A Delocalized Two-Electron Three-Center C–H–Metal Interaction. Single Crystal Neutron (30 and 110 K) and X-ray (298 K) Diffraction Study of $[Fe(P(OCH_3)_3)_3(\eta^3\text{-}C_8H_{13})]^+[BF_4]^-$

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Abstract: The crystal and molecular structure of $[Fe(P(OCH_3)_3)_3(\eta^3\text{-}C_8H_{13})][BF_4]$ has been determined at 298 K by X-ray diffraction and at 110 and 30 K by neutron diffraction techniques. The crystals belong to the monoclinic space group $P2_1/c$ [C_{2h}^5; no. 14] with unit cell dimensions of a = 9.018 (2) Å, b = 18.815 (4) Å, c = 16.974 (2) Å, β = 101.75 (1)°, and V = 2819.7 Å^3 at 298 K; a = 8.947 (6) Å, b = 18.508 (13) Å, c = 16.594 (11) Å, β = 101.71 (7)°, and V = 2690.7 Å^3 at 110 K; and a = 8.936 (2) Å, b = 18.401 (4) Å, c = 16.515 (5) Å, β = 101.75 (3)°, and V = 2658.7 Å^3 at 30 K, with Z = 4. Full-matrix least-squares refinement of the X-ray data led to $R(F_o) = 0.046$ and $R_w(F_o) = 0.043$ for the 3701 reflections (368 variables) with $F_o > 3\sigma(F_o)$. Full-matrix least-squares refinement of the neutron data led to $R(F_o^2) = 0.142$ and $R(F_o) = 0.156$ for all 3784 independent data at 110 K and to $R(F_o^2) = 0.077$ and $R(F_o) = 0.075$ for all 6354 independent data at 30 K. Considering only the nonhydrogen atoms, the coordination sphere about the iron atom would correspond to that of a distorted square pyramid with one axial and two basal phosphite ligands and with the allylic portion of the C_8H_{13} ligand encompassing the remaining two basal positions. The most significant structural finding is the existence of a C–H ··· Fe three-center interaction which contains a very short Fe···H distance of 1.874 (3) Å at 30 K. The hydrogen occupies the sixth coordination site of a distorted octahedron about the otherwise formally 16-electron Fe atom, thus relieving the coordinative and electronic unsaturation of the cationic iron complex. An even more striking feature in this three-center interaction is the *stretched* aliphatic C–H bond, the longest ever observed in a crystal, with an internuclear separation of 1.164 (3) Å. The other aliphatic C–H distances in the C_8H_{13} ring range from only 1.092 (3) to 1.100 (3) Å. A discussion of the origin and the nature of the unusual C–H ··· Fe interaction, and its relationship to C–H bond "activation" in catalysis, is presented.

Introduction

The activation of C–H bonds by the metal center of a discrete molecular complex is a critical step in the homogeneous catalysis of many reactions involving the efficient synthesis or transformation of hydrocarbons.[2] In the past, the nature of the C–H ··· M (M = transition metal) intermediate has been investigated by various spectroscopic and indirect structural methods.[3-8] More direct evidence has occasionally been obtained from crystal structures, although most of these results are based on X-ray diffraction data which do not provide accurate hydrogen positions relative to the metal atom center.

Of particular relevance is the study of the pyrazolylborate complex $\{[(C_2H_5)_2B(\text{pyrazolyl})_2]Mo(CO)_2(\eta^3\text{-}C_3H_5)\}$ by Trofimenko.[3,4] The observed low-frequency (2704, 2664 cm^{-1}) C–H stretching bands in the infrared spectrum, and the upfield shift in the ^{1}H NMR of one of the methylene groups of the $(C_2H_5)_2B$ moiety, indicated a bridging C–H ··· Mo interaction. In X-ray diffraction structural studies of the closely related complexes $\{[(C_2H_5)_2B(\text{pyrazolyl})_2Mo(CO)_2(\eta^3\text{-}CH_2CPhCH_2)\}$ and $\{[(C_2H_5)_2B(\text{pyrazolyl})_2]Mo(CO)_2(\eta^3\text{-}C_7H_7)\}$, Cotton and co-workers[9] reported H ··· Mo distances of ~2.15 and ~1.93 Å, respectively. These values were determined after correcting the observed hydrogen positions for the systematically underestimated C–H distances derived using X-ray data. If the short CH ··· Mo approach is considered a two-electron three-center (2e-3c) C ··· H ··· Mo bond, these formally 16-electron systems thereby achieve an inert-gas configuration by delocalizing the electrons in the C–H bond. However, the actual degree of electron delocalization throughout the three-center moiety could not easily be ascertained.

Dihapto norbornene and norbornadiene complexes have been reported which exhibit possible C–H–metal interactions involving one of the bridge methylene protons. A recent X-ray structure analysis of $[Cu(\text{diethylenetriamine})(C_7H_{10})]^+$ indicated the presence of a Cu–H distance of 2.01 (15) Å.[10] In the X-ray study of $(\eta^5\text{-}C_5H_5)Mn(CO)_2(C_7H_8)$, the hydrogen atoms were not located but a close CH ··· Mn approach is very strongly indicated.[11]

Strong spectroscopic evidence for $C_\alpha H_\alpha$–metal interactions in a series of electron-deficient tantalum-alkyl and -alkylidene complexes has been reported by Schrock and co-workers.[12a] From the neutron diffraction determined structure of $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$, a Ta–$C_\alpha$–$H_\alpha$ angle of 84.8 (2)° and a considerably lengthened C_α–H_α distance of 1.131 (3) Å were observed.[12b] It was suggested that this type of electrophilic C–H bond activation leads to α-hydrogen abstraction in related electron-deficient Nb(V) and Ta(V) alkyl complexes.

Characterization of the product obtained by protonation of $Fe(\eta^4\text{-diene})L_3$ complexes (where L has traditionally been CO but may also be phosphorus ligands) with noncoordinating acids has had a long, complicated history.[6,13-20] Protonation of $Fe(\eta^4\text{-diene})P_3$ complexes (where P = phosphite[21] and phosphine[22] ligands) yields isolable species.[22-24] We have reported[23] the isolation of $[Fe(P(OMe)_3)_3(\eta^3\text{-}C_8H_{13})]^+$ (**1**)

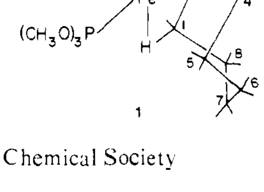

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Table I. Experimental Details of the X-ray and Neutron Diffraction Studies of $[Fe(P(OCH_3)_3)_3(C_8H_{13})][BF_4]$

	298 K X-ray	110 K neutron	30 K neutron
	A. Crystal Parameters[a]		
a	9.018 (2) Å	8.947 (6) Å	8.936 (2) Å
b	18.815 (4) Å	18.508 (13) Å	18.401 (5) Å
c	16.974 (2) Å	16.594 (11) Å	16.515 (5) Å
β	101.75 (1)°	101.71 (7)°	101.75 (3)°
V	2819.7 $Å^3$	2690.7 $Å^3$	2658.7 $Å^3$
λ	0.71069 Å	1.142 (1) Å	1.1629 (2) Å
ρ_c	1.470 g cm^{-3}	1.541 g cm^{-3}	1.560 g cm^{-3}
μ_c	7.9 cm^{-1}	3.01 cm^{-1}	3.05 cm^{-1}
transmission factors		0.353-0.485	0.389-0.485
	B. Measurement of Intensity Data		
total reflections	6477	4138	7038
total unique reflections	6477	3784	6354
scan technique	ω scan	θ-2θ step	θ-2θ step
$(\sin \theta/\lambda)_{max}$	0.65 $Å^{-1}$	0.56 $Å^{-1}$	0.66 $Å^{-1}$
	C. Least-Squares Results		
no. variables (n)	368	677	677
reflections used in refinement (m)	$3701 > 3\sigma(I)$	all 3784	all 6354
m/n	10.6	5.59	9.39
function minimized	$\Sigma w(\lvert F_o\rvert - S\lvert F_c\rvert)^2$	$\Sigma w\lvert F_o^2 - S^2F_c^2\rvert^2$	$\Sigma w\lvert F_o^2 - S^2F_c^2\rvert^2$
$R(F_o)$	0.046	0.156	0.073
$R_w(F_o)$	0.043		
$R(F_o^2)$		0.142	0.075
$R_w(F_o^2)$		0.158	0.077
σ_1		1.53	1.28
g		0.29 (4) × 10^{-4}	0.18 (1) × 10^{-4}

[a] Space group $P2_1/c$ [C_{2h}^5, no. 14], $Z = 4$.

previously. Spectroscopic characterization indicated a reasonably strong C-H ··· Fe interaction involving the endo hydrogen atom on C(1).[23] Interpretation of the NMR results was hampered by a site exchange which rapidly equilibrated the endo hydrogen atoms on C(1) and C(5) on the NMR time scale. A preliminary X-ray crystallographic study provided evidence for a possibly significant C-H ··· Fe interaction in the solid state. In order to directly and unambiguously determine the geometry of the C-H ··· Fe interaction, we undertook a single crystal neutron diffraction investigation of this complex. A preliminary account of this work[25] and a detailed account of the synthesis and spectroscopic characterization of related $[Fe(P(OMe)_3)_3(\eta^3\text{-enyl})]^+$ complexes have been presented.[24]

Experimental Section

Very large, well-formed crystals of $[Fe(P(OCH_3)_3)_3(C_8H_{13})][BF_4]$ were grown by slow evaporation under N_2 from dry methylene chloride solutions.

Collection and Treatment of Data. Crystals of $[Fe(P(OCH_3)_3)_3(C_8H_{13})][BF_4]$ are monoclinic (space group $P2_1/c$ [C_{2h}^5, no. 14]). For the neutron diffraction investigations, a 30-mg single crystal with dimensions 1.8 × 2.4 × 3.4 mm was sealed under N_2 in a lead-glass capillary in a general orientation. Experimental details of the X-ray and neutron diffraction experiments are given in Table I. All 110 K neutron data were collected using an Electronics-and-Alloys four-circle diffractometer at the Argonne CP-5 reactor in a manner previously described.[26] The unit cell dimensions and orientation at 110 K were determined from a least-squares fit of the diffractometer setting angles 2θ, χ, and ϕ for 23 intense reflections with $40° < 2\theta < 60°$ (λ = 1.142 (1) Å). The temperature at the crystal was maintained with a nitrogen gas flow system of the Strouse design.[27] The same crystal was used for the 30 K neutron data measurements on a four-circle diffractometer at the Brookhaven High Flux Beam Reactor.[38] The crystal was placed in a helium-filled inner chamber of a specially adapted closed-cycle helium refrigerator (Air Products and Chemicals, Inc., DISPLEX Model CS-202). The unit cell constants were refined by a least-squares procedure based on the sin θ values of 32 reflections with $47° \leq 2\theta \leq 60°$ (λ = 1.1629 (2) Å). The 298 K X-ray data were collected on a Syntex P3 diffractometer using Mo Kα radiation. A crystal of approximate dimensions 0.11 × 0.16 × 0.50 mm was placed in a thin-wall glass capillary and mounted with the a axis nearly parallel to the instrument ϕ axis. The unit cell constants and orientation were determined from 50 centered reflections. All X-ray and neutron data were corrected for Lorentz effects and the X-ray data were also corrected for polarization effects. The X-ray data were corrected for absorption using a ψ-scan technique and the maximum variance in the transmission factors was 10%. The 30 K neutron data were corrected for absorption using empirical techniques and an analytical correction was applied to the 110 K data.

Structure Solution and Refinement. Ths structure was solved from the room temperature X-ray data using MULTAN.[29] A difference Fourier map phased using the heavy atom coordinates was used to locate the hydrogen atoms. We were unable to satisfactorily refine the methoxy group hydrogen atoms from the X-ray data. Therefore, these atoms were fixed at C-H = 1.00 Å and B = 10.0 $Å^2$. Full-matrix least-squares refinement employing anistropic thermal parameters for the heavy atoms and isotropic thermal parameters for the hydrogen atoms of the cyclooctenyl ring led to $R(F_o) = 0.046$ and $R_w(F_o) = 0.043$ for the 3701 reflections with $F_o > 3\sigma(F_o)$.

The nonhydrogen atom coordinates from the room temperature X-ray investigation were used to phase the 110 K neutron data for a difference Fourier synthesis. The 40 hydrogen atoms were clearly defined in the difference map. Two cycles of isotropic full-matrix least-squares refinement of all 75 atoms led to $R(F_o^2) = 0.246$ and $R_w(F_o^2) = 0.272$ for all 3784 independent reflections. To facilitate computing, upon conversion to anisotropic temperature factors the structure was blocked into four sections and full-matrix least-squares refinement was continued. The four sections were defined as follows: (1) S, g, Fe, and the cyclooctenyl ligand; (2) S, g, Fe, and the phosphite ligand at P(1); (3) S, g, Fe, and the phosphite ligand at P(2); (4) S, g, Fe, the phosphite ligand at P(3), and the BF_4 anion, where S is the scale factor and g is the isotropic extinction factor. After several cycles of refinement in this fashion, two cycles of full-matrix least-squares refinement using all structural parameters (75 atoms, 677 parameters) led to $R(F_o^2) = 0.142$ and $R(F_o) = 0.156$ for all 3784 independent data and to $R(F_o^2) = 0.122$ and $R(F_o) = 0.098$ for the 2748 data with $F_o^2 > 3\sigma(F_o^2)$. The correction for isotropic extinction is based on the Zachariasen[30] approximation.

The refinement of the 30 K neutron data was initiated with the

Table II. Positional[a] and Thermal[b] Parameters ($Å^2$)($\times 10^4$) for $[Fe(P(OCH_3)_3)_3(C_8H_{13})][BF_4]$

ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
FE	3255(1)	96	2119	75(4)	27(3)	44(3)	5(3)	52(3)	3(3)
C1	2459	-537(1)	861(1)	107(6)	69(5)	66(5)	-8(5)	57(5)	-2(4)
C2	1496(1)	50(1)	1118(1)	114(6)	53(5)	75(5)	7(5)	59(5)	12(5)
C3	928(1)	-48(1)	1848(1)	100(6)	55(5)	86(6)	-2(5)	58(5)	0(4)
C4	1514(1)	-590(1)	2447(1)	114(6)	53(5)	77(6)	-14(5)	64(5)	-3(4)
C5	1684(2)	-1404(1)	2296(1)	136(7)	55(5)	79(6)	-15(5)	54(5)	6(4)
C6	347(2)	-1737(1)	1673(1)	141(7)	74(6)	102(6)	-39(5)	52(5)	-2(5)
C7	129(2)	-1429(1)	794(1)	119(6)	81(6)	99(6)	-25(5)	47(5)	-14(5)
C8	1619(2)	-1250(1)	511(1)	144(7)	72(6)	98(6)	-18(5)	64(5)	-23(5)
H1A	3387(3)	-703(1)	1434(2)	219(14)	187(13)	160(12)	37(11)	41(11)	3(10)
H1B	3103(3)	-336(2)	412(2)	255(15)	232(13)	189(12)	-40(12)	158(11)	-23(11)
H2	1105(4)	499(2)	699(2)	321(16)	166(13)	192(13)	51(12)	63(12)	65(11)
H3	212(3)	378(2)	2022(2)	215(14)	194(13)	249(14)	60(11)	119(11)	-17(11)
H4	1200(3)	-485(2)	3041(2)	295(15)	202(13)	166(12)	9(12)	149(11)	3(10)
H5A	2749(3)	-1539(1)	2100(2)	216(14)	190(13)	246(13)	3(11)	123(12)	-44(11)
H5B	1758(4)	-1677(2)	2893(2)	349(17)	180(13)	171(13)	-38(12)	54(12)	50(11)
H6A	555(4)	-2325(1)	1644(2)	357(17)	124(13)	278(15)	-51(12)	42(13)	-6(11)
H6B	-722(3)	-1677(2)	1897(2)	236(15)	309(15)	211(13)	-51(12)	119(12)	-33(12)
H7A	-581(4)	-939(2)	733(2)	269(15)	192(14)	303(15)	44(12)	106(13)	32(11)
H7B	-494(4)	-1831(2)	361(2)	290(16)	223(14)	217(13)	-104(13)	64(12)	-75(11)
H8A	2399(4)	-1714(2)	628(2)	261(15)	149(13)	389(17)	42(12)	124(13)	-14(12)
H8B	1356(4)	-1183(2)	-162(2)	355(17)	316(15)	177(13)	-88(14)	109(12)	-35(12)
P1	4597(2)	793(1)	1479(1)	102(8)	41(7)	61(7)	-3(6)	63(6)	12(6)
O1	5713(2)	438(1)	931(1)	153(7)	72(6)	102(6)	23(6)	102(6)	15(5)
O2	3539(2)	1272(1)	774(1)	124(7)	86(6)	94(6)	7(6)	62(6)	35(5)
O3	5619(2)	1406(1)	2004(1)	127(7)	94(7)	101(6)	-46(6)	61(6)	-44(5)
C11	6540(2)	-231(1)	1121(1)	147(7)	86(6)	110(6)	17(5)	85(5)	-5(5)
C12	4162(2)	1832(1)	335(1)	195(7)	99(6)	148(6)	-5(6)	97(6)	54(5)
C13	7232(2)	1504(1)	2097(1)	106(7)	134(7)	242(7)	-23(6)	59(6)	-8(6)
H111	5900(4)	-620(2)	1406(2)	387(19)	256(15)	474(19)	14(14)	267(16)	139(14)
H112	7612(4)	-135(2)	1546(3)	282(18)	371(18)	564(22)	73(16)	-83(17)	-99(17)
H113	6739(5)	-445(2)	542(2)	680(25)	310(17)	248(15)	210(17)	257(15)	6(13)
H121	4842(5)	1606(2)	-68(2)	646(26)	326(18)	501(21)	38(17)	455(20)	75(16)
H122	3211(4)	2132(2)	-15(3)	344(20)	444(21)	576(23)	48(17)	95(17)	351(19)
H123	4858(5)	2205(2)	758(2)	724(28)	271(16)	371(19)	-259(18)	143(19)	-5(15)
H131	7489(5)	1838(4)	1644(5)	269(23)	1485(59)	1409(56)	-95(29)	113(28)	1073(52)
H132	7622(6)	1758(4)	2666(4)	332(25)	1657(65)	1089(46)	-259(33)	211(27)	-931(49)
H133	7804(5)	1009(2)	2107(4)	301(22)	319(21)	1555(54)	4(17)	308(27)	-50(26)
P2	3070(2)	969(1)	2937(1)	86(8)	33(6)	74(7)	-2(6)	62(6)	-5(5)
O4	4585(2)	1220(1)	3556(1)	106(7)	57(6)	95(6)	2(5)	44(5)	-11(5)
O5	1915(2)	759(1)	3517(1)	113(7)	67(6)	78(6)	-10(5)	83(5)	-3(5)
O6	2493(2)	1749(1)	2567(1)	104(7)	41(6)	94(6)	-2(5)	49(5)	0(5)
C14	5042(2)	1966(1)	3734(1)	126(7)	96(6)	128(6)	-20(5)	31(5)	-35(5)
C15	1749(2)	1211(1)	4208(1)	152(7)	111(6)	102(6)	-2(5)	95(5)	-29(5)
C16	1030(2)	1830(1)	2023(1)	123(6)	75(6)	138(6)	7(5)	50(5)	-2(5)
H141	4128(4)	2268(2)	3910(2)	309(18)	281(16)	566(22)	-6(14)	209(16)	-176(15)
H142	5352(5)	2213(2)	3196(2)	550(23)	268(15)	362(18)	-147(19)	236(17)	-32(14)
H143	6036(4)	1949(2)	4241(2)	335(19)	307(16)	373(18)	-43(14)	-141(15)	-23(14)
H151	876(4)	972(2)	4481(2)	380(19)	391(17)	298(15)	-119(15)	271(15)	-93(13)
H152	1406(5)	1755(2)	4005(2)	581(23)	187(15)	356(17)	88(15)	212(15)	-12(13)
H153	2823(4)	1233(2)	4661(2)	295(18)	576(22)	234(15)	35(16)	34(14)	-172(15)
H161	828(4)	2406(2)	1925(2)	327(18)	151(14)	441(18)	53(12)	6(15)	59(12)
H162	1033(4)	1577(2)	1427(2)	368(19)	400(19)	220(15)	86(15)	5(13)	-115(13)
H163	143(4)	1608(2)	2304(2)	194(15)	429(19)	417(18)	-29(14)	118(14)	125(15)
P3	5132(2)	-360(1)	3011(1)	76(7)	46(7)	41(6)	5(6)	38(6)	0(5)
O7	6738(2)	22(1)	3031(1)	93(7)	86(7)	91(6)	-1(5)	56(5)	0(5)
O8	5197(2)	-400(1)	3984(1)	120(7)	70(6)	57(6)	-8(6)	58(5)	3(5)
O9	5363(2)	-1190(1)	2751(1)	108(7)	58(6)	93(6)	11(5)	42(5)	-8(5)
C17	7960(2)	118(1)	3748(1)	118(7)	141(6)	117(6)	-20(5)	31(5)	-2(5)
C18	4016(2)	-758(1)	4315(1)	154(7)	111(6)	81(6)	-7(5)	75(5)	24(5)
C19	6638(2)	-1613(1)	3186(1)	146(7)	81(6)	144(6)	38(5)	47(5)	3(5)
H171	8200(5)	-376(2)	4092(2)	446(22)	353(19)	458(21)	-81(17)	-134(17)	170(16)
H172	8956(4)	265(3)	3518(2)	241(18)	774(29)	270(16)	-149(18)	70(14)	2(17)
H173	7673(5)	548(2)	4131(2)	404(21)	460(21)	432(20)	65(17)	32(16)	-255(17)
H181	5575(4)	775(2)	5018(2)	399(18)	484(20)	131(14)	-41(16)	85(13)	62(13)
H182	6182(4)	3697(2)	926(2)	467(21)	232(15)	416(18)	144(15)	229(16)	66(14)
H183	2961(4)	-447(2)	4171(2)	228(16)	400(18)	426(18)	53(15)	149(14)	134(15)
H191	2301(4)	3585(2)	1952(2)	233(17)	383(18)	486(20)	-41(14)	146(15)	-112(15)
H192	3558(4)	2831(2)	2026(2)	394(19)	127(13)	478(20)	-77(13)	1(16)	57(13)
H193	3293(4)	3409(2)	1149(2)	490(22)	389(18)	201(15)	-165(16)	70(14)	-35(13)
B	-733(2)	3132(1)	358(1)	121(9)	69(8)	99(8)	-8(6)	73(6)	-6(5)
F1	752(2)	2851(1)	470(1)	117(8)	94(7)	111(7)	7(6)	50(6)	17(6)
F2	-1620(2)	2702(1)	778(1)	177(8)	117(7)	150(7)	-44(6)	109(7)	5(6)
F3	-1392(2)	3132(1)	-490(1)	133(8)	142(7)	132(7)	-2(6)	49(6)	33(6)
F4	-658(2)	3844(1)	659(1)	186(9)	82(7)	265(9)	-17(6)	138(7)	-66(6)

[a] x, y, and z are fractional coordinates. Estimated standard deviations in parentheses. [b] Anisotropic temperature factors of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$.

positional parameters obtained from the 110 K neutron study and with individual atom isotropic temperature factors set at $B = 1.25$ Å^2. In the final stages of least-squares refinement all atoms were treated anisotropically and a secondary extinction parameter[30] ($g = 0.18$ (1) $\times 10^{-4}$) was refined. The final agreement factors for all 6354 independent data were $R(F_o^2) = 0.075$ and $R_w(F_o^2) = 0.077$. The largest shift to error ratio in the final cycle of refinement was 0.10. A final difference nuclear density map was essentially featureless. Final positional and thermal parameters for the 30 K neutron structure are given in Table II. The neutron scattering amplitudes used in this study were $\bar{b}_{Fe} = 0.95$, $\bar{b}_P = 0.51$, $\bar{b}_O = 0.58$, $\bar{b}_C = 0.665$, $\bar{b}_H = -0.374$, $\bar{b}_F = 0.56$, and $\bar{b}_B = 0.54$ (all in units of 10^{-12} cm).

Results and Discussion

General Description of the Structure. The crystal structure consists of discrete $[Fe(P(OCH_3)_3)_3(C_8H_{13})]^+$ cations and $[BF_4]^-$ anions. The shortest intermolecular contacts are be-

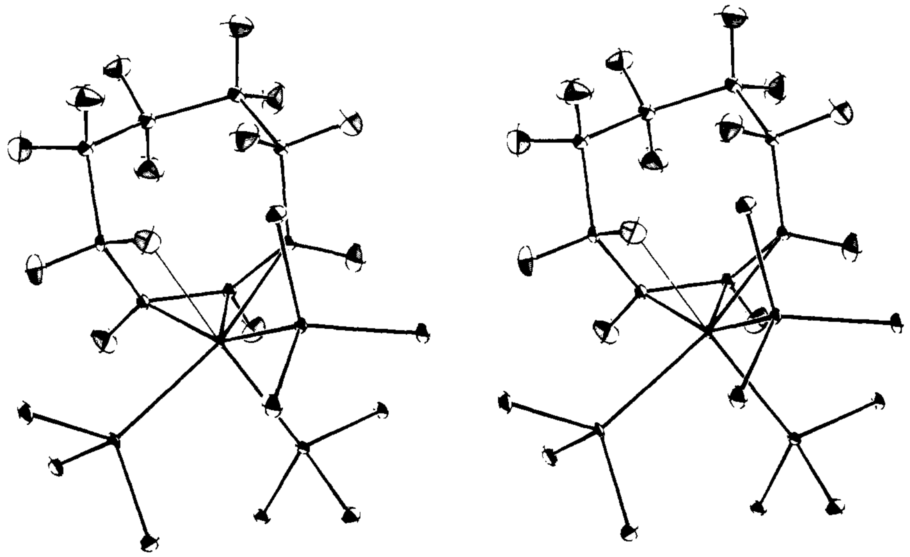


Figure 1. Stereoscopic view of the [(Fe(P(OCH$_3$)$_3$)$_3$(η^3-C$_8$H$_{13}$)]$^+$ cation (-CH$_3$ groups omitted) which clearly shows the C$_8$H$_{13}$ ring distortion which accompanies the formation of the strong C-H ··· Fe interaction (indicated by a faint line). All figures presented here represent results derived from the 30 K neutron study. The thermal ellipsoids of nuclear motion in all figures are scaled to enclose 50% probability and important internuclear distances (uncorrected for thermal motion) are given in angstroms with their estimated standard deviations.

Table III. Bond Distances (Å) and Angles (deg) for [Fe(P(OCH$_3$)$_3$)$_3$(C$_8$H$_{13}$)][BF$_4$] from the 30 K Neutron Crystallographic Investigation[a]

Distances to the Fe Atom			
Fe-C(1)	2.362(2)	Fe-H(1A)	1.874(3)
Fe-C(2)	2.038(2)	Fe-H(5A)	3.034(9)
Fe-C(3)	2.053(2)	Fe-P(1)	2.172(2)
Fe-C(4)	2.156(2)	Fe-P(2)	2.126(2)
Fe-C(5)	3.138(3)	Fe-P(3)	2.163(2)
C-C Distances in the C$_8$H$_{13}$ Ring			
C(1)-C(2)	1.500(2)	C(5)-C(6)	1.536(2)
C(2)-C(3)	1.411(2)	C(6)-C(7)	1.533(2)
C(3)-C(4)	1.427(2)	C(7)-C(8)	1.534(2)
C(4)-C(5)	1.532(2)	C(8)-C(1)	1.563(2)
C-H Distances in the C$_8$H$_{13}$ Ring			
C(1)-H(1A)	1.164(3)	C(6)-H(6A)	1.100(3)
C(1)-H(1B)	1.092(3)	C(6)-H(6B)	1.098(3)
C(2)-H(2)	1.090(3)	C(7)-H(7A)	1.096(3)
C(3)-H(3)	1.087(3)	C(7)-H(7B)	1.098(3)
C(4)-H(4)	1.092(3)	C(8)-H(8A)	1.094(3)
C(5)-H(5A)	1.095(3)	C(8)-H(8B)	1.095(3)
C(5)-H(5B)	1.096(3)		
Nonhydrogen Distances in the P(OCH$_3$)$_3$ Ligands			
P(1)-O(1)	1.615(2)	O(1)-C(11)	1.437(2)
P(1)-O(2)	1.606(2)	O(2)-C(12)	1.436(2)
P(1)-O(3)	1.593(2)	O(3)-C(13)	1.430(2)
P(2)-O(4)	1.589(2)	O(4)-C(14)	1.446(2)
P(2)-O(5)	1.592(2)	O(5)-C(15)	1.444(2)
P(2)-O(6)	1.604(2)	O(6)-C(16)	1.436(2)
P(3)-O(7)	1.593(2)	O(7)-C(17)	1.449(2)
P(3)-O(8)	1.598(2)	O(8)-C(18)	1.443(2)
P(3)-O(9)	1.610(2)	O(9)-C(19)	1.445(2)
Methoxy C-H Distances			
C(11)-H(111)	1.083(3)	C(15)-H(152)	1.081(3)
C(11)-H(112)	1.081(4)	C(15)-H(153)	1.091(4)
C(11)-H(113)	1.081(3)	C(16)-H(161)	1.081(3)
C(12)-H(121)	1.073(4)	C(16)-H(162)	1.088(3)
C(12)-H(122)	1.076(4)	C(16)-H(163)	1.078(3)
C(12)-H(123)	1.081(4)	C(17)-H(171)	1.070(4)
C(13)-H(131)	1.030(5)	C(17)-H(172)	1.071(4)
C(13)-H(132)	1.044(6)	C(17)-H(173)	1.075(4)
C(13)-H(133)	1.044(5)	C(18)-H(181)	1.088(4)
C(14)-H(141)	1.076(4)	C(18)-H(182)	1.080(4)
C(14)-H(142)	1.083(4)	C(18)-H(183)	1.086(4)
C(14)-H(143)	1.090(4)	C(19)-H(191)	1.083(4)
C(15)-H(151)	1.071(3)	C(19)-H(192)	1.084(4)
		C(19)-H(193)	1.088(4)
B-F Distances			
B-F(1)	1.401(2)	B-F(3)	1.403(2)
B-F(2)	1.400(2)	B-F(4)	1.398(2)
Angles Involving the Fe Atom			
P(1)-Fe-P(2)	89.17(7)	H(1A)-Fe-P(2)	177.28(10)
P(1)-Fe-P(3)	97.60(7)	H(1A)-Fe-P(3)	88.35(10)
P(2)-Fe-P(3)	90.61(7)	H(1A)-Fe-C(2)	67.05(9)
P(1)-Fe-C(2)	92.34(6)	H(1A)-Fe-C(3)	87.27(10)
P(1)-Fe-C(3)	127.21(7)	H(1A)-Fe-C(4)	80.18(10)
P(1)-Fe-C(4)	164.99(7)	Fe-H(1A)-C(1)	99.4(2)
P(2)-Fe-C(2)	113.57(7)	Fe-P(1)-O(1)	120.0(1)
P(2)-Fe-C(3)	91.70(6)	Fe-P(1)-O(2)	112.1(1)
P(2)-Fe-C(4)	97.43(6)	Fe-P(1)-O(3)	117.7(1)
P(3)-Fe-C(2)	154.01(7)	Fe-P(2)-O(4)	117.5(1)
P(3)-Fe-C(3)	135.15(7)	Fe-P(2)-O(5)	110.1(1)
P(3)-Fe-C(4)	95.80(6)	Fe-P(2)-O(6)	119.6(1)
C(2)-Fe-C(3)	40.34(5)	Fe-P(3)-O(7)	114.4(1)
C(2)-Fe-C(4)	72.67(6)	Fe-P(3)-O(8)	124.5(1)
C(3)-Fe-C(4)	39.55(5)	Fe-P(3)-O(9)	108.1(1)
H(1A)-Fe-P(1)	93.45(10)		
Angles within the C$_8$H$_{13}$ Ring			
C(2)-C(1)-C(8)	116.8(1)	C(2)-C(3)-H(3)	117.9(2)
C(2)-C(1)-H(1A)	108.3(2)	C(4)-C(3)-H(3)	118.2(2)
C(2)-C(1)-H(1B)	111.2(2)	C(3)-C(4)-C(5)	127.3(1)
C(8)-C(1)-H(1A)	106.8(2)	C(3)-C(4)-H(4)	112.0(2)
C(8)-C(1)-H(1B)	108.3(2)	C(5)-C(4)-H(4)	111.8(2)
H(1A)-C(1)-H(1B)	104.7(2)	C(4)-C(5)-C(6)	114.2(1)
C(1)-C(2)-C(3)	118.6(1)	C(5)-C(6)-C(7)	114.7(1)
C(1)-C(2)-H(2)	119.8(2)	C(6)-C(7)-C(8)	114.7(1)
C(3)-C(2)-H(2)	121.0(2)	C(7)-C(8)-C(1)	116.6(1)
C(2)-C(3)-C(4)	122.4(1)		
Angles within the P(OCH$_3$)$_3$ Ligands			
P(1)-O(1)-C(11)	124.9(1)	P(2)-O(6)-C(16)	120.9(1)
P(1)-O(2)-C(12)	121.9(1)	P(3)-O(7)-C(17)	126.7(1)
P(1)-O(3)-C(13)	127.0(1)	P(3)-O(8)-C(18)	121.5(1)
P(2)-O(4)-C(14)	125.1(1)	P(3)-O(9)-C(19)	120.6(1)
P(2)-O(5)-C(15)	121.3(1)		

[a] Estimated standard deviations in parentheses.

Table IV. Selected Bond Distances (Å) and Angles (deg) for $[Fe(P(OCH_3)_3)_3(C_8H_{13})][BF_4]$ from the Room Temperature X-ray Crystallographic Investigation[a]

	Distances		
Fe-C(1)	2.384(4)	C(3)-H(3)	0.95(3)
Fe-C(2)	2.037(3)	C(4)-C(5)	1.523(5)
Fe-C(3)	2.058(3)	C(4)-H(4)	0.99(3)
Fe-C(4)	2.161(3)	C(5)-C(6)	1.539(5)
Fe-H(1A)	1.95(3)	C(5)-H(5A)	0.99(3)
Fe-P(1)	2.182(1)	C(5)-H(5B)	0.97(3)
Fe-P(2)	2.130(1)	C(6)-C(7)	1.524(6)
Fe-P(3)	2.172(1)	C(6)-H(6A)	0.95(4)
C(1)-C(2)	1.480(5)	C(6)-H(6B)	0.99(4)
C(1)-C(8)	1.553(5)	C(7)-C(8)	1.520(6)
C(1)-H(1A)	1.07(3)	C(7)-H(7A)	0.90(4)
C(1)-H(1B)	0.99(3)	C(7)-H(7B)	1.02(4)
C(2)-C(3)	1.407(4)	C(8)-H(8A)	0.95(3)
C(2)-H(2)	0.93(2)	C(8)-H(8B)	1.00(3)
C(3)-C(4)	1.403(4)		
	Angles		
C(2)-Fe-C(3)	40.2(1)	H(1A)-Fe-C(3)	85.8(8)
C(3)-Fe-C(4)	38.8(1)	H(1A)-Fe-C(4)	80.9(8)
C(2)-Fe-C(4)	71.6(1)	H(1A)-Fe-P(1)	90.3(8)
C(2)-Fe-P(1)	92.2(1)	H(1A)-Fe-P(2)	177.4(8)
C(2)-Fe-P(2)	113.5(1)	H(1A)-Fe-P(3)	91.0(9)
C(2)-Fe-P(3)	152.8(1)	C(1)-H(1A)-Fe	100(2)
C(3)-Fe-P(1)	127.4(1)	C(2)-C(1)-C(8)	118.3(3)
C(3)-Fe-P(2)	92.0(1)	C(1)-C(2)-C(3)	118.6(3)
C(3)-Fe-P(3)	133.6(1)	C(1)-C(2)-H(2)	120(2)
C(4)-Fe-P(1)	163.7(1)	C(2)-C(3)-C(4)	122.1(3)
C(4)-Fe-P(2)	98.2(1)	C(4)-C(3)-Fe	74.6(2)
C(4)-Fe-P(3)	95.0(1)	C(3)-C(4)-C(5)	127.7(3)
P(1)-Fe-P(2)	90.05(4)	C(4)-C(5)-C(6)	114.1(3)
P(1)-Fe-P(3)	98.83(4)	C(5)-C(6)-C(7)	114.4(3)
P(2)-Fe-P(3)	91.46(3)	C(6)-C(7)-C(8)	114.8(4)
H(1A)-Fe-C(2)	64.0(9)	C(7)-C(8)-C(1)	115.9(4)

[a] Estimated standard deviations in parentheses.

tween hydrogen atoms of the phosphite ligands and are all greater than 2.36 Å. A stereoview of the cation is displayed in Figure 1. Pertinent bond distances and angles derived from the 30 K neutron study are given in Table III and for clarity are included in Figure 2. All structural parameters mentioned in the text refer to the 30 K neutron study unless otherwise noted. Structural parameters from the 110 K neutron study have been communicated previously[25] and selected parameters from the 298 K X-ray study are given in Table IV.

The structure of the cation may be viewed as a distorted square pyramid with P(2) occupying the axial site, P(1) and P(3) occupying basal sites, and the η^3-enyl portion of the C_8H_{13} group spanning the two remaining basal sites. This description yields a 16-electron configuration for the complex. However, examination of Figure 2 and consideration of the Fe-H(1A) separation clearly indicates the inadequacy of this description. The H(1A) atom is located at the sixth coordination site of a distorted octahedron, trans to P(2) [P(2)-Fe-H(1A) = 177.3 (1)°] and cis to P(1) and P(3) [P(1)-Fe-H(1A) = 93.5 (1)° and P(3)-Fe-H(1A) = 88.3 (1)°]. Since the only electrons available to H(1A) for coordination are initially localized in the C(1)-H(1A) bond, it is possible to consider the complex as an 18-electron system containing a C-H-Fe three-center bonding interaction. The distance of H(1A) from the equatorial plane defined by Fe, P(1), and P(3) is 1.870 (2) Å, which is identical with the Fe-H(1A) separation. This is the expected result for an atom in an octahedral coordination site.

The allylic portion of the C_8H_{13} group is not symmetrically positioned about the two octahedral coordination sites which it spans. The C(2)-Fe distance of 2.038 (2) Å is significantly shorter than the C(4)-Fe distance of 2.156 (2) Å, with the C(3)-Fe separation being intermediate at 2.053 (2) Å. While these Fe-C distances are within the range observed for other iron-allyl species, the central Fe-C distance is usually the shortest of the three.[31] It is apparent from Figure 2 that this asymmetric coordination arises from the Fe-H(1A) attractive interaction resulting in displacement of C(2) toward the Fe atom. This same trend was also observed in both the 298 K X-ray study and the 110 K neutron study.

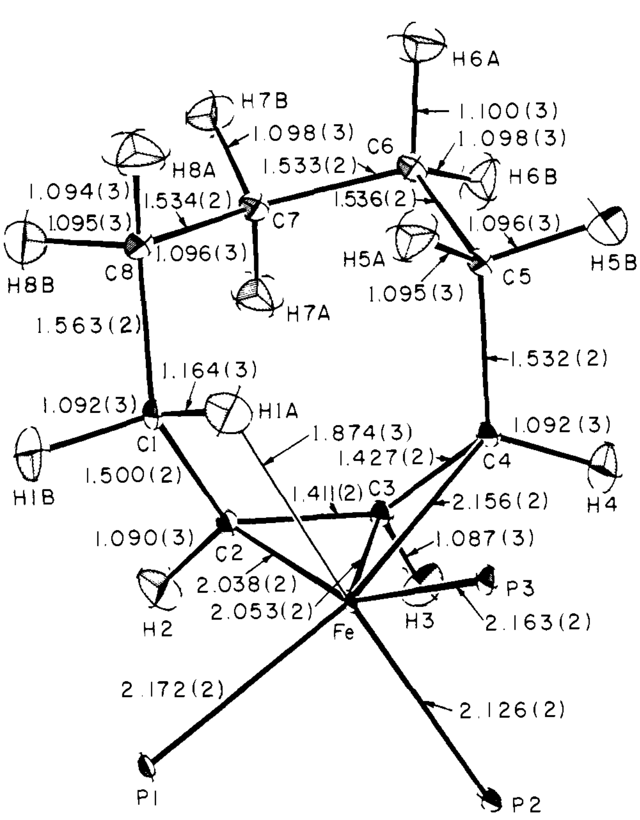


Figure 2. Atom labeling scheme for the $[(Fe(P(OCH_3)_3)_3(\eta^3\text{-}C_8H_{13})]^+$ cation (-OCH_3 groups omitted for clarity) showing the distorted octahedral coordination around the Fe atom with the aliphatic H atom [H(1A)] occupying a coordination site. The C1-H1A distance of 1.164 (3) Å is the longest such separation ever observed in a crystalline complex.

Other indications of the distortion of the coordinated portion of the C_8H_{13} ring due to the strong Fe-H(1A) interaction are the following.

(1) C(3) is asymmetrically located with respect to P(1) and P(3) [C(3)-Fe-P(1) = 127.21 (7)°, C(3)-Fe-P(3) = 135.15 (7)°].

(2) C(2) is displaced 0.317 (3) Å toward C(3) from a plane defined by Fe, P(2), and P(3), whereas C(4) is displaced 0.500 (2) Å toward C(3) from a plane defined by Fe, P(1), and P(2).

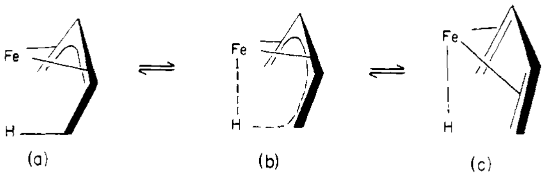
(3) C(2) and C(4) are 0.830 (2) and 0.253 (2) Å, respectively, from the equatorial plane defined by Fe, P(1), and P(3).

(4) C(3) is only 0.057 (2) Å from the equatorial plane, but the deviation is in the same direction as C(2) and C(4). In the normal coordination of allyl ligands, the central carbon atom and the two terminal carbon atoms are on opposite sides of the equatorial plane.[31] However, the dihedral angle of 131.57 (5)° between the equatorial plane (Fe, P(1), P(3)) and the allylic plane (C(2), C(3), C(4)) is only slightly less than the angle of 134.1° in $(\eta^3\text{-}C_3H_5)Fe(CO)_2(PPh_3)I$.[32]

In the absence of the Fe-H(1A) interaction one would expect the C_8H_{13} ring to be symmetrical about a plane passing through C(3) and C(7), with C(2) equivalent to C(4), C(1) equivalent to C(5), and C(8) equivalent to C(6). This would correspond to the time-averaged structure observed in the NMR experiments.[23,24] However, in addition to causing the asymmetric placement of the C_8H_{13} ring about the two iron coordination sites, the C(1)-H(1A) ··· Fe interaction gives rise to internal C_8H_{13} ring distortions. As an example, the C(1)-C(2)-C(3) angle of 118.6 (1)° differs significantly from the C(3)-C(4)-C(5) angle of 127.3 (1)°. The significant differences between the angles C(1)-C(2)-Fe [82.38 (8)°] and C(5)-C(4)-Fe [115.58 (8)°], and to a lesser extent between C(2)-C(3)-Fe [69.23 (8)°] and C(4)-C(3)-Fe [74.10 (8)°], are dependent on both asymmetric ring placement and internal ring distortions. These values are all in excellent agreement with the values determined in the X-ray investigation (see Table IV).

As mentioned in the Introduction, the temperature-dependent NMR studies[23,24] indicate a fluxional process involving site exchange of the endo hydrogen atoms on C(1) and C(5) giving alternating Fe-H(1A) and Fe-H(5A) interactions. The observed solid-state structure corresponds to one of the extremes of the dynamic fluxional process. If the FeP_3 framework is held rigid, the H(1A)-H(5A) separation of 2.038 (4) Å is presumably the distance H(5A) must travel to reach the octahedral site vacated by H(1A) during the fluxional process. During the fluxional process the Fe-H(5A) distance decreases by only 1.15 Å; the remainder of the motion is required to move H(5A) trans to P(2) and into the octahedral site. Since the degree of C-H bond stretching (vide infra) and the degree of angular deformation of C(1) are small compared to the Fe ··· H distance, as are the differences in the Fe to C(2), C(3), and C(4) distances, it is very likely that C(1) and C(5) also move by ca. 2 Å during the fluxional process. A major portion of this translational motion is accounted for by the deformation of the C-C-C angles subtended at C(2) and C(4) (vide supra). The Fe-H(5A) distance of 3.034 (9) Å must of course also be reduced to 1.874 (3) Å (the Fe-H(1A) distance) during the fluxional process.

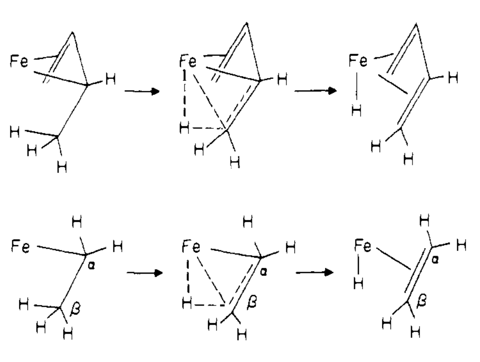
The C-C distances in the allylic portion of the cyclooctenyl group (C(2)-C(3) and C(3)-C(4) of 1.411 (2) and 1.427 (2) Å, respectively) are predictably shorter than the aliphatic C-C distances between C(4)-C(5) through C(8)-C(1), which range from 1.532 (2) to 1.563 (2) Å. It is significant that the C(1)-C(2) distance of 1.500 (2) Å lies between these two ranges and that it is considerably shorter than the corresponding C(4)-C(5) distance on the opposite side of the ring. Thus, the C(1)-C(2) bond exhibits partial multiple bond character. This is indicative of structure **2b**, which can be considered an intermediate in the conversion of a metal-(η^3-allyl) complex, **2a**, to a metal-hydride-(η^4-dienyl) complex, **2c**. Therefore, even a two-electron three-center bonding picture is not adequate to fully describe the bonding in this complex; the hydrogen interaction with the metal affects the entire four-carbon fragment shown in **2**.



2

The range of aliphatic C-C distances (excluding C(1)-C(8)) is 1.532 (2) to 1.536 (2) Å. The anomalously high value of 1.563 (2) Å for C(1)-C(8) is 0.03 Å longer than the average aliphatic C-C separation. This lengthening of the C(1)-C(8) bond is due to the small H(1A)-C(1)-C(8)-H(8A) and H(1B)-C(1)-C(8)-H(8B) torsion angles of 30.6 and 30.8°, respectively, which are induced by the C(1)-H(1A)-Fe interaction. These are the smallest aliphatic H-C-C-H torsion angles in the cyclooctenyl ring.

Scheme I. The Relationship between the Structure Observed in This Study (Top) and the Course of β-Hydride Elimination (Bottom)



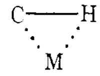
The $[BF_4]^-$ anion possesses normal tetrahedral geometry. All boron-fluorine bond distances are within the range 1.398 (2) to 1.403 (2) Å. Bond distances and angles for the anion are included in Tables III and IV.

Description of the Bonding. A delocalized (2e-3c) C(1)-H(1A)-Fe interaction should lead to lengthening of the C(1)-H(1A) bond as electron density is removed from this bond and delocalized over the C(1)-H(1A)-Fe three-center system. The most dramatic structural feature we observe is the lengthened aliphatic C(1)-H(1A) bond. The aliphatic C-H distances in the C_8H_{13} ring (excluding C(1)-H(1A)) range from 1.092 (3) to 1.100 (3) Å, a range of only 0.008 Å. To our knowledge the C(1)-H(1A) bond distance of 1.164 (3) Å is the longest C-H bond ever to be definitively characterized.

There is also a possibility of direct interaction of the metal center with C(1) of the C_8H_{13} ring. Two proposed[9] models for interaction of an sp^3 C-H bond with a transition metal are shown in configurations **3a** and **3b**. The collinear configuration

$C—H\cdots M$

3a



$\overset{C—H}{\cdot\,M\,\cdot}$

3b

3a was favored in the molybdenum pyrazolylborate complexes studied by Cotton.[9] In configuration **3b**, both carbon and hydrogen interact with the metal center much in the manner proposed by Brookhart and Whitesides[6] for a cyclohexadienyl iron complex. The current system has features which are very closely represented by **3b**. Although the Fe-C(1) distance of 2.362 (2) Å is seemingly long for such an interaction, it is noted that *both* the Fe-C(1) and Fe-H(1A) distances are ~0.2 Å longer than the sums of the appropriate covalent radii (Fe = 1.25, H = 0.37, and C = 0.77 Å).[33] The obtuse Fe-H(1A)-C(1) angle (99.4 (2)°) is also consistent with this interpretation. An interaction which would result in equidistant Fe-C(1) and Fe-H(1A) separations as idealized in **2b** allows for little M-H interaction even when there is a strong M-C bond, due to the small covalent radius of hydrogen. However, it should be stressed that the location of H(1A) in an exact octahedral coordination site about the Fe atom strongly implies that the close Fe-C(1) approach is a fortuitous result of the structural constraints dictated by the allyl, Fe-H(1A), and internal C_8H_{13} ring bonding. A geometry such as **3a** is indeed unlikely within these additional constraints. Thus, the degree of direct Fe-C(1) participation in the overall bonding remains unclear.

C-H Bond Activation. Recent chemical and spectroscopic investigations of the activation and eventual cleavage of a variety of C-H bonds by transition-metal complexes provides evidence for concerted reaction pathways involving intermediates such as **3a** and **3b**.[2,34-37] Oxidative addition of an alkyl C-H bond to a coordinately unsaturated metal center proceeds through an intermediate of the form **3b** and involves simultaneous attack on C and H by the metal, or, more aptly, attack on the C–H bond. Complete cleavage of the C–H bond, however, would result in an increase of +2 in the oxidation state of the metal, giving a cis hydrido alkyl species. Such is not the case in this system.

An alternative formalism for C–H bond cleavage is that of β-hydride elimination in which the oxidation state of the metal remains unchanged. The essential mechanistic process of β-hydride elimination as it would apply to this structure is illustrated in Scheme I by figuratively breaking the π-allyl system **2** into its σ and π components. It is clear that the structure reported here has all the necessary requirements of β-hydride elimination: (1) initial coordinative unsaturation of the metal center, (2) an Fe · · · H interaction, (3) a weakened H–C_β bond, (4) increasing multiple bond character between C_α and C_β (where C_α = C(2) and C_β = C(1)), and (5) potential for coordination of the resultant olefinic group.

Acknowledgment. This work was performed under the auspices of the Office of Basic Energy Sciences of the U.S. Department of Energy. We also wish to acknowledge the partial support of this collaborative research by the National Science Foundation (Grant CHE-78-20698) through a grant to J.M.W. We would like to thank J. Henriques for technical assistance.

Supplementary Material Available: A listing of structure factors (36 pages). Ordering information is given on any current masthead page.

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