1393 (s), 1368 (s), 1242 (s), and 1010 cm^{-1} (s); μ (C_6H_6, 30 °C) 5.13 ± 0.03 D ($\alpha' = 33.93$, $\beta' = -1.40$, $P_{2\infty} = 628.1$ cm, MR$_{\text{calcd}}$ 97.9 cm^{-1}).

Tri-(3-guaiazulenyl)cyclopropenium Perchlorate (6). A magnetically stirred suspension of trichlorocyclopropenium tetrachloroaluminate prepared as described above from tetrachlorocyclopropene (1.78 g, 10 mmol) and anhydrous aluminum chloride (1.47 g, 11 mmol) in dry dichloromethane (85 ml) was cooled to −70 °C and treated dropwise, below −70 °C, under anhydrous inert atmosphere, during 50 min, with a solution of guaiazulene (**8**, 5.58 g, 28.2 mmol) in dry dichloromethane (50 ml). The resulting red complex, which darkened during the addition, was kept at −70 °C for 40 min, heated gradually to room temperature, and kept at room temperature overnight. The complex was decomposed below −60 °C by the addition of aqueous acetone (20%, 50 ml). The mixture was heated to room temperature, water and dichloromethane were added, and the organic fraction was washed with water and dried over magnesium sulfate. The solution was concentrated under vacuum to a volume of 100 ml and treated with perchloric acid (70%, 15 ml), and stirred magnetically for 150 min. The layers were separated, the organic layer was washed with water and dried over magnesium sulfate, and the solvent evaporated under vacuum. Treatment of the remaining oil with petroleum ether gave crude **6** as a dark solid (4.48 g, 69%). Purification was effected by column chromatography on microcrystalline cellulose, using 15% dichloromethane in petroleum ether. The resulting oily product was dissolved in dichloromethane and precipitated with petroleum ether (four times) to give **6** as a dark solid, mp 171–173 °C dec (23% yield), R_f [microcrystalline cellulose, petroleum ether–dichloromethane (1:1)] 0.66. Anal. Calcd for $C_{48}H_{51}ClO_4$: C, 79.25; H, 7.07. Found: C, 79.52; H, 7.15%. Ir $\nu_{\max}$ (KBr) 2955 (m), 2920 (m), 2860 (m), 1760 (w), 1705 (w), 1524 (m), 1468 (vs), 1448 (vs), 1392 (vs), 1368 (vs), 1335 (s), 1270 (vs), 1215 (s), 1120 (m), 1090 (s), 1010 (s), 891 (m), 649 (m), 618 (m), and 592 cm^{-1} (m).

Acknowledgment. We thank Professor H. Selig and Dr. A. Loewenschuss of the Hebrew University of Jerusalem for the Raman spectra determinations.

Registry No.—**6**, 58815-85-3; **7**, 58815-87-5; **8**, 489-84-9; trichlorocyclopropenium tetrachloroaluminate, 10438-65-0.

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Organometallic Chemistry. 10.[1] Carbon-13 Nuclear Magnetic Resonance Study of *cis*-π-Pentadienyliron Tricarbonyl Cations and Protonated Norbornadieneiron Tricarbonyl

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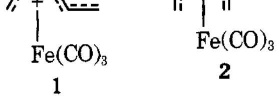
Acyclic and cyclic cisoid π-pentadienyliron tricarbonyl cations were studied by ^{13}C NMR spectroscopy in strong acids. The origin of the unusual stability of these ions and their fluxional behavior are discussed. The nature of bonding and the structure of the protonated norbornadieneiron tricarbonyl were also studied and are discussed.

The preparation of the tropyliummolybdenum tricarbonyl cation via hydride abstraction from tropylidenemolybdenum tricarbonyl by Dauben and Honnen[3] and that of cyclohexadienyliron tricarbonyl cation by Fischer and Fischer[4] have drawn considerable interest from both organic and inorganic chemists, and particularly theoretical chemists, in recent years. A large variety of organometallic cations has since been prepared and their chemistry reviewed.[5] All these cationic species exhibit remarkable stability due to the complexation of the unsaturated organic moiety with the metal atom (i.e., transition metals).

Acyclic *trans*-pentadienyliron tricarbonyl cations **1** have



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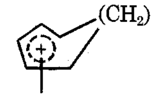
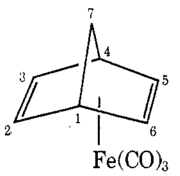


3, $n = 1$; **4**, $n = 2$

been demonstrated to rearrange to the related cis isomer 2[6] indicating the greater thermodynamic stability of 2. Although ample work has been carried out in the obtaining of the ${}^1H$ NMR spectra of these ions, limited ${}^{13}C$ NMR data have been reported.[7] In the continuation of our interest in metal stabilized cations, we wish to report a study of the relative charge distribution pattern in a series of cyclic and acyclic cisoid π-pentadienyliron tricarbonyl cations via ${}^{13}C$ NMR spectroscopy.

Furthermore, protonated diene–iron complexes are of substantial current interest. Depending on the acidity of the media differing species are obtained.[8] In contrast to iron tricarbonyl derivatives of conjugated dienes, norbornadieneiron tricarbonyl (5) was reported to undergo protonation on iron.[9] Based on a ${}^1H$ NMR study, structure 6 was proposed for protonated norbornadieneiron tricarbonyl. An unusual stereospecific coupling (J = 13 Hz) of the hydrido hydrogen with H_2 and H_6 was observed. Recently, the protonated species of 5 was suggested to be formulated in terms of rapidly equilibrating homoallylic σ,π species 7.[10]



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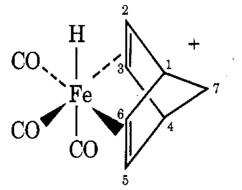

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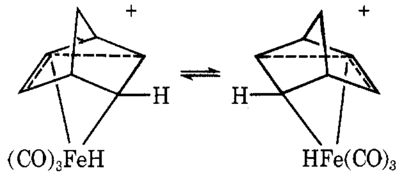

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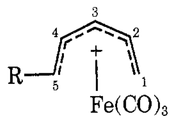
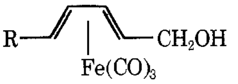
In order to provide better understanding of the bonding nature and the structure of the protonated norbornadieneiron tricarbonyl, we also report the high-resolution ${}^{13}C$ NMR spectra of the parent and the protonated species.

Results and Discussion

***cis*-π-Pentadienyliron Tricarbonyl Cations.** The parent and methyl substituted *cis*-π-pentadienyliron tricarbonyl cations were prepared from their corresponding alcohols 9 in



2, R = H
8, R = CH$_3$



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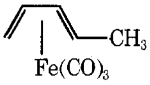
R = H or CH$_3$



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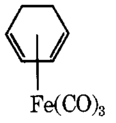
fluorosulfuric acid–sulfur dioxide solution at dry ice–acetone bath temperature (ca. −78 °C). The ${}^1H$ NMR spectra of these ions are in good agreement with those previously reported.[6] The Fourier transform carbon-13 proton-noise nondecoupled NMR spectra of 2 and 8 were then obtained. Assignments of carbon resonances, multiplicities, and coupling constants are summarized in Table I. The symmetrical nature of the parent *cis*-π-pentadienyliron tricarbonyl cation is clearly seen from the observation of three carbon resonances in the dienyl region and two in the carbonyl region. Both ${}^1H$ and ${}^{13}C$ NMR spectra thus rule out a transoid conformation 1.

Upon methyl substitution at one of the terminal positions (C_5), a deshielding of approximately 25 ppm of this carbon absorption is observed, while carbon resonances of the other positions did not much vary. There are, however, three carbonyl absorptions found in 8 indicating the unsymmetrical nature of this ion. The deshielding at C_5 in 8 reflects the methyl substituent effect at this carbon.

Cyclohexadienyl- and Cycloheptadienyliron Tricarbonyl Cations. The cyclohexadienyliron tricarbonyl cation 3[4,11] was prepared from their corresponding dienyliron tricarbonyl precursors 11 via hydride abstraction by trityl tetrafluoroborate in CH_2Cl_2 solution at room temperature. Cycloheptadienyliron tricarbonyl cation 4 was obtained by the protonation of free double bond in cycloheptadieneiron tricarbonyl 12 with HBF_4.[12] Both ${}^1H$ and ${}^{13}C$ NMR parameters



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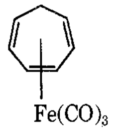

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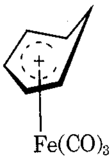
are summarized in Table I along with their assignments.

Going from 2 to 3 does not produce much effect on the C_1, C_2, and C_3 carbon shifts. The insertion, however, of an ethylidene group (two methylene groups) causes about 30 ppm deshielding effect on the terminal pentadienyl carbons (C_1 and C_5) and 10 ppm on the central carbon (C_3), while only minimal changes on the C_2 and C_4 carbons. The negligible methyl substituent effect observed in 3 is consistent with previous studies that the six-membered ring is nonplanar and highly distorted with the methylene carbon C_6 moving out of the C_1–C_5 plane and away from the iron tricarbonyl moiety.[13]

Another interesting aspect was revealed when a cyclopropanyl group was introduced into the *cis*-π-pentadienyliron tricarbonyl cation 2 at the terminal carbons. Carbon resonances of the cycloheptadienyl moiety going from *cis*-π-cycloheptadienyl- (4) to bicyclo[5.1.0]octadienyliron tricarbonyl (13)[13] does not seem to draw much positive charge from the *cis*-π-cycloheptadienyl moiety.



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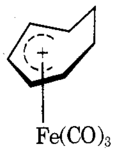

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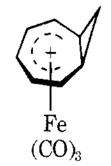

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The nature of bonding in dieneiron tricarbonyls was originally discussed by Pettit et al.[13] by modifying the Dewar–Chatt–Duncanson description.[14] The bonding has been pictured as derived from the σ forward donation from filled π orbitals to vacant metal orbitals and π back-donation from filled metal orbital to π-antibonding orbitals.[15] The origin of the unusual stability of the pentadienyl tricarbonyl cations has been attributed to the formation of a nonbonding orbital upon ionization.[13,16] The decrease of the energy level of the lowest unoccupied orbital favors back-donation. In the case of the *cis*-π-pentadienyliron tricarbonyl cations back-donation is of particular importance. It not only strengthens the metal–ligand bonding but also transmits the electron density into the pentadienyl tricarbonyl cations studied; the C_2 carbon is generally more deshielded than both C_1 and C_3, whereas the reverse is seen in the uncomplexed pentadienyl cations. The present ${}^{13}C$ NMR shielding pattern is thus in agreement with a bonding picture in which the dienyl carbons (C_1 and C_3) which are not at the nodal in the nonbonding orbital become less deshielded because of greater back-donation effect from the metal atom.

Protonation of Norbornadieneiron Tricarbonyl. The ${}^{13}C$ NMR spectrum of 5 in $CDCl_3$ at −20 °C consists of a triplet at δ_C 59.77 (J_{CH} = 133.0 Hz) for the methylene carbon, doublets at 44.00 (151.6 Hz) and 38.74 (180.7 Hz) for the bridgehead, tertiary, and olefinic carbons, respectively, and

Table I. ^{13}C NMR Data of Pentadienyliron, Cycloalkyldienyliron, and Norbornadieneiron Tricarbonyl Cations[a]

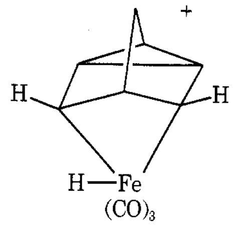
Ion	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	CO
2	65.43 (d-d, 165.4, 164.4)[c]	104.62 (d-m, 170.8)	98.58 (d-t, 180.3)						206.02 197.29
8[b]	62.19 (d-d, 166.6, 165.6)[c]	103.53 (d, 171.1)	94.84 (d, 178.5)	104.07 d, 170.4)	91.31 (d, 166.0)				207.46 198.50 198.06
3	63.74 (d, 175.4)	101.35 (d, 175.3)	89.0 (d, 183.5)			23.07 (t, 139.9)			208.12 198.36
4	92.58 (d, 161.8)	102.60 (d, 171.4)	99.43 (d, 179.3)			31.09 (t, 131.6)			107.89 198.24
13	97.90 (d, 174.3)	104.00 (d, 164.2)	99.20 (d, 178.7)			35.80 (d, 171.6)		47.0 (d-d)	210.0 196.3
5	44.00 (d, 180.7)	38.74 (d, 151.6)					59.77 (t, 133.0)		218.27
6	42.83 (d, 155.7)	39.78 (d-d, 177.1)	55.84 (d, 181.4)	44.15 (d, 157.6)			59.18 (t, 137.2)		205.61 197.32

[a] All carbon shifts are referred to external Me_4Si (capillary). Multiplicity and coupling constants (Hz) are given in parentheses: d = doublet, t = triplet, d-d = doublet of doublets, d-m = doublet of multiplets, d-t = doublet of triplets, t-d = triplet of doublets, q-d = quartet of doublets. [b] Shift for methyl carbon $\delta_{^{13}C}$ 20.37 (q-d, 129.4, 4.0). [c] Each doublet is further split into a doublet with $J_{C-H} \simeq 8$ Hz.

a singlet at δ_C 218.27 for the carbonyl carbons (Table I). The substantial shielding (Δ 105 ppm) of the olefinic carbons upon complexation (compared with the parent norbornadiene) indicates the importance of the back-donation in diene–iron bonding.[17] The shielding of C_7 (Δ 15 ppm) is also consistent with the reduced participation of π bonding being responsible for the effect,[18] because of the drastic decrease of the π-electron density on the exo side of the norbornadiene ligand upon coordination.[19,20]

Consistent with the C_s symmetry structure with the mirror plane containing C_1, C_7, and C_4, the ^{13}C NMR spectrum of protonated **5** in SO_2 solution at −50 °C consists of a triplet at δ_C 59.18 (J_{C-H} = 133.0 Hz) for the methylene carbon, two doublets at δ_C 42.83 (155.7) and 44.15 (157.6) for the bridgehead tertiary carbons, a doublet at δ_C 55.85 (181.4) for olefinic C_3 and C_5 carbons, a doublet of doublets at δ_C 39.78 (177.1 and 37.8) for C_2 and C_6 carbons, and two singlets at δ_C 205.61 and 197.32 ppm for the axial and equatorial carbonyl carbons, respectively. The unusual long-range ^{1}H–Fe–^{13}C coupling (38 Hz) of the hydrido proton with C_2 and C_6 olefinic carbons, and the large difference in the shielding (Δ 16 ppm) between the two olefinic carbon resonances, are rather striking and are difficult to rationalize based on the proposed structure **6**. To account for the experimental data the hydrido proton may be in simultaneous interaction with the iron and the olefinic C_2 and C_6 carbon atoms instead of being solely bound to iron. Since C_3 and C_5 do not seem to interact with the hydrido hydrogen, no coupling is observed. The slight upfield shifts of C_2 and C_6 compared with C_3 and C_5 probably occur because of the further decrease in the π character and (or) the forward donation in metal bonding by the formation of a four-center bond. It is of interest to note that shielding of C_7 is nearly unaffected upon protonation indicating the net change of π electron density on the exo side of the ligand diene is negligible.

The proposed structure **7**, a rapidly equilibrating σ,π species, provides a reasonable explanation for the long-range $J_{^1H-Fe-^{13}C}$ coupling and the upfield shifts of C_2 and C_6 by the direct bonding with iron.[21,22] However, the observed J_{C-H} coupling (157.6 Hz) on C_4 is not different from that on C_1 (155.7 Hz) and is too small to indicate the homoallylic participation by comparison with J_{C-H} in the quadricyclene (170.5 Hz)[20d] and 3-nortricyclyl cations (~185 Hz).[23] By the same argument, the possible structures **14** and **15** are also excluded.



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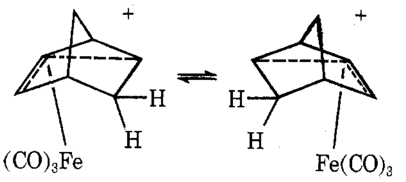

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Carbonyl Region. The fluxional behavior of dieneiron tricarbonyls has been demonstrated recently by ^{13}C NMR study.[24] Consistent with a tetragonal pyramidal structure,[25] the limiting spectra of these compounds with conjugated dienes show the two expected resonances for the basal and apical carbonyls in the ratio 2:1 at −90 °C or below. On the other hand, the fluxionality increases drastically in **5**, and no broadening of the carbonyl resonance is observed down to −110 °C.[24a,26] It is of interest to note that the fluxionality decreases substantially upon the formation of cations via protonation, and in some cases two resonances are observed even up to −30 °C for carbonyl carbons. The observed upfield shifts of the carbonyl absorptions is compatible with the corresponding increase in their ir stretching frequency.[27] Both are attributed to the decrease of the electron density of the iron.

Experimental Section

$Fe(CO)_5$, $Fe_2(CO)_9$, divinylcarbinol, 2,4-hexadien-1-ol, 1,4-cyclohexadiene, cycloheptatriene, cyclooctatetraene, and norbornadiene are commercially available. 2,4-Pentadien-1-ol was prepared by the rearrangement of divinylcarbinol with the presence of 1% sulfuric acid solution at room temperature for 24 h under nitrogen.[28] 2,4-Pentadien-1-ol- and 2,4-hexadien-1-oliron tricarbonyls were prepared by the reaction of freshly distilled corresponding alcohols with excess $Fe_2(CO)_9$ in anhydrous diethyl ether with reflux under nitrogen for 12 h.[6e] Norbornadieneiron tricarbonyl was prepared from the reaction of norbornadiene with iron pentacarbonyl in benzene with uv irradiation at 80 °C for 48 h. After workup, the fraction 98–103 °C (1.0 mmHg) was collected. Norbornadieneiron tricarbonyl was protonated in SO_2 at −80 °C with excess fluorosulfuric acid.

cis-Pentadienyl- and *cis*-1-methylpentadienyliron tricarbonyl cations were generated by the slow addition of excess cooled HSO_3F–SO_2 at −78 °C.

Cyclohexadienyliron Tricarbonyl Cation. 1,3-Cyclohexadieneiron tricarbonyl was prepared by the reaction of 1,4-cyclohexadiene with $Fe(CO)_5$ in benzene at 80 °C with uv irradiation under nitrogen for 48 h.[10c] Cyclohexadieneiron tricarbonyl cation was prepared by the hydride abstraction of distilled 1,3-cyclohexadieneiron tricarbonyl with triphenylmethyl tetrafluoroborate in methylene chloride.

Cycloheptadienyliron Tricarbonyl Cation. Cycloheptatrieneiron carbonyl was prepared by the reaction of cycloheptatriene with $Fe(CO)_5$ in methylcyclohexane with reflex under nitrogen for 48 h.[11d] Cycloheptadienyliron tricarbonyl cation is formed upon protonation of the free double bond in distilled cycloheptatrieneiron tricarbonyl with 40% aqueous HBF_4 in acetic anhydride at 0 °C.

Bicyclo[5.1.0]octadienyliron Tricarbonyl Cation. Cyclooctatetraeneiron tricarbonyl was prepared by the reaction of cyclooctatetraene with $Fe_2(CO)_9$ in anhydrous diethyl ether with reflux under nitrogen for 4 h. Bicyclo[5.1.0]octadienyliron tricarbonyl cation was obtained upon protonation of one of the free double bonds in chromatographically purified cyclooctatetraeneiron tricarbonyl with excess HSO_3F in SO_2 at −50 °C.

Instrumentation. The carbon-13 spectra were obtained on a Varian XL-100 spectrometer equipped with Fourier transform accessory, a spin decoupler, and a variable-temperature probe. A Varian 620L computer was used to accumulate data. Fluorobenzene was used as external lock and all chemical shifts are referred to external Me_4Si (5% ^{13}C enriched) capillary.

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