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Synthesis, alkylation, crystal structure and molecular mechanics investigations of the (methylthio) acetyliron complex [(η^5-C_5H_5)Fe(CO)(PPh_3)$COCH_2SCH_3$]

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Abstract

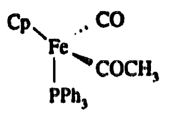
The air stable (methylthio)acetyliron complex **4** was obtained by methylthiolation with dimethyldisulphide of the anion generated from acetyliron complex **1** with butyllithium. Alkylthiolation could not be achieved with a number of thiolating reagents **5–11**. The enolate generated from **4** reacted readily and with high stereoselectivity with alkyl halides and with aldehydes. X-ray structural determination confirmed the pseudo-octahedral structure of **4**. Decomplexation of benzylation products **16a** and of aldol **18f** yielded several products, the majority of them without sulphur atoms.

Keywords: Iron; Acyliron complexes; Methylthioacetyliron; Crystal structure; Molecular mechanics calculations

1. Introduction

Reactions of the anion, obtained from the chiral acetyliron complex (η^5-C_5H_5)Fe(CO)(PPh_3)$COCH_3$ (**1**) [1] by deprotonation with butyllithium, with a variety of electrophiles (alkyl or aryl halides [2]; aldehydes [3,4]; epoxides [5]; sugar aldehydes [6,7]; sugar epoxides [8]) occur usually with high diastereoselectivity. After decomplexation and isolation of the expanded acyl ligand, many natural products have been obtained in this way [7,9].

Analogous alkoxyacetyl-ligand-containing complexes, such as benzyloxyacetyliron ((η^5-C_5H_5)Fe(CO)(PPh_3)$COCH_2OCH_2Ph$, **2**) [10], and methoxyacetyliron ((η^5-C_5H_5)Fe(CO)(PPh_3)$COCH_2OCH_3$, **3**) [11] have also been obtained and investigated in acyl ligand expansion reactions.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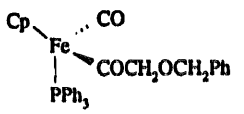
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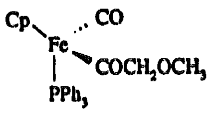
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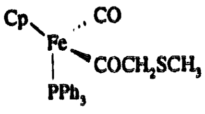
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As the sulphur-atom-containing compounds have interesting properties and are important intermediates in organic synthesis, we chose to study the reactions of (alkylthio)acetyliron complexes [(η^5-C_5H_5)Fe(CO)(PPh_3)$COCH_2SR$].

There are only a few examples of acetyliron-type complexes containing sulphur atoms. Reactions of acetyliron anion with (1*S*)-10-mercaptoisoborneol thiolsulphonate gave a mixture of diastereoisomers which has been used for separation of enantiomers of acetyliron complex [12].

Thioalkylation of (*R*)-propionyliron complex [(η^5-

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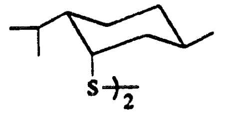
$C_5H_5)Fe(CO)(PPh_3)COCH_2CH_3]$ with diphenyl disulphide afforded a 16:1 mixture of stereoisomeric sulphides which, after oxidation of the sulphur atom, and decomplexation, gave an enantiomerically pure (*S*)-sulphoxide [13].

2. Results and discussion

2.1. Synthesis of (methylthio)acetyliron complex (rac-4)

Deprotonation of acetyliron complex (**1**) with butyllithium at −78 °C, followed by reaction with dimethyl disulphide at the same temperature, led to the (methylthio)acetyliron complex $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_2SCH_3$, *rac*-**4**] in very high yield (94% after chromatography). Orange crystals of *rac*-**4** are air stable and may be stored in a refrigerator without decomposition over a period of several months. However, in the presence of air, solutions of *rac*-**4** decompose slowly to form a brown precipitate.

As resolution of racemic acetyliron complex *rac*-**1** into enantiomers remains an important target, we tried to prepare optically active, diastereoisomeric complexes through reaction of *rac*-**1** with a chiral auxiliary. Unfortunately, all attempts at introduction of a variety of R* S groupings (where R* was in enantiomeric form, cf. compounds **5**–**11**) to the enolate generated from *rac*-**1** have failed.



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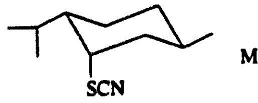

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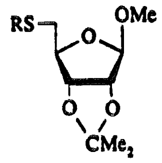
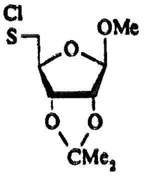
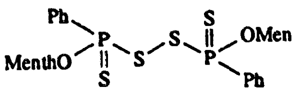
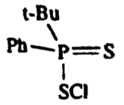


9: R = CN
10: R = Cl
11: R = S–





(SS)-**7**



(-)-**8**

2.2. The molecular structure of rac-4

Several acylirons have been investigated by X-ray diffractometric methods [3,11,14]. According to Davies and Seeman [15], these structures can be described in terms of a pseudo-octahedral arrangement of ligands around the iron atom. It is interesting to note that the chirality of the propeller-like PPh_3 ligand is, in all cases studied up to now, always the same: $R_{Fe}P_{P-Ph}$ ($S_{Fe}M_{P-Ph}$) (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 *rac*-**4**, suitable for X-ray analysis, were obtained by crystallization from dichloromethane–heptane solution. Crystal data and structure refinement for **4** are reported in Table 1. Atomic coordinates are given in Table 2. Selected interatomic bond distances and angles are presented in Table 3. The structure of complex **4** is shown in Fig. 1.

It is evident from the data that the structure of **4** corresponds closely to the generalized picture of other acetyliron complexes. Angles C1–Fe–C2, C1–Fe–P, and C2–Fe–P are approximately 90° and are characteristic for the pseudo-octahedral arrangement (Table 3). The mean angle Cp–Fe–P corresponds to 123.5°. The CO ligand is approximately anti oriented towards the acyl carbonyl group.

Comparison of the molecular structures of **3** [11] and **4** shows many similarities and only a few differences. The main bond lengths differ only a little: Fe–P (2.203 Å for **3** and 2.199 Å for **4**); $Fe–C_{CO}$ (1.727 and 1.733 Å); $Fe–C_{acyl}$ (1.966 and 1.964 Å respectively), although the sulphur–carbon bond (1.765 Å for **4**) is larger than for the oxygen–carbon bond (1.413 Å for **3**). The $O{=}C–C_\alpha–SMe$ grouping is in a cisoid arrangement (−5°) and the torsion angle $O{=}C–C_\alpha–OMe$ in **3** is 1.7°.

2.3. Molecular mechanics calculations of 4

Molecular mechanics calculations [16] reproduced the X-ray geometry of **4** rather well (Table 4), the main differences being found for the bond lengths for Fe–C(1) and Fe–C(2) and the torsion angle O(2)–C(2)–C(3)–S. The cisoid arrangement of the O=C–C–S atom system is satisfactorily reproduced, although the torsion angle of the calculated minimum energy conformation increased its value to ca. −16°.

Table 1
Crystal data and structure refinement for **4**

Empirical formula	$C_{27}H_{25}FeO_2PS$
Formula weight	500.35
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	7.862(2)
b (Å)	19.304(4)
c (Å)	15.579(3)
α (deg)	90
β (deg)	91.35(3)
γ (deg)	90
Volume (Å^3)	2363.7(9)
Z	4
Density (calculated) (Mg m^{-3})	1.406
Absorption coefficient (mm^{-1})	0.816
$F(000)$	1040
Crystal size (mm^3)	0.44 × 0.31 × 0.25
θ range for data collection (deg)	2.11 to 22.50
Index range	$-8 \leq h \leq 0$, $-20 \leq k \leq 0$, $-16 \leq l \leq 16$
Reflections collected	3322
Independent reflections	3083 (R_{int} = 0.0225)
Absorption correction	Semi-empirical
Max. and min. transmission	0.537 and 0.489
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	3082/20/355
Goodness-of-fit on F^2	1.060
$I > 2\sigma(I)$	2286
Final R indices ($I > 2\sigma(I)$)	$R1$ = 0.0547, $wR2$ = 0.1380
R indices (all data)	$R1$ = 0.0807, $wR2$ = 0.1573
Largest diff. peak and hole (e Å^{-3})	1.596 and −0.503

Table 2
Atomic coordinates (× 10^4), and equivalent isotropic displacement parameters (Å^2 × 10^3) for **4**

	x	y	z	U_{eq} [a]
Fe	1567(1)	3419(1)	6814(1)	37(1)
P	2976(2)	3584(1)	8033(1)	34(1)
C(1)	3420(9)	3289(3)	6255(4)	49(2)
O(1)	4643(6)	3179(3)	5867(3)	70(1)
C(2)	1533(7)	4420(3)	6585(4)	45(2)
O(2)	948(6)	4854(2)	7060(3)	57(1)
C(3)	2246(11)	4640(4)	5717(5)	74(2)
S	2017(4)	5512(1)	5392(2)	99(1)
C(4)	3575(11)	5914(4)	6044(7)	94(3)
C(11)	4542(7)	2905(3)	8309(4)	39(1)
C(12)	4344(8)	2247(3)	7960(5)	54(2)
C(13)	5510(10)	1721(4)	8172(5)	65(2)
C(14)	6861(9)	1856(4)	8715(5)	62(2)
C(15)	7073(8)	2506(4)	9050(5)	55(2)
C(16)	5912(7)	3029(3)	8861(4)	44(2)
C(21)	1670(7)	3649(3)	8991(4)	37(1)
C(22)	1955(8)	3242(3)	9721(4)	45(2)
C(23)	958(10)	3330(4)	10442(4)	57(2)
C(24)	−340(10)	3808(4)	10431(5)	62(2)
C(25)	−660(8)	4206(4)	9702(5)	55(2)
C(26)	333(8)	4129(3)	8992(4)	46(2)
C(31)	4315(7)	4364(3)	8117(4)	36(1)
C(32)	4154(9)	4859(3)	8750(4)	53(2)
C(33)	5217(10)	5438(4)	8769(5)	65(2)
C(34)	6448(9)	5511(4)	8172(5)	65(2)
C(35)	6640(8)	5022(4)	7547(5)	57(2)
C(36)	5578(8)	4452(3)	7523(4)	48(2)
C(41)	−922(7)	3229(4)	7264(4)	48(2)
C(42)	34(9)	2603(4)	7264(5)	63(2)
C(43)	472(9)	2465(4)	6418(6)	66(2)
C(44)	−163(8)	3006(4)	5892(4)	55(2)
C(45)	−1026(7)	3463(3)	6414(4)	46(2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Selected bond lengths (Å) and bond angles (deg) for **4**

Fe–P	2.199(2)	C(1)–O(1)	1.167(7)
Fe–C(1)	1.733(7)	C(2)–O(2)	1.215(7)
Fe–C(2)	1.964(6)	C(2)–C(3)	1.537(9)
Fe–C(41)	2.126(6)	C(3)–S	1.765(8)
Fe–C(42)	2.114(7)	C(4)–S	1.753(9)
Fe–C(43)	2.120(7)	C(41)–C(42)	1.424(10)
Fe–C(44)	2.111(6)	C(42)–C(43)	1.396(11)
Fe–C(45)	2.119(6)	C(43)–C(44)	1.411(11)
P–C(11)	1.841(6)	C(44)–C(45)	1.388(9)
P–C(21)	1.836(6)	C(41)–C(45)	1.399(9)
P–C(31)	1.841(6)		
C(1)–Fe–C(2)	93.4(3)	O(1)–C(1)–Fe	177.5(6)
C(1)–Fe–P	92.4(2)	O(2)–C(2)–Fe	124.8(5)
C(2)–Fe–P	91.1(2)	O(2)–C(2)–C(3)	119.8(6)
C(2)–C(3)–S	118.6(6)	C(11)–P–Fe	114.8(2)
C(4)–S–C(3)	101.0(4)	C(21)–P–Fe	115.6(2)
P–Fe–Cp (ring centroid)	123.8	C(31)–P–Fe	117.1(2)

2.4. Acyl ligand expansion reactions

One of the hydrogen atoms (pro-R) can readily reach the vertical orientation towards the O=C–C$_\alpha$ plane. Therefore, its base-induced removal should be easier than of the other (pro-S) hydrogen atom (stereoelectronic condition of deprotonation) [17].

In the first experiment, the enolate generated with butyllithium, was quenched with deuterium oxide to yield stereoisomeric mono-deuterated products **12** in greater than 15:1 proportion. Methylation of the enolate with methyl iodide yielded monomethylated stereoisomeric products **13** (12:1) of $R_{Fe}R_\alpha$ [1] and $R_{Fe}S_\alpha$. The configurations were assigned based on characteristic chemical shifts of the introduced methyl groups (δ 1.35 and 0.47) [18]. Ethylation gave both stereoisomeric products **14** in a moderate yield (26%) in greater than 24:1 proportion. The results of allylation and of benzy-

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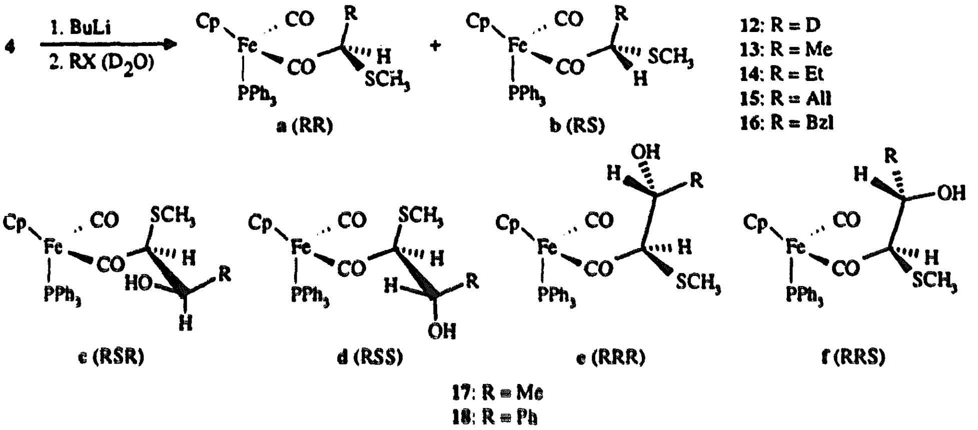
[1] Although all complexes were in the racemic form, only R_{Fe} enantiomers are shown in this paper, for convenience.

lation were similar, and the yields of products (**15** and **16** respectively) were good (cf. Section 4).

Quite interesting were the results of aldol reactions. Usually, from enolates of acylirons, the aldols are formed with little stereoselectivity [19]. From the reaction of the enolate generated from *rac*-**4** with acetaldehyde, four possible stereoisomeric aldols **17c**–**17f** were obtained in the proportion 2.3:1:1:17.2, i.e. with **17f** in a distinct predominance. ^{1}H NMR spectra enabled the assignment of relative configuration to all three centres of chirality, i.e. at Fe, C_α and C_β atoms, as RSR, RSS, RRR, and RRS respectively. The SMe signal occurred in the spectra of **17c** and **17d** above δ 2.0, and in the spectra of **17e** and **17f** at δ 1.20 and 1.39; this clearly proved the $R_{Fe}S_\alpha$ configuration for the first two complexes and $R_{Fe}R_\alpha$ for the remaining two. The configuration at the β carbon atoms could be determined from the aldol reactions with Et_2Al^+ and Sn^{2+} cations replacing Li^+. It is known [20] that diethylaluminium promotes the formation of $R_{Fe}R_\beta$ aldols, whereas $R_{Fe}S_\beta$ aldols are predominantly formed with the tin(II) cation [4]. The diethylaluminium cation promoted the formation of **17c** and **17e** aldols, whereas, in the presence of divalent tin, aldol **17f** was practically the exclusive product. The results of the aldol reaction of *rac*-**4** with benzaldehyde, leading to complexes **18c**–**18f**, were similar (cf. Section 4). It must be mentioned that the results described here strongly resemble the results achieved in aldol reactions of methoxyacetyliron [11], although preferences for RRS aldols are more pronounced.



2.5. Decomplexation

The product of benzylation **16a** was decomplexed with *N*-bromosuccinimide in methanol and the resulting product mixture examined with ^{1}H NMR spectra and the GC-MS method. The main products have been identified as *E*- and *Z*-2-(methylthio)-1-phenylethylene, phenylacetaldehyde and its dimethyl acetal. Minute amounts of 1,2-diphenylethane, methyl dihydrocinnamate, methyl cinnamate and 1,3-diphenyl-2-propanone have also been found. With chlorine in methanol–dichloromethane (at −100°C), besides the same products, trace amounts of monothio dimethyl acetal, phenylacetaldehyde, and of 2-(methylthio)-3-phenylpropionic acid have been recorded.

Decomplexation of **18f** led to mandelaldehyde dimethyl acetal in 78%. Other products, formed in trace amounts, included methyl cinnamate, 3-hydroxy-2-methoxy-3-phenylpropionic acid and three unidentified products $C_9H_{10}O$. Formation of the majority of these products can be understood, if we assume initial formation of a radical cation on oxidation of the complex [4], cleavage of acyl (or alkyl) radical which is next oxidized to cation, and a series of follow-up reactions [21].

3. Conclusion

The reactions aiming at expansion of the methylthioacetyl ligand in *rac*-**4** are highly stereoselective and high yielding. Exploitation of these reactions for stereocontrolled syntheses of MeS-grouping-containing products is promising. However, a further search for new decomplexation methods enabling preservation of the acyl ligand in its full entity, is necessary.

4. Experimental section

4.1. General methods

All manipulations on organometallic complexes were performed under argon. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ under a stream of argon prior to use. Butyllithium was used as a 1.6 M solution in hexane. TLC was performed on silica gel HF-254 and column chromatography on silica gel 230–400 mesh (Merck). ^1H NMR spectra were recorded with a Bruker AM-500 (500 MHz) spectrometer. High resolution mass spectra (HR-MS) were measured with AMD-604 and GC-MS spectra with GC/MS HP 5972A MSD mass spectrometers. IR spectra were recorded on a Perkin–Elmer 1640 FT-IR spectrophotometer. Compounds **6** [22], **9** [23], and **11** [23] were prepared according to literature methods.

4.2. $CpFe(CO)(PPh_3)COCH_2SMe$ (*rac*-4)

A solution of the acetyliron complex *rac*-**1** (3.0 g, 6.6 mM) in THF (20 ml) was cooled to −78 °C and butyllithium (6.6 mM) was added. After 20 min, a solution of dimethyl disulphide (930 mg, 10.0 mM) in THF (10 ml) was added and the mixture was stirred at −78 °C for 1 h. Methanol (5 ml) was added to the mixture which was then allowed to attain room temperature. The solution was concentrated to dryness. Column chromatography (hexane–acetone, 2:1) of the residue gave *rac*-**4** (3.1 g, 94%), m.p. 162–163 °C (dichloromethane-heptane); IR (KBr) ν_{max}: 1912 and 1620 cm^{-1}. ^1H NMR (C_6D_6) δ, 4.26 (d, 5H, $J_{H,P}$ 1.2 Hz, Cp), 3.88 and 3.52 (ABq, 2H, J 15.2 Hz, CH_2), 1.80 (s, 3H, CH_3). HR-MS/EI for $C_{25}H_{20}^{56}FeO_2P$ $(M - CH_2SCH_3)^+$ calc.: 439.0550. Found: 439.0549.

4.3. [(1S,2S,5R)-2-Isopropyl-5-methylcyclohexyl] disulphide (5)

To a mixture of neomenthanethiol [22] (1.60 g, 9.30 mM) and 20% sodium hydroxide (2.10 g = 0.42 g NaOH, 10.5 mM), iodine (1.2 g) and benzene (5 ml) was added. The stirring was continued overnight. The product was extracted with ether (3 × 10 ml). Combined organic extracts were washed with sat. aq. $Na_2S_2O_3$ (10 ml), water (2 × 10 ml) and brine (10 ml). The solution was dried over Na_2SO_4 and concentrated to dryness. Column chromatography (heptane) of the residue gave **5** (895 mg, 56%), m.p. 54–56 °C; $[\alpha]_D^{20} + 385.5°$ (c 1.3, chloroform). ^1H NMR ($CDCl_3$) δ, 3.22 (m, 1H, SCH), 0.8–2.4 (m, other protons). HR-MS/EI for $C_{20}H_{38}S_2$ $(M)^+$ calc.: 342.2415. Found. 342.2415.

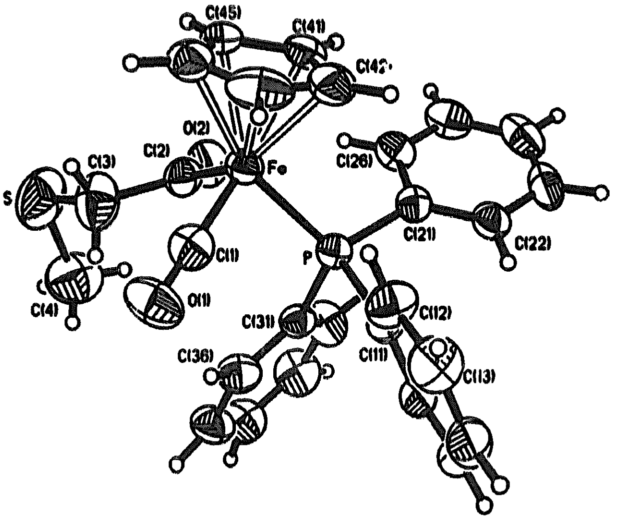


Fig. 1. Molecular structure of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_2SCH_3$ (**4**).

Table 4
Comparison of selected bond lengths (Å), angles (deg), and torsion angles (deg) from X-ray data and the MM-calculated model of **4**

	X-ray	MM
Fe–C(1)	1.733	1.85
Fe–C(2)	1.964	2.05
Fe–P	2.199	2.20
C(1)–Fe–C(2)	93.4	100.5
C(1)–Fe–P	92.4	88.6
C(2)–Fe–P	91.1	92.8
C(2)–Fe–P–C(11)	94.1	100.7
C(2)–Fe–P–C(21)	−144.5	−140.3
C(2)–Fe–P–C(31)	−26.4	−20.6
C(1)–Fe–C(2)–O(2)	−150.2	−153.3
O(2)–C(2)–C(3)–S	−5.0	−15.8
C(2)–C(3)–S–C(4)	75.5	78.3
Fe–P–C(11)–C(12)	−56.2	−55.7
Fe–P–C(21)–C(22)	−53.1	−67.4
Fe–P–C(31)–C(32)	−23.0	−35.1
O(2)–C(2)–C(3)–H(2)	−130.0	−140.5
O(2)–C(2)–C(3)–H(3)	119.9	109.0

4.4. Alkylation of $CpFe(CO)(PPh_3)COCH_2SMe$ (*rac*-4)

4.4.1. General method

To a cooled (−78 °C) solution of *rac*-**4** (1 mmol) in THF (5 ml) 1.3 mol/eq of butyllithium solution was added and the resulting dark red solution was stirred at −78 °C for 30 min. Alkyl halide or D_2O (1.5 mol/eq) was added and the solution stirred at −78 °C for 1.5 h. The reaction was quenched with methanol (5 ml) and the solvent removed in vacuo. The residue was dissolved in dichloromethane and the solution filtered through a column filled with alumina (Grade V). The filtrate was concentrated under diminished pressure and the mixture of products separated from the unreacted substrate by flash chromatography with a mixture of ether and hexane (1:9) as eluent. The proportion of stereoisomers was determined by integration of the ^1H NMR Cp signals. Crystallization from a mixture of ethyl acetate and hexane afforded pure products.

4.4.2. $CpFe(CO)(PPh_3)FeCOCH(D)SMe$ (12a,b)

12a:**12b** > 15:1; yield 95%, m.p. 160–161 °C; IR (KBr) ν_{max}: 1911 and 1610 cm^{-1}. ^1H NMR ($CDCl_3$) δ, **12a**: 4.45 (d, 5H, $J_{Cp,P}$ 1.2 Hz, Cp), 3.20 (s, 1H, H-1B), 1.71 (s, 3H, SMe); **12b**: 4.45 (d, 5H, $J_{Cp,P}$ 1.2 Hz, Cp), 3.71 (s, 1H, H-1A), 1.71 (s, 3H, SMe). MS/LSIMS: 502(M + H$^+$, 3), 439(50), 383(30). HR-MS/LSIMS for $C_{27}H_{25}DFeO_2PS$ $(M + H)^+$ calc.: 502.0833. Found: 502.0804.

4.4.3. CpFe(CO)(PPh$_3$)FeCOCH(SMe)CH$_3$ (13a,b)

13a:**13b** 12:1; yield 98%, m.p. of the mixture: 153–157°C; IR (KBr) ν_{max}: 1920 and 1599 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ, **13a**: 4.43 (d, 5H, $J_{Cp,P}$ 1.3 Hz, Cp), 3.62 (q, 1H, $J_{H,CH3}$ 7.1 Hz, H_α), 1.36 (s, 3H, SMe), 1.35 (d, 3H, CH_3); **13b**: 4.50 (d, 5H $J_{Cp,P}$ 1.2 Hz, Cp), 3.53 (q, 1H, $J_{H,CH3}$ 6.8 Hz, H_α), 1.89 (s, 3H, SMe), 0.47 (d, 3H, CH_3). MS/LSIMS: 537(M + Na$^+$, 2), 515(M + H$^+$, 5), 439(100), 383(70). Anal. Found: C, 65.64; H, 5.35. $C_{28}H_{27}FeO_2PS$. Calc.: C, 65.38; H, 5.29%.

4.4.4. CpFe(CO)(PPH$_3$)FeCOCH(SMe)CH$_2$CH$_3$ (14a,b)

14a:**14b** > 24:1; yield 26%, m.p. of the mixture 172–175°C; IR (KBr) ν_{max}: 1914 and 1597 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ, **14a**: 4.40 (d, 5H, $J_{Cp,P}$ 1.3 Hz, Cp), 3.45 (dd, 1H, $J_{H\alpha,H\beta}$ 4.6 Hz, $J_{H\alpha,H\beta'}$ 9.3 Hz, H_α), 1.81 and 1.56 (ABq, 2H, $J_{H\beta,H\beta'}$ 14.4 Hz, H_β, $H_{\beta'}$), 1.21 (s, 3H, SMe), 0.96 (t, 3H, $J_{H\beta,CH_3}$ 7.31 Hz, CH_3); **14b**: 4.51 (d, 5H, $J_{Cp,P}$ 1.2 Hz, Cp), 3.22 (dd, 1H, $J_{H\alpha,H\beta}$ 10.8 Hz, $J_{H\alpha,H\beta}$ 6.1 Hz, H_α), 2.84 and 2.52 (ABq, 2H, $J_{H\beta,H\beta'}$ 14.4 Hz, H_β, $H_{\beta'}$) 1.81 (s, 3H, SMe), 0.61 (t, 3H, $J_{H\beta,CH_3}$ 7.3 Hz, CH_3). MS/LSIMS: 551(M + Na$^+$, 2), 529(M + H$^+$, 1), 439(20), 383(15). Anal. Found: C, 65.78; H, 5.51. $C_{29}H_{29}FeO_2PS$. Calc.: C, 65.92: H, 5.53%.

4.4.5. CpFe(CO)(PPh$_3$)FeCOCH(SMe)CH$_2$CH = CH$_2$ (15a,b)

15a:**15b** > 23:1; yield 67%, m.p. of the mixture 160–162°C; IR (KBr) ν_{max}: 1915 and 1601 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ, **15a**: 5.87 (m, 1H, olefinic CH), 5.07 (m, 2H, olefinic CH_2), 4.39 (d, 5H, Cp), 3.75 (dd, 1H, $J_{H\alpha,H\beta}$ 5.6 Hz, $J_{H\alpha,H\beta'}$ 8.5 Hz, H_α), 2.54 and 2.31 (AB, 2H, $J_{H\beta,H\beta'}$ 14.4 Hz, H_β, $H_{\beta'}$), 1.25 (s, 3H, SMe); **15b**: 4.51 (d, Cp). MS/LSIMS: 563(M + Na$^+$, 2), 541(M + H$^+$, 7), 439(100), 383(60). Anal. Found: C, 66.74; H, 5.30. $C_{30}H_{29}FeO_2PS$. Calc.: C, 66.67; H, 5.41%.

4.4.6. CpFe(CO)(PPh$_3$)FeCOCH(SMe)CH$_2$Ph (16a,b)

16a:**16b** > 36:1; yield 72%, m.p. of the mixture 139–143°C; IR (KBr) ν_{max}: 1913 and 1606 cm^{-1}. ^{1}H NMR($CDCl_3$) δ, **16a**: 4.06 (d, 5H, $J_{Cp,P}$ 1.2 Hz, Cp), 3.85 (t, 1H, $J_{H\alpha,H\beta}$ 7.3 Hz, H_α), 3.25 and 2.61 (dd, 2H, $J_{H\beta,H\beta'}$ 13.4 Hz, H_β, $H_{\beta'}$), 1.17 (s, 3H, SMe); **16b**: 4.50 (d, 5H, Cp). MS/LSIMS: 1203(2M + Na$^+$, 0.2), 613(M + Na$^+$, 1), 591(M + H$^+$, 2), 439(100), 383(90). Anal. Found: C, 69.09; H, 5.37. $C_{34}H_{31}FeO_2PS$. Calc.: C, 69.16; H, 5.29%.

4.4.7. Aldol reactions of rac-4

To a cooled (−78°C) solution of *rac*-**4** (100 mg, 0.2 mmol) in THF (2.5 ml) 1.6 M solution of butyllithium in hexane (0.4 mmol) was added. After 30 min acetaldehyde (or benzaldehyde) 1.5 mol/eq was added and the mixture stirred for 45 min whereupon methanol (0.5 ml) and sat. aqueous solution of sodium–potassium tartrate (1 ml) were added and the stirring continued at room temperature for an additional 30 min. The mixture was filtered through a short column filled with alumina, and the filtrate concentrated to dryness. The residue was dissolved in dichloromethane, introduced onto a silica gel column and eluted with the same solvent. The eluates were concentrated to dryness.

With other counterions, after generation of the anion with BuLi for 15 min, a solution of diethylaluminium chloride (0.32 ml (0.58 mmol) of a 1.8 M solution in toluene) or of tin(II) chloride (0.5 ml (0.5 mmol) of a 1 M solution in THF) were added and the solution stirred for 1 h before addition of the aldehyde.

4.4.8. CpFe(CO)(PPh$_3$)FeCOCH(SMe)CH(OH)CH$_3$ (17c–f)

17c($R_{Fe}S_\alpha R_\beta$):**17d**(RSS):**17e**(RRR):**17f**(RRS) 2.3:1:1:17.2 (for Li$^+$, yield 98%, m.p. of the mixture 164–170°C), 3.8:1:4.6:7.4 (for Et_2Al^+, 65%), and practically only **17f** (for Sn^{2+}, 97%); IR (KBr) ν_{max}: 1915 and 1591 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ, **17c**: 4.54 (d, 5H, Cp), 3.19 (d, 1H, $J_{H\alpha,H\beta}$ 2.0 Hz, H_α), 2.74 (dd, 1H, $J_{H\beta,OH}$ < 0.8 Hz, H_β), 2.22 (s, 3H, SMe), 0.79 (d, 3H, CH_3); **17d**: 4.51 (d, 5H, Cp), 3.37 (d, 1H, $J_{H\alpha,H\beta}$ 7.4 Hz, H_α), 3.70 (d, 1H, H_β), 2.08 (s, 3H, SMe), 0.91 (d, 3H, CH_3); **17e**: 4.44 (d, 5H, Cp), 3.51 (d, 1H, $J_{H\alpha,H\beta}$ 9.2 Hz, H_α), 4.04 (dd, 1H, $J_{H\beta,OH}$ 4.0 Hz, H_β), 1.20 (s, 3H, SMe), 1.28 (d, 3H, CH_3); **17f**: 4.45 (d, 5H, Cp), 3.55 (d, 1H, $J_{H\alpha,H\beta}$ 4.76 Hz, H_α), 4.24 (d, 1H, H_β), 1.39 (s, 3H, SMe), 1.26 (d, 3H, CH_3). MS/LSIMS: 545(M + H$^+$, 3), 439(50), 383(30). HR-MS/LSIMS for $C_{29}H_{30}FeO_3PS$ $(M + H)^+$ calc.: 545.1003. Found: 545.1005.

4.4.9. CpFe(CO)(PPh$_3$)FeCOCH(SMe)CH(OH)Ph (18c–f)

18c($R_{Fe}S_\alpha R_\beta$):**18d**(RSS):**18e**(RRR):**18f**(RRS) 1:1.4:1.5:5.0 (for Li$^+$, yield 94%, m.p. of the mixture **18c** + **18d**: 158–164°C); 4.5:1:3.8:9.2 (for Et_2Al^+, 86%), and practically only **18f** (for Sn^{2+}, 91%); IR (KBr) ν_{max}: 1918 and 1561 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ, **18c**: 4.56 (d, 5H, Cp), 3.54 (d, 1H, $J_{H\alpha,H\beta}$ ca. 1.0 Hz, H_α), 4.03 (dd, 1H, $J_{H\beta,OH}$ 1.0 Hz, H_β), 1.69 (s, 3H, SMe); **18d**: 4.52 (d, 5H, Cp), 3.39 (d, 1H, $J_{H\alpha,H\beta}$ 9.6 Hz, H_α), 4.64 (d, 1H, $J_{H\beta,OH}$ 2.3 Hz, H_β), 1.60 (s, 3H, SMe); **18e**: 4.32 (d, 5H, Cp), 3.84 (d, 1H, $J_{H\alpha,H\beta}$ 8.2 Hz, H_α), 4.86 (dd, 1H, $J_{H\beta,OH}$ 4.6 Hz, H_β), 1.32 (s, 3H, SMe); **18f**: 4.02 (d, 5H, Cp), 3.94 (d, 1H, $J_{H\alpha,H\beta}$ 6.8 Hz, H_α), 5.07 (d, 1H, $J_{H\beta,OH}$ 3.3 Hz, H_β), 1.02 (s, 3H, SMe). MS/LSIMS: 607(M + H$^+$, 2), 439(30), 383(25). Anal. Found: C, 67.02; H, 5.05. $C_{34}H_{31}FeO_3PS$. Calc.: C, 67.33; H, 5.15%.

4.4.10. Decomplexation of 16a and 18f

To a cooled (−78 °C) solution of **16a** (100 mg, 0.17 mmol) or **18f** (520 mg, 0.86 mmol) in a 1:1 mixture of CH_2Cl_2 and methanol (2.5 ml) *N*-bromosuccinimide (36 mg, 0.18 mmol) or a solution of chlorine (0.15 M) in CH_2Cl_2 were added and the reaction mixture stirred. After 1 h the solution was brought to room temperature, concentrated to dryness and the residue dissolved in chloroform and separated by column chromatography with hexane–ethyl acetate 8:3. The fractions obtained were analysed by GC-MS and with ^1H NMR spectra.

From **16a** a mixture of *Z*- and *E*-1-(methylthio)-2-phenylethene (5 mg, 20%) in the first fraction and benzaldehyde and phenylacetaldehyde (10 mg, 52%) in the second fraction were obtained.

From **18f** mandelaldehyde dimethyl acetal (120 mg, 78%) in the first fraction and a mixture of products (24 mg) in the second fraction were obtained.

4.4.11. X-ray structural analysis of rac-4

Details of the data collection and structure refinement are presented in Table 1. Intensities were collected on a Siemens P4 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods (SHELXS) and refined against F^2 (SHELX-93). Group isotropic temperature factors were introduced for the hydrogen atoms. The remaining atoms were refined anisotropically.

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