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Syntheses and NMR Spectra of the Substituted Methylferrocenes

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Several 1′- and 2-substituted 1-methylferrocenes were prepared, and their NMR spectra were measured. From the consideration of the chemical shifts, the transmission coefficient of the electronic effect through the ferrocene nucleus was calculated to be 0.28. 1′-Substituted 1-acetylferrocenes were also prepared, and their NMR spectra were discussed in connection with those of methylferrocenes.

Since the discovery of the fact that the unsubstituted ring of acetylferrocene was acetylated about 10^4 times slower than those of ferrocene itself,[1] the transmissivity of the electronic effect of substituents through the ferrocene system has been widely studied. For example, linear relationships have been observed between the Hammett σ constants and various reaction constants, such as the dissociation constants of various heteroannularly-substituted ferrocenecarboxylic acids,[2,3] the quarter-wave potentials in the chronopotentiometric oxidation of mono- and disubstituted ferrocenes,[4] the shifts of the carbonyl stretching frequencies in the IR spectra of substituted ferrocenecarboxylic acids and esters,[5] the rates of the esterification of heteroannularly-substituted ferrocenecarboxylic acids with diphenyldiazomethane,[6] the rates of the desilylation of 1′-alkyl-1-(trialkylsilyl)ferrocenes,[7] the rates of the protodemercuration of bis(1′-substituted ferrocenyl)mercury,[8] and the rates of the solvolysis of 1′-substituted ferrocenylmethylcarbinyl acetates.[9] However, the electronic effect of homoannular substituents has been little studied. Only a few investigations concerning the chemical shifts of the ring protons in monosubstituted ferrocenes[10] and p-substituted phenylferrocenes,[11] and the rates of the acetylation of alkylferrocenes[7] are available.

The chemical shifts of the benzene protons or the side-chain protons in the substituted benzene derivatives have been reported to correlate with Hammett σ constants. For example, the chemical shifts of the methyl groups in p-substituted toluenes have linear correlations with the σ^+ constants.[12] In the present study, the NMR spectra of 1′- and 2-substituted methylferrocenes and of 1′-substituted acetylferrocenes were measured in order to get some information about the transmission of the electronic effect through the ferrocene system. An improved method for preparing these compounds will be presented, together with a discussion of the NMR spectra.

Results and Discussion

Syntheses of 1′-Substituted Methylferrocenes. Since methylferrocene is more reactive toward electrophilic reagents than is ferrocene itself, it always affords a mixture of three isomers on acetylation, dimethylaminomethylation, and chloromercuration.[13] Because of the difficulty of separating the isomers each other, some indirect routes which lead selectively to 1′-isomers were devised in the following manner. When formyl-

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[1] M. Rosenblum, J. O. Santer and W. G. Howells, *J. Amer. Chem. Soc.*, **85**, 1450 (1963).

[2] A. N. Nesmeyanov and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, **115**, 518 (1957).

[3] W. F. Little and R. Eisenthal, *J. Org. Chem.*, **26**, 3609 (1961).

[4] W. F. Little, C. N. Reilley, J. D. Johnson and A. P. Sanders, *J. Amer. Chem. Soc.*, **86**, 1382 (1964).

[5] L. A. Kazitsyna, B. V. Lokshin and A. N. Nesmeyanov, *Dokl. Akad. Nauk SSSR*, **127**, 333 (1959).

[6] W. F. Little and R. Eisenthal, *J. Amer. Chem. Soc.*, **83**, 4936 (1961).

[7] R. A. Benkeser, Y. Nagai and J. Hooz, *ibid.*, **86**, 3742 (1964).

[8] A. N. Nesmeyanov, E. G. Perevalova, S. P. Gubin and A. G. Kozlovskii, *Dokl. Akad. Nauk SSSR*, **178**, 616 (1968).

[9] D. W. Hall, E. A. Hill and J. H. Richards, *J. Amer. Chem. Soc.*, **90**, 4972 (1968).

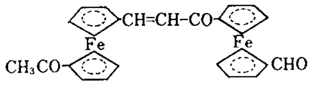
[10] G. G. Dvoryantseva, S. L. Partnova, K. I. Grandgerg, S. P. Gubin and Yu. N. Sheinker, *Dokl. Akad. Nauk SSSR*, **160**, 1075 (1965).

[11] M. Rosenblum, "Chemistry of the Iron Group Metallocenes," Part 1, John Wiley and Sons, Inc., New York, N. Y. (1965), p. 215.

[12] Y. Yukawa, M. Sakai, K. Kabazawa and Y. Tsuno, *Mem. Inst. Sci. Ind. Research Osaka Univ.*, **17**, 185 (1960).

[13] G. R. Knox, I. G. Morrison, P. L. Pauson, M. A. Sandhu and W. E. Watts, *J. Chem. Soc., C*, **1967**, 1853.

ferrocene was acetylated with three molar amounts of acetyl chloride and aluminum chloride in dichloromethane under cooling, only 1′-acetyl-1-formylferrocene was obtained in a 41% yield. Under somewhat severer conditions, two additional products were isolated. The minor product of the two, which was eluted ahead of 1′-acetyl-1-formylferrocene on chromatographic separation on alumina, seemed to be 3-acetyl-1-formylferrocene, judging from its IR and NMR spectra. The other (1.2% yield), which was eluted after 1′-acetyl-1-formylferrocene, was identified to be 1-(1′-formylferrocenyl)-3-(1″-acetylferrocenyl)-2-propen-1-one (**1**) on the basis of its IR and NMR spectra and its elemental analysis. In view of the large coupling constant (15.7 Hz) of the vinyl protons of **1**, it can be concluded that **1** has a *trans* configuration with respect to the olefinic double bond. On the reduction of 1′-acetyl-1-formylferrocene by lithium aluminum hydride-aluminum chloride compelx,[14] 1′-ethyl-1-methylferrocene was obtained in a good yield.



(**1**)

We have reported in a previous paper[15] that when 1,1′-diiodoferrocene was treated with copper(I) cyanide in boiling pyridine, 1′-iodo-1-cyanoferrocene was exclusively obtained. This compound proved to be useful as a starting material for the preparation of 1′-substituted methylferrocenes. On the hydrolysis of 1′-iodo-1-cyanoferrocene in a boiling 40% aqueous potassium hydroxide solution for 15 hr, 1′-iodo-1-ferrocenecarboxylic acid was obtained in a 74% yield, whereas the reaction for 4 hr gave 1′-iodo-1-ferrocenecarboxamide as the main product (77% yield). This can be explained by assuming that the reaction may be suppressed by the electron-attracting effect of the iodo group, since 1′-ethyl-1-cyanoferrocene can be hydrolyzed within a shorter period to give, quantitatively, 1′-ethyl-1-ferrocenecarboxylic acid.[16] 1′-Iodo-1-ferrocenecarboxylic acid gave its methyl ester when treated with diazomethane in an ice bath. The reduction of the ester with lithium aluminum hydride and aluminum chloride afforded 1′-iodo-1-methylferrocene in a poor yield. Since no dehalogenated product was detected, this low yield seems to be due to the decomposition of the starting material by the action of the reducing agent. 1′-Iodo-1-methylferrocene was converted into 1′-cyano- and 1′-chloro-1-methylferrocene when treated with copper(I) cyanide and chloride respectively.[15]

Syntheses of 2-Substituted 1-Methylferrocenes. It has recently been reported that 2-haloferrocenylmethanol[17] could be obtained from 2-lithio-1-(dimethylaminomethyl)ferrocene.[18,19] This procedure has now been applied to the synthesis of 2-halo-1-methylferrocenes; 2-bromo- and 2-chloro-1-ferrocenylmethanol thus obtained were reduced with lithium aluminum hydride-aluminum chloride complex to give the corresponding 2-halo-1-methylferrocene in a moderate yield. When 2-chloro-1-methylferrocene was heated with copper(I) cyanide in γ-picoline at 145°C, 2-cyano-1-methylferrocene was obtained in a 22% yield. On the other hand, 2-ethyl-1-methylferrocene was obtained in a good yield on the Clemmensen reduction of 2-acetyl-1-methylferrocene.[20]

NMR Spectra. The NMR spectra of 2- and 1′-substituted methylferrocenes thus obtained were measured as about a 20% solution in carbon tetrachloride, while those of 1′-substituted acetylferrocenes were measured in deuteriochloroform.

Table 1. The chemical shifts of acetyl protons in 1′-substituted 1-acetylferrocenes in deuteriochloroform

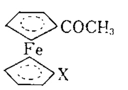
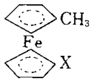
	Substituent (X)	Chemical shift(δ) (Hz)	$\Delta\delta$ (Hz)
	C_2H_5	142.1	−1.1
	H	143.2	0.0
	Cl	144.1	0.9
	CN	145.7	2.5
	$COCH_3$	140.8	−2.4
	$COOCH_3$	141.8	−1.4

Table 2. The chemical shifts of methyl protons in 1′-substituted 1-methylferrocenes in carbon tetrachloride

	Substituent (X)	Chemical shift (δ) (Hz)	$\Delta\delta$ (Hz)
	C_2H_5	116.2	−1.0
	H	117.2	0.0
	Cl	118.1	0.9
	CN	120.5	3.3

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[14] K. Schlögl, A. Mohar and M. Peterlik, *Monatsh. Chem.*, **92**, 921 (1961).

[15] M. Sato, T. Ito, I. Motoyama, K. Watanabe and K. Hata, This Bulletin, **42**, 1976 (1969).

[16] A. N. Nesmeyanov, V. A. Sazonova and V. N. Drozd, *Dokl. Akad. Nauk SSSR.*, **137**, 102 (1961).

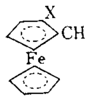
[17] G. Marr, R. E. Moore and B. W. Rockett, *J. Chem. Soc., C*, **1968**, 24.

[18] D. W. Slocum, B. W. Rockett and C. R. Hauser, *J. Amer. Chem. Soc.*, **87**, 1241 (1965).

[19] R. L. Gay, T. F. Crimmins and C. R. Hauser, *Chem. Ind.* (London), **1966**, 1635.

[20] E. A. Hill and J. H. Richards, *J. Amer. Chem. Soc.*, **83**, 4216 (1961).

TABLE 3. THE CHEMICAL SHIFTS OF METHYL PROTONS IN 2-SUBSTITUTED 1-METHYLFERROCENES IN CARBON TETRACHLORIDE

	Substituent (X)	Chemical shift (δ) (Hz)	$\Delta\delta$ (Hz)
	C_2H_5	114.8	−2.4
	H	117.2	0.0
	Cl	121.9	4.7
	CN	129.5	12.3
	$COCH_3$	134.3	17.1

The chemical shifts of these methyl and acetyl protons are summarized in Tables 1, 2, and 3.

In order to examine the substituent effects, the relative chemical shifts ($\Delta\delta$) of the protons in each series were plotted *versus* the Hammett σ_p constants. These results are shown in Fig. 1 for 1′-substituted acetylferrocenes and in Fig. 2 for 1′- and 2-substituted methylferrocenes. It is clear from Fig. 1 that an excellent linear correlation is present between the Hammett σ_p constants and the chemical shifts of the acetyl protons of 1′-substituted 1-acetylferrocenes and acetylferrocene itself, except for those of 1′-acetyl- and 1′-methoxycarbonyl-1-acetylferrocene. An irregularity observed in the compounds containing an extra carbonyl substituent is considered to be due to the large magnetic anisotropy of the carbonyl group.[21] Therefore, the substituent effects will be discussed on the basis of the shifts observed with substituents other than the carbonyl-containing substituent. The same limitation was applied in the consideration of the chemical-shift differences between 1′- and 2-substituted methylferrocenes, and good correlations were observed between the chemical shifts of the methyl protons and the Hammett σ_p constants in either series. The following equations are those of the regression lines, shown in Figs. 1 and 2, which were calculated by the method of least squares:

$$\Delta\delta = 4.4\,\sigma_p + 0.1$$

for 1′-substituted 1-acetylferrocenes,

$$\Delta\delta = 5.2\,\sigma_p - 0.2$$

for 1′-substituted 1-methylferrocenes, and

$$\Delta\delta = 18.3\,\sigma_p + 0.3$$

for 2-substituted 1-methylferrocenes.

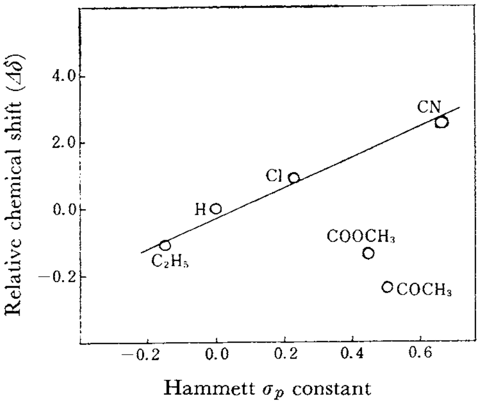


Fig. 1. Plot of the relative chemical shifts of 1′-substituted 1-acetylferrocenes against Hammett σ_p constant.

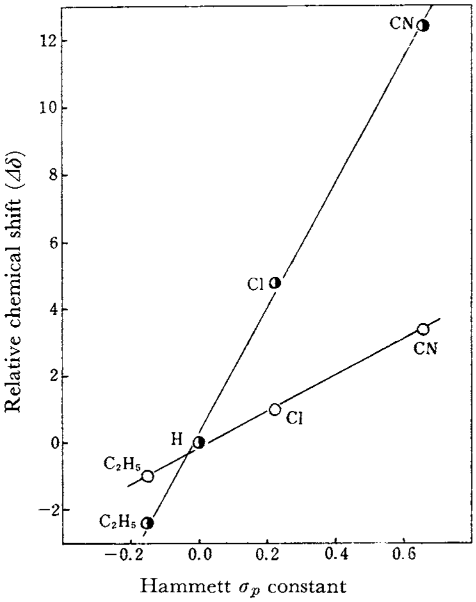


Fig. 2. Plot of the relative chemical shifts of substituted methylferrocenes against Hammett σ_p constant: ◑, 2-derivatives; ○, 1′-derivatives.

It is quite interesting that an excellent linear relationship, one with a correlation coefficient more than the 0.99 for the methylferrocene series, was found between the chemical shifts in the acetylferrocenes or methylferrocenes and the Hammett σ_p constants, while good correlations were not found with the other σ constants, such as σ_m, σ^+, and σ^*. In accordance with these observations, there have been reported many findings that various chemical behaviors of ferrocene derivatives correlated with Hammtt σ_p constants.[2-9]

As may be seen in Fig. 2, the chemical shifts of methyl protons in 2-substituted 1-methylferrocenes were found to correlate with Hammett σ_p constants, while no linear correlation was found with the σ^+ constants. A similar tendency had already been reported for those of the cyclopentadienyl ring protons in *p*-substituted phenylferrocenes, but without any detailed discussion.[11] On the other hand, it has been found that the chemical shifts of methyl protons in *p*-substituted toluenes and acetyl protons in *p*-substituted acetophenones correlated linearly

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[21] M. I. Levenberg and J. H. Richards, *J. Amer. Chem. Soc.*, **86**, 2634 (1964).

with the σ^+ constants.[12] The difference between the observations of ferrocene derivatives and of benzene derivatives suggests that the transmission of an electronic effect in 2-substituted methylferrocene might be through some way different from such a resonance effect of the substituent as was seen in benzene derivatives. The transmission of an electronic effect in ferrocene derivatives is probably through the total electron density of the ferrocene nucleus, without the loss of its stability due to the aromaticity.

It is clear from Fig. 2 that the regression lines for 1′- and 2-substituted methylferrocenes have different slopes. These differences can undoubtedly be attributed to the differences in the transmissivity of the electronic effect of the substituent. Hence, the ratio of these slopes, 0.28, may be considered to be the transmission coefficient of the electrnoic effect through the ferrocene nucleus. A similar value (0.22) was reported by Butter and Beachell,[22] who calculated it on the basis of the data reported by Nagai *et al.*[23] On the other hand, a transmission coefficient through a benzene ring was reported to be 0.37;[24] this was calculated on the basis of the dissociation constants of substituted 4-biphenylcarboxylic acids. In view of the intervention of an iron atom in the transmission of the electronic effect through the ferrocene ring, a smaller value is to be expected for the transmission coefficient through the ferrocene nucleus than for that through the benzene ring. Therefore, the value (0.28) obtained in this investigation seems reasonable.

Experimental

1′-Iodo-1-ferrocenecarboxylic Acid. 1′-Iodo-1-cyanoferrocene (1.12 g), which had been prepared from 1,1′-diiodoferrocene by a procedure reported previously,[15] was refluxed for 15 hr with 7.5 m*l* of a 40% aqueous potassium hydroxide solution and 16 m*l* of ethanol. The dark reaction mixture was then filtered out. The filtrate was acidified with dilute hydrochloric acid and extracted with ether, and then the ethereal solution was dried over anhydrous magnesium sulfate. The evaporation of the solvent gave red-orange crystals of 1′-iodo-1-ferrocenecarboxylic acid in a 73.7% yield; the acid was then recrystallized from benzene, mp 138.5°C (decomp.).

Found: C, 37.43; H, 2.42%. Calcd for $C_{11}H_9IFe$: C, 37.08; H, 2.52%.

The dark orange solid remaining after the filtration of the reaction mixture was dissolved in chloroform. After the insoluble matters had been filtered off, the filtrate was washed with water and dried over anhydrous magnesium sulfate. By evaporating the solvent, orange crystals of 1′-iodo-1-ferrocenecarboxamide were obtained (0.21 g, 18.7% yield); these were recrystallized from *n*-hexane, mp 136—137.5°C.

Found: C, 37.76; H, 3.17; N, 4.11%. Calcd for $C_{11}H_{10}ONIFe$: C, 37.18; H, 2.82; N, 3.94%.

When the same reaction was stopped after 4 hrs' heating, the main product was the amide (77.1% yield), while the minor product was the acid (14.6%). No recovery of unchanged nitrile was observed in either reaction.

Methyl 1′-Iodo-1-ferrocenecarboxylate. A solution of 1′-iodo-1-ferrocenecarboxylic acid (1.27 g) in 20 m*l* of ether was added, drop by drop, with vigorous stirring into an ethereal solution of diazomethane prepared from 1.0 g of nitrosomethylurea. After the addition of the acid had been completed, stirring was continued further an additional hour. After the solvent had been removed under reduced pressure, the residue was dissolved again in ether. The solution was washed successively with an aqueous sodium hydroxide solution and with water, and then dried. After the removal of the solvent, the residue was chromatographed on alumina to give methyl 1′-iodo-1-ferrocenecarboxylate in a 75.8% yield; the ester was recrystallized from *n*-hexnae, mp 71—72.5°C.

Found: C, 39.19; H, 3.03%. Calcd for $C_{12}H_{11}O_2IFe$: C, 38.92; H, 3.00%.

From the sodium hydroxide solution, 0.30 g (23.6%) of the starting material was recovered.

1′-Iodo-1-methylferrocene. Methyl 1′-iodo-1-ferrocenecarboxylate (1.2 g, 3.2 mmol) was added, little by little, to a suspension of 0.25 g (6.5 mmol) of lithium aluminum hydride in 20 m*l* of dry ether, and then a solution of 0.47 g (3.5 mmol) of aluminum chloride in 15 m*l* of dry ether was added, drop by drop, to the reaction mixture under a nitrogen atmosphere and in an ice-water bath. After stirred for 15 min, the mixture was poured into cold water and the aqueous layer was extracted with ether. The combined ethereal solution was washed with dilute hydrochloric acid and dried over anhydrous magnesium sulfate. After the removal of the solvent, the residue was chromatographed on alumina to give an orange liquid which was then distilled under reduced pressure, bp 102—104°C/0.2 mmHg. The yield of 1′-iodo-1-methylferrocene was 0.49 g (18.8%).

Found: C, 40.62; H, 3.65%. Calcd for $C_{11}H_{11}IFe$: C, 40.49; H, 3.37%.

1′-Chloro-1-methylferrocene. 1′-Iodo-1-methylferrocene (0.2 g, 0.6 mmol) and copper(I) chloride (0.12 g, 1.2 mmol) were refluxed in 2 m*l* of pyridine for 2 hr. After the reaction had been completed, a small amount of pyridine was added; then the reaction mixture was cooled. The cooled mixture was diluted with ether and filtered. The residue was then washed with ether. The combined ethereal solution was washed several times with dilute hydrochloric acid, and finally with water; it was then dried over anhydrous magnesium sulfate. After the removal of the solvent, the residue was purified by chromatography on alumina with *n*-hexane to give 0.07 g (51% yield) of 1′-chloro-1-methylferrocene, which was recrystallized from methanol, mp 47.5—48.5°C.

Found: C, 56.54; H, 5.11%. Calcd for $C_{11}H_{11}ClFe$: C, 56.38; H, 4.69%.

1′-Cyano-1-methylferrocene. After a mixture of 0.129 g (0.4 mmol) of 1′-iodo-1-methylferrocene, 0.180 g

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[22] S. A. Butter and H. C. Beachell, *Inorg. Chem.*, **5**, 1820 (1966).

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

[24] E. Berliner and E. A. Blommers, *J. Amer. Chem. Soc.*, **73**, 2479 (1951).

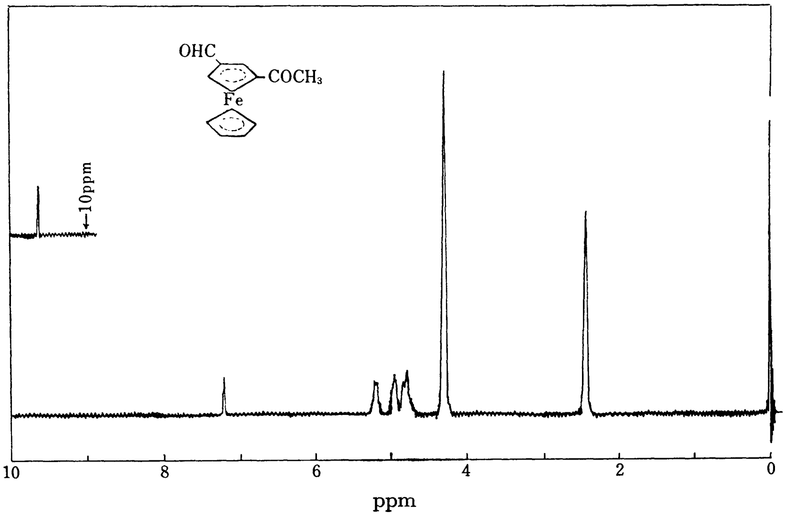

Fig. 3. NMR spectrum of 3-acetyl-1-formylferrocene (in $CDCl_3$).

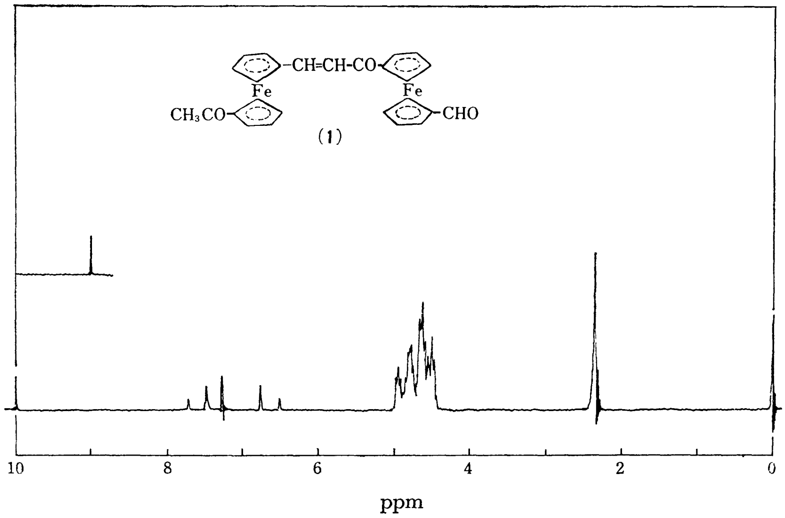

Fig. 4. NMR spectrum of compound **1** (in $CDCl_3$).

(2 mmol) of copper(I) cyanide, and 1 m*l* of pyridine had been heated at 120°C for 2.5 hr in a sealed tube, the mixture was treated in the manner described above to give 0.041 g (52% yield) of 1′-cyano-1-methylferrocene, mp 72.5—73.5°C (lit,[25] mp 72—73°C).

1′-Acetyl-1-formylferrocene. A solution of the complex, which had been prepared in advance from 2.2 m*l* (0.03 mol) of acetyl chloride and 4.0 g (0.03 mol) of anhydrous aluminum chloride in 20 m*l* of dichloromethane, was added to a solution of 2.2 g (0.01 mol) of formylferrocene in 50 m*l* of dichloromethane over a period of 15 min in an ice bath and with stirring under a nitrogen atmosphere. In order to keep the reaction out of the light, the flask was covered with aluminum foil during the reaction. After being stirred for 4 hr in the ice bath, the reaction mixture was hydrolyzed by ice and water containing tin(II) chloride as a reducing agent. The aqueous layer was extracted with dichloromethane, and then the combined dichloromethane solution was washed with water and dried over anhydrous magnesium sulfate. After the removal of the solvent under reduced pressure, the residue was chromatographed on alumina which had previously been deactivated by exposure to the air for 0.5 hr. The chromatography gave 0.62 g (28.2% recovery) of formylferrocene from the first fraction, eluted by ether-*n*-hexane (1 : 1), and then 1.08 g (41.1% yield) of 1′-acetyl-1-formylferrocene from the second fraction, eluted by ether. The product was recrystallized from *n*-hexane-ether, mp 94—95°C (lit,[26] mp 90—93°C).

When the same reaction was carried out initially in

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[25] G. G. Dvoryantseva, Yu. N. Sheinker, L. P. Yur'eva and A. N. Nesmeyanov, *Dokl. Akad. Nauk SSSR*, **156**, 873 (1964).

[26] K. Schlögl, M. Peterlik and H. Seiler, *Monatsh. Chem.*, **93**, 1309 (1962).

an ice bath for 1 hr, and subsequently at room temperature for 3 hr, the chromatographic separation of the product gave different results. After the recovery of the starting material (40.4%), the second fraction with *n*-hexane–ether (1 : 1) gave a trace of orange crystals. This compound was identified to be 3-acetyl-1-formyl ferrocene, mp 106—107.5°C, by a study of its IR and NMR spectra. The NMR spectrum is shown in Fig. 3.

Found: C, 60.70; H, 4.69%. Calcd for $C_{13}H_{12}O_2Fe$: C, 60.94; H, 4.69%.

From the third fraction, which was eluted with ether, 1′-acetyl-1-formylferrocene was obtained in a 33% yield. Further elution with ether gave a fourth fraction consisting of reddish-violet crystals (1.2% yield), which were then recrystallized from benzene–dichloromethane, mp 163°C (decomp.). This compound was identified to be 1-(1′-formylferrocenyl)-3-(1″-acetylferrocenyl)-2-propen-1-one (**1**) by means of its IR and NMR spectra. The NMR spectrum is shown in Fig. 4.

Found: C, 63.26; H, 4.43%. Calcd for $C_{26}H_{22}O_3Fe$: C, 63.16; H, 4.45%.

1′-Ethyl-1-methylferrocene. A solution of 1′-acetyl-1-formylferrocene (190 mg, 0.75 mmol) in 10 m*l* of dry ether was added, drop by drop, to a solution of lithium aluminum hydride (280 mg, 7.4 mmol) and aluminum chloride (1.0 g, 7.5 mmol) in 10 m*l* of dry ether in an ice bath and under an atmosphere of nitrogen. After being stirred for 0.5 hr, the mixture was poured into cold water. Then the ethereal layer was separated, and the aqueous layer was extracted with ether. The combined ethereal solution was then washed with dilute hydrochloric acid and dried over anhydrous magnesium sulfate. After the removal of the solvent, the residue was chromatographed on alumina to give an orange liquid; the liquid was then distilled under reduced pressure, bp 75—77°C/0.21 mmHg. The yield of 1′-ethyl-1-methylferrocene was quantitative.

Found: C, 68.87; H, 6.92%. Calcd for $C_{13}H_{16}Fe$: C, 68.44; H, 7.08%.

2-Chloro-1-methylferrocene. 2-Chloro-1-ferrocenylmethanol (1.45 g, 6 mmol), prepared by Marr's method,[17] was treated for half an hour with a solution of a complex composed of 0.46 g (12 mmol) of lithium aluminum hydride and 0.80 g (6 mmol) of aluminum chloride in 40 m*l* of dry ether under a nitrogen atmosphere. The chromatographic purification of the crude product thus obtained gave 0.94 g (69% yield) of 2-chloro-1-methylferrocene, which was recrystallized from methanol, mp 55.2—56.0°C.

Found: C, 56.68; H, 4.80%. Calcd for $C_{11}H_{11}ClFe$: C, 56.38; H, 4.69%.

2-Bromo-1-methylferrocene. Similarly, 1.01 g (3.4 mmol) of 2-bromo-1-ferrocenylmethanol[17] was converted into 0.57 g (59.7% yield) of 2-bromo-1-methylferrocene, which was then recrystallized from methanol, mp 64—65°C.

Found: C, 47.31; H, 3.94%. Calcd for $C_{11}H_{11}BrFe$: C, 47.45; H, 4.19%.

2-Cyano-1-methylferrocene. 2-Chloro-1-methylferrocene (0.47 g, 2 mmol) was refluxed with 1.8 g (0.02 mol) of copper(I) cyanide for 4 hr in the presence of 1 m*l* of γ-picoline. After the reaction mixture had been treated as has been described for the preparation of 1′-cyano-1-methylferrocene, 0.10 g (22.2% yield) of 2-cyano-1-methylferrocene was obtained and subsequently recrystallized from *n*-hexane, mp 49—50.0°C (lit,[25] mp 51—52°C).

2-Ethyl-1-methylferrocene. A solution of 0.145 g (0.6 mmol) of 2-acetyl-1-methylferrocene in 2 m*l* of acetic acid and 2 m*l* of concentrated hydrochloric acid was added, drop by drop, to amalgamated zinc dust, after which the mixture was refluxed for 5 min. After cooling, the reaction mixture was filtered and the residual zinc dust was thoroughly washed with ether. The filtrate, diluted with water, was also extracted with ether. The combined ethereal solution was washed with a dilute aqueous sodium hydroxide solution and then with water, and subsequently dried over anhydrous magnesium sulfate. After the removal of the solvent, the residue was chromatographed on alumina to give 2-ethyl-1-methylferrocene in an 87% yield as a yellow liquid, bp 68—69°C/0.16 mmHg (lit,[27] bp 70—80°C/0.02 mmHg).

NMR Spectra. The NMR spectra were measured on a Varian Associates A-60 NMR spectrometer.

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27) K. Schlögl, M. Fried and H. Falk, *ibid.*, **95**, 576 (1964).