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ASYMMETRIC INDUCTION IN CARBON–CARBON BOND FORMING REACTIONS OF PROCHIRAL NUCLEOPHILES WITH ELECTROPHILES CONTAINING CHIRAL IRON CENTERS

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Summary

Alkylations of the chiral electrophiles $CpFe(CO)(L)CH_2Cl$ and $CpFe(CO)(L)(CH_2{=}CH_2)^+\ SO_3CF_3^-$ ($L = PPh_3$ and tri(*o*-biphenyl)phosphite) by the prochiral nucleophiles sodium t-butyl acetoacetate and pyrrolidine cyclohexanone enamine yielded six of the eight possible alkyliron products. The two products where L was *o*-biphenylphosphite and t-butylacetoacetate was the nucleophile did not form, presumably because of excessive steric hindrance. Relative quantities of the two diastereomers formed in each case were easily determined from the diastereomeric resonances in their NMR spectra. Product ratios from alkylation by acetoacetate were thermodynamic, while those from alkylation by the enamine were presumed to be kinetic. The excess of one diastereomer over the other, relating in principle to an "optical yield" at the new chiral carbon center induced by the existing metal chirality, ranged from 10 to 64% depending on the nucleophile and the electrophile, but most pronouncedly, on the ligand L.

Introduction

Iron complexes of the type $CpFe(CO)_2R$ ($Cp = \eta^5\text{-}C_5H_5$) have been shown by Rosenblum and others [1,2] to be of potential utility as stoichiometric reagents in organic synthesis. This utility arises by virtue of the ability of iron to behave as both an electron donor and an electron acceptor in reactions of organic ligands. Since these organoiron species are both inexpensive and synthetically relatively tractable on a large scale, their potential as reagents seems to be more real than illusory.

For some time, we have been interested in the uses of chirality in the elucidation of organometallic mechanisms, with major emphasis on the synthesis and use of optically active organoiron species of the type $CpFe(CO)(L)R$ (L = phosphine, phosphite, or isonitrile) in such studies [3]. In light of the relative ease of incorpora-

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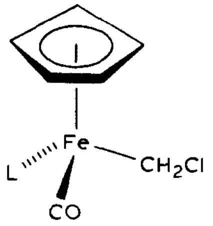
tion of L into $CpFe(CO)_2R$, and in view of the potential added dividend of asymmetric induction which might accrue to the synthetic reactions alluded to above, we have examined the asymmetric induction which could be achieved in several typical carbon–carbon bond forming reactions using electrophiles containing a chiral iron center and prochiral nucleophiles.

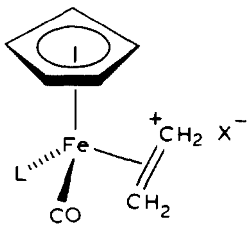
Two examples of asymmetric induction involving chiral iron species have appeared. $CpFe(CO)(PPh_3)(CH_2O$-menthyl) effects cyclopropanation upon treatment with acid in the presence of *trans*-β-methylstyrene, affording *trans*-1,2-methylphenylcyclopropane [4], and $CpFe(CO)(PPh_3)(CH_2Br)$ will cyclopropanate the same olefin in an uncatalyzed reaction [5]. Optical yields were up to 38 and 9%, respectively.

Results

Based upon our own work [5] and that of Rosenblum [1], complexes **1a** and **2a** were selected as alkylating agents for this study. In order to substantially enhance



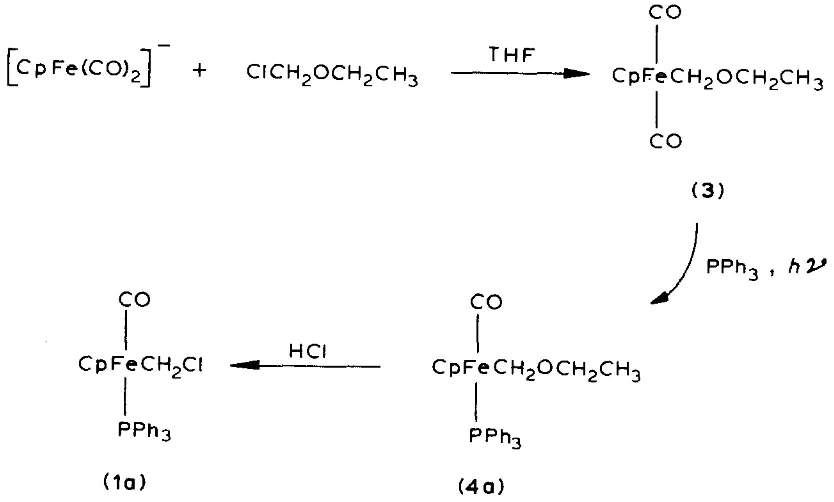
(**1a**, L = PPh_3 ;
1b, L = *o*-BP)



(**2a**, L = PPh_3 ;
2b, L = *o*-BP)

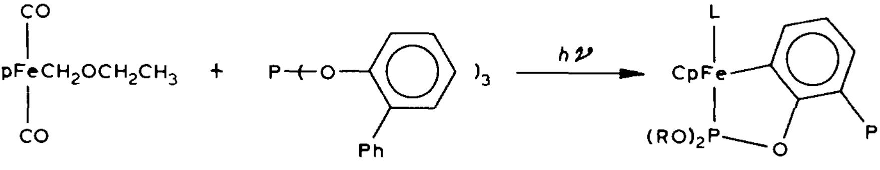
the steric bulk of L in comparison to PPh_3, and thus to increase the steric asymmetry about the metal complexes, **1b** and **2b** were prepared where tri(*o*-biphenyl)phosphite (*o*-BP) replaces PPh_3.

The preparation of **1a** was accomplished as shown in Scheme 1, by a procedure completely analogous to that used for optically active **1a** [5]. An attempt to photochemically incorporate *o*-BP into **3** to form **4b**, however, instead generated two



SCHEME 1

materials which NMR spectra indicated had no alkyl group. These species were tentatively assigned structures **5** (L = CO, *o*-BP) consistent with the known photochemical transformation of $CpFe(CO)_2Ph$ with $P(OPh)_3$ to yield the corresponding analogs of **5** [6]. Literature precedent [6,7] suggested that **4b** might be prepared by a

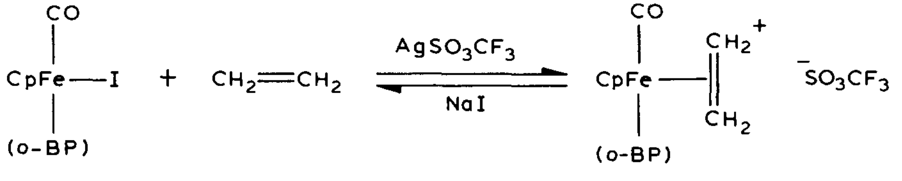


(3) (*o*-BP) (5)

(L = CO, *o*-BP) (1)

thermal exchange between excess *o*-BP and **4a**. This exchange proceeded in acceptable yield in benzene at reflux. Conversion of **4b** to **1b** by treatment with anhydrous HCl was somewhat more difficult than the corresponding preparation of **1a** because of the greater solubility of **1b** and the general instability of chloromethyliron species. Although a satisfactory combustion analysis could not be obtained, the spectra and reaction chemistry of **1b** leave no question as to its structure.

Complex **2a** was prepared by the standard procedure of β-hydride abstraction from $CpFe(CO)(PPh_3)CH_2CH_3$ using trityl fluoroborate. Again the analogous reaction with $CpFe(CO)(o\text{-BP})CH_2CH_3$ failed, presumably because of excessive steric hindrance between the reactants. Nevertheless, the precedented [8] reaction of eq. 2 worked well in the preparation of **2b**. The Cp and *o*-BP resonances of **2b** were well defined in its ^1H NMR spectrum, but the ethylenic resonance was not decisively located, perhaps because of rapidly reversible dissociation. To conclusively establish the presence of ethylene, **2b** was treated with NaI in acetone with the resultant regeneration of CpFe(CO)(*o*-BP)I and the evolution of ethylene [9].

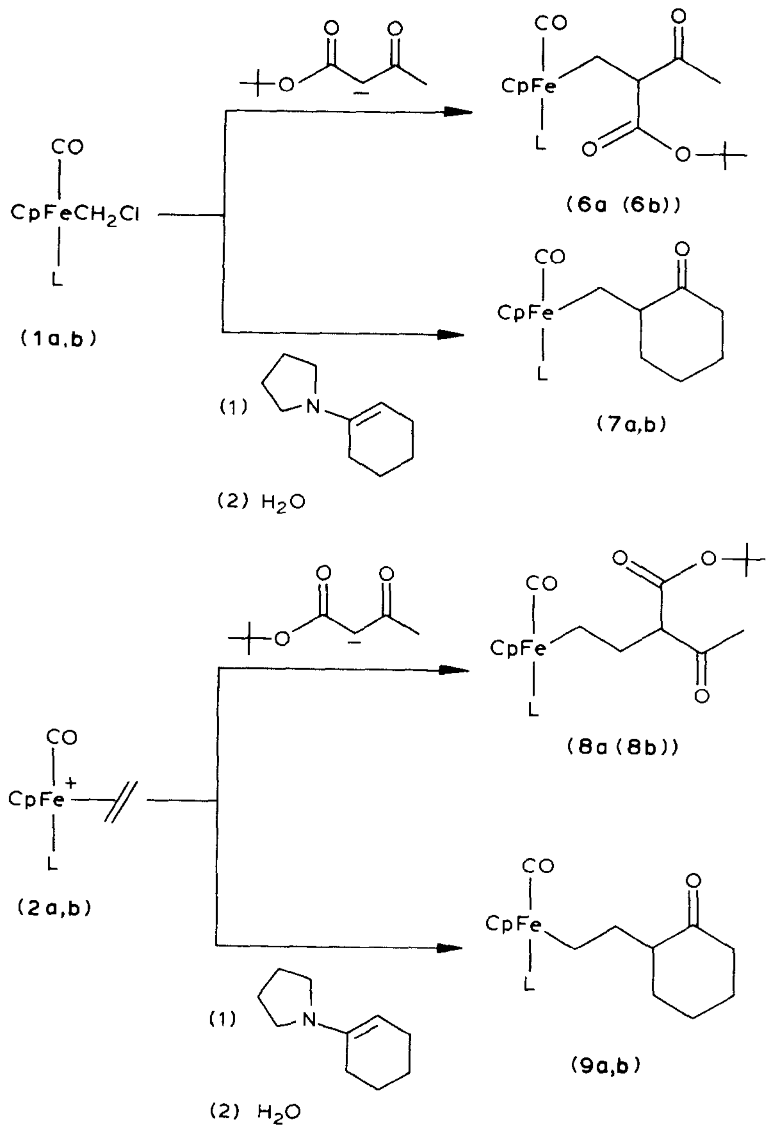


(2)

(2b)

The carbon–carbon bond-forming reactions chosen for study were those employing the prochiral nucleophiles shown in Scheme 2 [1]. Sodium t-butyl acetoacetate was generated in THF and reactions of this reagent were conducted in the same solvent. Compounds **6a**–**9a** as well as **7b** and **9b** were all prepared in yields between 65 and 95%. Attempted syntheses of **6b** and **8b** were unsuccessful, presumably because of the excessive steric bulk of the reactants.

In all cases in Scheme 2, enantiomeric iron species are converted into diastereomers. Since our interest was in the optical yield induced in formation of the second center by the presence of the first, use of enantiomerically resolved **1** and **2** was not necessary, although it would have been easy to achieve, at least for $L = PPh_3$. Assessment of the $[(RS)+(SR)]/[(RR)+(SS)]$ ratio was simple because



(a series, L = PPh_3; b series, L = *o*-BP)

SCHEME 2

in all cases diastereomeric resonances were well resolved in the NMR spectra. Generally, the most useful resonances were those of the cyclopentadienyl group which were usually base-line resolved, except in the case of **8a** wherein the Cp resonances were coincident, but in this case the diastereomeric acetyl-methyl and t-butyl resonances were well resolved. Diastereomeric ratios were determined as early in the reaction work-up as possible in order to avoid enrichment of one diastereomer over another by selective decomposition or by crystallization. The first useful NMR was generally obtainable on the bulk sample after rapid filtration of the

TABLE 1

STEREOSPECIFICITY OF ALKYLATIONS OF CHIRAL IRON ELECTROPHILES BY PROCHIRAL NUCLEOPHILES

	CpFe(CO)(L)R		Diastereomer ratio (% ee) [a]
	L	R	
6a	PPh_3	$CH_2CH(COCH_3)CO_2$-t-Bu	61/39 (22)
7a	PPh_3	$CH_2CHC(O)(CH_2)_4$	59/41 (18)
8a	PPh_3	$CH_2CH_2CH(COCH_3)CO_2$-t-Bu	73/27 (46)
9a	PPh_3	$CH_2CH_2CHC(O)(CH_2)_4$	55/45 (10)
7b	*o*-BP [b]	$CH_2CHC(O)(CH_2)_4$	80/20 (60)
9b	*o*-BP [b]	$CH_2CH_2CHC(O)(CH_2)_4$	82/18 (64)

[a] % ee is the enanthiomeric excess induced in the carbon center by the presence of the iron center.
[b] *o*-BP = tri(*o*-biphenyl)phosphite.

extracted product through a plug of alumina. The diastereomeric ratios of the products obtained are given in Table 1.

Fractional crystallization of complex **6a** yielded the less soluble diastereomer in pure form, and the more soluble in ca. 80% purity. To check for configurational stability, each diastereomer was treated independently with triethylamine and with sodium t-butyl acetoacetate and the progress of the reaction was followed by NMR. In all cases equilibration was rapid, within an hour with the use of acetoacetate anion. No equilibration was noted in the absence of base.

Several lines of evidence indicate that alkylation of **1a** and **2a** by acetoacetate anion resulted in *C*-alkylation and not *O*-alkylation. First, the IR carbonyl stretching frequencies of **6a** were 1713 and 1690 cm^{-1}, and those of **8a** were 1730 and 1710 cm^{-1}, while the ethyl enol ether of ethyl acetoacetate absorbs at 1650 and 1742 cm^{-1} [10]. Secondly, the *O*-alkylated product from reaction of **1a** would itself be exceptionally labile to C–O cleavage by HCl, while brief treatment of **6a** with anhydrous HCl had no effect. Thirdly, the α-carbons in $Fe-CH_2-O$ groups exhibit a ^{13}C resonance at ca. δ 70 ppm [5], while the resonance of the α-carbon in **6a** is a clear diastereomeric pair of phosphorus-coupled doublets (J 19.5 Hz) at δ -1.37 ppm.

Discussion

Asymmetric induction in catalytic reactions is a subject of current interest [11]. In view of the potential synthetic utility of carbon–carbon bond forming reactions mediated by iron-containing reagents, and in view of the readily obtainable chirality present in systems of the type CpFe(CO)(L)X, we have examined the extent of asymmetric induction which can be achieved in the reactions shown in Scheme 2. Since induction may be caused by a number of factors such as steric bulk, solvation, dipolar and charge effects, trans and other electronic effects, etc. whereby asymmetry can exert itself, it is not an easy matter to determine which factor or factors may be of primary importance in a given reaction. Nevertheless, we have sought to briefly investigate the effects of variation in steric bulk by replacement of the triphenylphosphine ligand by tri(*o*-biphenyl)phosphite. Tolman's "cone angles" for these two ligands are 145 and 152°, respectively [12], but these numbers are relevant to the size of the ligand in the immediate coordination sphere of the metal. The two alkylation reactions studied here involve no prior coordination of a reagent directly to the metal center, and, therefore, in the transition state for C–C bond formation the chiral and prochiral centers of the two reactants will lie relatively far apart. Space filling models clearly indicate that *o*-BP will exert substantially more steric influence somewhat farther from the metal than will PPh_3.

Whether the asymmetric induction exhibited in these alkylation reactions is kinetically or thermodynamically determined is, of course, a matter of importance, although the induction observed in either case is equally interesting. The base catalyzed epimerization of **6a** described above indicates that the product diastereomer ratio obtained from the preparation of that material is almost certainly the thermodynamic one. Since the destabilizing effect of the iron center on the carbanionic intermediate in the epimerization of **6a** should be attenuated by the additional CH_2 in **8a**, it is highly likely that the **8a** diastereomer ratio is also thermodynamically determined. It is considered unlikely that the ratio arising from enamine alkylation is the result of epimerization, since the less stable product is often the predominant one in such reactions [13], and the presence of the iron atom is expected to further destabilize an enolate anion racemization intermediate.

Other mechanisms which might alter the kinetic product ratio include metal epimerization by phosphine dissociation, and selective decomposition or accidental enrichment of one diastereomer over another during handling or workup. The latter problem was avoided, as mentioned above, by measuring the product ratio of the bulk sample as early as possible in the reaction workup. Phosphine dissociation is unlikely to be of significance at ambient temperature, as shown by thermolysis studies of this type of iron alkyl [14], and by the demonstrated configurational stability of the separated diastereomers of **6a** in the absence of base. Even the extremely hindered **9b** exhibited the same diastereomer ratio before and after column chromatography.

Although a complete, corresponding set of products with both phosphite and phosphine could not be obtained, some trends are present in the extent of asymmetric induction reported in Table 1. With $L = PPh_3$, higher asymmetric induction was obtained with the use of sodium t-butyl acetoacetate (t-BAA) than with pyrrolidene cyclohexanone enamine (enamine). Although this effect is minimal for alkylation of the chloromethyl complex **1a**, yielding 22% ee for **6a** and 18% ee for **7a**, the effect is more pronounced for the ethylene complex **2a** for which 46% ee (**8a**) and 10% ee (**9a**) were obtained in the two reactions. Steric demands may be more pronounced in the fully bonded products (**6a** and **8a** are equilibrated products) than in the more distant interactions of the transition state for approach of the enamine to the electrophiles (**7a** and **9a** are presumably kinetic products). Alternatively, space-filling molecular models indicate that the t-BAA anion may be more sterically hindered than the enamine in its approach as well. This would be consistent with the lack of alkylation of the much more highly hindered phosphite-substituted electrophiles **1b** and **2b** by t-BAA. Quite possibly the steric requirements are too severe to allow reaction.

In conclusion, the extent of asymmetric induction in the alkylation reactions of chiral electrophiles **1** and **2** with prochiral enamines and acetoacetic esters to generate new chiral alkyl centers is variable. The extent of induction can be substantial, especially considering the fact that the incoming nucleophile is itself never attached to the metal center, and so is at some distance from the chiral environment. Highly bulky phosphine ligands on **1** and **2** can lead to reasonably high induction, giving some promise for real synthetic utility.

Experimental section

General. Proton magnetic resonance spectra were recorded on Varian Instruments T-60, XL-100, and EM-360 spectrometers. Carbon spectra were recorded on the XL-100 spectrometer. Chemical shifts are reported in ppm (δ) and are referenced to tetramethylsilane. Infrared spectra were recorded on Perkin–Elmer 281 and Beckman IR-12 spectrometers. Melting points (Thomas–Hoover apparatus) are uncorrected. Preparative photolyses were performed using a Hanovia 450-W medium-pressure mercury arc lamp in a quartz immersion apparatus, using a Vycor filter sleeve. Microanalyses were performed by Elek (Torrance, CA) Cal. Tech. (Pasadena, CA), and Galbraith (Knoxville, Tenn.) Microanalytical Laboratories. The purity of all organoiron compounds was checked by thin-layer chromatography.

All reactions were carried out under an atmosphere of prepurified nitrogen or ultra high purity argon. THF, benzene, and toluene were distilled under nitrogen atmosphere from a solution of disodium benzophenone dianion. All other solvents were reagent grade and were deoxygenated by vigorously passing a stream of nitrogen through them. Column chromatography, or in many cases "filtration through alumina", was carried out on "acid-washed" alumina (alumina treated with ethyl acetate for several days and then reactivated) [15] prepared using hexane solvent. A THF solution of $Na[CpFe(CO)_2]$ [16a], and $CpFe(CO)_2I$ [16b], $P[O(o\text{-}C_6H_5)C_6H_4]_3$ [17], and $CpFe(CO)(PPh_3)Et$ [5] were all prepared by literature methods.

*Preparation of $CpFe(CO)(PPh_3)CH_2OCH_2CH_3$ (**4a**)*

A solution of $Na[CpFe(CO)_2]$ (ca. 0.48 mol) in THF (750 ml) was cooled to 0°C and transferred by forced siphon (cannula) to chloromethyl ethyl ether (0.53 mol) in THF (300 ml), also at 0°C. Following stirring at room temperature overnight, THF was removed at reduced pressure, the residual oil was taken up in ether/hexane (1/1), this solution was filtered through a cake of anhydrous $MgSO_4$ powder, and the solvent was again removed under reduced pressure. Chromatography on alumina yielded a redbrown fraction which upon solvent removal amounted to 96 g (ca. 85%) of crude $CpFe(CO)_2CH_2OCH_2CH_3$ (**3**) as an oil. ^1H NMR ($CDCl_3$) δ 1.10 (t, 3, J 6.5 Hz), 3.32 (q, 2, J 6.5 Hz), 4.55 (s, 5), 4.77 (s, 2); IR (thin film) 1995, 1930 (CO) cm^{-1}.

Crude **3** (0.16 mol) in 250 ml of ethyl ether and PPh_3 (0.16 mol) in 50 ml of benzene were added to the 300-ml immersion well photolyses apparatus, which was itself immersed in a 0°C bath. The solution was irradiated for 2.5 h during which product crystallized. Solid was removed, and the irradiation was continued an additional hour. The combined solids were washed with cold ether/hexane (1/1). The remaining solution was reduced in volume and stored at −20°C overnight to induce further crystallization. This portion was recrystallized from CH_2Cl_2/ether/hexane (2/1/4) by slow removal of CH_2Cl_2 and ether at reduced pressure. The total yield of **4a** was 65 g (86%), m.p. 130–131.5°C. ^1H NMR (C_6D_6) δ 1.35 (t, 3, J(HH) 8

Hz), 2.73–3.73 (m, 2), 4.33 (dd, 1, *J*(HH) 4, *J*(PH) 7 Hz, diastereotopic $FeCH_2$), 4.50 (d, 5, *J*(PH) 1 Hz), 4.84 (dd, 1, *J*(HH) 4, *J*(PH) 4 Hz, diastereotopic $FeCH_2$), 7.2–7.6 (m, 15, PPh_3) ppm. ^{13}C NMR ($CDCl_3$) δ 14.9 (CH_3), 65.2 (d, *J*(PC) 18 Hz, $FeCH_2$), 68.4 (CH_2), 84.9 (Cp), 127–139 (PPh_3), 222.7 (d, *J*(PC) 30 Hz, CO) ppm. IR (thin film) 1900 cm^{-1} (CO). Anal. Found: C, 68.92; H, 5.92. $C_{27}H_{27}FeO_2P$ calcd.: C, 68.95; H, 5.79%.

*Preparation of $CpFe(CO)(o\text{-}BP)CH_2OCH_2CH_3$ (**4b**)*

Tri(*o*-biphenyl)phosphite (37 mmol) and $CpFe(CO)(PPh_3)CH_2OCH_2CH_3$ (**4a**) (10.6 mmol) in THF (200 ml) were heated at reflux under nitrogen for several days during which time the solution was carefully protected from light. Solvent was removed at reduced pressure, and the brown oil was dissolved in ether/methylene chloride (50 ml, 2/1) and chromatographed on alumina. Phosphine and excess phosphite were eluted with hexane, and then benzene/chloroform (9/1) eluded the bright yellow product. Solvent removal and vacuum drying yielded 2.9 g (37%) of **4b**, m.p. 143–145°C. ^1H NMR ($CDCl_3$) δ 0.84 (t, 3, *J* 7.2 Hz), 2.4–3.6 (m, 2), 3.66 (d, 5, *J*(HP) 1 Hz), 4.38 (m, 2, $FeCH_2$), 7.15 (m, 27) ppm. ^{13}C NMR ($CDCl_3$) 15.2 (CH_3), 62.8 (d, *J*(PC) 30 Hz, $Fe\mathit{C}H_2$), 66.8 (OCH_2), 83.9 (Cp), 120.5–149 (m, aromatic) ppm; the CO resonance was too weak to observe. IR (thin film) 1940 cm^{-1} (CO). Analysis was obtained on a sample recrystallized from hexane, Found: C, 72.49; H, 5.39. $C_{45}H_{39}FeO_5P$ calcd.: C, 72.39; H, 5.27%.

*Preparation of $CpFe(CO)(PPh_3)CH_2Cl$ (**1a**)*

A suspension of **4a** (5.3 mmol) in 60 ml of ether at 0°C was treated with a slow stream of anhydrous HCl gas bubbled through via a syringe needle. After a short time the mixture became homogeneous, and then a bright orange solid separated. The HCl flow was stopped and the mixture was stirred an additional 10 min. The cold mixture was filtered in the air, and the solid was washed with cold ether (2 × 5 ml) and vacuum dried: yield 2.1 g (86%), m.p. 123–124°C. Spectra agreed with those reported [5].

*Preparation of $CpFe(CO)(o\text{-}BP)CH_2Cl$ (**1b**)*

Anhydrous HCl was bubbled through a solution of **4b** (0.67 mmol) in THF (10 ml) at 0°C until the color changed to lemon yellow. The solvent was removed at reduced pressure. ^1H NMR ($CDCl_3$) δ 3.71 (m, 2, diastereotopic $Fe\mathit{CH_2}$), 3.80 (s, 5), 7.1–7.3 (aromatic) ppm. IR (KBr) 1955 cm^{-1} (CO). Attempts to recrystallize **1b** from a variety of solvents yielded only less pure material. Anal. Found: C, 70.17; H, 5.71. $C_{43}H_{34}ClFeO_4P$ calcd.: C, 70.08; H, 4.66%.

*Preparation of $[CpFe(CO)(PPh_3)(\eta^2\text{-}CH_2{=}CH_2)]^+ BF_4^-$ (**2a**)*

$CpFe(CO)(PPh_3)CH_2CH_3$ (2.3 mmol) and $(C_6H_5)_3C^+ BF_4^-$ (2.5 mmol) were combined as solids and 10 ml of CH_2Cl_2 was added. After 5 min of stirring at room temperature, 20 ml of ether was added, and the solution was cooled to 0°C. The resultant crystals were collected and washed with ether, yielding 1.0 g (85%). Recrystallization could be accomplished from a minimum of CH_2Cl_2, followed by two volumes of ether. ^1H NMR (acetone-d_6) 3.2–3.6 (m, 4), 5.3 (d, 5, *J*(PH) 1 Hz), 7.3–7.8 (m, PPh_3). IR (thin film) 1980 cm^{-1} (CO). This compound has been reported previously [18].

Preparation of $[\mathrm{CpFe}(o\text{-}\mathrm{BP})(\mathrm{CO})(\eta^2\text{-}\mathrm{CH_2{=}CH_2})]^+\ \mathrm{SO_3CF_3}^-$ *(**2b**)*

A benzene (150 ml) solution of $\mathrm{CpFe(CO)_2I}$ (18.1 mmol) and tri(*o*-biphenyl)phosphite (19.9 mmol) was heated at reflux for 10 h. The solvent volume was reduced and the residue was chromatographed on alumina. The product, CpFe(CO)(*o*-BP)I, eluted as a green band using $\mathrm{CHCl_3}$/hexane (1/1) yield 11.7 g (78%). This was recrystallized by dissolution in a minimum of $\mathrm{CH_2Cl_2}$, addition of 2 volumes of heptane, and slow removal of $\mathrm{CH_2Cl_2}$ under vacuum; m.p. 158–159°C (sealed tube). ^{1}H NMR ($\mathrm{CDCl_3}$) δ 3.70 (s, 5, Cp) and 7.1–7.3 (m, 27) ppm. IR (thin film) 1978 $\mathrm{cm^{-1}}$ (CO).

A solution of CpFe(CO)(*o*-BP)I (3.1 mmol) in $\mathrm{CH_2Cl_2}$ (15 ml) at -10°C was treated with a toluene solution (17 ml) of $\mathrm{AgSO_3CF_3}$ (3.0 mmol) while ethylene gas was passed through the solution. The solution was warmed to ambient temperature with continued ethylene bubbling. Ethylene flow was stopped and after stirring for 30 min the AgI was packed by centrifugation and the supernatant was evaporated. Heptane (50 ml) was added, the solution was filtered, and the $\mathrm{CH_2Cl_2}$ was removed slowly at reduced pressure, leaving burgundy-colored crystals; yield 2.1 g (80%), m.p. 68–70°C in air (At 130–131°C (sealed tube) a sharp color change from burgundy to yellow occurred without melting). ^{1}H NMR ($\mathrm{CDCl_3}$) δ 3.90 (s, 5, Cp) and 7.1–7.3 (m, 27, aromatic) ppm. The ethylene resonances were not obvious, but may have been among poorly defined but persistent minor resonances between 0.9 and 1.5 δ. To test for the presence of ethylene, some pure **2b** was treated with NaI in acetone, resulting in reisolation of pure CpFe(CO)(*o*-BP)I and generation of a gas which gave a single peak upon coinjection with ethylene on VPC (Porapak Q, 1 m, 50°C). IR (thin film) 2010 $\mathrm{cm^{-1}}$ (CO). Anal. Found: C, 62.40; H, 4.28. $\mathrm{C_{45}H_{36}F_3FeO_7PS}$ calcd.: C, 62.51; H, 4.20%.

Preparation of $\mathrm{CpFe(CO)(PPh_3)CH_2CH(COCH_3)CO_2\text{-}t\text{-}Bu}$ *(**6a**)*

Sodium t-butyl acetoacetate was prepared as a 0.5 *M* solution in THF (20 ml) by the action of NaH (20% excess) on t-butyl acetoacetate. A solution of **1a** (4.6 mmol) in THF (100 ml) at -10°C was treated dropwise with 9.2 ml of the above solution over five minutes, and the mixture was stirred for one hour. Solvent was removed at reduced pressure without heating, and the residue was taken up in ether and filtered through a 2 cm × 10 cm plug of alumina. The orange-red filtrate was evaporated to dryness and then vacuum dried yielding 2.6 g (96%) of solid, m.p. 115°C (dec.). Crystallization of the sample from ether/acetone afforded the pure, less-soluble diastereomer, m.p. 114–115.6°C (sealed tube). ^{1}H NMR ($\mathrm{C_6D_6}$) δ 1.2–2.3 (m, partially obscured, $\mathrm{FeCH_2}$), 1.44 (s, t-Bu), 1.88 (s, $\mathrm{COCH_3}$), 3.6 (m, unresolved, $\mathrm{CO{-}\overset{|}{C}H{-}CO}$), 4.21 (d, $J \sim 1$ Hz, Cp), 6.6–7.5 (m, $\mathrm{PPh_3}$) ppm. Crystallization of the residue from ether/pentane gave ca. 80% pure, more-soluble diastereomer, m.p. 116.9–117.2°C (sealed tube). ^{1}H NMR ($\mathrm{C_6D_6}$) δ 1.2–2.3 (m, partially obscured, $\mathrm{FeCH_2}$), 1.44 (s, t-Bu), 2.06 (s, $\mathrm{COCH_3}$), 3.56 (dd, *J* 4 and 8 Hz, $\mathrm{CO{-}\overset{|}{C}H{-}CO}$), 4.07 (d, $J \sim 1$ Hz, Cp), 6.6–7.5 (m, $\mathrm{PPh_3}$) ppm. ^{13}C NMR (mixture of diastereomers in $\mathrm{C_6D_6}$) δ -1.89 and -0.85 (two d, *J*(CP) 20 Hz, Fe*C*$\mathrm{H_2}$), 26.6, 26.9 (*C*$\mathrm{H_3}$CO), 27.4 (OC(*C*$\mathrm{H_3})_3$), 70.1, 69.3 ($\mathrm{CO{-}}\overset{|}{C}\mathrm{H{-}CO}$), 79.7, 80.0 (O*C*$\mathrm{(CH_3)_3}$), 85.1 (Cp), 127–138 (m, $\mathrm{PPh_3}$), 171.1, 171.5, (*C*$\mathrm{O_2}$), 204.1 (br, s, C–*C*O–C), 222.5 (d, *J* 33 Hz, FeCO) ppm. IR (thin film) 1890 (C≡O), 1713 and 1690 (C=O) cm^{-1}. Anal. Found (mixture of diastereomers): C, 68.04; H, 5.85. $C_{33}H_{35}FeO_4P$ calcd.: C, 68.05; H, 6.06%.

To test for racemization, 25 mg of the pure less-soluble diastereomer in $CDCl_3$ was treated with 0.1 ml of a 1 *M* solution of sodium t-butylacetoacetate in THF in an NMR tube. NMR revealed that the 60/40 equilibrium of the two diastereomers, also the ratio observed in freshly prepared **6a**, had been reached within an hour.

Preparation of CpFe(CO)(PPh$_3$)CH$_2$-c-C$_6$H$_9$O (7a)

Freshly distilled cyclohexanone pyrrolidine enamine (3.3 mmol) was added to a solution of **1a** (3.6 mmol) in THF (70 ml) at − 12°C and this was stirred for an hour. Solvent was removed under vacuum without heating, and the residue was hydrolyzed by addition of water (20 ml), ether (20 ml), and CH_2Cl_2 (30 ml). The organic layer was separated, the aqueous phase washed once with CH_2Cl_2 (20 ml), and the combined organic layers were washed once more with water (30 ml). The organic layer was taken to dryness, the residue taken up in CH_2Cl_2, and this solution filtered through a 2 cm × 5 cm plug of alumina. Evaporation of the solvent and vacuum drying yielded 1.5 g (80%) of red-orange solid, m.p. 136–138°C (dec.). ^1H NMR ($CDCl_3$) δ 1.0–2.6 (broad, 11), 4.13 and 4.20 (two s, total of 5, diastereomeric Cp), 7.33 (m, 15) ppm. IR (thin film) 1905 (C≡O) and 1685 (C=O) cm^{-1}. Anal. Found (mixture of diastereomers): C, 71.38; H, 6.48. $C_{31}H_{31}FeO_2P$ calcd.: C, 71.27; H, 5.98%.

Preparation of CpFe(CO)(o-BP)CH$_2$-c-C$_6$H$_9$O (7b)

In a manner analogous to the above procedure, **1b** and cyclohexanone pyrrolidine enamine were submitted to reaction, affording the ketone **7b** in 68% yield. ^1H NMR (C_6D_6) δ 0.8–2.3 (m, ~ 11), 3.62 and 3.88 (two s, total of 5, diastereomeric Cp), and 7.1–7.3 (m, 27, aromatic) ppm. IR (thin film) 1895 (C≡O) and 1685 (C=O) cm^{-1}. Anal. Found (mixture of diastereomers): C, 73.09; H, 5.76. $C_{49}H_{43}FeO_5P$ calcd.: C, 73.69; H, 5.43%.

Preparation of CpFe(CO)(PPh$_3$)CH$_2$CH$_2$CH(COCH$_3$)CO$_2$-t-Bu (8a)

Ethylene complex **2a** (1.9 mmol) was suspended in THF (50 ml) at − 78°C and 3.2 ml of sodium t-butyl acetoacetate (1.6 mmol) in THF was added dropwise. The mixture was allowed to warm to room temperature (2 h) and the solvent was removed without heating. The residue was dissolved in 10 ml of CH_2Cl_2 and this solution was filtered through a 2 cm × 5 cm plug of alumina, eluted with ether. Solvent removal left a red-orange solid which crystallized when dried at high vacuum; yield 0.62 g (65%), m.p. 53–55°C. ^1H NMR (C_6D_6) δ 0.90 (m, 2), 1.32 and 1.38 (two s, total of 9, diastereomeric t-Bu), 1.88 and 1.92 (two s, total of 3, diastereomeric CH_3), 2.35 (m, 2), 3.35 (t, 1, *J* 6.6 Hz), 4.20 (s, 5, Cp) and 7.0–7.5 (m, 15) ppm. IR (thin film) 1905 (C≡O), 1730 (ester), and 1710 (ketone) cm^{-1}. Anal. Found (mixture of diastereomers): C, 69.05; H, 6.23. $C_{34}H_{37}FeO_4P$ calcd.: C, 68.46; H, 6.25%.

Preparation of CpFe(CO)(PPh$_3$)CH$_2$CH$_2$-c-C$_6$H$_9$O (9a)

Ethylene complex **2a** (1.7 mmol) was suspended in THF (50 ml), cooled to − 78°C, and cyclohexanone pyrrolidine enamine (1.7 mmol) was added dropwise.

The mixture was allowed to warm to room temperature (2.5 h) and the solvent was removed without warming. Water (20 ml) and ether (30 ml) were added with agitation. The separated aqueous phase was extracted with a second portion of ether. The combined ether fractions were concentrated to 15 ml and filtered through a 2 cm × 5 cm plug of acid-washed alumina. Evaporation of solvent afforded 0.67 g (73%) of red-orange crystals, m.p. 123–125°C. ^{1}H NMR (C_6D_6) δ 0.8–2.6 (m, 13), 4.2 and 4.3 (two d, total of 5, *J*(PH) 1 Hz, diastereomeric Cp), 7.0–7.6 (m, 15) ppm. IR (thin film) 1900 ($C\equiv O$) and 1700 ($C=O$) cm^{-1}. Anal. Found (mixture of diastereomers): C, 71.43; H, 6.54. $C_{32}H_{33}FeO_2P$ calcd.: C, 71.65; H, 6.20%.

*Preparation of CpFe(CO)(o-Bp)CH_2CH_2-c-C_6H_9O (**9b**)*

Ethylene complex **2b** (0.29 mmol) was dissolved in THF (5 ml) and cooled to −20°C. Freshly distilled cyclohexanone pyrrolidine enamine (0.35 mmol) was added and the mixture was stirred for 30 min at −20°C and then 30 min at room temperature. Water (5 ml) was added and the mixture was stirred 10 min more, then CH_2Cl_2 (10 ml) was added. The separated organic layer was evaporated leaving a yellow solid, 150 mg (65% yield), m.p. 185–190°C (dec.). ^{1}H NMR ($CDCl_3$) δ 1.1–2.3 (broad m), 4.12 and 4.51 (two s, total of 5, diastereomeric Cp), and 6.6–7.3 (m, 27, aromatic) ppm. IR (thin film) 1963 ($C\equiv O$) and 1730 ($C=O$) cm^{-1}. Satisfactory elemental analysis was obtained without further purification. Analyses: Found: C, 73.69; H, 5.78. $C_{50}H_{45}O_5P_{Fe}$ calcd.: C, 73.89; H, 5.58%.

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