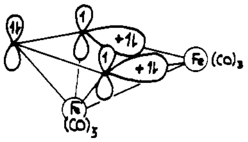
order between the apical iron and B_2 compared to B_1 and B_3. Within experimental error the apical iron–basal boron bond distances are equal (Table II) which means either that the bonding description is oversimplified or that intracage distances are not very sensitive to net bond order.[24] Other differences in bonding between B_5H_9 and $(CO)_6Fe_2B_3H_7$ are expected when compared in detail; however, the qualitative similarities presented here are fully supported by the observed geometrical structure. Hence, the ferraborane may be usefully described as a nido ($n + 2 = 7$ electron pairs) cage or cluster.

An alternative description of the bonding results if one investigates the effective atomic number, EAN, of each iron atom. The $(CO)_6Fe_2B_3H_7$ molecule can be formally considered as formed by the addition of $B_3H_7{}^{2-}$ to $Fe_2(CO)_6{}^{2+}$ as depicted in VI. In this view the π system of the borallyl ion donates four electrons to one iron while the two BH bonds donate four electrons to the other iron.[25] Hence, as each iron is d^7, has three CO ligands, and shares an Fe–Fe bond, the 18-electron rule is satisfied. However, as pointed out above, the geometry of B_3H_7 in $(CO)_6Fe_2B_3H_7$ is substantially different from that of the B_3 unit in the structurally characterized borallyl complex $L_2PtB_3H_7$.[14] The organometallic description may be formally correct, but the cage description of the bonding is more realistic in terms of geometry.[26]



VI

Acknowledgment. The aid of Professor W. R. Scheidt as well as the support of the National Science Foundation under Grant CHE 78-11600 is gratefully acknowledged.

Registry No. $(CO)_6Fe_2B_3H_7$, 71271-99-3.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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(24) Extended Hückel calculations on this molecule also suggest a significant difference in bond order.[19]

(25) There are precedents for considering the Fe–H–B as a two-electron donor to the metal. See, for example: Doi, J. A.; Teller, R. G.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1980**, 80.

(26) There is a similarity between the ferraborane and ferracyclopenadiene complexes. The latter complexes have a semi-bridging carbonyl primarily attached to the apical iron. With Cotton's method of electron counting, there is no need to invoke a semi-bridging carbonyl in the case of $(CO)_6Fe_2B_3H_7$ and indeed none is found: Cotton F. A. *Prog. Inorg. Chem.* **1976**, *21*, 1.

Contribution from the Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439,
and the Occidental Research Corporation, Irvine, California 92713

Crystal and Molecular Structure of the 1:2 Charge-Transfer Salt of Trimethyleneferrocene and 7,7,8,8-Tetracyano-*p*-quinodimethane: $[Fe(C_5H_4)_2(CH_2)_3{}^{+}\cdot][(TCNQ)_2{}^{-}\cdot]$[1]

C. WILLI,[2a,b] A. H. REIS, JR.,* E. GEBERT,[2a] and JOEL S. MILLER*[2c]

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The charge-transfer reaction between trimethyleneferrocene ($Fc(CH_2)_3$) and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) results in a 1:2 salt of composition $[Fe(C_5H_4)_2(CH_2)_3{}^{+}\cdot][(TCNQ)_2{}^{-}\cdot]$. The crystal and molecular structures of this substance have been determined by single-crystal X-ray diffraction. The complex crystallizes as block plates in the centrosymmetric space group $C2/c$ with the unit cell constants of $a = 13.608$ (1) Å, $b = 7.738$ (1) Å, $c = 28.788$ (3) Å, $\beta = 94.336$ (8)°, $V = 3022.66$ Å^3, and $Z = 4$. The structure was solved by a combination of direct methods, Fourier, and full-matrix least-squares refinement techniques. A final $R_F = 0.049$ was obtained for 2328 reflections where $F_o{}^2 > \sigma(F_o{}^2)$. The structure consists of segregated stacks of $[(TCNQ)_2{}^{-}\cdot]$ dimers and trimethyleneferrocenium $[Fc(CH_2)_3{}^{+}\cdot]$ ions, respectively. The stacking distance between the $TCNQ^{1/2-}$ planes of each dimer is 3.162 (5) Å, while the distance between dimers is 3.423 (10) Å. The $[(TCNQ)_2{}^{-}\cdot]$ dimers form stacks which are inclined along the *b* axis, while the $[Fc(CH_2)_3{}^{+}\cdot]$ ions are aligned along the *a* axis and rotated 45° about the *b* axis. The sterically hindering trimethylene bridge causes the C_5 planes of the $[Fc(CH_2)_3{}^{+}\cdot]$ ion to be tilted at an angle of 13.7 (9)° with respect to each other. This amount is significantly greater than the ring tilt observed for other nonoxidized ferrocenes containing three-membered bridges. The bridging carbon atoms between the rings exhibit disorder. The bond distances of the exocyclic carbon–carbon bonds of the $[(TCNQ)_2{}^{-}\cdot]$ ion are 1.390 (3) and 1.394 (4) Å, which are consistent with a charge transfer of 0.5 e/TCNQ.

Introduction

We have undertaken a study of the charge-transfer reactions between metallocenes (principally substituted ferrocenes) and organic electron-accepting bases (principally 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) and 2,3-dichloro-5,6-dicyanoquinone (DDQ)). Such charge-transfer complexes should be sublimable and, thus, permit the wide variety of physical studies that have been undertaken for (TTF)(TCNQ) (TTF = tetrathiafulvalene) to be extended to these materials. We have observed several unique and unusual materials: (1) 1:1 $[Fe(C_5(CH_3)_5)_2{}^{+}\cdot][TCNQ^{-}\cdot]$, a metamagnetic material with alternating ions along a stack,[3,4] (b) 1:1 $[Fe(C_5(CH_3)_5)_2{}^{+}\cdot]_2[(TCNQ)_2{}^{2-}]$, a paramagnetic dimeric material,[5,6]

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* To whom correspondence should be addressed: A.H.R., Department of Chemistry, Brandeis University, Waltham, MA 02254; J.S.M., Occidental Research Corp.

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(2) (a) Argonne National Laboratory. (b) Undergraduate research participant from Luther College, Decorah, IA. (c) Occidental Research Corporation.

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(c) 1:2 $[Fe(C_5(CH_3)_5)_2](TCNQ)_2$, which is conducting, (d) 1:2 $[Fe(C_5H_4(CH_3))_2{}^{+}\cdot][(TCNQ)_2{}^{2-}]$, which is conducting and possesses stacks of uniformly spaced TCNQ anions in different electronic polarizations,[8,9] and (e) 1:1 $[Fe(C_5(CH_3)_5)_2{}^{+}\cdot][DDQH^{-}]$, the first reported one-dimensional paramagnet.[10] To date, no studies have been carried out with bridging ferrocene-type molecules in order to probe the effect of increased steric effects on the charge-transfer reaction and on the electrical and magnetic properties. Therefore, we have undertaken an investigation of the charge-transfer reaction of 1,1′-trimethyleneferrocene, $Fc(CH_2)_3$, and TCNQ. Herein, we report the molecular and crystal structure of the 1:2 charge-transfer complex $[Fc(CH_2)_3{}^{+}\cdot][(TCNQ)_2{}^{-}\cdot]$, which is similar to $Fe(C_5H_4Me)_2(TCNQ)_2$,[9,11] $Fe(C_5H_5)_2(TCNQ)_2$,[1,11] and $Fe(C_5H_5)(C_5H_4Me)(TCNQ)_2$, as it is the only product formed in the reaction.

Experimental Section

Preparation of $[Fc(CH_2)_3{}^{+}\cdot][(TCNQ)_2{}^{-}\cdot]$. A warm filtered acetonitrile solution containing 116.5 mg of $Fc(CH_2)_3$ (0.515 mmol) was added to a hot filtered acetonitrile solution containing 221.6 mg of freshly recrystallized TCNQ (Aldrich) (108 mmol). After reduction of the volume to ca. 25 mL, the solution was slowly cooled to room temperature in a preheated Dewar which was allowed to slowly equilibrate with the ambient temperature. After 48 h, 118.9 mg (36%) of purple block crystals was harvested via vacuum filtration and air-drying. The acetonitrile utilized was dried via distillation over phosphorus pentoxide.[11]

X-ray Data Collection. Preliminary Weissenberg and precession photographs of several block crystals of $[Fc(CH_2)_3{}^{+}\cdot][(TCNQ)_2{}^{-}\cdot]$ indicated a monoclinic unit cell. Systematic absences hkl with $h + k = 2n + 1$ and hkl with $l = 2n + 1$, indicative of the space group Cc or $C2/c$, were observed. The space group $C2/c$ was later confirmed to be correct. A crystal of 0.02 × 0.02 × 0.03 cm was attached to the end of glass fiber with epoxy cement and subsequently mounted on a Syntex $P2_1$ automatic diffractometer. The b axis of the crystal was approximately aligned along the ϕ axis of the goniometer. Fifteen reflections were chosen to use in the automatic centering, indexing, and unit cell least-squares routines which indicated the same monoclinic unit cell as found in the preliminary photographic study.[14] A detailed description of the crystal alignment procedure has been reported previously.[15] Final unit cell parameters and other experimental information are given in Table I. Intensity data in the range of $4° \leq 2\theta \leq 50°$ (Mo $K\bar{\alpha}$) were obtained during data collection. Three check reflections were automatically measured every 47 reflections and were found to remain unchanged. A total of 2678 independent reflections were measured.

Solution and Structure Refinement. Absorption, Lorentz, and polarization corrections were applied to the data by using the DATALIB program,[16] and all equivalent reflections were averaged with use of the program DATASORT[16] ($R_{F_{av}} = 0.02$). The structure was solved by direct methods using the program MULTAN-74.[17] This routine indicated a centrosymmetric structure based on the E statistics and the Fe atom at the special position (0, y, 0.75). All of the atoms of the unique $(TCNQ^{1/2-})$ molecule of the $(TCNQ)_2{}^{-}\cdot$ dimer were also located. An initial Fourier map based on the MULTAN-74 solution revealed the C atoms of the unique C_5 ring. Subsequent difference-Fourier maps revealed the four hydrogen atoms of the TCNQ and the four hydrogen atoms of the unique C_5 ring. A disordered trimethylene carbon atom bridge was also located, but the hydrogen atoms attached to it were unresolved. The bridging carbon atom C6 was allowed 50% occupancy (C6A and C6B) in two possible disorder sites. The second bridging carbon atom is also disordered; however, the sites are related by the twofold axis ((−0.181 (6), 0.3938 (8), 0.7388 (2)) and (0.181 (6), 0.3938 (8), 0.7612 (2))). Anisotropic full-matrix least-squares refinement of nonhydrogen and nondisordered atoms and isotropic refinement of the disordered C6 and C7 atoms (the hydrogen atoms remaining fixed) resulted in a final $R_F = 0.049$ for the 2328 reflections with $F_o{}^2 > \sigma(F_o{}^2)$. In the final cycle of refinement, an isotropic extinction factor[18] was refined to $g = 1.31$. A final difference-Fourier synthesis indicated the largest residual peak to be 0.3 e/Å^3.

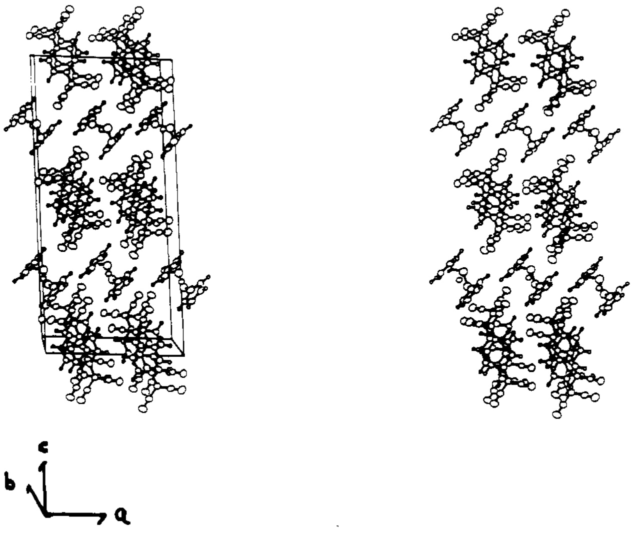

Figure 1. Stereoview of the unit cell of $[Fc(CH_2)_3{}^{+}\cdot][(TCNQ)_2{}^{-}\cdot]$ showing an arbitrary alternation of the disordered C6 and C7 methylene carbon atoms.

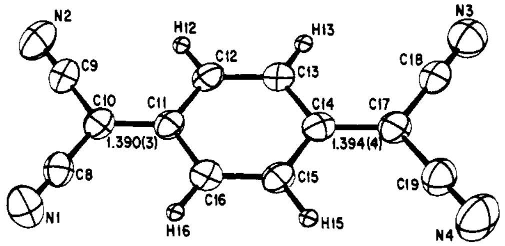

Figure 2. The $TCNQ^{1/2-}$ anion with atom labels.

The quantity minimized during refinement is $\sum w(|F_o{}^2 - F_c{}^2|)^2$, where F_o and F_c are the observed and calculated structure factor amplitudes. Weights are assigned as $w = 1/(\sigma(F_o{}^2))^2$; $\sigma(I) = [SC + \tau^2(B_1 + B_2) + P^2I^2]^{1/2}$. SC is the scan count, τ is the scan to background time ratio, B_1 and B_2 are the background counts on each side of the peak, I is the net intensity, and P is a systematic error factor, set to 0.02. The agreement indices are defined as

$$R_F = \sum||F_o| - |F_c||/\sum|F_o|$$

$$R_{wF^2} = [\sum w|F_o{}^2 - F_c{}^2|^2/\sum w(F_o)^2]^{1/2}$$

$$GOF = [\sum w|F_o{}^2 - F_c{}^2|^2/(N_o - N_R)]^{1/2}$$

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(16) DATALIB and DATASORT were written by H. A. Levy and locally adapted for the IBM 370/195.

(17) MULTAN-74 was written by P. Main, M. M. Woolfson, and G. Germain and locally adapted for the IBM 370/195.

(18) The extinction correction has the form $F_c = F_o(1 + gIc)$. The value of g is varied in the least-squares matrix. See: Coppens, P.; Hamilton, W. C. *Acta Crystallogr.* **1966**, *120*, 149.

Table I. Experimental Details for $[Fc(CH_2)_3^{+}\cdot][(TCNQ)]_2^{-}\cdot]$

mol formula: $[Fe(C_5H_4)_2(CH_2)_3^{+}\cdot][(C_6H_4(C(CN)_2)_2)_2^{-}\cdot]$
mol wt of asymmetric unit: 634.49
space group: $C2/c$ (C_{2h}^6, No. 15), $Z = 4$
extinctions: hkl ($h + k = 2n + 1$), $h0l$ ($l = 2n + 1$)
cell constants: $a = 13.608$ (1) Å, $b = 7.738$ (1) Å, $c = 28.788$ (3) Å, $\beta = 94.336$ (8)°, $V = 3022.66$ Å^3
cal density: 1.394 g cm^{-3}
measd density: 1.396 g cm^{-3} (flotation in CCl_4/xylene)
no. of molecules in asymmetric unit: 1.5 [i.e., TCNQ + $^1/_2Fc(CH_2)_3$]
radiation: Mo $K\bar{\alpha}$, $\lambda = 0.71069$ Å
abs coeff: 5.65 cm^{-1}
max 2θ: 50°
scan width: variable $(1.4 + \Delta(\alpha_2-\alpha_1))°$
scan speed: variable, 1.96–29.30°/min
crystal: general orientation block; vol 2.14×10^{-5} cm^3
max transmissn factor: 0.91
min transmissn factor: 0.86
no. of reflctns above σ: 2328
total no. of reflctns collected: 2671
R_F for all reflctns: 0.062
R_F for all reflctns above σ: 0.049
GOF = 2.120

Table II. Positional Atomic Coordinates of $[Fc(CH_2)_3^{+}\cdot][(TCNQ)_2^{-}\cdot]$ and Isotropic Thermal Parameters with Estimated Standard Deviations in Parentheses

atom	x	y	z	B,[a] Å^2
Fe	0.0	−0.03469 (7)	$^3/_4$	
C1	−0.0266 (2)	0.0295 (4)	0.8174 (1)	
C2	−0.0572 (2)	−0.1416 (4)	0.8049 (1)	
C3	−0.1286 (2)	−0.1437 (4)	0.7731 (1)	
C4	−0.1442 (2)	0.0278 (5)	0.7570 (1)	
C5	−0.0808 (2)	0.1363 (4)	0.7845 (1)	
C6A	−0.0886 (5)	0.3256 (9)	−0.2282 (2)	4.7 (1)
C6B	−0.0471 (6)	0.3364 (9)	−0.2137 (2)	4.9 (1)
C7	−0.0181 (6)	0.3938 (8)	0.7388 (2)	5.7 (1)
N1	0.7303 (2)	0.6614 (4)	0.8544 (1)	
N2	1.0011 (2)	0.8305 (4)	0.9296 (1)	
N3	0.5554 (2)	0.1851 (4)	1.0948 (1)	
N4	0.8270 (2)	0.3505 (4)	1.1710 (1)	
C8	0.7760 (2)	0.6695 (4)	0.8896 (1)	
C9	0.9274 (2)	0.7618 (4)	0.9310 (1)	
C10	0.8345 (2)	0.6773 (3)	0.9324 (1)	
C11	0.8054 (2)	0.5978 (3)	0.9724 (1)	
C12	0.7120 (2)	0.5125 (3)	0.9728 (1)	
C13	0.6845 (2)	0.4333 (3)	1.0118 (1)	
C14	0.7470 (2)	0.4393 (3)	1.0543 (1)	
C15	0.8390 (2)	0.5201 (4)	1.0540 (1)	
C16	0.8680 (2)	0.5989 (3)	1.0150 (1)	
C17	0.7180 (2)	0.3507 (2)	1.0939 (1)	
C18	0.6275 (2)	0.2600 (4)	1.0944 (1)	
C19	0.7794 (2)	0.3498 (4)	1.1368 (1)	
H1	0.019	0.061	0.845	3.84
H2	−0.204	0.038	0.734	4.37
H3	−0.156	−0.231	0.760	4.11
H4	−0.026	−0.225	0.824	3.92
H12	0.665	0.527	0.942	3.03
H13	0.616	0.385	1.014	3.00
H15	0.880	0.527	1.085	2.97
H16	0.930	0.650	1.007	2.90

[a] Atoms with unlisted isotropic thermal parameters were refined anisotropically.

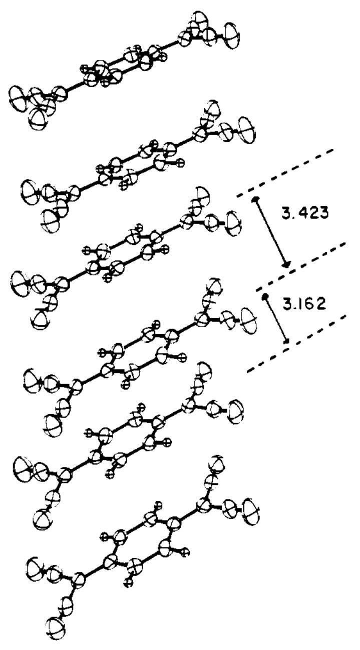

Figure 3. Stacking of the $[(TCNQ)_2^{-}\cdot]$ dimers along the b axis.

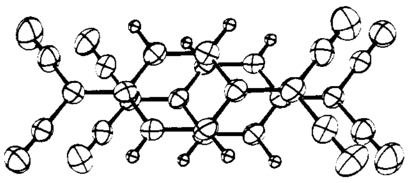

Figure 4. The $[(TCNQ)_2^{-}\cdot]$ dimer showing slippage of the planes along the long molecular axis.

N_0 is the number of independent reflections and N_R is the number of parameters varied. The programs S5FOUR[19] and S5XFLS[19] were used in the Fourier synthesis and least-squares refinements. Bond distances, angles, and estimated standard deviations (esd's) were determined from the program S5FFE.[19] LS PLANES[20] was used to determine deviations from various molecular planes. Molecular drawings were prepared with use of ORTEP.[21] Atomic coordinates are listed in Table II, and the corresponding anisotropic thermal parameters are listed in Table III. Scattering factors for nonhydrogen atoms were taken from the compilation of Cromer and Waber[22a] and modified for the real and imaginary components of anomalous dispersion.[22b] Hydrogen scattering factors were taken from ref 22c. A listing of F_o and F_c is given as supplementary material.

Structure Description

The crystal structure of $[Fc(CH_2)_3^{+}\cdot][(TCNQ)_2^{-}\cdot]$ consists of segregated stacks of $[(TCNQ)_2^{-}\cdot]$ dimers and $[Fc(CH_2)_3^{+}\cdot]$ ions. The interatomic distances and angles with estimated standard deviations (esd's) of the $Fc(CH_2)_3^{+}\cdot$ and $TCNQ^{1/2-}$ ions are respectively presented in Tables IV and V. Figure 1 shows a stereoview of the packing of $[Fc(CH_2)_3^{+}\cdot]$-$[(TCNQ)_2^{-}\cdot]$ units in the unit cell and displays the $[(TCNQ)_2^{-}\cdot]$ stacking arrangement along the b axis.

$[(TCNQ)_2^{-}\cdot]$ Dimer Anions. Figure 2 shows the bond distances and atom labels of each individual $TCNQ^{1/2-}$ anion of the dimer. The bond distances and angles are similar to those found in other $TCNQ^{1/2-}$ moieties as well as other $(TCNQ)^{z-}$ dimers.[5,23–25] The exocylic carbon–carbon bond distances of 1.390 (3) and 1.394 (4) Å agree with a postulated charge transfer of 0.5 e/TCNQ.[25] The $TCNQ^{1/2-}$ anion is essentially planar (Table VI), where the largest deviations from the plane are N1 = 0.172 (3) Å and N3 = 0.118 Å while N2 = 0.040 (3) Å and N4 = 0.006 (3) Å. The $[(TCNQ)_2^{-}\cdot]$ dimer is stacked along the b axis (Figure 3) of the crystal with alternating interplanar spacings within a dimer of 3.162 (5) Å and

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(19) S5FOUR, S5XFLS, and S5FFE are Sigma 5 versions of the programs FOURIER by R. J. Dellaca and W. T. Robinson, ORXFLS3 is by W. R. Busing and H. A. Levy, and ORFFE is by W. R. Busing and H. A. Levy.
(20) LS PLANES was written by M. E. Pippy.
(21) ORTEP was written by C. K. Johnson.
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Table III. Anisotropic Thermal Parameters[a] for $[Fc(CH_2)_3^{+}\cdot][(TCNQ)_2^{-}\cdot]$

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	0.0355 (3)	0.0462 (3)	0.0296 (3)	0.0	0.0052 (2)	0.0
C1	0.056 (2)	0.071 (2)	0.030 (1)	−0.002 (2)	0.011 (1)	−0.010 (1)
C2	0.065 (2)	0.065 (2)	0.037 (1)	0.003 (2)	0.017 (1)	0.006 (1)
C3	0.049 (2)	0.075 (3)	0.054 (2)	−0.016 (2)	0.019 (2)	−0.006 (2)
C4	0.033 (2)	0.103 (3)	0.051 (2)	0.013 (2)	0.009 (1)	0.004 (2)
C5	0.067 (2)	0.053 (2)	0.059 (2)	0.014 (2)	0.030 (2)	0.000 (2)
N1	0.080 (2)	0.110 (3)	0.044 (1)	−0.027 (2)	−0.010 (1)	0.003 (2)
N2	0.051 (2)	0.083 (2)	0.058 (2)	−0.013 (2)	0.004 (1)	0.007 (1)
N3	0.069 (2)	0.073 (2)	0.060 (2)	−0.017 (2)	0.014 (1)	−0.007 (1)
N4	0.078 (2)	0.119 (3)	0.051 (2)	0.000 (2)	−0.013 (1)	0.022 (2)
C8	0.052 (2)	0.056 (2)	0.038 (1)	−0.011 (2)	0.002 (1)	0.000 (1)
C9	0.043 (2)	0.056 (2)	0.032 (1)	0.000 (2)	0.002 (1)	0.002 (1)
C10	0.040 (1)	0.042 (2)	0.035 (1)	−0.001 (1)	0.002 (1)	−0.004 (1)
C11	0.038 (1)	0.034 (1)	0.036 (1)	0.005 (1)	0.002 (1)	−0.004 (1)
C12	0.042 (1)	0.043 (2)	0.032 (1)	−0.002 (1)	−0.003 (1)	−0.004 (1)
C13	0.040 (1)	0.039 (2)	0.040 (1)	−0.001 (1)	0.003 (1)	−0.004 (1)
C14	0.040 (1)	0.034 (2)	0.036 (1)	0.002 (1)	0.002 (1)	0.000 (1)
C15	0.038 (1)	0.049 (2)	0.034 (1)	0.003 (1)	−0.004 (1)	0.002 (1)
C16	0.033 (1)	0.044 (2)	0.041 (1)	0.002 (1)	0.000 (1)	0.001 (1)
C17	0.046 (2)	0.039 (2)	0.041 (1)	0.001 (1)	0.001 (1)	0.001 (1)
C18	0.054 (2)	0.046 (2)	0.037 (1)	0.000 (2)	0.009 (1)	−0.003 (1)
C19	0.055 (2)	0.061 (2)	0.042 (2)	0.002 (2)	0.003 (1)	0.011 (1)

[a] The form of the thermal parameter is $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^*)]$.

Table IV. Bond Distances (Å) within $[Fc(CH_2)_3^{+}\cdot][(TCNQ)_2^{-}\cdot]$ with Estimated Standard Deviations in Parentheses

	$[Fc(CH_2)_3^{+}\cdot]$		
Fe–C1	2.062 (2)	C6B′–C5′	1.614 (8)[a]
Fe–C2	2.102 (3)	C6A–C7	1.595 (11)[a]
Fe–C3	2.096 (3)	C7–C6B′	1.519 (10)[a]
Fe–C4	2.046 (3)	C6A–C6B	0.682 (10)
Fe–C5	2.028 (3)	C7–C6B	0.519 (10)
C1–C2	1.402 (5)	C7–C7′	0.782 (14)
C2–C3	1.374 (4)	C1–H1	1.02
C3–C4	1.416 (5)	C2–H2	0.86
C4–C5	1.405 (4)	C3–H3	0.84
C5–C1	1.420 (4)	C4–H4	1.01
C5–C6A	1.512 (8)[a]		
	$[(TCNQ)_2^{-}\cdot]$		
C8–C10	1.417 (4)	C17–C18	1.419 (4)
C9–C10	1.427 (4)	C17–C19	1.439 (4)
C10–C11	1.390 (3)	C8–N1	1.149 (4)
C11–C12	1.433 (3)	C9–N2	1.137 (4)
C11–C16	1.440 (3)	C18–N3	1.141 (4)
C12–C13	1.357 (3)	C19–N4	1.136 (4)
C13–C14	1.435 (3)	C12–H12	1.04
C14–C15	1.417 (4)	C13–H13	1.01
C15–C16	1.362 (3)	C15–H15	1.03
C14–C17	1.394 (4)	C16–H16	0.93

[a] Average value is 1.560 Å.

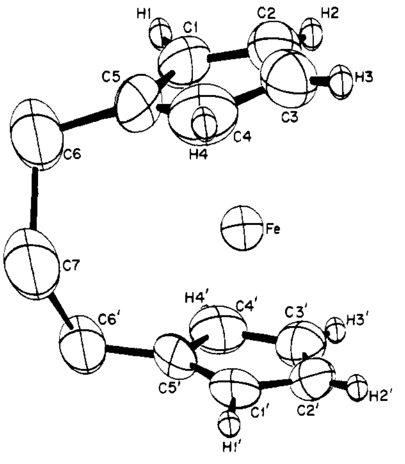

Figure 5. The $[Fc(CH_2)_3^{+}\cdot]$ ion showing atom labels and the disordered trimethylene side chain.

Table V. Interatomic Angles (Deg) within $[Fc(CH_2)_3^{+}\cdot][(TCNQ)_2^{-}\cdot]$ with Estimated Standard Deviations in Parentheses

	$[Fc(CH_2)_3^{+}\cdot]$		
C5–C1–C2	107.9 (2)	C6B′–C5′–C4′	113.9 (3)
C1–C2–C3	108.6 (3)	C6B′–C5′–C1′	138.7 (3)
C2–C3–C4	108.5 (3)	H1–C1–C2	120.8
C3–C4–C5	107.8 (3)	H2–C2–C3	130.8
C4–C5–C1	107.1 (3)	H3–C3–C4	124.5
C4–C5–C6	138.5 (4)[a]	H4–C4–C5	138.7
C1–C5–C6	114.4 (4)[a]	H1–C1–C5	130.7
C5–C6A–C7	108.6 (5)	H2–C2–C1	120.0
C6A–C7–C6B′	112.1 (6)	H3–C3–C2	126.8
C7–C6B′–C5′	110.2 (5)	H4–C4–C3	112.1
	$[(TCNQ)_2^{-}\cdot]$		
N1–C8–C10	178.5 (3)	C15–C14–C17	121.7 (2)
N2–C9–C10	179.2 (3)	C14–C15–C16	121.6 (2)
N3–C18–C17	179.1 (3)	C15–C16–C11	120.7 (2)
N4–C19–C17	179.1 (3)	C14–C17–C18	122.6 (2)
C8–C10–C9	115.9 (2)	C14–C17–C19	121.5 (2)
C8–C10–C11	121.7 (2)	C18–C17–C19	115.8 (2)
C9–C10–C11	122.3 (2)	H12–C12–C11	115.3
C10–C11–C12	121.2 (2)	H12–C12–C13	123.4
C10–C11–C16	121.2 (2)	H13–C13–C12	123.1
C12–C11–C16	117.6 (2)	H13–C13–C14	115.0
C12–C12–C13	121.0 (2)	H15–C15–C14	116.7
C12–C13–C14	121.3 (2)	H15–C15–C16	121.5
C13–C14–C17	120.5 (2)	H16–C16–C11	118.5
C13–C14–C15	117.8 (2)	H16–C16–C15	120.6

[a] Average value is 126.4°.

between dimers of 3.423 (10) Å. Each $TCNQ^{1/2-}$ plane within a stack is inclined at an angle of 22° to the *ac* plane. Due to the *C*2/*c* space group symmetry, only one $TCNQ^{1/2-}$ ion of the dimer is unique, being related to the second ion by an inversion center. The pair of $TCNQ^{1/2-}$ anions within the dimer are offset along the long axis of the TCNQ molecule (Figure 4).

$[Fc(CH_2)_3^{+}\cdot]$ Cations. The atom labeling and structure of the $Fc(CH_2)_3^{+}\cdot$ cations are shown in Figures 5 and 6. The C_5 rings appear eclipsed, and the Fe–C distances are 2.028 (3), 2.046 (3), 2.062 (2), 2.096 (3), and 2.102 (3) Å. The spread of distances is due primarily to the nonparallel C_5 rings where the angle between the least-squares planes of the two rings is 13.8° and the Fe to C_5 ring distance is 1.658 (1) Å. The carbon–carbon C_5 ring distances are 1.402 (5), 1.374 (4), 1.416 (5), 1.405 (4), and 1.420 (4) Å, where the 1.374 (4) Å

Table VI. Least-Squares Planes within $[Fc(CH_2)_3{}^{+}\cdot][(TCNQ)_2{}^{-}\cdot]$

atom	dev	wt	atom	dev	wt
C_5 Plane of $[Fc(CH_2)_3{}^{-}\cdot]$: $0.7572x - 0.1203y - 0.6420z + 16.71 = 0$[a]					
C1	−0.002 (3)	1	C4	0.001 (3)	1
C2	0.001 (3)	1	C5	0.003 (3)	1
C3	−0.002 (3)	1	Fe	1.685 (1)	0
C_6 Plane of $[(TCNQ)_2{}^{-}\cdot]$: $0.4471x - 0.8513y - 0.2745z + 7.6518 = 0$[b]					
C11	0.004 (2)	1	C10	0.012 (3)	0
C12	−0.005 (2)	1	C17	0.025 (3)	0
C13	0.003 (2)	1	C18	0.066 (3)	0
C14	0.001 (2)	1	C19	0.024 (3)	0
C15	−0.002 (2)	1	N1	0.172 (3)	0
C16	0.001 (2)	1	N2	0.040 (3)	0
C8	0.087 (3)	0	N3	0.118 (3)	0
C9	0.033 (3)	0	N4	0.006 (3)	0

[a] $\chi^2 = 2.5258$; dihedral angle between C_5 planes 13.7 (9)°.
[b] $\chi^2 = 10.0531$.

distance is between atoms C2 and C3 lying the greatest distance from the Fe atom. The trimethylene bridge is disordered whereby the C6 and C7 atoms may exist in different sites. Figure 5 shows these sites unresolved. The C6 and C7 disorder appears to be caused by a combination of ring rotation about the C_5 axis and the possibility of two equivalent sites generated by the twofold axis. Figure 6 shows one possible combination of these sites to give a trimethylene moiety which appears ordered; however, the carbon–carbon bond distances and angles are somewhat distorted from normal values (Tables IV and V). These distortions are due to large correlations between atom parameters of C6 and C7 and the unresolved rotational disorder about the C_5 axis. The $[Fc(CH_2)_3{}^{+}\cdot]$ ions are aligned along the *a* axis of the crystal in rows that isolate the TCNQ stacks (Figure 1); however, the $[Fc(CH_2)_3{}^{+}\cdot]$ cations do not stack upon each other, rather each ion is rotated 45° with respect to the *b* axis, allowing for better crystal packing.

Discussion

The structure of $[Fc(CH_3)_3{}^{+}\cdot][(TCNQ)_2{}^{-}\cdot]$ is unusual with respect to the other charge-transfer ferrocene–TCNQ complexes. Additionally, the $[Fc(CH_2)_3{}^{+}\cdot]$ ion is unusual when compared to the structures of other ferrocenium cations previously determined by X-ray diffraction. In other ferrocene–TCNQ materials, several different types of stacks of anions (A) and cations (C) have been observed. These include alternating stacks comprised of ···ACACAC··· where adjacent stacks are parallel to each other.[3,4] Isolated dimers, e.g., CAAC, which show no intradimer interactions, have also been reported.[5] Additionally, 1-D chains of evenly spaced anions with stacks of cations running parallel[8,9] and zigzag chains of alternating ···ACACAC··· ions weaving throughout the lattice have been reported.[23,24] In $[Fc(CH_3)_3{}^{+}\cdot][(TCNQ)_2{}^{-}\cdot]$, the $TCNQ^{1/2-}$ forms a 1-D dimeric anion stack (along the *b* axis) with the $[Fc(CH_2)_3{}^{+}\cdot]$ cations being rotated by 45° with the respect to the *b* axis. This localized dimeric structure is consistant with the observed intermediate value for the room-temperature conductivity ($3 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$).[46]

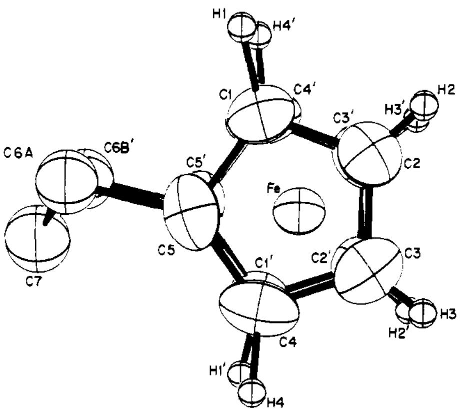

Figure 6. The $[Fc(CH_2)_3{}^{+}\cdot]$ ion showing the geometry of the C_5 rings and one possible resolved trimethylene side chain.

This substance is the first study of a ferrocene–TCNQ charge-transfer complex which has a bridging side chain. In all other materials, even those with methyl-substituted cyclopentadienide rings, cation stacking was observed. In this material, however, the C_5 rings are not parallel to each other, but they are inclined toward each other by 13.7 (9)°. This causes severe difficulty in cation stacking along a single axis. Also, the observed disorder of the methylene side chain shows that crystalline packing is not maximized as there is the possibility that the methylene side chain will be in one of two possible conformations. The lattice appears to be made up of $[(TCNQ)_2{}^{-}\cdot]$ anions with the $[Fc(CH_3)_3{}^{+}\cdot]$ cations being poured into the vacancies. Another interesting aspect of the structure is the inclination of the TCNQ ions along the *b* axis. Instead of lying flat and stacked, they lie canted with respect to the *b* axis. This canting is not unusual for monoclinic TCNQ-based charge-transfer complexes. Each $TCNQ^{1/2-}$ is crystallographically equivalent and is typical of other previously reported $TCNQ^{1/2-}$ anions.[5,23-25]

The $[Fc(CH_2)_3{}^{+}\cdot]$ cation radical possesses a large degree of C_5 ring inclination, i.e., 13.7 (9)°. Typically the C_5 ring tilt is invarient of the iron oxidation state; however, the ob-

Table VII. Ring-Tilt Angles for Various Bridged Ferrocenes

compd	ring bridge atoms	ring-tilt, deg	ref
α-oxo-1,1′-trimethyleneferrocene	3	8.8	26, 27
(1,1′-trimethylenebenzenecyclopentadiene)iron	3	7	28, 29
α-keto-α′-phenyl-1,1′-trimethyleneferrocene	3	10	30
α-phenyl-α′-(2-hydroxypropyl)-1,1′-trimethyleneferrocene	3	10	31
1,1′-(1,3-cyclopentylene)ferrocene	3	11	32
1,1′-trimethyleneferrocenium	3	13.7 (9)	this work
1,1′:2,2′:3,4:4′,5′-tetrakis(trimethylene)ferrocene	3[a]	11.1	33
1,1′:3,3′-bis(trimethylene)ferrocene	3[a]	9	34
1,1′:2,2′:3,3′:4,5:4′:5′-pentakis(trimethylene)ferrocene	3[b]	12.5	35
1,1′:2,2′:4,4′-tris(trimethylene)ferrocene	3[b]	2.4	36
1,1′-trithiaferrocene	3[c]	2.85	37
1,1′:3,3′-bis(1,3-cyclopentylene)ferrocene	3[b]	14.4	38
1,1′-tetramethyleneferrocene	2	23.2	39
1,1′-(tetraphenyl-o-phenylene)ferrocene	2	23.7	40
dipentalenyliron	2	23.6	41
[2]ferrocenophanethiazine 1,1′-dioxide	2	23	42

[a] Contains two bridges. [b] Contains three bridges. [c] Sulfur bridges.

served 13.7 (9)° is significantly larger than that observed for other substances containing a three-membered bridge (Table VII) and significantly smaller than that for ferrocenes containing two-membered bridges (Table VII). Recently, the correlations between the iron-to-C_5 crossing distance, ring tilt, and Mössbauer parameters have been established.[47] Several groups[43,44] have theorizied that the ring-tilt distortion would lead to a change in the electronic structure of the ferrocene. Ferrocene oxidation should lead to the loss of a weakly bonding e_{2g} ($3d_{xy}$, $3d_{x^2y^2}$) electron; however, the only previous report[48] of changes in the ferrocene conformation upon oxidation is a change is symmetry from D_{5d} to D_{5h}. Ballhausen and Dahl[43] also point out that ring-tilt distortions of up to 45° are not reflected in metal–ring bond energy changes. Consequently, the observed 13.7 (9)° ring tilt may result from the minimization of crystal packing forces.

In view of this large ring tilt, another structural anomoly of the $[Fc(CH_2)_3{}^{+}\cdot]$ radical ion should be discussed. The average carbon–carbon bond length in C_5 rings of ferrocenium ions is 1.42 Å.[4,5,9,45] In $[Fe(CH_2)_3{}^{+}\cdot]$, however, four of the carbon–carbon bond distances average 1.411 Å, while the C2–C3 distance is significantly shorter, 1.374 (4) Å, between atoms that are the farthest from the Fe atom (i.e., Fe–C2 is 2.102 (3) Å and Fe–C3 is 2.096 (3) Å). For the ferrocene compounds α-oxo-1,1′-trimethyleneferrocene and α-keto-α′-phenyl-1,1′-trimethyleneferrocene, which have smaller C_5 inclinations (Table VII) and which are not oxidized, similar bond shortening is not observed. With removal of a $3d_{xy}$, $3d_{x^2-y^2}$ electron of the Fe from the e_{2g} weakly bonding orbital and a decrease in the interaction distance between the Fe and C2 and C3, the possibility increases of localizing the electrons on C2 and C3, therefore enhancing the C2–C3 double-bond character.

Registry No. $[Fc(CH_2)_3{}^{+}\cdot][(TCNQ)_2{}^{-}\cdot]$, 75600-07-6; $Fc(CH_2)_3$, 12302-04-4; TCNQ, 1518-16-7.

Supplementary Material Available: A listing of F_o and F_c (8 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
University of California, Irvine, California 92717

Cumulene-Derived Metallocyclic Complexes. 2. Syntheses and Characterization of 2,5-Diethylidene- and 2,4-Dimethylenemetallocyclopentanes

J. RUSSELL SCHMIDT and D. MICHAEL DUGGAN*

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Two new exo unsaturated metallocyclopentanes have been obtained in high yield by the reaction of allene and 1,3-dimethylallene with $[(C_5Me_5)_2ZrN_2]_2N_2$. The allene-derived complex, I, has been structurally characterized by using single-crystal X-ray crystallography and both ^1H and ^{13}C NMR spectroscopy of solutions. The *exo*-methylene groups are found in the 2 and 4 positions on the metallocyclic ring. Rapid ring inversion averages axial and equational environments on the ^1H NMR time scale at room temperature in toluene solution. A ^{13}C NMR absorption at ~205 ppm downfield from Me_4Si is a characteristic of an sp^2 carbon bound to the zirconium atom. The structure of the product derived from 1,3-dimethylallene was defined from the consideration of ^1H and ^{13}C NMR data in comparison to I. The ethylidene groups are found to substitute the metallocyclopentane ring in the symmetrically disposed 2 and 5 positions, with the methyl substitutents in the *E,E* configuration (relative to the metal). This product (including its enantiomer) is the only compound found to have been formed out of 48 possible geometric isomers, region isomers, and stereoisomers. In that the 1,3-dimethylallene used was a racemic mixture, the identity of the metallocyclic product demonstrates greater than 95% chiral selectivity in that only *R,R* and *S,S* pairs are oxidatively coupled in the carbon–carbon bond-forming process.

Introduction

We have been studying the organometallic chemistry of cumulenes for three reasons: (1) There is much inherent interest in the use of CO_2 as a natural resource; (2) Heterocumulenes such as ketenes, carbodiimides, and ketenimines have displayed considerable use in organic synthesis, yet their utilization in the presence of metal complexes has not been thoroughly explored: (3) The formation and characterization of metallocyclic complexes has attacted much attention in recent years, and we often find metal–cumulene reactions to give rise to metallocyclic products.

In this paper, we shall discuss the preparation and physical properties of two new metallocyclic complexes—these being derived from allene and 1,3-dimethylallene. These complexes complete the list of observed structural types for the coupling of common unsaturated organic molecules into 5-membered metallocycles. For enumeration, saturated metallocyclopentanes can be formed from a carbon–carbon coupling process

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