The Synthesis and Unexpected Structure of η^5-Cyclopentadienyl-η^6-fluorenyliron

J. W. Johnson and P. M. Treichel*

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received July 26, 1976*

Abstract: The yellow cyclopentadienyl(arene)iron(II) complex, $[Fe(C_5H_5)(\eta^6\text{-}C_{13}H_{10})]PF_6$ ($C_{13}H_{10}$ = fluorene), was prepared by a standard route from $Fe(C_5H_5)_2$, fluorene, Al and $AlCl_3$, followed by metathesis with NH_4PF_6. When treated with 1 equiv of *tert*-butoxide ion in benzene, a proton is lost from C(9) of the fluorene ligand giving an air-sensitive green compound $Fe(C_5H_5)(C_{13}H_9)$. The ^1H NMR spectrum of this compound showed that coordination of the metal to one of the six-membered rings of the fluorenyl ligand was retained; subsequently a crystal structure confirmed this. (Crystal data: space group $P2_1/c$; a = 8.944 (3), b = 14.600 (4), c = 20.201 (5); β = 100.08 (2)°; V = 2597 (1) Å^3; Z = 8; d_{calcd} = 1.46, d_{obsd} = 1.45 g cm^{-3}. A total of 2323 independent ($F > 2\sigma(F)$) observations were collected by diffractometric techniques. The structure, solved by direct methods, was refined by anisotropic block-diagonal least-squares techniques to a value of R_1 = 0.045.) In this structure it was found that all six carbon atoms of this ring are coordinated to the metal; this unusual structure is represented by a zwitterionic formulation, with a positive charge on the metal and a negative charge primarily on C(9). Reactivity of this complex is in accord with this representation. The metal complex reacts as a nucleophile with alkyl halides (CH_3I, CH_3OSO_2F, p-$BrC_6H_4CH_2Br$) to give stereospecifically the *exo*-9-alkylfluorene(cyclopentadienyl)iron(II) complex. The exo stereochemistry was determined by a crystallographic study of the methyl compound. Reactions with acyl halides give two products, $[Fe(C_5H_5)(\eta^6\text{-}C_{13}H_{10})]^+$ and $[Fe(C_5H_5)(C_{13}H_8(COR)_2)]^+$, in equal quantities. Presumably this is a consequence of rapid proton transfer to starting material from the C(9) position of a monoacylated species. The compound $Fe(C_5H_5)(C_{13}H_9)$ was shown to slowly add 1 equiv of hydrogen, giving at least two isomers of the formula $Fe(C_5H_5)(C_{13}H_{11})$. These same products are also obtained on hydride addition to $[Fe(C_5H_5)(\eta^6\text{-}C_{13}H_{10})]PF_6$, and are assigned a cyclohexadienyl-metal structure.

Fluorene forms the fluorenide anion, $[C_{13}H_9]^-$, on treatment with bases of appropriate strength or when reacted with alkali metals. Not surprisingly the fluorenide anion (formally the dibenzocyclopentadienide anion) has been considered a likely candidate to form metal complexes, and, in the rapid expansion of the field of hydrocarbon-metal complex chemistry that followed the characterization of ferrocene, some substantial effort was probably directed to the formation of fluorenyl-metal complexes.[1] Notably, such efforts were largely unsuccessful and to date only a few fluorenyl complexes have been prepared wherein a metal is bonded to the five-membered ring of this ligand, all described in the last 7 years. King and Efraty[2] prepared the compound $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ (Throughout this paper, the term $\eta^5\text{-}C_{13}H_9$ will be used to designate coordination to the five-membered ring; more specifically the designation could be 9,10,11,12,13-η^5. The terms $\eta^6\text{-}C_{13}H_{10}$ or $\eta^6\text{-}C_{13}H_9$ refer to coordination to one six-membered ring, i.e., 1,2,3,4,10,11-η^6 for fluorene and fluorenyl ligands.) from $Mn(CO)_5Cl$ and $Na[C_{13}H_9]$, in poor yield; from this compound they prepared a triphenylphosphine derivative, $Mn(C_{13}H_9)(CO)_2[P(C_6H_5)_3]$. In addition an anionic complex $[Cr(\eta^5\text{-}C_{13}H_9)(CO)_3]^-$ has been prepared in solution but not isolated.[3] Very recently some work on fluorenyl–zirconium compounds appeared.[4] Remarkably, no fluorenyl–iron compounds were known prior to this work. Pauson[1] commented on this fact in an early review article, as did King and Efraty[2] in their paper on the manganese compounds.

In earlier work we reported on protonation–deprotonation reactions of bis(indenyl)iron.[5] These reactions were accompanied by facile migration of metal coordination between the five- and six-membered rings, viz.,

$$Fe(\eta^5\text{-}C_9H_7)_2 + H^+ \rightleftarrows [Fe(\eta^5\text{-}C_9H_7)(\eta^6\text{-}C_9H_8)]^+$$

Although these reactions proceed only with low yields, they suggested a reasonable route to the elusive η^5-fluorenyl complexes of iron. Deprotonation of the known complex $[Fe(C_5H_5)(\eta^6\text{-}C_{13}H_{10})]^+$ might be expected to occur with migration of coordination to give $Fe(C_5H_5)(\eta^5\text{-}C_{13}H_9)$. Support of this proposal is also found in the analogous reaction of $Cr(\eta^6\text{-}C_{16}H_{10})(CO)_3$ with base, said to give $[Cr(\eta^5\text{-}C_{13}H_9)(CO)_3]^-$.[3]

Further interest in this proposed study was derived from the hope that the stereochemistry of the protonation–deprotonation reaction of $Fe(C_5H_5)(\eta^5\text{-}C_{13}H_9)$ could be unequivocally determined. Determination of the stereochemistry of protonation of bis(indenyl)iron had been a goal in our earlier work on this species.[5]

In fact, as work proceeded on this project our interest was drawn from these original goals. Deprotonation of $[Fe(C_5H_5)(\eta^6\text{-}C_{13}H_{10})]^+$ yielded an unexpected product in which metal coordination to the six-membered ring (1,2,3,4,10,11-η^6 coordination) was retained; no migration of metal coordination to the five-membered ring occurred. A crystal structure study provided details of this unprecedented structure which may best be described by a zwitterionic representation, positive charge on the metal and negative charge at C(9) of the fluorenyl ligand.[6] Herein we discuss the synthetic, structural, and reactivity studies on this complex and the implications which derive from these results.

Experimental Section

All reactions were carried out under dry nitrogen. When noted, solvents were dried by appropriate measures; otherwise, all reagents were used as received. Solutions containing $Fe(C_5H_5)(C_{13}H_9)$ were handled using Schlenk techniques. Analyses were performed by Galbraith Laboratories. High resolution mass spectra were obtained on an AEI-MS9. ^1H NMR spectra were recorded on JEOL-MH100 or Bruker WH-270 instruments, and ^{13}C NMR spectra were recorded on the JEOL-FX60 at 15 MHz using ~30 000 pulses. All chemical shifts are expressed in parts per million downfield from internal Me_4Si. ^1H NMR and ^{13}C NMR data are presented in Tables I and II, respectively. Melting points were determined in sealed capillaries and are uncorrected.

The known compound $[Fe(C_5H_5)(\eta^6\text{-}C_{13}H_{10})]PF_6$ was prepared by the published method.[7]

Isolation of $Fe(C_5H_5)(C_{13}H_9)$. Potassium *tert*-butoxide (0.148 g, 1.30 mmol) was added to a suspension of $[Fe(C_5H_5)(C_{13}H_{10})]PF_6$ (0.580 g, 1.34 mmol) in toluene. The mixture was stirred at room temperature for 1.5 h and filtered. Addition of heptane to the filtrate, followed by slow evaporation under nitrogen flow, resulted in large,

Table I. ^{1}H NMR Data for Fluorene–Iron Complexes[a]

Compound	Uncomplexed 6-membered ring protons	Complexed 6-membered ring protons	5-Membered ring protons	C_5H_5 protons[b]	Other
$Fe(C_5H_5)(C_{13}H_9)$[c]	8.13, d, 8; 7.92, d, 8; 7.62, t, 8; 7.21, t, 8	6.13, d, 6; 5.96, d, 6; 4.62, t, 6; 4.43, t, 6	6.12, s	3.42, s	
$[Fe(C_5H_5)(C_{13}H_{10})]PF_6$	8.08, m; 7.56–7.82, m (int = 3)	7.29, m; 7.08, m; 6.50, m (int = 2)	4.42, AB (J = 22, $\Delta\nu$ = 37)	4.87, s	
$[Fe(C_5H_5)(exo\text{-}9\text{-}CH_3C_{13}H_9)]PF_6$	8.08, m; 7.51–7.76, m (int = 3)	7.20, m; 7.03, m; 6.47, m (int = 2)	4.63, q, 8	4.87, s	1.59, d, 8 (int = 3)
$[Fe(C_5H_5)(endo\text{-}9\text{-}CH_3C_{13}H_9)]PF_6$[d]	*e*	*e*	4.22, q, 7	4.94, s	1.96, d, 7 (int = 3)
$[Fe(C_5H_5)(exo\text{-}9\text{-}(p\text{-}BrC_6H_4CH_2)C_{13}H_9)]PF_6$[d]	8.02, m; 6.97–7.53, m (int = 8)[g]	6.75, m; 6.38, m (int = 2)	4.97, t, 7	4.79, s	3.31, d, 7 (int = 2)
$[Fe(C_5H_5)((C_6H_5CO)_2C_{13}H_8)]PF_6$[f]	7.4–8.3, m (int = 14)[h]	7.0, m (int = 2); 6.5, m (int = 2)		4.93, s	
$[Fe(C_5H_5)((CH_3CO)_2C_{13}H_8)]PF_6$	*i*	*i*		4.79, s	2.74, s; 2.60, s (both int = 3)
$Fe(C_5H_5)(C_{13}H_{11})$[c,j]	7.02–7.36, m (int = 4)	6.37, d, 5.0; 4.15, t, 5.6; 3.29, dd, 12.8, 6.4; 2.30, t, 6.3; 2.13, d, 12.7	3.39, d, 20.0; 3.07, d, 20.0	3.70, s	

[a] 100 MHz, $(CD_3)_2CO$ solution, except as noted; data given: chemical shift (δ), multiplicity, J (Hz). [b] Relative intensity = 5. [c] C_6D_6 solution. [d] The ^{1}H NMR spectrum of the mixture of isomers was used to give these data. [e] Same as for exo. [f] $(CD_3)_2SO$ solution. [g] Includes resonances for p-BrC_6H_4 and one proton of complexed ring. [h] Includes benzoyl resonances. [i] Recorded in presence of $[Fe(C_5H_5)(C_{13}H_{10})]PF_6$, six-membered resonances similar. [j] 270 MHz.

Table II. ^{13}C NMR Data for Fluorene–Iron Complexes

	Uncomplexed 6-membered ring		Complexed 6-membered ring		5-Membered ring	Cyclopentadienyl
Compound	C–H carbons	Quaternary carbons	C–H carbons	Quaternary carbons	C–H carbons	C–H carbons
$Fe(C_5H_5)(\eta^6\text{-}C_{13}H_9)$[a]	125.2, 120.7, 119.4, 115.5	124.7, 119.6	76.9, 76.5, 69.9, 69.1	75.6, 67.9	86.8	72.4
$[Fe(C_5H_5)(C_{13}H_{10})]PF_6$[b]	130.8, 128.3, 126.5, 122.9	144.7, 138.1	86.7, 86.3, 86.0, 81.0	107.5, 105.5	37.8	78.4
$C_{13}H_{10}$[c]	126.5 (2), 125.8, 119.7				36.8	

[a] C_6D_6 solution. [b] $(CD_3)_2CO$ solution. [c] $CDCl_3$ solution (L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra", Wiley-Interscience, New York, N.Y., 1972, p 452).

well-formed, dark green crystals, mp 105 °C. In contrast to the extreme air sensitivity of solutions of this compound, these crystals were much less reactive to air, undergoing only slight surface decomposition in about 10 min (while being mounted for the x-ray crystallographic study).

Anal. Calcd for $C_{18}H_{14}Fe$: C, 75.55; H, 4.93; Fe, 19.52. Found: C, 75.80; H, 4.90; Fe, 19.52. Mass spectrum parent peak found 286.0450. $^{12}C_{18}{}^{1}H_{14}{}^{56}Fe$ requires 286.0445.

Reprotonation of $Fe(C_5H_5)(C_{13}H_9)$. Preparation of a solution of $Fe(C_5H_5)(C_{13}H_9)$ was accomplished as described above. Addition of various proton donors such as HCl quantitatively regenerated the starting complex, $[Fe(C_5H_5)(C_{13}H_{10})]^+$.

Deuteration with gaseous DCl in dry benzene gave a mixture of d_0, d_1 (exo and endo), and d_2 derivatives of the product indicating rapid hydrogen-deuterium exchange must occur in this system. Addition of D_2O and DCl gave only the d_2 compound. The presence of these deuterated compounds was ascertained by consideration of the ^{1}H (^{2}D decoupled) NMR spectra of the products.

Reaction of $Fe(C_5H_5)(C_{13}H_9)$ with CH_3OSO_2F. A solution of $Fe(C_5H_5)(C_{13}H_9)$ was prepared in benzene as described above from 1.20 g (2.78 mmol) of $[Fe(C_5H_5)(C_{13}H_{10})]PF_6$. The solution was filtered; then CH_3OSO_2F (0.5 ml, 6 mmol) was added to the filtrate and the mixture stirred for 5 min. An oily yellow solid appeared. The reaction mixture was then treated with ~200 ml of H_2O. The aqueous layer was separated and treated with excess NH_4PF_6 to give a yellow solid which, upon recrystallization from CH_3OH, yielded 0.95 g (77%) of $[Fe(C_5H_5)(exo\text{-}9\text{-}CH_3C_{13}H_9)]PF_6$ as yellow plates, mp 135–137 °C. The presence of a single isomer was ascertained by ^{1}H NMR data (see Table I). The exo conformation was determined by single-crystal x-ray diffraction (vide infra).

Anal. Calcd for $C_{19}H_{17}F_6FeP$: C, 51.14; H, 3.84. Found: C, 51.12; H, 3.86.

Reaction with methyl iodide yielded the same product.

Deprotonation of $[Fe(C_5H_5)(exo\text{-}9\text{-}CH_3C_{13}H_9)]PF_6$ with *tert*-butoxide ion in benzene could be accomplished by the same method used for $[Fe(C_5H_5)(C_{13}H_{10})]PF_6$. The product, not isolated, could be reprotonated by CF_3COOH, giving approximately equimolar quantities of endo and exo isomers of the complex $[Fe(C_5H_5)(9\text{-}CH_3C_{13}H_9)]^+$.

Reaction of $Fe(C_5H_5)(C_{13}H_9)$ and p-$BrC_6H_4CH_2Br$. This reaction was carried out in a manner similar to that just described, giving yellow microcrystalline $[Fe(C_5H_5)(exo\text{-}9\text{-}BrC_6H_4CH_2C_{13}H_9)]PF_6$, mp 216–217 °C dec, in 47% yield.

Anal. Calcd for $C_{25}H_{20}BrF_6FeP$: C, 49.94; H, 3.35. Found: C, 49.56; H, 3.14.

Reaction of $Fe(C_5H_5)(C_{13}H_9)$ and C_6H_5COCl. Preparation of $Fe(C_5H_5)(C_{13}H_9)$ in benzene from 0.79 g (1.83 mmol) of $[Fe(C_5H_5)(C_{13}H_{10})]PF_6$ was carried out as described above. After filtration benzoyl chloride (0.31 ml, 2.5 mmol) was added; yellow solid was immediately deposited. Water was added and the mixture was stirred vigorously for 30 min. The aqueous layer was separated and treated with excess NH_4PF_6. The resulting solid was filtered and dried in vacuo to yield 0.537 g (55%) of a yellow microcrystalline product. A ^{1}H NMR spectrum indicated the presence of equimolar amounts of $[Fe(C_5H_5)(C_{13}H_{10})]PF_6$ and a diacylated product. The sample was extracted for 2 h with a small volume of acetone. The remaining solid was recrystallized from CH_2Cl_2/hexane to yield pure $[Fe(C_5H_5)((C_6H_5CO)_2C_{13}H_8)]PF_6$, mp >180 °C dec.

Anal. Calcd for $C_{32}H_{23}F_6FeO_2P$: C, 60.02; H, 3.62. Found: C, 58.75; H, 3.44. Infrared spectrum (Nujol mull): 1730 cm^{-1} ($\nu_{C=O}$), 1640 cm^{-1} ($\nu_{C=C}$).

Reaction of $Fe(C_5H_5)(C_{13}H_9)$ with CH_3COCl. This reaction was carried out in the manner described above, giving a 78% yield of a yellow microcrystalline solid. A ^1H NMR spectrum indicated an equimolar mixture of $[Fe(C_5H_5)(C_{13}H_{10})]PF_6$ and $[Fe(C_5H_5)((CH_3CO)_2C_{13}H_8)]PF_6$. An infrared spectrum of the mixture, in CH_2Cl_2 solution, gave absorptions at 1765 and 1650 cm^{-1}; presumably these are attributable to $\nu_{C=O}$ and $\nu_{C=C}$ in the latter compound. Separation of the two compounds was not accomplished.

Hydrogenation of $Fe(C_5H_5)(C_{13}H_9)$. A solution of $Fe(C_5H_5)(C_{13}H_9)$, prepared from 1.37 g (3.2 mmol) of $[Fe(C_5H_5)(C_{13}H_{10})]PF_6$, was injected into an atmospheric pressure hydrogenation apparatus with 0.3 g of 10% Pd/C catalyst. After 36 h at 21 °C 2.2 mmol of H_2 was absorbed. The reaction mixture was filtered through Celite to remove the catalyst and the filtrate was evaporated. The resulting red solid was dissolved in hexane and chromatographed on Florisil with hexane eluent. A small yellow band was discarded and the following large red band was collected, concentrated, and chilled to −20 °C. Red crystals (0.10 g) were deposited. A ^1H NMR spectrum indicated the presence of two isomers. Fractional crystallization from hexane afforded 0.050 g (5%) of the major isomer, $Fe(C_5H_5)(C_{13}H_{11})$, as red crystals, mp 106-108 °C.

Anal. Calcd for $C_{18}H_{16}Fe$: C, 75.02; H, 5.60; Fe, 19.38. Found: C, 75.15; H, 5.52; Fe, 19.26. Mass spectrum parent peak found 288.0555. $^{12}C_{18}{}^1H_{16}{}^{56}Fe$ requires 288.0601.

Reaction of $[Fe(C_5H_5)(C_{13}H_{10})]PF_6$ with $NaBH_4$. Excess $NaBH_4$ (1.3 g) was added to $[Fe(C_5H_5)(C_{13}H_{10})]PF_6$ (2.00 g, 4.63 mmol) in ~100 ml of dry dimethoxyethane and the mixture stirred at room temperature for 4 h. Water and hexane were added. The red organic layer was separated, dried over $MgSO_4$, and concentrated in vacuo. Upon cooling to −20 °C, 0.75 g (56%) of $Fe(C_5H_5)(C_{13}H_{11})$ was deposited as red crystals. The ^1H NMR spectrum of this product was identical with that of the major isomer isolated from the hydrogenation of $Fe(C_5H_5)(C_{13}H_9)$. Further cooling of the red filtrate resulted in deposition of 0.11 g (8%) of a mixture of the two isomers.

Reaction of $Fe(C_5H_5)(C_{13}H_{11})$ with $[Ph_3C]PF_6$. Samples of the compounds $Fe(C_5H_5)(C_{13}H_{11})$ (either the major isomer or the mixture of isomers) were converted by $[Ph_3C]PF_6$ in CH_2Cl_2 to $[Fe(C_5H_5)(C_{13}H_{10})]PF_6$ in yields greater than 80%, after recrystallization from CH_2Cl_2/ether.

Single-Crystal X-ray Diffraction Study of $Fe(C_5H_5)(C_{13}H_9)$. Collection and Reduction of the Single-Crystal X-ray Data for $Fe(C_5H_5)(C_{13}H_9)$. The crystal chosen for data collection was a parallelepiped of dimensions (each defined by the perpendicular distance between the pair of opposite crystal faces) of 0.5 mm (001) × 0.3 mm (100) × 0.40 mm (021). It was mounted on a glass fiber and sealed in a capillary tube under argon. The crystal was accurately centered on a Syntex P$\bar{1}$ four-circle automated diffractometer equipped with a graphite monochromator. Mo Kα radiation (λ 0.7107 Å) was used throughout the alignment and data collection procedures. ω-Scans on two strong diffraction maxima near χ = 90° exhibited sharp, well-defined peaks of half-width 0.17°. Diffraction maxima (12) (8° < 2θ <14°) were automatically centered in 2θ, ω, and χ. Preliminary Syntex routines[8] indicated a monoclinic lattice with dimensions: $\bar{a}$ = 8.944 (3), $\bar{b}$ = 14.600 (4), $\bar{c}$ = 20.201 (5) Å; β = 100.08 (2)°; and V = 2597 (1) $Å^3$. The experimental density of 1.45 g cm^{-3}, measured by flotation in CCl_4/CBr_4/heptane mixtures, agreed with the calculated density of 1.46 g cm^{-3} for Z = 8. The monoclinic lattice symmetry and associated axis lengths were verified by partial rotation photographic projections along the reciprocal axes.

Intensity data were collected using the 2θ-θ scan technique with variable scan speeds from 2 to 24° min^{-1}. Two standard peaks were counted after every 50 reflections and showed no significant deviation in intensity (±3.6%). A total of 3875 reflections, distributed through the octants $\bar{h}\bar{k}l$ and $h\bar{k}\bar{l}$ for which 2° < 2θ < 45°, were collected. These data were then corrected, reduced, and merged in the usual manner[9] to yield 2318 independent reflections, for which $I \geq 2\sigma(I)$, which were used in the solution of the structure. Later, the data were corrected for absorption. The linear absorption coefficient was μ = 11.69 cm^{-1}, and the transmission factors varied from 0.70 and 0.86. The observed systematic absences for $h0l$ ($l = 2n + 1$) and $0k0$ ($k = 2n + 1$) uniquely define the space group as $P2_1/c$.

Table III. Bond Distances for $Fe(C_5H_5)(C_{13}H_9)$

Molecule A		Molecule B	
C1-C2	1.402 (8)[a]	C1′-C2′	1.391 (8)
C2-C3	1.407 (8)	C2′-C3′	1.410 (8)
C3-C4	1.403 (7)	C3′-C4′	1.416 (8)
C1-C10	1.429 (7)	C1′-C10′	1.408 (8)
C10-C11	1.464 (7)	C10′-C11′	1.460 (7)
C4-C11	1.409 (7)	C4′-C11′	1.426 (7)
C9-C10	1.372 (7)	C9′-C10′	1.397 (7)
C11-C12	1.445 (7)	C11′-C12′	1.449 (7)
C9-C13	1.435 (8)	C9′-C13′	1.413 (7)
C5-C6	1.378 (8)	C5′-C6′	1.392 (8)
C6-C7	1.390 (9)	C6′-C7′	1.393 (8)
C7-C8	1.380 (8)	C7′-C8′	1.364 (8)
C5-C12	1.373 (7)	C5′-C12′	1.356 (8)
C12-C13	1.413 (7)	C12′-C13′	1.417 (7)
C8-C13	1.415 (8)	C8′-C13′	1.426 (8)
Fe-C1	2.122 (5)	Fe′-C1′	2.104 (6)
Fe-C2	2.053 (5)	Fe′-C2′	2.047 (6)
Fe-C3	2.039 (5)	Fe′-C3′	2.032 (6)
Fe-C4	2.072 (5)	Fe′-C4′	2.074 (6)
Fe-C10	2.316 (5)	Fe′-C10′	2.300 (5)
Fe-C11	2.152 (5)	Fe′-C11′	2.175 (5)
C14-C15	1.408 (8)	C14′-C15′	1.395 (9)
C15-C16	1.396 (8)	C15′-C16′	1.352 (9)
C16-C17	1.405 (8)	C16′-C17′	1.367 (9)
C17-C18	1.398 (8)	C17′-C18′	1.394 (10)
C14-C18	1.406 (8)	C14′-C18′	1.385 (11)
Fe-C14	2.042 (5)	Fe′-C14′	2.034 (6)
Fe-C15	2.041 (5)	Fe′-C15′	2.025 (6)
Fe-C16	2.048 (5)	Fe′-C16′	2.036 (6)
Fe-C17	2.030 (6)	Fe′-C17′	2.024 (7)
Fe-C18	2.031 (6)	Fe′-C18′	2.031 (6)
Fe-C9	3.385 (5)	Fe′-C9′	3.421 (6)

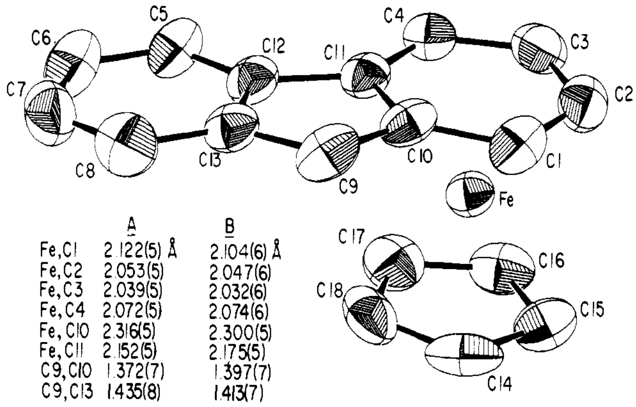
[a] Distances are given in Å. The number in parentheses is the estimated standard deviation in the last digit in this and the following tables.

Solution and Refinement of the Structure of $Fe(C_5H_5)(C_{13}H_9)$. For space group $P2_1/c$, Z = 8 requires two molecules in the crystallographically independent unit. Standard Patterson techniques led only to false structures, so the structure was solved by direct method and Fourier techniques.[10] Subsequent inspection suggested that the heavy-atom method failed due to substantial overlap in the Patterson map. Isotropic full-matrix least-squares refinement converged at R_1 = 9.6% and R_2 = 11.0%.[11] At this point, the data were corrected for absorption and refined two more cycles isotropically to R_1 = 8.8% and R_2 = 10.4%. A difference map revealed the hydrogen atom positions, but attempts at refining them led to inconsistent results, so the hydrogen atoms were placed at idealized positions with C-H distances of 1.0 Å. Block-diagonal anisotropic least-squares refinement (four blocks) converged to R_1 = 4.5%, R_2 = 4.9%. The final cycle was done in two steps: first, the thermal parameters and the scale factor were varied, holding the positional parameters fixed; next, the positional parameters and the scale factor were varied, holding the thermal parameters fixed. The maximum shift in a thermal parameter was 0.16σ and in a positional parameter was 0.04σ. The final error of fit was 1.06.

Bond distances and bond angles in this compound are presented in Tables III and IV, respectively. Final positional and thermal parameters are given in Tables V and VI. Observed and calculated structure factors are available in the supplementary material for this paper.[12]

Discussion of the bonding in this structure is facilitated by considering various planes within the molecules defined by the carbon atoms of the two hydrocarbon ligands. Data on several planes are given in Table VII.

Figure 1 presents a drawing of one of the two crystallographically independent molecular units for this compound, along with selected bond distances. A comparison of the fluorene ligand bond distances with analogous distances in alkali metal fluorenides[13] is given in Figure 2.



	A	B
Fe,C1	2.122(5) Å	2.104(6) Å
Fe,C2	2.053(5)	2.047(6)
Fe,C3	2.039(5)	2.032(6)
Fe,C4	2.072(5)	2.074(6)
Fe,C10	2.316(5)	2.300(5)
Fe,C11	2.152(5)	2.175(5)
C9,C10	1.372(7)	1.397(7)
C9,C13	1.435(8)	1.413(7)

Figure 1. View of $Fe(C_5H_5)(C_{13}H_9)$, molecule A.

Table IV. Bond Angles for $Fe(C_5H_5)(C_{13}H_9)$

Molecule A		Molecule B	
C1-C2-C3	120.4 (5)	C1′-C2′-C3′	120.6 (5)
C2-C3-C4	120.6 (5)	C2′-C3′-C4′	120.2 (5)
C3-C4-C11	118.9 (5)	C3′-C4′-C11′	118.5 (5)
C4-C11-C10	122.2 (5)	C4′-C11′-C10′	121.2 (5)
C11-C10-C1	115.0 (5)	C11′-C10′-C1′	116.3 (5)
C10-C1-C2	121.6 (5)	C10′-C1′-C2′	121.9 (5)
C9-C10-C11	109.3 (5)	C9′-C10′-C11′	108.7 (5)
C10-C11-C12	106.5 (5)	C10′-C11′-C12′	106.5 (5)
C11-C12-C13	106.7 (5)	C11′-C12′-C13′	106.8 (5)
C12-C13-C9	109.8 (5)	C12′-C13′-C9′	110.1 (5)
C13-C9-C10	107.7 (5)	C13′-C9′-C10′	107.9 (5)
C5-C6-C7	119.9 (6)	C5′-C6′-C7′	119.9 (6)
C6-C7-C8	122.8 (6)	C6′-C7′-C8′	121.8 (6)
C7-C8-C13	117.8 (6)	C7′-C8′-C13′	118.8 (6)
C8-C13-C12	118.4 (5)	C8′-C13′-C12′	118.3 (5)
C13-C12-C5	122.4 (5)	C13′-C12′-C5′	121.7 (6)
C12-C5-C6	118.7 (6)	C12′-C5′-C6′	119.5 (6)
C14-C15-C16	108.6 (6)	C14′-C15′-C16′	108.2 (7)
C15-C16-C17	107.4 (5)	C15′-C16′-C17′	109.3 (6)
C16-C17-C18	108.7 (5)	C16′-C17′-C18′	107.8 (7)
C17-C18-C14	107.8 (5)	C17′-C18′-C14′	107.4 (6)
C18-C14-C15	107.5 (5)	C18′-C14′-C15′	107.3 (7)

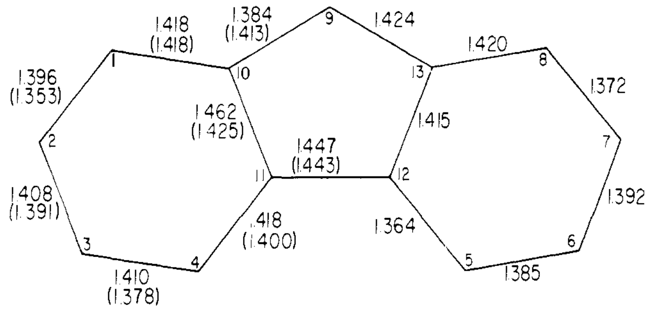


Figure 2. Comparison of averaged bond lengths in $Fe(C_5H_5)(C_{13}H_9)$ with symmetry averaged bond lengths of alkali metal–fluorenyl salts (values in parentheses).

Single-Crystal X-ray Study of $[Fe(C_5H_5)(exo\text{-}9\text{-}CH_3C_{13}H_9)]PF_6$. Collection and Reduction of the Single-Crystal X-ray Data for $[Fe(C_5H_5)(exo\text{-}9\text{-}CH_3C_{13}H_9)]PF_6$. Large prismatic crystals were grown by slow evaporation of a CH_3OH solution of the compound in a nitrogen-filled desiccator over $Mg(ClO_4)_2$. One of these crystals was cut to an approximate cube of dimension 0.2 mm and mounted in a capillary tube under argon. The crystal was accurately centered on a Syntex $P\bar{1}$ diffractometer equipped with a graphite monochromator. Mo Kα radiation (λ 0.7107 Å) was used throughout the alignment and data collection procedures. An ω-scan on a strong diffraction maximum near $\chi = 90°$ exhibited a sharp, well-defined peak of half-width 0.18°. Different maxima (15) ($7° < 2\theta < 26°$) were automatically centered in 2θ, ω, and χ. The preliminary Syntex routines[7] indicated a triclinic lattice of dimensions: $\bar{a} = 20.360$ (6), $\bar{b} = 21.858$ (9), $\bar{c} = 10.137$ (4) Å; $\alpha = 110.88$ (3)°, $\beta = 96.83$ (3)°, $\gamma = 113.07$ (3)°; and $V = 3699$ (2) Å^3. The experimental density of 1.59 g cm^{-3}, measured by flotation in CCl_4/heptane mixtures, agrees with the calculated density of 1.60 g cm^{-3} for $Z = 8$. The axis lengths and the absence of lattice symmetry were verified by partial rotation photographic projections along the axes chosen, as well as along other trial axes.

Intensity data were collected using the 2θ-θ scan technique with variable scan speeds from 4 to 24° min^{-1}. Two standard peaks were monitored after every 100 reflections and showed no significant deviation in intensity (±4.6%). A total of 7379 reflections distributed through the octants hkl, $\bar{h}kl$, $h\bar{k}l$, and $\bar{h}\bar{k}l$ for which $2° < 2\sigma < 40°$ were collected. These data were then corrected, reduced, and merged in the usual manner[8] to yield 4975 independent reflections for which $I > 2\sigma(I)$.[14] The effects of absorption were ignored ($\mu = 9.85$ cm^{-1}).

Solution and Refinement of the Structure of $[Fe(C_5H_5)(9\text{-}exo\text{-}CH_3C_{13}H_9)]PF_6$. The space group was assumed to be $P\bar{1}$. $Z = 8$ requires four cations and four anions in the crystallographically independent unit. A Patterson map revealed the positions of three of the Fe atoms.[10] Successive Fourier syntheses showed the positions of the remaining Fe, the four P, as well as all of the C and F atoms, except for four F atoms in one anion and four C atoms scattered among the four cations. Two cycles of block-diagonal least-squares refinement (three blocks) on the positional parameters lowered the reliability factors to $R_1 = 26.4\%$ and $R_2 = 33.6\%$.[11] A difference map showed the missing C positions and indicated that one of the PF_6^- anions was severely disordered. Various disorder models were tried, and the isotropic block-diagonal least-squares refinement (six block) progressed with $R_1 = 13.2\%$ and $R_2 = 16.9\%$. At this point, it became apparent that the disorder was not being modeled in a meaningful manner, and another difference map revealed disorder in another of the PF_6^- anions. The organometallic cations had all refined quite reasonably, however, to configurations identical within experimental error. The methyl group at C(9) was seen on difference maps to be clearly in the exo position with respect to the metal atom. The determination of the stereochemistry of addition to $Fe(C_5H_5)(C_{13}H_9)$ was the primary purpose in the structural analysis and this had been accomplished at this point. No attempts were made at further refinement, because of the uncertainty of obtaining final results due to the anion disorder, and because the large number of atoms caused further attempts to be very expensive.

Results

A suspension of the yellow salt $[Fe(C_5H_5)(\eta^6\text{-}C_{13}H_{10})]PF_6$ in benzene reacts with potassium *tert*-butoxide to give a deep green, air-sensitive solution and a white insoluble solid (presumably KPF_6). Both the air sensitivity and the color suggest that something unusual had occurred; in contrast, ferrocene and the various cyclopentadienyl(indenyl)iron compounds that we had worked with earlier[5] are yellow to red, and of moderate stability in air.

A ^1H NMR spectrum of the green solution indicates that coordination of the metal to one six-membered ring of the fluorenyl ligand is still retained in this compound (Table I). Two sets of resonances for the protons on the six-membered rings are seen. Two doublets and two triplets, $J = 8$ Hz, appear in the range δ 7.2–8.1, assigned to protons in the uncomplexed six-membered ring. Another set of two doublets and two triplets, $J = 6$ Hz, appears in the range δ 4.4–6.1. The upfield shift and reduced coupling constant are typical of protons bound to a transition metal-complexed arene ring. Resonances of appropriate intensity, assigned to the cyclopentadienyl protons at δ 3.24 and to the proton on C(9) at δ 6.12 are also found.

Similar information is obtained from the ^{13}C NMR spectrum (Table II). Four signals in the range δ 115–125 are assignable to the protonated carbons in the uncomplexed six-

Table V. Positional Parameters for $Fe(C_5H_5)(C_{13}H_9)$[a]

Molecule A	x	y	z	Molecule A	x	y	z
C18	1115 (6)	2656 (4)	0690 (4)	C1	3180 (6)	4839 (4)	0935 (3)
Fe	1540.9 (8)	3886.3 (5)	1153.8 (4)	C2	2153 (6)	5236 (4)	1302 (3)
H1[b]	3256	5086	0481	C3	1899 (6)	4835 (4)	1906 (3)
H2	1598	5808	1134	C4	2638 (6)	4019 (4)	2141 (3)
H3	1186	5133	2170	C5	4582 (6)	2109 (4)	2347 (3)
H4	2413	3714	2556	C6	5486 (7)	1353 (4)	2308 (3)
H5	3955	2158	2709	C7	6343 (7)	1293 (4)	1798 (4)
H6	5528	0849	2645	C8	6363 (6)	1975 (5)	1326 (3)
H7	6971	0732	1773	C9	5181 (6)	3561 (4)	0952 (3)
H8	7002	1923	0968	C10	4125 (5)	4086 (4)	1194 (3)
H9	5688	3702	0560	C11	3704 (5)	3636 (3)	1783 (3)
HP1	1042	3483	−0198	C12	4560 (6)	2793 (4)	1878 (3)
HP2	−0976	4440	0261	C13	5446 (5)	2756 (4)	1364 (3)
HP3	−1405	3719	1377	C14	0656 (6)	3367 (5)	0230 (3)
HP4	0376	2326	1614	C15	−0448 (6)	3886 (4)	0481 (3)
HP5	1894	2177	0648	C16	−0681 (6)	3499 (4)	1086 (3)
				C17	0291 (7)	2739 (4)	1214 (3)

Molecule B	x	y	z	Molecule B	x	y	z
Fe′	−1853.6 (8)	0841.7 (6)	−1347.3 (4)	C17′	−3140 (10)	1798 (5)	−0987 (4)
C1′	−0178 (6)	−0100 (4)	−1514 (3)	C18′	−1941 (9)	1538 (7)	−0484 (4)
C2′	−1499 (7)	−0191 (4)	−1987 (3)	H1′	0188	−0631	−1216
C3′	−2160 (7)	0577 (5)	−2349 (3)	H2′	−1989	−0805	−2074
C4′	−1484 (7)	1452 (4)	−2232 (3)	H3′	−3108	0503	−2690
C5′	0768 (8)	3201 (4)	−1713 (3)	H4′	−1979	2007	−2464
C6′	1902 (8)	3805 (4)	−1426 (3)	H5′	−0121	3433	−2041
C7′	3142 (7)	3483 (5)	−0970 (3)	H6′	1826	4470	−1546
C8′	3293 (6)	2580 (4)	−0798 (3)	H7′	3939	3929	−0764
C9′	2024 (6)	0992 (4)	−1037 (3)	H8′	4187	2353	−0471
C10′	0665 (6)	0719 (4)	−1440 (3)	H9′	2779	0583	−0757
C11′	−0082 (6)	1526 (4)	−1774 (3)	HP1′	−1396	0221	−0047
C12′	0883 (6)	2301 (4)	−1545 (3)	HP2′	−3747	−0338	−0859
C13′	2146 (6)	1953 (4)	−1094 (3)	HP3′	−4956	1026	−1517
C14′	−2085 (8)	0608 (6)	−0378 (3)	HP4′	−3327	2429	−1175
C15′	−3370 (8)	0308 (5)	−0818 (4)	HP5′	−1127	1949	−0246
C16′	−4005 (7)	1038 (6)	−1172 (3)				

[a] The positional parameters have all been multiplied by 10^4. The estimated standard deviation in the last digit is given in parentheses in this and in the other tables. [b] The hydrogen parameters are the idealized coordinates used for the final least-squares cycle.

membered ring, by comparison to the spectra of free $C_{13}H_{10}$ and $[Fe(C_5H_5)(C_{13}H_{10})]^+$. The quaternary carbons in this ring (and the complexed ring) are distinguishable by their lower intensity due to the lack of enhancement by the nuclear Overhauser effect. They appear at δ 120 and 125, shifted upfield some 20 ppm from the corresponding carbon resonances in $[Fe(C_5H_5)(C_{13}H_{10})]^+$. The complexed six-membered ring protonated carbons appear in the range δ 69–77, shifted upfield from the corresponding resonances in $[Fe(C_5H_5)(C_{13}H_{10})]^+$ by ~10 ppm. The quaternary carbons in the complexed six-membered ring resonate at δ 68 and 76, shifted upfield from the corresponding resonance in the protonated cation by ~30 ppm. The cyclopentadienyl carbon resonances of $Fe(C_5H_5)(C_{13}H_9)$ are at δ 72.4, shifted upfield from that of $[Fe(C_5H_5)(C_{13}H_{10})]^+$ by 6 ppm. These shifts to higher field can be explained by the increased electron density on the carbon atoms in the ligand in the deprotonated species. Presumably this increased electron density is located primarily on the five-membered ring, but is partially delocalized through the complexed six-membered ring and also to the $Fe(C_5H_5)^+$ group. The resonance for C(9) of the five-membered ring in $Fe(C_5H_5)(C_{13}H_9)$ is found at δ 86.8, shifted downfield by 49 ppm as compared to $[Fe(C_5H_5)(C_{13}H_{10})]^+$. This can be explained by the effect of rehybridization of C(9) from sp^3 to sp^2, which must be dominant over the effect of increased electron density at this carbon atom.

Well-shaped single crystals of $Fe(C_5H_5)(C_{13}H_9)$ were grown by slow evaporation of a filtered toluene-heptane solution under a nitrogen stream. After mounting the crystals in capillaries sealed under argon, satisfactory x-ray diffraction data were obtained. The space group was uniquely determined to be $P2_1/c$, and density measurements indicated $Z = 8$. This requires the presence of two molecules in the crystallographically independent unit. Solution of the structure confirmed this, and refinement by standard techniques converged to discrepancy factors $R_1 = 4.5\%$ and $R_2 = 4.9$.

The two crystallographically independent molecules are well separated, with no intermolecular distances less than 2.5 Å being observed. They are almost identical, with only minor conformational differences. A drawing of molecule A is presented in Figure 1, along with several selected bond distances. Other bond distances and angles are given in Tables III and IV.

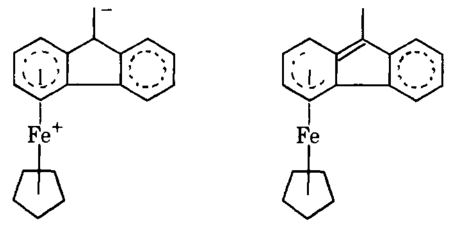
The crystal structure determination confirms the original prediction, from NMR evidence, that coordination of the iron atom to one of the six-membered rings on the fluorenyl ligand is retained. In addition, it provides an insight into the bonding in this species. It may be noted here that two limiting repre-

Table VI. Anisotropic Thermal Parameters ($\times 10^4$)[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Molecule A						
Fe	83 (1)	38.5 (5)	19.5 (2)	−3.4 (6)	3.6 (4)	−0.8 (3)
C1	108 (9)	53 (4)	26 (2)	−12 (5)	6 (3)	10 (2)
C2	115 (9)	35 (4)	36 (2)	−8 (4)	−6 (4)	1 (2)
C3	123 (9)	49 (4)	27 (2)	2 (5)	5 (3)	−11 (2)
C4	114 (9)	43 (4)	21 (2)	−5 (5)	2 (3)	−3 (2)
C5	104 (9)	58 (4)	27 (2)	3 (5)	3 (3)	10 (2)
C6	132 (10)	68 (5)	39 (3)	15 (6)	0 (4)	13 (3)
C7	136 (11)	50 (5)	45 (3)	17 (5)	0 (4)	−6 (3)
C8	93 (9)	72 (5)	40 (3)	3 (5)	18 (4)	−7 (3)
C9	78 (8)	77 (5)	25 (2)	−4 (5)	9 (3)	6 (2)
C10	83 (8)	51 (4)	21 (2)	−20 (4)	−1 (3)	5 (2)
C11	82 (8)	41 (4)	21 (2)	−7 (4)	−1 (3)	−1 (2)
C12	91 (8)	46 (4)	24 (2)	−4 (4)	−5 (3)	1 (2)
C13	77 (8)	55 (4)	23 (2)	0 (4)	1 (3)	−1 (2)
C14	120 (10)	87 (5)	21 (2)	−37 (6)	10 (3)	−16 (3)
C15	113 (9)	66 (4)	26 (2)	−8 (5)	−2 (4)	1 (2)
C16	95 (8)	64 (4)	27 (2)	−20 (5)	13 (3)	−8 (2)
C17	154 (11)	46 (4)	33 (2)	−29 (5)	3 (4)	0 (2)
C18	115 (10)	42 (4)	48 (3)	−3 (5)	−2 (4)	−17 (3)
Molecule B						
Fe′	96 (1)	54.6 (6)	20.6 (3)	−2.4 (6)	10.6 (4)	−3.2 (3)
C1′	136 (10)	52 (4)	33 (2)	14 (5)	20 (4)	4 (2)
C2′	163 (11)	59 (4)	26 (2)	−13 (5)	16 (4)	−7 (2)
C3′	134 (10)	80 (5)	20 (2)	−6 (6)	5 (3)	−7 (2)
C4′	161 (11)	65 (4)	20 (2)	25 (6)	17 (4)	7 (2)
C5′	233 (14)	54 (5)	30 (2)	27 (6)	38 (5)	6 (3)
C6′	260 (15)	44 (4)	31 (2)	−12 (6)	36 (5)	1 (2)
C7′	195 (13)	56 (4)	35 (2)	−33 (6)	45 (4)	−8 (2)
C8′	125 (10)	65 (5)	30 (2)	2 (5)	26 (4)	−6 (2)
C9′	123 (9)	56 (4)	29 (2)	27 (5)	7 (4)	5 (2)
C10′	112 (9)	53 (4)	23 (2)	13 (5)	18 (3)	0 (2)
C11′	139 (10)	41 (3)	23 (2)	−3 (5)	27 (4)	−5 (2)
C12′	143 (10)	45 (4)	23 (2)	21 (5)	29 (4)	2 (2)
C13′	151 (10)	39 (4)	29 (2)	12 (5)	35 (4)	2 (2)
C14′	144 (12)	153 (8)	26 (2)	9 (8)	23 (4)	14 (4)
C15′	162 (12)	84 (6)	44 (3)	−35 (7)	41 (5)	0 (3)
C16′	111 (10)	109 (6)	36 (2)	16 (7)	17 (4)	−5 (3)
C17′	271 (17)	60 (5)	60 (4)	8 (7)	75 (6)	−7 (3)
C18′	199 (14)	151 (8)	39 (3)	−98 (10)	55 (5)	−48 (4)

[a] Anisotropic temperature factors are of the form $\exp\{-[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]\}$.

sentations for bonding are possible; these are drawn below. One is a cyclohexadienyl–iron structure, with an uncoordinated exocyclic double bond required between C(9) and C(10). The second is a zwitterionic formation with a negative charge at C(9) and a positive charge residing at the metal. The crucial differences between these two structures are several bond lengths including those between C(10) and Fe, and between C(9) and C(10), and the planarity or lack of it for the fluorenyl ligand. Of course a structure intermediate between these two is probable (and in fact is found).



The fluorenyl ligand shows substantial deviation from planarity (see Table VII, plane 1). This can best be visualized by considering the ligand in segments. First, the carbon atoms in the uncomplexed six-membered rings of both molecules are coplanar (plane 4) within 0.009 Å. However, the complexed six-membered rings are not coplanar, primarily caused by a displacement of C(10) away from the iron atom. The remaining carbons in the complexed six-membered ring (plane 2) are coplanar within 0.027 Å. The C(10) atoms are 0.151 and 0.134 Å out of this plane in molecules A and B, respectively, in the direction opposite the metal. The dihedral angle formed between plane 2 and the plane formed by C(10), C(11), and C(1) (plane 3) is 11.0° in molecule A and 10.1° in molecule B. Planes 2 and 4, defining the complexed and uncomplexed rings, respectively, form dihedral angles of 7.7 and 2.0° in molecules A and B. It is here that the conformations of the two molecules differ most noticeably. The ends of the fluorenyl ligand are bowed towards the iron atom to a higher degree in molecule A than in molecule B. The cause of this is probably a subtle difference in crystal packing, and the energy difference between the two conformations is probably very slight.

For comparison, dihedral angles for several cyclohexadienyl-metal compounds are noted. In η^5-cyclohexadienylmanganese tricarbonyl[15] the methylene carbon is substantially out of the plane of the other carbon atoms in this ligand; the dihedral angle is 43°. The same angle is observed in the crystal structure of bis(6-*tert*-butyl-1,3,5-trimethylcyclohexadienyl)iron.[16] The degree of bending found here for $Fe(C_5H_5)(C_{13}H_9)$ is 11.0° and 10.1°, less than in these examples, but indicative of some cyclohexadienyl character in the bonding of the complex. The polycyclic nature of the ligand

Table VII. Least-Squares Planes for $Fe(C_5H_5)(C_{13}H_9)$

Atom	Distance from plane (Å)	Atom	Distance from plane (Å)	Atom	Distance from plane (Å)	Atom	Distance from plane (Å)
Plane 1A		Plane 1B		Plane 3A		Plane 3B	
$-0.6451X - 0.4957Y$		$0.6372X - 0.1645Y$		$-0.5009X - 0.6242Y$		$0.5247X - 0.2188Y - 0.8227Z$	
$0.5815Z + 6.3523 = 0$[b]		$- 0.7530Z - 2.6355 = 0$		$- 0.5995Z + 6.7837 = 0$		$- 2.7061 = 0$	
C1*[b]	0.148	C1′*	−0.105	C1*	0.0	C1′*	0.0
C2*	0.112	C2′*	−0.020	C10*	0.0	C10′*	0.0
C3*	−0.012	C3′*	0.043	C11*	0.0	C11′*	0.0
C4*	−0.067	C4′*	0.015				
C5*	0.003	C5′*	−0.015	Plane 4A		Plane 4B	
C6*	0.065	C6′*	−0.010	$-0.6648X - 0.4497Y$		$0.6336X - 0.1623Y - 0.7564Z$	
C7*	0.087	C7′*	−0.011	$- 0.5965Z + 6.3396 = 0$		$-2.6355 = 0$	
C8*	0.020	C8′*	−0.004	C5*	−0.002	C5′*	0.003
C9*	−0.098	C9′*	0.066	C6*	−0.006	C6′*	0.004
C10*	−0.093	C10′*	0.052	C7*	0.009	C7′*	−0.005
C11*	−0.072	C11′*	0.008	C8*	−0.002	C8′*	−0.002
C12*	−0.043	C12′*	−0.023	C13*	−0.006	C13′*	0.009
C13*	−0.051	C13′*	0.004	C12*	0.008	C12′*	−0.009
Fe	1.580	Fe′	−1.573	C9	0.015	C9′	0.069
Plane 2A		Plane 2B		Fe	1.774	Fe′	−1.557
$-0.6562X - 0.5489Y$		$0.6656X - 0.1904Y - 0.7217Z$		Plane 5A		Plane 5B	
$-0.5178Z + 6.4970 = 0$		$- 2.4685 = 0$		$-0.6393X - 0.5870Y$		$0.6889X - 0.1925Y - 0.6989Z$	
C1*	0.007	C1′*	−0.018	$0.4967Z + 3.4379 = 0$		$+0.8345 = 0$	
C2*	−0.001	C2′*	0.012	C14*	0.002	C14′*	−0.003
C3*	−0.012	C3′*	0.010	C15*	−0.002	C15′*	0.008
C4*	0.020	C4′*	−0.027	C16*	0.002	C16′*	−0.009
C11*	−0.013	C11′*	0.022	C17*	0.000	C17′*	0.006
Fe	1.558	Fe′	−1.555	C18*	−0.002	C18′*	−0.002
C10	−0.151	C10′	0.134	Fe	−1.653	Fe′	1.657
C9	−0.157	C9′	0.193				

Angles between Normals of Planes				Angles between Normals of Planes			
Planes	Angle (deg)	Planes	Angle (deg)	Planes	Angle (deg)	Planes	Angle (deg)
1A, 5A	7.2	1B, 5B	4.6	2A, 3A	11.0	2B, 3B	10.1
2A, 5A	2.7	2B, 5B	1.9	2A, 4A	7.3	2B, 4B	3.1

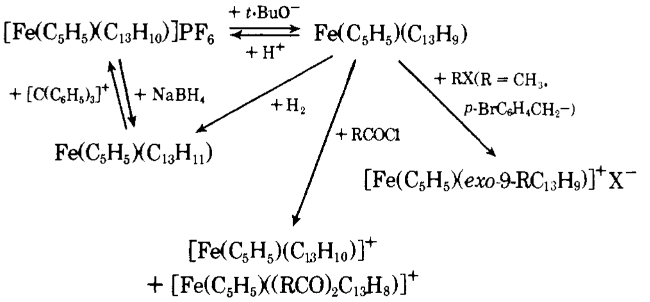
[a] The equation of each least-squares plane is expressed in orthogonal coordinates (X, Y, Z) which are related to the triclinic cell coordinates (x, y, z) by the transformation: $X = x \sin\gamma + 2 \cos\phi$, $Y = y + z \cos\alpha + x \cos\gamma$, and $Z = z \cos\rho$ where $\cos\phi = (\cos\beta - \cos\gamma \cos\alpha/\sin\gamma$ and $\cos\rho = (1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2 \cos\alpha \cos\beta \cos\gamma)^{1/2} \sin\gamma$. In this transformation X lies in the xy plane, Y coincides with y, and Z is perpendicular to the xy plane. [b] Atoms used in calculating the least-squares plane are marked with an asterisk.

probably prohibits a high degree of bending around the C(1)-C(11) axis. Of course, a metal arene structure, as represented by the zwitterionic formulation, should show no significant deviation from planarity in the complexed six-membered ring.

Variations of corresponding carbon-carbon bond lengths in the two molecules of $Fe(C_5H_5)(C_{13}H_9)$ are not significant. Figure 2 compares the averaged bond lengths of molecules A and B with the published symmetry-averaged bond lengths of two amine-complexed alkali metal salts of the fluorenide anion.[13] The bonds C(9)-C(13) and C(10)-C(11), formally single bonds in the cyclohexadienyl structure, are lengthened by 0.011 and 0.037 Å with respect to the bond lengths in the free anion. The C(9)-C(10) bond is shortened by 0.029 Å. These changes are in this direction predicted for a cyclohexadienyl structure. However, the cyclohexadienyl resonance structure also predicts a lengthening of the C(1)-C(10) bond, which is not observed. The magnitude of the bond length changes is small, and other less readily explainable differences of comparable magnitude exist. For example, the C(5)-C(12) bond length in $Fe(C_5H_5)(C_{13}H_9)$ is 0.036 Å shorter than the same distance in the free anion. More significant is the fact that in the complexed six-membered ring the average carbon-carbon bond length is 1.419 Å,while in the uncomplexed six-membered ring the average carbon bond length is 1.392 Å. This increase in bond length on complexation can be explained by donation of bonding π-electron density to the metal atom from the fluorenyl ligand.

The iron-carbon distances of the cyclopentadienyl ring average 2.034 Å. This compares favorably to the reported average Fe-C distance of 2.040 Å for other cyclopentadienyliron complexes.[17] The Fe-C bond lengths in the complexed six-membered ring exhibit variations reminiscent of cyclohexadienyl systems. The center carbon of the dienyl unit, C(3), is nearest the iron atom, at an average distance of 2.036 Å. The inner carbons, C(2) and C(4), are at intermediate distances from the metal, 2.050 and 2.074 Å. The outer carbons, C(1) and C(11), are farthest among the dienyl carbon atoms from the metal, at 2.113 and 2.175 Å. This structural pattern has been observed in other cyclohexadienyl transition metal complexes.[15,16] Farther from the iron atom than the dienyl carbons is C(10), at an average Fe-C distance of 2.308 Å. Here lies the significant difference from other cyclohexadienyl[15,16] complexes, in which the saturated carbon of this ring lies farther than 2.7 Å from the metal atom. In $Fe(C_5H_5)(C_{13}H_9)$, C(10) is definitely within bonding distance of the iron. This is evidence for the zwitterionic bonding representation.

Most of the chemical reactions of $Fe(C_5H_5)(C_{13}H_9)$ appear to be dictated by carbanion character at C(9). Addition of electrophiles occurs rapidly in benzene at room temperature, giving substituted fluorene–iron compounds. The chemistry of this compound is summarized below.



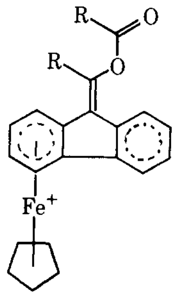
Protonation of $Fe(C_5H_5)(C_{13}H_9)$ can be accomplished with protonic acids, regenerating $[Fe(C_5H_5)(C_{13}H_{10})]^+$ in a nonstereospecific reaction. When a solution of $Fe(C_5H_5)(C_{13}H_9)$ in dry benzene is treated with anhydrous DCl, the rapidly formed $[Fe(C_5H_5)(C_{13}H_{10})]^+$ is a mixture of d_2, *exo*-d_1, *endo*-d_1, and d_0 at the methylene group, as indicated by a $^1H\{^2D\text{-decoupled}\}$ NMR spectrum. Relative amounts were not measured due to peak overlap. When a benzene solution of $Fe(C_5H_5)(C_{13}H_9)$ is placed in contact with D_2O and stirred, no noticeable reaction is apparent after 15 min. Addition of DCl at this point results in immediate precipitation of $[Fe(C_5H_5)(C_{13}H_{10})]^+$. After metathesis with NH_4PF_6, an ^1H NMR spectrum indicates complete deuterium substitution at the C(9) methylene group. These reactions suggest that exo and endo protonations occur at comparable rates. Proton–deuterium ion exchange with solvent also occurs readily and nonspecifically.

Further evidence in another system corroborates the nonspecificity of the protonation reaction. Solutions of $Fe(C_5H_5)(9\text{-}CH_3C_{13}H_8)$ can be generated by deprotonation of $[Fe(C_5H_5)(9\text{-}CH_3C_{13}H_9)]PF_6$. Reprotonation with CF_3CO_2H results in a mixture of 9-*exo*- and 9-*endo*-methylfluorenecyclopentadienyliron(II) cations. The 9-*endo*-methyl isomer is present in slight excess over the exo isomer, the difference being very small however.

Methyl iodide, or more cleanly, CH_3OSO_2F, readily reacts with $Fe(C_5H_5)(C_{13}H_9)$ to give after metathesis $[Fe(C_5H_5)(9\text{-}CH_3C_{13}H_9)]PF_6$ in good yield. The ^1H NMR spectrum displays only one doublet in the methyl region, indicating the addition to be stereospecific, to at least about 90%, the limits imposed by the ^1H NMR intensity measurements. A single-crystal x-ray diffraction study of $[Fe(C_5H_5)(9\text{-}CH_3C_{13}H_9)]PF_6$ was undertaken to determine the stereochemistry of this compound. The compound crystallizes in the space group $P\bar{1}$ with $Z = 8$, which requires four cations and four anions to be present in the crystallographically independent unit. Solution of the structure by standard heavy atom methods confirms this. Although difficulties were encountered in refinement due to disorder in two of the PF_6^- anions, the organometallic cations all refine in a well-behaved manner to configurations identical within the rough error limits. The discrepancy factors (isotropic refinement) are $R_1 = 13.2\%$ and $R_2 = 16.9\%$. Difference maps clearly demonstrate that the methyl group (shaded atom) is in the exo position at C(9). Since the primary information desired had been obtained and severe difficulty was found in modeling the disorder in the anions, further attempts at refinement of this structure were not carried out.

A similar reaction of $Fe(C_5H_5)(C_{13}H_9)$ with $p\text{-}BrC_6H_4CH_2Br$ was carried out to yield $[Fe(C_5H_5)(9\text{-}p\text{-}BrC_6H_4CH_2C_{13}H_9)]Br$, which was converted to the PF_6^- salt by metathesis. The ^1H NMR spectrum of the product contains one doublet for the methylene group, again indicating stereospecific alkylation. The product is assigned exo stereochemistry, by analogy with the methylation reaction. Trimethylsilyl bromide also reacts with $Fe(C_5H_5)(C_{13}H_9)$ to deposit a yellow oil. However, metathesis and workup result in the isolation only of $[Fe(C_5H_5)(C_{13}H_{10})]PF_6$, presumably due to hydrolysis of the fluorenyl–silicon bond.

A green solution of $Fe(C_5H_5)(C_{13}H_9)$ reacts rapidly at room temperature with acetyl or benzoyl chloride to deposit a yellow oil. Contrary to expectation, a cyclopentadienyl(9-acylfluorene)–iron complex is not formed. An ^1H NMR spectrum shows the presence of $[Fe(C_5H_5)(C_{13}H_{10})]^+$ and a diacylated cation. In the case of the benzoyl compound, this product mixture is separable and the diacylated cation is identified as an enol benzoate by its ^1H NMR and IR spectra. Formation of this product probably occurs by initial acylation at C(9) to give a monoacylated cation. The remaining proton at C(9) in this intermediate, in an enolic position, has an enhanced acidity and is rapidly transferred to a molecule of $Fe(C_5H_5)(C_{13}H_9)$ giving $[Fe(C_5H_5)(C_{13}H_{10})]^+$ and an enolate zwitterion, which is subsequently acylated at oxygen to give the enol benzoate product, shown below. This proposed mechanism of formation requires that proton transfer from the monoacylated cation is rapidly compared with acylation. Attempts to synthesize substantial amounts of monoacylated cation by inverse addition experiments, in which $Fe(C_5H_5)(C_{13}H_9)$ solution is added very slowly to an excess of acyl halide, resulted only in disubstitution.



All of the reactions with electrophilic reagents emphasize the zwitterionic formulation of bonding in $Fe(C_5H_5)(C_{13}H_9)$. In hope that reactions appropriate to a cyclohexadienyl–metal structure might also be observed, hydrogenation was attempted. It was determined that $Fe(C_5H_5)(C_{13}H_9)$ in benzene reacts with H_2 (1 atm, Pd/C catalyst) quite slowly. Only after 36 h did hydrogen uptake cease, after approximately 0.66 equiv had been absorbed. The red solution was chromatographed on Florisil with hexane eluent to give first a small yellow band which was not identified followed by a larger red band. The ^1H NMR spectrum of the product isolated from the red band indicates a mixture of the two isomers. The major isomer could be isolated by fractional crystallization in 5% overall yield. The total yield of product is about 30–40%.

Hydrogenation in tetrahydrofuran rather than benzene results in uptake of a full equivalent of hydrogen, but workup affords a smaller yield of the same products. No hydrogen uptake is observed in the absence of catalyst.

The 270-MHz ^1H NMR spectral data for the major isomer $Fe(C_5H_5)(C_{13}H_{11})$ are presented in Table I. The spectrum can be best rationalized as a structure in which hydrogen was added at the C(9) and at either the C(1) or C(4) on the complexed ring, rather than across the double bond. The spectrum exhibits the expected resonances for the uncomplexed arene protons and an AB quartet for the 9-methylene group. The cyclohexadienyl portion of the spectrum is of primary interest. The lowest signal, at δ 6.37, is a doublet. Many examples of cyclopentadienylcyclohexadienyliron compounds exist,[18,19] and the lowest field peak, in the range δ 6–7, is the center proton of the dienyl unit. Since this resonance is coupled to only one other proton in $Fe(C_5H_5)(C_{13}H_{11})$, the center of the dienyl unit must be at C(1) or C(4). The next signal is a triplet at δ 4.15, corresponding to the inner proton of the dienyl unit, coupled to the center and outer protons. The outer proton of the dienyl unit appears as a triplet, coupled to the inner proton and to the endo proton of the methylene group in the cyclohexadienyl ring. The exo proton of this methylene group does not couple to the adjacent outer proton of the dienyl unit because the Karplus angle[20] is ~90°. The remaining resonances are attributed to the methylene group. The exo proton is a doublet at δ 2.22 with a geminal coupling constant of 12.7 Hz and the endo proton is a doublet of doublets, coupled both to the exo proton and the outer dienyl proton. All chemical shifts and coupling constants are consistent with known examples of compounds of this type.

Arenecyclopentadienyliron cations[18,19] undergo hydride addition to give cyclopentadienylcyclohexadienyliron species. Similarly, $[Fe(C_5H_5)(C_{13}H_{10})]PF_6$ reacts with $NaBH_4$ to give $Fe(C_5H_5)(C_{13}H_{11})$ in 64% yield. Again a mixture of isomers is obtained. However, one isomer (the one which had previously been isolated in pure form) predominates, representing about 90% of the overall product. This cyclohexadienyl compound may in turn be reacted with a hydride abstracting reagent such as triphenylcarbenium ion[18,19,21] to regenerate the starting material.

Discussion and Conclusions

The unexpected structure of $Fe(C_5H_5)(C_{13}H_9)$ is the focal point of the work described in this paper. Rather than assuming a ferrocene-like structure, with the metal coordinated to five-membered rings of the cyclopentadienyl and fluorenyl ligands, a structure retaining metal coordination to one six-membered ring of the latter ligand is found.

Initial concern was directed to rationalization of this structure with a simple bonding model. Two limiting bonding representations can be considered. The first is a zwitterionic structure, with the negative charge localized at C(9) and the positive charge on the metal. The second structure involves coordination of the fluorenyl ligand to the metal through five carbons (C(1), C(2), C(3), C(4), C(11)); in this formulation C(10) would not be coordinated to the metal but would be bonded to C(9) with a double bond. This is formally a methylenecyclohexadienyl-metal structure.

Not surprisingly, the structural data show that neither limiting structure precisely defines the bonding in this compound. The coordinated six-membered ring of the fluorenyl ligand is not planar with C(10) above the plane. However, this distortion from planarity is not great; the angle made is only about 11°, in contrast to angles of more than 40° established for most cyclohexadienyl complexes. The fusion of five- and six-membered rings will constrain this bending. Still the iron atom is close to C(10); certainly it is well within bonding distance, and far closer than normal van der Waals distances. It seems most unlikely that these atoms could be constrained to this short distance if some degree of bonding between metal and C(10) were not involved. Bond length data, summarized in Figure 2, are also undecisive to distinguish the best structure. Particularly, the C(9)–C(10) distance is rather close to the C(9)–C(13) distance, intermediate between single and double bond character.

The chemistry of $Fe(C_5H_5)(C_{13}H_9)$ argues more strongly for structure approaching the zwitterionic representation. The formation of this compound from $[Fe(C_5H_5)(C_{13}H_{10})]PF_6$ requires a strong base such as *tert*-butoxide ion; methoxide ion is not strong enough. This means that the pK_a for this compound is probably between 16 and 19, the pK_a values for methanol and *tert*-butyl alcohol, respectively,[22] uncertainty being due to solvent; pK_a comparisons in these solvents are not available. This is not vastly different from the pK_a for fluorene ($pK_a \sim 23$). If the basicity of $Fe(C_5H_5)(C_{13}H_9)$ and the fluorenide anion are comparable it is likely that the charge distributions of the two species are somewhat similar. In the fluorenide anion substantial negative charge (−0.4 e) resides at C(9); the remaining negative charge is distributed in the six-membered rings.[23] It may be concluded that substantial negative charge also resides at C(9) in the complex.

The reactivity of the complex $Fe(C_5H_5)(C_{13}H_9)$ argues in favor of this structure. The complex is a strong nucleophile and readily displaces halide ion from CH_3I, p-$BrC_6H_4CH_2Br$, and fluorosulfonate ion from CH_3OSO_2F. It also is easily protonated by protonic reagents. Parenthetically it is noted that the alkylation reactions are stereospecific, the alkyl group entering from the least hindered side. There is apparently little distinction on protonation. With the 9-methylfluorenyliron compound both endo and exo products are obtained in comparable quality. With $Fe(C_5H_5)(C_{13}H_9)$ and DCl rapid proton–deuterium exchange occurs giving a mixture of d_0, d_1, and d_2 products. With DCl and D_2O, only a d_2 complex is formed.

A paper has appeared recently by Jaouen et al.[24] which discusses a related type of reactivity. In arenechromium tricarbonyl complexes enhanced acidity has been observed for α-protons in alkyl substituents on the arene ring. In the presence of strong bases deprotonation is accomplished; products of this reaction have not been isolated directly but were subsequently alkylated. Similarly, base catalyzed proton–deuterium exchange of exo protons only was reported for indanechromium tricarbonyl;[25] contrasting with our work is the specific stereochemistry of this reaction.

It is appropriate to consider at least qualitatively why a compound with this structure might result. There are two possible rationales, kinetic and thermodynamic. Either the observed structure is the preferred one, or, alternatively, the observed structure is less stable, but interconversion from η^6 to η^5 coordination to the fluorenyl ligand is not rapid. Only indirect evidence can be provided to distinguish these alternatives.

We are less inclined at this time to favor the kinetic argument. The original idea for this study was that ring migration ought to occur. Facile metal migration between five- and six-membered rings had been seen in the protonation–deprotonation reaction of bis(indenyl)iron.[5] A more direct comparison is found in the deprotonation reaction of $Cr(\eta^6\text{-}C_{13}H_{10})(CO)_3$, which is believed to give $[Cr(\eta^5\text{-}C_{13}H_9)(CO)_3]^-$.[3] More recently we observed the relatively slow migration of coordination[5] in $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$, to form $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$; the latter species is a known compound.[2] However, all attempts here to convert $Fe(C_5H_5)(\eta^6\text{-}C_{13}H_9)$ to the isomeric $Fe(C_5H_5)(\eta^5\text{-}C_{13}H_9)$ were unsuccessful. This reaction did not occur at room temperature for prolonged periods, nor did it occur at higher temperatures for either solid or solutions; forcing conditions led only to complete decomposition.

The migration of metal coordination might be an interesting and substantial problem. A recent theoretical paper[26] is at least peripherally related to this work. Calculations suggest a substantial barrier to interconversion between methylenecyclohexadienyliron tricarbonyl cation and an isomeric species in which the iron tricarbonyl group is coordinated to the trimethylenemethane fragment, the remaining uncoordinated allyl portion of the molecule bearing the positive charge. If the metal atom moves to a position intermediate between these two structures the principal ligand–metal interactions are eliminated according to symmetry considerations. A somewhat similar situation may be involved here.

Assuming a kinetic barrier is not the reason that $Fe(C_5H_5)(C_{13}H_9)$ has its unusual structure, it is appropriate to assess the other alternative, that the observed structure may in fact be the thermodynamically preferred one. It is possible to rationalize this result, qualitatively, and after the fact. First it has been recognized that the supposed similarity of fluorenide anion to the cyclopentadienide anion is really not accurate. It is suggested that metal coordination to the five-membered ring would distort the electronic distribution of the arene rings with concurrent loss of aromatic stabilization.[2] Simple calculations on the fluorenide ion charge distribution place a substantial negative charge on C(9), −0.4 e; the remaining negative charge is distributed more or less evenly at carbons 1, 3, 6, 8, 11, and 12.[23] There is less negative charge on the five-membered ring of the fluorenyl anion, and this group should be a poorer donor than the cyclopentadienide anion to a metal. Similarly, the LUMO orbitals for the fluorenide anion are substantially on the six-membered rings, and only in small part on the five-membered ring. Thus there should be a poorer overlap between LUMO and filled metal orbitals resulting in less back-donation to the metal. In effect, the η^5-fluorenide anion is a poorer acceptor than the cyclopentadienide anion, and should bond to a metal more weakly.

There are no qualitative bonding arguments against a η^6-fluorenyl structure, except possibly a reservation concerning charge separation. This concern is minimal, though, due to the extent to which the cyclohexadienyl–metal structure is assumed. The negative charge formally assigned on C(9) is expected to be partly delocalized over metal and ligand systems. This delocalization probably accounts for the stabilization of the anionic intermediates in the reactions described by Jaouen[24] and others. This does not speak fully to the question of relative stabilization of the two possible structures, of course; perhaps the problem is really too complex to address directly. Nonetheless a qualitative observation can be suggested. By assuming the observed structure rather than the alternative η^5-fluorenyl structure, the iron atom retains some measure of positive charge; in contrast electron density at the metal in the η^5-fluorenyl complex would be higher. The actual metal electron density would be determined by the ligands' ability to remove charge from the metal. Neither ligand is particularly adept in this regard. On the other hand fluorenyl complexes of other metals with good acceptor ligands might behave differently, and a η^5-structure preferred. Indeed, this is the result for the manganese tricarbonyl system.[6]

Acknowledgment. Fellowship support for J.W.J. from the University of Wisconsin Graduate School and from the National Science Foundation is acknowledged. The Syntex diffractometer and various NMR facilities, all Departmental equipment, were obtained with partial support from the National Science Foundation under their major instrument grants program.

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

References and Notes

(1) P. L. Pauson, *Q. Rev., Chem. Soc.*, **9**, 396 (1955).

(2) R. B. King and A. Efraty, *J. Organomet. Chem.*, **23**, 527 (1970).

(3) K. M. Nicholas, R. C. Kerber, and E. I. Stiefel, *Inorg. Chem.*, **10**, 1519 (1971).

(4) E. Samuel, H. G. Alt, D. C. Hrncir, and M. D. Rausch, *J. Organomet. Chem.* **113**, 331 (1976).

(5) P. M. Treichel and J. W. Johnson, *J. Organomet. Chem.*, **88**, 207, 215, 227 (1975).

(6) J. W. Johnson and P. M. Treichel, *J. Chem. Soc., Chem. Commun.*, 688 (1976).

(7) A. N. Nesmeyanov, N. A. Vol'Kenau, and I. N. Bolesnova, *Dokl. Akad. Nauk SSSR*, **166**, 607 (1966).

(8) R. A. Sparks et al., "Operations Manual, Syntex P$\bar{1}$ Diffractometer", Syntex Analytical Instruments, Cupertino, Calif. 1970.

(9) The integrated intensity (I) was calculated according to the expression $I = [S - (B_1 + B_2)/B_R]T_R$ where S is the scan count, B_1 and B_2 are the background counts, B_R is the ratio of background time to scan time ($B_R = 0.67$ for this data set), and T_R is the scan rate in degrees per minute. The standard deviation of I was calculated as $\sigma(I) = T_R[S + (B_1 + B_2)/B_R{}^2 + q(I)^2]$ where $q = 0.003$.

(10) All crystallographic programs used in structure determination and refinement were written by J. C. Calabrese, with the exception of the direct methods program MULTAN (Main, Woolfson, and Germain). The absorption correction program DEAR (J. F. Blount) uses the Gaussian integration method of Busing and Levy. Plots were made using ORTEP2 (C. K. Johnson).

(11) $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|] \times 100\%$ and $R_2 = \Sigma\omega_i/|F_o| - |F_c||^2/\Sigma\omega_i|F_o|^2] \times 100\%$ where $\omega_i = [\sigma(F)]^{-2}$. Refinement was based on R_2.

(12) Supplementary material available. See note at end of paper.

(13) R. Zerger, W. Rhine, and G. D. Stucky, *J. Am. Chem. Soc.*, **96**, 5441 (1974).

(14) For 1892 reflections $I < 2\sigma(I)$.

(15) M. R. Churchill and F. R. Scholer, *Inorg. Chem.*, **8**, 1950 (1969).

(16) M. Mathew and G. J. Palenik, *Inorg. Chem.*, **11**, 2809 (1972).

(17) P. J. Wheatley, *Persp. Struct. Chem.*, **1**, 1 (1967).

(18) I. U. Khand, P. L. Pauson, and W. E. Watts, *J. Chem. Soc. C*, 2257, 2261 (1968); 116, 2025 (1969).

(19) J. F. McGeer and W. E. Watts, *J. Organomet. Chem.*, **110**, 103 (1976).

(20) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(21) A. N. Nesmayanov, N. A. Vol'kenau, L. S. Shilovtseva, and V. A. Petrakova, *J. Organomet. Chem.*, **85**, 365 (1975).

(22) D. J. Cram, "Fundamentals in Carbanion Chemistry", Academic Press, New York, N.Y., 1965.

(23) J. J. Brooks, W. Rhine, and G. D. Stucky, *J. Am. Chem. Soc.*, **94**, 7339 (1972).

(24) G. Jaouen, A. Meyer, and G. Simonnieux, *J. Chem. Soc., Chem. Commun.*, 813 (1975).

(25) W. S. Trahanovsky and R. J. Card, *J. Am. Chem. Soc.*, **94**, 2897 (1972).

(26) R. Hoffmann and P. Hofmann, *J. Am. Chem. Soc.*, **98**, 598 (1976).

Studies of the Molecular and Electronic Structure of Dicyclopentadienylberyllium

Dennis S. Marynick

Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138. *Received June 14, 1976*

Abstract: The molecular and electronic structure of dicyclopentadienylberyllium is investigated by the method of partial retention of diatomic differential overlap. Six possible structures are considered, and the most stable structure is calculated to be one in which the beryllium is π bonded to one ring and σ bonded to the other, although the structure analogous to ferrocene appears to be only ~6 kcal/mol less stable. No evidence is found for a stable structure of C_{5v} symmetry. Several different mechanisms of intramolecular tautomerism are explored, and the bonding is analyzed in terms of localized molecular orbitals and population analyses.

Since the discovery of ferrocene[1] in 1951, a large number of dicyclopentadienyl–metal complexes have been synthesized. The smallest of these is dicyclopentadienylberyllium, $(C_5H_5)_2Be$.