ORGANOMETALLICS

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Sterically Crowded Organometallics. 2.[1] Influence of Complexation and Intramolecular Edge-to-Face Aromatic–Aromatic Interactions upon the Solid-State Conformational Preference of Arboroles

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The solid-state conformations of the prototypal doubly branched "arborole" molecule 1,2,4,5-$C_6H_2\{CH(CH_2Ph)_2\}_4$, **4**, and its $FeCp^+$ complex, **3a**, have been determined via single-crystal X-ray crystallography. **4** adopts a conformation with two of the eight benzyl groups roughly in the plane of the central C_6 ring and opposite the unsubstituted C_6 ring carbon atoms. The other six benzyl groups are oriented away from the central ring in a manner that suggests edge-to-face aromatic–aromatic interactions between phenyl rings on branches attached to adjacent ring carbon atoms (C–H···C_6 plane distances of 2.72 Å). **3a** adopts a conformation with four benzyl groups distal to the $FeCp^+$ moiety and four proximal. The proximal benzyl groups are roughly coplanar with each other and the central C_6 ring whereas the distal groups are oriented toward each other and away from the central C_6 plane. Once again edge-to-face aromatic–aromatic interactions appear to be occurring, between distal phenyl rings attached to branches on adjacent carbon atoms (C–H···C_6 plane distances of 2.57 and 2.61 Å). Steric crowding and/or electronic effects in **3a** appear to manifest themselves by causing a clear distortion in the C_6 ring toward a boat conformation. The conformations observed in **3a** and **4** therefore appear to limit the ability of this particular arborole to act as a host via encapsulation of small molecules. Indeed, both **3a** and **4** crystallize with acetone solvate molecules that do not interact with the arborole. Crystal data: **3a**, $C_{71}H_{67}FePF_6\cdot 3$(acetone), monoclinic, $P2_1$, $a = 13.100\ (6)$ Å, $b = 18.972\ (10)$ Å, $c = 15.542\ (4)$ Å, $\beta = 112.42\ (3)°$, $Z = 2$, $R = 0.060$; **4**, $C_{66}H_{62}\cdot$acetone, monoclinic, $A2/a$, $a = 17.584\ (5)$ Å, $b = 12.3220\ (18)$ Å, $c = 24.313\ (9)$ Å, $Z = 4$, $R = 0.051$.

Introduction

The ability of transition metal moieties to activate arenes has attracted a considerable amount of attention, particularly if the arene is activated toward reactions that are unfavorable or even unknown in the free arene.[2] Nucleophilic addition to afford cyclohexadienyl complexes represents perhaps the most studied such mode of activation,[2,3] but the ability of the transition metal moiety, in particular $FeCp^+$, to activate an arene to facile deprotonation of α-C–H bonds, including alkyl substituents, has received increasing attention in recent years.[4-6] The latter work is perhaps best and most dramatically highlighted by perfunctionalization of $[FeCp(C_6Me_6)]^+$, **1**, which occurs via facile one-pot base-promoted deprotonation/electrophilic addition of alkyl and functionalized alkyl groups. Early work focused upon conversion of **1** to the corresponding C_6Et_6[5] complex and recently culminated with the generation of a novel class of molecules with longer functionalized chains called "tentacled sandwiches".[6]

The steric effects of complexation upon crowded arene molecules, especially those with flexible substituents, has also been a matter of considerable interest and, in the context of the dynamic behavior of $M(CO)_2L$–arene (M = Cr, Mo; L = CO, CS, PPh_3, $P(OR)_3$) "piano stool" complexes, controversy.[7,8] Our interest in the field lies primarily with X-ray crystallographic determination of favored conformations adopted by bulky arenes with

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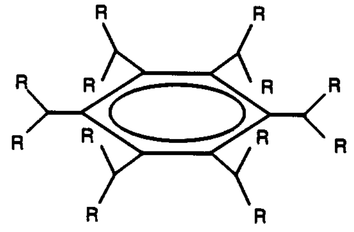
flexible substituents. For example, the $FeCp^+$ moiety in $[FeCp\{C_6(CH_2R)_6\}]^+$, **2** (R = Et (**2a**), CH_2Ph (**2b**)), promotes unfavorable[9] ligand conformations such that five (**1a**[10]) or even six (**1b**[1]) distal groups are observed. Unfortunately, the steric congestion in **2** precludes further functionalization at the α-carbon atom except for R = allyl, in which case Astruc very recently demonstrated that dodecasubstitution to afford a doubly branched "arborole" is feasible[11] (I). However, greater levels of



I

functionalization are routinely possible for tri- and tetramethylated benzenes. $[FeCp(mesitylene)]^+$ has been converted via nine alkylations to $[FeCp(1,3,5\text{-}tBu_3\text{-}benzene)]^+$,[5] and $[FeCp(1,2,4,5\text{-}Me_4benzene)]^+$ may be functionalized via eight alkylations to complexed double branched arboroles of general formula $[FeCp\{C_6H_2(CHR_2)_4\}]^+$, **3** (R = CH_2Ph (**3a**), allyl (**3b**), C_3H_6OH (**3c**)).[11] It has been suggested that the new arborole molecules might be exploited in several ways, including as hosts for encapsulation of small guest molecules.[11] In order to determine the feasibility of this intriguing proposition and to investigate the effects of steric crowding in these novel molecules, we have undertaken determination of the solid-state geometry of a prototypal arborole complex, **3a**, and the corresponding free arene, $1,2,4,5\text{-}C_6H_2\{CH(CH_2Ph)_2\}_4$, **4**. We report herein the results of our X-ray structural investigation.

Experimental Section

Synthesis. $1PF_6$ was prepared according to the literature.[12] THF was distilled over benzylketyl immediately prior to use. NMR spectra were recorded at the Atlantic Region Magnetic Resonance Centre, Dalhousie University, Halifax, Nova Scotia, Canada, and elemental analyses were obtained through Canadian Microanalytical Services, Ltd., Delta, British Columbia, Canada.

$3aPF_6$. To 0.55 g (1.5 mmol) of $1PF_6$ in 10 mL of THF were added 30 mL of 1.0 M *t*-BuOK (Aldrich, 30 mmol) and 5.99 g of benzyl bromide (Aldrich, 35.0 mmol) over a 30-min period. The reaction mixture was stirred under dinitrogen at ambient conditions for 16 h and refluxed for a further 5 h to ensure completion of the reaction. The solvent was removed in vacuo, and the pale yellow product was washed with diethyl ether and filtered out. A 1.31-g amount (1.17 mmol, 78%) of $3aPF_6$ was isolated after drying. ^1H and ^{13}C NMR spectra agreed closely with those reported by Astruc.[11] Anal. Calcd for $C_{71}H_{67}FePF_6$: C, 76.06; H, 6.02. Found: C, 76.00; H, 5.98.

Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

	compd	
	$3aPF_6\cdot3$(acetone)	**4**·acetone
color	orange	colorless
fw	1295.4	913.2
cryst system	monoclinic	monoclinic
space group	$P2_1$	$A2/a$
temp, °C	17	17
cell consts[a]		
a, Å	13.100 (6)	17.584 (5)
b, Å	18.972 (10)	12.3220 (18)
c, Å	15.542 (4)	24.313 (9)
β, deg	112.42 (3)	97.666 (10)
cell vol, Å^3	3571 (3)	5221 (3)
F(000)	1368	1960
Z	2	4
D_{calc}, g cm^{-3}	1.20	1.16
μ_{calc}, cm^{-1}	2.8	0.6
scan type	$\omega/2\theta$	$\omega/2\theta$
radiation	Mo Kα	Mo Kα
max xtal dimens, mm	0.30 × 0.55 × 0.65	0.25 × 0.35 × 0.53
scan width	0.80 + 0.35 tan θ	0.70 + 0.35 tan θ
transm range	0.62, 0.95	0.94, 0.99
decay of stds, %	−16	−2
no. of reflcns measd	5065	4215
2θ range, deg	2–45	2–48
no. of unique reflcns	4819	4061
no. of reflcns obsd[b]	3431	1721
computer programs[c]	NRCVAX[d]	NRCVAX[d]
structure solution	direct	direct
no. of params	759	317
weight modifier, *k*	0.0001	0.0002
GOF	2.85	1.89
R	0.060	0.051
R_w	0.059	0.051
final diff map, e/Å^3	0.46	0.35

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ for 24 reflections $\theta > 14°$. [b] $I > 3\sigma(I)$. Corrections: Lorentz–polarization and absorption (empirical ψ scan). [c] Neutral scattering factors and anomalous dispersion corrections from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4. [d] An Interactive Program System for Structure Analysis. Gabe, E. J.; Le Page, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

4. A 1.00-g amount (0.77 mmol) of $3aPF_6$ was dissolved in ca. 15 mL of acetone/water. The solution was exposed to light at ambient temperature for a period of 1 week, at which point 0.65 g (0.71 mmol, 92%) of colorless crystals of **4**·acetone were recovered by filtration and air drying. ^1H and ^{13}C NMR spectra agreed closely with those reported by Astruc.[11] Anal. Calcd for $C_{66}H_{62}$·acetone: C, 90.75; H, 7.51. Found: C, 90.56; H, 7.69.

X-ray Crystallography. Crystals of $3aPF_6$ suitable for X-ray crystallography were grown via cooling a saturated acetone/water solution to −15 °C whereas crystals of **4** were used as obtained directly from synthesis. Both $3aPF_6$ and **4** are air stable but were observed to lose solvent over a period of several hours. The crystals were therefore sealed in thin-walled glass capillaries prior to being placed on the goniometer. Details of crystallographic intensity data collection and structure refinement parameters are presented in Table I. All crystallographic calculations were conducted on IBM-compatible 40486 computers.

$3aPF_6$. The space group was determined to be the acentric $P2_1$ from systematic absences and subsequent structure solution using direct methods. Least-squares refinement of all non-hydrogen atoms with isotropic temperature factors revealed the presence of three independent acetone solvent molecules per asymmetric unit. Full-matrix least squares refinement of all non-hydrogen atoms with hydrogen atoms fixed in calculated positions (d_{C-H} = 1.08 Å), except for the solvent molecules, which were refined with isotropic thermal parameters and without hydrogen atoms, afforded final values of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.060$ and $R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2} = 0.059$. Final fractional coordinates are presented in Table II.

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[9] The most favorable conformer for C_6Et_6 is that with an alternating 3-up/3-down arrangement of the methyl groups whereas the least favorable is that with all six methyl groups on the same face of the C_6 ring. The relative energies of the eight possible conformers of the free ligand have been calculated: see ref 7f and references therein. Upon complexation, groups that orient toward the metal are termed proximal whereas those that face away are termed distal.

[10] Whereas the PF_6^- salt of $[FeCp(C_6Et_6)]^+$ adopts a four distal/two proximal conformation (see ref 5), the BPh_4^- analogue adopts a five distal/one proximal conformation: Dubois, R. H.; Zaworotko, M. J.; White, P. S. *J. Organomet. Chem.* **1989**, *362*, 155.

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Table II. Atomic Parameters *x, y, z* and B_{iso} Values (Å^2) for 3a

	x	*y*	*z*	B_{iso}^{a}		*x*	*y*	*z*	B_{iso}^{a}
Fe	0.37860 (10)	0.91610	0.94749 (7)	3.88 (6)	C234	−0.1816 (8)	0.9563 (6)	0.9151 (7)	7.7 (7)
P	0.65479 (24)	0.69972 (17)	−0.05631 (21)	6.53 (18)	C235	−0.1163 (8)	0.9051 (6)	0.9792 (6)	7.0 (7)
F1	0.5866 (6)	0.6417 (3)	−0.1241 (5)	10.6 (5)	C236	−0.0060 (7)	0.9187 (6)	1.0283 (5)	5.0 (5)
F2	0.5628 (5)	0.6988 (5)	−0.0142 (5)	12.7 (6)	C41	0.1448 (7)	0.9407 (4)	0.7533 (5)	4.3 (5)
F3	0.7234 (6)	0.6423 (4)	0.0174 (5)	12.3 (5)	C42	0.1811 (7)	1.0170 (5)	0.7450 (6)	5.0 (5)
F4	0.5880 (6)	0.7576 (4)	−0.1248 (6)	15.3 (6)	C421	0.1190 (8)	1.0505 (5)	0.6504 (6)	6.0 (6)
F5	0.7429 (6)	0.6968 (6)	−0.1000 (6)	14.9 (7)	C422	0.0523 (11)	1.1067 (7)	0.6412 (8)	10.2 (9)
F6	0.7213 (6)	0.7573 (4)	0.0150 (6)	13.2 (5)	C423	−0.0025 (15)	1.1414 (10)	0.5573 (10)	15.8 (14)
Cp1	0.5455 (7)	0.9213 (8)	1.0103 (7)	9.7 (7)	C424	0.0037 (14)	1.1113 (8)	0.4846 (11)	14.1 (10)
Cp2	0.5212 (7)	0.9236 (7)	0.9180 (8)	7.9 (7)	C425	0.0723 (10)	1.0553 (7)	0.4850 (7)	9.8 (9)
Cp3	0.4597 (8)	0.9783 (6)	0.8863 (7)	7.0 (7)	C426	0.1288 (9)	1.0230 (6)	0.5732 (7)	7.4 (7)
Cp4	0.4452 (9)	1.0154 (5)	0.9515 (10)	10.1 (10)	C43	0.0206 (7)	0.9393 (5)	0.7387 (5)	5.3 (6)
Cp5	0.4993 (12)	0.9805 (9)	1.0346 (7)	13.2 (11)	C431	−0.0370 (7)	0.8689 (5)	0.7121 (6)	5.1 (5)
C1	0.3213 (7)	0.8412 (4)	1.0216 (5)	3.5 (4)	C432	−0.0582 (8)	0.8405 (5)	0.6231 (6)	6.0 (6)
C2	0.2632 (6)	0.9046 (4)	1.0167 (5)	3.4 (4)	C433	−0.1156 (10)	0.7815 (6)	0.5951 (7)	9.0 (8)
C3	0.2161 (7)	0.9378 (4)	0.9261 (5)	3.8 (5)	C434	−0.1532 (10)	0.7442 (6)	0.6536 (9)	10.4 (8)
C4	0.2121 (6)	0.9053 (5)	0.8437 (5)	3.5 (4)	C435	−0.1354 (9)	0.7696 (7)	0.7386 (8)	8.5 (8)
C5	0.2714 (7)	0.8416 (4)	0.8512 (5)	3.5 (5)	C436	−0.0721 (8)	0.8311 (6)	0.7707 (6)	7.0 (7)
C6	0.3265 (7)	0.8122 (4)	0.9389 (5)	3.6 (5)	C51	0.2691 (7)	0.8015 (4)	0.7643 (5)	3.7 (5)
C11	0.3729 (7)	0.7981 (4)	1.1115 (5)	4.1 (5)	C52	0.3418 (8)	0.8389 (5)	0.7161 (6)	4.9 (5)
C12	0.4980 (7)	0.7910 (5)	1.1445 (5)	5.0 (5)	C521	0.3359 (8)	0.8034 (5)	0.6278 (6)	5.0 (5)
C121	0.5523 (7)	0.7516 (5)	1.2375 (5)	4.6 (5)	C522	0.2396 (9)	0.8077 (6)	0.5491 (6)	6.7 (7)
C122	0.5908 (9)	0.6833 (6)	1.2444 (6)	7.5 (7)	C523	0.2357 (10)	0.7718 (6)	0.4680 (7)	9.3 (8)
C123	0.6337 (10)	0.6500 (6)	1.3299 (8)	9.4 (8)	C524	0.3267 (13)	0.7371 (7)	0.4687 (8)	11.8 (11)
C124	0.6465 (10)	0.6857 (7)	1.4094 (7)	8.9 (8)	C525	0.4166 (12)	0.7302 (7)	0.5425 (8)	11.0 (10)
C125	0.6098 (9)	0.7503 (6)	1.4045 (6)	7.8 (7)	C526	0.4253 (9)	0.7656 (6)	0.6274 (6)	7.1 (7)
C126	0.5622 (9)	0.7841 (5)	1.3194 (6)	6.7 (7)	C53	0.3061 (7)	0.7245 (5)	0.7812 (6)	4.7 (5)
C13	0.3137 (7)	0.7258 (5)	1.1005 (5)	4.8 (5)	C531	0.2368 (7)	0.6759 (4)	0.8143 (5)	4.3 (5)
C131	0.2011 (7)	0.7278 (4)	1.1003 (5)	4.1 (5)	C532	0.2895 (8)	0.6231 (5)	0.8789 (7)	6.1 (6)
C132	0.1100 (7)	0.7262 (5)	1.0238 (6)	5.4 (5)	C533	0.2309 (9)	0.5723 (5)	0.9057 (7)	6.7 (7)
C133	0.0078 (9)	0.7247 (6)	1.0256 (7)	7.5 (7)	C534	0.1209 (8)	0.5727 (5)	0.8673 (7)	6.6 (6)
C134	−0.0063 (8)	0.7273 (6)	1.1113 (8)	7.9 (8)	C535	0.0676 (8)	0.6256 (6)	0.8092 (6)	6.1 (6)
C135	0.0884 (9)	0.7314 (7)	1.1918 (7)	8.8 (8)	C536	0.1251 (8)	0.6773 (5)	0.7802 (6)	5.2 (6)
C136	0.1909 (8)	0.7311 (7)	1.1882 (6)	7.5 (7)	OS1	0.6425 (8)	0.9555 (5)	0.2769 (7)	13.6 (3)
C21	0.2501 (7)	0.9379 (4)	1.1015 (5)	4.1 (5)	CS11	0.6608 (13)	1.0666 (9)	0.3489 (11)	14.4 (5)
C22	0.3578 (7)	0.9657 (4)	1.1734 (6)	4.4 (5)	CS12	0.6899 (11)	0.9921 (8)	0.3489 (9)	11.8 (4)
C221	0.3500 (8)	0.9832 (5)	1.2677 (6)	5.1 (6)	CS13	0.7551 (13)	0.9523 (9)	0.4374 (11)	14.4 (5)
C222	0.3386 (9)	0.9294 (6)	1.3236 (6)	7.2 (7)	OS2	0.9728 (10)	0.8508 (8)	0.3811 (8)	18.1 (4)
C223	0.3357 (11)	0.9462 (6)	1.4099 (7)	9.8 (9)	CS21	0.8303 (17)	0.8009 (13)	0.2737 (14)	20.5 (8)
C224	0.3418 (10)	1.0123 (6)	1.4405 (7)	8.8 (8)	CS22	0.8958 (17)	0.8551 (14)	0.2865 (14)	21.0 (8)
C225	0.3564 (11)	1.0650 (6)	1.3869 (7)	9.5 (9)	CS23	0.9617 (16)	0.9084 (13)	0.2691 (13)	20.3 (7)
C226	0.3565 (9)	1.0502 (5)	1.2997 (6)	6.7 (7)	OS3	0.4845 (9)	0.4761 (7)	0.3098 (8)	16.2 (4)
C23	0.1616 (8)	0.9972 (4)	1.0776 (6)	4.9 (5)	CS31	0.3741 (12)	0.5512 (10)	0.3516 (10)	14.1 (5)
C231	0.0457 (7)	0.9786 (5)	1.0163 (6)	4.4 (5)	CS32	0.4051 (12)	0.4787 (9)	0.3319 (10)	13.2 (5)
C232	−0.0179 (8)	1.0287 (5)	0.9520 (6)	6.3 (6)	CS33	0.3742 (12)	0.4137 (11)	0.3668 (10)	15.0 (5)
C233	−0.1285 (8)	1.0162 (6)	0.9021 (6)	7.4 (7)					

^{a} B_{iso} is the mean of the principal axes of the thermal ellipsoid.

4. The space group was found to the centric *A*2/*a* (nonstandard setting of *C*2/*c*, No. 15) following examination of systematic absences and subsequent structure solution and refinement. The molecule of 4 was found to lie around an inversion center and, following isotropic refinement of all non-hydrogen atoms, one molecule of acetone was located lying on a 2-fold axis. Refinement of this model with anisotropic thermal parameters for all non-hydrogen atoms and fixed hydrogen atom positions (d_{C-H} = 1.08 Å) for 4 afforded values of R = 0.051 and R_w = 0.051. Final fractional coordinates are presented in Table III, and selected interatomic distances and angles for both 3aPF$_6$ and 4 are given in Table IV.

Results and Discussion

3aPF$_6$. ORTEP[13] perspective and overhead views of cation **3a** are illustrated in Figure 1. They reveal that, as might be expected from steric considerations and NMR spectroscopy, there are four distal and four proximal benzyl moieties. An interesting feature is that the four proximal benzyl groups are disposed roughly parallel to the coordinated C_5 and C_6 planes (average angle between planes 23.5°) whereas the four distal groups are roughly normal to the C_5 and C_6 planes (average angle between planes 72.1°). This is presumably a manifestation of steric effects around the metal and has important consequences since it means that the distal benzyl groups are forced toward each other, thereby precluding the existence of an intraligand cavity. Steric strain within the arborole ligand appears to manifest itself by distortion in the C_6 ring rather than in the flexible substituents. A number of structural parameters support this assertion: (i) Fe–C_6 distances are significantly shorter to the unsubstituted ring carbon atoms (average 2.070 (3) Å vs 2.169 (12) Å). (ii) The C_6 plane is only planar to 0.057 Å whereas the planes formed by C1, C2, C3, C6 and C3–C6 are planar to 0.013 Å and the plane formed by the four substituted carbon atoms (C1, C2, C4, C5) is planar to less than .001 Å. (iii) The average angles around the α-carbon atoms are the same in the complex as in the free ligand (112.7 (1.8) and 112.7 (7)°, respectively). (iv) The average Fe–C_5 ring and Fe–C_6 ring bond distances and Fe–plane distances are comparable to those seen in less crowded Fe(II) arene and Fe(II) cyclopentadienyl complexes.[14] The net result is

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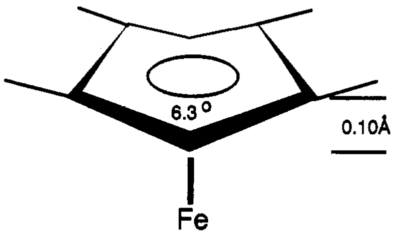
Table III. Atomic Parameters *x*, *y*, *z* and B_{iso} Values (Å^2) for 4

	x	*y*	*z*	B_{iso}[a]
C1	0.56467 (25)	0.2873 (3)	0.23235 (17)	3.65 (20)
C2	0.4949 (3)	0.3207 (3)	0.20396 (16)	3.51 (21)
C3	0.57265 (25)	0.2185 (3)	0.27862 (17)	3.59 (22)
C21	0.59305 (23)	0.3999 (3)	0.15559 (17)	3.95 (21)
C22	0.5542 (3)	0.4892 (3)	0.16710 (17)	4.53 (22)
C221	0.5448 (3)	0.5827 (3)	0.12585 (17)	4.13 (24)
C222	0.4753 (3)	0.6306 (4)	0.11043 (22)	5.8 (3)
C223	0.4668 (3)	0.7136 (4)	0.07180 (24)	6.4 (3)
C224	0.5286 (4)	0.7522 (4)	0.04967 (21)	6.5 (3)
C225	0.5985 (4)	0.7058 (5)	0.0648 (3)	7.9 (4)
C226	0.6068 (3)	0.6214 (4)	0.10279 (22)	6.6 (3)
C23	0.49508 (25)	0.3424 (3)	0.09896 (17)	4.46 (22)
C231	0.5614 (3)	0.2671 (4)	0.09461 (17)	4.5 (3)
C232	0.6295 (4)	0.3046 (4)	0.07897 (21)	6.7 (3)
C233	0.6885 (4)	0.2319 (7)	0.0731 (3)	8.6 (4)
C234	0.6795 (4)	0.1231 (7)	0.0818 (3)	8.3 (4)
C235	0.6125 (5)	0.0860 (5)	0.09662 (23)	7.8 (4)
C236	0.5539 (3)	0.1574 (5)	0.10349 (20)	6.0 (3)
C31	0.65323 (25)	0.1913 (3)	0.30537 (17)	3.96 (22)
C32	0.70450 (24)	0.2922 (4)	0.31928 (18)	4.64 (23)
C321	0.67393 (25)	0.3698 (4)	0.35896 (19)	4.22 (23)
C322	0.6369 (3)	0.4650 (4)	0.34114 (19)	5.5 (3)
C323	0.6095 (3)	0.5363 (4)	0.37781 (24)	6.3 (3)
C324	0.6187 (3)	0.5130 (4)	0.43370 (22)	5.8 (3)
C325	0.6559 (3)	0.4195 (4)	0.45239 (19)	5.5 (3)
C326	0.6830 (3)	0.3482 (4)	0.41537 (22)	4.9 (3)
C33	0.69407 (24)	0.1123 (4)	0.26940 (18)	4.84 (25)
C331	0.6648 (3)	–0.0032 (4)	0.26726 (19)	4.31 (23)
C332	0.6033 (3)	–0.0351 (4)	0.22957 (20)	5.9 (3)
C333	0.5799 (3)	–0.1433 (5)	0.22646 (22)	6.7 (3)
C334	0.6166 (4)	–0.2186 (4)	0.2617 (3)	6.4 (3)
C335	0.6764 (3)	–0.1882 (4)	0.29988 (22)	5.9 (3)
C336	0.7011 (3)	–0.0810 (4)	0.30319 (19)	4.95 (25)
CS1	$^1/_4$	0.4799 (12)	0.00000	21.6 (23)
CS2	0.3058 (8)	0.5090 (10)	0.0417 (5)	20.2 (9)
OS	$^1/_4$	0.3785 (12)	0.00000	21.1 (10)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

that the C_6 ring can be viewed as having adopted a boat conformation (II). Although this observation might be intuitively expected to be a consequence of steric effects, it should be noted that such a conformation may also be at least partially attributed to electronic factors that result from the 1,2,4,5 disposition of the C_6 ring substituents.[15] This latter explanation is not feasible for hexasubstituted C_6 systems such as **2a,b**, and as a result, **2b** exhibits more manifestations of intraligand strain than **3a**.



II

The four distal substituents are oriented with respect to each other in a manner that suggests intraligand edge-to-face aromatic–aromatic interactions (i.e. C–H···arene π hydrogen bonding) is influencing the conformation of the phenyl rings. This is illustrated by Figure 1b, which highlights the two phenyl–phenyl interactions that might be regarded as π hydrogen bonds. The following C–H···C_6 plane distances are consistent with such interactions: H235···C13(C_6 plane) = 2.57 Å; H536···C43(C_6 plane) = 2.61 Å. These interactions occur between phenyl groups on branches attached to adjacent carbon atoms. π-Hydrogen bonds have only recently been characterized experimentally in the solid state. For O–H···C_6 plane hydrogen bonding O···C_6 plane distances of 3.11 Å have been calculated[16] and 3.2 Å have been observed.[17] Furthermore, spectroscopic characterization of the 1:1 cluster of benzene with H_2O, D_2O, and HDO confirms the ability of benzene to act as hydrogen-bond acceptor.[18] Given that C–H hydrogen bonds would be expected to be weaker than O–H hydrogen bonds, the C–H···C_6 plane distances are reasonable and agree well with those recently reported for an intermolecular host–guest interaction.[19] Weaker C–H···C_6 plane interactions on the order of 2.73 Å or more are seen between a C–H methylene group on one branch and a phenyl ring of another branch which is not attached to an adjacent carbon atom. It should be noted that although such aromatic–aromatic interactions are energetically weak and are quite rare in terms of experimental characterization they are considered to be capable of profoundly influencing tertiary structure of biological important molecules[20] and the nature of host–guest interactions.[19,21] All other bond distances and angles are within expected ranges (Table IV). The three independent acetone solvate molecules lie in channels with PF_6^- anions and do not interact with the organometallic cation.

Table IV. Summary of Important Bond Distances (Å) and Angles (deg)

	av C–C distances	
	3a	**4**
central C_6 ring, sp^2–sp^2	1.416 (18)	1.396 (5)
central C_6 ring, sp^2–sp^3	1.527 (15)	1.521 (5)
outer C_6 rings, sp^2–sp^2	1.37 (3)	1.378 (12)
outer C_6 rings, sp^2–sp^3	1.513 (21)	1.512 (7)
α-carbon atom, sp^3–sp^3	1.546 (20)	1.546 (6)

	av C–C–C angles	
	3a	**4**
central C_6 ring, sp^2–sp^2–sp^2	120 (3)	120 (3)
central C_6 ring, sp^2–sp^3–sp^3	112.7 (1.8)	112.7 (7)
outer C_6 ring, sp^2–sp^2–sp^2	120.0 (2.1)	120.0 (1.1)
outer C_6 ring, sp^2–sp^3–sp^3	115.1 (1.5)	115.1 (1.2)
methyne carbon, sp^3–sp^3–sp^3	109.8 (1.9)	110.1 (1.9)

	Fe–C distances in **3a**	
	Fe–arene	Fe–Cp
	2.138 (8)	2.029 (9)
	2.175 (7)	2.091 (8)
	2.067 (8)	2.049 (9)
	2.172 (7)	2.067 (10)
	2.147 (8)	2.047 (10)
	2.073 (6)	
Fe–plane	1.592 (4)	1.708 (7)

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(15) Electron-donating substituents have been shown to predictably distort arene planarity in (arene)$Cr(CO)_3$ complexes by forcing the ipso carbon atoms away from the metal moiety. The distortions are only dependent upon the steric bulk of the substituent in extreme cases: Hunter, A. D.; Shilliday, L.; Furey, W. S.; Zaworotko, M. J. *Organometallics* **1992**, *11*, 1550.

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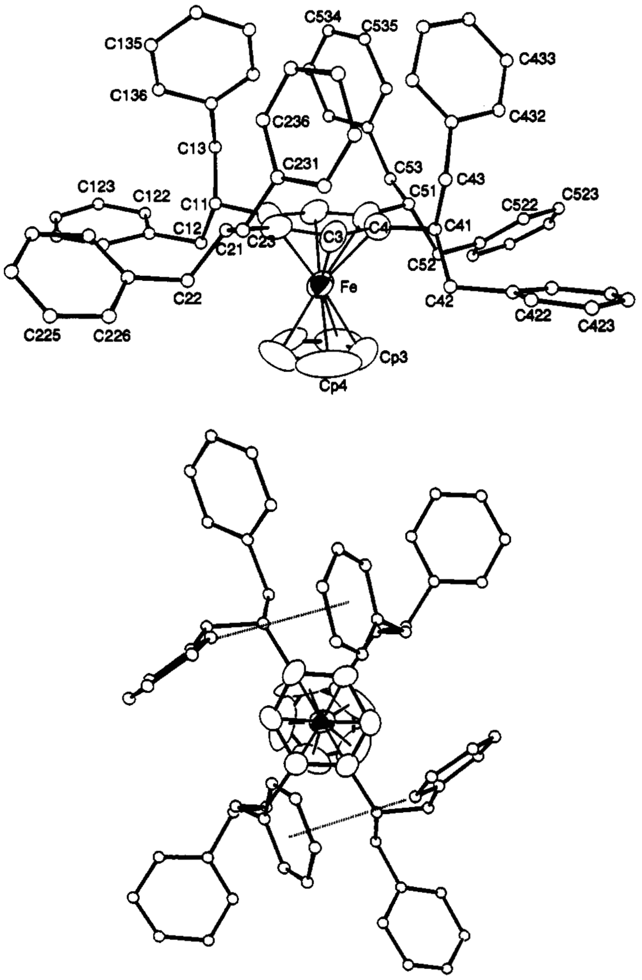

Figure 1. Perspective (a, top) and overhead (b, bottom) views of cation **3a**.

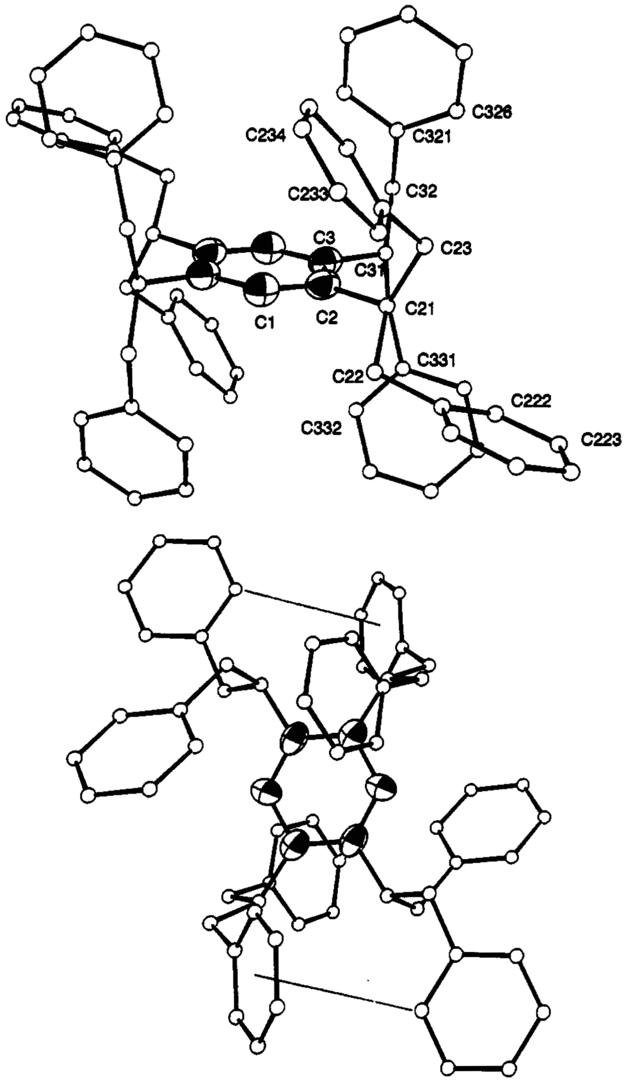

Figure 2. Perspective (a, top) and overhead (b, bottom) views of arborole **4**.

4. Perspective and overhead views of **4** are given in Figure 2. They reveal a markedly different conformation compared to that adopted by the complex. Two of the eight phenyl rings orient in a manner so that they are almost coplanar (14.8°) with the central C_6 ring (lying opposite the unsubstituted C_6 ring carbon atoms) whereas the other six are oriented in a more vertical fashion with respect to the central C_6 ring (49–68°). The observed conformation presumably relieves steric congestion among the benzyl moieties, and the central C_6 plane is planar to 0.006 Å. Once again there is strong evidence for edge-to-face interactions between phenyl groups, specifically *o*-C–H···arene hydrogen bonds. The interactions are highlighted in Figure 2b and arise from H236···C32(C_6 plane) distances of 2.72 Å. All covalent bonds and angles are within expected ranges (Table IV), and the acetone solvate molecule is not in proximity with the arborole.

Conclusion

The most salient result from this study concerns the identification of intramolecular edge-to-face aromatic–aromatic interactions (i.e. C–H π hydrogen bonds) in both **3a** and **4**. Although the attractive energies that result from such interactions would be expected to be small (ca. 2 kcal/mol[16] per bond), they might still be large enough to influence two important or potentially important aspects of the chemistry of bulky arenes. First, the nature of the lowest energy conformer, particularly upon complexation, could be determined by intramolecular aromatic–aromatic interactions since the difference in energies between sterically crowded conformers (i.e. those that often occur upon complexation) are calculated to be as little as 1 kJ/mol.[7f] Second, the ability of bulky arenes such as **4** to act as host molecules through noncovalent bonding is likely to be limited since the observed intramolecular interactions inherently work against formation of cavities. A positive aspect of our observations is the suggestion that control of ligand stereochemistry can become great upon complexation. The order of flexible groups at the exo face of the ligand suggests that control of self-assembly based upon molecules such as arboroles would be great if suitable functionalization could be introduced.

Acknowledgment. We gratefully acknowledge the financial support of the NSERC of Canada (operating grant, M.Z.) and Saint Mary's University (Senate Research Award; purchase of the X-ray diffractometer).

Supplementary Material Available: For $\mathbf{3aPF_6}$ and **4**, tables of bond lengths and angles, anisotropic thermal parameters, hydrogen atom parameters, and best least-squares planes (18 pages). Ordering information is given on any current masthead page.

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