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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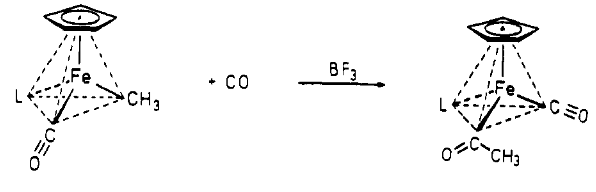
Scheme I



L	*(SS)/(S)*	*(RS)/(R)*
$P(C_6H_5)_2N(CH_3)$-(*S*)-$CH(CH_3)(C_6H_5)$	1*RS* $(-)_{436}$	2*SS* $(-)_{436}$
$P(C_6H_5)_2N(CH_3)$-(*S*)-$CH(CH_3)(C_6H_5)$	1*SS* $(+)_{436}$	2*RS* $(+)_{436}$
$P(C_6H_5)_2F$	-	3*S* $(-)_{436}$
$P(C_6H_5)_2F$	-	3*R* $(+)_{436}$
$P(C_6H_5)_2N(CH_2Ph)$-(*S*)-$CH(CH_3)(C_6H_5)$	4*RS* $(-)_{436}$	5*SS* $(-)_{436}$
$P(C_6H_5)_2N(CH_2Ph)$-(*S*)-$CH(CH_3)(C_6H_5)$	4*SS* $(+)_{436}$	5*RS* $(+)_{436}$
$P(C_6H_5)_3$	6*S* $(+)_{578}$	7*R* $(-)_{546}$

proceeding by alkyl migration.[17] The carbonylation of CpFe(CO)(L)Et, L = $P(C_6H_5)_3$ and $P(OCH_2)_3CCH_3$, showed a continuum of stereochemical behavior from >90% inversion to 75% retention at the Fe atom depending critically on the solvent.[18] We now report a study of the BF_3-promoted carbonylation of optically active compounds $CpFe(CO)(CH_3)L$ in toluene solution (Scheme I), which is a stereospecific reaction at low temperatures. The overall stereochemistry corresponds to a methyl to carbonyl migration in divergence to the conclusion drawn in a preliminary communication.[26]

Starting materials and products, involved in the present study, are characterized by a number and the italic symbol of the Fe configuration (followed by the symbol for the asymmetric carbon atom in compounds 1, 2, 4, and 5). The absolute configurations shown in the formulas of Scheme I refer to the starting materials with *S*,*S* configuration (1*SS*, 4*SS*) and *S* configuration (6*S*) and the corresponding carbonylation products with *R*,*S* configuration (2*RS*, 5*RS*) and *R* configuration (7*R*). Starting materials 1*RS* and 4*RS* and products 2*SS* and 5*SS* have opposite configurations at the Fe atoms.

Experimental Section

Materials. The preparation of 1*RS*/1*SS*,[19] 2*RS*/2*SS*,[20] 4*RS*/4*SS*,[19] 5*RS*/5*SS*,[20] 6*R*/*S*,[21] and 7*R*/*S*[17,22] was reported. The enantiomeric excess of 6 and 7 was determined by measurement of the optical rotation; the enantiomeric excess of 3 and 7 was checked NMR spectroscopically by addition of the optically active shift reagent $Eu(TBC)_3$.[23] The diastereoisomeric purity of 1, 2, 4, and 5 was determined by NMR analysis, based on the different chemical shifts of the Cp doublets of the two diastereomers, which did not overlap. The peak intensities were determined by averaging the results of five planimetries of the expanded signals. The values obtained were about 2% higher than the computer integral printouts and about 1% lower than the plotted integrals.

Scheme I correlates the absolute configurations, assigned as discussed in The Overall Stereochemistry, with those optical rotations that were used to characterize the compounds in the resolution procedures cited above.

Boron trifluoride (Merck-Schuchardt) was used as received. All the solvents were distilled under nitrogen from potassium, $LiAlH_4$, sodium benzophenone ketyl, or molecular sieves prior to use. Solid compounds and solutions were handled in N_2 atmosphere by the Schlenk technique.

Spectra. Proton NMR spectra were recorded in benzene-d_6 solution on a Bruker WH 90-MHz or WM 250-MHz instrument; chemical shifts are reported in parts per million downfield from tetramethylsilane. Infrared spectra were taken on a Beckman 4240 spectrometer. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. Circular dichroism spectra were run on a Jasco J-40A spectropolarimeter connected with a data processor J-DPY using *n*-hexane for all spectra at concentrations of ca. 1 mg/mL. Mass spectra were recorded on an Atlas CH5 or a Varian MAT 311A instrument.

High-Pressure Carbonylations in the Presence of BF_3. Boron trifluoride was transferred from a lecture bottle into a vacuum line equipped with a −80 °C trap to remove impurities of low volatility, a mercury manometer, a calibrated tube with a volume of 12.5 mL between two stopcocks, and a 17-mL ampule ready for sealing. The whole system was evacuated, and boron trifluoride was allowed to flow into the calibrated tube until the pressure reached the value necessary for a certain molar quantity on the basis of a *pVT* calculation. Then, the boron trifluoride in the calibrated tube was condensed into the ampule which was sealed under vacuum. With this technique, ampules containing 0.05–0.50 mmol of BF_3 could be obtained.

A 100-mL rotating autoclave consisting of CrNiMo steel with a maximum pressure capacity of 1000 bar was used for the carbonylations, the wall of which was covered with Teflon. The solution of the compound to be carbonylated was placed into the autoclave. The BF_3 ampule was added so that the fragile seal was below the surface of the liquid. The autoclave was closed and repeatedly flushed with 3–5 bar of CO, which removed traces of air and moisture without breaking the ampule. When the CO pressure was increased, the ampule burst, sometimes only at the seal and sometimes as a whole. In all cases BF_3 was released only in the presence of a large excess of CO.

For low-temperature carbonylations the autoclave was cooled after air and moisture were removed by flushing with CO. Two hours later, when the autoclave had reached the temperature of the cryostat, the reaction was started breaking the BF_3 ampule by increasing the CO pressure.

Reaction of $(-)_{436}$-$CpFe(CO)(CH_3)P(C_6H_5)_2N(CH_3)$-(*S*)-$CH(CH_3)(C_6H_5)$ (1*RS*) with CO. A red solution of 120 mg (0.24 mmol) of a diastereomer mixture of 1*RS*/1*SS* (91:9) in 5 mL of toluene was treated in an autoclave with 400 bar of CO at 30 °C for 20 h. The still red solution was concentrated and chromatographed on a silica column (15 × 2 cm). Elution with toluene afforded 104 mg (88%) of the unreacted starting materials

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(23) $Eu(TBC)_3$: Tris[3-(1-hydroxy-2,2-dimethylpropylidene)-*d*-camphorato]europium(III)

Table I. Carbonylation of **1**, **4**, and **6** in Toluene Solution with 400 bar of CO in the Absence and in the Presence of Boron Trifluoride

run	compd	opt purity (*RS*/*SS* or *R*/*S*)	reactn conditns	chemical yield, % starting mat.	chemical yield, % products		recovered start. mat. (*RS*/*SS*)	product (*SS*/*RS* or *S*/*R*)	% stereoselectivity of product formation
1	1*RS*/1*SS*	91:9	no BF_3, 30 °C, 24 h	88	7 (2)	...	88:12	52:48	4
2	1*RS*/1*SS*	91:9	no BF_3, room temp, 24 h	87	2 (2)	...	89:11		
3	1*RS*/1*SS*	91:9	no BF_3, −30 °C, 16 h	77	0	...			
4	4*RS*/4*SS*	50:50	no BF_3, room temp, 18 h	83	2 (5)	...			
5	4*RS*/4*SS*	50:50	no BF_3, −30 °C, 16 h	88	0	...			
6	6*R*/6*S*	50:50	no BF_3, 30 °C, 16 h	78	5 (7)	...			
7	6*R*/6*S*	50:50	no BF_3, room temp, 16 h	77	5 (7)	...			
8	6*R*/6*S*	50:50	no BF_3, −30 °C, 16 h	72	0	...			
9	1*RS*/1*SS*	91:9	30% BF_3, room temp, 24 h		23 (2)	7 (3)		78:22	68
10	1*RS*/1*SS*	91:9	100% BF_3, 4 h[a]		27 (2)[b]	12 (3)		71:29	51
11	1*RS*/1*SS*	91:9	100% BF_3, room temp, 24 h		51 (2)	9 (3)		77:23	66
12	1*RS*/1*SS*	91:9	120% BF_3, 15 h[a]		63 (2)	6 (3)		78:22	68
13	1*RS*/1*SS*	15:85	150% BF_3, 15 h[a]		46 (2)	6 (3)		27:73	66
14	4*RS*/4*SS*	5:95	120% BF_3, room temp, 17 h		35 (5)	5 (3)		25:75	55
15	6*R*/6*S*	5:95	120% BF_3, 16 h[a]		48 (7)	-		12:88[c]	84
16	1*RS*/1*SS*	91:9	120% BF_3, −40 °C, 17 h		30 (2)	18 (3)		97:3	105
17	1*RS*/1*SS*	91:9	120% BF_3, −40 °C, 20 h		37 (2)	9 (3)		88:12	93
18	1*RS*/1*SS*	91:9	120% BF_3, −40 °C, 15 h		41 (2)	4 (3)		91:9	100
19	1*RS*/1*SS*	91:9	120% BF_3, −20 °C, 15 h		34 (2)	6 (3)		89:11	95
20	1*RS*/1*SS*	91:9	120% BF_3, −30 °C, 16 h		46 (2)	14 (3)		87:13	90
21	1*RS*/1*SS*	91:9	220% BF_3, −40 °C, 15 h		40 (2)	16 (3)		84:16	83
22	1*RS*/1*SS*	15:85	120% BF_3, −30 °C, 15 h		31 (2)	8 (3)		12:88	108
23	1*RS*/1*SS*	15:85	120% BF_3, −30 °C, 16 h		49 (2)	5 (3)		14:86	103
24	4*RS*/4*SS*	95:5	120% BF_3, −30 °C, 15 h		35 (5)	10 (3)		87:13	82
25	4*RS*/4*SS*	5:95	120% BF_3, −40 °C, 14 h		37 (5)	6 (3)		2:98	107
26	6*R*/6*S*	50:50	120% BF_3, −30 °C, 16 h		65 (7)	...			
27	6*R*/6*S*	5:95	120% BF_3, −30 °C, 15 h		44 (7)	...		5:95	100
28	6*R*/6*S*	5:95	120% BF_3, −40 °C, 15 h		56 (7)	...		4:96	102

[a] The BF_3 ampule burst while being flushed with CO at room temperature. Autoclave was cooled to −30 °C within 2 h. Then the carbonylation with 400 bar of CO was carried out at −30 °C. [b] A 52% yield of starting material was recovered with a diastereomer ratio of 1*RS*/1*SS* = 88:12. [c] Determined by integration of the Cp signals in the ^1H NMR spectrum on addition of 80 mol % of optically active shift reagent $Eu(TBC)_3$.[23]

1*RS*/1*SS* (88:12). The product $CpFe(CO)(COCH_3)P(C_6H_5)_2N(CH_3)$-(*S*)-$CH(CH_3)(C_6H_5)$ (9 mg (7%); **2***SS*/**2***RS* 58:42) was eluted with diethyl ether.

The results of other carbonylations in the absence of BF_3 at different temperatures and with the starting materials **4** and **6** are given in Table I (upper part).

BF_3-Promoted Carbonylation of $CpFe(CO)(CH_3)L$ (1, 4, and 6). A red solution of 0.1 or 0.2 mmol of **1**, **4**, and **6**, respectively, in 5 mL of toluene and an ampule with a 0.3–1.2 M amount of BF_3 were put into an autoclave, which was flushed with CO as described above. When the CO pressure was increased to 400 bar, the ampule burst. After 16 h at room temperature the concentrated yellow solution was chromatographed. Elution with toluene showed that there was no starting material left. Elution with diehtyl ether in the case of **6** yielded only $CpFe(CO)(COCH_3)P(C_6H_5)_3$, **7**. In the cases of **1** and **4** a mixture of the compounds $CpFe(CO)(COCH_3)P(C_6H_5)_2R$ (R = $N(CH_3)$-(*S*)-$CH(CH_3)(C_6H_5)$, **2**; R = $N(CH_2C_6H_5)$-(*S*)-$CH(CH_3)(C_6H_5)$, **4**) and $CpFe(CO)(COCH_3)P(C_6H_5)_2F$, **3**, respectively, was isolated. This mixture could be separated by chromatography on prepacked Merck-Lobar columns, size B, filled with LiChroprep Si60 (40–63 μm).[24,25] With the solvent petroleum ether/toluene/diethyl ether (5:1:1) two separate yellow bands were formed, the first band containing compound **2** or **5** and the second smaller band containing compound **3**.

The yield of **3** (Table I) was determined from the proton NMR integral of the Cp doublet of **3** relative to the integrals of the Cp doublets of **2** and **5**, respectively.

$CpFe(CO)(COCH_3)P(C_6H_5)_2F$, **3**: yellow solid; mp 67 °C; ^1H NMR (benzene-d_6) δ 2.42 (3 H, d), 4.31 (5 H, d), 6.91–7.99 (10

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H, m), J(P–Cp) = 1.2 Hz, J(P–COCH$_3$) = 0.7 Hz; IR (KBr) 1936 (vs, CO), 1924 (vs, CO), 1608 (vs, COCH$_3$), (petroleum ether) 1950 (CO), 1614 cm^{-1} (COCH$_3$); MS (70 eV), *m/e* (relative intensity) 396 (M$^+$, 6), 381 (M$^+$ − CH$_3$, 8), 368 (M$^+$ − CO, 13), 340 (M$^+$ − 2CO, 38), 325 (M$^+$ − CO − COCH$_3$, 71), 260 (FeP(C$_6$H$_5$)$_2$F$^+$, 13), 183 (PC$_{12}$H$_8$$^+$, 100). Anal. Calcd for $C_{20}H_{18}FFeO_2P$: C, 60.63; H, 4.58; mol wt, 396.18. Found: C, 60.45; H, 4.61.

In very low yield there was another byproduct, [CpFe(CO)$_2$P(C$_6$H$_5$)$_2$N(CH$_3$)-(*S*)-CH(CH$_3$)(C$_6$H$_5$)]BF$_4$, insoluble in toluene, soluble in chloroform, and acetone: brown-yellow solid; mp 162 °C; IR (acetone) 2048 (CO), 2004 cm^{-1} (CO); MS (field desorption from acetone), *m/e* 496 (M$^+$ cation).

The reaction conditions, yields, and stereochemical results of the carbonylations in the presence of BF$_3$ are summarized in Table I (lower part).

The yields given in Table I are isolated yields. To some extent the values were determined by the necessity to work with quantities of 60–80 mg, where the loss of some material during workup reduced the yield considerably. The total yields of runs 1–8, in which there were no byproducts, range between 95% and 72%. The yields of the BF$_3$-promoted reactions (runs 9–28) must therefore be corrected correspondingly. Besides starting material, carbonylation product, compound 3 (where indicated), and traces of the salt [CpFe(CO)$_2$P(C$_6$H$_5$)$_2$N(CH$_3$)-(*S*)-CH(CH$_3$)(C$_6$H$_5$)]BF$_4$, no other products could be detected.

Reaction of (+)$_{436}$-CpFe(CO)(COCH$_3$)[P(C$_6$H$_5$)$_2$N(CH$_3$)-(*S*)-CH(CH$_3$)(C$_6$H$_5$)] (2*RS*) with (C$_2$H$_5$)$_3$O$^+$BF$_4^-$. A solution of 250 mg (1.32 mmol) of (C$_2$H$_5$)$_3$O$^+$BF$_4^-$ in 1.5 mL of CH$_2$Cl$_2$ was added to the solution of 233 mg (0.46 mmol) of 2*RS* in 10 mL of CH$_2$Cl$_2$ at 0 °C. The resulting yellow solution was concentrated, and the excess of (C$_2$H$_5$)$_3$O$^+$BF$_4^-$ was separated by repeated precipitation with ether at −18 °C: yield 121 mg (42%) of *RS*-(−)$_{436}$-{Cp(CO)[P(C$_6$H$_5$)$_2$NCH$_3$-(*S*)-CH(CH$_3$)(C$_6$H$_5$)]FeC(OC$_2$H$_5$)CH$_3$}$^+$BF$_4^-$; yellow solid; mp 39 °C; soluble in polar solvents; MS (field desorption from acetone), *m/e* 540 (M$^+$, cation); IR (CH$_2$Cl$_2$) 1988 cm^{-1} (CO); specific rotations (*c* 0.08, CH$_2$Cl$_2$) $[\alpha]^{20}_{578}$ −90°, $[\alpha]^{20}_{546}$ −135°, $[\alpha]^{20}_{436}$ −550°.

Reduction of (*RS*)-(−)$_{436}$-{Cp(CO)[P(C$_6$H$_5$)$_2$NCH$_3$-(*S*)-CH(CH$_3$)(C$_6$H$_5$)]FeC(OC$_2$H$_5$)CH$_3$}$^+$BF$_4^-$ with NaBH$_4$. Reaction of 93 mg (0.148 mmol) of (*RS*)-(−)$_{436}$-{Cp(CO)[P(C$_6$H$_5$)$_2$NCH$_3$-(*S*)-CH(CH$_3$)(C$_6$H$_5$)]FeC(OC$_2$H$_5$)CH$_3$}$^+$BF$_4^-$ in 6 mL of EtOH with a solution of 9.1 mg (0.239 mmol) of NaBH$_4$ in 4 mL of EtOH, followed by a chromatography of the crude red oil (SiO$_2$/toluene) afforded 53 mg (68%) of (*RS*)-(+)$_{436}$-CpFe(CO)(C$_2$H$_5$)[P(C$_6$H$_5$)$_2$NCH$_3$-(*S*)-CH(CH$_3$)(C$_6$H$_5$)]: red oil; soluble in all common organic solvents; MS (field desorption from toluene), *m/e* 497 (M$^+$); IR (petroleum ether) 1915 cm^{-1} (CO); specific rotations (*c* 0.09, toluene) $[\alpha]^{20}_{578}$ +250°, $[\alpha]^{20}_{546}$ +435°, $[\alpha]^{20}_{436}$ −1125°.

By BF$_3$-promoted carbonylation CpFe(CO)(C$_2$H$_5$)[P(C$_6$H$_5$)$_2$NCH$_3$-(*S*)-CH(CH$_3$)(C$_6$H$_5$)] could be converted into CpFe(CO)(COC$_2$H$_5$)[P(C$_6$H$_5$)$_2$NCH$_3$-(*S*)-CH(CH$_3$)(C$_6$H$_5$)], the spectral and analytical data of which proved to be identical with CpFe(CO)(COC$_2$H$_5$)[P(C$_6$H$_5$)$_2$NCH$_3$-(*S*)-CH(CH$_3$)(C$_6$H$_5$)] prepared according to ref 20.

Results

All the carbonylations of compounds 1, 4, and 6 have been carried out in toluene solution by using 400 bar of CO. The reaction variables were temperature, time, and especially presence or absence of boron trifluoride. The results are summarized in Table I.

In the absence of BF$_3$ the carbonylation of 1 at room temperature and at 30 °C after 24 h gave only 2% and 7% of the carbonylation product 2 (runs 1 and 2); 87% and 88% of 1 could be recovered. Starting with a diastereomer enrichment of 1*RS*/1*SS* (91:9), it could be shown for the 30 °C reaction (run 1) that the unreacted starting material was slightly epimerized (1*RS*/1*SS* = 88:12), whereas the product was almost completely epimerized (2*SS*/2*RS* = 52:48). A reaction time of 5 days did not increase the yield of 2 substantially. Reaction temperatures of 70 and 100 °C afforded complicated mixtures of compounds like CpFe(CO)$_2$CH$_3$, CpFe(CO)$_2$COCH$_3$, and [CpFe(CO)$_2$]$_2$ together with decomposition products, no starting material being left. At a reaction temperature of −30 °C there was no carbonylation at all. Only unreacted starting material was recovered (run 3), a relevant point for the discussion of the BF$_3$-promoted carbonylation, which proved to be fast at −30 °C. Similarly, the carbonylation of 4 and 6 at room temperature in the absence of BF$_3$ yielded 2% and 5% of the acetyl compounds 5 and 7, while at −30 °C there was no reaction at all (runs 4–8).

Addition of boron trifluoride in the carbonylation of 1, 4, and 6 increased both the chemical yield and the stereoselectivity of product formation. In the first experiments, some BF$_3$ from a lecture bottle was admitted directly into the autoclave containing the solution of the compound to be carbonylated, and the autoclave was closed and pressurized with 400 bar of CO as quickly as possible. This technique did not allow the use of definite quantities of BF$_3$, partial hydrolysis could not be avoided during the assembly of the autoclave, and the CO came into contact with the solution only after about 10 min. Low and varying yields and stereoselectivities were the consequence.

Therefore, we developed the following technique: definite amounts of BF$_3$ were condensed into an ampule. The ampule together with the solution of the compound to be carbonylated were placed into an autoclave under N$_2$. The assembled autoclave was vented several times with CO to remove the nitrogen and traces of air and moisture. Increasing the CO pressure made the ampule burst, allowing an interaction of substrate and BF$_3$ only in the presence of a large excess of CO.

With this technique the following results were obtained: for compound 1 (1*RS*/1*SS* = 91:9) stoichiometric amounts of BF$_3$ gave a 51% yield, whereas 30 mol % of BF$_3$ gave only a 23% yield; the two reactions gave identical stereoselective 2*SS*/2*RS* (77:23) (runs 9, 11). Similar results were obtained with compound 4 (run 14). A large excess of BF$_3$ reduced the yield of carbonylation products slightly (runs 13 and 21), a small excess of BF$_3$ giving the best results. Therefore, in all subsequent experiments BF$_3$ quantities of 120 mol % were used.

Control experiments verified that the diastereomer or enantiomer enrichments used did not change during workup, in agreement with the known configurational stability of the Fe chirality in the compounds 1, 2, 4, 5, 6, and 7.[19–22,26] However, it was not known whether starting materials and carbonylation products were also configurationally stable in the presence of BF$_3$. It had been shown that a reaction with electrophiles leads to racemization and epimerization at the Fe center in compounds of the type CpFe(CO)LX[27] and that Lewis acids in such compounds add to the metal atom.[28] For BF$_3$ we could demonstrate that the carbonylation product 2*SS* did not epimerize at room temperature in the presence of BF$_3$. However, after compound 1 (1*RS*/1*SS* = 95:5) in toluene was treated with boron trifluoride for 2 days, 82% of the starting material was recovered with a diastereomer ratio of 65:35. Compound 6*S* behaved similarly. Reaction with 0.8 equiv of BF$_3$ at room temperature for 5 min reduced the enantiomer ratio from 95:5 to 88:12.

These results demonstrate the configurational lability of the starting material 1 (and probably also 4 and 6) in the presence of BF$_3$. However, we found that racemization or epimerization at the Fe atom prior to the carbonylation can be avoided by carbonylation at temperatures between

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[26] Brunner, H.; Vogt, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 405.

[27] Brunner, H. *Adv. Organomet. Chem.* **1980**, *18*, 183.

[28] Ginzburg, A. G.; Aleksandrov, G. G.; Struchkov, Yu. T.; Setkina, V. N.; Kursanov, D. N. *J. Organomet. Chem.* **1980**, *199*, 229.

-20 and -50 °C. For these experiments the autoclave had to be cooled to these temperatures before the BF_3 ampule was cracked by the CO pressure.

At reaction temperatures of -30 and -40 °C the BF_3-promoted carbonylation of **1***RS* and **1***SS* turned out to be stereospecific, the average value of runs 16–23 being 99 ± 9%. The reason for the high limits of error is the fact that the diastereomeric purity of both starting material and reaction product had to be determined by ^1H NMR spectroscopy. Compound **6** (**6***R*/**6***S* = 5:95) at -30 and -40 °C could be carbonylated stereospecifically (runs 27, 28). For compound **4**, a reaction temperature of -30 °C obviously was not low enough to prevent epimerization completely (run 24), whereas at -40 °C no epimerization was found. In some experiments the BF_3 ampules burst during venting the autoclave at room temperature (runs 10, 12, 13, 15). In these cases the autoclave was cooled to -30 °C within 2 h, before a pressure of 400 bar of CO was applied. The stereochemical results of these experiments were intermediate between the room-temperature and the low-temperature runs. We did not succeed in extending the BF_3-promoted carbonylation to $CpFe(CO)(CH_2Ph)PPh_2N(CH_3)$-(*S*)-$CH(CH_3)(C_6H_5)$.[19] Only unreacted starting material and no carbonylation product at all could be isolated in the reaction with 400 bar of CO and 120% boron trifluoride at -30 °C.

In all the experiments 16–28 we burst the BF_3 ampule with 400 bar of CO pressure, so that BF_3 was released in the presence of a large excess of CO. In control experiments with **1***RS* and **1***SS* we flushed the loaded autoclave at -30 °C with nitrogen and burst the ampule by increasing the nitrogen pressure to 100 bar. After 10 min at -30 °C, CO (300 bar) was added. The stereoselectivity of these reactions was 68% and 86%, respectively, indicating that in 10 min at -30 °C, BF_3 had started to epimerize **1***RS* and **1***SS* before conversion into the configurationally stable carbonylation products. A similar experiment with **1***RS* carried out at -50 °C gave stereospecific product formation. Obviously, at -50 °C the epimerization of **1***RS* by BF_3 is a slow reaction and the BF_3-promoted carbonylation still is a fast reaction. Therefore, necessary conditions for a stereospecific BF_3-promoted carbonylation of **1***RS* are either reaction temperatures of -30 °C in the presence of a large excess of CO or reaction temperatures of -50 °C, where the CO can be added afterwards.

As shown in column 7 of Table I in the BF_3-promoted carbonylations there is about 10% $CpFe(CO)(COCH_3)P(C_6H_5)_2F$, **3**, formed by BF_3 cleavage of the P–N bond in **2** and **5**, even at low temperatures (runs 9–25). In one experiment the enantiomeric excess of byproduct **3** was determined by addition of $Eu(TBC)_3$[23] to a sample of **3** separated from **2** by chromatography. Starting with **1***RS*/**1***SS* (91:9, 100% BF_3, room temp, 24 h), the yield of **2** was 51% with the average room-temperature stereoselectivity of 66% (**2***SS*/**2***RS* = 77:23), whereas the yield of **3** was 30% with a higher selectivity of **3***S*/**3***R* (82:18). In a control experiment 120 mg of optically pure **2***RS* in toluene was treated with 110% BF_3 in a sealed ampule at room temperature for 5 days. Chromatographic workup gave 24 mg of **2***RS* (20%) and 42 mg of **3** (45%), the latter showing an enantiomer ratio of **3***R*/**3***S* = 97:3 (limits of error ca. 5%). These results show that only little epimerization at the Fe atom takes place during P–N cleavage. Similarly, the P–N bond in $CpFe(CO)(I)P(C_6H_5)_2NHCH(CH_3)(C_6H_5)$ was cleaved by HF with high stereoselectivity.[29]

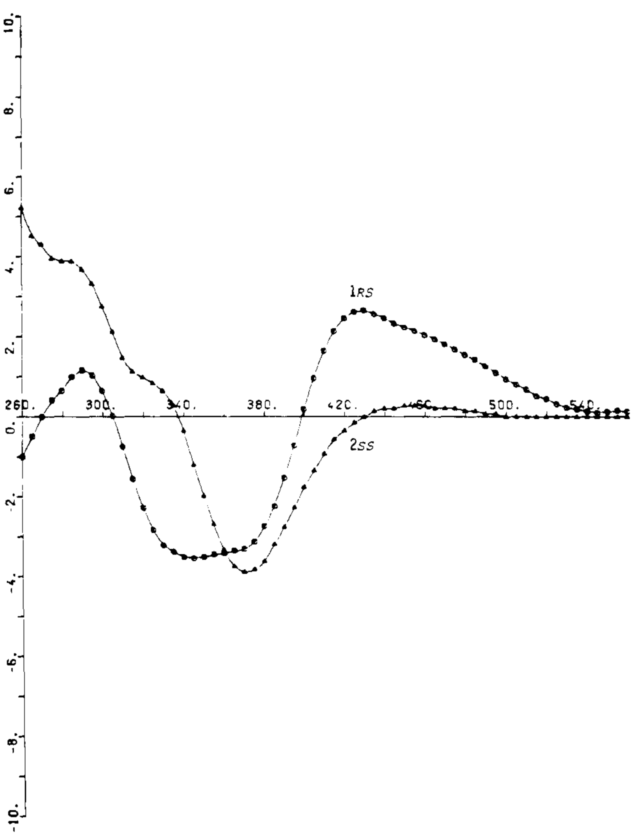

Figure 1. CD spectra of **1***RS* and **2***SS* (run 20, Table I) (2×10^{-3} M in *n*-hexane; ordinate scale $10^{-3}[\theta]_\lambda$).

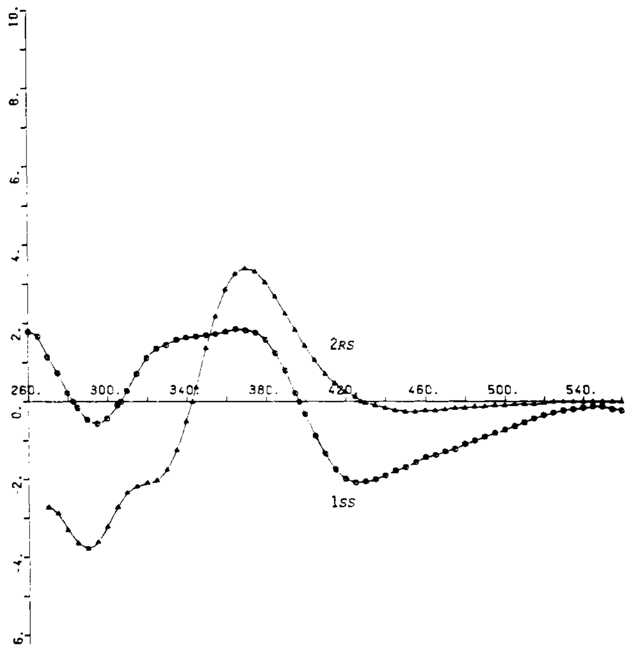

Figure 2. CD spectra of **1***SS* and **2***RS* (run 23, Table I) (2×10^{-3} M in *n*-hexane; ordinate scale $10^{-3}[\theta]_\lambda$).

The Overall Stereochemistry. For the five systems **1***RS* → **2***SS*, **1***SS* → **2***RS*, **4***RS* → **5***SS*, **4***SS* → **5***RS*, and **6***S* → **7***R* the CD spectra of the starting materials and the corresponding products of the BF_3-promoted carbonylation

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[29] Brunner, H.; Muschiol, M.; Dove, M. F. A. *J. Chem. Soc., Dalton Trans.* **1982**, 1527.

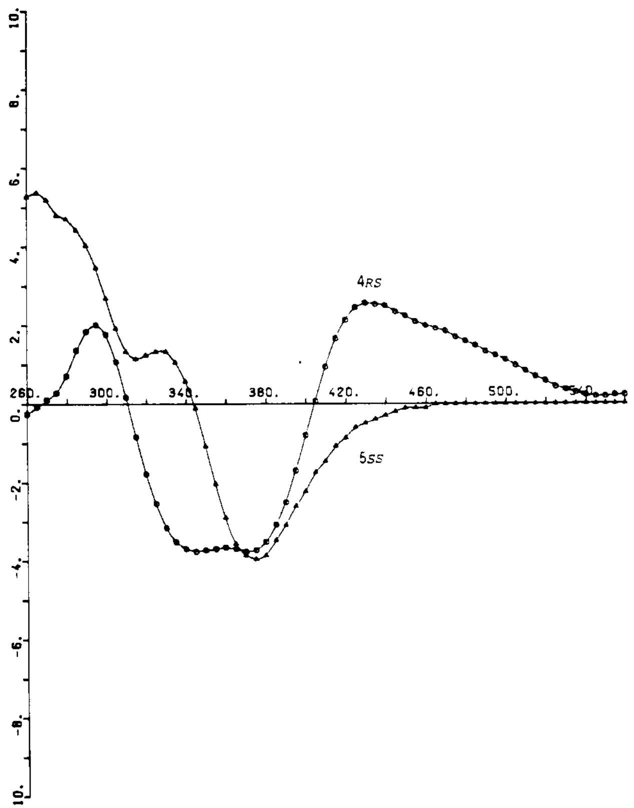
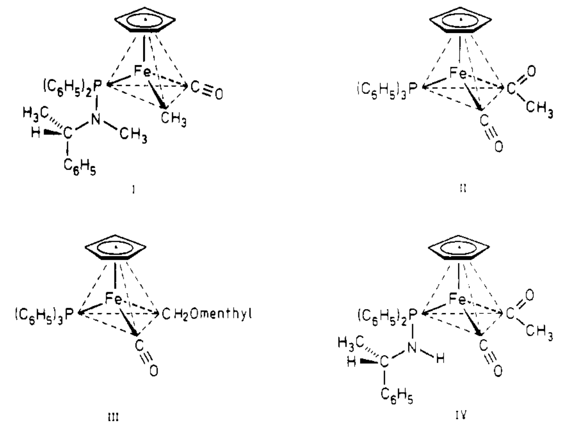


Figure 3. CD spectra of 4*RS* and 5*SS* (run 24, Table I) (2×10^{-3} M in *n*-hexane; ordinate scale $10^{-3}[\theta]_\lambda$).

Scheme II



are depicted in figures 1–5. The absolute configuration of compound 7*S* (II in Scheme II) has been determined by X-ray crystallography,[30] and the corresponding results for compound 1*RS* (I in Scheme II), a key compound for the present study, are presented in Tables II–IV. For compounds 6*S*, 2*SS*, and 5*SS* correlations are possible with the known absolute configurations of $(+)_{578}$-CpFe(CO)[P(C_6H_5)$_3$]$CH_2OC_{10}H_{19}$[31] and $(-)_{436}$-CpFe(CO)[P(C_6H_5)$_2$NH-(*S*)-CH(CH_3)(C_6H_5)]$COCH_3$[32] (III and IV in Scheme II). The absolute configuration of $(+)_{578}$-CpFe(CO)[P(C_6H_5)$_3$]CH_3, 6*S* (CD spectrum in Figure 5), is derived from its precursor $(+)_{578}$-CpFe(CO)[P(C_6H_5)$_3$]$CH_2OC_{10}H_{19}$ (III in Scheme II) to be *S* at the Fe atom. In ref 20 the CD spectra of a series of compounds $(-)_{436}$-CpFe(CO)[P(C_6H_5)$_2$N(R)-(*S*)-CH(CH_3)(C_6H_5)]$COCH_3$ were shown, including that for R = H, the absolute configuration of which is known (IV in Scheme II), and those for R = CH_3, the present 2*SS*, and R = $CH_2C_6H_5$, the present 5*SS*. All these CD spectra are extremely similar,

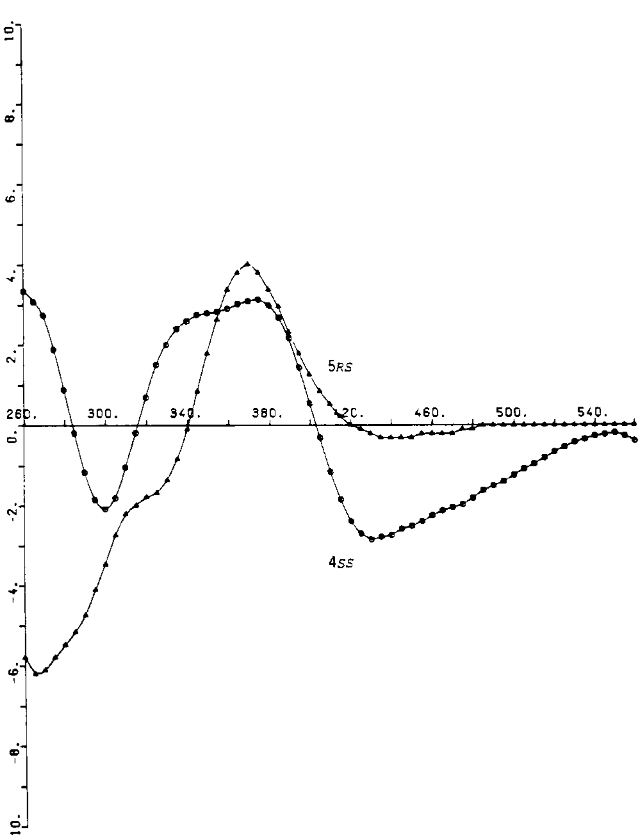


Figure 4. CD spectra of 4*SS* and 5*RS* (run 25, Table I) (2×10^{-3} M in *n*-hexane; ordinate scale $10^{-3}[\theta]_\lambda$).

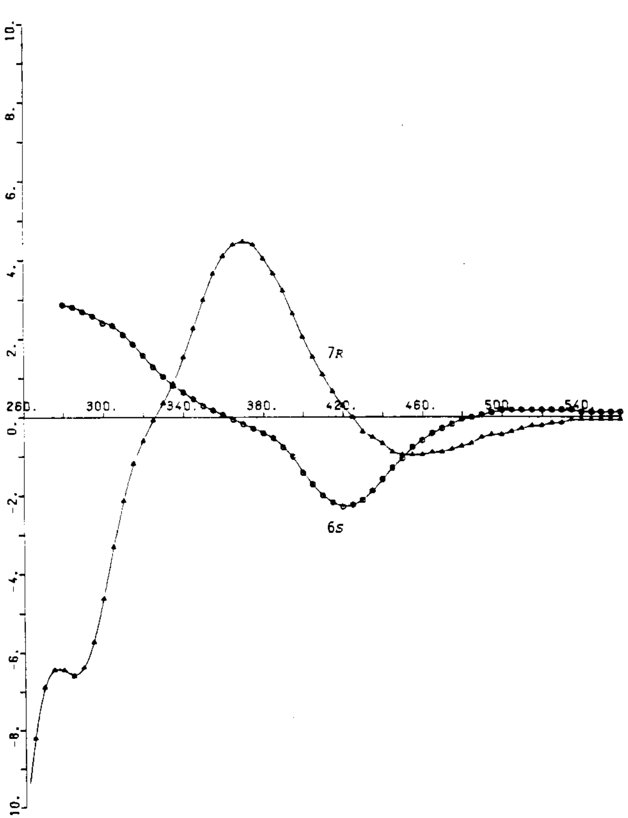


Figure 5. CD spectra of 6*S* and 7*R* (run 28, Table I) (3×10^{-3} M in *n*-hexane; ordinate scale $10^{-3}[\theta]_\lambda$).

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[30] Bernal, I.; Brunner, H.; Muschiol, M., publication in preparation.

[31] Chou, C.-K.; Miles, D. L.; Bau, R.; Flood, T. C. *J. Am. Chem. Soc.* **1978**, *100*, 7271.

[32] Korp, J. D.; Bernal, I. *J. Organomet. Chem.* **1981**, *220*, 355.

Table II. Summary of Data Collections and Processing Parameters for 1*RS*

space group	$P2_12_12_1$
cell const	$a = 12.394\ (9)$ Å $b = 13.875\ (3)$ $c = 13.959\ (4)$
cell volume	$V = 2400.35$ Å^3
mol formula	$C_{28}H_{30}NOPFe$
mol wt	483.38 g·mol^{-1}
d(calcd)	1.34 g·cm^{-3}
abs coeff	$\mu = 6.61$ cm^{-1}
data collect range	$4° \leqslant 2\theta \leqslant 50°$
scan width	$\Delta 2\theta = 2(1.0 + 0.35 \tan\theta)$
max scan time	240 s
scan speed range	0.38–3.35 deg·min^{-1}
total data collected	2585
data with $I > 3\sigma(I)$	1359
total variables	138
$R = \Sigma \lVert F_o\rvert - \lvert F_c\rVert / \Sigma \lvert F_o\rvert$	0.046
$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$	0.040
weights	$w = [\sigma(F_o)]^{-2}$
radiation used (Mo Kα)	$\lambda = 0.710\,73$ Å

especially with respect to the intense negative band at 370 nm. On this basis the *S* configuration at the Fe atom is assigned to 2*SS* (CD in Figure 1) and 5*SS* (CD in Figure 3), in analogy to the corresponding NH compound IV in Scheme II. In contrast, the virtually opposite CD spectra of 2*RS* (Figure 2) and 5*RS* (Figure 4) and also of the P$(C_6H_5)_3$ derivative 7*R* (Figure 5) demand *R* configuration at the Fe atom.

On the basis of these configurational assignments the overall stereochemistry of the BF_3-promoted carbonylations at low temperatures is as shown for 1*SS* → 2*RS*, 4*SS* → 5*RS*, and 6*S* → 7*R* in the formulas of Scheme I. The acetyl group ends up at the former position of the original carbonyl ligand, and the incoming carbonyl ligand occupies the former position of the methyl group.

This conclusion is corroborated by a chemical correlation of starting materials and products according to Davison's procedure.[17] CpFe(CO)[P$(C_6H_5)_2NCH_3$-(*S*)-$CH(CH_3)(C_6H_5)$]($COCH_3$), 2*RS*, was alkylated at the acetyl oxygen with $OEt_3{}^+BF_4{}^-$ to give (*RS*)-CpFe(CO)[P$(C_6H_5)_2NCH_3$-(*S*)-$CH(CH_3)(C_6H_5)$][C(OC_2H_5)CH_3]$^+BF_4{}^-$ which was reduced by $NaBH_4$ to (*RS*)-CpFe(CO)[P$(C_6H_5)_2NCH_3$-(*S*)-$CH(CH_3)(C_6H_5)$](C_2H_5), the ethyl analogue of 1*RS*. Figure 6 shows the CD spectra of 2*RS*, the isolated intermediate (*RS*)-CpFe(CO)[P$(C_6H_5)_2NCH_3$-(*S*)-$CH(CH_3)(C_6H_5)$][C(OC_2H_5)CH_3]$^+BF_4{}^-$ and (*RS*)-CpFe(CO)[P$(C_6H_5)_2NCH_3$-(*S*)-$CH(CH_3)(C_6H_5)$](C_2H_5). As in the reduction of the acetyl group in 2*RS* to the ethyl group in the ethyl analogue of 1*RS* the Fe configuration does not change,[17] the CD's of 2*RS* (Figure 2), of the ethyl analogue of 1*RS* (Figure 6), and of 1*RS* (Figure 1) derive from the *R* configuration at the Fe atom. In the BF_3-promoted carbonylation, however, 1*RS* is converted to 2*SS* (and 1*SS* to 2*RS*), the CD spectra of which demonstrate the inversion of configuration at the Fe atom, consistent with a methyl to carbonyl migration.

In our preliminary communication[26] the configurational correlation between $(-)_{436}$-starting material (the present 1*RS*) and $(-)_{436}$-carbonylation product (the present 2*SS*) was based on the CD spectra, because the absolute configurations of the optically active iron methyl and acetyl compounds were unknown. Three types of correlations

Table III. Atomic Coordinates and Thermal Parameters (×10^3) for 1*RS*

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(11)	*U*(22)	*U*(33)	*U*(12)	*U*(13)	*U*(23)
Fe	0.4740 (1)	−0.1145 (1)	0.4461 (1)	37 (1)	33 (1)	51 (1)	−3 (1)	−3 (1)	1 (1)
P	0.4885 (2)	0.0430 (2)	0.4530 (2)	28 (1)	32 (1)	37 (1)	−2 (1)	−2 (2)	0 (2)
O	0.4700 (6)	−0.1374 (5)	0.2420 (5)	79 (6)	80 (6)	67 (5)	21 (5)	−20 (5)	−27 (5)
N	0.6146 (5)	0.0904 (4)	0.4319 (5)	24 (4)	27 (4)	51 (5)	−6 (3)	8 (4)	0 (4)
C(6)	0.4728 (8)	−0.1236 (7)	0.3258 (7)	46 (6)	32 (5)	70 (7)	5 (6)	−9 (7)	−12 (6)
C(7)	0.3082 (5)	−0.0999 (7)	0.4472 (8)	31 (5)	62 (7)	77 (7)	−6 (5)	1 (7)	−4 (8)
C(8)	0.6293 (6)	0.1958 (5)	0.4396 (8)	30 (5)	41 (6)	60 (7)	−3 (5)	−1 (6)	0 (7)
C(21)	0.6849 (6)	0.0421 (7)	0.3607 (6)	40 (5)	52 (6)	28 (6)	−10 (6)	9 (5)	−15 (6)
C(22)	0.6607 (8)	0.0699 (8)	0.2583 (7)	55 (7)	105 (11)	45 (7)	−9 (7)	13 (6)	−12 (7)

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*, Å^2	atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*, Å^2
C(1)	0.5260 (6)	−0.2581 (4)	0.4680 (5)	77 (3)	H(5)	0.6832 (6)	−0.1967 (4)	0.4383 (5)	70 (0)
C(2)	0.4480 (6)	−0.2325 (4)	0.5380 (5)	60 (3)	H(7A)	0.2737 (5)	−0.0864 (7)	0.5170 (8)	70 (0)
C(3)	0.4897 (6)	−0.1542 (4)	0.5920 (5)	54 (3)	H(7B)	0.2334 (5)	−0.1702 (7)	0.4224 (8)	70 (0)
C(4)	0.5935 (6)	−0.1314 (4)	0.5554 (5)	51 (3)	H(7C)	0.2805 (5)	−0.0456 (7)	0.3975 (8)	70 (0)
C(5)	0.6159 (6)	−0.1956 (4)	0.4788 (5)	58 (3)	H(8A)	0.5932 (6)	0.2160 (5)	0.5070 (8)	70 (0)
C(9)	0.4597 (4)	0.0847 (3)	0.5747 (3)	30 (2)	H(8B)	0.5873 (6)	0.2313 (5)	0.3817 (8)	70 (0)
C(10)	0.3527 (4)	0.0981 (3)	0.6027 (3)	41 (3)	H(8C)	0.7131 (6)	0.2172 (5)	0.4391 (8)	70 (0)
C(11)	0.3283 (4)	0.1170 (3)	0.6985 (3)	54 (3)	H(10)	0.2935 (4)	0.0942 (3)	0.5542 (3)	70 (0)
C(12)	0.4109 (4)	0.1224 (3)	0.7661 (3)	55 (3)	H(11)	0.2516 (4)	0.1266 (3)	0.7185 (3)	70 (0)
C(13)	0.5179 (4)	0.1091 (3)	0.7381 (3)	49 (2)	H(12)	0.3934 (4)	0.1360 (3)	0.8348 (3)	70 (0)
C(14)	0.5423 (4)	0.0902 (3)	0.6423 (3)	41 (3)	H(13)	0.5771 (4)	0.1130 (3)	0.7866 (3)	70 (0)
C(15)	0.3961 (4)	0.1194 (4)	0.3798 (4)	34 (2)	H(14)	0.6190 (4)	0.0806 (3)	0.6222 (3)	70 (0)
C(16)	0.3700 (4)	0.2126 (4)	0.4092 (4)	42 (3)	H(16)	0.3970 (4)	0.2375 (4)	0.4720 (4)	70 (0)
C(17)	0.3061 (4)	0.2711 (4)	0.3509 (4)	51 (3)	H(17)	0.2874 (4)	0.3379 (4)	0.3720 (4)	70 (0)
C(18)	0.2685 (4)	0.2364 (4)	0.2633 (4)	58 (3)	H(18)	0.2227 (4)	0.2783 (4)	0.2215 (4)	70 (0)
C(19)	0.2947 (4)	0.1432 (4)	0.2339 (4)	61 (3)	H(19)	0.2677 (4)	0.1183 (4)	0.1711 (4)	70 (0)
C(20)	0.3585 (4)	0.0847 (4)	0.2922 (4)	45 (3)	H(20)	0.3773 (4)	0.0179 (4)	0.2711 (4)	70 (0)
C(23)	0.8043 (3)	0.0581 (4)	0.3891 (4)	38 (3)	H(21)	0.6680 (6)	−0.0343 (7)	0.3624 (6)	70 (0)
C(24)	0.8429 (3)	0.0102 (4)	0.4700 (4)	53 (3)	H(22A)	0.7165 (8)	0.0386 (8)	0.2077 (7)	70 (0)
C(25)	0.9501 (3)	0.0219 (4)	0.4982 (4)	72 (3)	H(22B)	0.6667 (8)	0.1475 (8)	0.2554 (7)	70 (0)
C(26)	1.0186 (3)	0.0816 (4)	0.4456 (4)	63 (3)	H(22C)	0.5795 (8)	0.0482 (8)	0.2403 (7)	70 (0)
C(27)	0.9800 (3)	0.1295 (4)	0.3647 (4)	61 (3)	H(24)	0.7938 (3)	−0.0326 (4)	0.5077 (4)	70 (0)
C(28)	0.8728 (3)	0.1178 (4)	0.3365 (4)	54 (3)	H(25)	0.9778 (3)	−0.0124 (4)	0.5562 (4)	70 (0)
H(1)	0.5188 (6)	−0.3109 (4)	0.4196 (5)	70 (0)	H(26)	1.0954 (3)	0.0900 (4)	0.4659 (4)	70 (0)
H(2)	0.3762 (6)	−0.2640 (4)	0.5476 (5)	70 (0)	H(27)	1.0291 (3)	0.1723 (4)	0.3270 (4)	70 (0)
H(3)	0.4525 (6)	−0.1209 (4)	0.6463 (5)	70 (0)	H(28)	0.8451 (3)	0.1521 (4)	0.2785 (4)	70 (0)
H(4)	0.6422 (6)	−0.0793 (4)	0.5794 (5)	70 (0)					

Table IV. Intramolecular Bond Distances (Å) and Angles (deg) in 1*RS*

	Bond Distances		
Fe-C(1)	2.117 (6)	O-C(6)	1.186 (9)
Fe-C(2)	2.105 (7)	N-C(8)	1.477 (8)
Fe-C(3)	2.119 (7)	N-C(21)	1.481 (9)
Fe-C(4)	2.139 (6)	C(21)-C(22)	1.511 (10)
Fe-C(5)	2.138 (6)	C(21)-C(23)	1.549 (8)
Fe-CpCent[a]	1.746 (2)		
Fe-P	2.195 (2)	Cp(ideal)C-C	1.420
Fe-C(6)	1.684 (9)	phen(ideal)C-C	1.395
Fe-C(7)	2.066 (6)	C-H(ideal)	1.00
P-N	1.721 (6)		
P-C(9)	1.829 (4)	methyl(ideal)C-H including C(21)-H(21)	1.080
P-C(15)	1.865 (4)		
	Bond Angles		
P-Fe-C(6)	96.8 (3)	C(21)-N-C(8)	115.1 (7)
P-Fe-C(7)	89.0 (3)	N-C(21)-C(22)	113.7 (7)
C(6)-Fe-C(7)	90.3 (4)	N-C(21)-C(23)	109.0 (6)
N-P-Fe	116.6 (2)	N-C(21)-H(21)	103.5 (6)
C(9)-P-Fe	109.9 (2)	C(22)-C(21)-C(23)	113.3 (7)
C(15)-P-Fe	119.4 (2)	C(22)-C(21)-H(21)	103.5 (6)
N-P-C(9)	102.5 (3)	C(23)-C(21)-H(21)	108.7 (4)
N-P-C(15)	104.3 (3)		
C(9)-P-C(15)	102.1 (3)	P-Fe-CpCent[a]	120.9 (2)
Fe-C(6)-O(6)	174.8 (9)	C(6)-Fe-CpCent[a]	122.6 (3)
P-N-C(21)	118.4 (5)	C(7)-Fe-CpCent[a]	115.8 (3)
P-N-C(8)	118.5 (5)		

[a] CpCent = the geometric center of the Cp ring.

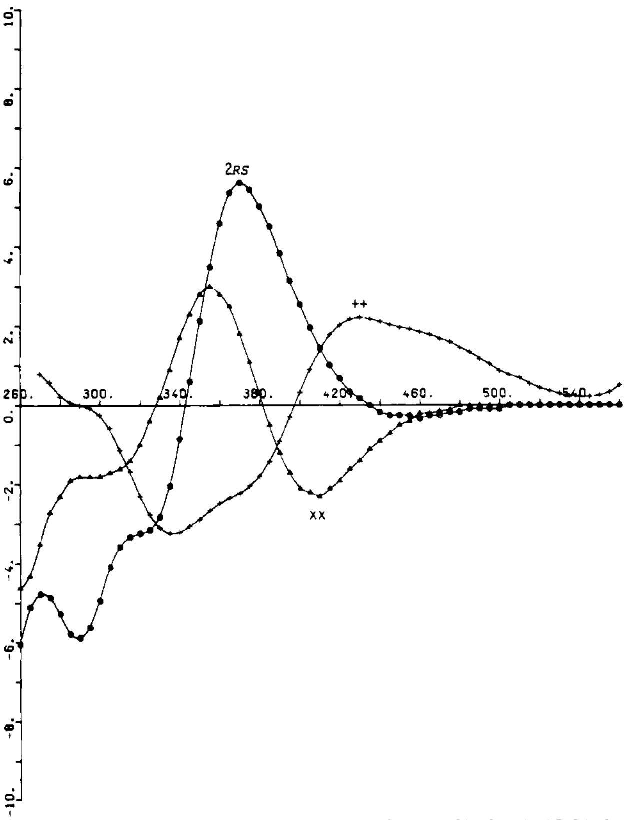
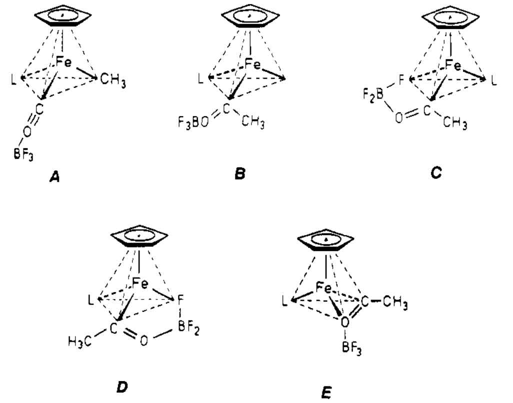


Figure 6. CD spectra of 2*RS*, (*RS*)-CpFe(CO)[P-$(C_6H_5)_2NCH_3$-(*S*)-$CH(CH_3)(C_6H_5)$][$C(OC_6H_5)CH_3$]BF_4 (×), and (*RS*)-CpFe(CO)[$P(C_6H_5)_2NCH_3$-(*S*)-$CH(CH_3)(C_6H_5)$]C_2H_5 (+) (2×10^{-3} M in *n*-hexane; ordinate scale $10^{-3}[\theta]_\lambda$).

were made (in terms of the numbering scheme of the present paper): (i) $(-)_{436}$-1*RS* and $(-)_{436}$-**2***SS* (Figure 1) (conclusion: on the one hand the 430-nm band of 1*RS* and the weak 450-nm maximum of **2***SS* and on the other hand the double maximum at 370 and 340 nm of 1*RS* and the 370-nm maximum of **2***SS* correlate, indicating the same configuration at the Fe atom (substituents methyl and acetyl at the same position)); (ii) $(-)_{436}$-1*RS* and $(+)_{578}$,$(-)_{436}$-**6***S* (Figures 1 and 5) (conclusion: the broad positive CD ending at 400 nm for 1*RS* and at 480 nm for **6***S* as well as the double maximum at 370 and 340 nm of 1*RS* and the maximum at 420 nm of **6***S* correlate, indicating the same configuration at the Fe atom); (iii) $(-)_{436}$-**2***SS* and $(-)_{546}$,$(+)_{436}$-**7***R* (Figures 1 and 5) (conclusion: the almost opposite CD curves of **2***SS* and **7***R* indicate opposite configurations at the Fe atom). With the advent of the absolute configurations of compounds I and IV in Scheme II[32] conclusions i and ii turned out to be wrong. So, in the preliminary communication[26] the wrong configuration was assigned to the starting material 1*RS*, another example of how dubious configurational assignments exclusively on the basis of CD spectra can be.[31]

Scheme III



Mechanism. According to Shriver the Lewis acid BF_3 in the reaction with a compound of type **1**, **4**, or **6** in the first step adds to the oxygen atom of the carbonyl group making the whole system more susceptible to carbonylation.[8-13] Starting with intermediate A and taking into account the known stereochemistry of the carbonylation product a lot of pathways can be envisaged, resulting in the observed stereochemistry (Scheme I).

If in A methyl migrates to the carbonyl without any further rearrangement, an intermediate of type B is formed containing a vacant coordination site.[33] Attack of one of the fluorine atoms at the Fe atom before a rotation around the Fe–C(acetyl) bond[34] inverts its configuration, giving intermediate C. If in B rotation around the Fe–C bond[34] is fast compared to process B → C, an F ligand can fill the empty coordination position without inversion at the Fe atom, giving intermediate D, the enantiomer of C. Likewise, a concerted formation of C starting from A is conceivable. A S_N2-type attack of CO opposite to the F ligand in C or a S_N1-type substitution of the F ligand at the front side of D both would give the observed stereochemistry after loss of BF_3. If the carbonylation starts by a BF_3-promoted CO insertion into the Fe–CH_3 bond, intermediate C results either directly or by ring enlargement via E. So, the possible intermediates overlap for the two fundamental pathways of carbonylation, CH_3 migration and CO insertion. BF_3, on the one hand, promotes the low-temperature carbonylation in a stereospecific manner and, on the other hand, however, increases the number of possibilities, so that a decision as to whether the reaction is a CH_3 migration or a CO insertion cannot be arrived at,

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(33) Intermediates of that type have been shown to possess an appreciable pyramidal stability. Hofmann, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 536.

(34) 20 kcal/mol have been calculated for the barrier to rotation around the manganese–acetyl bond in five-coordinate $(CO)_4Mn(COCH_3)$.[6]

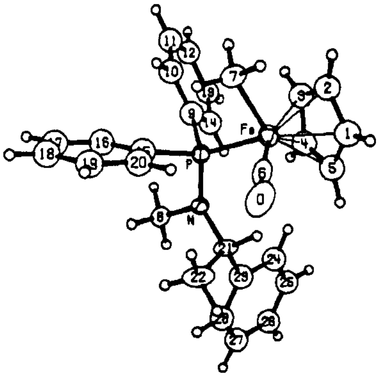

Figure 7. ORTEP of compound 1*RS* in its correct absolute configuration showing the numbering system used.

although the overall stereochemistry can be established.

BF_3 addition to the Fe atom in **1**, **4**, and **6**, giving a square-pyramidal intermediate, which can pseudorotate,[28,35,36] explains the epimerization at the Fe center of the Fe–methyl compounds in the presence of BF_3 at room temperature. However, a possible BF_3 addition to the Fe center in starting materials and products has no stereochemical impact regarding the low temperature carbonylations, because there is no loss of stereoselectivity with respect to the Fe atom. BF_3 addition to the almost planar N atoms of the aminophosphine ligands does not seem to be a necessary condition for the carbonylation reaction, because the triphenylphosphine derivative **6***S* and the aminophosphine derivatives **1***RS*, **1***SS*, **4***RS*, and **4***SS* react under comparable conditions. The BF_3 addition to the N atom of the aminophosphine ligands might, however, be the first step for the P–N cleavage reaction, giving about 10% of $CpFe(CO)(COCH_3)P(C_6H_5)_2F$, **3**, even in the low-temperature reactions (Table I). In addition to the byproducts due to cleavage of the P–N bond small amounts of $[CpFe(CO)_2P(C_6H_5)_2N(CH_3)CH(CH_3)(C_6H_5)]BF_4$ are formed in the BF_3-promoted carbonylation of 1*RS*/1*SS*. Products of this type frequently are found in the reaction of CpFe(CO)(L) alkyls with electrophiles.[37-39]

X-ray Crystallographic Study of 1*RS*. A crystal of 1*RS* suitable for X-ray analysis was obtained from an ether solution by slow evaporation of ether at -20 °C. The X-ray analysis was carried out as described previously.[40-42] Table II summarizes the crystal data and processing parameters. Figure 7 shows an ORTEP of 1*RS*. Table III contains the atomic parameters and Table IV the intramolecular bond lengths and bond angles.

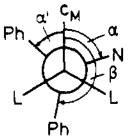

Figure 8. Newman projection along the Fe–P bond and conformational parameters α, α', and β for 1*RS*.

The absolute configuration of the molecule was determined by the Bijvoet test.[43] The configuration at the iron atom is *R*, given the priority sequence of the ligands is Cp > P > CO > CH_3,[44,45,27] and the configuration at the carbon atom is *S* in agreement with the fact that the optically pure aminophosphine derived from (*S*)-1-phenylethylamine was used.

The conformation found for 1*RS* in the crystal is very similar to other complexes containing the aminophosphine $(C_6H_5)_2PN(CH_3)$-(*S*)-$CH(CH_3)(C_6H_5)$.[40,46,47] Looking along the Fe–P bond (Figure 8) reveals a slightly distorted staggered conformation with phenyl C(15)–C(20) trans to the Cp ring centroid C_M and phenyl C(9)–C(14) as well as NCH_3-(*S*)-$CH(CH_3)(C_6H_5)$ gauche to the ring centroid. Similar to the other four X-ray structure analyses of three-legged pianostool compounds with the same aminophosphine ligand the N substituent forms the large gauche angle ($\alpha = 66.6°$) and the phenyl C(9)–C(14) the small gauche angle ($\alpha' = 49.3°$). The angle β of the trans-phenyl C(15)–C(20) is 193.4° (Figure 8). The value for α (66.6°) is well in the range, between 64 and 71°, found in the other cases.[40]

Registry No. **1*RS***, 59727-90-1; **1*SS***, 59568-04-6; **2*RS***, 67291-26-3; **2*SS***, 67375-04-6; **3*S***, 87039-41-6; **3*R***, 87069-56-5; **4*RS***, 78548-73-9; **4*SS***, 78506-14-6; **5*RS***, 74984-61-5; **5*SS***, 74945-68-9; **6*R***, 53318-87-9; **6*S***, 56907-97-2; **7*R***, 36548-61-5; **7*S***, 36548-60-4; $[CpFe(CO)_2P(C_6H_5)_2N(CH_3)$-(*S*)-$CH(CH_3)(C_6H_5)]BF_4$, 87039-43-8; *RS*-$(-)_{436}\{Cp(CO)[P(C_6H_5)_2NCH_3$-(*S*)-$CH(CH_3)(C_6H_5)]FeC(OC_2H_5)CH_3\}^+BF_4^-$, 87039-45-0; (*RS*)-$(+)_{436}$-$CpFe(CO)(C_2H_5)[P(C_6H_5)_2NCH_3$-(*S*)-$CH(CH_3)(C_6H_5)]$, 87039-46-1; $CpFe(CO)(COC_2H_5)[P(C_6H_5)_2NCH_3$-(*S*)-$CH(CH_3)(C_6H_5)]$, 87039-47-2; $(C_2H_5)_3O^+BF_4^-$, 368-39-8.

Supplementary Material Available: A listing of structure factor amplitudes for 1*RS* (9 pages). Ordering information is given on any current masthead page.

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