

cule. Evidently the geometric factor dominates the structural factor when primary hydrogen atoms are involved in the Barton reaction, while the inverse is true when secondary hydrogen atoms are involved.

The photolysis of cyclohexylmethyl nitrite gave a very small yield (4%) of nitroso dimer while 2-cyclohexyl-1-ethyl nitrite gave a fair yield (30%) of nitroso dimer (Table II). These results are consistent with the behavior of alkyl substituted cyclohexyl nitrites in that good yields of nitroso dimers were obtained only when a stable six-membered ring intermediate could be formed, as with the latter substance.

Further evidence in support of the basic prerequisite of a six-membered ring intermediate in the Barton reaction was obtained during the photolysis of three nitrites which had tertiary hydrogen atoms in appropriate positions, 2-cyclohexyl-1-ethyl, 3-cyclohexyl-1-propyl and 4-cyclohexyl-1-butyl nitrites. In the three compounds cited above, a tertiary hydrogen atom was available for intramolecular hydrogen abstraction which would involve five-, six- and seven-membered ring intermediates, respectively. Evidence of the attack on the tertiary hydrogen atom would be obtained easily from the fact that the resulting tertiary

nitroso monomer which would not dimerize in solution, would show a weak visible absorption band at $680\text{ m}\mu$ ($\epsilon \sim 20$).

No evidence for the formation of any tertiary nitroso monomer was found during the photolyses of 2-cyclohexyl-1-ethyl and 4-cyclohexyl-1-butyl nitrites. Only in the photolysis of 3-cyclohexyl-1-propyl nitrite where the tertiary hydrogen atom available for hydrogen abstraction can take part in a six-membered ring intermediate was there any evidence for the production of tertiary nitroso monomer (31%). The nitroso dimer yield fell to zero.

Experimental

Material, apparatus, photolysis procedure and analytical methods were as described in Parts I, II and III. The *cis* and *trans* isomer contents of the cyclohexyl alcohols were determined by vapor phase chromatography following the procedure of Komers, Kochloeff and Bazant.⁶

Acknowledgments.—The authors wish to acknowledge the technical assistance of members of this Laboratory and in particular Mr. R. Armswood. The authors are indebted to Prof. D. H. R. Barton and Dr. E. B. Hershberg for their helpful interest in this work.

(6) R. Komers, K. Kochloeff and V. Bazant, *Chemistry & Industry*, 1405 (1958).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF BRANDEIS UNIVERSITY, WALTHAM 54, MASS.]

The Structure and Chemistry of Ferrocene. VI. Mechanism of the Arylation Reaction¹

BY M. ROSENBLUM, W. GLENN HOWELLS,² A. K. BANERJEE AND C. BENNETT³

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The reaction of ferrocene with aryldiazonium salts prepared from aniline, *p*-aminoacetophenone and *p*-anisidine yields not only mono- and 1,1'-diarylfereocenes, but 1,2- and 1,3-diarylfereocenes as well. Structural assignments for these latter two types of derivatives have been made on the basis of unambiguous synthesis and infrared spectral correlations. The view that arylfereocenes are formed in these reactions by attack of free aryl radicals on either ferrocene or on the ferricinium cation is shown to be without experimental support. A new mechanism involving internal rearrangement of a ferrocene-diazonium salt charge-transfer complex is proposed. The broader theoretical implications of these conclusions are discussed.

Introduction

The very great reactivity of ferrocene toward electrophilic reagents prompted an early examination of its reaction with aryldiazonium salts with the expectation of securing azoferrocenes.⁴ Although these designs were frustrated, the outcome proved nevertheless to be of considerable interest since the products were the otherwise difficultly accessible arylfereocenes. At present this reaction constitutes the simplest and most direct method for the preparation of these substances.

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(2) Taken in part from a dissertation submitted by W.G.H. in partial fulfillment of the requirements for the Ph.D. degree, June, 1961.

(3) National Science Foundation Undergraduate Research Participant, under grant 13867, Summer, 1961.

(4) (a) A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya and O. A. Nesmeyanova, *Doklady Akad. Nauk S.S.S.R.*, **97**, 459 (1954); (b) A. N. Nesmeyanov, E. G. Perevalova and R. V. Golovnya, *ibid.*, **99**, 539 (1954); (c) C. D. Broadhead and P. L. Pauson, *J. Chem. Soc.*, 367 (1955).

Our interest in these reactions was initially confined to the preparation of a variety of arylfereocenes to be used in connection with other studies. However, certain observations led us to examine the reaction in greater detail. The present report is an account of these studies and of our conclusions regarding the mechanism of these transformations and their broader implications.

Results

The arylation of ferrocene has been reported to afford monoarylfereocenes together with 1,1'-diarylfereocenes. Broadhead and Pauson^{4c} alone have described the isolation of a substance isomeric with 1,1'-bis-*p*-methoxyphenylferrocene, obtained in the treatment of ferrocene with diazotized *p*-anisidine. They were unable to determine whether this substance was an authentic diarylfereocene (structure II or III) or a biphenyl derivative similar in constitution to *p*-biphenylferrocene isolated from the reaction of ferrocene with phenyl diazonium chloride.⁵ Mostly on the basis of their

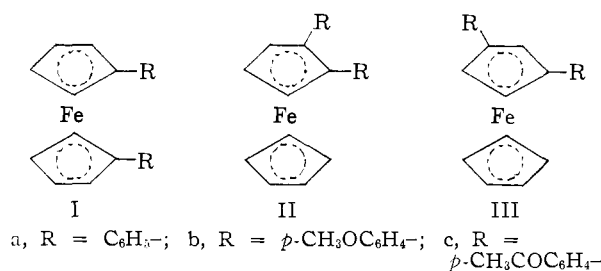
(5) P. L. Pauson, *Quart. Revs.*, **9**, 391 (1955).

TABLE I

Arylferrocene	M.p., °C.	Characteristic infrared absorption peaks, μ^a				
<i>p</i> -Methoxyphenyl-	108-110	11.25	10.00	9.05
1,1'-Bis- <i>p</i> -methoxyphenyl-	172-174	11.25	9.02
1,2-Bis- <i>p</i> -methoxyphenyl-	119-121	10.83	10.00
1,3-Bis- <i>p</i> -methoxyphenyl-	159-161	...	11.17	11.06	...	10.00
<i>p</i> -Acetylphenyl-	176-178	11.25	9.98
1,1'-Bis- <i>p</i> -acetylphenyl-	246-248	11.25
1,2-Bis- <i>p</i> -acetylphenyl-	146-147	10.83	9.97
1,3-Bis- <i>p</i> -acetylphenyl-	202-204	...	11.17	11.07	...	9.99
Phenyl-	114-115	11.27	10.00
1,1'-Diphenyl-	155-156	11.27	9.94
1,2-Diphenyl-	109-110	10.93	9.96
1,3-Diphenyl-	107	...	11.15	11.05	...	9.97
<i>o</i> - or <i>m</i> -Biphenyl ^b	128-130	11.23	9.90
<i>o</i> - or <i>m</i> -Biphenyl ^b	132-133	11.23	10.93	9.95
α -(4-Methoxyphenyl)-4-methoxyphenyl-	154-155	...	11.17	9.96

^a All spectra were determined in chloroform solution. ^b The *p*-isomer has m.p. 161-162° (P. L. Pauson, private communication).

own experience, Nesmeyanov and Perevalova concluded that diarylation of ferrocene yields 1,1'-diarylferrocenes exclusively.⁶ The present results, far from supporting such an inference, suggest that in general all possible structurally isomeric diarylferrocenes (I, II and III) are formed in these reactions.



The melting points and infrared spectral data for the arylferrocenes obtained in a series of reactions employing the diazonium salts derived from aniline, *p*-anisidine and *p*-aminoacetophenone are summarized in Table I. Included in this table are several biphenylferrocenes isolated from certain of these reactions. Separation of isomers was achieved by careful chromatography on alumina columns.

The arylferrocenes are generally accompanied by varying amounts of biphenyls, by the deaminated aromatic amine and by azo compounds. Thus, treatment of ferrocene with diazotized *p*-nitroaniline afforded nitrobenzene, 3,4'-dinitrobiphenyl⁷ and 2,4'-dinitrobiphenyl, while reaction with diazotized *p*-aminoacetophenone yielded acetophenone and a colorless substance of m.p. 122°.⁸ Arylation with diazotized *p*-anisidine gave a dimethoxybiphenylferrocene, m.p. 154°, in addition to a considerable amount of 4,4'-azoanisole. The azo compound also has been isolated by Nesmeyanov and co-workers^{4b} from a similar reaction.

(6) A. N. Nesmeyanov and E. G. Perevalova, *Uspekhi Khim.*, **27**, 3 (1958).

(7) The identity of this substance was established by comparison with an authentic sample kindly supplied to us by Professor D. H. Hey.

(8) Its analysis does not correspond to that calculated for a diacetyl-biphenyl but rather to *p*-acetylphenylcyclopentadiene.

Excluding biphenylferrocenes, the relative adsorbabilities of the isomeric diarylferrocenes were found to be 1,2-diarylferrocene < 1,1'-diarylferrocene < 1,3-diarylferrocene. This order, which is maintained with solvents of such diverse polarity as low boiling petroleum ether and diethyl ether, follows with remarkable regularity the sequence previously observed for isomeric acetyl-alkylferrocenes and acetyl-arylferrocenes. As yet no exception to this pattern has been observed either in our own work or in that reported by others,⁹ and it would therefore appear to constitute a useful primary indication of structure.

Structure Determination.—Within each series of diarylated ferrocenes, the heteroannularly substituted derivatives are identified readily by the absence of absorption at 9 and 10 μ in their infrared spectra.¹⁰ The structures of the remaining diarylferrocenes were rigorously established by independent syntheses, while the corresponding isomers in the other series were correlated with these through their infrared spectra (*vide infra*).

Preparation of 1,4-bis-*p*-methoxyphenylcyclopentadiene was carried out following the procedure employed by Drake and Adams for the synthesis of 1,4-diphenylcyclopentadiene¹¹ (Fig. 1). Conversion of the diene to 1,3-bis-*p*-methoxyphenylferrocene (IIIb) was accomplished readily by treatment of an ethereal solution of the diene containing a large excess of cyclopentadiene with methylmagnesium bromide and then with ferric chloride. Ferrocene, which is the only other product of the reaction, was readily separated from the desired derivative by chromatography on alumina.

The synthesis of 1,2-bis-*p*-methoxyphenylferrocene (IIb) is outlined in Fig. 3. Initial attempts to effect pinacol reduction of the diketone IV¹² with either zinc dust in acetic acid or with magnesium and iodine failed. Conversion of this substance

(9) K. L. Rinehart, K. L. Motz and S. Moon, *J. Am. Chem. Soc.*, **79**, 2749 (1957).

(10) (a) M. Rosenblum, *Chemistry & Industry*, 953 (1958); (b) M. Rosenblum and R. B. Woodward, *J. Am. Chem. Soc.*, **80**, 5443 (1958); (c) A. N. Nesmeyanov, L. A. Kazitsina, B. V. Lokshin and I. I. Kritskaya, *Doklady Akad. Nauk S.S.S.R.*, **117**, 433 (1957).

(11) N. L. Drake and J. R. Adams, *J. Am. Chem. Soc.*, **61**, 1326 (1939).

(12) S. G. P. Plant and M. E. Tomlinson, *J. Chem. Soc.*, 856 (1935).

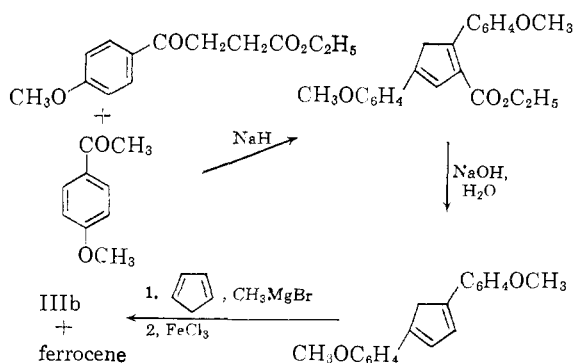


Fig. 2.

directly to 1,2-bis-*p*-methoxyphenylcyclopentadiene ultimately was achieved in one step by prolonged treatment with a large excess of aluminum amalgam. The transformation of the diene to 1,2-bis-*p*-methoxyphenylferrocene followed the procedure employed for the synthesis of IIIb, and does not require special comment.

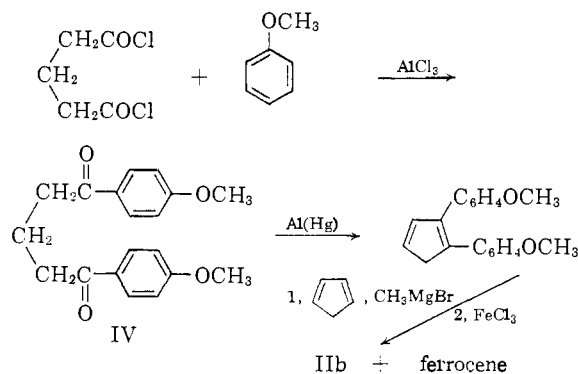


Fig. 3.

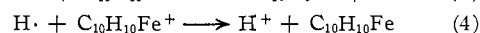
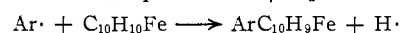
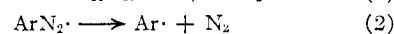
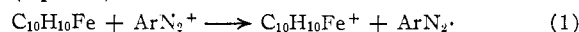
The infrared spectral correlations, so useful in assigning structures to homoannularly substituted isomeric acetyl-alkylferrocenes^{10a,b} and acetyl-arylferrocenes,¹³ may be extended with equal success to similarly constituted diarylferrocenes. For the acetyl-alkylferrocenes, absorption at 11.20 μ , characteristic of an acetyl substituted ferrocene ring, is replaced in the 1,2-isomers by an absorption near 10.90 μ , while for the 1,3-isomers disappearance of the long wave length absorption is attended by the emergence of two peaks near 10.85 and 11.05 μ . Similar regularities have been observed in the spectra of homoannularly substituted acetyl-arylferrocenes for which the absorption at 11.27 μ , indicative of an aryl substituted ferrocene ring, is replaced by absorption at 10.95 μ in the 1,2-isomers and by a doublet absorption at 11.05 and 11.15 μ in the 1,3-isomers. For the isomeric diarylferrocenes these significant peaks appear near 10.85 μ in the 1,2-isomers and at 11.05 and 11.15 μ in the 1,3-isomers. The appearance of these peaks is again accompanied by the disappearance of absorption near 11.25 μ .

Discussion

The arylation of ferrocene has been effected under various closely related experimental condi-

(13) M. Rosenblum, *J. Am. Chem. Soc.*, **81**, 4530 (1959); M. Rosenblum and W. G. Howells, *ibid.*, **84**, 1167 (1962).

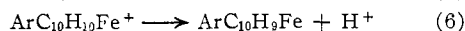
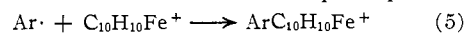
tions. Broadhead and Pauson^{4c} utilized aqueous acetic acid or acetone solutions of the aryldiazonium salts, while Nesmeyanov, Perevalova and Golovnya^{4a,b} carried out their reactions with aryloacetates in water-ether media. Both of these procedures, in particular the latter, afford primarily the monoarylferrocenes. Weinmayr later reported the arylation of ferricinium salts in aqueous acid solutions, a procedure which generally affords higher yields of diaryl- and polyarylferrocenes.¹⁴ Significantly, this reaction fails in the absence of a small amount of ferrocene.⁵ Both Pauson⁵ and Nesmeyanov^{4b} have concluded that the reaction is of a free radical type, and no doubt the analogy between these transformations, especially those effected in neutral solutions, and the Gomberg-Bachmann-Hey reaction is a particularly attractive one.¹⁵ In strongly acidic media, appreciable homolytic decomposition of the diazonium salt must be considered unlikely. For these reactions Pauson has suggested a mechanism involving an initial electron transfer process, in which ferrocene effects reduction of the diazonium cation to a diazo radical, which subsequently decomposes to give molecular nitrogen and an aryl radical¹⁶ (eq. 1-4).



The plausibility of the first step may not be questioned, for such electron transfer processes are a fundamental aspect of the chemistry of ferrocene. Furthermore, arylations carried out in acetone solution are attended by the rapid formation of a blue-green precipitate reminiscent of ferricinium salts, and the cation may be shown to be present at the conclusion of this reaction as well as those effected in other media.

However, serious objection may be raised to the replacement process depicted in step 3, for it is without adequate mechanistic analogy and involves a reaction which, on energetic grounds, is unlikely.¹⁶

Largely with the view of circumventing these difficulties, Little recently has suggested that the ferricinium cation itself, rather than ferrocene, is the active substrate for attack by aryl radicals¹⁷ (eq. 5, 6). Such a mechanism is in principle more



agreeable and appears to account for the observed arylation of ferrocene by treatment of aqueous ferricinium salt solutions containing a catalytic amount of ferrocene with aryldiazonium salts. However, the proportion of mono- and diarylferrocenes formed in these reactions with a series of *p*-substituted phenyldiazonium salts is not consonant with the above mechanism. Instead, Weinmayr's data,¹⁴ summarized in Table II, accord with the view

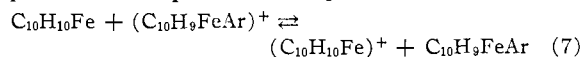
(14) V. Weinmayr, *ibid.*, **77**, 3012 (1955).

(15) For review of this reaction cf. W. E. Bachmann and R. H. Hoffman in "Organic Reactions," J. Wiley and Sons, Inc., New York, N. Y., Vol. 2, p. 224.

(16) Cf. C. Walling in "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 482.

(17) W. R. Little and A. K. Clark, *J. Org. Chem.*, **25**, 1979 (1960).

that it is the neutral species rather than the cation which undergoes substitution. In particular, the variation in the ratio of these products is precisely that expected from the known effect of the *p*-substituents upon the oxidation potentials of the intermediate monoarylfereocenes¹⁸ and hence on the position of equilibrium expressed in eq. 7. The



attainment of such an equilibrium is undoubtedly quite rapid, as is indicated by the fact that electron exchange reactions between 10^{-4} molar solutions of ferrocene and ferricinium nitrate or perchlorate have half-times of a few microseconds at -75° .¹⁹

TABLE II

YIELDS OF ARYLFERROCENES OBTAINED IN THE ARYLATION OF FERROCENE-FERRICINIUM SALT MIXTURES^a

Aromatic amine employed	Yield of monoarylferrocene, %	Yield of 1,1'-diarylferrocene, %
<i>p</i> -Hydroxyaniline	60	0
Aniline	17	20
<i>p</i> -Nitroaniline	10	60

^a From reaction of approximately equimolar quantities of aryldiazonium sulfates and oxidized ferrocene (ref. 14).

At this point we considered it important to examine the premise, central to each of these mechanisms, that free radicals are the active arylation agents in these reactions. This view rests in part upon an inferred analogy between these transformations and the Gomberg-Bachmann-Hey reactions, but less obliquely upon the observations that side reaction products, evidently of a radical origin, are encountered and that phenylation can be achieved in cyclohexane solution in the presence of *N*-nitrosoacetanilide.^{4c} However, the modes of formation of side reaction products and of arylfereocenes need not be identical, and the reactions of *N*-nitrosoacetanilides are by no means confined to the radical type. Huisgen and Horeld²⁰ have shown that decomposition of these substances in solutions containing phenols results in the quantitative formation of azo compounds, confirming and extending earlier observations of Hantzsch²¹ and of Bamberger.²² Azo coupling takes place rapidly in both non-polar as well as polar media, and its rate is at least four orders of magnitude greater than those decomposition processes which give rise to products of homolytic fission.^{23,24} Thus, the successful phenylation of ferrocene with nitrosoacetanilide cannot constitute evidence for a radical mechanism. Moreover, such a formulation is beset with serious inconsistencies, for the ability of ferrocene to compete effectively with solvent cyclohexane implies a relatively high order of reactivity toward phenyl radicals. Nevertheless, Broadhead

and Pauson have reported that ferrocene is not attacked by phenyl radicals generated from a mixture of phenylmagnesium bromide and bromobenzene with cobaltous chloride, by decomposition of benzoyl peroxide or by decomposition of phenylazotriphenylmethane in cyclohexane solutions.^{4c}

The latter observation now has been extended and amplified by carrying out the decomposition of phenylazotriphenylmethane in acetic acid in the presence of a mixture of ferrocene and the ferricinium cation. Under these conditions no detectable amounts of arylfereocenes are formed. It is clear then that neither ferrocene nor the ferricinium cation is susceptible to radical substitution, notwithstanding the very great reactivity of ferrocene itself in electrophilic substitution processes.

We believe that these reactions are explicable in terms of a transient complex (V) formed between the diazonium cation and the *metal* atom of ferrocene.²⁵ Decomposition of this complex may give the ferricinium cation and either an arylazo radical or an aryl radical and nitrogen directly. Such radical species are no doubt responsible for the formation of the side reaction products observed in these reactions but *not* apparently for the arylfereocenes. These substances must arise instead through an alternate mode of decomposition of V involving internal migration of an aryl group and concurrent loss of nitrogen to give the endocyclic σ -complex VI. For the present we must leave open a more exact description of character and extent of bonding in the transition state pertaining to this rearrangement and in particular the question as to whether the migrating group is a cationic or radical species. However, in view of the inferred analogy between these transformations and the Meerwein reaction (*vide infra*) the latter formulation seems the more reasonable.

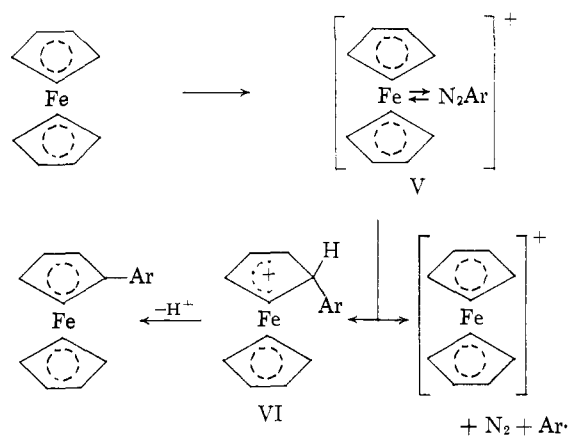


Fig. 4.

These mechanisms also account quite naturally for the failure of aryldiazonium salts to react normally with diacetylferrocene.²⁶ In these reactions, the formation of a complex similar to V is suppressed due to the increased oxidation poten-

(25) Broadhead and Pauson (ref. 4c) had earlier suggested the possible formation of a complex in these reactions, but did not define its nature.

(26) A. N. Nesmeyanov, *et al.*, *Izvest. Akad. Nauk SSSR*, 638 (1957).

(18) J. G. Mason and M. Rosenblum, *J. Am. Chem. Soc.*, **82**, 4208 (1960).

(19) D. R. Stranks, *Disc. Faraday Soc.*, **29**, 73 (1960).

(20) R. Huisgen and G. Horeld, *Ann.*, **562**, 137 (1949).

(21) A. Hantzsch and E. Wechsler, *ibid.*, **325**, 241 (1902).

(22) E. Bamberger, *Ber.*, **57**, 914 (1894); **53**, 2308 (1920).

(23) R. Huisgen, *Ann.*, **573**, 163 (1951).

(24) It is, in any event, doubtful whether free radicals as such are generated in the decomposition of *N*-nitrosoacetanilides: *cf.* R. Huisgen and H. Nakaten, *ibid.*, **573**, 181 (1951), and also H. Zollinger in "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961, p. 156.

tial of the metal atom. However, to the extent that such a complex is formed, its rearrangement to a σ -complex analogous to VI is precluded by the consequent transfer of positive charge from the metal atom to the acylated ring. The alternate mode of decomposition of the complex to a ferricinium salt is not as energetically prohibitive, but for diacetylferrocene as contrasted with ferrocene, the cation resulting is unstable.²⁷ The likely products of its decomposition are ferric ions and acetylcyclopentadiene. The latter may be expected to react rapidly with the aryldiazonium cation affording initially arylazoacetylcyclopentadiene and subsequently the products which are reported by Nesmeyanov.^{26,28} The decreasing proportion of diacetylferrocene reported to be recovered in these reactions with *p*-tolyl-, phenyl- and *p*-nitrophenyl-diazonium chlorides is likewise in accord with these deductions.

In principle two limiting structures (Va and Vb) each involving donor-acceptor bonds formed by overlap of metal and ligand orbitals of compatible local symmetry may be considered for the complex V. In each of these, bonding is partially achieved through overlap of a filled, weakly bonding e_{2g} ($3d_{xy}3d_{x^2-y^2}$) metal orbital with the anti-bonding orbital of the diazonium group. Back bonding from the diazonium function may involve interactions of its bonding π - or non-bonding p -orbital electrons with a vacant metal orbital of largely $4s$ or $4p_{x,y}$ character or a combination of these.²⁹

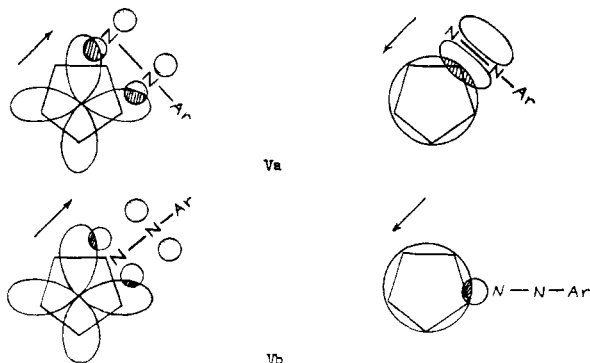
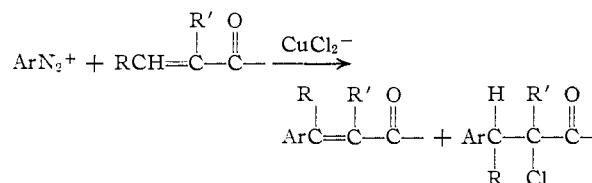


Fig. 5.

Structures of lower symmetry in which the angle between the N-N axis and the ligand-metal bond is intermediate between 90 and 180° may not be excluded. This geometry apparently obtains in certain Co(II) nitric oxide complexes,³⁰ and in Pd(II) complexes with styrene.³¹

These arylation reactions of ferrocene bear a remarkable similarity to the Meerwein reaction, in which addition of aryl groups to α,β -unsaturated

carbonyl compounds and related systems is effected by the agency of diazonium salts in the presence of cuprous halides.



Although a radical type mechanism is at present accepted for these reactions, free aryl radicals as such do not appear to be involved.³² Vogl and Rondestvedt have proposed a mechanism involving the formation and decomposition of a complex between diazonium cation, the olefin and the metal ion.³³ The internal rearrangement of such a complex to give the substituted olefin is a process in principle identical with that invoked in the arylation of ferrocene. The disparity in over-all result is a consequence simply of the difference in stability of the metal olefin portion of the complex in each case.

Internal rearrangements of ligand groups are a familiar occurrence in transition metal complexes containing carbonyl and acetylenic ligands.³⁴ There is no reason to believe that a fundamentally similar process involving diazo nitrogen groups could not operate, and that free nitrogen might not be lost in the course of such a rearrangement. The involvement of the metal atom of ferrocene in solvolysis reactions,³⁵ in intramolecular hydrogen bonding³⁶ and in protonation reactions³⁷ is well documented. While there is not as yet conclusive evidence for participation of the metal atom in ring substitution by electrophiles, such an inference is supported by the commonly encountered oxidation of ferrocene with oxidizing electrophiles and carbonium ions.³⁸ Moreover, the apparently anomalous reaction of ferrocene with aryldiazonium salts and its failure to react with aryl radicals, notwithstanding its very great reactivity toward

(32) For a review of the evidence bearing on this point cf. H. Zolinger (ref. 24), p. 162, and C. S. Rondestvedt in "Organic Reactions," J. Wiley and Sons, Inc., New York, N. Y., Vol. 11, 1960, p. 189.

(33) These authors prefer to invoke cupric rather than cuprous ion as the active metal species [O. Vogl and C. Rondestvedt, *J. Am. Chem. Soc.*, **78**, 3799 (1956)]. However, the weight of evidence would appear to be against such a formulation, although cupric ion may play an important role as a radical chain-terminating species, or as component in the cuprous complex. For relevant evidence on these points, cf. E. Pfeil and O. Velten, *Angew. Chem.*, **65**, 155 (1953); J. K. Kochi, *J. Am. Chem. Soc.*, **77**, 5090 (1955); **78**, 1228, 4815 (1956), and ref. 24.

(34) Cf. for example, R. F. Heck and D. S. Breslow, *ibid.*, **83**, 4223 (1961), and references cited therein; H. W. Sternberg and I. Wender in "International Conference on Co-ordination Chemistry," London, 1959, p. 35; M. Tsutsui and H. Zeiss, *J. Am. Chem. Soc.*, **82**, 6255 (1960), and preceding papers; P. L. Pauson, *Proc. Chem. Soc.*, 297 (1960).

(35) E. A. Hill and J. H. Richards, *J. Am. Chem. Soc.*, **83**, 3841, 4217 (1961); D. S. Trifan and R. Bacskai, *Tetrahedron Letters*, No. **13**, 1 (1960); G. R. Buell, W. E. McEwen and J. Kleinberg, *ibid.*, No. **5**, 16 (1959); A. Berger, W. E. McEwen and J. Kleinberg, *J. Am. Chem. Soc.*, **83**, 2274 (1961), have considered, but apparently rejected, metal interactions with the azido nitrogen function in ferrocenylphenylcarbinyl azide.

(36) D. S. Trifan and R. Bacskai, *J. Am. Chem. Soc.*, **82**, 5010 (1960).

(37) T. J. Curphey, J. O. Santer, M. Rosenblum and J. H. Richards, *ibid.*, **82**, 5249 (1960).

(38) M. F. Hawthorne, *J. Org. Chem.*, **21**, 363 (1956).

(27) M. Rosenblum, Thesis, Harvard University, 1953.

(28) A. N. Nesmeyanov, et al., *Doklady Akad. Nauk SSSR*, **133**, 851 (1960).

(29) Cf. F. A. Cotton and G. Wilkinson in "Progress in Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1959, p. 85, for a summary of molecular orbital treatments of ferrocene. C. J. Ballhausen and J. P. Dahl, *Acta Chem. Scand.*, **15**, 1333 (1961), have employed a somewhat different mixing of molecular orbitals in a discussion of the bonding in certain protonated metallocenes.

(30) R. H. Alderman and P. G. Owston, *Nature*, **178**, 1071 (1956).

(31) J. R. Holden and N. C. Baenziger, *J. Am. Chem. Soc.*, **77**, 4987 (1955).

electrophiles, are readily accounted for in terms of these concepts. An analogous mechanism may be operable in the recently reported electrophilic substitution of transition metal acetylacetonates,³⁹ certain aspects of which closely parallel similar reactions with ferrocene. These conclusions, if correct, will necessitate a fundamental revision in current concepts of the aromaticity of ferrocene and related metallocenes. Moreover, they provide a new vantage point from which to examine electrophilic substitution reactions of complex ions having formally unsaturated ligands.

Experimental⁴⁰

Reaction of Ferrocene-Ferricinium Chloride with Phenyl-diazonium Sulfate in Aqueous Solution.—Ferrocene (15 g., 0.08 mole) was dissolved in anhydrous ether and oxidized with an ethereal solution of ferric chloride (20 g., 0.12 mole). The resulting mixture was washed three times with 500-ml. portions of water and the aqueous extracts combined. A solution of benzenediazonium sulfate was prepared from 15 g. of aniline (0.16 mole), 11.6 g. of sodium nitrite (0.17 mole) and 25.8 g. of concentrated sulfuric acid. Excess nitrous acid was destroyed with urea and the diazonium salt solution together with 2 g. of ferrocene was added to the aqueous ferricinium salt solution. The mixture was stirred at ice-bath temperature for 20 hours, then decomposed with excess sodium bisulfite solution and extracted thoroughly with ether. The combined ether extracts were washed to neutrality, dried over magnesium sulfate and finally treated with excess ferric chloride. The resulting mixture of ferricinium salts was extracted into water and the combined aqueous solutions were washed several times with ether to ensure the complete removal of non-ferrocene compounds. The aqueous solution was then treated with excess sodium bisulfite and extracted with ether. The combined ether extracts were washed to neutrality and dried over magnesium sulfate. Drying reagent was filtered off and the ether removed. The residue was taken up in 100 ml. of petroleum ether (b.p. 30–60°). This solution was placed on an alumina column prepared from 850 g. of Merck alumina, and the products eluted with petroleum ether (b.p. 30–60°).

The four main bands which developed were collected separately. The first band contained unreacted ferrocene, and the second 900 mg. of phenylferrocene, m.p. 112–114° (lit.^{4c} 109–110°). The third fraction was concentrated to a volume of 10 ml. Crystallization gave a mixture of orange rods and red octahedral blocks which were separated by hand and recrystallized from petroleum ether (b.p. 20–40°). Additional material was obtained from the mother liquors by careful seeding and interrupted crystallization. In total, 450 mg. of 1,2-diphenylferrocene (IIa), m.p. 108.5–110°, and 260 mg. of *x*-biphenylferrocene, m.p. 131.5–132.5° were obtained.

Anal. Calcd. for C₂₂H₁₈Fe (IIa): C, 78.11; H, 5.33. Found: C, 77.65; H, 5.21. Calcd. for C₂₂H₁₈Fe: C, 78.11; H, 5.33. Found: C, 77.91; H, 5.41.

The fourth band was collected in three separate fractions. The first two of these gave 1.03 g. of 1,1'-diphenylferrocene (Ia), m.p. 156–157° (lit.^{4c} 154°). The third fraction gave 150 mg. of material, m.p. 106–121°. This was recrystallized six times from petroleum ether (b.p. 20–40°) to give 70 mg. of *x*'-biphenylferrocene, m.p. 128–130°.

Anal. Calcd. for C₂₂H₁₈Fe: C, 78.11; H, 5.33; Found: C, 77.75; H, 5.35.

The mother liquors from these recrystallizations gave impure 1,3-diphenylferrocene (IIIa) identified by comparison of its infrared spectrum with an authentic sample.⁴¹

(39) J. P. Collman, R. A. Moss, H. Maltz and C. C. Heindel, *J. Am. Chem. Soc.*, **83**, 531 (1961), and references cited therein; Abstracts of Papers, 140th Meeting, Am. Chem. Soc., Chicago, Ill., 1961, p. 4-N.

(40) All melting points were determined using a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer double beam recording spectrophotometer, model 21. Analyses were performed at the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., at the Alfred Bernhard Microanalytical Laboratory, Mulheim, Germany, and by Dr. C. Fitz, Needham, Mass.

Reaction of Ferrocene with Diazotized *p*-Anisidine in Aqueous Acetone.—A solution of diazotized *p*-anisidine was prepared by the usual method from 67.5 g. of *p*-anisidine (0.55 mole), 38 g. of sodium nitrite (0.55 mole) and 114 ml. of concentrated hydrochloric acid. Excess nitrous acid was destroyed with urea, and the cold solution was then added with stirring to 20 g. of ferrocene (0.11 mole) dissolved in 350 ml. of acetone. The reaction was allowed to continue for a period of 12 hours at 0° and then at 20° for 5 hours. Excess sodium bisulfite was added to reduce ferricinium salts and the aqueous acetone solution was repeatedly extracted with chloroform until the extracts were colorless. These extracts were combined, washed to neutrality and dried over magnesium sulfate. The drying reagent was filtered off and solvent was removed leaving a dark brown viscous oil. The crude product was taken up in 200 ml. of a 3:1 benzene-Skellysolve B solution and placed on a chromatographic column prepared from 3 kg. of Merck alumina (2% water added). Elution was begun with 1:5 mixtures of benzene-Skellysolve B and continued with 1:1 mixtures of these solvents. Four main bands developed and these were eluted and collected separately.

Band 1 yielded 1.76 g. of *p*-methoxyphenylferrocene, m.p. 108–110° (lit.^{4c} m.p. 112–114°).

The product obtained from band 2 was rechromatographed on 500 g. of Merck alumina (2% water added) employing Skellysolve B as eluent. A single fraction was collected, solvent was removed and the product taken up in cyclohexane. This solution on cooling gave a crop of mixed crystals, m.p. 110–116°, consisting of red blocks and more soluble small yellow needles. Careful fractional crystallization from cyclohexane gave 0.04 g. of *x*-(4-methoxyphenyl)-4-methoxyphenylferrocene as yellow needles, m.p. 154–155°.

Anal. Calcd. for C₂₄H₂₂O₂Fe: C, 72.4; H, 5.5. Found: C, 72.2; H, 5.5.

The second isomer, 1,2-bis-*p*-methoxyphenylferrocene (IIb) (1.07 g.), was obtained as red blocks, m.p. 119–121°.

Anal. Calcd. for C₂₄H₂₂O₂Fe: C, 72.4; H, 5.5. Found: C, 72.1; H, 5.5.

Recrystallization from cyclohexane of the product obtained from band 3 gave 1.13 g. of 1,1'-bis-*p*-methoxyphenylferrocene (Ib), m.p. 172–174° (lit.^{4c} 167–168°).

The product obtained from band 4 was recrystallized from cyclohexane to give an additional 0.44 g. of 1,1'-bis-*p*-methoxyphenylferrocene.

All mother liquors then were recombined and rechromatographed on 500 g. of alumina using Skellysolve B as eluent. The following compounds were eluted and isolated: 0.58 g. of *p*-methoxyphenylferrocene, 0.43 g. of 1,2-bis-*p*-methoxyphenylferrocene, 0.25 g. of *x*-(4-methoxyphenyl)-4-methoxyphenylferrocene and lastly 0.06 g. of 1,3-bis-*p*-methoxyphenylferrocene (IIIb), m.p. 159–161°.

Anal. Calcd. for C₂₄H₂₂O₂Fe: C, 72.4; H, 5.5. Found: C, 71.9, 72.7; H, 5.5, 5.8.

p-Methoxyphenylferrocene was also prepared in 43% yield by treatment of 20 g. of ferrocene with diazotized *p*-anisidine in water-ether mixture according to the procedure of Nesmeyanov, Perevalova and Golovnyia.^{4b} This reaction also gave 5 g. of 4,4'-azobenzene, m.p. 164–167° (lit.⁴² 164°), which had $\lambda_{\text{max}}^{\text{ethanol}}$ 242, 355 m μ ; ϵ 13,400, 23,600 (lit.⁴³, $\lambda_{\text{max}}^{\text{ethanol}}$ 246, 357 m μ ; ϵ 11,000, 29,000).

Reaction of Ferrocene with Diazotized *p*-Aminoacetophenone in Aqueous Acetic Acid.—A solution of diazotized *p*-aminoacetophenone was prepared from 34 g. of the amine (0.25 mole), 20 g. of sodium nitrite (0.30 mole) and 8.3 ml. of concentrated sulfuric acid in 150 ml. of water. This was added rapidly to a solution of 10 g. of ferrocene (0.05 mole) in 350 ml. of acetic acid. The resulting dark brown solution was allowed to stir overnight at 10–15°, and was then poured into 1 liter of water containing sodium bisulfite. The aqueous solution was extracted several times with chloroform, the extracts were combined, washed with sodium carbonate and water to neutrality and dried over magnesium sulfate. The drying reagent was filtered off and solvent removed leaving a deep orange solid.

(41) We are indebted to Professor P. L. Pauson for providing us with a sample of this substance.

(42) R. Walter, *Ber.*, **58**, 2306 (1925).

(43) M. P. Grammaticakis, *Bull. soc. chim. France*, 951 (1951).

The crude product was taken up in a small volume of chloroform-benzene, placed on a chromatographic column prepared from 1 kg. of Merck alumina (2% water added) and eluted with a 4:1 benzene-Skelly B solution. The following compounds were obtained in order of their elution: ferrocene, 100 mg.; acetophenone, 250 mg.; *p*-acetylphenylferrocene, 2.5 g., m.p. 174-175° (lit.¹³ 176-178°); and a colorless compound, m.p. 121-123°.

Anal. Calcd. for C₁₈H₁₂O: C, 85.59; H, 6.51. Found: C, 84.75; H, 6.51.

These substances were followed by 1,2-bis-*p*-acetylphenylferrocene (IIc), 150 mg., m.p. 146-147° (orange plates from ether-petroleum ether. *Anal.* Calcd. for C₂₆H₂₀O₂Fe: C, 73.95; H, 5.25. Found: C, 73.83; H, 5.38. 1,1'-bis-*p*-acetylphenylferrocene (Ic), 1.0 g., m.p. 243-245° (lit.¹³ 243-245°), and finally 1,3-bis-*p*-acetylphenylferrocene (IIIc) m.p. 202-204° (orange needles from methylene chloride-petroleum ether. *Anal.* Calcd. for C₂₆H₂₀O₂Fe: C, 73.95; H, 5.25. Found: C, 74.24; H, 5.51).

Synthesis of 1,3-Bis-*p*-methoxyphenylferrocene.— γ -*p*-Anisoylpropionic acid (79 g., 0.33 mole) was esterified with ethanol in the presence of sulfuric acid in the usual manner to give 55.5 g. of ethyl γ -*p*-anisoylpropionate, m.p. 49-50° (lit.⁴⁴ m.p. 52°). The ester (30 g., 0.13 mole) and 19 g. of *p*-methoxyacetophenone (0.13 mole) were added to a suspension of 6.1 g. of sodium hydride (0.254 mole) in 750 ml. of sodium-dried benzene. The reaction was stirred and heated at 70° in a nitrogen atmosphere for a period of 12 hours, then cooled and poured into 1 liter of ice-water contained in a separatory funnel. After extraction, the aqueous phase was withdrawn and set aside. The benzene solution was concentrated to a volume of 100 ml. and then refluxed in the presence of 50 ml. of a 10% sodium hydroxide solution. The aqueous phase was again withdrawn, combined with the previous aqueous extract and warmed on the steam-bath until the product separated from solution. The crude product was collected, washed with water and dried by suction. Recrystallization from benzene gave 8.54 g. (24%) of 1,4-bis-*p*-methoxyphenylcyclopentadiene as yellow crystals, m.p. 251-253°.

Anal. Calcd. for C₁₉H₁₈O₂: C, 82.0; H, 6.5. Found: C, 82.2; H, 6.8.

To a solution of methylmagnesium iodide prepared from 1.17 g. of magnesium turnings (0.15 mole) and 6.8 g. of methyl iodide (0.16 mole) in 300 ml. of tetrahydrofuran was added 0.80 g. of 1,4-bis-*p*-methoxyphenylcyclopentadiene (3.0 mmoles). The solution was stirred at reflux overnight, then allowed to cool to room temperature at which point 5 ml. of freshly cracked cyclopentadiene (0.07 mole) and additional methylmagnesium iodide (0.10 mole) were added. The solution was stirred at room temperature for 1 hour, then refluxed for 4 hours, and finally cooled in an ice-bath. Ferric chloride (16.2 g., 0.1 mole) partially dissolved in ether was added and the resulting dark red solution was allowed to stir at room temperature for 2 hours, then at reflux temperature for 30 minutes. The reaction mixture was cooled, washed with water containing sodium bisulfite, then with water to neutrality and dried over magnesium sulfate. Drying reagent was filtered off and solvent was removed leaving 2.5 g. of crystalline material. Chromatography on 200 g. of Merck alumina (2% water added) gave 1.7 g. of ferrocene from the first band and 0.75 g. of a yellow solid which, after two recrystallizations from cyclohexane, gave 0.23 g. of 1,3-bis-*p*-methoxyphenylferrocene (IIIb), m.p. 159-160°, identical with the substance, m.p. 159-160°, obtained in the arylation of ferrocene with diazotized *p*-anisidine.

Synthesis of 1,2-Bis-*p*-methoxyphenylferrocene.—Glutaryl chloride (134 g., 0.79 mole) was added dropwise over a period of 1 hour to a cold solution of 164 g. of anisole (1.5 moles) in 1 liter of methylene chloride, containing 225 g. of aluminum chloride. Following addition, the reaction was allowed to continue for an additional 2 hours. The deep red solution then was poured onto a mixture of 2 kg. of ice and 200 ml. of concentrated hydrochloric acid; the organic

phase was withdrawn, and the aqueous phase extracted with four 1-liter portions of benzene. The combined organic solutions were washed with water, sodium carbonate solutions and again with saturated sodium chloride solution to neutrality. Benzene was removed on the steam-bath and replaced gradually by ethanol until the volume of solution was 500 ml. On cooling to room temperature the solution deposited 66 g. of 1,3-bis-*p*-methoxybenzoylpropane as colorless needles, m.p. 99.5-100.5° (lit.¹³ m.p. 99°).

The above diketone (31.2 g., 0.10 mole) was dissolved in a mixture of 600 ml. of 95% ethanol and 300 ml. of water. Amalgamated aluminum was added in 6-g. batches to the refluxing solution over a period of 7 days, each portion being added over a period of 2 to 3 hours. The mixture was then poured into 5 liters of water, extracted several times with ether, and the combined ether extracts (3.5 liters) were washed to neutrality and dried over magnesium sulfate. The drying reagent was filtered off and solvent was removed, leaving 27.5 g. of viscous orange oil. A portion of this product (7 g.) was vacuum distilled and the fraction b.p. 190° (0.01 mm.) was collected. Addition of ether gave 450 mg. of material, m.p. 102-108°, which on recrystallization from ether gave 1,2-bis-*p*-methoxyphenylcyclopentadiene as colorless crystals, m.p. 107.5-109.5°. Chromatography of the remainder of the distillate gave an additional 120 mg. of diene.

Anal. Calcd. for C₁₉H₁₈O₂: C, 82.0; H, 6.5. Found: C, 81.6; H, 6.4.

To a solution of methylmagnesium iodide prepared from 23.0 g. of methyl iodide (0.16 mole) and 3.51 g. of magnesium turnings (0.15 mole) in 200 ml. of anhydrous ether and 300 ml. of benzene was added 0.40 g. of 1,2-bis-*p*-methoxyphenylcyclopentadiene (1.5 mmoles). The solution was refluxed for 2.5 hours and then 2.5 ml. of freshly prepared cyclopentadiene (0.03 mole) was added and the solution allowed to reflux for an additional 24 hours. The solution was cooled, 10.7 g. of ferric chloride (0.07 mole) partially dissolved in anhydrous ether was added, and the dark red brown mixture was stirred at room temperature for 4 hours and then heated at reflux for 30 minutes. After cooling, the mixture was poured into saturated sodium chloride solution containing sodium bisulfite. The organic phase was separated, washed to neutrality and dried over magnesium sulfate. Drying reagent was filtered off and solvent removed leaving 2.5 g. of crystalline product. This was placed on a chromatographic column prepared from 200 g. of Merck alumina (2% water added) and eluted with benzene. The first band eluted yielded 1.55 g. of ferrocene, while the second band gave 230 mg. of 1,2-bis-*p*-methoxyphenylferrocene (IIa), m.p. 119-121°, as red blocks, identical with the substance, m.p. 119-121°, obtained in the arylation of ferrocene with diazotized *p*-anisidine.

Reaction of Ferrocene-Ferricinium Cation with Phenylazotriphenylmethane.—Ferrocene (2.0 g., 0.011 mole) was dissolved in 75 ml. of acetic acid. The solution was stirred in a nitrogen atmosphere while 0.43 ml. of 30% hydrogen peroxide (0.0036 mole), dissolved in 25 ml. of acetic acid was added dropwise. Phenylazotriphenylmethane (4 g., 0.012 mole), dissolved in 100 ml. of acetic acid was then added and the reaction mixture was heated for 24 hours at 75°. The solution then was cooled to 0° and poured into 1.5 liters of water. The turbid aqueous solution was extracted with ether until the ether extracts were colorless and the combined ether extracts were washed to neutrality and dried over magnesium sulfate. Drying reagent was filtered off and the ethereal solution was poured into a solution of ferric chloride in anhydrous ether. The ferricinium salt was extracted with water until the aqueous extracts were colorless. The combined aqueous washings containing ferricinium salts were reduced with sodium bisulfite and extracted with ether. The ether extracts were combined, washed to neutrality and dried over magnesium sulfate. Drying reagent was filtered off, the solution reduced in volume to 25 ml. and placed on a chromatographic column prepared from 400 g. of alumina (Merck, acid-washed). Elution was carried out with petroleum ether (b.p. 30-60°). Only one band developed. This was eluted and gave 930 mg. of pure ferrocene.