CO Insertion into the Iron–Carbon σ Bond in Optically Active CpFe(CO)(L)R. Preparations and Optical Assay

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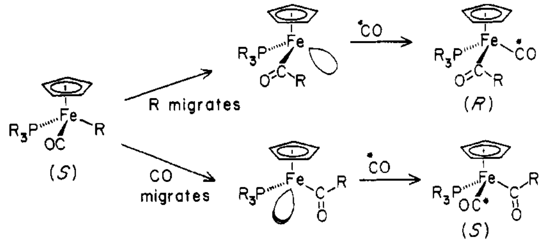
New chiral organoiron complexes of the type CpFe(CO)(mtpb)R [Cp = η^5-C_5H_5, mtpb = $P(OCH_2)_3CCH_3$, and R = CH_2OMen (**6**), CH_2Cl (**7**), Et (**8**), and $S(O)_2Et$ (**10**)] have been prepared in optically pure form. The CO insertion into the iron–ethyl bond in **8** and in $CpFe(CO)(PPh_3)Et$ (**3**) induced by both CO and cyclohexyl isocyanide (chi) has been investigated under a variety of conditions, with stereospecificity which varies widely but reproducibly with conditions. The best stereospecificity has been found in two solvents, the results of which are reported here for preparative utility. In nitroethane under CO pressure **3** and **10** yield $CpFe(CO)(PPh_3)C(O)Et$ (**4**) and CpFe(CO)(mtpb)C(O)Et (**9**), respectively, with >95% *formal* alkyl migration. Under CO pressure **4** forms with 73% net *formal* CO migration in HMPA, while **9** is formed with only 8% *formal* CO migration in Me_2SO (reaction is very slow in HMPA). Insertion induced in **3** by chi yields $CpFe(chi)(PPh_3)C(O)Et$ (**11**) with *formal* alkyl migration in both nitroethane and HMPA. Complex **8** yields CpFe(chi)(mtpb)C(O)Et (**12**) in both nitroethane and Me_2SO with some excess of the same enantiomer in each case, but the configuration, although probably corresponding to formal alkyl migration, cannot be reliably assigned. Insertion has been induced into racemic **8** by using (+)-*endo*-bornyl isocyanide (ebi) to yield $CpFe(ebi)(PPh_3)C(O)Et$ (**13**) as a mixture of optically pure diastereomers that could not be completely separated. Optical assay by NMR/EuL_3 analysis and configurational assignments based on circular dichroism spectroscopy are presented and discussed.

Introduction

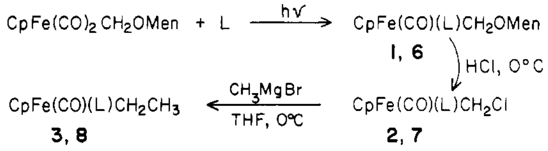
The stereochemistry of the important reaction of insertion of CO into metal–carbon bonds has been a subject of considerable interest.[1,2] It is now well documented that the insertion always proceeds with retention of configuration at the migrating carbon center. Studies of insertions in octahedral systems of Mn,[3] Fe,[4] Ru,[5] Rh,[6] and Ir[7] have shown that the situation at the metal is far more variable. In perhaps the simplest example, $MeMn(CO)_5$ has been shown to undergo insertion with unimolecular alkyl migration, without the detectable intervention of an η^2-acyl, via a relatively rigid square-pyramidal intermediate.[3] In other cases, trans effects can become important, which lead to overall stereochemistry which does not correspond to either simple alkyl or CO migration but instead to some more far reaching reorganization of ligands.[4–7]

Similar to the Mn system above, "pseudotetrahedral" systems of the type CpM(CO)(L)R should have an advantage over more complicated octahedral systems in that trans effects with their complicating cis–trans isomerizations should be absent. Only formal retention, inversion, or racemization is possible (these terms only apply even formally when the incoming ligand is CO) where, as shown in Scheme I, "inversion" corresponds to overall migration of the alkyl group to CO, while "retention" corresponds to overall migration of CO to the alkyl position.

Scheme I



Scheme II



Some related studies of iron complexes have been reported. Photochemical decarbonylation of species such as (η^5-C_5H_3RR')$Fe(CO)(PPh_3)Me$ was reported by Wojcicki to proceed with greater than 85% stereospecificity,[8] and the stereochemistry was shown first by Davison[9] and later by Wojcicki[10] to be formal alkyl migration to CO. No successful attempts to study the thermal insertion had been reported, but it seemed likely to us that some stereospecificity should be observable since species such as $(MeCO)Mn(CO)_4$[3b] and $[CpFe(CO)(PPh_3)]^+$[11] are at least transiently configurationally stable, consistent with theoretical rationale.[12] We therefore set about to examine the stereochemistry of the thermal CO insertion into CpFe(CO)(L)R. This paper describes the preparation of some new chiral organoiron complexes, their resolution and

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[1] Flood, T. C. *Top Stereochem.* **1981**, *12*, 37.

[2] Reviews concerning the CO insertion in general: (a) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87. (b) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299.

[3] (a) Noack, K.; Calderazzo, F. *J. Organomet. Chem.* **1967**, *10*, 101. (b) Flood, T. C.; Jensen, J. E.; Statler, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 4410.

[4] (a) Pankowski, M.; Bigorgne, M. *J. Organomet. Chem.* **1971**, *30*, 227. (b) Pankowski, M.; Samuel, E.; Bigorgne, M. *Ibid.* **1975**, *97*, 105. (c) Pankowski, M.; Bigorgne, M. "Abstracts", The 13th International Conference on Organometallic Chemistry; Kyoto, Japan, 1977; Abstract 5B 02. (d) Jablonski, C. R.; Wang, Y.-P. *Inorg. Chem.* **1982**, *21*, 4037–4044.

[5] Barnard, C. F. J.; Daniels, J. A.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1979**, 1331–1338.

[6] (a) Egglestone, D. L.; Baird, M. C.; Lock, C. J. L.; Turner, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1576–1582. (b) Bennett, M. A.; Jeffery, J. C.; Robertson, G. B. *Inorg. Chem.* **1981**, *20*, 323–330.

[7] (a) Glyde, R. W.; Mawby, R. J. *Inorg. Chim. Acta* **1971**, *5*, 317. (b) Bennett, M. A.; Jeffery, J. C. *Inorg. Chem.* **1980**, *19*, 3763–3767.

[8] (a) Attig, T. G.; Wojcicki, A. *J. Organomet. Chem.* **1974**, *82*, 397. (b) Reich-Rohrwig, P.; Wojcicki, A. *Inorg. Chem.* **1974**, *13*, 2457.

[9] Davison, A.; Martinez, N. *J. Organomet. Chem.* **1974**, *74*, C17.

[10] Attig, T. G.; Teller, R. G.; Wu, S.-M.; Bau, R.; Wojcicki, A. *J. Am. Chem. Soc.* **1979**, *101*, 619.

[11] Miles, S. L.; Miles, D. L.; Bau, R.; Flood, T. C. *J. Am. Chem. Soc.* **1978**, *100*, 7278.

[12] Hofmann, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 536.

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Table I

FeR[a]	ligand[b]	prod	time, h	temp, °C	prod % yield	prod % ee	starting material % ee	material balance
			Reactions in Nitroethane					
(*S*)-3a	CO	(*R*)-4b	18	amb	82	95	90	92
(*S*)-8a	CO	(*R*)-9b	118	amb	29	>95	>95	90
(*S*)-3a	chi	(*S*)-11b	24	amb	71	41	87	78
(*S*)-8a	chi	(*S*)-12b	190	39	47	20	64	89
rac-8	ebi	13	70[c]	60	67			
			Reactions in HMPA (3) and Me_2SO (8)					
(*S*)-3a	CO	(*S*)-4a	86	amb	5	73	71	86
(*S*)-8a	CO[d]	(*S*)-9a	135	39	2	8	20	45
(*S*)-3a	chi	(*S*)-11b	32	amb	35	20	87	70
(*S*)-8a	chi	(*S*)-12b	219	39	27	16	18	91

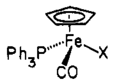
[a] Reactions run at 50 psi of CO or ca. 1 M isocyanide; FeR at (1-8) × 10^{-3} M. [b] chi = cyclohexyl isocyanide and ebi = *endo*-bornyl isocyanide. [c] Nitromethane solvent. [d] CO pressure was 1180 psi.

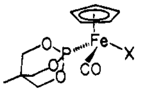
optical assay, and the insertion of CO induced by CO and by isocyanides into these and some previously reported iron alkyls. The stereochemical picture that emerges is one of significant complexity, where the insertion can proceed with a high degree of formal alkyl migration or CO migration depending on the solvent and the incoming ligand. Thus, generally in geometrically more complex systems, not only will trans effects determine the stereochemistry of the insertion but also the work reported here illustrates that solvation effects and the influence that incoming nucleophiles have on them will also have importance.

Brunner and co-workers[13] have recently found that BF_3 catalyzes the insertion of CO into the Fe–C bond of $CpFe(CO)(PPh_3)Me$ and several $CpFe(CO)(PPh_2NRR')$-Me below 0 °C in toluene with high stereospecificity and formal alkyl migration. These results are consistent with our acid catalysis and solvent dependence studies.[14]

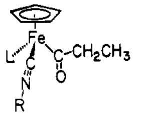
Results and Discussion

Preparation of Starting Materials.[15] The triphenylphosphine-substituted series of compounds 1–3 and 5 and the phosphite-substituted series 6–8 were prepared as shown in Scheme II, in essentially the manner reported previously for the PPh_3 series.[16] The use of $P(OCH_2)_3C$-CH_3 (mtpb) in place of PPh_3 imparts greater stability and resistance to oxidation, somewhat greater ease of crystallization, and generally reduced rates of various reactions of the compounds. The yield of 6 formed in the photolysis is, however, significantly lower compared to that of 1 due to the formation of unidentified side products. However 6 was very easily resolved in two crystallizations. The alkyls 3 and 8 were submitted to insertion of SO_2 to afford alkanesulfinates 5 and 10. These were used for optical assay as described below and previously.[16]





	X	
(*S*)-1a	$-CH_2OMenthyl$	(*S*)-6a
(*R*)-2a	$-CH_2Cl$	(*R*)-7a
(*S*)-3a	$-CH_2CH_3$	(*S*)-8a
(*S*)-4a	$-C(O)CH_2CH_3$	(*S*)-9a
(*S*)-5a	$-S(O)_2CH_2CH_3$	(*S*)-10a



	L	R
(*R*)-11a	PPh_3	*cyclo*-C_6H_{11}
(*R*)-12a	mtpb	*cyclo*-C_6H_{11}
13	mtpb	*endo*-bornyl

CO Insertions. The insertion of CO into 3 and 8 has been carried out in a variety of solvents using both CO and isocyanides as insertion-inducing ligands. *The stereochemical results are reproducible but highly variable, depending on several factors.*[14] The greatest stereospecificity was found by using CO as the incoming ligand and nitroethane or HMPA as solvent; under these conditions enantiomeric excesses (% ee) are above 90% and 70%, respectively, but the two solvents give *opposite stereochemistry.* Using isocyanides as incoming ligands results in far lower ee's. In this paper we report the best stereochemical results as examples and as general means of preparing optically active iron acyls.

Insertions induced by CO were carried out under from 1 to 100 atm of CO on 3 and 8. At 1 atm of CO, extensive racemization of both starting material and product was observed. At 4 atm of CO or above, good stereospecificity was obtained (see Table I). Insertion into 8 in nitroethane required more than seven times as long as it did for 3, consistent with the generally much reduced reactivity of the phosphite-substituted series of compounds. In both cases the reaction resulted in formal migration of the alkyl group to CO. Insertion in 3 was very much slower in HMPA, and reaction of 8 was so slow in HMPA that Me_2SO had to be used to obtain reasonable rates. Both products 4 and 9 from reaction in HMPA or Me_2SO were of the configuration resulting from CO migration to the alkyl site, but optical purity was reduced to ca. 70% for the former and to only 8% for the latter.

Insertion of CO in 3 in the presence of 1 M cyclohexyl isocyanide (chi) in nitroethane to produce 11 proceeded at qualitatively the same rate as did the insertion in the presence of CO in this solvent. Insertion into 8 to form 12 was much slower than for 3. In the isocyanide induced insertions, however, the stereospecificity was not nearly as high as for the CO-induced reactions (see Table I). The lower optical purity of 11 and 12 was not due to racemization after their formation, since no racemization of 11

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[13] Brunner, H.; Hammer, B.; Bernal, I.; Draux, M. *Organometallics*, following paper in this issue.

[14] Flood, T. C.; Campbell, K. D., submitted for publication.

[15] The conventions for configurational designations used in this paper are those of: Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6598. Since a minor change in structure can lead to a reversal of *R–S* designation without a change in configuration, in order to reduce confusion this paper has taken the convention of designating all species of the configuration corresponding to (*S*)-1 as the "a" series and the species enantiomeric to this at iron as the "b" series.

[16] Flood, T. C.; Disanti, F. J.; Miles, D. L. *Inorg. Chem.* **1976**, *15*, 1910.

Table II. Maximal NMR Chemical Shifts (δ) with Eu(hfc)$_3$ in C$_6$D$_6$

	FeS(O)$_2$Et	FeC(O)Et	Fe(CN-c-C$_6$H$_{11}$)C(O)Et
PPh$_3$	5a 8.8	4a 8.7	11a 8.6
	5b 8.5	4b 9.3	11b 8.7
mtpb	10a 6.4	9a 6.7	12a 5.5
	10b 9.7	9b 9.8	12b 8.4

(expected to be the more labile of the two) was detected upon its resubmission to reaction conditions, and rechromatography led to only ca. 5% racemization. As anticipated, when the isocyanide-induced insertions were carried out on **3** in HMPA and on **8** in Me$_2$SO the rates were retarded over the same reactions in nitroethane, and the stereospecificity was similarly not high. The particularly surprising feature of the isocyanide reactions in comparison to the CO reactions is that **3** in either nitroethane or HMPA yielded **11** with overall alkyl migration. The configuration of **12** could not be reliably assigned from its CD spectrum.

We wished to resolve a diastereomeric analogue of **12** in order to establish its absolute configuration by X-ray crystallography. Racemic **8** was therefore treated with excess (+)-*endo*-bornyl isocqcyanide in MeNO$_2$ at 60 °C as indicated in Table I. A nearly 1:1 diastereomer ratio of **13** was generated that could not be separated by crystallization or HPLC. It is possible that because of the greater steric bulk of bornyl isocyanide the product was far less configurationally stable.

NMR Spectra and Optical Assay. The NMR spectra and optical assay of complexes **1**–**3** and **5** have been reported previously.[16] Spectra are reported for new complexes in the Experimental Section. Optical assay of **6** was readily achieved because the FeCH$_2$ group exhibits diastereotopic ^{1}H resonances that are different for the two diastereomers. In (*R*)-**6** there are resonances at δ 4.47 (d of d, $J_{\mathrm{PH}} = 6.5$, $J_{\mathrm{HH}} = 3.8$ Hz) and 5.51 (d of d, $J_{\mathrm{PH}} = 4.5$ Hz), while in (*S*)-**6** the two multiplets for the FeCH$_2$ group overlap at 4.9 ppm. Optical assay was not attempted on **7**, but its minimum purity was apparent from the purity of iron alkyls subsequently prepared from it.

In the case of the enantiomeric iron alkyls, optical assay was conducted on the SO$_2$-inserted derivatives by the use of optically active europium shift reagents, as described previously.[16] For acyls **4** and **9**, the optical purity could be determined directly since the acyl oxygen is itself a good ligand for shift reagents. In all cases, changes in chemical shift, as well as diastereomeric chemical shift differences, maximized after the addition of 0.6–1 molar equiv of shift reagent. Approximate optimum chemical shifts are listed in Table II.

Notice from Table II that complexes bearing the phosphite ligand mtpb exhibit very large diastereomeric chemical shift differences in the presence of shift reagents. For example, Figure 1 shows the spectra of **9a** and **9b** wherein the two Cp resonances are separated by 3.1 ppm. The CH$_2$O resonances of the phosphite are similarly different by 3 ppm and are further divided into two diastereotopic peaks with a separation of ca. 0.4 ppm. We believe that this large enhancement of peak separation arises from the ability of the phosphite oxygen and the oxygen of the sulfinate or acyl group to chelate to the shift reagent.

Most of the compounds listed in Table I exhibit an apparently precedented but unusual property in that addition of small amounts of shift reagent results in extensive broadening of the resonances of the iron substrate. Upon addition of ca. 1 molar equiv of reagent, the peaks sharpen again at the maximally shifted positions. Even when special care was taken to ensure that reagents and solvents were totally dry, the effect was reproducible. The origin of the effect in PPh$_3$-substituted molecules, where it is much less pronounced, is not clear to us. Perhaps in this case, in spite of rigorous efforts, small amounts of water were present that lead to broadening and that effect was overcome upon addition of larger amounts of shift reagent. In the case of phosphite-substituted complexes, the major part of this effect, which is quite large, may arise from exchange phenomena having their origin in the chelation mentioned above. Similar effects have been reported for certain methoxyl-containing flavones where chelation is also possible.[17]

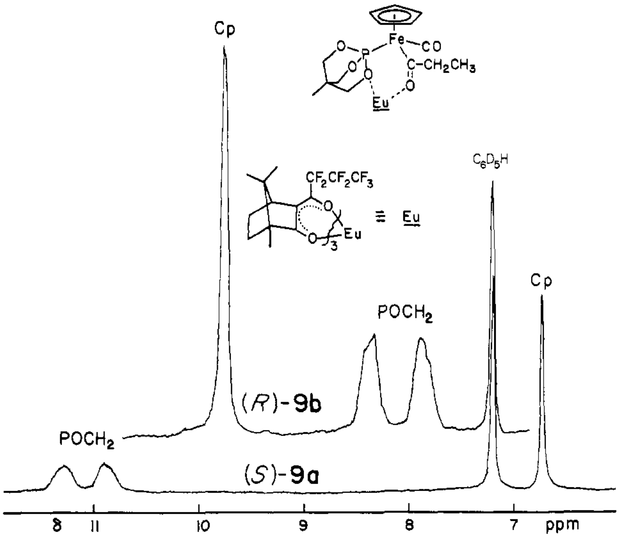

Figure 1. ^{1}H NMR spectra at 100 MHz of CpFe(CO)(mtpb)C(O)Et, **9a** and **9b**, in C$_6$D$_6$ in the presence of Eu(hfc)$_3$.

Absolute Configurations. The configurations of **1**–**3** are known from an X-ray structure determination of **1**[18] and that of **5** from a structure determination of a close analogue.[11] The configuration of **4** has been established beyond reasonable question by the work of Davison,[9] in conjunction with our own crystallographic work.[18]

It has been found that while assignment of transitions in the CD spectra of these compounds is not possible, nevertheless, empirical configurational assignments can be made based on the morphology of the CD curves, provided that both the compounds and their CD curves are very similar.[18] Since no large electronic effect is anticipated upon the substitution of the carbonyl oxygen in **4** by (cyclohexyl nitrogen) of the isocyanide in **11**, one anticipates that the CD spectra should be comparable. Indeed, Figure 2 shows that the CD spectra of **11** and **4** are similar in the diagnostic region of the bands at ca. 300 and 350–400 nm,[18] but, more convincing, the spectra of starting material **3** and **11** are essentially superimposable (or mirror images in this case). We believe there is little doubt of the configuration of **11** based on these data. It is to be noted that at least one strong transition that presumably appears near 375 nm in the CD spectrum of **4** has been significantly red-shifted to 430 nm in the spectrum of **11**.

The CD spectra of **5** and **10** are rather similar, and this and the presence of a maximum in the diagnostic region of 350–400 nm in the phosphite complexes[19] led us to believe we could assign the absolute configuration of the

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(17) Okigawa, M.; Kawano, N. *Chem. Ind.* (*London*) **1973**, 850.

(18) Chou, C.-K.; Miles, D. L.; Bau, R.; Flood, T. C. *J. Am. Chem. Soc.* **1978**, *100*, 7271.

(19) Flood, T. C.; Statler, J. A.; Campbell, K. C., submitted for publication.

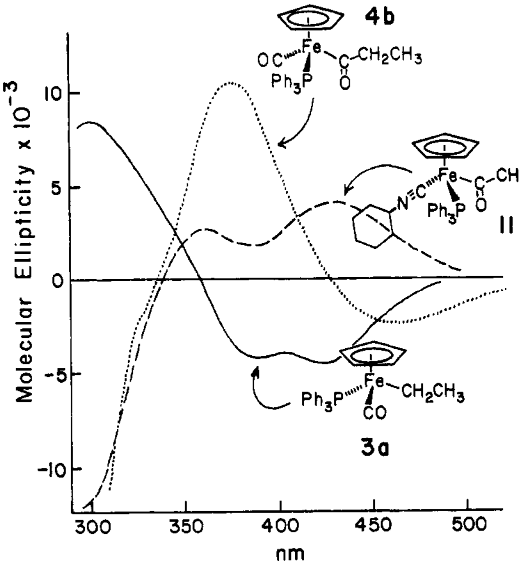

Figure 2. CD spectra of starting alkyl complex **3a** and of acyl products **4b** and **11b** resulting from insertion in EtNO$_2$ in the presence of CO and cyclohexyl isocyanide, respectively.

phosphite-substituted series. Nevertheless, substitution of PPh$_3$ by mtpb does lead to significant changes in the CD spectra. Therefore, to corroborate these CD-based empirical configurational assignments, the absolute configuration of **6** was determined directly by X-ray crystallography,[19] thus establishing the configurations of **7**, **8**, and almost certainly[11] **10** as well.

Figure 3 shows the CD spectra of **8a** and of products **9** and **12** resulting from insertion in EtNO$_2$ in the presence of CO and cyclohexyl isocyanide, respectively. The spectrum of **9** is similar to that of **4b** and is extremely similar to the CD spectra of a series of acetyl complexes CpFe(CO){PPh$_2$[N(R)CHMePh]}C(O)Me prepared by Brunner and Vogt.[20] The configuration of one of the latter has been established by X-ray crystallography.[21] The CD curve in Figure 3 therefore corresponds to the *R* configuration for **9** (i.e., **9b**).

Configurational assignment of **12** presents a problem. It is clear from Figure 3 that there is no simple morphological correspondence between the spectrum of **12** and that of any of the other phosphite-substituted complexes. Recall that there is a band in the spectrum of **11** at 430 nm that is red shifted with respect to what may be the corresponding transition in **4** (see above). It may be that the transition of **12** at 420 nm is the red-shifted band of **9** at 370 nm. If this is so, then the CD spectrum in Figure 3 would correspond to this isomer of **12** having the *S* configuration, i.e., **12b**. Nevertheless, this leaves the strong negative maximum at 360 nm unexplained. Also suggestive is the fact that if this configurational assignment were correct for **12**, then the relative magnitude of the pseudocontact shift for the two enantiomeric series of mtpb substituted molecules, as revealed in Table II, would also be internally consistent. And finally, it would be chemically reasonable for the isocyanide-induced insertion to give the same stereochemical result with both **3** and **8** under the same conditions. It seems likely, therefore, that the CD spectrum shown in Figure 3 does correspond to the (*S*)-**12b**. We emphasize, however, that this assignment is *highly* tentative. Our attempts to establish it via a crystal structure of **13** have been thwarted by our inability to resolve **13**.

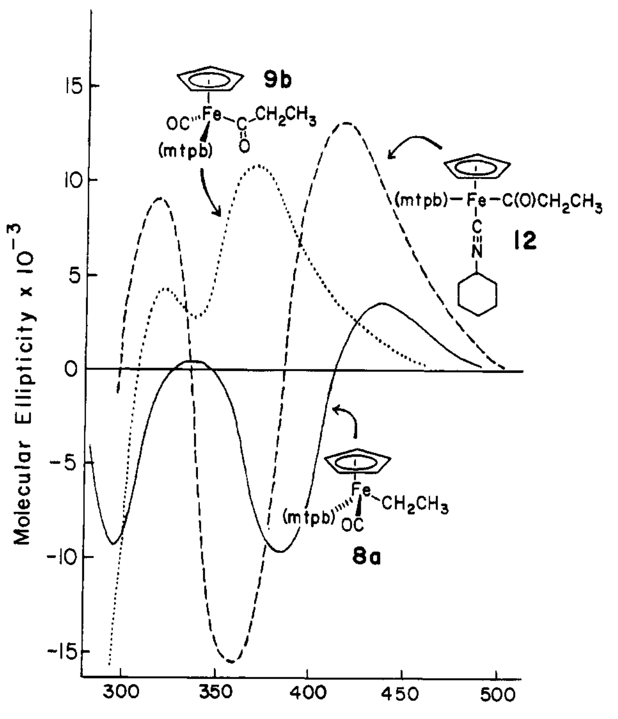

Figure 3. CD spectra of starting alkyl complex **8a** and of acyl products **9b** and **12** resulting from insertion in EtNO$_2$ in the presence of CO and cyclohexyl isocyanide, respectively.

Conclusions

The insertion of CO into the Fe–C bond of **3** and **8** in the presence of CO is a highly stereospecific reaction proceeding with *formal* ethyl migration when carried out under mild and convenient conditions in nitroethane. This reaction should be of significant general synthetic utility for the preparation of enantiomeric acyliron complexes of this type. Products enriched in the *opposite* enantiomer are produced when the reaction is carried out in HMPA. Insertion induced by cyclohexyl isocyanide is much less stereospecific but produces products enriched in the enantiomer corresponding to *formal* alkyl migration, regardless of the solvent. These enigmatic stereochemical results naturally invite interpretation, but we have been unable to construct a unique and compelling rationalization. On the basis of further work with these systems—kinetics of the chi-induced insertion, additional solvent dependence data, acid catalysis, etc.—we currently believe that the most internally consistent explanation involves the presence of two intermediates in rapid equilibrium: a coordinately unsaturated acyl species and an η^2-acyl-coordinated species. These mechanistic studies and interpretations are the subject of another publication.[14]

Experimental Section

General Comments. NMR spectra were recorded on a Varian XL-100 FT spectrometer; chemical shifts are reported in parts per million downfield from tetramethylsilane for both ^{1}H and ^{13}C spectra; all coupling constants are reported in hertz. For shift reagent experiments, 5–15-mg samples in 0.3 mL of degassed C$_6$D$_6$ were carefully treated with small aliquots of a 0.1-g/mL C$_6$D$_6$ solution of shift reagent, generally Eu(hfc)$_3$, tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]europium(III), until maximum resolution was achieved; typically ca. 0.6–1.0 molar equiv was required. Infrared spectra were recorded on a Perkin-elmer 337 spectrometer. Optical rotations were measured on a Perkin-Elmer 241 polarimeter; all rotations reported were taken at ambient temperature. UV–vis spectra were recorded on a Beckman ACTA MVI spectrometer and are reported over the

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(20) Brunner, H.; Vogt, H. *J. Organomet. Chem.*, **1980**, *191*, 181–192.
(21) Korp, J. D.; Bernal, I. *J. Organomet. Chem.* **1981**, *220*, 355–364.

range of ca. 300–600 nm. Circular dichroism spectra were recorded on a Varian Carey 61 CD spectrometer. Preparative photolyses, unless otherwise noted, were performed by using a Hanovia 450-W medium-pressure mercury arc lamp in a quartz immersion apparatus, with a Pyrex filter sleeve. Reactions above 1 atm pressure were carried out in a 1-L Parr Instruments Co. autoclave with fittings to allow venting, sample removal, and repressuring without admission of air; a 125-mL Erlynmeyer flask served as a reaction vessel inside the bomb. Reactions in the bomb were stirred magnetically. Microanalyses were obtained from the CalTech microanalytical laboratories.

All reactions involving organometallic compounds were carried out under an atmosphere of nitrogen purified over reduced copper catalyst and in flamed-out glassware. All reactions and samples, including those for NMR, CD, and optical rotations, were always kept totally in the dark. Chromatography columns were wrapped in aluminum foil. THF, benzene, and toluene were distilled from purple solutions of disodium benzophenone dianion. Nitroethane was distilled from P_4O_{10}, treated with anhydrous sodium carbonate, and passed through a column of active alumina. CpFe(CO)(PPh_3)X (X = CH_2OMen, CH_2Cl, Et, S(O)$_2$Et),[16] CpFe(CO)$_2CH_2OMen$,[16] and mtpb[22] were all prepared by literature methods. The CO was CP grade specified to contain less than 600 ppm of O_2. Alumina for column chromatography was Brockmann grade IV (deactivated with 10% H_2O).

Preparation of CpFe(CO)(mtpb)CH_2OMen (6a and 6b). CpFe(CO)$_2CH_2OMen$ (28 g, 81 mmol) and mtpb (14.5 g, 98 mmol) were dissolved in 200 mL of hexane and 100 mL of toluene. After irradiation for 1.5 h in the Hanovia apparatus, the solution was reduced in volume, the resulting yellow oil was taken up in a minimum of CH_2Cl_2, and this was filtered through a column of alumina by using 25% ether/hexane. This solution was reduced to ca. 200 mL in volume and was stored overnight at −20 °C. Collection of the crystals gave 4.5 g (12% yield) of partially resolved diastereomer $(+)_{436}$-**6a**. Recrystallization of 3 g of this material from ether/hexane yielded 1.6 g of optically pure **6a**: mp 187–187.5 °C dec; $[\alpha]_{436}$ +98° (*c* 0.02, toluene); UV–vis (toluene) λ_{max} 288 nm (ϵ 2.1 × 10^3); NMR (C_6D_6) δ −0.33 (s, 3), 0.7–1.7 (m, 16), 2.4–2.8 (m, 2), 3.20 (dt, 1, J_d = 4, J_t = 10 Hz, −OCH−), 3.49 (d, 6, J_{PH} = 4.5 Hz), 4.47 (dd, 1, J_{HH} = 3.8, J_{PH} = 6.5 Hz, FeCHaO), 4.69 (s, 5), 5.51 (dd, 1, J_{HH} = 3.8, J_{PH} = 4.5 Hz, $FeCH_bO$); IR (film) 1955 cm^{-1}.

After several additional days at −20 °C, the mother liquor deposited 2.1 g of pure **6b**: mp 115–116.5 °C; $[\alpha]_{436}$ −530° (*c* 0.02, toluene); NMR (C_6D_6) δ −0.28 (s, 3), 0.7–1.7 (m, 16), 2.4–2.8 (m, 2), 3.07 (dt, 1, J_d = 3, J_t = 9 Hz, −OCH−), 3.53 (d, 6, J_{PH} = 4.7 Hz), 4.67 (d, 5, J_{PH} = 0.7 Hz), 4.8–5.0 (m, 2, −OCH_2−); Ir (film) 1940 cm^{-1}. Anal. Calcd for $C_{22}H_{35}FeO_5P$: C, 56.66; H, 7.56. Found: C, 56.51; H, 7.31.

Preparation of CpFe(CO)(mtpb)CH_2Cl (7a or 7b). The same procedure is used to prepare either enantiomer. Pure diastereomer **6a** or **6b** (1.5 g, 3.2 mmol) was dissolved in 50 mL of anhydrous ether, and this solution was cooled to −15 °C. Anhydrous HCl was passed through the solution for 2 min, after which the solvent volume was reduced to 15 mL by rotary evaporation. The resulting yellow solid was collected and washed several times with ice-cold ether, yielding 0.97 g (86%): mp >100 °C dec; $[\alpha]_{436}$ −640° (*c* 0.02, toluene); UV–vis (toluene) λ_{max} 285 nm (ϵ 1.7 × 10^5); NMR (C_6D_6) δ −0.34 (s, 3), 3.41 (d, 6, J_{PH} = 5 Hz), 4.53 (s, 5), 4.5–4.8 (m, 2); IR (film) 1940 cm^{-1}. Anal. Calcd for $C_{12}H_{16}ClFeO_4P$: C, 41.59; H, 4.65. Found: C, 41.05; H, 4.45.

Preparation of CpFe(CO)(mtpb)Et (8a or 8b). Either enantiomer of 7 (0.85 g) was dissolved in 50 mL of THF, and the solution was cooled to 0 °C. Then 3 mmol of methyl Grignard reagent in THF was added, and the solution was stirred an additional 15 min. The solvent was removed at reduced pressure, and the residue was taken up in ether and chromatographed on deactivated alumina by using 1/1 ether–hexane. The yellow product typically amounted to ca. 0.70 g (87%): mp 145 °C dec; $[\alpha]_{436}$ −1300° for one enantiomer and +1250° for the other (*c* 0.01, toluene); UV–vis (toluene) λ_{max} 295 (ϵ 3.1 × 10^2), 360 nm (ϵ 720); NMR (C_6D_6) δ −0.19 (s, 3), 1.6–1.9 (m, 5), 3.56 (d, 6, J_{PH} = 4.6 Hz), 4.48 (s, 5); IR (film) 1925 cm^{-1}. Anal. Calcd for $C_{13}H_{19}FeO_4P$: C, 47.88; H, 5.87. Found: C, 48.24; H, 5.90.

Preparation of CpFe(CO)(mtpb)S(O)$_2$Et (10a or 10b). Anhydrous SO_2 was bubbled into a solution of **8a** or **8b** (ca. 28 mg, 0.086 mmol) in 10 mL of CH_2Cl_2 at −15 °C for 2 min. After an additional 15 min at −15 °C, the solvent was removed at reduced pressure and the residue taken up in CH_2Cl_2 and chromatographed on deactivated alumina. After impurity elution with CH_2Cl_2, product was eluted with CH_3CN and typically amounted to 20 mg (60%). This was shown to be optically pure by the use of an optically active shift reagent and NMR (see Results). Recrystallization (CH_2Cl_2–hexane) then yielded a material with a melting point 169–170 °C dec; $[\alpha]_{436}$ (from **8b**) −1900° (*c* 0.01, toluene); UV–vis (CH_2Cl_2) λ_{max} 305 (ϵ 5.9 × 10^3); NMR (C_6D_6) δ −0.8 (s, 3), 1.44 (t, 3, J_{HH} = 7.0 Hz) 3.14 (q, 2, J_{HH} = 7.0 Hz), 3.68 (d, 6, J_{PH} = 5.0 Hz), 4.54 (d, 5, J_{PH} = 0.7 Hz) IR (film) 1980 (CO), 1160 and 1040 (SO_2), 1005 (PO) cm^{-1}. Anal. Calcd for $C_{13}H_{19}FeO_6PS$: C, 40.02; H, 4.91. Found: C, 40.04; H, 5.32.

General CO Insertion Procedure. The Parr high-pressure apparatus was assembled, including the internal Erlynmeyer flask, and this was evacuated and refilled with a CO atmosphere. a solution of iron alkyl (typically 50–100 mg, ca. 0.16–0.32 mmol, in 25 mL of nitroethane) was injected via a septum-sealed valve into the Erlynmeyer flask, and the pressure was increased to 50 psi of CO. Progress of the reaction was followed by venting excess CO pressure, removing samples via the valve, and repressuring the system. For workup, reaction mixtures were removed by forced syphon (cannula) from the reactor and the solvent was removed at reduced pressure. The residue was chromatographed on alumina, resulting in isolation of unreacted starting material and product. Recovered starting material was converted to its sulfinate insertion product as described above, and its optical purity was determined by the shift reagent NMR experiment. The optical purity of the product was determined directly by using shift reagent NMR. Reaction conditions, yields, and optical yields are given in Table I.

CpFe(CO)(PPh_3)COEt (4b). Recovered starting material and product were eluted in chromatography using 25% ether–hexane $[\alpha]_{436}$ 1800 (*c* 0.03, toluene); NMR (C_6D_6) δ 0.86 (t, 3, J_{HH} = 7 Hz), 2.91 (q, 2, J_{HH} = 7 Hz), 4.24 (d, 5, J_{PH} = 1 Hz), 7.0–7.8 (m, 15); IR (film) 1910, 1610 cm^{-1} (physical constants and spectra agreed well with the literature[24]).

CpFe(CO)(mtpb)COEt (9). Starting material was eluted with 50% ether–hexane and product with CH_2Cl_2: mp 114–115 °C dec; $[\alpha]_{436}$ 470° (*c* 0.01, toluene); UV–vis (toluene) λ_{max} 330 nm (ϵ 3.2 × 10^3); NMR (C_6D_6) δ −0.33 (s, 3), 1.22 (t, 3, J_{HH} = 7 Hz), 3.18 (q, 2, J_{HH} = 7 Hz), 3.48 (d, 6, J_{PH} = 5 Hz), 4.50 (d, 5, J_{PH} = 1 Hz); IR (film) 1930, 1620 cm^{-1}. Anal. Calcd for $C_{14}H_{19}FeO_5P$: C, 47.48; H, 5.41. Found: C, 47.67; H, 5.31.

Preparation of CpFe(PPh_3)(chi)COEt (11). A solution of 54 mg (0.12 mmol) of **3a** and 2.75 mL of cyclohexyl isocyanide (25 mmol) in 22.25 mL of nitroethane was left for 24 h after which the solvent was removed and the residue was chromatographed on alumina by using 25% ether–hexane. The first band was starting material (4 mg, 7%), and the second was product amounting to 48 mg (71%): mp 113–114 °C; $[\alpha]_{546}$ +120° (*c* 0.04, toluene) for material of 41% ee; NMR (C_6D_6) δ 0.9–1.5 (m, 13), 2.9–3.3 (m, 3), 4.34 (d, 5, J_{PH} = 1 Hz), 7.0–7.9 (m, 15); IR (film) 2040 (CN), 1585 (C=O) cm^{-1}. Anal. Calcd for $C_{33}H_{36}FeNOP$: C, 72.13; H, 6.60; N, 2.55. Found: C, 72.07; H, 6.89; N, 2.62. Optical yields were determined as in other cases and are reported in Table I.

Preparation of CpFe(mtpb)(chi)COEt (12). A solution of 24 mg (0.07 mmol) of **8b** and 1.4 mL of cyclohexyl isocyanide (11.2 mmol) in 11 mL of nitroethane was heated for 190 h at 39 °C. The solvent was removed and the residue chromatographed on alumina. Starting material was eluted by using 25% ether–hexane (10 mg, 42%) and product by using CH_3CN to yield 15 mg (47%) of yellow crystals: mp 87–87.5 °C; UV–vis (toluene) λ_{max} 300 nm (ϵ 4.1 × 10^3); NMR (C_6D_6) δ −0.22 (s, 3), 1.0–1.6 (m, 13), 3.0–3.6 (m, 3), 3.62 (d, 6, J_{PH} = 4.5 Hz), 4.64 (d, 5, J_{PH} = 1.0 Hz); IR (film) 2080 (CN), 1590 (C=O) cm^{-1}. Anal. Calcd for $C_{20}H_{30}FeNO_4P$:

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C, 55.19; H, 6.95; N, 3.22. Found: C, 55.26; H, 6.49; N, 3.11.

Preparation of (+)-*endo*-Bornyl Isocyanide (ebi). The formamide {4.0 g, 22 mmol, mp 81–83 °C, $[\alpha]_D$ −40° (*c* 0.5, MeOH)} of (+)-*endo*-bornylamine {as the hydrochloride, mp >250 °C, $[\alpha]_D$ +19° (*c* 0.4, EtOH)[23]} was treated with 6.0 g of tosyl chloride in 50 mL of pyridine at 25 °C for 3 h. This was poured onto ice, and the solid that formed was washed several times with water. Sublimation at 85 °C (0.07 mm) yielded 88% of white solid: mp 126–127.5 °C, $[\alpha]_D$ +41° (*c* 0.4, MeOH); NMR ($CDCl_3$) δ 0.815, 0.896, 0.915 (3 × Me), 0.8–2.4 (m, 7), 3.5–3.7 (br d, 1); IR (pyridine) 2140 cm^{-1}. Anal. Calcd for $C_{11}H_{17}N$: C, 80.92; H, 10.50; N, 8.58. Found: C, 80.69; H, 10.70; N, 8.76.

Preparation of CpFe(mtpb)(ebi)COEt (13). A solution of 400 mg (1.23 mmol) of racemic **8** and 1.1 g of (+)-*endo*-bornyl isocyanide in 7 mL of nitromethane was heated at 60 °C for 70 h. Solvent was removed, and the residue was chromatographed on alumina; starting material was eluted with ether–hexane (1:1) and product using acetonitrile (400 mg, 67%). Repeated crystallizations from a variety of solvent systems afforded only slight enrichment of either diastereomer: mp 149–151 °C (sealed tube, ca. 1/1 diastereomer ratio); (C_6D_6) NMR δ −0.14 (s, 3), 0.61 (s, 3, 7-Me), 0.78 (s, 3, 7-Me), 0.99 (d, 3, diastereomeric 1-Me, $\Delta\delta$ = 0.013 ppm), 1.42 (t, 3, J_{HH} = 7.2 Hz), 1.1–2.5 (m, 8), 3.21 (dq, 2, J_{HH} = 7.2 Hz, $\Delta\delta$ = 0.03 ppm), 3.66 (d, 6, J_{PH} = 4.5 Hz), 4.68 (d, 5, J_{PH} = 0.9 Hz); IR (KBr) 2080 (CN), 1575 (C=O) cm^{-1}. Anal. Calcd for $C_{24}H_{36}FeNO_4P$: C, 58.90; H, 7.42; N, 2.89. Found: C, 59.11; H, 7.57; N, 2.79.

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Registry No. (*S*)-**3a**, 53318-85-7; (*S*)-**4a**, 53403-10-4; (*R*)-**4b**, 87069-62-3; (*S*)-**5a**, 59367-41-8; (*R*)-**5b**, 87098-83-7; (*S*)-**6a**, 87040-84-4; (*R*)-**6b**, 87069-67-8; (*S*)-**7a**, 87069-68-9; (*R*)-**7a**, 87040-85-5; (*S*)-**8a**, 87040-83-3; (*R*)-**8b**, 87069-69-0; *rac*-**8**, 87069-65-6; (*S*)-**9a**, 87069-63-4; (*R*)-**9b**, 87040-79-7; (*S*)-**10a**, 87050-19-9; (*R*)-**10b**, 87098-84-8; (*R*)-**11a**, 87069-64-5; (*S*)-**11b**, 87040-80-0; (*R*)-**12a**, 87040-81-1; (*S*)-**12b**, 87069-66-7; **13**, 87040-82-2; ebi, 87040-86-6.

Optically Active Transition-Metal Complexes. 85. The BF_3-Promoted Carbonylation of $CpFe(CO)(L)CH_3$ Compounds—A Reaction Stereospecific at Low Temperatures[1]

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The carbonylation of optically active $CpFe(CO)(CH_3)L$, L = $P(C_6H_5)_2N(CH_3)$-(*S*)-$CH(CH_3)(C_6H_5)$, in toluene solution at room temperature leads to $CpFe(CO)(COCH_3)L$ in low yield, almost completely epimerized at the Fe atom. Addition of boron trifluoride increases both yield and stereoselectivity of the reaction. Below −20 °C the BF_3-promoted carbonylation of optically active $CpFe(CO)(CH_3)L$, L = $P(C_6H_5)_2N(CH_3)$-(*S*)-$CH(CH_3)(C_6H_5)$, $P(C_6H_5)_2N(CH_2C_6H_5)$-(*S*)-$CH(CH_3)(C_6H_5)$, and $P(C_6H_5)_3$, proceeds stereospecifically. Correlations with known absolute configurations demonstrate the following overall stereochemistry: the acetyl group ends up where the carbonyl ligand was bonded and the incoming carbonyl ligand occupies the position of the former methyl group.

Introduction

The carbon monoxide insertion into metal–carbon σ bonds is a reaction of both scientific and technical importance.[2-5] The system most extensively studied is the carbonylation of $CH_3Mn(CO)_5$ that has been demonstrated by calculation[6] and proven by labeling experiments[7] to undergo methyl migration from the Mn atom to a carbonyl group in a cis position. In a recent series of papers, Shriver showed that Lewis acids promote alkyl group migration in $RMn(CO)_5$ and $CpFe(CO)_2R$.[8-13] It has been established that the carbonylation and decarbonylation reactions occur with retention of configuration at the migrating carbon center.[14] The photochemical decarbonylation of compounds of the type $CpFe(CO)(PR_3)COCH_3$ was found to be highly stereoselective with respect to the Fe atom,[14-16]

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