π-Stacking between Pentafluorophenyl and Phenyl Groups as a Controlling Feature of Intra- and Intermolecular Crystal Structure Motifs in Substituted Ferrocenes. Observation of Unexpected Face-to-Face Stacking between Pentafluorophenyl Rings

Mélanie D. Blanchard,[†] Russell P. Hughes,*,[†] Thomas E. Concolino,[‡] and Arnold L. Rheingold[‡]

Departments of Chemistry Burke Chemistry Laboratory, Dartmouth College, Hanover, New Hampshire 03755-3564, and University of Delaware, Newark, Delaware 19716

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Ferrocenes containing phenyl and pentafluorophenyl substituents on the cyclopentadienyl rings have been prepared, and their solid-state structures were determined by single-crystal X-ray studies. In the homoleptic ferrocene $Fe(Me_2PhCp)_2$ (**5**), no intra- or intermolecular face-to-face π-stacking of the aryl rings is observed, as expected. The intramolecular conformation has staggered cyclopentadienyl rings with the phenyl groups in an anti conformation. However, the mixed ferrocene $Fe(Me_2PhCp)(C_6F_5Cp)$ (**6**) crystallizes with eclipsed cyclopentadienyl rings and intramolecular π-stacking between the phenyl and pentafluorophenyl substituents. In addition the π-stacking between phenyl and pentafluorophenyl rings occurs between neighboring molecules, and controls the intermolecular crystal motif. Yet a different molecular architecture is observed in the homoleptic ferrocene $Fe(C_6F_5Cp)_2$ (**2**) which crystallizes surprisingly with intramolecularly π-stacked pentafluorophenyl rings. The overall crystal architecture in this case in controlled by π-stacking between pentafluorophenyl rings on one molecule with the cyclopentadienyl rings of neighbors, to afford a third structural motif. These results illustrate that both the intra- and intermolecular solid-state structures of simple organometallic molecules can be controlled by stacking interactions involving pentafluorophenyl rings and suggest that these attractive interactions can be added to the repertoire of attractive forces used to effect crystal engineering in organometallic systems.

Introduction

One of the principal impeti behind the field of crystal engineering is to design molecular crystals with specific properties for a variety of physical and chemical applications.[1,2] Noncovalent attractive forces, such as hydrogen bonding or electron donor/acceptor interactions, in molecular crystals can generate structures defined as "supramolecular synthons" which can be crucial to the topochemical reactivity of molecules in the crystalline state.[3−6] Aromatic π-stacking interactions have been studied extensively and are responsible for a wide array of phenomena in chemistry and biology, including organic transformations,[7,8] molecular recognition,[9] and the organization of molecular solids.[3−5] It seems reasonable therefore that π-stacking should become an increasingly important component of the construction toolbox for molecular crystals.

π-Stacking interactions between perfluoroaryl and aryl rings have been the subject of considerable attention in recent years.[3,4,10−16] This phenomenon was first observed by Patrick and Prosser who noted that an equimolar mixture of benzene (mp = 5.5 °C) and hexafluorobenzene (mp = 4 °C) formed a crystalline product (mp 24 °C).[10] The molecular structure of this material[10−12] showed columns of alternating benzene

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[†] Dartmouth College.

[‡] University of Delaware.

(1) Desiraju, G. R. *Crystal engineering: the design of organic solids*; Elsevier: Amsterdam, 1989; Vol. 54.

(2) Braga, D.; Greponi, F.; Desiraju, G. R. *Chem. Rev.* **1998**, *98*, 1375−405.

(3) Coates, G. W.; Dunn, A. R.; Henling, L. M.; Dougherty, D. A.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 248−51.

(4) Coates, G. W.; Dunn, A. R.; Henling, L. M.; Ziller, J. W.; Lobkovsky, E. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 3641−9.

(5) Dai, C.; Nguyen, P.; Marder, T. B.; Scott, A. J.; Clegg, W.; Viney, C. *Chem. Commun.* **1999**, 2493−4.

(6) Martin, C. B.; Patrick, B. O.; Cammers-Goodwin, A. *J. Org. Chem.* **1999**, *64*.

(7) Trost, B. M.; O'Krongly, D.; Belletire, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 7595−6.

(8) Siegel, C.; Thornton, E. R. *Tetrahedron Lett* **1988**, *29*, 5225−8.

(9) Benzing, T.; Tjivikura, T.; Wolfe, J.; Rebek, J., Jr. *Science* **1993**, *242*, 266−8.

(10) Patrick, C. R.; Prosser, G. S. *Nature* **1960**, *187*, 1021.

(11) Williams, J. H. *Acc. Chem. Res.* **1993**, *26*, 593.

(12) Williams, J. H.; Cockcroft, J. K.; Fitch, A. N. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1655−7.

(13) Dahl, T. *Acta Chem. Scand., Ser. A* **1988**, *A42*, 1−7.

(14) Dahl, T. *Acta Crystallogr., Sect. B: Struct. Sci.* **1990**, *B46*, 283−8.

(15) Dahl, T. *Acta Chem. Scand.* **1994**, *48*, 95−106.

(16) Luhmer, M.; Bartik, K.; Dejaegere, A.; Bovy, P.; Reisse, J. *Bull. Soc. Chim. Fr.* **1994**, *131*, 603−6.

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and hexafluorobenzene molecules stacked in an slightly offset parallel manner, with a staggered face-to-face arrangement; weak H···F contacts align neighboring columns, building a network of weakly polarized hydrogen bonds which provide stabilization to the crystal lattice. The interplanar distance within columns is 3.77 Å. This stacked structure contrasts with the structures of a pure benzene dimer, in which neighboring molecules are perpendicularly oriented and the shortest neighboring distance between the plane centers is 4.97 Å.[11,12] In the gas phase, Jorgensen and Severance have suggested a slightly tilted T-structure as the global energy minimum for benzene−benzene interaction with a ring center−ring center separation of 4.99 Å.[17] Similarly, the X-ray structure of pure hexafluorobenzene shows an L-shaped arrangement, with ring center−ring center separation of 5.4 Å, rather than a face-to-face orientation.[18]

This fluoroaryl−aryl stacking interaction persists outside the crystalline state. Liquid−gas critical temperatures of hexafluorobenzene with aromatic hydrocarbons and alicyclic hydrocarbons were measured, and in all cases the hexafluorobenzene−aromatic hydrocarbon interaction was determined to be stronger than the corresponding hexafluorobenzene−alicyclic hydrocarbon interaction.[19] Gas-phase investigations of the benzene/hexafluorobenzene adduct, with molecular beam electric resonance spectroscopy, detected an induced dipole moment of 0.44 D.[11] This intermolecular polarization has, to date, been attributed to common noncovalent interactions between the aromatic fluorocarbon and hydrocarbon. Electron donor−acceptor interactions have been eliminated, and electrostatic interactions favored, to explain the noncovalent interactions in arylnaphthalenes in which two interacting aromatic rings are held in a face-to-face stacked geometry.[20−22]

The electrostatic potential map of benzene reveals concentration of negative charge in the center and positive charge on the periphery of the ring. Conversely, the high electronegativity of fluorine provides perfluorobenzene with a negative outer torus and a positive center. Not surprisingly therefore, the quadrupole moments of benzene and perfluorobenzene have similar magnitudes ($\sim 30 \times 10^{-40}$ Cm^2) but opposite charge distribution, providing an explanation for the observed structure of the benzene−hexafluorobenzene molecular crystal.[11]

Recently, these interactions between fluoroaryl and aryl rings have been used to align diyne molecules, and alkene molecules, for subsequent photochemical reaction in the crystalline phase.[3,4] There is also evidence that this stacking interaction exists outside the crystalline phase, as evidenced by relatively high barriers (9.3 ± 0.3 kcal/mol) to rotation of stacked phenyl and pentafluorophenyl rings in solution.[3,23] These observations suggest that the stacked arrangement first observed by Patrick and Prosser[10] may be a fairly general supramolecular motif and that the interaction is clearly strong enough to be a controlling factor in favoring intramolecular conformation and intermolecular packing in crystals.

On the basis of these observations, and the desire to enter the field of crystal engineering, we were moved to investigate whether analogous interactions could be used to control both the intra- and intermolecular structural architecture of organometallic complexes in the crystalline state. We were encouraged by recent reports of crystal structures in which ferrocene, decamethylferrocene, and bis(benzene)chromium each cocrystallize and form stacked structures with perfluoroaromatic compounds, with inter-ring distances in ferrocene/perfluorophenanthrene (∼3.6 Å),[24] decamethylferrocene/perfluorophenanthrene (∼3.7 Å),[25] and bis(benzene)chromium/perfluorobenzene (∼3.5 Å).[26] The classical sandwich structure of ferrocene embraces the metal between two parallel cyclopentadienyl rings set at approximately the correct distance for an optimum π-stacking arrangement between appended aryl and pentafluorophenyl groups.[27] It provides an attractive organometallic structural motif with an appealing combination of stability and inexpensiveness, so we set out to investigate the synthesis and solid-state structures of phenyl- and pentafluorophenylferrocenes.

Results and Discussion

We were fortunate that the synthesis of pentafluorophenylcyclopentadiene **1** (Chart 1) and the ferrocene **2** derived from it were reported as we started this work.[28] We were able to repeat both syntheses with no problems. The crystal structure of **2** was not reported in the original paper,[28] and we were able to grow a suitable crystal, the X-ray structure of which is discussed later. While the synthesis of phenylcyclopentadiene **3** and some complexes of its anion have also been reported in the literature,[29] its seemingly simple preparation was problematical in our hands. Phenylcyclopentenol was obtained by reaction of phenylmagnesium bromide with 2-cyclopentenone, and is reported to spontaneously dehydrate upon vacuum distillation to produce a mixture of phenylcyclopentadiene isomers in 50−80% yield.[29] In our hands, however, these dehydration conditions, as well as distillation under higher vacuum, resulted in a considerably lower yield than reported in the literature and was unforgiving of attempts to scale-up the reaction. H_2SO_4, P_4O_{10}, and BF_3-etherate, and activated alumina were all tried as dehydrating agents, each giving good results on a small scale but proving inefficient on larger scales. Conse-

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(17) Jorgensen, W. L.; Severance, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 4768.

(18) Boden, N.; Davis, P. P. *Mol. Phys.* **1973**, *25*, 81−6.

(19) Fenby, D. V. *Pure Appl. Chem.* **1972**, *22*, 55.

(20) Cozzi, F.; Ponzini, F.; Annunziata, R.; Cinquini, M.; Siegel, J. S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1019−20.

(21) Cozzi, F.; Cinquini, M.; Annuziata, R.; Siegel, J. S. *J. Am. Chem. Soc.* **1993**, *115*, 5330−1.

(22) Cozzi, F.; Siegel, J. S. *Pure Appl. Chem.* **1995**, *67*, 683−9.

(23) Parks, D. J.; Piers, W. E.; Parvez, M.; Atencio, R.; Zaworotko, M. J. *Organometallics* **1998**, *17*, 1369−77.

(24) Burdeniuc, J.; Crabtree, R. H.; Rheingold, A. L.; Yap, G. P. A. *Bull. Soc. Chim. Fr.* **1997**, *134*, 955−8.

(25) Beck, C. M.; Burdeniuc, J.; Crabtree, R. H.; Rheingold, A. L.; Yap, G. P. A. *Inorg. Chim. Acta* **1998**, *270*, 559−62.

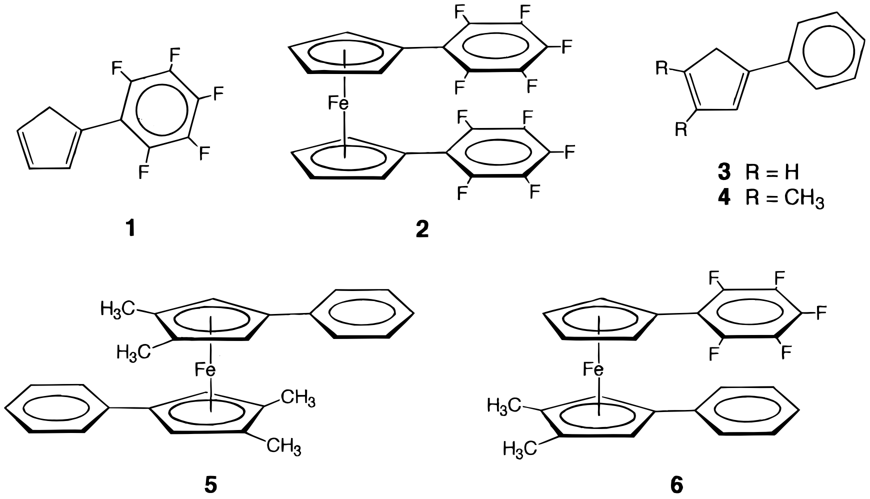
(26) Aspley, C. J.; Boxwell, C.; Buil, M. L.; Higgitt, C. L.; Long, C.; Perutz, R. N. *Chem. Commun.* **1999**, 1027−8.

(27) Togni, A.; Hayashi, T. *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, and Material Science*; VCH: Weinheim, Germany, 1995.

(28) Deck, P. A.; Jackson, W. F.; Fronczek, F. R. *Organometallics* **1996**, *15*, 5287−91.

(29) Singh, P.; Rausch, M. D.; Bitterwolf, T. E. *J. Organomet. Chem.* **1988**, *352*, 273−82.

Chart 1



quently we turned our attention to a more substituted phenylcyclopentadiene, and utilized 3,4-dimethyl-1-phenyl-1,3-cyclopentadiene **4**, prepared from reaction of the known 3,4-dimethyl-1-phenyl-2-cyclopentenone[30] with PhMgBr followed by dehydration of the resultant alcohol with *p*-toluenesulfonic acid, as previously reported.[31]

Bis[η^5-(1,2-dimethyl-4-phenylcyclopentadienyl)]iron(II) **5** was synthesized by the reaction between $FeCl_2$ and potassium 1,2-dimethyl-4-phenylcyclopentadienide; NMR spectroscopic characterization and crystallization was straightforward.

Our approach to the mixed ferrocene **6** utilized the method initially reported by Manriquez;[32] reaction of $Fe(acac)_2$ with 1 equiv of lithium dimethylphenylcyclopentadienide led to a red-brown solution containing the putative intermediate (η^5-$PhMe_2Cp$)Fe(acac), which was not isolated. This reaction mixture was then added to a solution of C_6F_5CpNa in THF at −80 °C to ultimately give the mixed metallocene **6**, albeit in poor yield, with considerable amounts of the homoleptic ferrocene **5** being formed. However separation was achieved and suitable crystals grown. ^1H and ^{19}F NMR confirmed the composition of **6**.

The homoleptic ferrocene $Fe(Me_2PhCp)_2$ (**5**) crystallizes as orange plates in the space group $P2_1/c$. An ORTEP depiction is presented in Figure 1, and the structure is relatively unremarkable. Details of the crystallographic data acquisition, and cell parameters for all compounds are presented in Table 1. Compound **5** displays the classic ferrocene sandwich geometry, with a crystallographically imposed center of inversion at the iron atom, such that the intramolecular conformation has staggered cyclopentadienyl rings with the phenyl groups in an anti conformation. The average iron−carbon distance of 2.061(7) Å is essentially the same as the 2.055(9) Å Fe−C distance in $Fe(Cp^{3i})_2$ (Cp^{3i} = 1,2,4-tri-isopropylcyclopentadienyl),[33] and only slightly longer than the 2.050(2) Å found in Fe Cp^*_2 ($Cp^* = C_5Me_5$),[34] or than that in ferrocene itself (2.030 Å).[35,36] There is insignificant variation of 2.055(3)−2.067(3) (Δ = 0.012 Å) between individual Fe−C distances. Each cyclopentadienyl ring is essentially coplanar with its appended

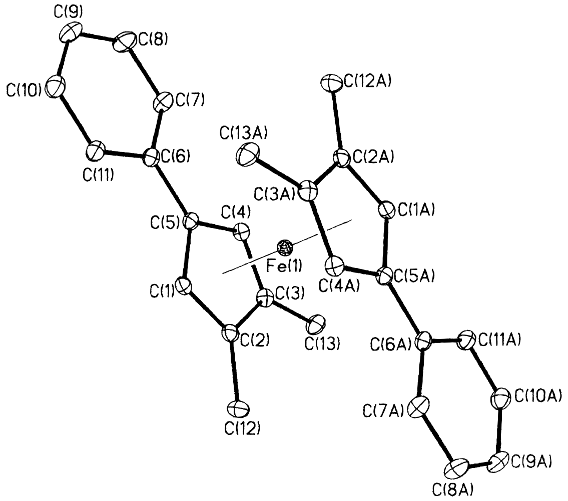


Figure 1. ORTEP drawing of **5**. Atoms are drawn at 30% probability with hydrogen atoms omitted for clarity.

Table 1. Crystallographic Data for Compounds 5, 6, and 2

compound	5	6	2
formula	$C_{26}H_{26}Fe$	$C_{24}H_{17}F_5Fe$	$C_{22}H_8F_{10}Fe$
formula weight	394.32	456.23	518.13
space group	$P2_1/c$	$P\bar{1}$	$P2_1$
a, Å	9.6395(2)	7.5442(14)	10.7378(3)
b, Å	8.0062(2)	10.5836(21)	13.9667(5)
c, Å	12.7395(2)	12.1279(23)	13.4215(4)
α, deg		86.346(4)	
β, deg	97.0381(11)	83.046(4)	108.2627(3)
γ, deg		73.886(3)	
V, Å^3	975.77(4)	923.0(5)	1911.44(16)
Z	2	2	4
D(calcd), g cm^3	1.342	1.642	1.800
T, K	173(2)	173(2)	173(2)
radiation	Mo Kα (λ = 0.71073 Å)		

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(30) Conia, J. M.; Leriverend, M. L. *Bull. Soc. Chim. Fr.* **1970**, 2981−91.

(31) Petoff, J. L. M.; Bruce, M. D.; Waymouth, R. M.; Masood, A.; Lal, T. K.; Quan, R. W.; Behrend, S. J. *Organometallics* **1997**, *16*, 5909−16.

(32) Bunel, E. E.; Valle, L.; Manriquez, J. M. *Organometallics* **1985**, *4*, 1680−2.

(33) Burkey, D. J.; Hays, M. L.; Duderstadt, R. E.; Hanusa, T. P. *Organometallics* **1997**, *16*, 1465−75.

(34) Freyburg, D. P.; Robbins, J. L.; Raymond, K. N.; Smart, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 892.

(35) Seiler, P.; Dunitz, J. D. *Acta Crystallogr., Sect. B* **1979**, *B35*, 1068−74.

(36) Takusagawa, F.; Koetzle, T. F. *Acta Crystallogr., Sect. B* **1979**, *B35*, 1074−81.

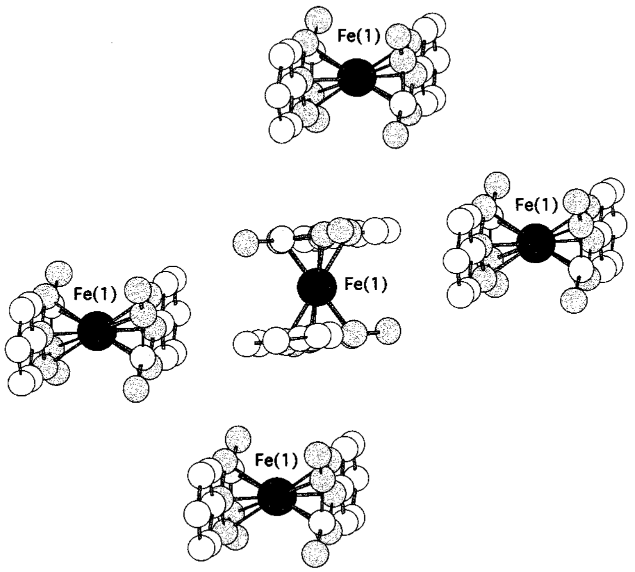

Figure 2. A detail of the crystal packing diagram of **5**, showing nearest neighbors. Carbon atoms are depicted in gray, while the C_6H_5 rings are shown in white. Hydrogen atoms are omitted for clarity.

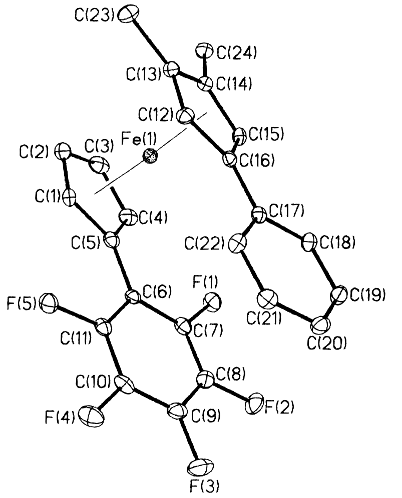

Figure 3. ORTEP drawing of **6**. Atoms are drawn at 30% probability with hydrogen atoms omitted for clarity.

phenyl substituent, as indicated by insignificant values (0.5(3)° and 0.9(3)°) for the C(4)−C(5)−C(6)−C(7) and C(1)−C(6)−C(5)−C(1) torsion angles, respectively. The packing diagram, a detail of which is shown in Figure 2, provides no evidence of significant intermolecular interactions between phenyl and/or cyclopentadienyl rings. Indeed neighboring molecules are oriented at 90° to one another.

In contrast, the mixed ferrocene Fe(Me_2PhCp)(C_6F_5-Cp) (**6**) crystallizes as large yellow blades in the *P*1 space group (Table 1). An ORTEP drawing is shown in Figure 3. The average iron−carbon distances to the fluoroarylCp ligand and phenylCp ligands are identical at 2.047(9) and 2.048(9) Å respectively, only marginally shorter than that of Fe(Me_2PhCp)$_2$ (**5**). The range of Fe−C distances is 2.035(4)−2.059(4) (Δ = 0.024 Å) for the pentafluorophenylcyclopentadienyl and 2.039(4)−2.056(4) (Δ = 0.017 Å) for the phenylcyclopentadienyl rings. The most dramatic difference is that the cyclopentadienyl rings are eclipsed and the phenyl and pentafluorophenyl rings are in a syn-stacked conformation.

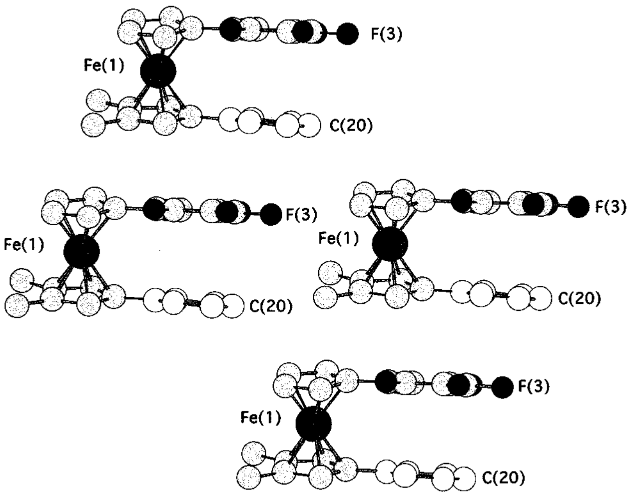

Figure 4. A detail of the crystal packing diagram of **6**, showing nearest neighbors. Carbon atoms are depicted in gray, while the C_6H_5 rings are shown in white, and the fluorine atoms of the C_6F_5 rings are in black. Hydrogen atoms are omitted for clarity.

The structure reveals a distance between the center of the respective phenyl and pentafluorophenyl rings of 3.54(1) and 3.53 Å for the normal between the centroid of one aryl plane and the projection of the other aryl group. Thus, the two aromatic rings are almost perfectly eclipsed, although not perfectly parallel with each other. The Cp centroid−Fe−Cp centroid angle is 177.3(3)°. with an angle of 3.5° between the least squares planes of the two aryl rings. The intramolecular interplanar distance is slightly shorter than that found by Patrick and Prosser in the benzene−hexafluorobenzene complex (3.77 Å).

Unlike the structure of **5**, the phenyl and pentafluorophenyl groups in **6** are not coplanar with their respective cyclopentadienyl ligands. Two slightly different torsion angles [16.8(2)° for C(1)−C(5)−C(6)−C(11) and 15.7(2)° for C(4)−C(5)−C(6)−C(7)] for the pentafluorophenyl group are observed, whereas those for the phenyl group [C(15)−C(16)−C(17)−C(18) and C(12)−C(16)−C(17)−C(22)] are identical at 13.0(2)°. We rationalize these observations as follows. Fluorine is sterically more demanding than hydrogen,[37,38] resulting in the favored conformation of the pentafluorophenyl ring being tilted out of the Cp ring plane by about 15°. However, to retain the favorable π-stacking arrangement between the aryl rings, the phenyl group rotates to give a similar torsion angle.

The phenyl/pentafluorophenyl stacking controls not only the intramolecular conformation of **6**, but also its intermolecular packing. Part of the packing diagram is shown in Figure 4, and illustrates that the iron centers adopt a chain structure, with the fluoroaryl group from one molecule being stacked with a phenyl group of its neighbor ferrocene. The intermolecular distance between pentafluorophenyl and phenyl centroids (4.23(1) Å) and the short distance for the normal between the

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(37) Smart, B. E. *Chemistry of Functional Groups, Supplement D*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1983; Vol. Chapter 14, pp 603−55.

(38) Smart, B. E. *Mol. Struct. Eng.* **1986**, *3*, 141−91.

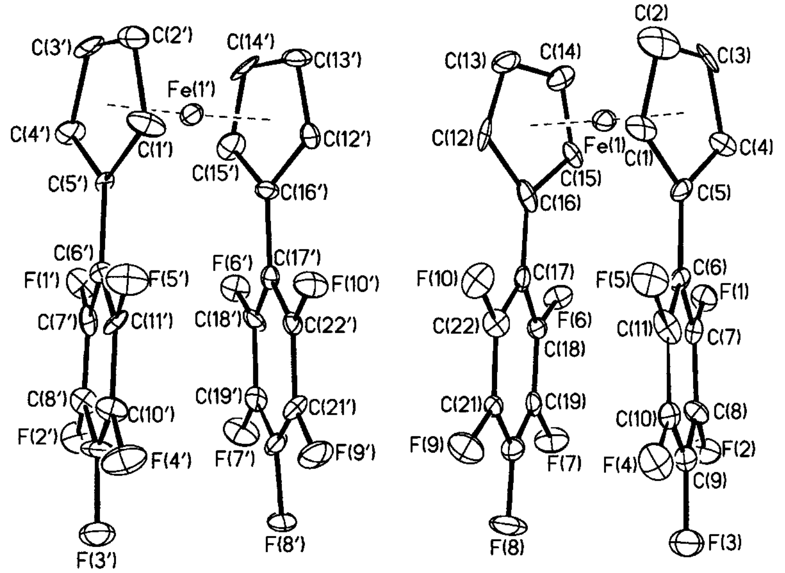

Figure 5. ORTEP drawings of the two enantiomers of **6**. Atoms are drawn at 30% probability with hydrogen atoms omitted for clarity.

centroid of one aryl plane and the projection of the other aryl group (3.50 Å) indicates that the intermolecular π-stacking interactions are between rings that are significantly more slipped with respect to each other.

As mentioned earlier, we were able to grow crystals of the homoleptic ferrocene (**2**), whose synthesis had been previously reported. X-ray-quality crystals were obtained by slow evaporation of a toluene solution at ambient temperature as orange plates (Table 1). The compound crystallizes in the space group $P2_1$ with two crystallographically independent molecules, which happen to be of opposite hand with regard to the twist angle of the five- and six-membered ring systems. The ORTEP drawings of each enantiomer are presented in Figure 5. The structure of **2** displays the expected planar sandwich geometry (centroid−Fe−centroid angle = 178.7(6)°), but the structure showed the surprising feature that the pentafluorophenyl rings adopt a syn-stacked conformation in the solid state. The average iron−carbon distance is 2.11(3) Å for Fe−[C(1)−C(2)−C(3)−C(4)−C(5)] and 2.08(3) for Fe−[C(12)−C(13)−C(14)−C(15)−C(16)], quite similar to that in (Me$_2$PhCp)-Fe(C$_6$F$_5$Cp) **(6)**. The range of Fe−C distance is 2.038(14)−2.124(15) ($\Delta = 0.086$). Distances of 3.58(1) Å between the aryl centroids and 3.57 Å for the normal between one centroid of a pentafluorophenyl ring and the projection of the other group are observed in both enantiomers.

A detail of the packing diagram for **2** is shown in Figure 6, and illustrates another different intermolecular stacking motif in which the pentafluorophenyl ring of one ferrocene stacks with the cyclopentadienyl ring of another complex. This interaction is similar to the intermolecular interactions between decamethylferrocene[24,25] and bis(benzene)chromium[26] with perfluoroaromatic compounds. The distance between a Cp centroid and a pentafluorophenyl centroid in a neighboring ferrocene complex (3.61(1) Å) and the short distance of the normal between these two planes (3.61 Å) suggest that π-stacking interactions can also occur between cyclopentadienyl and pentafluorophenyl rings of different molecules in the unit cell.

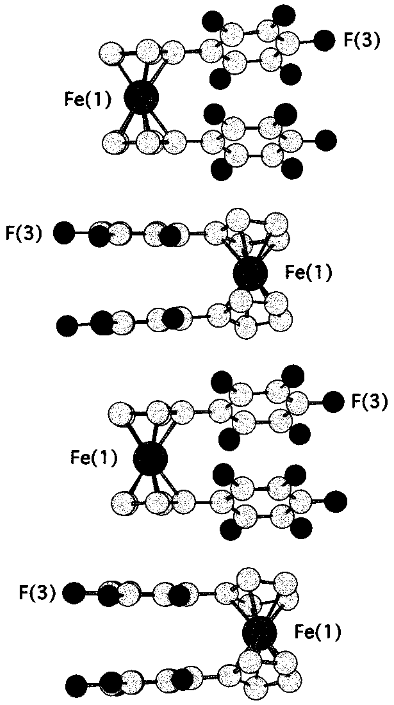

Figure 6. Detail of the packing diagram of **2** showing the intermolecular stacking of pentafluorophenyl rings in one molecule with the cyclopentadienyl rings of its neighbor. Carbon atoms are depicted in gray, while the fluorine atoms of the C$_6$F$_5$ rings are in black. Hydrogen atoms are omitted for clarity.

Finally, the pentafluorophenyl groups in **2** appear to be tipped with respect to the planes of the cyclopentadienyl rings, as shown in Figure 7. Intramolecular distances as short as 3.23 and 3.27 Å are observed between *ortho*-fluorine and carbon atoms of different rings, but 3.38 and 3.50 Å separate the *meta*-atoms and angles of 4.9° and 3.6° are measured between the pentafluorophenyl rings in the two different enantiomers. Moreover, four different torsion angles [24.1(5)° for C(4)−C(5)−C(6)−C(7), 26.0(5)° for C(1)−C(5)−C(6)−C(11), 25.3(5)° for C(15)−C(16)−C(17)−C(18), and 24.5°(5) for C(12)−C(16)−C(17)−C(22)] are measured

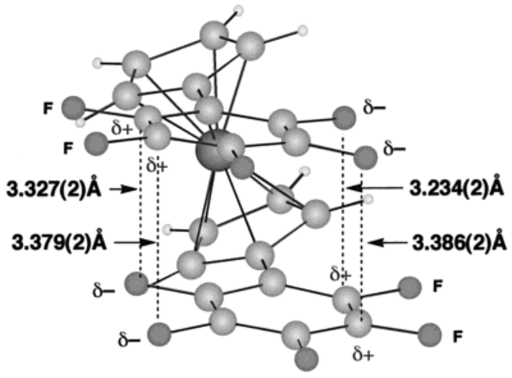

Figure 7. Suggested dipole−dipole interactions between C−F bonds on adjacent pentafluorophenyl rings to account for the intramolecular structure of **2**.

for one enantiomer; these four values are considerably higher than that found in the previous ferrocenes and we rationalize them, and the observation of stacking between perfluoroaryl rings, as follows. We have already commented that, since the pentafluorophenyl ring is bulkier than the phenyl ring, it tends to orient itself with a greater torsion angle with respect to the Cp ring. We suggest that the stacking arrangement between pentafluorophenyl rings is driven, not by quadrupolar interactions as in the heteroleptic case, but by dipole−dipole interactions between C−F bonds. Such interactions are likely to be more significant in fluoroaryl groups than in their hydrocarbon counterparts, due to the significantly more polar CF bond compared to a CH bond, and consequently no stacking is observed between the aryl rings in **5**. In compound **2**, to maximize attractive dipole−dipole interactions between carbons and fluorines on stacked rings, the torsion angle for the fluoroaryl rings must increase, as shown in Figure 7.

Conclusions

Stacking interactions between aryl and perfluoroaryl rings clearly represent an important mechanism for controlling the intramolecular and intermolecular structure of organometallic complexes in the solid state. Phenyl−phenyl interactions appear to be insignificant, whereas phenyl−perfluorophenyl, cyclopentadienyl−perfluorophenyl, and perfluorophenyl−perfluorophenyl stacking interactions are significant, and do seem to control intra- and intermolecular organization in ferrocenes.

Experimental Section

General Procedures. All reactions were performed in oven-dried glassware, using standard techniques, under an atmosphere of dinitrogen, unless otherwise noted, which had been deoxygenated over BASF catalyst and dried over Aquasorb, or in a Braun Drybox. THF, hexane, toluene, and diethyl ether were distilled under nitrogen from potassium benzophenone ketyl; dichloromethane was refluxed over calcium hydride under nitrogen and distilled immediately before use. Benzene, pentane, and 2-propanol were used without previous distillation. IR spectra were recorded on a Perkin-Elmer FTIR 1600 Series spectrometer. NMR spectra were recorded on a Varian Unity Plus 300 or 500 FT spectrometers. ^{1}H NMR spectra were referenced to the protio impurity present in the solvent, and ^{19}F NMR spectra are referenced to internal $CFCl_3$. 2-Cyclopentenone, crotonic acid, polyphosphoric acid, *n*-butyllithium, pentane-2,4-dione, and piperidine (Aldrich), hexafluorobenzene and KH (Alfa), and anhydrous $FeCl_2$ (Strem Chemicals) were used as received. $FeCl_2{\cdot}2THF$,[39] $Fe(acac)_2$,[32] sodium cyclopentadienide,[40] pentafluorophenylcyclopentadiene,[28] and 3,4-dimethyl-1-phenyl-1,3-cyclopentadiene[31] were prepared according to literature procedures.

Bis[η^5-(1,2-Dimethyl-4-phenylcyclopentadienyl)]iron(II) (5). 3,4-Dimethyl-1-phenyl-1,3-cyclopentadiene (0.5 g, 2.94 mmol) dissolved in THF (10 mL) was added slowly to a suspension of KH in THF (20 mL) at 0 °C in a 100 mL Schlenk flask. The solution was stirred for 2 h while slowly warming to room temperature. Anhydrous $FeCl_2$ (0.18 g, 1.40 mmol) in THF (10 mL) was added via cannula to the potassium salt. This mixture was heated to reflux and stirred overnight. After cooling, the solvent was removed under reduced pressure. Water (40 mL) was added, and the product was extracted with benzene (3 × 40 mL). The solvent was removed from the separated organic layer to yield a crude orange solid, which was redissolved and filtered through neutral alumina. Removal of the solvent afforded orange crystals of the desired product in 52% yield, mp = 186.9−188.2 °C. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.28 (overlapping m, 10H, *Ar*−*H*); 4.13 (s, 4H, 4*CH*); 1.72 (s, 12H, 4CH_3). X-ray quality crystals were grown by slow evaporation of a hexane/CH_2Cl_2 mixture (1:1). Calcd for $C_{26}H_{26}Fe$: C, 79.19; H, 6.64. Found: C, 79.43, H, 6.72.

η^5-(1,2-Dimethyl-4-phenylcyclopentadienyl)(η^5-pentafluorophenylcyclopentadienyl)]iron(II) (6). 3,4-Dimethyl-1-phenyl-1,3-cyclopentadiene (1.0 g, 5.87 mmol) was dissolved in diethyl ether (20 mL) in a 100 mL Schlenk flask. *n*-Butyllithium (1.6 M in hexanes, 3.70 mL, 5.92 mmol) was added dropwise by means of a syringe at 0 °C to give a creamy yellow precipitate. The reaction was allowed to warm to room temperature and stirred for 0.5 h, then cooled to −80°. $Fe(acac)_2$ (1.49 g, 5.87 mmol) dissolved in THF (50 mL) was added using a cannula and the solution was stirred for 4 h while slowly warming to room temperature. The mixture was cooled to −80 °C again when a THF solution (30 mL) of potassium pentafluorophenylcyclopentadienide (1.36 g, 5.87 mmol) (prepared from the diene and KH) was cannulated into the solution. This resulting mixture was allowed to stir for 2 h while slowly letting the temperature reach 25 °C. The solvent was removed under vacuum to give a brown solid. This residue was extracted with pentane (6 × 10 mL) and filtered. Upon removal of the solvent, a red-brown oily solid mixture was obtained. Crystallization of the mixture from pentane gave a first crop containing bis[η^5-1,2-dimethyl-4-phenylcyclopentadienyl)iron(II)] (50%); a subsequent crop afforded the desired mixed ferrocene in 20% yield, mp = 154−156 °C. ^{1}H NMR ($CDCl_3$) δ ppm): 7.26 (m, 2H, *Ar*−*H*); 7.18 (m, 1H, *Ar*−*H*); 7.11 (m, 2H, *Ar*−*H*); 4.81 (apparent s, 2H, *CH* α to C_6F_5); 4.56 (s, 2H, *CH* α to C_6H_5); 4.10 (apparent s, 2H, 2*CH* β to C_6F_5); 1.70 (s, 6H, CH_3). ^{19}F NMR ($CDCl_3$) δ ppm): −140.55 (m, 2F, *ortho*-C*F*); −161.38 (t, $^3J_{FF}$ = 15 Hz, 1F, *para*-C*F*); −164.28 (m, 2F, *meta*-C*F*). X-ray-quality crystals were grown by slow evaporation of a pentane solution. Calcd for $C_{24}H_{17}F_5Fe$: C, 63.18; H, 3.75. Found: C, 63.33, H, 3.82.

Bis(η^5-pentafluorophenylcyclopentadienyl)iron(II) (2).[28] Pentafluorophenylcyclopentadiene (0.2 g, 0.86 mmol) in THF (10 mL) was added slowly to a suspension of KH (0.03 g, 0.86 mmol) in THF (10 mL) at 0 °C in a 100 mL Schlenk flask. The solution was stirred for 1 h while slowly warming to room temperature. Anhydrous $FeCl_2$ (0.05 g, 0.43 mmol) dissolved in THF (10 mL) was added via cannula to the potassium salt. This mixture was heated to reflux and stirred overnight. After cooling, the solvent was removed under reduced pressure. Water (20 mL) was added, the aqueous layer was extracted with toluene (3 × 40 mL), the combined organic layers were dried over $MgSO_4$, and toluene was evaporated to give a crude orange paramagnetic solid. The solid was dissolved in pentane, filtered through activated neutral alumina, and the pentane was removed to yield a red solid. Recrystallization from toluene

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(39) Herzog, S.; Gusatev, K.; Krüger, E.; Oberender, H.; Schuster, R. *Z. Chem.* **1963**, *3*, 428.

(40) Hagen, A. P.; Russo, P. J. *Inorg. Synth.* **1977**, *17*, 172−5.

afforded the desired product in 41% yield. ^{1}H NMR ($CDCl_3$) δ ppm): 4.82 (apparent t, $^{3}J_{HH} = 2.10$ Hz, 4H, *CH* α to C_6F_5); 4.46 (apparent t, $^{3}J_{HH} = 2.10$ Hz, 4H, *CH* in β to C_6F_5). ^{19}F NMR ($CDCl_3$) δ ppm): −140.04 (m, 4F, *ortho*-C*F*); −158.50 (t, $^{3}J_{FF} = 22.58$ Hz, 2F, *para*-C*F*); −163.39 (m, 4F, *meta*-C*F*). X-ray-quality crystals were obtained by slow evaporation of a toluene solution at 0 °C.

Crystallographic Determinations. The single-crystal X-ray diffraction experiments were performed on a Siemens P4/CCD diffractometer. Crystal, data collection, and refinement parameters are given in Table 1. Systematic absences and diffraction symmetry are consistent with the space groups $P1$ and $P\bar{1}$ for **5**, with $P2_1$ and $P2_1/m$ for **2**, and uniquely consistent with $P2_1/c$ for **6**. The E-statistics suggested the centrosymmetric option for **5**, and the noncentrosymmetric option for **2**, which yielded chemically reasonable and computationally stable results of refinement in each case. Compound **6** exists as one-half molecule per asymmetric unit lying on an inversion center. Crystals of **2** were found to be composed of racemic twins; refinement of a partitioning factor indicated that the enantiomeric forms were about equally represented. All structures were solved by direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix, least squares procedures. All non-hydrogen atoms were refined with anisotropic displacement coefficients and all hydrogen atoms were treated as idealized contributions. An empirical absorption correction as applied to the data using the program DIFABS.

All software and sources of the scattering factors are contained in the SHELXTL (5.10) program library (G. Sheldrick, Siemens XRD, Madison WI), and the program DIFABS is described in the literature.[41]

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Supporting Information Available: Atomic coordinates and isotropic thermal parameters, bond distances, bond angles, anisotropic thermal parameters, H atom coordinates, and isotropic thermal parameters. This material is available free of charge via the Internet at http://www.pubs.acs.org.

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(41) Walker, N.; Stuart, D. *Acta Crystallogr. Sect. A.* **1983**, *39*, 158−66.