(All operations were conducted in an apparatus protected from atmospheric moisture.) In a flame-dried, 250-ml round-bottom flask is condensed 100 ml (170 g) of methyl bromide. The reaction flask is cooled to $-20°$. Anhydrous fluoroantimonic acid, 71 g (0.3 mol), is added dropwise with vigorous agitation over a period of 20 min. The reaction mixture is agitated an additional 40 min and excess methyl bromide is removed under vacuum through a glass tube with a frit end. The light-colored salt is washed with 50 ml of methyl bromide and dried under vacuum. The yield is 100 g, 97% of theoretical, mp $\sim110°$ dec. The product gives correct analysis and nmr spectra. It is stable at room temperature and can be stored.

Elemental Analyses. Ion salt **3** had mp 153–157° (dec with evolution of I_2). *Anal.* Calcd for $C_2H_6SbF_6I$: C, 6.12; H, 1.54; Sb, 31.00; F, 29.02; I, 32.31. Found: C, 6.58; H, 1.37; Sb, 30.57; F, 29.38; I, 32.08. Melting points determined for samples in both open and sealed capillaries were identical: **2**, mp 74–79° dec. *Anal.* Calcd for $C_2H_6Sb_2F_{11}Br$: C, 4.27; H, 1.07; Sb, 43.28; F, 37.15; Br, 14.22. Found: C, 5.61; H, 1.52, Sb, 39.84; F, 37.46; Br, 15.82. Calcd for $C_2H_6SbF_6Br$: C, 6.95; H, 1.75; Sb, 35.22; F, 32.97; Br, 23.11. Ion salt **1** had mp 108–113° (decomposing at 116° with gas evolution). *Anal.* Calcd for $C_2H_6Sb_2F_{11}Cl$: C, 4.64; H, 1.16; Sb 47.00; F, 40.43; Cl, 6.84. Found: C, 5.89; H, 1.51; Sb, 40.93; F, 37.98; Cl, 7.12. Calcd for $C_2H_6SbF_6Cl$: C, 7.97; H, 2.01; Sb, 40.41; F, 37.84; Cl, 11.77. The discrepancies in the calculated and found analysis of salts **1** and **2** are easily accounted for by considering the presence of a small amount of hexafluoroantimonate anion. The presence of $Sb_2F_{11}{}^-$ anions in these salts is substantiated by the ^{19}F nmr spectra of the isolated salts in SO_2 solutions in which signals characteristic of this anion are observed. This question was discussed previously in our work.[34]

Nmr Spectra. A Varian Associates Model A56/60A nmr spec-trometer equipped with a variable-temperature probe was used for ^1H and ^{19}F nmr spectra. Proton coupling constants are believed accurate to ±0.1 Hz. Unless otherwise indicated, proton chemical shifts (δ) are in SO_2 solvent from external capillary TMS. Fourier transform carbon-13 nmr spectra were recorded on a Varian Associates Model XL-100 nmr spectrometer. Experimental details on obtaining carbon-13 spectra have been previously reported.[35]

Laser Raman and Ir Spectra. Raman spectra were obtained on a Cary 81 Raman spectrometer with laser source (50 mW gas laser using the 6328 Å He Ne line). The detailed experimental conditions have been previously reported.[34] Ir spectra were recorded as Nujol and Fluorolube mulls on ITRAN and KRS-5 plates with a Beckman IR-10 spectrometer. All manipulations were carried out in a drybox.

Alkylation of Aromatics. Solutions of the ions **1–3** and **7–9** (ca. 1 M) were prepared as described in SO_2ClF; an approximate 0.5-ml aliquot of the resulting solution was added with vigorous stirring to an approximate 10 mol excess of toluene in SO_2ClF. At the completion of the reaction, a 0.25-ml portion of the mixture was quenched with ca. 30 ml of a saturated solution of sodium carbonate and extracted with ether. Glc of the resulting ether solutions utilizing a Perkin-Elmer 226 gas chromatograph in conjunction with Infotronics CRS-1 Digital Chromotograph Readout System was used to obtain the isomer distribution of the xylenes formed.

Alkylation of n-Donor Substrates. In general, reactions were performed by addition of an aliquot portion of halonium ion in SO_2 at ca. $-60°$ to a calculated amount of the heteroorganic n-base substrate at $-78°$. The solutions then were allowed to warm up to $-15°$ for about 5 min and cooled back to $-60°$, and anion ions summarized in Table VII were identified by nmr spectroscopy.

(34) A. Commeyras and G. A. Olah, *J. Amer. Chem. Soc.*, **91**, 2929 (1969).

(35) G. A. Olah and P. W. Westerman, *J. Amer. Chem. Soc.*, **95**, 3706 (1973).

The Crystal Structure of Ferrocenyldiphenylcyclopropenium Tetrafluoroborate, a Stable Carbonium Ion Salt

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Abstract: The crystal and molecular structure of ferrocenyldiphenylcyclopropenium tetrafluoroborate has been determined by an X-ray diffraction study of a single crystal specimen. The monoclinic cell, space group $P2_1/c$, with $a = 8.219$ (3), $b = 14.708$ (3), and $c = 17.857$ (3) Å and $\beta = 103.60$ (5)°, contains four formula units ($C_{25}H_{19}$-$FeBF_4$); the calculated X-ray density is 1.53 g/cm.^{3} The structure was refined to a weighted R_2 factor of 0.046 and $R = 0.057$. Of the 2003 measured reflections, the number with nonzero weight was 1410. The structure consists of a $C_{25}H_{19}Fe$ cation and a BF_4 anion. The structure and stability of the cation are consistent with interaction between iron d orbitals and empty orbitals of the cyclopropenium moiety.

Although a wide variety of carbonium ions are known to be stable in solution, the number which have been isolated as stable solids is much smaller.[1] One such stable solid is the carbonium ion salt: ferrocenyldiphenylcyclopropenium tetrafluoroborate, the crystal and molecular structure of which we report here. The factors stabilizing the carbonium ion center in α-ferrocenyl cations have been the subject of study and debate for some time. It has been argued by some[2] that conjugation with the π electrons is the source of the un-usual stability of α-ferrocenyl cations, while others[3–6] have suggested that direct interaction of nonbonding e_{2g} metal orbital electrons with the carbonium ion orbital leads to stabilization. The relative merits of these two points of view have been reviewed,[7] and recently the structure of the ferrocenylmethyl cation has

(1) G. A. Olah, *Science*, **168**, 1298 (1970).

(2) T. G. Traylor and J. C. Ware, *J. Amer. Chem. Soc.*, **89**, 2304 (1967).

(3) J. H. Richards and E. A. Hill, *J. Amer. Chem. Soc.*, **81**, 3484 (1959).

(4) E. A. Hill and J. H. Richards, *J. Amer. Chem. Soc.*, **83**, 3840 (1961).

(5) E. A. Hill and J. H. Richards, *J. Amer. Chem. Soc.*, **83**, 4216 (1961).

(6) D. S. Trifan and R. Backsai, *Tetrahedron Lett.*, **13**, 1 (1960).

(7) M. Cais, *Rec. Chem. Progr.*, **27**, 177 (1966).

been calculated using a self-consistent charge procedure based on an extended Hückel model.[8] Since various distortions from expected symmetry have been predicted to accompany metal orbital participation in the bonding and stabilization, we have undertaken a crystallographic investigation of ferrocenyldiphenyl-cyclopropenium tetrafluoroborate, a stable carbonium ion salt.

Experimental Section

Professor Richard W. Fish of this department kindly supplied us with single crystals of $C_{25}H_{19}FeBF_4$, prepared by the method of Cais.[9] The crystals were in the form of dark red needles, elongated along [010]. The crystal used for the intensity measurements was about 0.1 mm $\times$ 0.1 mm in cross-section and mounted with the b axis as the rotation axis. Preliminary investigation by Weissenberg and Buerger precession film methods revealed the following systematic extinctions: $h0l, l = 2N + 1$; $0k0, k = 2N + 1$. The unit cell is monclinic and the space group is $P2_1/c$.

The crystal was transferred to a Picker automatic four-circle diffractometer to refine the cell dimensions and collect diffraction intensity data. Two cycles of least-squares refinement gave unit cell dimensions: $a = 8.219 (3), b = 14.708 (3)$, and $c = 17.857 (3)$ Å and $\beta = 103.60 (5)°$. With $Z = 4$ molecules/cell, $d_{\text{calcd}} = 1.53$ g cm^{-3}. The density was not measured, but is consistent with the densities of other substituted ferrocenes of comparable molecular weight.[10,11]

Intensity data were collected by the θ–2θ scan technique out to a limiting 2θ of 40°. The integrated intensity of each reflection was measured by scanning in 2θ across the peak beginning 0.90° below the 2θ value for diffraction at Kα_1, scanning at a rate of 1°/min until 2θ reached 0.90° above the 2θ value at which the Kα_2 beam was diffracted. Ten-second background counts were taken with the apparatus stationary, 0.50° below and above the 2θ scan limits. In order to check on systematic variations in the intensity data, two standard reflections were measured periodically, but no systematic variation was observed. The molybdenum radiation was monochromatized with a graphite crystal ($2\theta = 11.8°$).

The data were processed and the structure was refined on a CDC3150 computer.[12] The net intensity was calculated from

$$I = C - (B_1 + B_2)(T_c/2T_B)$$

in which C is the total recorded counts in scan time T_c and B_1 and B_2 are background counts for time T_b each. The standard deviation of I is

$$\sigma(I) = [C + (T_c/2T_b)^2(B_1 + B_2) + (qI)^2]^{1/2}$$

in which q is an arbitrary factor of 0.05 used to prevent the relative error in large counts from becoming unrealistically small. The standard deviation in the structure factor is given by

$$\sigma(F) = F_o - [F_o^2 - S\sigma(I)/Lp]^{1/2}$$

in which S is the scaling factor in the equation

$$F_o = (SI/Lp)^{1/2}$$

where L and p are the Lorentz and polarization factors. No correction for absorption was made.

The full-matrix least-squares program minimizes the function

$$R_2^2 = \sum w(\Delta F)^2/\sum w|F_o|^2$$

(8) R. Gleiter and R. Seeger, *Helv. Chim. Acta*, **54**, 1217 (1971).
(9) M. Cais, *J. Amer. Chem. Soc.*, **89**, 5468 (1967).
(10) A. P. Krukonis, J. Silverman, and N. F. Yannoni, *Acta Crystallogr.*, **28**, 987 (1972).
(11) R. Churchill and J. Wormald, *Inorg. Chem.*, **8**, 720 (1969).
(12) The following computer programs, which were used, were furnished by A. Zalkin, University of California Radiation Laboratory, Berkeley, Calif.: MAGPIK, to calculate net intensities; INCOR, to calculate F_o's; FORDAP, to calculate Patterson and Fourier functions; LSLONG, to refine the structure; DISTAN, to calculate interatomic distances and angles; LSPLAN, to calculate atomic planes; DIHED, to calculate dihedral angles between planes; HFINDR, to locate hydrogen atoms; and LIST to prepare a table of F_o's and F_c's. The programs, originally written for a CDC6600 (118K core), were adapted to a CDC3150(16K core).

where ΔF is the difference between the magnitudes of the observed and calculated structure factors F_o and F_c (see paragraph at end of paper regarding supplementary material). For each reflection w was set to $1.0/F_o$ with the exception that $w = 0$ when I (net count) $\leq \sigma(I)$. Of the 2003 measured reflections, the number of reflections for which $w = 0$ was 1410. The conventional R was also calculated where

$$R = \sum|\Delta F|/\sum|F_o|$$

Atomic scattering factors for hydrogen were taken from International Tables,[13] and for the remaining atoms from the compilations of Cromer and Waber.[14] Real and imaginary corrections for anomalous dispersion by the iron atom were those calculated by Cromer.[15]

Determination of the Structure

In the Harker sections of the three-dimensional Patterson function, it was possible to locate the Fe–Fe vectors. A three-dimensional Fourier map phased on the iron revealed most of the 31 non-hydrogen atoms. Several cycles of least-squares refinement (diagonal approximation) with all temperature factors isotropic (of the form $\exp(-B \lambda^{-2} \sin^2 \theta)$) except that of the iron atom resulted in $R_2 = 0.129$ and $R = 0.150$. At this point all temperature factors were made anisotropic and further refinement was carried out by full-matrix least squares. The anisotropic temperature factors have the form $\exp(-\beta_{10}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$. However, because of the severe limitations of core storage in our computer, it is possible to refine a maximum of *seven* anisotropic atoms by full-matrix least squares, holding the positions of remaining atoms constant. Consequently, the atoms were grouped into sets of seven, and three cycles of full-matrix least squares were carried out as shown in Table I.

Table I. Least-Squares Refinement

Run	Atoms refined	R_2	R
1	Fe, C: 1–6	0.082	0.116
2	Fe, C: 7–12	0.076	0.111
3	Fe, C: 13–18	0.072	0.105
4	Fe, C: 19–24	0.071	0.105
5	Fe, C(25), B, F: 1–4	0.061	0.094
6	H: 1–16	0.055	0.088
7	H: 7–22	0.053	0.086
8	All non-H atoms	0.046	0.057

Runs 1–5 were full-matrix least-squares refinements, with anisotropic temperature factors for non-hydrogen atoms. After run 6, a difference Fourier was calculated and the positions of the hydrogen atoms became quite clear. Two runs, 6 and 7, were required to refine the hydrogen atom positions (full matrix, but with isotropic temperature factors). Finally, to place all the positional parameters and their standard deviations on a single magnetic tape for a subsequent calculation of interatomic distances and angles, three cycles of least squares (diagonal approximation) were carried out (run 8) on all non-hydrogen atoms. At the end of the refinement process, R_2 stood at 0.046, R at 0.057, and the standard deviation of an observation of unit weight was 1.13. Total CPU time on the CDC3150 was 8.49 hr.

(13) J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. III, C. H. MacGillavry, G. D. Rieck, and K. Lonsdale, Ed., Kynoch Press, Birmingham, England, 1968, p202.
(14) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
(15) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

Table II. Positional Coordinates of the Nonhydrogen Atoms[a]

	X	Y	Z		X	Y	Z
Fe	0.4426 (1)	0.1693 (0.7)	0.2117 (0.6)	C(16)	0.1357 (8)	0.0859 (5)	0.4586 (4)
C(1)	0.6194 (10)	0.2614 (6)	0.1955 (5)	C(17)	0.7673 (7)	0.2848 (4)	0.4499 (4)
C(2)	0.5771 (10)	0.1996 (6)	0.1316 (4)	C(18)	0.9060 (8)	0.1862 (5)	0.0047 (4)
C(3)	0.4034 (11)	0.2101 (5)	0.0989 (4)	C(19)	0.9080 (8)	0.1014 (5)	0.0377 (4)
C(4)	0.3348 (11)	0.2727 (5)	0.1413 (4)	C(20)	0.7708 (9)	0.0434 (5)	0.0140 (4)
C(5)	0.4692 (13)	0.3044 (5)	0.1999 (4)	C(21)	0.6289 (9)	0.4260 (5)	0.4584 (4)
C(6)	0.5226 (8)	0.1076 (4)	0.3131 (4)	C(22)	0.6267 (8)	0.3392 (5)	0.4273 (3)
C(7)	0.5005 (9)	0.0402 (4)	0.2521 (4)	C(23)	0.6804 (8)	0.1368 (4)	0.3615 (4)
C(8)	0.3288 (9)	0.0419 (5)	0.2132 (4)	C(24)	0.8487 (8)	0.1225 (4)	0.3940 (4)
C(9)	0.2461 (9)	0.1100 (5)	0.2491 (4)	C(25)	0.7681 (7)	0.1994 (4)	0.4127 (4)
C(10)	0.3639 (7)	0.1521 (5)	0.3114 (4)	B	0.1060 (10)	0.3523 (6)	0.3379 (4)
C(11)	−0.0091 (7)	0.0654 (4)	0.4036 (3)	F(1)	0.0298 (7)	0.2872 (4)	0.2908 (4)
C(12)	0.0230 (9)	0.4874 (4)	0.1427 (4)	F(2)	−0.0072 (5)	0.4141 (4)	0.3469 (3)
C(13)	0.8853 (10)	0.4274 (6)	0.1303 (4)	F(3)	0.1890 (6)	0.3168 (3)	0.4062 (2)
C(14)	0.7426 (9)	0.4476 (5)	0.0754 (4)	F(4)	0.2231 (6)	0.3899 (4)	0.3043 (3)
C(15)	0.2698 (6)	0.0253 (4)	0.4692 (2)				

[a] Numbers in parentheses in this and subsequent tables are estimated standard deviations of the last digits.

Table III. Anisotropic Thermal Parameters

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	2.65 (3)	2.33 (3)	3.22 (4)	−0.02 (4)	0.60 (3)	−0.26 (5)
C(1)	6.80 (43)	7.31 (51)	6.22 (42)	−2.73 (4)	1.92 (35)	3.31 (38)
C(2)	7.44 (43)	6.81 (50)	4.90 (36)	0.52 (39)	1.84 (33)	0.75 (36)
C(3)	8.91 (48)	5.64 (83)	2.89 (33)	−0.39 (40)	0.79 (33)	0.13 (32)
C(4)	9.40 (50)	4.47 (39)	3.86 (36)	1.57 (39)	0.78 (34)	0.73 (33)
C(5)	12.82 (61)	3.46 (38)	4.12 (37)	−2.19 (40)	1.39 (38)	−0.04 (33)
C(6)	4.89 (35)	3.01 (30)	3.98 (32)	−0.79 (29)	1.02 (26)	−0.45 (28)
C(7)	4.94 (34)	3.10 (33)	5.18 (33)	0.46 (30)	0.99 (27)	−0.06 (0)
C(8)	4.03 (33)	3.30 (35)	6.34 (39)	−0.62 (30)	0.59 (29)	0.52 (33)
C(9)	4.21 (33)	4.34 (36)	5.27 (37)	−1.16 (33)	1.19 (28)	−0.18 (32)
C(10)	2.06 (27)	4.68 (37)	4.29 (32)	0.53 (27)	0.19 (32)	0.19 (28)
C(11)	2.63 (27)	3.91 (32)	2.74 (28)	1.04 (26)	−0.00 (23)	−0.22 (26)
C(12)	5.02 (35)	4.69 (36)	4.22 (32)	−2.01 (32)	0.57 (28)	0.25 (31)
C(13)	5.35 (40)	6.18 (46)	6.13 (42)	−0.93 (37)	0.47 (42)	0.83 (38)
C(14)	4.49 (36)	4.53 (38)	6.81 (40)	−1.22 (32)	1.08 (31)	0.48 (36)
C(15)	4.91 (37)	6.17 (43)	6.44 (40)	0.12 (35)	0.54 (32)	−1.55 (35)
C(16)	3.26 (32)	4.21 (37)	4.42 (35)	0.64 (29)	−0.50 (27)	0.10 (30)
C(17)	2.84 (28)	3.13 (30)	4.04 (30)	−0.58 (26)	1.01 (23)	−1.32 (26)
C(18)	4.88 (33)	3.70 (37)	4.94 (33)	1.14 (31)	1.16 (27)	0.63 (30)
C(19)	5.45 (35)	3.50 (34)	5.75 (37)	1.03 (31)	1.90 (29)	0.75 (31)
C(20)	5.88 (37)	4.45 (39)	5.26 (34)	0.42 (34)	2.06 (29)	0.81 (33)
C(21)	5.63 (36)	5.17 (39)	4.13 (34)	1.38 (33)	1.26 (37)	−0.05 (33)
C(22)	5.21 (32)	3.77 (32)	3.48 (28)	1.98 (29)	1.70 (24)	0.05 (29)
C(23)	4.43 (33)	3.35 (33)	3.51 (32)	0.88 (28)	0.85 (23)	0.73 (23)
C(24)	2.98 (29)	3.55 (32)	4.40 (33)	0.29 (27)	0.69 (29)	0.31 (25)
C(25)	3.45 (31)	3.77 (36)	3.34 (30)	−0.014 (27)	0.01 (25)	0.23 (28)
B	4.13 (39)	7.01 (56)	3.50 (38)	1.38 (46)	0.08 (32)	−0.72 (39)
F(1)	9.83 (34)	8.55 (29)	12.58 (35)	1.01 (29)	−3.29 (28)	−3.74 (30)
F(2)	7.25 (23)	9.82 (30)	9.14 (29)	5.08 (21)	1.87 (20)	−0.15 (25)
F(3)	8.03 (24)	9.49 (28)	5.53 (20)	3.68 (23)	0.90 (18)	1.98 (23)
F(4)	7.88 (25)	12.38 (37)	11.97 (30)	1.53 (27)	5.12 (21)	5.49 (28)

The final positional parameters of the non-hydrogen atoms are given in Table II, and the corresponding anisotropic thermal parameters in Table III. The positional and thermal parameters of the hydrogen atoms are listed in Table IV.

Description of the Structure

The interatomic distances are shown in Figures 1 and 2, while interatomic bond angles are listed in Table V. The three rings attached to ring C, the cyclopropenium moiety, are twisted propeller-like, in a manner similar to sym-triphenylcyclopropenium pechlorate (TPCP) as indicated in Table VI. Rings A and B, the cyclopentadienyl rings, are eclipsed and are offset from parallelism by 2.7°, which is slightly more than in the recently studied 2,2-dicyanovinylferrocene,[10] but

comparable with results listed in Churchill's survey[11] of X-ray diffraction and electron diffraction studies on ferrocene derivatives. Average bond distances are listed in Table VII.

The details of the structure are reasonably consistent with the structure calculated by Gleiter and Seeger.[8] Although their model indicates a staggered configuration for the ferrocene system, the energy difference[16,17] between the staggered and eclipsed configuration, 0.9 kcal/mol, is probably too small to invalidate the comparison. In particular, three details of the structure agree with the metal orbit participation.

(1) The bending of ring C up toward the ferrocenyl

(16) R. K. Bohn and A. Haaland, J. Organometal. Chem., 5, 470 (1966).

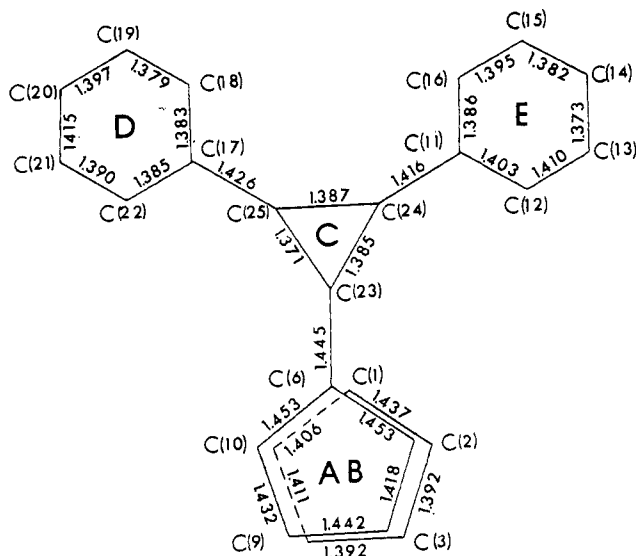(17) A. Haaland and J. E. Nilsson, Chem. Commun., 88 (1968).

Figure 1. The five rings making up the $C_{25}H_{19}Fe^-$ moiety are shown with the measured carbon–carbon bond distances. The average standard deviation equals 0.008 Å.

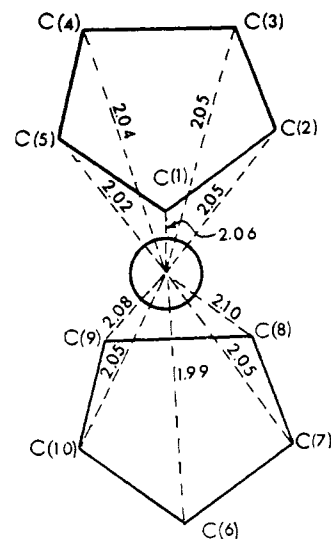

Figure 2. The ferrocene moiety in $C_{25}H_{19}FeBF_4$ with the measured iron–carbon distances indicated. The average standard deviation is 0.007 Å.

Table IV. Positional and Thermal Parameters of the Hydrogen Atoms

	X	Y	Z	B
H(1)	0.6772	0.2304	0.2396	23.1
H(2)	0.6470	0.1426	0.9848	19.3
H(3)	0.3381	0.1733	0.0527	7.3
H(4)	0.1704	0.2973	0.1314	38.2
H(5)	0.4728	0.3407	0.2454	13.6
H(7)	0.6019	0.0017	0.2264	11.2
H(8)	0.2734	0.0002	0.1449	8.3
H(9)	0.0920	0.1255	0.2278	5.3
H(10)	0.3483	0.2251	0.3546	7.5
H(12)	0.8389	−0.0395	0.3037	12.3
H(13)	1.1109	−0.1408	0.3335	11.8
H(14)	1.3616	−0.1014	0.4402	8.4
H(15)	1.3692	0.0417	0.5061	14.3
H(16)	1.1391	0.1654	0.4907	11.4
H(18)	1.0097	0.2669	0.5233	9.1
H(19)	0.9958	0.4427	0.5793	12.4
H(20)	0.7389	0.5401	0.5329	6.8
H(21)	0.5229	0.4699	0.4374	6.4
H(22)	0.5255	0.3343	0.3765	8.2

Table VI. Dihedral Angles (deg)

Rings	This work	TPCP[a]
C and D	7.5	7.6
C and E	11.2	12.1
C and A	14.6	21.2

[a] M. Sundaralingam and L. H. Jensen, *J. Amer. Chem. Soc.*, **88**, 198 (1966).

Table VII. Average Bond Distances

Ring	Bond	Av, Å	"Best"	Ref
A + B	Fe–C	2.049	2.058	a
A + B	C–C	1.424	1.419	b
C	C–C	1.381	1.373	c
D + E	C–C	1.392	1.395	d

[a] R. K. Bohn and A. Haaland, *J. Organometal. Chem.*, **5**, 470 (1966). [b] P. J. Wheatley in "Perspectives in Structural Chemistry," Vol. I, J. D. Dunitz and J. A. Ibers, Ed., Wiley, New York, N. Y., 1967, p 9. [c] Footnote a, Table VI. [d] H. Ondik and D. Smith in ref 13.

Table V. Bond Angles

Atoms	Angle, deg	Atoms	Angle, deg
(a) Within the Ferrocene System			
C(1)–Fe–C(2)	40.9 (3)	C(6)–Fe–C(7)	42.1 (3)
C(2)–Fe–C(3)	40.4 (3)	C(7)–Fe–C(8)	40.0 (3)
C(3)–Fe–C(4)	39.8 (3)	C(8)–Fe–C(9)	40.4 (3)
C(4)–Fe–C(5)	40.7 (3)	C(9)–Fe–C(10)	40.6 (3)
C(5)–Fe–C(1)	40.4 (4)	C(10)–Fe–C(6)	42.1 (3)
C(1)–C(2)–C(3)	106.8 (7)	C(6)–C(7)–C(8)	106.8 (6)
C(2)–C(3)–C(4)	110.3 (7)	C(7)–C(8)–C(9)	108.3 (6)
C(3)–C(4)–C(5)	106.0 C (8)	C(8)–C(9)–C(10)	110.0 (6)
C(4)–C(5)–C(1)	110.8 (7)	C(9)–C(10)–C(6)	105.1 (6)
C(5)–C(1)–C(2)	106.1 (7)	C(10)–C(6)–C(7)	110.0 (6)
(b) Within the Cyclopropenyl System			
C(23)–C(24)–C(25)	59.3 (5)	C(18)–C(17)–C(25)	120.7 (6)
C(24)–C(25)–C(23)	60.3 (5)	C(22)–C(17)–C(25)	117.9 (6)
C(25)–C(23)–C(24)	60.5 (5)	C(16)–C(11)–C(24)	120.2 (6)
		C(12)–C(11)–C(24)	117.6 (6)
C(23)–C(6)–C(10)	123.6 (6)	C(17)–C(25)–C(24)	152.2 (6)
C(23)–C(6)–C(7)	126.0 (6)	C(17)–C(25)–C(23)	147.5 (6)
C(25)–C(23)–C(6)	148.6 (6)	C(11)–C(24)–C(25)	151.7 (6)
C(24)–C(23)–C(6)	150.9 (6)	C(11)–C(24)–C(23)	148.8 (6)

group facilitates interaction of the filled nonbonding $3d_{z^2}$ orbital of the iron with the empty orbital of the cyclopropenium moiety. Gleiter and Seeger predict an angle of 40°, but admit that this value "may be somewhat too large," while the measured value is 14.6°.

(2) The slight elongation of the exocyclic bond distance C(6)–C(23) (Figure 1) is consistent with mixing metal orbitals with empty orbitals, resulting in a weakening and lengthening of the C(6)–C(23) bond and ease of bending C(23) toward the iron.

(3) The C(6)–Fe bond distance, 1.99 Å, is the shortest of all the C–Fe bond distance, the direction of which shift would tend to facilitate orbital overlap. The slight distortion from D_{5h} symmetry of the ferrocenyl group was also predicted by Hill and Richards.[4]

The structure of the anion, BF_4^-, is tetrahedral: average bond distances and angles are 1.346 Å and 109.45°

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Latent Homoallylic Ions in Carbocyclic Ring Construction. α-Cedrene

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Abstract: A synthetically useful concept for construction of complex carbocyclic ring systems by cationic cyclization is developed. Transformations theoretically attributable to homoallylic cations which are unachievable in practice can be performed by *partial* generation and consumption of such bifunctional intermediates in *different* steps. A short and efficient total synthesis of α-cedrene illustrates the approach.

The utilization of latent functionality[1] has become a powerful consideration in total syntheses of complex organic molecules. Whereas the use of blocking groups[2] continues to play an indispensable role in peptide and nucleotide synthesis *inter alia*, latent carbonyl compounds such as furans, anisoles, pyridines, and isoxazoles have become increasingly popular synthetic building blocks for terpenes, steroids, etc. Not only does latent functionality increase efficiency (*e.g.*, by eliminating blocking and deblocking steps) but the possibility exists of partially generating "asymmetric difunctionality" before fully revealing two similar or identical groups. Thus, while hydrogenolysis and hydrolysis of isoxazoles ultimately yield a β-diketone, modified conditions allow a single intermediate β-enamino ketone to form and react selectively.[3] Chloroalkenes are latent ketones which have found use in nonconcerted cationic cyclizations leading stereoselectively to cycloalkanones and acylcycloalkanes, and in [2,3]- and [3,3]-sigmatropic rearrangements.[4] In this paper, such a group is employed along with a *latent* homoallylic cation to facilitate the construction, *via* spiroannelation, of the fascinating sesquiterpene α-cedrene[5-8] (1). As will be clear below, actual homoallylic ions can and do rearrange (→B) prior to intended spirocyclization (→C), when only a weakly nucleophilic terminus is present, *e.g.*, see Scheme I.

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(4) P. T. Lansbury, *Accounts Chem. Res.*, **5**, 311 (1972).
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(6) Biogenesis: W. Parker, J. S. Roberts, and R. Ramage, *Quart. Rev., Chem. Soc.*, **21**, 331 (1967).
(7) First total synthesis: G. Stork and F. H. Clarke, Jr., *J. Amer. Chem. Soc.*, **83**, 3114 (1961).
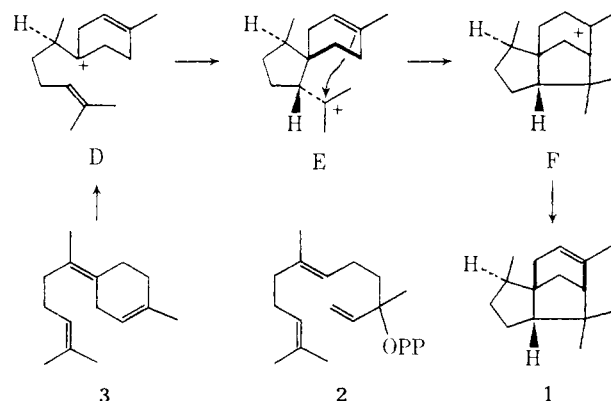(8) Biogenetic-type syntheses: (a) E. J. Corey, N. N. Girotra, and C. T. Mathew, *J. Amer. Chem. Soc.*, **91**, 1557 (1969); (b) T. G. Crandall and R. G. Lawton, *ibid.*, **91**, 2127 (1969); (c) N. H. Andersen and D. D. Syrdal, *Tetrahedron Lett.*, 2455 (1972).

Scheme I
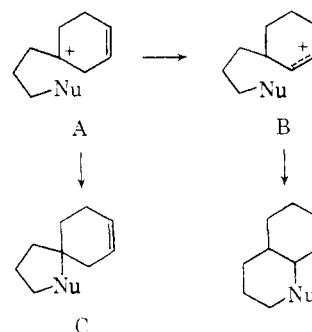
Examination of a proposed biosynthesis of cedrene as depicted in Scheme II indicates that nerolidyl pyro-

Scheme II

phosphate (2), or perhaps *cis*-farnesyl pyrophosphate, cyclizes to γ-bisabolene (3) and that subsequent enzyme-catalyzed steps (3 → D → E → F) should eventually produce 1. The viability of this scheme has been demonstrated recently by the acid-catalyzed biogenetic-like cyclization of nerolidol to 1, epicedrene and an aromatic isomer of the curcumenes in comparable yields.[8c] The complexity of the product mixture arises