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(Phenylthio)acetyliron complex [(η^5-C_5H_5)Fe(CO)(PPh_3)$COCH_2SPh$] Configuration of aldols

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Abstract

(Phenylthio)acetyliron complex **3** was obtained by reaction of the anion generated with butyllithium from acetyliron complex **4** with diphenyl disulphide. Alkylation and aldol reactions of the anion of **3** were investigated. X-Ray structural determination of four aldols and reactions with aldehydes in the presence of Et_2Al^+ or Sn^{2+} permitted the assignment of configuration to all aldols.

Keywords: Acyliron complexes, phenylthioacetyliron, crystal structure.

Introduction

Acylirons (cyclopentadienyl-carbonyl-triphenylphosphine-acylirons, **1**), stable, readily available iron(II) complexes have found applications in organic synthesis as chiral auxiliaries [1]. These applications are connected with the possibility of elaboration of the acyl ligand *via* highly stereoselective alkylation or aldol reactions of the anion generated from **1** with strong bases. Mild oxidative decomplexation affords acyl ligand in the form of an ester or amide, depending on the medium employed. Racemic acylirons can be efficiently resolved into enantiomers on optically active chromatographic columns [2].

Recently we have studied the synthesis and reactions of (methylthio)acetyliron (**2**). This complex underwent readily acyl ligand expansion reactions [3]. Decomplexation of the products was concomitant with decarbonylation and compounds containing the MeSCH grouping were obtained. Condensation of the anion of **2** with sugar aldehydes was investigated [4].

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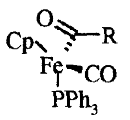
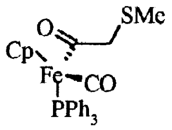
We next turned our attention to (phenylthio)acetyliron [**3**, (η^5-C_5H_5)Fe(CO)(PPh$_3$)COCH$_2$SPh], an acyliron complex capable of providing a PhSCH group, a prochiral structural unit, in acyl ligand expansion reactions. This unit offers valuable synthetic potential in further elaboration of carbon skeletons.



1



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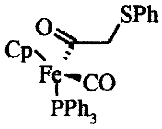

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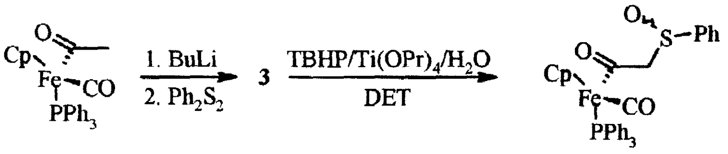


4 **5**

Results and discussion

The synthesis of **3** followed the route used for the synthesis of **1** [1]. Deprotonation of the racemic acetyliron complex (**4**) with butyllithium at -78°C followed by reaction with diphenyl disulphide at the same temperature led to the (phenylthio)acetyliron complex [(η^5-C_5H_5)Fe(CO)(PPh$_3$)COCH$_2$SPh] in high yield (80% after crystallisation). Orange crystals of **3** are air stable and can be stored in refrigerator without decomposition for several months.

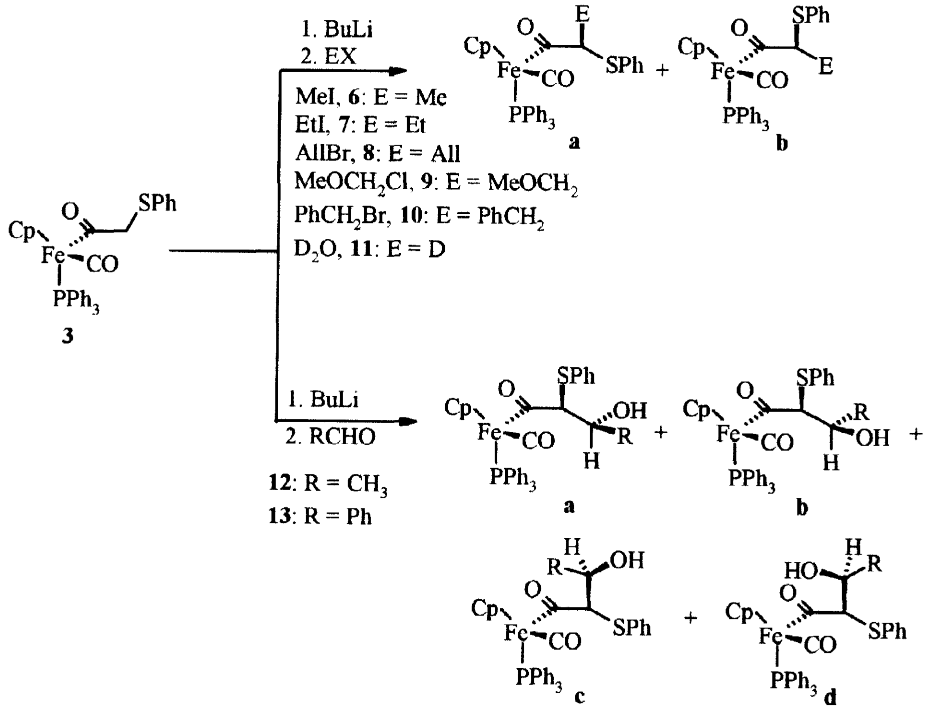
Non-symmetrical sulphides can be oxidized to optically active sulphoxides [5,6] with the Sharpless oxidant [t-butyl hydroperoxide, Ti(OiPr)$_4$, (-)- or (+)-diethyl tartrate]. Oxidation of *rac*-**3** according to this method [using D(-)-diethyl tartrate, D(-)-DET] led to two stereoisomeric sulphoxides **5a** and **5b** in 45% yield and 3:1 proportion. Regenerated **3** was racemic. Optical purity of sulphoxides **5a** and **5b** was tested with ^{1}H NMR spectra using the Pirkle alcohol [R(-)-1-(9-anthryl)-2,2,2-trifluoroethanol] to show only a weak enrichment (approx. 1.2:1) in one of the enantiomers. When the oxidation was performed in the presence of L(+)-DET, the proportion of **5a** and **5b** increased to 12:1 (51%), however, enantiomeric purity of products remained within the same limits. It should be noted that Davies and Gravatt [7], starting from R-propionyliron (enantiomer of **1**, R=Et), prepared α-(phenylthio) derivative of $R_{Fe}S_\alpha$ configuration which was transformed into optically pure R-sulphoxide. This result clearly indicated that the presence of a chiral center at the α carbon atom was essential for the stereospecific oxidation of the sulphur atom.

Expansion of the acyl ligand in **3** occurs *via* the anion generated with butyllithium. The anion was reacted with primary alkyl halides: methyl and ethyl iodides, allyl bromide, methoxymethyl chloride, and benzyl bromide to form mixtures of α-alkylated products (**6a,b-10a,b**). Secondary alkyl halides (isopropyl iodide and *sec*-butyl bromide) were unsuccessful in the reaction.

The majority of the reactions were carried out at -20 °C to afford good and very good yields of products. At -78 °C, only methyl iodide reacted fast enough, while the other electrophiles did not react at all, indicating a lower reactivity of the anion of **3** compared to **2** [1]. The proportion of **a** and **b** stereoisomers was 3 - 14 : 1. The configuration of the methylated products could be deduced from the ^{1}H NMR shift of the Me group signal: for the **6a** stereoisomer ($R_{Fe}R_\alpha/S_{Fe}S_\alpha$) it appeared at δ 1.41 and for the **6b** ($R_{Fe}S_\alpha/S_{Fe}R_\alpha$) at δ 0.60 (in the proximity of the PPh_3 shielding zone) [8]. This interpretation is based on the well-proven formation of the E-enolate which is attacked by the electrophile from the side opposite to the bulky triphenylphosphine ligand [9]. The configuration of the major alkylation products was assumed to be analogous, i.e. $R_{Fe}R_\alpha/S_{Fe}S_\alpha$. Quenching of the anion of **3** with D_2O at -78 °C led to monodeuterated complexes **11a,b** in 7.5:1 proportion.

*Aldol reactions of **3***

Aldol reactions of acylirons occur readily at -78 °C and provide stereoisomeric aldols in high yield. The reactions performed in the presence of Li^+ cation were, however, not stereoselecitve [10]. Distinct stereoselectivities can be obtained replacing Li^+ with other counter cations like Et_2Al^+ [11] or Sn^{2+} [12] . Diethylaluminum cation promotes the formation of $R_{Fe}R_\beta/S_{Fe}S_\beta$ and tin(II) - promotes $R_{Fe}S_\beta$/ $S_{Fe}R_\beta$ aldols.



Condensation of the anion of **3** with acetaldehyde leads to a mixture of four aldols **12a-d** in 1:1.3:4.3:3.5 proportion and 90% yield. The individual products have been isolated by chromatography. The assignment of configuration to all four products, knowledge of which is essential for further exploitation of these products, was based on X-ray structural determinations performed for crystalline **12a** and **12b** (*vide infra*). The configuration of the remaining two aldols, **12c** and **12d** as $R_{Fe}R_{\alpha}R_{\beta}/S_{Fe}S_{\alpha}S_{\beta}$ and $R_{Fe}R_{\alpha}S_{\beta}/S_{Fe}S_{\alpha}R_{\beta}$ respectively, was deduced from the results of the condensation reaction carried out in the presence of Et_2Al^+ and Sn^{2+} cations in which **12c** or **12d** were obtained as the major products (cf. Experimental).

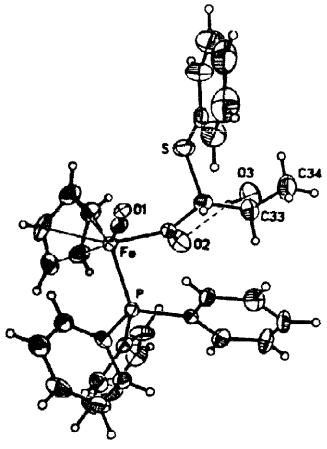
Similar results have been obtained when the anion of **3** (Li^+) was condensed with benzaldehyde: four aldols **13a** - **13d** were formed in 1.1:1:1.5:2.7 ratio (88%) and separated by chromatography. The structures of **13a** and **13b** were also determined by X-ray structural analyses. The configurations of **13c** and **13d** were deduced (as for **11c,d)** as $R_{Fe}R_{\alpha}R_{\beta}/S_{Fe}S_{\alpha}S_{\beta}$ and $R_{Fe}R_{\alpha}S_{\beta}/S_{Fe}S_{\alpha}R_{\beta}$, respectively.

*The molecular structure of complexes **12a, 12b, 13a,** and **13b***

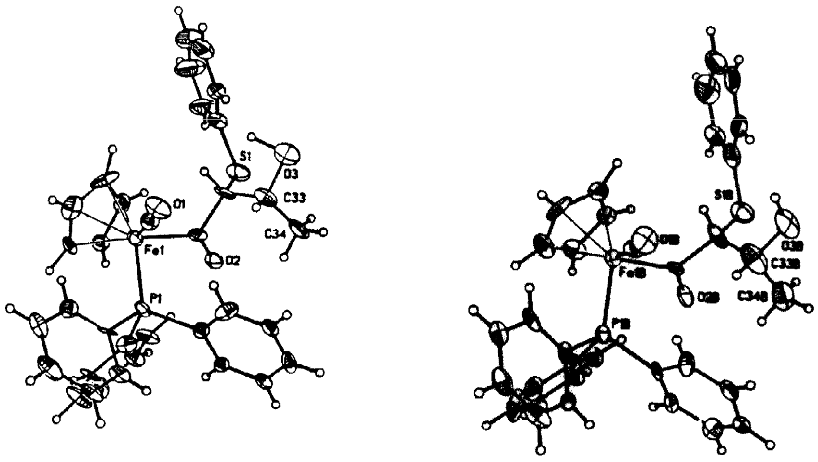
The molecular structures of several acylirons have been investigated by single crystal X-ray diffraction methods [9,13-19]. Davies and Seeman [9] describe these structures in terms of a pseudo-octahedral arrangement of ligands around the iron atom. The bond angles C_{CO}-Fe-C_{acyl}, C_{CO}-Fe-P, and C_{acyl}-Fe-P are near to 90°, and the Cp-Fe-P angle is *ca.* 125° (Cp is defined as the centroid of the cyclopentadienyl ligand). The CO ligand is approximately *anti* oriented towards the acyl carbonyl group. Chirality of the propeller-like PPh_3 ligand is, in all cases studied until now, always the same: $R_{Fe}P_{P\text{-}Ph}$ ($S_{Fe}M_{P\text{-}Ph}$) [P - plus (clockwise), M - minus (anticlockwise)]. (The acute torsion angles Fe-P-C-C_{ortho} are always negative for the P twist, and positive for the M twist.)

Crystals of **12a,b** and **13a,b**, suitable for X-ray measurements, were obtained by crystallization from ethyl acetate - heptane solution. Selected interatomic bond distances, angles, and torsion angles are presented in Table 1. The structures of all four complexes are shown in Figure 1; S_{Fe} enantiomers are shown. Crystals of **12b** and **13a** each contained two conformers in the asymmetric unit.

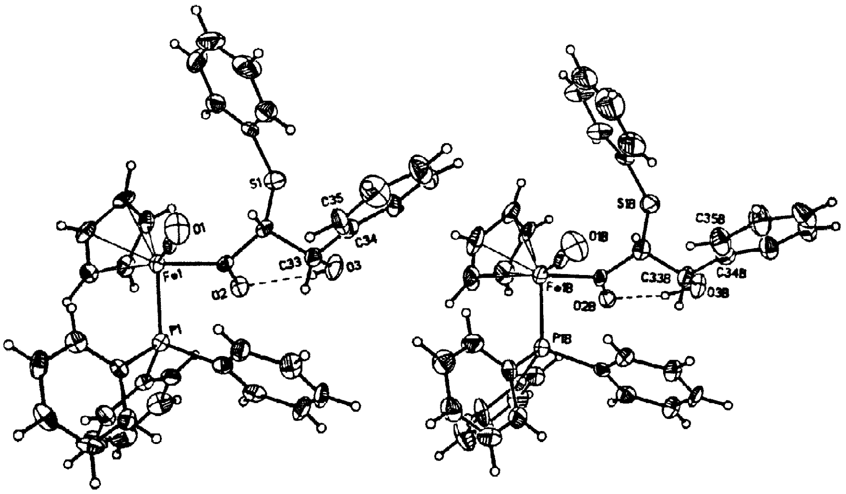
The configuration of **12a** and both conformers of **13a** are $S_{Fe}R_{\alpha}S_{\beta}/R_{Fe}S_{\alpha}R_{\beta}$ and that of both conformers of **12b** and of **13b** are $S_{Fe}R_{\alpha}R_{\beta}/R_{Fe}S_{\alpha}S_{\beta}$. From the data it follows that the structures of **12a,b** and **13a,b** correspond closely to the generalized picture of other acetyliron complexes: the C6-Fe-C25, C6-Fe-P, and C25-Fe-P angles are approximately 90° and are characteristic of a pseudo-octahedral arrangement (Table 1).



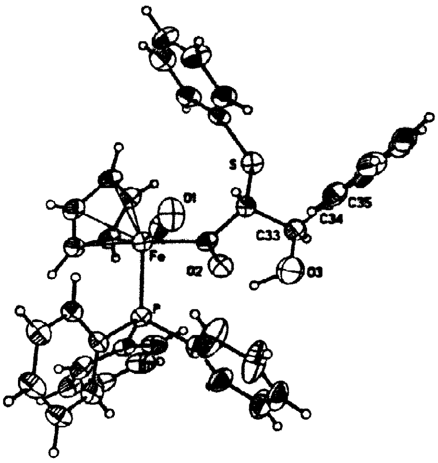
12a



12b



13a



13b

Fig. 1 ORTEP drawings of **12a**, **12b** (both conformers), **13a** (both conformers) and **13b**.

Table 1

Selected bond lengths, angles and torsion angels in complexes 12a, 12b, 13a and 13b; esds in parentheses

Bond lengths	**12a**	**12b**		**13a**		**13b**
C1, C2, C3, C4, C5-Fe	2.099 (7)	2.097 (12)	2.087 (12)	2.098 (7)	2.101 (8)	2.108 (5)
	2.099 (7)	2.109 (11)	2.107 (11)	2.103 (7)	2.106 (7)	2.109 (5)
	2.102 (7)	2.110 (13)	2.121 (13)	2.116 (7)	2.118 (7)	2.113 (5)
	2.120 (7)	2.128 (12)	2.125 (12)	2.122 (7)	2.133 (8)	2.132 (5)
	2.133 (7)	2.132 (12)	2.146 (12)	2.132 (7)	2.132 (8)	2.146 (5)
Fe-P.	2.200 (2)	2.206 (4)	2.199 (4)	2.207 (2)	2.208 (2)	2.198 (2)
Fe-C25	1.943 (6)	1.972 (13)	1.939 (12)	1.951 (7)	1.950 (8)	1.950 (5)
Fe-C6	1.736 (7)	1.766 (13)	1.743 (13)	1.728 (8)	1.737 (9)	1.735 (6)
Fe-Cp	1.741	1.743	1.752	1.741	1.739	1.745
Bond angles						
C25-Fe-C6	95.8 (3)	94.4 (5)	93.9 (6)	95.1 (3)	96.0 (3)	92.8 (2)
C6-Fe-P	92.7 (2)	92.9 (4)	93.0 (4)	92.5 (2)	92.6 (3)	95.3 (2)
C25-Fe-P	89.6 (2)	91.1 (4)	91.1 (4)	90.9 (2)	91.9 (2)	93.0 (2)
Cp-Fe-P	126.0	126.0	126.9	126.0	126.8	122.5
Cp-Fe-C6	124.4	125.5	125.6	125.1	124.4	125.8
Cp-Fe-C25	119.4	118.0	117.2	118.4	116.9	119.2
Torsion angles						
C6-Fe-C25-O2	173.7	136.5	142.3	156.9	156.8	147.5
S-C26-C25-O2	100.7	52.9	49.2	71.2	71.8	73.6
C25-C26-C33-C34	-172.9	56.1	70.7	-164.3	-164.1	-168.0
C26-S-C27-C32	-19.4	35.6	46.1	57.2	-139.0	50.2
Fe-P-C7-C12	54.6	56.5	56.3	57.7	53.6	68.1
Fe-P-C13-C14	14.0	19.8	21.9	15.4	18.3	-8.9
Fe-P-C19-C24	63.7	54.4	63.5	69.8	69.9	65.7

The Cp-Fe-P angles correspond to 122-127°. The Cp-Fe, Fe-P and Fe-C bond lenghts are nearly identical to those in other acylirons [15-19].

Several conclusions can be drawn from the torsion angles. The C6-Fe-C25-O2 angle in all 6 structures indicates an approximately *anti* arrangement of the CO and acyl carbonyl groups. Hydrogen bonding between the β-OH and carbonyl oxygen atom (O3-H30-O2) was found for **12a**, both conformers of **13a,** and for **13b**. In these structures the carbon atom chain C25-C26-C33-C34 is in an antiperiplanar arrangement, whereas in conformers of **12b** it is in the (+)synclinal form. Judging from the torsion angles of both complexes of **12a**, the structural differences are minor. In case conformers of **13a**, the torsion angles are also similar except for the C26-S-C27-C32 angle which indicates a different position of the SPh group relative to the Cp ligand. The fourth chirality unit of the complexes, i.e. the PPh_3 propeller, displays posivite acute torsion angles Fe-P-C7-C12 (-C13-C14, -C19-C24) indicating the M configuration. There is, however, one exception: the Fe-P-C13-C14 angle in **13b** is negative indicating disorder in the arrangement of the triphenylphosphine ligand.

Conclusions

(Phenylthio)acetyliron (**3**) can be readily obtained from acetyliron (**4**). The anion of **3** can be alkylated with reactive primary alkyl halides to form stereoisomers $R_{Fe}R_{\alpha}/S_{Fe}S_{\alpha}$ as the dominating products. Reactions with acet- or benzaldehyde yield crystalline aldols. In each case the structures of two of the four aldols could be unequivocally determined by X-ray analysis.

The configuration of the remaining two pairs was disclosed by experiments with counterions (Et_2Al^+ or Sn^{2+}). The reactions with both aldehydes, performed in the presence of Li^+, are unselective and yield all four aldols in similar amounts. When counterions are added, the products derived from the E-enolate clearly dominate: $R_{Fe}R_{\alpha}R_{\beta}/S_{Fe}S_{\alpha}S_{\beta}$ (for Et_2Al^+) and $R_{Fe}R_{\alpha}S_{\beta}/S_{Fe}S_{\alpha}R_{\beta}$ (for Sn^{2+}).

Experimental section

General methods

All manipulations of organometallic complexes were performed under argon. Tetrahydrofuran (THF) was distilled from potassium under a stream of argon prior to use. Butyllithium was used as a 2.5 M solution in hexane. TLC was performed on Silica Gel HF-254 and column chromatography on Silica Gel 230 - 400 mesh (Merck). ^1H and ^{13}C NMR spectra were recorded with a Varian AC-200 (200 MHz) spectrometer for solutions in $CDCl_3$. Signals of aromatic protons are omitted in the description of spectra. Coupling constant $J_{Cp,P}$ was approx. 1.3 Hz. High resolution mass spectra (HR-MS) were measured with an AMD-604 mass spectrometer. IR spectra were recorded on a Perkin -Elmer 1640 FT-IR spectrophotometer.

$CpFe(CO)(PPh_3)COCH_2SPh$ (3)

A solution of the acetyliron complex **4** (45.4 g, 100 mmol) [20,21] in THF (200 ml) was cooled to -78 °C and butyllithium (50 ml of a 2.5 M solution in hexane, 1.25 mol/eq) was added. After 30 min., a solution of diphenyl disulphide (27.3 g, 1.25 mol/eq) in THF (50 ml) was added dropwise and the mixture was stirred at -78°C for 2 h. The mixture was allowed to attain room temperature and sat. aq. ammonium chloride solution (200 ml) was added. The solution was extracted with dichloromethane, the extract dried, and then concentrated to approx. 200 ml. This solution was filtered through a short alumina column. The effluent was concentrated to dryness and the residue was crystallized from heptane-ethyl acetate: 45 g (80%), dark-red crystals, m.p. 157-159 °C. IR (KBr): ν_{max} 1900, 1622 cm^{-1}. ^1H NMR: δ 4.43 (d, 5H, Cp), 4.18 and 3.59 (ABq, 2 H, *J* 15.9 Hz, CH_2). HR-MS (LSIMS): for $C_{32}H_{28}FeO_2PS$ $(M+H)^+$ calc.: 563.0897. Found: 563.0890. Anal. Found: C, 67.97; H, 4.64. $C_{32}H_{27}FeO_2PS$. Calc.: C, 68.34; H, 4.84.

(η^5-C_5H_5)(CO)(PPh_3Fe)$COCH_2S(O)Ph$ (5)

To a solution of diethyl tartrate (DET, 1.71 ml) in dichloromethane (50 ml) titanium(IV) isopropoxide (1.49 ml) and water (90 : 1) were added. After 20 min of stirring **3** (2.81 g, 5 mmol) was added, the temperature was lowered to -20 °C, and *tert*-butyl hydroperoxide (2.1 ml of a 2.6 M solution in toluene) was added. After 18 h at -20 °C water (2 ml) was added, the mixture was allowed to attain room temperature and then was filtered through a layer of Celite. Aq. 25% NaOH solution (20 ml) was added and the mixture was intensively stirred for 1 h. The organic layer was dried and concentrated. The residue was purified on a silica gel column with hexane-ethyl acetate, 1:2. Unchanged **3** was recovered and the stereoisomeric sulphoxides **5a** and **5b** were separated by crystallization from hexane-dichloromethane.

Yield of **5a** and **5b** with D(-)-DET: 1.3 g (45%), proportion: 3:1. With L(+)-DET: 1.46 g (51%), proportion: 12:1.

5a: orange crystals, m.p. 165-167 °C. IR (KBr): 1910, 1628 cm^{-1}. ^1H NMR: δ, 4.51 (d, 5 H, Cp), 4.43, 3.24 (ABq, 2 H, J_{AB} 15.8 Hz, H-2,2'). Anal. Found: C, 66.70; H, 4.88. $C_{32}H_{27}FeO_3PS$. Calc.: C, 66.45; H, 4.70.

5b: orange crystals, m.p. 170-171 °C. IR (KBr): 1905, 1609 cm^{-1}. ^1H NMR: δ, 4.24 (d, 5 H, Cp), 4.14, 3.75 (ABq, 2 H, J_{AB} 15.4 Hz, H-2,2'). Anal. Found: C, 66.72; H, 4.83.

The ^1H NMR spectrum of recovered **3** recorded in the presence of R(-)-1-(9-anthryl)-2,2,2-trifluoroethanol showed equal peaks of both enantiomers. Analogous spectra of **5a** and of **5b** showed only weak differentiation of peaks belonging to both enantiomers.

Alkylation of (η^5-C_5H_5)(CO)(PPh_3)$FeCOCH_2SPh$ (3). General method.

To a cooled (-78°C) solution of **4** (560 mg, 1 mmol) in THF (10 ml), 0.5 ml (1.25 mol/eq) of butyllithium solution was added and the resulting dark red solution was stirred at -78 °C for 15 min. Alkyl halide (0.2 ml) or D_2O in THF (1:1, 0.2 ml) was added and the solution was stirred at -78°C for 1 h. The reaction was quenched with methanol (2 ml) and the solvent was removed *in vacuo*. The residue was dissolved in dichloromethane and the solution was filtered through a column filled with alumina (Grade V). The filtrate was concentrated under diminished pressure and the mixture of products was separated from the unreacted substrate by flash chromatography with a mixture of ether and hexane (1 : 8) as eluent. The proportion of stereoisomers was determined by integration of the ^{1}H NMR Cp signals. Crystallisation from a mixture of ethyl acetate and hexane afforded pure products as orange-coloured crystals.

Deuteration was performed as above by addition of D_2O in THF (1:1, 0.2 ml) to the anion generated from **3**.

(η^5-C_5H_5)(CO)(PPh_3)FeCOCH(SPh)CH_3 (**6**): 547 mg (95%). m.p.: 148-151 °C. IR (KBr): 1919, 1597 cm^{-1}. LSIMS (NBA): 577 $(M + H)^+$, 520. HRMS (LSIMS): for $C_{33}H_{30}FeO_2PS$ $(M + H)^+$ calc.: 577.1054. Found: 577.1062. Anal. for $C_{33}H_{29}FeO_2PS$ Calc.: C, 68.76; H 5.07%. Found: C, 68.77; H, 5.00%.

6a.^{1}H NMR ($CDCl_3$): δ 4.49 (d, 5 H, Cp), 4.04 (q, 1 H, $J_{2,3}$ 7.2 Hz, H-2), 1.41 (d, 3 H, H-3).

6b ^{1}H NMR ($CDCl_3$): δ 4.46 (d, 5 H, Cp), 4.17 (q, 1 H, $J_{2,3}$ 6.8 Hz, H-2), 0.60 (d, 3 H, H-3).

6a : **6b**; 3 : 1 (-20 °C), 8 : 1 (-78 °C)

(η^5- C_5H_5)(CO)(PPh_3)FeCOCH(SPh)CH_2CH_3 (**7**):

7a. 340 mg (58%), m.p. 156-158 °C. IR (KBr): 1904, 1617 cm^{-1}. LSIMS (NBA): 591$(M + H)^+$. HRMS (LSIMS): for $C_{34}H_{32}FeO_2PS$ $(M + H)^+$ Calc.: 591.1210. Found: 591.1201. Anal. For $C_{34}H_{31}FeO_2PS$ Calc.: C, 69.16; H, 5.29%. Found: C, 68.96; H, 5.22%. ^{1}H NMR ($CDCl_3$): δ 4.46 (d, 5 H, Cp), 4.10 (t, 1 H, $J_{2,3}{\approx}J_{2,3'}$ 5.2 Hz, H-2), 2.04, 1.72 (AB, 2 H, $J_{3,3'}$ 14.4 Hz, H-3, H-3'), 0.87 (t, 3 H, $J_{4,3}$ 7.3 Hz, H-4).

7b. 20 mg (3%), m.p. 153-154 °C. ^{1}H NMR ($CDCl_3$): δ 4.40 (d, 5 H, Cp), 3.95 (dd, 1 H, $J_{2,3}$ 3.7, $J_{2,3'}$ 9.1 Hz, H-2), 1.13, 0.81 (m, 2 H, $J_{3,3'}$ 14.5 Hz, H-3, H-3'), 0.55 (t, 3 H, $J_{4,3}$ 7.0 Hz, H-4).

7a : **7b**; 8 : 1 (-20 °C).

(η^5- C_5H_5)(CO)(PPh_3)FeCOCH(SPh)CH_2CH=CH_2 (**8**):

8a. 400 mg (66%), m.p. 153 - 155 °C. IR (KBr): 1911, 1612 cm^{-1} LSIMS (NBA): 603 $(M + H)^+$. HRMS (LSIMS): for $C_{35}H_{32}FeO_2PS$ $(M + H)^+$ Calc.: 603.1210. Found: 603.1213. Anal. For $C_{35}H_{31}FeO_2PS$ Calc.: C, 69.77; H, 5.19%. Found: C, 69.51; H, 5.08%. ^{1}H NMR ($CDCl_3$): δ 5.87 (m, 1 H, H-4), 5.00 (m, 2 H, H-5), 4.45 (d, 5 H, Cp), 4.13 (t, 1 H, $J_{2,3}{\approx}J_{2,3'}$ 5.3 Hz, H-2), 2.75, 2.45 (m, 2 H, $J_{3,3'}$ 15.2, $J_{3,4}$ 6.8, $J_{3',4}$ 6.2 Hz, H-3, H-3').

8b. 75 mg (12%), m.p. 159-161 °C. ^{1}H NMR ($CDCl_3$): δ 5.47 (m, 1 H, H-4), 4.78 (m, 2 H, H-5), 4.40 (d, 5 H, Cp), 3.98 (dd, 1H, $J_{2,3}$ 3.7, $J_{2,3'}$ 10.1 Hz, H-2), 1.82, 1.41 (m, 2 H, $J_{3,3'}$ 14.8, $J_{3,4}$ 7.3, $J_{3',4}$ 6.7 Hz, H-3, H-3').

8a : **8b:** 3.5 : 1 (-20 °C).

(η^5-C_5H_5)(CO)(PPh_3)FeCOCH(SPh)CH_2OCH_3 (**9**): 551 mg (91%), m.p. 165-168 °C. IR (KBr): 1907, 1610 cm^{-1}. LSIMS (NBA): 607 $(M + H)^+$. HRMS (LSIMS): for $C_{34}H_{32}FeO_3PS$ (M

+ H)$^+$ Calc.: 607.1159. Found: 607.1165. Anal. For $C_{34}H_{31}FeO_3PS$ Calc.: C, 67.33; H, 5.16%. Found: C, 67.41; H, 5.24%.

9a. ^{1}H NMR (C_6D_6): δ 4.77 (dd, 1 H, $J_{2,3'}$ 3.5, $J_{2,3}$ 9.0 Hz, H-2), 4.46 (d, 5 H, Cp), 4.03 (t, 1 H, H-3), 3.57 (dd, 1 H, $J_{3,3'}$ 9.3 Hz, H-3'), 3.01 (s, 3 H, OMe).

9b. ^{1}H NMR ($CDCl_3$): δ 4.44 (d, 5 H, Cp), 3.07 (s, 3 H, OMe).

9a : **9b**: 14 : 1 (-20 °C).

(η^5- C_5H_5)(CO)(PPh_3)FeCOCH(SPh)CH_2Ph (**10**): 567 mg (87%), m.p. 143-145 °C. IR (KBr): 1917, 1590 cm^{-1}. LSIMS (NBA): 653 (M + H)$^+$. HRMS (LSIMS): for $C_{39}H_{34}FeO_2PS$ (M + H)$^+$ Calc.: 653.1367. Found: 653.1368. Anal. For $C_{39}H_{33}FeO_2PS$ Calc.: C, 71.78; H, 5.10%. Found: C, 71.72; H, 4.93%.

10a. ^{1}H NMR ($CDCl_3$): 4.41 (dd, 1 H, $J_{2,3}$ 6.7, $J_{2,3'}$7.4 Hz, H-2), 4.09 (d, 5 H, Cp), 3.24, 2.66 (dd, 2 H, $J_{3,3'}$ 13.8 Hz, H-3, H-3').

10b. ^{1}H NMR ($CDCl_3$): 4.39 (d, 5 H, Cp), 4.22 (dd, 1 H, H-2).

10a : **10b**: 7.5 : 1 (-20 °C).

(η^5- C_5H_5)(CO)(PPh_3)FeCOCHDSPh (**11**): 518 mg (92%), m.p. 156-158 °C.

11a. ^{1}H NMR ($CDCl_3$): δ 4.43 (d, 5 H, Cp), 3.56 (s, 1 H, CHDPh).

11b. ^{1}H NMR ($CDCl_3$): δ 4.43 (d, 5 H, Cp), 4.15(s, 1 H, CHDPh).

11a : **11b**; 7.5 : 1 (-78 °C), 11 : 1 (-20 °C).

*Aldol reactions of **3***

To a cooled (-78 °C) solution of **3** (100 mg, 0.2 mmol) in THF (2.5 ml), 1.6 M solution of butyl lithium in hexane (0.4 mmol) was added. After 30 min acetaldehyde (or benzaldehyde) 1.5 mol/eq was added and the mixture was stirred for 45 min whereupon methanol (0.5 ml) and sat. aqueous solution of sodium-potassium tartrate (1 ml) were added. The stirring was continued at r.t. for an additional 30 min. The mixture was filtered through a short column filled with alumina, and the filtrate was concentrated to dryness. The residue was dissolved in dichloromethane, introduced onto a silicagel column and eluted with the hexane-ethyl ether 9 : 1.

With other counterions, after generation of the anion with BuLi for 15 min, a solution of diethylaluminum chloride [0.32 ml (0.58 mmol) of a 1.8 M solution in toluene] or of tin(II) chloride [0.32 ml (0.58 mmol) of a 1.8 M solution in THF] were added and the solution was stirred for 1 h before addition of the aldehyde.

(η^5-C$_5$H$_5$)(CO)(PPh$_3$)FeCOCH(SPh)CH(OH)CH$_3$ (**12**): For all diastereoisomers observed LSIMS (NBA): 629 (M + Na)$^+$, 607 (M + H)$^+$. HRMS (LSIMS): For $C_{34}H_{32}FeO_3PS$ (M + H)$^+$ Calc.: 607.1159. Anal. For $C_{34}H_{31}FeO_3PS$ Calc.: C, 67.33; H, 5.15%.

12a. m.p. 155-156°C. IR (KBr): 1905, 1605 cm^{-1}. HRMS (LSIMS): Found: 607.1146. Anal. Found: C, 67.05; H, 5.25%. ^{1}H NMR (CDCl$_3$): δ 4.38 (d, 5 H, Cp), 4.27 (d, 1 H, $J_{2,3}$ 5.2 Hz, H-2) 3.76 (dq, 1 H, H-3), 0.65 (d, 3 H, $J_{4,3}$ 7.2 Hz, H-4).

12b. m.p. 165-167°C. IR (KBr): 1915, 1558 cm^{-1}. HRMS (LSIMS): Found: 607.1128. Anal. Found: C, 66.94; H, 5.19%. ^{1}H NMR (CDCl$_3$): δ 4.38 (d, 5 H, Cp), 4.14 (d, 1 H, $J_{2,3}$ 1.1 Hz, H-2), 2.81 (dq, 1 H, H-3), 0.93 (d, 3 H, $J_{4,3}$ 6.4 Hz, H-4).

12c. m.p. 161-163°C. IR (KBr): 1906, 1588 cm^{-1}. HRMS (LSIMS): Found: 607.1159. Anal. Found: C, 67.10; H, 5.19%. ^{1}H NMR (CDCl$_3$): δ 4.45 (d, 5 H, Cp), 4.33 (d, 1 H, $J_{2,3}$ 6.6 Hz, H-2), 4.18 (dq, 1H, H-3), 1.19 (d, 3 H, $J_{4,3}$ 6.1 Hz, H-4).

12d. m.p.: 158-159°C. IR (KBr): 1906, 1579 cm^{-1}. HRMS (LSIMS): Found: 607.1140. Anal. Found: C, 66.97; H, 5.26%. ^{1}H NMR (CDCl$_3$): 4.52 (dq, 1 H, H-3), 4.51 (d, 5 H, Cp), 4.32 (1H, $J_{2,3}$ 1.7 Hz, H-2), 1.00 (s, 3H, $J_{4,3}$ 6.2 Hz, H-4).

	12a	**12b**	**12c**	**12d**	Yield %
Li$^+$	1	1.3	4.3	3.5	90
Sn^{2+}	1	10	22.5	55	82
Et$_2$Al$^+$	1	8.8	27.5	8.8	93
	SRS	*SRR*	*SSS*	*SSR*	

(η^5-C$_5$H$_5$)(CO)(PPh$_3$)FeCOCH(SPh)CH(OH)Ph (**13**): For all diastereoisomers observed LSIMS (NBA): 691 (M + Na)$^+$, 669 (M + H)$^+$. HRMS (LSIMS): For $C_{39}H_{34}FeO_3PS$(M + H)$^+$ Calc.: 669.1316. Anal. For $C_{39}H_{33}FeO_3PS$ Calc.: C, 70.06; H, 4.98%.

13a, m.p. 157-159 °C. IR (KBr): 1916, 1564 cm^{-1}. HRMS (LSIMS): Found: 669.1326. Anal. Found: C, 69.82; H, 4.96%. ^{1}H NMR (CDCl$_3$): δ 4.39 (d, 5 H, Cp), 4.33 (d, 1 H, $J_{2,3}$ 1.1 Hz, H-2), 4.11 (1H, H-3).

13b, m.p. 154-156 °C. IR (KBr): 1906, 1575 cm^{-1}. HRMS (LSIMS): Found: 669.1314. Anal. Found: C, 69.88; H, 4.98%. ^{1}H NMR (CDCl$_3$): δ 4.75 (d, 1 H, $J_{3,2}$ 9.3 Hz, H-3), 4.48 (d, 5 H, Cp), 4.07 (d, 1 H, H-2).

13c, m.p. 153-154 °C. IR (KBr): 1920, 1581 cm^{-1}. HRMS (LSIMS): Found: 669.1307. Anal. Found: C, 69.91; H, 4.99%. ^{1}H NMR (CDCl$_3$): δ 4.72 (d, 1 H, H-3), 4.56 (d, 1 H, $J_{2,3}$ 5.3 Hz, H-2), 4.04 (d, 5 H, Cp).

13d, m.p. 159-160 °C. IR (KBr): 1909, 1579 cm^{-1}. HRMS (LSIMS): Found: 669.1314. Anal. Found: C, 69.94; H, 4.93%. ^{1}H NMR (CDCl$_3$): δ 5.53 (d, 1 H, H-3), 4.57 (d, 1 H, $J_{2,3}$ 3.1 Hz, H-2), 4.41 (d, 5 H, Cp).

	13a	**13b**	**13c**	**13d**	Yield %
Li^+	1.1	1.0	1.5	2.7	88
Sn^{2+}	1	-	2.2	5.0	79
Et_2Al^+	5.4	1.0	13.5	9.1	90
	SRS	SRR	SSS	SSR	

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References

[1] Davies SG. Aldrichimica Acta 1990;23:31-37.

[2] Francotte ER, Bartnicka E, Pakulski Z, Wiśniewski K, Zamojski A. Enantiomer 1998; in press. See also: Case-Green S.C., Costello JF, Davies SG, Heaton N, Hedgecock ChJR, Humphreys VM, Metzler MR, Prime JC. J. Chem. Soc. Perkin Trans. I, 1994:933-941, Cook SJ, Costello JF, Davies SG, Kruk HT. J. Chem. Soc., Perkin Trans. I, 1994:2369-2372, and Baker RW, Davies SG. Tetrahedron Asymm., 1993;4:1479-1480.

[3] Wiśniewski K,. Pakulski Z, Zamojski A, Sheldrick WS. J. Organometal. Chem., 1995;523:1-7.

[4] Wiśniewski K, Zamojski A. Pol. J. Chem. 1998; in press.

[5] Pitchen P, DuZach E, Deshmukh MN, Kagan HB. J. Am. Chem. Soc. 1984;106: 8188-8193.

[6] Zhao SH, Samuel O, Kagan HB, Tetrahedron, 1987;43:5135-5144.

[7] Davies SG, Gravatt GL. J. Chem. Soc., Chem. Commun. 1988;780-781.

[8] Davies SG, Dordor IM, Walker JC, Warner P. Tetrahedron Lett. 1984;25:2709-2712.

[9] Davies SG, Seeman JI, Tetrahedron Lett., 1984;25:1845-1848.

[10] Aktogu N, Felkin H, Baird GJ, Davies SG, Watts O. J. Organometall. Chem., 1984;262:49-58.

[11] Davies SG, Dordor-Hedgecock IM., Warner P. Tetrahedron Lett, 1985;26:2125-2128.

[12] Liebeskind L,. Welker ME, Fengl RW. J. Am. Chem. Soc. 1986;108:6328-6343.

[13] Davies SG, Dordor - Hedgecock IM, Sutton KH, Walker JC, Jones RH, Prout K. Tetrahedron, 1986;42: 5123-5137.

[14] Bernal I,. Brunner H, Muschiol M. Inorg. Chim. Acta. 1988;142:235-242.

[15] Capon RJ, MacLeod JK, Coote SJ, Davies SG, Gravatt GL, Dordor-Hedgecock IM, Whittaker M. Tetrahedron, 1988;44:1637-1650.

[16] Lin HY, Koh LL., Eriks K, Giering WP, Prock A. Acta Cryst., 1990;C46:51-54.

[17] Krajewski JW, Gluziński P, Zamojski A, Mishnyov A, Kemme A, Guo ZW, J. Crystal. Spectrosc. Res. 1991;21:271-275.

[18] Guo ZW, Zamojski A, Krajewski JW, Gluziński P. J. Crystal. Spectrosc. Res. 1993;23:209-221.

[19] Wiśniewski K, Zamojski A, Guo ZW, Ciunik Z. Pol. J. Chem., 1996;70:446-457.

[20] Eisch JJ, King RB. Organometallic Synthesis, New York:Academic Press, vol. 1, 1965:145.

[21] Green M, Westlake DJ. J. Chem. Soc. A, 1971: 367-371.