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THE SYNTHESIS OF FERROCENE MONOMERS AND POLYMERS

HAROLD ROSENBERG
FREDERICK L. HEDBERG

TECHNICAL REPORT AFML-TR-69-68

NOVEMBER 1969

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THE SYNTHESIS OF FERROCENE MONOMERS AND POLYMERS

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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division, AFML. The work was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena," Task No. 734201, "Basic Factors in the Synthesis of Macromolecular Materials." It was administered under the direction of Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. Harold Rosenberg as project scientist.

This report covers work conducted from March 1965 to July 1968. The manuscript was released for publication by the authors in July 1968.

The authors are indebted to Mr. Charles A. Tobin for performing some of the experimental work. The assistance of Lt. J. N. Willis, Jr., and Mary T. Ryan of the Analytical Branch, Materials Physics Division, Air Force Materials Laboratory, in determining the infrared and nuclear magnetic resonance spectra is gratefully acknowledged.

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William E. Gibbs

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Chief, Polymer Branch
Nonmetallic Materials Division
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ABSTRACT

The development of a new procedure for preparing lithiated derivatives of ferrocene [bis(cyclopentadienyl)iron] is reported. The reactivity and synthetic utility of these lithiated derivatives are shown by their reactions with halides of Group III, IV, and V elements to yield novel ferrocene derivatives containing the Group III, IV, or V element directly bonded to the ferrocene moieties. The new ferrocene derivatives have potential applications as thermally stable and radiation-resistant materials. The role of lithiated ferrocenes in the synthesis of ferrocene polymers derived from α-ferrocenylcarbinols is also described.

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SECTION I
INTRODUCTION

This research program is concerned with the synthesis and study of novel derivatives of ferrocene [bis (cyclopentadienyl) iron]. The high thermal stability and radiation resistance displayed by compounds in the ferrocene class have encouraged the exploration of this class as a potential source of polymers and fluids for use in high temperature or high radiation level environments.

The lithiated derivatives of ferrocene, ferrocenyllithium and 1,1'-dilithioferrocene, have proved to be highly reactive and very useful for incorporating the ferrocene group into both monomers and polymers. Previous methods of forming lithiated ferrocenes either have afforded mixtures of both the mono- and dilithiated derivatives or have concurrently produced reactive mercury compounds. As a result of this research, a new method has been developed for the preparation of either pure mono- or dilithiated ferrocene in the general absence of any other reactive species. This method involves an exchange reaction between n-butyllithium and either bromoferrocene or 1,1'-dibromoferrocene.

The reactivity and versatility of lithiated ferrocenes as synthetic intermediates have been demonstrated by the synthesis of a number of novel ferrocene derivatives of elements of Groups III, IV, and V. Oxidative coupling of ferrocenyllithium derivatives to the corresponding biferrocenyl derivatives has been accomplished. Ferrocenyllithium has also been used for the synthesis of triferrocenylcarbinol, which in turn was converted to a stable carbonium ion salt as part of a study being initiated on the formation of polymers via α-ferrocenylcarbinol intermediates. Infrared spectra and nuclear magnetic resonance (NMR) spectra were obtained for all compounds synthesized and were used in the identification of new compounds.

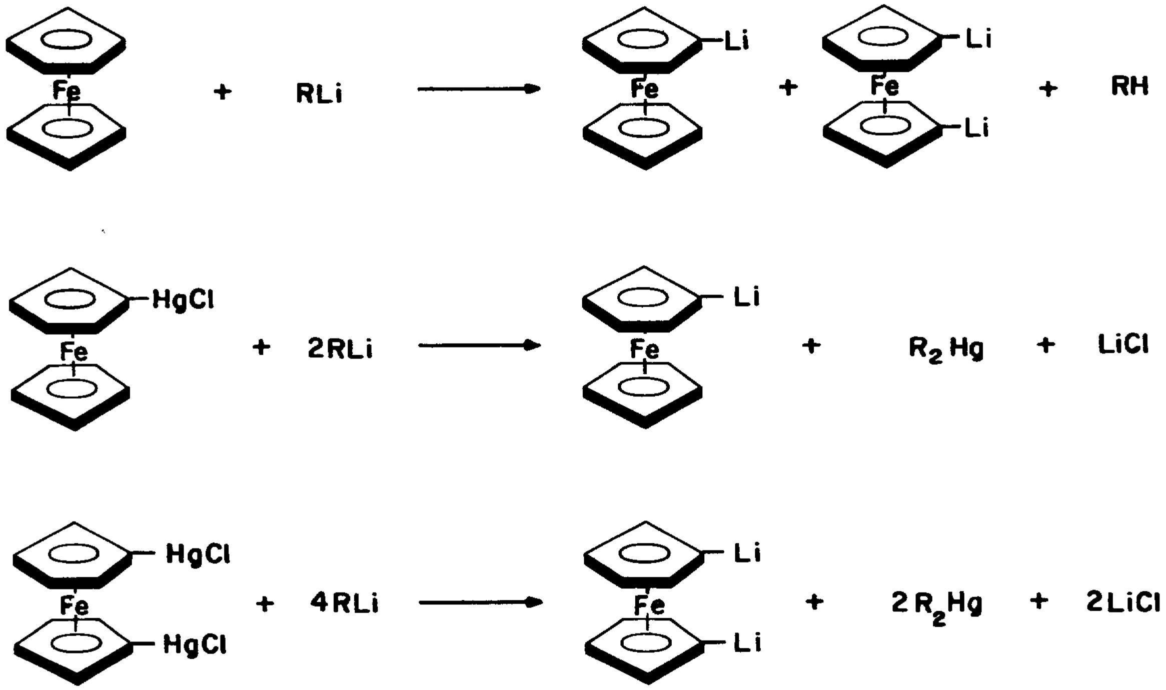
In conjunction with the new ferrocene lithiation method, an improved route to one of the starting materials, bromoferrocene, was developed. The lithiation of other haloferrocenes was also investigated.

SECTION II

DISCUSSION

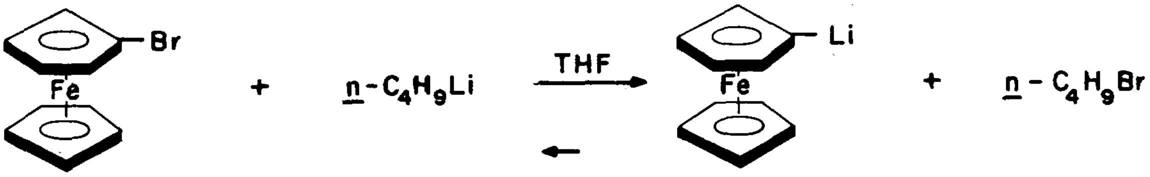
A. Formation of Lithiated Ferrocenes

Ferrocenyllithium and 1,1'-dilithioferrocene have been prepared by modifications of two general procedures: The direct abstraction of a proton or protons from ferrocene by an alkyllithium (References 1-3), or an exchange reaction between a chloromercurated ferrocene and an alkyllithium (References 4 and 5).

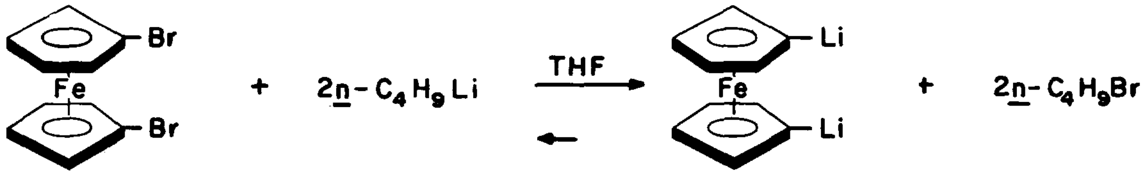


The abstraction procedure leads to a mixture of both the mono- and dilithiated species. In addition, a large excess (ca 6:1) of n-butyllithium is required in order to obtain reasonable yields of lithiated ferrocenes. The exchange procedure affords a unique lithiated species in good yield and employs a stoichiometric amount of alkyllithium, but is complicated by the concurrent formation of a reactive dialkylmercury compound. Use of the exchange procedure in this laboratory has resulted in the formation of both alkylated and mercury-containing derivatives of ferrocene as undesirable side products.

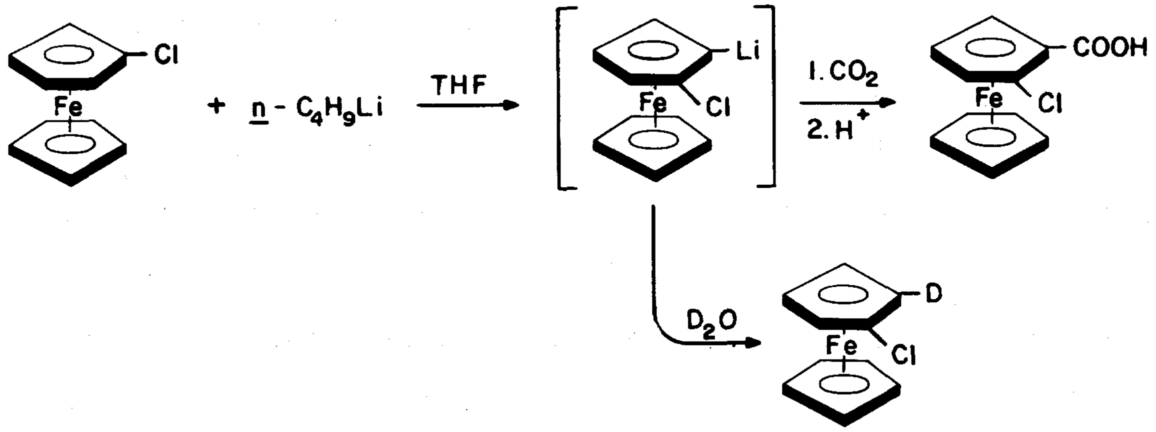
Previous attempts in this laboratory to form ferrocenyllithium by the reaction of haloferrocenes with lithium metal in various forms were not successful (Reference 6). An exchange reaction between n-butyllithium and bromoferrocene proved much more fruitful. Yields of ferrocenyllithium from this procedure, as determined by carbonation, ranged from 50-75%. Stoichiometric amounts of bromoferrocene and n-butyllithium were used. Less than 1% of unreacted bromoferrocene was detected by vapor phase chromatography. No disubstituted ferrocene derivatives were ever isolated from reactions with ferrocenyllithium prepared in this manner, indicating the absence of any appreciable amounts of 1,1'-dilithioferrocene. The reaction temperature was varied from -78 to 0°C with no noticeable correlation with yield. Reactions, involving excess ferrocenyllithium, which were allowed to stand at 0-25°C for a few hours or more showed small amounts (1-5%) of n-butylferrocene upon vapor phase chromatographic analysis of the products. Some reaction can apparently take place at higher temperatures between ferrocenyllithium and n-butyl bromide, but this reaction is quite slow.



Extension of the exchange reaction to 1,1'-dibromoferrocene and n-butyllithium afforded yields of 1,1'-dilithioferrocene, determined by carbonation, of 98-100%. We have been unable to determine a reason for the variance in yield between the mono- and dilithiated species, but are presently studying variations of conditions which may increase the yield of ferrocenyllithium.

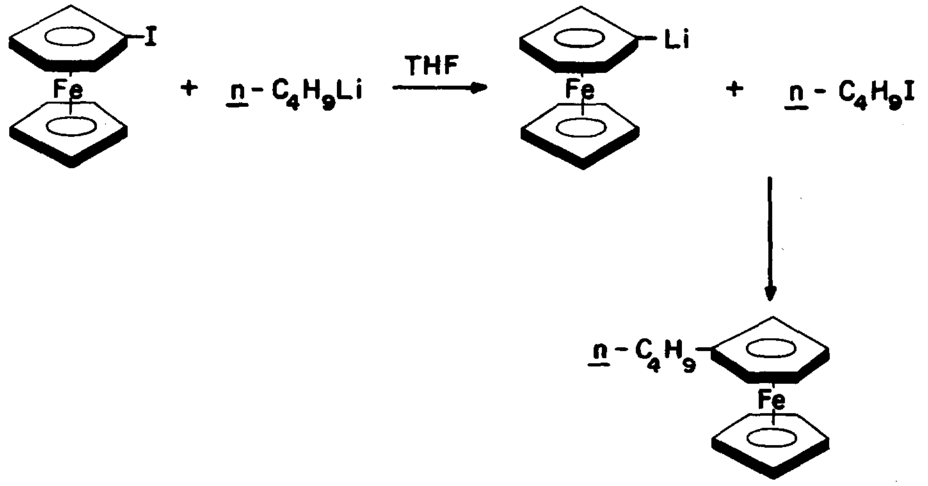


The uniqueness of the exchange reaction between n-butyllithium and bromoferrocene or 1,1'-dibromoferrocene can be seen by comparison with the results obtained from the reaction of n-butyllithium with chloroferrocene or iodoferrocene. Chloroferrocene has been reacted with n-butyllithium in hexane-ether (2:1) solution at room temperature for 7 hours to give, after carbonation, a 78% yield of 2-chloroferrocenecarboxylic acid (Reference 7). Chloroferrocene and n-butyllithium have been reacted together at 0° in tetrahydrofuran for 1 hour in this laboratory to give a quantitative yield of 2-chloroferrocenecarboxylic acid (Reference 8). We have reacted chloroferrocene with n-butyllithium at 0° in tetrahydrofuran to obtain a quantitative yield of 2-chloroferrocenecarboxylic acid upon carbonation, and a 97% conversion to 2-deuterochloroferrocene of 98.8% isotopic purity upon deuteration.

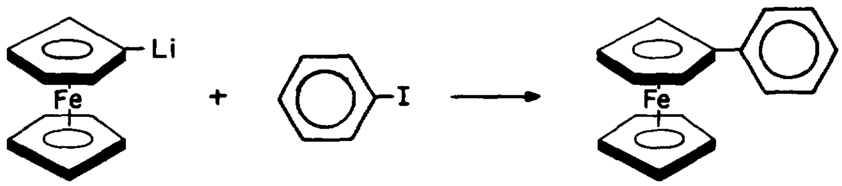


The chloroferrocene-n-butyllithium proton abstraction reaction proved to be much slower than the exchange reaction between bromoferrocene and n-butyllithium, since carrying out the reaction at -40 C for 30 minutes effected only about a 25% conversion to 2-lithiochloroferrocene.

Iodoferrocene, like bromoferrocene, underwent an exchange reaction with n-butyllithium. In this case, however, the side product from the reaction, n-butyl iodide, proved to be quite reactive toward the ferrocenyllithium formed, affording a 27% yield on n-butylferrocene in one instance. The time-temperature dependence of yields of ferrocenyllithium obtained from this reaction have led us to investigate other organolithiums as exchange agents with

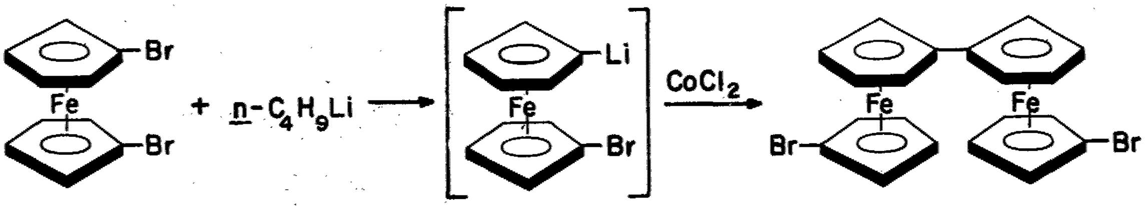


iodoferrocene. The only related result in this area so far is the room temperature reaction of ferrocenyllithium with iodobenzene to give a 19% yield of phenylferrocene. The low temperature exchange reaction between phenyllithium and iodoferrocene may thus afford a convenient synthesis of ferrocenyllithium.



The usefulness of bromoferrocene and 1,1' -dibromoferrocene as starting materials for the formation of ferrocenyllithium and 1,1' -dilithioferrocene prompted an investigation into the synthesis of these brominated ferrocenes. The bromoferrocenes have been prepared by three routes: direct bromination of chloromercuriferrocene or 1,1' -bis (chloromercuri) ferrocene (Reference 9); the reaction of cupric bromide with ferrocenylboronic or ferrocenyl-1,1' -diboronic acids (References 10 and 11); and the reaction of chloromercuriferrocene or 1,1' -bis(chloromercuri)ferrocene with N-bromosuccinimide (Reference 12). A modification of the third route employing tetrahydrofuran as the solvent for the reaction, rapid addition of N-bromosuccinimide, and high-speed stirring gave excellent results with chloromercuriferrocene. Yields of 68-72% of bromoferrocene were obtained. The purity of the product determined by vapor phase chromatography, ranged from 96.5% to greater than 99%. Attempts to extend the modification to the synthesis of 1,1'-dibromoferrocene were unsuccessful.

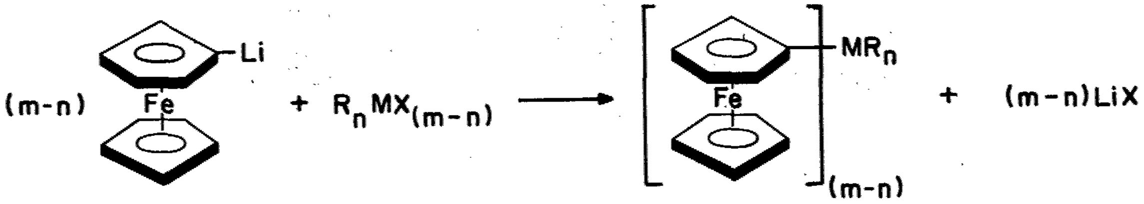
The reaction of 1,1'-dibromoferrocene with half an equivalent of n-butyllithium followed by coupling with cobaltous chloride was used to prepare 1',6'-dibromobiferrocenyl.



Extension of the n-butyllithium exchange reaction to this compound may afford a route to substituted 1',6'-biferrocenyls via 1',6'-dilithiobiferrocenyl.

B. Reactions of Ferrocenyllithium

The general reaction of ferrocenyllithium with an organometallic halide is of the following type for the organic moiety, R, and the halide, X.



where m = 3, 4, or 5 for elements, M, of
Group III, IV, or V, respectively, and
n = 1 to m.

Table I contains a list of the novel compounds which we have synthesized by the above route (X = Cl throughout, unless otherwise indicated).

TABLE I

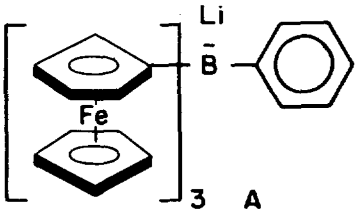
Novel Ferrocene Derivatives from Ferrocenyllithium

Compound	M	n	R
Diferrocenylphenylborane	B	1	C_6H_5
Triferrocenylborane (X = F)	B	0	
Diferrocenyldimethylgermane	Ge	2	CH_3
Diferrocenyldiphenylgermane	Ge	2	C_6H_5
Methyltriferrocenylgermane	Ge	1	CH_3
Ferrocenyltrimethyltin	Sn	3	CH_3
Diferrocenyldimethyltin	Sn	2	CH_3
Ferrocenyltriphenyllead	Pb	3	C_6H_5
Diferrocenyldiphenyllead	Pb	2	C_6H_5

Two known compounds were also made by this route, ferrocenyltriphenylgermane and diferrocenylphenylphosphine oxide. The germane was previously made in much lower yield from a mixture of mono- and disodiated ferrocenes (Reference 13). The phosphine oxide was previously made via a Friedel-Crafts reaction between ferrocene and dichlorophenylphosphine (References 14 and 15). The low solubility of diferrocenylphosphine oxide in tetrahydrofuran discouraged any attempt at polymer formation from the reaction of dichlorophenylphosphine oxide with 1,1'-dilithioferrocene under similar conditions.

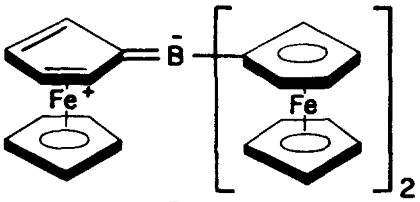
An attempt to synthesize triferrocenylborane by an alternate route, reaction of excess ferrocenyllithium with tri-n-butylborate, resulted in the attachment of only 2 ferrocene groups to boron to give (upon hydrolysis) diferrocenylborinic acid. Although this result would seem to indicate some difficulty in adding a third ferrocenyl group to boron derivatives with poor leaving groups, a contrasting result was obtained during the synthesis of diferrocenylphenylborane. Some triferrocenylborane was produced as a side product in this reaction.

The formation of triferrocenylborane in this reaction represents exchange of a phenyl group for a ferrocenyl group. The replacement of a group or groups on a trialkyl-substituted borane has been observed to occur upon reaction with an alkyl (Reference 16) or aryl (Reference 17) Grignard reagent. Since an excess of ferrocenyllithium was used in this reaction, further attack by ferrocenyllithium upon diferrocenylphenylborane may have occurred, with subsequent elimination of a phenyl group from the sterically crowded tetrasubstituted intermediate (A).



A

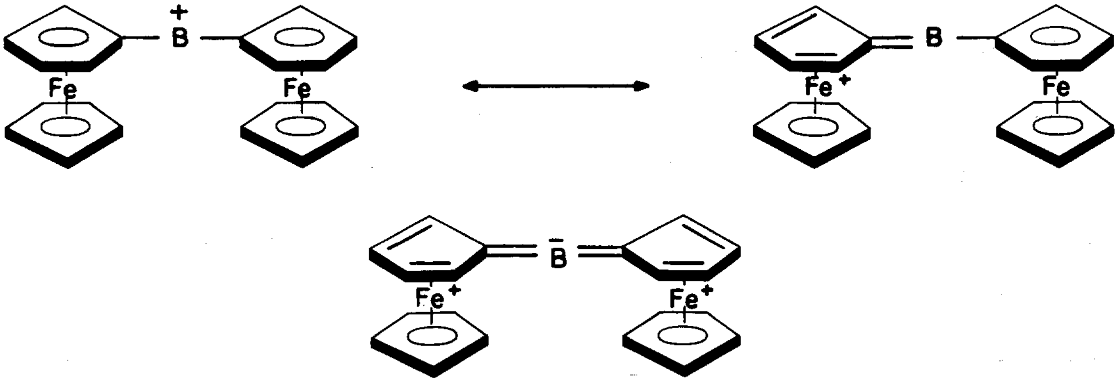
The yield of triferrocenylborane from this reaction could not be determined accurately due to the facile decomposition of triferrocenylborane upon alumina chromatography, but appeared to be roughly equivalent to the yield of diferrocenylphenylborane by thin layer chromatographic analysis of the crude reaction mixture. The production of so much triferrocenylborane in this reaction is probably caused both by the mass law effect and the thermodynamic stability of triferrocenylborane. Triferrocenylborane decomposes slowly in hexane solution, but is quite stable toward both air and moisture in the solid state. Its NMR spectrum (Figure 21) shows an unusually high downfield shift for the substituted ferrocene ring protons (280 and 296 cps versus 248 cps for ferrocene) indicating considerable withdrawal of electron density from the ferrocene ring by boron. Structures such as (B) may be considered in describing the ground state of the molecule.



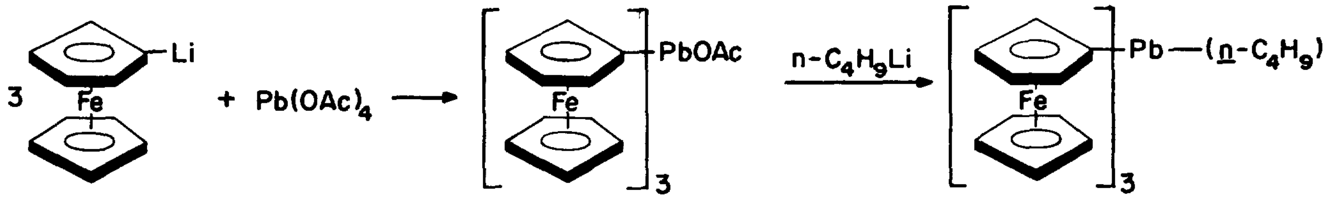
B

The ferrocenyl-substituted boron compounds obtained represent the only reported derivatives of boron with more than one ferrocene group bonded directly to a boron atom. The only previously reported boron derivatives of ferrocene are ferroceneboronic acid and 1,1'-ferrocenediboronic acid (References 10 and 11).

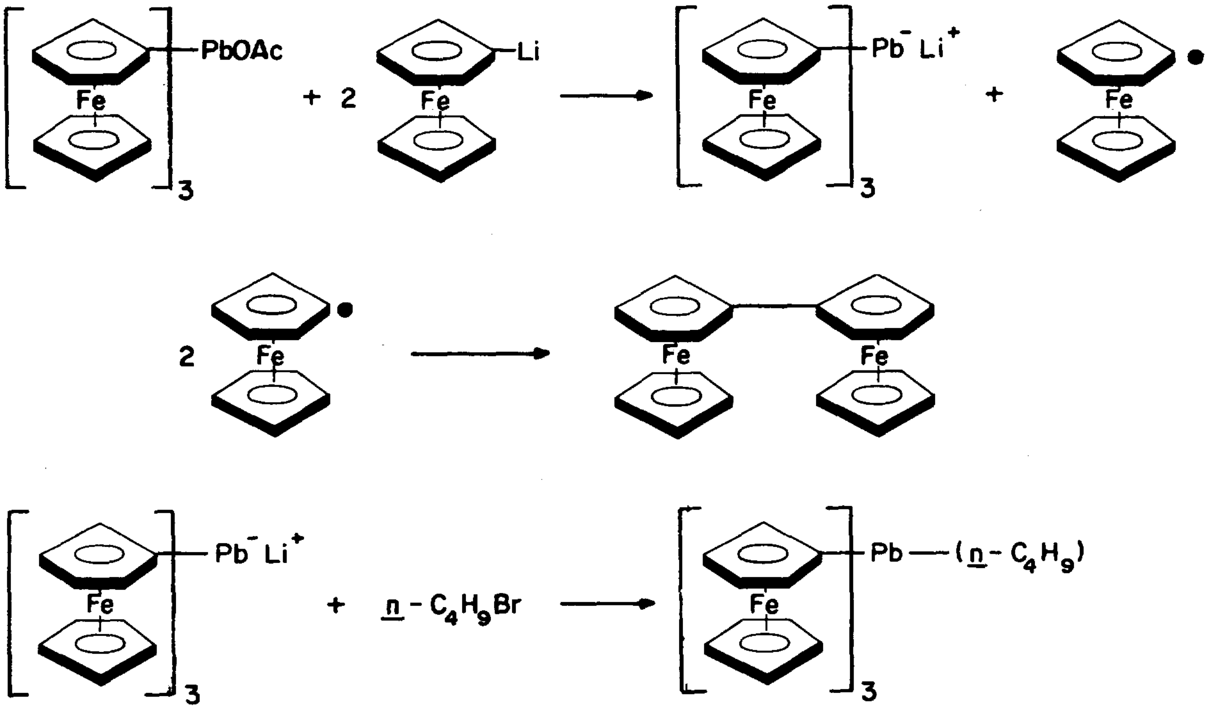
The addition of a few drops of 40% fluoboric acid to a yellow acetone solution of diferrocenylborinic acid was accompanied by the instantaneous formation of a deep blue color. No color change occurred upon addition of fluoboric acid to an acetone solution of triferrocenylborane. Diferrocenylborinic acid also dissolved in trifluoroacetic acid to give a deep blue colored solution. An NMR spectrum of this solution showed no peak broadening (which would be expected if a ferricinium ion species were present). The absorption for the unsubstituted ring protons was shifted 6 cps upfield from the corresponding absorption in deuterochloroform as solvent. The substituted ring protons of diferrocenylborinic acid, however, which appeared as a single broad peak centered at 272 cps in deuterochloroform, appeared as two separate sets of peaks centered at 287 and 324 cps in trifluoroacetic acid. The possibility that the blue color of an acidic solution of diferrocenylborinic acid may be due to generation of the ferrocene analog (C) of the diphenylboronium ion (References 18 and 19) is currently under investigation.



The reaction of excess ferrocenyllithium with lead tetraacetate afforded a very low yield of the expected product, tetraferrocenyllead, giving rise instead to n-butyltriferrocenyllead as the major product of the reaction. In rationalizing this result, it is necessary to remember that the reaction between bromoferrocene and n-butyllithium is essentially an equilibrium. When 3 ferrocene groups have been substituted onto the lead atom, it is conceivable that the rate of reaction of the resultant triferrocenyllead acetate intermediate could be slowed by steric considerations to such an extent that the bromoferrocene-n-butyllithium equilibrium could be shifted back to the left as attack by the more reactive and sterically favored n-butyllithium takes precedence.

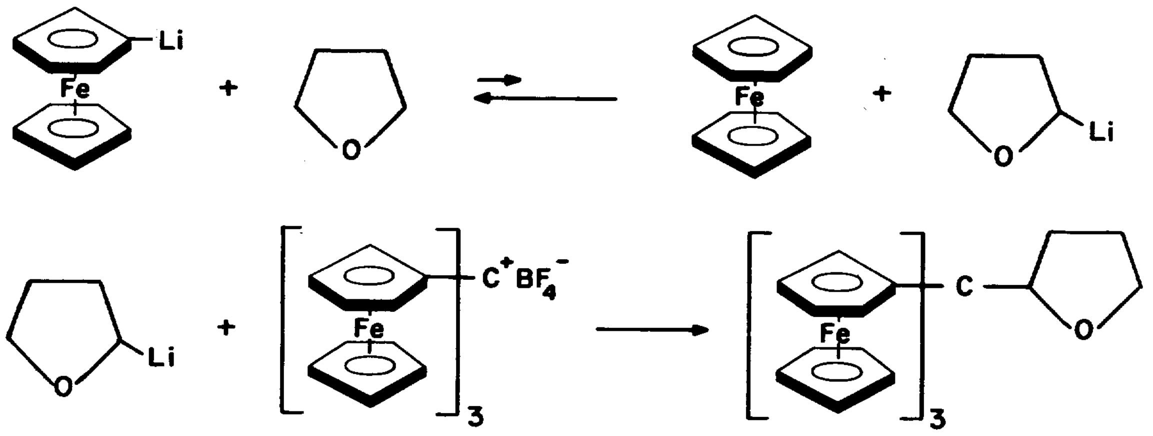


The presence of a relatively large amount of biferrocenyl among the reaction products, however, suggests another mechanism which might also be operative: the transfer of 2 electrons to the triferrocenyllead acetate, followed by reaction of the resultant triferrocenyllead anion with n-butyl bromide.

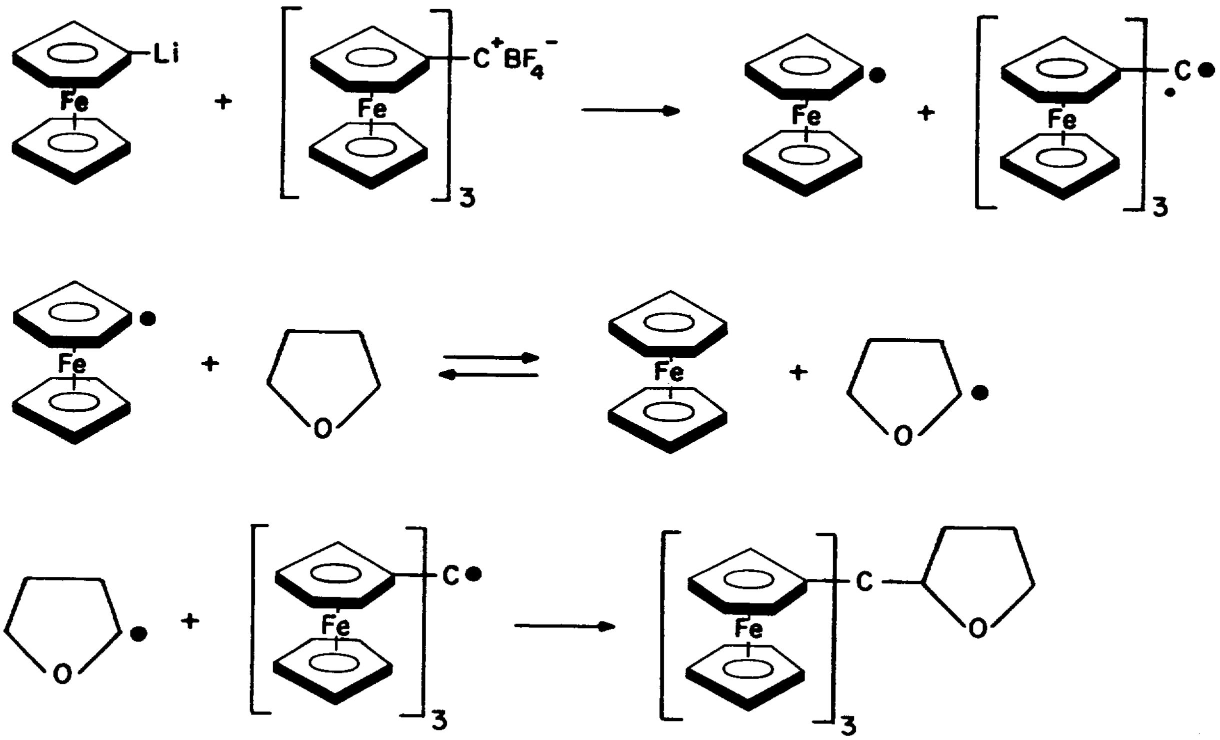


A related complication arose during an attempt to synthesize tetraferrocenylmethane. Ferrocenyllithium was reacted with diferrocenyl ketone to make triferrocenylcarbinol. The carbinol was converted to the novel carbonium ion salt, triferrocenylmethyl fluoborate, by reaction with fluoboric acid. The major reaction product obtained from adding triferrocenylmethyl fluoborate to a tetrahydrofuran solution of ferrocenyllithium was not the expected tetraferrocenylmethane, but instead proved to be the novel compound, 2-(triferrocenylmethyl)tetrahydrofuran. The formation of this compound can be accounted for by either an ionic or a radical mechanism, since, here also, steric considerations inhibit the attachment of a fourth ferrocene group to a triferrocenyl-substituted methane.

Ionic Mechanism:

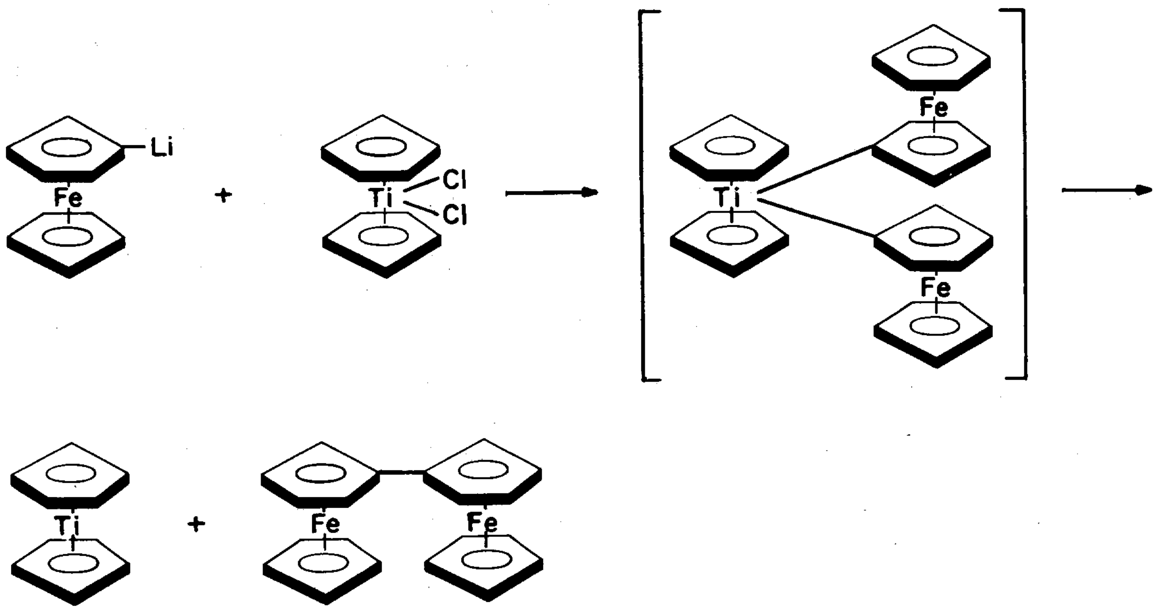


Radical Mechanism:

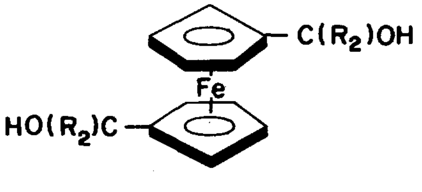


The intense purple color formed during the initial period of the reaction can be considered as evidence for the radical mechanism, since no purple-colored species would be expected for the ionic mechanism, while the triferrocenylmethyl radical might be expected to be highly colored. Reaction of ferrocenyl radical with tetrahydrofuran would also explain the poor yields of biferrocenyl obtained (0-20%) in this laboratory from coupling ferrocenyllithium with cobaltous chloride in tetrahydrofuran as solvent (Reference 8).

A successful coupling of ferrocenyllithium was accomplished by the use of titanocene dichloride [bis-(cyclopentadienyl)titanium dichloride]. From the results of previous studies on the thermal decomposition of diphenyl-(bis-cyclopentadienyl)titanium to biphenyl in aprotic solvents (Reference 20), it seems reasonable to postulate an unstable diferrocenyl-(bis-cyclopentadienyl)titanium intermediate. The proximity of ferrocenyl radicals resulting from the intramolecular decomposition of such an intermediate would favor coupling over hydrogen abstraction from the solvent;

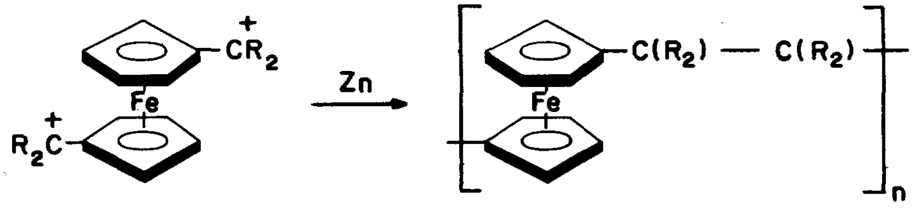


The syntheses of triferrocenylcarbinol and triferrocenylmethyl fluoborate represent the initiation of a study on the use of α-ferrocenylcarbinols of the form, (D), as precursors to ferrocene-containing polymers.



D

The formation of stable carbonium ion salts from the carbinols followed by reductive coupling should lead to substituted poly-ethyleneferrocenylenes.

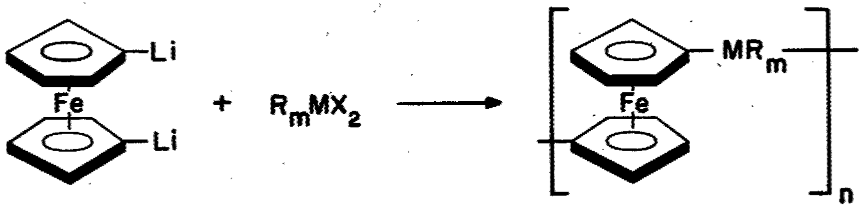


Although heat sensitive in solution and hygroscopic, triferrocenylmethyl fluoborate is fairly stable when stored in the solid state in a desiccator. Nuclear magnetic resonance absorption of the substituted ring protons shows a large downfield shift (334 and 340 cps versus 248 cps for ferrocene). The salt was characterized by sodium borohydride reduction to triferrocenylmethane.

An attempt to reduce triferrocenylcarbinol to triferrocenylmethane by heating in formic acid resulted instead in polymerization of the carbinol. The same polymer was also formed by heating the carbinol in acetic acid. The structure of the polymer could not be determined from infrared and NMR studies. Elemental analysis agrees with the carbon-hydrogen analysis for diferrocenylfulvene, recently identified as the maroon decomposition product of triferrocenylchloromethane hydrochloride (Reference 28). This polymer may therefore result from Diels-Alder polycondensation of diferrocenylfulvene (which could be expected to form under these conditions). An attempt either to form a similar polymer or to effect reduction to the methane derivative with ferrocenyl-(bis-trifluoromethyl)-methanol by heating in formic acid led only to recovery of starting material.

C. Reactions of 1,1'-Dilithioferrocene

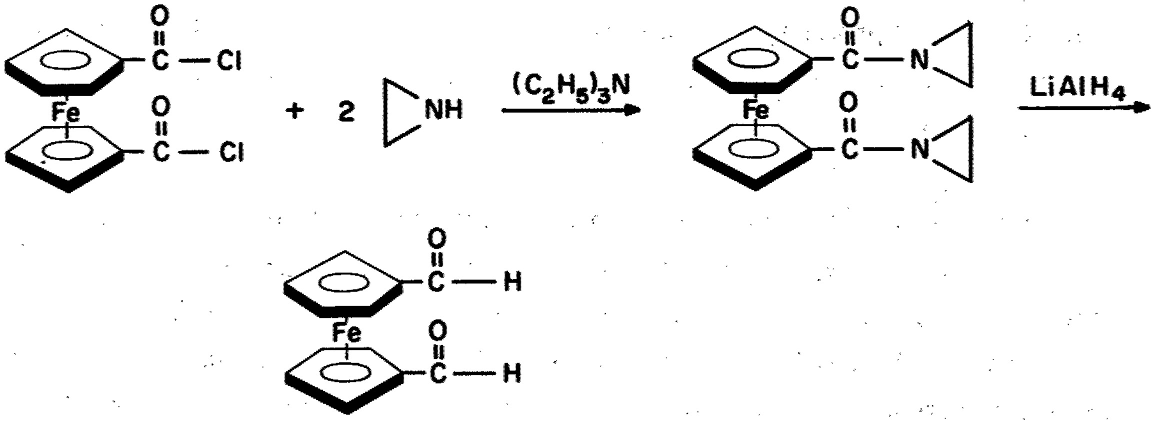
1,1'-Dilithioferrocene can theoretically react with a dihalo derivative of Group III, IV, or V to give the corresponding polymer.



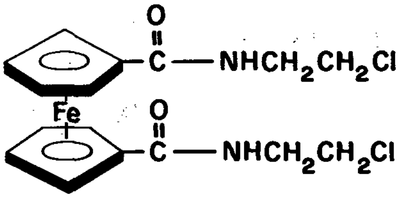
When this type of reaction was carried out with dichlorodiphenyllead to give the derivative where R = phenyl, m = 2, and M = Pb, only very low molecular weight material was obtained (mol wt 2250, corresponding to 4.1 monomer units).

D. Miscellaneous Reactions

An attempt was made to synthesize 1,1'-ferrocenedicarboxaldehyde via an acylaziridine intermediate according to the procedure developed by H. C. Brown (Reference 21). The only synthesis of the dialdehyde reported previously involves oxidation of 1,1'-(bis-hydroxymethyl)ferrocene by manganese dioxide (Reference 22). The only product obtained from the initial reaction of the di-acid chloride with ethylenimine,



however, appears to be N,N'-di-β-chloroethyl-1,'-ferrocenedicarboxamide (E) arising from ring opening of the ethylenimine ring.



E

SECTION III

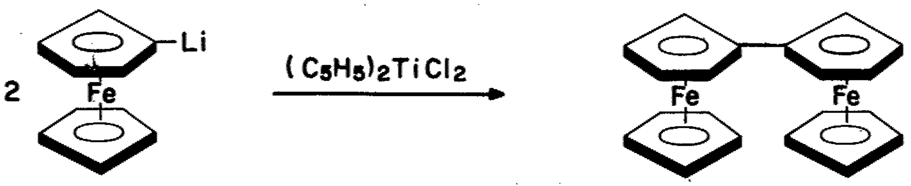
EXPERIMENTAL

A. General

All melting points were taken in a sealed capillary under nitrogen and are uncorrected. Molecular weights were determined by vapor phase osmometry unless otherwise specified. Elemental analyses were carried out by either Schwarzkopf, Crobaugh, or Huffman Microanalytical Laboratories. Nuclear magnetic resonance spectra were obtained on a Varian model A-60. Infrared spectra were obtained as KBr pellets on a Perkin-Elmer Model 21 Spectrophotometer. Woelm alumina used for column chromatography was neutral, activity grade 1, which was deactivated to the specified activity grade by the addition of 1.5% water for activity grade 1.5 and 3% water for activity grade 2.

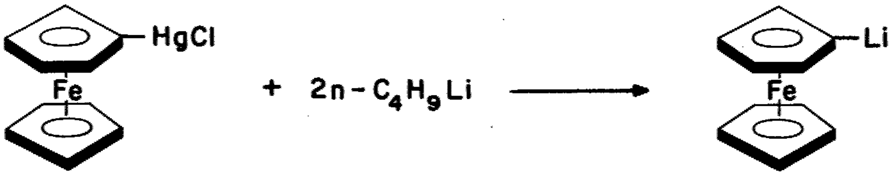
Nuclear magnetic resonance absorption spectra and infrared spectra are given at the end of the experimental section. Deuterochloroform was used as the solvent for all NMR spectra except triferrocenylmethyl fluoborate for which perdeuterodimethyl sulfoxide was used.

B. Biferrocenyl



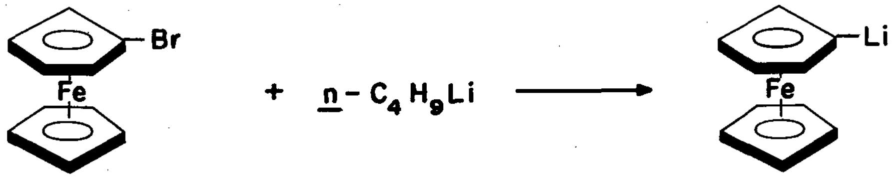
Bis(cyclopentadienyl)titanium dichloride (4.98 g, 0.020 mole) was added to a stirred solution of ferrocenyllithium (from chloromercuriferrocene [25.3 g, 0.060 mole]) in dry tetrahydrofuran (420 ml) at 0°C. The dark, blue-green colored reaction mixture was stirred for 1 hour at 0°C, then poured onto Dry Ice and allowed to evaporate to dryness. The residue was washed successively with water and petroleum ether, then continuously extracted with boiling benzene for three days. The benzene extracts were evaporated to dryness and the residue was continuously extracted with boiling methanol for 12 hours. The residue left in the Soxhlet thimble after the methanol extraction was continuously extracted with boiling hexane for five days. Removal of hexane from the extracts left 4.11g (55%) of biferrocenyl of mp 237-241°C after recrystallization from benzene-methanol (reported: 239-240° in (Reference 23).

C. Ferrocenyllithium from Chloromercuriferrocene



A solution of chloromercuriferrocene (4.95 g, 0.0117 mole) in dry tetrahydrofuran was stirred at 0° under a nitrogen atmosphere while a solution of n-butyllithium in hexane (8.7 ml, 0.012 mole) was added over a 1-minute period. The yellow suspension formed was stirred at 0° for 30 minutes, then a second 8.7 ml portion of butyllithium was added, causing immediate clarification to a deep orange-brown solution, which was stirred at 0°C for 45 minutes. At the end of this period, a 10-ml aliquot was withdrawn and carbonated, and the reactant used was added to the remaining solution. Carbonation of the aliquots afforded yields ranging from 70-85%.

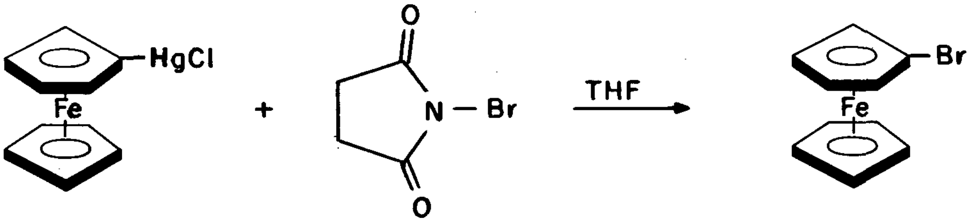
D. Ferrocenyllithium from Bromoferrocene



A solution of bromoferrocene (6.00 g, 0.0226 mole) in dry tetrahydrofuran (250 ml) was stirred at 5°C* under a nitrogen atmosphere while a solution of n-butyllithium in hexane (15 ml, 0.023 mole) was added. The reaction mixture was stirred at 0° for 30 minutes. At the end of this period, a 10-ml aliquot was withdrawn and carbonated and the reactant was added to the remaining solution. Carbonation of the aliquot afforded a 60% yield of ferrocenecarboxylic acid. Yields of ferrocenecarboxylic acid obtained by this procedure ranged from 50-75%. More concentrated solutions (from 6 g of bromoferrocene in less than 200 ml of tetrahydrofuran) afforded suspensions of ferrocenyllithium which only became homogeneous upon warming to *ca* 15°C.

E. Bromoferrocene

Bromoferrocene has been prepared by the reaction of cupric bromide with ferrocenylboronic acid (References 10 and 11) and, in low yield, by the reaction of bromine with chloromercuriferrocene (Reference 9). Recently, the preparation of bromoferrocene by the reaction of N-bromosuccinimide with chloromercuriferrocene has been reported (Reference 12). The following procedure is a modification of the last-named reaction.



The reaction is carried out in a 2-liter four-necked flask fitted with a high-speed stirrer, thermometer, and drying tube. The flask is charged with 42.1g (0.10 mole) of chloromercuriferrocene and 600 ml of dry tetrahydrofuran. The solution was cooled to 4° C,

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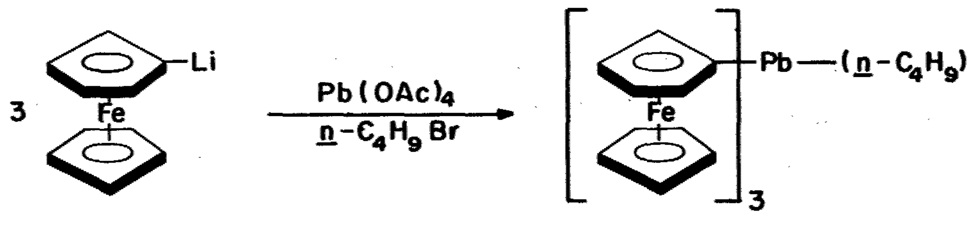
* Addition of butyllithium solution was carried out at temperatures ranging from -78 - 5°C with no noticeable correlation with yield.

and 39.0 g (0.22 mole) of N-bromosuccinimide was added quickly. A slight temperature rise occurred (1-2°C), and the nature of the reaction mixture gradually changed from an orange solution to a blue-green suspension. Stirring at 1-4° C was continued for 1 hour then a solution of sodium bisulfite (50 g) in water (450 ml) was added to the reaction mixture. After 5 minutes of stirring, the two-phase orange-colored reaction mixture was poured into a stirred solution of sodium carbonate (50 g) in water (2 liters). The upper, deep orange organic layer was separated and the lower aqueous layer extracted (4 x 200 ml) with petroleum ether. The combined organic extracts were washed with six 300 ml portions of water, filtered from residual mercury compounds, and dried over anhydrous sodium sulfate. After removal of solvent by rotary evaporator, the residual orange suspension was taken up in 100 ml of hexane, filtered from residual mercury compounds, and chromatographed on 1500 g of alumina (Woelm, activity grade 2). The first orange band eluted with petroleum ether afforded 18.2 g (69%) of bromoferrocene, mp 36-36.5°C (reported: 31-32°C) in Reference 12). Analysis by vapor phase chromatography indicated the presence of 0.5% ferrocene.

Bromoferrocene has also been made by this procedure with the amounts of all materials doubled. Purification in this case was accomplished by vacuum sublimation at 100°C rather than by column chromatography. The yield was 37.5 g (71%) of bromoferrocene of mp 32-32.5°C. Vapor phase chromatographic analysis showed ca 96.5% bromoferrocene and 3.5% ferrocene in the sublimed product.

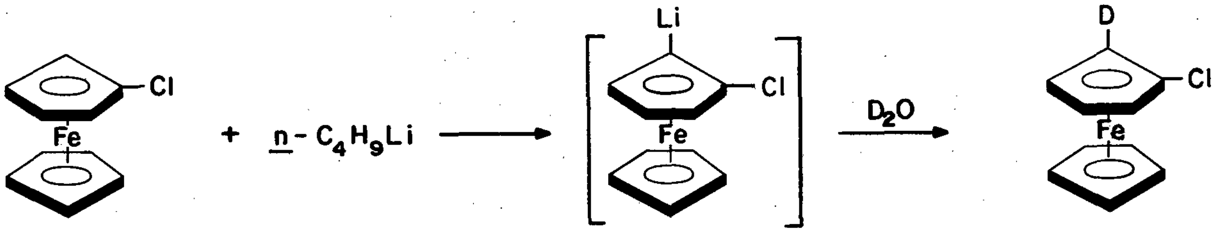
When diferrocenylmercury was used in place of chloromercuriferrocene for the reaction, a 61% yield of bromoferrocene was obtained. No 1,1' -dibromoferrocene was obtained when 1,1' -bis(chloromercuri) ferrocene was used under the same conditions. No chloroferrocene was obtained when N-chlorosuccinimide was used in place of N-bromosuccinimide for the reaction.

F. n-Butyltriferrocenyllead



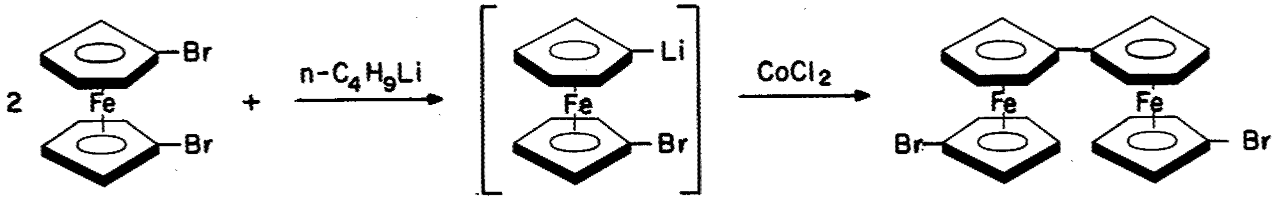
Lead tetraacetate (4.43 g, 0.0100 mole) was added to a stirred solution of ferrocenyllithium [from bromoferrocene(12.00 g, 0.0452 mole)] in dry tetrahydrofuran (250 ml) at 2°C. The reaction mixture was stirred at 2°C for 2 hours, then at room temperature for 18 hours. The reaction mixture was then evaporated to dryness, leaving 19.4 g of residue which was extracted thoroughly with hot benzene. The benzene extracts were concentrated to 100 ml and chromatographed on 1500 g of alumina (Woelm, activity grade 2). Benzene-petroleum ether (1:1) eluted a yellow band containing a mixture of 3 components. Benzene eluted an orange band containing 0.687 g of an orange oil which gradually solidified. Recrystallization of this material from methylene chloride-hexane gave a mp of 82-83°C. An infrared spectrum of the material exhibited carbonyl absorption at 6.05 μ, indicating that the material was probably triferrocenyllead acetate. The material from the first chromatographic band was rechromatographed. Continual elution with petroleum ether afforded three yellow bands. The first band contained 0.525 g (14%) of biferrocenyl. The third band contained 0.211 g (2.2%) of tetraferrocenyllead (infrared spectrum, mp and mixed mp identical to an authentic sample). The second band contained 1.689 g (21%) of n-butyltriferrocenyllead of mp 137-137.5°C after recrystallization from methylene chloride-hexane. Anal. Calcd for $C_{34}H_{36}Fe_3Pb$: C, 49.83; H, 4.43; mol wt, 819.4. Found: C, 49.86, 49.62; H, 4.71, 4.42; mol wt, 807, 779.

G. 2-Deuterochloroferrocene



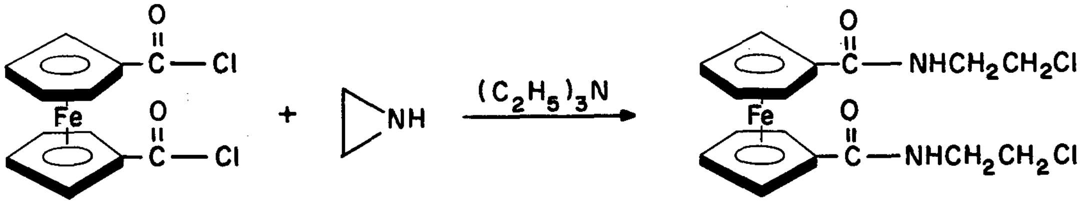
A solution of chloroferrocene (2.21 g, 0.0100 mole) in dry tetrahydrofuran (125 ml) was stirred at 2°C under nitrogen while a solution of n-butyllithium in hexane (15 ml, 0.022 mole) was added over a 5-minute period. The temperature of the reaction mixture rose to 4°C during the course of the addition, and the color changed to a deep orange. Stirring was continued at 2°C for 1.5 hours. A 10-ml aliquot of the reaction mixture was then withdrawn and carbonated. Deuterium oxide (1.0 ml, 0.050 mole) was added with stirring, causing immediate formation of a yellow suspension which was stirred for an additional 45 minutes. The reaction mixture was then evaporated to dryness, and the residue was triturated 3 x 25 ml with benzene. The combined benzene extracts were concentrated to ca 25 ml and chromatographed on 500 g of alumina (Woelm, activity grade 2). Elution with petroleum ether afforded a single orange band. Removal of solvent from the eluate left 1.99 g (97%) of 2-deuterochloroferrocene, mp 57-58°C. Mass spectral analysis indicated an isotopic purity of 98.8%. Carbonation of the aliquot afforded a quantitative yield of 2-chloroferrocenecarboxylic acid. The same reaction was run at -40°C for 30 minutes to give a 25% yield of 2-deuterochloroferrocene and a 26% yield of 2-chloroferrocenecarboxylic acid.

H. 1',6'-Dibromobiferrocenyl



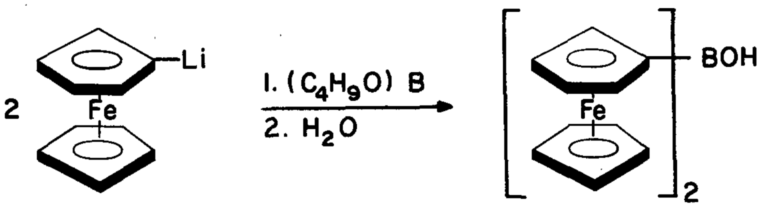
A solution of dibromoferrocene (6.00 g, 0.0175 mole) in dry tetrahydrofuran (100 ml) was stirred at 3°C under nitrogen while a solution of n-butyllithium in hexane (11 ml, 0.018 mole) was added at such a rate as to maintain the temperature below 9°C. The solution was stirred for 20 minutes at 5°C. Cobaltous chloride (2.27 g, 0.0175 mole) was added, resulting in the formation of a black suspension and a temperature rise to 21°C. The suspension was stirred for 1 hour at room temperature and then evaporated to dryness. The residue was triturated with water, then with methanol. The methanol extract was concentrated to dryness and the residue was taken up in benzene and chromatographed on 400 g of alumina (Woelm, activity grade 1.5). Petroleum ether eluted a band containing ferrocene and bromoferrocene. Benzene eluted a second band which, after removal of solvent, afforded 0.618 g (14%) of 1',6'-dibromobiferrocenyl. After two recrystallizations from methylene chloride-hexane, the material melted at 140-142°C. Anal. Calcd for $C_{10}H_{16}Br_2Fe_2$: C, 45.50; H, 3.06; Br, 30.28; Fe, 21.16; mol wt, 527.9. Found: C, 46.73, 46.75; H, 3.19, 3.29; Br, 29.67; Fe, 20.78; mol wt, 542.4.

I. N, N' -Di-β-chloroethyl-1, 1' -ferrocenedicarboxamide



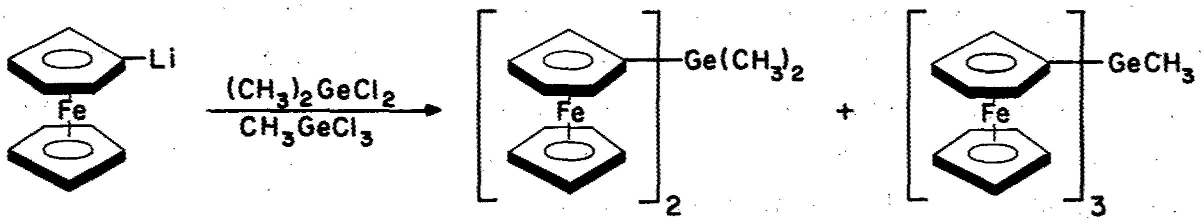
A solution of ethylenimine (0.83 g, 0.040 mole) and triethylamine (4.1g, 0.040 mole) in dry ether (100 ml) was stirred at 0°C while bis-chlorocarbonylferrocene (6.22 g, 0.020 mole) was added. The red suspension was stirred for 1 hour at 0°C, then filtered and washed with dry ether. The red filter cake was then extracted with chloroform to give a deep red chloroform filtrate. The chloroform was removed, and the resultant red oil was taken up in tetrahydrofuran. The red tetrahydrofuran suspension was filtered to remove a voluminous precipitate of triethylamine hydrochloride, and the filtrate was chromatographed on an alumina column (Woelm, activity grade 2). Tetrahydrofuran eluted a single orange band. The eluate was evaporated to dryness to leave an oily red solid which was taken up in methylene chloride and reprecipitated with hexane. Extensive decomposition took place upon attempts to recrystallize the substance. A melting point of 134.5-136.5°C was obtained after 1 recrystallization from benzene. The yield was 1.8 g (25%). Analysis by NMR and infrared spectroscopy, and a positive chlorine analysis support the structure N, N' -di-β-chloroethyl-1-1' -ferrocenedicarboxamide.

J. Diferrocenylborinic Acid



Tributyl borate (1.21 g, 0.00518 mole) was added to a stirred solution of ferrocenyllithium [from bromoferrocene (5.6 g, 0.021 mole)] in dry tetrahydrofuran (140 ml) at -75 °C. The reaction mixture was allowed to warm gradually to room temperature, and was stirred for 12 hours at room temperature. The volume was then reduced to ca 100 ml, and the syrupy brown concentrate was taken up in methylene chloride and extracted with water. The methylene chloride layer was dried by filtration through a bed of anhydrous sodium sulfate, then concentrated to 50 ml, and diluted to 175 ml with hexane. The hexane-methylene chloride solution was boiled down to 100 ml, cooled, and filtered. The filtrate was evaporated to dryness and the residue (3.46 g) was taken up in 25 ml of benzene and chromatographed on 800 g of alumina (Woelm, activity grade 2). Elution with petroleum ether afforded a band containing 1.47 g of a mixture of ferrocene, bromoferrocene, and n-butylferrocene (5:3:3 by vapor phase chromatographic analysis). Elution with petroleum ether-benzene mixtures afforded traces of biferrocenyl and triferrocenylborane. Elution with methylene chloride afforded 0.661 g (32%) of diferrocenylborinic acid, mp 178-181°C after recrystallization from benzene-hexane. Anal Calcd for $C_{20}H_{19}BFe_2O$: C, 60.37; H, 4.81; B, 2.72; Fe, 28.07; mol wt, 398. Found: C, 61.29, 61.51; H, 4.87, 4.88; B, 3.06, 3.06; Fe, 24.70, 24.56, mol wt, 423.1, 419.3.

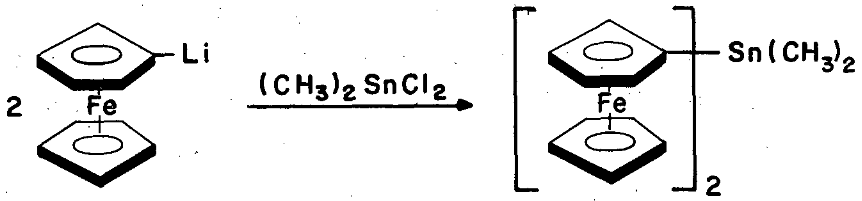
K. Diferrocenyldimethylgermane and Methyltriferrocenylgermane



A mixture of dichlorodimethylgermane (2.93 g, 0.017 mole) and methyltrichlorogermane (0.610 g, 0.0031 mole) was added to a stirred solution of ferrocenyllithium [(from chloromercuriferrocene (25.3 g, 0.060 mole)] in dry tetrahydrofuran (420 ml) at 0°C and the solvent was evaporated. Stirring at 0°C was continued for 45 minutes, and then the reaction mixture was poured onto a large excess of Dry Ice. The residue was triturated successively with water, petroleum ether, and methanol. The petroleum ether extracts were combined and concentrated to a thick brown oil which was heated in vacuo for 2 days to remove dibutylmercury and ferrocene. The pot residue was washed with petroleum ether, taken up in methanol, combined with the previous methanol extracts, and evaporated to dryness. The residue was taken up in benzene and chromatographed on an alumina column (Woelm, activity grade 2). Hexane eluted a small amount of ferrocene followed by 2 yellow bands. Removal of solvent from the first band afforded 5.549 g (70%) of diferrocenyldimethylgermane of mp 109.5-110.5°C after recrystallization from benzene-hexane.

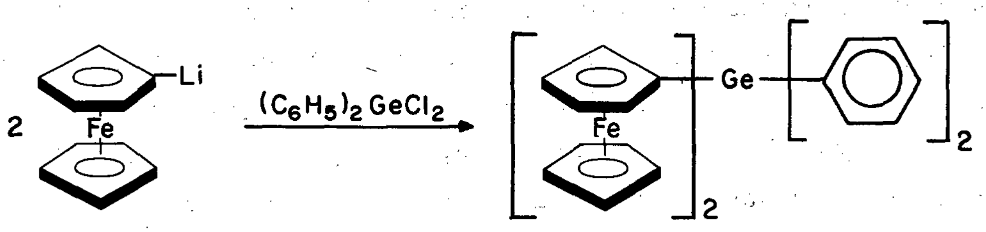
Anal Calcd for $C_{22}H_{24}Fe_2Ge$: C, 55.89; H, 5.12; Fe, 23.63; Ge, 15.36; mol wt 472.7. Found: C, 56.47, 56.10; H, 5.31, 5.11; Fe, 23.77, 24.05; Ge, 13.57; mol wt, 479.8, 470.1. Removal of solvent from the second band afforded 0.425 g (21%) of methyltriferrocenylgermane of mp 197.5-198.5°C after recrystallization from benzene-hexane. Anal. Calcd for $C_{31}H_{30}Fe_3Ge$: C, 57.93; H, 4.71; Fe, 26.07; Ge, 11.30; mol wt, 642.7. Found: C, 57.50, 57.77; H, 4.63, 4.50; Fe, 26.98, 27.26; Ge, 10.41, 10.70; mol wt, 626.8, 605.8.

L. Diferrocenyldimethyltin



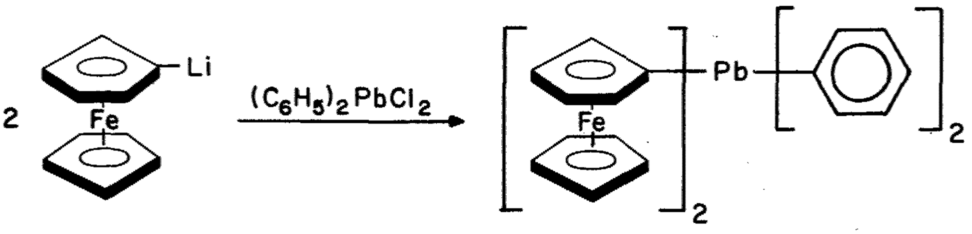
Dichlorodimethyltin (1.76 g, 0.00800 mole) was added to a stirred solution of ferrocenyllithium [from bromoferrocene (6.00 g, 0.0226 mole)] in dry tetrahydrofuran at 3°C. The reaction mixture was stirred at 0°C for 15 minutes, then evaporated to dryness. The residue was washed with water and extracted with methylene chloride, and the methylene chloride extracts were filtered. The filtrate was evaporated to dryness, and the residue was taken up in benzene and chromatographed on 800 g of alumina (Woelm, activity grade 1.5). Hexane eluted a yellow band containing mainly ferrocene. Benzene-hexane eluted a yellow band which, after removal of solvent, afforded 2.272 g (73% based upon a 53% yield of ferrocenyllithium determined by carbonation) of diferrocenyldimethyltin of mp 132.5-133°C after recrystallization from methylene chloride-hexane. Anal Calcd for $C_{22}H_{24}Fe_2Sn$: C, 50.93; H, 4.66; Fe, 21.53; Sn, 22.88; mol wt, 518.8. Found: C, 51.24, 51.54; H, 4.81, 4.91; Fe, 20.51, 20.63; Sn, 22.95, 22.65; mol wt. 522.9, 514.3.

M. Diferrocenyldiphenylgermane



Dichlorodiphenylgermane (5.95 g, 0.0200 mole) was added to a stirred solution of ferrocenyllithium [from chloromercuriferrocene (25.3 g, 0.060 mole)] in dry tetrahydrofuran (420 ml) at 0°C. The reaction mixture was stirred for 20 minutes at 0°C, then for 25 minutes more while warming to 17°C. At the end of this period, the reaction mixture was poured onto Dry Ice, and the solvent was allowed to evaporate to ca 200 ml. Water (500 ml) was added, forming a yellow suspension, which was filtered and washed with water. This was followed by a thorough washing with petroleum ether. The filter cake was then triturated with methylene chloride, and the methylene chloride extracts were filtered. The filtrate was evaporated to dryness, leaving 7.8 g of yellow solid. An additional 3.6 g of material precipitated from the petroleum ether washings upon standing overnight, and was collected. Recrystallization of the combined crude material (11.4 g) from benzene-hexane afforded 4.85 g of diferrocenyldiphenylgermane of mp 190-190.5°C. The mother liquor afforded an additional 2.29 g of mp 188-189.5°C. The total yield was thus 7.14 g (60%). Further recrystallization of the material melting from 190-190.5°C did not change the melting point. Anal. Calcd for $C_{32}H_{28}Fe_2Ge$: C, 64.39; H, 4.73; Fe, 18.72; Ge, 12.16; mol wt, 596.8. Found: C, 64.55, 64.31; H, 4.73, 4.69; Fe, 18.78, 18.28; Ge, 12.5, 12.7; mol wt, 576.8, 585.2.

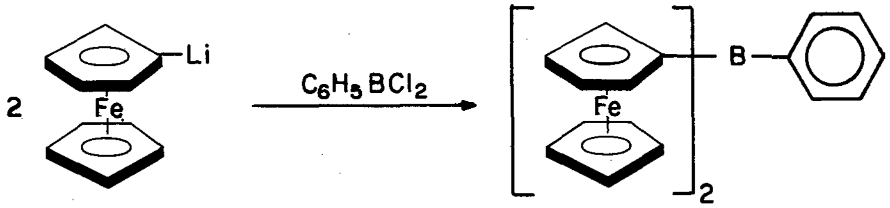
N. Diferrocenyldiphenyllead



Dichlorodiphenyllead (5.84 g, 0.00800 mole) was added to a stirred solution of ferrocenyllithium [from bromoferrocene (6.00 g, 0.0226 mole)] in dry tetrahydrofuran (250 ml) at 4°C. The reaction mixture was stirred at room temperature for 2 hours, poured onto Dry Ice, and allowed to evaporate to dryness. The residue was dried for 12 hours in a vacuum oven at 60°C, leaving 4.134 of yellow solid which was chromatographed on 800 g of alumina (Woelm, activity grade 2). Hexane eluted first a trace of ferrocene, then a band which, after removal of solvent, afforded 3.95 g (75%, based upon a 60% yield of ferrocenyllithium determined by carbonation) of diferrocenyldiphenyllead of mp 176-180°C: Recrystallization from methylene chloride-hexane raised the mp to 183-183.5°C. Anal. Calcd for

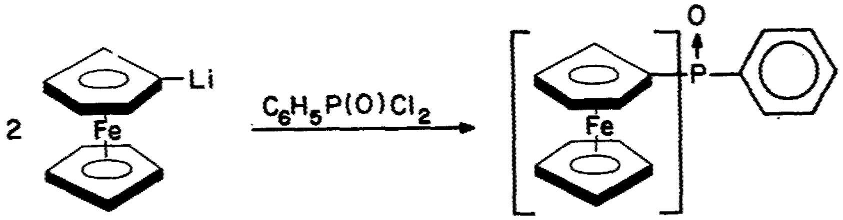
$C_{32}H_{28}FePb$: C, 52.54; H, 3.86; Fe, 15.27; Pb, 28.33; mol wt, 731.5. Found: C, 52.34, 52.49; H, 3.90, 3.92; Fe, 13.84, 13.62; Pb, 29.31, 29.65; mol wt, 746.3, 743.4.

O. Diferrocenylphenylborane



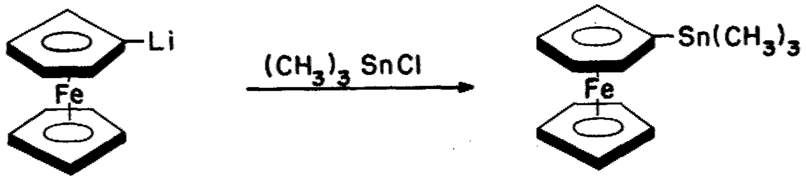
Phenylboron dichloride (1.56 g, 0.0098 mole) was added to a stirred solution of ferrocenyllithium [from bromoferrocene (12.4 g, 0.0468 mole)] in dry tetrahydrofuran (300 ml) at 2°C. The reaction mixture was stirred at room temperature for 13 hours, then poured into 1000 ml of water. The aqueous emulsion was extracted with 250 ml of ether. The ether layer was separated and washed with 1000 ml of water, forming an emulsion. After standing for 24 hours, the ether layer had separated and was removed, dried by filtration through a bed of anhydrous sodium sulfate, and evaporated to dryness. The residue was taken up in methylene chloride and chromatographed on 1860 g of alumina (Woelm, activity grade 2). Small amounts of ferrocene and biferrocenyl (0.114 g) were eluted with petroleum ether and petroleum ether-benzene (1:1). Benzene-methylene chloride (3:1) eluted two overlapping red bands. The first red band showed extensive decomposition on the column. Evaporation of solvent from the eluate afforded 0.170 g of a dark red solid whose infrared spectrum, melting point, and thin layer chromatographic behavior identified it as triferrocenylborane. The second red band eluted from the chromatographic cloumn afforded, after removal of solvent, 0.786 g (17%) of diferrocenylphenylborane of mp 225-227°C after 2 recrystallizations from methylene chloride-hexane. Anal. Calcd for $C_{26}H_{23}BFe_2$: C, 68.18; H, 5.06; mol wt, 458. Found: C, 69.26, 69.08, 68.37; H, 5.12, 5.16, 5.86; mol wt, 458 (mass spectrum). Diferrocenylphenylborane, like triferrocenylborane, is quite stable toward air or moisture.

P. Diferrocenylphenylphosphine Oxide



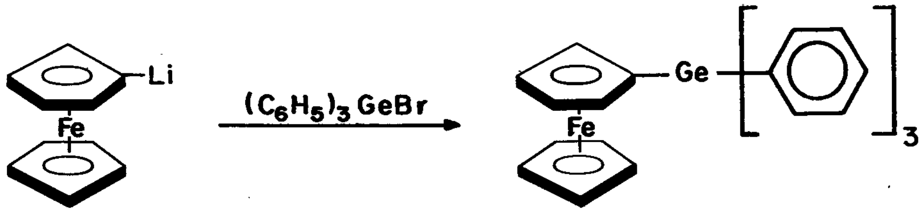
Dichlorophenylphosphine oxide (1.48 g, 0.0076 mole) was added to a stirred solution of ferrocenyllithium [from bromoferrocene (4.00 g, 0.0151 mole)] in dry tetrahydrofuran (100 ml) at 0°C. The reaction mixture was stirred for 1 hour at 0°C, then filtered, and the yellow filter cake was washed with tetrahydrofuran. The filter cake (wt: 1.03 g) was then taken up in methylene chloride and chromatographed on 400 g of alumina (Woelm, activity grade 2). Elution with tetrahydrofuran afforded 0.460 g (12%) of diferrocenylphenylphosphine oxide of mp 253-255°C (reported: 239-241 C; 249-251°C in References 14 and 15). The infrared spectrum of the material was identical to the spectrum reported for diferrocenylphenylphosphine oxide (Reference 15).

Q. Ferrocenyltrimethyltin



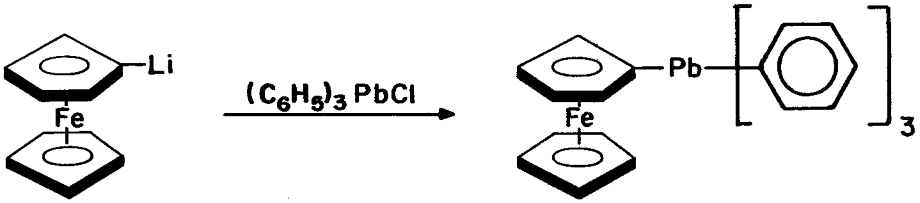
Chlorotrimethyltin (1.90 g, 0.00955 mole) was added to a stirred solution of ferrocenyllithium [from bromoferrocene (3.00 g, 0.0113 mole)] in dry tetrahydrofuran (92 ml) at 1°C. The reaction mixture was stirred for 105 minutes at 0°C, then poured into 400 ml of 10% potassium carbonate solution. The aqueous emulsion was extracted with petroleum ether (2 x 300 ml), and the combined organic extracts were washed with water and dried over anhydrous sodium sulfate. The petroleum ether was distilled from the extracts to a volume of ca 60 ml, and the resultant solution was chromatographed on 800 g of alumina (Woelm, activity grade 2). Petroleum ether eluted a single yellow band. Removal of solvent from the eluate left 1.897 g of an orange oil. Vapor phase chromatographic analysis indicated the presence of ferrocene, n-butylferrocene, and ferrocenyltrimethyltin (ca 81%, corresponding to a 75% yield on the basis of a 66% yield of ferrocenecarboxylic acid). Preparative vapor phase chromatography (F&M model 500; 2 meter x 1/4 in. O D stainless steel column packed with 15% SE-52 on Anakrom ABS (60-70 mesh)) afforded a small amount of purified ferrocenyltrimethyltin. Anal. Calcd for $C_{13}H_{18}FeSn$: C, 44.76; H, 5.20; Fe, 16.01; Sn, 34.03; mol wt, 348.8. Found: C, 45.44, 45.34; H, 5.72, 5.58; Fe, 11.28, 11.23; Sn, 30.35, 30.30; mol wt 318, 303.

R. Ferrocenyltriphenylgermane



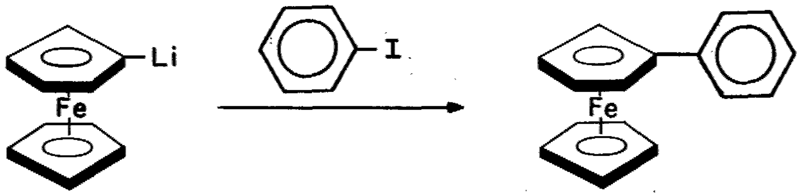
Bromotriphenylgermane (4.50 g, 0.0117 mole) was added to a stirred solution of ferrocenyllithium [from chloromercuriferrocene (4.95 g, 0.0117 mole)] in dry tetrahydrofuran (100 ml) at 0°C. The reaction mixture was stirred for 18 hours at room temperature. The solvent was removed, and the yellow residue was triturated successively with petroleum ether and chloroform. The chloroform extract was filtered and evaporated to dryness to leave 4.13 g of orange solid. Recrystallization from methylene chloride-hexane afforded 3.21 g (78% yield, based upon a 79% yield of ferrocenecarboxylic acid) of ferrocenyltriphenylgermane of mp 150-154°C. Further recrystallization raised the mp to 154-155°C (reported: 155-156°C in Reference 13). Anal. Calcd for $C_{28}H_{24}FeGe$: C, 68.78; H, 4.95; Fe, 11.42; Ge, 14.85; mol wt, 488.9. Found: C, 68.90, 68.90; H, 4.61, 4.84; Fe, 10.93, 11.11; Ge, 14.62, 14.50; mol wt, 480.3, 498.7.

S. Ferrocenyltriphenyllead



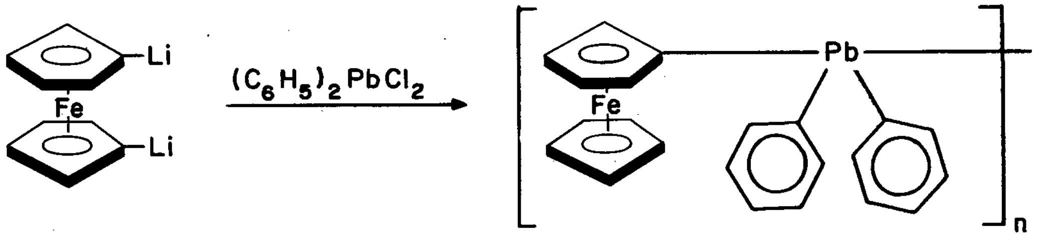
Chlorotriphenyllead (2.47 g, 0.0052 mole) was added to a stirred solution of ferrocenyllithium [from bromoferrocene (1.68 g, 0.00635 mole)] in dry tetrahydrofuran (100 ml) at 0° C. The reaction mixture was stirred 2 hours at room temperature, then concentrated to dryness. The residue was extracted with benzene-methylene chloride (1:1), and the extracts were filtered and chromatographed on 400 g of alumina (Woelm, activity grade 1). Extensive decomposition took place on the column, and acetonitrile was necessary to elute the ferrocenyltriphenyllead band. Removal of solvent from the eluate afforded 0.581 g (29%, based upon a 62% yield of ferrocenecarboxylic acid) of ferrocenyltriphenyllead of mp 160.5-162°C after recrystallization from methylene chloride-hexane. Anal. Calcd for $C_{28}H_{24}FePb$: C, 53.93; H, 3.88; Fe, 8.96; Pb, 33.23; mol wt, 623.5. Found: C, 53.88, 53.99; H, 3.84, 3.95; Fe, 8.53, 8.30; Pb, 34.23, 34.30; mol wt, 628,600.

T. Phenylferrocene



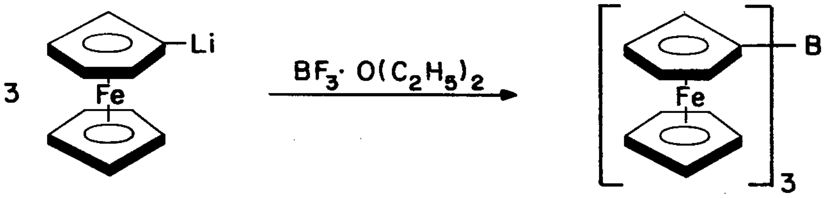
Iodobenzene (8.0 ml, 0.072 mole) was added to a stirred solution of ferrocenyllithium [from bromoferrocene (6.00 g, 0.0226 mole)] in dry tetrahydrofuran (125 ml) at 3°C. The reaction mixture was stirred at room temperature for 18 hours, then evaporated to a thick oil. The oil was extracted with water and ether. The ether layer was evaporated to a thick brown oil which was taken up in hexane. The hexane solution was filtered and the filtrate was chromatographed on 900 g of alumina (Woelm, activity grade 2). Petroleum ether elution afforded 2 yellow bands, containing respectively, ferrocene and phenylferrocene. A third band, containing 0.214 g of biferrocenyl, was eluted by benzene-petroleum ether (1:1). The yield of phenylferrocene was 0.669 g (19%, based upon a 65% yield of ferrocenecarboxylic acid) of mp 110-112°C after recrystallization from methylene chloride-hexane (reported: 110-111°C in Reference 24).

U. Poly [1, 1'-(diphenylplumbyl)-ferrocenylene]



A solution of 1, 1' -dibromoferrocene (6.88 g, 0.0200 mole) in dry tetrahydrofuran 250 ml) was stirred at 5°C under a nitrogen atmosphere while a solution of n-butyllithium in hexane (34 ml, 0.040 g) was added. The reaction mixture was stirred for 30 minutes at 4°C. A 10-ml aliquot was withdrawn and carbonated, affording a 98% yield of 1, 1' -ferrocenedicarboxylic acid. To the remainder of the reaction mixture was added dichlorodiphenyllead (8.34 g, 0.0193 mole), and stirring was continued at room temperature for 75 minutes. The reaction mixture was then evaporated to dryness, and the residue was extracted with hot benzene. The combined benzene extracts were filtered, concentrated to 120 ml, and added to 500 ml of petroleum ether with stirring. The resultant precipitate was taken up in methylene chloride and reprecipitated with petroleum ether. The precipitate was collected, continuously extracted for 24 hours with pentane, and dried in a vacuum oven at 60°C for 2 hours. The weight of the material after drying was 0.882 g. Upon heating in a sealed capillary under nitrogen, the material gradually turned viscous from ca 90°. Anal. Calcd for $(C_{22}H_{18}FePb)_n$: C, 48.44; H, 3.33; Fe, 10.24; Pb, 37.99; mol wt n x 545.4. Found: C, 49.47; 49.50; H, 3.05, 3.23; Fe, 11.08, 11.35; Pb, 17.29, 17.54; mol wt, 2250.

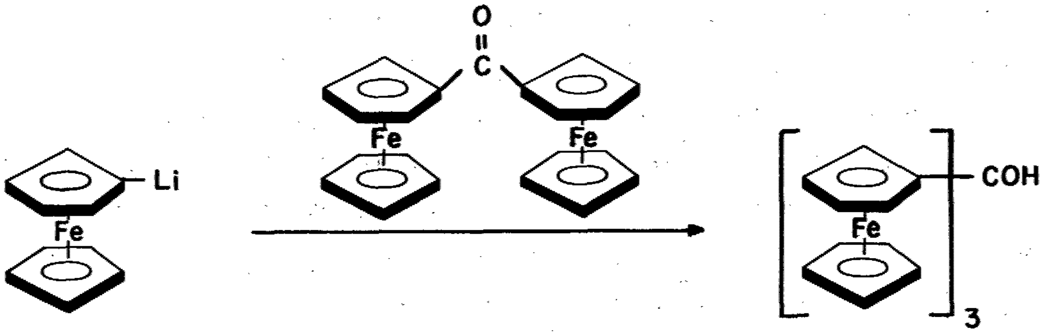
V. Triferrocenylborane



Boron trifluoride etherate (0.71 g, 0.0050 mole) was added to a stirred solution of ferrocenyllithium [from bromoferrocene (4.00 g, 0.0151 mole] in dry tetrahydrofuran (100 ml) at 0° C. The reaction mixture was stirred at 0°C for 75 minutes, then evaporated to dryness. The residue was washed thoroughly with water, then extracted with ether. The ether extract was filtered, concentrated to ca 20 ml, and diluted to 100 ml with methanol. The red precipitate which formed was collected and air dried to give 0.294 g (10%) of triferrocenylborane of mp 162-163°C after reprecipitation from methanol. Anal. Calcd for $C_{30}H_{27}BFe_3$: C, 63.67; H, 4.81; B, 1.91; Fe, 29.61; mol wt, 565.9. Found: C, 64.23, 64.20; H, 5.03, 5.04; B, 2.05, 2.08; Fe, 29.14, 29.32; mol wt, 565.8.

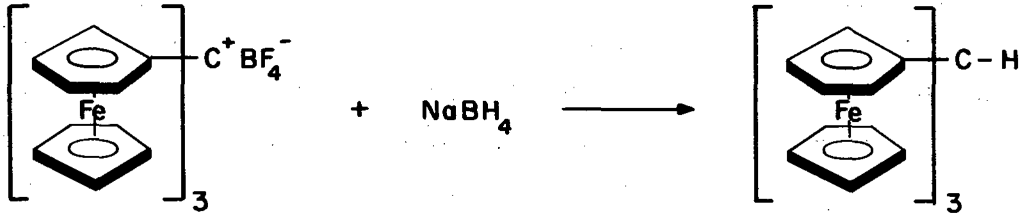
The ether insoluble residue from the reaction mixture was extracted with methylene chloride, and the dark methylene chloride extracts were added to methanol to give a black precipitate. Reprecipitation of the black precipitate from tetrahydrofuran by methanol gave a product of mp 151.5-152°C. Anal. Found: C, 64.31, 64.46; H, 5.10, 5.01; B, 1.62, 1.71; Fe, 29.25, 28.95.

W. Triferrocenylcarbinol



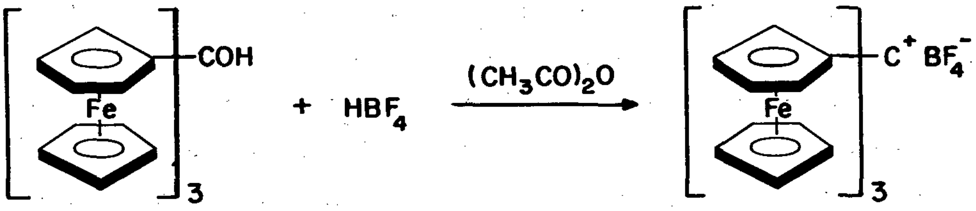
Diferrocenylketone (15.0 g, 0.0377 mole) was added to a stirred solution of ferrocenyllithium [from bromoferrocene (12.00 g, 0.0452 mole)] in dry tetrahydrofuran (300 ml) at 5°C. The reaction mixture was stirred at room temperature for 3.5 hours, then 30 ml of water was added and the reaction mixture was evaporated to dryness. The residue was washed with water, then triturated with methylene chloride. The methylene chloride extracts were filtered and chromatographed on an alumina column (Woelm, activity grade 2). Benzene eluted a mixture of ferrocene and biferrocenyl. Benzene-methylene chloride (4:1) eluted 12.16 g (94%, based upon a 51% yield of ferrocenecarboxylic acid) of triferrocenylcarbinol of mp 194.5 to 196.5°C after recrystallization from methylene chloride-acetone (reported: 160-162°C, 204-205°C, 200°C in References 25, 26, and 27).

X. Triferrocenylmethane



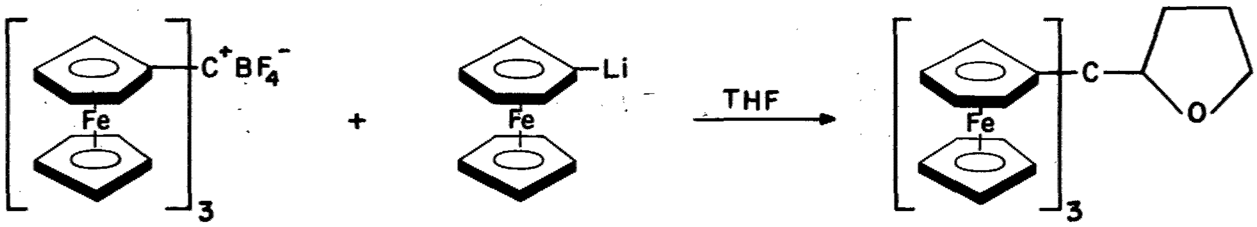
Triferrocenylmethyl fluoborate (1.28 g, 0.00196 mole) was stirred in dry tetrahydrofuran (25 ml) at 0°C. To the green suspension was added 1 g of sodium borohydride. The resultant brown-yellow solution was stirred for 5 minutes. Water (100 ml) was added and, after 1 minute of stirring, the reaction mixture was extracted with ether (2 x 50 ml) and the combined ether extracts were washed with water (4 x 50 ml). The ether layer was dried by filtration through a bed of anhydrous sodium sulfate, concentrated to ca 30 ml, and chromatographed on 300 g of alumina (Woelm, activity grade 2). Petroleum ether eluted a single yellow band which, after removal of solvent, afforded 0.408 g (37%) of triferrocenylmethane of mp 295.5-296.5°C (reported: 312-314°C; dec.>200°C, 290-293°C in References 21, 22, and 23).

Y. Triferrocenylmethyl Fluoborate



To a stirred suspension of triferrocenylcarbinol (0.870 g, 0.00149 mole) in acetic anhydride (30 ml) at 0°C, was added 8 drops of 40% fluoboric acid. The dark green reaction mixture was stirred at 0°C for 10 minutes, then poured, with stirring, into dry ether (600 ml). The ethereal suspension was stirred for 45 minutes, then filtered. The dark green filter cake was washed with ether and sucked dry. The product was dissolved in acetonitrile (75 ml) and poured, with stirring, into dry ether (650 ml). The suspension was stirred for 1 hour, then filtered. The filter cake was washed with ether and sucked dry to give 0.953 g (98%) of dark green triferrocenylmethyl fluoborate. No melting point was observed below 350°C, although ferrocene sublimed from the dark powder above 200°C in a sealed capillary. Triferrocenylmethyl fluoborate is very soluble in acetonitrile, acetic anhydride, and dimethyl sulfoxide; soluble in methylene chloride and acetone; slightly soluble in tetrahydrofuran; and insoluble in petroleum ether, ether, and benzene. It is very hygroscopic, but insensitive to oxygen and can be stored in a desiccator. Heating a solution of triferrocenylmethyl fluoborate above room temperature resulted in decomposition with an accompanying color change from green to dark brown. An NMR spectrum in deuterated dimethylsulfoxide showed no broadening of the absorption peaks, indicating the absence of any ferricinium ion species.

Z. 2-(Triferrocenylmethyl)tetrahydrofuran

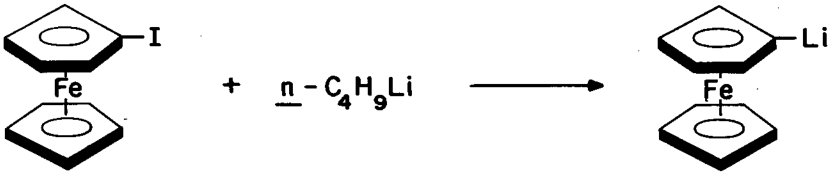


Triferrocenylmethyl fluoborate (1.56 g, 0.00239 mole) was added to a stirred solution of ferrocenyllithium (0.0045 mole determined by carbonation, from 0.0226 mole of bromoferrocene and 0.016 mole of n-butyllithium) in dry tetrahydrofuran (200 ml) at 0°C. The deep violet reaction mixture was stirred for 2 hours at 0°C, then for 18 hours at room temperature, during which time the color gradually turned to brownish-red. The reaction mixture was then concentrated to ca 100 ml and chromatographed on 1200 g of alumina (Woelm, activity grade 2). The products obtained from both petroleum ether elution and benzene-petroleum ether (1:1) elution contained the same 3 components. The products were combined, taken up in ca 100 ml of benzene, and rechromatographed on 1200 g of alumina (Woelm, activity grade 2).

Petroleum ether eluted a band containing a mixture of ferrocene and bromoferrocene. Petroleum ether-benzene (4:1) eluted a band containing 0.191 g of biferrocenyl. Petroleum ether-benzene (1:1) eluted first a violet band containing a trace of diferrocenylfulvene (Reference 28), followed by a yellow band containing 1.087 g (71%) of 2-(triferrocenylmethyl)tetrahydrofuran of mp 214-215°C after recrystallization from methylene chloride-hexane. Anal. Calcd for $C_{35}H_{34}Fe_3O$: C, 65.87; H, 5.37; Fe, 26.25; O, 2.51;

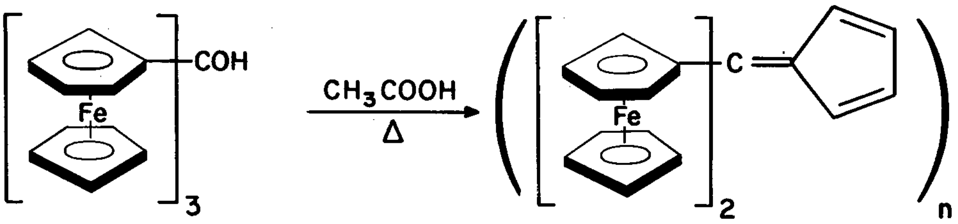
mol wt, 638.2. Found: C, 65.91, 65.99; H, 5.53, 5.46; Fe, 25.76, 25.80; mol wt, 647.3 (vapor phase osmometry), 638.2 (mass spectrum).

AA. Reaction of Iodoferrocene with n-Butyllithium



Addition under a nitrogen atmosphere of a solution of n-butyllithium in hexane to a stirred solution of an equimolar amount of iodoferrocene in dry tetrahydrofuran was carried out under the following conditions: (1) At -40°C, followed by 15 minutes of stirring at -40°C and subsequent carbonation; (2) at -76°C, followed by 30 minutes of stirring while warming to -10°C and subsequent carbonation; (3) at -78°C, followed by 30 minutes of stirring at -78°C and subsequent reaction with excess chlorotriphenyllead. The following results were obtained: from (1), a 52% yield of ferrocenecarboxylic acid; from (2), a 12% yield of ferrocenecarboxylic acid and a 27% yield of butylferrocene; from (3), a 35% yield of ferrocenyltriphenyllead. Although trace amounts of biferrocenyl were indicated by thin layer chromatographic analysis of the reaction products, no isolable amounts of biferrocenyl were obtained under any of the three reaction conditions employed.

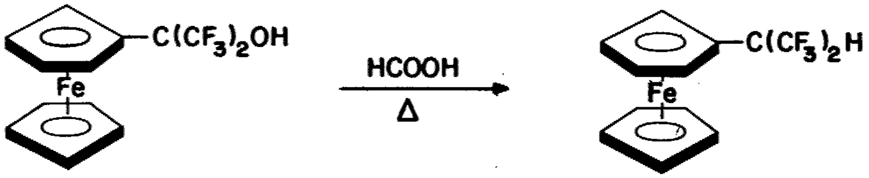
BB. Polymerization of Triferrocenylcarbinol



Triferrocenylcarbinol (0.521 g, 0.000893 mole) was dissolved by stirring in glacial acetic acid (75 ml) to give a yellow solution which turned deep green in color within a few minutes. The reaction mixture was heated to reflux temperature, during which time the color gradually changed from green to brown, and was refluxed with stirring for 1 hour, then poured into water (500 ml). The brown suspension which formed was collected, washed with water, and taken up in tetrahydrofuran (20 ml). The dark brown tetrahydrofuran solution was filtered, and the filtrate was diluted to 500 ml with methanol. The filter cake was washed with methanol and dried under vacuum for 2 hours at 60°C. The product weighed 0.268 g. An NMR spectrum showed a single very broad absorption centered around 240 cps (from tetramethylsilane), indicating the presence of paramagnetic centers in the molecule. The material was soluble in tetrahydrofuran, dimethylformamide, and chloroform; slightly soluble in benzene and acetic acid; and insoluble in petroleum ether and methanol. Heating the material in a sealed capillary under nitrogen effected gradual sublimation of ferrocene above 200°C, but no melting took place. After being heated to 300°C under nitrogen, the brown residue was no longer soluble in tetrahydrofuran, dimethylformamide, or chloroform. Anal. Calcd for $(C_{26}H_{22}Fe_2)_n$: C, 69.99; H, 4.97; Fe, 25.04. Found: C, 69.85, 69.55; H, 4.87, 4.97; Fe, 21.60, 21.64; mol wt, 3215.3.

A compound with an identical infrared spectrum and melting point behavior was obtained by the used of formic acid in place of glacial acetic acid for the reaction.

CC. Attempted Preparation of Ferrocenyl-(bis-trifluoromethyl)-methane



Ferrocenyl-(bis-trifluoromethyl)-methanol (1.03 g, 0.00293 mole) was refluxed in formic acid (75 ml) for 20 minutes. The reaction mixture turned dark green in color, and was then stirred at 40°C for 3 days. At the end of this period, the reaction mixture was poured into 600 ml of water, and sufficient stannous chloride was added to effect a change in color to light yellow with concurrent separation of a yellow upper organic layer. The organic layer was removed, and the water layer extracted (4 x 100 ml) with ether. The combined organic layers were washed with water, 10% sodium bicarbonate solution, and water again. Removal of ether left 0.991 g of recovered ferrocenyl-(bis-trifluoromethyl)-methane.

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ILLUSTRATIONS

PART ONE

Nuclear Magnetic Resonance Spectra

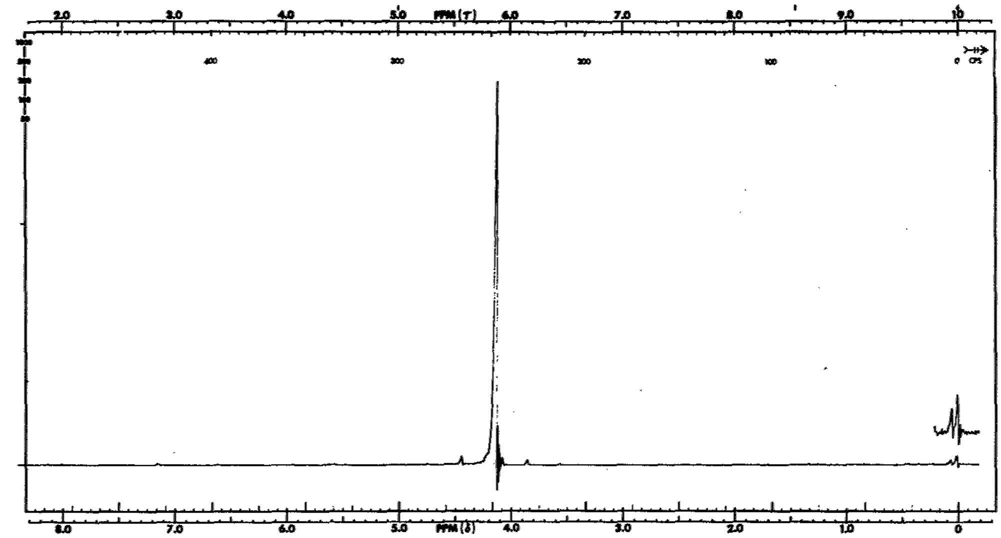

Figure 1. NMR Spectrum of Ferrocene

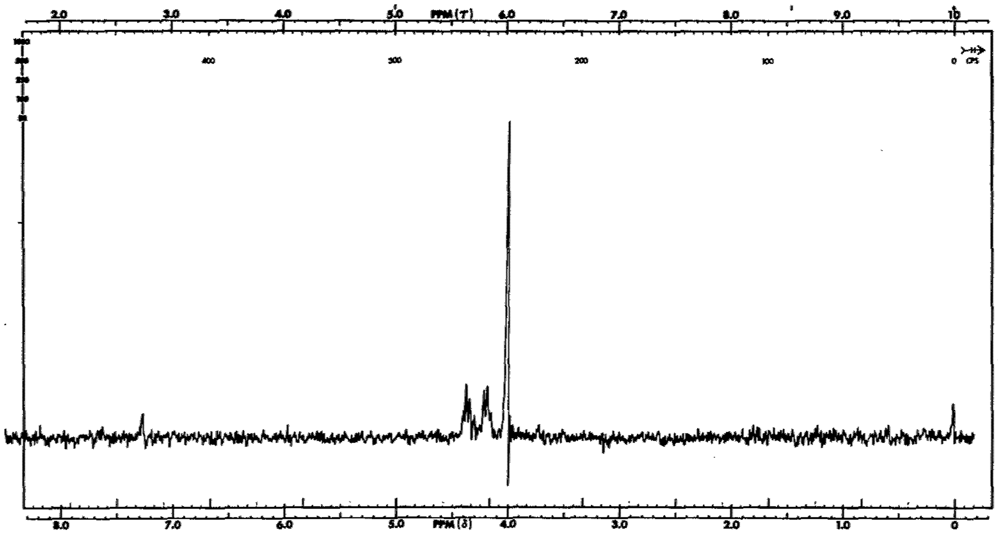

Figure 2. NMR Spectrum of Biferrocenyl

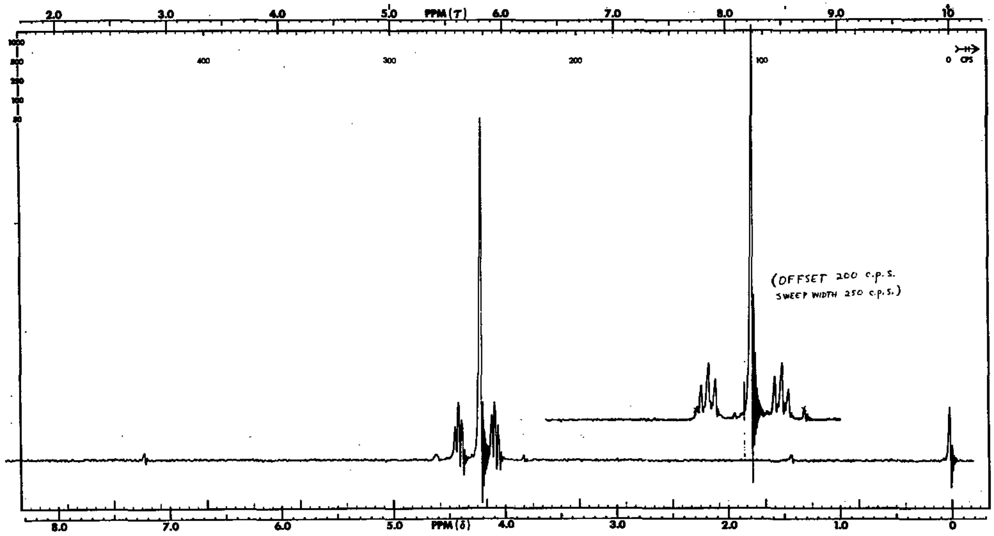

Figure 3. NMR Spectrum of Bromoferrocene

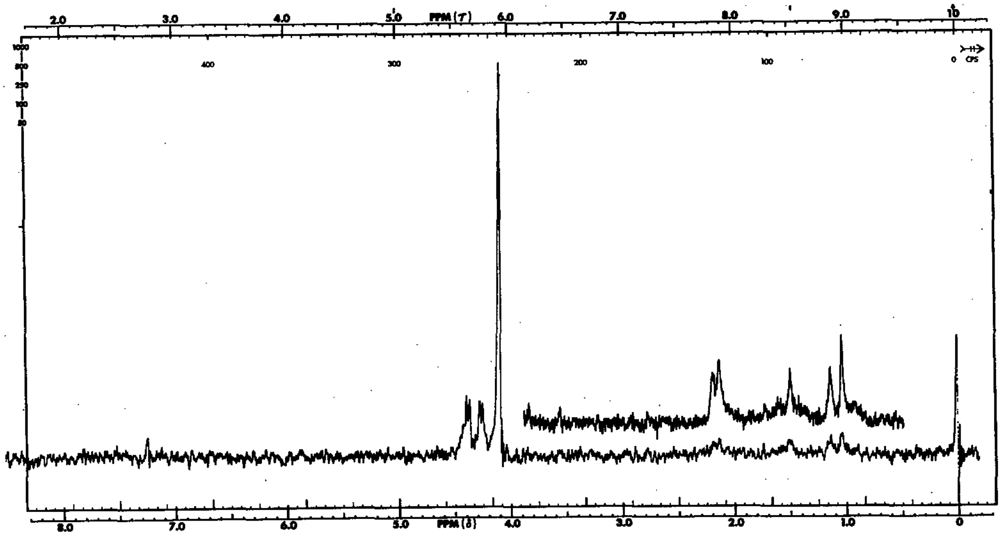

Figure 4. NMR Spectrum of n-Butyltriferrocenyllead

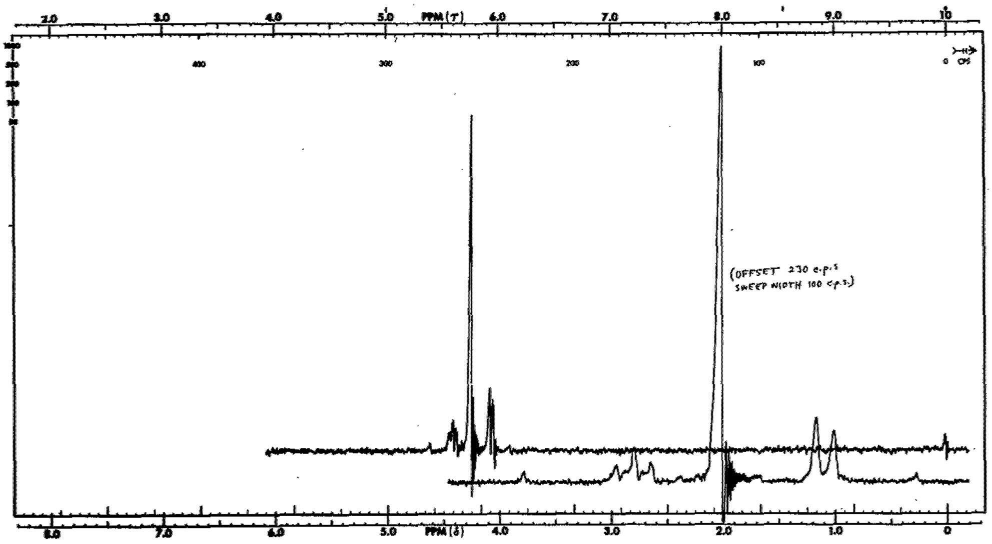

Figure 5. NMR Spectrum of 2-Deuterochloroferrocene

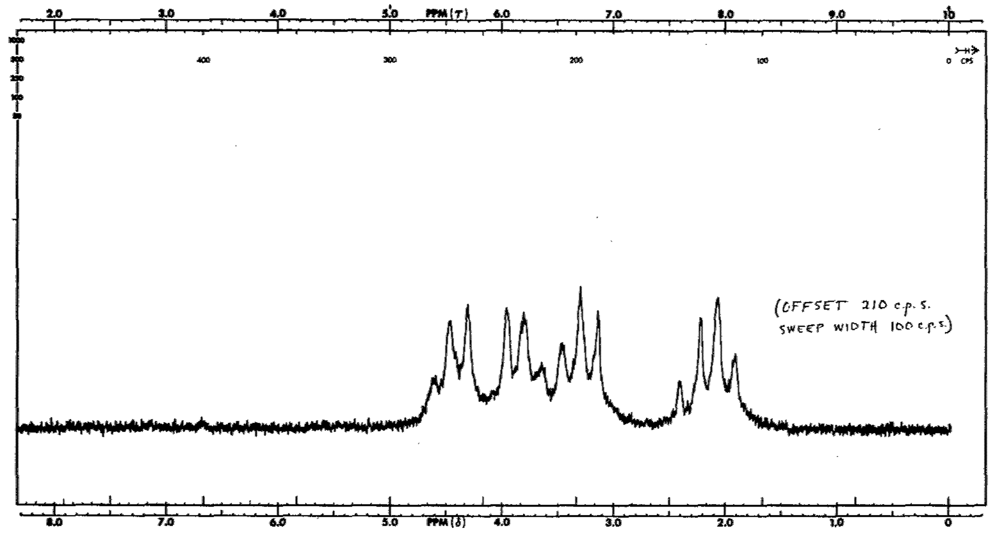

Figure 6. NMR Spectrum of 1′, 6′-Dibromobiferrocenyl

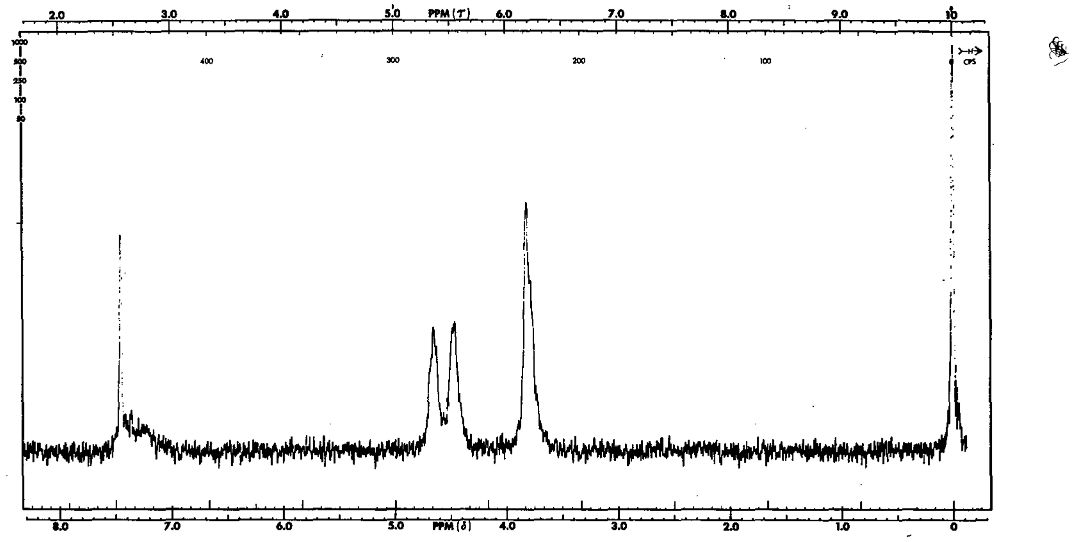

Figure 7. NMR Spectrum of N,N' -Di-β-chloroethyl-1,1' -ferrocenedicarboxamide

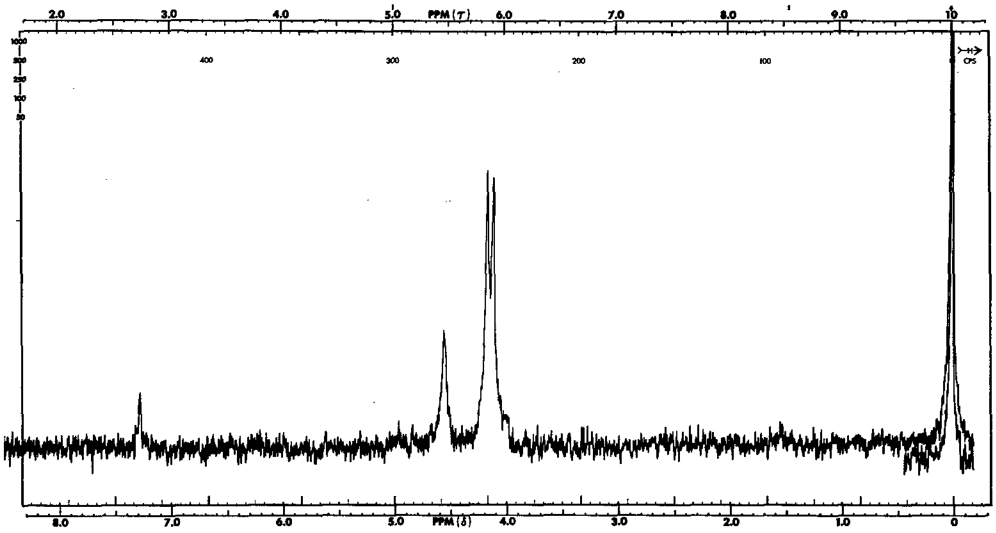

Figure 8. NMR Spectrum of Diferrocenylborinic Acid

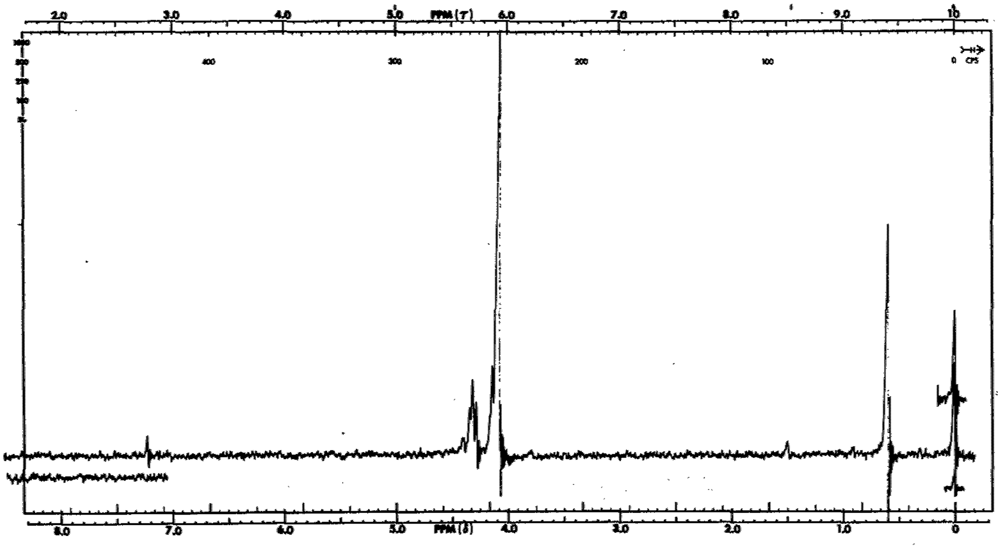

Figure 9. NMR Spectrum of Diferrocenyldimethylgermane

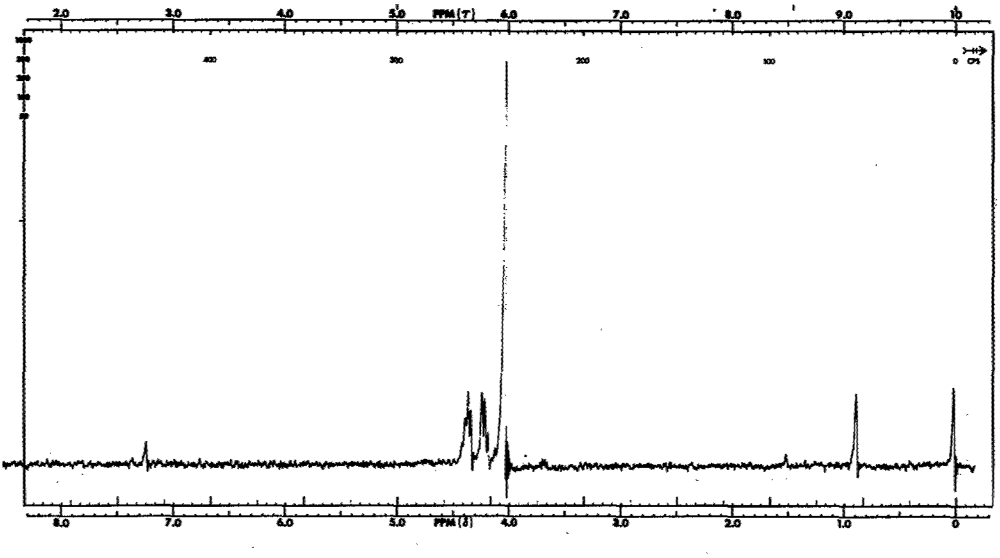

Figure 10. NMR Spectrum of Methyltriferrocenylgermane

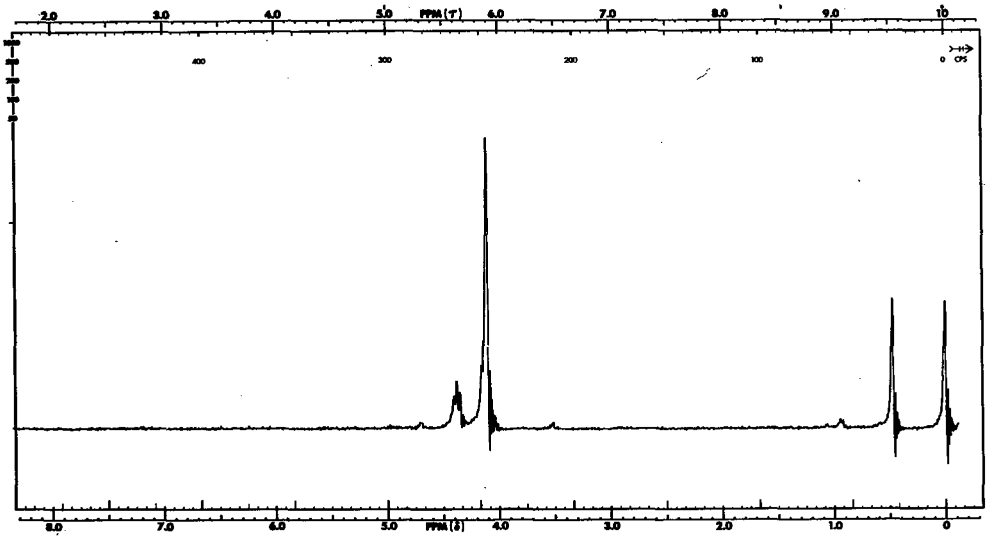

Figure 11. NMR Spectrum of Diferrocenyldimethyltin

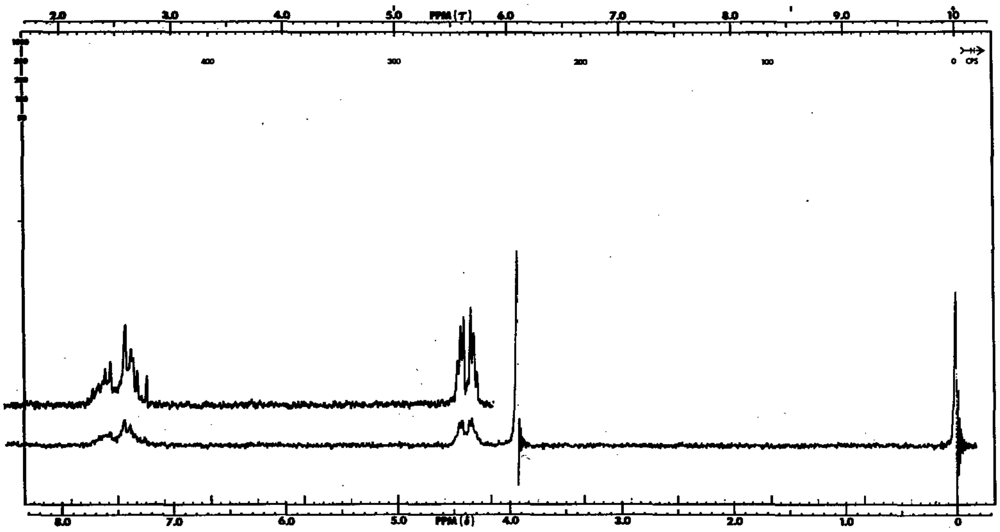

Figure 12. NMR Spectrum of Diferrocenyldiphenylgermane

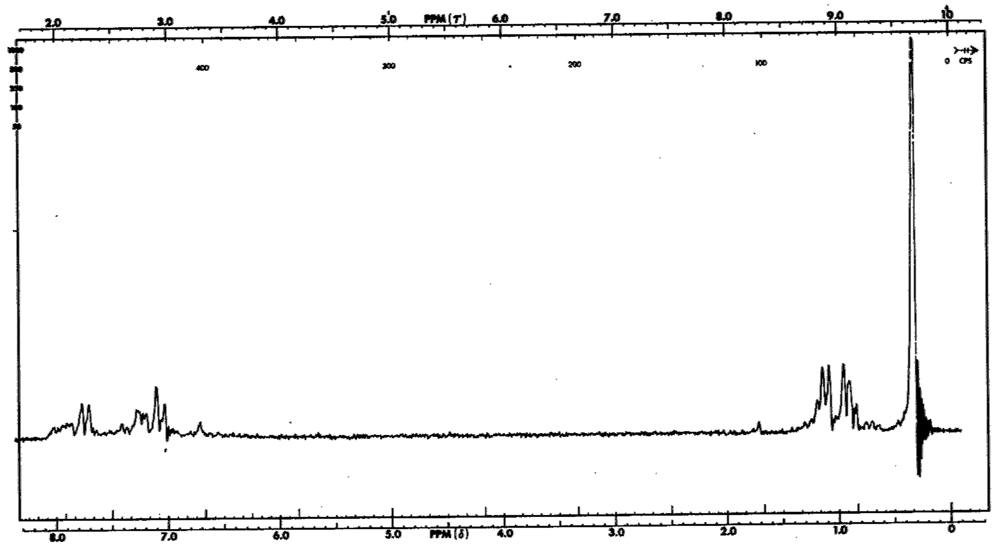

Figure 13. NMR Spectrum of Diferrocenyldiphenyllead

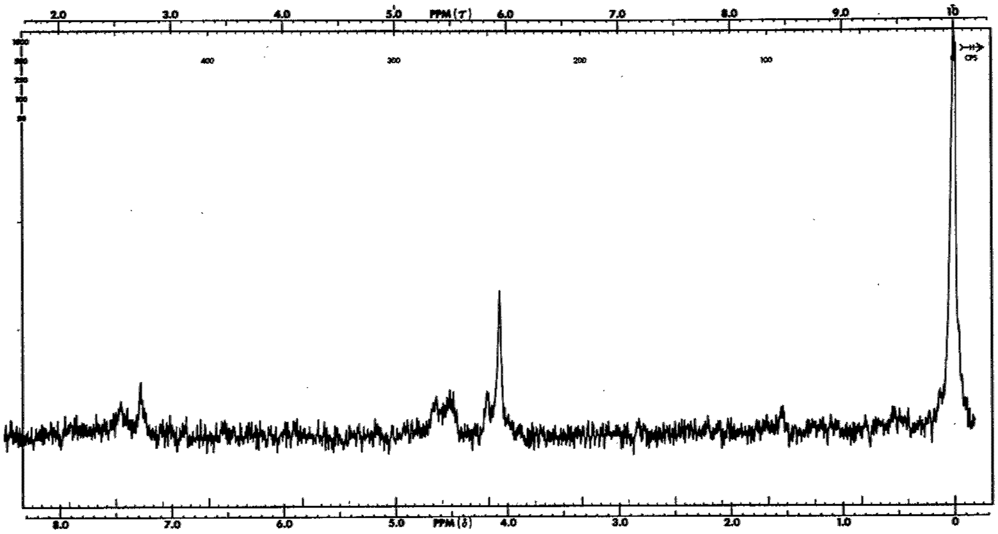

Figure 14. NMR Spectrum of Diferrocenylphenylborane

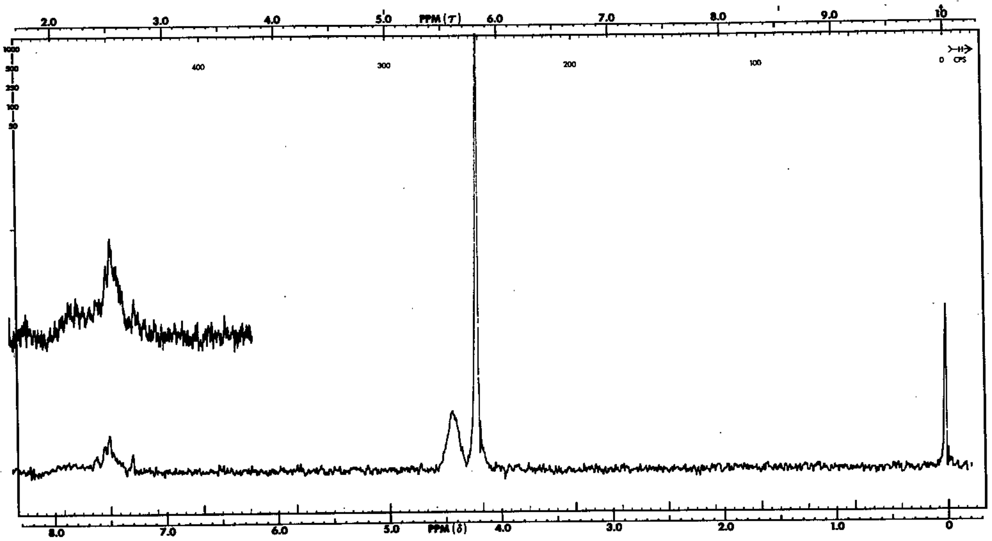

Figure 15. NMR Spectrum of Diferrocenylphenylphosphine Oxide

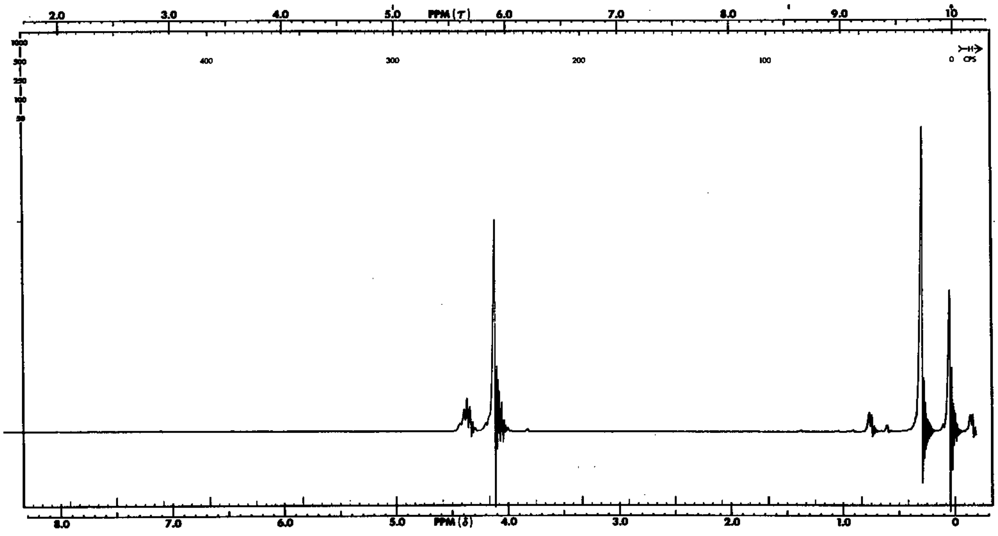

Figure 16. NMR Spectrum of Ferrocenyltrimethyltin

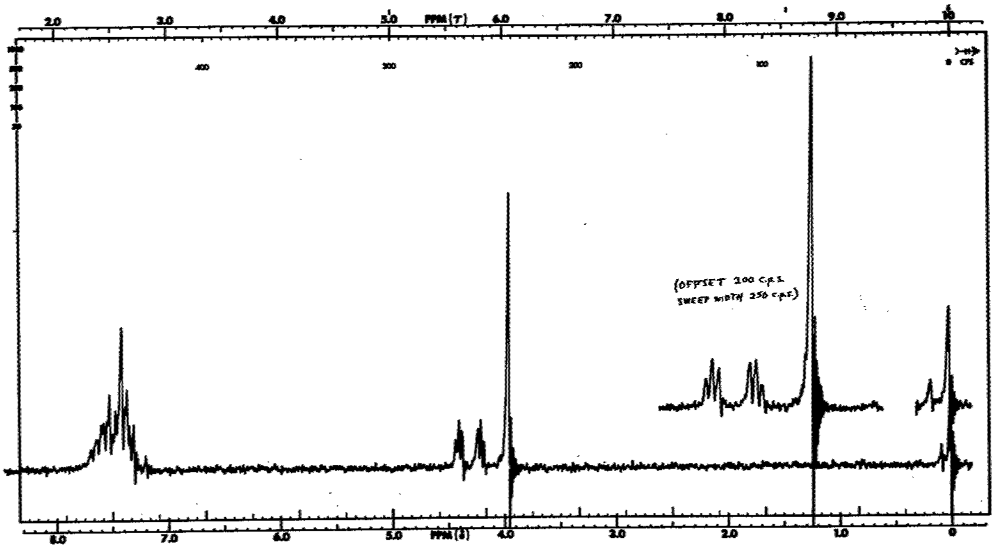

Figure 17. NMR Spectrum of Ferrocenyltriphenylgermane

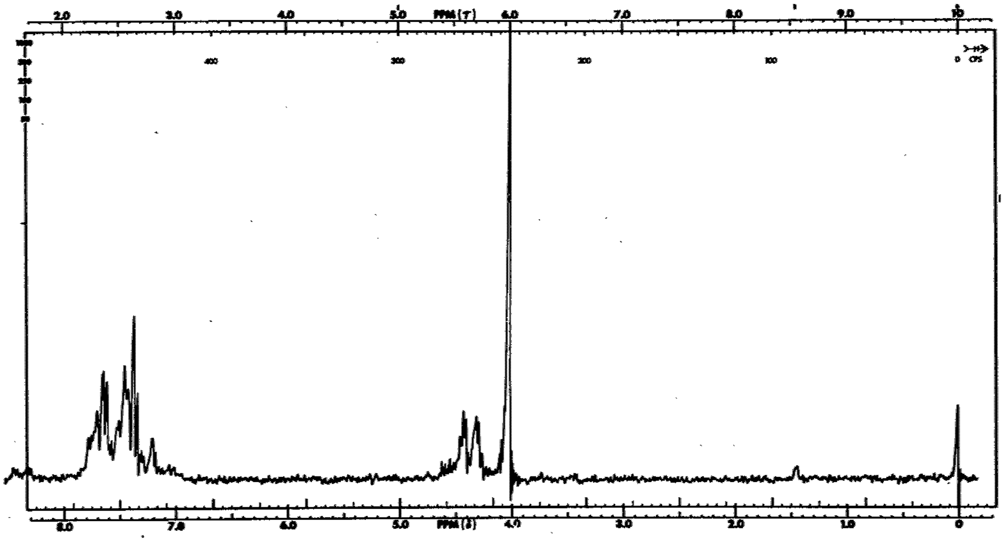

Figure 18. NMR Spectrum of Ferrocenyltriphenyllead

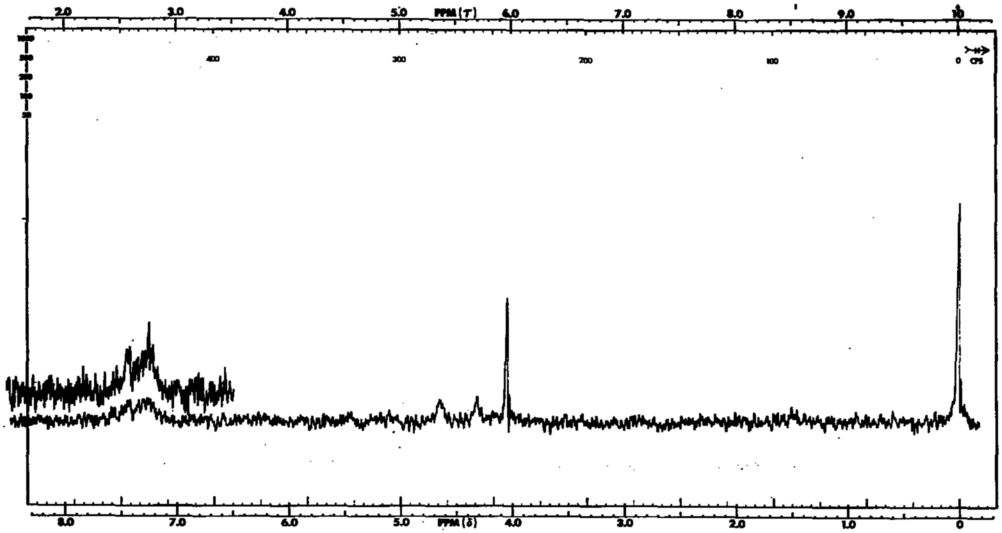

Figure 19. NMR Spectrum of Phenylferrocene

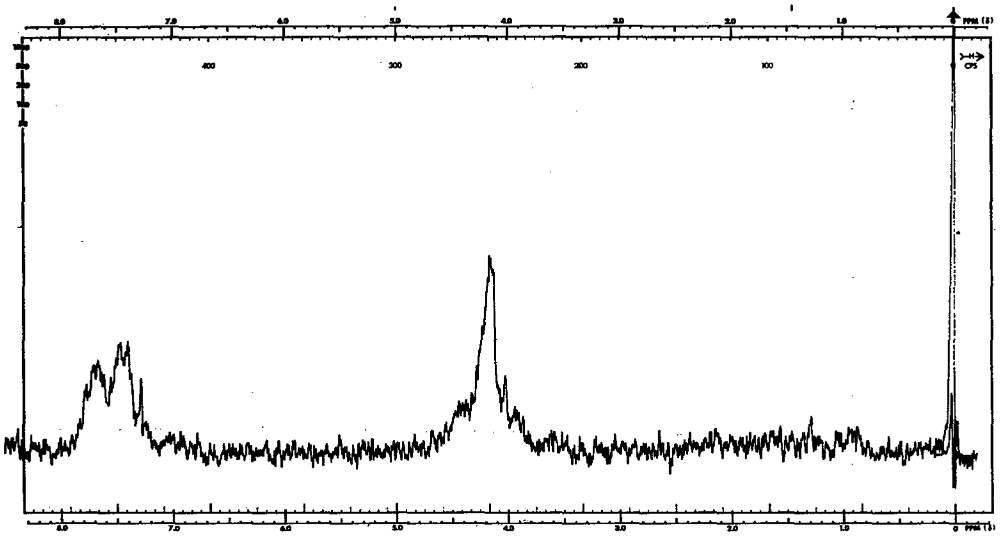

Figure 20. NMR Spectrum of Poly [1, 1' -(diphenylplumbyl)-ferrocenylene]

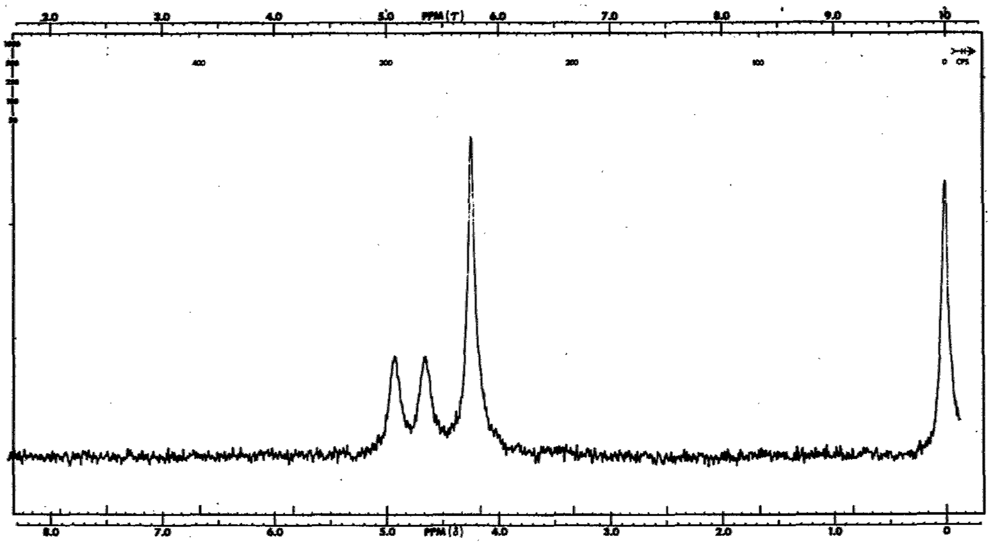

Figure 21. NMR Spectrum of Triferrocenylborane

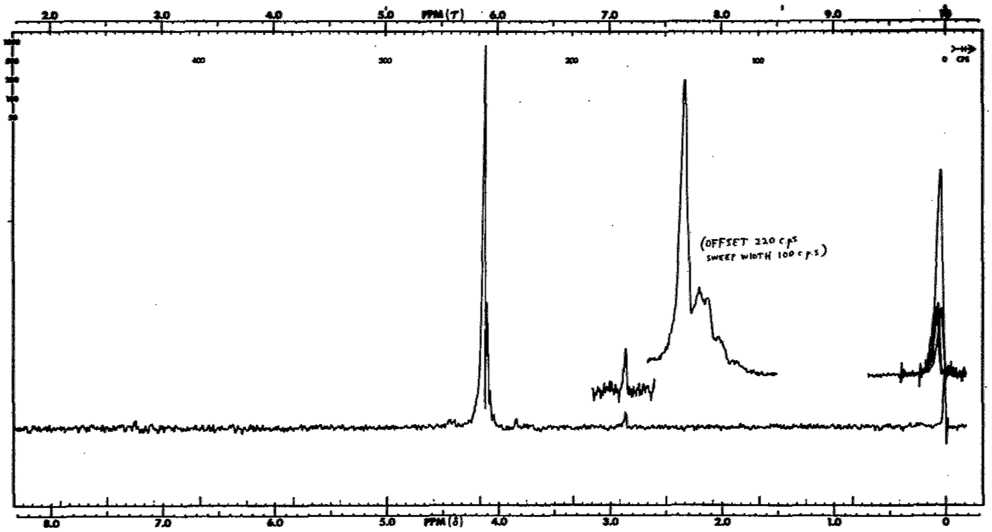

Figure 22. NMR Spectrum of Triferrocenylcarbinol

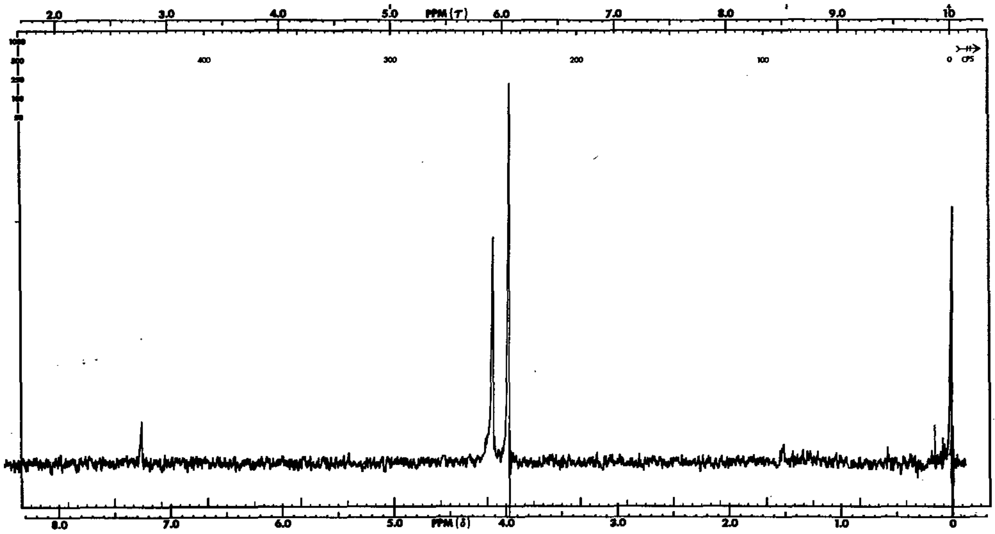

Figure 23. NMR Spectrum of Triferrocenylmethane

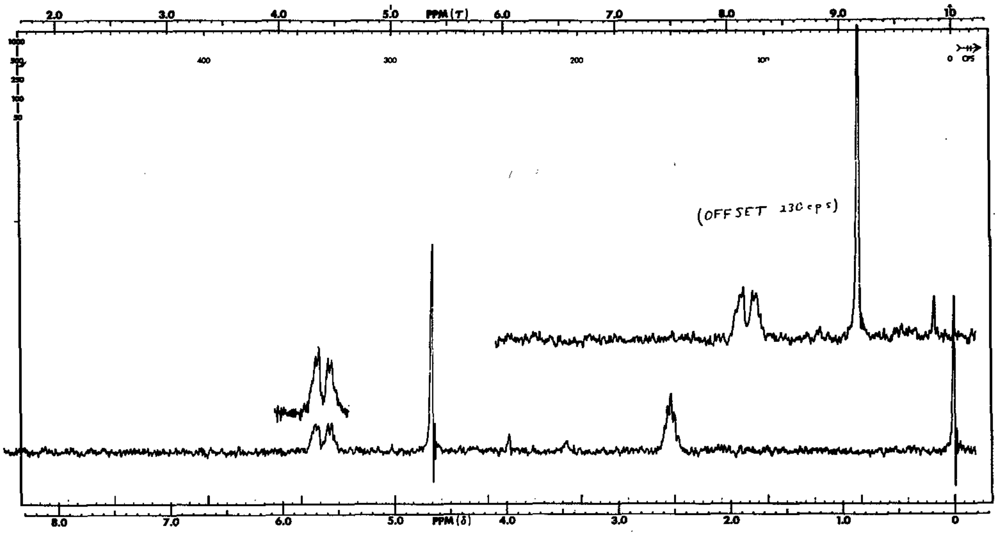

Figure 24. NMR Spectrum of Triferrocenylmethyl Fluoborate

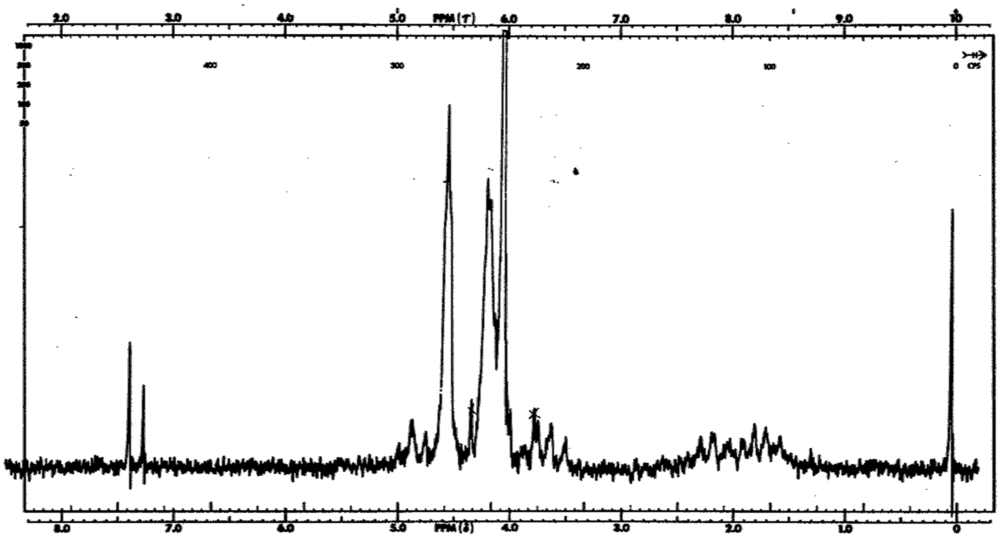

Figure 25. NMR Spectrum of 2-(Triferrocenylmethyl)tetrahydrofuran

ILLUSTRATIONS

PART TWO

Infrared Spectra

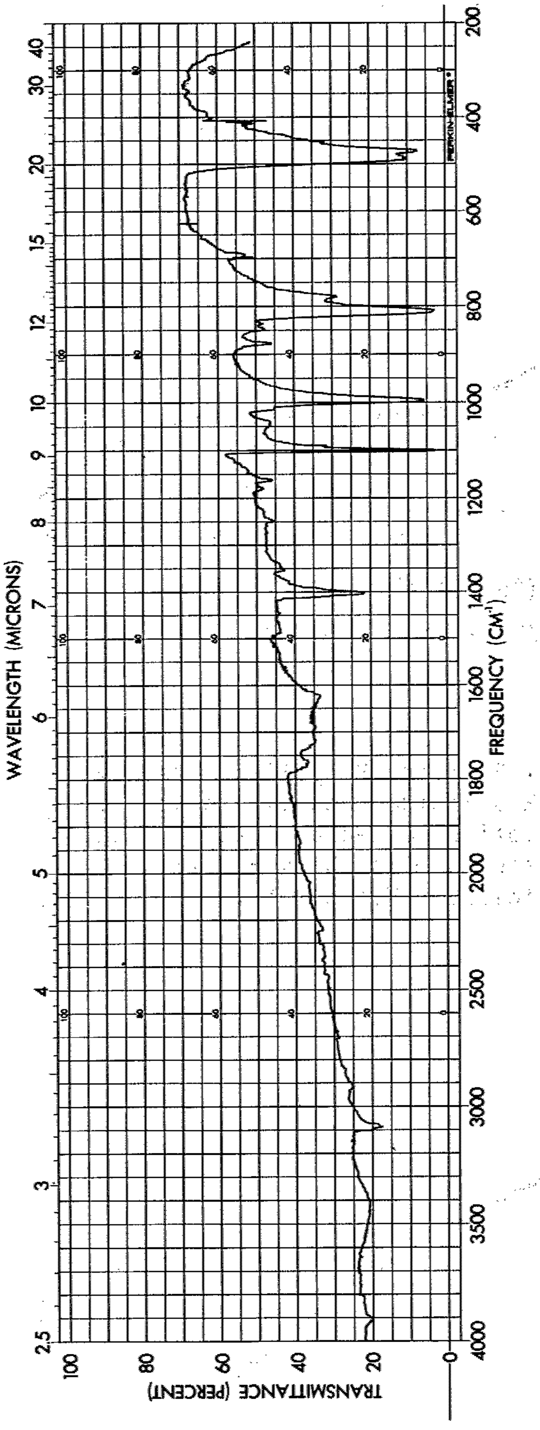

Figure 26. Infrared Spectrum of Ferrocene

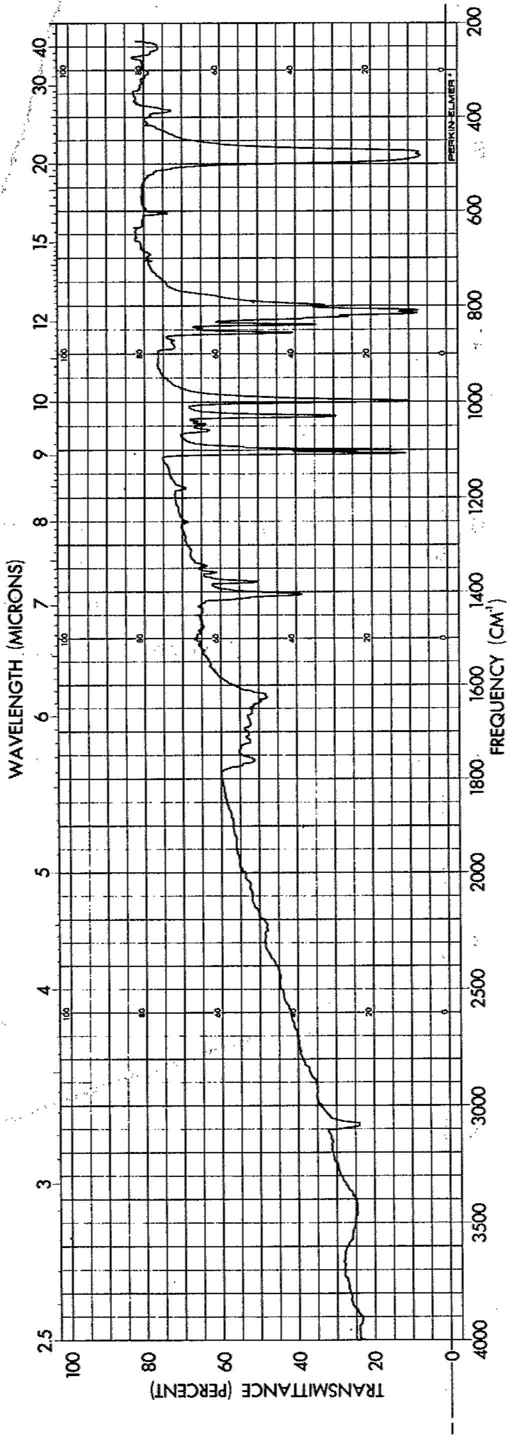

Figure 27. Infrared Spectrum of Biferrocenyl

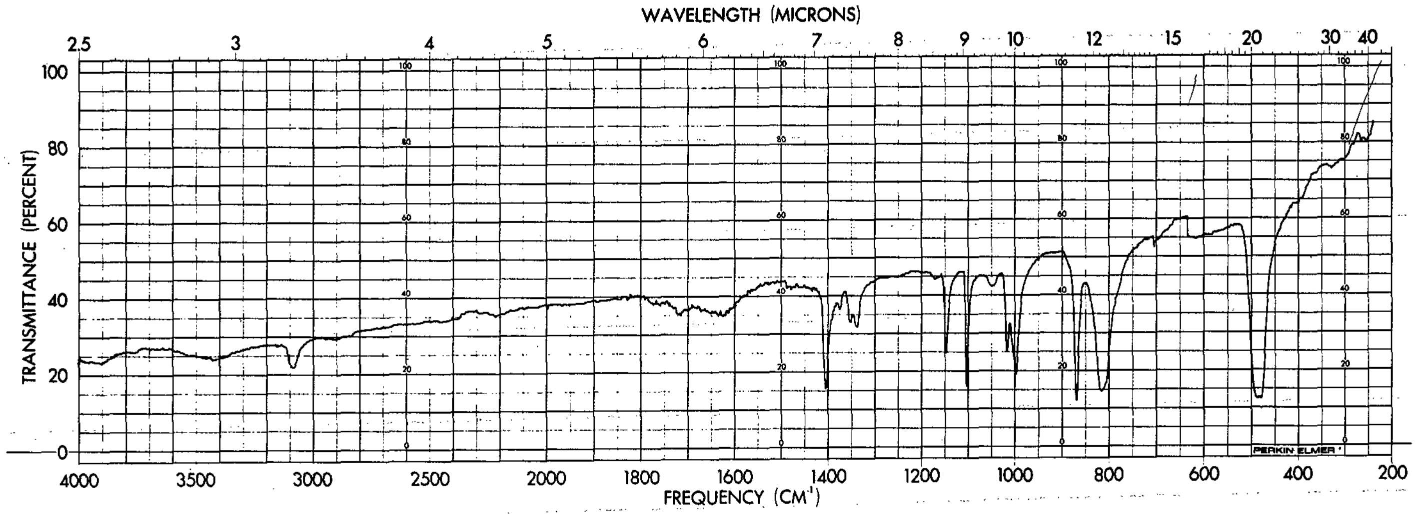

Figure 28. Infrared Spectrum of Bromoferrocene

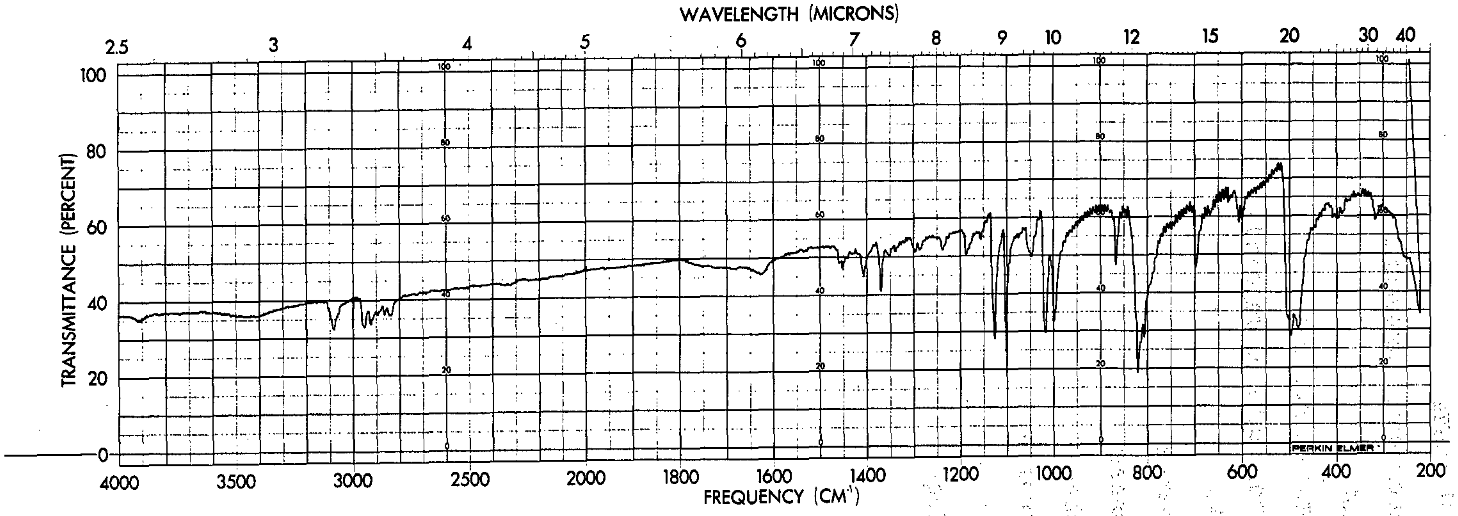

Figure 29. Infrared Spectrum of n-Butyltriferrocenyllead

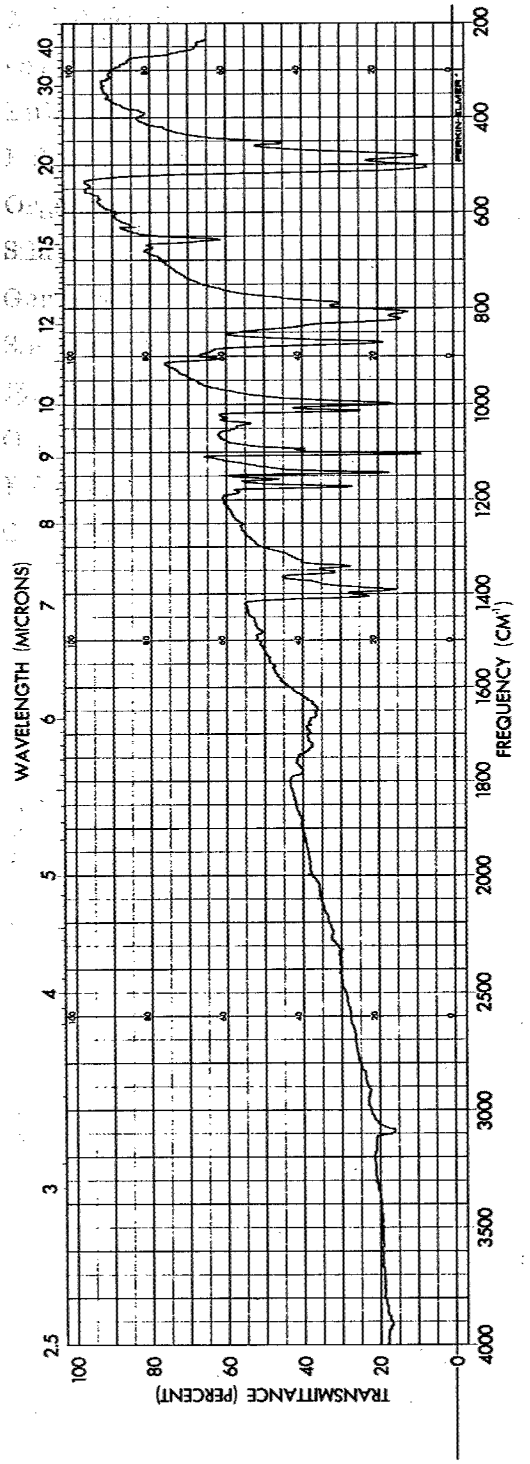

Figure 30. Infrared Spectrum of 2-Deuterochloroferrocene

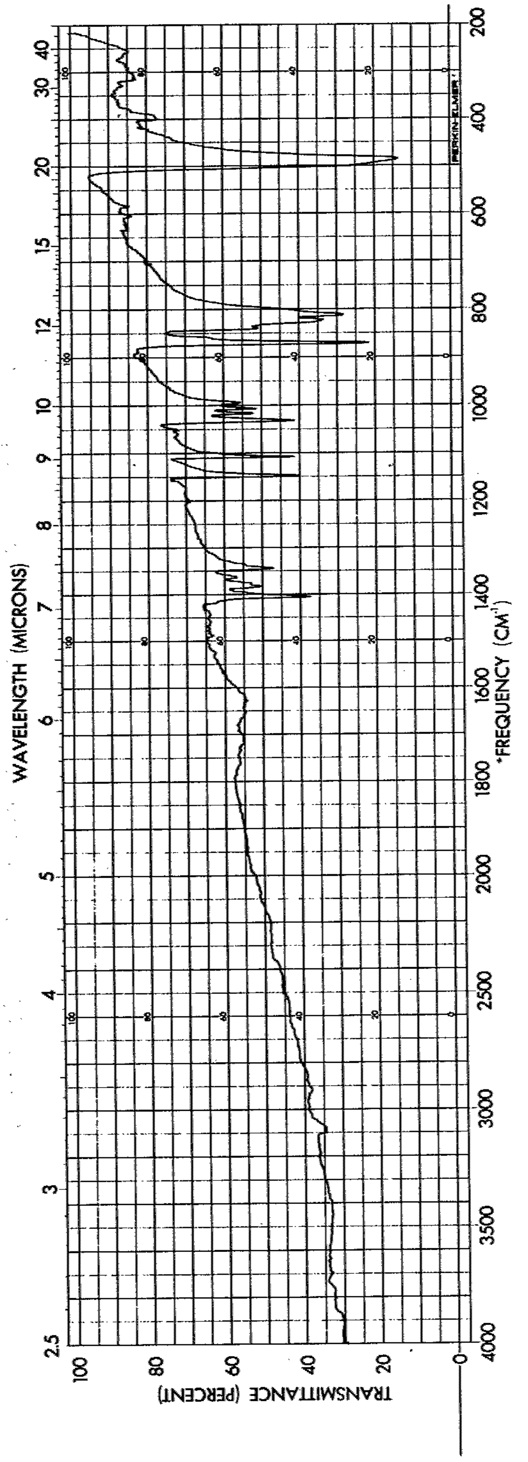

Figure 31. Infrared Spectrum of 1', 6' -Dibromobiferrocenyl

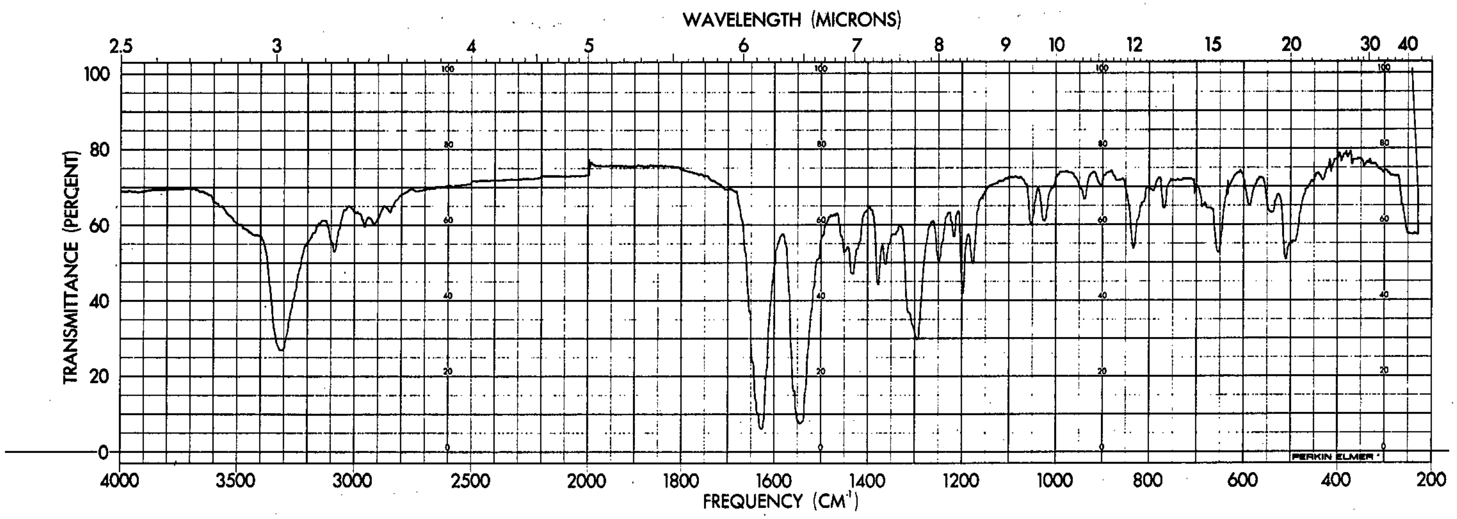

Figure 32. Infrared Spectrum of N,N' -Di-β-chloroethyl-1,1' -ferrocenedicarboxamide

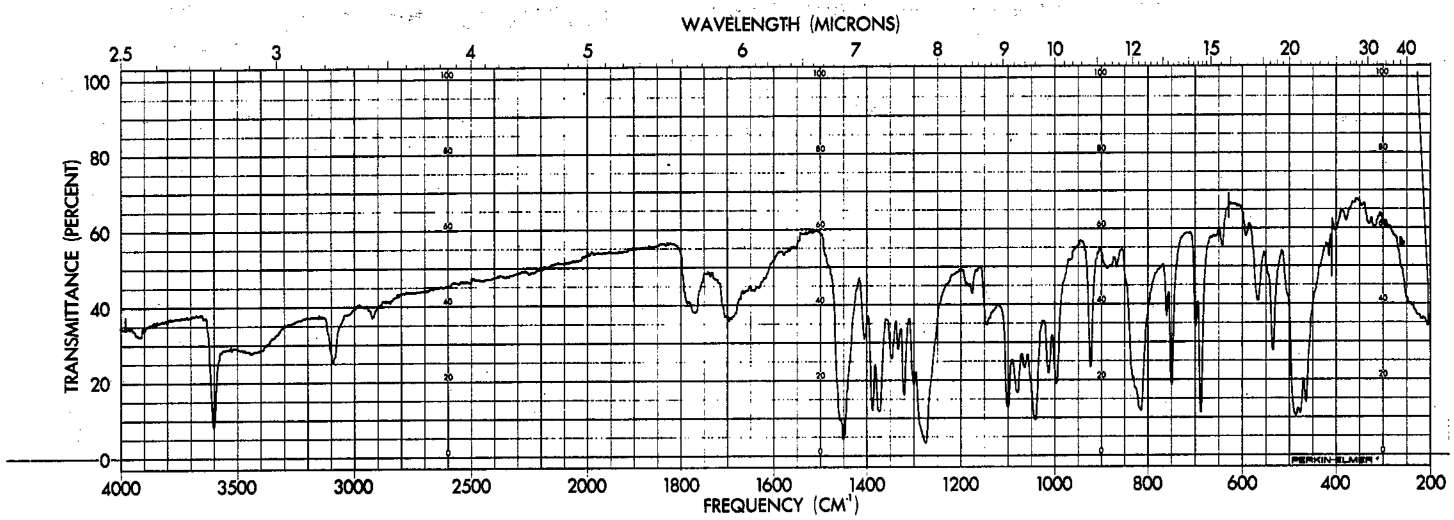

Figure 33. Infrared Spectrum of Diferrocenylborinic Acid

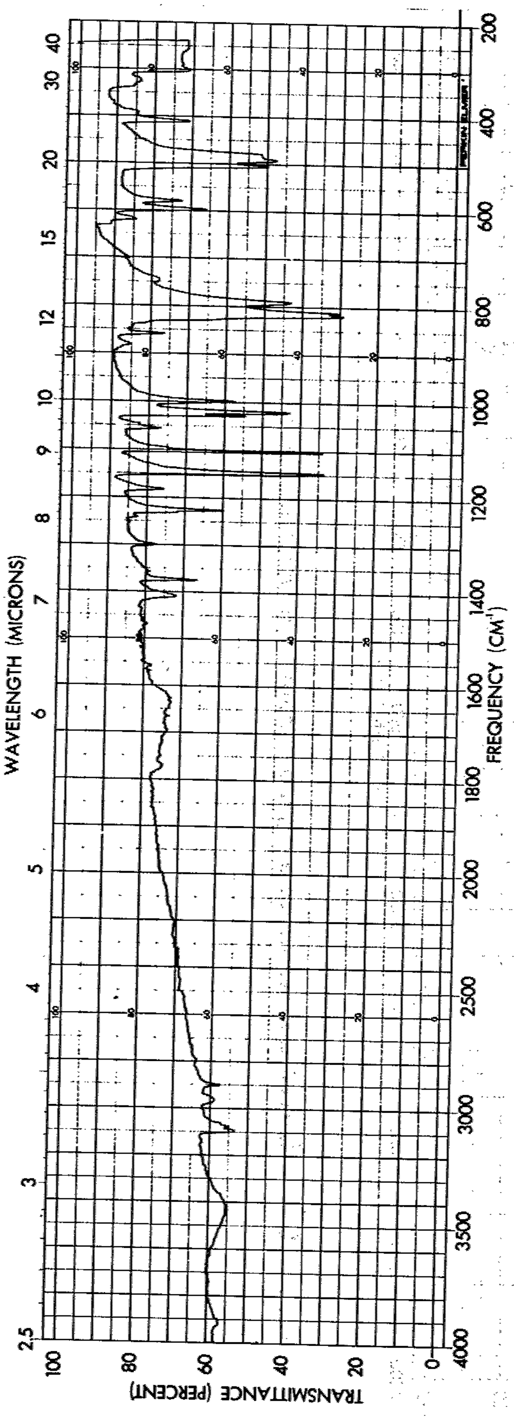

Figure 34. Infrared Spectrum of Diferrocenyldimethylgermane

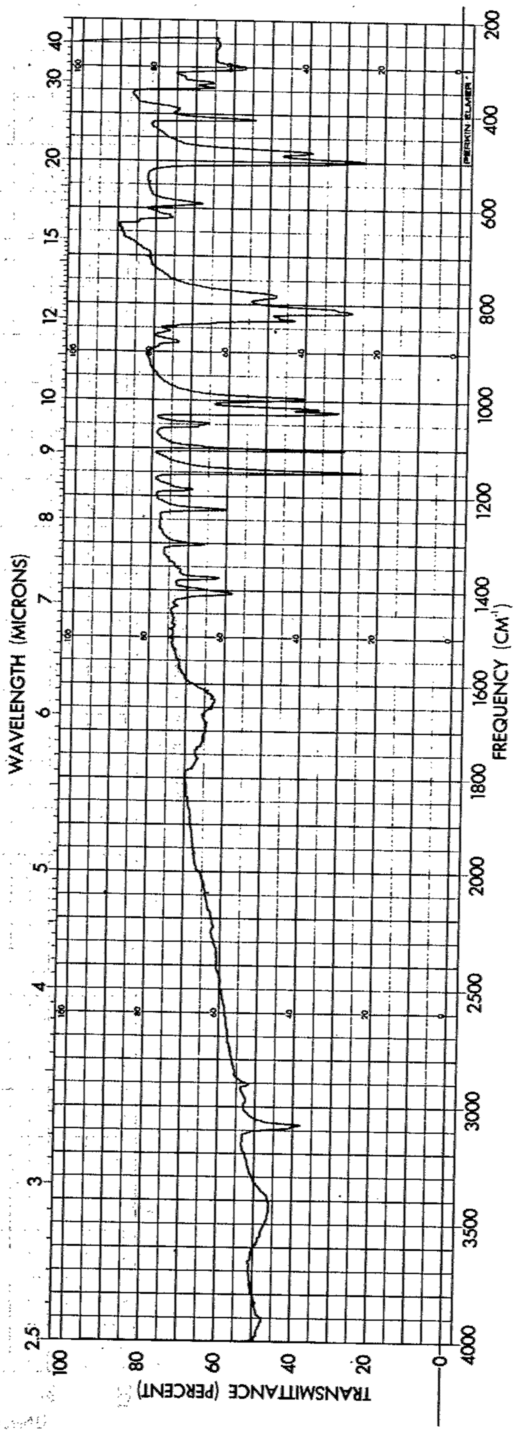

Figure 35. Infrared Spectrum of Methyltriferrocenylgermane

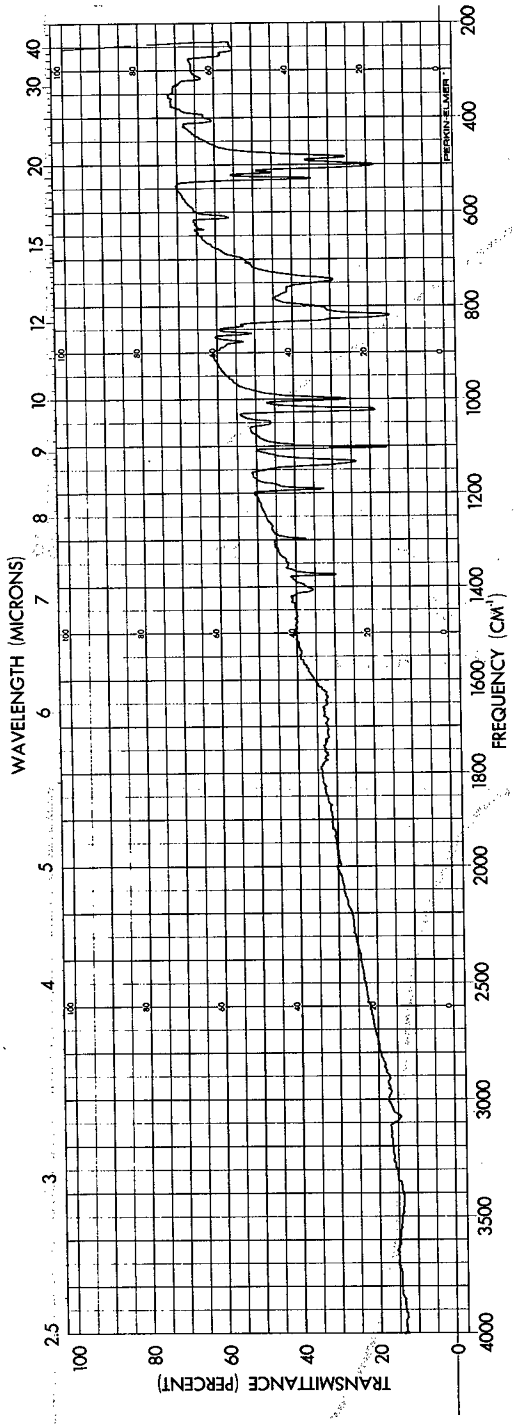

Figure 36. Infrared Spectrum of Diferrocenyldimethyltin

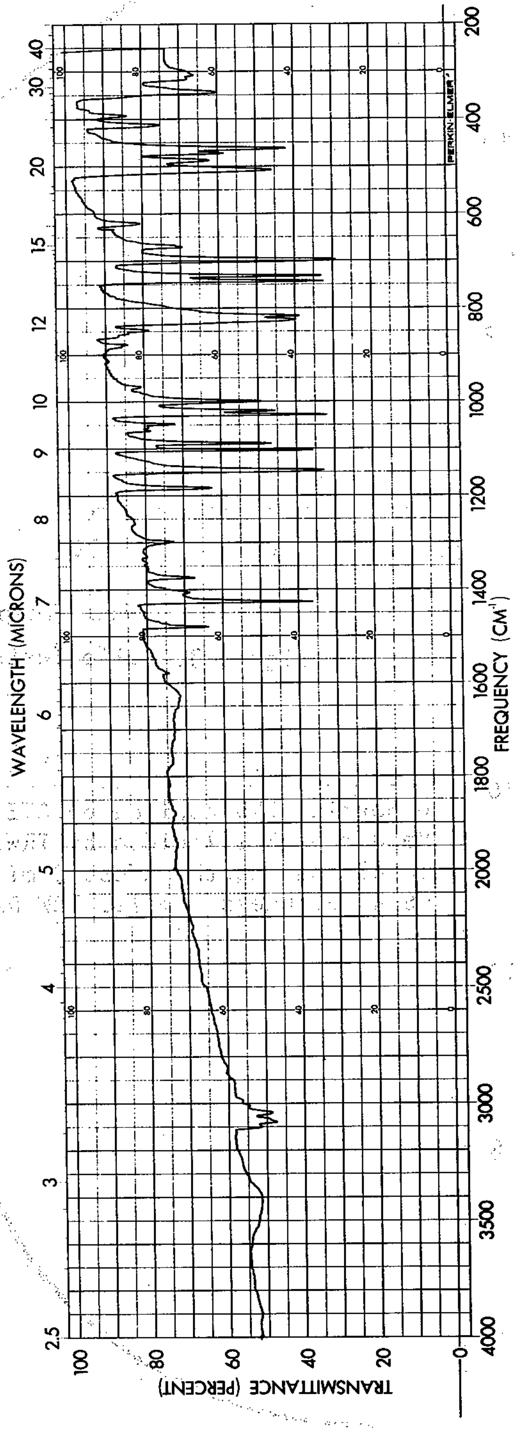

Figure 37. Infrared Spectrum of Diferrocenyldiphenylgermane

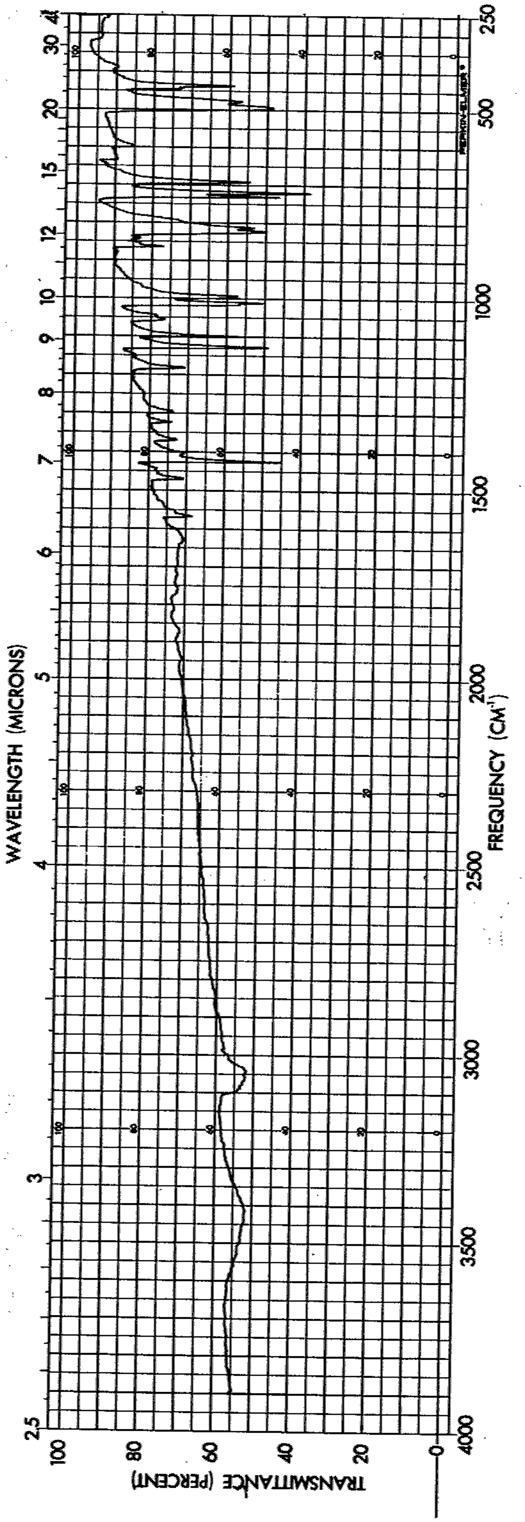

Figure 38. Infrared Spectrum of Diferrocenyldiphenyllead

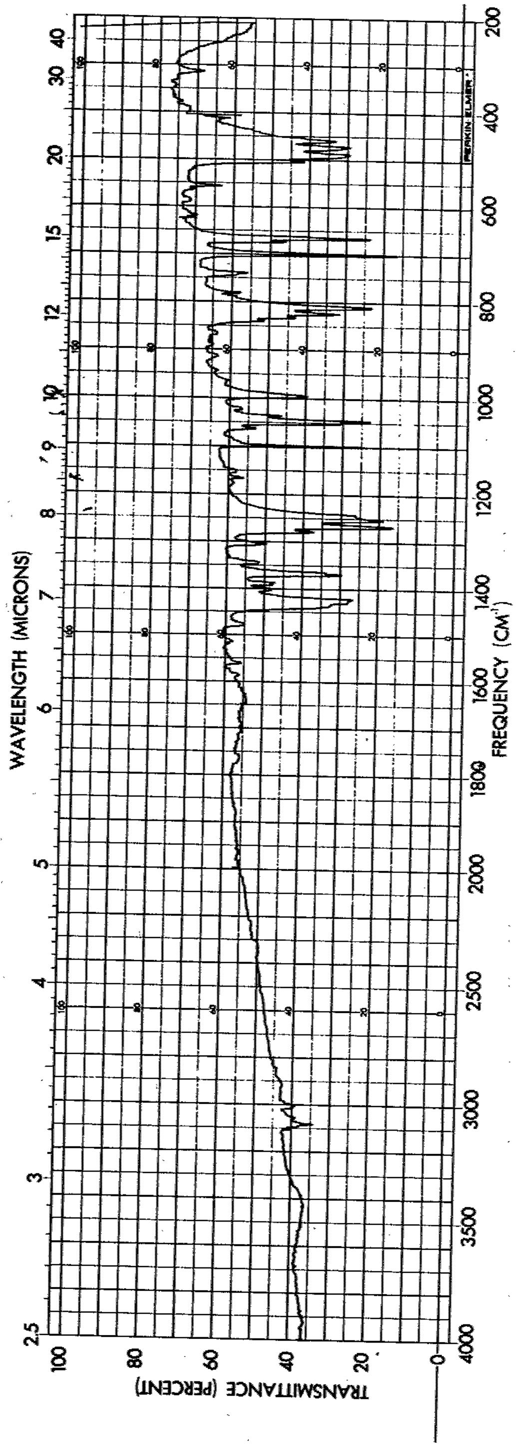

Figure 39. Infrared Spectrum of Diferrocenylphenylborane

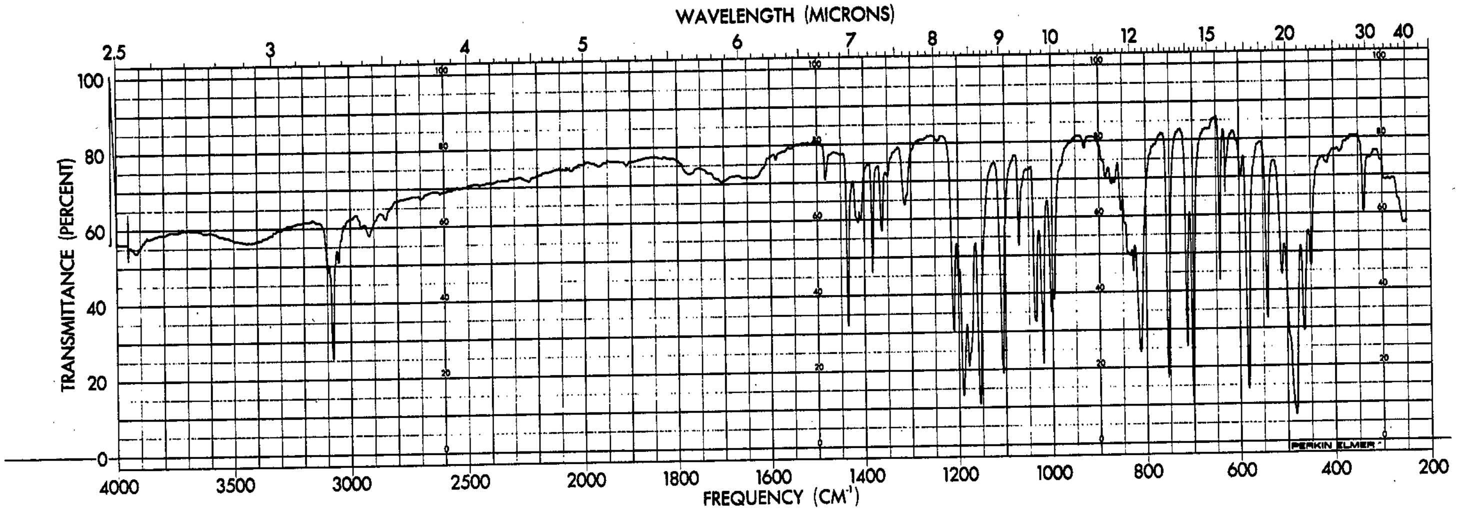

Figure 40. Infrared Spectrum of Diferrocenylphenylphosphine Oxide

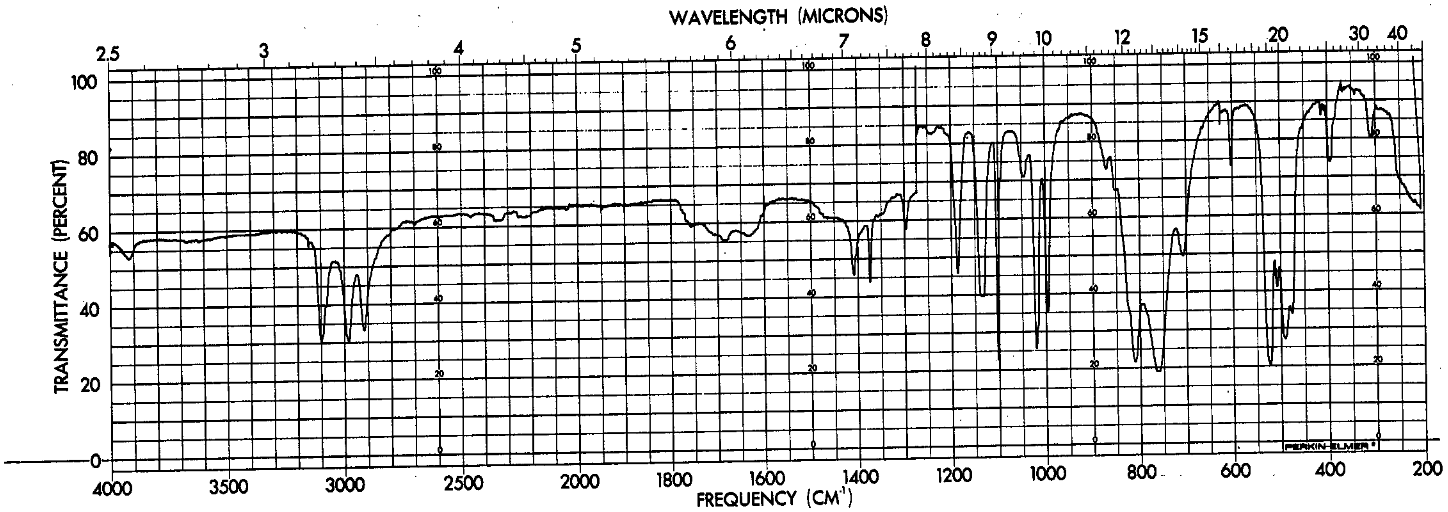

Figure 41. Infrared Spectrum of Ferrocenyltrimethyltin

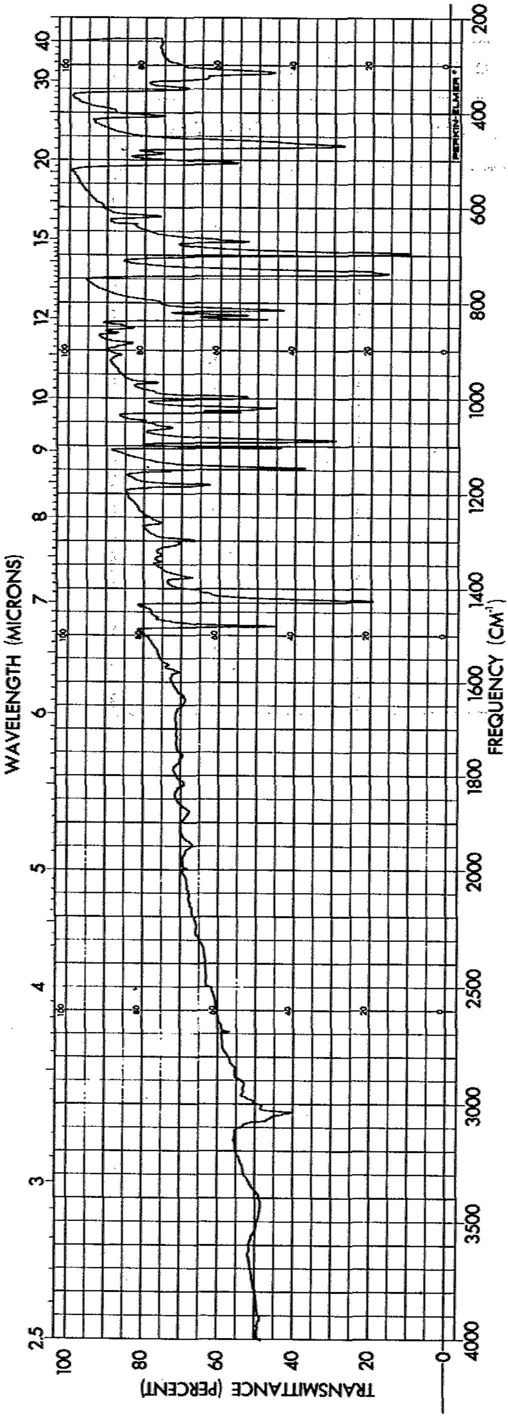

Figure 42. Infrared Spectrum of Ferrocenyltriphenylgermane

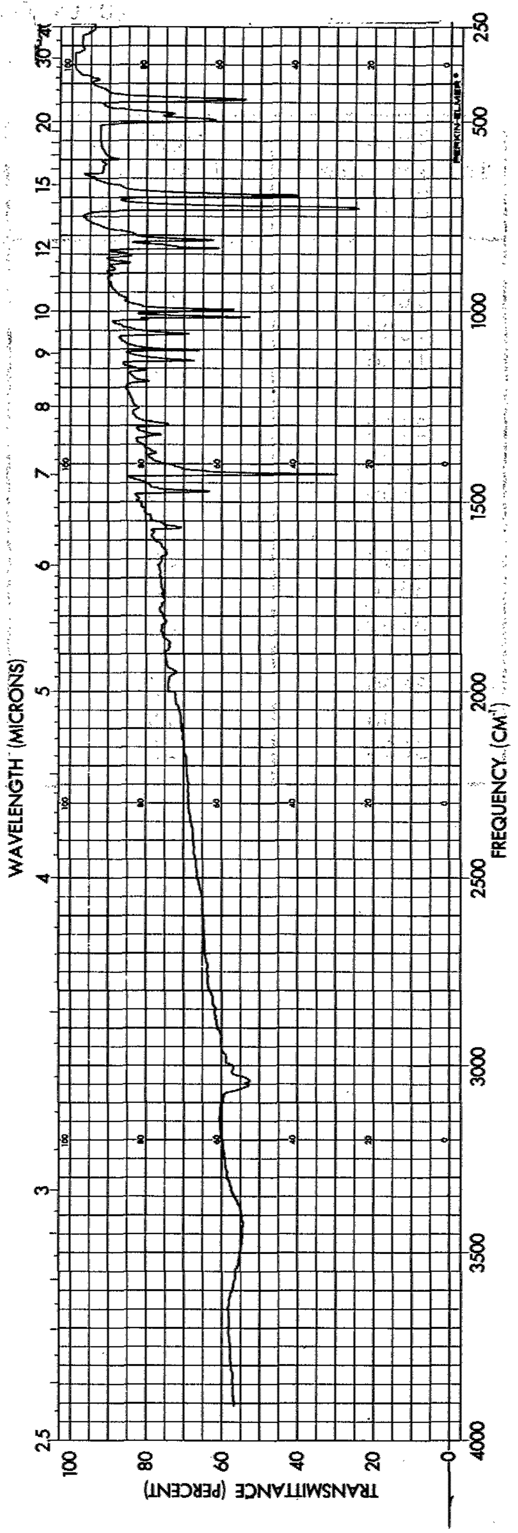

Figure 43. Infrared Spectrum of Ferrocenyltriphenyllead

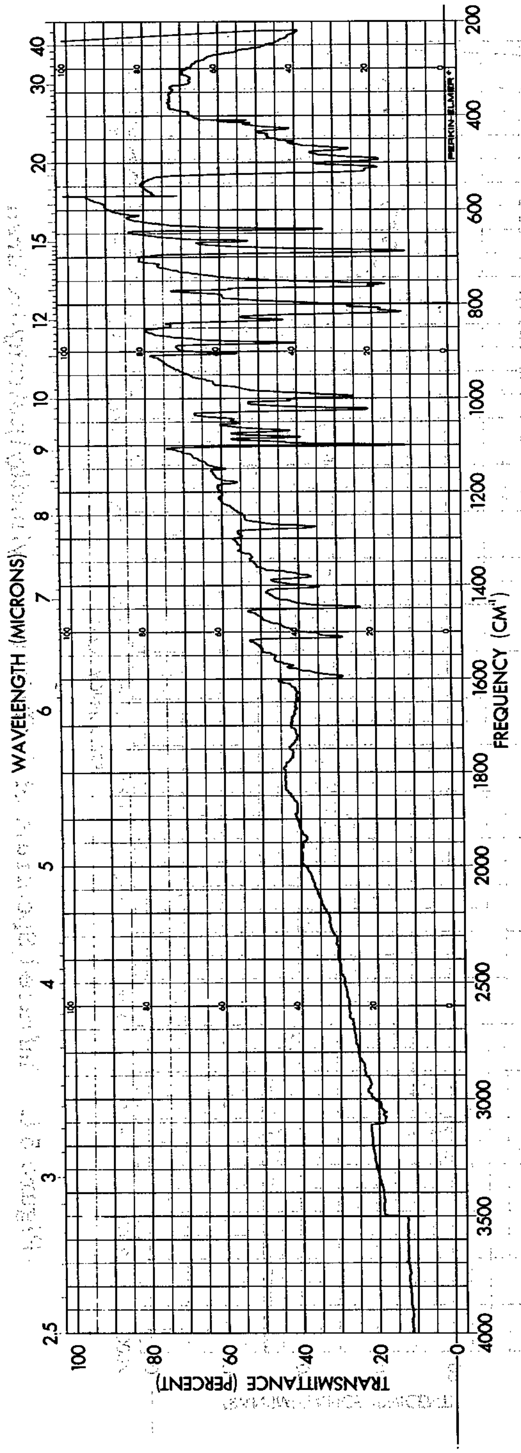

Figure 44. Infrared Spectrum of Phenylferrocene

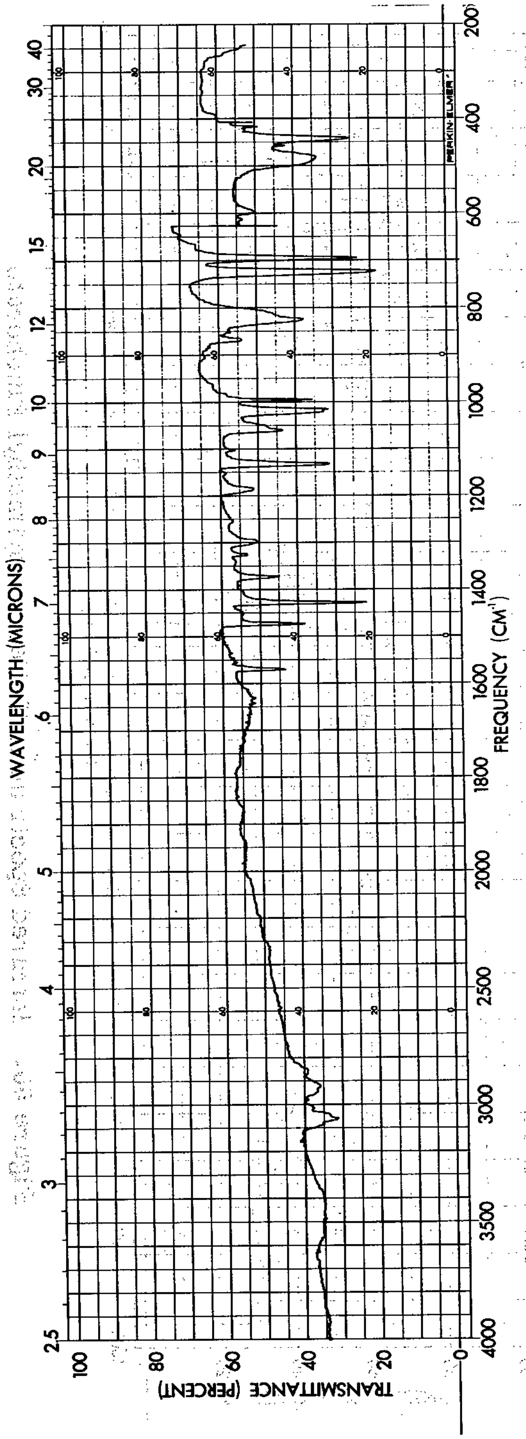

Figure 45. Infrared Spectrum of Poly [1, 1' -(diphenylplumbyl)-ferrocenylene]

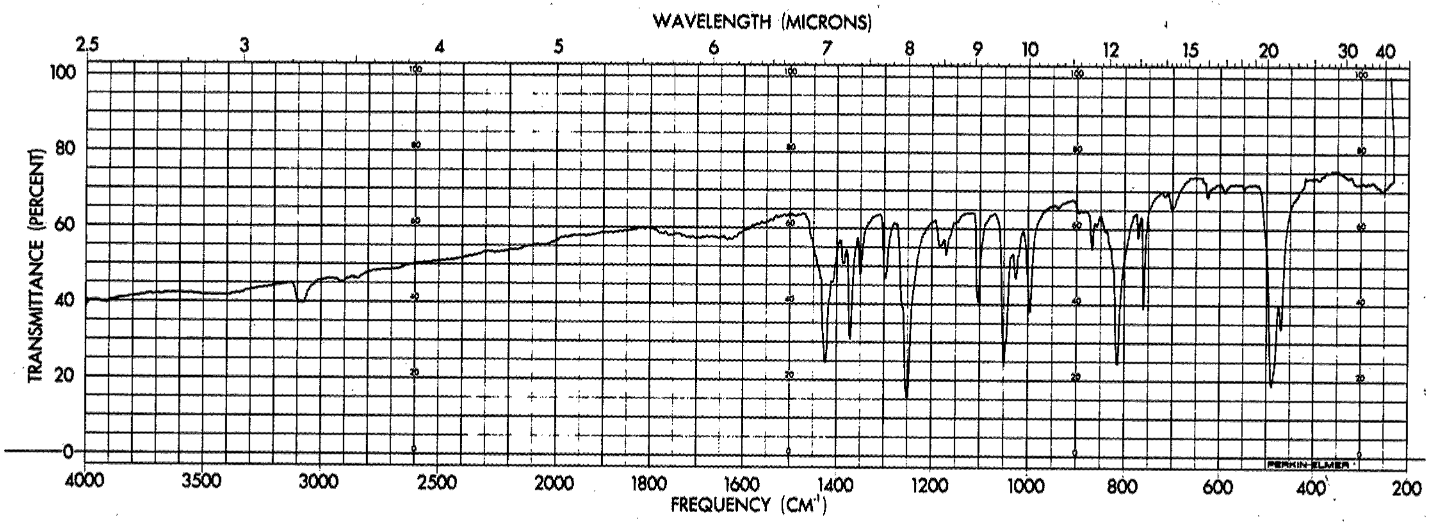

Figure 46. Infrared Spectrum of Triferrocenylborane

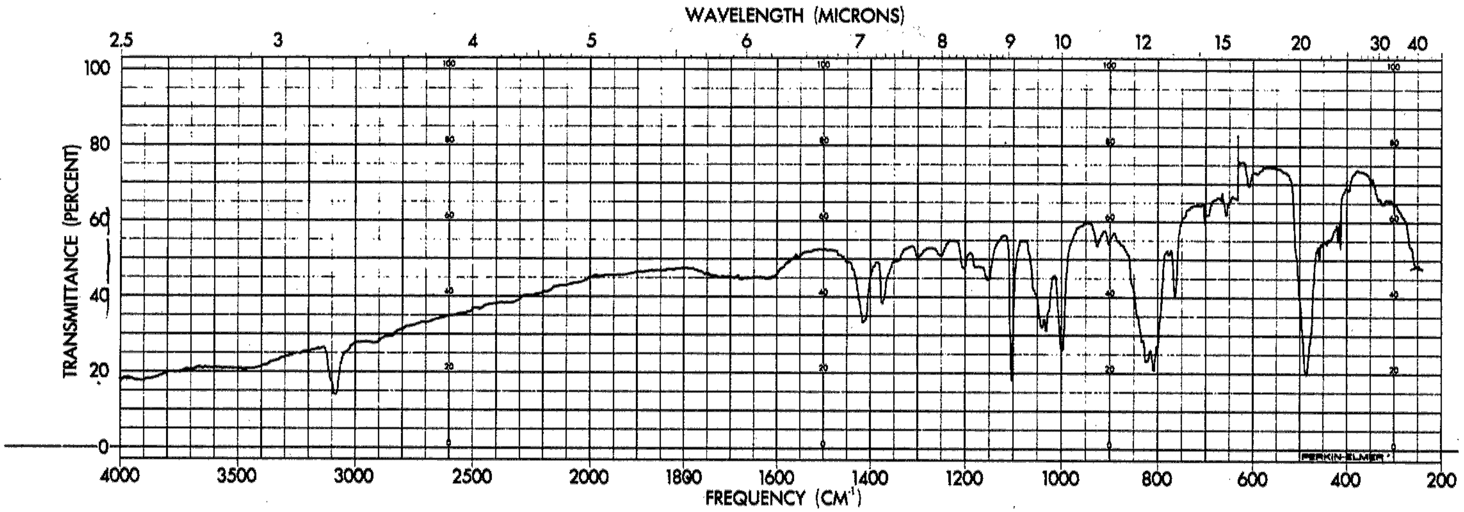

Figure 47. Infrared Spectrum of Black Byproduct from Triferrocenylborane Reaction

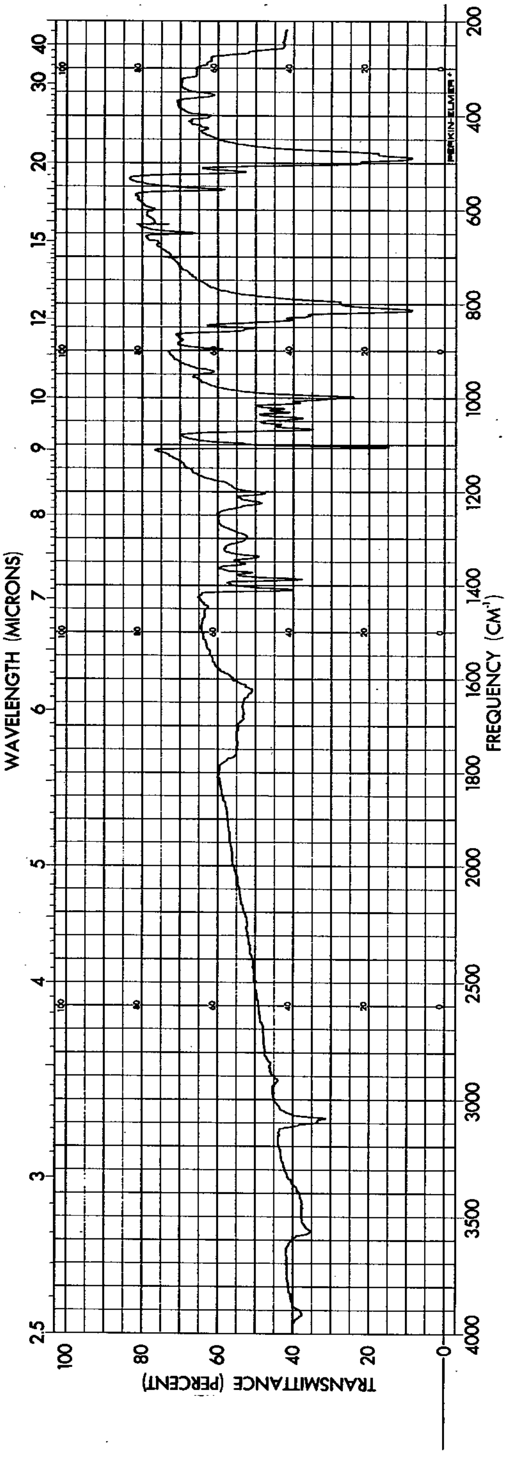

Figure 48. Infrared Spectrum of Triferrocenylcarbinol

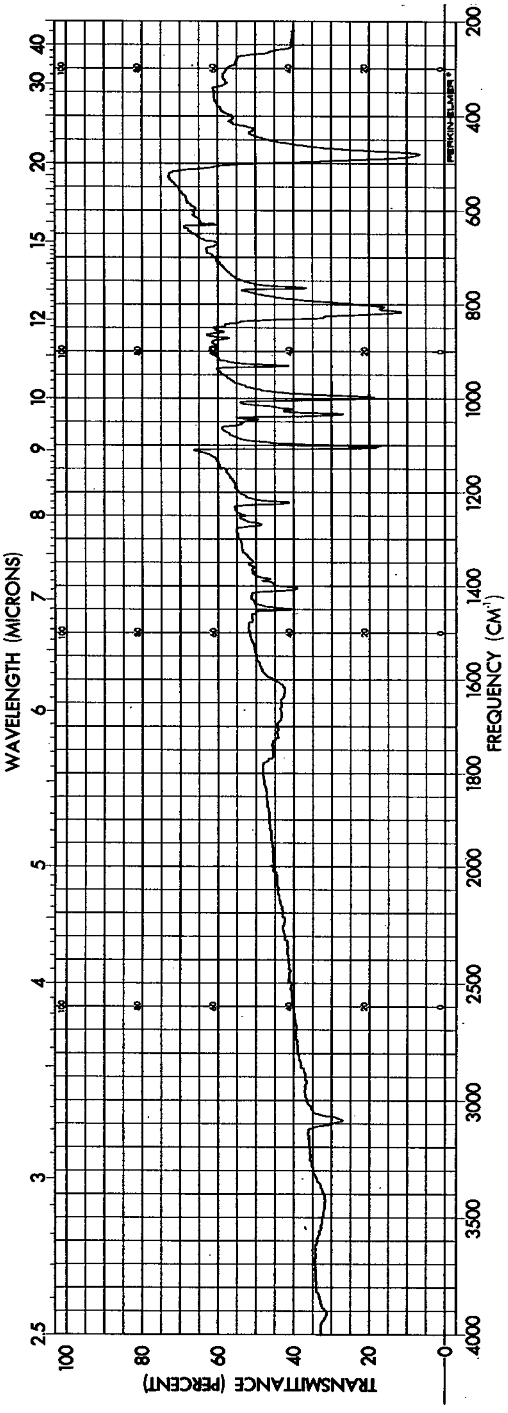

Figure 49. Infrared Spectrum of Triferrocenylmethane

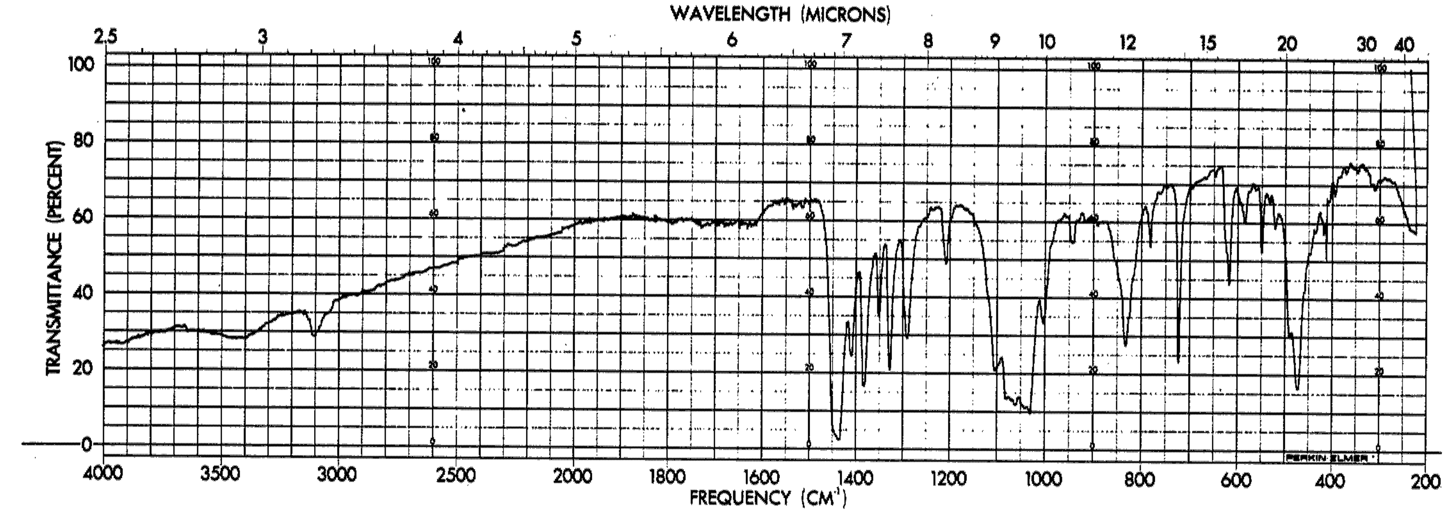

Figure 50. Infrared Spectrum of Triferrocenylmethyl Fluoborate

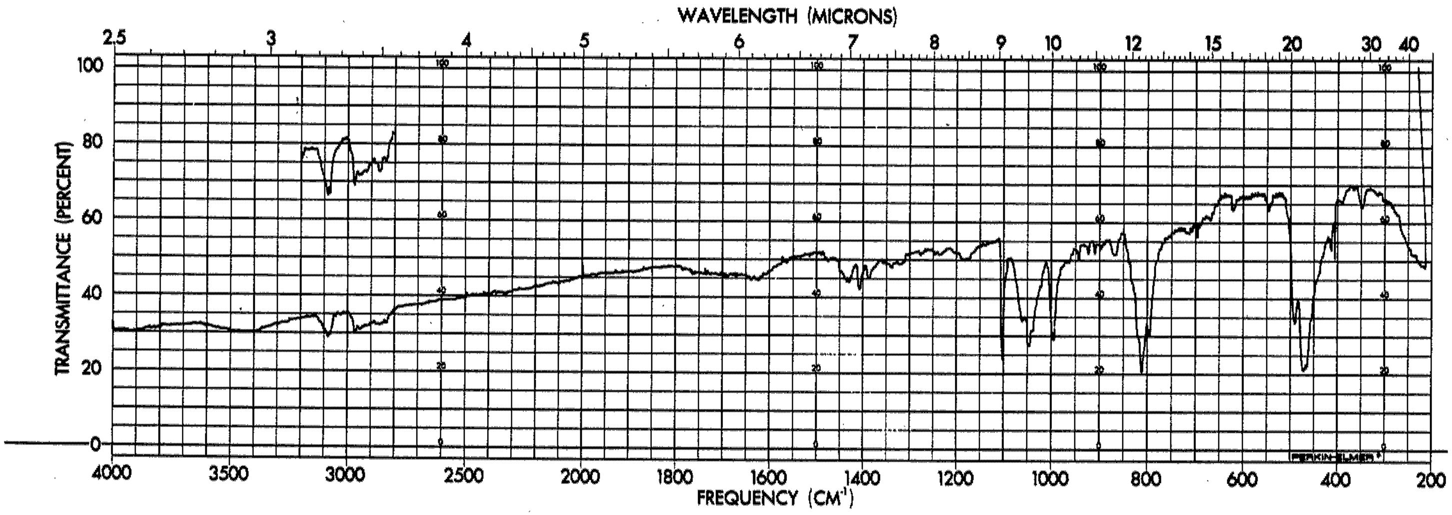

Figure 51. Infrared Spectrum of 2-(Triferrocenylmethyl)tetrahydrofuran

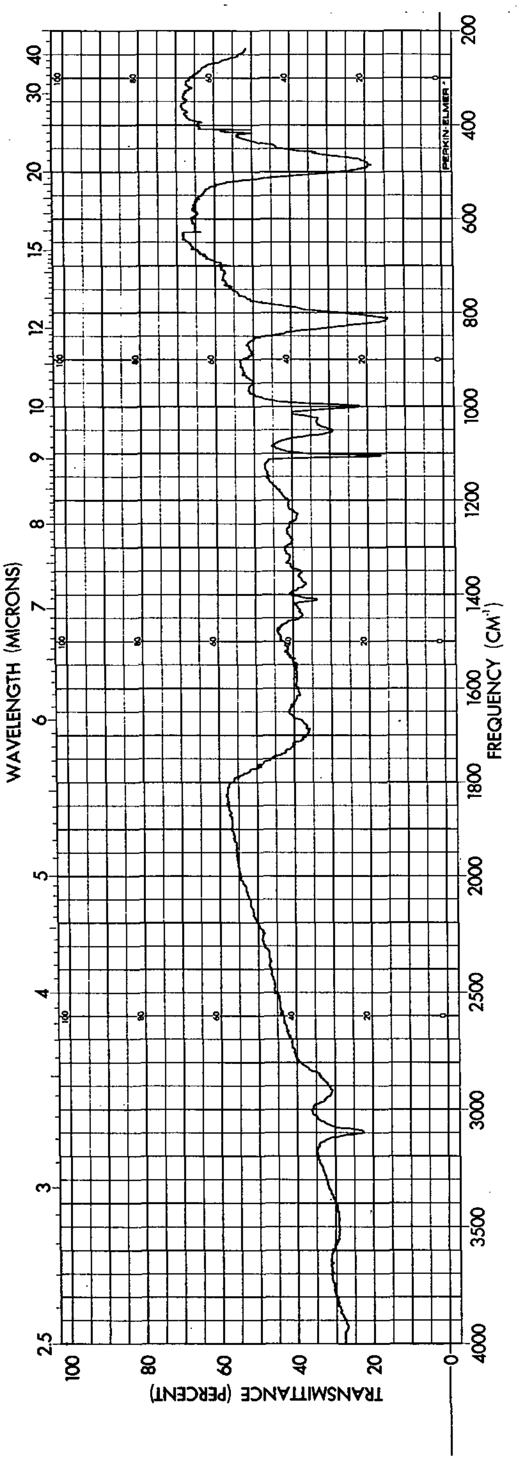

Figure 52. Infrared Spectrum of Polymer from Triferrocenylcarbinol

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13. ABSTRACT

The development of a new procedure for preparing lithiated derivatives of ferrocene [bis(cyclopentadienyl)iron] is reported. The reactivity and synthetic utility of these lithiated derivatives are shown by their reactions with halides of Group III, IV, and V elements to yield novel ferrocene derivatives containing the Group III, IV, or V element directly bonded to the ferrocene moieties. The new ferrocene derivatives have potential applications as thermally stable and radiation-resistant materials. The role of lithiated ferrocenes in the synthesis of ferrocene polymers derived from α-ferrocenylcarbinols is also described.

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Organometallic Compounds						
Silanes						
Germanes						
Stannanes						
Plumbanes						
Organoiron						
Polymers						
Carbinols						