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Alkylation and aldol reactions of acyl and phosphine ligand in $(\eta^5\text{-}C_5H_5)Fe(CO)(CH_3PPh_2)(COCH_2R)$

Halszka Stępowska and Aleksander Zamojski

Institute of Organic Chemistry, Polish Academy of Sciences, 01-224 Warsaw (Poland)

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Abstract

The effect of replacement of triphenylphosphine in $CpFe(CO)PPh_3(COR)$ by methyldiphenylphosphine on the reactivity of the acyl ligand attached to Fe has been investigated. Reactions of anions generated from complexes $(\eta^5\text{-}C_5H_5)Fe(CO)(CH_3PPh_2)COCH_3$ (**5**) and $(\eta^5\text{-}C_5H_5)Fe(CO)(CH_3PPh_2)COC_2H_5$ (**6**) with a variety of electrophilic reagents gave mixtures of diastereo- and regio-isomeric products. The proportion of these was found to be independent of the type of base used for deprotonation but dependent on the stoichiometric base-to-complex ratio. The product of benzylation **12** gave methyl 3-phenylpropionate after decomplexation with NBS in methanol.

1. Introduction

There has recently been increasing interest in the synthesis, structure and reactivity of chiral transition metal complexes [1]. The presence of an organic ligand bonded to the chiral centre on the metal offers a number of potential applications in asymmetric reactions [2–4].

In continuation of our work on the chemistry and synthetic application of iron(II) complexes of the general formula $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COCH_2R)$ (**1**, R = OMe, Ph) [5,6], we undertook a study of the effect of changing the phosphine ligand. To our knowledge, only two reports have appeared on the reactivity of acyliron complexes containing phosphine ligands other than PPh_3. Liebeskind [7] reported the synthesis of the acetyliron species **2** and **3**, the reactions of these complexes were rather disappointing. Davies [8] synthesized the enantiomeric complex (*R*)-4 and achieved enantioselective reduction of ethyl benzoylformate to ethyl mandelate.

We expected that the presence of a suitable phosphine ligand (including chiral phosphines) complexed to iron might provide an efficient chiral system for asymmetric induction. This hope prompted us to initiate a preliminary study on the reactivity of acylirons containing methyldiphenylphosphine as the phosphine ligand.

2. Results and discussion

Two acylirons of the formula $(\eta^5\text{-}C_5H_5)Fe(CO)(Ph_2PMe)(COR)$, R = Me (**5**) and R = Et (**6**) were prepared by the general method [9a,b] involving sodium amalgam reduction of dicyclopentadienyltetracarbonyldiiron, alkylation with methyl or ethyl iodides to form intermediate alkylation products and treatment with methyldiphenylphosphine. Complex **6** was described previously [9b]; we introduced modifications which improved its preparation. Full spectral data for the two complexes are listed in Table 1.

Although the conformation of **5** and **6** is not known, we suppose that it will be of pseudo-octahedral geometry, like other acylirons [10]. Molecular mechanics calculations [11] performed for **5** have shown that of three rotamers (around the Fe–P bond) that having the phosphine methyl group eclipsing the cyclopentadienyl ligand has the lowest strain energy, *ca.* 0.6 kcal/mol lower than the other two. It may be added that strain energy calculated for the acetyliron species, $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COCH_3)$, is *ca.* 6 kcal/mol higher than that for **5** indicating that additional strain is introduced when a phenyl replaces the methyl group

Correspondence to: Professor A. Zamojski.

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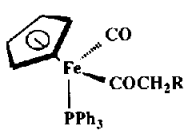
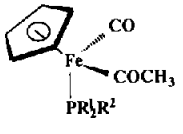
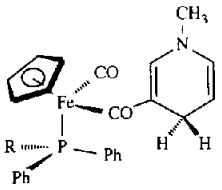


1: R = OCH_3, Ph *)

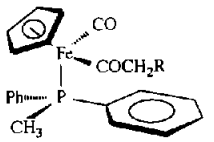


2: $R^1 = R^2 = OPh$

3: $R^1 = Ph_2$, $R^2 = NEt_2$



4: R = O-l-menthyl



5: R = H

6: $R = CH_3$

*) For simplicity, the formulae in this paper depict complexes of R configuration although all compounds were racemic.

in the phosphine ligand. A molecular model of **5** also shows that the phosphine methyl group should be readily accessible to the attacking base.

Elaboration of the acyl ligand in acylirons usually occurs via reactions of the anion generated in the acyl ligand with electrophiles [1,2]. In the case of **5** and **6**, it was conceivable that strong bases might deprotonate not only the α-position in acyl ligands but also in the methyl group in the phosphine ligand. For the low-temperature generation of anions, n-butyl lithium (^{n}BuLi) and lithium diisopropylamide (LDA) were employed as bases. Both bases behaved similarly, and so the majority of reactions were performed with ^{n}BuLi. Deprotonations of **5** were carried out in tetrahydrofuran solution at −78°C with complex-to-base ratios of 1:1, 1:2 and 1:5. The anions generated were quenched with alkyl halides or with aldehydes.

Formally, anions generated from **5** can exist as two regioisomers, **7** and **8**, and as a dianion **9** (Scheme 1).

2.1. Alkylation

When 1 molar equivalent of n-butyl lithium was used for deprotonation of **5** and the anion generated was treated with 1 molar equivalent of methyl iodide, a single product **10** was isolated, in 64% yield. Under similar conditions, allyl and benzyl bromides yielded the single coupling products **11** and **12**, respectively (Table 2). In the case of ethyl iodide, in addition to **13** (36%), a second product, **14**, was isolated in *ca.* 8% yield.

Compound **10** was found to be identical with **6** proving that methylation took place at the acetyl group. On the basis of ^{1}H NMR spectra, **11**–**13** were also shown to be products of alkylation in the acetyl group.

When the methylation reaction was repeated but with 2 molar equivalents of the base and 1 mol equivalent of methyl iodide, two products, **10** and **15**, were obtained, each in over 20% yield.

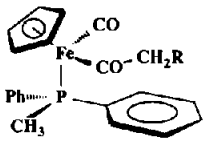
Complex **15** was found to be the product of methylation in the phosphinic methyl group. This conclusion was reached from the ^{1}H NMR spectral data which revealed replacement of P–Me by P–Et signals, with the acetyl group signal left unchanged. In the mass spectrum of **15** a strong peak of the $CpFePPh_2Et$ ion (*m/z* 35.0648, $C_{19}H_{20}PFe$) replaced the $CpFePPh_2Me$ ion ($C_{18}H_{18}PFe$, *m/z* 321.0494) found in the spectrum of **5**. A similar structure was assigned to **14**, also on the basis of ^{1}H NMR and MS data. A separate report will be published on the mass spectroscopy of acyliron complexes.

Metallation in the presence of a 2 molar amount of the base followed by methylation with 2 molar equivalents of methyl iodide led to three products: **10** (23%), **15** (5%) and **17** (67%). The major product was judged to be the bis-methylated product **17** from the ^{1}H NMR and MS data. The corresponding reactions of **5** with

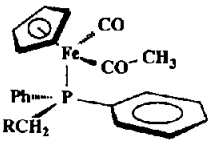
TABLE 1. Yields, m.p. and spectral data for **5** and **6**

Complex no.	Yield (%)	m.p. (°C)	^{1}H NMR (in C_6D_6 solution) [a] δ in ppm (J Hz)	Formula	MS (*m/z*)		IR (KBr) ν(CO) (cm^{-1})
					Calc	Found	
5	84	123–124	4.21 (d, 5H, J(PH) = 1.31, Cp) 2.43 (d, 3H, J(PH) = 0.76, $COCH_3$) 1.86 (d, 3H, J(PH) = 9.27, CH_3–P)	$C_{21}H_{21}FeO_2P$	392.0628	392.0632	1920 1615
6	89	109–110	4.23 (d, 5H, J = 1.28, Cp) 2.82 (dd, 1H, $J'_{\alpha\alpha}$ = 16.29, H_α) 2.46 (dd, 1H, H'_α) 1.86 (d, 3H, J(PH) = 9.34, CH_3–P) 0.95 (t, 3H, J = 7.27, CH_3CH_2)	$C_{22}H_{23}FeO_2P$	406.0785	406.0783	1930 1620

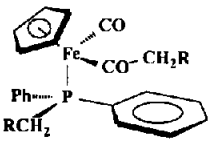
[a] The signals of the aromatic protons appear at δ 7.1–7.5.



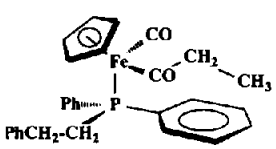
10: R = CH_3
11: R = $CH_2CH{=}CH_2$
12: R = CH_2Ph
13: R = C_2H_5



14: R = C_2H_5
15: R = CH_3
16: R = CH_2Ph



17: R = CH_3
18: R = C_2H_5
19: R = CH_2Ph



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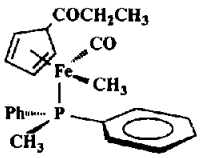

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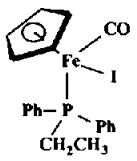
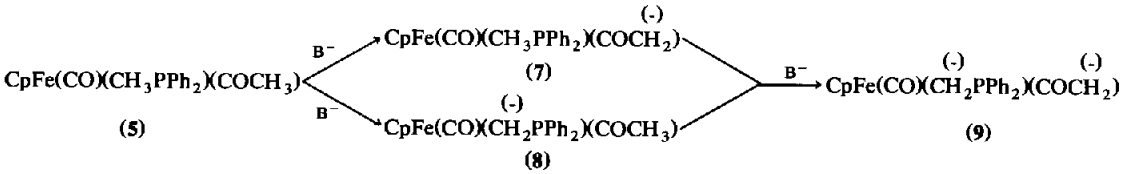


21a

ethyl iodide or benzyl bromide, with the reagents in 1:2:2 ratio, gave very similar results (Table 2, entries 7 and 8).

Alkylation of the other complex, the propionyliron **6**, was performed with a 1:1:1 ratio of complex, base and alkyl halide. From the methylation reaction, a single product was isolated and identified as **17**, *i.e.* methylation had occurred in the P-methyl group. The corresponding product **20** was obtained from benzyl bromide.

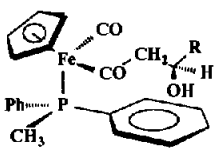
When the methylation was performed with 2 molar equivalents of the base, two products were obtained in 76% and 23% yield. One of them, complex **21**, was identified on the basis of ^1H NMR and HR-MS data (Tables 5 and 6) as the product of propionyl group migration from Fe to Cp and methylation at the iron atom. Davies [13] described a similar methylation with rearrangement for $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COC_6H_5)]$ and several other acylirons. The interpretation offered by Davies [13] involved deprotonation of the cyclopentadienyl ligand, migration of the benzoyl group from Fe to Cp, and methylation of the iron anion. Experiments with optically active complexes [12] have shown that rearrangement-methylation sequence is associated with racemization at the iron centre. We think that formation of **21** follows a similar pattern, indicating that deprotonation of the cyclopentadienyl ligand occurs more readily than that at the α-position of the propionyl ligand.



Scheme 1.

TABLE 2. Yields of alkylation products **10–19** for various molar ratios of reagents

Entry no.	Molar ratio **5** base RX	Complex no.	Yield (%)	Complex no.	Yield (%)	Complex no.	Yield (%)
1	1:1:1	**10**	64	–	–	–	–
2		**11**	35	–	–	–	–
3		**12**	74	–	–	–	–
4		**13**	36	**14**	8.5	–	–
5	1:2:1	**10**	21	**15**	21	–	–
6	1:2:2	**10**	23	**15**	5	**17**	67
7		**13**	17	**14**	7	**18**	61
8		**12**	6	**16**	6	**19**	78



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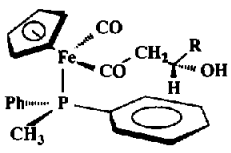


23

a: R = CH_3

b: R = Ph

c: R = p-$O_2NC_6H_4$

d: R = p-BrC_6H_4

e: R = CH_3CH_2

f: R = p-$H_3COC_6H_4$

g: R = PhCH=CH

The minor, iodine-containing product, was tentatively judged to be structure **21a** on the basis MS fragmentation data.

In order to confirm that decomplexation had followed the usual course [14], complex **12** was treated with N-bromosuccinimide in methanol, to yield methyl 3-phenylpropionate in 76% yield.

2.2. Aldol reactions

Aldol reactions were carried out with the anion generated from **5**. The reagents, *i.e.* the complex; ^{n}BuLi, and aldehyde were taken first in 1:1:1 ratio. Acetaldehyde gave two diastereoisomeric products, **22a** and **23a**, in 62% yield and in 4.8:1 ratio.

Similar results were obtained with benzaldehyde and *p*-nitrobenzaldehyde (Table 3, entries 2 and 3). Surprisingly, with *p*-bromobenzaldehyde, the proportion of diastereomeric products **22d** and **23d** was reversed (Table 3, entry 4). Under these conditions no substitution in the phosphine ligand was observed.

When 2 equivalents of the base were employed (**5**:^{n}BuLi:aldehyde = 1:2:1) for the reaction with acetaldehyde, besides the expected aldol products **22a** and **23a**, some of the phosphine-substituted product **24a** was isolated.

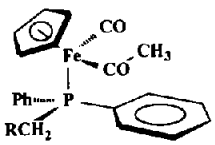
Propionaldehyde yielded only **22e**, in a low yield (12%), and traces of a phosphine-substituted product **24b**. With benzaldehyde and *p*-methoxybenzaldehyde the products **22b** and **22f** dominated over stereoisomers **23b** and **23f**; phosphine-modified products **24c** and **24d** were isolated in 7% and 14% yield, respectively. Again, *p*-bromobenzaldehyde yielded distinctly more **23d** than **22d** and the phosphine-modified product **24e** was also isolated, in 27% yield.

Increasing the amount of base for generation of the anion to 5 molar equivalents and treating the anion with *p*-bromobenzaldehyde, markedly enhanced the stereoselectivity of the reaction, but at the cost of a decreased yield (Table 3, entry 12). Cinnamaldehyde did not show any stereodiscrimination in this reaction, and yielded **22g** and **23g** in 1:1 ratio. When the ratio of acetaldehyde in this reaction was increased to two molar equivalents, the yield of aldol-type products **22a** and **23a** fell to 49%, with loss of the stereoselectivity, and the phosphine-modified product **24a** was obtained in 40% yield.

The phosphine-substituted products **24**, although not very stable, did not undergo further reaction, *e.g.* those leading to styrene-type products. This shows that the P-methylene anion **7** is not of the ylid type. Condensation of the anion generated from propionyliron **6**

TABLE 3. Yields of aldol condensation products **22a–g**, **23a–g** and **25a,b** for various molar ratios of reagents

Entry	Molar ratio **5** BuLI RCHO	Complex no.	Yield (%)	Complex no.	Yield (%)	Complex no.	Yield (%)
1	1:1:1	**22a**	51.4	**23a**	10.6	–	
2	1:1:1	**22b**	46.3	**23b**	17.7	–	
3	1:1:1	**22c**	33.3	**23c**	7.7	–	
4	1:1:1	**22d**	8.2	**23d**	29.8	–	
5	1:2:1	**22a**	46.4	**23a**	11.6	**24a**	5
6	1:2:1	**22e**	12.0	**23e**	–	**24e**	Trace
7	1:2:1	**22b**	46.5	**23b**	14.5	**24b**	7
8	1:2:1	**22d**	5.2	**23d**	52.8	**24d**	27
9	1:2:1	**22f**	44.6	**23f**	12.4	**24f**	14
10	1:2:1	**22g**	23.0	**23g**	23.0	**24g**	–
11	1:2:2	**22a**	24.5	**23a**	24.5	**24a**	40
12	1:5:1	**22d**	trace	**23d**	8.9	**24d**	30
	6 BuLi RCHO						
13	1:1:1					**25a**	36.1
14	1:1:1					**25b**	40.4



24

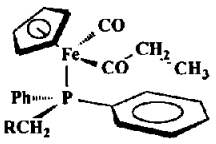
a: R = CH_3CHOH

b: R = CH_3CH_2CHOH

c: R = PhCHOH

d: R = p-$H_3COC_6H_4CHOH$

e: R = p-BrC_6H_4CHOH



25

a: R = CH_3CHOH

b: R = PhCHOH

with acetaldehyde or benzaldehyde (with the reagents taken in 1:1:1 ratio) led to products **25a** and **25b**, respectively. Their structures were derived from ^1H NMR and MS data (Tables 3, 5). As for alkylation, reaction took place only at the phosphine methyl group.

Products **24a–e** and **25a,b** were mixtures of diastereoisomers (two Cp signals in *ca.* 5–3:1 proportions). We did not succeed in separating these products.

It is known that replacement of the lithium cation by tin(II) or diethylaluminium cations [13,14] substantially increases the stereoselectivity of the anion generated from acetyliron in reactions with aldehydes. We examined the influence of these ions on the stereoselectivity of aldol reactions with the anion generated from **5**. As the results in Table 4 demonstrate, high stereoselectivity was achieved, but the yields of products were rather low.

3. Conclusions

Any interpretation of the results of alkylation must take account of steric and electronic factors. It seems that steric accessibility of the protons to the base plays a substantial role in the reactivity of complexes **5** and **6**. Apparently removal of a proton from a methyl group, whether located in the acetyl group or bonded to phosphorus atom, is easier than that from the methylene group in the propionyl ligand. In turn, deprotonation of the acetyl group in **5** occurs more readily than that of the P-methyl group. Alkylation of the anion **7** leads cleanly to the reaction at the acyl ligand. Some ion interchange **7** ⇌ **8** is obviously possible as evidenced by the ethylation reaction (Table 2, entry 4).

Use of 2 molar equivalents of the base in the deprotonation of **5** promotes the formation of di-anion **9**. Alkylation with 2 molar equivalents of alkyl halides leads to bis-alkylated complexes as the dominant products. The proportion of mono-alkylated side products is clearly in favour of the acyl-alkylated complexes which may arise from the higher nucleophilicity of the acetyl-derived anion or its easier steric accessibility to the reagent.

The results of the reaction of **5** with aldehydes strongly resemble those of alkylation. By controlling the complex to base ratio one can achieve reaction at the acetyl group or, with a 2 molar proportion of the base at the phosphine ligand.

In the case of complex **6**, even when an equimolar amount of the base is used for deprotonation, reaction with aldehydes takes place only at the phosphine methyl group.

The yields of alkylation and aldol reaction products are good. The pronounced stereoselectivity of the aldol reaction is remarkable. The proportion of stereoisomers remains at least 3–5:1, whereas practically no stereodiscrimination could be observed for reaction of lithium enolate of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_3$ with aldehydes [14].

We intend to continue further studies on reactions of acylirons containing other phosphine ligands.

4. Experimental details

All reactions were carried out under a dry argon atmosphere. Solvents were purified and distilled under argon before use. ^1H NMR spectra were recorded with Bruker AM-500 (500 MHz) and Varian Gemini (200 MHz) spectrometers, C_6D_6 solutions were used, with TMS as internal standard.

High resolution mass spectra (HR-MS) were obtained with a AMD-604 mass spectrometer. Infrared spectra were recorded on a Perkin-Elmer Model 597 double beam spectrophotometer calibrated with

TABLE 4. Yields of aldol condensation products **22b,c,e** and **23b,c** in the presence of counterions

Entry	Additive	Molar ratio 5 BuLi counterion RCHO	Complex no.	Yield (%)	Complex no.	Yield (%)
1	$SnCl_2$	1:2:3:1	**22b**	–	**23b**	17
2	$SnCl_2$	1:2:3:1	**22c**	1.5	**23c**	17.5
3	Et_2AlCl	1:2:3:1	**22b**	13.6	**23b**	1.4
4	Et_2AlCl	1:2:3:1	**22e**	28	**23e**	–

TABLE 5. ^{1}H NMR data for the selected alkylation and aldol condensation products from **5** and **6**

Entry	Complex no.	δ(Cp) J(P, H) Hz	δ(COR)	δ(CH_3P) J(P, H) Hz
1	**11**	4.21 (d, 0.88)	5.80 (m, 1H, Hγ); 5.05 (m, 2H, H_δ, H'_δ); 3.16 (ddd 1H, $J_{\alpha\alpha'}$ = 17.1, H_α); 2.15 (m, 2H, $H_\beta H'_\beta$)	1.82 (d, 9.20)
2	**12**	4.17 (d, 1.10)	3.27 (dd, 1H, $J_{\alpha\alpha'}$ = 16.32, H_α); 3.14 (dd, 1H, $J_{\alpha\beta}$ = 6.09, H_β); 2.78 (dd, 1H, $H_{\alpha'}$); 2.61 (dd, 1H, $J_{\beta\beta'}$ = 13.71, $H_{\beta'}$)	1.82 (d, 9.28)
3	**13**	4.23 (d, 1.28)	2.90 (dd, 1H, $J_{\alpha\alpha'}$ = 16.02, H_α); 2.50 (dd, 1H, $J_{\alpha\beta}$ = 6.84, $H_{\alpha'}$); 1.62 (m, 2H, H_β, $H_{\beta'}$); 0.81 (t, 3H, $J_{\beta\gamma}$ = 7.76)	1.83 (d, 9.28)
4	**15**	4.14 (d, 1.00)	2.65 (s, 3H, $COCH_3$); 2.24 (m, 2H, CH_2P); 0.81 (m, 3H, CH_3CH_2P)	
5	**17**	4.17 (d, 1.02)	2.91 (m, 2H, H_α, P–CH); 2.42 (m, 1H, $H_{\alpha'}$); 2.25 (m, 2H, CH_2P); 1.07 (t, 3H, CH_3CH_2CO); 0.78 (m, 3H, CH_3CH_2P)	
6	**21**	4.87 (bs, 2H, H-2, H-5) 3.95 (bs, 2H, H-3, H-4)	2.33 (q, $COCH_2$, J = 14.22); 1.15 (t, 3H, J = 7.32, CH_3CH_2); 0.11 (d, 3H, J = 6.2, CH_3Fe)	1.56 (d, 8.54)
7	**22a**	4.17 (d, 1.17)	3.95 (m, 1H, H_β); 2.92 (dd, 1H, $J_{\alpha\alpha'}$ = 17.47, H_α); 2.63 (dd, 1H, $J_{\alpha\beta}$ = 9.37, $H_{\alpha'}$); 1.05 (d, 3H, $J_{\beta\gamma}$ = 6.19, H_γ)	1.76 (d, 9.40)
8	**22b**	4.10 (d, 1.28)	4.85 (dd, 1H, J = 9.71, H_β); 4.65 (bs, 1H, OH); 3.26 (dd, 1H, $J_{\alpha\alpha'}$ = 17.40, H_α); 2.95 (dd, 1H, $J_{\alpha\beta}$ = 9.50, $H_{\alpha'}$)	1.79 (d, 9.34)
9	**22c**	4.12 (d, 1.29)	5.95 (m, 1H, H_β); 4.65 (s, 1H, OH); 3.01 (dd, 1H, $J_{\alpha\alpha'}$ = 17.48, H_α); 2.65 (dd, 1H, $J_{\alpha\beta}$ = 9.61, $H_{\alpha'}$)	1.77 (d, 9.40)
10	**22f**	4.12 (d, 1.32)	4.84 (m, 1H, H_β); 4.58 (s, 1H, OH); 3.30 (s, 3H, OCH_3); 3.28 (dd, 1H, $J_{\alpha\alpha'}$ = 17.48, H_α); 2.96 (dd, 1H, $J_{\alpha\beta}$ = 9.57, $H_{\alpha'}$)	1.78 (d, 9.38)
11	**22e**	4.17 (d, 1.32)	3.85 (bs, 1H, OH); 3.64 (m, 1H, H_β); 3.05 (dd, 1H, $J_{\alpha\alpha'}$ = 17.45, H_α); 2.72 (dd, 1H, $J_{\alpha\beta}$ = 8.80, $H_{\alpha'}$); 2.42 (m, 2H, H_α, $H_{\gamma'}$); 0.90 (t, 3H, $J_{\beta\gamma}$ = 7.22, CH_3)	1.77 (d, 9.38)
12	**23a**	4.19 (d, 1.16)	4.24 (m, 1H, H_β); 3.22 (dd, 1H, $J_{\alpha\alpha'}$ = 16.72, H_α); 2.42 (dd, 1H, $J_{\alpha\beta}$ = 9.37, $H_{\alpha'}$)	1.74 (d, 9.36)
13	**23b**	4.15 (d, 1.34)	5.27 (dt, 1H, $J_{\alpha\beta}$ = 10.07, H_β); 3.49 (dd, 1H, $J_{\alpha\alpha'}$ = 16.85, H_α); 2.78 (dd, 1H, H'_α)	1.72 (d, 9.30)
14	**23c**	4.17 (d, 1.34)	5.02 (m, 1H, H_β); 4.65 (bs, 1H, OH); 3.01 (dd, 1H, $J_{\alpha\alpha'}$ = 17.48); 2.65 (dd, 1H, $J_{\alpha\beta}$ = 9.61, $H_{\alpha'}$)	1.77 (d, 9.40)
15	**23d**	4.15 (d, 1.21)	5.05 (m, 1H, H_β); 3.35 (dd, 1H, $J_{\alpha\alpha'}$ = 16.85, $H_{\alpha'}$); 2.56 (dd, 1H, $J_{\alpha\beta}$ = 9.96, $H_{\alpha'}$)	1.72 (d, 9.30)
16	**23f**	4.16 (d, 1.30)	5.23 (m, 1H, H_β); 4.60 (bs, 1H, OH); 3.60 (dd, 1H, $J_{\alpha\alpha'}$ = 16.45, H_α); 3.30 (s, 3H, OCH_3); 2.76 (dd, 1H, $J_{\alpha\beta}$ = 10.06, $H_{\alpha'}$)	1.75 (d, 9.28)
17	**23b**	4.27 (d, 0.90)	5.03 (m, 1H, CH(OH); 3.36–3.26 (m, 2H, H_α, $H_{\alpha'}$); 2.81 (m, 2H, CH_2–P); 1.16 (t, 3H, CH_3)	
		δ (J(PH) Hz)		
18	**24e**	4.8–5.0 (m, 1H, C*H*OH); 4.26 and 4.20 (2d, 5H, J(Cp,P) 1.20, 1.40, two Cp signals in 1:3.5 proportion); 2.86 (s, 3H, CH_3CO); 2.60–2.72 (m, 3H, PCH_2, OH)		
19	**25b**	4.9–5.1 (m, 1H, C*H*OH); 4.33 and 4.28 (2s, 5H, two Cp signals in 1:4.7 proportion); 3.37 and 3.15 (AB system, 2H, $COCH_2CH_3$); 2.78–2.88 (m, 2H, PCH_2); 1.13 (t, 3H, $COCH_2CH_3$)		

polystyrene film (1602 cm^{-1}). Reactions were monitored by TLC on Merck Alu-Plates (0.2 mm), and column chromatography was performed on silica gel (70–230 mesh). Melting points are uncorrected.

Commercial n-butyllithium (1.6 M solution in n-hexane) and a 1.5 M solution of diethylaluminium chloride in toluene were used. Anhydrous tin dichloride was prepared by the reported method [15].

Complex **5** was obtained in 84% yield by a published method [9a,b].

4.1. Synthesis of $(\eta^5\text{-}C_5H_5)Fe(CO)(CH_3PPh_2)COC_2H_5$ (6)

To a solution of η^5-cyclopentadienyldicarbonyliron anion (obtained from 3.5 g of dicyclopentadienyltetracarbonyldiiron) in 30 ml THF ethyl iodide (3.2 g, 0.02 mol) was added dropwise. The mixture was stirred for 12 h at room temperature, then the THF was removed *in vacuo* and the residue was extracted under argon with hexane (2 × 50 ml). The extract was evaporated to dryness and the crude ethylation product, $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$, was obtained as pale yellow oil in 90% yield (3.6 g). This was refluxed in acetonitrile (50 ml) with methyldiphenylphosphine (3.8 g) for 60 h. After the reaction was complete (TLC), the solvent was removed and the residue was chromatographed on silica gel with hexane/ethyl acetate (3:1) as eluent. Compound **6** was obtained as an orange powder in 89% yield (6.3 g).

4.2. Alkylation of $(\eta^5\text{-}C_5H_5)Fe(CO)(CH_3PPh_2)COCH_3$ (5)

To a solution of **5** (0.15 g, 0.38 mmol) in THF (10 ml), cooled to −78°C was added, n-butyl lithium (0.25 ml, 0.38 mol in the case of 1:1 molar ratio of reagents). The mixture turned red, and was stirred for 15 min and then the appropriate amount of alkyl halide (*e.g.* benzyl bromide 0.065 g, 0.38 mmol) was added. The mixture was stirred at −78°C for a further 30 min and then allowed to warm to room temperature. Thereafter addition of 1 ml of methanol quenched the reaction. Solvent was removed *in vacuo* and the residue was separated by column chromatography using hexane/ethyl acetate (9:1) for elution. Eluted first was the product of alkylation at the phosphine methyl group (*e.g.* **16**). Continued elution with hexane/ethyl acetate (4:1) gave the unchanged substrate (10–20%) and after change of the ratio of components in the eluent to 3.5:1.5, the product of alkylation in the acetyl ligand (*e.g.* **12**) was obtained.

The same procedure was used for alkylation of **5** with methyl, ethyl, and allyl bromides. The yields of these reactions are listed in Table 2.

TABLE 6. High resolution mass spectral data for selected alkylation and aldol condensation products

Entry	Complex no.	m.p. (°C)	Formula	MS (*m/z*)	
				Calc	Found
1	**11**	97–99	$C_{24}H_{25}FeO_2P$	432.0941	432.0951
2	**12**	131–132	$C_{28}H_{27}FeO_2P$	482.1098	482.1100
3	**13**	103–105	$C_{23}H_{25}FeO_2P$	420.0941	420.0942
4	**15**	114–116	$C_{22}H_{23}FeO_2P$	406.0785	406.0783
5	**17**	113–115	$C_{23}H_{25}FeO_2P$	420.0941	420.0942
6	**21**	Oil	$C_{23}H_{25}FeO_2P$	420.0942	420.0942
7	**22a**	106–107	$C_{23}H_{25}FeO_3P$	436.0891	436.0889
8	**22b**	79–80	$C_{28}H_{27}FeO_3P$	498.1047	498.1049
9	**22e**	Oil	$C_{24}H_{27}FeO_3P$	450.1047	450.1033
10	**23a**	Oil	$C_{23}H_{25}FeO_3P$	436.0891	436.0889
11	**23d**	146–147	$C_{28}H_{26}FeO_3PBr$	576.0152	576.0147
12	**24e**	156–159	$C_{28}H_{26}FeO_3PBr$	576.0152	576.0147

4.3. Alkylation of $(\eta^5\text{-}C_5H_5)Fe(CO)(CH_3PPh_2)COCH_2CH_3$ (6)

n-Butyl lithium (0.52 ml, 0.74 mmol) was added dropwise with stirring to a solution of **6** (150 mg, 0.37 mol) in THF (10 ml) cooled to −78°C. A dark-red colour developed immediately. After 15 min methyl iodide (52 mg, 0.37 mmol) in THF (1 ml) was added, and the mixture was then evaporated to dryness *in vacuo* and the residue separated by column chromatography on a silica gel with hexane/ethyl acetate (4:1) as eluent. Eluted first was the green-coloured iodine-containing product **21a** (37 mg, 23%). MS data; 490 $[CpFeI(CO)(Ph_2PCH_2CH_3)]$, 462, 335, 248, 214 $(Ph_2PCH_2CH_3)$. Eluted second was the rearrangement product **21** (104 mg, 76.5%). ^1H NMR data are given in Table 5 and HR-MS data in Table 6.

4.4. Reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)(CH_3PPh_2)COCH_3$ (5) with aldehydes

For the generation of anions from **5**, the same procedure was employed as in the alkylation reaction. After addition of aldehyde, the mixture was stirred for 10 min at −78°C, then quenched with methanol and evaporated under reduced pressure to dryness. The products were isolated by column chromatography with hexane/ethyl acetate (1:1) as eluent. Eluted first were the *RR/SS* stereoisomers followed by those of *RS/SR* configuration.

The yields and proportions of the products are listed in Table 3. The ^1H NMR data are given in Table 5 and HR-MS data of selected products in Table 6. The experiments with counterions (Table 4) were performed as described previously [13].

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