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Synthesis and Characterization of Bis(pentadienyl)iron and Several Methylated Derivatives

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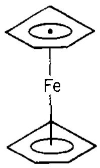
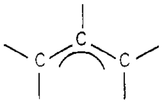
The synthesis of bis(pentadienyl)iron compounds, including 2-methyl, 3-methyl, 2,3-dimethyl, and 2,4-dimethyl derivatives, are reported. Their characterization has been achieved analytically as well as by infrared, ^1H and ^{13}C NMR, electronic, and mass spectroscopy. The properties of these red, air-stable compounds are discussed and compared with their cyclic ferrocene counterparts. An X-ray diffraction study of bis(2,4-dimethylpentadienyl)iron has been completed, which demonstrates a gauche-eclipsed ligand conformation and iron–carbon bond distances slightly exceeding those found in ferrocene. The structure has been refined to a conventional R index (on F) of 0.062 and a weighted index R_w of 0.082 for the 2697 unique reflections having $I > 3\sigma(I)$. The space group is C_i^1—$P\bar{1}$ (No. 2): $a = 7.778$ (5) Å, $b = 7.979$ (5) Å, $c = 11.198$ (8) Å, $\alpha = 85.77$ (5)°, $\beta = 80.46$ (5)°, $\gamma = 68.48$ (5)°, $V = 637.5$ Å^3, $Z = 2$.

Introduction

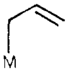
The accidental discovery of ferrocene (I), $Fe(C_5H_5)_2$, in 1951 is well recognized as a major cause of the subsequent explosive growth of organometallic chemistry.[2] Among the now classic properties of ferrocene are its high air and thermal stability as well as its capability of undergoing a wide variety of electrophilic substitution reactions.[3] As a result, the cyclopentadienyl ligand has achieved tremendous utility in organometallic chemistry, and very extensive studies have been carried out on its compounds, leading to a reasonable understanding of this ligand system.[4,5] In actually a much different fashion, the allyl ligand, C_3H_5 (II), and its various substituted derivatives, have also become tremendously important, in terms of both fundamental knowledge and practical applications.[5] While homoleptic metal–allyl complexes are often quite unstable thermally, the accessibility of both σ (IIIa) and π (IIIb) bonding schemes allows for a great deal of chemical versatility and catalytic activity.[5]



I



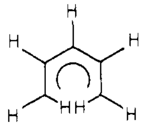
II



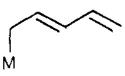
IIIa

IIIb

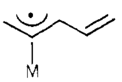
As opposed to the closed five-membered cyclopentadienyl and open three-membered allyl ligands, the open five-membered pentadienyl system IV has been explored only to a very slight extent,[6] although a number of straightforward routes are available to potential starting materials such as pentadienyl anions.[7] This is particularly surprising since the π-molecular orbitals (π-MO's) of the pentadienyl and cyclopentadienyl systems are quite analogous,[8] and in terms of energy considerations the open system could turn out to possess even stronger metal–ligand bonds. Of course, kinetic features are of utmost importance for catalytic activity, and this should be facilitated by the open nature of these ligands by virtue of possible η^1 (Va), η^3 (Vb), and η^5 (Vc) bonding modes. As an initial step in an extensive study of metal–pentadienyl chemistry, we have investigated the synthesis, physical, chemical, and structural properties of various bis(pentadienyl)iron compounds, which may be regarded as the



IV



Va



Vb

Vc

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"open ferrocenes". We report here our data and observations pertaining to these systems.[9]

Experimental Section

All operations involving organometallics were carried out under an atmosphere of prepurified nitrogen in Schlenk apparatus or in a glovebox. Nonaqueous solvents were thoroughly dried and deoxygenated in a manner appropriate to each and were distilled immediately before use. Elemental analyses were performed by Galbraith Laboratories and have mostly been previously reported.[9] Lithium and potassium salts of the pentadienyl anions were prepared by reported procedures.[7] Overnight drying of the isolated potassium salts under high vacuum led to materials which contained no THF bands in the infrared spectrum. Anhydrous ferrous chloride was prepared by a method reported by King.[10] 1,3- or 1,4-Pentadienes, 3-methyl-1,3- or 3-methyl-1,4-pentadienes, 2,3-dimethyl-1,4-pentadiene, and 2,4-dimethyl-1,3-pentadiene were obtained commercially.

Spectroscopic Studies. Infrared spectra were recored with a Perkin-Elmer 298 spectrophotometer. Mulls were prepared in a glovebox with dry, degassed Nujol. All IR spectra were calibrated with polystyrene. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded in benzene-d_6 or toluene-d_8 on Varian FT-80, EM-360, and SC-300 spectrometers. ^{1}H NMR spectra are reported relative to Me_4Si using C_6D_5H (δ 7.23) as internal standard. ^{13}C NMR spectra were similarly referenced (C_6D_6 128 ppm vs. Me_4Si). Electronic spectra were recorded in cyclohexane on a Cary 17 spectrophotometer. The solutions were prepared in Schlenk apparatus and syringed into matched quartz cells under nitrogen. A conservative estimate of error in the reported extinction coefficients is ±15%. The error for the less stable $Fe(C_5H_7)_2$ and $Fe(2\text{-}C_6H_9)_2$ ($2\text{-}C_6H_9 = 2\text{-}CH_3C_5H_6$) compounds may well be somewhat greater. Wavelengths are reported in nanometers. Mass spectra were performed on a Varian MAT 112 spectrometer or on a VG Micromass 7070 double-focusing high-resolution mass spectrometer with VG Data System 2000 at 70 eV. Except for the parent fragment, peaks are only quoted if their relative intensities are at least 10% of the intensity of the strongest peak.

Bis(2,4-dimethylpentadienyl)iron, $Fe(2,4\text{-}C_7H_{11})_2$. A slurry of 1.00 g (7.89 mmol) of ferrous chloride in 40 mL of THF (THF = tetrahydrofuran) was cooled with stirring to −78 °C under a nitrogen atmosphere. To this was added dropwise a solution of 2.12 g (15.8 mmol) of the potassium salt of the 2,4-dimethylpentadienyl anion in 40 mL of THF. After the addition was complete, the mixture was slowly warmed to room temperature, by which time a deep red solution had resulted. After the mixture was stirred overnight, the solvent was removed in vacuo and the product was extracted with 60 mL pentane. After the solution volume was reduced, some product was isolated by cooling to −78 °C, after which the supernatant was taken down to a volume of 10 mL in vacuo, leading to a second batch of product after being cooled to −78 °C. After being drained, the supernatant was removed by syringe and the reddish crystalline product dried first under a nitrogen stream and then in vacuo. Complete infrared data (Nujol mull): 3077 (ms), 3058 (sh), 1494 (ms), 1469 (sh), 1440 (sh), 1390 (sh), 1285 (m), 1192 (w), 1060 (w), 1035 (s), 1016 (ms), 1000 (ms), 987 (sh), 940 (ms), 913 (ms), 886 (mw), 873 (s), 865 (sh), 809 (w), 792 (mw), 732 (mw), 715 (m) cm^{-1}. ^{1}H NMR: δ 4.40 (s, 1 H), 2.68 (s, 2 H), 1.85 (s, 6 H), 0.26 (s, 2 H). ^{13}C NMR: δ 99.2 (s), 93.4 (d, J = 157 Hz), 50.6 (t, J = 156 Hz), 26.3 (q, J = 127 Hz). Mass spectrum: m/e (relative intensity) 39 (33), 41 (49), 44 (13), 51 (11), 53 (22), 55 (50), 65 (15), 67 (100), 69 (10), 77 (32), 79 (46), 80 (11), 81 (17), 91 (41), 93 (36), 94 (19), 95 (42), 105 (25), 107 (36), 108 (18), 119 (31), 120 (10), 121 (23), 122 (12), 133 (15), 134 (11), 175 (16), 246 (2.2). Electronic spectrum: λ (ϵ) 234 (47600), 267 (12600), 305 (2510), 405 (448), 490 (190).

Bis(2,3-dimethylpentadienyl)iron, $Fe(2,3\text{-}C_7H_{11})_2$. To a magnetically stirred solution of 2.28 g (23.7 mmol) of 2,3-dimethyl-1,4-pentadiene in 10 mL of THF at −78 °C was slowly added 9.56 mL (23.7 mmol) of 2.48 M *n*-butyllithium. After addition was complete, the solution was allowed to warm to room temperature and was stirred for an additional 45 min. The resulting yellow-orange solution was transferred by syringe to a dropping funnel under nitrogen and then added dropwise to a stirred slurry of 1.5 g (11.8 mmol) anhydrous ferrous chloride in 50 mL of THF at −78 °C. After the mixture was allowed to slowly warm to room temperature, the solvent was then removed in vacuo from the dark solution. The residue was extracted with pentane and filtered under nitrogen through a frit of medium porosity and the crude product isolated by removal of pentane in vacuo. The product was then purified either by sublimation or recrystallization from pentane at −78 °C, yielding orange-red needles, which were air-stable for at least several hours. Complete infrared data (Nujol mull): 3073 (s), 3043 (m), 1502 (ms), 1253 (w), 1190 (ms), 1164 (m), 1027 (vs), 1005 (s), 950 (sh), 940 (m), 872 (m), 731 (s), 714 (m) cm^{-1}. The ^{1}H NMR spectrum was very complex, indicating the presence of two nonsuperimposable isomers. ^{13}C NMR: δ *102.6* (s), 100.2 (s), 96.4 (s), *93.3* (s), *90.6* (d), 89.9 (d), 52.3 (t), *51.5* (t), 50.5 (t), *50.3* (t), 22.9 (q), *21.5* (q), 18.8 (q), *18.7* (q). The italicized ^{13}C NMR parameters are those which belong to one of the two possible isomers. Mass spectrum: m/e (relative intensity) 39 (19), 41 (32), 53 (15), 55 (23), 55.8 (100), 57 (18), 67 (23), 71 (17), 77 (15), 79 (23), 82 (12), 83 (12), 91 (16), 93 (13), 95 (23), 96 (54), 108 (21), 110 (53), 124 (18), 134 (15), 148 (35), 150 (58), 152 (16), 246 (20). Electronic spectrum: λ (ϵ) 223 (76300), 262 (31000), 318 (2900), 390 (618), 460 (400).

Bis(3-methylpentadienyl)iron, $Fe(3\text{-}C_6H_9)_2$. This compound was synthesized in manners analogous to both bis(2,4-dimethylpentadienyl)iron and bis(2,3-dimethylpentadienyl)iron. In one route 2.50 g (30.4 mmol) of 3-methyl-1,4-pentadiene was first reacted with a stoichiometric amount of *n*-butyllithium to generate the 3-methylpentadienyl anion, after which the anion was treated with 1.84 g (14.5 mmol) of anhydrous ferrous chloride. Or, in an alternative fashion, 2.00 g (16.6 mmol) of potassium 3-methylpentadienide and 1.00 g (7.89 mmol) of anhydrous ferrous chloride were used. In both procedures sublimation (ca. 40–60 °C) followed by recrystallization from pentane at −78 °C led to the isolation of the compound as red diamond-shaped crystals. Complete infrared data (Nujol mull): 3060 (s), 3045 (sh), 1512 (vs), 1229 (s), 1202 (vs), 1168 (s), 1035 (s), 1017 (m), 966 (w), 953 (w), 940 (w), 924 (ms), 897 (m), 867 (m), 816 (m), 770 (w), 729 (ms), 632 (w) cm^{-1}. ^{1}H NMR: δ 3.83 (t, 2 H, J = 10 Hz), 2.87 (d of d, 2 H, J = 9, 2 Hz), 1.72 (s, 3 H), 0.35 (d of d, 2 H, J = 10, 2 Hz). ^{13}C NMR: δ 102.0 (s), 90.4 (d, J = 159 Hz), 49.3 (t, J = 157 Hz), 21.8 (q, J = 126 Hz). Mass spectrum: m/e (relative intensity) 41 (19), 53 (13), 55.8 (81), 57 (20), 79 (23), 81 (26), 82 (18), 83 (17), 96 (46), 108 (11), 109 (10), 110 (45), 121 (13), 134 (42), 135 (14), 136 (100), 137 (11), 138 (38), 148 (18), 162 (18), 216 (10), 218 (44). Electronic spectrum: λ (ϵ) 216 (64000), 255 (29700), 315 (2700), 385 (640), 465 (250).

2-Methyl-1,3-pentadiene. This compound has been synthesized by the reduction and subsequent dehydration of mesityl oxide.[11] A 50-g (0.51 mmol) sample of mesityl oxide in 60 mL of diethyl ether under nitrogen was added dropwise to a magnetically stirred slurry of 9.7 g (0.256 mmol) of $LiAlH_4$ in 130 mL of diethyl ether at 0 °C. After being stirred for several hours at room temperature, the reaction mixture was hydrolyzed and the aqueous layer was extracted with diethyl ether and dried and the product (a mixture of ca. 88% 4-methyl-3-penten-2-ol[12] and ca. 12% 4-methyl-4-penten-2-ol) isolated in good yield by removal of solvent in vacuo. A small amount of iodine was then added to the product mixture, which was then covered with a small wad of glass wool. Subsequent distillation led to a good yield of 2-methyl-1,3-pentadiene, which was recovered nearly completely as the trans isomer as judged by comparison of the ^{1}H NMR spectrum with that of an authentic sample.

Bis(2-methylpentadienyl)iron, $Fe(2\text{-}C_6H_9)_2$. The potassium salt of the 2-methylpentadienyl anion was prepared from 2-

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(12) Separation of the isomers could readily be achieved by preparative scale gas chromatography. The ^{1}H NMR of 4-methyl-3-penten-2-ol consisted of the following resonances: δ 5.27 (br d, 1 H, J = 9 Hz), 4.61 (br m, 1 H), 2.81 (s, 1 H (OH)), 1.73 (s, 6 H), 1.21 (d, 3 H, J = 6.6 Hz).

methyl-1,3-pentadiene by a manner strictly analogous to that reported for the 3-methylpentadienyl anion.[7b] $Fe(2-C_6H_9)_2$ could then be prepared from 2.00 g (16.6 mmol) of potassium 2-methylpentadienide and 1.00 g (7.89 mmol) of ferrous chloride in a manner similar to that described for the other compounds. The best and most consistent results, however, were obtained when the general preparation procedure of $Fe(C_5H_7)_2$ was employed. After extraction of the product in pentane, the compound was isolated by repeated low-temperature (−78 °C) crystallization as attempted sublimation of the low melting product was sometimes accompanied by substantial decomposition. The stability of this compound was intermediate between those of $Fe(3-C_6H_9)_2$ and $Fe(C_5H_7)_2$, and therefore the compound is best stored cold. Slow decomposition takes place at room temperature. Complete infrared data (Nujol mull): 3080 (ms), 3060 (sh), 3010 (sh), 3000 (s), 1493 (s), 1460 (s, sh), 1445 (s), 1246 (ms), 1230 (w), 1100 (w), 1030 (s), 1018 (ms), 975 (m), 930 (m), 902 (s), 863 (sh), 850 (s), 718 (w) cm^{-1}. The ^1H NMR spectrum was very complex, indicating the presence of two nonsuperimposable isomers. ^{13}C NMR: δ 101.2 (s), *98.4* (s), *95.6* (d), 91.6 (d), *90.6* (d), 86.3 (d), 51.3 (t), *50.2* (t), 49.7 (t), *49.4* (t), 25.9 (q), *24.9* (q). The italicized ^{13}C NMR parameters are those belonging to one of the two possible isomers. Mass spectrum: m/e (relative intensity) 51 (19), 53 (33), 55.8 (70), 57 (15), 69 (100), 71 (15), 79 (28), 81 (25), 95 (11), 96 (24), 119 (10), 131 (10), 134 (14), 218 (11). Electronic spectrum: λ (ϵ) 223 (33 000), 280 (5700), 296 (5500), 309 (5600), 325 (4400), 362 (800), 383 (609), 408 (445), 475 (138). Anal. Calcd for $FeC_{12}H_{18}$: C, 66.08; H, 8.32. Found: C, 64.29; H, 8.16.

Bis(pentadienyl)iron, $Fe(C_5H_7)_2$. To a magnetically stirred slurry of 1.29 g (9.46 mmol) of $ZnCl_2$ (or the equivalent weight of $MgBr_2$) in 30 mL of THF at 0 °C was added dropwise under nitrogen a solution of 0.99 g (9.46 mmol) of KC_5H_7 in 30 mL of THF. The dark red color of the pentadienyl anion rapidly decolorized upon addition to $ZnCl_2$. After addition had been completed, the pale reaction mixture was allowed to warm to room temperature and stirring was continued for an additional hour. The reaction mixture was transferred by syringe to a dropping funnel under nitrogen and subsequently added slowly to a slurry of 0.80 g (6.30 mmol) of $FeCl_2$ in 30 mL of THF at −78 °C. No visible color change occurred during the addition, and upon completion the reaction mixture was allowed to warm to room temperature. After 1 h at room temperature the mixture developed a reddish color. Stirring was continued for an additional 3 h by which time a small amount of black precipitate (metallic iron) was observed to be forming. The reddish mixture was filtered under nitrogen on a coarse frit yielding a cherry-red solution. After solvent removal in vacuo, the resulting orange-red solid was extracted with pentane and filtered a second time. Solvent removal yielded a thick orange oil which could be sublimed easily at ca. 40 °C under high vacuum. The compound was obtained in crystalline form by cooling a concentrated pentane solution of the orangish sublimate to −78 °C, draining and removing supernatant, and drying the product in vacuo. ^1H NMR: δ 4.77 (t of t, 1 H, J = 6.3, 0.9 Hz), 4.18 (m, 2 H), 2.92 (d of d of d, 2 H, J = 9.2, 2.1, 0.8 Hz), 0.41 (d of d of d, 2 H, J = 10.5, 2.2, 0.8 Hz). ^{13}C NMR: δ 90.9 (d, J = 161 Hz), 88.8 (d, J = 162 Hz), 49.8 (t, J = 160 Hz). The relative intensities of the first two peaks are virtually 1:2, leading to their assignments as C(3) and C(2,4), respectively. The first two coupling constants might be slightly in error due to the overlap of the coupled resonances. Mass spectrum: m/e (relative intensity) 38 (14), 39 (83), 40 (30), 41 (71), 56 (100), 57 (17), 65 (19), 66 (14), 67 (64), 71 (11), 82 (27), 95 (19), 96 (21), 121 (32), 122 (27), 124 (12), 134 (16), 148 (12), 190 (47). Electronic spectrum: λ (ϵ) 215 (9230), 228 (17 700), 273 (4160), 285 (4370), 301 (4100), 315 (3460), 334 (800), 353 (663), 375 (492), 397 (69), 425 (55).

Table I. Positional Parameters for the Non-Hydrogen Atoms of $Fe(2,4-C_7H_{11})_2$

atom	x	y	z
Fe	0.221 65 (7)	0.137 60 (7)	0.296 93 (5)
C(1)	0.224 51 (64)	0.148 50 (57)	0.482 88 (39)
C(2)	0.223 63 (55)	0.312 35 (53)	0.426 50 (38)
C(3)	0.100 58 (54)	0.408 48 (49)	0.344 31 (40)
C(4)	−0.030 20 (51)	0.350 84 (54)	0.302 94 (41)
C(5)	−0.068 46 (55)	0.199 68 (64)	0.355 29 (46)
C(6)	0.376 35 (72)	0.380 68 (66)	0.441 06 (51)
C(7)	−0.119 87 (77)	0.447 48 (79)	0.194 91 (58)
C(8)	0.299 29 (71)	−0.142 74 (56)	0.293 52 (43)
C(9)	0.227 23 (66)	−0.063 37 (59)	0.186 74 (40)
C(10)	0.281 08 (63)	0.068 43 (59)	0.115 10 (38)
C(11)	0.404 11 (59)	0.149 28 (60)	0.143 65 (41)
C(12)	0.510 90 (56)	0.077 32 (68)	0.236 34 (47)
C(13)	0.065 17 (93)	−0.104 85 (84)	0.154 32 (54)
C(14)	0.407 95 (90)	0.318 57 (81)	0.075 64 (52)

X-ray Diffraction Study of $Fe(2,4-C_7H_{11})_2$. Single crystals of either the 3-methyl or 2,3-dimethyl compounds (grown by slowly cooling pentane solutions) were generally well formed. However, these often waxy crystals were unsuitable for data collection due to either polycrystallinity and/or thermal disorder. In contrast, single crystals of 2,4-dimethyl compound were usually poorly formed but otherwise diffracted reasonable well (wide scan ranges were generally required, however). It was later observed that slow sublimation produced higher quality crystals. Unit cell data were determined from a combination of oscillation and Weissenberg photographs, along with standard Nicolet P$\bar{1}$ software programs, which allowed the location of the appropriate reduced cell. Accurate cell constants and their standard deviations were derived from a least-squares refinement of 15 centered relections for which 26° < 2θ < 35°, by using the Mo K$\bar{\alpha}$ peak at 0.710730 Å. The unit cell parameters are a = 7.778 (5) Å, b = 7.979 (5) Å, c = 11.198 (8) Å, α = 85.77 (5)°, β = 80.46 (5)°, γ = 68.48 (5)°, Z = 2, V = 637.5 Å^3.

The data crystal displayed acceptable mosaicity for the θ–2θ scan technique. Mo Kα radiation was monochromatized by using the 002 face of mosaic graphite. Scans were from 1.75° below the Mo Kα_1 peak to 1.25° above the Mo Kα_2 peak at a rate of 1°/min. A collimator with a diameter of 1.0 mm was used as the crystal edges varied from 0.2 to 0.44 mm. Data were collected in two concentric shells of 2θ, 0–50° and 50–60° with background time equal to half the total scan time. The intensities of five standard reflections were monitored for every 95 reflections and showed during data collection an average 0.6% decomposition for which a correction was made. All data were processed by using the X-RAY 70 program package.[13] An absorption correction (μ(Mo Kα) = 11.49 cm^{-1}) was applied for the bar-shaped crystal by using a modification of the Ibers program AGNOST.[14] The transmission coefficients ranged from 0.690 to 0.835. The faces of the crystal were indexed as (001), (00$\bar{1}$), (101), ($\bar{1}$0$\bar{1}$), 01$\bar{1}$), and (0$\bar{1}$1). A total of 4310 reflections were processed, yielding 3740 unique reflections, of which 2697 had intensities judged to be above background (I > 3σ (I)). These were used in subsequent calculations. The function minimized was $\sum w(|F_o| - |F_c|)^2$, with empirical weights assigned by the method of Cruikshank.[15] The atomic scattering factors were taken from a recent tabulation, as were the anomalous dispersion terms for iron.[16]

The position of the single iron atom was readily discerned from a Patterson map. All carbon atoms were located on a subsequent difference Fourier synthesis. Least-squares refinement led to an anisotropic agreement index ($R = \sum||F_o| - |F_c||/\sum|F_o|$) of 0.081 and a weighted index ($R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$) of 0.101. A series of difference Fourier maps and least-square refinements led sequentially to the location of all but one of the hydrogen atoms. These were placed in calculated or idealized positions. Final refinement led to agreement indices of R = 0.062 and R_w = 0.082. A final difference Fourier map revealed no peaks greater than 0.51 e/Å^3. The standard deviation of the map was 0.09 e/Å^3. The final positional parameters obtained from the last cycle of least-squares refinement are presented in Table I, along with their estimated standard deviations. The thermal parameters for non-hydrogen atoms (Table II) and hydrogen atom parameters

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[16] Cromer, D. T.; Waber, J. T. In "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2A and 2.3.1.

(Table III) are available as supplementary material. The final values of $10|F_o|$ and $10|F_c|$ in electrons are also available as supplementary material. Other than those mentioned later, intermolecular contacts are normal.

Synthetic and Spectroscopic Results and Discussion

The reaction of 2 mol of various pentadienyl anions with ferrous chloride in THF (eq 1) leads to the formation of

$$FeCl_2 + 2M(C_5H_4R_2R_3R_4) \rightarrow \underset{\text{VIc–e}}{Fe(C_5H_4R_2R_3R_4)_2} + 2MCl \quad (1)$$

$$M = Li, K$$

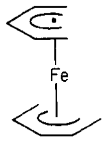
$$FeCl_2 + 2(C_5H_4R_2R_3R_4)MX \rightarrow \underset{\text{VIa,b}}{Fe(C_5H_4R_2R_3R_4)_2} + 2MXCl \quad (2)$$

$$M = Zn, Mg$$

a, $R_2 = R_3 = R_4 = H$; b, $R_2 = CH_3$, $R_3 = R_4 = H$; c, $R_3 = CH_3$, $R_2 = R_4 = H$; d, $R_2 = R_3 = CH_3$, $R_4 = H$; e, $R_2 = R_4 = CH_3$, $R_3 = H$

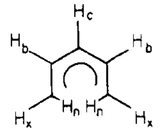
reddish bis(pentadienyl)iron complexes (VI), where R_2, R_3, and R_4 refer to substituents present on the carbon atoms at the 2-, 3-, and 4-positions of the pentadienyl group, respectively. In the case of VIa and VIb, isolation of product is aided greatly if one moderates the reaction conditions by employing a milder zinc or magnesium reagent[17] (eq 2). In fact, this alternative route seems highly desirable for the preparation of any of the iron compounds. After isolation of the crude product, purification is generally (except for VIb) best achieved by sublimation (ca. 60 °C) followed by low-temperature recrystallization. Attempted sublimation of VIa, however, is carried out at room temperature, while the low melting VIb sublimes with partial decomposition. The order of stability of these compounds as a function of ligand qualitatively appears to be $2,4\text{-}C_7H_{11} \approx 2,3\text{-}C_7H_{11} > 3\text{-}C_6H_9 > 2\text{-}C_6H_9 \geq C_5H_7$ where the first number(s), if any, refer to locations at which methyl groups are attached. As will be discussed subsequently, methylation has a very significant effect in controlling stability and chemical reactivity. The compounds are reasonably air stable and somewhat volatile, subliming in time within closed containers under a nitrogen atmosphere. In many respects, then, these compounds are quite similar to the ferrocenes, the most notable difference being the lack of aromatic character for the π-bound ligand.

The infrared spectra of these compounds lack absorptions due to C=C bonds, although "aromatic" C—C bands can be observed, consistent with η^5 coordination. All compounds displayed the appropriate parent ions and reasonable fragments in the mass spectra. ^{1}H and ^{13}C NMR have been obtained and are also consistent with the formulation of these compounds as "open sandwiches", VII. As will be seen, all data seem to indicate that the gauche-eclipsed conformation depicted below is favored.

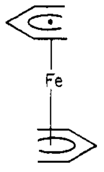


VII

The ^{1}H NMR spectra can be readily compared to the spectra for related complexes.[18] The H_n(endo) resonances are observed in the range 0.2–0.4 ppm, with H_x(exo) resonances around 2.7–2.9 ppm. Further downfield are the

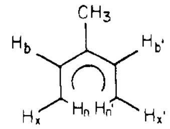


H_b (ca. 3.8–4.2 ppm) and the H_c resonances (ca. 4.4–4.8 ppm) while the methyl resonances appear around 1.7–1.9 ppm. These positions, as well as the observed coupling constants (see Experimental Section), are reasonably similar to those of metal–allyl and metal–butadiene complexes. For a symmetric ligand complex (e.g., VIa, VIc, or VIe), one observes only four resonances at room temperature, indicating equivalent ligands in which an apparent vertical mirror plane of symmetry (perpendicular to the ligand plane) is present. This would necessitate either a symmetric ground-state conformation such as the anti-eclipsed, VIII, or else a low barrier to ligand oscillation if a less symmetric geometry such as that in the solid-state gauche-eclipsed conformer (VII) is adopted.



VIII

In an attempt to determine whether the four-line spectra were the result of a symmetric ground-state conformation (i.e., the anti eclipsed) or of an unsymmetric ground state (presumably gauche eclipsed) characterized by a relatively low barrier to oscillation, variable-temperature ^{1}H NMR spectra of VIc and VIe were recorded in the range +26 to −105 °C in toluene-d_8.[19] Representative spectra for $Fe(3\text{-}C_6H_9)_2$ are presented in Figure 1. It is quite clear that as the temperature is lowered the four resonances broaden significantly, finally collapsing at ca. −69 °C and reappearing as a seven-line spectrum indicative of an unsymmetric conformation in which no vertical mirror plane of symmetry is present, i.e.



Quite analogous spectra are observed as well for $Fe(2,4\text{-}C_7H_{11})_2$, with the coalescence temperature appearing to be ca. −60 °C. Taken together with the results from the X-ray diffraction and theoretical studies,[20] it is quite clear that the ground-state conformation is gauche eclipsed. For $Fe(3\text{-}C_6H_9)_2$ and $Fe(2,4\text{-}C_7H_{11})_2$, the activation parameter

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(17) Yasuda, H.; Ohnuma, Y.; Nakamura, A.; Kai, Y.; Yasuoka, N.; Kasai, N. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1101.

(18) Marks, T. J. In "The Organic Chemistry of Iron"; Koerner von Gustorf, E. A., Grevels, F. W., Eds.; Academic Press: New York, 1978; Vol. 1.

(19) (a) Temperatures were calibrated from reported peak positions of methanol;[19b] the −105 °C temperature was reachable probably due to the melting point depression of the toluene and perhaps supercooling. (b) Van Geet, A. L. *Anal. Chem.* **1968**, *40*, 2227. (c) At the low-temperature limit for $Fe(3\text{-}C_6H_9)_2$ and $Fe(2,4\text{-}C_7H_{11})_2$, the resonances for the four protons attached to the terminal carbon atoms were observed to fall in the order H_{endo}, H_{exo}, H_{endo}', H_{exo}' (from high to low field).

(20) Böhm, M. C.; Eckert-Maksić, M.; Ernst, R. D.; Wilson, D. R.; Gleiter, R. *J. Am. Chem. Soc.* **1982**, *104*, 2699.

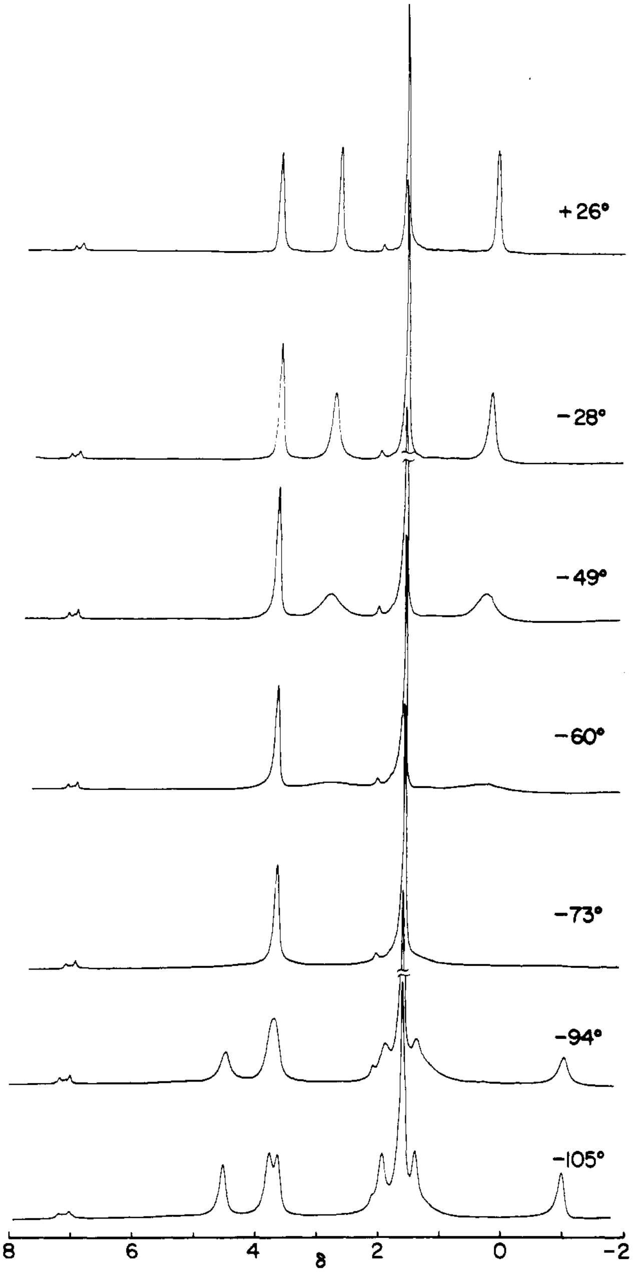


Figure 1. Variable-temperature ^1H NMR spectra of bis(3-methylpentadienyl)iron in toluene-d_8.

$\Delta G^\ddagger$ can be calculated as 8.7 and 9.1 kcal/mol,[21] respectively, with a probable maximum error of ca. 0.1 kcal/mol.[22] Finally, even though the ^1H NMR spectrum of $Fe(C_5H_7)_2$ is too complex to be similarly analyzed, variable-temperature proton-decoupled ^{13}C NMR spectra again demonstrate an unsymmetric ground state by -90 °C, and the activation barrier, $\Delta G^\ddagger$, is calculated to be 8.4 kcal/mol.

The ^1H NMR spectra of VIb and VId, on the other hand, are quite complex even at room temperature. Besides the lack of a possible vertical plane of symmetry for a given ligand, it is quite clear that two nonsuperimposable isomers are present in each case, e.g., VId_1 and VId_2. However, it must be recognized that each of these isomers actually exists as a pair of gauche-eclipsed rotamers (vide infra).

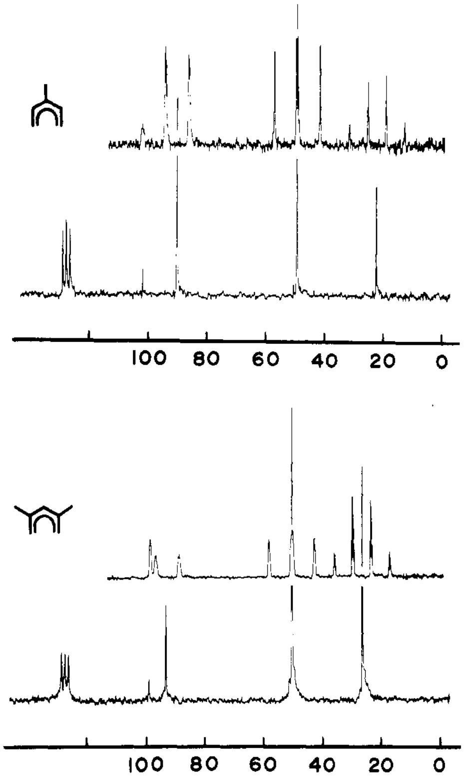
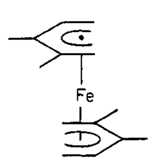
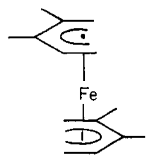


Figure 2. Proton-coupled (upper) and -decoupled (lower) ^{13}C NMR spectra for bis(3-methylpentadienyl)iron and bis(2,4-dimethylpentadienyl)iron in benzene-d_6.



VId_1



VId_2

The ^{13}C NMR spectra data (Figure 2) provide further information and confirmation of the above conclusions. Thus, the unmethylated C(1,5), C(2,4), and C(3) resonances in $Fe(C_5H_7)_2$ appear respectively at 49.8, 88.8, and 90.9 ppm. Methylation of a given carbon atom can be seen to bring about a downfield shift of ca. 11 ppm, while methylation of an adjacent carbon atom brings about a downfield shift of ca. 1–3 ppm (see Experimental Section). The methyl resonances appear in the range of 19–26 ppm. The assignments given above are readily confirmed by a comparison of the proton coupled with the proton-decoupled spectra and may be reasonably compared to metal complexes containing alkyl, allyl, or butadiene ligands.[23] As in the case of the proton NMR spectra, the ^{13}C NMR spectra of VIa, VIc, and VIe demonstrate patterns which are more simplified than would be expected on the basis of the unsymmetric gauche-eclipsed conformation. This is again consistent with the reasonably low (ca. 9 kcal/mol) barriers to ligand oscillation determined by the variable-temperature ^1H NMR studies.

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(21) (a) The rate constant $k = (k_bT/h)\exp(-\Delta G^\ddagger/RT)$; at the coalescence temperature, $k_c = \pi\Delta\nu(2)^{1/2}$.[21b] (b) Kessler, H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 219.

(22) Actually there is some coupling occurring between some of the protons in ^1H NMR spectra, especially for $Fe(3\text{-}C_6H_9)_2$. However, this coupling is small compared to the chemical shift difference in the low-temperature spectrum and therefore will not result in a major error in the calculation of $\Delta G^\ddagger$ but could mean that the barrier might be more comparable to that of 2,4-dimethyl compound.

(23) (a) Chisholm, M. H.; Godleski, S. *Prog. Inorg. Chem.* **1976**, *20*, 299. (b) Jolly, P. W.; Mynott, R. *Adv. Organomet. Chem.* **1981**, *19*, 257.

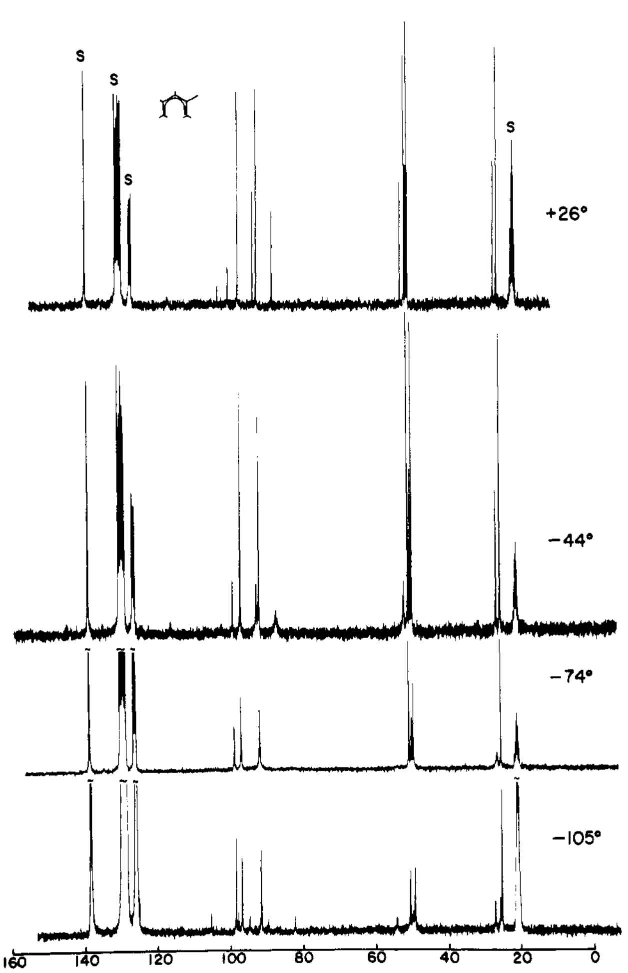
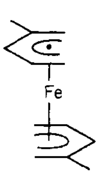
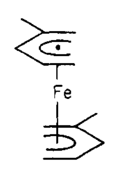


Figure 3. Variable-temperature proton-decoupled ^{13}C NMR spectra of bis(2-methylpentadienyl)iron in toluene-d_8. Solvent peaks are marked by an S.

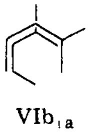
Because of the greater spectral shifts encountered in ^{13}C NMR studies, the spectra for VIb and VId conclusively demonstrate the presence of two isomers each, since respectively 12 and 14 resonances are observed at room temperature, each in a location consistent with those for the simpler compounds VIc and VIe. For Fe(2-C_6H_9)$_2$, these (diastereomeric) isomers can be most simply depicted as shown in VIb$_1$ and VIb$_2$. However, this is in fact an oversimplification of the matter since the gauche-eclipsed geometry will again be favored. In fact, evidence favoring the gauche-eclipsed conformer(s) can again be obtained from low-temperature proton-decoupled ^{13}C NMR spectra. Isomer VIb$_1$ actually should exist as the two enantiomeric rotational isomers VIb$_{1a}$ and VIb$_{1b}$, which can be seen to possess only the identity symmetry element. Thus, the six lines VIb$_1$ displays at room temperature should become 12 lines at low temperature. Further, VIb$_2$ should freeze out as VIb$_{2a}$ and VIb$_{2b}$, each of which possesses a twofold rotational axis but are entirely nonequivalent to one another in the absence of ligand oscillation. Thus, VIb$_{2a}$ and VIb$_{2b}$ should each exhibit different six-line ^{13}C NMR spectra. On this basis, a total of 24 resonances might be expected to be found at low temperatures. Interestingly, however, variable-temperature ^{13}C NMR spectra of Fe(2-C_6H_9)$_2$ (see Figure 3) demonstrate that by −90 °C, one set of six resonances has indeed collapsed and reappeared as 12 resonances such that each of the original six resonances is symmetrically surrounded by a pair of new resonances. Somewhat surprising at first glance, the other six resonances (belonging to the more abundant of the two room-temperature forms) were not observed to have undergone much of any change and still appeared as six sharp resonances at −90 °C. These resonances are italicized in the Experimental Section. One could attribute this behavior to the existence of a ground-state anti conformation or perhaps to the existence of a much lower barrier to ligand oscillation for one of the two (room-temperature isomers), either VIb$_1$ or VIb$_2$. However, since Fe(C_5H_7)$_2$, Fe(3-C_6H_9)$_2$, Fe(2,4-C_7H_{11})$_2$, and the other Fe(2-C_6H_9)$_2$ isomer all exhibit ground-state gauche-eclipsed conformations with barriers to oscillation equal to ca. 8.4–9.1 kcal/mol (vide infra), this does not seem reasonable. The key to properly interpreting these spectra would seem to lie in the fact that the rotamer pair VIb$_{1a}$ and VIb$_{1b}$ are mirror images of one another and therefore equivalent in their stabilities, while the rotamer pair VIb$_{2a}$ and VIb$_{2b}$ are essentially diastereomeric and may possess differing stabilities. One can readily observe that in the cases of symmetric ligands (C_5H_7, 3-C_6H_9, or 2,4-C_7H_{11}), the freezing out process also produces two rotamers which are mirror images of one another. Thus, the mirror-image rotamers VIb$_{1a}$ and VIb$_{1b}$ should behave similarly and are assigned to the six room-temperature resonances which become 12 resonances at low temperature.[24] The remaining six lines (at low or high temperature) must therefore be assigned to one or both of the nonequivalent rotamers VIb$_{2a}$ and VIb$_{2b}$. At room temperature, rapid ligand oscillation should ensure a six-line spectrum, whether or not both rotameric forms are substantially populated. However, the fact that only six lines remain at lower temperatures can be reasonably attributed to a higher stability of one rotamer over the other. Hence, as the temperature is lowered, the more stable rotamer (perhaps VIb$_{2a}$) is apparently preferentially populated while the less stable one is insufficiently populated to be observed. It can be noted that a related situation exists for bis(isoprene)iron monocarbonyl, for which only one isomer is observed in the ^1H NMR spectrum.[25]



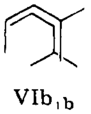
VIb$_1$



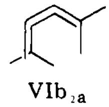
VIb$_2$



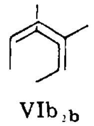
VIb$_{1a}$



VIb$_{1b}$



VIb$_{2a}$



VIb$_{2b}$

These arguments, of course, are also applicable to Fe(2,3-C_7H_{11})$_2$. In addition, it is important to note in both cases that the two diastereomers are not present in equivalent proportions but exist rather in approximate (presumably thermodynamic) ratios of ca. 1.5–2:1. One

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[24] It should be noted that for the symmetric ligand complexes (2,4-C_7H_{11}, 3-C_6H_9, C_5H_7), the freezing out process leaves the two ligands equivalent but removes the symmetry relating one end of the given ligand to another, while the 2-C_6H_9 and 2,3-C_7H_{11} ligands can never have one end equivalent to the other, and the freezing out process for VIb$_1$ instead involves removing the equivalence of the two ligands.[1] However, in each case the spectral changes are dependent on the freezing out of the unsymmetric conformation and therefore should be energetically similar.

[25] Koerner von Gustorf, E.; Buchkremer, J.; Pfajfer, Z.; Grevels, F.-W. *Angew. Chem., Intl. Ed. Engl.* **1971**, *10*, 260.

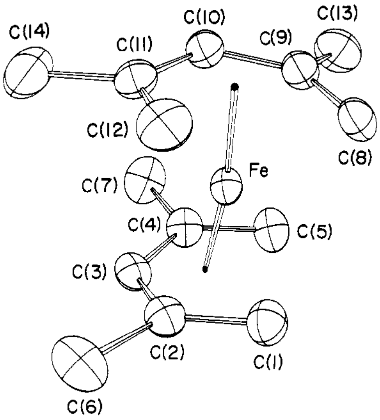


Figure 4. Perspective view and numbering scheme of bis(2,4-dimethylpentadienyl)iron. the 35% probability ellipsoids are shown.

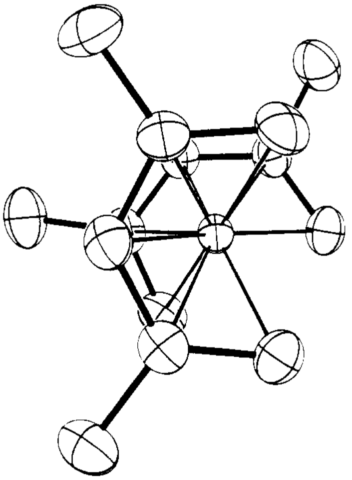
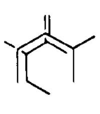
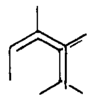


Figure 5. Perspective view of bis(2,4-dimethylpentadienyl)iron. The 25% probability ellipsoids are shown.

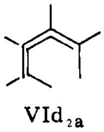
can speculate that the isomer VIb_{2a} above might be preferentially populated since there are no close $CH_3 \cdots CH_3$ interactions. Similarly, for $Fe(2,3\text{-}C_7H_{11})_2$, isomer VId_{2a} would seem favored.



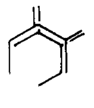
VId_{1a}



VId_{1b}



VId_{2a}



VId_{2b}

While a great deal of similarity appears to exist between these complexes and the ferrocenes, there is also some resemblance exhibited to the allylic systems. Thus, $Fe(C_5H_7)_2$ is least stable of all the compounds and readily decomposes on standing or heating, much like $Ni(C_3H_5)_2$.[26] In each case, methylation (of at least the nonterminal carbon atoms) brings about an increase in stability. Even so, however, NMR samples of $Fe(3\text{-}C_6H_9)_2$ produce metallic iron particles on standing for several weeks while the 2-methyl (and unmethylated) complexes are even less stable. It therefore appeared possible that these systems would be capable of exhibiting "naked iron" or other naked metal chemistry, much like Wilke's fascinating "naked nickel" contributions.[27] Indeed, such naked iron catalysis has recently been observed[28] and detailed efforts to investigate these possibilities are continuing.

Crystallographic Results and Discussion

The structural result for $Fe(2,4\text{-}C_7H_{11})_2$ is presented in Figure 4, along with the atom numbering scheme. The hydrogen atoms have also been numbered sequentially but have been deleted for clarity. The structural result clearly confirms the open sandwich configuration expected for the complex. The compound possesses idealized C_2 symmetry which relates a given C(n) atom to the C(n + 7) atom. An alternative view is presented in Figure 5 which emphasizes the adoption of a gauche-eclipsed conformation by the complex. The actual conformational state can be specified as the angle between two planes, each plane being defined by Fe, the carbon atom in position 3 (C(3) or C(10)), and the midpoint between the carbon atoms in positions 1 and 5 [$^1/_2$(C(1) + C(5)) or $^1/_2$(C(8) + C(12))]. The angle observed in this structure is 59.7°, quite close to the ideal 60° value (assuming 0° for the cis-eclipsed structure). It is noteworthy that similar conformations have been observed in various bis(cyclo-η^5-dienyl) complexes of iron and ruthenium, such as $Fe[\eta^5\text{-}6\text{-}t\text{-}C_4H_9\text{-}1,3,5\text{-}(CH_3)_3C_6H_3]_2$,[29] $Fe(\eta^5\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)$,[30] and $Ru(\eta^5\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)$,[31] which strongly suggests that the gauche-eclipsed conformation is generally more stable than the otherwise reasonable anti-eclipsed conformation. Interestingly, $V(2,4\text{-}C_7H_{11})_2$ and $Cr(2,4\text{-}C_7H_{11})_2$ display angles of 89.9° and 82.9° respectively.[32] Pertinent bond distances and angles are presented in Table IV, and least-squares plane information is contained in Table V (supplementary material).

Assuming the overall symmetry is C_2, the average[33] Fe-C bond distances can be seen to be Fe–C(1,8) = 2.095 (4) Å, Fe–C(2,9) = 2.085 (4) Å, Fe–C(3,10) = 2.084 (3) Å, Fe–C(4,11) = 2.062 (3) Å, and Fe–C(5,12) = 2.122 (3) Å. It is clear that in the solid-state structure the Fe–C bonds formed to one side of the ligand are not equivalent to those formed on the other side. To some extent this may reflect the presence of substantial repulsive C⋯C nonbonded contacts[34] between the ligands as the Fe–C(1) bond, for example, is not engaged in an eclipsing interaction while the Fe–C(5) bond is. The overall average Fe–C bond distance of 2.089 (1) Å[35] is observed to be somewhat longer than in ferrocene, 2.064 (3) Å.[36a] This may well reflect the presence of the nonbonded C⋯C contacts[34] brought on

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[26] (a) O'Brien, S.; Fishwick, M.; McDermott, B.; Wallbridge, M. G. H.; Wright, G. A. *Inorg. Synth.* **1972**, *13*, 73. (b) Actually the relative stabilities of the bis(pentadienyl)iron compounds are very much dependent on the criteria employed. Thus, the 2-methyl analogue can be prepared by direct reaction of the anion with $FeCl_2$ (although the results are inconsistent), whereas the unmethylated compound is not isolated under those reaction conditions. However, once a solid $Fe(C_5H_7)_2$ is isolated, the solid crystalline material appears more stable at room temperature than the liquid $Fe(2\text{-}C_6H_9)_2$.

[27] Jolly, P. W.; Wilke, G. "The Organic Chemistry of Nickel"; Academic Press: New York: 1974, Vol. I; 1975, Vol. II.

[28] Severson, S.; Cymbaluk, T. H.; Wilson, D. R.; Higashi, J.; Ernst, R. D.; Parry, R. W., experiments in progress.

[29] Mathew, M.; Palenik, G. J. *Inorg. Chem.* **1972**, *11*, 2809.

[30] Blackborow, J. R.; Grubbs, R. H.; Hildenbrand, K.; Koerner von Gustorf, E. A.; Miyashita, A.; Scrivanti, A. *J. Chem. Soc. Dalton Trans.* **1977**, 2205.

[31] Schmid, H.; Ziegler, M. L. *Chem. Ber.* **1976**, *109*, 125.

[32] (a) Ernst, R. D.; Campana, C. F.; Wilson, D. R.; Liu, J.-Z., unpublished results. (b) Wilson, D. R.; Liu, J.-Z.; Ernst, R. D. *J. Am. Chem. Soc.* **1982**, *104*, 1120.

[33] When average values are discussed, the standard deviation of the mean is reported.

[34] (a) C(2)–C(12) = 2.997 (6), C(3)–C(11) = 3.201 (6), C(4)–C(10) = 3.221 (6), and C(5)–C(9) = 2.977 (6) Å. (b) The van der Waals radius for carbon is 1.7 Å.[34c] (c) Pauling, L. "The Nature of the Chemical Bond", 3rd. ed.; Cornell University Press: Ithaca, N.Y., 1960.

[35] The standard deviation reported for the overall average Fe–C bond distance is not reflective of Fe–C bond distances but should reflect the accuracy of the average.

[36] (a) Bohn, R. K.; Haaland, A. *J. Organomet. Chem.* **1966**, *5*, 470. (b) The distances to the bonded ligand center of mass average 1.508 (2) Å.

Table IV. Selected Bond Distances (Å) and Angles (deg) for $(2,4\text{-}C_7H_{11})_2Fe$

Bond Distances

Fe-C(1)	2.095 (5)	Fe-C(8)	2.094 (5)	C(1)-C(2)	1.407 (6)	C(8)-C(9)	1.412 (7)
Fe-C(2)	2.091 (5)	Fe-C(9)	2.078 (5)	C(2)-C(3)	1.414 (6)	C(9)-C(10)	1.419 (7)
Fe-C(3)	2.086 (4)	Fe-C(10)	2.081 (4)	C(3)-C(4)	1.411 (7)	C(10)-C(11)	1.421 (8)
Fe-C(4)	2.065 (4)	Fe-C(11)	2.058 (5)	C(4)-C(5)	1.410 (7)	C(11)-C(12)	1.395 (7)
Fe-C(5)	2.122 (4)	Fe-C(12)	2.122 (4)	C(2)-C(6)	1.512 (8)	C(9)-C(13)	1.518 (10)
				C(4)-C(7)	1.514 (8)	C(11)-C(14)	1.509 (8)

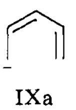
Bond Angles

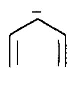
C(1)-C(2)-C(3)	123.8 (5)	C(3)-C(4)-C(7)	118.4 (4)	C(10)-C(9)-C(13)	117.3 (4)
C(1)-C(2)-C(6)	119.1 (4)	C(5)-C(4)-C(7)	120.2 (5)	C(10)-C(11)-C(12)	120.2 (5)
C(2)-C(3)-C(4)	125.4 (4)	C(8)-C(9)-C(10)	124.4 (5)	C(10)-C(11)-C(14)	118.2 (5)
C(3)-C(2)-C(6)	116.7 (4)	C(8)-C(9)-C(13)	117.9 (5)	C(12)-C(11)-C(14)	121.5 (5)
C(3)-C(4)-C(5)	121.2 (4)	C(9)-C(10)-C(11)	125.6 (4)		

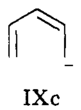
by the short distance from the iron atom to the idealized ligand planes (1.46 Å vs. 1.66 Å in $Fe(C_5H_5)_2$).[36] To some extent the large size of the ligand may also cost Fe–C bond overlap since much larger (methyl) substituent tilts (ca. 6, 6, 11, and 12°) toward the metal were observed relative to ferrocene (3.7 (9)°). Such tilting has been ascribed to an attempt by the ligand to better direct its p orbitals toward the metal.[37] The combination of the shorter metal–ligand plane distance and the substantial C···C nonbonded contacts (both of which are brought about by the large size of the ligand) appears to overwhelm what might have been expected to be stronger Fe–C bonds on the basis of energetic considerations (vide supra). The fact that an eclipsed configuration is adopted despite the close interligand contacts can be taken as evidence of a large electronic contribution to the favorability of the gauche-eclipsed conformer.

The Fe–C bond distances may also be compared to those in the bis(cyclo-η^5-dienyl)iron compounds. Thus, $Fe(\eta^5\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)$[30] possesses analogous average distances (defined to be consistent with our numbering scheme) of 2.086, 2.035, 2.080, 2.046, and 2.126 Å (average = 2.074 Å). Similarly, $Fe(6\text{-}t\text{-}C_4H_9\text{-}1,3,5\text{-}(CH_3)_3(C_6H_3)]_2$[29] is characterized by Fe–C distances of 2.135 (4), 2.055 (4), 2.062 (5), 2.047 (4), and 2.135 (3) Å (average = 2.087 Å) with the ligand plane 1.57 Å from the iron atom. It can be seen that the major difference between $Fe(2,4\text{-}C_7H_{11})_2$ and these cyclic ligand structures lies in the Fe–C(2) and Fe–C(4) distances, on which methyl groups are present in our complex. This difference, then, may well again be predominately a geometric effect brought about by C–C–C bond angle contraction for methylated sites.

The carbon–carbon bond distances within the ligand seem to fall in two sets (excluding the C–CH_3 bonds which average 1.513 (4) Å). The "external" set (formed between the C(1)–C(2) and C(4)–C(5) positions) ranges from 1.395 to 1.412 Å, averaging 1.406 (3) Å. The "internal" set (formed between the C(2)–C(3) and C(3)–C(4) positions) ranges from 1.411 to 1.421 Å, averaging 1.416 (4) Å. There is a difference between the two averages of two standard deviations which, when taken into consideration with the almost nonoverlapping ranges of each set, suggests that this difference may be real. Indeed, in $Nd(2,4\text{-}C_7H_{11})_3$,[38] the same effect was observed with a difference of three standard deviations. The origin of this can be traced to the resonance structures for a pentadienyl anion, IXa–c.


IXa


IXb


IXc

It can be seen that hybrids IXa and IXc bring about essentially equivalent shortening of both the internal and the external sets of C–C bonds. Hybrid IXb, however, can clearly be expected to bring about preferential shortening of the external set, in agreement with the recent theoretical results.[20]

The interior C–C–C bond angles are observed to fall in three sets, 124.1 (4)° around the C(2,9) atoms, 125.5 (3)° around the C(3,10) atoms, and 120.7 (3)° around the C(4,11) positions. On the average, those positions having an attached methyl group clearly have the smaller interior C–C–C bond angles. This observation may well relate to the apparent kinetic stabilizing influence of the methyl groups (theoretical calculations indicate a thermodynamically destabilizing effect in the absence of a change in geometry).[20] If the methyl groups contract the ligand size (by ca. 3° each in this case), the ligands may move further from the metal while the same M–C bond distances are retained, if not shortened. The net effect, then, of moving the ligand out farther is to reduce the interligand C···C nonbonded repulsions and perhaps increase the overlap between the metal and ligand orbitals. It might also be maintained that the presence of methyl groups serves to hinder a reductive coupling process (leading to dipentadienyl compounds[7b]), either by direct steric hinderance or less likely by the separation of the ligands from one another.

The bonded five atom ligand fragments are nearly planar (Table V). An angle of 15.0° is found between the two ligand planes such that the open ligand faces are bent toward one another resulting in C(2)···C(12) and C(5)···C(9) nonbonded contacts averaging 2.987 (4) Å and C(3)···C(11) and C(14)···C(10) nonbonded contacts averaging 3.211 (4) Å.[34] The methyl groups are also bent out of the ligand planes, in a direction toward the iron atom by 6.0, 10.7, 6.0, and 11.8° for C(6), C(7), C(13), and C(14), respectively. The much smaller substituent tilts observed for ferrocene (3.7 (9)°) illustrate the considerably larger size of the pentadienyl ligands (note in $Fe(C_5(CH_3)_5)_2$ the methyl groups are bent away from the metal[39]).

A somewhat related distortion is also observed for the terminal CH_2 groups in $Fe(2,4\text{-}C_7H_{11})_2$. It should be noted that while almost all of the hydrogen atoms could be located, a great deal of uncertainty is naturally associated with their locations. Even so, however, it was clear that significant bending of each of the C–H bonds occurred, which brought the two endo hydrogen atoms above the ligand plane (away from the iron atom) and (to a lesser extent) the two exo hydrogen atoms below the ligand plane. While a small amount of bending might be expected in order to increase the overlap between the p orbitals of the

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CH_2 groups and the iron atom, the larger magnitude of bending experienced by the endo hydrogen atoms might come about from an attempt to relieve $H_{endo}\cdots H_{endo}$ repulsions which would be substantial in a planar arrangement.[40,41]

It is worthwhile to note that both $Nd(2,4\text{-}C_7H_{11})_3$ and $V(2,4\text{-}C_7H_{11})_2$ possess substantially "wider" ligands, in that the interior C–C–C bond angles are noticeably larger (ca. 3–4° each).[32,38] Quite possibly the ligands in the iron complex have contracted themselves substantially so that they may move farther from the iron atom (in order to relieve the aforementioned interligand C···C contacts and to increase metal–ligand overlap) while still possessing comparable iron–carbon distances. In this regard, it can be noted that the contraction has resulted in C(1)···C(5) and C(8)···C(12) nonbonded contacts of 2.777 (7) and 2.794 (8) Å, respectively.[34b] Alternatively, since metal–allyl systems demonstrate a similar contraction of ligand as it becomes closer to the metal,[42] this contraction may be due to an attempt to maximize metal–ligand overlap in both of these systems. There is quite clearly a great deal of molecular crowding in the "open ferrocene" compounds, and indeed this seems to be the case in the other first-row transition-metal systems under investigation[32,43] and a key to understanding their chemistry.

The present study indicates that the "open ferrocene" compounds do share much in common with their cyclic ferrocene counterparts, and other detailed physical studies, notably theoretical calculations[20] and Mössbauer investigation[44] have provided further valuable information regarding these analogies and the general nature of the metal–pentadienyl bonding. At this point it appears that the pentadienyl ligands behave much like a hybrid between the cyclopentadienyl and allylic ligands in that both reasonable stability and chemical reactivity can be achieved. In this regard, it also appears that the introduction of substituents has a substantial and exploitable effect on these properties. These systems, then, appear to be favorably disposed for both detailed physical and chemical studies and may therefore allow a number of fruitful correlations to be made. Our efforts have thus far led to stable, often unusual, compounds of titanium,[43] vanadium, chromium, manganese,[32] and ruthenium[45] and are being further pursued.

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Registry No. VIb$_1$, 85883-08-5; VIb$_2$, 85922-64-1; VId$_1$, 85922-62-9; VId$_2$, 85922-63-0; VIII, 74910-62-6; $Fe(2,4\text{-}C_7H_{11})_2$, 74920-98-2; $Fe(3\text{-}C_6H_9)_2$, 74910-63-7; KC_5H_7, 79210-89-2; ferrous chloride, 7758-94-3; potassium 2,4-dimethylpentadienide, 74205-98-4; 2,3-dimethyl-1,4-pentadiene, 758-86-1; 3-methyl-1,4-pentadiene, 1115-08-8; potassium 3-methylpentadienide, 74206-00-1; potassium 2-methylpentadienide, 74205-99-5.

Supplementary Material Available: A listing of non-hydrogen atom thermal parameters (Table II), the hydrogen atom parameters (Table III), least-squares plane information (Table V), and the structure amplitude table (25 pages). Ordering information is given on any current masthead page.

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(40) Barrow, M. J.; Mills, O. S.; Haque, F.; Pauson, P. L. *Chem. Commun.* 1971, 1239.

(41) (a) It actually appears that the H_{endo} atoms have twisted above the ligand plane to a larger extent than the H_{exo} atoms have twisted below, consistent with the stated argument. (b) See also: Hoffmann, R.; Hofmann, P. *J. Am. Chem. Soc.* **1976**, *98*, 598.

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