Table VI. Solubilities of Benzene (20.0 ± 0.5 °C)

solvent	additive (M)	benzene solubility,[a] M
formamide	none	0.519 ± 0.013
	LiCl (2.32)	0.327 ± 0.011
	$LiClO_4$ (2.00)	0.388 ± 0.014
	GnCl (2.21)	0.399 ± 0.032
	Me_4NBr (0.485)	0.519 ± 0.005
	Bu_4NBr (0.500)	0.717 ± 0.015
	urea (4.16)	0.384 ± 0.006
ethylene glycol	none	0.658 ± 0.052
	LiCl (1.11)	0.464 ± 0.044
	$LiClO_4$ (1.01)	0.486 ± 0.014
	GnCl (1.09)	0.522 ± 0.012
	Me_4NBr (0.500)	0.625 ± 0.007
	Bu_4NBr (0.500)	1.05 ± 0.02
	urea (4.13)	0.373 ± 0.037

[a] Three measurements averaged; the errors are standard deviations.

waterlike. Probably all polar solutes in polar solvents have some antichaotropic effect, tending to decrease the solubility of hydrocarbons by tying up solvent molecules. In water solution with chaotropic materials such as urea or guanidinium ion this effect is overbalanced by the ability of the solute to break up solvent structure, but in formamide and ethylene glycol no such overbalancing is seen. The absence of chaotropic effects and of a greatly increased endo/exo product ratio for ethylene glycol and formamide could simply reflect a weaker waterlike structure. It is more likely that the existence of these phenomena in water solution reflects the detailed three-dimensional icelike cage structure of water,[29] in contrast to the structures of these other hydrogen-bonded solvents.

These results support the idea that the chaotropic effects of urea and similar substances in water reflect their interaction with water, not their interaction with hydrocarbon solutes. In our studies the chaotropic effects that are present in water solution are absent, with the same solutes, in the other hydrogen-bonding solvents.

The decreased rates (Table IV) and increased benzene solubilities (Table VI) with quaternary ammonium bromides in formamide and in ethylene glycol are a different matter. The contrast with the behavior of the other chaotropes suggests that these ammonium salts interact with the *solutes* in all polar solvents, acting as pseudodetergents. Indeed, micellelike structures may be formed.[14,15] As expected from this explanation, the tetrabutyl compound is more effective than is the tetramethyl compound. The contrasting behavior of the two classes of solubilizing agents makes it even clearer that the chaotropes urea and guanidinium cation, and perchlorate anion, are *not* acting as detergents. Instead, they are interacting uniquely with water.

Chaotropic effects are quite useful for confirming the existence of hydrophobic interactions in water solution. We have used them not only to study the Diels–Alder reaction[1-3] but also to detect hydrophobic packing of the transition state in the benzoin condensation.[30] However, there is apparently as yet no substance that produces a solvent-breaking chaotropic effect in solvents such as ethylene glycol or formamide. Thus, in this respect water is still unique.

Conclusions

(1) The Diels–Alder addition reactions of nitrosobenzene with 1,3-cyclohexadiene and of methyl vinyl ketone with 1,3-cyclopentadiene are faster in formamide or in ethylene glycol than in other organic solvents, but not as fast as in water solution.

(2) The reactions in these organic solvents are also accelerated by β-cyclodextrin.

(3) The kinetic results indicate that there is solvophobic binding of the reactants to each other, or into the cyclodextrin cavity, in these polar solvents.

(4) In spite of this, there is no striking increase in endo/exo selectivity, as there is in water. Furthermore, agents such as urea, guanidinium cation, and perchlorate anion that are normally chaotropic in water and thus decrease the hydrophobic effect, and the rate, show no such effect in the organic solvents. These agents also all *decrease* the solubility of benzene in ethylene glycol or in formamide, in contrast to their effects in water.

(5) The contrasts indicate that waterlike organic solvents still do not share some of the most striking properties of water itself.

(6) However, tetraalkylammonium salts do increase benzene solubility, and decrease the rate of the Diels–Alder reaction, in formamide and in ethylene glycol. This indicates that these particular salting-in agents interact with the organic solute, acting as detergents.

(7) The results and contrasts also indicate that chaotropic effects of urea and guanidinium cation in water reflect primarily the interaction of the chaotropes with the water, not with the hydrocarbon solutes.[31]

(29) Ben-Naim, A. *Water and Aqueous Solutions*; Plenum: New York, 1974; especially Chapters 6 and 8.

(30) Kool, E. T.; Breslow, R. *J. Am. Chem. Soc.* **1988**, *110*, 1596.

(31) Support of this work by the NIH is gratefully acknowledged.

Remarkable Effects of a Pentafluorophenyl Group on the Stereoselective Reactions of a Chiral Iron Acyl Complex

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Abstract: A novel chiral iron acyl complex, $[(C_6F_5)Ph_2P](CO)CpFeCOMe$ (PFCHIRAC), is synthesized. The stereoselective aldol and imine condensation reactions with benzaldehyde and benzylideneaniline using the lithium, tin, aluminum, and copper enolates of PFCHIRAC are studied. The reactions give (*R**,*S**) products regardless of the metal enolate species with high stereoselectivities (89–99% de). The observed unique stereodifferentiation is rationalized on the basis of an electron donor–acceptor type attractive interaction between the pentafluorophenyl moiety and the enolate oxygen. The variable-temperature NMR (^1H, ^{19}F, ^{31}P) study of the dynamic behavior of PFCHIRAC strongly supports the rationale.

Recently, the usefulness of chiral iron acyls (CHIRACs), $(PPh_3)(CO)CpFeCOR$ (Cp = η^5-cyclopentadienyl), in organic synthesis has been demonstrated by Davies and Liebeskind in their extensive studies on the stereoselective reactions with those com-

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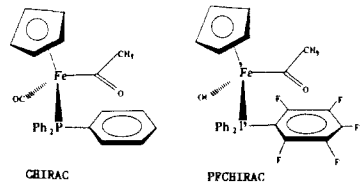
plexes.[1,2] In the stereoselective reactions of CHIRACs such as



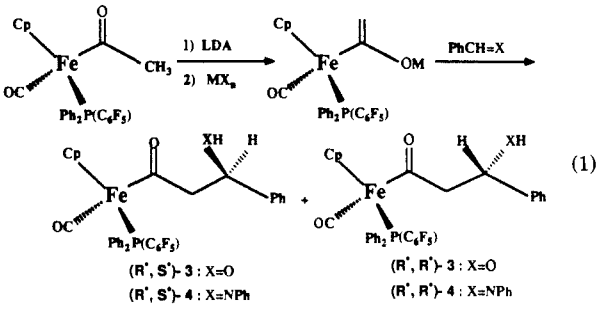
aldol and imine condensations and Michael type additions, the chiral iron metal acts as an effective stereogenic center for the newly forming chiral center at carbon. As for the mechanism of asymmetric induction, Davies proposed a unique blocking effect of a phenyl group of triphenylphosphine ligand, which directs the attack of electrophiles (for enolate reactions)[1h,i] or nucleophiles (for Michael additions):[1a] He has also demonstrated the fact that the enolate oxygen and CO ligand has an exo (or anti) geometry.[1g-j]

We synthesized a new CHIRAC having (pentafluorophenyl)diphenylphosphine as a ligand, $[(C_6F_5)Ph_2P](CO)CpFeCOMe$ (PFCHIRAC, **1**), on the basis of our hypothesis that strongly electron-accepting nature of the pentafluorophenyl group should bring about charge transfer or electron donor–acceptor type interactions with the acetyl ligand as well as the enolate oxygen so that PFCHIRAC would have unique properties in the stereoselective reactions.

The PFCHIRAC was prepared from $Cp(CO)_2FeMe$ in 68% yield through photolysis (>280 nm) in the presence of $PPh_2(C_6F_5)$ in THF or acetonitrile at 25 °C for 2 h followed by a Lewis acid catalyzed carbonylation ($BF_3{\cdot}OEt_2$, 15 mol %; CO, 150 psi [10.3 bar]) at 25 °C for 15 h.

First, the stereoselective aldol condensation of PFCHIRAC with benzaldehyde was studied. The reactions were carried out with the lithium, tin, and aluminum enolates of PFCHIRAC. The lithium enolate (**2a**) was generated by the reaction of PFCHIRAC with LDA (2 equiv) at −78 °C in THF, and the tin, aluminum, and copper enolates (**2b–d**) were generated through transmetalation of the lithium enolate with $SnCl_2$ (4 equiv), $AlClEt_2$ (4 equiv), and CuCN (4 equiv), respectively at −40 °C in THF. Results are summarized in Table I.

As Table I shows, the reactions give (*R**,*S**)-**3** (eq 1) with good to excellent stereoselectivity. The observed stereodifferentiation



(1)

forms a sharp contrast with that reported for the CHIRAC system; viz., (i) the lithium enolate of PFCHIRAC gives an excellent stereoselectivity whereas that of CHIRAC gives almost 1:1 mixture of two diastereomers,[1i,2f] and (ii) the direction of asymmetric induction in the PFCHIRAC system is independent of the metal species giving the (*R**,*S**) isomer selectively whereas that is highly dependent on the metal species in the CHIRAC system. E.g., the tin[2e] and copper[1i] enolates of CHIRAC give the (*R**,*S**) isomer as the major product while the aluminum enolate gives the (*S**,*S**) isomer selectively.[1d,2e]

Even a more remarkable difference is observed in the stereoselective imine condensation of PFCHIRAC with benzylideneaniline. We employed two methods to carry out the reactions. Method A is the simple reaction of enolates **2a–c** with the imine while method B is the reaction of the lithium enolate **2a** with imine–Lewis acid complexes. The reactions by method B proceeded much faster than those by method A, and method B gave higher stereoselectivities than method A: A similar enhancement of the reaction rate and the stereoselectivity is observed for method B in the aldol condensation as well (see Table I). The results of the stereoselective imine condensation are listed in Table II.

As Table II shows, the PFCHIRAC systems give (*R**,*S**)-**4** with 91–>98% de regardless of the metal used while the CHIRAC systems (Li and Et_2Al enolates) are reported to afford (*R**,*R**) isomer predominantly:[1e,2b] The lithium enolate of PFCHIRAC (**2a**) gives much higher stereoselectivity than that of CHIRAC by a factor of between 4 and 5.

Table I. Stereoselective Aldol Condensation of PFCHIRAC with Benzaldehyde[a]

			aldol **3**	
enolate	Lewis acid	method	yield,[b] %	(*R**,*S**)/(*R**,*R**)[c]
2a (Li)		A	88	60/1
2b (SnCl)		A	88	35/1
2c ($AlEt_2$)		A	63	8/1
2d (Cu)		A	51	9/1
2a (Li)	$SnCl_2$	B	47	80/1
2a (Li)	$BF_3{\cdot}OEt_2$	B	61	80/1
2a (Li)	$AlClEt_2$	B	58	80/1
CHIRAC (Li)		A	85–90	1/1.3[d]
			84	1/1[e]
CHIRAC (SnCl)		A	66	13/1[e]
CHIRAC ($AlEt_2$)		A	85–90	1/20[d]
CHIRAC (Cu)		A	85–90	1.2/1[d]

[a] All reactions were run with 0.22 mmol of the enolates of PFCHIRAC (**2**) and 1.10 mmol of benzaldehyde in 3–4 mL of THF in the presence or absence of Lewis acid (0.80 mmol) at −78 °C for 2 h (method B)–10 h (method A). [b] Isolated yield based on PFCHIRAC reacted. [c] Determined by ^1H NMR. [d] See ref 1i. [e] See ref 2a.

Table II. Stereoselective Imine Condensation of PFCHIRAC with Benzylideneaniline[a]

			amine **4**	
enolate	Lewis acid	method	yield,[b] %	(*R**,*S**)/(*R**,*R**)[c]
2a (Li)		A	65	25/1
2b (SnCl)		A	70	10/1
2c ($AlEt_2$)		A	62	30/1
2d (Cu)		A	73	8/1
2a (Li)	$SnCl_2$	B	78	30/1
2a (Li)	$BF_3{\cdot}OEt_2$	B	72	30/1
2a (Li)	$AlClEt_2$	B	92	50/1
CHIRAC (Li)		A	85	1/5.5[d]
		A	95	1/14[e]
CHIRAC ($AlEt_2$)		A	55	1/5.7[d]

[a] All reactions were run with 0.22 mmol of the enolates of PFCHIRAC (**2**) and 1.10 mmol of benzaldehyde in 3–4 mL of THF in the presence or absence of Lewis acid (0.66 mol) at −78 °C for 2 h (method B)–10 h (method A). [b] Isolated yield based on PFCHIRAC reacted. [c] Determined by ^1H NMR. [d] LDA (1.2 equiv) was used for the reaction. See ref 2b. [e] *n*-Butyllithium (2.3 equiv) and excess imine (5 equiv) was used. Although Davies reported[1e] the formation of only one diastereomer, the formation of a minor isomer was clearly detected by ^1H NMR.

(1) E.g.: (a) Davies, S. G.; Walker, J. C. *J. Chem. Soc., Chem. Commun.* **1985**, 209. (b) Seeman, J. I.; Davies, S. G. *Ibid.* **1984**, 1019. (c) Curtis, P. J.; Davies, S. G. *Ibid.* **1984**, 747. (d) Davies, S. G.; Dordor, I. M.; Warner, P. *Ibid.* **1984**, 956. (e) Broadley, K.; Davies, S. G. *Tetrahedron Lett.* **1984**, *25*, 1743. (f) Davies, S. G.; Dordor, I. M.; Walker, J. C.; Warner, P. *Ibid.* **1984**, *25*, 2709. (g) Davies, S. G.; Seeman, J. I. *Ibid.* **1984**, *25*, 1845. (h) Baird, G. J.; Bandy, J. A.; Davies, S. G.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1983**, 1202. (i) Davies, S. G.; Dordor-Hedgecock, I. M.; Warner, P.; Jones, R. H.; Prout, K. *J. Organomet. Chem.* **1985**, *283*, 213. (j) Davies, S. G.; Seeman, J. I.; Williams, I. H. *Tetrahedron Lett.* **1985**, 2125. (k) Davies, S. G.; Seeman, J. I.; Williams, I. H. *Tetrahedron Lett.* **1986**, *27*, 619.

(2) (a) Liebeskind, L. S.; Welker, M. E.; Fengle, R. W. *J. Am. Chem. Soc.* **1986**, *108*, 6328. (b) Liebeskind, L. S.; Welker, M. E.; Goedken, V. *Ibid. 106*, **1984**, 441. (c) Liebeskind, L. S.; Fengl, R. W.; Welker, M. E. *Tetrahedron Lett.* **1985**, *26*, 3075. (d) Liebeskind, L. S.; Welker, M. E. *Ibid.* **1985**, *26*, 3079. (e) Liebeskind, L. S.; Welker, M. E. *Ibid.* **1984**, *25*, 4341. (f) Liebeskind, L. S.; Welker, M. E. *Organometallics* **1983**, *2*, 194.

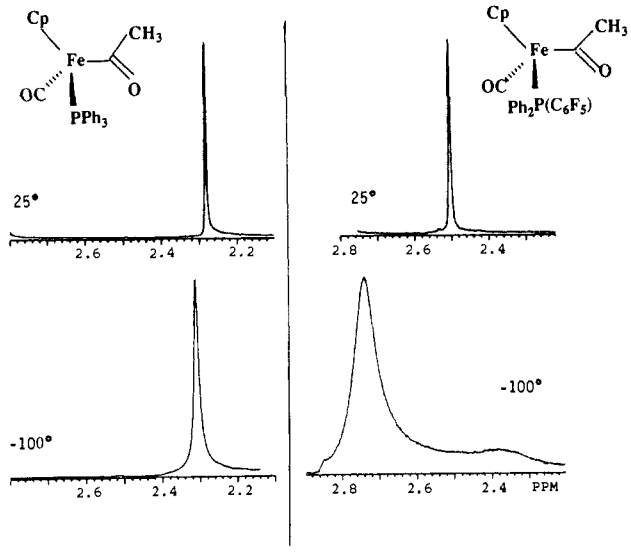


Figure 1. Variable-temperature ^1H NMR spectra of the acetyl region of PFCHIRAC. The corresponding spectra of CHIRAC are shown for comparison.

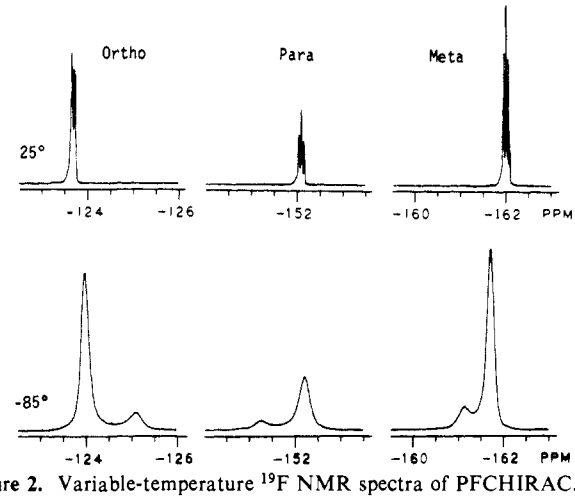
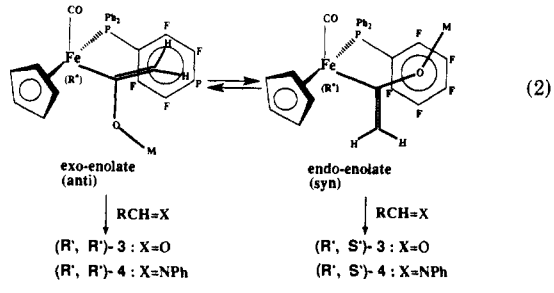


Figure 2. Variable-temperature ^{19}F NMR spectra of PFCHIRAC.

The observed remarkable difference between PFCHIRAC and CHIRAC is best rationalized by assuming the highly selective generation of endo (or syn) enolate in the PFCHIRAC system,[3] contrary to the CHIRAC system, which favors the selective generation of exo (or anti) enolate,[1h] because of electron donor–acceptor type attractive interaction between the enolate oxygen (electron donor) and the pentafluorophenyl group (electron acceptor) (eq 2). From the *endo*-enolate (*R*,S**) isomers should be formed through a quasi-boat-like transition state, which has been proposed by Davies.[1i]



(2)

In order to confirm the proposed electron donor–acceptor type interaction between the enolate oxygen and the pentafluorophenyl group, the dynamic behavior of PFCHIRAC itself as a model for its enolates was looked at by means of NMR spectroscopy. We performed ^1H, ^{19}F, and ^{31}P variable-temperature NMR measurements.

The following conclusions are deduced from the variable-temperature NMR study: (i) The rotation around the Fe–COMe bond is completely fixed at −100 °C (the coalescence temperature varies depending upon the nucleus),[4] and two diastereomers (ca.

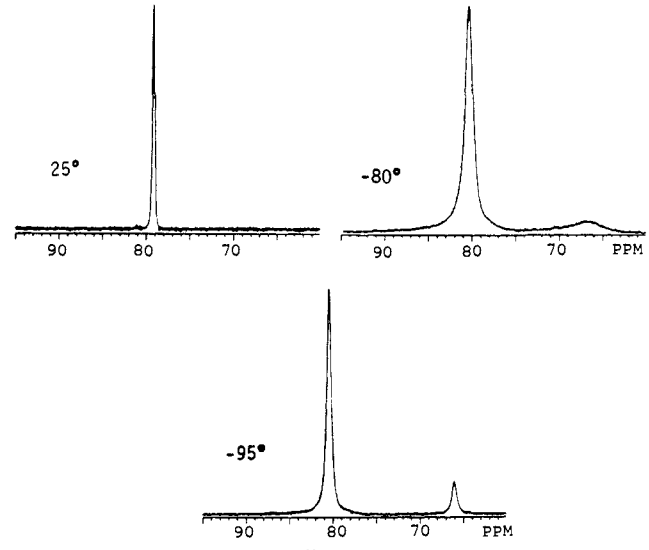


Figure 3. Variable-temperature ^{31}P NMR spectra of PFCHIRAC.

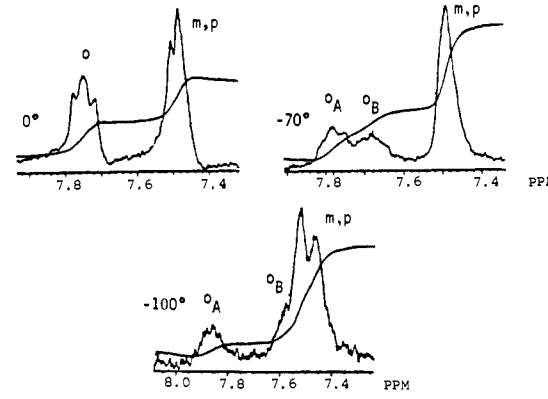


Figure 4. Variable-temperature ^1H NMR of the aromatic region of PFCHIRAC.

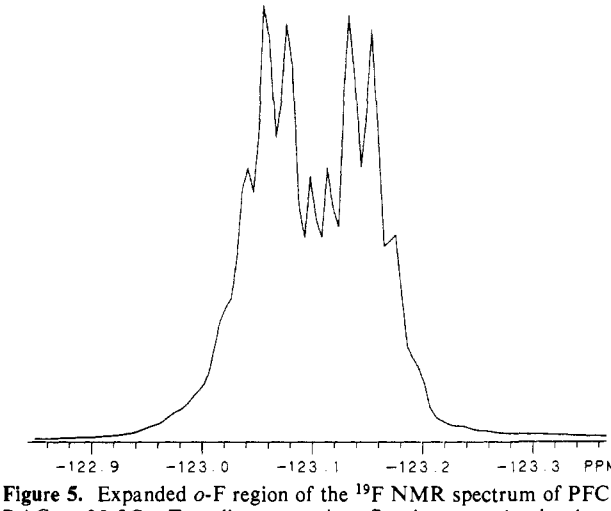


Figure 5. Expanded *o*-F region of the ^{19}F NMR spectrum of PFCHIRAC at 25 °C. Two diastereotopic *o*-fluorines are clearly observed ($J_{F_0^A-F_0^B}$ = 10.6 Hz; $J_{F_0^{A,B}-F_p}$ = 5.3 Hz; $J_{F_0^{A,B}-F_m}$ = 21.2 Hz; J_{F-P} is negligible on the basis of ^{31}P NMR).

(3) Ab initio SCF calculations for a CHIRAC model in which PPh_3 is substituted by PH_3 indicate that the endo (or syn) conformer is more favorable than the exo (or anti) conformer by 2.7 kcal/mol.[1k]

(4) The estimated activation energy of the rotational barrier around the Fe–COMe bond is 8.5 kcal/mol: The calculations from the ^1H, ^{19}F, and ^{31}P NMR data give the consistent value.

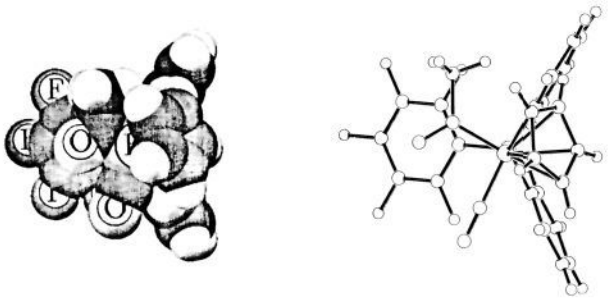


Figure 6. Computer-generated structure of PFCHIRAC with favorable endo conformation.

8:1) are observed below a coalescence temperature;[5] the ratio of the two diastereomers is consistent in ^1H, ^{19}F, and ^{31}P NMR spectra (see Figures 1–3). (ii) Two P–Ph correlated rotations *(or flipping) are coalesced at ca. −50 °C (^1H NMR) and fixed* at lower temperature[6] (see Figure 4). (iii) The rotations around Fe–P and P–C_6F_5 bonds are fixed at 25 °C.[7] The expanded *o*-F region of the ^{19}F NMR spectrum of PFCHIRAC clearly shows that the two *o*-fluorines are diastereotopic (Figure 5), which indicates the rotation about P–C_6F_5 being fixed.

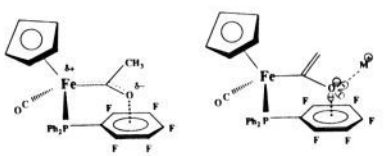
It should be noted that the predominant diastereomer shows an acetyl peak at δ 2.74 and the minor at δ 2.38 in the ^1H NMR spectrum. The results strongly suggest that the methyl moiety of the predominant isomer is located just outside of the shielding zone of the pentafluorophenyl group whereas that of the minor isomer sits right above the pentafluorophenyl group (see Figure 6) and thus receives substantial shielding effects.

As for the interpretation of the 8:1 ratio mixture of conformers, there is a possible assignment of the observed result to rotamers around the Fe–P bond. However, this possibility is excluded on the basis of careful inspection of the space-filling model of PFCHIRAC based on the X-ray crystal structure of CHIRAC reported by Davies; viz., it is apparent that the pentafluorophenyl group is substantially larger than simple phenyl group and the *free* rotation around P–C_{ipso} bond is virtually impossible in any conformations including rotamers around Fe–P bond. Moreover, the rotation of three aryl groups is correlated because of severe ortho–ortho rotational barriers. Thus, only the flipping mode seems likely to occur. We inspected diastereomers based on clockwise and anticlockwise propeller structures for $FePPh_2(C_6F_5)$ and found that those conformations severely suffer from steric conflicts with other ligands, e.g., Cp, acetyl, and CO. Thus, the conformation shown in Figure 6 is by far the most favorable. We also observed the freeze of correlated rotation or most likely flipping of two phenyl groups below −60 °C (Figure 4): The coalescence temperature is ca. −50 °C (^1H NMR). This means that the rotation around the Fe–P bond should be frozen below this temperature as well because of the extremely crowded coordination sphere. The rotational barriers for those metal–PPh_3 complexes have been studied by Faller,[8] and the values are ca. 18 kcal/mol for Ru–PPh_3 and 10–12 kcal/mol for Fe–PPh_3: It has been found that the rotational barrier for Fe–PPh_3 is higher than that for P–C_{ipso}. As Figure 1 shows, the acetyl region is frozen at ca. −100 °C (coalescence temperature is ca. −90 °C), *which clearly indicates that this phenomenon is not related to rotamers nor propeller type diastereomers.* Also, if the observed two species are rotamers around the Fe–P bond, there should be three isomers. But, only two isomers are observed.

Consequently, the possible interpretation based on the rotational isomers around the Fe–P bond is very unlikely. Moreover, this interpretation cannot explain the *observed* remarkable effects of pentafluorophenyl group on the stereoselectivity since it is quite unlikely that the rotamers can change the stereoselectivity on the basis of the widely accepted mechanism proposed by Davies.

The IR study of PFCHIRAC also strongly supports the existence of the proposed electron donor–acceptor type interaction. Wojcicki disclosed a very consistent trend in the CO stretching frequencies of MC≡O and MC(O)Me in $(R_3P)Cp(CO)FeC(O)Me$ systems when the group electronegativity of the phosphine ligand was changed.[9] Namely, both CO stretching frequencies are sensitive to the group electronegativity of the PR_3 ligand, and an electron-releasing ligand decreases both CO stretching frequencies and an electron-withdrawing ligand increases them. For *example, PBu_3 gives 1916 cm^{-1} for $\nu_{C\equiv O}$ and 1590 cm^{-1} for $\nu_{C=O}$* while $P(OBu)_3$ gives 1959 cm^{-1} for $\nu_{C\equiv O}$ and 1625 cm^{-1} for $\nu_{C=O}$ in $CHCl_3$. The values for PPh_3 (CHIRAC) are 1920 and 1598 cm^{-1} in $CHCl_3$. We measured the IR spectra of CHIRAC nPR_3 = PPh_3) and PFCHIRAC [PR_3 = $PPh_2(C_6F_5)$] in CCl_4. The values for CHIRAC are 1919 and 1602 cm^{-1}, which are very close to those in $CHCl_3$. The values for PFCHIRAC are 1935 and 1603 cm^{-1}. The best interpretation of these values is as follows. Since $PPh_2(C_6F_5)$ is much more electron withdrawing than PPh_3, the through-bond induction effect should substantially increase both $\nu_{C\equiv O}$ and $\nu_{C=O}$ frequencies compared with the PPh_3 case. In fact, the $\nu_{C\equiv O}$ frequency is increased by 26 cm^{-1}. Thus, it is reasonable to assume that the $\nu_{C=O}$ frequency is increased by ca. 10 cm^{-1}; i.e., the value should be between 1598 (1602) cm^{-1} (PPh_3) and 1625 cm^{-1} [$P(OBu)_3$]. *However, the observed $\nu_{C=O}$ frequency is 1603 cm^{-1}. This clearly indicates the existence of compensating effects, which polarize the FeC(O)Me to $Fe^+{=}C(Me)\ O^-$.* This compensating effect is ascribed to the electron donor–acceptor type interaction between C_6F_5 and –C(O)Me.

All these results indicate that there is indeed the electron donor–acceptor type attractive interaction between the acetyl moiety and the pentafluorophenyl moiety as we expected, which fixes the conformation of PFCHIRAC. In the corresponding enolates (**2**), the attractive interaction may well be stronger than that in PFCHIRAC itself because of larger negative charge on the enolate oxygens.



In conclusion, remarkable "fluorine" effects of the pentafluorophenyl group on the stereoselective reactions in the CHIRAC system are disclosed. The results are very intriguing and important for the design of a new series of chiral ligands for asymmetric synthesis and catalysis since it is obvious that we can introduce an electron donor–acceptor type attractive interaction to the chiral recognition in the coordination sites of metal complexes by using the pentafluorophenyl group or its derivatives in addition to the well-established steric interactions.

Further study along this line is actively under way.

Experimental Section

General Methods. Boiling points and melting commercially are uncorrected. The ^1H NMR spectra were measured with a General Electric QE-300 or a Nicolet NT-300 using Me_4Si as the internal standard. The ^{19}F and ^{31}P NMR spectra were recorded on the Nicolet NT-300 using $CFCl_3$ as the internal standard for ^{19}F NMR and 85% H_3PO_4 as the external standard for ^{31}P NMR. The IR spectra were recorded on a Perkin-Elmer 1310 or 1430 spectrophotometer using samples as KBr disks. Analytical thin-layer chromatography (TLC) was carried out on

(5) It is noteworthy that such a freeze of the rotation or formation of two diastereomers is not observed at all in the case of CHIRAC even at −100 °C. See Figure 1.

(6) The variable-temperature ^1H NMR study on the aromatic region indicates that two phenyl ligands are located in almost identical environments, and the two ortho protons in a phenyl group are clearly distinguished (δ 0.3) at −100 °C, which indicates that one of the two ortho protons is in the shielding region of the pentafluorophenyl ligand whereas the other is not. Those observations strongly suggest a structure bearing a hypothetical plane of symmetry that bisects the $(C_6F_5)Ph_2PFeCp$ moiety. For the stereomodel, see Figure 6.

(7) No appreciable change in the ^1H NMR spectrum of PFCHIRAC was observed even at 100 °C.

(8) Faller, J. W., private communication.

(9) Bibler, J. P.; Wojcicki, A. *Inorg. Chem.* **1966**, *5*, 889.

precoated alumina plates (neutral aluminum oxide 60, Type E) and/or silica gel plates (silica gel 60) available from E. M. Chemicals. Preparative chromatography was performed on activated neutral or basic alumina (80–200 mesh) purchased from Fisher Scientific. Elemental Analyses were performed by M-H-W Laboratories, Phoenix, AZ.

Materials. Cyclopentadienyliron dicarbonyl (Fp) dimer was commercially available from Strem Chemicals, Inc., and was used as purchased. Diethylaluminum chloride, stannous chloride, cuprous cyanide, boron trifluoride etherate, methyl iodide, and *n*-butyllithium in hexane were purchased from Aldrich Chemical Co. and used as received. Benzaldehyde and aniline were purchased from Aldrich and distilled prior to use.

Synthesis of PFCHIRAC. A Pyrex photoreaction vessel containing a yellow solution of diphenyl(pentafluorophenyl)phosphine (352 mg, 1.0 mmol) and $Cp(CO)_2FeMe$ (450 mg, 2.34 mmol) in degassed THF (35 mL), which was equipped with a tap-water cooling jacket and a magnetic stirring bar, was irradiated with 550-W Hg lamp for 2 h. The resulting red solution was transferred to a Pyrex reaction vessel in a stainless-steel autoclave, and boron trifluoride etherate (21 mg, 15 mol%) was added to it. After the air was substituted by carbon monoxide, the autoclave was pressurized with carbon monoxide (150 psi; 10.2 bar), and the reaction mixture was stirred for 20 h at room temperature. Then, carbon monoxide was discharged and water (10 mL) was added to the reaction mixture. The mixture was extracted with dichloromethane (25 mL × 3) and dried over anhydrous sodium sulfate, and solvent was removed to give a crude PFCHIRAC as brown oil, which was purified on a neutral alumina column (Fischer, 80–200 mesh) with hexane/ethyl acetate as eluent (hexane/EtOAc = 8) to yield pure PFCHIRAC (353 mg, 65%) as orange solid.

PFCHIRAC: orange solid; mp 122–123 °C; IR (KBr disk) 1935 ($\nu_{C\equiv O}$), 1601 ($\nu_{C=O}$) cm^{-1}; ^1H NMR ($CDCl_3$, TMS) δ 2.55 (s, 3 H), 4.39 (d, J = 1.2 Hz, 5 H), 7.2–8.2 (m, 10 H); ^{19}F NMR ($CDCl_3$, CF_3Cl) δ −121.6 (m, 2 F), −150.2 (m, 1 F), −160.2 (m, 2 F); ^{31}P NMR ($CDCl_3$, H_3PO_4 (external, 85%)) δ 77.2 (m). Anal. Calcd for $C_{26}H_{18}F_5FeO_2P$: C, 57.38; H, 3.33. Found: C, 57.43; H, 3.43.

Although the procedure described above does not require the isolation of $Cp(CO)[(C_6F_5)Ph_2P]FeMe$, this complex was isolated from the reaction mixture of photolysis as stable orange oil through a chromatographic separation on a neutral alumina column: IR (neat) 1935 ($\nu_{C\equiv O}$) cm^{-1}; ^1H NMR ($CDCl_3$, TMS) δ −0.12 (d, J = 7.4 Hz, 3 H), 4.30 (d, J = 0.7 Hz, 5 H), 7.0–7.7 (m, 10 H); ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ −127.6 (m, 2 F), −150.5 (m, 1 F), −160.8 (m, 2 F). Anal. Calcd for $C_{25}H_{18}F_5FeOP$: C, 58.16; H, 3.51. Found: C, 57.92; H, 3.32.

Typical Procedure for the Aldol Condensation of a Lithium Enolate (2a) with Benzaldehyde (Method A). A solution of lithium diisopropylamide (LDA) was prepared by mixing diisopropylamine (49 mg, 0.48 mmol) and 1.6 M *n*-butyllithium in hexane (0.275 mL, 0.44 mmol) in THF (1.0 mL) at 0 °C for 15 min. The resulting LDA solution was added to a solution of PFCHIRAC (120 mg, 0.22 mmol) in THF (2.0 mL) at −78 °C, and the mixture was stirred for 45 min. During the reaction the orange color of PFCHIRAC turned to deep red, which indicated the generation of an enolate (**2a**). To the enolate solution was added benzaldehyde (0.112 mL, 1.10 mmol), and the mixture was stirred overnight at −78 °C. The reaction was quenched by adding saturated aqueous sodium bicarbonate (1.0 mL) at −78 °C. The reaction mixture was then allowed to warm to room temperature, and another 5.0 mL of saturated aqueous sodium bicarbonate was added to it. The usual workup followed by a column chromatography on alumina (vide infra) with hexane/ethyl acetate (hexane/EtOAc = 8) gave the aldol (**3**) (111 mg, 78%) as orange solid and unreacted PFCHIRAC (14.4 mg, 12%).

3: orange solid; mp 173–175 °C (for the sample in which (*R**,*S**)/(*R**,*R**) = 60/1); IR (KBr disk) 3400 (ν_{NH}), 1920 ($\nu_{C\equiv O}$), 1580 ($\nu_{C=O}$) cm^{-1}; ^1H NMR ($CDCl_3$, TMS). (*R**,*S**) isomer: δ 1.70 (br s, 1 H), 3.22 (dm, J = 17.8 Hz, 1 H), 3.78 (br d, J = 17.8 Hz, 1 H), 4.49 (d, J = 1.2 Hz, 5 H), 4.50 (m, 1 H), 7.25–8.20 (m, 15 H). (*R**,*R**) isomer: δ 1.70 (br s, 1 H), 2.77 (m, 2 H), 4.34 (d, J = 1.2 Hz, 5 H), 4.36 (m, 1 H), 7.25–8.20 (m, 15 H). Anal. Calcd for $C_{33}H_{24}F_5FeO_3P$: C, 60.94; H, 3.72. Found: C, 61.00; H, 3.66.

The chemical shifts and the coupling patterns of the key signals of (*R**,*S**)-**3** and (*R**,*R**)-**3** are clearly distinctive, which correspond well to those of the aldols obtained with CHIRAC.[1i,2a] Thus, the stereochemistry of **3** can unambiguously be determined.

For a typical procedure of method B, see below.

Procedures for the Imine Condensation of Enolates (2) with Benzylideneaniline. Method A. The reaction of tin enolate (**2b**) is typically described. The lithium enolate of PFCHIRAC (**2a**, 0.22 mmol) was generated in the same manner to that described for the aldol condensation. To the enolate solution was added stannous chloride (125 mg, 0.66 mmol) and THF (1.0 mL) at −78 °C. The mixture was warmed to −42 °C, stirred for 1 h, and then cooled again to −78 °c. A solution of benzylideneaniline (198 mg, 1.10 mmol) in THF (1.0 mL) was added to this tin enolate solution, and the mixture was stirred for 10 h at −78 °C. The workup, same as that for the aldol condensation followed by a column chromatography on alumina (vide infra) with hexane/ethyl acetate as eluent (hexane/EtOAc = 8), gave the amine **4** (104 mg, 65%) as orange solid and unreacted PFCHIRAC (13.9 mg, 12%).

Method B. The reaction of lithium enolate (**2a**) with benzylideneaniline–diethylaluminum chloride complex is typically described.

To the lithium enolate solution (0.22 mmol) in THF (3 mL) prepared from LDA (0.44 mmol) and PFCHIRAC (120 mg, 0.22 mmol) was added a solution of benzylideneaniline (198 mg, 1.10 mmol)–diethylaluminum chloride (0.45 mL, 1.8 M solution in toluene; 0.80 mmol) complex in THF (1.0 mL) at −78 °C and stirred for 2 h at the same temperature. The workup and column chromatography on alumina, which are the same as those for method A, gave the amine **4** (89 mg, 55%) and unreacted PFCHIRAC (49 mg, 40%).

4: orange solid; mp 177–179 °C (for the sample in which (*R**,*S**)/(*R**,*R**) = 30/1); IR (KBr disk) 3450 (ν_{NH}), 1930 ($\nu_{C\equiv O}$), 1580 ($\nu_{C=O}$) cm^{-1}; ^1H NMR ($CDCl_3$, TMS). (*R**,*S**) isomer: δ 3.28 (dm, J = 17 Hz, 1 H), 3.82 (br d, J = 17 Hz, 1 H), 4.49 (d, J = 1.1 Hz, 5 H), 4.50 (m, 1 H), 6.65 (d, J = 9.5 Hz, 1 H), 7.1–8.0 (m, 20 H). (*R**,*R**) isomer: δ 2.50 (m, 2 H), 4.35 (d, J = 1.1 Hz, 5 H), 4.36 (m, 1 H), 6.75 (d, J = 9.5 Hz, 1 H), 7.1–8.0 (m, 20 H). Anal. Calcd for $C_{39}H_{29}F_5FeNO_2P$: C, 64.57; H, 4.03. Found: C, 64.89; H, 3.63.

The stereochemistry of **4** can unambiguously be determined on the basis of the comparison of the coupling patterns and the chemical shifts of the key signals with those of the adducts obtained from the corresponding CHIRAC reaction.[2a]

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