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Optically Active Transition-Metal Complexes. 104.[1] Asymmetric Michael Reactions of (R_{Fe})- and (S_{Fe})-[(η^5-C_5H_5)Fe(CO)(PPh_3)COCH=CH_2]. Synthesis of an Enantiomerically Pure Precursor for Verapamil. X-ray Crystal Structure of ($R_{Fe}R_C$)-{(η^5-C_5H_5)Fe(CO)(PPh_3)$COCH_2CH_2C$(CN)(^{i}Pr)-[3,4-$C_6H_3(OMe)_2$]}

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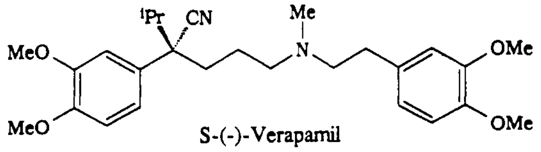
Michael addition of the anion of 3,4-dimethoxy-α-isopropylbenzeneacetonitrile, having no H substituent at the carbanionic C atom, to the acryloyl complexes (R_{Fe})- and (S_{Fe})-[(η^5-C_5H_5)-Fe(CO)(PPh_3)COCH=CH_2] followed by protonation of the resulting enolate gave diastereomerically pure ($R_{Fe}R_C$)- and ($S_{Fe}S_C$)-{(η^5-C_5H_5)Fe(CO)(PPh_3)$COCH_2CH_2C$(CN)(^{i}Pr)[3,4-C_6H_3-$(OMe)_2$]} after fractional crystallization. The absolute configuration of the newly formed stereogenic carbon atom in these complexes was established by X-ray crystallography. The enantiomerically pure (*S*)-(−)- and (*R*)-(+)-γ-cyano-3,4-dimethoxy-γ-isopropylbenzenebutanoic acids, precursors for the drug verapamil, were obtained on decomplexation by treatment with bromine/water. In the Michael reaction, the new bis-addition product {(η^5-C_5H_5)-Fe(CO)(PPh_3)$COCH_2CH_2CH$[CH_2C(CN)(^{i}Pr)[3,4-$C_6H_3(OMe)_2$]][CO(PPh_3)(CO)Fe(η^5-C_5H_5)]} was formed as a byproduct, which, after decomplexation, gave the α-substituted glutaric acid α-[2-cyano-2-(3,4-dimethoxyphenyl)-2-isopropylethyl]glutaric acid. Michael addition of the anion of 3,4-dimethoxybenzeneacetonitrile, having a H substituent at the carbanionic C atom, to the acryloyl complex (S_{Fe})-[(η^5-C_5H_5)Fe(CO)(PPh_3)COCH=CH_2] gave the α-enolate (S_{Fe})-{(η^5-C_5H_5)Fe(CO)(PPh_3)$COCHCH_2CH$(CN)[3,4-$C_6H_3(OMe)_2$]}$^-$, which transformed to the anion (S_{Fe})-{(η^5-C_5H_5)Fe(CO)(PPh_3)$COCH_2CH_2C$(CN)[3,4-$C_6H_3(OMe)_2$]}$^-$, having the negative charge at the γ-position. This anion added again to the acryloyl complex to build up the bis-addition product ($S_{Fe}S_{Fe}$)-{[(η^5-C_5H_5)Fe(CO)(PPh_3)$COCH_2CH_2]_2C$(CN)[3,4-$C_6H_3(OMe)_2$]} after protonation. In addition, a further acryloyl complex added to the enolate of this complex. In this way the tris-addition product {(η^5-C_5H_5)Fe(CO)(PPh_3)$COCH_2CH_2C$(CN)[3,4-$C_6H_3(OMe)_2$]CH_2-CH[CH_2CH_2COFe(CO)(PPh_3)(η^5-C_5H_5)][COFe(CO)(PPh_3)(η^5-C_5H_5)]} was synthesized with three (S_{Fe})-(η^5-C_5H_5)Fe(CO)(PPh_3) substituents and two diastereomerically pure stereogenic carbon atoms.

Introduction

As a rule, the enantiomers of chiral drugs show different physiological activities. Frequently, one enantiomer is effective whereas the other is less effective, not effective, or even toxic.[2,3] The two enantiomers of verapamil (1; Chart I) differ considerably in their activity, (*S*)-(−)-verapamil being much more effective as a coronary dilator than the (*R*)-(+) enantiomer.[4] In addition, verapamil seems to be a promising candidate to avoid the development of resistance in the chemotherapy of cancer. To exclude a reaction to circulation, only the *R* isomer of verapamil can be used for this purpose. Thus, both enantiomers of verapamil are of interest. Attempts to build up verapamil constituents by enantioselective catalysis have proved to be unsatisfactory.[5] In the present study we report on the enantioselective synthesis of γ-cyano-3,4-dimethoxy-γ-isopropylbenzenebutanoic acid, a precursor for verapamil, using the [(η^5-C_5H_5)Fe(CO)-(PPh_3)] group as the chiral auxiliary.

Chart I



1

Starting from the chiral iron acetyl complex [(η^5-C_5H_5)-Fe(CO)(PPh_3)$COCH_3$] (2), Davies et al. succeeded in the stereospecific buildup of new stereogenic centers at the

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α-, β-, and γ-positions of the acyl substituent using several reaction types.[6–11] Prompted by the high stereocontrol of the chiral auxiliary $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)]$, we tried to synthesize optically active γ-cyano-3,4-dimethoxy-γ-isopropylbenzenebutanoic acid via a Michael reaction of the lithium salt of 3,4-dimethoxy-α-isopropylbenzeneacetonitrile (DIBA, **6**) and the enantiomerically pure acryloyl complex $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH{=}CH_2]$ (**5**). In Michael reactions high diastereomeric excess (de) values have been reported for systems in which the new stereogenic center is formed at the α- or β-position of the acyl substituent bound to $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)]$.[12–16] In the present Michael reaction the new stereogenic center is built up at the γ-position.

Experimental Section

All the reactions were performed under nitrogen using standard vacuum line and Schlenk techniques. $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COMe]$ (**2**) and chloromethyl menthyl ether were prepared as described in the literature.[17,18] DIBA (**6**) was used as received from BASF AG. Melting points were determined with a Büchi SMP 20 apparatus. IR spectra were taken on a Beckman IR 4240 spectrometer. Proton NMR spectra were recorded with a Bruker WM 250 instrument at 250 MHz and a Varian EM 360 L spectrometer at 60 MHz using $CDCl_3$ as the solvent and TMS as the internal standard. Mass spectra were measured with a Finnigan MAT 95 instrument using the field desorption (FD) technique. Specific rotations were determined with a Perkin-Elmer 241 polarimeter.

Preparation of (*S*)-(+)- and (*R*)-(−)-$[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_2CH_2OMen]$ (4).[19] *n*-Butyllithium (6.1 mL of a 1.6 M solution in hexane, 9.8 mmol) was added to an orange solution of *rac*-**2** (2.0 g, 4.4 mmol)[17] in THF (15 mL) at −78 °C to give a dark reddish brown reaction mixture containing the enolate **3**. After this mixture was stirred for 1.5 h, chloromethyl menthyl ether,[18] prepared from (−)-menthol, was slowly added dropwise. Then, the solution was stirred for 1 h at −78 °C. Gradual warming to room temperature and removal of the solvent gave a red oil which was dissolved in CH_2Cl_2 and filtered through alumina (grade II-III). The solution was concentrated to 10 mL and transferred to an alumina (grade II-III) column (2.5 × 100 cm). With 1/1 CH_2Cl_2/petroleum ether (40–60 °C), *rac*-**2** and chloromethyl menthyl ether were eluted as the first orange band. The diastereomers (*S*)-**4** and (*R*)-**4** were eluted with CH_2Cl_2 as an orange-yellow band which after removal of the solvent gave an orange air-stable powder (1.75 g, 64% yield). IR (KBr): 3050 (m), 2910 (s), 2940 (s), 2855 (s), 1915 (vs), 1610 (s), 1480 (m), 1450 (m), 1332 (s), 1381 (w), 1365 (w), 1340 (w), 1257 (w), 1180 (w), 1105 (s), 1087 (vs), 1025 (w), 1010 (w), 995 (w), 930 (m), 885 (m), 815 (s), 743 (s), 690 (s) cm^{-1}.

A second chromatography procedure on two commercial silica gel Lobar columns (Merck, type B) connected in series was carried out to separate the two diastereomers. With 1/4 ether/petroleum ether (40–60 °C) the isomers (*S*)-**4** and (*R*)-**4** were eluted as two orange bands which after evaporation of the solvent gave orange powders (0.85 g each).

The diasteromer eluted first was (*S*)-**4**: mp 59–60 °C. ^1H NMR (250 MHz): δ 7.53–7.30 (15 H, m, phenyl H); 4.421 (5 H, d, J_{PH} = 1.2 Hz, Cp H); 3.29–3.14 (2 H, m, CH_2O); 2.88–2.76 (2 H, m, CH_2CO); 2.15–2.06 (1 H, m, CHO); 2.04–1.93 (1 H, m, $CHCHMe_2$); 1.63–1.53 (2 H, m, CH_2CHO); 1.25–0.80 (12 H, m, menthyl H), 0.734 (3 H, d, J = 7.0 Hz, CH_3CH). $[\alpha]^{25}{}_D$ = +65° (c = 0.4; benzene).[19]

The diastereomer eluted second was (*R*)-**4**: mp 126–127 °C. The ^1H NMR of (*R*)-**4** was nearly the same as that of (*S*)-**4**. The following signals, however, were different: δ 4.423 (5 H, d, J_{PH} = 1.2 Hz, Cp H); 0.728 (3 H, d, J = 7.0 Hz, CH_3CH). $[\alpha]^{25}{}_D$ = −150° (c = 0.4; benzene).[19] Anal. Calcd for $C_{37}H_{43}FeO_3P$ (622.6): C, 71.38; H, 6.96. Found: C, 71.19; H, 7.25.

Preparation of (*S*)-(+)- and (*R*)-(−)-$[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH{=}CH_2]$ (5).[16,20] (*R*)-**4** (1.5 g, 2.4 mmol) was dissolved in THF (10 mL) and treated 48 h at room temperature with sodium hydride (0.29 g; 12 mmol). After removal of the solvent and extraction with CH_2Cl_2 the concentrated solution was chromatographed on an alumina (grade II-III) column (2.0 × 80 cm) with CH_2Cl_2. After the orange band of (*R*)-**4** the orange-brown band of (*R*)-**5** was eluted. Concentration provided 0.95 g (85% yield) of a red-orange air-stable powder of (*R*)-**5**: mp 93–95 °C. IR (KBr): 3050 (w), 1900 (vs), 1600 (m), 1565 (s), 1480 (m), 1435 (s), 1390 (w), 1270 (w), 1190 (w), 1100 (s), 1022 (w), 1005 (w), 980 (w), 950 (m), 935 (m), 830 (m), 762 (m), 745 (w), 710 (s) cm^{-1}. $[\alpha]^{25}{}_D$ = −202° (c = 0.11; benzene).[20] ^1H-NMR (250 MHz):[23] δ 7.51–7.30 (15 H, m, phenyl H); 6.58 (1 H, dd, J_{trans} = 17.0 Hz, J_{cis} = 10.2 Hz, $CH{=}CH_2$); 4.92 (1 H, dd, J_{trans} = 17.0 Hz, J_{gem} = 1.9 Hz, $CHH{=}CH$); 4.52 (1 H, dd, J_{cis} = 10.2 Hz, J_{gem} = 1.9 Hz, $CHH{=}CH$); 4.44 (5 H, d, J_{PH} = 0.7 Hz, Cp H). MS (FD, toluene; *m/e* (relative intensity)): 466.3 (100).

(*S*)-**5** was prepared from (*S*)-**4** by following the same procedure. $[\alpha]^{25}{}_D$ = +202° (c = 0.11; benzene).[20] Anal. Calcd for $C_{27}H_{23}FeO_2P$ (466.3): C, 69.54; H, 4.97. Found: C, 69.23; H, 5.21.

Preparation of $\{(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_2CH_2C(CN)(^iPr)[3,4\text{-}C_6H_3(OMe)_2]\}$ (8) and $\{(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_2CH_2CH\{CH_2C(CN)(^iPr)[3,4\text{-}C_6H_3(OMe)_2]\}[CO(PPh_3)(CO)Fe(\eta^5\text{-}C_5H_5)]\}$ (9). *n*-Butyllithium (2.8 mL of a 1.6 M solution in hexane, 4.5 mmol) and THF (10 mL) were cooled to −30 °C, and diisopropylamine (0.63 mL, 4.5 mmol) was added to produce lithium diisopropylamide (LDA). 3,4-Dimethoxy-α-isopropylbenzeneacetonitrile (DIBA, **6**) (0.984 g, 4.5 mmol) was dissolved in THF (7 mL) and added to the LDA solution to give a yellow solution which was stirred for 1 h and then cooled to −78 °C. (*S*)-**5** (0.95 g, 2.04 mmol) dissolved in THF (15 mL) was added within 30 min. The dark red solution was stirred for 1 h at −78 °C. On addition of methanol (0.6 mL, 15 mmol) at −78 °C the solution became bright orange. The solvent was evaporated to give a red oil, which was dissolved in CH_2Cl_2 and filtered through alumina (grade II-III). The solution was concentrated and transferred to an alumina (grade II-III) column (2.0 × 90 cm). With 1/1 petroleum ether (40–60 °C)/ether unchanged DIBA (**6**) was eluted first. Using ether as the eluent,

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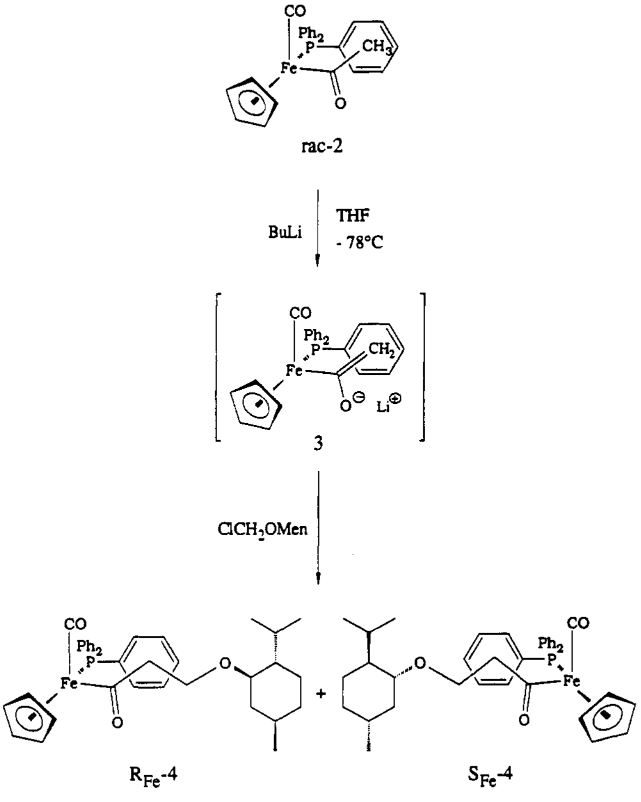
Table I. Crystal Data and Data Collection Parameters for $(R_{Fe}R_C)$-$\{(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_2CH_2C(CN)(^iPr)\text{-}[3,4\text{-}C_6H_3(OMe)_2]\}$ (8)

mol formula	$C_{40}H_{40}FeNO_4P$
fw	685.58
cryst syst	rhombic
space group	D_2^4
cell dimens	
a, Å	7.914(4)
b, Å	16.43(1)
c, Å	27.43(2)
V, Å^3	3566.6
Z	4
T, K	296
d_{calc}, g cm^{-3}	1.28
linear abs, μ, cm^{-1}	5.0
$F(000)$	1440
diffractometer	Syntex R3
radiation, Å	λ(Mo K_α) = 0.710 73
scan type	Ω
rflns measd	h, 0–10; k, 0–20; l, 0–33
2θ range, deg	3.0–50.0
no. of rflns measd	3604
abs cor; range of transmission	empirical, 4 rflns; 0.92–1.00
no. of unique obsd data	1903 ($I > 2.5\sigma(I)$)
no. of params (NV)	425
$R(F)$	0.056
$R_w(F)$	0.043
GOF	1.52
residual ρ, e Å^{-3}	0.38

Scheme I



the two iron complexes 8 and 9 could be separated, both being a mixture of diastereomers.

The first yellow band contained 8, which after evaporation of the solvent gave a yellow powder (1.06 g, 76% yield): mp 142–144 °C. IR (KBr): 3050 (w), 2950 (m), 2930 (m), 2870 (w), 2830 (w), 2240 (w), 1900 (vs), 1585 (s), 1515 (s), 1480 (m), 1460 (m), 1435 (s), 1410 (m), 1390 (w), 1370 (w), 1330 (m), 1262 (s), 1212 (w), 1185 (m), 1150 (s), 1095 (s), 1032 (s), 920 (m), 885 (m), 860 (m), 830 (s), 760 (s), 705 (s), 655 (m) cm^{-1}. ^{1}H NMR (250 MHz): δ 7.50–7.24 (15 H, m, phenyl H); 6.89–6.67 (3 H, m, phenyl H); 4.38, 4.27 (5 H, 2d, J_{PH} = 1.2 Hz, Cp H, intensity ratio 82:18); 3.91–3.84 (6 H, m, OMe); 3.12–3.01 (1 H, m, C*H*HCO); 2.35–2.24 (1 H, m, CH*H*CO); 2.09–1.86 (2 H, m, C*H*Me$_2$, C*H*HCCN); 1.60–1.49 (1 H, m, CH*H*CCN); 1.09, 1.01 (3 H, 2d, J = 6.6 Hz, J = 6.7 Hz, C*H*$_3$CH); 0.73–0.68 (3 H, m, C*H*$_3$CH). MS (FD, toluene; m/e (relative intensity)): 685.2 (100), 686.3 (41). $[\alpha]^{25}_D$ = +58° (c = 0.4; toluene). Anal. Calcd for $C_{40}H_{40}FeNO_4P$ (685.6): C, 70.02; H, 5.88; N, 2.04. Found: C, 69.29; H, 5.97; N, 2.22.

The second orange band of the chromatography contained **9**, which after removal of the solvent gave red crystals (0.19 g, 19% yield): mp 114 °C. IR (KBr): 3600–3200 (broad), 3050 (m), 2960 (m), 2930 (m), 2820 (w), 2240 (w), 1985 (w), 1990 (vs), 1600 (s), 1515 (s), 1480 (m), 1465 (w), 1435 (s), 1420 (w), 1390 (w), 1265 (s), 1190 (w), 1155 (m), 1120 (w), 1100 (s), 1080 (w), 1035 (s), 1010 (w), 850 (w), 836 (s), 760 (s), 705 (s) cm^{-1}. ^{1}H NMR (250 MHz): 7.71–7.34 (30 H, m, phenyl H); 7.01–6.75 (3 H, m, phenyl H); 4.42, 4.26, 4.20, 4.17 (10 H, 4d, J_{PH} = 1.2 Hz, J_{PH} = 1.3 Hz, J_{PH} = 1.2 Hz, J_{PH} = 1.3 Hz, Cp H, intensity ratio 35:65:65:35); 3.95–3.81 (6 H, m, OMe); 3.21 (1 H, m); 2.52–2.24 (3 H, m); 1.83–0.58 (10 H, m). MS (FD, toluene; m/e (relative intensity)): 1151.9 (100). $[\alpha]^{25}_D$ = +75° (c = 0.4; toluene). Anal. Calcd for $C_{67}H_{63}Fe_2NO_6P_2$ (1151.9): C, 69.99; H, 5.51; N, 1.22. Found: C, 69.51; H, 5.49; N, 1.36.

When (R)-**5** was used as the starting material, the mirror image mixture of diastereomers of **8** ($[\alpha]^{25}_D$ = −58° (c = 0.4; toluene)) and of **9** ($[\alpha]^{25}_D$ = −75° (c = 0.4; toluene)) was obtained.

Isolation of the Main Diastereomer of 8. 8 (1.0 g, 1.5 mmol), the (+)-diastereomer mixture as described above, was dissolved in CH_2Cl_2 (4 mL) at room temperature and treated with ether (12 mL). The main diastereomer precipitated at −20 °C as a yellow powder, which was filtered off and washed with ether. Diastereomerically pure 8 could be obtained by a second recrystallization with reduced solvent quantities (0.56 g, 56% yield): mp 170–171 °C. ^{1}H NMR (250 MHz): δ 7.42–7.24 (15 H, m, phenyl H); 6.82 (2 H, s, phenyl H_{ortho}); 6.68 (1 H, s, phenyl H_{meta}); 4.38 (5 H, d, J_{PH} = 1.2 Hz, Cp H); 3.91 (3 H, s, OMe); 3.84 (3, H, s, OMe); 3.12–3.02 (1 H, m, C*H*HCO); 2.35–2.25 (1 H, m, CH*H*CO); 2.09–1.90 (2 H, m, C*H*Me$_2$, C*H*HCCN); 1.59–1.50 (1 H, m, CH*H*CCN); 1.09 (3 H, J = 6.6 Hz, C*H*$_3$CH); 0.72 (3 H, d, J = 6.6 Hz, CH$_3$CH). $[\alpha]^{25}_D$ = +64° (c = 0.4; toluene).

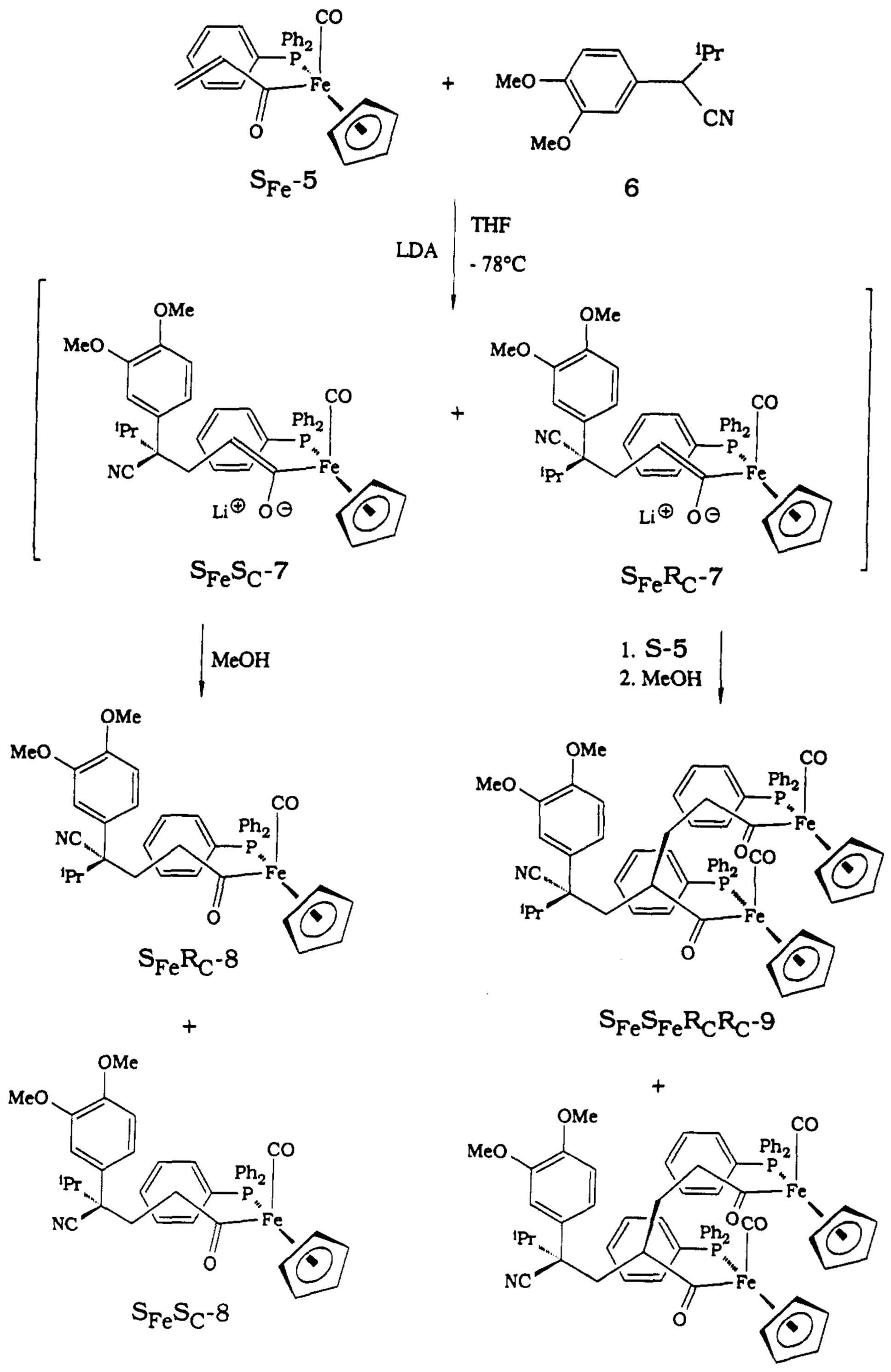
When the (−)-diastereomer mixture of 8 was used as the starting material, diastereomerically pure 8 ($[\alpha]^{25}_D$ = −64° (c = 0.4; toluene)) was obtained.

Preparation of γ-Cyano-3,4-dimethoxy-γ-isopropylbenzenebutanoic Acid (10). Bromine (0.13 mL, 2.6 mmol) in THF (4 mL) was added dropwise to a cooled solution (0 °C) of diastereomerically pure (+)-8 (0.90 g, 1.3 mmol) in THF (10 mL) containing water (0.5 mL) to give a dark brown solution. After the mixture was stirred (0 °C, 2 h), a saturated $Na_2S_2O_3$ solution in water (1 mL) was added and the THF was removed. Upon further addition of water (15 mL) and acidification with aqueous HCl to pH 1, the aqueous solution was extracted with ether (3 × 20 mL). The resultant green solution was concentrated and washed with a saturated solution of $NaHCO_3$ in water (20 mL) and then with water (3 × 20 mL). The combined aqueous washings were reacidified with HCl to pH 1 and extracted with ether (3 × 15 mL). After the ether extracts were dried over Na_2SO_4, the solvent was removed to give 10 as a pale yellow oil (0.25 g, 67% yield). IR (film): 3600–2500 (broad), 2240 (m), 1700 (vs), 1610 (m), 1590 (m), 1510 (s), 1450 (m), 1410 (m), 1370 (w), 1250 (vs), 1145 (s), 1020 (s), 945 (w), 875 (w), 850 (w), 805 (m), 770 (m), 720 (w), 700 (w) cm^{-1}. ^{1}H NMR (60 MHz):[5] δ 9.50 (1 H, broad, COOH); 6.90 (3 H, m, phenyl H); 3.90 (6 H, s, OMe); 2.50–1.90 (5 H, m, C*H*Me$_2$, C*H*$_2$C*H*$_2$); 1.20 (3 H, d, J = 6.7 Hz, C*H*$_3$CH); 0.80 (3 H, d, J = 6.7 Hz, C*H*$_3$CH). $[\alpha]^{25}_D$ = +36.5° (c = 10.0; ethanol) (lit.[4] $[\alpha]^{25}_D$ = +36.5° (c = 10.0; ethanol)[4]).

When (−)-8 is used, $[\alpha]^{25}_D$ = −36.5° (c = 10.0; ethanol).

Preparation of α-[2-Cyano-2-(3,4-dimethoxyphenyl)-2-isopropylethyl]glutaric Acid (11). In the same way as described above, 9 (0.20 g, 0.17 mmol) was treated with bromine/water to give 11 as a colorless oil (0.04 g, 63% yield). IR (KBr): 3500–2400 (broad), 2400 (w), 1700 (vs), 1600 (m), 1580 (m), 1500 (vs), 1450 (s), 1400 (s), 1375 (m), 1250 (vs), 1130 (s), 1100 (m), 1005 (s), 780 (m), 745 (w), 700 (w), 670 (w) cm^{-1}. ^{1}H NMR (250

Scheme II



MHz): δ 7.68–7.47 (2 H, m, COOH); 7.05–6.78 (3 H, m, phenyl H); 3.91–3.84 (6 H, m, OMe); 3.77–3.11 (1 H, m); 2.86–1.68 (7 H, m); 1.32–1.18 (3 H, m, C*H*$_3$CH); 0.79–0.76 (3 H, m, C*H*$_3$CH). MS (FD, toluene; *m*/*e* (relative intensity)): 363.4 (70) [M$^+$].

Preparation of {[(η^5-C$_5$H$_5$)Fe(CO)(PPh$_3$)COCH$_2$CH$_2$]$_2$C(CN)[3,4-C$_6$H$_3$(OMe)$_2$]} (16) and {(η^5-C$_5$H$_5$)Fe(CO)(PPh$_3$)COCH$_2$CH$_2$C(CN)[3,4-C$_6$H$_3$(OMe)$_2$]CH$_2$CH[CH$_2$CH$_2$COFe(CO)(PPh$_3$)(η^5-C$_5$H$_5$)][COFe(CO)(PPh$_3$)(η^5-C$_5$H$_5$)]} (17). *n*-Butyllithium (1.4 mL of a 1.6 M solution in hexane, 2.2 mmol) and THF (8 mL) were cooled to –30 °C, and diisopropylamine (0.31 mL, 2.2 mmol) was added to produce lithium diisopropylamide (LDA). 3,4-Dimethoxybenzeneacetonitrile (DBA; 12) (0.39 g, 2.2 mmol) was dissolved in THF (7 mL) and added to the LDA solution to give a green solution which was stirred for 1 h and then cooled to –78 °C. (*S*)-5 (0.50 g, 1.07 mmol) dissolved in THF (10 mL) was added. The dark red solution was stirred for 1 h at –78 °C. After methanol was added (0.3 mL, 7.5 mmol) at –78 °C, the solution became bright orange. The solvent was evaporated to give a red oil, which was dissolved in CH$_2$Cl$_2$ and filtered through alumina (grade II-III). The solution was concentrated and transferred to an alumina (grade II-III) column (2.0 × 100 cm). With 8/1 CH$_2$Cl$_2$/ether the two iron complexes **16** and **17** could be separated.

The first yellow band contained **16**, which after evaporation of the solvent gave an orange powder (0.25 g, 42% yield): mp 108–109 °C. IR (KBr): 3060 (w), 3000 (w), 2960 (m), 2940 (m),

Table II. Atomic Coordinates (×10^{-4}) and Equivalent Isotropic Displacement Parameters (×10^{-4} Å^2) for ($R_{Fe}R_C$)-{(η^5-C_5H_5)Fe(CO)(PPh_3)$COCH_2CH_2C$(CN)(^{i}Pr)-[3,4-$C_6H_3(OMe)_2$]} (8)

atom	*x*	*y*	*z*	U_{eq}[a]
Fe(1)	1825(2)	8793(1)	1658(1)	45(1)
P(1)	644(3)	9590(2)	2212(1)	41(1)
C(1)	4167(15)	8211(7)	1788(6)	84(6)
C(2)	3448(20)	7901(8)	1359(4)	78(6)
C(3)	1924(22)	7541(7)	1484(6)	86(6)
C(4)	1696(18)	7622(6)	1984(6)	74(6)
C(5)	3092(20)	8039(7)	2170(4)	64(5)
C(6)	−4(14)	11051(6)	1727(4)	77(5)
C(7)	−972(18)	11648(7)	1502(5)	85(6)
C(8)	−2700(19)	11586(8)	1492(5)	86(7)
C(9)	−3427(15)	10926(8)	1715(5)	86(6)
C(10)	−2464(14)	10329(6)	1937(4)	65(5)
C(11)	−729(14)	10394(6)	1951(3)	43(4)
C(12)	3725(13)	10022(7)	2646(4)	74(5)
C(13)	4766(14)	10461(7)	2958(4)	76(5)
C(14)	4166(16)	11097(7)	3222(4)	72(5)
C(15)	2507(16)	11307(7)	3172(4)	68(5)
C(16)	1430(13)	10870(6)	2860(4)	61(4)
C(17)	2062(14)	10206(6)	2601(3)	44(4)
C(18)	−1758(13)	8432(5)	2510(3)	46(4)
C(19)	−2741(13)	7979(6)	2830(4)	62(4)
C(20)	−2627(13)	8138(7)	3334(4)	66(5)
C(21)	−1579(16)	8758(7)	3481(3)	70(5)
C(22)	−612(13)	9215(6)	3160(3)	56(4)
C(23)	−685(12)	9053(5)	2667(3)	40(4)
C(24)	−2707(13)	10834(7)	145(3)	59(4)
C(25)	−2517(14)	11661(6)	25(4)	58(5)
C(26)	−1363(13)	11904(6)	−325(4)	48(4)
C(27)	−368(12)	11310(7)	−545(3)	46(4)
C(28)	−610(14)	10479(6)	−441(3)	49(4)
C(29)	−1792(16)	10236(6)	−105(3)	55(4)
C(30)	2697(13)	9595(7)	1335(4)	61(5)
O(30)	3384(11)	10098(5)	1109(3)	93(4)
C(31)	−288(13)	8784(6)	1277(3)	48(4)
C(32)	−436(12)	9239(6)	785(3)	55(4)
C(33)	−2132(13)	9096(6)	537(3)	64(4)
C(34)	−2214(17)	9335(6)	−5(3)	58(5)
C(35)	−4115(22)	9170(7)	−200(5)	129(8)
C(36)	−4250(15)	9404(6)	−726(4)	120(7)
C(37)	−4606(21)	8341(9)	−133(5)	183(10)
C(38)	−977(19)	8829(8)	−272(4)	73(6)
N(38)	17(18)	8443(6)	−471(4)	106(6)
C(39)	−2203(15)	13298(6)	−290(4)	95(6)
C(40)	1829(16)	11051(6)	−1112(4)	114(6)
O(1)	−1481(10)	8363(4)	1393(2)	75(3)
O(2)	−1116(9)	12690(4)	−487(2)	65(3)
O(3)	789(9)	11604(4)	−871(3)	65(3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

2840 (w), 2230 (w), 1910 (vs), 1600 (s), 1515 (s), 1480 (m), 1460 (w), 1450 (w), 1432 (s), 1420 (w), 1260 (s), 1240 (s), 1190 (w), 1140 (m), 1090 (s), 1025 (s), 900 (w), 840 (w), 815 (m), 745 (s), 693 (s), 600 (m), 560 (s), 520 (s), 505 (m) cm^{-1}. ^{1}H NMR (250 MHz): δ 7.56–7.18 (30 H, m, phenyl H): 6.79–6.54 (3 H, m, phenyl H); 4.43 (5 H, d, J_{PH} = 1.0 Hz, Cp H); 4.40 (5H, d, J_{PH} = 0.9 Hz, Cp H); 3.91–3.81 (6 H, m, OMe); 3.23–2.16 (5 H, m, CH_2); 1.80–0.96 (3 H, m, CH_2). MS (FD, toluene; *m/e* (relative intensity)): 1110.9 (3), 643.7 (100). $[\alpha]^{25}_D$ = +85° (*c* = 0.4; toluene). Anal. Calcd for $C_{67}H_{57}Fe_2NO_6P_2$ (1110.9): C, 69.27; H, 5.18; N, 1.26. Found: C, 69.38; H, 5.24; N, 1.16.

The second orange band of the chromatograph contained 17, which after removal of the solvent gave a red powder (0.32 g, 38% yield): mp 142–143 °C. IR (KBr): 3070 (w), 3050 (m), 3000 (w), 2955 (m), 2920 (m), 2850 (w), 2225 (w), 2000 (w), 1915 (vs), 1605 (s), 1518 (m), 1482 (m), 1463 (w), 1435 (s), 1415 (m), 1360 (w), 1260 (m), 1182 (m), 1145 (m), 1090 (s), 1070 (w), 1025 (m), 997 (m), 840 (w), 817 (m), 745 (m), 695 (s), 600 (m), 560 (m), 525 (vs), 503 (m) cm^{-1}. ^{1}H NMR (250 MHz): δ 7.67–7.31 (45 H, m, phenyl H); 6.99–6.83 (3 H, m, phenyl H); 4.42 (5 H, d, J_{PH} = 0.8 Hz, Cp H); 4.25 (5 H, d, J_{PH} = 0.9 Hz, Cp H); 4.14 (5 H, d, J_{PH} = 0.9 Hz, Cp H); 3.94 (3 H, s, OMe); 3.89 (3 H, s, OMe); 2.94–2.81 (1 H, m); 2.65–2.35 (4 H, m); 1.89–1.70 (2 H, m); 1.40–1.01 (4 H, m). $^{13}C\{^1H\}$ NMR (62.896 MHz): 221.5–219.8 (m, C≡O); 148.9 (s, *C*OMe); 148.1 (s, *C*OMe); 137.2–136.1 (m, Ph C_{ipso}); 133.6–133.1 (m, Ph C_{ortho}); 130.6 (s, Ph C_{ipso}); 129.6–127.8 (m, Ph C_{para}, Ph C_{meta}); 123.0 (s, CN); 119.5 (s, Ph C_{ortho}); 111.0 (s, Ph C_{ortho}); 109.9 (s, Ph C_{meta}); 85.2 (s, Cp), 85.1 (s, Cp), 85.0 (s, Cp); 68.9 (s, CH); 63.4 (s, CH_2); 61.3 (s, CH_2); 56.1 (s, OMe); 56.0 (s, OMe); 44.5 (s, *C*CN), 38.7 (s, CH_2); 37.7 (s, CH_2); 24.5 (s, CH_2). $[\alpha]^{25}_D$ = +72° (*c* = 0.4; toluene). Anal. Calcd for $C_{91}H_{80}Fe_3NO_8P_3$ (1576.1): C, 69.75; H, 5.15; N, 0.89. Found: C, 69.61; H, 5.05; N, 0.93.

Crystallographic Studies. An orange crystal of (−)-8 ($C_{40}H_{40}$-$FeNO_4P$) obtained from dichloromethane/hexane, having approximate dimensions of 0.15 × 0.20 × 0.25 mm, was mounted on a Syntex R3 diffractometer. The unit cell was determined and refined from 23 reflections (3.8 < 2θ < 13.7°). Relevant crystal and data collection parameters are given in Table I. The structure was solved by using standard Patterson methods, least-squares refinement, and Fourier techniques. All non-hydrogen atoms were refined anisotropically; the hydrogen atoms were included riding in calculated positions (HFIX option of SHELXTL PLUS[26]). All calculations were performed with the SHELXTL PLUS program;[26] scattering factors were taken from ref 27.

Results and Discussion

Reaction of 3,4-Dimethoxy-α-isopropylbenzeneacetonitrile (DIBA, 6) with [(η^5-C_5H_5)Fe(CO)(PPh_3)-COCH=CH_2] (5). Treatment of racemic [(η^5-C_5H_5)Fe(CO)(PPh_3)COMe] (2)[17] in THF at −78 °C with *n*-butyllithium gave the corresponding lithium enolate 3.[21–23] Its reaction with chloromethyl menthyl ether, derived from (−)-menthol, resulted in a 1:1 mixture of the diastereomers of 4 (Scheme I).[19] This reaction is only briefly described in the literature. The two diastereomers can be separated on two silica gel columns (Merck Lobar type B) connected in series, with 4/1 petroleum ether/ether as the eluent. In this way two diastereomerically pure orange powders are obtained. The diastereomeric purity is evident from the cyclopentadienyl resonances in the ^{1}H NMR spectrum. (*S*)-4 (first eluted band) exhibits a doublet at δ 4.423 and (*R*)-4 (second eluted band) a doublet at δ 4.421, the coupling constant ^3J(CpP) being 1.2 Hz in both cases.

The reaction of (*S*)-4 or (*R*)-4 with sodium hydride is described in the literature, giving the enantiomerically pure acryloyl complexes (*S*)-5 and (*R*)-5.[20,24]

The acryloyl complex 5 was treated with the anion obtained by deprotonation of 3,4-dimethoxy-α-isopropylbenzeneacetonitrile (DIBA; 6) with lithium diisopropylamide. *n*-Butyllithium and diisopropylamine were cooled to −30 °C and treated with a solution of DIBA (6) in THF. The solution became yellow, and after the temperature had been lowered to −78 °C the acryloyl complex 5 was added dropwise.

In the first reaction step the anion of 6 adds to the acryloyl complex 5 to form the corresponding enolate 7, which gives the product 8 in 76% yield on subsequent protonation with methanol. However, the enolate 7 competes with the DIBA anion in the addition to the acryloyl complex 5. In this way, additionally, the bis-addition product 9 containing two (η^5-C_5H_5)Fe(CO)(PPh_3) groups is produced after protonation with 19% yield (Scheme II). This type of complex had only been described

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[26] SHELXTL PLUS, Release 4.3, Siemens Analytical X-Ray Instruments, Inc., 1989.

[27] *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

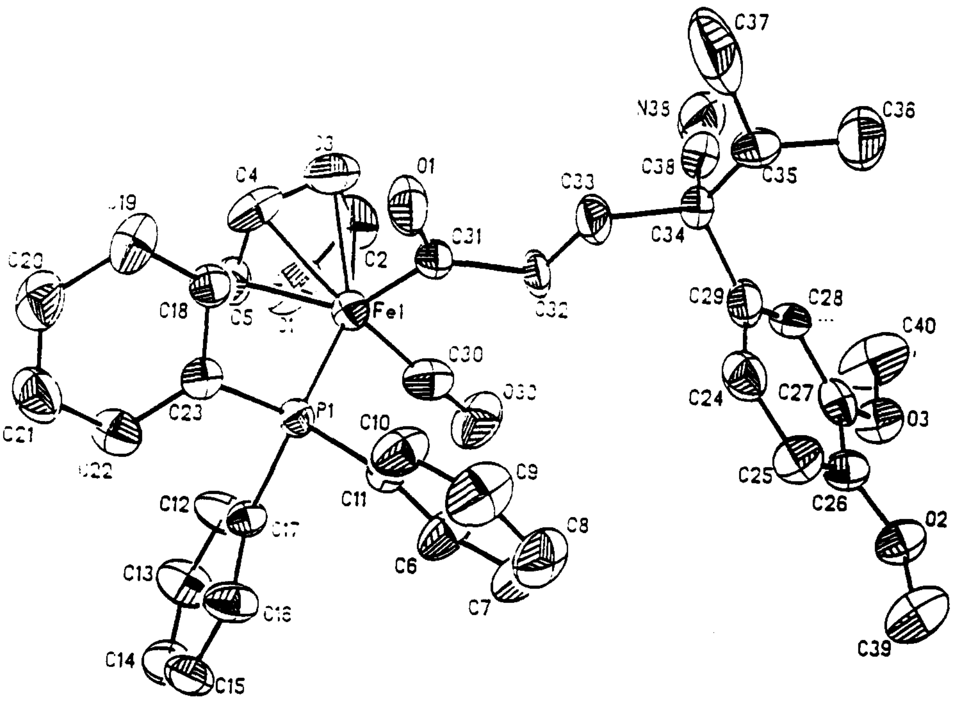


Figure 1. Molecular structure of $(R_{Fe}R_C)$-$\{(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_2CH_2C(CN)(^iPr)[3,4\text{-}C_6H_3(OMe)_2]\}$ (8).

Table III. Selected Bond Lengths (Å) and Angles (deg) for $(R_{Fe}R_C)$-$\{(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_2CH_2C(CN)(^iPr)$-$[3,4\text{-}C_6H_3(OMe)_2]\}$ (8)

	Distances		
Fe(1)-P(1)	2.212(3)	C(32)-C(33)	1.523(14)
Fe(1)-C(30)	1.732(11)	C(33)-C(34)	1.539(13)
Fe(1)-C(31)	1.973(10)	C(31)-O(1)	1.213(12)
C(31)-C(32)	1.546(12)		
	Angles		
C(31)-Fe(1)-P(1)	90.6(3)	C(30)-Fe(1)-C(31)	94.1(4)
C(30)-Fe(1)-P(1)	94.0(4)	O(1)-C(31)-Fe(1)	121.6(7)

once before.[25] The mixture of the complexes 8 and 9 was separated by chromatography on Al_2O_3. (*S*)-5 gave the product (+)-8 with a specific rotation of $[\alpha]^{25}{}_D$ = +58°, whereas (*R*)-5 resulted in (−)-8 with a specific rotation of $[\alpha]^{25}{}_D$ = −58° (c = 0.4; toluene). The specific rotations of the complexes 9, obtained from (*S*)-5 and (*R*)-5, were $[\alpha]^{25}{}_D$ = +75° and $[\alpha]^{25}{}_D$ = −75° (c = 0.4; toluene).

Product 8 contains two stereogenic centers, one at the Fe atom, introduced enantiomerically pure with the acryloyl complexes (*S*)-5 and (*R*)-5, respectively, and one at the C atom, newly formed in the synthesis. Thus, there are two diastereomers in each series with $S_{Fe}S_C$,$S_{Fe}R_C$ and $R_{Fe}S_C$,$R_{Fe}R_C$ configuration, respectively. The diastereomers can be differentiated on the basis of their ^1H NMR spectra. The resonances of the Cp ligands at δ 4.38 and 4.27 are most suitable for the determination of the diastereomeric excess. Integration gives a diastereomer ratio of 82:18. Furthermore, the two doublets of the diastereotopic methyl groups of the two diastereomers have the same intensity ratio, 82:18. The diastereotopic methylene groups form an ABCD system, with the methylene protons of the AB group neighboring the carbonyl group at lower field than the protons of the CD group neighboring the quaternary stereogenic center.

From the 82:18 mixture of the two diastereomers of 8, obtained from (*S*)-5, a single diastereomer can be isolated by fractional crystallization in dichloromethane/ether. At −20 °C the major isomer crystallizes as a yellow powder. After two crystallizations the specific rotation of $[\alpha]^{25}{}_D$ = +64° (c = 0.4; toluene) is constant. The diastereomer separation can be monitored by ^1H NMR spectroscopy. The major diastereomer of 8 exhibits one doublet at δ 4.38 for the Cp resonances and two doublets at δ 1.09 and 0.72 for the diastereotopic methyl resonances of the isopropyl groups. The absolute configuration of the new stereogenic center in (−)-8, obtained from (*R*)-5, was established by X-ray crystallographic analysis (Table II, Figure 1) as $R_{Fe}R_C$. Selected distances and angles are listed in Table III.

Complex 9 contains four stereogenic centers, two at the Fe atoms, introduced enantiomerically pure with the acryloyl complexes (*S*)-5 and (*R*)-5, respectively, and two at the C atoms, newly formed in the synthesis. In principle, the two stereogenic carbon atoms give rise to a total of four diastereomers in each series. However, only the two diastereomers $(S_{Fe}S_{Fe}R_{C_\alpha}R_{C_\gamma})$-9 and $(S_{Fe}S_{Fe}R_{C_\alpha}S_{C_\gamma})$-9 ($(R_{Fe}R_{Fe}S_{C_\alpha}S_{C_\gamma})$-9 and $(R_{Fe}R_{Fe}S_{C_\alpha}R_{C_\gamma})$-9) are obtained experimentally (for the determination of the configurations, see below). In the range of the Cp signals four doublets at δ 4.42, 4.26, 4.20, and 4.17 are observed, two of them having the same intensity (Figure 2). The integral ratio of the more intense to the less intense pair of doublets is 65:35. The two pairs of doublets are assigned to the two different cyclopentadieyl ligands in the two diastereomers $(S_{Fe}S_{Fe}R_{C_\alpha}R_{C_\gamma})$-9 and $(S_{Fe}S_{Fe}R_{C_\alpha}S_{C_\gamma})$-9, arising from (*S*)-5, as indicated in Figure 2 (left side). This assignment is corroborated by the appearance of four doublets for the diastereotopic methyl groups of the isopropyl substituents. The formation of only two diastereomers of 9 means that the addition of the enolate 7, generated in the reaction of the DIBA anion with 5, to the acryloyl complex 5 is highly stereoselective. This is not too surprising, as in this Michael addition a new stereogenic center is built up at the α-position, a process known to be highly stereoselective.[13,15,16] According to the integration of the Cp resonances, the diastereomeric excess is 30% de in favor of $(S_{Fe}S_{Fe}R_{C_\alpha}R_{C_\gamma})$-9.

Thus, the de values of 8 (64%) and 9 (30%) differ significantly, although they arise from the same inter-

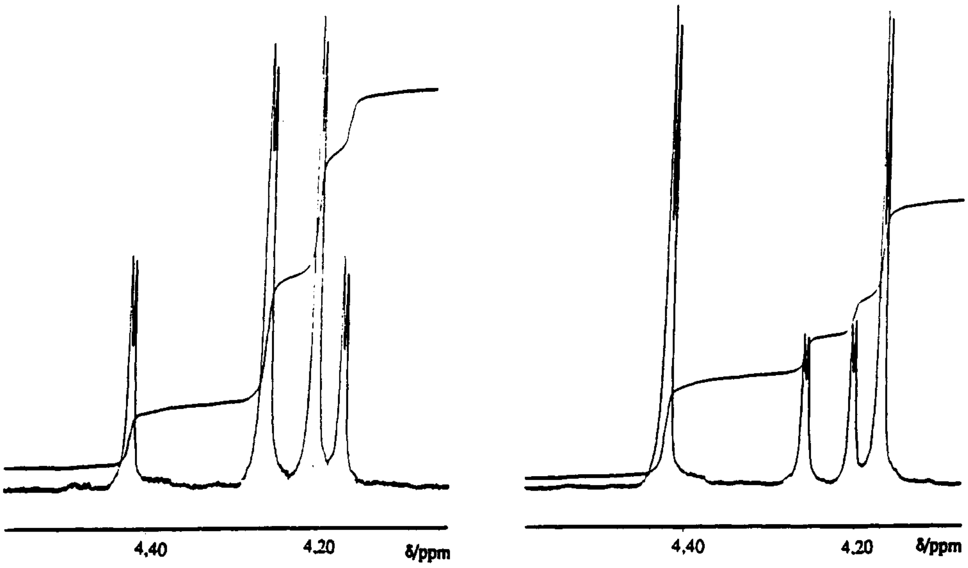
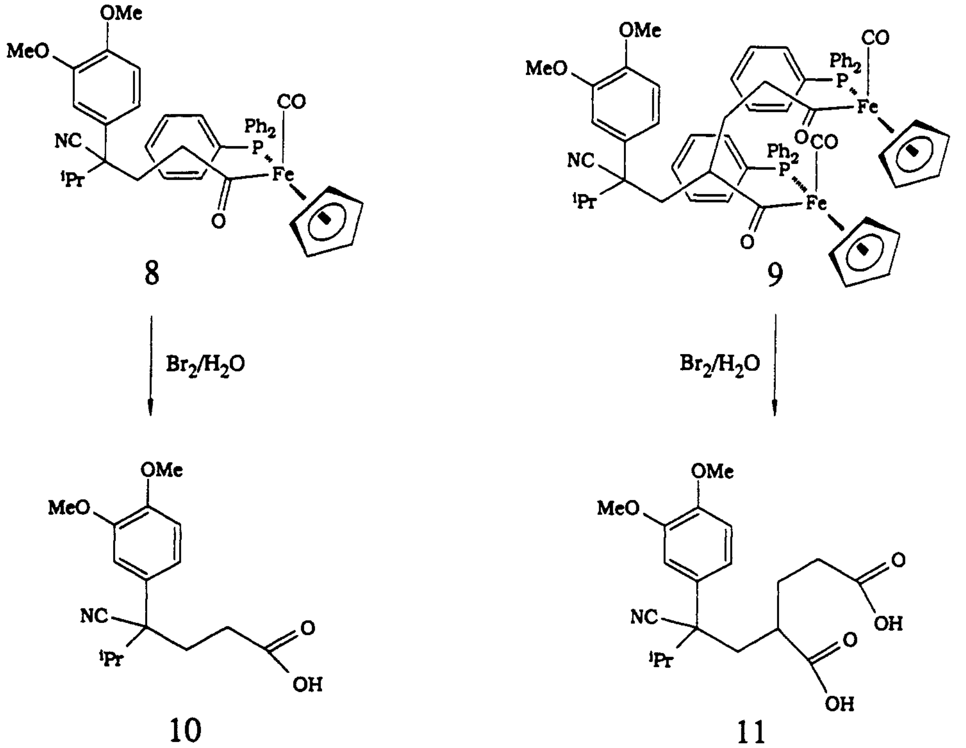


Figure 2. ^{1}H NMR resonances (250 MHz) of the cyclopentadienyl ligands in complex **9**: (left side) variant 1, $(S_{Fe}S_{Fe}R_{C_\alpha}R_{C_\gamma})$-**9** dominating; (right side) variant 2, $(S_{Fe}S_{Fe}R_{C_\alpha}S_{C_\gamma})$-**9** dominating. Cp signals of $(S_{Fe}S_{Fe}R_{C_\alpha}R_{C_\gamma})$-**9** are at 4.26 and 4.20 ppm, and Cp signals of $(S_{Fe}S_{Fe}R_{C_\alpha}S_{C_\gamma})$-**9** are at 4.42 and 4.17 ppm.

Scheme III

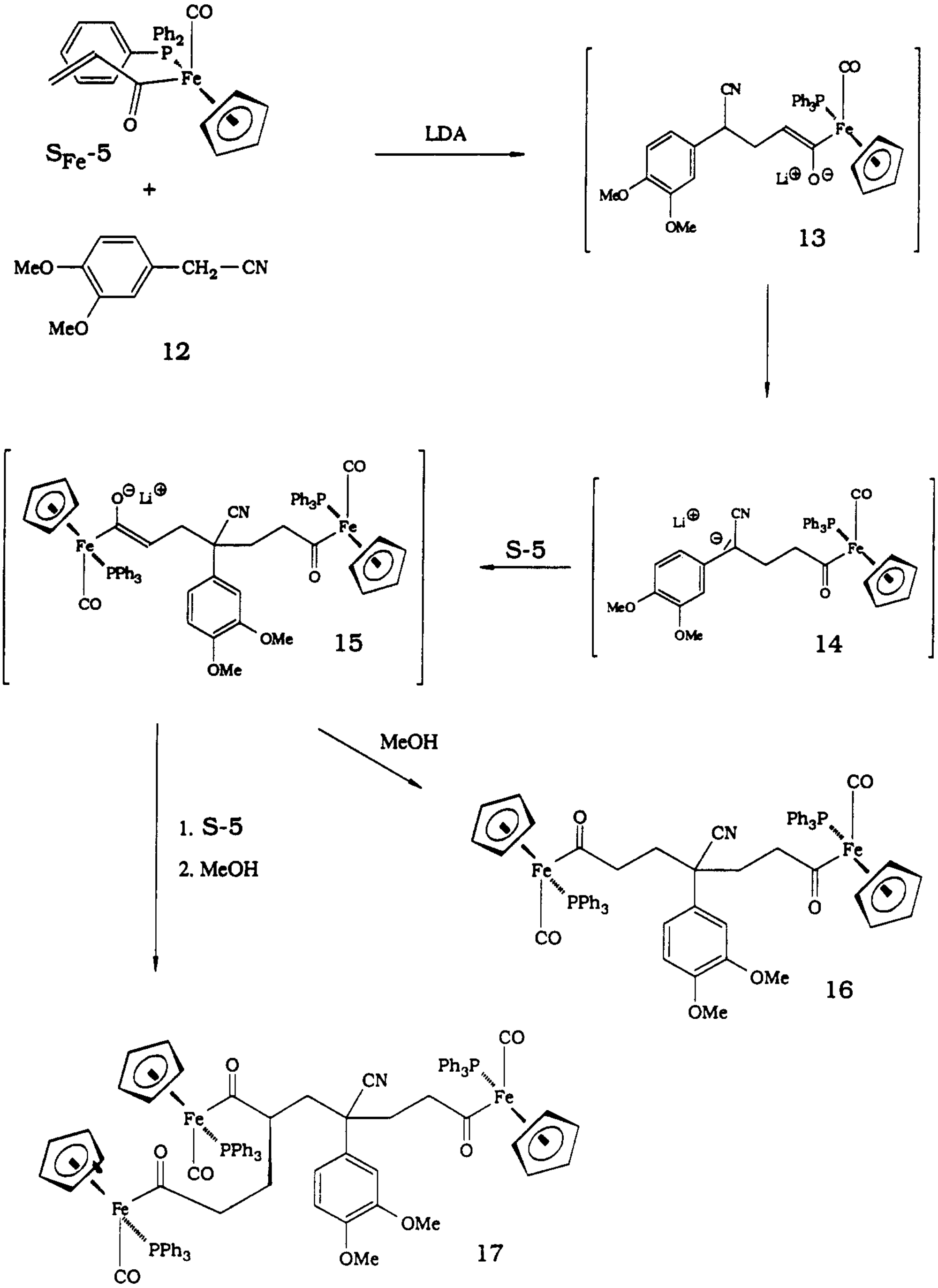


mediate, the diastereomers of the enolate **7**, in which the configuration of the newly formed stereogenic carbon atom at the γ-position is already established. This indicates an appreciable diastereoselectivity in the reaction of the acryloyl complex **5** with the enolate **7**. We investigated how the yields and the de values were affected by a change in the reaction conditions. An increase of the addition time of **5** to the solution containing the DIBA anion from 5 min to 1.5 h did not change the yield ratio of **8**:**9** = 4:1, the de values of **8** and **9** being 64% and 30%, respectively (variant 1). However, inverting the order of addition of the components had a profound effect. When the DIBA anion was added dropwise to **5**, complex **8** was not formed at all and compound **9** was obtained in 50% yield (variant 2). Thus, the inverse addition, in which the concentration of complex **5** is high with respect to the anion of **6**, is the best procedure to synthesize compound **9**. The inverse addition gave compound **9** with a de value of 44%, surprisingly in favor of diastereomer $(S_{Fe}S_{Fe}R_{C_\alpha}S_{C_\gamma})$-**9** (Figure 2, right side), having the specific rotation $[\alpha]^{25}_{D}$ = +92.1° (c = 0.4; toluene).

In another experiment, complex **8**, having a $R_{Fe}R_C$:$R_{Fe}S_C$ diastereomer ratio of 82:18, was treated with an equimolar quantity of n-BuLi at −78 °C and afterwards (R)-**5** was added dropwise to the enolate **7**. After protonation and purification by chromatography, **8** and **9** were obtained in 26% and 16% yield, respectively (variant 3). Complex **8** was enriched to 92% de in favor of $(R_{Fe}R_C)$-**8**, and compound **9** had a de value of 66%, once again in favor of diastereomer $(R_{Fe}R_{Fe}S_{C_\alpha}R_{C_\gamma})$-**9**.

Using the de values and the yields of **8** and **9** in the variants 1 and 2, the de value of the enolate **7** can be

Scheme IV



calculated. For the calculation it is assumed that the minor diastereomer of 7 reacts faster with the acryloyl 5 than the major diastereomer. Hence, which of the diastereomers of 9 predominates depends on the extent of conversion. Only this assumption allows a rationalization of the results. On this basis 45% de is calculated for the enolate 7 (72.5% of $(S_{Fe}S_{C})$-7 and 27.5% of $(S_{Fe}R_{C})$-7). In the Michael conversion of 7 to 9 the minor diastereomer $(S_{Fe}R_{C})$-7 reacts faster with 5 than $(S_{Fe}S_{C})$-7. Therefore, the configurations of the newly formed stereogenic centers in the products can be determined as $(S_{Fe}S_{Fe}R_{C_\alpha}R_{C_\gamma})$-9 and $(S_{Fe}S_{Fe}R_{C_\alpha}S_{C_\gamma})$-9. In variant 1 the major diastereomer of 9 is $(S_{Fe}S_{Fe}R_{C_\alpha}R_{C_\gamma})$-9 or $(R_{Fe}R_{Fe}S_{C_\alpha}S_{C_\gamma})$-9, respectively. For variant 2 the distribution 72% of $(S_{Fe}S_{Fe}R_{C_\alpha}S_{C_\gamma})$-9 and 28% of $(S_{Fe}S_{Fe}R_{C_\alpha}R_{C_\gamma})$-9 is found.

By treatment with bromine in the presence of water,[15] 8 and 9 are converted into $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)Br]$ and the acids 10 and 11 (Scheme III). γ-Cyano-3,4-dimethoxy-γ-isopropylbenzenebutanoic acid (10), a building block for the verapamil synthesis, is known in its (+)- and (−)-forms.[4] 11 is an α-substituted glutaric acid not described in the literature up to now. In the transformation with bromine/water the diastereomer mixture of complex 8 with 64% de gave the acid 10 with a specific rotation of $[\alpha]^{25}_{D} = +23.1°$ ($c = 10.0$; ethanol), corresponding to an enantiomeric excess of 63%. The conversion of diastereomerically pure $(S_{Fe}S_{C})$-8 resulted in the acid (S)-(−)-10 having the specific rotation reported in the literature. In the same way complex 9 was treated with bromine/water to give the dicarboxylic acid 11 as a colorless oil.

Reaction of 3,4-Dimethoxybenzeneacetonitrile (DBA, 12) with $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH{=}CH_2]$ (5). In the addition of DIBA (6) to the acryloyl complex 5 a new stereogenic center at the γ-position of the acyl substituent is formed in the two complexes **8** and **9** with high diastereoselectivity. Further investigations should demonstrate the influence of the isopropyl group on the stereoselectivity of the Michael reaction. Therefore, 3,4-dimethoxybenzeneacetonitrile (DBA, **12**) was deprotonated by lithium diisopropylamide in the same way as described for DIBA (**6**). The acryloyl complex (*R*)-**5** was added dropwise to the green solution of the anion of **12**. The anion of **12** added to **5** to form the enolate **13**, which should give the corresponding compound after protonation. However, in this reaction no product comparable to complex **8** was found.

The enolate **13**, generated in the addition of the anion of **12** to complex **5**, has the carbanionic center at the α-position of the acyl substituent. However, **13** also contains an acidic proton at the γ-position of the acyl substituent. Obviously, in a fast reaction the anion **14** with the carbanionic center at the γ-position is formed, its negative charge being stabilized by the cyano and phenyl substituents. This new anion adds to the acryloyl complex **5**, and the bis-addition compound **16** is obtained after treatment with methanol in 42% yield (Scheme IV).

The enolate **15**, formed in the addition of the anion **14** to complex **5**, competes with the anion **14** in adding to another complex **5**. In this way the tris-addition compound **17** is produced after protonation with 38% yield. The mixture of the complexes **16** and **17** was separated by chromatography on Al_2O_3. (*S*)-**5** gave the complexes **16** and **17** with a specific rotation of $[\alpha]^{25}{}_D = +85°$ and $[\alpha]^{25}{}_D = +72°$ ($c = 0.4$; toluene), respectively.

Complex **16** contains only the two stereogenic centers at the Fe atoms, introduced enantiomerically pure. The quaternary C atom is not a stereogenic center, because it bears two identical substituents. The resonances at δ 4.43 and 4.40, having an integral ratio of 1:1, correspond to the diastereotopic Cp ligands in **16**.

Complex **17** contains five stereogenic centers, three at the Fe atoms, introduced enantiomerically pure with the acryloyl complex (*S*)-**5**, and two at the C atoms, newly formed in the synthesis. The stereogenic center at the α-position of the acyl substituent is built up with the known high stereoselectivity. The γ-position becomes stereogenic on addition of the enolate **15** to the acryloyl complex **5**. The structure of complex **17** was determined by NMR spectroscopy. Three doublets at δ 4.42, 4.25, and 4.14 of the same intensity are observed for the three different Cp ligands and two singlets of the same intensity for the two different methoxy groups. This indicates that only one diastereomer of complex **17** is formed, in contrast to the case for complex **9**. Thus, in the reaction of the anion **14** with the acryloyl complex **5**, the enolate **15** was built up with a diastereoselectivity of nearly 100%, whereas the reaction of the anion of **6** with complex **5** gave complex **9** with a diastereoselectivity of only 64%.

The structure of the complex **17** was determined on the basis of a $^{13}C\{^1H\}$ NMR spectrum in combination with a DEPT spectrum. The resonances could be assigned unambiguously, including the five CH_2 signals and the signal of the newly formed quaternary C atom.

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Supplementary Material Available: Tables of atomic coordinates and equivalent isotropic displacement parameters, bond lengths, bond angles, anisotropic displacement parameters, and H atom coordinates and isotropic displacement parameters for $(R_{Fe}R_C)$-$\{(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_2CH_2C(CN)(^iPr)[3,4\text{-}C_6H_3(OMe)_2]\}$ (**8**) (5 pages). Ordering information is given on any current masthead page. Further details of the structure determination have been deposited with the number CSD-57211 at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, Federal Republic of Germany.

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