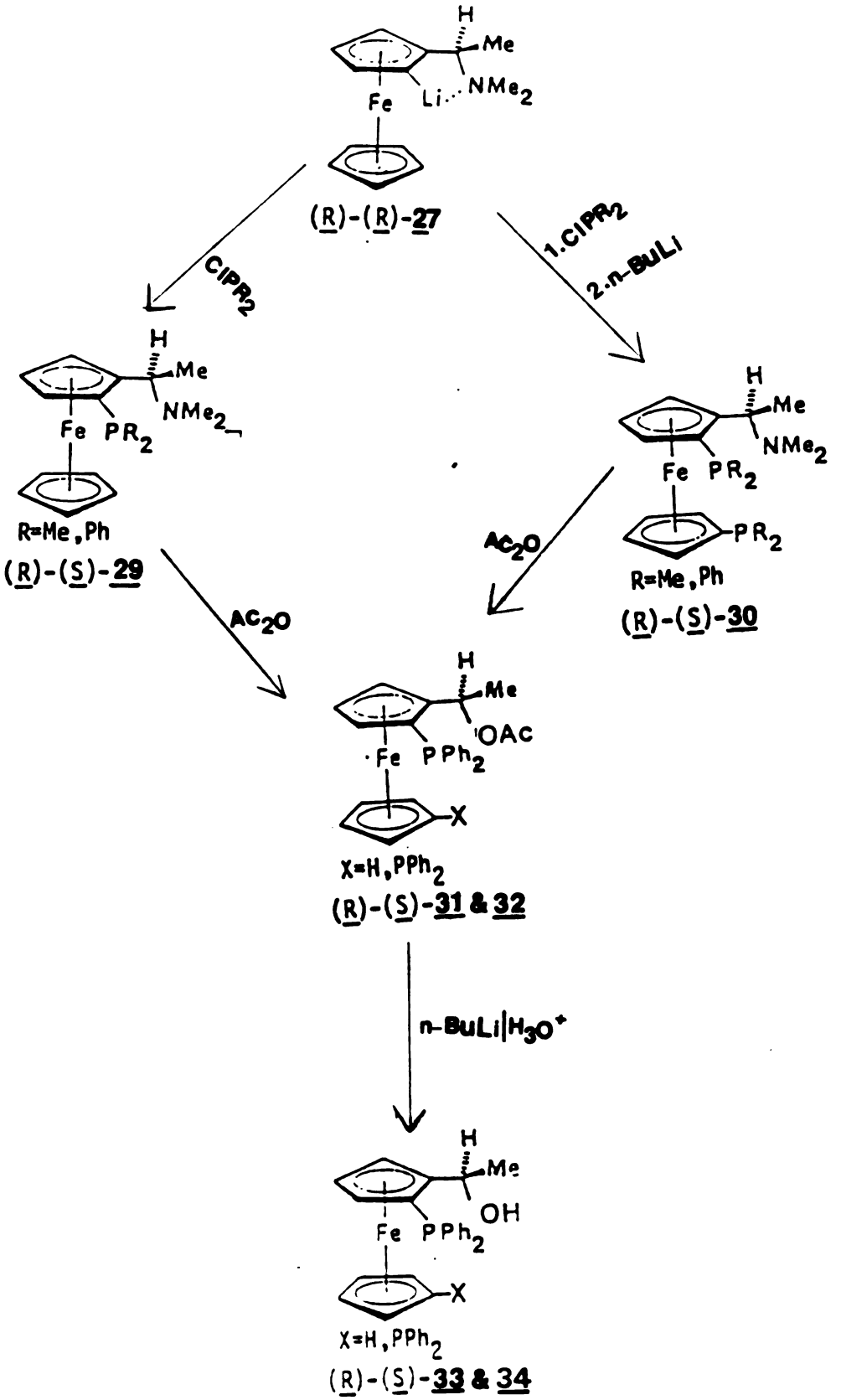


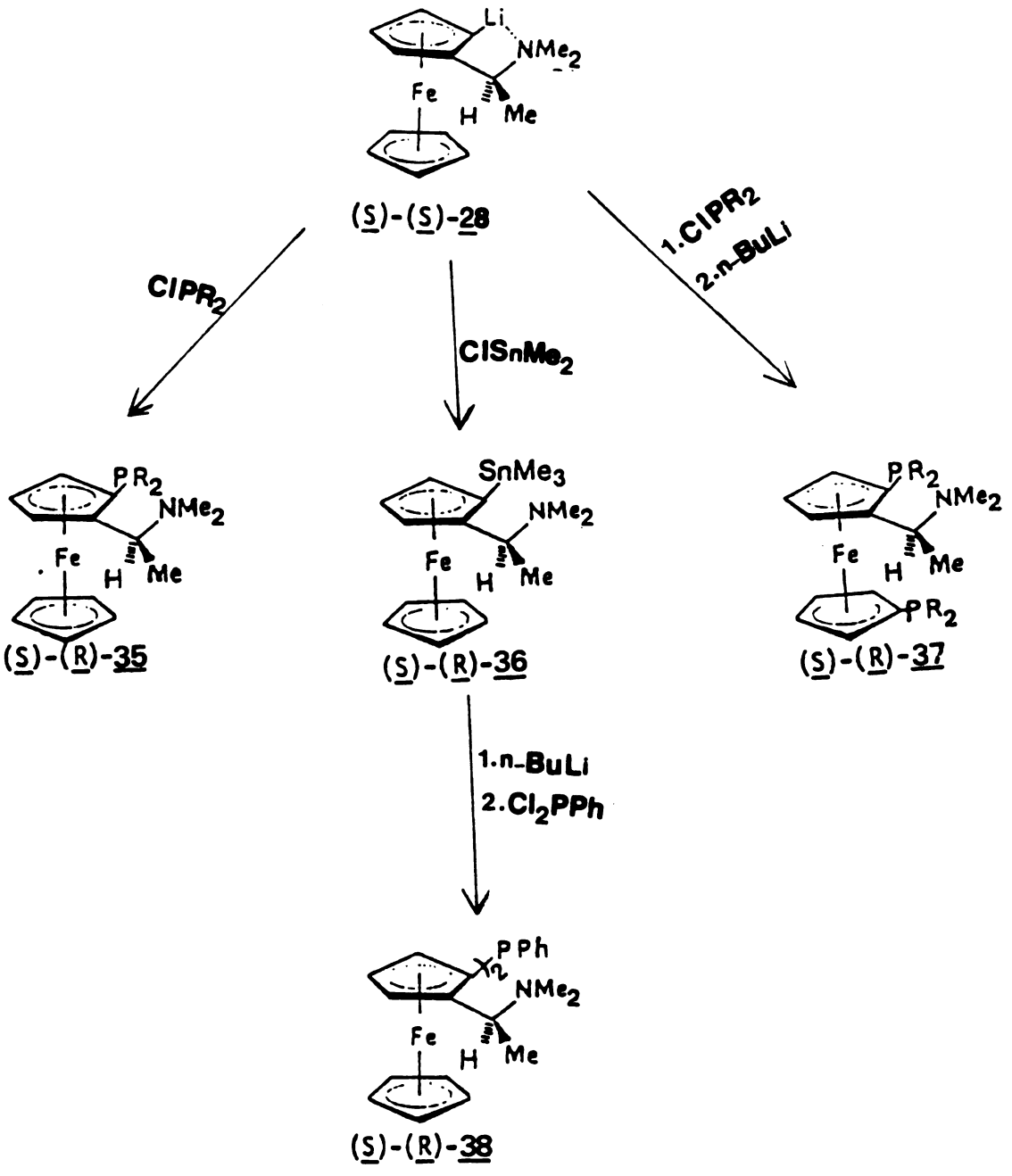
Scheme 1: Some Characteristic Reactions of Dilithioferrocene.



Scheme 2: Selected Reactions of 1-Dimethylaminomethyl-2-lithioferrocene



Scheme 3: **Some Reactions of (R)-(R)-N,N-Dimethyl-1-Lithioferrocenyl-ethylamine.**



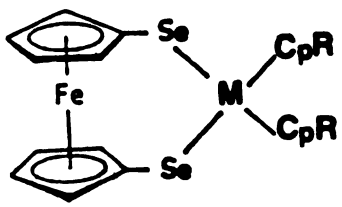
Scheme 4: Some Reactions of (S)-(S)-N,N,-dimethyl-1-Lithioferrocenylethylamine

The organic chemistry of ferrocene and its derivatives is extensive and literally thousands of reactions have been reported. One of the more recent applications is their use as ligands in transition metal complexes.[14-16] Metallation has proved to be a useful synthetic technique for the introduction of potential donors such as phosphines and arsines on to the cyclopentadienyl ring. Schemes 1,2,3 and 4 illustrate the variety of different donor substituents that may be incorporated into ferrocene, dimethylaminomethylferrocene (6), and N,N-dimethyl--1-ferrocenylethylamine (7) respectively. Davison[17] synthesized ferrocenylphosphines and ferrocenylarsines in high yield from 1,1'-dilithioferrocene. Addition of elemental sulfur to dilithioferrocene gave 1,2,3-trithia-[3]-ferrocene (9) which can be reduced quantitatively to 1,1'-dithioferrocene (10). The selenium analog (11) has also been reported.[18]

The [1]ferroceneophanes, which have phosphorus, arsenic or Group 6A elements as the bridging atoms, are another interesting class of compounds that have been obtained from the reaction of dilithioferrocene with $RPCl_2$, $RAsCl_2$[19,20] or R_2MCl_2 (M = Ge, R = Ph; M = Si; R = Ph, Cl)[21] respectively. These compounds exhibit unusual spectroscopic properties as the cyclopentadienyl rings are severely tilted towards the bridge atom. Wrighton and co-workers have used (1,1'-ferrocenediyl)dichlorosilane to derivatize a number of electrode and silica surfaces by opening the highly reactive, strained C-Si-C bond in the ferrocenophane.[22]

The ferrocenophanes are cleaved by alkyllithium reagents to give a ring opened ferrocenyllithium reagent. Subsequent reaction with electrophiles gives rise to ferrocene derivatives with mixed functionality as in (15). Cullen[20] has also reported to preparation of ring-substituted ferrocenophanes with phosphorus and arsenic bridges. These are precursors to chiral ferrocenes with mixed functionality that have important applications in asymmetric synthesis.

Recently Gautheron[23] reported the synthesis of new metalladiselenaferrocenophanes of the type $Fe(\eta^5\text{-}C_5H_4Se)_2M(\eta^5\text{-}C_5H_4R)_2$ (where M = Zr, Hf; R = H, to -Bu) known as [3]ferrocenophenes.



M = Zr, Hf; R = t-Bu, H

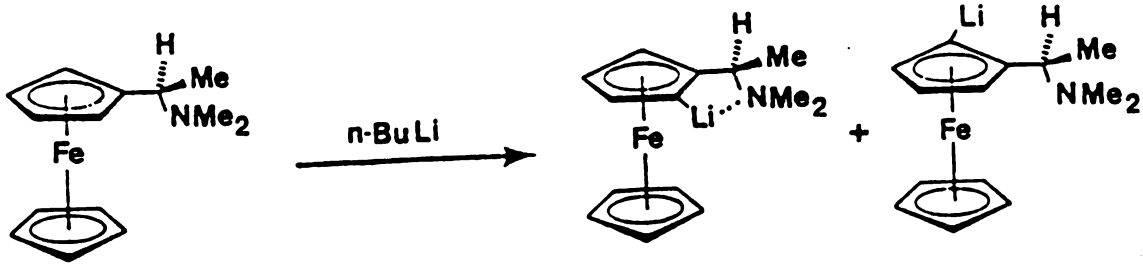
In solution at ambient temperature, these complexes appear to be non-fluxional by a bridge reversal process and show a staggered conformation of the ferrocene moiety.

The coordination chemistry of 19 (Scheme 2, available from 18 via nucleophilic substitution of chlorodiphenylphosphine) with chormium, molybdenum, tungsten, iron, and cobalt carbonyls has been investigated.[14] The ligand was bidentate with the group VIB carbonyls, but monodentate through phosphorus with Fe and Co. Compound 18 adds in Grignard manner to carbonyl species giving 20[24,25] and the addition products of acetylferrocene and acetaldehyde[15,26]. Pyridine undergoes a nucleophilic aromatic substitution to yield 23, whose CoX_2 complexes (X = Cl, Br, and SCN) have been studied.[15]

Marr and co-workers[27] reported that 18 reacts with paraformaldehyde and dimethylformamide giving 1-dimethylaminomethyl-2-hydroxymethylferrocene and 1-dimethylaminomethyl-2-formylferrocene, respectively. Several derivatives of these compounds were reported. Trimethylchlorosilane reacts with 18 to give 21[28] and 18 undergoes reaction with hexachloroethane to give the 2-chloro compound.[29] The latter reaction involves lithium-halogen exchange followed

by β-elimination giving tetrachloroethylene. Tri-n-butyl borate reacts with 18 to yield, after hydrolysis, boronic acid 24,[30] which is an amino acid with the same properties as natural amino acids: it has an isoelectric point and is soluble in aqueous base and acid. More important, 24 undergoes replacement of the boronic acid portion with Cl, Br, and I using cupric chloride, cupric bromide and iodine as the reagents. Finally, various quinones have been added to 18 giving the corresponding Keto-alcohols, eg., 25.[31] An excess of quinone was used and no evidence was found for addition of two molecules of 18 to the quinone.

Chiral ferrocenylphosphines[32] are readily prepared by lithiation of optically resolved N,N-dimethyl-1-ferrocenylethylamine 7, followed by treatment with chlorophosphines. The lithiation of (R)-7 with n-butyllithium was previously reported by Ugi and co-workers[33] to proceed with high stereoselectivity to give preferentially (R)-N,N-dimethyl(-1-[(R)-2-lithioferrocenyl]-ethylamine[(R)--(R)-7].

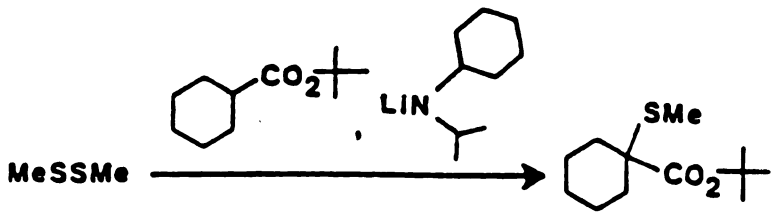


(R)-7 (R)-(R)-27(96%) (R)-(S)-28 (4%)

(R)-N,N-dimethyl-1-[(S)-2-(diphenylphosphino)ferrocenyl]-amine [(R)-(S)-PPfA] (29) and (S)-N,N-dimethyl-1-[(R)-2-(diphenylphosphino)ferrocenyl]ethylamine, [(S)-(R)-PPfA] (35), was obtained in high yield from (R)-(R)-27 and (S)-(S)-28 respectively. The stepwise lithiation of (R)-7 or (S)-7 with n-butyllithium, in ether and with n-butyllithium/TMEDA followed by treatment with chlorodiphenylphosphine led to the introduction of two diphenylphosphino groups, one onto each of the cyclopentadienyl rings to give (R)-N,N-dimethyl-1-[(S)-1',2-bis-(diphenylphosphino)ferrocenyl]ethylamine, [(R)-(S)-BPPfA] (30) or (S)-N,N-dimethyl--1-[(R)-1',2-bis(diphenylphosphino)-ferrocenyl[ethylamine[(S)-(R)-BPPfA](37). The analogous bis(dimethylphosphine) derivatives were also prepared. The preparation of (S)-(R)-38 was achieved by transmetallation of (S)-N,N-dimethyl--1-[(B)-2-(trimethylstannyl)-ferrocenyl]ethylamine 26 that had once been isolated as a precursor for lithioferrocene (S)-(S)-28.[34] The acetate (R)-(S)-31 was converted quantitatively into a ferrocenyl phosphine with the hydroxyl group, (R)-1-1[(S)-1',2-bis(diphenylphosphino)ferrocenyl]ethanol, [(R)-(S)-BPPfOH], (R)-(S)-34, and (R)-1-[(S)-2-diphenylphosphine]ferrocenyl]ethanol [(R)-(S)-PPfOH]-(R)-(S)-33.

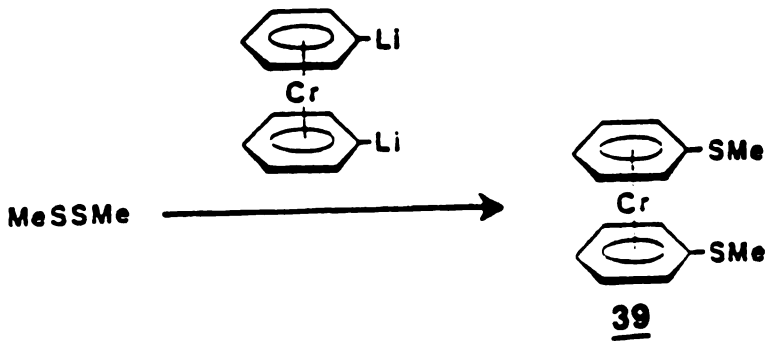
So far it is obvious that there are a multitude of electrophiles that will react with lithioferrocenes 2, 18, 27, and 28. There are also many lithiated compounds that will react with disulfides and diselenides.

The reaction of disulfides with anions has been known for many years, and involves electrophilic rather than nucleophilic sulfur. In organic chemistry, the reaction is used with enolate anions to produce α-sulfenyl carbonyl species (Scheme 5), intermediates on the path to α, β-unsaturated carbonyl compounds.[35-37]



Scheme 5: Reaction of Methyldisulfide with a t-butylester Enolate

In 1981, bis(η^6-benzene)chromium was lithiated and the product reacted with methyl disulfide (Scheme 6)[38].



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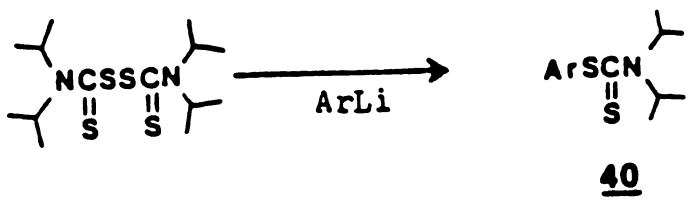
Scheme 6: Reaction of Methyldisulfide with bis(η^6-phenyl Lithium) Chromium

Thioether sandwich complex 36 acted as a chelating agent with $Mo(CO)_4$. Cava's group[39] has found that phenyllithium and a number of lithiated aromatics react with tetraisopropyl thiuram disulfide to give S-aryl-N,N-diisopropyldithiocarbamates (40, Scheme 7). The bulk of the isopropyl groups prevents attack at the thione carbons, in contrast to the tetramethyl analog. With tetraisopropylthiuram disulfide replaced by tetramethylthiuramdisulfide, a major side product,

thioamide, results.

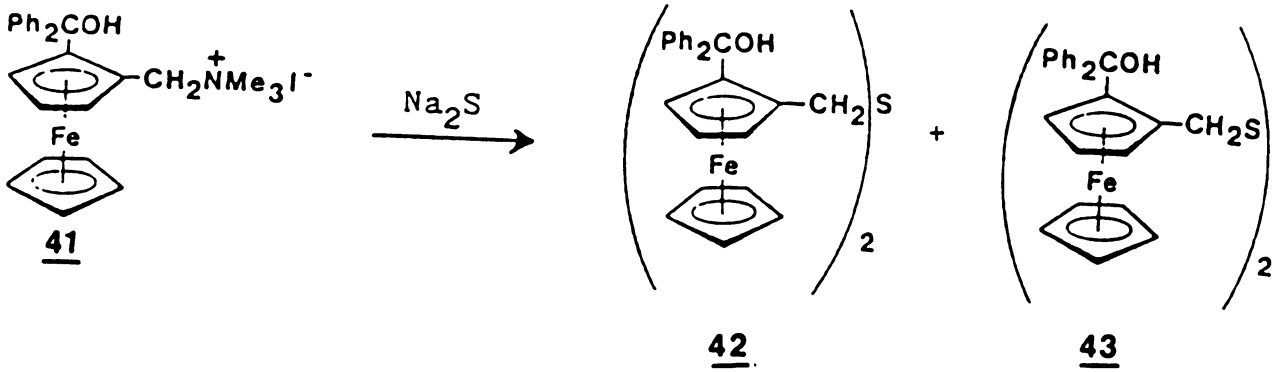


40

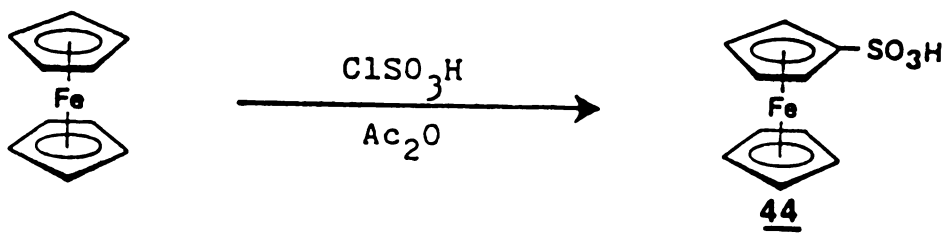
Scheme 7: Reaction of Tetraisopropylthiuram Disulfide with Aryllithium Species

The authors hydrolyzed dithiocarbamates, 40 to the thiols in high yield, so that the sequence represents a new synthesis of aromatic thiols.

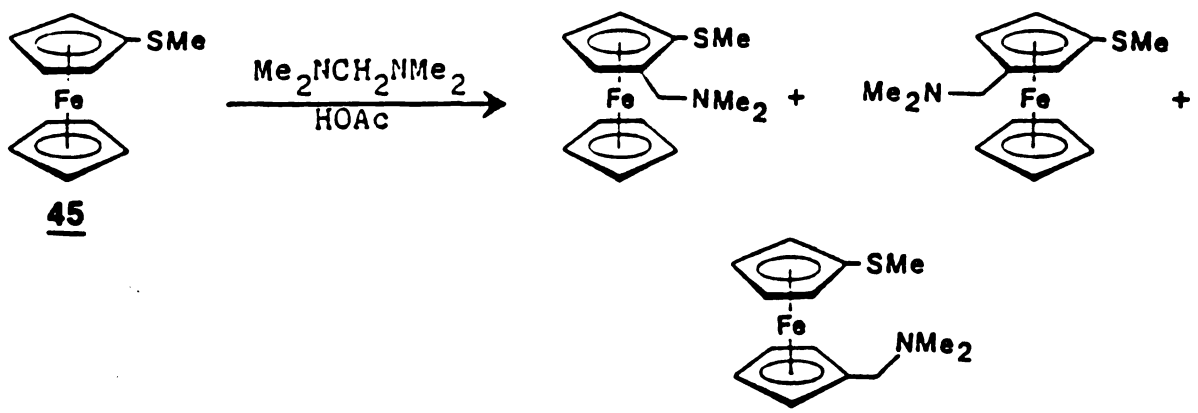
Recently in our laboratory,[40-42] it was found that lithioferrocene and 1,1'-dilithioferrocene react with various disulfides to give thioethers 16 and dithiocarbamates 17 (Scheme 1). Other ferrocene derivatives with sulfur in side chains have been made, but these were the products of a nucleophilic substitution in the side chain (Scheme 8) or electrophilic sulfonation (Scheme 9). Reaction of tetraalkylammonium iodide 41 (Scheme 8), with sodium sulfide gave thioether 42 and disulfide 43.[43] Sulfur was introduced directly to a ferrocenyl ring via electrophilic sulfonation (Scheme 9).[44] Sulfonic acid 44 was converted to the sulfonyl chloride and then the thiol. The thiol was converted to its methyl thioether. The methyl thioether (45, Scheme 10), was subjected to electrophilic substitution with bis(dimethylamino)methane[45].



Scheme 8: **Nucleophilic Substitution Leading to Ferrocenes with Sulfur in the Side Chain**



Scheme 9: **Introduction of Sulfur to a Ferrocene Ring by Electrophilic Aromatic Substitution**



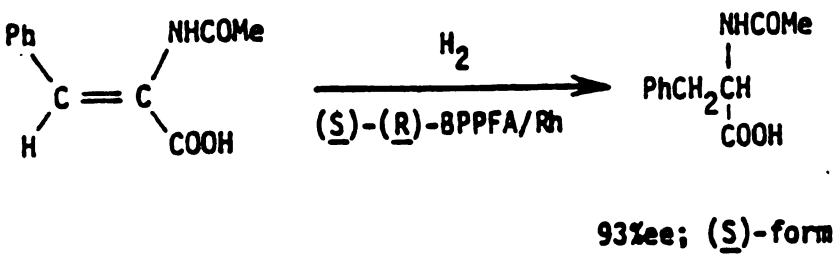
Scheme 10: Aminomethylation of Methylthioferrocene

All three possible monosubstituted products were obtained as was expected from the activating nature of the methylthio group. The lithiation procedure yielding 18, 27, and 28, described previously, offers a distinct advantage over electrophilic substitution in that only a single lithiation product is obtained.

Symmetrically 1,1'-disubstituted ferrocenes Fe(η^5-C_5H_4E), where E is a potential electron donor such as phosphine or arsine, have generated much interest in functioning as rigid chelating ligands.[4,16,17,46-48] In particular, 1,1'-bis(diphenylphosphino)-ferrocene (fdpp) strongly chelates Ni and Pd and such complexes have been shown to exhibit extremely high catalytic activity for selective cross-coupling reactions.[49] Hughes[50] and Christenson[51] have reported that fdpp complexes of rhodium are highly selective hydroformylation catalysts. Brubaker and co-workers[40,41] has reported the properties of some 1,1'-bis(thioether)ferrocene derivatives. We have also reported that the Pd complex of dimethylaminomethylferrocenyl sulfide is an efficient selective

hydrogenation catalyst.[52]

Another recent development in ferrocene chemistry is the use of chiral ferrocene derivatives as ligands in transition metal catalyzed asymmetric synthesis. Rhodium and palladium complexes with chiral ferrocenylphosphine ligands have been used as catalysts in asymmetric hydrogenation,[55-62] Grignard cross-coupling[55,63-70] and hydrosilylation reactions[55,71-73]. In particular, acylamino acids have been produced in 93% optical purity by the asymmetric hydrogenation of α-acetaminocinnamic acids catalyzed by a rhodium complex of (S)-N,N-dimethyl-1-[(R)-1',2-bis(di-phenylphosphino)ferrocenyl]ethylamine. [(S)-(R)-BPPfA] (Scheme 11).



Scheme 11: Asymmetric Hydrogenation by Using [(S)-(R)-BPPFA]

Table 1 shows a number of various possible ligands - mostly bidentate phosphine derivatives. N,N-dimethyl-1-[2-(diphenylphosphino)ferrocenyl]-ethylamine (PPFA) is the parent member of the ferrocene derived ligands. It has two kinds of chirality, one on the side chain (central element of chirality) and a second on the 1,2-disubstituted cyclopentadiene ring.

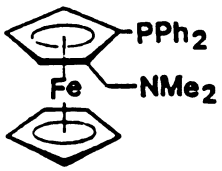
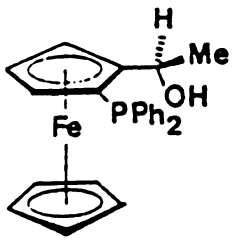
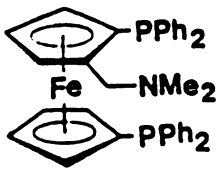
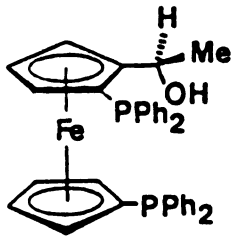
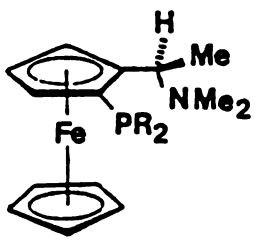
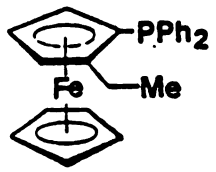
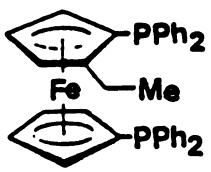
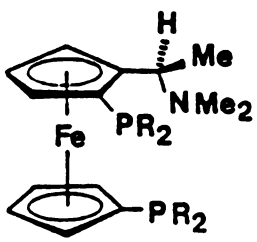
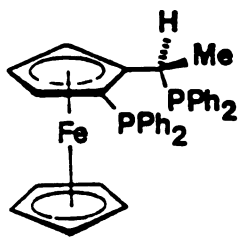
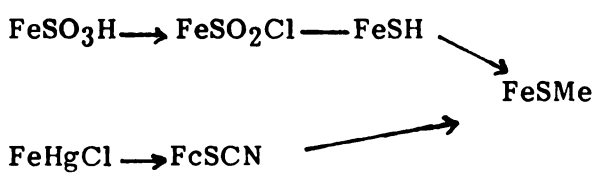
Ligand	Abbreviation	Ligand	Abbreviation
	FcPN		PPFOH
	FcPPN		BPPFOH
	R=Ph; PPFA R=Me; MPFA		PPEF
			BPPEF
	R=Ph; BPPFA R=Me; BMPFA		(1-(2-(Diphenylphosphino)ferrocenyl)ethyl)diphenylphosphine

Table 1. Chiral Ferrocenylphosphines for Asymmetric Catalysts.

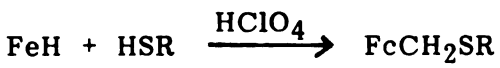
(R)-(S)-PPFA

The aim of this research was to develop a new class of chiral chelating ferrocenyl thioether ligands. The recent interest in transition metal sulfides led to the investigation of the preparation and application of ferrocenyl thio and seleno ethers.[52]

A few ferrocenyl thioether complexes are known. Pauson[44] has reported synthesis of methylthioferrocene from ferrocenesulfonic acid whereas Russian workers[74] prepared this complex from thiocyanatoferrocene



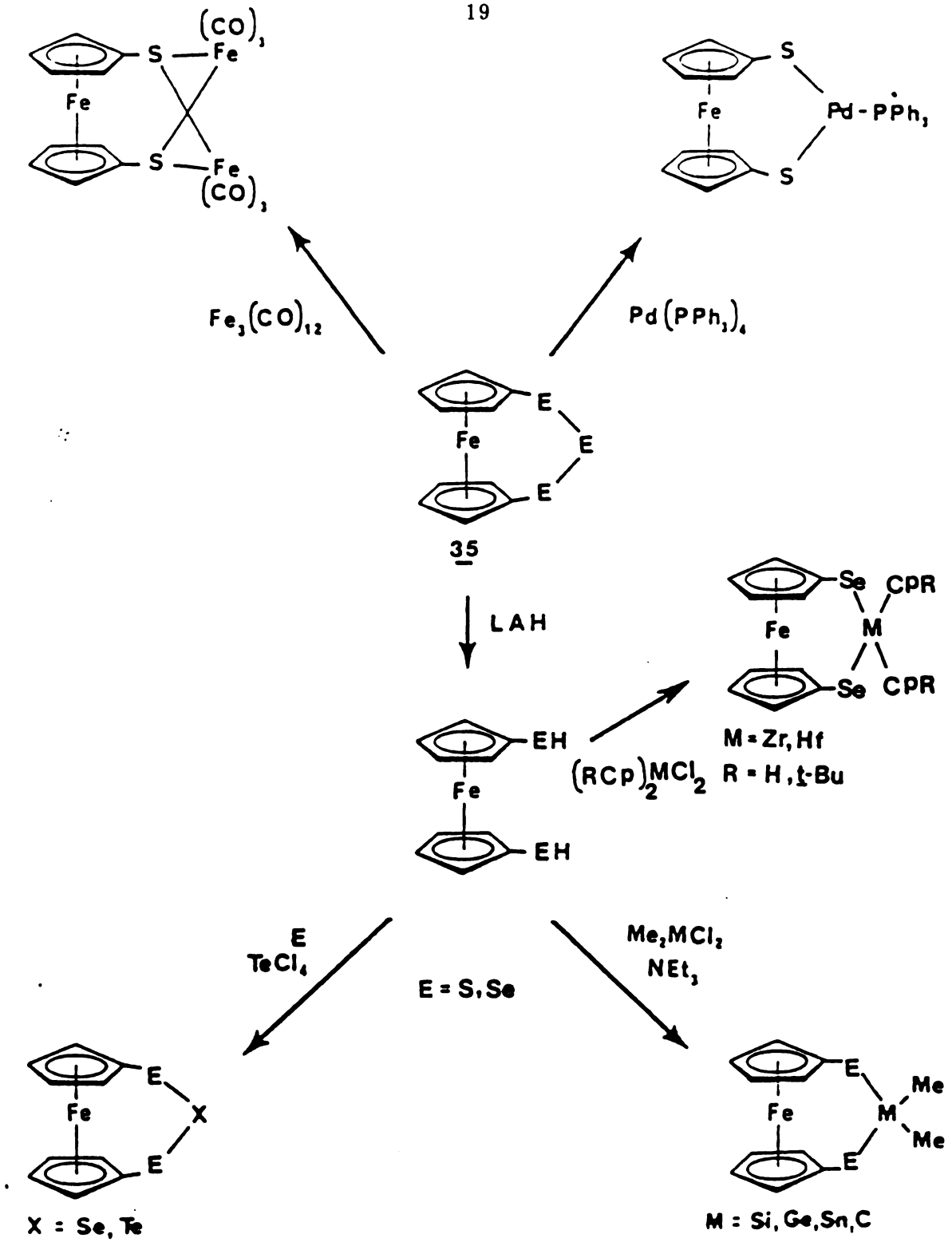
Ferrocenylmethylsulfides have also been prepared from ferrocene and mercaptans in one step syntheses.[75]



These procedures are limited to the preparation of specific ferrocenylsulfide complexes. A new synthetic method[42,52] has been developed similar to that reported by Elschenbroich[38]). This procedure is a one-pot, high yield general synthesis of substituted ferrocenylsulfides and has been applied in this work.

Some metal complexes of these new ferrocenyl thio ether chelating ligands have been prepared and their application as catalysts for selective hydrogenation and asymmetric Grignard cross-coupling reactions examined.

In addition the reaction of tetraalkylthiuram disulfides with 27 was examined.



Scheme 12: Some Ferrocenylsulfide and Ferrocenylselenide Metal Complexes

II. EXPERIMENTAL

EXPERIMENTAL

Air sensitive reagents were manipulated in prepurified argon or nitrogen atmosphere. Standard schlenk-tube techniques and vacuum line were employed. Where necessary a nitrogen-filled glovebox was used for transfers.

Infrared spectra (IR) were obtained by use of a Perkin-Elmer 457 grating spectrophotometer or a Perkin-Elmer 599 grating spectrophotometer by using neat films of liquid samples, Nujol mulls between CsBr plates or in KBr pellets for solid samples. Ultraviolet and visible spectra (UV-VIS) were recorded by use of a Cary 17 spectrophotometer and acetonitrile solutions. Mass spectra (MS) were obtained by means of a Finnigan 4000 instrument with an Incos data system at 70 eV. Optical rotations were determined with a Perkin-Elmer 141 polarimeter. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee. Gas chromatography (GC) was carried out by using a Hewlett-Packard 5880A instrument.

All melting points were determined by using a Thomas-Hoover capillary melting point apparatus and were uncorrected.

Proton NMR spectra were obtained by use of a Bruker WM-250 spectrometer at 250 MHz in chloroform-d_1 solutions with chemical shifts reported in parts per million downfield from a tetramethylsilane internal standard. Carbon-13 NMR (broadband proton decoupled and gated decoupled) were obtained by use of a Bruker WM-250 spectrometer at 62.9 MHz. A pulse width (PW) of 8 μs and a relaxation delay (RD) of 6s were generally employed.

All solvents used were A·C·S reagent grade and were distilled by standard methods[76] before use. (R)-N,N-dimethyl-1-ferrocenylethylamine(R-7) and (S)-N,N-dimethyl-1-ferrocenylethylamine (S-7) were prepared according to Ugi's procedure.[77] Dimethylaminomethyl ferrocene (6) was made by the standard

method.[78] Bis(benzonitrile) complexes, $[(PhCN)_2MCl_2]$ where M = Pd, Pt, were prepared according to published procedures.[79,80] The hydrogenation substrate 1,3-cyclooctadiene was obtained from Columbian Carbon Co., 1,3-cyclohexadiene was obtained from Columbian Organic Chemical Co., and cyclohexene was obtained from Aldrich Chemical Co. These reagents were retreated by standard methods before use. The Grignard cross-coupling substrate, 1-phenylethyl chloride, was prepared as previously reported;[81] allylmagnesium chloride (2 M solution in THF) and allylmagnesium bromide (1 M solution in ether) were obtained from Aldrich Chemical Co. The ^1H NMR chiral shift reagents, Tris(d,d—dicampholymethanato)europium(III) [Eu(dcm)$_3$], was obtained from Alfa Products. A pressure bottle with gauge was used to perform hydrogenations.

X-ray structure determinations were performed on a Nicolet P3F computer controlled 4-circle diffractometer equipped with a graphite crystal incident beam monochromator.

A. Preparation of Ligands

(R)-1-(Dimethylamino)-ethylferrocene[(R)-7] and (S)-1-(Dimethylamino)-ethylferrocene [(S)-7].

N,N-dimethyl-1-ferrocenylethylamine (7) was prepared and resolved by using (R)-(+)tartaric acid as described by Ugi.[77] The (R)-(+)amine tartarate crystals were recovered from the mother liquor by treatment with diethylether and then recrystallized three times from 10:1 acetone:water, allowing about 17 mL of solvent for each gram of salt. The (S)-(-)amine tartarate crystals filtered off readily as previously reported.[77] The tartarate salts were dissolved in 20% aqueous NaOH solution and extracted with methylene chloride. The amine solutions were dried over anhydrous K_2CO_3 and evaporated to give a dark brown oil that partially solidified on cooling. $[\alpha]_D^{25}$ + 14.1° for (R)-1—(dimethylamino)-ethylferrocene [(R)-7], and $[\alpha]_D^{25}$ - 14.1° for (S)-1-(dimethyl-

amino)-ethylferrocene [(S)-7], lit.[2] $[\alpha]_D^{25}$ + 14.1° and -14.1°, respectively. MS m/e (relative intensity), 257 (83, M^+), 242 (95, M^+-Me), 213 (100, M^+-NMe_2), 212 (36, M^+-$HNMe_2$), 121 (66, FeCp), 72 (18, $CHMeNMe_2$), 65 (3, Cp), 56 (21, Fe), 44 (4, NMe_2). ^1H NMR (δ ppm) 4.11 (m, 4H, C_5H_4); 4.08 (s, 5H, Cp); 3.60 (q, J = 6.8 Hz, 1H, CH); 2.09 (s, 6H, NMe_2); 1.46 (d, J = 6.8 Hz, 3H, $NCHCH_3$). ^{13}C NMR (δ ppm) 86.2 (s, C_1); 68.5 (d, J = 91 Hz, C_{2-5}), 67.7 (d, J = 88 Hz, Cp); 66.5 (d, J = 92.4 Hz, C_2, C_3, C_4, C_5) 66.3 (d, J = 9.2 Hz, C_2, C_3, C_4, C_5); 65.9 (d, J = 91.4 Hz, C_2, C_3, C_4, C_5); 57.8 (d, J = 67.3 Hz, NCH); 40.2 (q, J = 47.4 Hz, NMe_2); 14.8 (q, J = 42.9 Hz, NCHMe).

(R,S)-1-(1-Dimethylaminoethyl)-2-methylthioferrocene (46, R=Me).

The amine (R)-7 (1.5 g, 5.8 mmol) was dissolved in 50 mL dry ether and placed in a 100 mL round-bottomed schlenk flask equipped with a side arm and rubber septum. The solution was cooled to -78°C and while being stirred 4.0 mL (6.4 mmol) of n-BuLi was added dropwise via a syringe. The orange suspension was allowed to reach room temprature and stirred overnight. Me_2S_2 (0.53 mL, 5.9 mmol) was added dropwise via syringe at -78°C. The solution was allowed to reach room temperature and stirred under N_2 for 24 h. After refluxing for 7 h, the reaction mixture was cooled and then 20 mL of saturated aqueous $NaHCO_3$ was added. The resulting organic layer and ether extracts from the aqueous layer were combined, washed twice with ice water, dried over anhydrous Na_2SO_4, and evaporated to give a dark oily residue. The oil was chromatographed on alumina by eluting first with hexane and then with CH_2Cl_2 to give the product which upon recrystallization from hexane/petroleum ether gave yellow crystals: yield 65%; mp 64-66°C; MS m/e (relative intensity), 303 (19, M^+), 213 (100, M^+-NMe_2), 121 (92, FeCp), 72 (57, $CHMeNMe_2$), 56 (60, Fe). IR (Nujol, CsI) 1260 (C-N stretch), 1104, 1092 (asymmetric ring breathing), 988 (ring-H bend parallel to ring), 810 (ring-H bend perpendicular to ring),

450 cm^{-1} (asymmetric ring-Fe stretch). ^1H NMR (δ ppm) 4.28 (m, 1H, H_3, H_4, H_5); 4.18 (m, 1H, H_3, H_4, H_5); 4.17 (m, 1H, H_3, H_4, H_5); 4.10 (S, 5H, Cp); 3.94 (q, J = 7 Hz, 1H, NC<u>H</u>); 2.30 (S, 3H, SCH_3); 2.13 (s, 6H, NMe_2); 1.40 (d, J = 7 Hz, 3H, NCH<u>C</u>H_3).

^{13}C NMR (δ ppm) 84.0 (s, C_2); 75.1 (s, C_1); 71.0 (d, C_3, C_4, C_5); 69.9 (d, Cp); 67.3 (d, C_3, C_4, C_5); 66.5 (d, C_3, C_4, C_5); 56.1 (d, NCH); 40.5 (q, NMe_2); 19.8 (q, SCH_3); 13.1 (q, NCH<u>C</u>H_3).

Anal. Calcd. for $C_{15}H_{21}FeNS$: C, 59.41; H, 6.93.

Found: C, 59.54; H, 6.89.

(<u>R</u>,<u>S</u>)-1-(Dimethylaminoethyl)-2-ethylthioferrocene (<u>47</u>, R = Et).

The amine (<u>R</u>)-<u>7</u> (1.5 g, 5.8 mmol) was dissolved in 50 mL dry ether and placed in a 100 mL round-bottomed schlenk falsk equipped with a side arm and rubber septum. The suspension was cooled to -78°C and while being stirred 4.0 mL (6.4 mmol) <u>n</u>-BuLi was added dropwise via a syringe. The orange suspension was allowed to reach room temperature and stirred overnight. Et_2S_2 (0.73 mL, 5.9 mmol) was added dropwise via a syringe at -78°C. The solution was allowed to reach room temperature and stirred under N_2 for 24 h. After refluxing for 7 h, the reaction mixture was cooled and 20 mL of water added. The organic layer was separated, dried and evaporated to give a brown oil. The oil was chromatographed on alumina by gradient elution (hexane/ether/CH_2Cl_2), giving a brown oil: yield 45%; MS m/e (relative intensity), 317 (53, M^+), 302 (23, M^+-CH_3), 272 (44, M^+-$HNMe_2$), 121 (29, FeCp), 72 (9, $CHMeNMe_2$), 56 (17, Fe), 40 (100).

IR (neat, KBr) 1360 (C-N stretch), 1100, 1000 (asymmetric ring breathing—unsubstituted ring), 452 cm^{-1} (asymmetric ring-Fe stretch).

^1H NMR (δ ppm) 4.20 (m, 3H, C_5H_3; 4.10 (s, 5H, Cp); 3.95 (q, J = 7.0 Hz, 1H, -C<u>H</u>-); 2.75 (q, 1H, CH_2CH_3); 2.60 (q, 1H, CH_2CH_3); 2.10 (s, 6H, NMe_2); 1.35

(d, 3H, -$CHCH_3$); 1.15 (t, 3H, CH_2CH_3).

(R,S)-1-(1-Dimethylaminoethyl)-2-isopropylthioferrocene (48, R = i-Pr)

The amine (R)-7 (1.5 g, 5.8 mmol) was dissolved in 50 mL dry ether and placed in a 100 mL round-bottomed schlenk falsk equipped with a side arm and rubber septum. The suspension was cooled to -78°C and while being stirred 4.0 mL (6.4 mmol) of n-BuLi was added dropwise via a syringe. The orange suspension was allowed to reach room temperature and stirred overnight. Then 0.94 mL $(i\text{-Pr})_2S_2$ (5.9 mmol) was added dropwise via a syringe at -78°C. The reaction mixture was allowed to reach room temperature and stirred under N_2 for an additional 24 h, after which saturated aqueous $NaHCO_3$ was added to the mixture. 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 product mixture which was chromatographed on a silica gel column (hexane/ether) to give orange crystals. The product was recrystallized from hexane to give bright orange needles: yield 80.4 %; mp 34-35°C. MS m/e (relative intensity), 331 (85, M^+), 316 (25, M^+-Me), 287 (35, M^+-NMe_2), 286 (60, M^+-$HNMe_2$), 244 (48, M^+-$CHMeNMe_2$), 210 (5, M^+-CpFe), 121 (78, FeCp), 56 (35, Fe), 43 (100, i-Pr).

IR (neat, KBr), 3096 (ring-H stretch), 2870, 2820, 2778, 2930 (alkyl C-H stretch), 1450, 1380 (methyl C-H bond), 1260, 1245 (alkyl C-H bend), 1190 (C-N stretch), 1103, 1090 (asymmetric ring breathing), 998, 930 (ring-H bend parallel to ring), 815 (ring-H bend perpendicular to ring), 532 (asymmetric ring tilt), 465 cm^{-1} (asymmetric ring-Fe stretch).

^1H NMR (δ ppm), 4.33 (m, 1H, H_3, H_4, H_5); 4.21 (m, 1H, H_3, H_4, H_5); 4.17 (m, 1H, H_3, H_4, H_5); 4.09 (s, 5H, Cp), 4.00 (q, J = 7.0 Hz, 1H, -C<u>H</u>NMe_2); 3.20 (m, J = 7.0 Hz, 1H, SC<u>H</u>Me_2); 2.12 (s, 6H, NMe_2), 1.34 (d, J = 7.0 Hz, 3H, NCHC<u>H</u>$_3$); 1.22 (d, J = 7.0 Hz, 3H, β CH_3); 1.15 (d, J = 7.0 Hz, 3H, β CH_3).

^{13}C NMR (δ ppm), 94.6 (s, C_2), 78.3 (s, C_1); 75.2 (d, J = 91.0 Hz, C_3, C_4, C_5); 69.9 (d, J = 97.4 Hz, Cp), 67.8 (d, C_3, C_4, C_5); 66.7 (d, C_3, C_4, C_5); 55.8 (d, J = 66.5 Hz, N<u>C</u>H); 39.9 (q, NMe_2), 39.2 (d, J = 63.0 Hz, SCH); 23.8 (q, J = 38.0 Hz, β <u>CH_3</u>), 22.6 (q, J = 39.0 Hz, β <u>C</u>H_3); 10.6 (q, J = 39.2 Hz, NCH<u>C</u>H_3).

Anal. Calcd. for $C_{17}H_{25}FeNS$: C, 61.63; H, 7.55; S, 9.67.

Found: C, 61.70; H, 7.75; S, 9.90.

(<u>R</u>,<u>S</u>)-1-(1-Dimethylaminoethyl)-2-<u>n</u>-propylthioferrocene (<u>49</u>, R = <u>n</u>-Pr).

The procedure was the same as for <u>48</u>, R = <u>i</u>-Pr, except that 0.92 mL (5.9 mmol) of (<u>n</u>-Pr)$_2S_2$ was added. The product was recrystallized from hexane/CH_2Cl_2 to give dark organe crystals; yield 65%, mp 32-33°C. MS m/e (relative intensity), 331 (100, M^+), 316 (36, M^+-Me), 288 (13, M^+-<u>n</u>-Pr), 287 (48, M^+-NMe_2), 286 (71, M^+-$HNMe_2$), 256 (5, M^+-S-<u>n</u>-Pr), 210 (5, M^+-FeCp), 121 (17, FeCp), 65 (3, Cp), 56 (7, Fe), 43 (38, <u>n</u>-Pr), 41 (62, CH_2=$CHCH_3$).

IR (neat KBr), 3096 (ring-H stretch), 2830, 2870, 2850, 2818 (alkyl C-H stretch), 1454 (CH_2 scissoring of SCH_2), 1362 (methyl C-H bend), 1260, 1245 (alkyl C-H bend), 1190 (C-N stretch), 1152 (C-H deformation), 1104 (asymmetric ring stretch), 998, 970 (ring-H bend parallel to ring), 815 (ring-H bend perpendicular to ring), 454 cm^{-1} (asymmetric ring-Fe stretch).

^1H NMR (δ ppm), 4.32 (m, 1H, H_3, H_4, H_5); 4.19 (m, 1H, H_3, H_4, H_5); 4.16 (m, 1H, H_3, H_4, H_5); 4.10 (s, 5H, Cp); 3.97 (q, J = 7.0 Hz, NC<u>H</u>CH_3); 2.77 (m, 1H, SCH_2); 2.58 (m, 1H, SCH_2); 2.12 (s, 6H, NMe_2); 1.56 (m, 2H, βCH_2); 1.36 (d, J = 7.0 Hz, 3H, $NCHCH_3$); 0.95 (t, J = 7.1 Hz, 3H, γ CH_3).

^{13}C NMR (δ ppm), 93.2 (s, C_2); 80.5 (s, C_1); 73.3 (d, J = 95.8, C_3, C_4, C_5); 69.9 (d, J = 92.4, Cp); 67.4 (d, J = 92.6, C_3, C_4, C_5); 66.5 (d, J = 92.4, C_3, C_4, C_5); 55.9 (d, J = 71.4, N<u>C</u>HMe); 40.2 (q, J = 51.9, NMe_2); 38.7 (t, J = 58.0, SCH_2); 22.9 (t, J = 43.0, β CH_2); 13.5 (q, J = 37.0, γ CH_3); 12.0 (q, J = 42.5, NCH-<u>C</u>H_3).

Anal. Calcd. for $C_{17}H_{25}FeNS$: C, 61.63; H, 7.55.

Found: C, 61.90; H, 7.62.

(R,S)-1-(1-Dimethylaminoethyl)-2-t-butylthioferrocene (50, R = t-Bu)

The amine (R)-7 (1.0 g, 3.9 mmol) was dissolved in 40 mL dry ether in a 100 mL round-bottomed schlenk flask equipped with a side arm and rubber septum. The suspension was cooled to -78°C and while being stirred 1.8 mL of 2.7 M n-BuLi (4.8 mmol) was added dropwise via a syringe. The orange suspension was allowed to reach room temperature and stirred overnight. Then 0.78 mL t-Bu_2S_2 (4.0 mmol) was added dropwise via a syringe at -78°C. The reaction mixture was allowed to reach room temperature and stirred under N_2 for an additional 24 h, after which saturated aqueous $NaHCO_3$ was added to the mixture. The resulting organic layer and ether extracts from the aqueous layer were combined washed with cold water and dried over anhydrous K_2CO_3. Evaporation of the solvent gave a brown oil that was chromatographed on a silica gel column by eluting first with hexane, then with ether and finally with MeOH. The product obtained was orange oil: yield 64%.

MS m/e (relative intensity), 345 (35, M^+), 301 (5,M^+-NMe_2), 300 (5, M^+-$HNMe_2$), 244 (100, M^+-t-Bu-NMe_2), 121 (131, FeCp), 89 (4, S-t-Bu), 57 (33, t-Bu), 56 (15, Fe).

IR (neat, CsI), 3100 (ring C-H stretch), 2960, 2940, 2860, 2820 (alkyl C-H stretch), 1450 (asymmetric C-H bend), 1390, 1370 (symmetric C-H bend of CH_3), 1260, 1245 (alkyl C-H bend), 1190 (C-N stretch), 1000, 930 (unsubstituted ring stretch), 818 (ring C-H bend perpendicular to ring), 656 (C-S stretch), 468 cm^{-1} (asymmetric ring-Fe stretch).

^1H NMR (δ ppm); 4.41 (m, 1H, H_3, H_4, H_5); 4.25 (m, 1H, H_3, H_4, H_5); 4.21 (m, 1H, H_3, H_4, H_5); 4.08 (s, 5H, Cp), 3.88 (q, J = 6.9 Hz, 1H, NCHMe); 2.12 (s, 6H, NMe_2); 1.30 (d, J = 6.9 Hz, 3H, $NCHCH_3$); 1.24 (s, 9H, β CH_3).

^{13}C NMR (δ ppm), 95.5 (s, C_2); 77.8 (s, C_1); 77.7 (d, J = 94.1 Hz, C_3, C_4, C_5);

70.8 (d, J = 88.9 Hz, Cp); 68.9 (d, J = 90.3 Hz, C_3, C_4, C_5); 68.2 (d, J = 91.7 Hz, C_3, C_4, C_5); 55.9 (d, J = 68.4 Hz, NCHMe), 45.9 (s, SC); 39.9 (q, J = 51.6 Hz, NMe_2); 31.7 (q, J = 41.5 Hz, β CH_3); 9.3 (q, J = 42.0 Hz, $NCHCH_3$).

Anal. Calcd. for $C_{18}H_{27}FeNS$: C, 62.61; H, 7.83.

Found: C, 62.70; H, 8.00.

(R,S)-1-(1-Dimethylaminoethyl)-2-isobutylthioferrocene (51, R = i-Bu)

The procedure was the same as for 50, R = t-Bu, except that 0.75 mL (4.0 mmol) of i-Bu_2S_2 was used. The product was obtained as brownish orange oil: yield 84.5%.

MS m/e (relative intensity), 345 (80, M^+), 330 (28, M^+-Me), 301 (38, M^+-NMe_2), 300 (42, M^+-$HNMe_2$), 256 (3, M^+-S-i-Bu), 244 (24, M^+-NMe_2-i-Bu), 121 (36, FeCp), 89 (6, S-i-Bu), 72 (100, $HCMeNMe_2$), 65 (5, Cp), 57 (26, i-Bu), 56 (48, Fe), 45 (16, $HNMe_2$), 44 (34, NMe_2).

IR (neat, CsI), 3100 (ring C-H stretch), 2960, 2940, 2870, 2820 (alkyl C-H stretch), 1460 (asymmetric C-H bend), 1383, 1365 (symmetric C-H bend of methyl), 1260 (alkyl C-H bend), 1190 (C-N stretch), 1106 (asymmetric ring breathing), 1000 (unsubstituted Cp ring stretch), 818 (ring C-H bend perpendicular to ring), 532, 496 (asymmetric ring tilt), 452 cm^{-1} (asymmetric ring-Fe stretch).

^1H NMR (δ ppm), 429 (m, 1H, H_3, H_4, H_5); 4.17 (m, 1H, H_3, H_4, H_5); 4.13 (m, 1H, H_3, H_4, H_5); 4.10 (s, 5H, Cp); 3.97 (q, J = 7.0 Hz, 1H, NCHMe); 2.72 (dd, J_{gem} = 12.0 Hz, J_{vic} = 6.0 Hz, 1H, SCH_2); 2.47 (dd, J_{gem} = 12. Hz, J_{vic} = 8 Hz, 1H, SCH_2), 2.12 (s, 6H, NMe_2); 1.76 (M, 1H, β CH); 1.35 (d, J = 7.0 Hz, 3H, $NCHCH_3$); 0.99 (d, J = 7.0 Hz, 3H, γ CH_3); 0.93 (d, J = 7.0 Hz, 3H, γ CH_3).

^{13}C NMR (δ ppm), 93.2 (s, C_2); 80.8 (s, C_1); 73.2 (d, J = 88.1 Hz, C_3, C_4, C_5); 69.9 (d, J = 84.5, Cp); 67.4 (d, J = 84.5 Hz, C_3, C_4, C_5); 66.5 (d, J = 84.6 Hz, C_3, C_4, C_5); 55.9 (d, J = 84.8 Hz, NCHMe); 45.9 (t, J = 84.5, SCH_2), 40.2 (q,

J = 47.7 Hz, $N\underline{Me}_2$); 28.4 (d, J = 42.0 Hz, βCH); 22.3 (q, J = 35.6 Hz, γ CH_3); 21.7 (q, J = 35.5 Hz, γ CH_3); 11.8 (q, J = 38.8, $NCH\underline{C}H_3$).

Anal. Calcd. for $C_{18}H_{27}FeNS$: C, 62,61; H, 7.83.

Found: C, 62.81; H, 7.99.

(R,S)-1-(1-Dimethylaminoethyl)-2-n-butylthiferrocene (52, R = n-Bu)

The procedure was the same as for 50, R = t-Bu, except that 0.76 mL (4.0 mmol) of n-Bu_2S_2 was used. The product was obtained as brownish orange oil: yield 81.2%.

MS m/e (relative intensity), 345 (91, M^+), 330 (31, M^+-Me), 302 (11, M^+-Pr), 301 (48, M^+-NMe_2), 300 (51, M^+-$HNMe_2$), 256 (5, M^+-SBu), 121 (42, FeCp), 65 (6, Cp), 56 (48, Fe), 45 (20, $HNMe_2$), 44 (42, NMe_2).

IR (neat, CsI), 3100 (ring C-H stretch), 2970, 2940, 2860, 2820 (alkyl C-H stretch), 1460 (asymmetric C-H bend), 1380 (symmetric C-H bend), 1265, 1245 (alkyl C-H bend), 1190 (C-N stretch), 1106 (asymmetric ring breathing), 1000 (unsubstituted Cp ring stretch), 818 (ring C-H bend perpendicular to ring), 532 (asymmetric ring tilt), 452 cm^{-1} (asymmetric ring-Fe stretch).

^1H NMR (ppm), 4.31 (m, 1H, H_3, H_4, H_5); 4.10 (s, 5H, Cp), 3.97 (q, J = 6.8 Hz, 1H, $NC\underline{H}Me$); 2.79 (ddd, J_{gem} = 13.0 Hz, J_{vic} = 7.0 Hz, 1H, SCH_2); 2.61 (ddd, J_{gem} = 13.0 Hz, J_{vic} = 7.0 Hz, 1H, SCH_2); 2.12 (s, 6H, NMe_2), 1.51 (m, 2H, β CH_2); 1.37 (m, 2H, γ CH_2); 1.36 (d, J = 6.8 Hz, 3H, $NCH\underline{CH}_3$); 0.88 (t, J = 6.8 Hz, 3H, δ CH_3).

^{13}C NMR (δ ppm), 93.5 (s, C_2); 80.5 (s, C_1); 73.5 (d, J = 89.4 Hz, C_3, C_4, C_5); 69.9 (d, J = 86.4 Hz, Cp); 67.5 (d, J = 86.4 Hz, C_3, C_4, C_5); 66.5 (d, J = 87.5 Hz, C_3, C_4, C_5); 55.9 (d, J = 66.3 Hz, $NC\underline{H}Me$); 40.2 (q, J = 49.0 Hz, NMe_2); 36.4 (t, J = 56.3 Hz, SCH_2); 31.8 (t, J = 38.5 Hz, β CH_2); 21.9 (t, J = 36.9 Hz, γ CH_2), 13.7 (q, J = 34.0 Hz, δ CH_3); 11.9 (q, J = 39.5 Hz, $NCH\underline{CH}_3$).

Anal. Calcd. for $C_{18}H_{27}FeNS$: C, 62.61; H, 7.88.

Found: C, 62.50, H, 8.00.

(R,S)-1-(1-Dimethylaminoethyl)-2-isopentylthioferrocene (53, R = i-Pent.)

The amine (R)-7 (0.5 g, 1.95 mmol) was dissolved in 40 mL dry ether in a 100 mL round-bottomed schlenk flask equipped with a side arm and a rubber septum. The suspension was cooled to -78°C and while being stirred 0.8 mL of 2.8 M n-BuLi (2.14) mmol) was added dropwise via a syringe. The orange suspension was allowed to reach room temperature and stirred overnight. Then 0.41 g isopentyldisulfide (1.99 mmol) dissolved in 30 mL hexane was added dropwise via cannula to the orange solution at -78°C. The reaction mixture was allowed to reach room temperature and stirred under N_2 for an additional 24 h, after which saturated aqueous $NaHCO_3$ was added to the mixture. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with cold water, dried, and evaporated to a brown oil that was chromatographed on a silica gel (hexane/CH_2Cl_2/Et_2O). The product was obtained as a light brown oil: yield 72%.

MS m/e (relative intensity), 359 (60, M^+), 344 (20, M^+-Me), 315 (25, M^+--NMe_2), 314 (32, M^+-$HNMe_2$), 121 (10, FeCp), 103 (8, S-Pent), 56 (12, Fe).

^1H NMR (δ ppm), 4.31 (m, 1H, H_3, H_4, H_5); 4.20 (m, 1H, H_3, H_4, H_5); 4.16 (m, 1H, H_3, H_4, H_5); 4.10 (s, 5H, Cp); 3.98 (q, J = 7.0 Hz, 1H, NCHMe); 2.85 (m, 1H, α CH_2); 2.63 (m, 1H, αCH_2); 2.10 (S, 6H, NMe_2); 1.71 (m, 2H, βCH_2); 1.45 (m, 1H, CH); 1.35 (d, J = 7.0 Hz, 3H, $NCHCH_3$), 0.82-0.90 (dd, 6H, $CHMe_2$).

(R,S)-1-(1-Dimethylaminoethyl)-2-phenylthioferrocene (54, R = Ph)

The amine (R)-7 (1.5 g, 5.8 mmol) was dissolved in 50 mL dry ether and placed in a 200 mL round bottomed flask equipped with a side arm and rubber septum. The suspension was cooled to -40°C and 4.0 mL (6.4 mmol) n-BuLi was added slowly via a syringe. the orange suspension was allowed to reach room temperature and stirred overnight. Ph_2S_2 (1.29 g, 5.91 mmol), dissolved

in 30 mL warm hexane, was added dropwise via cannula to the orange suspension at -78°C. The resulting solution was allowed to reach room temperature and then refluxed overnight under N_2. Upon cooling the reaction mixture to room temperature, 30 mL H_2O was added. The resulting organic layer was separated, dried and evaporated to give a dark oily residue. Unreacted Ph_2S_2 was removed by sublimation. The oil was chromatographed on activated alumina by eluting first with hexane and then with CH_2Cl_2, to the product, which was recrystallized from hexane/CH_2Cl_2 to give orange crystals: yield 85%, mp 70-72°C.

MS m/e (relative intensity), 365 (70, M^+), 320 (78, M^+-$HNMe_2$), 212 (31, vinylferrocene), 121 (54, FeCp), 72 (100, $CHMeNMe_2$), 56 (45, Fe).

^1H NMR (δ ppm) 7.05-7.25 (m, 5H, Ph); 4.53 (m, 1H, H_3, H_4, H_5); 4.42 (m, 1H, H_3, H_4, H_5); 4.30 (m, 1H, H_3, H_4, H_5); 4.18 (s, 5H, Cp); 3.85 (q, J = 7.0 Hz, NC<u>H</u>Me); 1.90 (s, 6H, NMe_2); 1.45 (d, J = 7.0 Hz, NCHC<u>H</u>$_3$).

Anal. Calcd. for $C_{20}H_{23}FeNS$: C, 65,75; H, 6.30.

Found: C, 65.32; H, 6.21.

(<u>R,S</u>)-1-(1-Dimethylaminoethyl)-2-benzylthioferrocene (<u>55</u>, R = CH_2PH)

The procedure was the same as for <u>54</u>, R = Ph, except that 1.45 g (5.88 mmol) of $(PhCH_2)_2S_2$ was used. The product was obtained as a brown oil: yield 75%.

MS m/e (relative intensity), 379 (25, M^+), 334 (54, M^+-$HNMe_2$), 244 (39), 121 (57, FeCp), 91 (100, CH_2Ph), 72 (84, $CHMeNMe_2$), 56 (54, Fe).

IR (neat), 3090-3000 (ring C-H stretch), 1490 (CH_2 scissoring of SCH_2), 1000 (unsubstituted Cp stretch), 456 cm^{-1} (asymmetric ring-Fe stretch).

^1H NMR (δ ppm), 7.18 (m, 5H, Ph); 4.20 (m, 1H, H_3, H_4, H_5; 4.15 (m, 1H, H_3, H_4, H_5); 4.11 (m, 1H, H_4, H_5); 4.06 (s, 5H, Cp); 4.0 (q, J = 7.0 Hz, 1H, N<u>CH</u>Me); 3.90 (m, 2H, SCH_2); 2.21 (s, 6H, NMe_2); 1.38 (d, J = 6.8 Hz, 3H, CH<u>Me</u>).

^{13}C NMR (δ ppm), 138.9 (s); 129.1(d), 128.3(d), 126.7 (d, Ph), 79.3, 74.5, 71.6,

69.99 (d, Cp), 67.99, 67.03, 56.4 (d, CHMe), 41.45 (t, SCH_2), 39.95 (q, NMe_2), 10.88 (q, CHMe).

Anal. Calcd. for $C_{21}H_{25}FeNS$: C, 66.49; H, 6.60.

Found: C, 66.52, H, 6.65.

(R,S)-1-(1-Dimethylaminoethyl)-2-(p-tolyl)thioferrocene (56, R = p-tolyl).

The amine (R)-7 (0.5 g, 1.95 mmol) was dissolved in 30 mL dry ether and placed in a 100 mL round-bottomed schlenk flask equipped with a side arm and rubber septum. The suspension was cooled to -70°C and 0.8 mL (2.14 mmol) of 2.7 M n-BuLi was added slowly via a syringe. The orange suspension was allowed to reach room temperature and stirred overnight. Then p-tolyl disulfide (0.48 g, 1.94 mmol), dissolved in 30 mL warm hexane, was added dropwise via cannula to the orange suspension at -70°C. The reaction mixture was allowed to reach room temperature and stirred for 12 h under N_2. Saturated aqueous $NaHCO_3$ was added to the mixture and the resulting organic layer and ether extracts of the aqueous layer were combined. After drying and evaporation of solvent, the resulting product mixture was chromatographed on a silica gel column (hexane/CH_2Cl_2/ether). The product was obtained as yellow crystals upon recrystallization from hexane/CH_2Cl_2: yield 85%, mp 66-67°C.

MS m/e (relative intensity), 379 (81, M^+), 364 (27, M^+-CH_3), 335 (52, M^+—NMe_2), 334 (19, M^+HNMe_2), 121 (90, FeCP), 72 (100, $CHMeNMe_2$), 56 (55, Fe).

^1H NMR (δ ppm), 7.11-6.94 (m, 4H, C_6H_4); 4.49 (m, 1H, H_3, H_4, H_5); 4.30 (m, 1H, H_3, H_4, H_5); 4.25 (m, 1H, H_3, H_4, H_5); 4.15 (S, 5H, Cp); 3.86 (q, J = 7.0 Hz, 1H, NCHMe); 2.24 (s, 3H CH_3Ph); 1.94 (s, 6H, NMe_2), 1.46 (d, J = 7.0 Hz, 3H, $NCHCH_3$).

^{13}C NMR (δ ppm), 138.0 (s, substituted phenyl C); 135.2 (s, para substituted phenyl C); 129.6 (d, J = 103.0 Hz, phenyl C); 128.2 (d, J = 106.2 Hz, phenyl

C); 94.3 (s, C_2); 77.9 (s, C_1); 76.0 (d, J = 97.0 Hz, C_3, C_4, C_5); 70.9 (d, J = 92.2 Hz, Cp); 69.1 (d, J = 93.2 Hz, C_3, C_4, C_5); 68.7 (d, J = 94.2 Hz, C_3, C_4, C_5); 56.6 (d, J = 70.0 Hz, NCHMe); 40.4 (q, J = 50.0 Hz, NMe_2); 20.9 (q, J = 51.0 Hz, CH_3-Ph); 12.7 (q, J = 43.3 Hz, $NCHCH_3$).

Anal. Calcd. for $C_{21}H_{25}FeNS$: C, 66.49; H, 6.60.

Found: C, 66.25; H, 6.82.

(R,S)-1-(1-Dimethylaminoethyl)-2-(4-chlorophenyl)thioferrocene (57, R = 4-chlorophenyl).

The amine (R)-7 (1.0 g, 3.89 mmol) was dissolved in 50 mL dry CH_2Cl_2 and placed in a 200 mL round-bottomed schlenk flask equipped with a side arm and rubber septum. The solution was cooled to -70°C and 1.6 mL (4.28 mmol) of 2.7 M n-BuLi was added slowly via a syringe. The orange solution was allowed to reach room temperature and stirred overnight under N_2. Then 4-chlorophenyl disulfide (1.12 g, 3.9 mmol), dissolved in 50 mL dry CH_2Cl_2, was added dropwise via cannula to the solution at -70°C. The reaction mixture was allowed to reach room temperature and stirred for 12 h under N_2. Saturated aqueous $NaHCO_3$ was added and the resulting organic layer and ether extracts of the aqueous layer were combined. After drying and evaporation of solvent, the resulting product mixture was chormatographed on a silica gel column (hexane/ether). The product was obtained as yellowish orange crystals upon recrystallization from CH_2Cl_2/petroleum ether: yield 72%, mp 97-98°C.

MS m/e (relative intensity), 399.5 (21, M^+), 355 (27, M^+-NMe_2), 354 (20, M^+-$HNMe_2$, 143 (7, S-4-chlorophenyl), 121 (75, FeCp), 72 (100, $HCMeNMe_2$), 56 (55, Fe), 44 (34, NMe_2).

IR (KBr pellet), 3100-3050 (ring C-H stretch), 2970, 2930, 2820 (alkyl C-H stretch), 1575 (phenyl C-C stretch), 1185 (C-N stretch), 1001 (unsubstituted Cp stretch), 470 cm^{-1} (asymmetric ring-Fe stretch).

^{1}H NMR (δ ppm), 7.12-7.04 (m, 4H, C_6H_4); 4.47-4.25 (m, 3H, H_3, H_4, H_5); 4.17 (s, 5H, Cp), 3.87 (q, J = 7.0 Hz, 1H, NC<u>H</u>Me); 1.92 (s, 6H, NMe_2); 1.40 (d, J = 7.0 Hz, 3H, NCHC<u>H</u>$_3$).

^{13}C NMR (δ ppm), 141.0 (s, substituted phenyl C); 130.5 (s, p-phenyl C); 128.8 (d, J = 105.0 Hz, phenyl C); 128.8 (d, J = 105.3 Hz, phenyl C); 95.0 (s, C_2); 76.2 (d, C_3, C_4, C_5); 76.1 (s, C_1); 70.8 (d, J = 90.0 Hz, Cp); 69.4 (d, C_3, C_4, C_5); 69.0 (d, C_3, C_4, C_5); 56.5 (d, J = 66.0 Hz, N<u>C</u>H); 39.8 (q, J = 48.5 Hz, NMe_2),; 11.0 (q, NCH<u>C</u>H$_3$).

B. Preparation of Metal Complexes

The complexes (<u>R</u>,<u>S</u>)-$C_5H_5Fe(C_5H_3$-1-CHMeNMe_2-2-SR)MCl_2 where R = Me, i-Pr, n-Pr, i-Bu, Ph, p-tolyl, 4-chlorophenyl; M = Pd, Pt, were prepared from benzene solutions of the appropriate $(PhCN)_2MCl_2$[79] species and a slight excess of the ferrocenylsulfide ligand in an approximate 1:1.1 molar ratio. The reaction mixture was stirred for 10 h in the case of Pd complexes, and for a week in the case of Pt complexes. The resulting precipitates were filtered, washed with benzene, then with petroleum ether, and recrystallized from CH_2Cl_2/-hexane by slow evaporation.

Dichloro[(<u>R</u>)-1-(<u>S</u>)-2-Methylthioferrocenylethyldimethylamine]-palladium(II)-<u>58</u>

Deep purple needles decomposed at 162-164°C.

^{1}H NMR (δ ppm), 4.51 (m, 1H, H_3, H_4, H_5); 4.40 (m, 2H, H_3, H_4, H_5); 4.23 (s, 5H, Cp); 3.87 (q, J = 6.8 Hz, 1H, NCHMe); 3.21 (s, 3H NMe_2); 2.70 (s, 3H, SMe); 2.31 (s, 3H, NMe_2); 1.55 (d, 3H, NCHC<u>H</u>$_3$).

MS m/e (relative intensity), 303 (2, M^+-$PdCl_2$), 258 (100, M^+-$PdCl_2$-$HNMe_2$), 121 (34, FeCp), 56 (16, Fe).

Anal. Calcd. for $C_{15}H_{21}FeNSPdCl_2$: C, 37.47; H, 4.37.

Found: C, 36.43; H, 4.31.

Dichloro[(R)-1-(S)-2-isopropylthioferrocenylethyldimethylamine]-palladium(II)-59.

Deep brown crystals decomposed at 151-153°C.

^{1}H NMR (δ ppm), 4.63 (m, 1H, H_3, H_4, H_5); 4.48 (m, 2H, H_3, H_4, H_5); 4.27 (s, 5H, Cp); 3.88 (m, 1H, SC<u>H</u>Me_2); 3.80 (q, J = 7.0 Hz, 1H, NC<u>H</u>Me); 3.17 (s, 3H, NMe_2), 2.24 (s, 3H, NMe_2); 1.93 (d, J = 7.0 Hz, NCHC<u>H</u>$_3$); 1.75 (d, J = 7.0 Hz, 3H, β CH_3); 1.53 (d, J = 7.0 Hz, 3H, β CH_3).

IR (KBr pellet), 493 (b), 460 (Sh, Pd-N stretch), 320 (b, Pd-Cl or Pd-S stretch); 300 cm^{-1} (b, Pd-Cl or Pd-S stretch).

Anal. Calcd. for $C_{17}H_{25}FeNSPdCl_2$: C, 40.15, H, 4.95.

Found: C, 39.90; H, 4.19.

Dichlor[(R)-1-(S)-2-propylthioferrocenylethyldimethylamine]-palladium(II)-60

Deep brown crystals decomposed at 162-164°C.

^{1}H NMR (δ ppm), 4.49 (m, 1H, H_3, H_4, H_5); 4.40 (m, 2H, H_3, H_4, H_5); 4.21 (s, 5H, Cp); 3.86 (q, J = 6.8 Hz, 1H, NC<u>H</u>Me); 3.57 (m, 1H, SCH_2); 3.05 (m, 1H, SCH_2); 3.19 (s, 3H, NMe_2); 2.30 (s, 3H, NMe_2); 2.24 (m, 1H, CH_2); 2.03 (m, 1H, β CH_2); 1.52 (d, J = 6.8 Hz, 3H, NCHC<u>H</u>$_3$); 1.17 (t, J = 7.0 Hz, 3H, γ CH_3).

IR (KBr pellet), 465 (sh, Pd-N stretch), 322 cm^{-1} (b, Pd-Cl or Pd-S stretch).

Dichloro[(R)-1-(S)-2-isobutylthioferrocenyl ethyldimethylamine]-palladium(II)-61.

Dark brown crystals decomposed at 144-145°C.

^{1}H NMR (δ ppm), 4.44 (m, 1H, H_3, H_4, H_5); 4.39 (m, 2H, H_3, H_4, H_5); 4.21 (s, 5H, Cp); 3.83 (q, J = 7.0 Hz, 1H, NC<u>H</u>Me); 3.67 (d, 1H, SCH_2); 3.19 (s, 3H, NMe_2); 2.82 (d, 1H, SCH_2); 2.37 (m, 1H, β CH); 2.33 (s, 3H, NMe_2); 1.52 (d, J = 7.0 Hz, 3H, NCHC<u>H</u>$_3$); 1.20 (d, J = 7.0 Hz, 3H, γ CH_3); 1.18 (d, J = 7.0 Hz, 3H, γ CH_3).

^{13}C NMR (δ ppm), 80.2 (s, C_2); 71.0 (d, C_3, C_4, C_5); 68.2 (d, C_3, C_4, C_5); 67.8 (d, C_3, C_4, C_5); 64.5 (s, C_1); 63.2 (d, NCH); 50.1 (t, SCH_2); 50.1 (q, NMe_2); 41.0 (q, NMe_2); 27.5 (d); 22.3 (q, $^{\gamma}CH_3$); 21.4 (q, $^{\gamma}CH_3$); 10 (q, $NCH\underline{C}H_3$).

Anal. Calcd. for $C_{18}H_{27}FeNSPdCl_2$: C, 41.37; H, 5.21.

Found: C, 41.10; H, 5.15.

Dichloro[(R)-1-(S)-2-phenylthioferrocenylethyldimethylamine]-palladium(II)—62.

Greenish black crystals decomposed at 165-166°C.

^1H NMR (δ ppm), 8.00-7.50 (m, 5H, C_6H_5); 4.36 (m, 1H, H_3, H_4, H_5); 4.25 (m, 1H, H_3, H_4, H_5); 4.10 (s, 5H, Cp); 4.03 (q, J = 6.8 Hz, 1H, $HC\underline{H}Me$); 4.02 (m, 1H, H_3, H_4, H_5); 3.28 (s, 3H, NMe_2); 2.36 (s, 3H, NMe_2); 1.52 (d, J = 6.8 Hz, 3H, $NCHC\underline{H}_3$).

IR (KBr pellet), 482 (sh), 443, 323 (b, Pd-Cl or Pd-S stretch), 298 cm^{-1} (s, Pd-Cl or Pd-S stretch).

Anal. Calcd. for $C_{20}H_{23}FeNSPdCl_2$: C, 44.25; H, 4.24.

Found: C, 44.18, H, 3.96.

Dichloro[(R)-1-(S)-2-paratolythioferrocenylethyldimethylamine]-palladium(II)—63.

Dark brown needles decomposed at 158-159°C.

^1H NMR (δ ppm), 7.80-7.28 (m, 4H, C_6H_4); 4.33 (m, 1H, H_3, H_4, H_5); 4.21 (m, 2H, H_3, H_4, H_5); 4.00 (s, 5H, Cp); 3.96 (q, J = 7.0 Hz, 1H, $NC\underline{H}CH_3$); 3.16 (s, 3H, NMe_2); 2.36 (s, 3H, para CH_3); 2.22 (s, 3H, NMe_2); 1.44 (d, J = 7.0 Hz, 3H, $NCHC\underline{H}_3$).

IR (Nujol) 550, 500 (b, asymmetric ring tilt), 460 (sh, Pd-N stretch), 330 (sh, Pd-Cl or Pd-S stretch), 297 cm^{-1} (m, Pd-Cl or Pd-S stretch).

Dichloro[(R)-1-(S)-2-(4-chlorophenyl)thioferrocenylethyl-dimethylamine]palladium(II)-64.

Greenish brown powder decomposed at 198-200°C.

^{1}H NMR (δ ppm), 8.04-7.55 (m, 4H, C_6H_4); 4.68 (m, 1H, C_3, C_4, C_5); 4.50 (m, 2H, C_3, C_4, C_5); 4.21 (q, J = 6.8 Hz, 1H, NCHMe); 4.12 (s, 5H, Cp); 3.18 (s, 3H, NMe_2); 2.24 (s, 3H, NMe_2); 1.50 (d, J = 7.0 Hz, 3H, $NCHCH_3$).

Dichloro[(R)-1-(S)-2-(4-chlorophenyl)thioferrocenylethyldimethylamine]platinum(II)-65.

Yellow flakes decomposed at 218-220°C.

^{1}H NMR (δ ppm), 7.40-7.22 (m, 4H, C_6H_4); 4.5-4.2 (m, 3H, H_3, H_4, H_5); 4.13 (s, 5H, Cp); 3.88 (q, 1H, NCHMe); 3.18 (s, 3H, NMe_2); 2.25 (s, 3H, NMe_2); 1.45 (d, 3H, NCHMe).

IR (KBr pellet), 4.58 (sh, Pt-N), 336 cm^{-1} (sh, Pt-Cl or Pt-S), 320 cm^{-1} (W,Pt-Cl).

Anal. Calcd. for $C_{20}H_{22}FeNSPtCl_3$: C, 36.06; H, 3.31.

Found: C, 36.29; H, 4.22.

(R,S)-1-(1-Dimethylaminoethyl)-2-(dimethyldithiocarbamate)-ferrocene(66).

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-(dimethylamino)-ethylferrocene (1.0 g, 3.9 mmol) in 50 mL dry diethyl ether at -78°C. The solution was allowed to reach room temperature and stirred for an additional 12 h water N_2. Tetramethylthiuram 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 then 40 mL saturated aqueous $NaHCO_3$ 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 103-105°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, $CSNMe_2$), 72 (11, $CHMeNMe_2$).

IR (KBr pellet), 2980, 2940, 2780, 1495 cm^{-1}.

^1H NMR (δ ppm) at 22°C; 4.63 (dd, 1H, H_3, H_5); 4.46 (t, 1H, H_4); 4.40 (dd, 1H, H_3, H_4); 4.15 (s, 5H, Cp); 3.71 (q, J = 7.0 Hz, 1H, NC<u>H</u>Me); 3.50 (s, 6H, NMe_2); 2.10 (s, 6H, NMe_2); 1.52 (d, J = 7.0 Hz, 3H, NCHC<u>H</u>$_3$).

^{13}C NMR (δ ppm) at 27°C; 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); 69.6 (d, C_3, C_4, C_5) 68.6 (d); 68.4 (s); 55.6 (t, N<u>C</u>HMe); 40.8 (q, NMe_2), 18.0 (q, NCH<u>C</u>H$_3$).

Anal. Calcd. for $C_{17}H_{24}FeN_2S_2$: C, 54.25; H, 6.38.

Found: C, 53.62; H, 6.63.

(<u>R</u>,<u>S</u>)-1-(1-Dimethylaminoethyl)-2-(diethyldithiocarbamate)-ferrocene(<u>67</u>).

A 2.5 <u>M</u> solution <u>n</u>-BuLi in hexane (1.0 mL, 2.57 mmol), was slowly added via a syringe to a solution of (<u>R</u>)-1-(dimethylamino)-ethylferrocene (0.65 g, 2.57 mmol) in 30 mL 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 toluene was added. The solution was stirred overnight at room temperature and 30 mL 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/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 (δ ppm) at 27°C, 4.60 (dd, 1H, H_3, H_5); 4.48 (t, 1H, H_4); 4.40 (dd, 1H, H_3, H_5); 4.12 (s, 5H, Cp); 3.96 (q, J = 7.0 Hz, 2H, $C\underline{H}_2CH_3$); 3.82 (q, J = 7.0 Hz, 2H, $C\underline{H}_2CH_3$); 3.63 (q, J = 7.0 Hz, 1H, $NC\underline{H}Me$); 2.15 (s, 6H, NMe_2); 1.46 (d, 3H, $NCHC\underline{H}_3$); 1.3-1.42 (tt, 6H, carbamate CH_3).

^{13}C NMR (δ ppm); 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, $N\underline{C}HMe$); 66.6; 66.4; 57.9; 51.0 (t, NCH_2); 46.8 (t, carbamate CH_2); 39.9; 15.2 (q, $NCH\underline{C}H_3$); 12.9 (q, carbamate CH_3); 10.0 (q, carbamate CH_3).

C. Catalytic Applications of Complexes

(i) Asymmetric Grignard Cross-Coupling Reactions

The cross-coupling reactions were carried out in essentially the same manner as was previously reported.[67] Since the optical rotation of the coupling product (4-phenyl-1-pentene) was strongly affected by small impurities,[70] in addition racemization of products always occurred, it was difficult to determine the optical purity of the product by use of polarimeter. The alkene was thus converted into the methyl ester, of which the enantiomeric purity was determined by ^1H NMR spectroscopy in the presence of a chiral shift reagent, $Eu(dcm)_3$.[82] Detailed procedures for cross-coupling reactions and conversion of 4-phenyl-1--pentene to methyl 3-phenyl-butyrate follow.

Grignard cross-coupling reaction of allylmagnesium chloride to 4-phenyl-1--pentene using complex 58, 59, 62, 63, or 64.

The catalyst (0.0499 mmol) was placed in a 100 mL round-bottomed schlenk flask equipped with a stirring bar and a septum. The vessel was evacuated

and filled with Ar several times. After being cooled to -78°C, the reaction vessel was charged with 1.41 g (10.0 mmol) 1-phenylethyl chloride in 20 mL dry ether and stirred for 2 h at room temperature before addition of allylmagnesium chloride (20 mmol, 10 mL of a 2 M solution in THF) via syringe at -78°C. The reaction mixture was allowed to warm to 0°, stirred for 40 h, and hydrolyzed with 10% HCl. The organic layer and ether extracts from the aqueous layer were combined, washed with saturated $NaHCO_3$ solution and water, and dried over Na_2SO_4. Evaporation of solvent and chromatography on a silica gel column (hexane/CH_2Cl_2) gave 93 to 98.5% of 4-phenyl-1-pentene. ^1H NMR (δ ppm) 1.25 (d, 3H, CH_3), 2.35 (m, 2H, CH_2), 2.80 (m, 1H, $CHCH_3$), 5.00 (m, 2H, $CH=CH_2$), 5.70 (m, 1H, $CH=CH_2$), 7.25 (m, 5H, Ph); Lit.[83] ^1H NMR (ppm) 1.24 (d, 3H, CH_3), 2.32 (m, 2H, CH_2), 2.75 (sex, 1H, $CHCH_3$), 4.80 (s, 1H, $CH=CH_2$), 4.92 (split d, 1H, $CH=CH_2$), 5.52 (m, 1H, $CH-CH_2$), 7.0 (5H, Ph); MS m/e (relative intensity), 41 (5, $CH_2CH=CH_2$), 77 (15, C_6H_5), 105 (100, $PhCHCH_3$), 146 (15, M^+). Results are shown in Table 20.

Conversion of 4-phenyl-1-pentene to methyl 3-phenylbutyrate

The reported precedure[84] for oxidation of 3-phenyl-1-butene was followed. To a solution of 4-phenyl-1-pentene (0.453 g, 3.1 mmol) in 80 mL tert-butyl alcohol were added a solution of 1.24 g (9.0 mmol) K_2CO_3 in 60 mL of water and a solution of 5.13 g (24 mmol) of sodium periodate and 0.63 g (4.0 mmol) of $KMnO_4$ in 60 mL of water. The solution was adjusted to pH 8.5 with 2N aqueous NaOH and was stirred overnight. After tert-butyl alcohol was removed under reduced pressure, the aqueous solution was acidified with concentrated HCl to pH 2.5, and sodium bisulfite was added until the solution became off-white. The solution was extracted with ether and the extracts were dried over Na_2SO_4, concentrated and distilled [120-135°C (2mm)]. A solution of the acid thus obtained (0.295 g, 1.8 mmol) and p-toulenesulfonic acid (40 mg) in 10 mL of

methanol was refluxed for 3 h. The solvent was removed under reduced pressure, and the residue was taken up in ether. The solution was washed with 10% aqueous sodium hydroxide dried over anhydrous Na_2SO_4, and evaporated. The residue was distilled [110-130°C (2mm)] to give about 72-85% of methyl 3-phenyl-butyrate; ^1H NMR (δ ppm), 1.29 (d, J = 7.0 Hz, 3H, $CHC\underline{H}_3$), 2.53 (dd, J_{gem} = 15 Hz, J_{vic} = 8 Hz, 1H, $C\underline{H}_2CH$), 2.63 (dd, J_{gem} = 15 Hz, J_{vic} = 8 Hz, 1H, $C\underline{H}_2CH$), 3.28 (sex, J = 7.0 Hz, 1H, $CH_2C\underline{H}PhMe$), 3.61 (s, 3H, OCH_3), 7.16-7.45 (m, 5H, Ph). ^1H NMR spectroscopy with the chiral shift reagent $Eu(dcm)_3$ showed varying enantiomeric excess (e.e) values as the catalyst was varied (results in Table 20).

(ii) Selective Hydrogenation of Conjugated Dienes to Alkenes with 58, 62-65.

In all the cases studied, a period of induction was observed except when additives were introduced. The induction time was dependent on the catalyst.

Hydrogenation of 1,3-cyclooctadiene with 58, 62-64 in acetone at 67 psi.

The complex (2.0×10^{-5} mol), acetone (9.0 mL) and 1,3 cyclooctadiene (0.91 mL, 7.45×10^{-3} mol) were added to a 100 mL pressure bottle with a pressure gauge and stirring bar. The bottle was evacuated and filled several times with H_2 to a pressure of 67 psi. After an induction period, uptake of H_2 began and slowed after absorption of about 5.5×10^{-3} mol of H_2. The initial turnover rate, product analysis at the end of reaction, and the calculated selectivity are shown in Table 17.

Solvent Effects on Hydrogenation of 1,3-Cyclohexadiene at Room Temperature

The complex (2.0×10^{-5} mol), 1,3-cyclohexadiene (7.45×10^{-3} mol) and 9.0 mL of various solvents (acetone, CCl_4/acetone, 2:1 and 1:1, and CCl_4)

were added to a 100 mL pressure bottle with a pressure gauge and stirring bar. The bottle was evacuated and filled several times with H_2 to a predetermined pressure. The hydrogenation was dependent on the chosen solvent. Results are shown in Table 18.

X-ray Structure Determination of dichloro[(R-1-(S)-2-Methylthioferrocenylethyl-dimethylamine]palladium(II)-58.

Data Collection

A deep purpule pyramidal crystal of dichloro[(R)-1-(S)-2-Methylthioferrocenyl-ethyldimethylamine]palladium(II), $C_{15}H_{21}Cl_2FePdNS$, having approximate dimensions of 0.20 x 0.25 x 0.45 mm, was mounted in a glass capillary in a random orientation. Preliminary examination and data collection were performed with MoK_α radiation (λ = 0.71073 A) on a Nicolet P3F computer controlled 4-circle diffractometer equipped with a graphite crystal incident beam monochromator.

Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 20 reflections in the range $35 < 2\theta < 30°$. The orthorhombic cell parameters and calculated volume are: a = 9.226(3), b = 12.219(4), c = 15.448(5) A, V = 1741.5(8) A^3. For Z = 4 and F.W. = 480.56 the calculated density is 1.83 g/cm^3. From the systematic absences of:

h00 h = 2n+1

0k0 k = 2n+1

001 1 = 2n+1

and from subsequent least-squares refinement, the space group was determined to be $P2_12_12_1$ (# 19).

The data were collected at a temperature of 23(1)°C using the 2theta-theta scan technique. The scan rate varied from 4 to 30 °/min (in 2 θ). The variable

scan rate allows rapid data collection for intense reflections where a fast scan rate is used and assures good counting statistics for weak reflections where a slow scan rate is used. Data were collected to a maximum 2θ of 60°. The scan range (in deg.) was determined as a function of 2θ to correct for the separation of the K_α doublet[1]; the scan width was calculated as follows:

$$2\theta \text{ scan width} = 2.00 \quad (2\theta(K_{\alpha\,2}) - (2\theta(K_{\alpha\,1}))$$

The ratio of peak counting time to background counting time was 1:1. The diameter of the incident beam collimator was 1.0 mm and the crystal to detector distance was 19 cm.

Data Reduction

A total of 2937 reflections were collected, of which 2912 were unique and not systematically absent. As a check on crystal and electronic stability 3 representative reflections were measured every 45 reflections. The slope of the least-squares line through a plot of intensity versus time was -17(16) counts/hour which corresponds to a total loss in intensity of 0.3%. A linear decay correction was applied with correction factors on I ranging from 1.000 to 1.003 and with an average value of 1.002.

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 22.7 cm^{-1} for Mo K_α radiation. An empirical absorption correction based on a series of psi-scans was applied to the data. Relative transmission coefficients ranged from 0.892 to 0.999 with an average value of 0.959. A secondary extinction correction was applied.[128] The final coefficient, refined in least-squares, was -0.344×10^{-8} (in absolute units).

Structure Solution and Refinement

The structure was solved using the Patterson heavy-atom method which

revealed the position of the Pd atom. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were located and their positions and isotropic thermal parameters were refined.

Scattering factors were taken from Cromer and Waber.[129] Anomalous dispersion effects were included in Fc;[130] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[1] Only the 2175 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. The final cycle of refinement included 275 variable parameters and converged (largest parameter shift was 0.25 times) with unweighted and weighted agreement factors of:

$$R1 = \Sigma \; || Fo | - | Fc || \; / \; \Sigma \; | Fo | = 0.029$$

$$R2 = SQRT (\Sigma \; w \; (\; |Fo| - | Fc |)^2 \; / \; \Sigma \; w \; Fo^2) = 0.029$$

The standard deviation of an observation of unit weight was 1.29. The standard deviation of an observation of unit weight was 1.29. The highest peak in the final difference Fourier had a height of 0.59 e/A^3 with an estimated error based on σF of 0.09.[131] Plots of $\Sigma w(|Fo| - |Fc|)^2$ versus $| Fo |$, reflection order in data collection, sin θ/λ, and various classes of indices showed no unusual trends.

All calculations were performed on a VAX-11 computer using SDP-PLUS.[132]

III. RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

A. (R,S)-$C_5H_5FeC_5H_3[CH(CH_3)N(CH_3)_2][SR]$

(R = Me, Et, i-Pr, n-Pr, n-Bu, i-Bu, t-Bu, Ph, CH_2Ph, i-Pent, p-toly, 4-Cl-Ph

There has been considerable interest in chiral ferrocenylphosphine ligands that possess planar chirality due to a 1,2-unsymmetrically substituted cyclopentadienyl ring and are highly effective as ligands in transition metal catalyzed asymmetric synthesis.[85,86] Though few sulfide complexes have been used as ligands in catalysis, the preparation of several chiral ferrocenylsulfide complexes was undertaken so that possible catalytic applications to hydrogenation and asymmetric synthesis could be investigated.

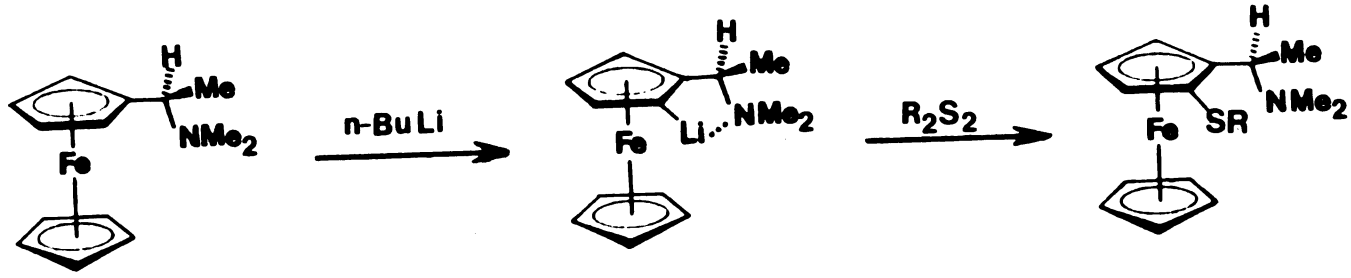
Earlier results[53] obtained in the syntheses of ferrocenylamine sulfides in our laboratory revealed poor yields (from 0.1% yield for phenyl derivative to 45% yield for ethyl derivative) and products were obtained as yellow powders, suggesting that products may be salts of the amine and not free ligands. To circumvent this problem, it was observed that it is necessary to deprotonate the product by washing with aqueous $NaHCO_3$ prior to final separation. This has eventually resulted in high yeilds in this work. Nesmeyanov has also reported that quaternary ammonium salts of the general formula $[C_5H_5FeC_5H_4CH_2N(CH_3)_2-CH_2R]X^-$, were prepared in high yields by the action of the corresponding alkyl halides on (dimethylamino-methyl)ferrocene even at low temperature.[87,88] This factor will decrease the yield of the chiral ferrocenyl tertiary amine thioethers. To avoid the problem, we have consistently used dry ether as the solvent in the synthesis and not halogenated organic solvents (CH_2Cl_2, $CHCl_3$, CCl_4), even though the starting material is highly soluble in such solvents.

1. Preparation

A number of previously unknown chiral ferrocenylamine thioether ligands of the type (R,S)-$C_5H_5FeC_5H_3[CH(CH_3)N(CH_3)_2][SR]$ where R = Me, Et, i-Pr, n-Pr, n-Bu, i-Bu, t-Bu, i-Pent, Ph, CH_2Ph, p-toyl, 4-Cl-Ph, have been prepared in a general, high yield, one step synthesis shown in scheme 13. The starting material (R)-N,N-dimethyl-1-ferrocenyl ethylamine [(R)-7] was prepared from ferrocene according to Ugi's procedure[77] and was resolved by using (R)-(+)-tartaric acid. As illustrated by Ugi,[33] the (R)-amine [(R)-7], is stereoselectively lithiated by n-butyllithium to give 96% of the (R)-(R)-7. The (R)-(R) derivative is thought to be stabilized by the coordination of the adjacent nitrogen atom (in the side chain) to the lithium atom. The lithiated chiral ferrocene derivative is then treated with the appropriate disulfides to produce the product as (R)-(S)-amines. In some cases (like in preparation of the phenyl derivative), it may be necessary to reflux the reaction mixture before work-up. The chiral ferrocenyl-amine sulfide products (46-57) are usually deprotonated by washing with aqueous $NaHCO_3$ before separation by chromatography on alumina or silica gel column. It should be noted here that the chiral ferrocenylamine sulfide compounds 46-57 contain two elements of chirality. The (R) configuration refers to the asymmetric carbon while the (S) configuration refers to the planar chirality. The yields of these products are fairly high (ranging from 45% yield in the ethyl derivative to 85% yield in the p-tolyl derivative) basically due to the modified procedure adopted in this work.[87] The (R)-N,N-dimethyl-1-[(R)-2-lithio-ferrocenyl]ethylamine, [(R)-(R)-7], was not isolated here but rather was prepared fresh for each reaction.

2. ^1H NMR

The 250 MHz ^1H NMR data for the chiral ferrocenylamine thioethers



(R)-7 (R)-(R)-27 46–57

Scheme 13

R = Me,
Et,
i-Pr,
n-Pr,
n-Bu,
t-Bu,
i-Pent
Ph,
CH_2Ph,
p-tolyl,
4-chlorophenyl(4-Cl-Ph)

Table 2

250 MHz ^{1}H NMR Data for (R,S)-$C_5H_5FeC_5H_3$[CH(CH_3)N(CH_3)$_2$][SR] R = Me, Et, i-Pr, n-Pr, n-Bu, t-Bu, Ph, CH_2Ph, i-Pent, p-tolyl, 4-Cl-Ph. Spectra Obtained in $CdCl_3$/TMS at Room Temperature: δ, ppm (J,Hz)

							SR				
Compound	Ph	C_5H_3	C_5H_5	NCH	NM_2	$NCCH_3$	αH	βH	γH	δH	$CH(CH_3)_2$ $PhCH_3$
*(R)-7		4.11	4.08 s	3.60 d (6,8)	2.09 s	1.46 d					
(R,S)-46		4.28 t[a]									
		4.18 m[b,c]									
		4.17 m[b,c]	4.10 s	3.94 q (7)	2.13 s	1.40 d (7)	2.30 s				
(R,S)-47		4.20 m	4.10 s	3.95 q (7)	2.10 s	1.35 d	2.60 q	1.15 t			
							2.75 q				
(R,S)-48		4.33 t[a]									1.22 d (7)
		4.21 m[b,c]									1.15 d (7)
		4.17 m[b,c]	4.09 s	4.00 q (7)	2.12 s	1.34 d (7)	3.20 m				
(R,S)-49		4.32 t[a]					2.58 q		0.95 t (7.1)		
		4.19 m[b,c]	4.10 s	3.97 q (7)	2.12 s	1.36 d (7)	2.77 q	1.56 m			
		4.16 m[b,c]									

Table 2 continued

Compound	Ph	C_5H_3	C_5H_5	NCH	NM_2	$NCCH_3$	SR αH	SR βH	SR γH	SR δH	$CH(CH_3)_2$ $PhCH_3$
(R,S)-50		4.41 t[a]									
		4.25 m[b,c]									
		4.21 m[b,c]	4.08 s	3.88 q (6.9)	2.12 s	1.30 d (6.9)		1.24 s			
(R,S)-51		4.29 t[a]									
		4.17 m[b,c]					2.72 d		0.99 d (7)		
		4.13 m[b,c]	4.10 s	3.97 q (7)	2.12 s	1.35 d (7)	2.47 d		0.93 d (7)		
(R,S)-52		4.31 t[a]									
		4.18 m[b,c]					2.79 m				
		4.15 m[b,c]	4.10 s	3.97 q (6.8)	2.12 s	1.36 d (6.8)	2.61 m	1.51 m	1.37 m	0.88 t	
(R,S)-53		4.31 t[a]					2.85 m			0.82-	0.82-
		4.20 m[b,c]									
		4.16 m[b,c]	4.10 s	3.98 q (7)	2.10 s	1.35 d	2.63 m	1.71 m	1.45 m	0.90 m	0.90m
(R,S)-54	7.25-	4.53 t[a]									
	7.05	4.42 ,[b,c]									
		4.30 m[b,c]	4.18 s	3.85 q (7)	1.90 s	1.45 d (7)					

Table 2 continued

Compound	Ph	C_5H_3	C_5H_5	NCH	NM_2	$NCCH_3$	αH	βH	SR γH	δH	$CH(CH_3)_2$ $PhCH_3$
(R,S)-55	7.18 m	4.20 t[a]									
		4.15 m[b,c]									
		4.11 m[b,c]	4.06 s	4.0 q (7)	2.21 s	1.38 d (6.8)	3.90 m				
(R,S)-56	7.11-	4.49 t[a]									
	6.94	4.30									
		4.25 m[b,c]	4.15 s	3.86 q (7)	1.94 s	1.46 d (7)					2.24 s
(R,S)-57	7.12-	4.47-									
	7.04 m	4.25 m	4.17 s	3.87 q (7)	1.92	1.40 d (7)					

Note: a = H_3

b = H_4

c = H_5

ligands (46-57) are given in Table 2. The ^1H NMR spectra of these compounds are typical of 1,2-unsymmetrically disubstituted ferrocenes in which one of the rings is unsubstituted. Rosenblum and Woodward[89] have shown that there is free rotation about the Fe-Cp axis in ferrocenes. The barrier to rotation in ferrocene is only about one-third that of the 2 methyl groups in ethane.[90] Consequently, the unsubstituted C_5H_5 ring appears as a singlet at 4.06-4.17 ppm region (see figures 1-4). Another striking feature of these spectra is the diastereotopic nature of the S-CH_2 protons. The 2 methylene protons appear at different positions with their appropriate multiplicity. Their splitting pattern is given in diagramatic form in Figure 5. In the case of the isopentyl derivative, (R,S)-53 (Figure 3), the total number of peaks expected from the methylene protons should be $2(2^3) = 16$. However, the actual number observed was 15 due to overlap of the central peaks.

The upfield peaks (1.90-2.12 ppm) of NMe_2 in these compounds are due to the ring current effect. The inversion of the pyramidal N of NMe_2 is faster than the NMR time scale at room temperature, so the nitrogen methyls appear as singlet in these compounds. Assignments of the disubstituted ring protons H_3, H_4, and H_5 cannot be made with absolute certainty, since a number of ^1H NMR studies[91-93] have shown that a single substituent may deshield or shield positions 3 and 4, in any combination relative to ferrocene. However, tentative assignments for H_3, H_4, and H_5 have been given in Table 2 and deuteration studies may be necessary to make unambiguous assignments.

The 250 MHz ^1H NMR (R-S)-55, R = CH_2Ph is given in Figure 1. One point is striking here. The benzylic protons, although diastereotopic, this property was not observed in the ^1H NMR spectra because, the resonance due to the benzylic protons is partially obscurred probably, by a combination of the cyclopentadienyl and phenyl ring protons. In contrast, the diastereotopic nature

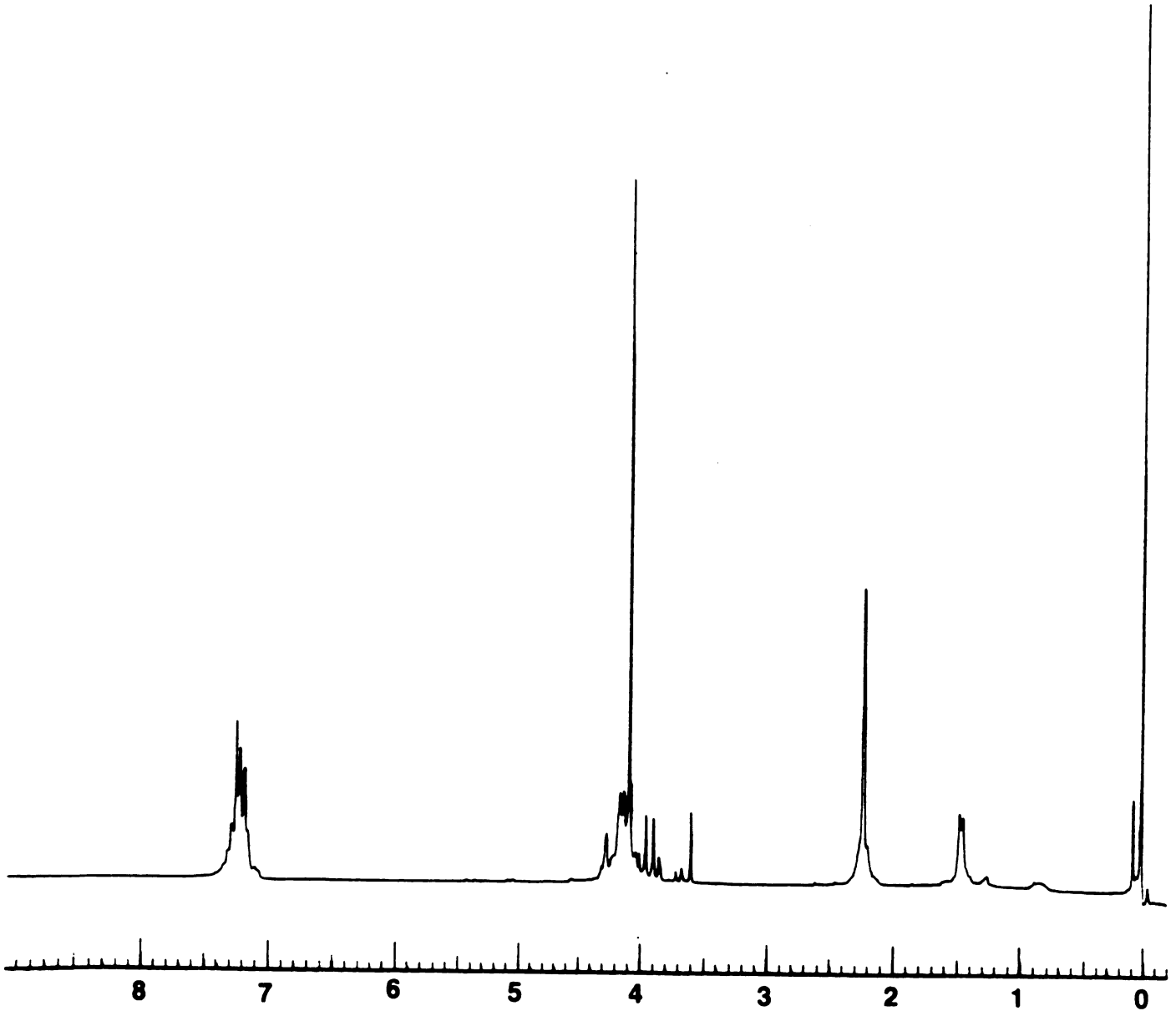


Figure 1. 250 MHz ^{1}H NMR spectrum of 55, R = CH_2Ph.

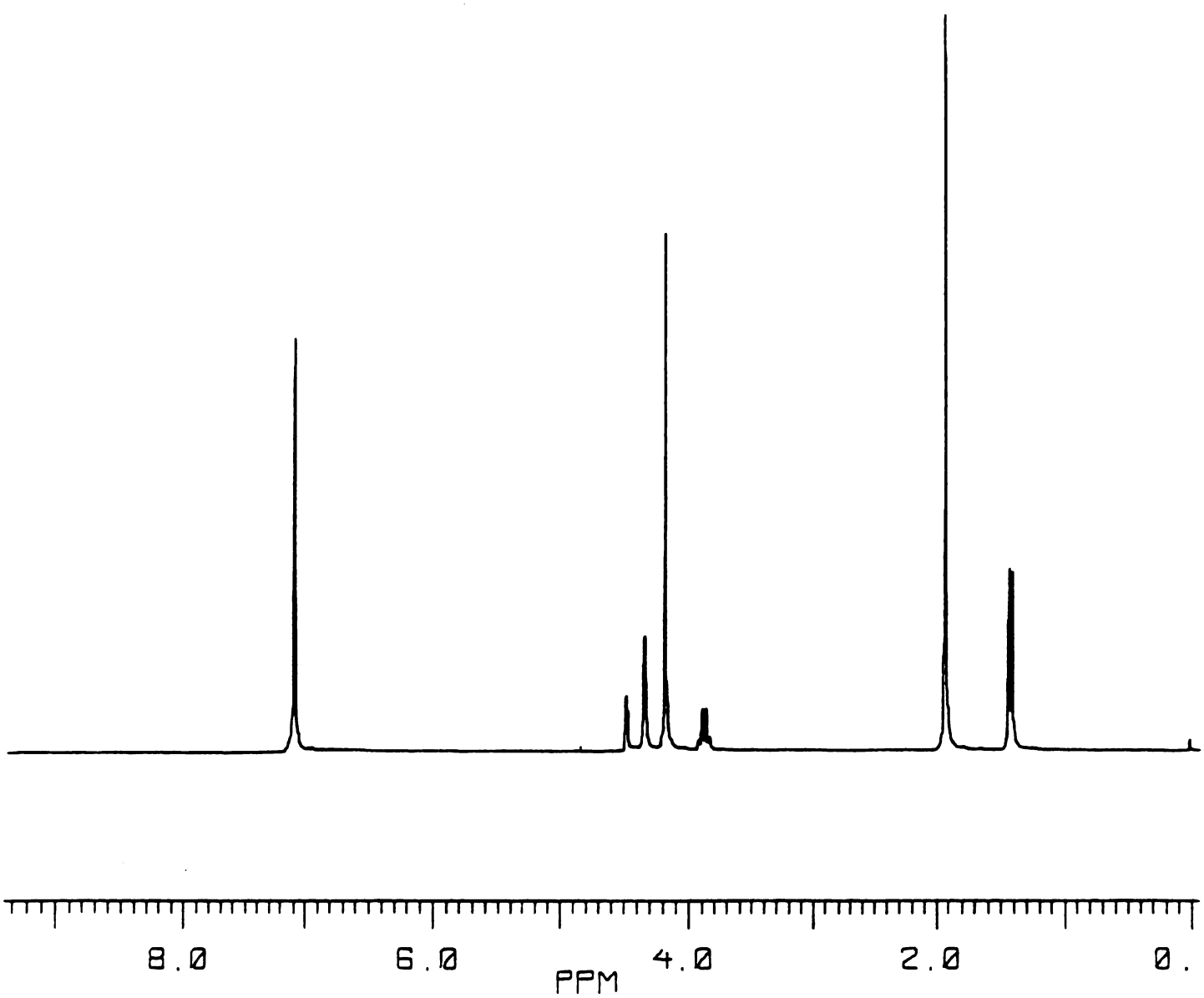


Figure 2. 250 MHz ^{1}H NMR spectrum of 57, R = 4-Cl-Ph.

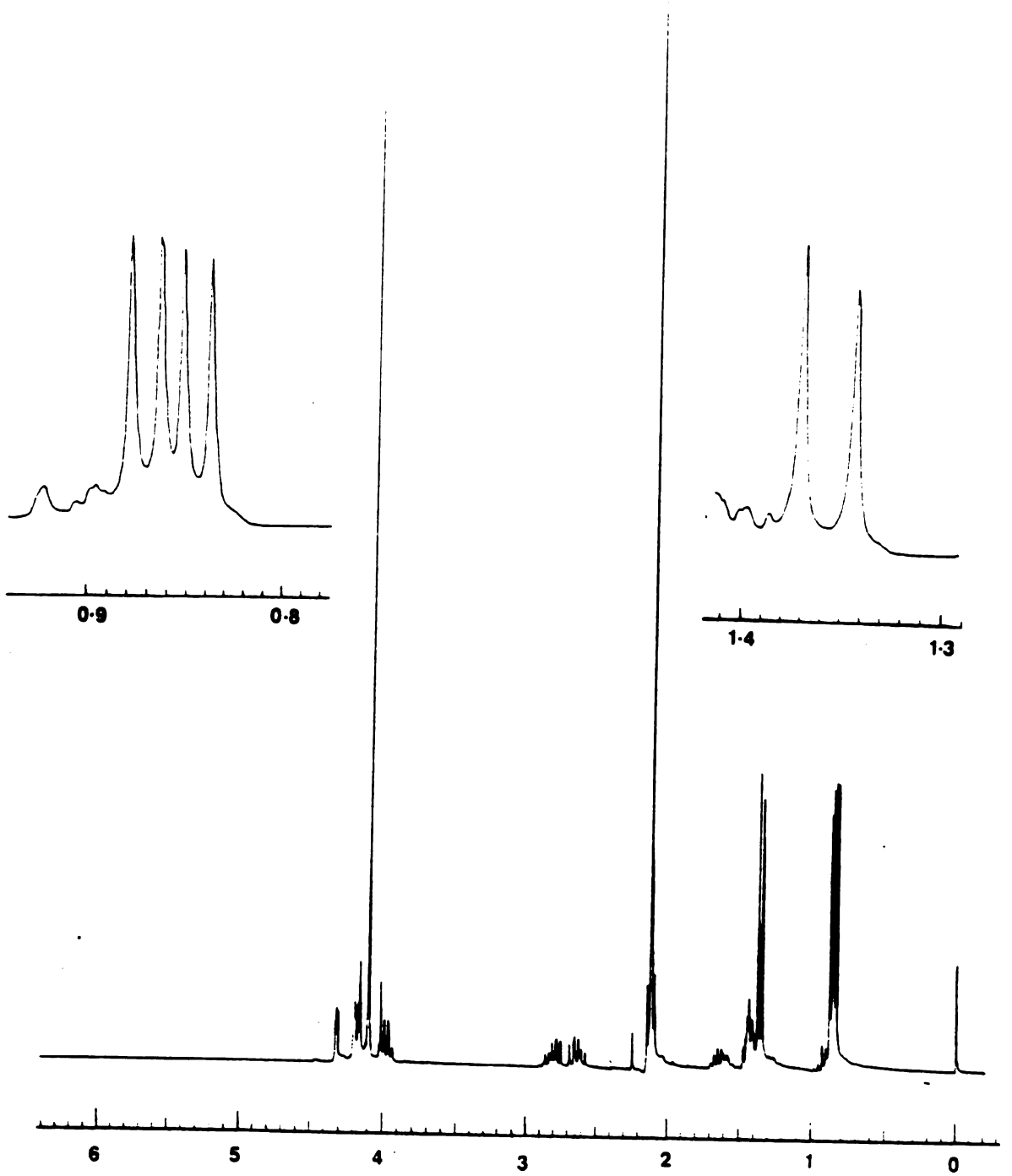


Figure 3. 250 MHz ^{1}H NMR spectrum of 53, R = i-pentyl.

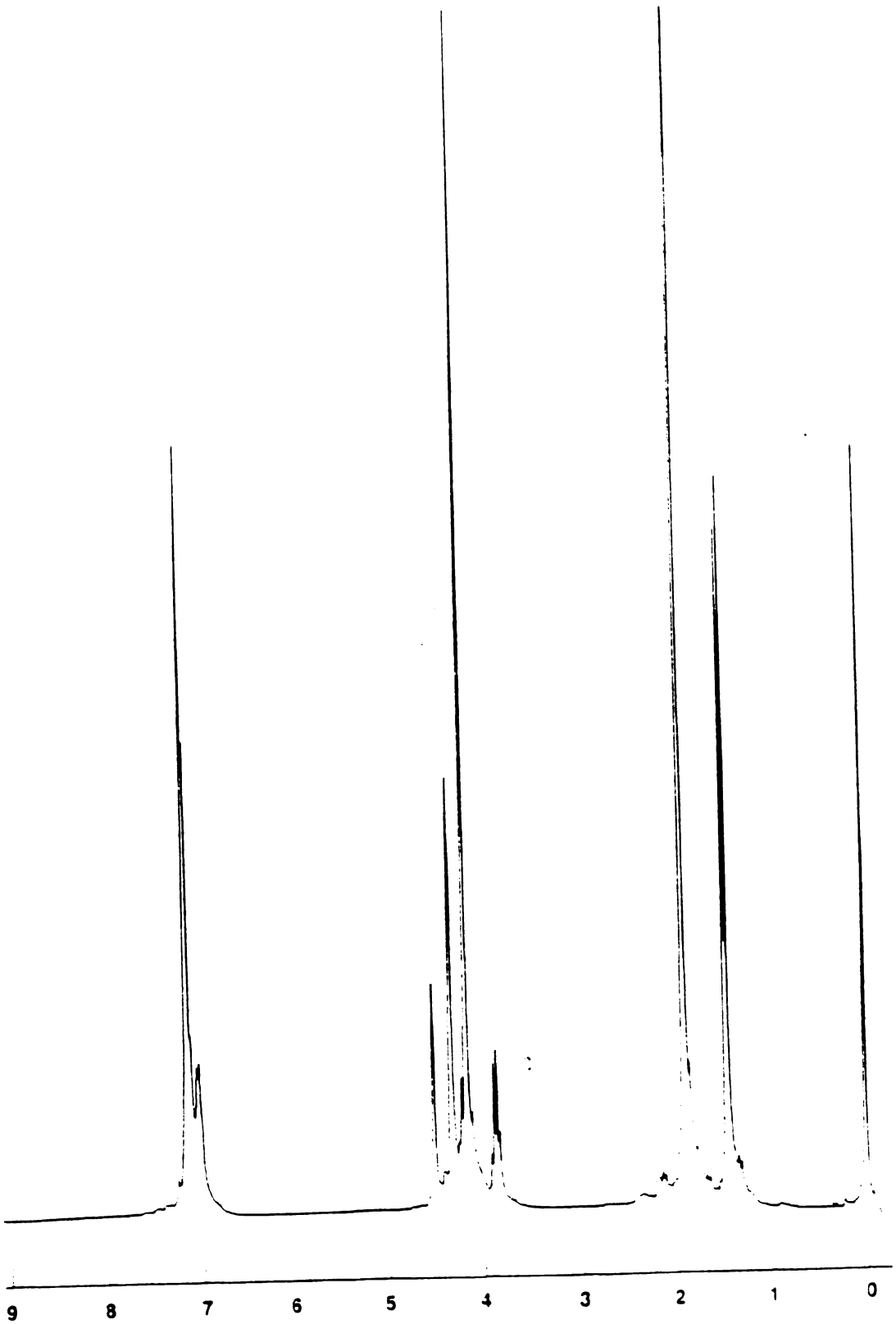


Figure 4. 250 MHz ^{1}H NMR spectrum of 54, R = Ph.

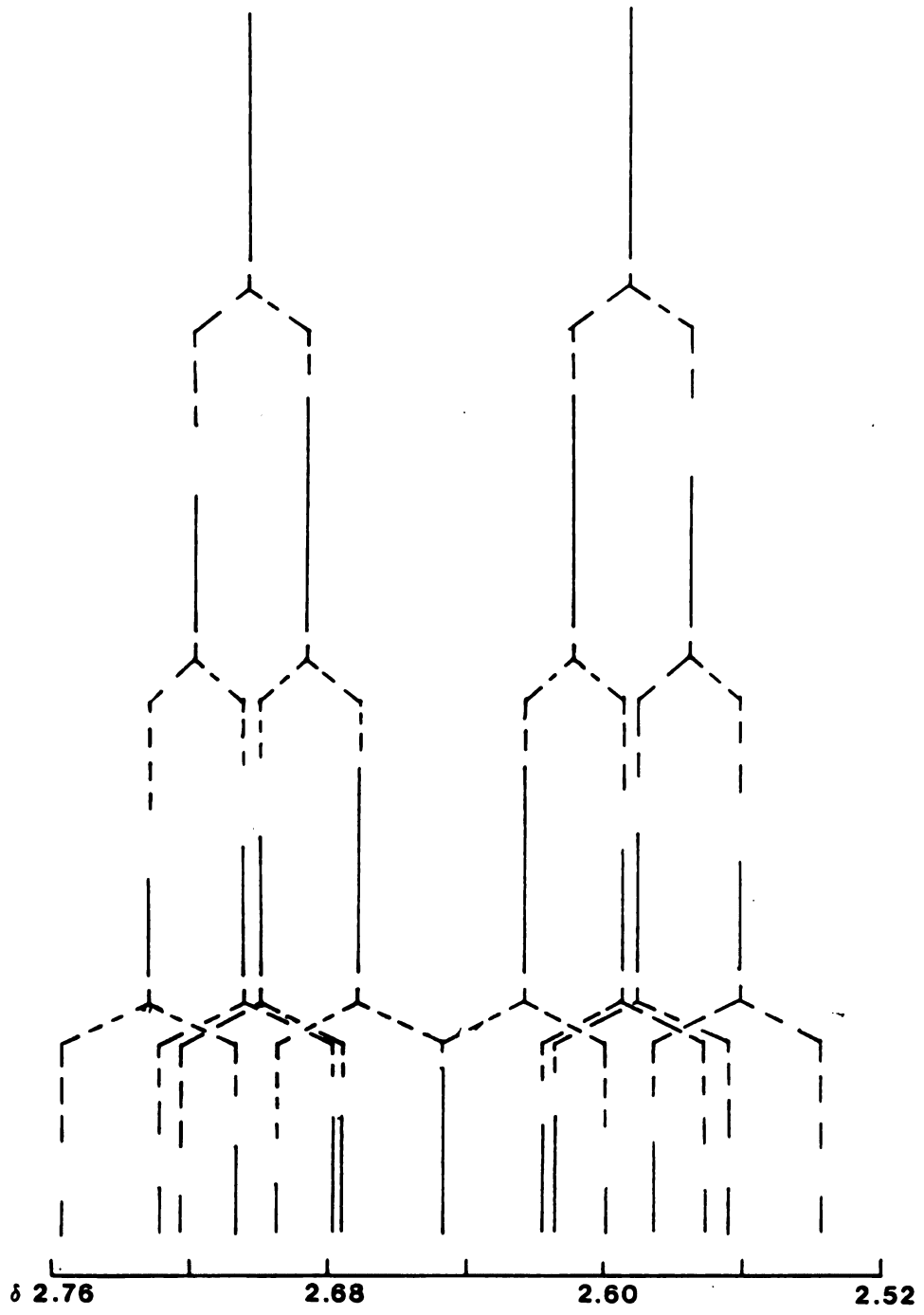
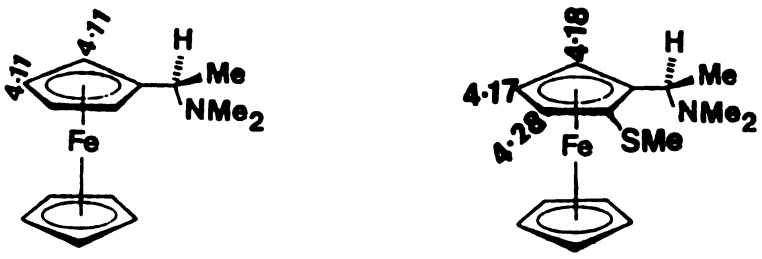


Figure **5** Splitting pattern of SCH_2 protons in **53**, R = i-pentyl.



(R)-7 (R)-(S)-46

Figure 5B: The Chemical Shifts of Substituted Ring Protons (H_3, H_4, H_5) In (R)-7 and (R,S)-46

of the methylene protons in the ethyl derivative, (R-S)-47, were observed as two distinct quartets at 2.60 and 2.75 ppm. The methyl protons of the sulfide link gave an upfield triplet signal at 1.15 ppm as expected, while the methyl protons at the chiral carbon appeared as a doublet at 1.35 ppm. The appearance of a singlet peak at 4.10 ppm confirmed the presence of an unsubstituted cyclopentadienyl ring, while the multiplet peaks at 4.20 ppm accounted for the disubstituted Cp ring.

3. ^{13}C NMR

^{13}C NMR is a sensitive tool for measuring the electron density distribution on the cyclopentadienyl ring in ferrocene.[42] Substituents on the ring induce screening of the nuclei in two different ways, one being due to the magnetic anisotropy of the substituent and the second to the electronic effect of the substitutent that consists of both resonance and inductive components.

The ^{13}C NMR data for the chiral ferrocenylamine thio ether ligands (46-57) are presented in Table 3. Koridze[94] has assigned the signals in methoxyferrocene on the basis of deuterium labelling studies. Since such labelling studies were not carried out in this work, most of the assignments here could be considered as tentative. However, the assignment of C_1 and C_2 in the 1,2-disubstituted cyclopentadienyl ring appear reasonable. C_2 reflects the inductive and field effects of the substituents (-SR) and exhibits the widest range of values of any of the ring carbons. The C_2 resonance in (R,S)-56 (i.e. p-tolyl derivative) is shifted downfield by 26.1 ppm, relative to ferrocene (68.2 ppm[94]), whereas the 4-chlorophenyl derivative, (R,S)-57, is deshielded by 24.9 ppm. the assignments of C_1 and the unsubstituted cyclopentadienyl ring are reasonable, but assignments of C_3, C_4 and C_5 are more difficult. In addition, it is incorrect to extrapolate ^{13}C data to ^{1}H data. In some cases the chemical shift ordering is the same,

Table 3

250 MHz ^{13}C NMR Data for (R,S)-$C_5H_5FeC_5H_3$]$CH(CH_3)N(CH_3)_2$][SR] (46-57) in $CDCl_3$/TMS at Room Temperature: δ ppm,

Compound	Ph	C_2-C_5[a] C_2	C_1	C_5H_5	C_3,C_4,C_5	NCH	NMe_2	SC	βC	PhMe δ SC γ C	$NCCH_3$
*(R)-7		68.5 d									
		66.5 d									
		66.3 d	86.2 s	67.7 d		57.8 d	40.2 q				14.8 q
(R,S)-46					71.0 d						
					67.3 d						
		84.0 s	75.1 s	69.9 d	66.5 d	56.1 d	40.5 q	19.8 q			13.1 q
(R,S)-48					75.2 d						
					67.8 d				22.6 q		
		94.6 s	78.3 s	69.9 d	66.7 d	55.8 d	39.9 q	39.2 d	23.8 q		10.6 q
(R,S)-49					73.3 d						
					67.4 d						
		93.2 s	80.5 s	69.9 d	66.5 d	55.9 d	40.2 q	38.7 t	22.9 t	13.7 q	12.0 q

Table 3 continued

Compound	Ph	C_2-C_5[a] C_2	C_1	C_5H_5	C_3,C_4,C_5	NCH	NMe_2	SC	C	PhMe SC C	$NCCH_3$
(R,S)-50					77.7 d						
					68.9 d						
		95.5 s	77.8 s	70.8 d	68.2 d	55.9 d	39.9 q	45.9 s	31.7 q		9.3 q
(R,S)-51					73.2 d						
					67.4 d					21.7 q	
		93.2 s	80.8 s	69.9 d	66.5 d	55.9 d	40.2 q	45.9 t	28.4 d	22.3 q	11.8 q
(R,S)-52					73.5 d						
					67.5 d					13.7 q[b]	
		93.5 s	80.5 s	69.9 d	66.5 d	55.9 d	40.2 q	36.4 t	31.8 t	21.9 t	11.9 q
(R,S)-55	138.9 s, 129.1 d			69.9 d	71.6 d						
	128.3 d, 126.7 d				68.0 d						
					67.0 d	56.4 d	39.9 q	41.45 t			10.9 q
(R,S)-56	138.0 s				76.0 d						
	135.2 s	94.3 s	77.9 s	70.9 d	69.1 d	56.6 d	40.4 q			20.9 q	12.7 q
	129.6 d				68.7 d						
	128.2 d										

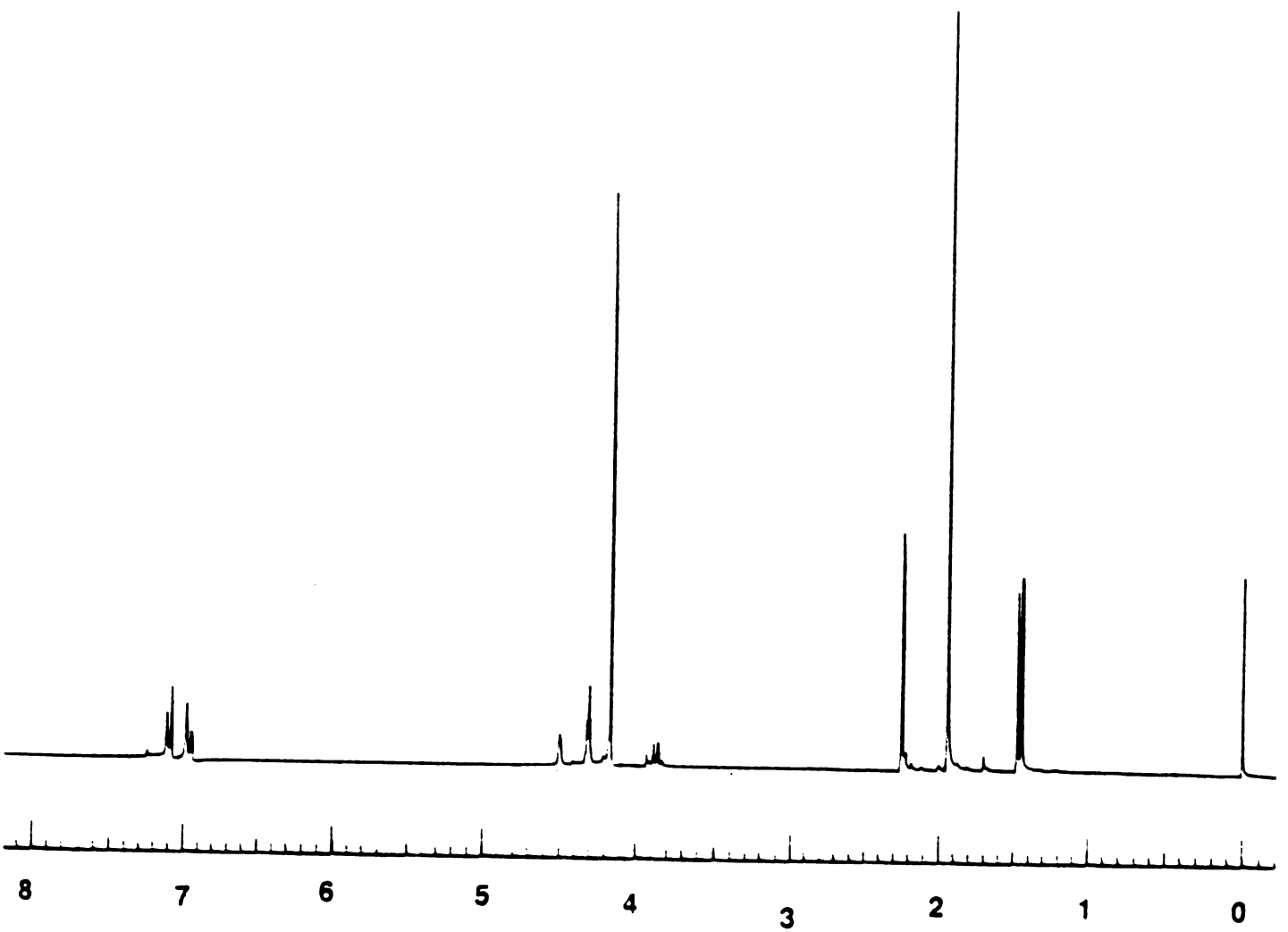


Figure 6. 250 MHz ^{1}H NMR spectrum of 56, R = p-tolyl.

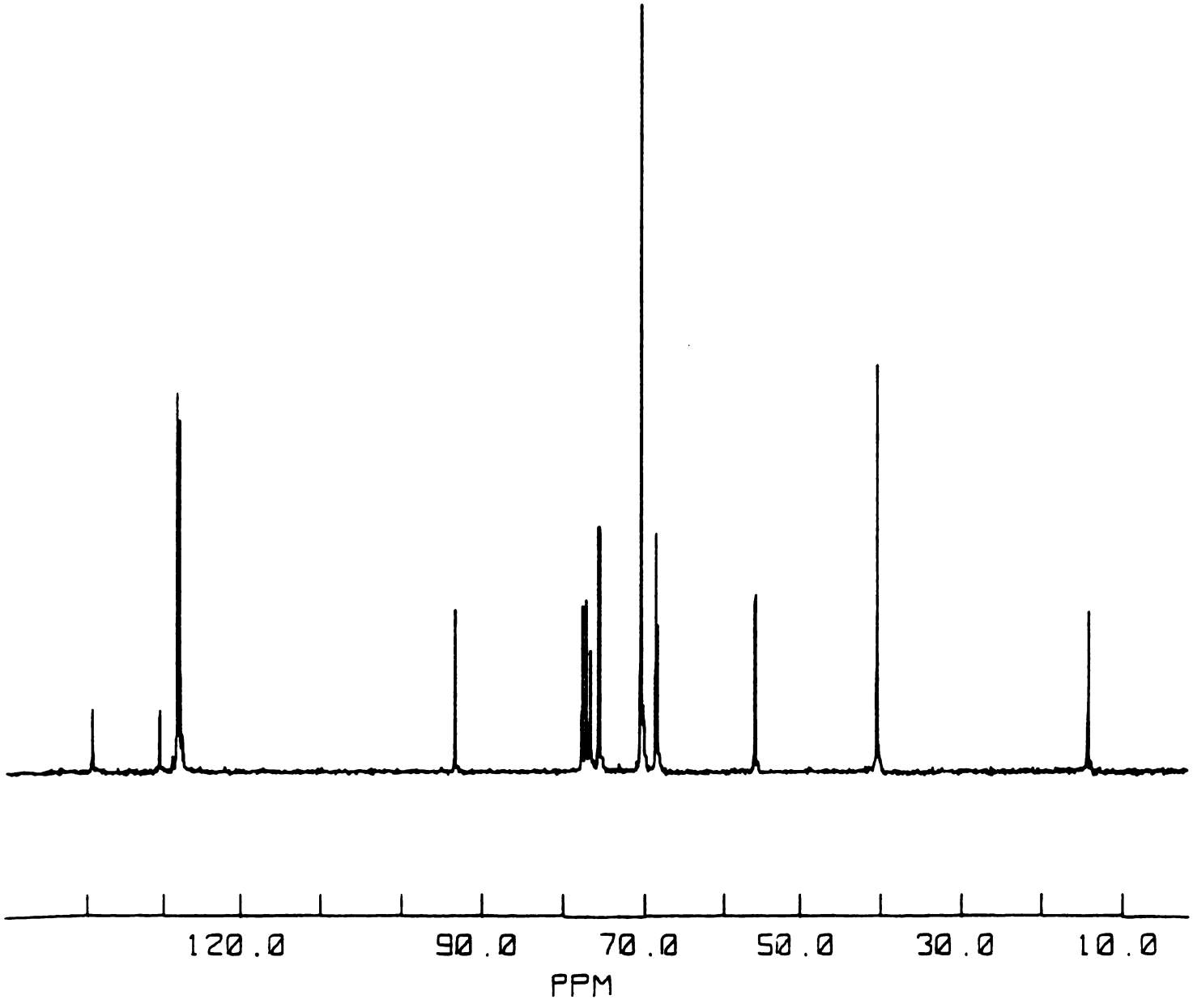


Figure 7. Gated decoupled ^{13}C NMR spectrum of 57,

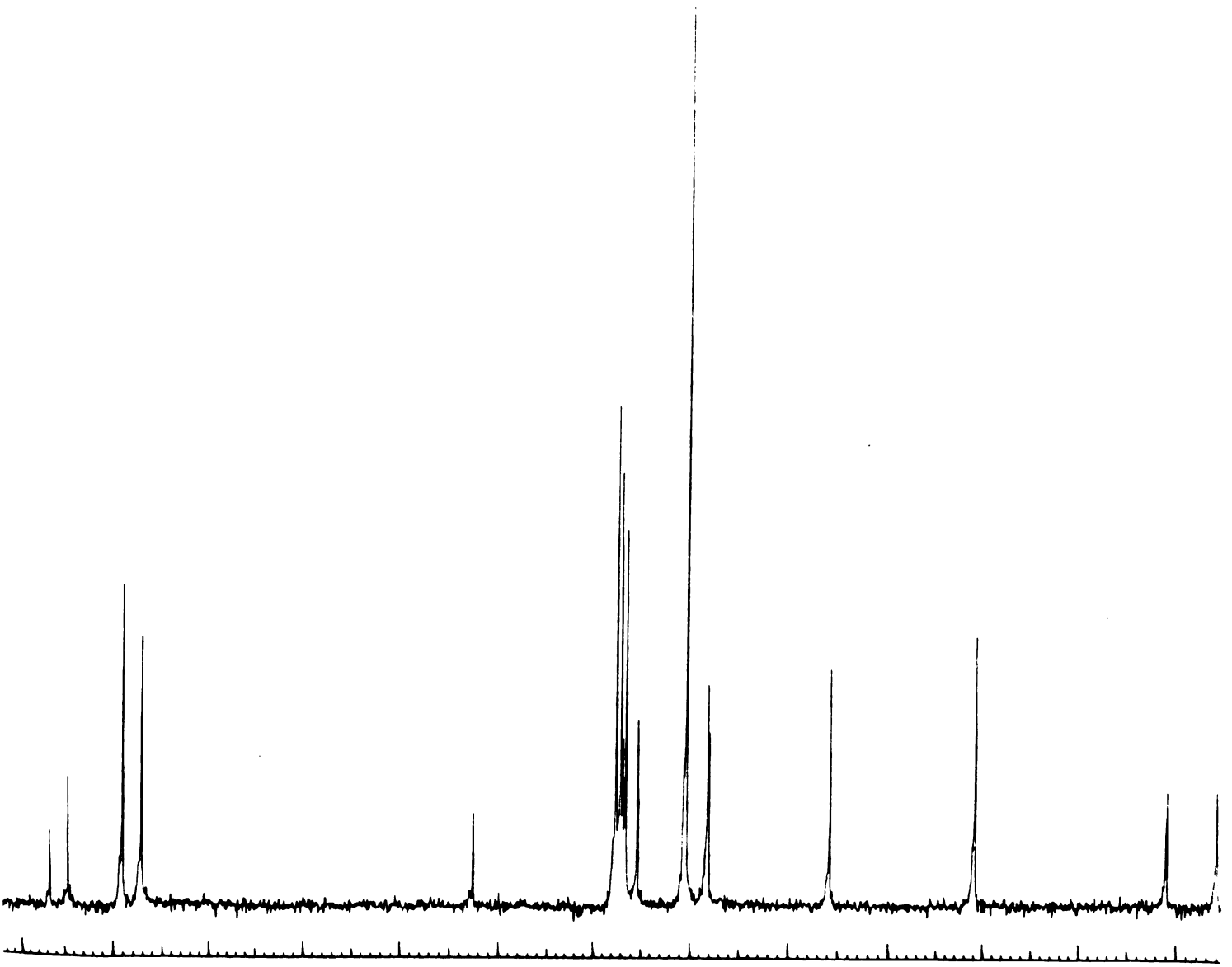


Figure 8. Gated decoupled ^{13}C NMR spectrum of 56.

but in ferrocenylaldehyde, for example, the carbon order is $C_3 > C_2$,[95] while the proton order is $H_2 > H_3$.[91-93, 96, 97].

4. Infrared (IR) Spectra

As reported by Rosenblum,[2] the two most important peaks in the infrared spectra of ferrocenederivatives, in which one ring is unsubstituted, appear around 1000 and 1100 cm^{-1}. In all the chiral ferrocenylamine thioether ligands (46-57), peaks were observed in this region, thus confirming substitution in one ferrocenyl ring of these compounds. The IR data are shown in the experimental section. A general inspection of the IR data indicates that certain frequencies are common to all the chiral ferrocenylamine thioether compounds (46-57). These frequencies have been tentatively assigned by comparison with the vibrational spectra of ferrocene[2] and dimethylferrocene.[98]

The high frequency infrared bands at 3100-2860 cm^{-1} are assigned to C-H stretching frequencies. The strong absorption around 1450-1380 cm^{-1} may be associated with alkyl C-H bend whereas the strong absorption at 1100-1050 cm^{-1} could be assigned to ring breathing modes. The broad band absorptions in the region of 500-450 cm^{-1} may be associated with ring-metal vibrations such as an asymmetric ring-metal tilt and an asymmetric ring-metal stretch.

The mass spectral data (shown in the experimental section) reveal some important fragments such as M^+, FeCp, C_5H_5, $HCMeNMe_2$, vinylferrocene and M^+-SR. In addition to these fragments, peaks consistent with the less abundant isotopes ^{54}Fe, ^{57}Fe, and ^{34}S were observed.

Cullen[57,99] has determined the crystal structure of [(PPFA)Rh(NBD)]PF_6, where PPFA is (R,S)-1-(2-di-phenylphosphinoferrocenyl)ethyldimethylamine; NBD is norbornadiene, and concluded that the chiral ferrocenyl phosphine

ligand coordinated to rhodium through both the phosphorous and nitrogen atoms. Since there is much interest in ligands which have both "hard" and "soft" properties, investigation of the chelation of the chiral ferrocenylamine sulfide, (46-57) with transition metals, such as palladium and platinum, forms the basis of interest in this work. In addition, the effectiveness of these chiral ligands in transition metal catalyzed asymmetric synthesis has been explored.

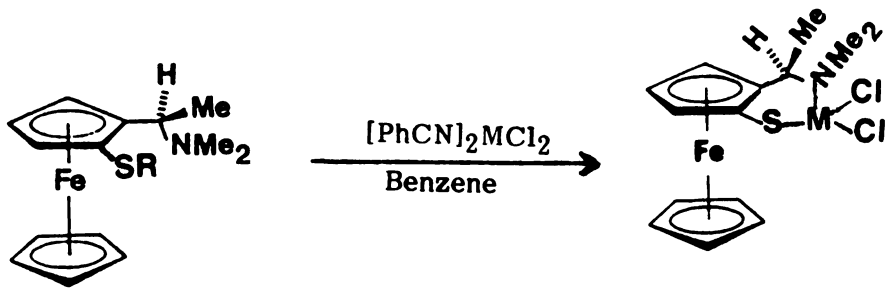
B. Palladium Complexes of (R,S)-$C_5H_5FeC_5F_3$[CHMeNMe$_2$][SR] (R = Me, i-Pr, n-Pr, i-Bu, Ph, p-tolyl, 4-Cl-Ph) and Platinum Complexes of (R-S)-$C_5H_5FeC_5H_3$-[CHMeNMe$_2$][S-4-Cl-Ph]

1. Preparation

Palladium and platinum complexes, (58-65), were made by allowing a benzene solution of the chiral ferrocenylamine sulfides, (46, 48, 49, 51, 54, 56, 57), to react with bis(benzonitrile) adducts of palladium and platinum chloride salts (Scheme 14). The heterobimetallic complexes are insoluble in benzene: the chiral palladium ferrocenylamine sulfide complexes precipitated immediately while the platinum analog precipitated after being stirred for 8 days.

The palladium complexes are soluble in acetone, methylene chloride and chloroform, except the phenyl and tolyl derivatives which were only slightly soluble in these solvents. The platinum complex (57) is also soluble in these solvents. Analytically pure samples were obtained by the slow evaporation of the mixed solvent system, methylene chloride-petroleum ether.

Dichloro[(R)-1-(S)-2-methylthioferrocenylethyldimethyl-amine]palladium(11), (58), gave the best crystals as reflected in the elemental analysis and x-ray crystal structure.



(R,S)-Ligands

M = Pd, R = Me,
i-Pr,
n-Pr,
i-Bu,
Ph,
p-tolyl,
4-Cl-Ph

M = Pt, R = 4-Cl-Ph.

Scheme 14

Table 4

250 MHz ^{1}H Data for (R,S)$C_5H_5FeC_5H_3$(CHMeNMe$_2$)(SR)/MCl_2 Complexes (58-65) in $CDCl_3$/TMS at Room Temperature: δ ppm

Compound	M	Ph	C_5H_3	C_5H_5	NCH	SCH	NMe_2	$NCCH_3$	βH	γH	Ph-CH_3 δ CH_3
58	Pd		4.51 m				3.21 s				
			4.40	4.23 s	3.87 q	2.70 s	2.31 s	1.55 d			
59	Pd		4.63 m				3.17 s		1.75 d		
			4.48 m	4.27 s	3.80 q	3.88 m	2.24 s	1.93 d	1.53 d		
60	Pd		4.49 m			3.57 m	3.19 s		2.24 m		
			4.40 m	4.21 s	3.86 q	3.05 m	2.30 s	1.52 d	2.03	1.17 t	
61	Pd		4.44 m			3.67 d	3.19 s			1.20 d	
			4.39 m	4.21 s	3.83 q	2.82 d	2.33 s	1.52 d	2.37 d	1.18 d	
62	Pd	8.00-	4.36 m				3.28 s				
		7.50 m	4.25 m								
			4.02 m	4.10 s	4.03 q		2.36	1.52 d			
63	Pd	7.80-	4.33 m				3.16 s				
		7.28 m	4.21 m	4.00 s	3.96 q		2.22s	1.44 d			2.36 s
64	Pd	8.04-	4.68 m				3.18 s				
		7.55 m	4.50 m	4.12 s	4.21 q		2.44 s	1.50 d			
65	Pt	7.40-	4.50-				3.18 s				
		7.22 m	4.20 m	4.13 s	3.88 q		2.25 s	1.45 d			

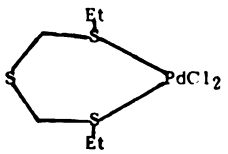
2. ^{1}H NMR

250 MHz ^{1}H NMR data for the chiral palladium and platinum complexes, (58-65), are presented in Table 4. The chiral ferrocenylamine thioether ligand undergoes a significant change in the ^{1}H NMR spectra upon complexing with platinum or palladium chlorides. Figure 9 indicates that the most striking difference in the ^{1}H NMR spectra of the complexed ligand relative to the free ligand is the large downfield shift of the resonance due to H_3, H_4 and H_5 of the substituted cyclopentadienyl ring. This deshielding effect was originally thought to be due to a severe tilting of the cyclopentadienyl rings where H_3, H_4 and H_5 were further from the shielding iron atom.[100] The crystal structure of the chiral methylthioether palladium complex (58), (discussed in detail in a later section) however, indicated that the cyclopentadienyl ring was tilted 3.2° from the plane. The large downfield shift of H_3, H_4 and H_5 is either due to the magnetic anisotropy or the inductive effect of the metal chloride. A further difference between the ^{1}H NMR spectra of the free ligand and complexed methyl ligand is the deshielding of the alkyl protons. In particular, the resonance due to sulfur methyl protons shifts from 2.30 to 2.70 ppm.

Sokolov had observed that the chemical shifts of two methyl groups in NMe_2 of a 2-dimethylaminomethylferrocenyl palladium chloride dimer are different (2.85 and 3.00 ppm respectively).[101] The same splitting of NMe_2 protons were observed in this case for the methyl complex (58), indicating the obvious diastereotopic nature of these methyl groups. The two peaks appeared at 2.31 and 3.21 ppm respectively (see Figure 9). The chemical shifts of the two methyl groups in NMe_2 of the metal complexes (58-65), are much more downfield than those of the corresponding free ligands and the chemical shift difference of the two methyl groups (0.90 ppm) is large because the inversion of the pyramidal N of these metal complexes is inhibited by a rigid 6-member

Table 5

Metal-S, Metal-N, and Metal-Cl Stretching Modes in Several Metal Complexes

Compound	$\bar{\nu}$, cm^{-1}	Stretching Mode	Reference
59	460 sh	Pd-N	a
	320 b	Pd-Cl, Pd-S,	a
	300 b	Pd-Cl, Pd-S	
60	465 sh	Pd-N	
	322 b	Pd-Cl, Pd-S	a
62	482 sh, 443 b	Pd-N	
	323 b	Pd-Cl, Pd-S	
	298 sh	Pd-Cl, Pd-S	a
63	460 sh	Pd-N	
	297 m	Pd-Cl, Pd-S	a
	273, 316	Pd-Cl	
	349, 396	Pd-S	102
Thioether-metal complexes	280-400	M-S	103
Unidentate amine-Metal complexes	370-500	M-N	103
$(PhSC_3H_6SPh)PdCl_2$	278 sh, 262 sh	Pd-Cl	
	323 sh, 308 sh	Pd-S	104

[a] This work.

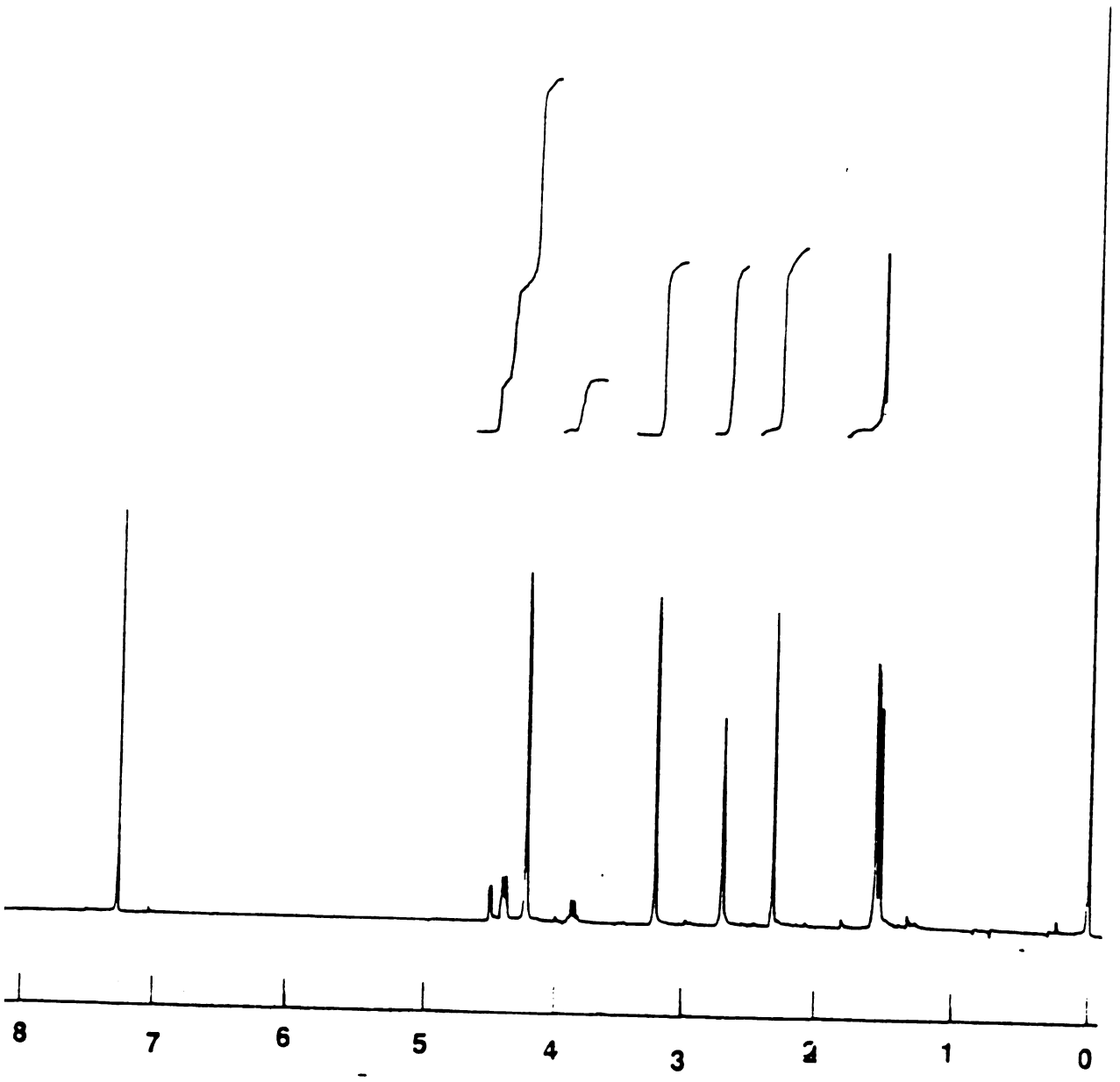


Figure 9. 250 MHz ^{1}H NMR spectrum of 58; $PdCl_2$ complex.

chelate ring structure in the complex (see structure).

3. Infrared Spectra (IR)

The metal-N, metal-Cl, and metal-S stretching modes of several complexes are given in Table 5. The most striking change occurs in the low frequency region where metal-ligand vibrations are prevalent. Metal-sulfur bands are often weak and occur in a region similar to metal-chloride bands. Consequently, the absorptions around 297 to 323 cm^{-1} region in complexes 59, 60, 62, and 63, have been assigned to Pd-S and/or Pd-Cl stretches. Metal-nitrogen stretches occur at a higher frequency region, so the peaks around 460 to 482 cm^{-1} region are assigned to Pd-N in the complexes. These assignments are, however, tentative since in complex molecules of low symmetry, more than one fundamental mode often contributes to a given peak.[105] It should be noted that the stretching frequencies assigned to complexes 59, 60, 62 and 63 are in close agreement with those reported for the chelated thioether complex, $(PhSC_3H_6SPh)PdCl_2$,[104] and most other values in the literature.[106,107]

4. Structure of Dichloro[(R)-1-(S)-2-methylthioferrocenylethyldimethylamine]palladium(11), 58.

The structure and numbering scheme of dichloro[(R)-1-(S)-2-methylthioferrocenylethyldimethylamine]palladium(11), 58, is shown in Figure 10, while a stereoview is given in Figure 11. Hydrogen atoms have been omitted for clarity. A total of 2937 reflections were collected, of which 2912 were unique and not systematically absent. As a check on crystal and electronic stability, three representative reflections were measured every 45 reflections. The slope of the least-squares line through a plot of intensity versus time was -17 (16) counts/hour which corresponds to a total loss in intensity of 0.3%. A linear

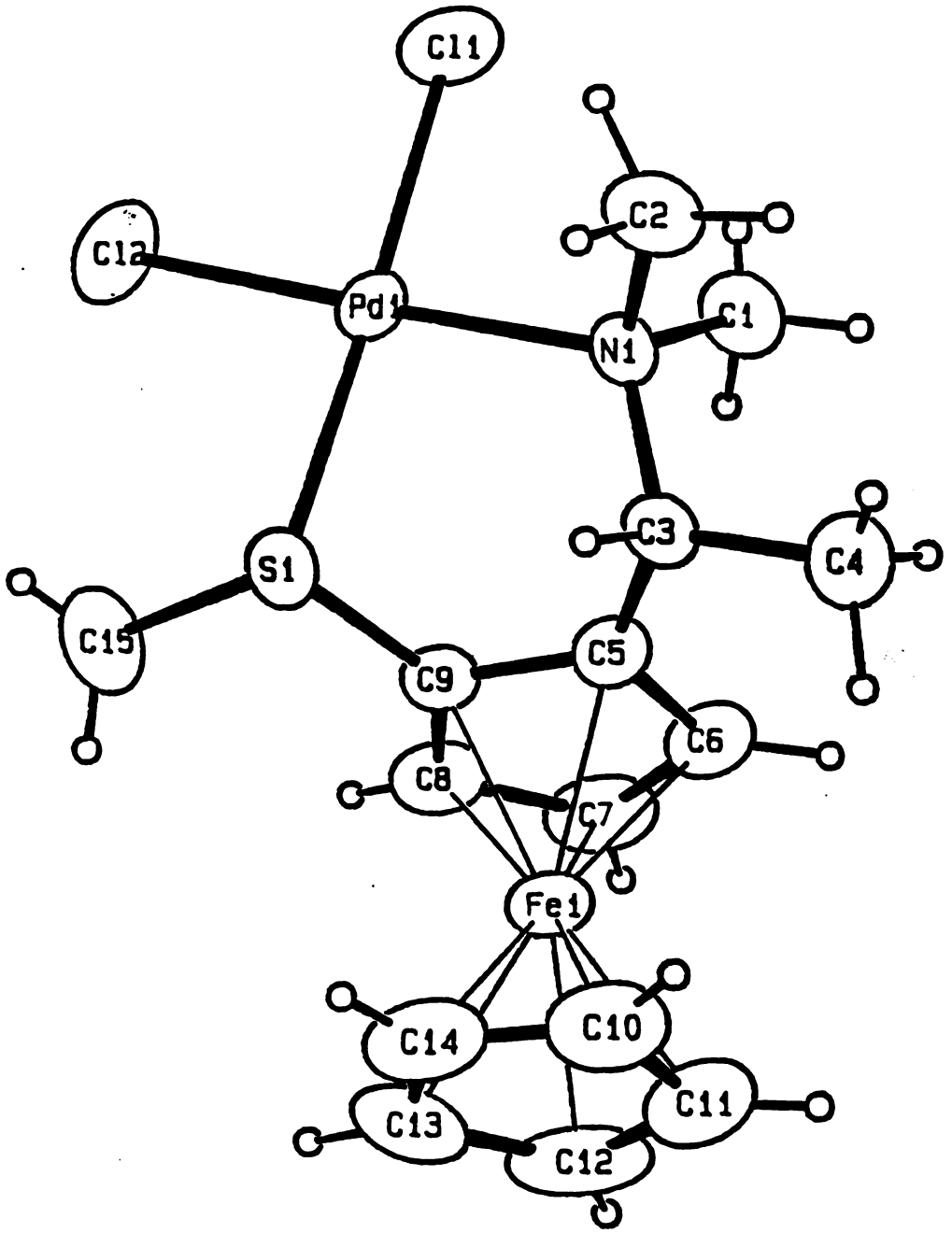


Figure 10: Structure and Numbering Scheme for the Comples $C_5H_5FeC_5H_3[CHMeNMe_2][SMe]/PdCl_2$, 58

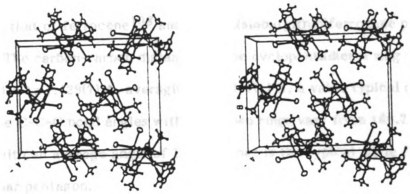


Figure 11:

Stereoview of the Complex $C_5H_5FeC_5H_3[CHMeNMe_2][SMe]/PdCl_2$, 58

decay correction was applied with correction factors on 1 ranging from 1.000 to 1.003 and with an average value of 1.002. The final coefficient, refined in least-squares, was -0.344×10^{-8} (in absolute units).

The positional parameters are given in Table 6, while general temperature factor expressions are given in Tables 7-9. The palladium atom is in a square planar environment where the ferrocenylamine thioether ligand chelates to the palladium atom through nitrogen and sulfur atoms.

The bond distances and bond angles for the complex are presented in Table 11 and Table 12 and are fairly typical. the iron-carbon distances range from 2.02(6) A to 2.050(6) A with an average value of 2.033(7) A that compares favorably with that of ferrocene[108] and 1,1'-bis(siobutylthio)ferrocene palladium-dichloride.[42] The carbon-carbon distances in the cyclopentadienyl ring vary from 1.378(12) A to 1.429(7) A, averaging at 1.407(1) A, a value typical of ferrocene. The C-C-C bond angles within the two rings vary from 106.7(7) to 109.2(7)°, with an average angle of 108.01° that is the typical angle for a regular, planar pentagon.

The Pd-S bond length is 2.288(1) A which compares favorably with the sum of the covalent radii (2.35 A)[109] and suggests that there is little or no π-bonding in the Pd-S bond. The Pd-Cl bond, which is trans to the sulfur atom, shows no apparent trans bond lengthening, indicating that the thioether ligand has a negligible trans-influence.[110] The Pd-Cl bond distances have an average value of 2.307(5) A almost equal to the sum of the Pauling covalent radii, 2.31 A.[109] The Pd-N bond length is 2.159(4) A, and is comparable to the sum of the Pauling covalent radii.

Seyferth[111] has reported a crystal structure of a heterobinuclear species $(Ph_3P)PdFe(C_5H_4S)_2$ where thiolate groups chelate to palladium. The cyclopentadienylthiolato groups, (C_5H_4S), are tilted away from the parallel plane by

Table6. Positional Parameters and
Their Estimated Standard Deviations for
dichloro[(R)-1-(S)-2-Methylthioferrocenylethyldimethylamine]palladium(II)

Atom	x	y	z	B(A2)
Pd1	0.24368(4)	0.95281(3)	0.32293(3)	2.565(5)
Fe1	0.72981(8)	1.06536(6)	0.42963(5)	2.76(1)
Cl1	0.1007(2)	0.9270(2)	0.2000(1)	4.81(4)
Cl2	0.1385(2)	0.7998(2)	0.3797(2)	6.08(5)
S1	0.3806(2)	0.9739(1)	0.44528(9)	2.79(2)
N1	0.3355(5)	1.0999(4)	0.2682(3)	2.42(8)
C1	0.3909(7)	1.0741(6)	0.1801(4)	3.7(1)
C2	0.2092(7)	1.1772(5)	0.2601(4)	3.7(1)
C3	0.4558(6)	1.1545(4)	0.3207(4)	2.65(9)
C4	0.5130(9)	1.2610(5)	0.2834(5)	4.4(1)
C5	0.5723(5)	1.0719(5)	0.3365(3)	2.7(1)
C6	0.7113(6)	1.0555(6)	0.2976(4)	3.5(1)
C7	0.7716(6)	0.9588(5)	0.3313(4)	4.0(1)
C8	0.6717(7)	0.9135(5)	0.3912(4)	3.6(1)
C9	0.5494(6)	0.9827(4)	0.3943(3)	2.48(9)
C10	0.740(1)	1.2111(5)	0.4940(4)	4.8(1)
C11	0.8733(8)	1.1861(7)	0.4558(5)	5.0(2)
C12	0.9229(7)	1.0884(7)	0.4890(5)	5.6(2)
C13	0.8183(9)	1.0498(7)	0.5498(5)	5.8(2)
C14	0.7074(8)	1.1265(7)	0.5514(5)	5.4(2)
C15	0.403(1)	0.8520(6)	0.5073(5)	5.1(2)

Positional Parameters and
Their Estimated Standard Deviations (contd.) in
dichloro[(R)-1-(S)-2-Methylthioferrocenylethyldimethylamine]palladium(II)

Atom	x	y	z	B(A2)
H1a	0.486(7)	1.020(5)	0.183(4)	4(1)*
H1b	0.433(7)	1.134(5)	0.149(4)	4(2)*
H1c	0.335(6)	1.055(5)	0.150(4)	4(1)*
H2a	0.179(8)	1.196(6)	0.316(5)	7(2)*
H2b	0.122(6)	1.132(4)	0.237(3)	3(1)*
H2c	0.239(9)	1.245(5)	0.232(4)	6(2)*
H3	0.411(7)	1.171(5)	0.370(4)	4(2)*
H4a	0.589(7)	1.292(5)	0.324(4)	5(2)*
H4b	0.450(8)	1.302(6)	0.279(4)	6(2)*
H4c	0.563(6)	1.250(4)	0.234(3)	3(1)*
H6	0.757(8)	1.112(5)	0.263(4)	4(1)*
H7	0.864(6)	0.924(4)	0.322(4)	3(1)*
H8	0.674(6)	0.846(5)	0.416(4)	4(1)*
H10	0.695(7)	1.271(5)	0.476(4)	5(2)*
H11	0.91(1)	1.237(8)	0.419(6)	9(3)*
H12	1.011(7)	1.054(5)	0.474(4)	4(1)*
H13	0.827(7)	0.973(6)	0.577(5)	6(2)*
H14	0.633(7)	1.117(5)	0.577(4)	4(2)*
H15a	0.329(7)	0.824(5)	0.523(4)	5(2)*
H15b	0.465(7)	0.875(5)	0.551(4)	5(2)*
H15c	0.436(8)	0.796(6)	0.477(4)	6(2)*

Starred atoms were refined isotropically.
Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:
(4/3) * [a^2*B(1,1) + b^2*B(2,2) + c^2*B(3,3)
+ ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3)
+ bc(cos alpha)*B(2,3)]

Table 7. General Temperature Factor Expressions - B's - for dichloro[(R)-1-(S)-2-Methylthioferrocenylethyldimethylamine]palladium(II)

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)	Beqv
Pd1	1.96(1)	2.75(1)	2.99(1)	-0.17(2)	0.20(1)	0.01(1)	2.565(5)
Fe1	2.08(2)	3.30(3)	2.91(3)	0.12(3)	-0.29(2)	-0.57(3)	2.76(1)
Cl1	3.75(6)	6.25(9)	4.45(7)	-1.13(7)	-0.97(6)	-0.92(7)	4.81(4)
Cl2	5.35(8)	5.42(8)	7.5(1)	-2.79(7)	-0.19(9)	2.03(8)	6.08(5)
S1	2.92(5)	2.92(5)	2.54(5)	0.27(5)	0.23(4)	0.47(4)	2.79(2)
N1	2.5(2)	2.6(2)	2.1(2)	0.2(2)	0.1(1)	0.4(1)	2.42(8)
C1	4.1(2)	5.1(3)	1.9(2)	-0.1(2)	0.3(2)	-0.2(2)	3.7(1)
C2	3.5(2)	3.2(2)	4.5(3)	1.0(2)	-0.7(2)	0.3(2)	3.7(1)
C3	3.0(2)	2.5(2)	2.4(2)	-0.1(2)	-0.4(2)	0.2(2)	2.65(9)
C4	4.8(3)	3.4(3)	5.1(3)	-0.9(3)	-0.9(3)	1.1(3)	4.4(1)
C5	2.5(2)	3.2(2)	2.4(2)	-0.2(2)	0.1(2)	-0.4(2)	2.7(1)
C6	2.6(2)	4.8(3)	3.1(2)	-0.4(2)	0.5(2)	-0.8(2)	3.5(1)
C7	2.7(2)	5.0(2)	4.4(2)	1.0(2)	0.1(2)	-2.4(2)	4.0(1)
C8	3.4(2)	2.8(2)	4.6(3)	0.2(2)	-0.9(2)	-0.9(2)	3.6(1)
C9	2.3(2)	2.5(2)	2.6(2)	0.2(2)	-0.3(2)	-0.3(2)	2.48(9)
C10	4.7(3)	4.7(3)	4.9(3)	-0.2(4)	-1.1(3)	-1.6(2)	4.8(1)
C11	3.8(3)	5.9(4)	5.2(3)	-1.3(3)	-0.3(3)	-0.8(3)	5.0(2)
C12	2.8(2)	7.4(4)	6.6(4)	1.1(3)	-1.8(3)	-2.9(3)	5.6(2)
C13	7.1(4)	5.9(4)	4.5(3)	-0.9(4)	-3.3(2)	0.2(3)	5.8(2)
C14	3.7(3)	8.7(4)	3.9(3)	-1.2(3)	-0.0(2)	-2.4(3)	5.4(2)
C15	6.3(4)	4.3(3)	4.8(3)	0.2(3)	-0.3(3)	2.0(3)	5.1(2)

The form of the anisotropic thermal parameter is:

$\exp[-0.25(h^2a^2B(1,1) + k^2b^2B(2,2) + l^2c^2B(3,3) + 2hkabB(1,2) + 2hlacB(1,3) + 2klbcB(2,3))]$

where a, b, and c are reciprocal lattice constants.

Table 8. Refined Temperature Factor Expressions - Beta's - for dichloro[(R)-1-(S)-2-Methylthioferrocenylethyldimethylamine]palladium(II)

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
Pd1	0.00575(3)	0.00461(2)	0.00313(1)	-0.00077(7)	0.00070(5)	0.00004(4)
Fe1	0.00609(7)	0.00553(5)	0.00304(3)	0.0005(1)	-0.00103(9)	-0.00150(7)
Cl1	0.0110(2)	0.0105(2)	0.00466(7)	-0.0050(3)	-0.0034(2)	-0.0024(2)
Cl2	0.0157(2)	0.0091(1)	0.0078(1)	-0.0124(3)	-0.0007(3)	0.0054(2)
S1	0.0086(1)	0.00489(9)	0.00266(5)	0.0012(2)	0.0008(2)	0.0013(1)
N1	0.0074(5)	0.0044(3)	0.0022(2)	0.0007(7)	0.0003(5)	0.0011(4)
C1	0.0119(7)	0.0086(5)	0.0020(2)	-0.000(1)	0.0010(7)	-0.0006(6)
C2	0.0104(7)	0.0054(4)	0.0047(3)	0.0044(9)	-0.0026(8)	0.0008(6)
C3	0.0089(6)	0.0042(3)	0.0026(2)	-0.0002(8)	-0.0015(7)	0.0006(5)
C4	0.0142(9)	0.0056(4)	0.0054(3)	-0.004(1)	-0.003(1)	0.0029(7)
C5	0.0073(5)	0.0053(4)	0.0025(2)	-0.0011(8)	0.0005(6)	-0.0012(5)
C6	0.0075(6)	0.0081(5)	0.0032(2)	-0.002(1)	0.0016(6)	-0.0021(6)
C7	0.0079(6)	0.0083(4)	0.0046(2)	0.004(1)	0.0003(7)	-0.0063(6)
C8	0.0100(7)	0.0046(4)	0.0048(3)	0.0011(9)	-0.0033(8)	-0.0024(6)
C9	0.0068(5)	0.0041(3)	0.0028(2)	0.0007(7)	-0.0010(6)	-0.0008(5)
C10	0.0139(9)	0.0078(4)	0.0051(3)	-0.001(2)	-0.004(1)	-0.0041(6)
C11	0.0112(8)	0.0099(6)	0.0054(4)	-0.006(1)	-0.001(1)	-0.0022(9)
C12	0.0082(7)	0.0124(7)	0.0069(4)	0.005(1)	-0.0064(9)	-0.0077(9)
C13	0.021(1)	0.0098(6)	0.0047(3)	-0.004(2)	-0.0115(9)	0.0005(9)
C14	0.0109(8)	0.0145(8)	0.0040(3)	-0.006(1)	-0.0000(9)	-0.0064(8)
C15	0.018(1)	0.0071(5)	0.0050(3)	0.001(1)	-0.001(1)	0.0053(7)

The form of the anisotropic thermal parameter is:

$\exp[-(B(1,1)*h^2 + B(2,2)*k^2 + B(3,3)*l^2 + B(1,2)*hk + B(1,3)*hl + B(2,3)*kl)]$.

Table 9. General Temperature Factor Expressions - U's - for dichloro[(R)-1-(S)-2-Methylthioferrocenylethyldimethylamine]palladium(II)

Name	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
Pd1	0.0248(1)	0.0349(1)	0.0378(2)	-0.0022(2)	0.0025(2)	0.0002(2)
Fe1	0.0263(3)	0.0418(4)	0.0368(3)	0.0015(3)	-0.0037(3)	-0.0072(3)
Cl1	0.0474(7)	0.079(1)	0.0564(9)	-0.0143(9)	-0.0123(7)	-0.0117(9)
Cl2	0.068(1)	0.069(1)	0.095(1)	-0.0353(8)	-0.002(1)	0.026(1)
S1	0.0369(6)	0.0370(7)	0.0322(6)	0.0034(6)	0.0029(6)	0.0060(6)
N1	0.032(2)	0.033(2)	0.027(2)	0.002(2)	0.001(2)	0.005(2)
C1	0.051(3)	0.065(4)	0.024(2)	-0.001(3)	0.004(3)	-0.003(3)
C2	0.045(3)	0.041(3)	0.056(3)	0.013(3)	-0.009(3)	0.004(3)
C3	0.038(2)	0.032(2)	0.031(2)	-0.001(2)	-0.005(2)	0.003(2)
C4	0.061(4)	0.043(3)	0.065(4)	-0.011(3)	-0.011(4)	0.014(3)
C5	0.031(2)	0.040(3)	0.031(2)	-0.003(2)	0.002(2)	-0.006(2)
C6	0.033(2)	0.061(3)	0.039(3)	-0.005(3)	0.006(2)	-0.010(3)
C7	0.034(3)	0.063(3)	0.056(3)	0.013(3)	0.001(3)	-0.030(3)
C8	0.043(3)	0.035(3)	0.058(3)	0.003(3)	-0.012(3)	-0.012(3)
C9	0.030(2)	0.031(2)	0.034(2)	0.002(2)	-0.004(2)	-0.004(2)
C10	0.060(4)	0.059(3)	0.061(3)	-0.003(5)	-0.013(4)	-0.020(3)
C11	0.048(3)	0.075(5)	0.066(4)	-0.016(4)	-0.004(4)	-0.011(4)
C12	0.035(3)	0.094(5)	0.084(4)	0.014(4)	-0.023(3)	-0.037(4)
C13	0.090(5)	0.074(5)	0.057(3)	-0.012(5)	-0.041(3)	0.003(4)
C14	0.047(4)	0.110(6)	0.049(3)	-0.016(4)	-0.000(3)	-0.031(4)
C15	0.079(5)	0.054(4)	0.061(4)	0.002(4)	-0.003(4)	0.025(3)

The form of the anisotropic thermal parameter is:

$$\exp[-2\pi^2(h^2a^2U(1,1) + k^2b^2U(2,2) + l^2c^2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3) + 2klbcU(2,3))]$$

where a, b, and c are reciprocal lattice constants.

Table 10. Root-Mean-Square Amplitudes of Thermal Vibration (in Angstroms) for dichloro[(R)-1-(S)-2-Methylthioferrocenylethyldimethylamine]palladium(II)

Atom	Min.	Int'med.	Max.
Pd1	0.155	0.188	0.196
Fe1	0.158	0.180	0.218
Cl1	0.178	0.255	0.294
Cl2	0.169	0.286	0.347
S1	0.168	0.185	0.209
N1	0.155	0.176	0.193
C1	0.153	0.227	0.255
C2	0.165	0.229	0.249
C3	0.164	0.180	0.204
C4	0.186	0.228	0.287
C5	0.167	0.174	0.209
C6	0.170	0.193	0.257
C7	0.147	0.201	0.302
C8	0.173	0.194	0.261
C9	0.165	0.169	0.196
C10	0.187	0.250	0.288
C11	0.195	0.255	0.292
C12	0.161	0.233	0.364
C13	0.168	0.268	0.348
C14	0.181	0.218	0.354
C15	0.177	0.282	0.288

Table 11. Bond Distances (in Angstroms) for
dichloro[(R)-1-(S)-2-Methylthioferrocenylethyldimethylamine]palladium(II)

Atom1	Atom2	Distance
Pd1	Cl1	2.334(2)
Pd1	Cl2	2.281(2)
Pd1	S1	2.288(1)
Pd1	N1	2.159(4)
Fe1	C5	2.046(5)
Fe1	C6	2.050(6)
Fe1	C7	2.038(6)
Fe1	C8	2.021(6)
Fe1	C9	2.022(5)
Fe1	C10	2.042(7)
Fe1	C11	2.023(8)
Fe1	C12	2.024(7)
Fe1	C13	2.037(7)
Fe1	C14	2.034(7)
S1	C9	1.749(5)
S1	C15	1.783(8)
N1	C1	1.487(7)
N1	C2	1.505(8)
N1	C3	1.529(7)
C3	C4	1.518(9)
C3	C5	1.495(7)
C5	C6	1.429(7)
C5	C9	1.425(8)
C6	C7	1.407(9)
C7	C8	1.418(9)
C8	C9	1.410(8)
C10	C11	1.395(11)
C10	C14	1.395(10)
C11	C12	1.378(12)
C12	C13	1.427(11)
C13	C14	1.387(11)

Bond Distances (Continued) for
dichloro[(R)-1-(S)-2-Methylthioferrocenylethyldimethylamine]palladium(II)

Atom1	Atom2	Distance
C1	H1a	1.10(6)
C1	H1b	0.96(6)
C1	H1c	0.73(6)
C2	H2a	0.93(8)
C2	H2b	1.04(6)
C2	H2c	0.97(7)
C3	H3	0.89(6)
C4	H4a	1.01(7)
C4	H4b	0.77(7)
C4	H4c	0.91(5)
C6	H6	0.97(6)
C7	H7	0.96(5)
C8	H8	0.91(6)
C10	H10	0.88(7)
C11	H11	0.90(9)
C12	H12	0.95(6)
C13	H13	1.03(8)
C14	H14	0.80(6)
C15	H15a	0.80(6)
C15	H15b	0.93(7)
C15	H15c	0.88(7)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 12. Bond Angles (in Degrees) for
dichloro[(R)-1-(S)-2-Methylthioferrocenylethyldimethylamine]palladium(II)

Atom1	Atom2	Atom3	Angle
Cl1	Pd1	Cl2	87.79(8)
Cl1	Pd1	S1	178.34(6)
Cl1	Pd1	N1	90.9(1)
Cl2	Pd1	S1	90.55(7)
Cl2	Pd1	N1	177.9(1)
S1	Pd1	N1	90.8(1)
C5	Fe1	C6	40.8(2)
C5	Fe1	C7	68.6(2)
C5	Fe1	C8	68.9(2)
C5	Fe1	C9	41.0(2)
C5	Fe1	C10	110.0(3)
C5	Fe1	C11	125.2(3)
C5	Fe1	C12	159.8(3)
C5	Fe1	C13	158.3(3)
C5	Fe1	C14	124.3(3)
C6	Fe1	C7	40.3(3)
C6	Fe1	C8	68.4(3)
C6	Fe1	C9	68.5(2)
C6	Fe1	C10	122.6(3)
C6	Fe1	C11	107.2(3)
C6	Fe1	C12	122.2(3)
C6	Fe1	C13	159.2(3)
C6	Fe1	C14	158.9(3)
C7	Fe1	C8	40.9(3)
C7	Fe1	C9	68.6(2)
C7	Fe1	C10	155.7(3)
C7	Fe1	C11	119.4(3)
C7	Fe1	C12	105.1(3)
C7	Fe1	C13	122.9(3)
C7	Fe1	C14	160.6(3)
C8	Fe1	C9	40.8(2)
C8	Fe1	C10	163.1(3)
C8	Fe1	C11	154.4(3)
C8	Fe1	C12	119.6(3)
C8	Fe1	C13	106.8(3)
C8	Fe1	C14	125.6(3)
C9	Fe1	C10	127.3(3)
C9	Fe1	C11	163.1(3)
C9	Fe1	C12	156.4(3)
C9	Fe1	C13	122.0(3)
C9	Fe1	C14	110.5(3)
C10	Fe1	C11	40.1(3)
C10	Fe1	C12	67.4(3)
C10	Fe1	C13	67.6(3)
C10	Fe1	C14	40.0(3)
C11	Fe1	C12	39.8(3)

Bond Angles (Continued) for
dichloro[(R)-1-(S)-2-Methylthioferrocenylethyldimethylamine]palladium(II)

Atom1	Atom2	Atom3	Angle
C11	Fe1	C13	67.9(3)
C11	Fe1	C14	67.3(3)
C12	Fe1	C13	41.1(3)
C12	Fe1	C14	67.6(3)
C13	Fe1	C14	39.8(3)
Pd1	S1	C9	97.3(2)
Pd1	S1	C15	114.5(3)
C9	S1	C15	100.8(3)
Pd1	N1	C1	108.5(4)
Pd1	N1	C2	104.5(3)
Pd1	N1	C3	116.1(3)
C1	N1	C2	108.9(4)
C1	N1	C3	109.2(4)
C2	N1	C3	109.4(4)
N1	C3	C4	115.1(5)
N1	C3	C5	108.3(4)
C4	C3	C5	113.0(5)
Fe1	C5	C3	130.6(4)
Fe1	C5	C6	69.7(3)
Fe1	C5	C9	68.6(3)
C3	C5	C6	132.1(5)
C3	C5	C9	120.8(5)
C6	C5	C9	106.8(5)
Fe1	C6	C5	69.5(3)
Fe1	C6	C7	69.4(3)
C5	C6	C7	108.5(5)
Fe1	C7	C6	70.3(3)
Fe1	C7	C8	68.9(4)
C6	C7	C8	108.2(5)
Fe1	C8	C7	70.2(4)
Fe1	C8	C9	69.6(3)
C7	C8	C9	108.0(5)
Fe1	C9	S1	130.0(3)
Fe1	C9	C5	70.4(3)
Fe1	C9	C8	69.5(3)
S1	C9	C5	117.5(4)
S1	C9	C8	133.7(4)
C5	C9	C8	108.6(5)
Fe1	C10	C11	69.2(4)
Fe1	C10	C14	69.7(4)
C11	C10	C14	107.3(7)
Fe1	C11	C10	70.6(4)
Fe1	C11	C12	70.1(5)
C10	C11	C12	108.9(7)
Fe1	C12	C11	70.1(4)
Fe1	C12	C13	69.9(4)

Bond Angles (Continued) for
dichloro[(R)-1-(S)-2-Methylthioferrocenylethyldimethylamine]palladium(II)

Atom1	Atom2	Atom3	Angle
C11	C12	C13	107.9(7)
Fe1	C13	C12	68.9(4)
Fe1	C13	C14	70.0(4)
C12	C13	C14	106.7(7)
Fe1	C14	C10	70.3(4)
Fe1	C14	C13	70.2(4)
C10	C14	C13	109.2(7)
N1	C1	H1a	111.(3)
N1	C1	H1b	116.(4)
N1	C1	H1c	114.(5)
H1a	C1	H1b	99.(5)
H1a	C1	H1c	113.(6)
H1b	C1	H1c	102.(6)
N1	C2	H2a	108.(5)
N1	C2	H2b	107.(3)
N1	C2	H2c	111.(5)
H2a	C2	H2b	102.(6)
H2a	C2	H2c	107.(6)
H2b	C2	H2c	121.(5)
N1	C3	H3	103.(4)
C4	C3	H3	107.(4)
C5	C3	H3	110.(4)
C3	C4	H4a	109.(4)
C3	C4	H4b	109.(5)
C3	C4	H4c	112.(3)
H4a	C4	H4b	109.(6)
H4a	C4	H4c	103.(5)
H4b	C4	H4c	114.(6)
Fe1	C6	H6	118.(4)
C5	C6	H6	121.(4)
C7	C6	H6	129.(4)
Fe1	C7	H7	124.(3)
C6	C7	H7	132.(3)
C8	C7	H7	120.(3)
Fe1	C8	H8	134.(4)
C7	C8	H8	128.(4)
C9	C8	H8	123.(4)
Fe1	C10	H10	123.(4)
C11	C10	H10	117.(4)
C14	C10	H10	135.(4)
Fe1	C11	H11	128.(6)
C10	C11	H11	115.(6)
C12	C11	H11	136.(6)
Fe1	C12	H12	126.(4)
C11	C12	H12	126.(4)

Bond Angles (Continued) for
dichloro[(R)-1-(S)-2-Methylthioferrocenylethyldimethylamine]palladium(II)

Atom1	Atom2	Atom3	Angle
C13	C12	H12	126.(4)
Fe1	C13	H13	119.(4)
C12	C13	H13	121.(4)
C14	C13	H13	132.(4)
Fe1	C14	H14	120.(5)
C10	C14	H14	128.(5)
C13	C14	H14	122.(5)
S1	C15	H15a	115.(5)
S1	C15	H15b	102.(4)
S1	C15	H15c	114.(5)
H15a	C15	H15b	115.(6)
H15a	C15	H15c	97.(7)
H15b	C15	H15c	115.(6)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 13. Torsional Angles (in Degrees) for
dichloro[(R)-1-(S)-2-Methylthioferrocenylethyldimethylamine]palladium(II)

Atom 1	Atom 2	Atom 3	Atom 4	Angle
Cl1	Pd1	S1	C9	131.3
Cl1	Pd1	S1	C15	25.9
Cl2	Pd1	S1	C9	127.3
Cl2	Pd1	S1	C15	21.8
N1	Pd1	S1	C9	-54.3
N1	Pd1	S1	C15	-159.8
Cl1	Pd1	N1	C1	-52.1
Cl1	Pd1	N1	C2	64.0
Cl1	Pd1	N1	C3	-175.4
Cl2	Pd1	N1	C1	-102.7
Cl2	Pd1	N1	C2	13.4
Cl2	Pd1	N1	C3	134.0
S1	Pd1	N1	C1	128.1
S1	Pd1	N1	C2	-115.9
S1	Pd1	N1	C3	4.8
C6	Fe1	C5	C3	-128.7
C6	Fe1	C5	C9	118.5
C7	Fe1	C5	C3	-165.6
C7	Fe1	C5	C6	-36.9
C7	Fe1	C5	C9	81.6
C8	Fe1	C5	C3	150.4
C8	Fe1	C5	C6	-80.9
C8	Fe1	C5	C9	37.6
C9	Fe1	C5	C3	112.9
C9	Fe1	C5	C6	-118.5
C10	Fe1	C5	C3	-11.5
C10	Fe1	C5	C6	117.2
C10	Fe1	C5	C9	-124.4
C11	Fe1	C5	C3	-53.9
C11	Fe1	C5	C6	74.8
C11	Fe1	C5	C9	-166.8
C12	Fe1	C5	C3	-90.3
C12	Fe1	C5	C6	38.3
C12	Fe1	C5	C9	156.8
C13	Fe1	C5	C3	68.0
C13	Fe1	C5	C6	-163.3
C13	Fe1	C5	C9	-44.9
C14	Fe1	C5	C3	30.9
C14	Fe1	C5	C6	159.6
C14	Fe1	C5	C9	-81.9
C5	Fe1	C6	C7	-120.2
C7	Fe1	C6	C5	120.2
C8	Fe1	C6	C5	82.4
C8	Fe1	C6	C7	-37.8
C9	Fe1	C6	C5	38.3
C9	Fe1	C6	C7	-81.9
C10	Fe1	C6	C5	-83.1

Torsional Angles (Continued) for
dichloro[(R)-1-(S)-2-Methylthioferrocenylethyldimethylamine]palladium(II)

Atom 1	Atom 2	Atom 3	Atom 4	Angle
C10	Fe1	C6	C7	156.7
C11	Fe1	C6	C5	-124.4
C11	Fe1	C6	C7	115.4
C12	Fe1	C6	C5	-165.3
C12	Fe1	C6	C7	74.5
C13	Fe1	C6	C5	162.6
C13	Fe1	C6	C7	42.5
C14	Fe1	C6	C5	-53.0
C14	Fe1	C6	C7	-173.2
C5	Fe1	C7	C6	37.4
C5	Fe1	C7	C8	-82.1
C6	Fe1	C7	C8	-119.5
C8	Fe1	C7	C6	119.5
C9	Fe1	C7	C6	81.6
C9	Fe1	C7	C8	-37.9
C10	Fe1	C7	C6	-54.1
C10	Fe1	C7	C8	-173.6
C11	Fe1	C7	C6	-82.0
C11	Fe1	C7	C8	158.5
C12	Fe1	C7	C6	-122.4
C12	Fe1	C7	C8	118.1
C13	Fe1	C7	C6	-163.4
C13	Fe1	C7	C8	77.1
C14	Fe1	C7	C6	172.6
C14	Fe1	C7	C8	53.1
C5	Fe1	C8	C7	81.2
C5	Fe1	C8	C9	-37.7
C6	Fe1	C8	C7	37.2
C6	Fe1	C8	C9	-81.7
C7	Fe1	C8	C9	-118.9
C9	Fe1	C8	C7	118.9
C10	Fe1	C8	C7	170.9
C10	Fe1	C8	C9	52.0
C11	Fe1	C8	C7	-47.6
C11	Fe1	C8	C9	-166.5
C12	Fe1	C8	C7	-78.5
C12	Fe1	C8	C9	162.6
C13	Fe1	C8	C7	-121.3
C13	Fe1	C8	C9	119.8
C14	Fe1	C8	C7	-160.9
C14	Fe1	C8	C9	80.2
C5	Fe1	C9	S1	-109.9
C5	Fe1	C9	C8	119.5
C6	Fe1	C9	S1	-148.1
C6	Fe1	C9	C5	-38.2
C6	Fe1	C9	C8	81.4
C7	Fe1	C9	S1	168.5

Torsional Angles (Continued) for
dichloro[(R)-1-(S)-2-Methylthioferrocenylethyldimethylamine]palladium(II)

Atom 1	Atom 2	Atom 3	Atom 4	Angle
C7	Fe1	C9	C5	-81.6
C7	Fe1	C9	C8	38.0
C8	Fe1	C9	S1	130.5
C8	Fe1	C9	C5	-119.5
C10	Fe1	C9	S1	-32.7
C10	Fe1	C9	C5	77.2
C10	Fe1	C9	C8	-163.2
C11	Fe1	C9	S1	-69.8
C11	Fe1	C9	C5	40.1
C11	Fe1	C9	C8	159.7
C12	Fe1	C9	S1	90.0
C12	Fe1	C9	C5	-160.1
C12	Fe1	C9	C8	-40.6
C13	Fe1	C9	S1	52.2
C13	Fe1	C9	C5	162.1
C13	Fe1	C9	C8	-78.4
C14	Fe1	C9	S1	9.3
C14	Fe1	C9	C5	119.2
C14	Fe1	C9	C8	-121.2
C5	Fe1	C10	C11	-121.3
C5	Fe1	C10	C14	119.9
C6	Fe1	C10	C11	-77.6
C6	Fe1	C10	C14	163.7
C7	Fe1	C10	C11	-39.2
C7	Fe1	C10	C14	-157.9
C8	Fe1	C10	C11	155.4
C8	Fe1	C10	C14	36.6
C9	Fe1	C10	C11	-164.3
C9	Fe1	C10	C14	77.0
C11	Fe1	C10	C14	-118.7
C12	Fe1	C10	C11	37.1
C12	Fe1	C10	C14	-81.6
C13	Fe1	C10	C11	81.8
C13	Fe1	C10	C14	-36.9
C14	Fe1	C10	C11	118.7
C5	Fe1	C11	C10	79.2
C5	Fe1	C11	C12	-161.3
C6	Fe1	C11	C10	120.6
C6	Fe1	C11	C12	-120.0
C7	Fe1	C11	C10	162.6
C7	Fe1	C11	C12	-77.9
C8	Fe1	C11	C10	-163.7
C8	Fe1	C11	C12	-44.2
C9	Fe1	C11	C10	48.1
C9	Fe1	C11	C12	167.5
C10	Fe1	C11	C12	119.5

Torsional Angles (Continued) for
dichloro[(R)-1-(S)-2-Methylthioferrocenylethyldimethylamine]palladium(II)

Atom 1	Atom 2	Atom 3	Atom 4	Angle
C12	Fe1	C11	C10	-119.5
C13	Fe1	C11	C10	-81.0
C13	Fe1	C11	C12	38.5
C14	Fe1	C11	C10	-37.7
C14	Fe1	C11	C12	81.8
C5	Fe1	C12	C11	49.3
C5	Fe1	C12	C13	168.0
C6	Fe1	C12	C11	77.9
C6	Fe1	C12	C13	-163.3
C7	Fe1	C12	C11	118.1
C7	Fe1	C12	C13	-123.2
C8	Fe1	C12	C11	159.7
C8	Fe1	C12	C13	-81.5
C9	Fe1	C12	C11	-171.0
C9	Fe1	C12	C13	-52.3
C10	Fe1	C12	C11	-37.4
C10	Fe1	C12	C13	81.3
C11	Fe1	C12	C13	118.7
C13	Fe1	C12	C11	-118.7
C14	Fe1	C12	C11	-80.9
C14	Fe1	C12	C13	37.8
C5	Fe1	C13	C12	-168.8
C5	Fe1	C13	C14	-50.9
C6	Fe1	C13	C12	43.0
C6	Fe1	C13	C14	160.9
C7	Fe1	C13	C12	74.3
C7	Fe1	C13	C14	-167.8
C8	Fe1	C13	C12	116.1
C8	Fe1	C13	C14	-126.0
C9	Fe1	C13	C12	158.1
C9	Fe1	C13	C14	-84.0
C10	Fe1	C13	C12	-80.8
C10	Fe1	C13	C14	37.0
C11	Fe1	C13	C12	-37.3
C11	Fe1	C13	C14	80.6
C12	Fe1	C13	C14	117.9
C14	Fe1	C13	C12	-117.9
C5	Fe1	C14	C10	-80.3
C5	Fe1	C14	C13	159.6
C6	Fe1	C14	C10	-41.1
C6	Fe1	C14	C13	-161.1
C7	Fe1	C14	C10	152.3
C7	Fe1	C14	C13	32.2
C8	Fe1	C14	C10	-167.7
C8	Fe1	C14	C13	72.3
C9	Fe1	C14	C10	-124.2
C9	Fe1	C14	C13	115.8
C10	Fe1	C14	C13	-120.0

Torsional Angles (Continued) for
dichloro[(R)-1-(S)-2-Methylthioferrocenylethyldimethylamine]palladium(II)

Atom 1	Atom 2	Atom 3	Atom 4	Angle
Cl1	Fe1	C14	C10	37.8
Cl1	Fe1	C14	C13	-82.2
Cl2	Fe1	C14	C10	81.1
Cl2	Fe1	C14	C13	-39.0
C13	Fe1	C14	C10	120.0
Pd1	S1	C9	Fe1	149.1
Pd1	S1	C9	C5	62.3
Pd1	S1	C9	C8	-111.1
C15	S1	C9	Fe1	-94.1
C15	S1	C9	C5	179.1
C15	S1	C9	C8	5.7
Pd1	N1	C3	C4	-176.9
Pd1	N1	C3	C5	55.6
C1	N1	C3	C4	60.2
C1	N1	C3	C5	-67.4
C2	N1	C3	C4	-58.9
C2	N1	C3	C5	173.5
N1	C3	C5	Fe1	-157.9
N1	C3	C5	C6	102.9
N1	C3	C5	C9	-70.7
C4	C3	C5	Fe1	73.3
C4	C3	C5	C6	-25.9
C4	C3	C5	C9	160.5
Fe1	C5	C6	C7	58.6
C3	C5	C6	Fe1	127.0
C3	C5	C6	C7	-174.4
C9	C5	C6	Fe1	-58.8
C9	C5	C6	C7	-0.2
Fe1	C5	C9	S1	125.7
Fe1	C5	C9	C8	-59.3
C3	C5	C9	Fe1	-125.5
C3	C5	C9	S1	0.2
C3	C5	C9	C8	175.2
C6	C5	C9	Fe1	59.5
C6	C5	C9	S1	-174.8
C6	C5	C9	C8	0.2
Fe1	C6	C7	C8	58.7
C5	C6	C7	Fe1	-58.6
C5	C6	C7	C8	0.1
Fe1	C7	C8	C9	59.6
C6	C7	C8	Fe1	-59.6
C6	C7	C8	C9	0.0
Fe1	C8	C9	S1	-126.3
Fe1	C8	C9	C5	59.8
C7	C8	C9	Fe1	-60.0
C7	C8	C9	S1	173.8
C7	C8	C9	C5	-0.1

Torsional Angles (Continued) for
dichloro[(R)-1-(S)-2-Methylthioferrocenylethyldimethylamine]palladium(II)

Atom 1	Atom 2	Atom 3	Atom 4	Angle
Fe1	C10	C11	C12	-59.9
C14	C10	C11	Fe1	59.5
C14	C10	C11	C12	-0.4
Fe1	C10	C14	C13	59.6
C11	C10	C14	Fe1	-59.2
C11	C10	C14	C13	0.4
Fe1	C11	C12	C13	-60.0
C10	C11	C12	Fe1	60.2
C10	C11	C12	C13	0.3
Fe1	C12	C13	C14	-60.1
C11	C12	C13	Fe1	60.0
C11	C12	C13	C14	0.0
Fe1	C13	C14	C10	-59.6
C12	C13	C14	Fe1	59.4
C12	C13	C14	C10	-0.2
C5	Fe1	C6	H6	115.6
C7	Fe1	C6	H6	-124.3
C8	Fe1	C6	H6	-162.1
C9	Fe1	C6	H6	153.9
C10	Fe1	C6	H6	32.4
C11	Fe1	C6	H6	-8.8
C12	Fe1	C6	H6	-49.8
C13	Fe1	C6	H6	-81.8
C14	Fe1	C6	H6	62.6
C5	Fe1	C7	H7	164.9
C6	Fe1	C7	H7	127.5
C8	Fe1	C7	H7	-113.0
C9	Fe1	C7	H7	-150.9
C10	Fe1	C7	H7	73.4
C11	Fe1	C7	H7	45.6
C12	Fe1	C7	H7	5.1
C13	Fe1	C7	H7	-35.9
C14	Fe1	C7	H7	-59.9
C5	Fe1	C8	H8	-154.9
C6	Fe1	C8	H8	161.1
C7	Fe1	C8	H8	123.9
C9	Fe1	C8	H8	-117.2
C10	Fe1	C8	H8	-65.2
C11	Fe1	C8	H8	76.3
C12	Fe1	C8	H8	45.4
C13	Fe1	C8	H8	2.6
C14	Fe1	C8	H8	-37.0
C5	Fe1	C10	H10	-11.4
C6	Fe1	C10	H10	32.3
C7	Fe1	C10	H10	70.8
C8	Fe1	C10	H10	-94.7
C9	Fe1	C10	H10	-54.3

Torsional Angles (Continued) for
dichloro[(R)-1-(S)-2-Methylthioferrocenylethyldimethylamine]palladium(II)

Atom 1	Atom 2	Atom 3	Atom 4	Angle
C11	Fe1	C10	H10	109.9
C12	Fe1	C10	H10	147.1
C13	Fe1	C10	H10	-168.2
C14	Fe1	C10	H10	-131.3
C5	Fe1	C11	H11	-27.9
C6	Fe1	C11	H11	13.4
C7	Fe1	C11	H11	55.5
C8	Fe1	C11	H11	89.2
C9	Fe1	C11	H11	-59.1
C10	Fe1	C11	H11	-107.1
C12	Fe1	C11	H11	133.4
C13	Fe1	C11	H11	171.9
C14	Fe1	C11	H11	-144.8
C5	Fe1	C12	H12	-70.9
C6	Fe1	C12	H12	-42.3
C7	Fe1	C12	H12	-2.1
C8	Fe1	C12	H12	39.5
C9	Fe1	C12	H12	68.8
C10	Fe1	C12	H12	-157.7
C11	Fe1	C12	H12	-120.2
C13	Fe1	C12	H12	121.1
C14	Fe1	C12	H12	158.8
C5	Fe1	C13	H13	76.4
C6	Fe1	C13	H13	-71.8
C7	Fe1	C13	H13	-40.5
C11	Fe1	C13	H13	-152.1
C12	Fe1	C13	H13	-114.8
C14	Fe1	C13	H13	127.3
C8	Fe1	C13	H13	1.3
C9	Fe1	C13	H13	43.3
C10	Fe1	C13	H13	164.4
C5	Fe1	C14	H14	42.8
C6	Fe1	C14	H14	82.1
C7	Fe1	C14	H14	-84.6
C8	Fe1	C14	H14	-44.5
C9	Fe1	C14	H14	-1.1
C10	Fe1	C14	H14	123.2
C11	Fe1	C14	H14	161.0
C12	Fe1	C14	H14	-155.8
C13	Fe1	C14	H14	-116.8
Pd1	S1	C15	H15a	-57.6
Pd1	S1	C15	H15b	177.0
Pd1	S1	C15	H15c	52.3
C9	S1	C15	H15a	-160.8
C9	S1	C15	H15b	73.7
C9	S1	C15	H15c	-50.9
Pd1	N1	C1	H1a	-69.0

Torsional Angles (Continued) for
dichloro[(R)-1-(S)-2-Methylthioferrocenylethyldimethylamine]palladium(II)

Atom 1	Atom 2	Atom 3	Atom 4	Angle
Pd1	N1	C1	H1b	179.0
Pd1	N1	C1	H1c	60.6
C2	N1	C1	H1a	177.8
C2	N1	C1	H1b	65.8
C2	N1	C1	H1c	-52.6
C3	N1	C1	H1a	58.4
C3	N1	C1	H1b	-53.6
C3	N1	C1	H1c	-172.0
Pd1	N1	C2	H2a	67.2
Pd1	N1	C2	H2b	-42.1
Pd1	N1	C2	H2c	-175.9
C1	N1	C2	H2a	-177.0
C1	N1	C2	H2b	73.7
C1	N1	C2	H2c	-60.1
C3	N1	C2	H2a	-57.8
C3	N1	C2	H2b	-167.1
C3	N1	C2	H2c	59.1
Pd1	N1	C3	H3	-60.7
C1	N1	C3	H3	176.3
C2	N1	C3	H3	57.3
N1	C3	C4	H4a	178.2
N1	C3	C4	H4b	58.6
N1	C3	C4	H4c	-68.7
C5	C3	C4	H4a	-56.7
C5	C3	C4	H4b	-176.2
C5	C3	C4	H4c	56.4
H3	C3	C4	H4a	64.6
H3	C3	C4	H4b	-54.9
H3	C3	C4	H4c	177.8
H3	C3	C5	Fe1	-46.5
H3	C3	C5	C6	-145.7
H3	C3	C5	C9	40.7
Fe1	C5	C6	H6	-110.9
C3	C5	C6	H6	16.1
C9	C5	C6	H6	-169.6
Fe1	C6	C7	H7	-119.1
C5	C6	C7	H7	-177.7
H6	C6	C7	Fe1	109.8
H6	C6	C7	C8	168.5
H6	C6	C7	H7	-9.3
Fe1	C7	C8	H8	-131.5
C6	C7	C8	H8	168.9
H7	C7	C8	Fe1	118.5
H7	C7	C8	C9	178.1
H7	C7	C8	H8	-13.0
H8	C8	C9	Fe1	130.5
H8	C8	C9	S1	4.2

Torsional Angles (Continued) for
dichloro[(R)-1-(S)-2-Methylthioferrocenylethyldimethylamine]palladium(II)

Atom 1	Atom 2	Atom 3	Atom 4	Angle
H8	C8	C9	C5	-169.6
Fe1	C10	C11	H11	123.7
C14	C10	C11	H11	-176.8
H10	C10	C11	Fe1	-117.1
H10	C10	C11	C12	-177.1
H10	C10	C11	H11	6.5
Fe1	C10	C14	H14	-112.9
C11	C10	C14	H14	-172.1
H10	C10	C14	Fe1	116.6
H10	C10	C14	C13	176.2
H10	C10	C14	H14	3.7
Fe1	C11	C12	H12	120.3
C10	C11	C12	H12	-179.4
H11	C11	C12	Fe1	-124.5
H11	C11	C12	C13	175.6
H11	C11	C12	H12	-4.1
Fe1	C12	C13	H13	112.1
C11	C12	C13	H13	172.1
H12	C12	C13	Fe1	-120.3
H12	C12	C13	C14	179.7
H12	C12	C13	H13	-8.2
Fe1	C13	C14	H14	113.3
C12	C13	C14	H14	172.8
H13	C13	C14	Fe1	-111.6
H13	C13	C14	C10	-171.2
H13	C13	C14	H14	1.8

Table 14. Least-Squares Planes for
dichloro[(R)-1-(S)-2-Methylthioferrocenylethyldimethylamine]palladium(II)

The equation of the plane is of the form:
$A*x + B*y + C*z - D = 0$
where A, B, C & D are constants and
x, y & z are orthogonalized coordinates.

Plane No. 1 A = -0.4255, B = -0.5241, C = -0.7378, D = -12.9444
Chi Squared = 0.

Atom	x	y	z	Distance	Esd
		Atoms in Plane			
C5	5.2802	13.0970	5.1980	-0.001	0.005
C6	6.5620	12.8976	4.5977	0.001	0.006
C7	7.1189	11.7152	5.1182	0.000	0.006
C8	6.1973	11.1620	6.0426	0.000	0.006
C9	5.0692	12.0072	6.0912	0.001	0.005
		Other Atoms			
C3	4.2053	14.1071	4.9545	0.107	0.005
S1	3.5110	11.9000	6.8786	0.139	0.001
Fe1	6.7332	13.0177	6.6369	-1.639	0.001
H6	6.9837	13.5890	4.0663	-0.149	0.060
H7	7.9680	11.2909	4.9684	-0.029	0.055
H8	6.2215	10.3403	6.4261	0.137	0.061

Plane No. 2 A = -0.4711, B = -0.4929, C = -0.7315, D = -16.0916
Chi Squared = 0.

Atom	x	y	z	Distance	Esd
		Atoms in Plane			
C10	6.8304	14.7983	7.6312	-0.002	0.007
C11	8.0572	14.4931	7.0408	0.002	0.008
C12	8.5146	13.2994	7.5545	-0.001	0.008
C13	7.5498	12.8274	8.4934	-0.001	0.008
C14	6.5269	13.7643	8.5177	0.002	0.007
		Other Atoms			
Fe1	6.7332	13.0177	6.6369	1.648	0.001
H10	6.4149	15.5251	7.3522	0.039	0.065
H11	8.3760	15.1209	6.4773	-0.045	0.093
H12	9.3308	12.8743	7.3235	-0.007	0.058
H13	7.6284	11.8917	8.9107	0.118	0.073
H14	5.8441	13.6453	8.9203	0.088	0.064

Least-Squares Planes (Continued) for
dichloro[(R)-1-(S)-2-Methylthioferrocenylethyldimethylamine]palladium(II)

Plane No. 3 A = 0.7252, B = -0.5526, C = -0.4108, D = -6.8656
Chi Squared = 1343.

Atom	x	y	z	Distance	Esd
			Atoms in Plane		
Pd1	2.2482	11.6424	4.9886	0.014	0.000
Cl1	0.9287	11.3271	3.0897	0.011	0.002
Cl2	1.2778	9.7731	5.8653	-0.017	0.002
N1	3.0949	13.4398	4.1426	-0.018	0.004
S1	3.5110	11.9000	6.8786	0.011	0.001
			Other Atoms		
C1	3.6068	13.1250	2.7825	1.086	0.006
C2	1.9297	14.3840	4.0175	-1.333	0.006
C3	4.2053	14.1071	4.9545	0.085	0.005
C9	5.0692	12.0072	6.0912	1.405	0.005
C15	3.7219	10.4108	7.8368	0.593	0.008

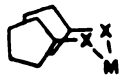
Dihedral Angles Between Planes:

Plane No.	Plane No.	Dihedral Angle
1	2	3.2
1	3	73.5
2	3	76.6

Table 16. Dihedral Angle and Bridgehead Angle of Selected [3]ferrocenophanes.

Compound	X	M	Dihedral[a] Angle	Bridgehead Angle
$Fe(C_5H_4S)_2Se$	S	Se	112.2°	100.5°
$Fe(C_5H_4S)_2S$	S	S	110.9°	103.9°
$Fe(C_5H_4S\text{-}iBu)_2PdCl_2$	S	Pd	75.4°	84.0°
$Fe(C_5H_4AsMe_2)_2Ni(CO)I_2$	As	Ni	46.6°	93.5°

[a]Dihedral angle obtained from least-squares planes calculation. Dihedral angle refers to angle between FeX_2 plane and MX_2 plane.



19.6. Seyferth proposed the presence of a weak dative Fe Pd bond on the basis of a Fe-Pd distance of 2.878(1) A. The structure of the methyl palladium complex, 58, makes it impossible for any interaction between Pd and Fe to occur.

The two cyclopentadienyl rings are eclipsed and are slightly tilted with respect to each other, the dihedral angle being, 3.2°. The planes containing the cyclopentadienyl rings are almost orthogonal to the plane containing the palladium, sulfur, nitrogen and chlorine atoms. Table 14 shows a list of atomic parameters refined in least squares.

C. (R,S)-$C_5H_5FeC_5H_3[CH(CH_3)N(CH_3)_2][SCSNR_2]$ (R = Me,Et)

The dithiocarbamate ligand has played a major role in the chemistry of transition-metal sulfide complexes.[112,113,114] Dithiocarbamates and thiuram disulfides have been used as fungicides, pesticides, vulcanization accelerators, antioxidants, floatation agents and high-pressure lubricants, and as drugs in medicine.[112] In particular, complexes of heavy metals with thiuram disulfides are effective fungicides and seed disinfectants. The rich and diverse chemistry of dithio acid and dithiolate complexes has been extensively covered in many reviews.[113]

1. Preparation

Tatraalkylthiuram disulfides undergo nucleophilic attack at the disulfide linkage by cyanide ions, amines and Grignard reagents.[115] Cava[116] has reported that aryllithium derivatives react with tetraisopropylthiuram disulfide to give dithiocarbamate esters that were precursors to aromatic thiols. Recently McCulloch[41] reported that dilithioferrocene and lithioferrocene reacted with a series of tetraalkylthiuram disulfides giving rise to bis(dialkyldithiocarbamate)-

ferrocene derivatives and monosubstituted dialkyldithiocarbamateferrocene derivatives respectively. Reaction of 1-dimethylaminomethyl-2-lithioferrocene with tetraalkylthiuram disulfide also gave rise to 1-dimethylaminomethyl-2-(dialkyldithiocarbamate)ferrocene derivatives.[54]

Reaction of (R,R)-1-dimethylaminoethyl-2-lithioferrocene, [(R)-(R)-27], with tetramethylthiuram disulfide and tetraethylthiuram disulfide gave rise to a high yield of (R,S)-1-(dimethylaminoethyl)-2-(dimethyldithiocar bamate)-ferrocene, 66, and (R,S)-1-(dimethylaminoethyl)-2-(diethyldithiocar-bamate)ferrocene, 67, respectively (Scheme 15). These new compounds contain a chiral center and plane of symmetry that is absent in bis(dialkyldithiocarbamate)-ferrocene derivates and dialkyldithiocarbamateferrocene derivatives.[41] They also contain a chiral center that is absent in 1-dimethylaminomethyl-2-dialkyl-(dithiocarbamate ferrocene.[54] In contrast to the results obtained by Cava, only the desired product and no thioamide derivative was obtained. The thioamide species arise from competing nucleophilic attack at the thione carbon rather than at the sulfur-sulfur bond in the tetraalkylthiuram disulfide.

2. ^{1}H NMR

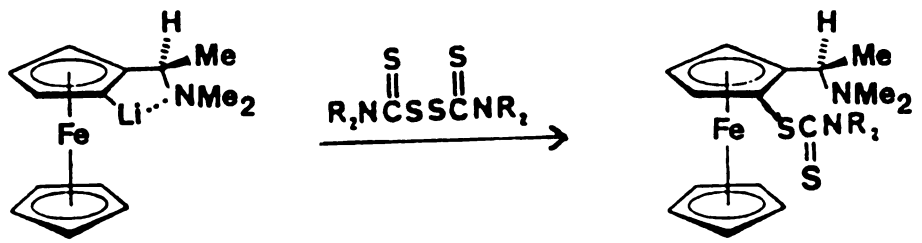
The 250 MHz ^{1}H NMR data for (R,S)-1-(dimethylaminoethyl)-2-(dialkyl-dithiocarbamate)ferrocene derivatives, 66 and 67, are given in Table 17. The ^{1}H NMR spectra of these ligands are similar to the spectra obtained for the chiral ferrocenyl-thioether compounds in the previous section, (Table 2). A comparison of the chemical shifts of the substituted ring protons in Table 17 and Table 2 revealed that the $SCSNR_2$ group substituted at ring exhibit more downfield peak than SR substituted ring. This is to be expected since the greater electron withdrawing effect of the $SCSNR_2$ group causes a greater deshielding of the ring protons, resulting in a more downfield peak.[91,92] At

Table 17

^{1}H NMR Data for (R)-7, (R,S)-$C_5H_5FeC_5H_3$[CHMeNMe$_2$][R], R = SCSNMe$_2$, 66, SCSNEt$_2$, 67, $C_5H_5Fe(C_5H_3$-1-CH_2NMe_2-2R), R = SCSNMe$_2$, SCSNEt$_2$; and $C_5H_5FeC_5H_4R$, R = SCSNMe$_2$, SCSNEt$_2$. (, ppm)

Compound	T(°C)	Substituted Ring	C_5H_5	NCH	NMe_2	CH_2	CH_3
(R)-7	25	4.11	4.08 s	3.60 d	2.09 s		1.46 d
(R,S)$C_5H_5FeC_5H_3$(CHMeNMe$_2$)-		4.63 dd			3.50 s		
(SCSNMe$_2$) 66	22	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$_2$)-		4.60 dd					
(SCSNEt$_2$) 67	27	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
[a]$C_5H_5Fe(C_5H_3$-1-CH_2NMe_2-2-SCSNMe$_2$)		4.43 t					
	27	4.45 dd		3.40 d			
		4.62 dd	4.16 s	3.18 d	2.21 s		3.50 s
[a]$C_5H_5Fe(C_5H_3$-1-CH_2NMe_2-2-SCSNEt$_2$)		4.42 t					
	27	4.49 dd		3.19 d		3.85	1.22 t
		4.59 dd	4.14 s	3.48 d	2.18 s	3.98	1.39 t
[b]$C_5H_5Fe(C_5H_4$SCSNMe$_2$)		4.44 t					
	22	4.34 t	4.24 s				3.51 s
[b]$C_5H_5Fe(C_5H_4$SCSNEt$_2$)		4.42 t				3.82 q	1.23 t
	22	4.34 t	4.22 s			3.96 q	1.37 t

[a]Reference 54; [b]Reference 41



(R)-(R)-27

R = Me, 66
R = Et, 67

Scheme 15

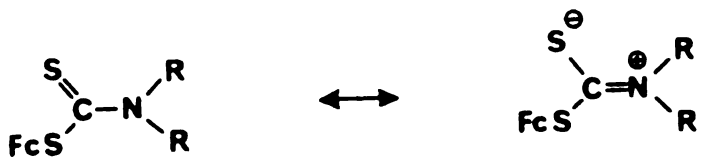
room temperature, single signal was observed for the NR_2 protons of the carbamate group due to incomplete restricted rotation around the C-N bond. At lower temperatures however, two separate signals were observed for the N,N--dialkyl signals a phenomenon that will be discussed in detail later.

3. ^{13}C NMR

The ^{13}C NMR data for the chiral carbamate derivatives, 66 and 67 are given in Table 18. During acquisition of the ^{13}C NMR data, the parameters PW = 4 μs and Rd = 4s were used since the thiocarbonyl carbon has a long relaxation time, T_1.[42] The low field signal around 198.9 ppm is attributed to the thiocarbonyl carbon. The other assignments shown in table 18 are tentative but results from other work do support these assignments.[41,54] The assignments of $C_3 < C_4 < C_5$ are based on previous conclusions about deshielding.[41]

4. Dynamic NMR Studies

There are two possible resonance forms for the dialkyldithiocarbamate ferrocene complexes,[41] as shown below.



Fc = ferrocenyl backbone.

Table 18

^{13}C NMR Data for (R)-7; (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, ppm)

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
(R)-7							
(R,S)$C_5H_5FeC_5H_3$(CHMeNMe$_2$)(SCSNMe$_2$)	198.9	91.7, 74.9, 68.6,	69.9	55.6	40.8		18
66		69.6, 76.2					
(R,S)$C_5H_5FeC_5H_3$(CHMeNMe$_2$)(SCSNEt$_2$)	197.3	86.6, 86.5, 67.8	68.6	51.0	39.9	46.8	12.9
67		68.6, 77.5				39.9	10.0
[a]$C_5H_5Fe(C_5H_3$-1-CH_2NMe_2-2-SCSNMe$_2$)	199.3	88.1, 75.0, 69.4	70.2	56.8	45.5		
		71.3, 76.3					
[a]$C_5H_5Fe(C_5H_3$-1-CH_2NMe_2-2-SCSNEt$_2$)	197.4	87.7, 75.2, 69.2	70.0	56.6	45.2	46.8	11.4
		71.2, 76.7				49.4	12.9
[b]$C_5H_5Fe(C_5H_4$SCSNMe$_2$)	199.9	70.3, 75.5, 75.2	69.4				
[b]$C_5H_5Fe(C_5H_4$SCSNEt$_2$)	198.7	72.0, 77.4, 76.4	69.5			47.2	11.5
						49.6	12.6

[a] Reference 54; [b] Reference 41

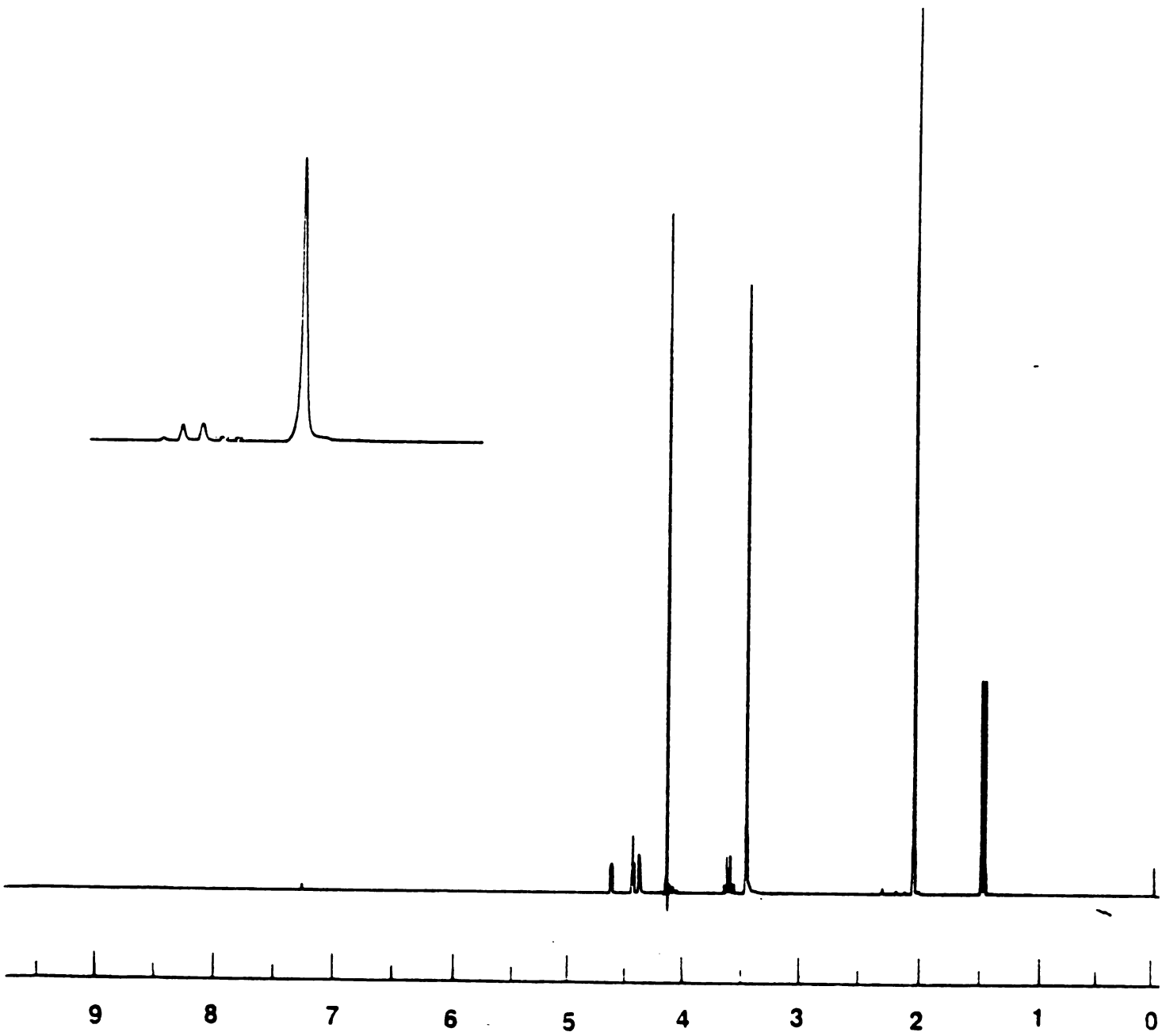


Figure 12. 250 MHz ^{1}H NMR spectrum of 66, R = $SCSNMe_2$.

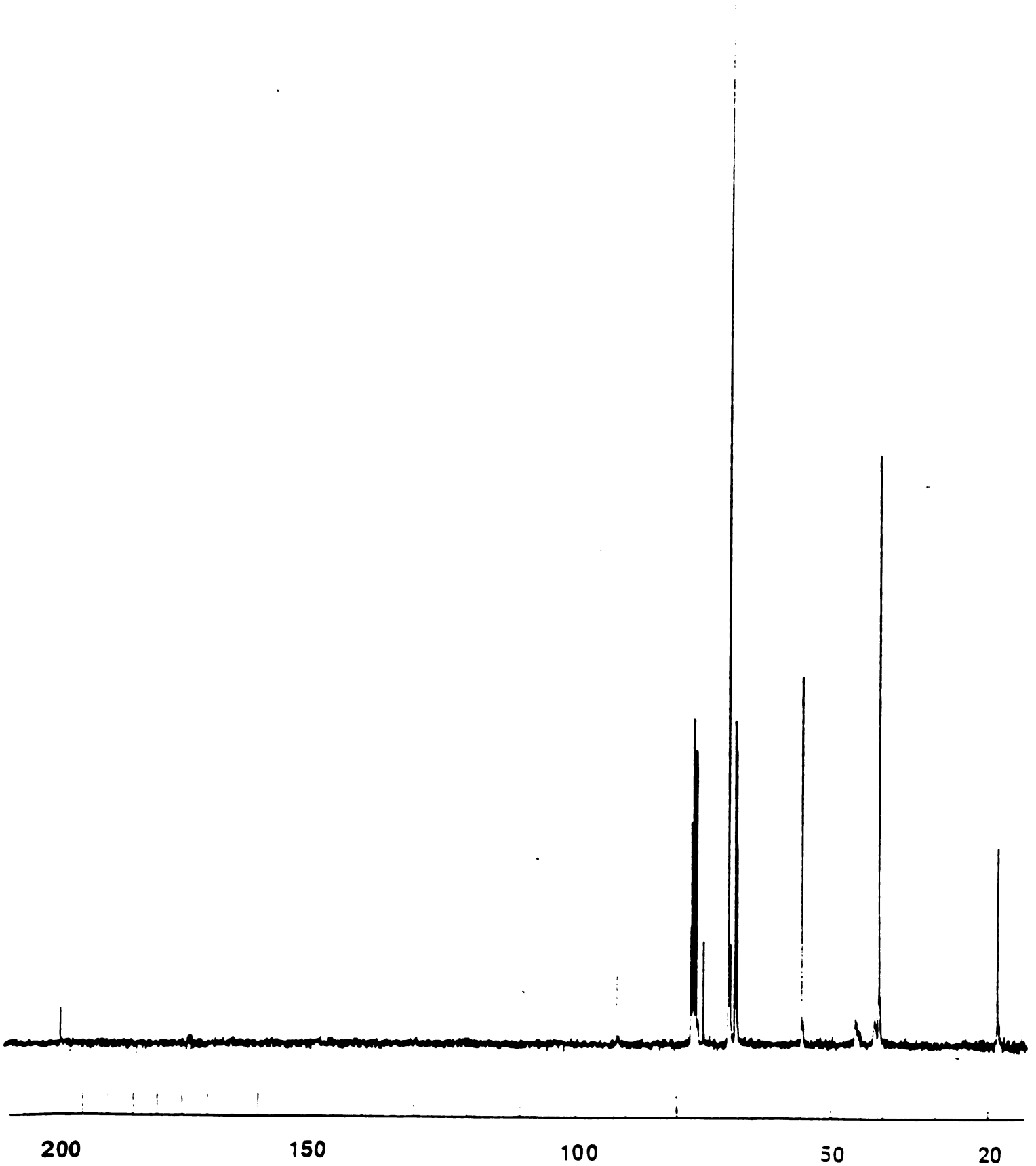


Figure 13. Gated decoupled ^{13}C NMR of 66.

The second resonance form introduces a degree of double bond character into the carbon-nitrogen bond which prevents free rotation around the C-N bond. The ^{1}H NMR and ^{13}C NMR data in Table 17 and Table 18 show that two separate signals were observed for the N,N-dialkyl group of the diethyldithiocarbamate ferrocene derivative, 67, at room temperature, but the dimethyldithiocarbamateferrocene derivative, 66, are observed only at a lower temperature (12°C). 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 such 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. NMR parameters, rate constants and an approximate value of the barrier to rotation in compounds 66, and 67, are given in Table 19. The rate constant, k_c, at the coalescence temperature, T_c, was determined from the peak separation, ΔV, at slow exchange by using the equation[117] $k_c = \pi\Delta V/(2)^{1/2}$. An approximate rotational free energy barrier was obtained from the Eyring equation:

$$\Delta G^{\ddagger} = 2.303RT\,[10.3-\log(K_c/T_c)].$$

The values of the rotational barriers are 15.36 and 15.81 kcal/mol for compounds 66 and 67, respectively. These ΔG values, though of fairly narrow range, reveal that the rotational barrier of the NEt_2 in 67 is higher than that of NMe_2 in 66. This is to be expected since the diethylamino group is more sterically hindered than the dimethylamino group in a 1,2-disubstituted cyclopentadienyl ring.

Hollaway[118] has determined rotational barriers about the carbamate

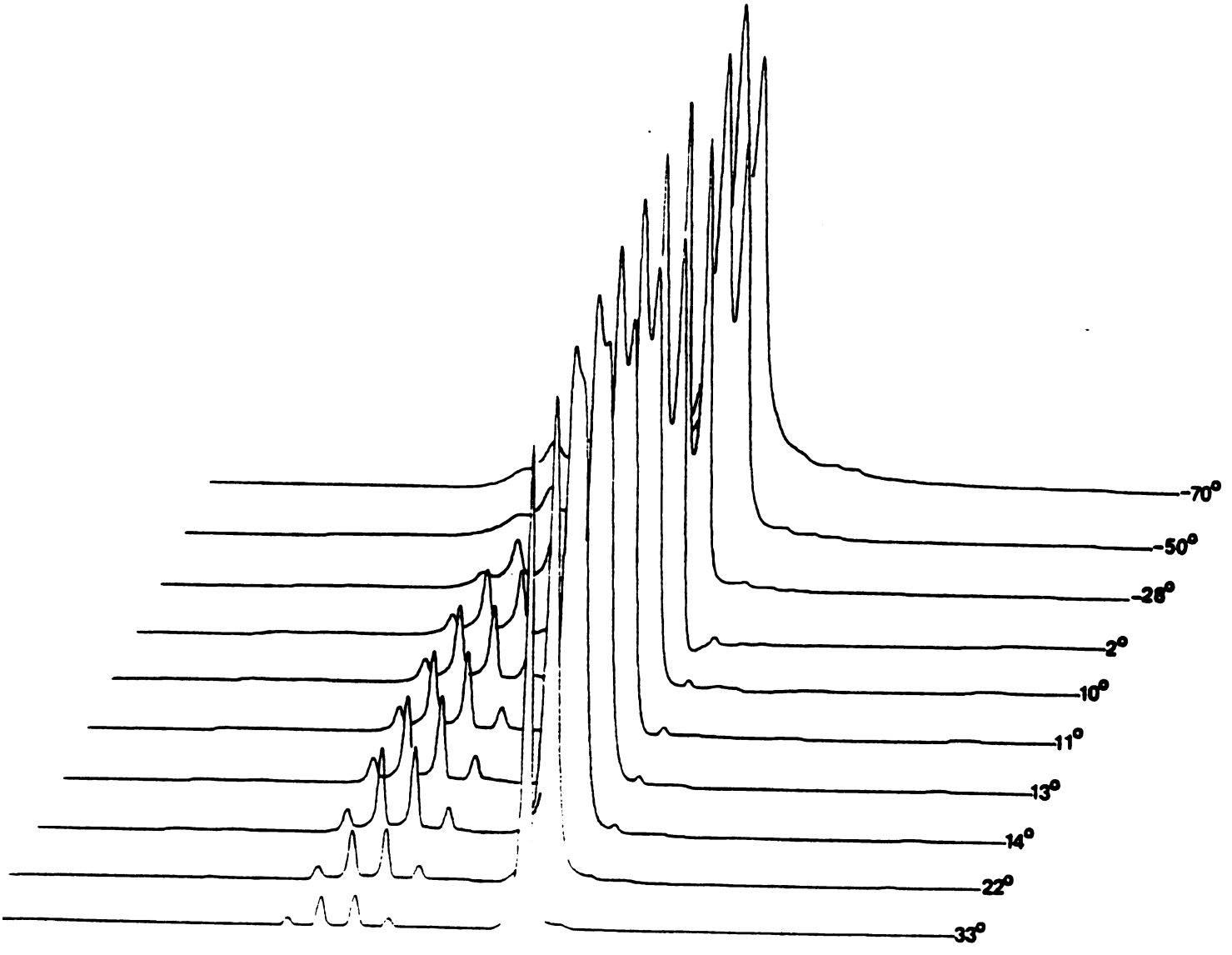


Figure 14. Variable-temperature ^1H NMR spectra of 66, R = $SCSNMe_2$.

Table 19

NMR Parameters, Kinetic and Infrared Data for (R,S)-$C_5H_5FeC_5H_3$[CHMeNMe$_2$][R]; $C_5H_5Fe(C_5H_3$-1-(H_2NMe$_2$-2R); and $C_5H_5FeC_5H_4R$ where R = $SCSNMe_2$, $SCSNEt_2$

Compound	(Hz)	K_c, (s^{-1})	T_c (°K)	$\Delta G^{\ddagger}$ (kcal/mol)	IR(cm^{-1})
66					
(R,S)$C_5H_5FeC_5H_3$(CHMeNMe$_2$)($SCSNMe_2$)	4.15	9.22	285	15.36	1495
67					
(R,S)$C_5H_5FeC_5H_3$(CHMeNMe$_2$)($SCSNEt_2$)	41.25	91.63	319	15.81	1498
[a]$C_5H_5Fe(C_5H_3$-1-CH_2NMe_2-2-$SCSNMe_2$)	5.28	11.73	296	15.83	1498
[a]$C_5H_5Fe(C_5H_3$-1-CH_2NMe_2-2-$SCSNEt_2$)	43.87	104.62	328	16.18	1487
[b]$C_5H_5Fe(C_5H_4SCSNMe_2)$	17.70	39.32	312	16.00	1475
[b]$C_5H_5Fe(C_5H_4SCSNEt_2)$	31.74	79.40	320	15.98	1480

[a] Reference 54; [b] Reference 41

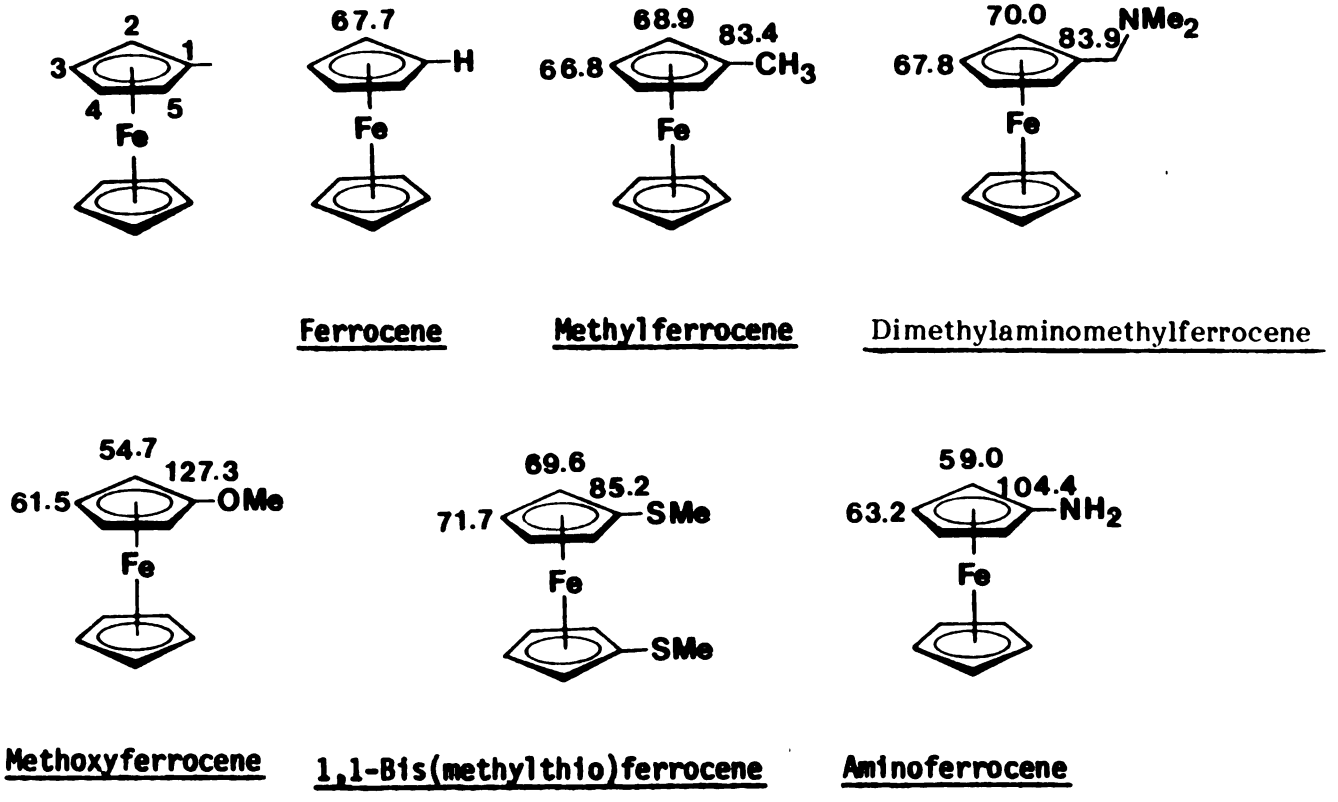


Figure 15. Assignments of the substituted ring carbons of some substituted ferrocenes.

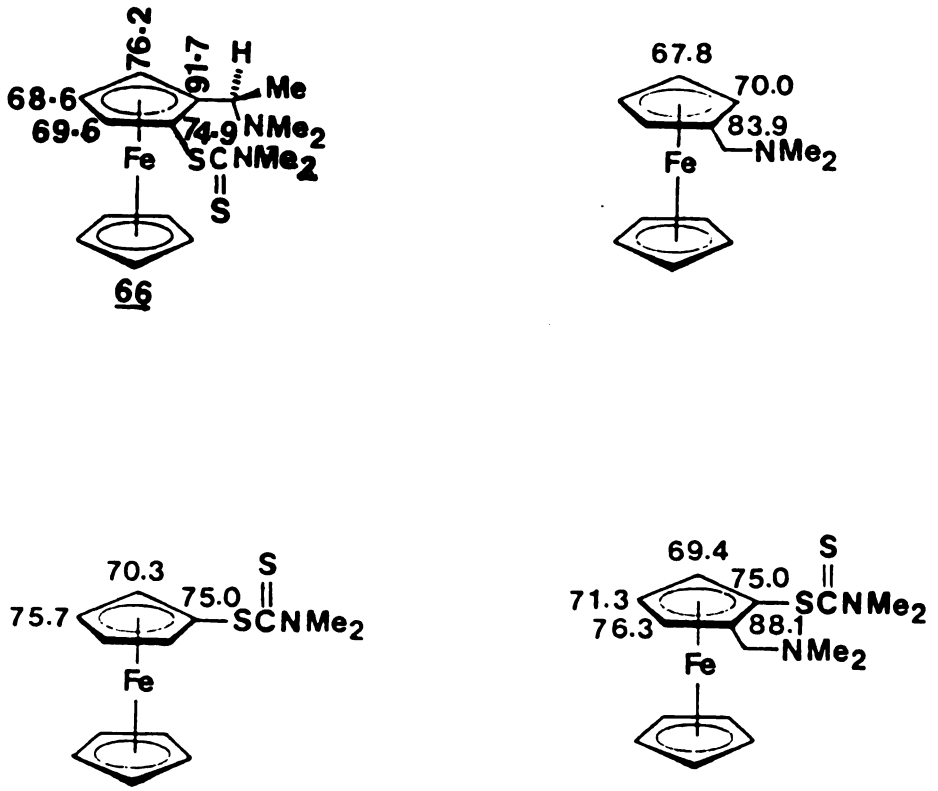


Figure 16. Assignment of ring carbons in some ferrocenyl carbamate derivatives.

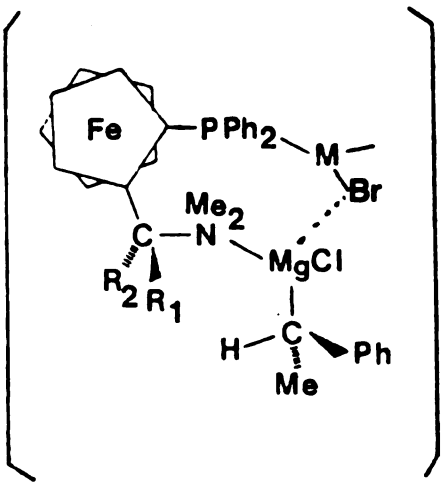
C-N bond in a series of N,N-dialkyldithiocarbamate esters. Activation energies of 10 to 12 kcal/mol suggested that an appreciable amount of C-N double bond character was present. Hollaway was able to correlate the C-N double bond character with the "thioureide" band between 1489 and 1498 cm^{-1} in the infrared region. The "thioureide" band, which has been assigned to the partial double bond character in the carbon-nitrogen bond, was observed at 1495 cm^{-1} for the chiral dimethylaminoethyldimethyldithio carbamate derivative 66, and 1489 cm^{-1} for the dimethylaminoethyldiethyldithio carbamate derivative 67. The variable temperature ^1H NMR spectrum for the chiral dimethylaminoethyl-dimethyldithio carbamate derivative, 66, is shown in Figure 14.

D. Catalytic Applications of Complexes

1. Asymmetric Grignard Cross-Coupling Reactions

Asymmetric carbon-carbon bond-forming reactions are of great significance for the synthesis of optically active compounds, and the use of chiral transition—metal catalysts for such reactions has recently attracted considerable attention due to a number of advantages of catalytic asymmetric synthesis.[120] The first report on asymmetric Grignard cross-coupling appeared in 1973, where 2,3-o-isoproylidene—2,3-dihydroxyl-1,4-bis(diphenylphosphino)butane (DIOP) was used as a chiral ligand on a nickel catalyst and 7-16% of the products were obtained in the reaction of (1-phenylethyl)magnesium chloride. Since the first report in 1975 that Pd complexes catalyze the coupling of Grignard reagents with organic halides,[122] the method has been used with a variety of Grignard reagents and halogenated species. Kumada and co-workers[123] has examined various types of chiral ferrocenylphosphine ligands for the nickel- or palladium-catalyzed reaction of (1-phenylethyl)-magnesium chloride with vinyl bromide and found that the ferrocene planar chirality played an important

role rather than the carbon centered chirality on the side chain of the ferocene and concluded that the asymmetric induction on the coupling product was mainly determined by transmetallation of the alkyl group from the Grignard reagent to the transition-metal catalyst and the most important intermediate of the reaction was the diastereomeric transition state shown below.



The development of such transition metal catalysis depends largely on the availability of suitable ligating compounds. Up to now only chiral phosphines or phosphineamine combinations have provided satisfactory results.[67,124] This is a severe limitation for the synthesis of phosphines is not simple and the derived ligands, once obtained, are often sensitive, especially to oxidation by air.

These condiderations induced us to investigate application of our new chiral ferrocenylthioether compounds as potential ligands. While in the process of this work, Kellogg and his co-workers,[69] reported the asymmetric Grignard cross-coupling reactions of 1-phenylethylmagnesium chloride with vinyl bromide by using nickel catalyzed bi- and polydentate sulfide ligands and obtained good

Table 20

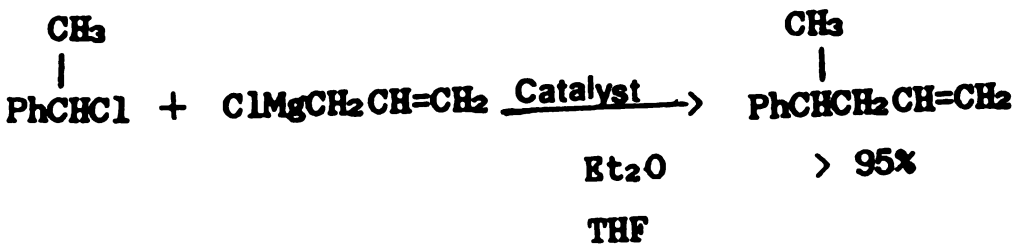
Asymmetric Grignard Cross-Coupling Reactions Using Chiral Thioether Complexes

Catalyst	Chemical Yield(%)	e.e.(%)	Configuration
58, R = Me	97.5	26.0	S
59, R = i-Pr	95.0	22.3	S
62, R = Ph	96.0	18.2	S
63, R = p-tolyl	96.0	25.5	S
64, R = 4-Cl-Ph	94.5	16.5	S
[a]Ni	100	16.9	S

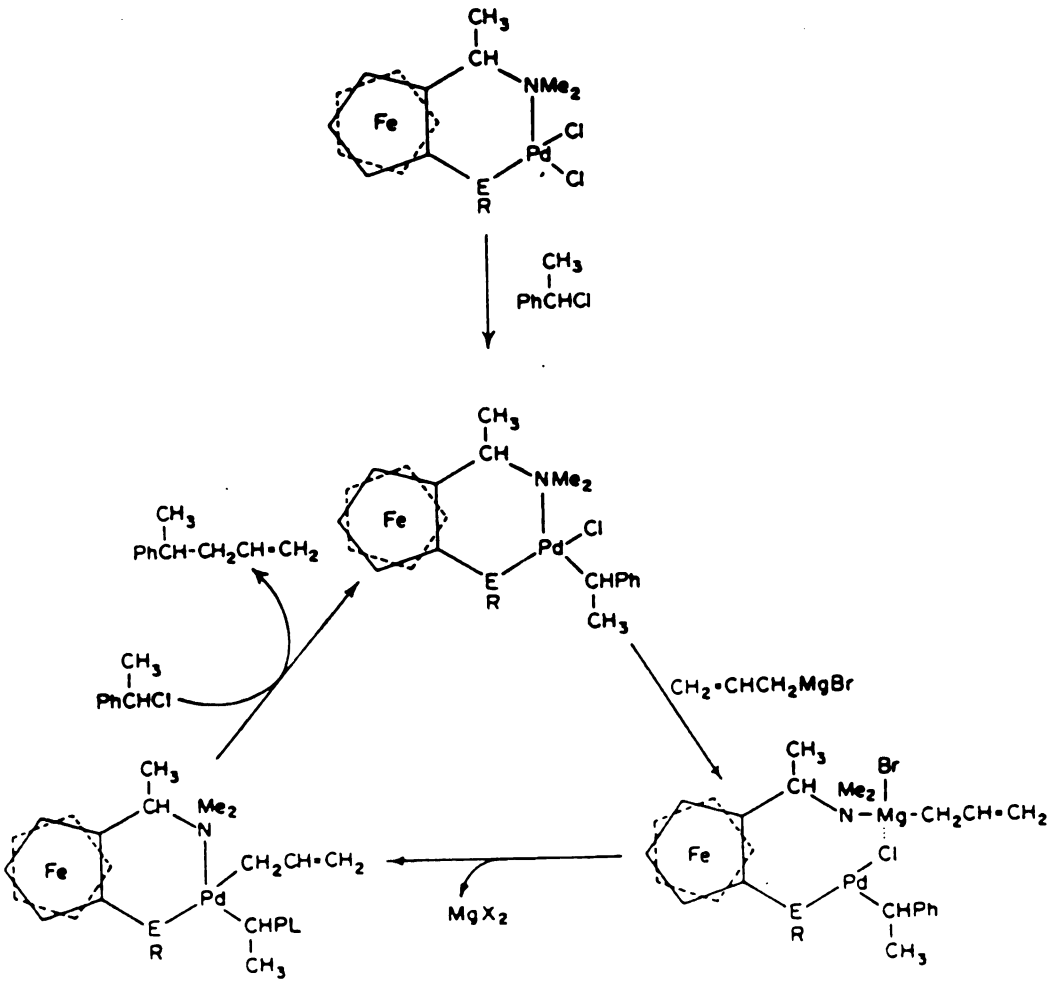
[a] Reference 69

chemical yield but poor enantiomeric purity (0.8-16.9% e.e.).

The new chiral ferrocenylaminethioether palladium complexes, 58, 59, 62-64, was tested for asymmetric Grignard cross-coupling reactions represented below



The results are shown in Table 20. Since the optical rotation of the coupling product 4-phenyl-1-pentene was strongly affected by small impurities[70] and in addition recemization of products always occur, it was difficult to determine the optical purity by use of a polarimeter. The alkene was converted into the methylester, the enantiomeric purity of which was determined by ^{1}H NMR spectroscopy in the presence of a chiral shift reagent, Eu(dcm)$_3$.[82] The chemical shift (δ), and the enantiomeric shift difference ($\Delta\Delta\delta$) depend on the concentration of the chiral shift reagent and the temperature at a constant concentration of the substrate (0.5 M) in $CDCl_3$ as shown in Figures 17 and 18 respectively. At room temperature the ^{1}H NMR signal of the methyl protons of the methyl ester is a singlet when no chiral shift reagent is present. Upon addition of the shift reagent the signal separates into two distinct singlets. The signal shifted downfield and $\Delta\Delta\delta$ increased as the concentration of the chiral shift reagent increased. When the concentration of the chiral shift reagent was 0.27 M, $\Delta\Delta\delta$ was large enough for the determination of the enantiomeric excess (e.e.) (see Figure 17 and 18). Kumada[125] had reported that the methyl



Scheme 16 Proposed Mechanism for Grignard Cross Coupling Reaction.

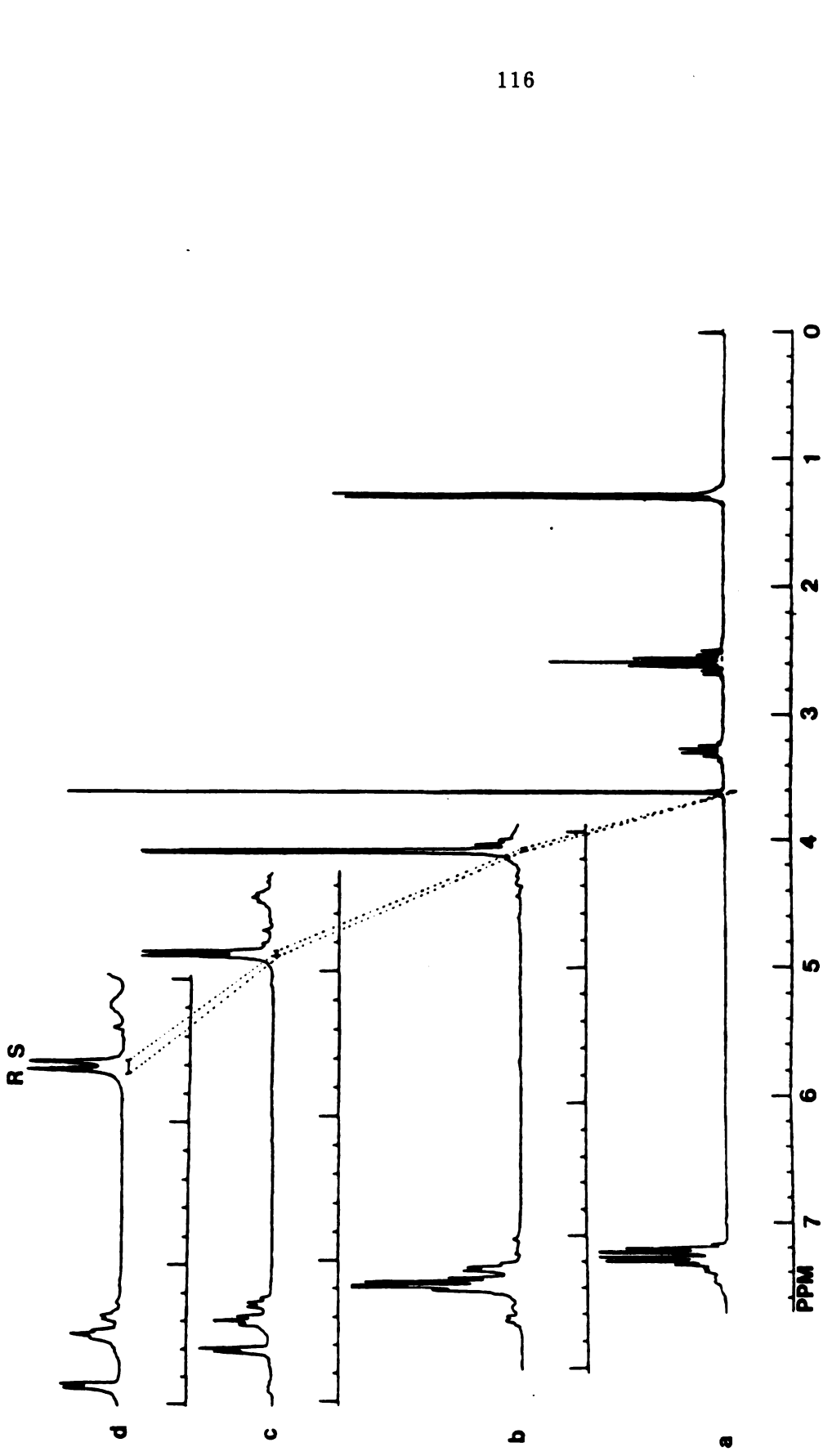


Figure 17. ^{1}H NMR spectra of (R) and (S)-methyl 3-phenyl butyrate in the presence of increasing concentrations of chiral shift reagent, $Eu(dcm)_3$. The concentration of substrate in these spectra is 0.5M in $CDCl_3$/TMS, and that of $Eu(dcm)_3$ is (a) 0.0M, (b) 0.09M, (c) 0.18M, and (d) 0.27M.

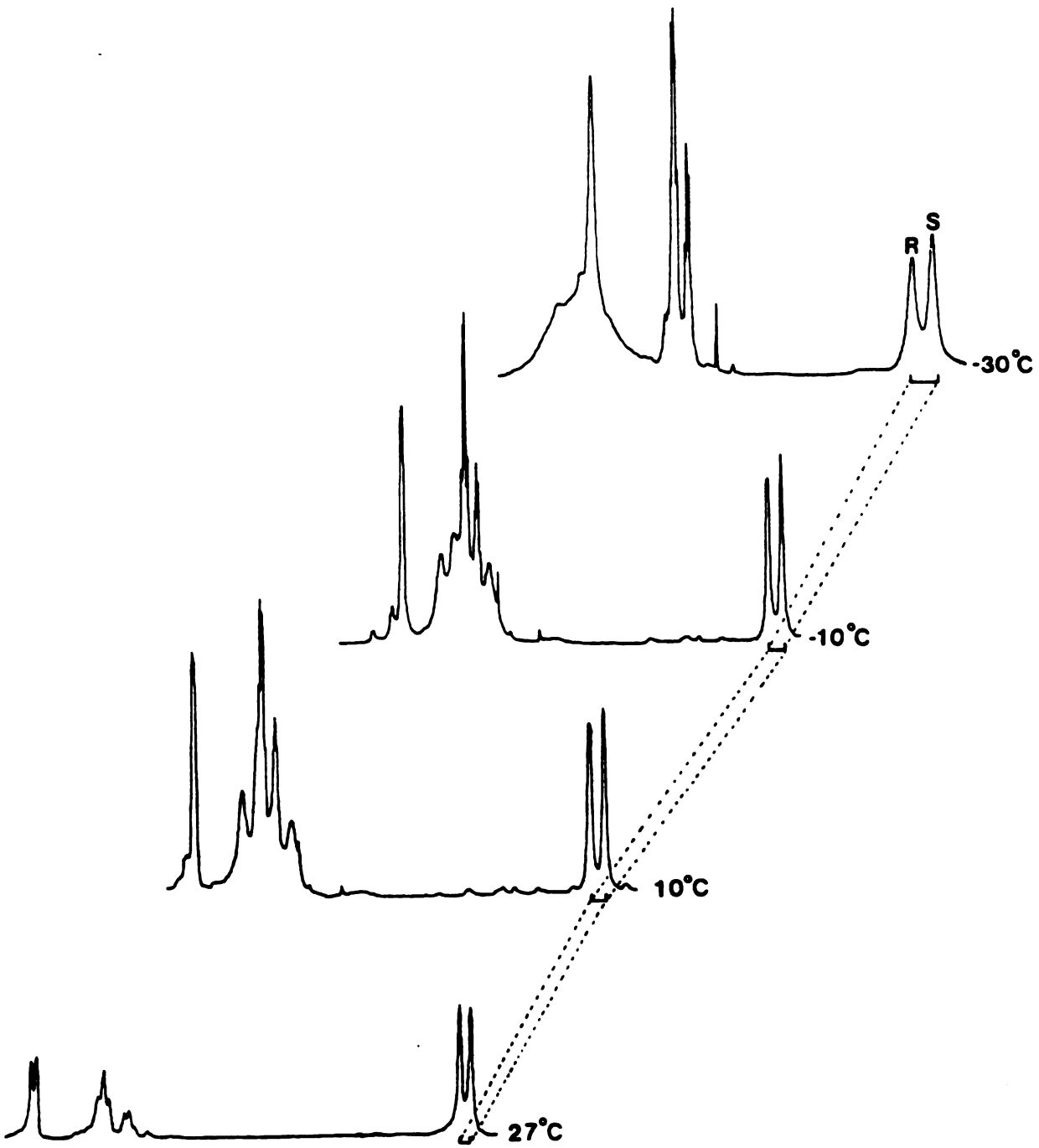


Figure 18. The magnitudes of $\Delta\Delta\delta$ increase for methyl 3-phenylbutyrate with decreasing temperature in the presence of chiral shift reagent, $Eu(dcm)_3$. The concentration of substrate and chiral shift reagent in $CDCl_3$/TMS are 0.5 and 0.27 M, respectively.

signal of (S)-methyl 3-phenyl butyrate appears at a higher field than that of the R enantiomer.

The chiral ferrocenylamine thioether complexes with Pd, 58, 59, 62-64, catalyzed formation of 4-phenyl-1-pentene from 1-phenyl-1-chloroethane and allylmagnesium chloride at 0° in high yield (>95%). The resulting configuration in all cases were S (see Table 20). The enantiomeric excess (e.e) range from 16.5 to 26.0 e.e (S) and is much higher than those reported by Kellogg.[69] The Grignard cross-coupling reaction mechanism using phosphine-amine-palladium complex was postulated by Kumada.[123] Based on that we have also proposed a mechanism for the chiral thioether-palladium catalyzed reaction (Scheme 16). It should be noted from our results that the planar chirality played an important role rather than the carbon centered chirality of the side chain of the ferrocenyl ligand in the asymmetric induction. Thus the configuration of the coupling product was consistent with the planar chirality of the chiral ferrocenylaminethioether-Pd catalysts.

2. Selective Hydrogenation of Conjugated Dienes to Alkenes

Hydrogenation by homogeneous catalysts is well-developed.[133] Of the many known complexes, those of Group VIII metals with amines and sulfides have been used with varying degrees of success. In 1967 $PtCl_2(SPh_2)_2$ was found to be selective for the hydrogenation of dienes to monoenes in the presence of $SnCl_2$.[134] Treatment of $PdCl_2$ or Na_2PdCl_4 with tertiary amines resulted in an active selective catalyst.[135] The same was true of $PdCl_2$ when treated with 2,2'-bipyridine and $NaBH_4$.[136] Palladium chloride and thioethers gave complexes which upon reduction by diisobutylaluminum hydride, were selective catalysts.[137] The thioetherrhodium complex, $RhCl_3(SEt_2)_3$ hydrogenates maleic acid, provided maleic acid is present in excess.[138-141]

Table 21

Selective Hydrogenation of 1,3-cyclooctadiene at Room Temperature[a].

***Solvent in All Cases was Acetone.**

Catalyst	Induction Time (h)	Initial Turnover Rate(mol/mol.Pd.h)	Products		Reference
			Cyclooctene (%)	Cyclooctane(%)	
$PdCl_2/CpFeC_5H_3[CHMeNMe_2][SCH_3]$ 58	45.00	15.65	86.3	13.7	This work
$PdCl_2/CpFeC_5H_3[CHMeNMe_2][SPh]$ 62	0.00	256.3	89.9	10.1	This work
$PdCl_2/CpFeC_5H_3[CHMeNMe_2][SPhMe]$ 63	0.00	462.00	95.5	4.5	This work
$PdCl_2/CpFeC_5H_3[CHMeNMe_2][S\text{-}PhCl]$ 64	0.50	353.43	87.6	12.4	This work
$PdCl_2/CpFeC_5H_3[CH_2NMe_2][SMe]$	49.7	13.96	94.08	5.92	142
$PdCl_2/CpFeC_5H_3[CH_2NMe_2][SPhMe]$	0.00	690.91	78.54	21.46	142
$PdCl_2/CpFeC_5H_3[CH_2NMe_2[S\text{-}t\text{-}Bu]$	0.00	345.46	97.22	2.78	142

[a] 9.0 mL acetone; 2.0×10^{-5} mol of catalyst; 7.45×10^{-3} mol of substrate; initial H_2 press. = 67 psi

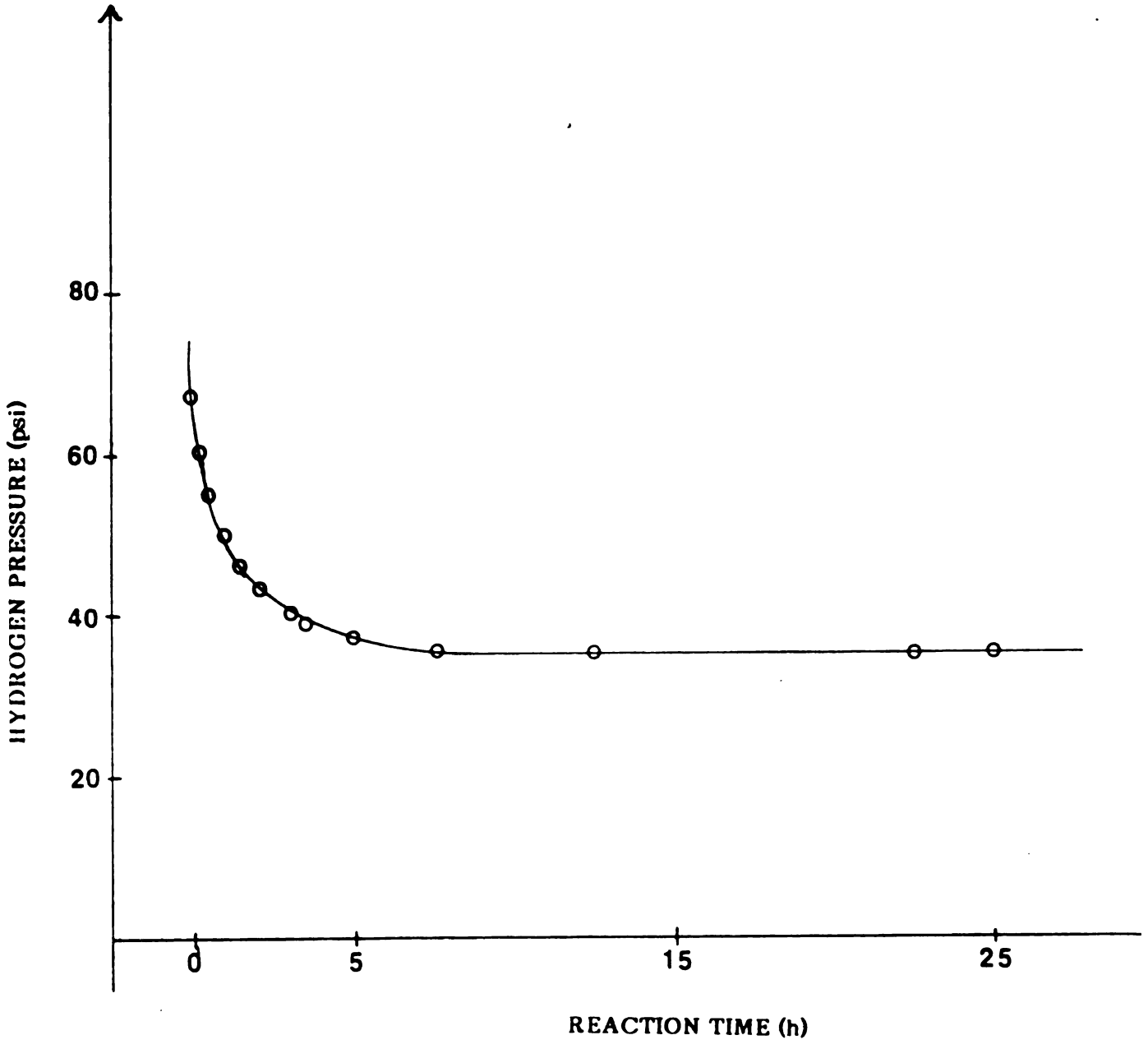


Figure 19: Selective Hydrogenation of 1,3-cyclooctadiene in Acetone at 27°C and 67 psi Using Complex 58. R = Me

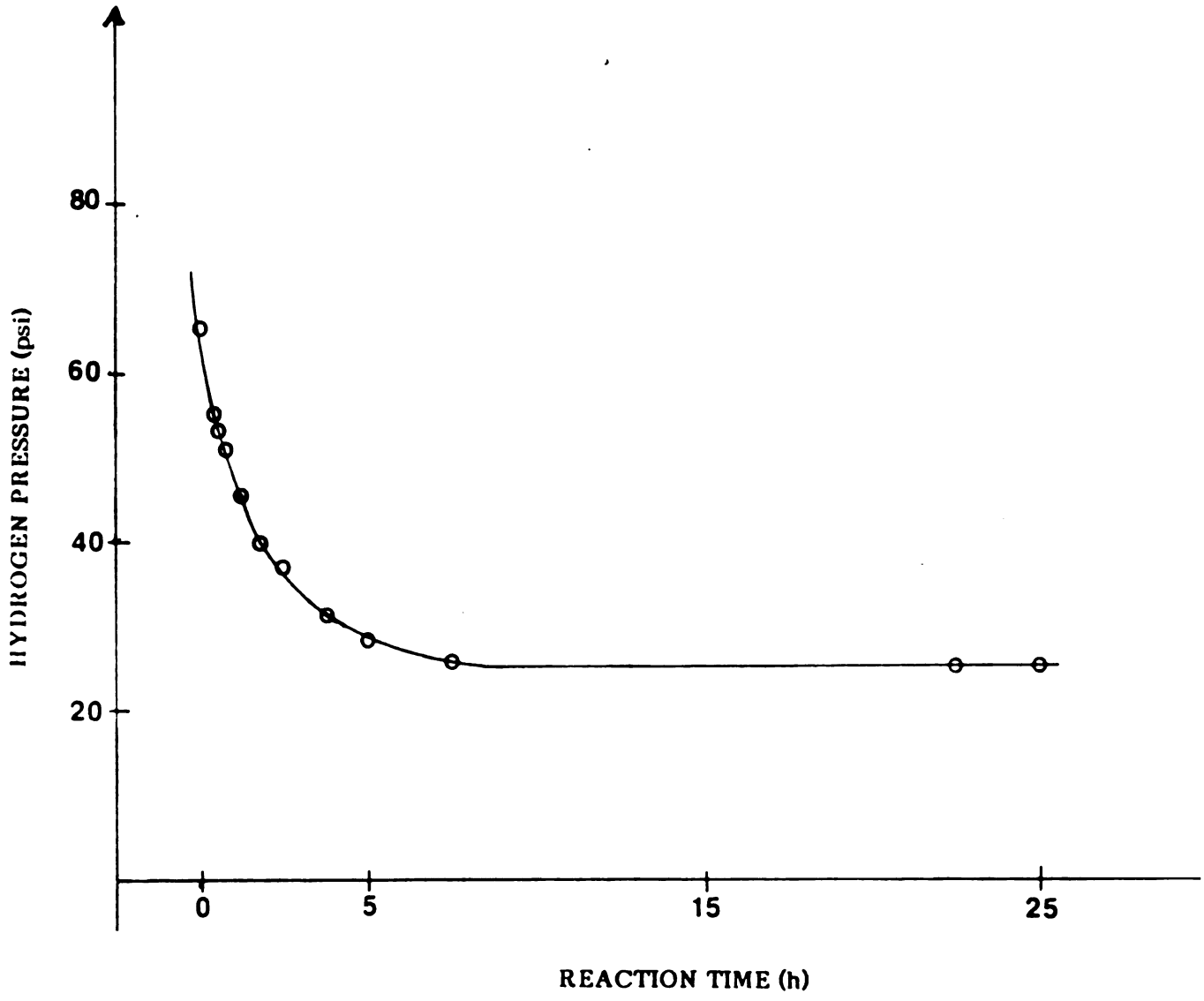


Figure 20: Selective Hydrogenation of 1,3-cyclooctadiene in Acetone at 27°C and 67 psi Using 62, R = Ph

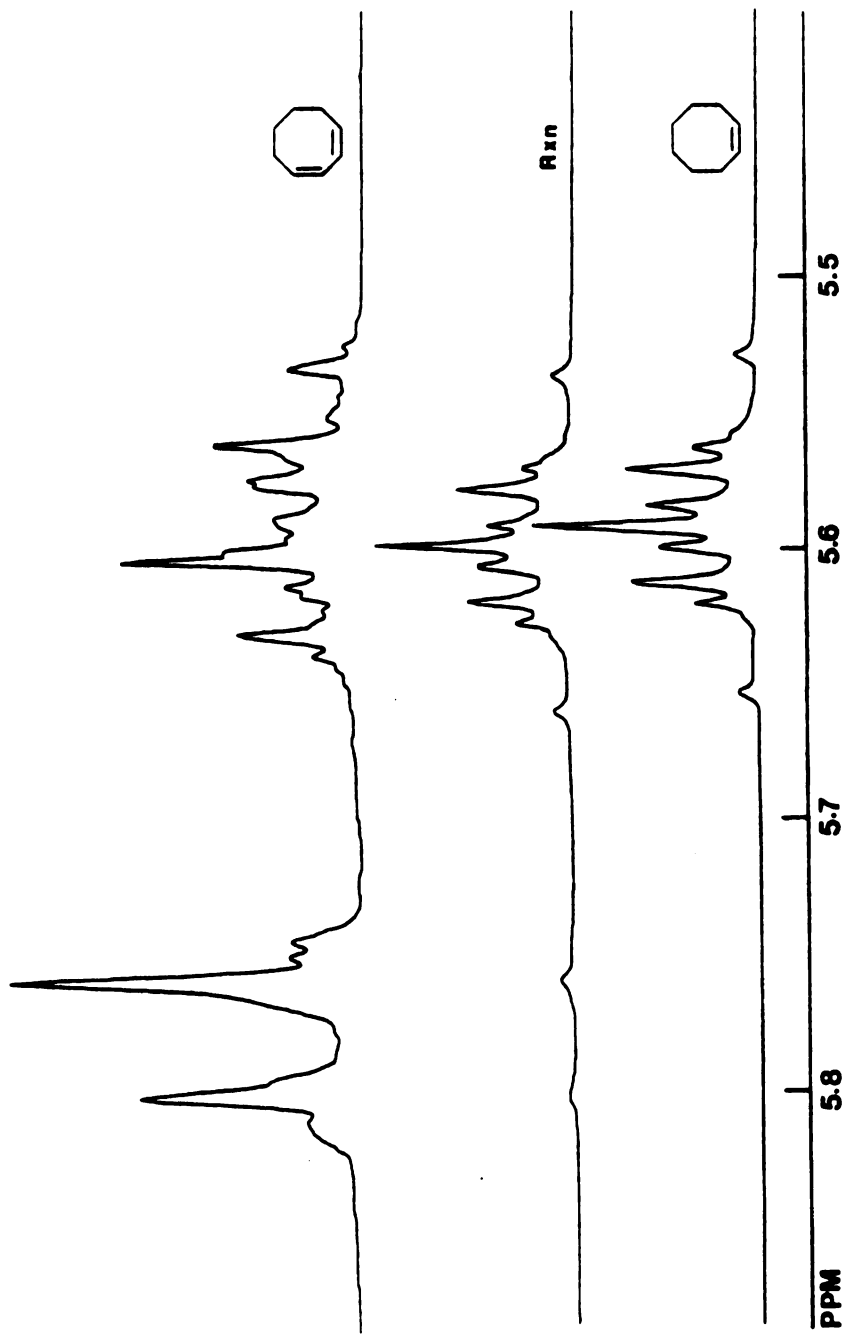


Figure 21. Olefinic region of 250 MHz ^{1}H NMR of 1,3-cyclooctadiene(top), the mixture of 1,3-cyclooctadiene and cyclooctene(middle), and cyclooctene(bottom).

In view of the selective hydrogenation of thioether-palladium complexes,[52,138] we have carried out selective hydrogenation of conjugated dienes to alkenes using ferrocenylamine thioether-palladium complexes 58, 62-64. Our results have previously reported that hydrogenations using thioether—palladium complex failed if reducing agents were added.[52] Hydrogenation of 1,3-cyclooctadiene proceeded conveniently in acetone at 67 psi (see Figure 18). This is a homogeneous reaction system without H_2O or reducing agents and reaction proceeds at a useful rate (up to 462 mol/mol Pd.Hr) to afford a high conversion of nearly 96%. As time passed the red solution became brown but remained homogeneous. Most of the product at the end of reaction was cyclooctene, but some cyclooctane was present. The compounds present after each of the hydrogenation reactions were 1,3-cyclooctadiene, cyclooctene and cyclooctane. The (diene + monoene):alkane ratio was determined by gas chromatography, the two peaks being separated typically by more than 0.8 minutes. The ratio of the diene to monoene was determined by ^1H NMR, as illustrated in Figure 21. The central olefinic protons of the diene appear near 5.8 ppm while the outer protons appear around 5.6 ppm. The olefinic protons of the monoene appear around 5.6 ppm. The ratio of monoene to diene is therefore given by;

$$\frac{\text{Monoene}}{\text{Diene}} = \frac{A_{5.6} - A_{5.8}}{A_{5.8}}$$

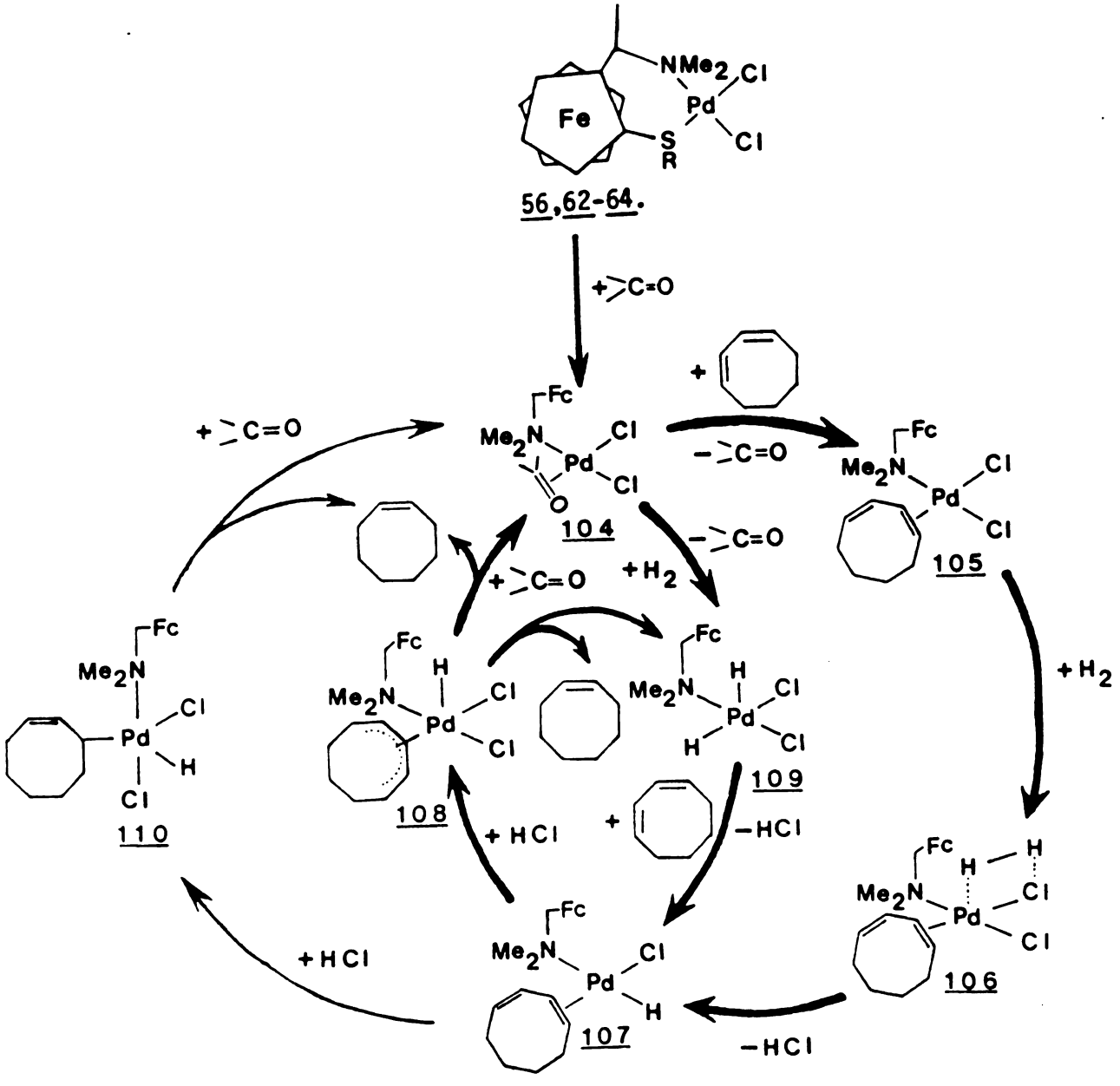
The selective hydrogenations of 1,3-cyclooctadiene in acetone at 27°C and 67 psi initial hydrogen pressure using thioether-palladium complexes 58 and 62 as catalysts are shown in Figure 19 and Figure 20 respectively. Table 21 shows that the ratio of products (selectivity) and initial turnover rates depend on the nature of the alkyl group present in the catalyst. Steric crowding rather

Table 22

Effect of Solvents on the Selective Hydrogenation of 1,3-cyclohexadiene[a]

Catalyst	Solvent	Initial H_2 Pressure (psi)	Turnover Rate (mol/ mol.Pd.h)	Conversion(%)	Products (%)	
					Cyclohexene	Cyclohexane
63	Acetone	67	462.00	100	95.5	4.5
63	Acetone/CCl_4 2:1	67	50.9	56	94.9	5.1
63	Acetone/CCl_4 1:1	67	16.4	51	96.3	3.7
63	CCl_4	67	-	-	-	-

[a] 9.0 mL of solvent; 2.0×10^{-5} mol of catalyst; 7.40×10^{-3} mol of substrate; T = 27°C



Scheme 17. Proposed Mechanisms for Homogeneous Selective Hydrogenation of 1,3-cyclooctadiene via a 4-coordinate intermediate. Fc- = 2-alkylthioetherferrocenylderivative.

than inductive effects of the aryl and alkyl groups present in the catalyst, favor selective hydrogenation.

The effect of solvents on the hydrogenation of 1,3-cyclohexadiene at room temperature is given in Table 22. The catalyst and substrate are soluble in CCl_4. However, the solution is catalytically inactive since H_2 is unable to add oxidatively to Pd. When the catalyst and substrate are dissolved in acetone, acetone replaces the thioether and coordinates to Pd, and thus induces hydrogenation. In a mixed solvent of actone and CCl_4, the hydrogenation turnover rate decreases but the selectivity increases slightly, indicating that proper choice of solvent is essential in the selective hydrogenation process.

IV. APPENDIX

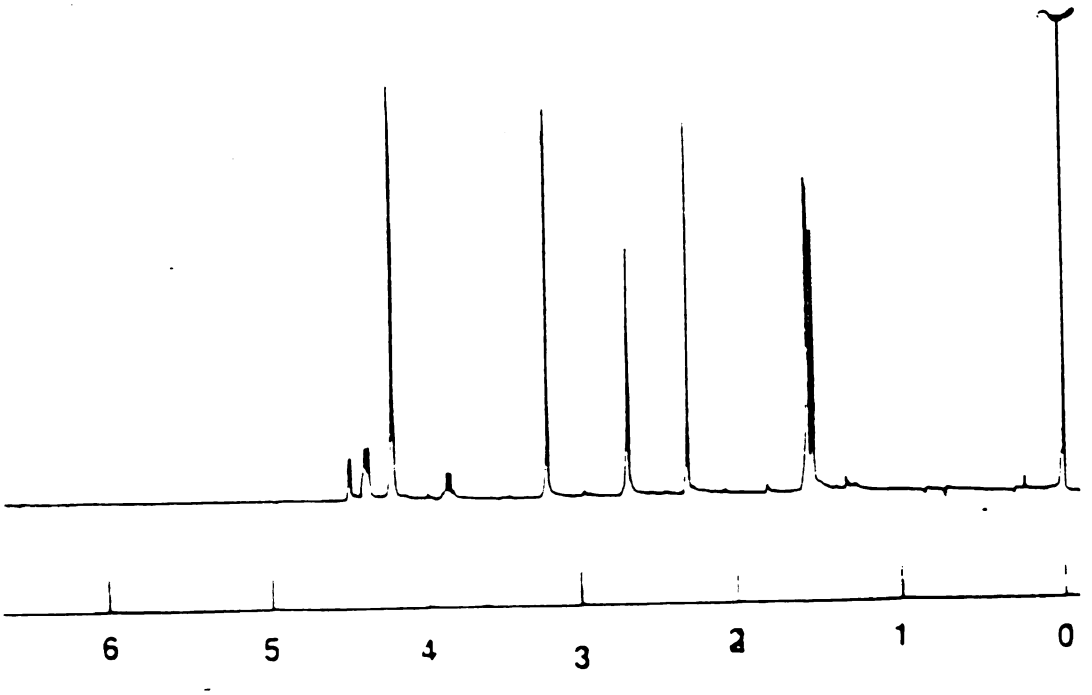


Figure 9. 250 MHz ^1H NMR spectrum of 58; $PdCl_2$ complex.

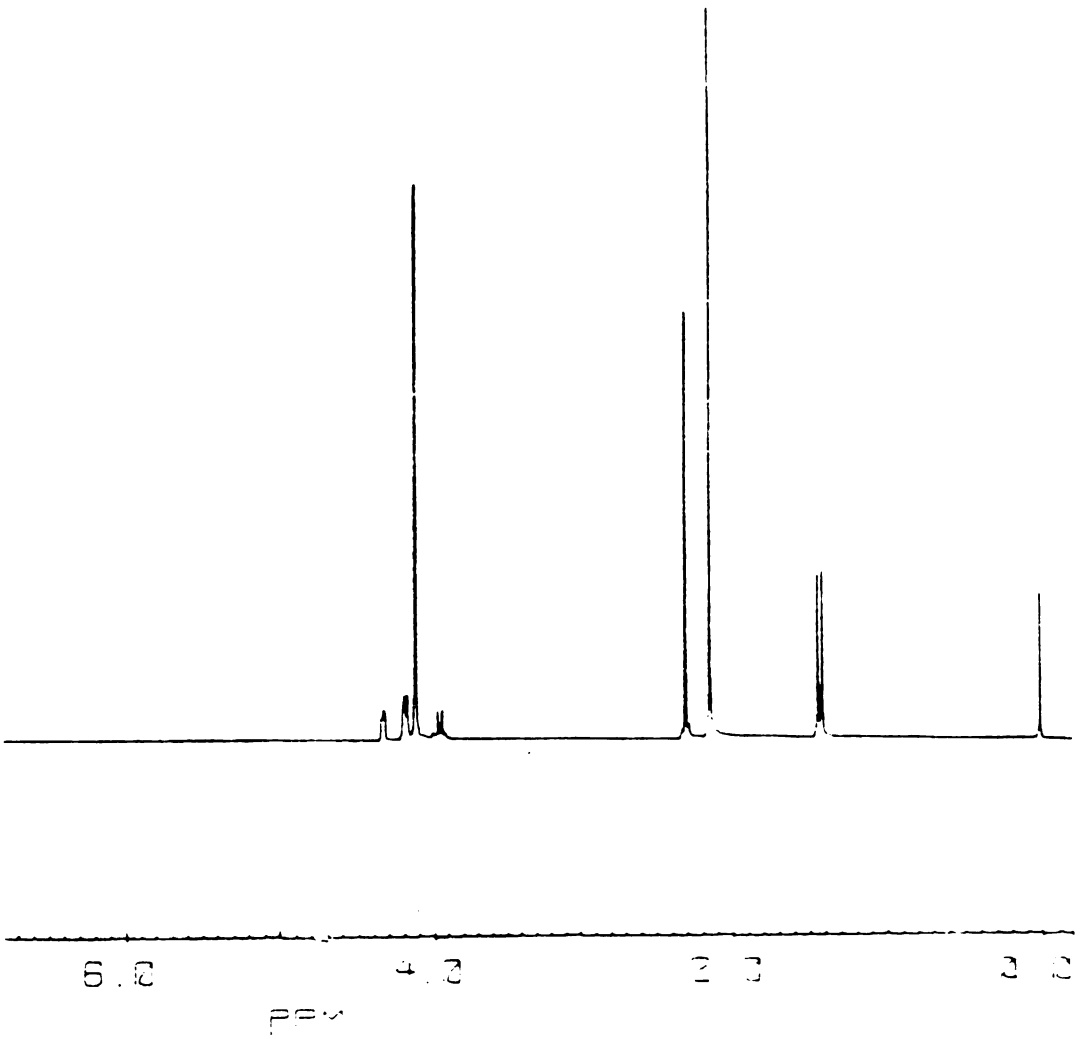


Figure 22. 250 MHz ^1H NMR Spectrum of 46, R=Me.

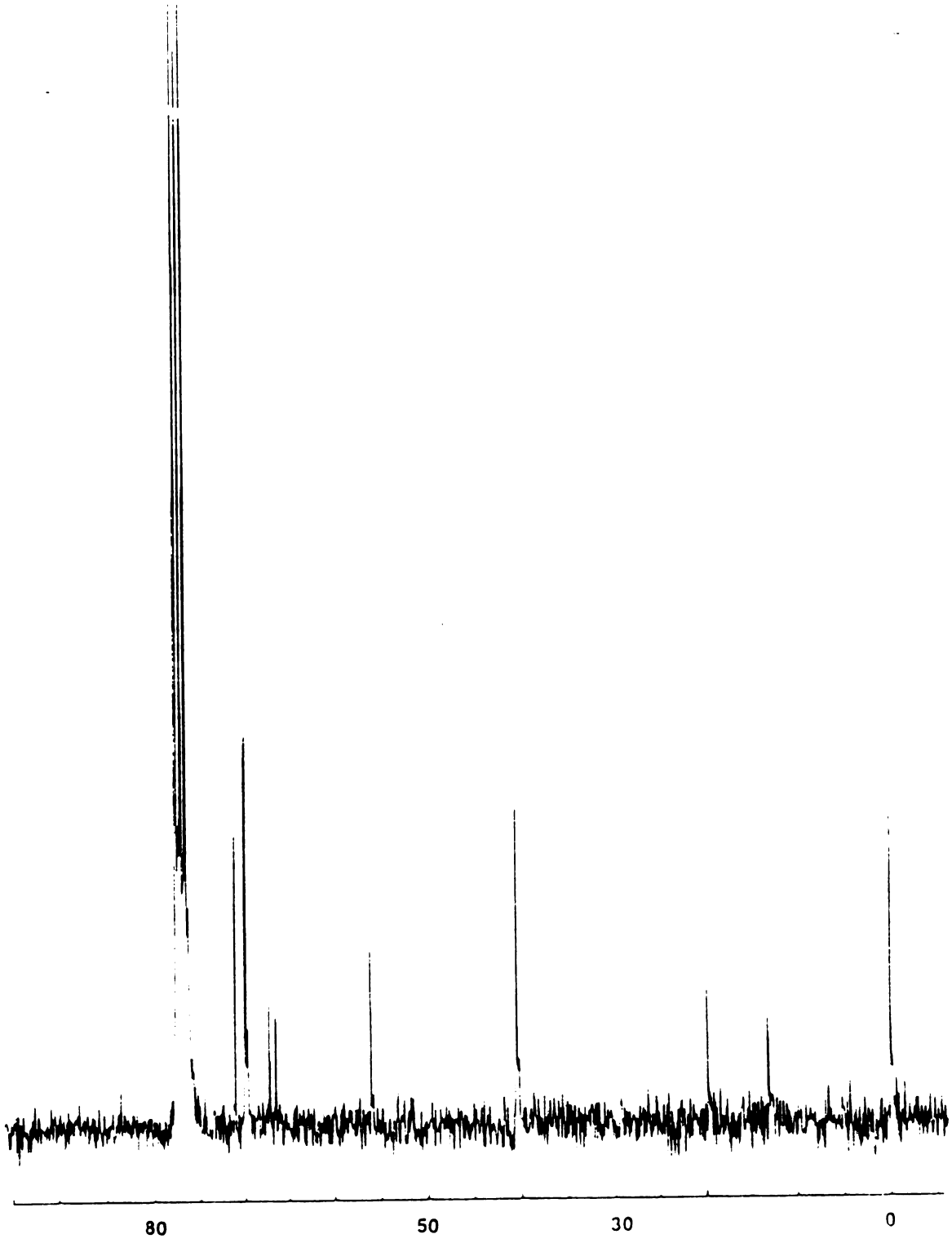


Figure 23. Gated decoupled ^{13}C NMR of 46, R=Me.

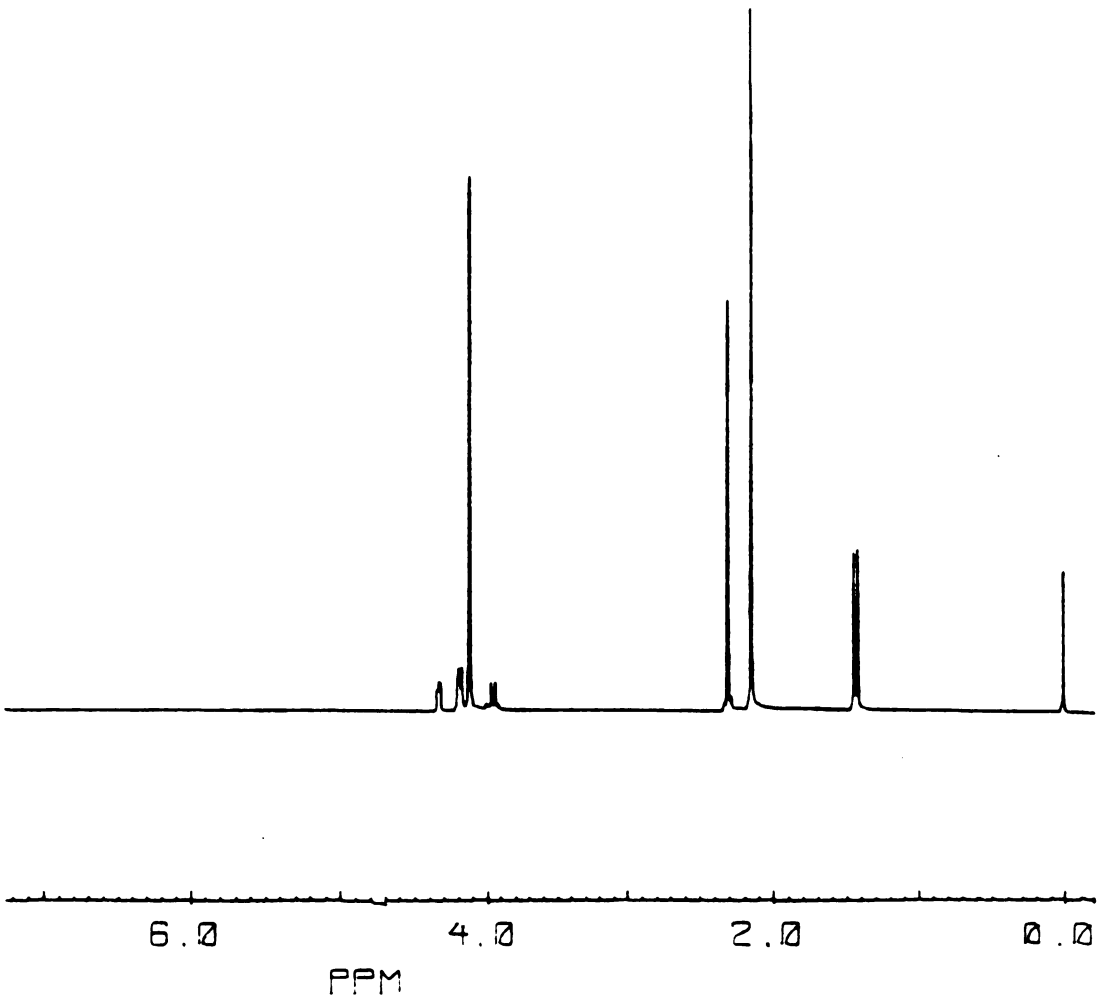


Figure 24: 250 MHz ^{1}H NMR Spectra of 46, R = Me

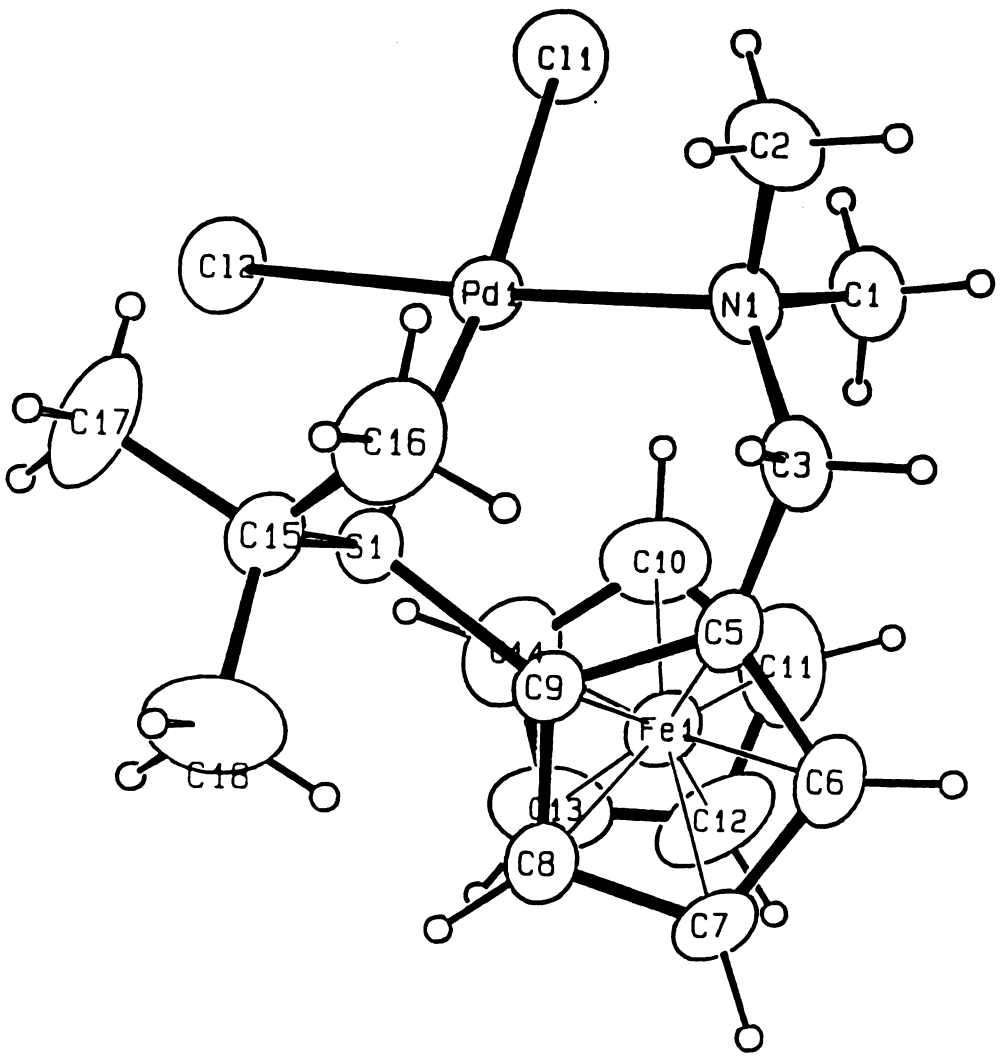


Figure 25: Structure of Dichloro[1-dimethylaminomethyl-2-t-butylthioferrocenyl]palladium(II).

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