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STABILIZATION OF THE CYCLOPROPENUM AND CYCLOPROPENONE RING SYSTEMS BY FERROCENE

A ^{13}C NUCLEAR MAGNETIC RESONANCE STUDY

ISRAEL AGRANAT* and ELIEZER AHARON-SHALOM
Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel

and

ALBERT J. FRY* and RICHARD L. KRIEGER
Hall-Atwater Laboratories of Chemistry, Wesleyan University, Middletown, CT 06457, U.S.A.

and

WILLIAM O. KRUG*
Department of Chemistry, The Johns Hopkins University, Baltimore, MD 21218, U.S.A.

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Abstract—The ^{13}C NMR spectra of diferrocenylcyclopropenone (1) and the triferrocenylcyclopropenium (2) and ferrocenyldiphenylcyclopropenium (3) cations in non-acidic media are analyzed with special reference to the information they afford concerning charge distribution in these species. A delocalization of the positive charge into the remote unsubstituted five-membered rings of 2 and 3 is indicated. The role of the metal as a conduit for this effect is suggested.

Diferrocenylcyclopropenone (1) and the triferrocenylcyclopropenium ion (2) were recently synthesized[1] with a view toward utilizing and studying the effect of ferrocene substituents as stabilizing groups in the cyclopropenone and cyclopropenium ring systems. The rationale underlying this approach was based on a combination of the remarkable stability of α-ferrocenylcarbenium ions[2] and the potential stabilization of the "aromatic" but highly strained $2\pi 3C$ ring systems of 1 and 2 by electron-donating substituents. In the event, it turned out that the ferrocene substituent does indeed strongly stabilize these ring systems, as exemplified, for example, in the very high value of the pK_{R+} of 2 (> 10).[1] In the present work, a ^{13}C NMR spectroscopic study of 1 and 2 and ot the related 1-ferrocenyl-2,3-diphenylcyclopropenium ion (3) was undertaken. The ^{13}C NMR method provides a more quantitative (relative to ^{1}H NMR) and reliable estimate of the π-electron charge density distribution in the remainder of the molecule. ^{13}C NMR studies of the individual components of 1–3, viz., α-ferrocenylcarbenium ions in acidic media,[5-9] cyclopropenium ions,[10] cyclopropenones,[10,11] and ferrocenes,[12] have recently been reported.

RESULTS

The ^{13}C NMR parameters of several neutral 1,2,3-triferrocenylcyclopropenes (4, X = H, CN, or OCH_3) served as a model for the interpretation of the spectra of 1–3. Compounds 4 were prepared by appropriate nucleophilic attack on 2-BF_4. In these compounds, in which the conjugation of the cyclopropenium ion has been destroyed by introduction of an additional substituent at C-3, the ferrocene carbons appear over a relatively narrow range: 68.8–70.2 ppm for C_2, C_3 and C_4, and 66.9–67.8 for C_1. These values deviate only slightly from the absorption of the reference compound ferrocene (68.0 ppm). It appears therefore, that the cyclopropene ring does not exert a significant effect on the ferrocene carbons attached at the "sp^2" or "sp^3" carbons. As will be seen, this is far from true in compounds 1–3.

Diferroncenylcyclopropenone

The proton-decoupled ^{13}C spectrum of 1 consisted of six lines, associated with the six non-equivalent C atoms (Table 1). The assignment of quarternary carbons (C_1, C_5, C_6) was based not only on model systems (see below) but on the very reduced intensity of their signals relative to the proton-bearing carbons (C_2, C_3, C_4), arising from the long relaxation times customarily associated with the quarternary carbons.[4] C_1 is readily assigned as the resonance at 65.2 ppm, since the quarternary carbon of ferrocenes bearing electron-withdrawing groups generally appear in the range 51–79 ppm.[12] The two remaining resonances at 144.9 and 152.2 ppm are assigned as C_5 and C_6, respectively, by analogy to diphenylcyclopropenone (5) in which the corresponding C_5 and C_6 resonances appear at 148.4 and 155.8 ppm, respectively.[10] The upfield shift of C_5 and C_6 in 1 relative to 5 is associated with the greater electron-supplying power of the ferrocene group relative to phenyl and finds parallel in the observation that both types of cyclopropene ring carbon in triferrocenylcyclopropene (4a) resonate at higher field that the corresponding carbons of triphenylcyclopropene (6). The assignments of C_5 and C_6 in 1 are also consistent with those in other cyclopropenones.[10,11]

The assignments of the remaining carbons, i.e. 70.8 for C_2, 71.8 for C_3, and 69.9 for C_4 are based upon known unambiguous assignments of the ^{1}H NMR signals for H_2, H_3 and H_4 of 1,[1] combined with off-resonance decoupling experiments which correlate the ^{13}C and ^{1}H NMR experiments. For comparison, similar off-resonance

Table 1. ^{13}C NMR spectra of cyclopropenones and cyclopropenium ions

Compound	C_1	C_2	C_3	C_4	C_5	C_6	C_{ipso}	C_{ortho}	C_{meta}	C_{para}
1	65.2[a]	70.8[b]	71.8[c]	69.9[d]	144.9[a]	152.2[a]				
2	59.5[a]	73.7[d]	77.1[e]	71.5[f]	147.8[a]					
3	56.2	76.6	80.3	73.2	148.6, 156.2		120.7	135.8	131.6	138.0
5					148.4	155.8	124.0	131.5	129.4	132.7
8					154.0		119.2	135.0	130.3	138.3
Ferrocene:		68.0								
Benzene									128.7	

Multiplicities of the proton-coupled ^{13}C NMR spectra lines: [a]singlet, [b]doublet, 176.6 Hz, [c]doublet, 178.5 Hz. [d]doublet, 177.6 Hz. [e]doublet, 181.4 Hz. [f]doublet, 180.4 Hz.

experiments on ferrocenecarboxaldehyde (7) gave the following unambiguous assignments: C_1, 79.5; C_2, 69.6; C_3, 73.1; C_4, 69.6 ppm (see Discussion).[6c,12a,13]

Triferrocenylcyclopropenium perchlorate (2)

The simple 5-line ^{13}C spectrum of 2 was assigned on the same principles used in interpretation of the spectrum of 1 (Table 1). Weak signals at 59.5 and 147.8 ppm were assigned to quarternary carbons C_1 and C_5, respectively. The assignment of C_5 is supported by previous determination that the 3-membered ring carbons of triphenylcyclopropenium ion (8) and the unsubstituted cyclopropenium ion (9) appear at 154.0 and 175.0 ppm, respectively.[10] The relevant chemical shifts in the dimethylferrocenylcarbinyl cation 10 are 100.1 (C_1) and 155.1 ($C_{5'}$) ppm.[6b]

It was possible to assign the ^{13}C resonance of 2 at 71.5 ppm unambiguously to C_4 by an off-resonance decoupling experiment. Assignment of C_2 and C_3 presented some difficulties, however, in view of the fact that H_2 and H_3 have almost identical ^{1}H NMR chemical shifts[1] and cannot be assigned unambiguously. Two alternatives could be considered for the ^{13}C assignments: (a) C_2 at 73.7 and C_3 at 77.1 ppm, or conversely, (b) C_2 at 77.1 and C_3 at 73.7. A decision between these alternatives may be made by applying Nesmeyanov's correlations between the ^{13}C NMR shieldings of ferrocene derivatives and their benzene analogues (π-C_5H_5Fe-πC_5H_4X vs C_5H_5X).[12a] The screening of the C_2 and C_3 nuclei in the ferrocene compounds was found to correlate satisfactorily with the screening of the C_{ortho} and C_{para} nuclei, respectively, of the benzene derivatives, and not to correlate at all with the corresponding C_{meta} nuclei.[12a] In the case of 2, the appropriate benzene analogue is 8, for which the shieldings of C_{ortho} and C_{para} relative to benzene are ΔC_{ortho} (8) = δC_{ortho} (8)–$\delta(C_6H_6)$=6.3 ppm and ΔC_{para}(8)=δC_{para}(8)–$\delta(C_6H_6)$=9.6 ppm.[10] This trend, in which the deshielding of the *para*-carbon is more pronounced than that of the *ortho*-carbon, favors alternative (a) for which $\Delta C_2[= \delta C_2(2) - \delta(C_{10}H_{10}Fe)] = 5.7$ and $\Delta C_3[= \delta C_2(2) - \delta(C_{10}H_{10}Fe)] = 9.1$, rather than alternative (b); for which $\Delta C_2 = 9.1$ and $\Delta C_3 = 5.7$ ppm. A similar trend, though smaller in magnitude, was observed with the cyclopropenone derivatives 1 and 5: $\Delta C_{ortho}(5) = 2.8$ and $\Delta C_{para}(5) = 4.0$ ppm vs $\Delta C_2(1) = 2.8$ and $\Delta C_3(1) = 3.8$ ppm. Indeed, the absorptions of C_2 and C_3 in 1, assigned as described above, do fit Nesmeyanov's correlation lines.

Ferrocenyldiphenylcyclopropenium tetrafluoroborate (3)

The proton-decoupled ^{13}C spectrum of 3 exhibited the expected lines for the ten types of C atoms (four phenyl, four ferrocenyl, and two cyclopropenium ring) in 3 (Table 1). Assignments in the case of 3 were based upon principles already used in assignment of the spectra of 1 and 2, and by direct analogies with the spectra of 2 and 8.

Quarternary carbons C_1 and C_{ipso} exhibited weak signals at 56.2 and 119.1 ppm respectively. Quanternary carbons 5 and 5' exhibited signals in the cyclopropenium carbon region at 148.6 and 156.2 ppm. It is tempting to assign δ148.6 ppm to C_5 and δ156.2 ppm to $C_{5'}$ by analogy with spectrum of 2 and 8 ($\delta C_5(2) = 147.8$ ppm and $\delta C_5(8) = 154.0$ ppm). Such an assignment would indicate that the effect of single ferrocenyl group of 3 in delocalizing the available positive charge is comparable to the corresponding effect of each of the three rerrocenyl group of 2. An analysis of the chemical shifts of C_2, C_3 and C_4 (*vide infra*) does not support this conclusion. The low field resonance at 156.2 ppm is more likely due to C_5 and the high field resonance at 148.6 ppm to $C_{5'}$. The assignment is consistent with the fact that the latter resonance is the larger of the two.

Assignment of C_2, C_3 and C_4 were made in routine fashion. The largest peak in the spectrum is at 73.2 ppm and is certainly associated with C_4, i.e. the unsubstituted cyclopentadienyl ring. C_2 and C_3 are assigned to the resonances at 76.6 and 80.3 ppm, respectively. The reverse assignments seem very unlikely, given the corresponding assignments of C_2 and C_3 in the spectrum of 2 (*vide supra*). Assignment of C_{ortho}, C_{meta} and C_{para} is made in straightforward fashion to the resonances at 135.9, 131.6 and 138.0 ppm, respectively. The chemical shifts of compounds 1–3 are summarized in Table 1, together with the corresponding data for 5 and 8.

DISCUSSION

The preceeding assignments of the spectra of 1–3 permits an interpretation of the spectra in terms of the charge delocalization in these species. For convenience, the following discussion is organized according to the various types of carbons in the 3-membered rings and the ferrocenyl system, using the numbering system shown in the introduction.

The absorption of C_6 in 1 is at somewhat higher field than the corresponding absorptions of unsubstituted cyclopropenone (155.1 ppm) and many other cyclopropenones.[10,11] In 5, this resonance is at 155.8 and has been interpreted as associated with a degree of enhanced polarization of the carbonyl group relative to, e.g. acetone, to the extent that the dipolar ("aromatic") cyclopropenium oxide form 11 makes a contribution to the ground state of the molecule.[11] By extension of this reasoning, the degree of charge separation in 1 must be even greater than in 5. The difference in chemical shifts between C_6 in 1 and 5 is rather small but real (3.6 ppm), though not as large as in *bis*-diisopropylaminocyclopropenone (21.8 ppm) and diethoxycyclopropenone (18.4 ppm).[10] It is likely that cyclopropenones do have an enhanced contribution of charge separation as in 11, but this may not be a major effect. Tobey has argued that the relatively high dipole moments exhibited by cyclopropenones, originally attributed to a high contribution of cyclopropenium oxide structure 11, are rather associated with that in ordinary ketones, but spread over a larger distance because conjugation of the CO with the 3-membered ring shifts the center of positive charge into the 3-membered ring.[14] On the other hand, and X-ray crystallographic investigation of 5, in conjugation with CNDO/2 calculations,[15] suggests that there is some cyclopropenium ion character in the cyclopropenone ring, and to this extent the ferrocene groups ought to be able to stabilize 11 more effectively, as observed.

The ^{13}C resonance position of cyclopropenium ring carbons is very sensitive to substituents, as the 21.0 ppm difference between 8 and 9 demonstrates.[10] Introduction of OMe and dimethylamine substituents results in even greater shielding of the ring carbons.[10] Any conclusions drawn from comparisons involving δC_5 should be viewed with caution. The following point is, however, worthy of note. δC_5 (3) is substantially deshielded relative to δC_5 (2), while $\delta C_{5'}$ (3) is shielded relative to δC_5 (8). This may suggest the enhanced polarization of the positive charge in the 3-membered ring of 3, from $C_{5'}$ towards C_5.

The resonances of C_2, C_3 and C_4 in 1–3 are all shifted downfield relative to ferrocene. In each compound the deshielding is the smallest at C_4: $\delta C_4(1) = 1.9$, $\delta C_4(2) = 3.5$, and $\delta C_4(3) = 5.2$ ppm (Table 1). In 1, the effect is similar to that in 7 [$\delta C_4(7) = 1.6$ ppm] and many other substituted ferrocenes.[12] However, δC_4 is significantly larger in 2 and 3, implying a significant *delocalization of the positive charge into the remote unsubstituted 5-membered ring*. Such long-range delocalization may shed light on the controversy concerning the origin of the unusually potent stabilization of the carbenium ions by adjacent metallocenes.[2,6] *The role of the metal may be to provide a conduit for transmission of the positive charge into the unsubstituted ring.* It has been suggested that the positive charge for α-ferrocenylcarbenium ion is effectively delocalized throughout the entire ferrocenyl system, including the unsubstituted ring.[6b,7b] The enhanced stability of α-metallocenylcarbenium ions has been attributed to an interaction between occupied metal orbitals and an electron deficient center via the cyclopentadienyl ring system.[6c] The previously reported downfield shifts of the resonances of C_2, C_3 and C_4 in α-metallocenylcarbenium ions have all been obtained in moderately or strongly acidic media,[5-9] (e.g. trifluoroacetic acid, sulphuric acid). Under such circumstances, the metallocenyl systems undergo two kinds of interactions with the acidic media, viz. π-H bonding in which the cyclopentadienyl ring is the electron donor and, in the most strongly protic solvents, metal protonation.[9] For comparison, in ferrocene, $\delta C(CDCl_3) = 68.0$ ppm while $\delta^{13}C(BF_3 \cdot H_2O) = 78.0$ ppm,[6b] and $\delta^{57}Fe(CDCl_3) = 0$ while $\delta^{57}Fe(BF_3 \cdot H_2O) = -1099$ ppm.[6b] The effect of the acidic media is indeed reflected in the ^{13}C NMR chemical shifts of 2: in trifluoroacetic acid, the resonances of C_1, C_2 C_3 and C_4 appear at 61.70, 75.09, 79.00 and 73.40 ppm, respectively. In the α-ferrocenylcarbenium ions, the deshielding of the carbon resonances should therefore be attributed, to a certain extent, to the effects of the acidic media and their complexation with the metallocene substrate. By contrast, the ^{13}C NMR chemical shifts of 2 and 3 could be obtained in dichloromethane or chloroform. The comparison with neutral ferrocenes is justified, so that the observed downfield shifts of C_4 as well as C_3 are a true reflection of the effective positive charge delocalization over the entire metallocenyl unit.

C_2 and C_3 are deshielded to a greater extent than C_4: $\Delta C_2(1) = 2.8$ and $\Delta C_3(1) = 3.8$ ppm; $\Delta C_2(2) = 5.7$ and $\Delta C_2(2) = 9.1$ ppm; and $\Delta C_2(3) = 8.6$ and $\Delta C_3(3) = 12.3$ ppm. For comparison, $\Delta C_2(7) = 1.6$ and $\Delta C_3(7) = 5.1$ ppm; $\Delta C_2(FcCN) = 2.5$ and $\Delta C_3(FcCN) = 3.5$ ppm (or *vice versa*). The magnetic anisotropy of the substitutent contributes to the screening of C_2 of a substituted ferrocene, and hence the measured chemical shifts may not be significant as an indicator of the charge of these nuclei. On the other hand, C_3 is unaffected by the anisotropic effect of the substituent, and ^{13}C parameters related to this position may be used to assess the electron-density distribution at this position remote from the subsequent.[12a] The strong deshielding at C_3 (9.1 in 2 and 12.3 ppm in 3) indicates a substantial delocalization of the positive charge of the 3-membered ring into the 5-membered ring, in agreement with the weaker deshielding of C_5 relative to 8 or even 1 (*vide supra*). The corresponding deshielding of C_5 in α-ferrocenylcarbenium ions is greater (25.6 ppm in 10).[5] However, in 2 three ferrocene groups share the unit positive charge, so the anticipated deshielding should only be one-third of than in species such as 10, as observed. Even if the assignment of C_2 and C_3 in 2 is reversed, the deshielding of C_3 would be substantial. Attention should also be drawn to the downfield shift of 5.3 ppm of C_3 in 2 relative to 1. This is the best measure in the ^{13}C NMR data of the superior delocalization of positive charge into the ferrocenyl moiety in 2 as compared with cyclopropenone 1. The downfield shift of C_2 and C_3 in 1 relative to ferrocene, show, however, that a small but real amount of positive charge is indeed delocalized into the ferrocene ring in species 1, as also may be concluded from the ^{13}C shifts of C_5 and C_6 (*vide supra*). It may be noted that the electric dipole moment of 1 (5.37D)[1] is only slightly higher than that of 5 (5.08D). It was previously concluded that this evidence and also the ^1H NMR data did not demonstrate any substantial displacement of the (modest) positive charge on the 3-membered ring of 1 into the ferrocenyl groups.[1] In view of the ^{13}C NMR data on C_3 and also C_5 and C_6 (*vide supra*) this conclusion must now be modified somewhat. The cumulative ^{13}C NMR evidence points toward some contribution from dipolar structure 11 in the ground state. It is not clear whether, however, there is any significant delocalization of positive charge in 1 into the unsubstituted cyclopentadienyl rings. Even if there were, it need not necessarily contribute to an enhancement of the overall dipole moment of the molecule. Indeed, since the dipole moment is an overall global property of the molecule, this effect may even reduce it, depending on the exact geometry taken up by the ferrocene groups.

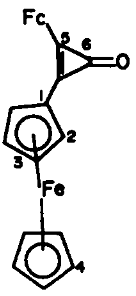
The comparison between the ^{13}C NMR signals of the remote carbons of 2 and 3 is impressive. The deshielding of C_3 and C_4 is significantly greater in 3 than in 2 [$\Delta C_3(3) = 12.3$ ppm vs $\Delta C_3(2) = 9.1$ ppm; $\Delta C_4(3) = 5.2$ ppm vs $\Delta C_4(2) = 3.5$ ppm]. On the other hand, $C_{para}(3)$ is not deshielded at all compared with $C_{para}(8)$. It appears that the ferrocenyl substituent in 3 carries the heaviest share of the load of delocalization of the positive charge in the ring. (This effect is also exemplified by the larger pK_{R^+} of 3 relative to 8, 5.4 vs 3.1). The ^{13}C NMR data on 3 demonstrate unequivocally substantial delocalization of the positive charge into the ferrocenyl group.

In order to obtain a crude estimate of the extra π-charge delocalization in the remote ferrocenyl carbons (C_3 and C_4) of 2 (relative to ferrocene), the simple Spiesecke and Schneider relationship[16]

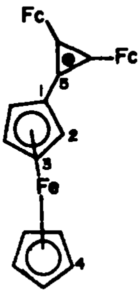
$$\delta_c = -159.5\rho + 288.5$$

may be applied to the corresponding ^{13}C chemical shifts. Thus, $\Delta\rho(C_3)(2) = \rho C(\text{ferrocene}) - \rho C_3(2) = 0.06$ and $\Delta\rho(C_4)(2) = \rho C(\text{ferrocene}) - \rho C_4(2) = 0.02$. (Of course, the absolute values of ρ have no significance). However, in each ferrocenyl group of 2 there are two C_3 positions and five C_4 positions, so the $\Sigma\rho(C_3)(2) = 0.12$, while $\Sigma\rho(C_4)(2) = 0.10$. Furthermore, $\Delta\rho(C_{para})(8) = \rho C(\text{benzene}) - \Delta\rho(C_{para})(8) = 0.06$, but only one *para* position is available in each phenyl group of 8. Thus, (a) the total extra positive π-charge on the unsubstituted cyclopentadienyl rings in 2 is actually comparable to that at the C_3 positions, and (b) both the C_3 and C_4 values considerably exceed the corresponding charge on C_{para} in 8. Similarly, $\Delta\rho(C_3)(3) = 0.08$ and $\Delta\rho(C_4)(3) = 0.03$, and $\Delta\rho(C_{para})(3) = 0.06$. Including the statistical correction for differing numbers of C_3 and C_4 and C_{para} sites, $\Sigma\rho(C_3)(3) = 0.16$, $\Sigma\rho(C_4)(3) = 0.15$ and $\Sigma\rho(C_{para})(3) = 0.12$. Thus, it can be seen that (a) as with 2, the C_4 and C_3 sites of 3 share the charge almost equally, and (b) the single ferrocene unit carries a greater fraction of the charge than do the other two phenyl groups combined.

One of the most striking observations in the spectra of 1–3 are the unusual high field shifts of the substituted (C_1) carbon atoms relative to a variety of ferrocene derivatives,[12] even those carrying electron-withdrawing substituents, e.g. ferrocenecarboxaldehyde (7) (Table 2).



1



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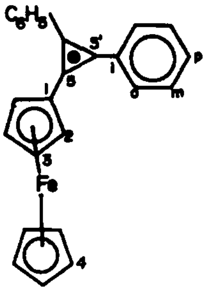
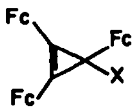
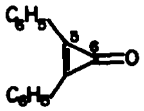


3

Fc = $C_5H_5FeC_5H_4$



4a, X = H
b, X = CN
c, X = OCH_3



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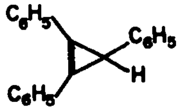
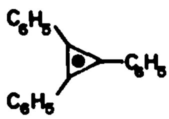


6

FeCHO

7



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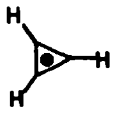

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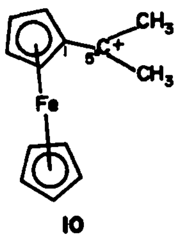


10

11

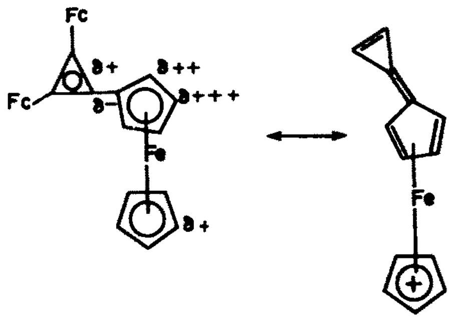
$FcC{\equiv}CH$ $FcC{\equiv}N$

12 13

Thus, $\Delta C_1(1)$ $[\equiv \delta C_1(1) - \delta C(C_{10}H_{10}Fe)] = -2.8$ ppm, and $\Delta C_1(2) = -8.8$ ppm, while $\alpha C_1(7) = +11.3$ ppm. The effect is even more pronounced in 3: $\Delta C_1(3) = 11.8$ ppm. The positive value of $\Delta C_1(7)$, as mentioned above, is representative of ferrocenes bearing electron-withdrawing substituents. However, it may be noted that ethynylferrocene (12) and cyanoferrocene (13) represent exceptions to this generality: ΔC_1 is -4.5 and -16.6 ppm for 12 and 13, respectively. In these derivatives the substituent sp bond directly bonded to C_1 has a greater degree of "s-character" than all other derivatives. It is the greater electronegativity of this sp carbon which is probably responsible for the upfield shift of C_1 in 12 and 13. An analogous effect may be responsible for the unusual shielding of C_1 in 1, 2 and 3. The hydridization of the three-membered ring carbons in these species must, like many other strained small-ring substances, be such that the exocylic bonds have a high degree of s-character, though it is not possible to estimate its magnitude using the simple relationship ($\%s = J13_{C-H}/5$) often used for this purpose, since this relationship[17] works well only for estimating the hydridization in strained hydrocarbons, and is not valid for charged and polar systems.[18] A similar upfield shift of C_{ipso} in 3, 5 and 8 ought to be expected if the effect on C_1 arises from the unusual hydbridization of the cyclopropenium and cyclopropenone rings, and indeed is observed: $\Delta C_{ipso}(3) = -8.0$, $\Delta C_{ipso}(5) = -4.7$ and $\Delta C_{ipso}(8) = -9.5$ ppm (Table 1). It should be noted that C_1 in other α-ferrocenylcarbenium ions does not exhibit this upfield shift,[3-9] thought this comparison should perhaps be taken with a grain of salt, since the reported spectra of α-ferrocenylcarbenium ions have all been measured in acidic media, in which π-hydrogen complexation and/or protonation on iron may have occurred[3-9] (*vide supra*). Surprisingly, compound 2 showed in trifluoroacetic acid an upfield shift of δC_1, larger than those of all other carbons. The π-electrons in 1–3 must also exert an influence. To paraphrase Nesmeyanov,[12a] the sign of the shift of C_1 is opposite to that which could be expected on the basis of the simplest concepts, taking account only of the σ-inductive and mesomeric effect of the substituents. It should be noted that, in contrast to the ^{13}C NMR spectra, the ^{1}H NMR spectra of 1 and 7 closely resemble each other. The shift of H_2 in 1 to lower field was attributed mainly to the anisotropy of the cyclopropenone system, including the diamagnetic anisotropy of the CO group.[1] The above analysis indicates that 7 is not a suitable model for the ^{13}C NMR shifts of C_1 in 1–3.

The unusually high shielding at C_1 in 1, 2 and 3 may be due in part to mixing of the filled non-bonding $d_z{}^2$ orbital of iron with the empty π-antibonding orbital of the "fulvene" moiety.[19] In this connection, it may be noted that an X-ray structure determination of ferrocenyldiphenylcyclopropenium tetrafluorate (3-BF_4) showed that the C_1–Fe bond length at 1.99Å is the shortest of all C–Fe bond distances in the ion.[20] An alternate explanation for the unusual π-electron charge distribution at C_1 of 1–3 can be postulated. It is based on similar observations for mono-substituted ferrocenes with conjugated electron-withdrawing groups.[12a] For 2 the relative charge distribution can be represented qualitatively as shown in 14a in Fig. 1. In unsaturated systems electronic effects may be transmitted in three ways. The σ-inductive effect is clearly in contradiction of the observed shielding of C_1. However, a π-resonance effect, indicated as fulvenoid resonance contribution 14b in Fig. 1, could account for part of the observed shielding. The third effect, a π-inductive effect could also afford stability to this system by polarization of the π-system in the observed manner. This π-inductive effect has been observed for numerous monosubstituted benzenes[21] and the corresponding monosubstituted ferrocenes.[12a]

It is interesting to note that the central C atom (Cα) of cation 15 also resonates at quite high field (68.6 ppm),



14a 14b

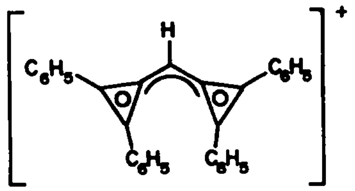
Fig. 1.

Table 2. ^{13}C NMR shifts of carbons in substituted ferrocenes relative to ferrocene[a]

Compound	ΔC_1	ΔC_2	ΔC_3	ΔC_4
1[b]	-2.8	2.8	3.8	1.9
2[b]	-8.5	5.7	9.1	3.5
3[b]	-11.8	8.6	12.3	5.2
$FcOCH_3$[c]	10.9	-1.2	-3.9	0.5
FcC_2H_5[c]	22.9	-0.6	-1.0	0.3
FcCHO[c]	10.8	0.8	4.4	0.8
$FcC\equiv CH$(12)[c]	-4.4	3.3	0.4	1.7
$FcC\equiv N$(13)[c]	-16.5	3.3	2.5	2.2

[a] ΔC_n = chemical shift of C_n - 68.0 ppm

[b] This work. [c] Ref. 12a



15

indicating a high electron density at this position.[22] The relation of this observation to that unusual shielding of C_1 in 1–3 is not obvious, however.

The novelty of the cyclopropenium subtituent in 2 and 3 is manifested in the combination of the chemical shifts of the various carbon nuclei C_1, C_2, C_3 and C_4 relative to ferrocene as compared with representative monosubstituted ferrocenes (Table 2). The ^{13}C NMR spectra of 2 and 3 features in each case a unique combination of a shielding effect in $C_1[\Delta C_1(2) = -8.5$ and $\Delta C_1(3) = -11.8$ ppm] and a deshielding effect in $C_3[\Delta C_3(2) = 9.1$ and $\Delta C_3(3) = 12.3$ ppm] with similar absolute values.

EXPERIMENTAL

M. ps were taken on a Unimelt Thomas-Hoover capillary m.p. apparatus and are uncorrected. IR spectra were recorded on a Perkin–Elmer Model 457 spectrophotometer in Nujor and in KBr disks. UV spectra were recorded on a Unicam Model SP800A spectrophotometer. The ^1H NMR spectra were taken on a Varian HA-100 spectrometer at 100 MHz. ^1H chemical shifts are reported in parts per million downfield from Me_4Si (internal standard). Mass spectra were measured on a Varian MAT-311 double focusing instrument operating at 70 eV, employing the direct insertion technique. Metasable transitions were detected by the defocusing method (alteration of accelerating voltage mode). Analytical tlc separations were carried out a 24° on precoated plastic sheets (layer thickness 0.2 mm), Polygam Sil M-HR/UV_{254} and Polygam Cel 400/UV_{254} (Machery-Nagel and Co.). Materials were detected with UV light. Column chromatography separations were performed on silica gel 60 (Kieselgel 60 Merck) and on microcrystalline cellulose (Merck). For dry column chromatography, silica was deactivated with EtOAc. Dipole moment was determined in benzene solution at 30°. The dielectric constants of the solns were measured in a heterodyne beat apparatus (500 kHz), the specific volumes, with a Sprengel–Oswald type pycnometer. The molar refraction was calculated according to LeFevre and Steel. The polarization $P_{2\infty}$ and the dipole moment were calculated according to Halverstadt and Kumler.[24] The pH measurements were calculated according to Halverstadt and Kumler.[24] The pH measurements were made in a Radiometer Type TTTICpH meter equipped with glass—calomel electrodes. The pH meter was standardized with an appropriate buffer before each measurement. Raman spectra were obtained on a rotating KBr pellet. Instrumentation consists of a Spex ·1401 monochromator, a Spex 1419A sample illuminator, and a Spectra Physics Model 164 Kr^+ laser sypplying about 50 MW power at the sample. Tetrachlorocyclopropene was obtained from Aldrich Chemical Co., Inc., Milwaukee, Wisconsin.

^{13}C NMR spectra were obtained on Varian CFT-20 and Bruker WH-270 high resolution spectrometers in $CDCl_3$ for 1 and 2 and in CH_2Cl_2 for 3 and are reported in ppm relative to interval tetramethylsilane.

Diferrocenylcyclopropenone (1). A soln of tetrachlorocyclopropene (3.56, 20 mmole) in dry CH_2Cl_2 (5 ml) was added dropwise, at −40°, under an argon atmosphere, to a magnetically stirred suspension of $AlCl_3$ (2.67 g, 20 mmole) in dry CH_2Cl_2 (200 ml). The mixture was gradually heated to 20° and left at this temp. for 15 min to give a white ppt of trichlorocyclopropenium tetrachloroaluminate. The resulting suspension was cooled to −80° and treated dropwise, during 90 min at −80° to −70°, with a soln of ferrocene (7.44 g, 40 mmole) in dry CH_2Cl_2 (200 ml). The resulting dark red soln was stirred at −90° to 80° for an additional 150 min heated to 20° for 30 min cooled to −70°, and treated with aqueous acetone (20%, 100 ml), keeping the temp. below −60°. After gradual heating to 20°, additional CH_2Cl_2 and water were added, the layers were separated, and the organic reaction was washed with water to neutrality, dried over $MgSO_4$ and evaporated to dryness under vacuum. The resulting crude oily product was triturated with petroleum-ether to give a dark solid (4.72 g). It was purified by dry column chromatography on silica, using EtOAc as a developer. The red spot (R_f = 0.25) was extracted with MeOH, the solvent was evaporated under vacuum, and the remaining solid was dissolved in CH_2Cl_2, dried over $MgSO_4$ and the solvent evaporated to dryness under vacuum to give 1 (0.567 g, 7%) m.p. 160–162°.

Recrystallization from a mixture of benzene and petroleum ether afforded 1 as dark red crystals, m.p. 181° (dec); tlc, R_f silica, EtOAc-petroleum ether (1:1) = 0.25. (Found: C, 65.30; H, 4.20; Fe, 26.69. Calc. for $C_{23}H_{18}Fe_2O$: C, 65.46; H, 4.30; Fe, 26.47%).

Spectral properties of this material were all consistent with its formulation as 1. Mass spectrum: *m/e*: 422 (parent, 6%), 394 (base peak, –CO). IR V_{max}(KBr): 3095(w), 2920(w), 1850(vs), 1820(m), 1612(vs), 1475(s), 1105(s), 892(m), 839(s), 815(s), 727(m), 514(m), 496(s), 482(s) cm^{-1}. The bands at 1850, 1820 and 1612 cm^{-1} are characteristic of the cyclopropenone nucleus.[25] UV: λ_{max} (EtOH) (log ϵ): 243 (4.15), 275 (4.08), 300 (4.08), 348 (3.71) and 477 (3.33) nm. ^1H NMR ($CDCl_3$): δ 4.23 (10H, s, H_4), 4.56 (4H, t, J = 2Hz, H_3), and 4.83 (4H, t, J = 2 Hz, H_2); (C_6H_6): δ 3.94 (10H, S), 4.13 (4H, broad sing), and 4.60 (4H, broad sing). (This pattern closely resembles that of 7.)[26] The dipole moment of 1 (benzene, 30°) is 5.37 D ($\alpha' = 41.60$; $\beta' = 3.09$; MR_{calc} = 109.56 cm^3; $P_{2\infty}$ = 689.4 cm^3).

Triferrocenylcyclopropenium perchlorate (2). A magnetically stirred suspension of trichlorocyclopropenium tetrachloroaluminate prepared as described above from tetrachlorocyclopropene (3.56 g, 20 mmole) and anhyd $AlCl_3$ (2.80 g, 21 mmole) in dry CH_2Cl_2 (55 ml) was cooled to −70° (acetone-dry ice bath) and treated dropwise, at −70°, under an argon atmosphere, during 105 min with a soln of ferrocene (11.5 g, 60 mmole) in dry CH_2Cl_2. The resulting red complex was kept at −70° for 60 min heated gradually to room temp., kept at room temp. overnight, and refluxed for 2 hr. The complex was decomposed below −60° by the dropwise addition of aqueous acetone (20%, 50 ml). The mixture was heated to room temp., water and CH_2Cl_2 were added, the layers were separated, and the organic fraction was washed with water to neutrality, and dried over $MgSO_4$. The soln was concentrated under vacuum to a volume of 100 ml and treated with perchloric acid (70%, 35 ml), and stirred magnetically for 4 hr. The layers were separated, the organic layer was washed with water and dried over $MgSO_4$, and the solvent evaporated under vacuum. Trituration of the remaining pasty solid with benzene afforded a crystalline red-purple solid (9.47, 68%). Purification was effected by column chromatography on microcyrstalline cellulose, using CH_2Cl_2-petroleum ether mixtures as developers. (The product decomposes slowly during the chromatography; therefore, contact with the cellulose should not be prolonged). The column was first developed with 30% CH_2Cl_2 in petroleum ether and the concentration of CH_2Cl_2 was gradually increased to 100%. Purification of 3.0 g of crude 2 gave 1.68 g of a red-purple solid. Recrystallization from CH_2Cl_2-petroleum ether afforded 2 as dark red crystals, m.p. 171° (explosive) in 38% yield; tlc, R_f microcrystalline cellulose, petroleum ether-dichloromethane (1:1) 0.28. (Found: 56.23; H, 4.04; Fe, 23.14. Calc. for $C_{33}H_{27}ClFe_3O_4H_2O$: C, 55.94%; H, 3.84; Fe, 23.65%). Recrystallization of 2 from CH_2Cl_2-benzene afforded a 1:3 complex of 2 with benzene. *Warning*. The perchlorate salt of 2 is stable up to 171°. However, it can explode upon friction even at room temp.

The analogous *triferrocenylcyclopropenium tetrafluoroborate* was prepared in a similar manner, applying tetrafluoroboric acid (50%, 50 ml) instead of perchloric acid. Purification of the crude dark red solid (8.76 g, 65%) was effected by column chromatography on microcrystalline cellulose using CH_2Cl_2-petroleum ether mixtures (30%–70%) as developer. The main red fraction was collected. The product was dissolved in CH_2Cl_2 and precipitated by adding petroleum-ether. After repeating this operation for several times, the salt was obtained as dark red crystals, m.p. 127° (dec), in 26% yield. (Found: C, 59.60; H, 5.01; F, 11.11; Fe, 22.96. Calc. for $C_{33}H_{27}BF_4Fe_3$: C, 58.41; H, 5.01: F, 11.20; Fe, 24.70%).

The spectral properties of these salts are all consistent with their formulation as salts of 2. UV, λ_{max} (CH_2Cl_2) (log ϵ): 309 (4.42), 363 (3.98) and 520 (3.85) nm. IR, λ_{max} (Kbr): 3120(w), 2930(w), 1860(w), 1494(vs), 1412(m), 1384(s), 1359(m), 1146(m), 1120(s), 1100(vs), 1052(m), 1030(m), 1000(m), 900(m), 820(m), 675(w), 620(m), 490(s) and 478(s) cm^{-1}. The band at 1494 cm^{-1} is characteristic of cyclopropenium ions; it is assigned to the unsymmetric degenerated (E′) stretching vibration of the cebtral ring.[25c,27] The presence of a cyclopropenium ring in 2 is proven by the Raman band at 1860 cm^{-1} associated with the totally symmetric (A_1) stretching vibration of the 3-membered ring. ^{1}H NMR: ($CDCl_3$): δ 4.38 (15H, S, H_4), and 5.13 (12H, broad sing., H_2 and H_3): (CD_3CN): δ 4.35 (15H, S), 5.08 (6H, broad sing.) and 5.17 (6H, broad sing.). The pK_{R^+} of 2 was found to be > 10 by potentiometric titration in 50% aqueous CH_3CN.

1-*Ferrocenyl-2,3-diphenylcyclopropenium tetrafluoroborate* (3). A suspension of 2.6 g of 1,2-diphenyl-3-ethoxycyclopropenium tetrafluoroborate (prepared by the reaction between 5 and triethoxoxonium tetrafluoroborate in ether)[28] in 30 ml of 1,2-dichloroethane was added slowly to a suspension of 1.56 g of ferrocene in 20 ml of dichloroethane at 0° under argon. As the solution warmed to room temp. the suspended salt dissolved, yielding a red soln. After 24 hr at room temp. the solvent was removed *in vacuo*. The residue was washed with pentane, subjected to Soxhlet extraction with cyclohexane to remove residual ferrocene, and final crystallization from CH_2Cl_2 ether to afford 1.01 g of 3 (29% based on the oxonium salt). Spectral properties of this material were identical to a sample prepared by the literature procedure.[3]

1,2,3-*Triferrocenylcyclopropene* (4a). To a stirred suspension of $NaBH_4$ (5 g) in 50 ml CH_2Cl_2 under N_2 was added a soln of 1.00 g of 2 in CH_2Cl_2 at a rate sufficient to permit each drop to change color. After 3 hr the solvent was removed *in vacuo*, extracted with ether, and the extracts purified by dry column chromatograpyy over neutral alumina (deactivated with 6% H_2O)[29] using CCl_4 as developer, to afford 872 mg (92%) of 4a as an orange solid, m.p. 179°, UV (cyclohexane) at λ_{max} nm (log ϵ): 465 (3.13), 323 (4.11), 278 (4.08) and 240 sh (4.23). ^{1}H NMR ($CDCl_3$): δ 2.23 (1H, S, cyclopropene) and 3.9–4.5 (15H, multiplet, Fc). ^{13}C NMR ($CDCl_3$): δ 20.9, 67.3, 68.9, 69.2, 69.4, 69.6, 69.8, 69.9 and 110.47 IR ν_{max} (KBr) 1845 cm^{-1} (disubstituted cyclopropene).

1,2,3-*Triferrocenyl-3-cyanocyclopropene* (4b). A soln of 1.015 g of 2 in 20 ml dry acetonitrile was added dropwise to a stirred suspension of 2 g dry NaCN in 25 ml of acetonitrile at 25° under N_2. After 1 hr the mixture was poured into 200 ml of H_2O, and extracted with ether (3 × 100 ml); drying and evaporation of the ether gave 634 mg (69%) of crude product. Dry column chromatography over deactivated alumina (see previous synthesis) with benzene or CCl_4 developer afforded a dark orange oil which crystallized as a gold iridescent power upon trituration with ether, 114 mg (18%). A second crop, 242 mg (39%) was obtained by cooling the mother liquor to −78%. UV (EtOH) at λ_{max} nm (log ϵ): 457 (3.25), 3.65 sh (3.50), 312 (4.03), 273 (4.02), 242 (4.18), and 203 (4.77). IR ν_{max} (KBr): 1850 (disubstituted cyclopropene), 2220 cm^{-1} (CN). ^{13}C NMR ($CDCl_3$): δ 18.8, 66.9, 67.5, 68.8, 69.0, 69.2, 69.6, 69.8, 70.2, 105.7 and 122.7.

1,2,3-*Triferrocenyl-3-methoxycyclopropene* (4a). A 0.02 M soln of NaOMe in dry MeOH was added dropwise to a soln of 756 mg of 2 in 80 ml of dry MeOH at −20° under N_2; methoxide addition was stopped when a small excess of 2 remained, as seen by a slight reddish coloration. The methanolic soln was extracted with cyclohexane; removal of the cyclohexane *in vacuo* afforded 330 mg (47%) of crude product, purified by dry column chromatography on microcrystalline celulose (J. T. Baker Company) using cyclohexane as eluent to afford a dark orange solid, air-sensitive and even unstable over a period of days in an inert atmosphere at room temp. and hence stored at −78° until required for spectral characterization. IR ν_{max} (KBr) 1852 (disubstituted cyclopropene) and 1087 cm^{-1} (ether). ^{13}C NMR ($CDCl_3$): δ 27.2, 54.3, 67.3, 67.4, 69.0, 69.2, 69.7, 69.9, 70.0, 70.1 and 118.3.

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