methoxy-1-silacyclohexa-3-ene, 32297-02-2; 1,1-dimethyl-4,5-di(trimethylsiloxy)-1-silacyclohept-4-ene, 32297-03-3; 5,5-dimethyl-2-acetoxy-5-silacycloheptanone, 32297-04-4; dimethylbromomethylchlorosilane, 16532-02-8; dimethylallylbromomethylsilane, 32367-49-0; dimethylallyl-3-butenylsilane, 24171-43-5; dimethyl-(3-hydroxypropyl)(4-hydroxybutyl)silane, 32367-50-3, 32367-51-4 (diacetate); dimethyl(2-carbomethoxyethyl)(3-carbomethoxypropyl)silane, 32367-52-5; 1,1-dimethyl-4,5-di(trimethylsiloxy)-1-silacycloocta-4-ene, 32296-53-0; 5,5-dimethyl-2-acetoxy-5-silacyclooctanone, 32296-54-1; 6,6-dimethyl-2-acetoxy-6-silacyclooctanone, 32296-55-2; 4,4-dimethylsilacyclooctanone, 32296-56-3; 5-trimethylsilylpentan-2-one, 17012-93-0.

Acknowledgments.—This work was supported in part by a Biomedical Sciences Support Grant RR-07012-04 from the National Institutes of Health. We also thank the Caltech President's Fund and NASA Contract NAS 7-100.

Reactions of 2-Methylchloroferrocene. Evidence for the Ferrocyne Intermediate[1]

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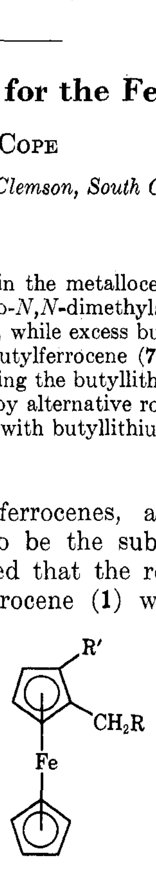
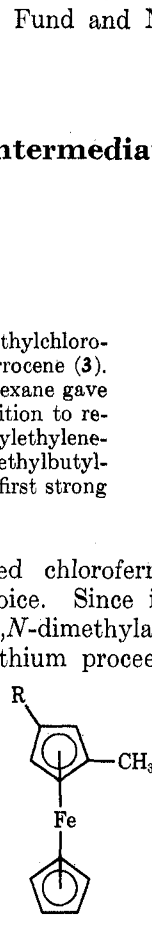
In an effort to investigate the possibility of aryne intermediates in the metallocene series, 2-methylchloroferrocene (**2**) was prepared by reduction of the methiodide of 2-chloro-*N*,*N*-dimethylaminomethylferrocene (**3**). Reaction of **2** with butyllithium in tetrahydrofuran gave α-lithiation, while excess butyllithium in hexane gave a mixture of approximately equal parts of 2-methyl- and 3-methylbutylferrocene (**7** and **8**) in addition to recovered **2** and methylferrocene (**6**). Similar results were obtained using the butyllithium–tetramethylethylenediamine complex. For reference samples, **7** and **8** were synthesized by alternative routes, and 1′-methylbutylferrocene (**9**) was also prepared. The results from the reaction of **2** with butyllithium provide the first strong evidence for an aryne intermediate in the ferrocene series.

Several years ago, in work carried out in these laboratories, reactions of chloroferrocene with butyllithium and butyllithium–lithium piperidide were carried out.[2] The products obtained in this study indicated that these reactions were probably proceeding *via* a ferrocyne intermediate, but alternative paths involving prior halogen–metal interconversion could not be excluded.[2] Following our earlier publication, there have been no additional studies on the intermediacy of arynes in the metallocene series, and the only related work appears to be the recent preparation and subsequent trapping of dehydrocyclopentadiene[3] and the selective α-lithiation experiments carried out on haloferrocenes by Hedberg and Rosenberg.[4]

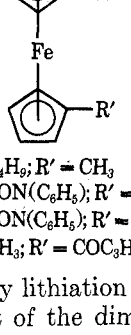
In order to establish whether the reaction of chloroferrocene with *n*-butyllithium to give butylferrocene was an example of an aryne reaction or simply Wurtz–Fittig coupling, a substrate which would give an unsymmetrical aryne was needed. The classical work in the benzene series was carried out using such compounds as *o*-bromoanisole and the halotoluenes,[5] and by analogy it appeared that the reaction of a 2- or 3-substituted chloroferrocene with butyllithium should serve to either establish or refute the existence of the ferrocyne intermediate. In view of the limited synthetic methods available for preparing 1,3-disubstituted ferrocenes, a 2-substituted chloroferrocene seemed to be the substrate of choice. Since it has been noted that the reaction of *N*,*N*-dimethylaminomethylferrocene (**1**) with *n*-butyllithium proceeds to give almost exclusively lithiation at the 2 position[6] and since the replacement of the dimethylamino group by hydrogen was quite feasible, 2-methylchloroferrocene (**2**) was chosen as the subject of our study. Initially



1, R = $N(CH_3)_2$; R′ = H
2, R = H; R′ = Cl
3, R = $N(CH_3)_2$; R′ = Cl
4, R = $N(CH_3)_2$; R′ = $B(OH)_2$
5, R = $N(CH_3)_3{}^+I^-$; R = Cl
6, R = R′ = H
7, R = H; R′ = C_4H_9
12, R = $N(CH_3)_2$; R′ = $CH{=}CHC_2H_5$
13, R = H; R′ = COC_3H_7



8, R = C_4H_9
14, R = COC_3H_7



9, R = C_4H_9; R′ = CH_3
10, R = $CON(C_6H_5)$; R′ = H
11, R = $CON(C_6H_5)$; R′ = COC_3H_7
15, R = CH_3; R′ = COC_3H_7

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[1] (a) Abstracted from the Ph.D. Dissertation of J. F. Cope, Clemson University, May 1971; (b) supported in part by Career Development Award GM-5433 from the National Institutes of Health.

[2] J. W. Huffman, L. H. Keith, and R. L. Asbury, *J. Org. Chem.*, **30**, 1600 (1965).

[3] J. C. Martin and D. R. Block, *J. Amer. Chem. Soc.*, **93**, 451 (1971).

[4] (a) F. L. Hedberg and H. Rosenberg, *Tetrahedron Lett.*, 4011 (1969). (b) A. N. Nesmeyanov, B. A. Sazonova, and N. S. Sazonova, *Dokl. Akad. Nauk SSSR*, **176**, 598 (1967), reported the preparation and thermal decomposition of 2-chloroferrocenylsilver, but observed no products indicative of an aryne reaction.

[5] (a) T. L. Gilchrist and C. W. Rees, "Carbenes, Nitrenes and Arynes," Appleton-Century-Crofts, New York, N. Y., 1969, pp 42–54 and 103–119, (b) H. Heaney, *Chem. Rev.*, **62**, 81 (1962), and (c) R. Huisgen in "Organometallic Chemistry," H. Zeiss, Ed., Reinhold, New York, N. Y., 1960, pp 36–88, have all reviewed the work which establishes the fact that arynes are intermediates in the reactions of halobenzenes with strong bases.

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

2-chloro-*N*,*N*-dimethylaminomethylferrocene (**3**) was prepared by means of a halogen–metal interconversion utilizing 3,3,3-trichloropropylene oxide as a halogen source;[7] however, the yields were rather poor and the product difficult to isolate. Subsequently the preparation of this compound by way of 2-(*N*,*N*-dimethylamino)ferrocenylboronic acid (**4**) was reported[8] and this method was used for the preparation of the bulk of the material used in this study. The conversion of the dimethylamine to the methiodide (**5**) and the sodium amalgam reduction to 2-methylchloroferrocene proceeded smoothly.

Initial reactions of **2** with butyllithium in hexane–tetrahydrofuran, even for prolonged periods at reflux, gave no evidence for either aryne reactions or coupling. The only volatile (glc) compounds which could be isolated were recovered **2** and methylferrocene (**6**), probably the result of halogen–metal interconversion.[1a] In order to ensure that lithiation was occurring at the position adjacent to the halogen atom[2,4] the reactions with *n*-butyllithium–tetrahydrofuran were repeated, and either quenched with deuterium oxide or carbonated. Quenching with deuterium oxide gave a 7:1 mixture of **2** and **6**, with 44% incorporation of deuterium in **2**. The only nmr peak which was affected by deuteration was the low-field multiplet at δ 4.22, which may be assigned to the proton α to the chlorine in **2**. Carbonation gave an unstable acid, the spectral data for which (see Experimental Section) were in accord with the structure 2-chloro-3-methylferrocenecarboxylic acid.

Since it was apparent that lithiation α to the halogen was taking place, but the lithioferrocene was not decomposing, the reaction conditions were varied in an effort to obtain the aryne. The use of an alternative solvent, tetrahydropyran, and a more reactive organometallic, *tert*-butyllithium in *n*-butyl ether, were explored. The latter reaction gave no identifiable products except methylferrocene (**6**), while the former gave **2**, **6**, and traces of compounds which were subsequently identified as 2- and 3-methylbutylferrocene.

It has been noticed recently that the *n*-butyllithium–tetramethylethylenediamine complex is a very powerful lithiating agent,[9] which is highly selective for reactions ortho to an electron-rich substituent on an aromatic ring.[9b] Reaction of **2** with this reagent in hexane–tetrahydrofuran, under conditions which favored first formation of the lithio derivative, and then prolonged heating with excess complex, gave a mixture which contained 40% of **6**, 52% of recovered **2**, and 8% of a 5:3 mixture of 2-methylbutylferrocene (**7**) and 3-methylbutylferrocene (**8**). Finally, since it had been noted that lithiation was occurring in tetrahydrofuran, but decomposition to the aryne was not, **2** was lithiated in tetrahydrofuran, and the lithioferrocene was treated with excess butyllithium in hexane and then heated at reflux for several hours. By this method a mixture containing 45% of **6**, 40% of **2**, and 15% of a 2:3 mixture of **7** and **8** was obtained. The overall yield of **7** plus **8** by this procedure was 6%. Various reactions of **2** with butyllithium in the presence of lithium piperidide gave only traces of material which may have been piperidylmethylferrocene, in contrast to the similar reaction of chloroferrocene which affords isolable quantities of piperidylferrocene.[2]

The mixture of **7** and **8** could be isolated by preparative glc, but could not be separated into its components. The infrared and nmr spectra of the mixture were indentical with the sum of the spectra of pure **7** and **8**, prepared as described below, as were the retention times on glc. In addition, the mass spectrum of the mixture was the same as that of **7** and **8**, while markedly different from that of 1′-methylbutylferrocene (**9**).[10] The mass spectral data are summarized in Table I.

Table I[a]

Mass Spectra of Methylbutylferrocenes

		Compd		
m/e	**7**	**8**	**7** + **8**[b]	**9**
257	24	20	21	20
256	100	100	100	100
254	18	31	18	16
214	18	12	17	
213	88	60	79	97
135	10	10	9	27
134	9	8	10	15
121	48	28	34	15
56	21	18	22	26

[a] All peaks reported in relative abundances. [b] From preparative glc of the reaction product of **2** and *n*-butyllithium.

Since the preparation of the three isomeric butylmethylferrocenes had not been reported, and it was necessary to have samples available in order to rigorously assign structures to the products of the above reactions, the syntheses of these compounds was carried out. The most accessible of the three isomers is 1′-methylbutylferrocene, which was prepared in a straightforward sequence from *N*,*N*-diphenylcarbamylferrocene (**10**).[11] Acylation of **10** with butyryl chloride gave keto amide **11**, which on hydrolysis followed by lithium aluminum hydride–aluminum chloride reduction gave **9**. It has been clearly established that electrophilic substitution reactions carried out on **10** proceed to give exclusively the heteroannular product.[11]

The most attractive approach to 2-methylbutylferrocene seemed to be *via* 2-lithio-*N*,*N*-dimethylaminomethylferrocene. However, the reaction with *n*-butyraldehyde did not proceed particularly well, and on isolation of the product it was found that the intermediate carbinol had dehydrated to a mixture of cis and trans butenyl compounds (**12**), contaminated with considerable **1**. The mixture was converted to the methiodides and reduced first with sodium amalgam and then catalytically to give a 1:1 mixture of **2** and **7**.

The only route available for the preparation of 3-methylbutylferrocene (**8**), and one which also afforded an alternative route to the 2 and 1′ isomers (**7** and **10**, respectively), was from the reaction of methylferrocene with butyryl chloride–aluminum chloride, which gave a mixture of 2-methylbutyrylferrocene (**13**, 18%), 3-methylbutyrylferrocene (**14**, 30%), and 1′-methylbutyrylferrocene (**15**, 52%). The heteroannular product **15** was easily distinguished due to the lack of

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[7] W. Reeve and E. F. Group, Jr., *J. Org. Chem.*, **32**, 22 (1967).

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

[9] (a) G. G. Eberhardt and W. A. Butler, *J. Org. Chem.*, **29**, 2928 (1964); (b) R. E. Ludt, G. P. Crowther, and C. Hauser, *ibid.*, **33**, 1288 (1970).

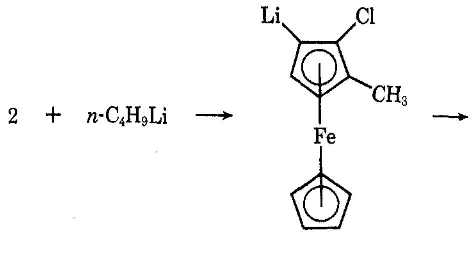
[10] The authors would like to thank the Research Triangle Institute for Mass Spectrometry, Research Triangle Park, N. C., for carrying out these determinations.

[11] W. F. Little and R. Eisenthal, *J. Amer. Chem. Soc.*, **82**, 1577 (1960).

"9–10 bands" in the infrared, and the presence of an A_2B_2 pattern in the aromatic region of the nmr, with two-proton multiplets centered about δ 4.38 and 4.60. The 2-methyl ketone **13** shows a deshielded aryl methyl singlet at δ 2.24, while that of the 3-methyl isomer **14** shows a methyl singlet at δ 1.98. Also, the aromatic region of the spectrum of **13** shows only one proton at significantly lower field, δ 4.40, than the other aromatic protons, while **14** shows a two-proton multiplet at δ 4.55.[12] These structural assignments were strengthened by the chromatographic behavior of these compounds, which paralleled that of the acetylmethylferrocenes,[13] and were confirmed by reduction of each isomer to the corresponding methylbutylferrocene, the structures of two of which had been established by the routes described above.

The three methylbutylferrocenes show slightly different but reproducible retention times on glc (two columns), and, although the mass spectra of the 2- and 3-methyl isomers (**7** and **8**) are very similar, that of 1′-methylbutylferrocene (**9**) is considerably different (see Table I). A comparison of these three compounds with the products of the reaction of 2-methylchloroferrocene (**2**) and butyllithium clearly shows that only the 2-methyl and 3-methylbutyl isomers are obtained. No trace of the 1′ isomer is found.

The results of the reaction of 2-chloromethylferrocene with butyllithium provide very strong evidence for intervention of an aryne intermediate, as outlined in eq 1. It is very difficult to envision any other mechanism which is consistent with the formation of approximately equimolar quantities of 2- and 3-methylbutylferrocenes, from these reactions.[14] The methylferrocene (**6**) obtained probably arises from halogen–metal interconversion to 2-lithiomethyl ferrocene which would afford methylferrocene on hydrolysis, or perhaps by way of a β-hydride transfer from butyllithium to the aryne.[15] On the basis of the data available, it is not possible to differentiate between these two reaction paths.



methylferrocyne ⟶ **7** + **8** (1)

Although the overall yields of butylmethylferrocenes from these reactions are not high, there is strong evidence that they proceed, at least in part, through an aryne intermediate, and indicate that the earlier reactions of chloroferrocene reported from these laboratories[2] probably proceed by a similar route.

Experimental Section[16]

2-Chloro-*N*,*N*-dimethylaminomethylferrocene. A.—The lithiation of 5.0 g of *N*,*N*-dimethylaminomethylferrocene was carried out following the published procedure.[6] The resulting solution of 2-lithio-*N*,*N*-dimethylaminomethylferrocene in 60 ml of dry ether and 5 ml of hexane was added dropwise to a chilled solution of 2.80 ml of 3,3,3-trichloropropylene oxide in 20 ml of anhydrous tetrahydrofuran. The reaction mixture was allowed to warm to room temperature, stirred for 6 hr, and then poured into water. The aqueous phase was drawn off, and the organic layer was extracted with 10% aqueous sulfuric acid. The acidic solution was made basic with 10% potassium hydroxide and extracted with ether. The ether extracts were washed with water and dried and the solvent was removed to give an orange oil. Tlc (alumina-G) indicated that the reaction product consisted of two compounds, one of which was *N*,*N*-dimethylaminomethylferrocene. Integration of the nmr spectrum indicated that this accounted for 60% of the product mixture, with the chloro compound accounting for the remaining 40%. Repeated chromatography on Bio-Rad neutral alumina and elution with hexane–benzene (2:1) gave a small quantity of pure 2-chloro-*N*,*N*-dimethylaminomethylferrocene, which formed crystals from pentane, mp 42–43° (lit.[8] mp 42–43°). The nmr spectrum of this compound was essentially the same as that reported subsequently by Slocum and Engelmann.[17]

Anal. Calcd for $C_{13}H_{16}NClFe$: C, 56.21; H, 5.80; N, 5.05; Cl, 12.78. Found: C, 56.40; H, 5.69; N, 4.95; Cl, 12.97.

B.—2-Chloro-*N*,*N*-dimethylaminomethylferrocene could be prepared more effectively from 2-(*N*,*N*-dimethylaminomethyl)-ferrocenylboronic acid by the following modification of the published procedure.[8] A suspension of 1.68 g of the aminoboronic acid in 50 ml of water was added to a solution of 2.1 g of cupric chloride dihydrate in 50 ml of water, which had been warmed to 40°. The solution was stirred mechanically and the temperature was raised to 55° for 1.5 hr. After cooling to room temperature, the reaction mixture was treated with excess concentrated ammonium hydroxide and extracted with ether. The organic solution was washed with water and saturated sodium chloride solution and dried over magnesium sulfate. Removal of solvent at reduced pressure gave 1.34 g (83%) of an orange oil which slowly crystallized, mp 41–42°, mmp 42.43° with material from part A. Both samples had identical infrared and nmr spectra.

2-Chloro-*N*,*N*,*N*-trimethylammonium Methylferrocene Methiodide.—To a solution of 0.210 g of 2-chloro-*N*,*N*-dimethylaminomethylferrocene in methanol at room temperature was added 0.50 ml of methyl iodide. The mixture was stirred for 20 min at room temperature and then heated on the steam bath with stirring for an additional 5 min. Ether was added and the crystals were collected, washed with anhydrous ether, and dried under reduced pressure, giving 0.290 g (92%) of yellow crystals, mp 186–189° dec (lit. darkening from 185°).[8]

Anal. Calcd for $C_{14}H_{19}NClFeI$: C, 40.07; H, 4.56; N, 3.34; Cl, 8.45; I, 30.25. Found: C, 40.03; H, 4.45; N, 3.28; Cl, 8.50; I, 30.48.

2-Methylchloroferrocene.—To sodium amalgam, formed from 65 g of mercury and 5 g of sodium maintained at 0°, was added

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[12] M. I. Levenberg and J. H. Richards, *J. Amer. Chem. Soc.*, **86**, 2634 (1964), have used a more or less similar argument in assigning the structure to a series of acetylated alkylferrocenes.

[13] J. H. Richards and E. A. Hill, *ibid.*, **83**, 4216 (1961).

[14] One can postulate a series of halogen–metal interconversions and coupling reactions leading to **7**. To arrive at **8**, 2-chloro-3-methyllithioferrocene would react with butyl chloride to give 3-methyl-2-chlorobutylferrocene, which would then undergo halogen–metal interconversion to give on hydrolysis 3-methylbutylferrocene. This route is highly unlikely for two reasons. First, **7** and **8** are formed in approximately equal amounts, while a preponderance of **7** would be predicted if this mechanism were operative. Second, no trace of a methylchlorobutylferrocene was found. Since a significant amount of **2** survives the reaction, a significant amount of chlorobutyl compound would be expected to be present in the final product mixture. The glc techniques used would have permitted the detection of even very small quantities of this substance if it were present.

[15] V. Franzen and H. I. Joschek, *Angew. Chem.*, **72**, 564 (1964).

[16] All melting points were taken on a Kofler hot stage and are uncorrected. The analytical vapor phase chromatography was carried out with an F & M research chromatograph, Model 810; unless otherwise noted a 6 ft × 0.125 in. SE-30 silicon gum column was employed. Preparative glc was carried out on an Aerograph Autoprep, Model A-700 using a 5-ft, 20% SF-96 silicone fluid column. All infrared spectra were taken on a Perkin-Elmer Model 137 spectrophotometer, as liquid or potassium bromide pellets, and are reported in microns. Nuclear magnetic resonance spectra were obtained on a Varian Associates A-60 nuclear magnetic resonance spectrophotometer using either deuteriochloroform or carbon tetrachloride as a solvent. All spectra are reported in parts per million relative to tetramethylsilane (δ). Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Unless otherwise noted, all reactions were carried in an atmosphere of dry nitrogen.

[17] D. W. Slocum and T. R. Engelmann, *J. Org. Chem.*, **34**, 4101 (1969).

0.416 g of methiodide **5** in 10 ml of water. The reaction was allowed to proceed for 10 min, after which 20 ml of benzene was added and the mixture was heated at reflux for 2 hr, at which point the aqueous phase was colorless. The organic phase was extracted with 10% aqueous sulfuric acid and dried and the solvent was removed at reduced pressure. The residue was dissolved in hexane and chromatographed on Merck alumina. Elution with hexane gave an orange oil which crystallized on standing. Recrystallization from pentane gave 0.052 g of yellow crystals (64%): mp 54–57°; nmr δ 2.05 (s, 3 H, CH_3), 3.91 (m, 2 H, FCH), 4.06 (s, 5 H, FCH), 4.22 (m, 1 H, FCH).

Anal. Calcd for $C_{11}H_{11}ClFe$: C, 56.33; H, 4.73; Cl, 15.12. Found: C, 56.29; H, 4.90; Cl, 15.00.

Reactions of 2-Methylchloroferrocene with *n*-Butyllithium. A.—To a solution of 0.270 g of 2-methylchloroferrocene, containing 8% methylferrocene in 25 ml of freshly distilled tetrahydrofuran, cooled to 0°, was added 1.6 ml of 0.9 *N* *n*-butyllithium in hexane. The mixture was stirred for 1.5 hr at this temperature and 25 ml of the reaction solution were withdrawn and mixed with 4 ml of deuterium oxide. After stirring for 5 min, the phases were separated, the organic solution was dried, and the solvent was removed at reduced pressure. Following chromatography on Bio-Rad neutral alumina and elution with hexane, the crystalline material was analyzed by glc and nmr. The former showed the sample to consist of 87% 2-methylchloroferrocene and 13% methylferrocene; nmr showed a 44% decrease in the intensity of the resonance at 4.22 assigned to the proton adjacent to the chloro substituent.

B.—The reaction of 0.970 g of 2-methylchloroferrocene with 2.0 ml of 2.1 *N* *n*-butyllithium was carried out as described above; however, the reaction was heated at reflux for 6.5 hr. A 25-ml aliquot of the reaction solution was removed and added, under nitrogen, to a slurry of anhydrous ether and Dry Ice. The carbonation mixture was extracted with 10% sodium hydroxide until the extracts were colorless. The extracts were washed with ether, acidified with 10% hydrochloric acid, extracted with ether, and dried and the solvent was removed to give 0.168 g of soft crystals. Recrystallization from ether gave orange crystals: mp 178–183°; ir 3.75 br, 5.98; nmr δ 2.14 (s, 3 H, CH_3), 4.25 (s, 5 H, FCH), 4.30 (m, 1 H, FCH), 4.76 (m, 1 H, FCH). Tlc (ethyl acetate, silica gel-G) showed a single spot with an R_f value only slightly different than that of ferrocenecarboxylic acid. This material, **2-chloro-3-methylferrocenecarboxylic acid**, decomposed in 12 hr when stored under nitrogen at −10 and could not be submitted for analysis.

The balance of the original reaction mixture was treated with 4 ml of deuterium oxide as described above to give 0.240 g of a mixture of methylferrocene and 2-methylchloroferrocene in which 15% deuterium incorporation in the chloro compound was observed.

C.—To a stirred solution of 0.215 g of freshly sublimed 2-methylchloroferrocene in 25 ml of tetrahydrofuran at 0° was added 3 ml of a mixture of 1.37 ml of tetramethylethylenediamine, 3.6 ml of hexane, and 10 ml of 0.9 *N* *n*-butyllithium. The reaction mixture was heated at reflux for 15 min and the remaining butyllithium solution was added dropwise to the hot reaction mixture. After heating for 18 hr the dark brown solution was poured into ice water and the aqueous layer was drawn off. The aqueous solution was treated with ascorbic acid and extracted with ether and the extracts were combined with the original organic phase. The combined extracts were washed with water and dried, and the solvent was removed to give a yellow oil. The oil was dissolved in hexane and chromatographed on Merck alumina to give 0.20 g of yellow oil which by glc contained 40% methylferrocene, 52% 2-methylchloroferrocene, 5% 2-methylbutylferrocene, and 3% 3-methylbutylferrocene.

D.—The reaction of 0.130 g of 2-methylchloroferrocene with *n*-butyllithium–tetramethylethylenediamine was carried out essentially as described in C above; however, the chloro compound was dissolved in 10 ml of hexane to which had been added 0.12 ml of piperidine. After heating at reflux for 11 hr the reaction mixture was poured over ice and the phases were separated. The organic phase was washed with water and extracted with 10% hydrochloric acid. The acidic extracts were cooled in an ice bath and made basic with 10% sodium hydroxide. Extraction with ether gave a yellow organic phase which was washed with with saturated sodium chloride and dried over magnesium sulfate. Removal of the solvent gave 0.032 g of brown material. Tlc (alumina-G, benzene–hexane 1:1) left most of the sample at the origin; however, two spots appeared, the R_f values of which were slightly greater than that of piperidylferrocene,[2] which was simultaneously chromatographed.

The neutral fraction was washed with saturated brine and dried, and the solvent removed to give 0.070 g of dark oil which was dissolved in hexane and chromatographed on 20 g of Merck alumina. Elution with hexane gave 0.030 g of yellow oil which was analyzed by glc and found to contain 79% methylferrocene, 9% 2-methylchloroferrocene, and 11% butylmethylferrocenes. A second fraction was eluted with benzene and was nonvolatile under glc conditions. Tlc showed that it had an R_f value virtually identical with that of biferrocenyl.[2] The infrared spectrum showed both alkyl and aromatic carbon hydrogen bands as well as the 9 and 10 bands characteristic of unsubstituted rings in ferrocene derivatives.

E.—To a solution of 1.00 g of feshly sublimed 2-methylchloroferrocene in 10 ml of tetrahydrofuran at 0° was added 2.5 ml of 2.18 *N* *n*-butyllithium in hexane. After 1.5 hr at 0°, 20 ml of purified hexane and an additional 10 ml of *n*-butyllithium in hexane were added. The reaction mixture was allowed to warm to room temperature and then heated at reflux for 6 hr. The products were isolated as described above, and on chromatography 0.386 g of material was obtained from the hexane fraction. This mixture was found to contain 45% (19% yield) methylferrocene, 40% (17% recovery) 2-methylchloroferrocene, 6% (2%) 2-methylbutylferrocene, and 9% (4%) 3-methylbutylferrocene. Preparative glc of this material gave 0.010 g of the mixture of 2- and 3-methylbutylferrocenes, the infrared, nmr, and mass spectra of which were identical with the summation of the spectra of the pure isomers.

1′-Butyldiphenylcarbamylferrocene.—To a chilled (−40°) solution of 2.19 g of diphenylcarbamylferrocene[11] in 50 ml of anhydrous dichloroethane was added 0.90 g of aluminum chloride and then a mixture of 6.87 ml of butryl chloride and 0.90 g of aluminum chloride was added dropwise. The mixture was stirred for 2 hr in the cooling bath and was then warmed to room temperature and stirred for an additional 1.5 hr. The reaction mixture was poured into water, the aqueous layer was drawn off, and the organic material was washed with two portions of 10% hydrochloric acid, sodium bicarbonate, and finally water. The dark organic solution was dried and the solvent was removed to give a dark oil which partially crystallized after standing under nitrogen at room temperature for several days. Crystallization from ether gave 1.48 g (56%) of dark red crystals: mp 125–127°; nmr 0.98 (t, 3 H, CH_3), 1.70 (m, 2 H, $CH_2CH_2C{=}O$), 2,70 (t, 2 H, $CH_2CH_2C{=}O$), 4.18 (s, 4 H, FCH), 4.52, 4.78 (A_2B_2, FCH), 7.28 (s, 10 H, Ar H).

Anal. Calcd for $C_{27}H_{25}NO_2Fe$: C, 71.85; H, 5.58; N, 3.10. Found: C, 72.04; H, 5.94; N, 3.06.

1′-Butyrylferrocenecarboxylic Acid.—A suspension of 0.490 g of diphenyl amide **11** in 25 ml of 10% ethanolic potassium hydroxide was heated at reflux for 7 hr. The reaction mixture was poured into ice water and washed with methylene chloride. The aqueous layer was acidified with 10% hydrochloric acid and extracted with three portions of methylene chloride. The organic extracts were combined, washed with water, and dried and the solvent was removed to give 0.263 g (70%) of orange crystals. Recrystallization from ether gave an analytical sample: mp 109–110°; resolidification then mp 119–120°; nmr δ 1.01 (t, 3 H, CH_3), 1.78 (m, 2 H, $CH_2CH_2C{=}O$), 2.78 (t, 2 H, $CH_2CH_2C{=}O$), 4.58 (m, 4 H, FCH), 4.89 (br s, 4 H, FCH).

Anal. Calcd for $C_{15}H_{16}O_3Fe$: C, 60.02; H, 5.37. Found: C, 60.00; H, 5.41.

Butyrylmethylferrocenes.—To a solution of 3.57 g of methylferrocene[18] in 25 ml of methylene chloride was added dropwise a mixture of 1.34 ml of butyryl chloride and 2.38 g of aluminum chloride in 30 ml of methylene chloride. The mixture was stirred at room temperature for 4 hr and the poured over ice. The organic layer was drawn off and the aqueous solution was extracted with methylene chloride. The organic extracts were combined, washed with water and saturated aqueous sodium bicarbonate, and dried and the solvent was removed to give 4.06 g of red oil. This oil was dissolved in hexane and chromatographed on Merck acid-washed alumina. Elution with hexane gave 0.637 g (18%) of recovered ferrocene, while 2:1 hexane-benzene gave 0.400 g (10%) of **2-methylbutyrylferrocene** as a red oil: nmr δ 0.99 (t, 3 H, CH), 1.70 (m, 2 H, $CH_2CH_2C{=}O$),

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[18] A. N. Nesmeyanov, E. G. Prevalova, L. S. Shilovtseva, and Z. N. Beinoreivichata, *Dokl. Akad. Nauk SSSR*, **121**, 117 (1958); *Chem. Abstr.*, **53**, 323 (1959).

2.21 (s, 3 H, FC CH_3), 2.55 (m, 2 H, $CH_2C\mathbf{H}_2C{=}O$), 3.98 (s, 5 H, FCH), 4.15 (m, 2 H, FCH), 4.39 (m, 1 H, FCH).

Anal. Calcd for $C_{15}H_{18}FeO$: C, 66.60; H, 6.72. Found: C, 66.92; H, 6.48.

Later fractions eluted with hexane–benzene mixtures gave 2.30 g (57%) of a mixture of 2-, 3-, and 1′-methylbutyrylferrocene. The major fraction (1.68 g) of this mixture, which as relatively rich in the 3 and 1′ isomers, was dissolved in benzene and rechromatographed on Woelm activity I neutral alumina. Elution with 2:1 methylene chloride–ether gave 0.370 g of a mixture of 94% 1′-methyl ketone and 6% of the 3 isomer, while later fractions eluted with the same solvent pair gave first 0.440 g of a mixture of 44% of the 1′ and 56% of the 3′ compound and finally 0.500 g containing 84% of 3-methylbutyrylferrocene and 16% of the 1′ isomer. The nmr assignments could be made on the enriched fractions and follow: **1′-methylbutyrylferrocene,** δ 1.00 (t, 3 H, CH_3), 1.75 (m, 2 H, $C\mathbf{H}_2CH_2C{=}O$), 1.82 (s, 3 H, FC CH_3), 2.59 (t, 2 H, $CH_2C\mathbf{H}_2C{=}O$), 3.91 (s, 4 H, FCH), 4.24 (m, 2 H, FCH), 4.60 (m, 2 H, FCH); **3-methylbutyrylferrocene,** 0.98 (t, 3 H, CH_3), 1.68 (m, 2 H, $C\mathbf{H}_2CH_2C{=}O$), 1.99 (s, 3 H, FCH), 2.55 (m, 2 H, $CH_2C\mathbf{H}_2C{=}O$), 3.96 (s, 5 H, FCH), 4.21 (m, 2 H, FCH), 4.59 (m, 2 H, FCH). The middle fraction consisting of the 44:56 mixture was submitted for analysis.

Anal. Calcd for $C_{15}H_{18}FeO$: C, 66.69; H, 6.72. Found: C, 66.89; H, 6.67.

2-Methylbutylferrocene. A.—To a chilled suspension of 0.080 g of aluminum chloride and 0.265 of lithium aluminum hydride in 20 ml of dry ether was added dropwise 0.100 g of 2-methylbutyrylferrocene in 20 ml of ether. The reaction mixture was allowed to warm to room temperature and stirred for 30 min, and ice water was added cautiously. The aqueous layer was drawn off, the organic layer was dried, and the solvent was removed to give a yellow oil which was dissolved in hexane and filtered through a column of Woelm neutral alumina to give 0.048 g (50%) of 2-methylbutylferrocene, homogenous to glc: nmr δ 0.92 (m, 3 H, CH_3), 1.32 (m, 4 H, $-CH_2CH_2-$), 1.98 (s, 3 H, $FcCH_3$), 2.28 (m, 2 H, $FcCH_2-$), 3.78 (m, 3 H, FCH), 3.81 (s, 5 H, FCH).

Anal. Calcd for $C_{15}H_{20}Fe$: C, 70.33; H, 7.87. Found: C, 70.63; H, 7.91.

B.—To a solution of 2-lithio-*N*,*N*-dimethylaminomethylferrocene, from 1.67 g of *N*,*N*-dimethylamminomethylferrocene, was added 3.1 g of redistilled *n*-butyraldehyde and the reaction was stirred at reflux for 5 hr. Ice water was added and the layers were separated. The ethereal solution of products was extracted with 10% hydrochloric acid, and the acid extracts were made basic with 10% sodium carbonate and extracted with ether. The ether extracts were washed with water and dried, and the solvent was removed to give 2.56 g of various viscous oil. Tlc (alumina-G; 1:1 benzene–ether) indicated the presence of starting material and a second compound of similar polarity. The ir showed no hydroxyl absorption and the nmr showed vinyl protons in the δ 5.85–6.18 region. Attempted chromatographic separation was unsuccessful and the mixture was converted to the methiodides and reduced with sodium amalgam as described above for the preparation of 2-methylchloroferrocene. From 2.56 g of starting mixture, 1.50 g of amber oil was obtained. Glc analysis showed that the product consisted of 49% methylferrocene, 45% 2-methylbutenylferrocenes (cis and trans), and 6% of a third component: nmr 1.83–2.42 (m, $-CH_2$, CH_3), 3.60, 3.65 (s, $FeCH_3$), 3.95–4.34 (m, FCH), 5.96 (m, CH=CH).

Again, chromatographic separation was unsuccessful and 1.00 g of the mixtue was dissolved in 40 ml of methanol and hydrogenated at 30 psig using 0.100 g of Adams catalyst. The catalyst was filtered off and the solvent was removed to leave 0.802 g of yellow oil. Glc showed that the product contained 42% methylferrocene, 45% 2-methylbutylferrocene, and 13% minor components. The retention time of material prepared in this manner was identical with that prepared in part A, and differed from that of the other two isomers.

3-Methylbutylferrocene.—This compound was prepared from the corresponding ketone contaminated with 15% of the 1′ isomer, by the procedure described above. From 0.100 g there was obtained 0.060 g (63%) of reduced material: nmr 0.91 (m, 3 H, CH_3), 1.32 (m, 4 H, CH_2CH_2), 1.98 (s, 3 H, $FcCH_3$), 2.21 (m, 2 H, $FcCH_2$), 3.79 (m, 3 H, FCH), 3.85 (s, 5 H, FCH).

Anal. Calcd for $C_{15}H_{20}Fe$: C, 70.33; H, 7.87. Found: C, 70.42; H, 7.71.

1′-Methylbutylferrocene. A.—The reduction of 1′-butyrylmethylferrocene, contaminated with 5% of the 3 isomer, was carried out as described above for the preparation of 2-methylbutylferrocene. From 0.100 g of ketone there was obtained 0.73 g (75%) of 1′-methylbutylferrocene, contaminated with 5% of the 3 isomer: nmr δ 0.90 (m, 3 H, CH_3), 1.34 (m, 4 H, CH_2CH_2), 1.91 (s, 3 H, $FcCH_3$), 2.22 (m, 2 H, $FcCH_2$), 3.80 (br s, 8 H, FCH).

Anal. Calcd for $C_{15}H_{20}Fe$: C, 70.33; H, 7.87. Found: C, 69.64; H, 7.33.[19]

B.—The reduction of 1′-butyrylferrocenecarboxylic acid was carried out by the same procedure used for the reduction of the methylbutyryl compounds. From 0.030 g of acid 0.032 g of product, which was homogenous to glc, was obtained. The retention time of this material was identical with that of material prepared by method A, as were the ir and nmr spectra.

Registry No.—**2**, 31852-03-6; **7**, 32241-91-1; **8**, 32241-92-2; **9**, 32241-93-3; **11**, 32241-94-4; **13**, 32241-95-5; **14**, 32241-96-6; **15**, 32241-97-7; *n*-butyllithium, 109-72-8; 2-chloro-3-methylferrocenecarboxylic acid, 32241-98-8; 1′-butyrylferrocenecarboxylic acid, 32241-99-9.

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(19) Completely acceptable analytical data could not be obtained for this compound; however, ir, nmr, and mass spectral data (see Table I) are in accord with the assigned structure.