The solid reaction mixture left after the distillation was extracted with hot chloroform and filtered. On cooling it deposited a white solid melting 200–210°. Recrystallization of this solid from chloroform and then from benzene–heptane raised the melting point to 228–231°, which showed no depression on admixture melting point with known hexaphenylditin.

The chloroform filtrate was evaporated *in vacuo* and the resulting yellow solid was washed with ethanol leaving a white solid, m.p. 120–130°, and a yellow ethanol solution. Recrystallization of this white solid from benzene–heptane gave a product melting 143.5–145.0°. A mixture melting point with a sample of known bis-(triphenyltin) sulfide showed no depression.

Benzalaniline with Triphenyltin Hydride.—Benzalaniline (1.81 g., 0.10 mole) was mixed with 10.5 g. (0.030 mole) triphenyltin hydride and heated at 124° for 22 hr. On cooling, the reaction mixture solidified and was extracted with hot methanol. The solid remaining was recrystallized from chloroform and an admixture melting point with hexaphenylditin showed no depression.

The methanol solution was evaporated under vacuum leaving a brownish oil, which was taken up in ether and extracted with 10% hydrochloric acid. Treatment with 10% sodium hydroxide, extraction with ether, drying the ether layer over sodium sulfate, and distillation of the ether left a brownish red oil to which pentane was added. Upon standing in a refrigerator overnight, a solid was obtained, m.p. 32.6–35.3°. Recrystallization from ethanol–water gave 0.65 g. (35%) of colorless product, 35.4–36.5° (lit. 37°).

The **phenylthiourea derivative** was prepared by mixing 0.185 g. of the N-phenylbenzylamine with 0.135 g. of phenyl isothiocyanate and allowing the mixture to stand overnight. Addition of hexane with cooling and scratching gave a white solid with a melting point of 80–83°. Recrystallization from ethanol–water gave colorless crystals, m.p. 104.6–105.6° (lit. 103°).

Multi-nuclear Ferrocenes. I. Biferrocenyl[1a,b]

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In its initial isolation, biferrocenyl (I) was obtained in small yield during distillation of the reaction products produced from treatment of a mixture of lithio- and dilithioferrocene with tri-*n*-hexylbromosilane[2,3]; since publication of a preliminary account of this work,[4] a number of additional reports concerning biferrocenyl have appeared.[5–9] Russian workers prepared biferrocenyl *via* reaction of ammoniacal silver oxide with ferroceneboronic acid,[5,10] and by catalytic pyrolysis of diferrocenylmercury.[6,11] Shechter and Helling[8] have shown that biferrocenyl may be obtained from ferrocenyl Grignard reagents, while still another method for preparation of biferrocenyl parallels the Ullmann procedure for biaryls in that iodoferrocene is heated in the presence of activated copper bronze.[7,9]

Because of the increasing interest in biferrocenyl, and because our spectral data[13] have been used to establish identity of biferrocenyl obtained by various methods,[8,9,12] we wish to report the experimental evidence upon which our original structural assignment to biferrocenyl was based, and present additional evidence in confirmation of that structure.

Initial data (combustion analysis, molecular weight determinations, and infrared C—H stretching absorption)[4] were clearly consistent with the biferrocenyl formulation, and comparison of absorption intensities (absorbance) of the 9- and 10-bands[14] of biferrocenyl with those of ferrocene showed the unsubstituted ring content of the former to be equal to that of the latter (Table I).

TABLE I

9–10-BAND ABSORBANCE OF FERROCENE AND BIFERROCENYL[a]

Molarity × 10^{-3}	9-Band		10-Band	
	Ferrocene	Biferrocenyl	Ferrocene	Biferrocenyl
3.41	0.054	0.061	0.056	0.054
5.08	.082	.076	.082	.076
8.49	.134	.141	.136	.123
11.1	.176	.179	.177	.165
14.1	.222	.218	.223	.200

[a] Measurements carried out in carbon disulfide solution.

The possibility of fortuitous agreement in this case was ruled out by examining similarly the 9–10 infrared absorption of a variety of known ferrocene derivatives (see Experimental). For each compound a Lambert–Beer plot was made of absorbance *vs.* molarity (carbon disulfide solution). Straight line relationships were obtained, while upper limits of concentration were determined for ferrocene, palmitoylferrocene, and hexadecylferrocene. Deviations from linearity for these compounds occurred above concentrations of 14 × 10^{-3} *M* for the 9-band, and above concentrations of 22 × 10^{-3} *M* for the 10-band. Working concentrations for all compounds, therefore, were kept below these limits. Difficulties due to base-line variations were overcome by use of the so-called base-line technique introduced by Wright.[15] A more serious limitation, however, lay in the fact that in some cases the 9- and/or the 10-band may be greatly distorted by the close proximity of other absorption. In such cases quantitative use of the 9–10 Rule is not applicable. For this reason the

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[1] (a) This research was supported in part by grants from Research Corporation (Frederick Gardner Cottrell Fund) and National Science Foundation (G-24083) for which the authors express sincere gratitude. Grateful acknowledgment is further made to National Science Foundation for an institutional grant which allowed purchase of the n.m.r. spectrometer used in this work; (b) preliminary aspects of this work were presented before the Division of Organic Chemistry, 135th National Meeting of the American Chemical Society, Boston, Mass., April, 1959; (c) Department of Chemistry, Bowdoin College, Brunswick, Me.; (d) National Science Foundation Undergraduate Research Participant.

(2) S. I. Goldberg, D. W. Mayo, M. Vogel, H. Rosenberg, and M. Rausch, *J. Org. Chem.*, **24**, 824 (1959).

(3) Formation of biferrocenyl, as described in this work, was first observed in 1957 by D. W. Mayo (Wright Air Development Center technical report 57-62, Part II, February, 1958; ASTIA document no. 150979). Efforts to accumulate additional material for investigation were aided by a subsequent preparation carried out by M. D. Rausch. In that case, tri-*n*-dodecylbromosilane was used instead of the tri-*n*-hexylbromosilane employed in the original and in subsequent runs.

(4) S. I. Goldberg and D. W. Mayo, *Chem. Ind.* (London), 671 (1959).

(5) A. N. Nesmeyanov, V. A. Sazonova, and V. N. Drozd, *Dokl. Akad. Nauk, SSSR*, **126**, 1004 (1959).

(6) O. A. Nesmeyanova and E. G. Perevalova, *ibid.*, **126**, 1007 (1959).

(7) E. G. Perevalova and O. A. Nesmeyanova, *ibid.*, **132**, 1093 (1960).

(8) H. Shechter and J. F. Helling, *J. Org. Chem.*, **26**, 1034 (1961).

(9) M. D. Rausch, *ibid.*, **26**, 1802 (1961).

(10) The experimental procedures originally reported in ref. 5 have been translated into German and republished [A. N. Nesmeyanov, V. A. Sazonova, and V. N. Drozd, *Chem. Ber.*, **93**, 2717 (1960)].

(11) Most of the work reported in ref. 6 has been repeated by M. D. Rausch.[12]

(12) M. D. Rausch, *Inorg. Chem.*, **1**, 414 (1962).

(13) Infrared and ultraviolet spectra of biferrocenyl are given in ref. 4.

(14) M. Rosenblum, Doctoral dissertation, Harvard University, 1953; K. L. Rinehart, Jr., K. L. Motz, and S. Moon, *J. Am. Chem. Soc.*, **79**, 2749 (1957); M. Rosenblum and R. B. Woodward, *ibid.*, **80**, 5443 (1958); A. N. Nesmeyanov, L. A. Kazitsyna, B. V. Lokshin, and V. D. Vilchevskaya, *Dokl. Akad. Nauk, SSSR*, **125**, 1037 (1959).

(15) N. Wright, *Ind. Eng. Chem., Anal. Ed.*, **13**, 1 (1941).

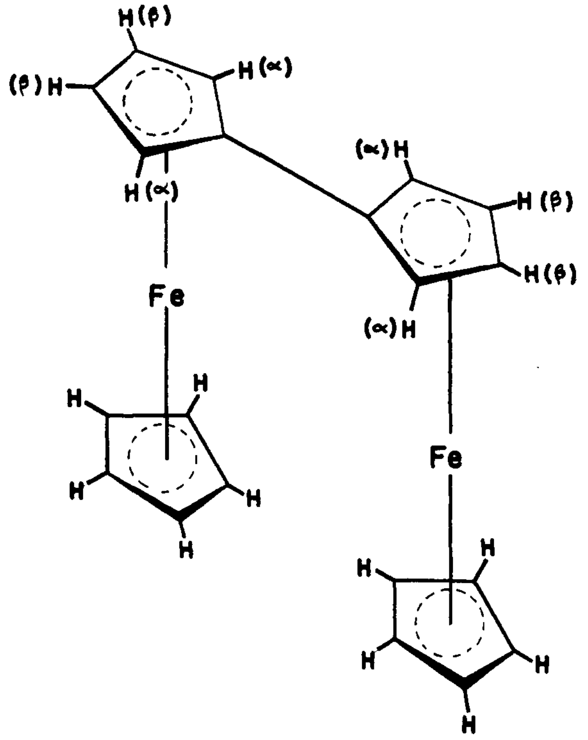
9-bands of α-hydroxyethylferrocene and acetylferrocene were found to be unusable, but the 10-band of each gave satisfactory results. Likewise, while the 10-band of *p*-phenoxyphenylferrocene proved to be too distorted by other close-lying absorption, its 9-band gave the expected results.

It was found, not unexpectedly, that in quantitative comparisons of 9–10 absorption of two given ferrocene derivatives (one of which treated as an unknown), a lack of close agreement between absorbance was usually the case. Nevertheless, the ultimate determination—the number of unsubstituted cyclopentadienyl rings—is one for which a relatively large lack of precision may be tolerated. Differences in measured absorbance between compounds which contain an equal number of unsubstituted rings or between compounds which contain a 100% difference in the number of unsubstituted rings (one *vs.* two), fell between 15 and 25%. In no case, except in those with the serious band distortions noted above, was there any difficulty in judging the unsubstituted ring content of the "unknown."

These data, therefore, constituted the basis of our structural assignment to biferrocenyl.[4] Confirmation of that assignment may now be seen in the n.m.r. spectrum obtained from biferrocenyl.[16] The pattern of signals displayed—two symmetrical four-proton triplets (5.82 and 5.68 τ[17], $J = 2$ c.p.s.) arising from the two equivalent A_2B_2 systems[18] present in I, and a ten-proton signal (6.03 τ) due to the ten equivalent protons in the two unsubstituted rings of I—is typical of that given by a monosubstituted ferrocene.[19]

In view of the known high nucleophilic character of ferrocene, one may expect two directly bonded ferrocene nuclei to exert a mutal shielding effect on all protons present. That this is the case may be seen from the fact that the n.m.r. signal which arises from protons in the unsubstituted rings of biferrocenyl (6.03 τ) appears upfield from that due to the protons in ferrocene itself (5.95 τ). Assignment, therefore, of the higher field triplet (5.82 τ) is made to the α-protons and the lower field triplet (5.68 τ) to the β-protons.

The effect of conjugation between the two ferrocene nuclei of biferrocenyl may be seen from its ultraviolet spectrum.[13] The situation is analogous to the effect of conjugation between two benzene nuclei as seen in the ultraviolet spectra of benzene and biphenyl.[20] Benzene gives rise to a K-band at 202 mμ (log ε 3.8), while in biphenyl this band appears at 252 mμ (log ε 4.3). A similar bathochromic shift, as well as a similar increase in extinction, was found in a comparison of the ultraviolet absorption of ferrocene—K-band below 220 mμ (log ε ~ 3.7, cyclohexane)—with that of biferrocenyl-absorption shoulder at 257 mμ (log ε 4.1, cyclohexane).[21]



I

It is tempting to ascribe the mode of formation of biferrocenyl in this work to a free radical process. Although no direct evidence for participation of ferrocenyl free radicals was obtained, generation of this species *via* thermally induced homolysis of ferrocenyl–silicon bonds[22] was indicated by results of a separate experiment in which ferrocene was formed in 16% yield when pure tri-*n*-hexylsilylferrocene[2] was heated in air to about 250°. While no biferrocenyl was detected in the sublimate of ferrocene obtained, conclusions regarding its formation could not be drawn since the compound, if formed, would not have survived the conditions of the experiment. Other attempts to promote the suspected homolysis of ferrocenyl–silicon bonds, carried out in the absence of air, were not successful. Apparently, a limited amount of air or some other activating agent is required, while in the presence of air, enough for the formation of ferrocene, biferrocenyl is known to suffer decomposition. Homolytic cleavage of arene–silicon bonds also seems to be indicated by the formation of biphenyl during heating of 1,5-bis-(4-biphenylyl)hexamethyltrisiloxane.[23]

In this regard it is pertinent to note that all presently known methods for biferrocenyl production[6–8,12,24] also give rise to ferrocene. While it is true that co-formation of ferrocene and biferrocenyl was not reported in one case[9] which involved heating iodoferrocene in the presence of activated copper

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(16) N.m.r. spectrum of biferrocenyl [saturated solution in chloroform containing tetramethylsilane (3%, v./v.)], determined with a Varian A-60 spectrometer (room temperature probe).

(17) G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).

(18) L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1959, p. 92 ff.

(19) See for example the n.m.r. spectrum of *p*-nitrophenylferrocene in, "High Resolution N.M.R. Spectra Catalog," Varian Associates, Palto Alto, Calif.

(20) E. A. Braude in "Determination of Organic Structures by Physical Methods," E. A. Braude and F. C. Nachod, Ed., Academic Press, Inc., New York, N. Y., 1955.

(21) We are grateful to Prof. K. L. Rinehart, University of Illinois, for calling our attention to this analogy.

(22) Generation of ferrocenyl free radicals *via* lithio- and dilithioferrocene, analogous to the work with dilithiobiphenyl [G. Wittig and G. Lehmann, *Chem. Ber.*, **90**, 875 (1957)], does not appear to be applicable here since no suitable metal halides were present in the reaction mixtures under discussion. Furthermore, attempts by Prof. P. D. Shaw (University of Illinois, personal communication) to promote coupling of the lithioferrocenes by introduction of various metal halides (*cf.*, Witting and Lehmann, ref. given) were not successful.

(23) R. L. Schaaf and P. T. Kan, Wright Air Development Center technical report 58-187, Part III, 1960, p. 27.

(24) A. N. Nesmeyanov, E. G. Perevalova, and O. A. Nesmeyanova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **47** (1962).

bronze, Russian workers[7] have noted the formation of ferrocene in this modified Ullmann process. The reaction been repeated several times in this laboratory—each run giving rise to a significant amount of ferrocene in addition to biferrocenyl (Table II), even under conditions slightly milder than those previously reported.[7,9]

TABLE II

PRODUCTS FROM TREATMENTS OF IODOFERROCENE (20 G., 0.064 MOLE) WITH ACTIVATED COPPER BRONZE AT 90° DURING 24 HR. UNDER NITROGEN

	Biferrocenyl[a]		Ferrocene[a]	
Run	Grams	% Yield[b]	Grams	% Yield[b]
1	7.50	63.4	2.80	23.7
2	7.50	63.4	2.90	24.3
3	8.20	69.4	2.50	20.9

[a] Data obtained from purified products. [b] Calculations based on complete conversion of iodoferrocene.

Experimental[25]

Biferrocenyl from Silylferrocenes.—Isolation of biferrocenyl from the complex reaction mixtures obtained from treatment of lithioferrocenes with trialkylbromosilanes may be illustrated by one such procedure in which tri-*n*-hexylbromosilane was used. After preparation of a mixture of lithio- and dilithioferrocene by reaction of ferrocene (18.0 g., 0.097 mole) with *n*-butyllithium (0.71 mole), and then treatment with tri-*n*-hexylbromosilane (35.0 g., 0.096 mole), the reaction mixture was prepared for distillation as previously described.[2] Distillation was carried through collection of a forerun [150–165° (0.2 mm.)] and then collection of tri-*n*-hexylsilylferrocene [184–187° (0.05 mm.)]. At pot temperature of 200–220° (0.05 mm.) biferrocenyl appeared as an orange colored, crystalline sublimate in the column. After all of the material had sublimed and the apparatus was allowed to cool to room temperature, the sublimate was washed out in chloroform solution. Evaporation of the chloroform yielded 170 mg. of crude biferrocenyl (0.11% yield based on 0.097 mole of ferrocene). Initial purification, accomplished by chromatography on alumina and evaporation of the elution solvent, benzene, afforded reasonably pure biferrocenyl. Constant melting material (227.5–229.0°) was obtained, however, only after repeated recrystallizations from benzene–petroleum ether (b.p. 40–50°). Melting range determinations of biferrocenyl were carried out in carefully evacuated capillary tubes since decomposition of the compound (pure or slightly impure) usually started near 200° in the presence of air.

Anal. Calcd. for $(C_{10}H_9Fe)_2$: C, 64.91; H, 4.90; Fe, 30.19; mol. wt., 372. Found: C, 65.03; H, 5.08; Fe, 30.39; mol. wt. (cryoscopic), 385, 389 (camphor), and 397, 361 (naphthalene).

Ferrocene *via* Thermal Decomposition of Tri-n-hexylsilylferrocene.—Tri-*n*-hexylsilylferrocene[2] (5.00 g., 10.7 moles) was slowly heated in a 100-ml. flask fitted with an air condenser. The amber-colored fluid started to darken at about 220°, and decomposition proceeded rapidly near 250°. During the rapid period of the decomposition a mass of orange colored, crystalline material sublimed into the air condenser. The sublimate was collected and shown to be ferrocene (16% yield) by means of comparison of infrared spectra and by admixture melting with authentic material. An ultraviolet spectrum of the sublimate also was found to be identical with that of ferrocene. It did not exhibit any of the intense absorption characteristic of the presence of biferrocenyl.[4]

Similar treatment of another sample of tri-*n*-hexylsilylferrocene except that heating was carried out in an atmosphere of purified nitrogen, merely caused the material to reflux gently with no sign of decomposition.

Biferrocenyl and Ferrocene from Iodoferrocene.[26]—Iodoferrocene (20 g., 0.064 mole), prepared by means of treatment of chloromercuriferrocene[27] with iodine in methylene dichloride solution according to the procedure reported by Shechter and Helling,[8] and activated copper bronze[28] (40 g.) were intimately mixed and placed into a 100-ml. Kjeldahl flask. The flask and contents were flushed with purified nitrogen during 30 min. at room temperature, and then maintained under a slight head of nitrogen during 20 hr. while the system was heated at 90°. Some of the ferrocene formed during the reaction could be seen sublimed on the neck of the flask after several hours. When the reaction mixture had been allowed to cool to room temperature it was extracted with 15-ml. portions of warm benzene until the extracts appeared colorless. Evaporation of the combined extracts *in vacuo* yielded a mass of crystalline material which was dissolved in hot hexane and the resulting solution allowed to cool to room temperature. The initial crop of crystalline material was collected, and the supernatent reduced slightly in volume. This caused a second crop of crystalline material to be deposited which was collected, and again the volume of the supernatent reduced. By repeating this procedure many times it was possible to effect a clean separation between biferrocenyl and ferrocene, the former being less soluble in hexane. Individual crops were each recrystallized from hexane giving, in this representative run, purified biferrocenyl (7.5 g., 63.4%) and purified ferrocene (2.9 g., 24.3%) which each gave rise to infrared and ultraviolet spectra identical to those obtained from respective authentic samples.

TABLE III

COMPOUNDS USED

Compound	9-Band	10-Band
Ferrocene	9.012	9.942
Biferrocenyl	8.986	9.985
m-Tolylferrocene	9.029	9.978
Diferrocenylketone	9.025	9.971
2-Biphenylylferrocene	9.034	9.942
α-Hydroxyethylferrocene	9.036	9.977
Diferrocenylmercury	9.029	9.979
Palmitoylferrocene	9.027	9.976
Hexadecylferrocene	9.036	9.983
Chloromercuriferrocene	9.037	9.990
Trimethylsilylferrocene	9.025	9.975
Benzoylferrocene	9.019	9.963
Benzylferrocene	9.035	9.979
p-Phenoxyphenylferrocene	9.031	9.978
Acetylferrocene	8.996	9.968

Infrared Measurements.—All of the compounds examined (Table III) were samples of analytical purity. Measurements were carried out with a Perkin-Elmer Model 21 double beam recording spectrophotometer, equipped with a sodium chloride prism interchange unit. Absorption intensity data were recorded at the wave lengths given in Table III, with slit settings of 0.0212 and 0.0282 μ at 9 and 10 μ, respectively. Measurements were made from several concentrations (usually four) of each ferrocene derivative in solutions of purified carbon disulfide. The same liquid absorption cell of 1-mm. thickness was used throughout the study. Absorbences were calculated with the use of base lines[15] drawn in each case as nearly parallel as possible to the background radiation of the solvent. Background radiation was checked before and after a series of runs.

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[25] All temperature readings are uncorrected. Analysis by the Schwartzkopf Microanalytical Laboratory, Woodside, N. Y. Molecular weight determinations by the Huffman Microanalytical Laboratories, Wheatridge, Colo.

[26] Procedure based upon those previously reported.[7,9]

[27] A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya, and O. A. Nesmeyanova, *Dokl. Akad. Nauk, SSSR*, **97**, 459 (1954).

[28] A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., Inc., New York, N. Y., 1948, p. 188.

Preparation of Bicyclo[4.3.1]dec-7-en-10-one

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Although bicyclo[4.3.1]dec-7-en-10-one has not been reported, the preparation of a few derivatives has