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The Direct Formation of Biferrocenyl and Polyferrocenyls from Ferrocenyllithium

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In the presence or absence of *n*-butyl bromide, ferrocenyllithium and cobaltous chloride reacted to give various polyferrocenyls and butylated polyferrocenyls. They were isolated, mainly by alumina chromatography, and their structures were established, principally from the NMR spectra, to be heteroannularly-bonded ones. The formation of these compounds is considered to be due to the coupling reactions of the ferrocenyl radical, the ferrocenylene biradical and the butyl radical, which were formed by homolytic fissions of some reactive intermediate and butyl halide. The presence of the alkyl halide greatly affected the sorts and yields of the products. No cyclic polyferrocenylene was obtained. The "9—10 rule" concerning the infrared spectra of ferrocene derivatives was found not to apply to di-substituted biferrocenyls. It was found, by a study of the X-ray diffraction patterns and the infrared spectra, that terferrocenyl crystallizes in polymorphic forms according to the method and the solvent of crystallization. The polymorphism may be attributable to the rotational isomerism around the central ferrocene nucleus.

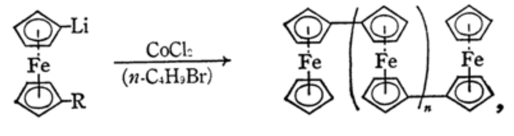
In connection with the synthesis of glycidylferrocenes and the related compounds,[1,2] the direct formation of biferrocenyl from ferrocenyllithium was previously reported by the present authors.[3] It was supposed that the formation of biferrocenyl is attributable to the Wurtz-type reaction,[4] in which the coupling of ferrocenyl radicals, produced by the homolytic fission of ferrocenyllithium molecules, gives rise to biferrocenyl. It has been shown by Kharasch and his co-workers[5] that small quantities of cobaltous chloride favor the formation of biphenyl from phenyllithium. Wittig and Lehmann[6] have also reported the coupling reaction of biphenyldilithium in the presence of cobaltous chloride. With reference to their experiments, the present authors attempted the reaction of ferrocenyllithium and cobaltous chloride in order to establish the radical mechanism. The mechanism has already been presumed from the results of the reaction which partly reported in a previous paper.[3]

Just after the present experiment was finished, Spilners and Pellegrini[7] reported a similar reaction of lithiated ferrocene and cobaltous chloride in ether-tetrahydrofuran. The reaction of ferrocenyl magnesium halide and cobaltous chloride to give biferrocenyl has also been reported by Shechter and Helling.[8] These investigators proposed the radical mechanism. However, no detailed description of a reaction of this type affording many sorts of polyferrocenyls has ever appeared.

The present paper will deal in full detail with the direct formation of biferrocenyl and polyferrocenyls from ferrocenyllithium. The reaction of ferrocenyllithium and cobaltous chloride was accomplished in dry ether under an atmosphere of nitrogen, in the presence or absence of an equimolar amount of alkyl halide, such as *n*-butyl bromide, to the ferrocene used. After the reaction of ferrocenyllithium and cobaltous chloride, the reaction mixture was poured into ice water in order to quench the reactive compounds. The organic layer was then separated from the inorganic aqueous layer. After the solvent has been removed from the organic layer, many products were isolated from the solid mixture by various procedures. The isolated crude products were then purified by rechromatography or recrystallization.

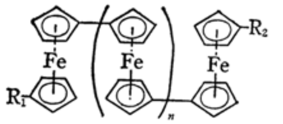
Results and Discussion

The reaction scheme and the products are as follows:



R=H or Li

I $n=0$
II $n=1$
III $n=2$
IV $n=3$
V $n=4$



VI $n=0$, $R_1=n\text{-}C_4H_9$, $R_2=H$
VII $n=0$, $R_1=R_2=n\text{-}C_4H_9$
VIII $n=1$, $R_1=n\text{-}C_4H_9$, $R_2=H$
IX $n=2$, $R_1=n\text{-}C_4H_9$, $R_2=H$

The reaction products in the presence of *n*-butyl bromide were found to be biferrocenyl (I), terferrocenyl (II), quaterferrocenyl (III), quinqueferrocenyl (IV), sexiferrocenyl (V), monobutyl-biferrocenyl (VI), dibutyl-biferrocenyl (VII), monobutyl-terferrocenyl (VIII), and monobutyl-quaterferrocenyl (IX). In the reaction without the halide, however, it was found that biferrocenyl, terferrocenyl and monobutyl-terferrocenyl were the main products. All of these products except biferrocenyl were confirmed to be heteroannularly-bonded compounds. Their structures were established by means of their infrared, NMR and ultraviolet spectra, molecular weight determinations, elemental analyses, and by the behavior of these compounds in the chromatographic separation.

The Reactions of Ferrocenyllithium and Cobaltous Chloride.—The reaction conditions and the rate of the conversion of ferrocene into the condensation products are shown in Table I. The conversion rate in Run A was 36.2%, while in Run B it was 4.8%, in spite of the longer reaction period. This indicates that the presence of alkyl halide greatly affected the conversion of ferrocenyllithium into the condensation products. The reaction products, separated by chromatography, are listed in Table II.

In the reaction without the halide the present authors observed the formation of orange-red crystals which are apparently different from ferrocene and may be suspected to be an intermediate compound. Moreover, it is noticeable that, after the reaction was complete, a fine, almost black solid was found in the bottom of the flask. This solid was proved to be so sensitive to water that it rapidly changed

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[1] K. Hata, I. Motoyama and H. Watanabe, This Bulletin, **36**. 1698 (1963).

[2] K. Hata, I. Motoyama and H. Watanabe, ibid., **39**, 784 (1966).

[3] K. Hata, I. Motoyama and H. Watanabe, ibid., **37**, 1719 (1964).

[4] D. Bryce-Smith, *J. Chem. Soc.*, **1956**, 1603.

[5] M. S. Kharasch, D. W. Lewis and W. R. Reynolds, *J. Am. Chem. Soc.*, **65**, 498 (1943).

[6] G. Wittig and G. Lehmann, *Chem. Ber.*, **90**, 875 (1957).

[7] I. J. Spilners and J. P. Pellegrini; The 148th National Meeting of the American Chemical Society, Division of Organic Chemistry, Chicago, Illinois, August 31 to September 4, 1964; *Chem. & Eng. News*, **42**, 47 (1964); *J. Org. Chem.*, **30**, 3800 (1965).

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

Table I. The reaction conditions and the results

Run	Lithiation		Reaction with $CoCl_2$		Conversion rate of ferrocene %
	Mol. ratio *n*-BuLi/FcH	Time, hr. Temp., °C	Mol. ratio *n*-BuBr : $CoCl_2$: FcH	Time, hr. Temp., °C	
A	2	73 $^1/_6$ −30 to room temp.	1 : 0.23 : 1	45 5 to 35	36.2
B	2	71 $^1/_{12}$ −30 to room temp.	0 : 0.23 : 1	72 room temp. to 33	4.8

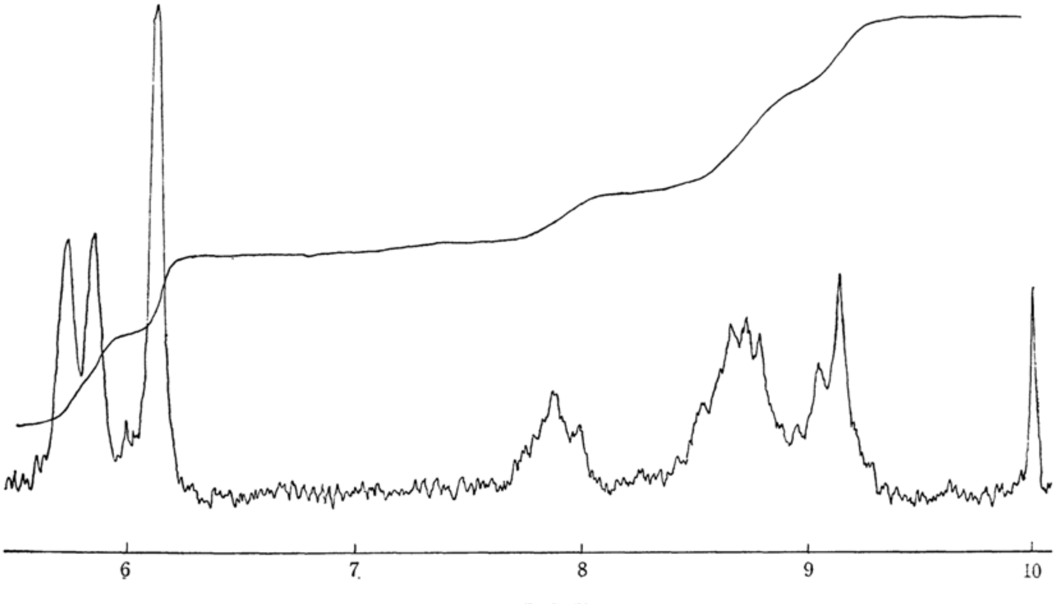


Fig. 1. NMR spectrum of dibutyl-biferrocenyl (VII).

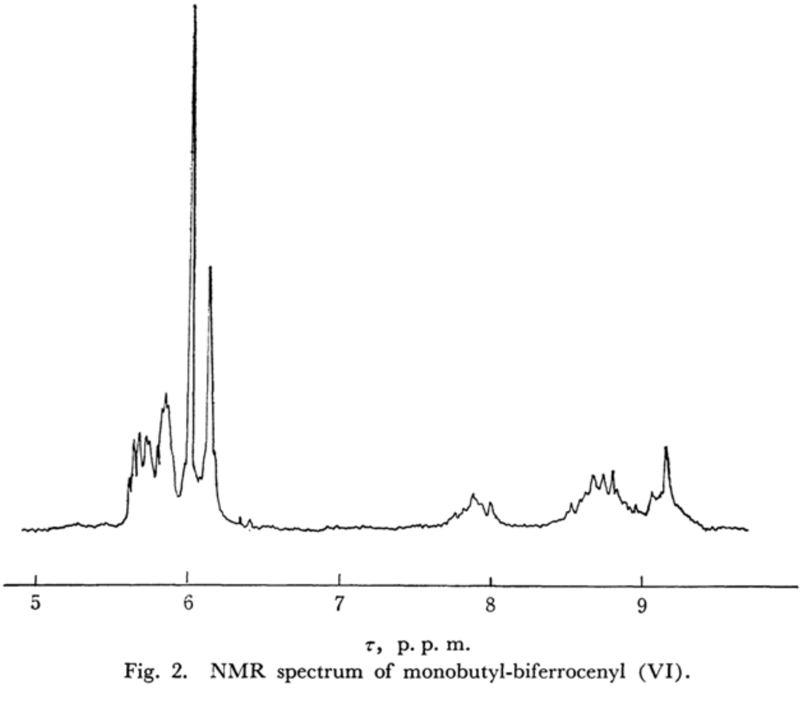


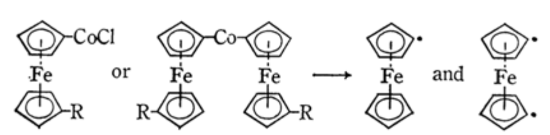
Fig. 2. NMR spectrum of monobutyl-biferrocenyl (VI).

TABLE II. THE PRODUCTS OBTAINED BY CHROMATOGRAPHIC SEPARATION AND THE ANALYTICAL RESULTS

Order of the elution	Product	M. p., °C[a]	Composition[b] and yields,[c] %	
			Run A	Run B
1st	Dibutyl-biferrocenyl (VII)	52.0—53.0	1.0 (0.3)	±
2nd	Monobutyl-biferrocenyl (VI)	68.2—70.2	11.0 (3.4)	16.1 (0.5)
3rd	Biferrocenyl (I)	233.8—234.5	27.9(11.2)	45.5 (1.9)
4th	Monobutyl-terferrocenyl (VIII)	113.0—115.0	2.5 (0.8)	±
5th	Terferrocenyl (II)	226.5—227.2	11.9 (5.7)	5.9 (0.2)
6th	Monobutyl-quaterferrocenyl (IX)	177.4—179.4	0.7 (0.2)	0
7th	Quaterferrocenyl (III)	280	17.9 (4.0)	±
—	Quinqueferrocenyl (IV)	240—245	0.2 (0.1)	±
—	Sexiferrocenyl (V)	252—256	2.8 (1.1)	±

a) All melting points were measured in sealed capillary.
b) Percentage composition of the products, any unidentified products being excluded in the table.
c) The yields, calculated on the basis of used ferrocene, are shown in parentheses.

into a fine orange solid, which seemed to be ferrocene, upon contact with water. Since ferrocenyllithium is yellow or orange, this reactive substance may be inferred to be an intermediate compound, something like X or XI, derived from ferrocenyllithium and cobaltous chloride. Probably, the homolytic fission of the intermediate affords the ferrocenyl radical (XII) and the ferrocenylene biradical (XIII), as has been reported in connection with phenyl derivatives by Kharasch and his co-workers⁵⁾ and by Wilds and McCormack.⁹⁾



X XI XII XIII

R=H, Li or CoCl R=H, Li, CoCl, or -Co-

In the present experiment, however, it could not be elucidated from which intermediate, X or XI, the ferrocenyl and ferrocenylene radicals were derived. Nevertheless, it may be concluded that the formation of many polynuclear ferrocenes is attributable to the coupling reactions of these radicals, and that the presence of alkyl halide in the reaction system facilitates the formation of these radicals. Besides, alkyl halide itself is subjected to homolytic fission to give the alkyl radical, which then couples with ferrocenyl and ferrocenylene radicals to afford alkylated polyferrocenyls. The formation of some cyclic product was expected from the radical mechanism, as has been reported by Wittig and Lehmann⁶⁾ on biphenyl series, but no cyclic compounds such as biferrocenylene and polyferrocenylene were isolated at all from the reaction product. This is probably due to the steric inhibition of the radical coupling reaction and/or to the termination of the chain coupling by the ferrocenyl or the butyl radical.

Spectroscopic Behavior of the Products.—The structures of the products which were soluble in organic solvents were mainly assigned by means of their NMR spectra.

In the chromatographic separation of the products (Table II), the first elution gave rise to a red-orange compound (VII; m. p. 52.0—53.0°C), the NMR spectra of which is shown in Fig. 1. Three multiplet signals of eighteen protons, centered at τ 7.89, 8.73 and 9.14, are apparently due to the two butyl groups on the biferrocenyl nuclei. Nagai and his co-workers¹⁰⁾ pointed out that, in general, the four protons of the cyclopentadienyl ring with an alkyl group are subjected to the shielding effect from the alkyl group, and that a singlet signal appears at

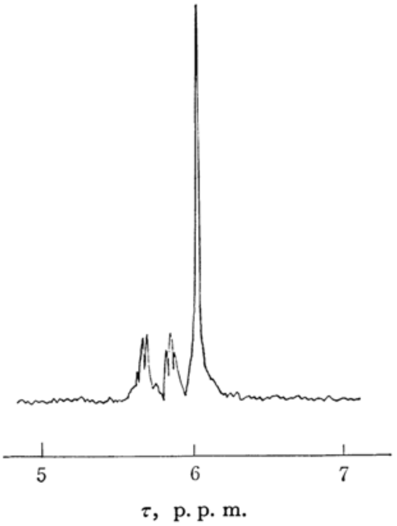


Fig. 3. NMR spectrum of biferrocenyl (I).

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9) A. L. Wilds and W. B. McCormack, *J. Org. Chem.*, ibid., **14**, 45 (1949).

10) Y. Nagai, J. Hooz and R. A. Benkeser., This Bulletin, **37**, 53 (1964).

TABLE III. THE CHEMICAL SHIFTS OF THE PRODUCTS1) (τ value)

Compound	$H_{u.r.}$2)	$H_{\alpha,\beta}$3)	$H_{s.r.}$4)	$H_{b.}$5)
FcH	5.85(10)	—	—	—
I	6.03(10)	5.68 (4); 5.85 (4)	—	—
II	6.03(10)	5.79 (8); 5.88 (8) 5.84 6)	—	—
VI	6.02 (5)	5.70 (4); 5.85 (4)	6.14 (4)	7.87, 8.85, 9.15 (9)
VII	—	5.73 (4); 5.85 (4)	6.13 (8)	7.89, 8.73, 9.14(18)
VIII	6.06 (5)	5.86 6)(16)	6.18 (4)	7.95, 8.75, 9.18 (9)
IX	6.07 (5)	5.91 6)(24)	6.18 (4)	8—9.5 (9)

1) The values in parentheses are relative intensities.
2) Unsubstituted ring protons.
3) Alpha and beta protons on directly bonded rings.
4) Protons on the ring substituted with one butyl group.
5) Protons of butyl group.
6) Value of the center of multiplet signal.

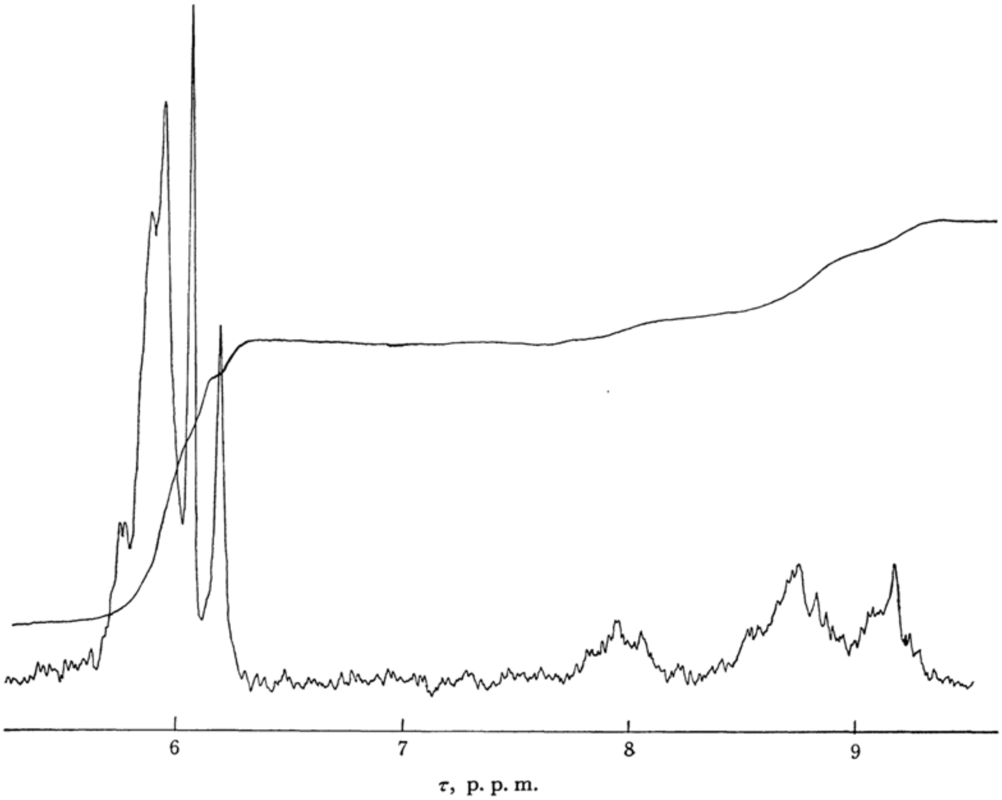

Fig. 4. NMR spectrum of monobutyl-terferrocenyl (VIII).

a higher field than that of the protons of the unsubstituted ring. Further, it is known that two directly-bonded ferrocene nuclei in biferrocenyl or its derivatives exert a strong mutual deshielding effect on the α and β protons in the bonded ring. From these facts, and by a comparison with the spectrum of monobutyl-biferrocenyl (Fig. 2. see below), the eight-proton singlet signal at τ 6.13 may be said to be due to the protons on the two rings respectively substituted with one butyl group, while the remaining two signals of four protons, centered at τ 5.73 and 5.85, are assignable to the α and β protons respectively. Therefore, this compound was determined to be heteroannularly-dibutylated biferrocenyl (VII).

The second elution gave a compound (VI; m. p. 68.2—70.2°C), the NMR spectrum of which is shown in Fig. 2. The singlet signal at τ 6.14 is due to the four protons on the substituted ring with a butyl group. The singlet signal at τ 6.02 is due to the five protons on an unsubstituted ring, and the two four-proton multiplet signals at τ 5.70 and

5.85 respectively to the α and β protons on the two directly-bonded rings. The signals of a butyl group appear at a higher field (centered at τ 7.87, 8.85 and 9.15). From these analyses this compound was identified as heteroannularly-monobutylated biferrocenyl (VI).

The NMR spectrum of biferrocenyl (I), obtained from the fraction of the third elution, shows only three signals (Fig. 3), as has been reported by Goldberg.[11] A singlet signal at τ 6.03 is attributable to ten protons on the two unsubstituted rings, and two triplet signals at τ 5.68 and 5.85 respectively to the α and β four protons on the directly-bonded rings.

The orange-red compound VIII melting at 113.0—115.0°C, obtained from the fraction of the fourth elution, shows a spectrum similar to that of monobutyl-biferrocenyl (see Fig. 4). By a compraison of the τ values of the signals and the intensities of the resonance peaks in Fig. 4 and Fig. 2, the compound VIII was identified as heteroannularly-bonded monobutyl-terferrocenyl.

The compound II, m. p. 226.5—227.2°C, obtained from the fraction of the fifth elution, was identified as terferrocenyl. Its NMR spectrum is shown in Fig. 5. A singlet signal at τ 6.03 is assignable to the ten protons on the two unsubstituted rings, while a multiplet signal centered at τ 5.84 is assignable to the sixteen protons on the four directly-bonded rings.

The orange-red compound IX melting at 177.4—179.4°C, obtained from the fraction of the sixth elution, exhibits the NMR spectrum shown in Fig. 6. By a treatment similar to that of monobutylterferrocenyl (VIII), the compound IX was presumed to be monobutylated quaterferrocenyl.

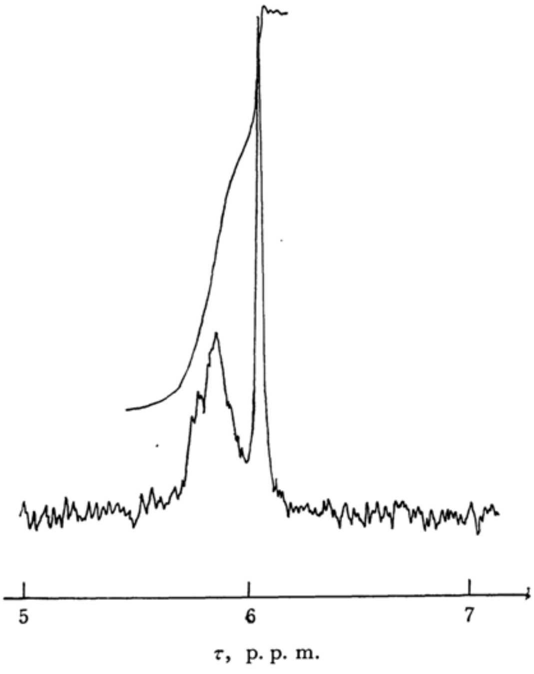

Fig. 5. NMR spectrum of terferrocenyl (II).

All of the peaks of the NMR spectra described above are summarized in Table III.

The NMR spectra of the remaining products, III, IV and V, were not available, for these compounds were insoluble in the solvent necessary for the observation of the spectra. The structures of these compounds were determined by other means to be heteroannularly-bonded quaterferrocenyl, quinqueferrocenyl and sexiferrocenyl.

As is shown in Figs. 7 and 8, the infrared absorption spectra of five polyferrocenyls (I—V) and of four butylated polyferrocenyls (VI—IX) are respectively very similar, while slight differences appeared mainly in the regions near 1100 and 900—800 cm^{-1}.

It is well known that the 9 and 10 μ bands are, respectively, due to unsubstituted ring breathing and to C–H bending in the plane. These absorption bands are very useful in distinguishing monosubstitution and heteroannular disubstitution in mononuclear ferrocene derivatives.[12] However, in the absorption spectra of heteroannularly-disubstituted biferrocenyl VII (Fig. 8), both 9 and 10 μ bands are observed in spite of the lack of an unsubstituted ring. Similar observations have been reported by several investigators.[13] Thus, it is obvious that the 9—10 rule is only applicable to mononuclear ferrocene derivatives.

By a careful comparison of the spectrum of compound VII with those of polyferrocenyls I—V, however, slight differences are found; there are two absorption bands in the latter in the 9 μ region (1105 and 1100 cm^{-1}). The band at 1105 cm^{-1} may be attributable to the directly-bonded ring breathing, and the band at 1100 cm^{-1}, to the unsubstituted ring breathing.

The ultraviolet absorption spectra of ferrocene, biferrocenyl (I) and terferrocenyl (II) in cyclohexane are shown in Fig. 9. As may be seen in the figure, the latter two compounds display the K-band at 220 and 225 mμ and the B-band in the region near 300 mμ, while ferrocene is inferred to show the K-band in a shorter wavelength region. The bathochromic shifts in this band are due to the increase in the conjugation in these polyferrocenyls. It is interesting that the position and the intensity of the absorption maxima of biferrocenyl are so

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[11] S. I. Goldberg, D. W. Mayo and J. A. Alford., *J. Org. Chem.*, **28**, 1708 (1963).

[12] 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. Kazitzyna, B. V. Lokshin and V. D. Vil'chevskaya, *Doklady Akad. Nauk S. S. S. R.*, **125**, 1037 (1959); *Chem. Abstr.*, **53**, 21857 (1959).

[13] S. I. Goldberg and J. S. Crowell, *J. Org. Chem.*, **29**, 996 (1964); A. N. Nesmeyanov, V. N. Drotz, V. A. Sazonova, V. I. Romanenko, A. K. Prokophiev and L. A. Nikonova, *Izvestia Akad. Nauk S. S. S. R.*, **1963**, 667; K. Yamakawa, N. Ishibashi and K. Arakawa, *Chem. Pharm. Bulletin*, **12**, 119 (1964).

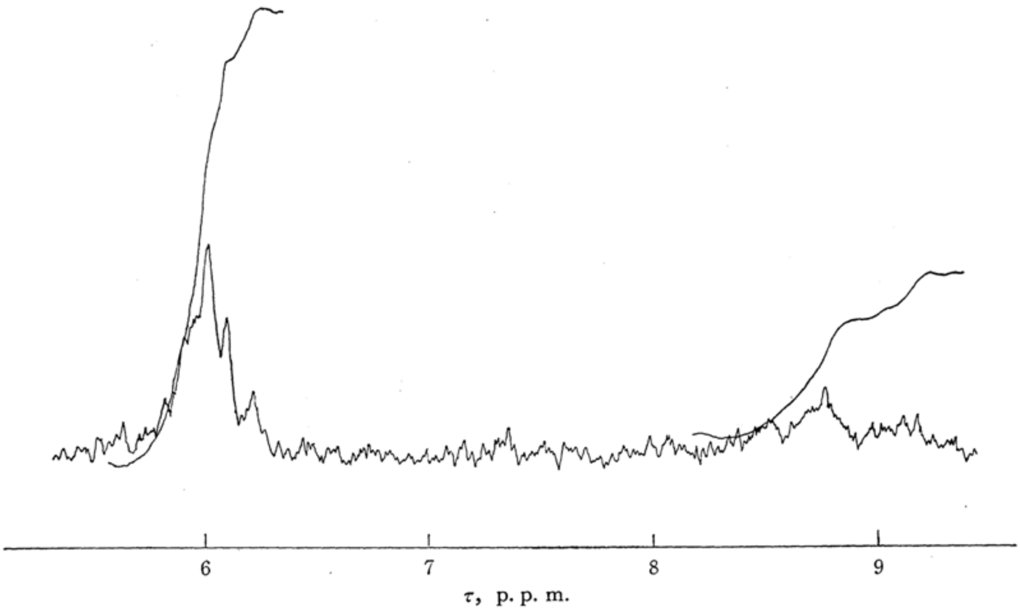

Fig. 6. NMR spectrum of monobutyl-quaterferrocenyl (IX).

similar to those of terferrocenyl that the effect of the accumulation of ferrocene nuclei on the spectra can hardly be recognized, while it is distinguished in para-polyphenyls.[14]

Chromatographic Behavior and Solubilities of the Products.—The order of the elution of the reaction products in the chromatographic separation (Table II) suggests that, in the series of polynuclear ferrocenes, the adsorbability on alumina increases according to the increase in the molecular weight, and that the increase in the number of butyl substituents on the polynuclear ferrocene nuclei causes a decrease in the adsorbability. Thus, as a whole, the order of the adsorbability on alumina is as follows: dibutyl-biferrocenyl < monobutyl-biferrocenyl < biferrocenyl < monobutyl-terferrocenyl < terferrocenyl < monobutyl-quaterferrocenyl < quaterferrocenyl < other polyferrocenyls (IV and V).

Among these compounds, alkylated polynuclear ferrocenes are soluble in common organic solvents, but polyferrocenyls without any alkyl group are less soluble than those of alkylated compounds. The solubilities of the series of polynuclear ferrocenes decrease with the increase in the molecular weight; quaterferrocenyl is almost insoluble, and quinque- and sexiferrocenyl are quite insoluble. Therefore, the latter two compounds could not be purified by the recrystallization method. In contrast, terferrocenyl was purified by recrystallization and chromatography on alumina.

The Polymorphism of Terferrocenyl.—It was found that, when the sample of terferrocenyl was crystallized from different solvents, the crystals were obtained in polymorphic forms, although no remarkable difference was observed between their melting points (around 226°C). The crystals obtained from benzene, ethanol, and ethyl acetate solution showed identical infrared absorption bands (Fig. 10). On the other hand, the spectrum of the crystals obtained by the crystallization from a large amount of petroleum ether (Fig. 11) was quite different in the region of the finger print from those of the former. The sample crystallized from the mixture of benzene and petroleum ether again showed a different spectrum (Fig. 12). The X-ray diffraction pattern of each crystal was also observed; the results were consistent with those of the infrared spectra, as is shown in Figs. 10—12. It was also found from the infrared spectra and X-ray diffraction patterns that the crystals obtained by the rapid cooling method in the crystallization are mixtures of the polymorphic forms described above, even when the same solvents were used.

The polymorphism of terferrocenyl may be accounted as a rotational isomerism (which belongs to the molecular polymorphism) about the central ferrocene nucleus, caused by rotation around the axis connecting the two cyclopentadienyl rings through an iron atom. It is also probable that the polymorphism is due to the variation in the arrangement of molecules in the crystal lattice caused by any hydrogen bonding possibly present.

Experimental

General.—Ferrocene was prepared according to the method previously reported by the present authors.[15]

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[14] A. E. Gillam and D. H. Hey, *J. Chem. Soc.*, **1939**, 1170.

[15] H. Watanabe, I. Motoyama and K. Hata, This Bulletin, **38**, 853 (1965).

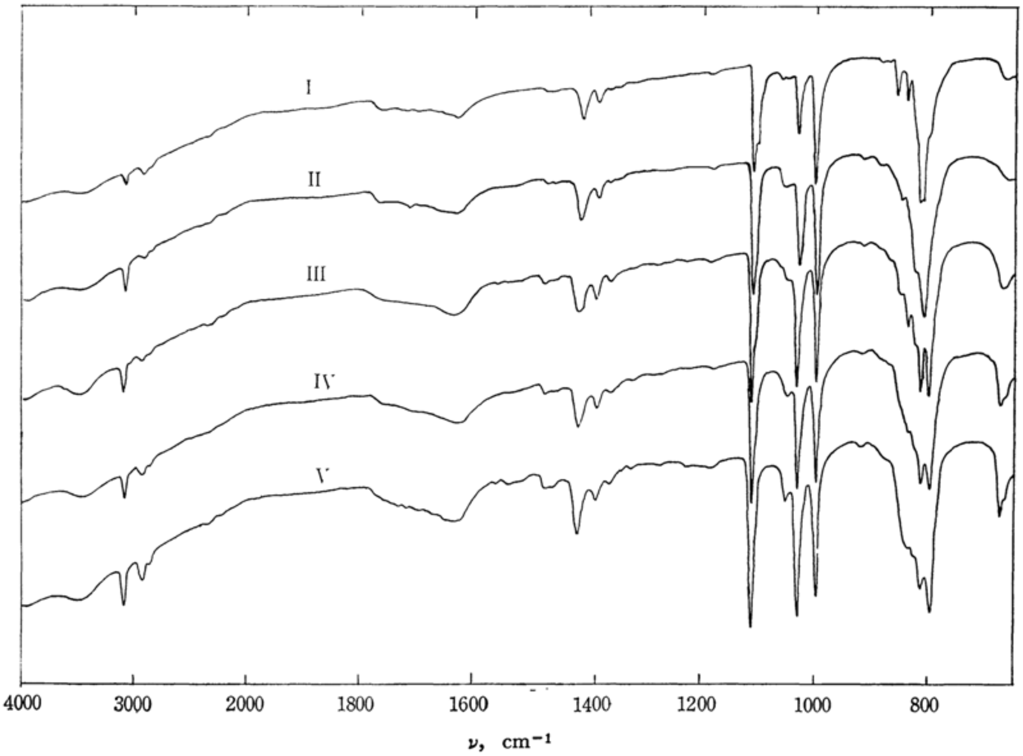

Fig. 7. Infrared spectra of polyferrocenyls (KBr disk method).

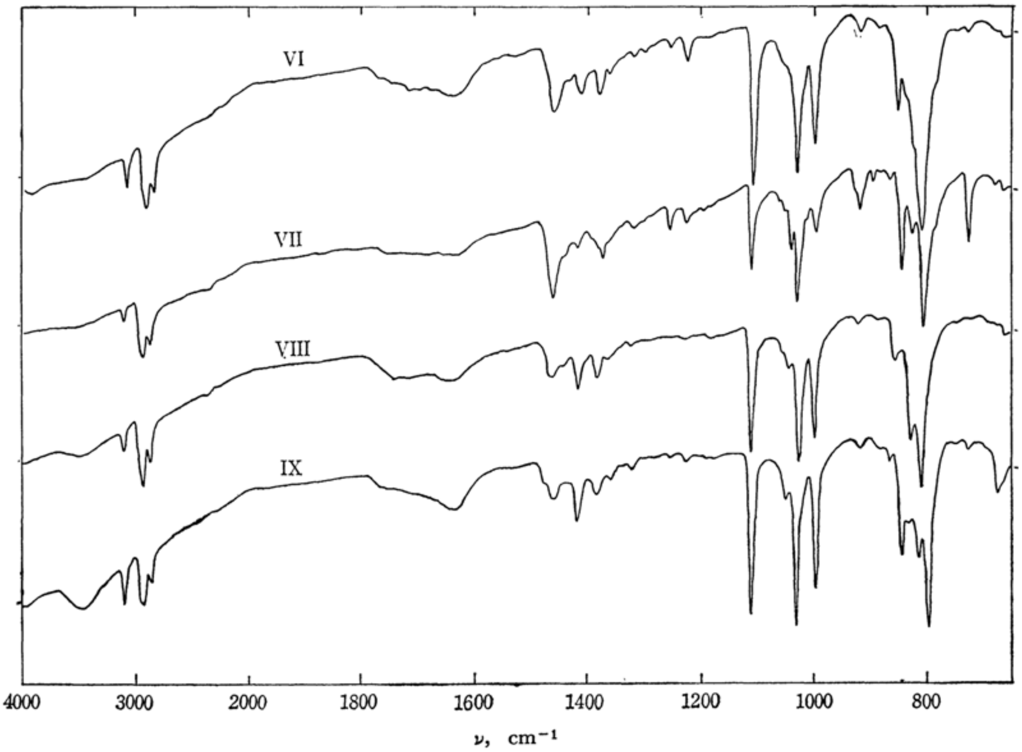

Fig. 8. Infrared spectra of butylated polyferrocenyls (KBr disk method).

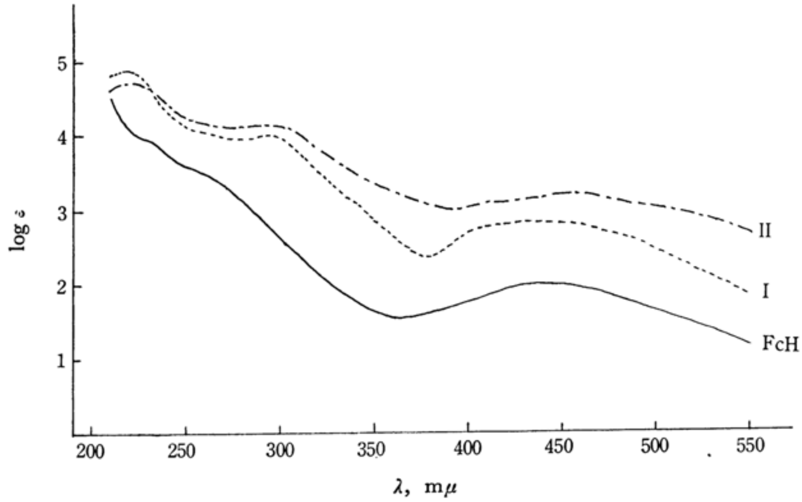

Fig. 9. Ultraviolet spectra of ferrocene, biferrocenyl (I) and terferrocenyl (II) in cyclohexane.

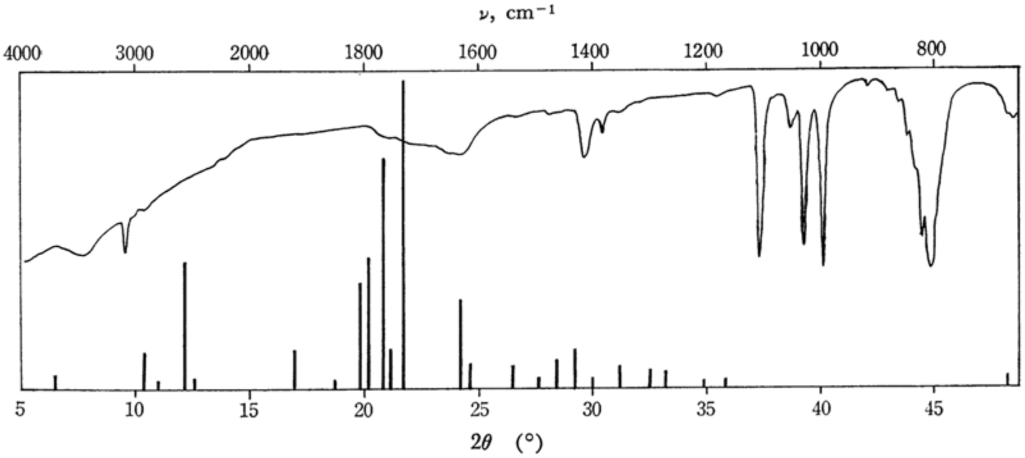

Fig. 10. Infrared spectrum and X-ray diffraction pattern of terferrocenyl from benzene, ethanol, or ethyl acetate.

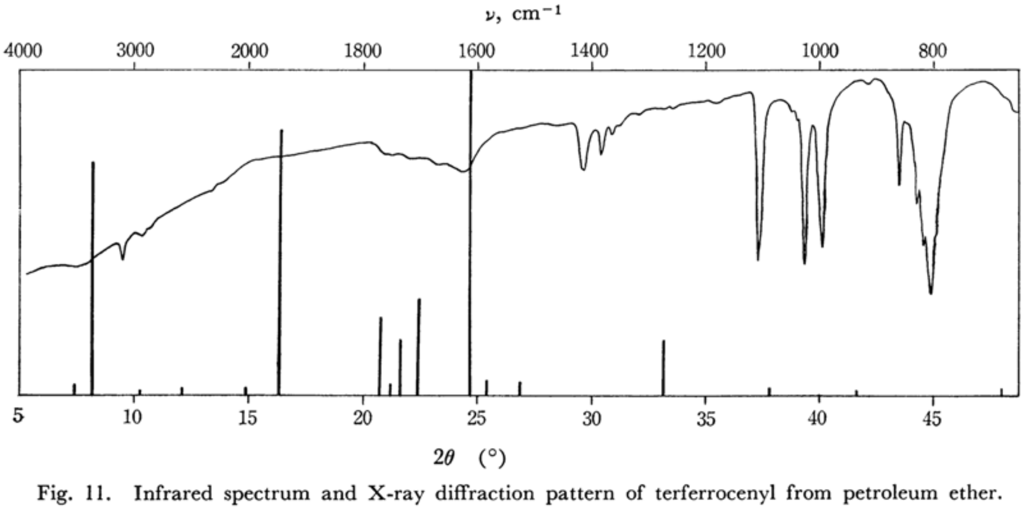

Fig. 11. Infrared spectrum and X-ray diffraction pattern of terferrocenyl from petroleum ether.

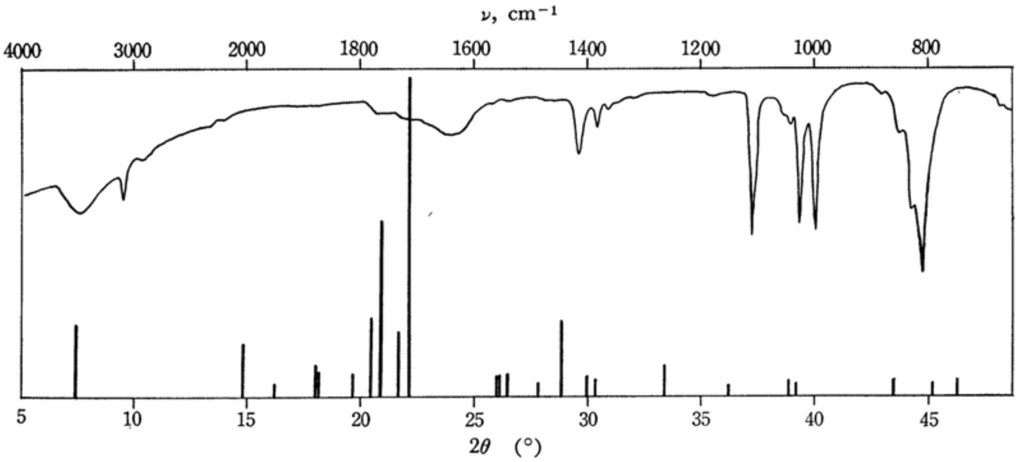

Fig. 12. Infrared spectrum and X-ray diffraction pattern of terferrocenyl from a mixture of benzene and petroleum ether.

The temperatures in the reactions and measurements were uncorrected, and each melting point was determined in a sealed capillary except for the case of the particular description. The NMR spectra were determined at 60 Mc. on a Model JNM-C-60 spectrometer (Japan Electron Optics Laboratory Co.) and a Model A-60 spectrometer (Varian Associates) in deuteriochloroform, containing tetramethylsilane as the internal standard. Molecular weight measurements with a vapor pressure osmometer were carried out on a Model 301-A (The Mechrolab Inc.). The infrared spectra were obtained on a Model EPI-S2 spectrometer (Hitachi Co.) by means of potassium bromide disks. The ultraviolet spectra were determined on a Model EPS-3 recording spectrometer (Hitachi Co.) in cyclohexane. Chromatographies were performed on Sumitomo Chemicals' activated alumina (150—250 meshes). After benzene solutions of the samples had been placed on alumina packed into a column with hexane, each component was developed and eluted with the appropriate solvent, as described below. The X-ray diffraction patterns⁽16⁾ of terferrocenyl were obtained on a Model ADX-103 spectrometer (Toshiba Electric Co.) by the powder method. The differences among polymorphic forms from various crystallization methods were determined by a study of the X-ray diffraction patterns and infrared spectra.

The Reaction of Ferrocenyllithium and Cobaltous Chloride in the Presence of *n*-Butyl Bromide (Run A).—According to the method described in a previous paper,⁽2⁾ a suspension of ferrocenyllithium was prepared by stirring 55.8 g. (0.3 mol.) of ferrocene and 0.6 mol. of *n*-butyllithium in anhydrous ether under an atmosphere of nitrogen. In this experiment, the lithiation took 72 hr. at room temperature.

Anhydrous cobaltous chloride (9.1 g., 0.07 mol.), obtained from its hydrate,⁽17⁾ was added to the oragne suspension of ferrocenyllithium in an atmosphere of nitrogen, and then 14.4 g. (0.105 mol.) of *n*-butyl bromide was added at room temperature through a dropping funnel. An exothermic reaction took place with an evolution of gas and a vigorous refluxing, but the latter subsided when the flask was immersed into an ice-water bath. Then, the additional main part (26.70 g.; 0.195 mol.) of *n*-butyl bromide was added at one time. Immediately the vigorous refluxing of ether broke out again; it was again suppressed by cooling. After the mixture had been stirred for 44 hr. at room temperature, it was heated to reflux for another hour. The dark brown suspension thus obtained was poured into a large amount of ice water in order to hydrolyze the reactive compounds. On filtration, the reaction mixture was separated into two parts: (1) the filtrate, consisting of an ethereal layer and an aqueous layer, and (2) the residue on the filter. The following is the work-up for the two parts:

1) The ethereal layer was separated, and the aqueous layer was repeatedly extracted with ether. After the complete evaporation of ether from the combined ethereal solutions, the residue was submitted to sublimation in order to collect the unreacted ferrocene (35.6 g. recovery; the percentage of converted ferrocene: ca. 36.2%). After the sublimation, 15.5 g. of an orange-red solid (Substance A) remained; this was chromatographed on alumina.

2) The residue on the filter was washed with a sufficient amount of water and ether, and then left stand until it almost reached dryness in vacuo (water-jet pump). After it had been extracted with ether in a Soxhlet apparatus for ca. 100 hr., 14.7 g. of brown powder remained. This was further triturated with boiling benzene several times (total volume: 1.5 l.). After the trituration, 6.6 g. of a gray residue remained; this was interpreted as being an inorganic material derived from cobaltous chloride. Fine glittering orange-red crystals (0.67 g., Substance B), which separated when the hot benzene solution was cooled, were collected on a filter. The dark red mother liquor was evaporated to dryness in vacuo, and the solid was again dissolved in 600 ml. of boiling benzene. The undissolved material (0.44 g., Substance C) was collected by filtration while hot. After the hot solution had been cooled, 0.55 g. of an orange-red powder (Substance D) separated; this was collected on a filter. The filtrate was concentrated to about 200 ml. and cooled in order to separate

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16) The present authors wish to express their thanks to Dr. M. Ichikuni for taking the X-ray patterns and his kind suggestion.

17) "Inorganic Syntheses," Vol. 5, 153 (1957).

additional crystals. Upon filtration, 0.98 g. of another orange-red powder (Substance E) was obtained. Finally the filtrate was evaporated to remove the benzene; 2.05 g. of a dark red-brown solid (Substance F) was thus obtained.

When the ethereal solution obtained by the Soxhlet-extraction described above was left to stand, 0.33 g. of an orange-red solid material (Substance G) separated. After the filtration, the mother liquor was evaporated to give rise to a red-orange solid material (1.79 g., Substance H).

The Chromatographic Separation and the Identification of Each Product.—*Substance A* (15.5 g.).—After the development with hexane, the elutions of the colored bands in the column were successively performed in the following order.

1) The first elution, with petroleum-benzene (3:1 by volume), yielded 1.0 g. of a yellow-orange liquid, which was then rechromatographed with the same eluent to afford two fractions. The first was an orange liquid (0.22 g.) which solidified to orange crystals upon standing. It was found to be dibutyl-biferrocenyl (VII), which is very soluble in common organic solvents; m. p. 52.0—53.0°C.

Found: C, 70.35; H, 6.96. Calcd. for $C_{28}H_{34}Fe_2$: C, 69.74; H, 7.11%.

The second fraction (0.22 g.) also solidified by itself, upon standing, to orange crystals, which were identified as monobutyl-biferrocenyl (VI) (see below).

2) The second elution, with the same solvent as in 1), yielded 1.95 g. of red-orange crystals which were very soluble in common organic solvents. This compound was identified as monobutyl-biferrocenyl (VI); m. p. 68.0—70.0°C.

Found: C, 67.61; H, 5.95%; mol. wt., 446 (Rast), 400 (vapor pressure osmometer method). Calcd. for $C_{24}H_{26}Fe_2$: C, 67.64; H, 6.19%; mol. wt. 426.

3) The third elution, also with the same solvent as in 1), yielded 5.78 g. of biferrocenyl (I), which melted at 225—234°C under decomposition (in an open capillary).

4) The fourth elution, with petroleum ether - benzene (1 : 1), yielded monobutyl-terferrocenyl (VIII, 0.34 g.), which was purified by rechromatography; m. p. 113.0—115.0°C.

Found: C, 67.07; H, 5.49%; mol. wt., 565 (v. p. o. method). Calcd. for $C_{34}H_{34}Fe_3$: C, 66.93; H, 5.62%; mol. wt., 610.

5) The fifth elution, with the same solvent as in 4), yielded orange crystals of terferrocenyl (II, 1.54 g.). The pure compound, recrystallized from a mixture of benzene and petroleum ether, had a m. p. of 226.5—227.2°C.

Found: C, 65.03; H, 4.73%; mol. wt., 554 (Rast). Calcd. for $C_{30}H_{26}Fe_3$: C, 64.89; H, 4.81%; mol. wt., 554.

6) The last elution, with methanol, gave rise to ca. 1.0 g. of a dark red glassy material. It was supposed to be still a mixture, but no attempt was made to separate and identify the components.

Substance B (0.67 g.).—Substance B melted at 252—256°C and was almost insoluble in common organic solvents. From the various analytical results, this compound was identified as sexiferrocenyl (V).

Found: C, 65.23; H, 4.87%; mol. wt., 1089 (Rast). Calcd. for $C_{60}H_{50}Fe_6$: C, 65.15; H, 4.56%; mol. wt., 1106.

Substances C, D and E (1.97 g. in total).—These substances are in fact the same compound, as is revealed by the identity of their infrared absorption spectra (Fig. 7). From the various analytical results, it was identified as quaterferrocenyl (III). It was insoluble in most common organic solvents, but it could be recrystallized from a large amount of hot benzene; m. p. 280°C.

Found: C, 65.76, 65.84, 65.63; H, 4.83, 4.84, 4.53%; mol. wt., 717, 729 (Rast; perylene being used instead of camphor because of the high melting point of this compond).[6] Calcd. for $C_{40}H_{34}Fe_4$: C, 65.09; H, 4.64%; mol. wt., 738.

Substance F (2.05 g.).—This substance was separated by chromatography into the following six fractions.

1) The first elution, with petroleum ether - benzene (1 : 1), yielded 0.2 g. of crude biferrocenyl; this was recrystallized from a mixture of benzene and petroleum ether to give a pure compound (I); m. p. 228.0—231.0°C.

2) The second elution, with the same solvent as in 1), gave ca. 90 mg. of monobutyl-terferrocenyl (VIII).

3) The third elution, with benzene, provided 0.57 g. of crude terferrocenyl (II, m. p. 214—220°C). The pure compound was obtained by the recrystallization from a mixture of benzene and petroleum ether.

4) The fourth elution, also with benzene, gave orange-red crystals (0.14 g., m. p. 170—173°C). The pure compound, obtained by recrystallization from a mixture of benzene and petroleum ether, had a m. p. of 177.0—179.0°C and was soluble in common organic solvents. The compound was found from the various analytical results to be monobutyl-quaterferrocenyl (IX).

Found: C, 66.24; H, 5.30. Calcd. for $C_{44}H_{42}Fe_4$: C, 66.54; H, 5.33%. The ultraviolet absorption spectrum (in cyclohexane) showed λ_{max} 228 ($\log \varepsilon$ 4.89), 305 (4.29) and 450 mμ (3.25).

5) The fifth elution, also with benzene, gave rise to quaterferrocenyl (III) as an orange-red powder (0.3 g., m. p. 280°C). This was found to be the same compound as Substances C, D and E.

6) The last elution, with methanol, yielded 0.29 g. of a dark red glassy solid. It was supposed to be a mixture, but further treatments were not attempted.

Substance G (0.33 g.).—This substance was repeatedly triturated with a sufficient amount of hot benzene. After the trituration, 55 mg. of a light brown powder remained; m. p. 240—245°C. From various analytical results this compound was identified as quinqueferrocenyl (IV). It is insoluble in common organic solvents.

Found: C, 61.83; H, 4.59%; mol. wt., 903 (Rast: perylene being used). Calcd. for $C_{50}H_{42}Fe_5$: C, 65.11; H, 4.59%; mol. wt., 922.

On the other hand, the evaporation of the benzene solution after the trituration gave 0.254 g. of a red-orange powder. This was dissolved in a small amount of benzene, and then chromatographed on an alumina column.

1) The first elution, with benzene - petroleum ether (4 : 1), yielded biferrocenyl (I) as orange leaflets (10 mg., m. p. 218.0—222.0°C).

2) The second elution, with the same solvent as in 1), gave rise to terferrocenyl (II) as orange crystals (0.77 g.).

3) The third elution, also with the same solvent as

in 1), yielded monobutyl-quaterferrocenyl (IX) as orange-red crystals (20 mg.).

4) The fourth elution, with benzene, gave rise to quaterferrocenyl (III) as orange-red crystals (56 mg., m. p. 278.0—279.5°C, recrystallized from a large amount of benzene).

5) The last elution, with methanol, afforded a dark red glassy solid (47 mg.). This was assumed to be a mixture of many compounds, but their separation and identification were not attempted.

Substance H (1.79 g.).—This substance was dissolved in a small amount of benzene and placed on alumina. The following is the work-up of the elution:

1) The first elution, with petroleum ether - benzene (3 : 1), gave rise to orange crystals (leaflets, 0.25 g.) which were found to be biferrocenyl (I).

2) The second elution, with petroleum ether - benzene (1 : 1), yielded 0.13 g. of fine yellow-orange crystals; these were rechromatographed by using petroleum ether - benzene (3 : 1) to give a pure substance. The compound had a m. p. of 113.0—115.0°C and was identified as monobutyl-terferrocenyl (VIII).

3) The third elution, with the same solvent as in 2), gave terferrocenyl (II, 0.78 g.).

4) A dark red glassy solid was obtained from the fraction of the last elution, but no further treatments were attempted.

The Reaction of Ferrocenyllithium and Cobaltous Chloride (Run B).—To an orange suspension of ferrocenyllithium, prepared from 55.8 g. (0.3 mol.) of ferrocene and 0.6 mol. of *n*-butyllithium according to the method described above, 9.1 g. (0.07 mol.) of anhydrous cobaltous chloride was added at one time. After the addition, a gentle refluxing occurred because of the exothermic reaction, but no cooling procedure was applied. The mixture was allowed to cool to room temperature over a period of 3 hr. The dark brown suspension was then stirred for 70 hr. under a stream of nitrogen at room temperature, and then for an additional hour under refluxing on a water bath. After cooling, the suspension was poured into a large amount of ice water in order to hydrolyze the reactive compounds. The total mixture was filtered to separate it into a solid and a liquid part.

The solid material which remained on the filter was repeatedly washed with a sufficient amount of water and benzene, dried in vacuo at room temperature, and extracted with ether for 8 hr. in a Soxhlet apparatus. The residual gray-black powder (7.77 g.) was conceived to be an inorganic substance derived from cobaltous chloride.

On the other hand, the liquid part from the reaction mixture consisted of an ethereal layer and an aqueous layer. The liquid part was combined with the washings of the solid part and the ethereal solution from the Soxhlet extraction. The combined organic layer was separated from the aqueous layer, and the aqueous layer was repeatedly extracted with ether. All the parts of the organic solution were combined, dried over magnesium sulfate, filtered, and evaporated to obtain an orange-red crystalline substance. It was submitted to vacuum sublimation at 100—120°C under 0.5 mmHg to collect the unreacted ferrocene (53.4 g., 95.5% recovery). The remaining dark red-brown solid (2.33 g.) was dissolved in a small amount of benzene and chromatographed on alumina. The solution of the sample was placed on alumina packed into a column with benzene - pertroleum ether (1 : 1), and the same solvent was used as the developer. Elution was performed as follows:

1) The first elution, with petroleum ether - benzene (1 : 1), gave rise to monobutyl-biferrocenyl (VI, 0.38 g., m. p. 67.0—69.0°C).

2) The second elution, with the same solvent as in 1), yielded biferrocenyl (I, 1.06 g., m. p. 228.5—233.0°C).

3) The third elution, also with the same solvent as in 1), gave an orange solid (59 mg.) which was found to be butyl-polyferrocenyl by a comparison of its infrared spectrum with those of other butyl-polyferrocenyls, such as monobutyl-biferrocenyl and monobutyl-terferrocenyl. It might be crude monobutyl-terferrocenyl, but no further treatments were attempted.

4) The fourth elution, with benzene, yielded terferrocenyl (II, 0.14 g., m. p. 215.0—218.0°C).

5) A dark red-brown glassy solid (0.20 g.) was obtained from the fraction of the elution with methanol. This was inferred to be a mixture which might contain some polyferrocenyls of a greater molecular weight than that of terferrocenyl. However, no further investigation was undertaken.

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