Data were measured with variable scan speed to ensure constant statistical precision on the collected intensities. Three standard reflections were used to check the stability of the crystal and of the experimental conditions and measured every 1 h; no significant variation was detected. The orientation of the crystal was checked by measuring three reflections every 300 measurements. Data have been corrected for Lorentz and polarization factors and for decay, using the data reduction programs of the CAD4 SDP package.[34] An empirical absorption correction was applied by using azimuthal (ψ) scans of three "high-χ-angle" reflections ($\chi \geq 86.6°$, $8.6° \leq \theta \leq 17.4°$). Transmission factors were in the range 0.9665–0.9983. The standard deviations on intensities were calculated in terms of statistics alone, while those on F_o were calculated as reported in Table IV. Intensities were considered as observed if $|F_o^2| > 2.0\sigma|F^2|$ and used for the solution and refinement of the structure. An $F_o = 0.0$ value was given to those reflections having negative net intensities.

The structure was solved by a combination of Patterson and Fourier methods and refined by full-matrix least squares[34] (the function minimized was $[\sum w|F_o| - 1/k|F_c|)^2]$) with $w = [\sigma^2(F_o)]^{-1}$. No extinction correction was applied.

The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature.[34] Anisotropic temperature factors were used for all but the hydrogen atoms.

Most of the hydrogen atoms could be located in the final Fourier difference maps, in particular those of the allyl moiety and those bound to C(6) and C(6'), which were refined by using isotropic temperature displacements. The remaining hydrogens were also refined starting from their idealized positions (C–H = 0.95 Å, B = 5.0 Å^2).

Upon convergence (no parameter shift $\geq 0.4\sigma(p)$) the Fourier difference map showed no significant feature. All calculations were carried out by using the SDP crystallographic package.[35] Final atomic coordinates and thermal factors are given in Table V.

Modeling. The semiempirical MO package MOPAC V4.0[36] was used to generate molecular geometries on the AM1 level. The calculations used Zn instead of Pd as the metal center and were carried out for both C_3H_5 and C_4H_7 as the allyl ligand. The symmetry was defined as C_s. The separation between the metal atom and the center of the terminal C atoms of the π-allyl ligand was chosen as 1.85 Å, and a value of 109° was selected for the angle between the N–M–N and allyl planes. No other geometrical constraints were imposed. The total charge on the complex was assigned as +1 with the following found total charges: terminal allyl C, −0.52; central allyl C, +0.07; metal +0.703, nitrogen, −0.176.

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Supplementary Material Available: Tables of bond distances and bond angles (Table S1) and thermal parameters (Table S2) (4 pages); a listing of F_o and F_c values (Table S3) (27 pages). Ordering information is given on any current masthead page.

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Sterically Crowded Organometallics. Influence of Complexation upon the Conformation of Hexakis(phenylethyl)benzene

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In order to determine the relative importance of intraligand versus ligand–metal steric repulsions in sterically crowded arenes with flexible substituents, the effect of complexation upon the conformation of hexakis(phenylethyl)benzene (1) has been studied. X-ray crystallographic characterization of the free ligand and the hexafluorophosphate salt of its previously known complex with $[Fe(C_5H_5)]^+$, 2, reveals that, whereas the ligand itself adopts the expected alternating three-up/three-down conformation, complexation forces an energetically unfavorable six-up (distal) conformation. To our knowledge, the latter represents the first example of such a conformation being exclusively adopted in the solid state. Furthermore, a VT-NMR study of 2 reveals no evidence of dynamic behavior, suggesting that the six-distal conformation also persists in solution. These results are discussed in the context of more widely studied hexaethylbenzene analogues. Crystal data: 1, $C_{54}H_{54}$, triclinic, $P\bar{1}$, a = 11.567 (5) Å, b = 12.115 (6) Å, c = 15.887 (8) Å, α = 86.96 (5)°, β = 77.30 (5)°, γ = 76.01 (5)°, Z = 2, R = 0.070; 2, $C_{59}H_{59}F_6FeP$, orthorhombic, $Pn2_1a$, a = 26.192 (9) Å, b = 18.447 (6) Å, c = 10.066 (7) Å, Z = 4, R = 0.074.

Introduction

Arene π-complexes are prototypal organometallic compounds and exist for virtually all the transition metals.[1] As such, they have engendered considerable attention, in particular because of the profound effect complexation has upon arene reactivity.[2] The depletion of π-electron den-

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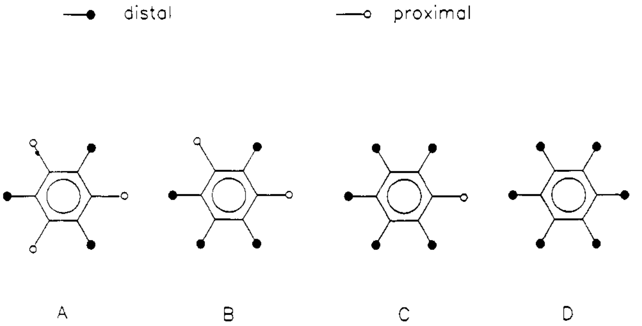
sity that causes the altered chemical reactivity, coupled with the stereochemical consequences of the presence of the metal moiety, has led to applications in organic synthesis.[2,3] However, an effect of complexation that has tended to be overlooked until quite recently is the steric influence of the metal and ancillary ligands upon the conformation of arenes with flexible substituents. The dramatic effect ancillary ligands have upon the conformation of hexaethylbenzene (heb) was demonstrated by Mislow, Hunter, et al. using (heb)M(CO)$_2$L (M = Cr, Mo) tripodal or "piano stool" complexes.[4] This series of papers outlined the effects of increasing the size of L upon the solid-state conformation and the solution-phase dynamic behavior of heb. In the process four conformations (A–D) of the possible eight[4a] were observed in the solid state.



More recently, related cationic complexes [(heb)Mo(CO)$_3$X]$^+$ (X = Cl, H) have been investigated[5] and the crystal structure of [(heb)Mo(CO)$_3$Cl][MoCl$_6$] revealed the presence of a fifth conformer, the 1,2,4,5-distal–3,6-proximal species.[5a]

The dynamic behavior of heb complexes in the solution phase is a subject of continuing interest and controversy since low-temperature spectra may be interpreted via invoking restricted rotation about either the arene–metal tripod bond[6] or the heb ethyl substituents.[7] The debate is complicated by observations that exceptional electronic or steric factors may unequivocally induce the former effect.[8] Nevertheless, such results do not necessarily preclude the existence of the latter effect for heb complexes.

Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement for $C_6(CH_2CH_2Ph)_6$ (1) and $[(C_5H_5)Fe(C_6(CH_2CH_2Ph)_6)]PF_6$ (2)

compd	1	2
color	colorless	yellow
fw	703.2	968.93
space group	$P\bar{1}$	$Pn2_1a$
temp, °C	20	20
cell constants[a]		
a, Å	11.567 (5)	26.192 (9)
b, Å	12.115 (6)	18.447 (6)
c, Å	15.887 (8)	10.066 (7)
α, deg	86.96 (5)	
β, deg	77.30 (5)	
γ, deg	76.01 (5)	
cell vol, Å^3	2107.4	4863.5
Z	2	4
D_{calc}, g cm^{-3}	1.11	1.32
μ_{calc}, cm^{-1}	0.67	4.18
scan type	$\omega/2\theta$	$\omega/2\theta$
radiation	Mo Kα	Mo Kα
max cryst dimens, mm	0.15 × 0.35 × 0.43	0.22 × 0.35 × 0.37
scan width, deg	0.80 + 0.35 tan θ	0.80 + 0.35 tan θ
decay of stds, %	+3	+3.9
no. of rflns measd	7412	4781
2θ range, deg	2–50	2–50
no. of rflns obsd[b]	1854	1807
computer programs[c]	SHELX[13]	SHELX[13]
structure soln	SHELXS[14]	SHELXS[14]
no. of params	487	569
weights, w[d]	0.0009	0.0002
GOF	1.08	2.38
R	0.070	0.074
R_w	0.088	0.079
final diff map, e Å^{-3}	0.2	0.6

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ for 25 reflections, $\theta >$ 15°. [b] Corrections: Lorentz-polarization, $F_o \geq 5\sigma(F_o)$. [c] Neutral scattering factors and anomalous dispersion corrections from ref 12. [d] $[\sigma(F_o)^2 + w(F_o)^2]^{-1}$.

Our recent observation that merely changing the counterion alters the solid-state conformation in the isoelectronic [(heb)Fe(C$_5$H$_5$)]$^+$ cation[9] supports EFF and EFF-EHMO calculations that indicate relatively small energy differences between heb conformations in the uncomplexed heb moiety.[4a] An added feature of interest concerning [Fe(C$_5$H$_5$)]$^+$ complexes is that an extremely facile method of arene functionalization may be invoked to prepare a variety of C$_6$R$_6$ complexes much wider than those readily accessible for Cr(CO)$_2$L.[10] It is therefore possible to study the influence of substituents larger than R = Et upon the conformation of C$_6$R$_6$. Such a situation is quite intriguing, as both intraligand and ligand–metal moiety steric repulsions would be expected to increase; however, they would compete against each other. In this contribution we report the effect of [Fe(C$_5$H$_5$)]$^+$ complexation upon such an arene, C$_6$(CH$_2$CH$_2$Ph)$_6$ (1).

Experimental Section

Synthesis. [(C$_5$H$_5$)Fe(C$_6$(CH$_2$CH$_2$Ph)$_6$)]PF$_6$ (2). 2 was prepared by a method based upon that described earlier by Astruc.[10] A 0.70-g (1.63-mmol) amount of [(C$_5$H$_5$)Fe(C$_6$Me$_6$)]PF$_6$[9], 3.63 g (32.3 mmol) of freshly prepared $K^{+t}BuO^-$, and 2.00 mL (16.8 mmol) of benzyl bromide were stirred in 50 mL of THF for 4 h, under an atmosphere of dinitrogen. The solvent was then removed in vacuo and the residue washed throughly with H$_2$O, filtered, and washed with ether. The resulting tan solid was subsequently recrystallized from acetone/H$_2$O, yielding 1.02 g (65%) of yellow air-stable crystals of 2. ^{1}H NMR ((CD$_3$)$_2$CO): δ 7.39 (s, 30 H), 5.28 (s, 5 H), 3.48 (dm, 24 H). ^{13}C NMR ((CD$_3$)$_2$CO): δ 141.6 s,

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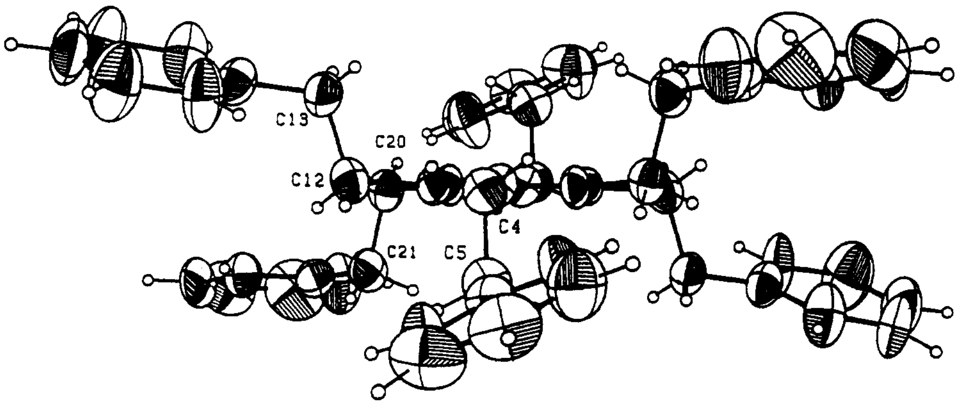

Figure 1. ORTEP view of one of the two independent molecules of $C_6(CH_2CH_2C_6H_5)_6$ (1).

129.6 d, 129.1 d, 127.5 d, 104.2 s, 79.5 d, 38.1 t, 33.7 t. Anal. Calcd for $C_{59}H_{59}F_6FeP$: C, 73.14; H, 6.14. Found: C, 72.50; H, 6.45.

$C_6(CH_2CH_2Ph)_6$ (1). An acetonitrile solution (0.40 g, 0.41 mmol in 100 mL) of **2** afforded colorless crystals of **1** after standing for 5 days. The crystals were collected by filtration and dried under vacuum; yield 0.21 g (72%). ^1H NMR ($(CD_3)_2CO$): δ 7.31 (m, 5 H), 2.97 (dm, 4 H). ^{13}C NMR ($(CD_3)_2CO$): δ 143.1 s, 137.3 s, 129.3 d, 129.0 d, 126.8 d, 38.5 t, 33.2 t. Anal. Calcd for $C_{54}H_{54}$: C, 92.26; H, 7.74. Found: C, 91.54; H, 7.87. All NMR spectra were recorded on a Nicolet 360-NB spectrometer, and elemental analyses were performed by Canadian Microanalytical Service, Ltd., Delta, British Columbia, Canada.

X-ray Crystallography. All intensity data were collected on an Enraf-Nonius CAD-4 diffractometer. Scattering factors for neutral atoms were taken from ref 12, and computations were effected with SHELX76[13] and SHELX.[14]

Compound 1. A colorless crystal of $C_6(CH_2CH_2Ph)_6$ was mounted on a pin and transferred to the goniometer. The space group was determined to be either the centric $P\bar{1}$ or acentric $P1$. Statistical tests indicated that the space group was centric, and subsequent solution and successful refinement of the structure were carried in the centric space group $P\bar{1}$. A summary of data collection and refinement parameters is given in Table I. Least-squares refinement with isotropic thermal parameters gave $R = 0.141$. The geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å^2. Refinement of non-hydrogen atoms with anisotropic temperature factors led to final values of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.070$ and $R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2} = 0.088$. High thermal motion was noted for C(43)–C(45); however, a disorder model could not be resolved. Final fractional coordinates are presented in Table II, and interatomic bond distances and angles are given as supplementary material.

Compound 2. A parallelepiped crystal of $[(C_5H_5)Fe(C_6(CH_2CH_2Ph)_6)]PF_6$ was mounted on a pin and transferred to the diffractometer. Cell dimensions and other pertinent crystallographic parameters are given in Table I. The space group was determined to be either the centric $Pnma$ or acentric $Pn2_1a$ (a nonstandard setting of $Pna2_1$) from the systematic absences. The subsequent solution and successful refinement of the structure was carried out in the acentric space group $Pn2_1a$. Least-squares refinement with isotropic thermal parameters led to $R = 0.113$. The geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å^2. High thermal motion was noted for the PF_6^- anion. It was not possible to resolve a disorder model, and these atoms were refined isotropically only.

Table II. Final Fractional Coordinates for $C_6(CH_2CH_2C_6H_5)_6$

atom	x/a	y/b	z/c	B(eqv),[a] Å^2
C(1)	0.9779 (8)	1.1172 (7)	0.5066 (5)	2.93
C(2)	0.9020 (7)	1.0716 (7)	0.4686 (5)	2.47
C(3)	0.9258 (7)	0.9523 (7)	0.4614 (5)	2.75
C(4)	0.9523 (8)	1.2465 (6)	0.5205 (5)	3.19
C(5)	0.8748 (8)	1.2818 (7)	0.6103 (6)	3.57
C(6)	0.8650 (9)	1.4023 (8)	0.6358 (5)	3.24
C(7)	0.7591 (9)	1.4844 (8)	0.6477 (6)	4.48
C(8)	0.751 (1)	1.5933 (9)	0.6744 (7)	5.45
C(9)	0.855 (1)	1.6241 (9)	0.6834 (6)	4.82
C(10)	0.963 (1)	1.540 (1)	0.6720 (6)	5.44
C(11)	0.9667 (9)	1.4330 (8)	0.6474 (7)	4.63
C(12)	0.8028 (7)	1.1472 (7)	0.4306 (5)	3.14
C(13)	0.8497 (7)	1.1738 (7)	0.3364 (5)	3.47
C(14)	0.7555 (9)	1.2434 (8)	0.2908 (6)	3.58
C(15)	0.7166 (9)	1.1974 (9)	0.2279 (7)	5.36
C(16)	0.632 (1)	1.261 (1)	0.1834 (7)	6.15
C(17)	0.587 (1)	1.374 (1)	0.2023 (8)	5.81
C(18)	0.619 (1)	1.417 (1)	0.2644 (9)	7.22
C(19)	0.707 (1)	1.356 (1)	0.3088 (7)	5.85
C(20)	0.8389 (7)	0.9003 (7)	0.4257 (5)	2.91
C(21)	0.7374 (8)	0.8736 (8)	0.4966 (6)	3.64
C(22)	0.6548 (9)	0.8094 (8)	0.4682 (6)	3.20
C(23)	0.679 (1)	0.694 (1)	0.4746 (7)	5.80
C(24)	0.605 (1)	0.634 (1)	0.4492 (9)	7.23
C(25)	0.512 (1)	0.693 (1)	0.4147 (9)	6.93
C(26)	0.486 (1)	0.806 (1)	0.4063 (7)	5.73
C(27)	0.5617 (9)	0.8652 (9)	0.4312 (6)	4.19
C(28)	0.4572 (8)	0.6073 (7)	0.0384 (5)	2.62
C(29)	0.3780 (7)	0.5332 (7)	0.0447 (5)	2.53
C(30)	0.4203 (8)	0.4274 (7)	0.0046 (5)	2.52
C(31)	0.4107 (7)	0.7251 (6)	0.0807 (5)	3.12
(C32)	0.4264 (8)	0.7283 (7)	0.1727 (6)	3.79
C(33)	0.4036 (9)	0.8488 (8)	0.2048 (5)	3.22
C(34)	0.285 (1)	0.9076 (9)	0.2426 (6)	4.52
C(35)	0.266 (1)	1.018 (1)	0.2742 (7)	5.51
C(36)	0.362 (2)	1.066 (1)	0.2620 (8)	6.17
C(37)	0.477 (1)	1.011 (1)	0.2225 (8)	6.53
C(38)	0.495 (1)	0.9025 (9)	0.1927 (5)	4.55
C(39)	0.2493 (7)	0.5707 (7)	0.0955 (5)	3.08
C(40)	0.1548 (7)	0.6347 (7)	0.0427 (5)	3.45
C(41)	0.0299 (9)	0.668 (1)	0.0988 (6)	3.90
C(42)	−0.047 (1)	0.595 (1)	0.1154 (7)	6.05
C(43)	−0.154 (2)	0.615 (2)	0.172 (1)	10.86
C(44)	−0.188 (3)	0.717 (2)	0.211 (2)	11.32
C(45)	−0.127 (2)	0.794 (2)	0.196 (2)	10.89
C(46)	−0.015 (1)	0.768 (1)	0.1394 (8)	6.83
C(47)	0.3320 (7)	0.3512 (7)	0.0067 (5)	3.27
C(48)	0.3289 (8)	0.2683 (7)	0.0829 (5)	3.74
C(49)	0.2423 (9)	0.1961 (9)	0.0802 (6)	3.59
C(50)	0.276 (1)	0.091 (1)	0.0408 (7)	6.06
C(51)	0.189 (2)	0.028 (1)	0.039 (1)	9.63
C(52)	0.072 (2)	0.077 (2)	0.070 (1)	11.37
C(53)	0.031 (2)	0.181 (2)	0.109 (1)	8.49
C(54)	0.118 (1)	0.237 (1)	0.1113 (7)	5.51

[a] $B(\mathrm{eqv}) = {}^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. [b] Isotropic refinement.

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The very low ratio of observed to unobserved reflections may have its origin in the diffuse scattering of the anion. Refinement of non-hydrogen atoms with anisotropic temperature factors led to the final values of $R = 0.074$ and $R_w = 0.079$. Final values of the positional parameters are given in Table III, whereas interatomic bond distances and angles are presented as supplementary material.

Results and Discussion

The structure of 1 is illustrated in Figure 1. 1 adopts the alternating up–down arrangement of phenylethyl groups that would be expected to predominate on the basis of steric repulsions between the phenylethyl moieties. Such a conformation was also adopted by heb in the solid state, for which it was predicted to be ca. 3.5 kcal mol^{-1} more stable than any of the other seven up–down isomers.[4a] The 360-MHz ^{1}H NMR spectrum of 2 exhibits two complex but symmetrical patterns in the ethylene region and is similar to that observed for the free ligand. The similarity between the two spectra might be anticipated since, with the assumption of fast rotation around the CH_2–Ph, CH_2–CH_2, and Fe–arene bonds, the six phenylethylene moieties are equivalent if the conformations adopted in the solid state predominate in solution (effective D_{3d} or S_6 symmetry for 1, C_{6v} for 2). Unfortunately, neither 1 nor 2 exhibits temperature dependence in their NMR spectra between room temperature and −92 °C. However, 1 appears to be approaching decoalescence at −92 °C, as the ethylene multiplets broaden considerably relative to the rest of the spectrum. The spectrum of 2 also broadens at lower temperatures, but this is presumably a solubility effect, as all peaks in the spectrum are affected. We cannot therefore unambiguously determine whether 1 and 2 are undergoing rapid interconversion of conformers on the NMR time scale (the observed solid-state conformations predominating) or whether they are rigid; however, the data are consistent with the former for 1 and the latter for 2.

There are two independent molecules of 1 in the unit cell, both of which lie around a center of inversion. There are only subtle differences between the molecules, with both adopting the same alternating three-up–three-down conformation. The phenyl groups dispose themselves roughly parallel to the plane of the central C_6 ring, presumably a result of packing effects. Molecule A, defined by C(1)–C(27), appears slightly more distorted than molecule B, which is defined by C(28)–C(54). This is confirmed by best least-squares plane calculations, which show that the phenyl groups in molecule A subtend angles of 26.45, 21.63, and 8.33° with the central C_6 ring whereas the corresponding values for molecule B are 4.81, 11.73, and 9.70°. The plane calculations also show that the ethylene groups in molecule A are slightly more distorted, with the first CH_2 unit lying an average of 0.084 Å and the second an average of 1.527 Å from the central C_6 plane. The corresponding values for molecule B are 0.055 and 1.324 Å. All other plane deviations, bond distances, and bond angles are entirely within expected ranges, with average C–C distances as follows: 1.40 (1) Å within the central benzene rings; 1.37 (3) Å within the phenyl rings; C_{sp^2}–C_{sp^3} = 1.51 (2) Å; C_{sp^3}–C_{sp^3} = 1.53 (1) Å. High thermal motion in the extremities of both molecules precludes detailed examination of the parameters.

Table III. Final Fractional Coordinates for $[(\eta^6\text{-}C_6(CH_2CH_2C_6H_5)_6)(\eta^5\text{-}C_5H_5)Fe]PF_6$

atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*(eqv),[a] Å^2
Fe	−0.97838 (7)	−0.2500	−0.1470 (2)	3.15
C(1)	−0.9581 (6)	−0.1971 (8)	−0.323 (1)	3.15
C(2)	−0.9374 (6)	−0.1604 (8)	−0.211 (2)	3.38
C(3)	−0.9714 (6)	−0.1381 (7)	−0.098 (1)	2.79
C(4)	−1.0224 (6)	−0.1542 (8)	−0.103 (1)	3.15
C(5)	−1.0443 (5)	−0.1958 (6)	−0.216 (1)	2.10
C(6)	−1.0111 (5)	−0.2139 (7)	−0.324 (1)	2.44
C(7)	−0.8816 (5)	−0.1420 (9)	−0.198 (2)	4.02
C(8)	−0.8628 (7)	−0.080 (1)	−0.288 (2)	5.27
C(9)	−0.8125 (6)	−0.0465 (9)	−0.236 (2)	3.74
C(10)	−0.7787 (6)	−0.077 (1)	−0.157 (2)	4.73
C(11)	−0.7326 (7)	−0.040 (1)	−0.114 (2)	5.16
C(12)	−0.7269 (9)	0.024 (1)	−0.159 (2)	6.94
C(13)	−0.761 (1)	0.060 (1)	−0.229 (3)	7.96
C(14)	−0.8051 (7)	0.025 (1)	−0.281 (2)	5.90
C(15)	−0.9219 (6)	−0.2202 (8)	−0.430 (1)	3.73
C(16)	−0.9208 (6)	−0.1756 (9)	−0.554 (2)	4.00
C(17)	−0.8786 (7)	−0.195 (1)	−0.649 (2)	4.01
C(18)	−0.8424 (9)	−0.141 (1)	−0.696 (2)	5.83
C(19)	−0.8045 (8)	−0.156 (1)	−0.782 (3)	6.86
C(20)	−0.7999 (9)	−0.229 (2)	−0.826 (3)	7.95
C(21)	−0.8318 (8)	−0.280 (1)	−0.781 (2)	6.25
C(22)	−0.8722 (6)	−0.261 (1)	−0.695 (1)	4.42
C(23)	−1.0322 (4)	−0.2523 (9)	−0.442 (1)	3.37
C(24)	−1.0603 (7)	−0.2026 (9)	−0.541 (2)	4.85
C(25)	−1.0911 (5)	−0.2358 (9)	−0.643 (1)	3.10
C(26)	−1.0793 (7)	−0.302 (1)	−0.702 (2)	4.73
C(27)	−1.1060 (7)	−0.334 (1)	−0.803 (2)	5.23
C(28)	−1.150 (1)	−0.295 (1)	−0.845 (2)	7.27
C(29)	−1.1652 (7)	−0.235 (1)	−0.786 (2)	6.15
C(30)	−1.1339 (8)	−0.201 (1)	−0.692 (2)	5.24
C(31)	−1.0992 (5)	−0.2259 (8)	−0.213 (2)	3.56
C(32)	−1.1410 (5)	−0.1791 (8)	−0.254 (2)	4.18
C(33)	−1.1912 (6)	−0.2157 (9)	−0.245 (2)	3.97
C(34)	−1.2177 (8)	−0.211 (1)	−0.127 (2)	6.08
C(35)	−1.2630 (8)	−0.252 (1)	−0.110 (2)	6.00
C(36)	−1.2830 (6)	−0.291 (1)	−0.206 (3)	5.52
C(37)	−1.2555 (9)	−0.295 (1)	−0.324 (3)	7.28
C(38)	−1.2104 (6)	−0.2608 (9)	−0.347 (2)	3.66
C(39)	−1.0584 (6)	−0.1314 (8)	0.005 (1)	3.59
C(40)	−1.0762 (7)	−0.0541 (8)	−0.017 (2)	4.04
C(41)	−1.1196 (9)	−0.030 (1)	0.073 (2)	5.03
C(42)	−1.1170 (8)	−0.019 (1)	0.199 (3)	5.45
C(43)	−1.155 (1)	−0.002 (1)	0.286 (2)	5.80
C(44)	−1.202 (1)	0.002 (1)	0.217 (3)	8.30
C(45)	−1.207 (1)	−0.006 (1)	0.092 (4)	9.40
C(46)	−1.169 (1)	−0.025 (1)	0.018 (2)	7.25
C(47)	−0.9477 (7)	−0.1027 (8)	0.026 (2)	4.65
C(48)	−0.9344 (7)	−0.0273 (8)	0.001 (2)	4.77
C(49)	−0.9088 (7)	0.0083 (9)	0.121 (2)	3.70
C(50)	−0.9331 (7)	0.0082 (8)	0.249 (2)	4.87
C(51)	−0.9090 (9)	0.041 (1)	0.353 (2)	6.30
C(52)	−0.8619 (9)	0.0778 (9)	0.335 (2)	5.68
C(53)	−0.8397 (8)	0.071 (1)	0.219 (2)	5.47
C(54)	−0.8624 (7)	0.0408 (9)	0.110 (2)	4.34
C(55)	−1.0070 (7)	−0.341 (1)	−0.078 (3)	5.97
C(56)	−0.979 (1)	−0.310 (1)	0.022 (2)	6.86
C(57)	−0.932 (1)	−0.304 (1)	−0.025 (3)	8.13
C(58)	−0.930 (1)	−0.331 (2)	−0.146 (3)	7.91
C(59)	−0.977 (1)	−0.3567 (9)	−0.172 (2)	4.20
P(1)	−1.0421 (3)	0.0331 (4)	0.5987 (7)	8.5 (2)[b]
F(1)	−1.0315 (6)	−0.0126 (8)	0.462 (2)	13.7 (5)[b]
F(2)	−1.0589 (8)	0.074 (1)	0.721 (2)	21.0 (8)[b]
F(3)	−1.0100 (9)	0.091 (1)	0.542 (3)	20.6 (8)[b]
F(4)	−1.0924 (8)	0.069 (1)	0.527 (2)	18.2 (7)[b]
F(5)	−1.0023 (9)	−0.005 (1)	0.669 (2)	20.0 (8)[b]
F(6)	−1.0851 (7)	−0.025 (1)	0.623 (2)	18.3 (7)[b]

[a] $B(\text{eqv}) = {}^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. [b] Isotropic refinement.

The conformation adopted by hexakis(phenylethyl)benzene when complexed to $[Fe(C_5H_5)]^+$ is quite different from that seen in the free molecule. Figure 2 illustrates how all six ethylene moieties are distal to the iron atom, making 2 the first compound to exclusively adopt conformation D for a C_6R_6 ligand in the solid state. A six-distal conformation was also observed for $(heb)Cr(CO)_2(PPh_3)$;[4a] however, one of the ethyl groups was seen to be disordered and to occupy a proximal site in approximately one-third of the molecules. The closest X-ray crystallographically characterized analogues to 2 are perhaps

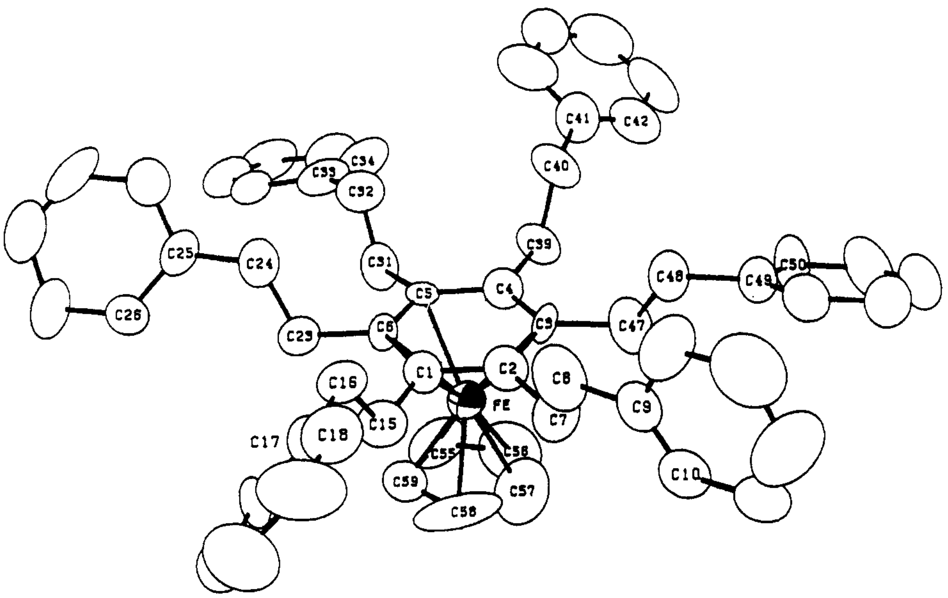

Figure 2. ORTEP perspective view of the cationic portion of 2.

$[(heb)Fe(C_5H_5)][PF_6]$[10] and $[(heb)Fe(C_5H_5)][BPh_4]$,[9] which are observed to adopt conformations B and C, respectively, in the solid state. The effect of increasing the size of the R group is therefore, at least in this instance, adoption of the conformation that is least energetically favored in the free ligand. A similar phenomenon was encountered with the pentabenzylcyclopentadienyl (pbzcp) ligand. $(pbzcp)Mn(CO)_3$[15] and $(pbzcp)Co(CO)_2$[16] adopt one-proximal–four-distal conformations, whereas for $(pbzcp)_2Fe$[15] all 10 benzyl groups are distal.

Steric strain might be expected to manifest itself, particularly in the Fe–C bond distances, the Fe–plane distances, and the angles around the ethylene moieties. Unfortunately, the quality and amount of data and high thermal motion in the phenyl moieties preclude close scrutiny of individual bond lengths and angles. However, there are two apparent manifestations of steric strain: the average angle subtended at the ethylene carbon atoms bonded to the coordinated C_6 ring is 115 (3)°; the Fe–C_5 plane distance of 1.64 Å is the shortest of a range of Fe(II)–plane distances whereas the Fe–C_6 plane separation of 1.54 Å is more typical.[17] Average bond distances are as follows: Fe–C_5H_5 = 1.99 (2) Å; Fe–arene = 2.11 (3) Å; 1.33 (4) Å within the C_5H_5 ring; 1.44 (4) Å within the coordinated arene ring; 1.37 (6) Å within the phenyl rings; C_{sp^2}–C_{sp^3} = 1.51 (3) Å; C_{sp^3}–C_{sp^3} = 1.50 (4) Å. The coordinated rings are planar to 0.02 Å, and surprisingly, four of the ethylene carbon atoms bonded to the coordinated C_6 ring point toward the Fe atom (by 0.05–0.24 Å). Bending of ring substituents toward the metal has been predicted in $(arene)M(CO)_n$ complexes.[18] The conformations adopted by the phenyl groups are markedly different from those adopted in 1. As might be expected, the phenyl groups are now unable to orient themselves parallel to the coordinated C_6 ring, and the result is random disposition of the phenyl groups. The observed orientations are presumably strongly influenced by a combination of intraligand and packing effects.

In summary, complexation of hexakis(phenylethyl)benzene by $[Fe(C_5H_5)]^+$ results in adoption of a six-distal conformation, the least energetically favored in the free ligand. That such control over conformation is feasible suggests that synthetic applications of transition-metal moieties might be extended to include steric control of reactivity at flexible substituents. In such a context we are investigating methods of incorporating reactive functional groups into arene moieties. Such a strategy appears reasonable in light of recent work by Astruc.[19]

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Supplementary Material Available: Tables of positional parameters for hydrogen atoms, thermal parameters, bond distances and bond angles, and least-squares plane calculations (16 pages); listings of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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