Journal of Organometallic Chemistry, 141 (1977) 355—370

Metallocene Basicity. IV. Conformational and Electronic Behaviour of Some Protonated Ferrocenes

Thomas E. Bitterwolf
The Department of Chemistry, U.S. Naval Academy, Annapolis, Md., 21402, USA

and

A. Campbell Ling*
The Nuclear Science Facility, San Jose State University, San Jose, Cal.,
95192, USA.
(Received March 16th, 1977)

SUMMARY

The PMR spectra of several substituted ferrocenes in HBF_3OH have been recorded and the metal protonated species are discussed. 1,3-di-t-butylferrocenonium compounds were found to exist as two noninterconverting rotamers in acid solution. Hammett substituent constants for ferrocene and ferrocenonium have been determined.

INTRODUCTION

In an earlier paper[1] we discussed the conformational behavior of ferrocenonium species with simple alkyl substituents. In this paper we shall describe the protonation of 1,3-substituted ferrocenes containing electron withdrawing groups. In addition, we have determined the Hammett substituent constants for ferrocene and ferrocenonium via ^{19}F-NMR spectrometry.

---

*To whom correspondence should be addressed

EXPERIMENTAL

PMR spectra were recorded on a Varian Associates Model T-60 NMR Spectrometer and ^{19}F-NMR spectra were recorded on a Varian Associates Model HA 60 Spectrometer operating at 56.5 MHz. All spectra were recorded at a temperature of 30°.

Sample preparation, and decomposition screening for ferrocene compounds in HBF_3OH, have been discussed elsewhere[1,2]. Tetramethyl ammonium bromide was used as an internal standard ($\tau = 6.67$) for PMR spectra in HBF_3OH. Trifluoroacetic acid was used as an internal standard for ^{19}F-NMR in HBF_3OH. The fluorine resonance of trifluoroacetic acid was found to lie 77.5 ppm downfield of CCl_3F and to be insensitive to the acid environment. CCl_3F was used as an internal standard for ^{19}F-NMR spectra of ferrocenes in CCl_4.

The *t*-butyl-ferrocenes were prepared by Friedel Crafts alkylation of ferrocene with *t*-butyl chloride as described by Leigh[3]. All compounds were characterized by NMR spectrometry. Gas chromatographic analysis of the purified compounds demonstrated that no impurities were present at levels which might be detectable by PMR. All PMR spectral parameters are quoted in τ-units relative to TMS at τ10.00.

Meta- and p-fluorophenyl-ferrocene. Arylation of ferrocene was performed using the procedure described by Broadhead and Pauson[4]; p-fluorophenylferrocene was isolated as red crystals: mp 101-104°. Analysis: calculated for $FC_6H_4(C_5H_4)(C_5H_5)Fe$: C, 70.0; H: 4.64. Found: C: 69.00; H: 4.82%. PMR: 2.66 (2H, triplet, J = 4.0 Hz), 3.10 (2H, triplet, J = 4.0 Hz), 5.53 (2H, broad singlet), 5.80 (2H, broad singlet), 6.06 (5H, singlet), m-fluorophenylferrocene was isolated as red crystals: mp 52-53°. Analysis: calculated for $FC_6H_4(C_5H_4)Fe$: C, 70.0; H, 4.64. Found: C, 69.85; H, 4.90. PMR: 2.5 - 3.5 (4H, broad multiplet), 5.50 (2H, broad multiplet), 5.80 (2H, broad multiplet), 6.06 (5H, singlet).

All other compounds were prepared by standard techniques and their identities were confirmed by melting point determinations and PMR spectral data. Gas and thin layer chromatographic techniques were used to determine purity.

RESULTS AND DISCUSSION

Protonation of t-Butyl Ferrocenes

The PMR spectra of five-t-butyl-substituted ferrocenes in HBF_3OH were recorded. The chemical shifts of the observed resonances and their assignments are presented in Table 1. Included in Table 1 is the iron hydride resonance for 1,3-di-t-butyl-1'-methylferrocene in the same medium. In this latter case contamination with about 20% of a second di-t-butyl-isomer obscured the ring resonance region, making interpretation impossible.

In a previous paper[1], methyl and ethyl substituted ferrocenes were shown to undergo protonation at the metal to produce a ring tilted species. The spectra of the protonated species were characterized by separations of the ring protons into two symmetric doublets with the H_3 and H_4 protons appearing at higher field than the H_2 and H_5 protons. The different proton environments were attributed to hindered ring rotation of the substituted ring, the hindrance being caused by the inability of the substituent to pass through the region of closest ring approach in the tilted species. A strong shielding field has been found to exist along the C_{2v} axis of the ferrocenonium ion.

The general observations seen for the mono-alkyl substituted ferrocenonium ions appear inappropriate to describe the ring proton resonances of mono- and 1,1' -di-t-butylferrocenonium, which show no resonance splitting at all. However, when these compounds are viewed in the context of a series of protonated ferrocenes involving decreasing chemical shift separation, the failure to observe a separation is less suprising; for example:

$$\text{Me}(19\ \text{Hz}) > \text{Me}_2(17\ \text{Hz}) > \text{Me-Et}(16\ \text{Hz}) > \text{Et}(14\ \text{Hz}) >$$

$$\text{Et}_2(13\ \text{Hz}) > \text{t-Bu}(\sim 0\ \text{Hz}) = \text{di-t-Bu}(\sim 0\ \text{Hz}).$$

This series has been interpreted as indicating an order of decreasing ring

(Continued on p. 360)

TABLE 1. PMR Parameters for τ-Butyl-ferrocenes
(all chemical shift parameters are given in τ-units)

COMPOUND	Ring protons in C_5H_4R' ring	Ring protons and substituent protons in C_5H_4R ring					
		H_2	H_3	H_4	H_5	R = τ-Butyl	Fe-H
t-Butylferrocene (R' = H)	6.06	5.99	5.99	5.99	5.99	8.85	
t-Butylferrocenonium (R' = H)	4.90	4.90	4.90	4.90	4.90	8.65	11.81
1,1,-di-t-butyl ferrocene		6.06	6.06	6.06	6.06	8.80	
1,1'-di-t-butyl ferrocenonium		4.61	4.61	4.61	4.61	8.58	11.81
1,3-ferrocene-di-t-butyl (R' = H)	5.99	6.16	--	6.16	6.16	8.78	
1,3-ferrocenonium-di-t-butyl (R' = H)	4.64	4.79	--	4.36	4.36	8.70	12.70 (0.5H) 12.90 (0.5H)

1,1',3-Tri-t-butyl-ferrocene (R' = H)	$H_{2'}$ & H_5 = 6.06 $H_{3'}$ & H_4 = 6.06 R' = 8.80	6.23	--	6.15	6.15	8.80	
1,1',3-Tri-t-butyl-ferrocenonium (R' = t-Bu)	$H_{2'}$, $H_{5'}$ = 4.64 $H_{3'}$, $H_{4'}$ = 5.23 R' = 8.51	4.64	--	4.43	4.43	8.71	12.28
1,1',3,3' -Tetra-t-butylferrocene		6.23	--	6.17	6.17	8.78	
1,1,'3,3'-Tetra-t-butylferrocenonium		5.13	--	4.73	4.73	8.65	13.00
1,3 Di-t-butyl-1'-methylferrocenonium							12.66(0.5 H) 12.86(0.5 H)

tilting [1]; and this latter would appear to be related to the relative abilities of the substitutents to release electrons.

It is possible to conclude from the absence of splitting of the proton resonances in t-butyl ferrocenonium spectra that the substituted rings in these compounds are free to rotate about the ring-metal axis. However, further evidence presented below indicates that such a conclusion may be premature. The failure to observe differentiation of the ring protons in the spectra of the t-butyl compounds may arise from two sources: Ring tilting may be so slight as to allow free rotation (and hence resonance averaging) about the ring-iron bond; or, the shielding field arising from the metal la, b_2, and 2a, orbitals[5] may be so tightly focussed that a small change in ring tilting moves the ring protons out of the field.

In contrast, the ring proton resonances of the three 1,3-di-t-butyl ferrocenonium ions provide a richer and more interesting subject than do the two compounds discussed above. The ring resonance region of the 1,3-di-t-butylferrocenonium ion was found to contain three resonances whose relative areas were 2:5:1. These resonances can be immediately assigned to the H_4 and H_5 protons, the unsubstituted ring, and the H_2 proton, respectively. The ring resonance region of 1,1',3,3'-tetra-t-butylferrocenonium ion was found to be very simple with only two resonances whose area ratio was 2:1. Again, the downfield resonance is assigned to the H_4 and H_5 proton pair and the upfield resonance to the H_2 proton.

This apparent tendency for the H_2 proton to be upfield of the H_4 and H_5 protons can be used to assign the protons in the ring resonance pattern of 1,1',3-tri-t-butylferrocenonium. In this compound, the ring resonance pattern has an integration area ratio of 2:3:2. Assuming that the H_2 proton resonance for the disubstituted ring contributes the odd proton to the central resonance, this requires that the H_4 and the H_5 protons of the disubstituted ring be assigned to the lowest of the resonances. This assignment leaves the remaining two resonances, which are separated by 37 Hz, to be assigned to the singly substituted ring. Based on the established tendency for the protons H_3 and H_4 to be upfield of the H_2 and H_5 protons, the remaining two resonances will be similarly assigned.

The observation of a strongly split resonance for the ring protons of a singly t-butyl-substituted ring contrasts sharply with the case of t-butylferrocenonium and 1,1' -di-t-butylferrocenonium. If the failure to observe resonance splitting in the latter compounds is due to a reduction in ring tilting, then it does not seem reasonable to invoke extreme ring tilting to explain the 37 Hz separation in the 1,1',3-tri-t-butylferrocenonium. A more consistent explanation suggests that the steric constraints produced by the 1,3-disubstituted ring are sufficiently severe to cause what may possibly be a small shielding effect in the region of closest ring approach to be magnified by the inability of the singly substituted ring to average its proton environments.

The most striking feature of the PMR spectra of the 1,3-di-t-butyl substituted compounds is the appearance of two clearly resolved and equal area iron-hydrogen resonances for the 1,3-di-t-butylferrocenonium and the 1,3-di-t-butyl-1' -methylferrocenonium, and a highly broadened iron-hydrogen resonance for the 1,1',3-tri-t-butylferrocenonium. 1,1'3,3'-tetra-t-butylferrocenonium itself has a single iron-hydrogen resonance. The iron-hydrogen resonances of these compounds are shown in Figure 1. Integration of the hydride resonances indicate that there is only one hydrogen per ferrocene attached to the central metal atom, precluding the possibility of multiple protonation. Gas chromatographic analysis of the starting compounds indicated that in every case except for 1,3-di-t-butyl-1'-methylferrocenonium there was no impurity that would be detectable by PMR.

The existence of two distinct hydride resonances requires that, despite the simplicity of the ring resonance patterns, two unique protonated species must be formed by 1,3-di-t-butylferrocenes. Additionally, the equal integrations of these resonances requires that the species have equal probabilities of formation.

The requirements outlined above are satisfied by the rotamers illustrated in Figure 2. Determination of which rotamer is formed is a random process controlled by the direction from which an incoming proton

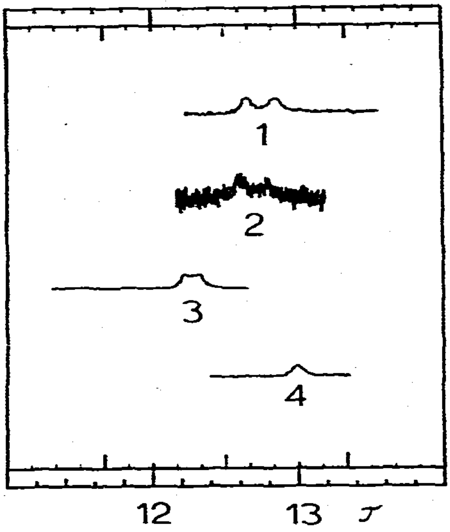

Fig. 1. Iron-hydrogen pmr spectra for:

(1) 1,3-di-t-butyl-ferrocenonium,

(2) 1,3-di-t-butyl-1'-methyl ferrocenonium,

(3) 1,1',3-tri-t-butyl-ferrocenonium,

(4) 1,1',3,3'-tetra-t-butyl-ferrocenonium.

approaches the metal. The integrity of the resulting rotamer is insured by the prohibition of ring rotation by the t-butyl groups. As the inductive electronic contributions to the iron should be equal in the two rotamers, the iron hydride chemical shift differences must be related to the relative proximity of the t-butyl groups to the hydride. It would seem that the dielectric shielding of the iron hydride by the t-butyl groups is greater in rotamer B of Figure 2 than it is in rotamer A; thus, the upfield resonance is assigned to the former rotamer.

This explanation of metal-proton shift differences based on dielectric shielding arguments is supported by the reduction in the separation between the resonances of the iron hydrides with increasing size of the substituent on the second ring,

i.e. H(12Hz) > Me(10Hz) > t-butyl (6Hz)

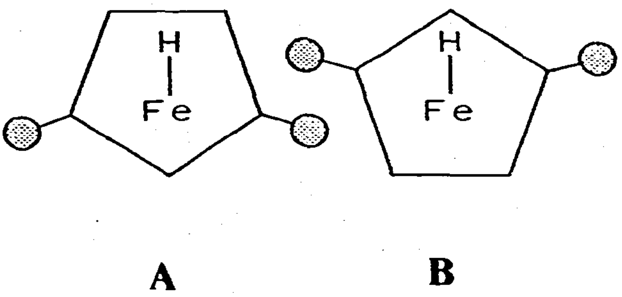

Fig. 2. Possible rotamers for the metal protonated ferrocene derivative 1,3-di-t-butylferrocenonium cation.

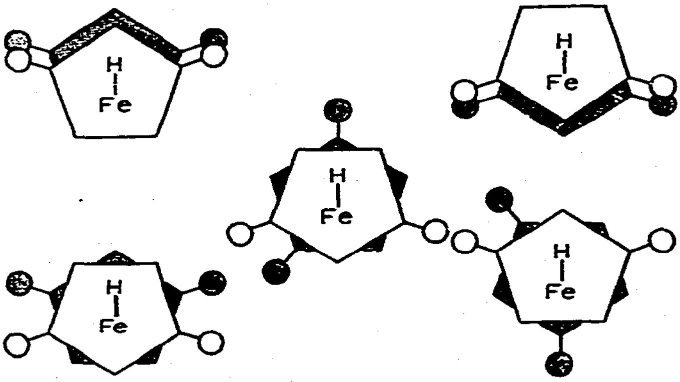

Fig. 3. Possible rotamers for the 1,1',3,3'-tetra-t-butylferrocenonium cation.

The additional dielectric shielding contributed by the second ring substituents reduces the contrast in shielding between the two rotamers.

The appearance of a single hydride resonance for the 1,1'3',3'-tetra-t-butylferrocenonium may indicate either that only one of the several possible rotamers shown in Figure 3 is stable, or that the hydride resonances of all of these rotamers are accidentally identical.

The observed 2:1 ring proton pattern for all of the 1,3-di-t-butyl substituted rings indicates that this pattern is determined by inductive effects within the rings or dielectric shielding by the t-butyl groups, and that it is not sensitive to the tilting of the ring. If ring tilting and its concurrent shielding were important, then much more complex ring patterns would be anticipated.

Electron Withdrawing Substituents

The introduction of an electron withdrawing substituent into a cyclopentadienyl ring in ferrocene is expected to reduce the basicity of the iron. If this reduction in basicity is great enough, the metal protonated species may be destabilized relative to the postulated σ-complex which is expected to precede electrophilic substitution on the ring. To examine the possibility of ring σ-complex formation, several ferrocene compounds containing electron withdrawing groups were studied in HBF_3OH.

Several attempts were made to observe PMR spectra from iodoferrocene, bromoferrocene, chloroferrocene, and 1,1'-dichloroferrocene, in HBF_3OH. In every case, acid addition to each system was followed by immediate oxidation. When the acid solutions were neutralized and reduced, only ferrocene was recovered. This finding is consistent with the protodehalogenation of halogeno-ferrocenes which has been reported by Nesmeyanov et al.[6]

Triphenylmethyl-ferrocene was found to undergo rapid cleavage in HBF_3OH to produce the triphenylmethenium ion and ferrocene (ferrocenonium). Several similar reactions have been reported[7] in which the leaving group is a ferrocenyl carbenium ion. Turbitt and Watts have proposed that these reactions follow the "ricochet" mechanism in which a metal protonated ferrocene undergoes a rapid hydrogen shift to produce a ring σ-complex at the carbon containing the substituent, followed by loss of the substituent.

Phenylferrocene and p- and m-fluorophenylferrocene were examined in HBF_3OH and found to undergo protonation to form a stable metal protonated species. The chemical shifts of the spectral resonances and their assignments are presented in Table 2. In every case, the spectrum of the phenylferrocenonium ion is found to consist of an AA'BB' doublet which is positioned slightly downfield of the sharp unsubstituted ring resonance. In keeping with the known tendency for the electron withdrawing groups to deshield the H_2 and H_5 ring protons more than the H_3 and H_4 protons, the resonances have been assigned accordingly. This assignment also corresponds to the expected tendency for the H_3 and H_4 protons to be shielded by the region of closest ring approach. The iron hydride resonance is clearly resolved at about τ12 in all three compounds.

(Trimethylammonium)methylferrocene iodide was found to undergo metal protonation in HBF_3OH. The spectrum has four broadened resonances below τ10 which are found by integration to have the relative areas 2:7:2:9 and a single resonance at τ12.13, which had an integration area of one and is immediately assignable to the iron hydride. Assignment of the ring resonances is complicated by the accidental superimposition of the unsubstituted ring resonance with a second two-proton resonance at τ4.53. By analogy with the phenylferrocenonium ions discussed above, the two-proton resonance at τ4.53 is assigned to the H_3 and H_4 protons of the substituted ring and the downfield resonance at τ4.00 assigned to the H_2 and H_5 protons of this ring. The two-proton resonance at τ5.87 can be assigned to the methylene protons of the substituent. This last assignment requires that the methylene resonance undergo a 15 Hz upfield shift upon protonation, which is in contrast to the usually observed downfield shift of methylene protons adjacent to the cyclopentadienyl ring. This shift can be explained if it is assumed that electrostatic repulsion between the ammonium group and the iron hydride is sufficiently strong to keep the two groups at a maximum distance. The repulsion would force the methylene hydrogens to rotate so that they are <u>endo</u> with respect to the iron hydride, where they would be subjected to the shielding field between the ferrocenonium rings. In a recent paper, Rimmelin, Sommer, Sandström, and Seita[8] have reported that acylferrocene in a super acid undergoes both oxygen protonation to form a carbenium center and also iron protonation. This observation, along with our own, indicates that metal protonation is preferred even in the presence of strong electron withdrawing substituents.

^{19}F-NMR of Protonated Ferrocenes

Table 3 presents the ^{19}F chemical shifts of m- and p-fluoro-phenyl-

TABLE 2

PMR Parameters for Variously Substituted Ferrocenes and their Metal Protonated Derivatives

COMPOUND	C_5H_5	H_2 & H_4	H_3 & H_4	R		Fe-H
Ferrocenylmethyltrimethylammonium iodide	5.62	5.30	5.62	CH_2	5.00	
				$(CH_3)_3N^+$	6.65	
Ferrocenonium-methyltrimethylammonium iodide	4.53	4.00	4.53	CH_2	5.87	12.13
				$(CH_3)_3N^+$	6.65	
Phenylferrocene	6.06	5.47	5.79	C_6H_5	2.5-3.0	
Phenylferrocenonium	4.92	4.12	4.75	C_6H_5	3.0	11.93
p-Fluorophenylferrocene	6.05	5.53	5.80	C_6H_4F	2.5-3.3	
p-Fluorophenylferrocenonium	4.99	4.29	4.78	C_6H_4F	1.9	12.05
m-Fluorophenylferrocene	6.05	5.49	5.80	C_6H_4F	2.6-3.2	
m-Fluorophenylferrocenonium	4.88	4.10	4.70	C_6H_4F	2.3	11.94

TABLE 3

^{19}F NMR Parameters for some Fluorophenyl-ferrocenes

COMPOUND in CCl_4 Solution	$CFCl_3$ Standard in Hz	$CFCl_3$ Standard in ppm	Fluorobenzene Standard in ppm
m-fluorophenyl-ferrocene	6476	114.8	+0.7
p-fluorophenyl-ferrocene	6762	119.8	+5.7

COMPOUND in HBF_3OH Solution	TFA Standard in Hz*	$CFCl_3$ Standard in ppm	Fluorobenzene Standard in ppm
m-fluorophenyl-ferrocenonium	2050	113.8	-0.3
p-fluorophenyl-ferrocenonium	2050	113.8	-0.3

*TFA was found to lie 77.5 ppm from $CFCl_3$ independent of the quantity of HBF_3OH present.

ferrocenes relative to fluorobenzene. The spectra were measured in both CCl_4 and HBF_3OH so that the parent and protonated species could be compared. Hammett constants were calculated using standard literature techniques.[9] The resulting values of σ_I, σ_R^o, σ_m, and σ_p, are presented in Table 4, along with values reported by other workers.* (See next page)

In this study, ferrocene was found to have an inductive contribution, $\sigma_I = -0.014$, on the order of that of an ethyl group, and a resonance contribution, $\sigma_R^o = -0.169$, comparable to that of bromine. These findings are in good qualitative agreement with the more classical techniques for measuring the substituent effects of ferrocene which have been used by Rausch[11], and Russian workers[12-16].

TABLE 4

HAMMETT σ-VALUES FOR FERROCENE,

AND CATIONS DERIVED FROM FERROCENE.

COMPOUND	σ_p	σ_m	σ_I	σ_R^o	REFERENCE
Ferrocene	-0.048	-0.118	-0.014	-0.169	This work
	-0.18	-0.15			12
	-0.10				13
	-0.05				11
	-0.03				11
Ferrocenonium[*]	+0.288	+0.0507	+0.127	0.00	This work
Ferricenium[**]	+0.29	+0.29			10

[*] Ferrocenonium = $(Cp_2Fe\text{-}H)^+$

[**] Ferricenium = $(Cp_2Fe)^+$

---

[*] Values recorded in Table 4 for ferricenium were attributed by Little *et al.*[10] to "protonated ferrocene." Little *et al.* tested indirectly for oxidation and found no evidence for it; however, their experimental details are sufficiently suggestive as to warrant re-iteration and comment at this time. Firstly, their original experiments were performed in H_2SO_4 with no described protection against air oxidation, which is known to occur easily in this medium. Secondly, their paper describes the "protonated ferrocene compound" as staying in solution with water, and requiring the addition of base to recover the original compound. These properties are more descriptive of ferricenium than of ferrocenonium.

Protonated ferrocene is found to be a moderately electron withdrawing substituent, $\sigma_I = +0.127$, which is similar to the chloromethyl group. The resonance contribution of protonated ferrocene, $\sigma_R^o = 0.00$, is identical to that of methylammonium.

These results indicate that the protonation of the iron in ferrocene causes electron withdrawal from both the σ and π-cyclopentadienyl frameworks. The net effect of this withdrawal is to compensate for the increased formal charge on the iron in the protonated species.

Comparison of the σ_m values of ferrocenonium and ferricenium indicates that the oxidized ferrocene (ferricenium) is a stronger electron withdrawing group than the metal protonated ferrocene (ferrocenonium). This is in accord with the full positive charge on the metal in the former case, and the partial charge in the latter. The similarity of the σ_p values is striking and suggests that despite the structural differences between the two species, their electronic behavior is closely related. An identifical suggestion has been made by Pavlik with his co-workers Klikorka[17] and Sübrt[18] on the basis of their IR spectral study of the protonated and oxidized ferrocenes.

ACKNOWLEDGEMENTS

We wish to thank Dr. William Watts for his suggestions which led to the investigation of t-butylferrocenonium compounds, and for his advice throughout. We thank the Research Corporation for partial support of this research.

REFERENCES

1. T.E. Bitterwolf and A.C. Ling, J. Organometal Chem., 40, (1972), 197.
2. T.E. Bitterwolf and A.C. Ling, Submitted for Publication.
3. T. Leigh, J. Chem. Soc., (1964), 3294.
4. G.D. Broadhead and P.L. Pauson, J. Chem. Soc., (1955), 367.
5. J.W. Lauher and R. Hoffman, J. Amer. Chem. Soc., 98, (1976), 1729.

6. A.N. Nesmeyanov, D.N. Dursanov, M.N. Nefedova, V.N. Setkina, and E.G. Perevalova, Dokl. Akad. Nauk. S.S.S.R., 161, (1965), 1349.

7. T.D. Turbitt and W.E. Watts, J. Chem. Soc., Perkin II, (1974), 189.

8. P. Rimmelin, J. Sommer, J. Sandström, and J. Seita, J. Organometal. Chem., 114, (1976), 175.

9. P.R. Wells, "Linear Free Energy Relationships", Academic Press, New York, 1968.

10. W.F. Little, R.A. Berry, and P. Kannan, J. Amer. Chem. Soc., 84, (1962), 2525.

11. M.D. Rausch, E.O. Fischer, and H. Grubert, J. Amer. Chem. Soc., 82, (1960), 76.

12. A.N. Nesmeyanov, Proc. Roy. Soc. London, 246A, (1958), 495.

13. A.N. Nesmeyanov and E.G. Perevalova, Ann. N.Y. Acad. Sci., 125, (1965), 67.

14. A.N. Nesmeyanov, E.G. Perevalova, and R.V. Golovnya, Dokl. Akad. Nauk. S.S.S.R., 103, (1955), 81.

15. A.N. Nesmeyanov, E.G. Perevalova, S.P. Gubin, K.I. Grendberg, and A.G. Kozlovsky, Tetrahedron Lett., (1966), 2381.

16. E.G. Perevalova, K.I. Grendberg, N.A. Zharikova, S.P. Gubin, and A.N. Nesmeyanov, Izvestia Akad. Nauk. S.S.S.R., Ser. Khim. 5, (1966), 832.

17. I. Pavlík and J. Klikorka, Proc. 9th. Int. Conf. Coord. Chem., (1965), 21.

18. I. Pavlík and J. Sǔbrt, Coll. Czech. Chem. Comm., 32, (1967), 76.