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Elaboration of the Acyl Ligand in Complex $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COCH_2Ph)$[1,2]

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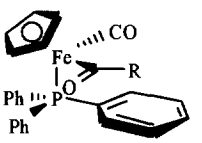
Abstract: Deuteration and alkylation of the acyl ligand in $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COCH_2Ph)$ (**2**) led to mixtures of the diastereomeric products, and the diastereomeric proportions varied with the base used for deprotonation of **2** at -78°C. When alkylation was performed at +16°C, the results of alkylation were similar, irrespective of the base used for deprotonation . The effect of experimental conditions on the stereochemical results of these reactions was also studied. Reactions of **2** with acetaldehyde and benzaldehyde were practically non-stereoselective and the diastereomeric proportions of the products were influenced by bases employed for deprotonation. Tin dichloride or diethylaluminum chloride promoted the predominant formation of single stereoisomers. The reaction of **2** with acetone was similar to its alkylation at -78°C. Decomplexation of alkylation products with NBS resulted in bromides, and decomplexation of aldol product **11** led to mixtures of stereomeric epoxides and bromides. Decomplexation was connected with decarbonylation of the acyl ligand.

Since the first report of highly stereoselective alkylations of complex **1** (R = Me),[3,4] the properties of **1** having different acyl ligands, e.g. R = acyl[5] or α,β-unsaturated acyl,[6] have been extensively studied and their applications to asymmetric synthesis have been fully demonstrated,[7] but before us,[2] there had been no research on complex **2**. We became interested in complex **2** not only because arylacetyl ligands represent an important kind of synthons in organic synthesis but also because the special properties of the aryl substituent may result in some unique behavior of such complexes. The special properties of aromatic substituents include: (1) their pronounced ability to stabilize a radical or a charge on the α-atom, which determines the special reactivity of aromatic compounds and also determines the conformational preference of their reactive intermediates; (2) their specific steric demands, e.g. phenyl group can be larger than t-butyl group or smaller than methyl group according to its different orientations. Therefore, we have synthesized complex **2** and carefully studied its various reactions.



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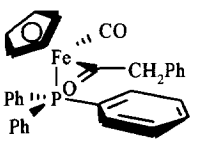

2

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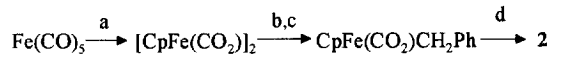
RESULTS

1. Synthesis of Complex 2

The orange, air-stable and brick-colored crystalline complex **2**, with a sharp m.p. of 157°C, first described by Brunner,[8] was prepared by reactions shown in Scheme 1. X-Ray structural determination[9] proved the typical pseudooctahedral[10] arrangement of ligands in **2**.

Scheme 1

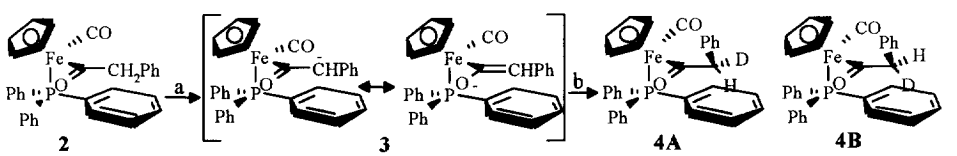


a. dicyclopentadiene, Ar., refl., 20h, 95% b. Na-Hg, THF, Ar., r.t., 2h
c. BnBr, THF, Ar., r.t., 4h d. PPh_3, CH_3CN, Ar., refl., 30h, 37%

2. Deuteration and Alkylation of 2

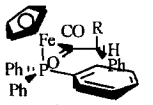
Treatment of the orange solution of **2** in THF with two equivalents of n-butyl lithium at -78°C led to a dark red solution of lithium enolate **3** (the use of an excess of the base was beneficial for the fast generation of **3** and for the high yield of alkylation products). The THF solution of **3** was very stable at -78°C under argon. Addition of deuterium oxide resulted in a mixture of two diastereomeric products, **4A** and **4B** (Scheme 2), in proportion of 5.2:1.0 (configuration of **4A** and **4B** was based on ^1H NMR spectra[11]). Therefore, the deuteration of **3** was of limited stereoselectivity.

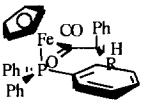
Scheme 2



a. 2eq. n-BuLi, THF, -78°C, 30min b. D_2O, THF, -78°C, 1h, 95%

Similarly, on addition of methyl iodide, ethyl, allyl and benzyl bromides to **3** at -78°C as above, inseparable diastereomeric mixtures of alkylation products **5A-8A** and **5B-8B**(configurations assigned by ^1H-NMR spectra[11]) were obtained in proportions close to 6.0:1.0 (Table 1). These results were very similar to that of deuteration, which confirmed that alkylation of **2** also was of limited stereoselectivity. It is interesting to note that these results were different from those obtained with all other complexes.[3-6] To our surprize, deuteration and alkylations of **3** generated from **2** with LDA led to diastereomeric products **A** and **B** in proportions close to 1:2.4. Here, in contrast to the results achieved with n-BuLi, isomers **B** were obtained as the major products (Table 1). To the best of our knowledge, this was the first observation of reversed stereoselectivity induced by an achiral base.





	A	B
5	R= Me	Me
6	Et	Et
7	All	All
8	Bzl	Bzl
9	i-Bu	i-Bu
10	i-Pr	i-Pr

Table 1. Deuteration and alkylation product-proportions in relation to bases at -78°C

Electrophile	Product	Base and product proportion		
		LDA	t-BuLi	n-BuLi
D_2O	**4A:4B**	1.0:2.4	-	5.2:1.0
MeI	**5A:5B**	1.0:2.4	1.6:1.0	6.3:1.0
EtBr	**6A:6B**	1.0:2.4	1.6:1.0	3.5:1.0
AllBr	**7A:7B**	1.0:1.8	-	6.4:1.0
BzlBr	**8A:8B**	1.0:2.3	1.4:1.0	8.2:1.0

We had also examined the alkylation reactions of **2** with t-butyl lithium as the base. These reactions resulted in diastereomeric product proportions close to 1.6:1 (Table 1).

As clearly shown in Table 1, the alkylating reagents had practically negligible influence on the product proportions for a given base. It was also proved by experiments in which a change of the interval time between deprotonation and alkylation reactions (from 5 to 180 minutes) did not affect the product proportions either. The results of all alkylation reactions were well reproducible under the same experimental conditions.

If the solution of **3,** generated at -78°C, was allowed to warm up gradually to ambient temperature (+16°C) and then quenched with methyl iodide or allyl bromide, the observed product proportions (Table 2) were distinctly different from those obtained at -78°C (Table 1). Reaction of **2** with isobutyl bromide at +16°C also led to products in similar proportions. However, the proportion of diastereomers produced by reaction with isopropyl bromide was different. The results in Table 2 clearly show that the product proportions of methylation, allylation and isobutylation of **2** were practically unaffected either by the base employed or by alkylating reagents. Evidently, different rate-determining steps were involved in reactions performed at +16°C and at -78°C. We found also that the final product proportions were not altered whether the enolate was kept at +16°C for 5 or for 35 minutes before adding the alkylating reagents.

Table 2. Alkylation product-proportions in relation to bases at room temperature

Electrophile	Reaction temp.(°C)	Product	Base and product-proportion	
			LDA	n-BuLi
MeI	+16	**5A:5B**	2.1:1.0	2.6:1.0
AllBr	+16	**7A:7B**	2.8:1.0	2.9:1.0
i-BuBr	+16	**9A:9B**	3.0:1.0	3.3:1.0
i-PrBr	+16	**10A:10B**	1.3:1.0	1.3:1.0

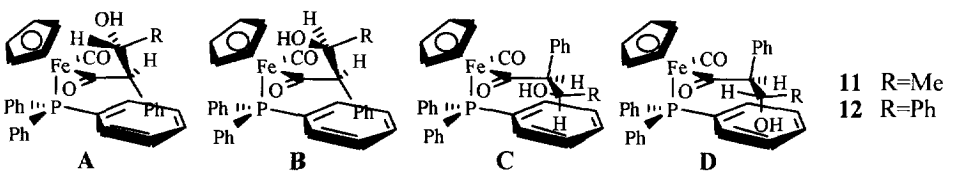
The study of the stability of lithium enolate **3** has shown that it was very stable in THF under argon at -78°C and it was also stable enough to be alkylated at ambient temperature without obvious decline in product yields (Table 3). Therefore, enolate **3** was much more stable than the enolates derived from other iron complexes[5,12]. These observations indicated the important influence of substituents on the stability of enolates.

Table 3. Influence of experimental conditions on yields of deuteration and alkylation products

Electrophile	Product	Reaction temp.(°C)	Time between deprot. & alkyl.	Base and yield(%) LDA	t-BuLi	n-BuLi
D_2O	**4A, 4B**	-78	20min	90.0	-	95.0
MeI	**5A, 5B**	-78	5-30min	88.0	92.0	87.0
		-78	180min	70.0	-	64.0
		+16	35min	86.0	-	47.0
		+16	60min	68.0	-	-
EtBr	**6A, 6B**	-78	20min	82.0	81.0	88.0
i-BuBr	**7A, 7B**	+16	35min	72.0	-	73.0
AllBr	**8A, 8B**	-78	20min	97.0	-	87.0
		+16	35min	85.0	-	88.0
BzlBr	**9A, 9B**	-78	5-30min	75.0	84.0	94.0
i-PrBr	**10A,10B**	+16	35min	41.0	-	57.0

3. Aldol Condensation of 2 with Carbonyl Compounds

On addition of acetaldehyde and benzaldehyde to lithium enolate **3** mixtures containing all four possible diastereomeric products were obtained in proportions of **11A:11B:11C:11D**=1.0:12.4:4.4:2.3 and **12A:12B:12C:12D**=1.0:3.3:2.7:1.1, respectively. These orange and air-stable mixtures were inseparable by flash column chromatography, but were easily separated by HPLC. The configurations of the products were assigned according to their ^{1}H-NMR spectra and one of the assignments was proved by X-ray study of crystalline **11D**[11].



As shown in Table 4 and 5, the product proportions of the aldol condensation between **2** and aldehydes at -78°C were again affected by the bases as in the case of alkylation at the same temperature. However, the proportions of products with opposite α-carbon configurations [**(A+B):(C+D)**] were not the same as those of alkylation, and furthermore, the product proportions were also dependent on aldehydes.

As generally observed in aldol condensation reactions,[5a,13] counter cations can alter the stereochemical outcome of reactions between **1** and aldehydes. Exchange of lithium cation in **3** for diethylaluminum cation or

divalent tin cation resulted in preferential formation of one diastereomer (Table 5 and 6). Diethylaluminum cation promoted the formation of **11C** or **12C**, whereas the divalent tin cation induced the predominant formation of **11A** or **12B**. It is evident that the major products have opposite configurations at the α-carbon atom.

Table 4. Product proportions in reactions between **2** and acetaldehyde in relation to bases

Base	Reaction Temp.(°C)	**11A**	**11B**	**11C**	**11D**	**(11A+11B):(11C+11D)**
LDA	-78	1.0	4.4	5.4	10.8	1.0:3.0
t-BuLi	-78	1.0	16.4	7.6	10.6	1.0:1.1
n-BuLi	-78	1.0	12.4	4.4	2.3	2.0:1.0

Table 5. Product proportions in reactions between **2** and benzaldehyde in relation to bases

Base	Reaction Temp.(°C)	**12A**	**12B**	**12C**	**12D**	**(12A+12B):(12C+1D)**
LDA	-78	1.3	1.0	5.5	1.0	1.0:3.5
t-BuLi	-78	1.0	2.4	4.3	1.0	1.0:1.7
n-BuLi	-78	1.0	3.3	2.7	1.1	1.2:1.0

This result is different from that of aldol condensations between other acyl iron complexes[5a,c] and aldehydes, where countercations only caused the preferred formation of products with different configurations at the β-carbon atom but with the same configuration at the α-carbon atom. In fact, in the reactions of **2**, the influences of counter cations on discrimination of the α-carbon atom configuration [**(A+B):(C+D)**] were even more evident than on the β-carbon atoms (**A:B** or **C:D**) (Table 6 and 7).

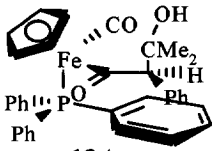
Table 6. Product proportion in reaction between **2** and acetaldehyde in relation to bases and cations

Base+cation	**11A**	**11B**	**11C**	**11D**	**(11A+11B):(11C+11D)**	Major Product
LDA+$SnCl_2$	5.2	1.0	2.4	1.2	1.7: 1.0	**A**
n-BuLi+$SnCl_2$	20.6	7.1	1.0	1.8	9.9: 1.0	**A**
LDA+Et_2AlCl	1.0	0.1	11.6	1.8	1.0:12.5	**C**
n-BuLi+Et_2AlCl	1.0	0.1	6.4	2.7	1.0: 8.3	**C**

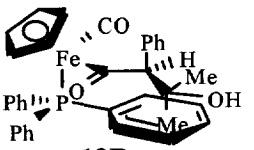
Table 7. Product proportion in reaction between **2** and benzaldehyde in relation to bases and cations

Base+cation	**12A**	**12B**	**12C**	**12D**	**(12A+12B):(12C+12D)**	Major Product
LDA+$SnCl_2$	20.7	42.9	2.0	1.0	21.2: 1.0	**B**
n-BuLi+$SnCl_2$	4.8	58.0	2.4	1.0	18.5: 1.0	**B**
LDA+Et_2AlCl	1.0	-	30.0	2.3	1.0:32.3	**C**
n-BuLi+Et_2AlCl	1.0	-	16.0	6.1	1.0:22.1	**C**

The reaction between **2** and acetone at -78°C, with n-butyl lithium as the base, resulted in a mixture of two diastereomeric products **13A** and **13B** (6.2:1.0). The configuration of the products was deduced from their ^{1}H-NMR spectra and the configurational assignment of **13A** was proved by X-ray determination.[9] The product proportion of this reaction was again influenced by bases (**13A:13B**=6.2:1.0 with n-BuLi, **13A:13B**=1.0:3.2 with t-BuLi), and these results were rather similar to those of alkylations of **2** at -78°C (Table 1).



13A

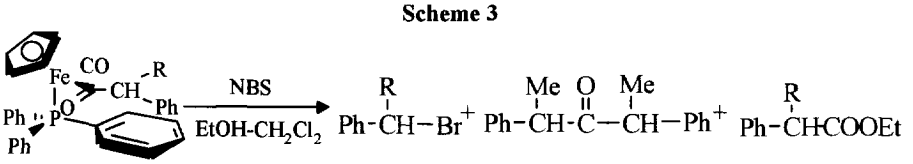


13B

4. Oxidative Degradation of Complexes Derived from 2

On decomplexation of **5** with NBS in dichloromethane and ethanol (Scheme 3), α-bromoethylbenzene **14** was isolated as the major product in a yield of 50%. Compound **15** was also obtained as a second product in a yield of ca. 10%. Only a trace amount of ethyl α-phenylpropionate **16** was observed in the HR-MS spectrum but not in the ^{1}H-NMR spectra. Similarly, decomplexation of benzylation product **8** with NBS in dichloromethane-ethanol resulted in 56% yield of bromide **17** and a trace amount of **18**.

Scheme 3

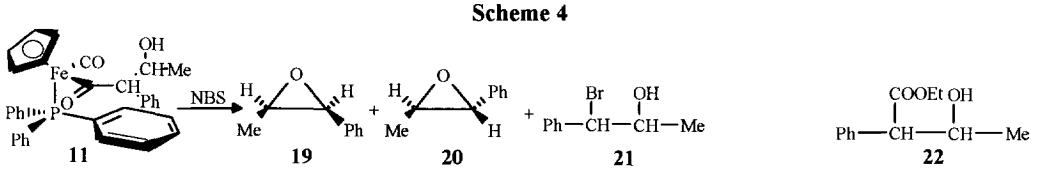


5 R=Me, **8** R=Bn

14 R=Me(50%), **17** R=Bn(56%) **15**(10%) **16** R=Me, **18** R=Bn

On decomplexation of **11** with NBS in dichloromethane and ethanol at -78°C for 0.5h and then at ambient temperature for 2h, a mixture of *cis*- and *trans*-epoxides **19** and **20** (1.0:1.6) was obtained in 84% yield. Decomplexation of **11** with NBS in dichloromethane and ethanol at -78°C for 2h and then at ambient temperature for 1h resulted in a mixture of diastereomeric bromides **21A** and **21B** (1.4:1.0) in 38% yield with a small amount of epoxides **19** and **20** (ca. 12%, Scheme 4). In both cases, a small amount of ester **22** was also detected in the ^{1}H-NMR spectrum.

Scheme 4



11 **19** **20** **21** **22**

DISCUSSION

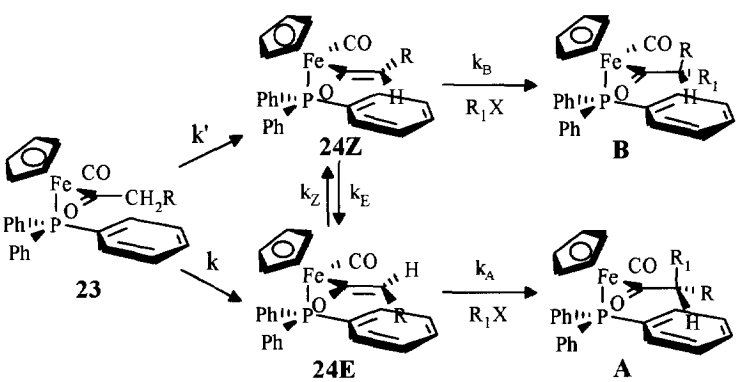
1. Alkylation Reactions of Complex 2

The alkylation reactions of **2** at -78°C were of low stereoselectivity and the stereochemical outcome was determined by the bases used. In a paper[14] Davies explained our results[2] by supposing that the poor stereoselectivity in these alkylations resulted from rapid decomposition of one product, and in order to provide support for his argument, he exposed a stirred mixture of **5A** and **5B** (5:1) to air at room temperature for 120h

to reach a ratio of **5A**:**5B**=1:6 in 7% yield. However, we think that this argument and experiment do not fit to our situation, because: (1) our experiments were conducted at -78°C under argon and purification was carried out under nitrogen. The enolates and products were indefinitely stable at low temperature and in inert atmosphere (Davies also pointed out that both isomers were stable under exclusion of air), (2) the products were isolated in very good yields (>85%), (3) the reaction and work-up usually took less than 3h; (4) Davies' reasoning cannot explain the different results achieved with various bases.

We decided to have a brief look at the kinetics of reactions shown in Scheme 5, where the alkylation reactions of **24E** and **24Z** are one-face selective.[3] In the first case, if E- and Z-enolates, **24Z** and **24E**, are in a quick equilibrium after they are formed, then, the product ratio ($P_{A/B}$) is the product of $K_{E/Z}(=k_E/k_Z)$ multiplied by k_A/k_B. $K_{E/Z}$ is a constant under certain reaction conditions and k_A/k_B is determined by the alkylating reagents R_1X. Therefore, the final product proportion should be influenced by the alkylating reagents. In the second case, if there is no equilibrium between **24Z** and **24E**, then, $P_{A/B}$ is only determined by k/k', which means that the final product proportion is only determined by the bases used for deprotonation. For complexes **24** (R=alkyl or alkoxyl), highly stereoselective alkylations can be the result of either $kk_A>>k'k_B$ in the first case or k>>k' in the second case. Therefore, if the influences of bases and R_1X on the product ratios were not observed and evaluated, just based on their highly stereoselective alkylation results, it cannot be concluded that **24E** and **24Z** are not in equilibrium.[3]

Scheme 5



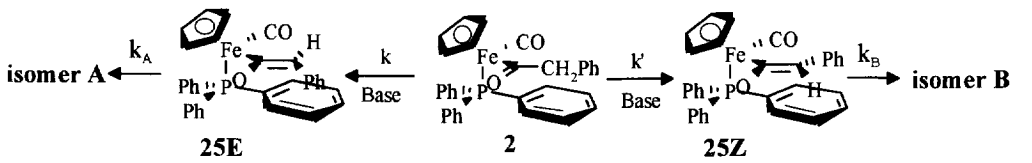
From the finding that the alkylation product proportions (**A**:**B**) of complex **2** at -78°C varied substantially with different bases used to generate **3**, whereas the proportion of products for a given base was practically the same for different alkylations, as well as from the results indicating that variation of the time interval between deprotonation and alkylation, from 5 to 180 minutes at -78°C, did not influence the product proportions of the reactions, the following conclusions could be drawn:

(1) A possible equilibrium between E- and Z-enolates under the experimental conditions employed is excluded. As discussed above, if E-enolate **25E** and Z-enolate **25Z** (shown in Scheme 6) were in a fast equilibrium, all reactions with different bases should lead to the same results.

(2) Alkylations of both, **25E** and **25Z**, are one-face selective what is consistent with Davies' observation[3,10] (the approach of the electrophile to the enolate can take place only from the open "upper" side whereas the side occupied by the triphenylphosphine ligand appears to be inaccessible due to the steric reasons).

Similarly, a quick equilibrium between *anti* and *syn* conformers of the enolates (with respect to the CO ligand) is also excluded. Otherwise, the influences of various alkylating reagents on the product proportions should be observed because of their different steric demands during the approach to the enolates.

Scheme 6



(3) These results proved that the alkylation product proportions ($P_{A/B}$) of **2** at -78°C were determined only by the deprotonation step, i.e. k_A/k_B, and therefore, $P_{A/B}$ roughly reflected the ratios of **25E** to **25Z.**

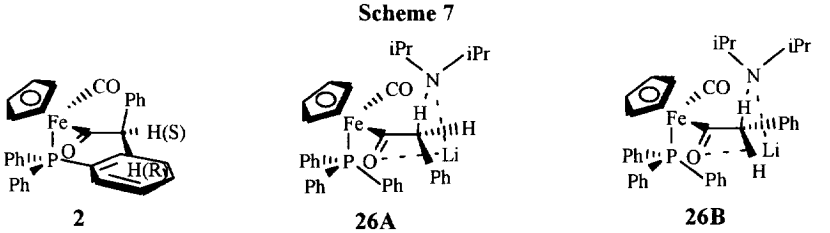
(4) n-BuLi and t-BuLi favor the generation of the enolate **25E** and LDA - of the enolate **25Z.**

Therefore, the low stereoselectivity on alkylations of **2** results from poorly discriminative formation of both enolates, and the final product proportions are only determined by the ratios of **25E** to **25Z** produced during the deprotonation reaction.

Then, how to explain the results that different bases induce different stereoselectivities in the reactions of **2**? The deprotonation of carbonyl compounds with organolithium reagents is rather complex[15]. We think that a feasible explanation of our results can be found if we assume that (a) deprotonation of phenylacetyl ligand with BuLi (and, to a major extent, with t-BuLi) meets the stereoelectronic requirement, i.e. proton to-be-removed must be perpendicularly oriented towards the Cα-C=O plane, and (b) deprotonation with LDA occurs in a cyclic transition state[16-18] (Scheme 7).

In case of bases like n-BuLi and t-BuLi, the stereoelectronic effect leads to two conformations of acyl ligand in **2**, exposing pro-R or pro-S protons to the base. In consequence, both stereoisomeric products are formed in a ratio reflecting strain energies of both transition states. On the other hand, cyclic transition state **26A** (with the Ph group inside) is obviously more strained than **26B** (with the hydrogen atom inside) and therefore, more favorable **26B** leads to the "unfavorable" Z-enolate **25Z** and isomers **A** are obtained as the major products. It is quite clear from above discussion that no matter what kind of transition state was involved in these reactions, it is the steric interactions between ligands and bases that determine the final stereochemical outcome of the reactions.

Scheme 7



Alkylation reactions of **2** carried out at ambient temperature (+16±1°C) have shown very different product proportions from those observed at -78°C (Table 2). As in these experiments, the solution of the anion **3** generated at -78°C was allowed to warm up to ambient temperature and then quenched with alkyl halides, the changed product proportions suggested an equilibrium between E- and Z-enolates at higher temperature. Furthermore, the fact that the product proportion ($P_{A/B}$=2.8±0.5) at +16°C was not affected by the base employed or the alkylating reagent, suggests that the rate of equilibration between **25E** and **25Z** should be much slower than that of alkylation and that $P_{A/B}$=2.8 roughly reflects the equilibrium constant between enolates **25E** and **25Z** ($K_{E/Z}$) at +16°C. The reaction of **2** with isopropyl bromide at +16°C led to a different product proportion ($P_{A/B}$=1.3). This difference suggests that the proportion of products of isopropylation was at least partially affected by k_A and k_B, then, the rates of isopropylation of **25E** and **25Z** were slow compared with the equilibrium between **25E** and **25Z**. The decreased rate of isopropylation may be the result of high steric hindrance of secondary bromide in reaction with the enolates. This conclusion is supported by the fact that the reaction between **3** and isopropyl bromide can only be realized at room temperature and by the observation that no reaction between **3** and cyclohexyl bromide occurs even at ambient temperature. It was estimated from these results that the reaction between Z-enolate **25Z** and isopropyl bromide is about two times as fast as with the E-enolate **25E**.

The lack of equilibration between **25E** and **25Z** at -78°C, what indicates the geometrical stability of these enolates, suggests a double-bond character of CO-Cα bond in these anions. However, the much lower equilibration temperature of enolates **25E** and **25Z** than that of a typical carbon-carbon double bond[19] suggests that CO-Cα bond possesses only a partial double-bond character. This observation may be indicative for the charge delocalization in the structures of enolates **25E** and **25Z**. Another experimental support for the delocalized structures of enolates **25E** and **25Z** is their outstanding stability compared to that of enolates **24**(R=alkyl and alkoxyl)[5,12].

2. Aldol Condensation Reaction of 2

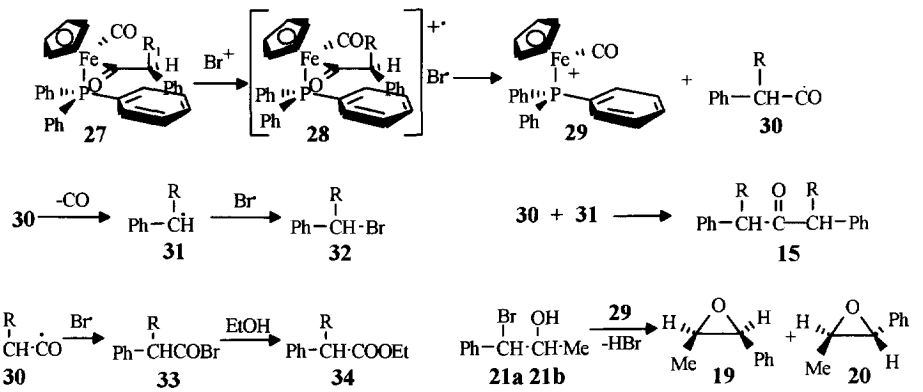
Although differences in stereochemical results of alkylation and of aldol condensation performed on acyl iron complexes have been observed since the early experiments[5a,11], a convincing model explaining the stereochemical course of aldol reactions is still lacking. As no equilibrium between E- and Z-enolates occurs at -78°C, the practically non-stereoselective aldol condensation can be caused only by a low-facial-selective attack of aldehydes on both sides of the enolates. Another possibility could be an attack of the aldehyde on **25E** and **25Z** or on their *syn* conformers (both C-O groupings *syn*), however, there is no evidence in favor of *syn* conformers occurring during the reaction. The attack of the aldehyde carbonyl group on **3** in the cleft between Ph_3P ligand and the enolate ligand seems to be improbable. As concerns the stereochemical course of aldol reactions in the presence of countercations: diethylaluminum or tin(II) the appropriate models have been proposed by Davies and Liebeskind.

3. Decomplexation

On oxidative degradation of elaborated structures of **2** with NBS, bromides or epoxides were isolated as the major products. All decomplexations were connected with decarbonylation. Because the degradations were carried out in ethanol but no trace amount of ethers were observed, the reactions most probably involve some radical intermediates. An important evidence for a radical intermediate is the isolation of coupling product **15** which can only be derived from radicals.

As shown in Scheme 8, one-electron oxidation of complex **27** by bromonium cation gave the corresponding radical cation **28** which splitted the acyl ligand as radical **30** by heterolysis. Decarbonylation of **30** formed radical **31** which was captured by bromine atom to give the major product as bromide **14**. Because decomplexation of **11** afforded a mixture of **21a**:**21b** = 1.4:1 [i.e. **32** R=CH(OH)Me], reactions of **31** with bromine atom must be practically non-stereoselective. Coupling of **30** with a small amount of **31** resulted in **15**. Only a very small amount of **30** reacted with bromine atom to form acyl bromide **33** which was then converted into corresponding esters **34** by ethanolysis. The epoxides **19** and **20** may be derived from the intramolecular nucleophilic substitution of bromides **21a,b** catalyzed by Lewis acid **29**.

Scheme 8



Isolation of bromides connected with decarbonylation on degradation of acyl iron complexes is a new observation. Only Liebeskind[5a] has briefly mentioned an iodide as a side product in a degradation reaction. Isolation of epoxides as the major product on degradation of acyl iron complexes is the first report of this kind.

CONCLUDING REMARKS

The fact that stereoselective alkylation of **2** with alkyl halides and n-butyl lithium or LDA as bases led to major products having reverse configurations at the α-carbon atoms and the fact that alkylating reagents did not affect the stereochemical outcome at -78°C proved that the product proportions of these reactions were only determined by the kinetic-controlled deprotonation of **2** and also excluded the possibility of an equilibrium between E- and Z-enolates **25E** and **25Z** or *syn* and *anti* conformations of these enolates at -78°C. The decisive influence of bases on the stereoselective deprotonation of complex **2**, which is the first case observed with achiral bases, suggests that these deprotonation reactions involve different transition states. The observations with alkylations of **2** are important for understanding the stereochemical behavior of ligands and enolates attached to $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)$ moiety.

Because there is no equilibration between E- and Z-enolates at -78°C, the practically non-stereoselective results of aldol condensations of acyl iron complexes indicates a decreased facial selectivity when aldehydes attack the enolates. This poor facial selectivity does not find a plausible model explaining the results.

The oxidative degradation of complexes **5**, **8** and **11** with NBS in ethanol furnished new results, namely, formation of bromides or epoxides as the main products was observed.. The reactions were connected with decarbonylation. These results, together with isolation of the coupling product **15**, suggest a decomplexation mechanism involving radical intermediates. This mechanism can also be used to explain the decomplexation reactions of other acyliron complexes.

All reactions connected with complex **2,** like alkylation, aldol condensation and decomplexation of its derivatives, are different from those of other acyliron complexes studied up to now. The proportions of the diastereomeric products obtained from alkylation and aldol condensation of complex **2** enabled a careful study of the influence of reagents, temperature, time and other reaction conditions on the stereochemical outcome of these reactions. We could discuss their kinetic properties and models of intermediates involved. These conclusions can be expanded to predict and explain the results of reactions of other similar complexes. The detailed conformational and configurational analysis of all stereoisomeric products, based on their ^{1}H-NMR spectra,[11] enabled us to assign configurations to all products obtained.

EXPERIMENTAL

General

^{1}H-NMR spectra were recorded with a Bruker AM-500 (500 MHz) and a Varian GEM-200 (200 MHz) spectrometers for solutions in $CDCl_3$ (internal Me_4Si). Melting points were not corrected. TLC was performed on Silica Gel G (Merck) and column chromatography on Silica Gel 40-63 mμ (Merck). Commercial n-butyl lithium and t-butyl lithium (1.5 M solution in n-hexane) were used. A 1.5 M solution of diethylaluminum chloride in toluene was employed. Anhydrous tin dichloride was prepared according to reported method[20]. THF was treated with sodium, lithium aluminum hydride ($LiAlH_4$) and kept over $LiAlH_4$. It was freshly distilled from $LiAlH_4$ under argon atmosphere just before use. All reactions were performed under argon atmosphere. Flash column chromatography was carried out using nitrogen pressure.

Dicyclopentadienyltetracarbonyldiiron was prepared by refluxing a mixture of pentacarbonyliron and dicyclopentadiene[21] at about 140°C for 18h.

Synthesis of (η^5-C_5H_5)Fe(CO)(PPh_3)($COCH_2Ph$) (2)

η^5-Cyclopentadienyldicarbonyliron anion (obtained from reduction of 5 g dicylclopentadienyltetracarbonyldiiron with sodium amalgam) was reacted with benzyl bromide (5 ml) and the resulting product was refluxed in acetonitrile (100 ml) with triphenylphosphine (15 g) for three days. The reaction mixture was concentrated to dryness and **2** (5.3 g, 35% yield) was purified by flash column chromatography (eluent: ethyl acetate and n-hexane 1:5). M.p. 175°C; *Anal.* $C_{32}H_{27}FeO_2P$ Calcd. : C, 72.46%; H, 5.13%. Found: C, 72.47%; H, 4.96%. I.R.(KBr) ν_{max}: 1915vs (C≡O), 1600s (C=O) cm^{-1}; ^{1}H-NMR(δ): 6.5-7.5 (m, 20H, H-Ph), 4.32(d, 5H, $J_{cp,P}$ 1.2Hz, H-Cp), 4.19(d, 1H, $J_{\alpha,\alpha'}$ 14.3 Hz, H-α), 3.67(d, 1H, H-α').

Deuteration and alkylation of 2 at -78°C

A1: n-butyl lithium as the base(general procedure)

To the orange solution of **2** (106 mg, 0.2 mmol) in THF (5 ml) was added n-butyl lithium (0.27 ml, 0.4 mmol) dropwise with stirring at -78°C. A dark-red coloration appeared quickly. Twenty minutes later, deuterium oxide or alkyl halide (methyl iodide, ethyl, allyl or benzyl bromides) (1 ml) was added. The mixture was stirred at -78°C for 1 h and then warmed up to room temperature followed by quenching with 5% aq. ammonium chloride solution (10ml). After extraction with dichloromethane and drying with magnesium sulfate, the solvent was evaporated under reduced N_2 pressure and the orange solid residue was purified by flash chromatography (eluent, ethyl acetate:n-hexane 1:5) on a silica gel column. ^{1}H-NMR spectrum of the product showed that the product was composed of two diastereomers in proportion close to 6:1 in each case (Table 1) and the isolated yield was between 87% and 95% (Table 3).

B1: t-butyl lithium as the base (general procedure)

Tert-butyl lithium (0.27 ml, 0.4 mmol) was dropped into the orange solution of **2** (106 mg, 0.2 mmol) in THF (5 ml) with stirring at -78°C. Ten minutes later, alkyl halide (methyl iodide, ethyl or benzyl bromides) (1 ml) was added. The mixture was stirred at -78°C for 1h and then warmed up to room temperature. After quenching, work-up and flash column chromatography as above, a mixture of diastereomeric products was obtained in a proportion close to 1.7:1.0 in each case (Table 1) and in a yield of 81-92% (Table 3).

C1: LDA as the base (general procedure)

A solution of n-butyl lithium (0.27 ml, 0.4 mmol) and diisopropylamine (50 mg, 0.5 mmol) in THF (1 ml) was stirred at 0°C for 20 minutes under argon. The LDA solution formed was then cooled down to -78°C and an orange solution of **2** (106 mg, 0.2 mmol) in THF (5 ml) was added slowly with stirring. Dark-red coloration of the mixture was developed in about half a minute. Twenty minutes later, deuterium oxide or alkyl halide (methyl iodide, ethyl, allyl or benzyl bromides) (1 ml) was added. The mixture was stirred at -78°C for 1 h and then warmed up to room temperature. After quenching, work-up and flash chromatography as above, a mixture of diastereomeric products was obtained in a proportion close to 1.0:2.4 in each case (Table 1) and in a yield of 75-97% (Table 3).

D1: influence of time interval between deprotonation and methylation on the diastereomeric proportion of methylation products

These experiments were performed only with n-butyl lithium or LDA as bases. Five, 10, 20, 30 and 180 min after addition of base to the solution of **2**, methyl iodide was added to the resulting dark-red solution of lithium enolate **3**. Thereafter, the experimental procedures were exactly the same as procedures *A1* and *C1*. The diastereomeric product proportions obtained in these experiments were practically the same as the methylation results in Table 1.

4A: ^{1}H-NMR(δ): 6.5-7.5(m, 20H, H-Ph), 4.32(d, 5H, $J_{Cp\text{-}P}$ 1.2Hz, H-Cp), 3.64(ws, 1H, H-α). **4B**: ^{1}H-NMR(δ): 6.5-7.5(m, 20H, H-Ph), 4.32(d, 5H, $J_{Cp\text{-}P}$ 1.2Hz, H-Cp), 4.16(ws, 1H, H-α).

5A and **5B:** *Anal.* $C_{33}H_{29}FeO_2P$ Calcd.: C, 72.81%; H, 5.37%. Found: C, 72.43%; H 5.39%. I.R.(KBr) ν_{max}: 1924(vs), 1606(vs) cm^{-1}; ^{1}H-NMR(δ): **5A:** 6.5-7.5(m, 20H, H-Ph), 4.47(d, 5H, $J_{Cp\text{-}P}$ 1.1Hz, H-Cp), 4.41(q, 1H, $J_{\alpha,Me}$ 7.2 Hz, H-α), 1.31(d, 3H, H-Me); **5B:** 6.5-7.5(m, 20H, H-Ph), 4.03(d, 5H, $J_{Cp\text{-}P}$ 1.1 Hz, H-Cp), 4.23(q, 1H, $J_{\alpha,Me}$ 6.1 Hz, H-α), 0.57(d, 3H, H-Me).

6A and **6B**: *Anal.* $C_{34}H_{31}FeO_2P$ Calcd.: C, 73.13%; H, 5.60%. Found: C, 72.68%; H, 5.30%. I.R.(KBr) ν_{max}: 1920(vs), 1600(vs) cm^{-1}; ^{1}H-NMR(δ): **6A**: 6.5-7.5(m, 20H, H-Ph), 4.45(d, 5H, $J_{Cp\text{-}P}$ 1.2 Hz, H-Cp), 4.20(dd, 1H, $J_{\alpha,\beta}$ 3.9 Hz, $J_{\alpha,\beta'}$ 11.0 Hz, H-α), 1.94(ddq, 1H, $J_{\beta,\beta'}$ 13.4 Hz, $J_{\beta,Me}$ 7.4 Hz, H-β), 1.59(ddq, 1H, $J_{\beta',Me}$ 7.4 Hz, H-β'), 0.63(t, 3H, H-Me); **6B**: 6.5-7.5(m, 20H, H-Ph), 4.02(d, 5H, $J_{Cp\text{-}P}$ 1.2 Hz, H-Cp), 3.93(dd, 1H, $J_{\alpha,\beta}$ 10.8 Hz, $J_{\alpha,\beta'}$ 3.4 Hz, H-α), 1.35(ddq, 1H, $J_{\beta,\beta'}$ 13.7 Hz, $J_{\beta,Me}$ 7.4 Hz, H-β), 0.61(ddq, 1H, $J_{\beta',Me}$ 7.4 Hz, H-β'), 0.30(t, 3H, Me-H).

7A and **7B**: *Anal.* $C_{35}H_{31}FeO_2P$ Calcd.: C, 73.69%; H, 5.48%. Found: C, 73.56%; H, 5.36%. I.R.(KBr) ν_{max}: 1920(vs), 1615(vs) cm^{-1}; ^{1}H-NMR(δ): **7A**: 6.5-7.5(m, 20H, H-Ph), 4.45(d, 5H, $J_{Cp\text{-}P}$ 1.3 Hz, H-Cp), 4.36(dd, 1H, $J_{\alpha,\beta}$ 4.8 Hz, $J_{\alpha,\beta'}$ 10.3 Hz, H-α), 2.61(ddddd, 1H, $J_{\beta,\beta'}$ 14.1 Hz, $J_{\beta,\gamma}$ 7.4 Hz, $J_{\beta,t}$ 1.4 Hz, $J_{\beta,c}$ 1.1 Hz, H-β), 2.33(ddddd, 1H, , $J_{\gamma,\beta'}$ 6.9 Hz, $J_{\beta',t}$ 1.4 Hz, $J_{\beta',c}$ 1.1 Hz, H-β'), 5.49(dddd, 1H, $J_{\gamma,t}$ 17.1 Hz, $J_{\gamma,c}$ 10.1 Hz, H-γ), 4.91(dddd, 1H, $J_{t,c}$ 2.2 Hz, H-t), 4.83(dddd, 1H, H-c); **7B**: 6.5-7.5(m, 20H, H-Ph), 4.02(d, 5H, $J_{Cp\text{-}P}$ 1.2 Hz, H-Cp), 4.04(dd, 1H, $J_{\alpha,\beta}$ 11.4 Hz, $J_{\alpha,\beta'}$ 3.0 Hz, H-α), 2.17(ddddd, 1H, $J_{\beta,\beta'}$ 14.1 Hz, $J_{\beta,\gamma}$ 6.5 Hz, $J_{\beta,t}$ 1.3 Hz, $J_{\beta,c}$ 1.4 Hz, H-β), 1.24(ddddd, 1H, , $J_{\gamma,\beta'}$ 7.8 Hz, $J_{\beta',t}$ 1.3 Hz, $J_{\beta',c}$ 1.1 Hz, H-β'), 5.17(dddd, 1H, $J_{\gamma,t}$ 16.8 Hz, $J_{\gamma,c}$ 10.2 Hz, H-γ), 4.61(dddd, 1H, $J_{t,c}$ 2.5 Hz, H-t), 4.63(dddd, 1H, H-c).

8A and **8B**: *Anal.* $C_{39}H_{33}FeO_2P$ Calcd.: C, 75.49%; H, 5.36%. Found: C, 75.52%; H, 5.37%. I.R.(KBr) ν_{max}: 1924(vs), 1610(vs) cm^{-1}; ^{1}H-NMR(δ): **8A**: 6.5-7.5(m, 25H, H-Ph), 4.25(d, 5H, $J_{Cp\text{-}P}$ 1.2 Hz, H-Cp), 4.63(dd, 1H, $J_{\alpha,\beta}$ 6.2 Hz, $J_{\alpha,\beta'}$ 8.5 Hz, H-α), 3.26(dd, 1H, $J_{\beta,\beta'}$ 13.4 Hz, H-β), 2.68(dd, 1H, H–β'); **8B**: 6.5-7.5(m, 25H, H-Ph), 4.03(d, 5H, $J_{Cp\text{-}P}$ 1.2 Hz, H-Cp), 4.25(dd, 1H, $J_{\alpha,\beta}$ 12.0 Hz, $J_{\alpha,\beta'}$ 3.0 Hz, H-α), 2.69(dd, 1H, $J_{\beta,\beta'}$ 13.8 Hz, H-β), 1.87(dd, 1H, H–β').

9A and **9B**: *Anal.* $C_{36}H_{35}FeO_2P$ Calcd.: C, 73.73%; H, 6.02%. Found: C, 73.82%; H 5.82%. I.R.(KBr) ν_{max}: 1920(vs), 1620(vs) cm^{-1}; ^{1}H-NMR(δ): **9A**: 6.5-7.5(m, 20H, H-Ph), 4.47(d, 5H, $J_{Cp\text{-}P}$ 1.2 Hz, H-Cp), 4.47(dd, 1H, $J_{\alpha,\beta}$ 3.4 Hz, $J_{\alpha,\beta'}$ 12.0 Hz, H-α), 1.72(ddd, 1H, $J_{\beta,\beta'}$ 13.8 Hz, $J_{\beta,\gamma}$ 11.7 Hz, H-β), 1.55(ddd, 1H, $J_{\gamma,\beta'}$ 3.5 Hz, H-β'), 1.06(ddqq, 1H, $J_{\gamma,Me}$ 6.1 Hz, $J_{\gamma,Me'}$ 6.5 Hz, H-γ), 0.86(d, 3H, H-Me), 0.76(d, 3H, H-Me'); **9B**: 6.5-7.5(m, 20H, H-Ph), 4.01(d, 5H, $J_{Cp\text{-}P}$ 1.2 Hz, H-Cp), 4.24(dd, 1H, $J_{\alpha,\beta}$ 11.7 Hz, $J_{\alpha,\beta'}$ 3.4 Hz, H-α), 1.73(ddd, 1H, $J_{\beta,\beta'}$ 13.7 Hz, $J_{\beta,\gamma}$ 1.5 Hz, H-β), 0.32(ddd, 1H, $J_{\gamma,\beta'}$ 10.3 Hz, H-β'), 0.63(d, 3H, $J_{\gamma,Me}$ 6.3 Hz, H-Me), 0.54(d, 3H, $J_{\gamma,Me'}$ 6.5 Hz, H-Me').

10A and **10B**: *Anal.* $C_{35}H_{33}FeO_2P$ Calcd.: C, 73.43%; H, 5.81%. Found: C, 73.43%; H 5.76%. I.R.(KBr) ν_{max}: 1930(vs), 1610(vs) cm^{-1}; ^{1}H-NMR(δ): **10A**: 6.5-7.5(m, 20H, H-Ph), 4.39(d, 5H, $J_{Cp\text{-}P}$ 1.2 Hz, H-Cp), 3.98(d, 1H, $J_{\alpha,\beta}$ 8.8 Hz, H-α), 2.18(dqq, 1H, $J_{\gamma,Me}$ 6.6 Hz, $J_{\gamma,Me'}$ 6.7 Hz, H-β), 0.98(d, 3H, H-Me), 0.47(d, 3H, H-Me'); **10B**: 6.5-7.5(m, 20H, H-Ph), 3.95(d, 5H, $J_{Cp\text{-}P}$ 1.3 Hz, H-Cp), 3.84(d, 1H, $J_{\alpha,\beta}$ 8.6 Hz, H-α), 1.85(m, 1H, $J_{\gamma,Me}$ 6.8 Hz, $J_{\gamma,Me'}$ 6.6 Hz, H-β), 0.35(d, 3H, H-Me), 0.04(d, 3H, H-Me').

Alkylation of 2 at ambient temperature (+16°C)

A2: n-butyl lithium as the base (general procedure)

The dark-red solution of **3** generated by procedure *A1* was stirred at -78°C for 20min and then allowed to warm up to ambient temperature (16±1°C) during 25 min. After stirring at +16°C for further 5min, alkyl halide (methyl iodide, allyl, iso-butyl or isopropyl bromides) (1 ml) was added. An hour later, the mixture was quenched with ammonium chloride solution. After work-up and column chromatography (eluent, ethyl acetate:n-hexane 1:5), a mixture of diastereomeric alkylation products was obtained in a proportion shown in Table 2 and in a yield of 47-88% (Table 3).

C2: LDA as the base (general procedure)

To the LDA solution formed by procedure *C1* was added the orange solution of **2** (106 mg, 0.2 mmol) in THF (5.0 ml) at -78°C. The mixture was stirred at -78°C for 20min and then warmed up to 16±1°C during 25min. After stirring at +16°C for further 5min, alkyl halide (methyl iodide, allyl, iso-butyl or iso-propanyl bromides) (1 ml) was added. One hour later, the reaction was quenched, processed and purified as above. A mixture of diastereomeric alkylation products was obtained in a proportion shown in Table 2 and in a yield of 41-86% (Table 3).

D2: influence of time interval between deprotonation and methylation on the diastereomeric proportion of methylation products

These experiments were performed only with n-butyl lithium and LDA as the base. The experimental procedures were the same as *A2* and *C2* except that the solution of lithium enolate **3** was kept at +16°C for 35min instead of 5min. The results obtained in these experiments were practically the same as those observed in procedures *A2* and *C2* (Table 2 and 3).

Note: When isopropyl bromide was added at -78°C to the dark-red solution of lithium enolate **3**, there was no reaction even after 2h at -78°C. Isopropylation of **3** could be carried out at ambient temperature. Work-up as above produced diastereomeric mixture of products (Table 2 and 3).

Aldol condensation of 2 with carbonyl compounds

A3: n-butyl lithium as the base (general procedure)

The procedure was the same as in *A1* except that acetone, acetaldehyde or benzaldehyde replaced alkyl halides as the nucleophiles. The ^{1}H-NMR spectra of the products showed that all four possible diastereomers were formed in proportion shown in Table 4, 5 and 8, in isolated yield of 83-87%.

B3: t-butyl lithium as the base (general procedure)

Procedure *B1* was employed with replacement of alkyl halides for aldehydes. The mixture of diastereomeric products was obtained in a proportion shown in Table 4 and 5, in a yield of 85-93%.

C3. LDA as the base (general procedure)

Procedure *C1* was employed with replacement of alkyl halides for acetaldehyde, benzaldehyde or acetone. The mixture of diastereomeric products was obtained in a proportion shown in Table 4, 5 and 8, in a yield of 85-93%.

11A-D: yields: 83% with *A3*, 93% with *B3* and 68% with *C3*; *Anal.* $C_{34}H_{31}FeO_3P$ Calcd.: C, 71.08%; H, 5.44%. Found: C, 70.84%; H 5.18%. I.R.(KBr) ν_{max}: 1925(vs), 1585(vs) cm^{-1}; ^{1}H-NMR(δ): **11A**: 6.5-7.5(m, 20H, H-Ph), 4.46(d, 5H, $J_{Cp\text{-}P}$ 1.3 Hz, H-Cp), 4.28(d, 1H, $J_{\alpha,\beta}$ 9.5 Hz, H-α), 4.07(ddq, 1H, $J_{\beta,Me}$ 6.3 Hz, $J_{\beta,OH}$ 3.0 Hz, H-β), 2.68(d, 1H, OH), 0.81(d, 3H, H-Me); **11B**: 6.5-7.5(m, 20H, H-Ph), 4.44(d, 5H, $J_{Cp\text{-}P}$ 1.3 Hz, H-Cp), 4.42(d, 1H, $J_{\alpha,\beta}$ 3.0 Hz, H-α), 4.16(ddq, 1H, $J_{\beta,Me}$ 6.2 Hz, $J_{\beta,OH}$ 0.5 Hz, H-β), 3.83(d, 1H, OH), 0.75(d, 3H, H-Me); **11C**: 6.5-7.5(m, 20H, H-Ph), 4.08(d, 5H, $J_{Cp\text{-}P}$ 1.3 Hz, H-Cp), 3.94(d, 1H, $J_{\alpha,\beta}$ 2.3 Hz, H-α), 2.99(ddq, 1H, $J_{\beta,Me}$ 6.4 Hz, $J_{\beta,OH}$ 1.2 Hz, H-β), 3.88(d, 1H, OH), 0.49(d, 3H, H-Me); **11D**: 6.5-7.5(m, 20H, H-Ph), 3.95(d, 5H, $J_{Cp\text{-}P}$ 1.2 Hz, H-Cp), 3.93(d, 1H, $J_{\alpha,\beta}$ 9.1 Hz, H-α), 4.05(m, 1H, $J_{\beta,Me}$ 6.2 Hz, $J_{\beta,OH}$ 2.1 Hz, H-β), 1.77(d, 1H, OH), 0.62(d, 3H, H-Me).

12A-D: yield: 81% with *A3*, 85% with *B3* and 92% with *C3*; *Anal.* $C_{39}H_{33}FeO_3P$ Calcd.: C, 73.59%; H, 5.23%. Found: C, 73.42%; H, 5.37%. I.R.(KBr) ν_{max}: 1920(vs), 1580(vs) cm^{-1}; ^{1}H-NMR(δ): **12A**: 6.5-7.5(m, 25H, H-Ph), 4.43(d, 5H, $J_{Cp\text{-}P}$ 1.2 Hz, H-Cp), 4.62(d, 1H, $J_{\alpha,\beta}$ 8.8 Hz, H-α), 4.88(dd, 1H, $J_{\beta,OH}$ 3.7 Hz, H-β), 3.27(d, 1H, OH); **12B**: 6.5-7.5(m, 25H, H-Ph), 4.26(d, 5H, $J_{Cp\text{-}P}$ 1.2 Hz, H-Cp), 4.70(d, 1H, $J_{\alpha,\beta}$ 4.7 Hz, H-α), 5.14(dd, 1H, $J_{\beta,OH}$ 1.0 Hz, H-β), 3.54(d, 1H, OH); **12C**: 6.5-7.5(m, 25H, H-Ph), 4.08(d, 5H, $J_{Cp\text{-}P}$ 1.2 Hz, H-Cp), 4.14(d, 1H, $J_{\alpha,\beta}$ 2.0 Hz, H-α), 4.05(dd, 1H, $J_{\beta,OH}$ 0.8 Hz, H-β), 4.66(d, 1H, OH); **12D**: 6.5-7.5(m, 25H, H-Ph), 3.98(d, 5H, $J_{Cp\text{-}P}$ 1.3 Hz, H-Cp), 4.15(d, 1H, $J_{\alpha,\beta}$ 9.6 Hz, H-α), 4.90(dd, 1H, $J_{\beta,OH}$ 1.7 Hz, H-β), 2.25(d, 1H, OH).

13A-B: yield: 87% with *A3* and 89% with *C3*; *Anal.* $C_{35}H_{33}FeO_3P$ Calcd.: C, 71.44%; H, 5.65%. Found: C, 71.11%; H, 5.49%. I.R.(KBr) ν_{max}: 1925(vs), 1590(vs) cm^{-1}; ^{1}H-NMR(δ): **13A**: 6.5-7.5(m, 20H, H-Ph), 4.38(d, 5H, $J_{Cp\text{-}P}$ 1.3 Hz, H-Cp), 4.27(s, 1H, H-α), 4.31(s, 1H, OH), 1.36(s, 3H, Me), 0.71(s, 3H, Me'); **13B**: 6.5-7.5(m, 20H, H-Ph), 3.95(d, 5H, $J_{Cp\text{-}P}$ 1.3 Hz, H-Cp), 4.08(s, 1H, H-α), 4.42(s, 1H, OH), 0.57(s, 3H, Me), 0.36(s, 3H, Me').

Influence of counter cations on aldol condensation of 2 with aldehydes

A4: influence of diethylaluminum or tin cations with n-butyl lithium as the base (general procedure)

Twenty minutes after addition of n-butyl lithium as in *A1*, diethylaluminum chloride (0.7 ml, 1.0 mmol) [or tin dichloride (76 mg, 0.4 mmol, in THF 5 ml)] was added and the mixture was stirred for 1h, whereupon an excess of aldehyde (acetaldehyde or benzaldehyde) (0.5 ml) was added. The mixture was stirred at -78°C for 0.5h and was then allowed to warm up to room temperature. After quenching, work-up and flash chromatography, the produced diastereomers were obtained in proportion shown in Table 6 and 7, in a yield of 87-96%.

C4. influence of diethylaluminum or tin cations with LDA as the base (general procedure)

Twenty minutes after generation of **3** with LDA as in *C1*, diethylaluminum chloride (0.7 ml, 1.0 mmol) [or tin dichloride (76 mg, 0.4 mmol, in THF 5 ml)] was added and the mixture was stirred for 1h, whereupon the same procedure as *A4* was employed. A mixture composed of all diastereomers was obtained in a proportion shown in Table 6 and 7, in a yield of 77-94%.

Decomplexation of elaborated complexes of 2

Decomplexation of **5**

The solution of **5** (200 mg, 0.37 mmol) in dichloromethane (5 ml) and ethanol (5 ml) was cooled to -78°C and NBS (80 mg, 0.45 mmol) in dichloromethane (5 ml) was added. The mixture was stirred for 30min at -78°C with little change of the orange color; cooling bath was removed and stirring was continued at room temperature for 2h during which time the color of the solution changed into deep green. 1N aqueous sodium hydroxide solution (30 ml) was added and the mixture was extracted with dichloromethane. The extract was dried ($MgSO_4$) and concentrated to dryness and the residue was taken into ether, again evaporated and chromatographed (eluent: ethyl acetate and n-hexane 1:10) to yield a colorless, oil mixture of two products **14** and **15**.

14: 34.5 mg (51%); I.R.(film) ν_{max}: 3010-3080(m), 1460(m), 760(m), 690(m) cm^{-1}; ^{1}H-NMR (δ): 7.15-7.45(m, 5H, Ph), 5.24(q, 1H, J 6.93 Hz, -CH<), 2.02(d, 3H, Me) [reported[22] δ: 5.25 and 2.02]; HR-MS (m/z): 186(M^++2), 183.9889(M^+, calcd. for C_8H_9Br, 183.9887)[(M+2):M=1:1](52%),105(M^+-Br)(100%).

15: 5.8 mg (13%); ^{1}H-NMR (δ): 7.15-7.45 (m, Ph), 3.89 (q, 1H, J 7.04 Hz, -CH<), 1.38 (d, 3H, Me); HR-MS: 238.1376(M^+), calcd. for $C_{17}H_{18}O$, 238.1358.

In addition to **14** and **15**, a third component was also noticed by high resolution mass spectrum with a molecular ion mass of 178.0994 which was suggested the presence of ester **16** (Calcd. for $C_{11}H_{14}O_2$, 178.0994). But this compound was formed in a yield too low to be observed by ^{1}H-NMR (200 MHz).

Decomplexation of ***8***

The experimental procedure was the same as above. Compound **17** was isolated as the major product in a yield of 56%.

17: colorless oil; I.R.(film) no C=O signal; ^{1}H-NMR (δ): 7.05-7.45 (m, 10H, Ph), 5.13(dd, 1H, -CH_X<), 3.49 and 3.55(ABX system, 2H, $J_{A,B}$ 14.1 Hz, $J_{A,X}$ 7.8 Hz, $J_{B,X}$ 7.4 Hz, -C$\underline{H}_A\underline{H}_BCH_X$<); HR-MS (m/z): 262($M^+$), 260.0201($M^+$+2, Calcd. for $C_{14}H_{13}Br$, 260.0201) [(M+2):M=1:1](24%), 181.1016(M^+-Br, Calcd. for $C_{14}H_{13}$, 181.1017)(100%), 168.9653 (M^+-Bn, Calcd. for C_7H_6Br, 168.6953), 103, 91, 77.

A second component observed only by MS with M^+ 254 ($C_{17}H_{18}O_2$) was suggested to be ester **18.**

Decomplexation of ***11***

a. The same procedure as above was employed for the degradation of **11.** After work-up, a colorless, oil mixture of products **19** and **20** in a proportion of 1.0:1.6 was obtained in 84% yield.

Mixture of **19** and **20:** 39.4 mg (84%); IR (film): no C=O signal; HR-MS (m/z): 134.0732(M^+, Calcd. for $C_9H_{10}O$, 134.0731)(79%), 105, 90(100%), 77; **19:** ^{1}H-NMR (δ): 7.2-7.4(m, 5H, Ph), 4.07(d, 1H, J 4.3 Hz, PhCH<), 3.40(dq, 1H, MeC$\underline{H}$<), 1.09(d, 3H, J 5.4 Hz, Me); **20**: ^{1}H-NMR (δ): 7.2-7.4(m, 5H, Ph), 3.58(d, 1H, J 2.1 Hz, PhCH<), 3.04(dq, 1H, MeC$\underline{H}$<), 1.46(d, 3H, J 5.1 Hz, Me).

b. A solution of **11** (200 mg, 0.35 mmol) in dichloromethane (5 ml) and ethanol (5 ml) was cooled to -78°C and NBS (80 mg, 0.45 mmol) in dichloromethane (5 ml) was added. The mixture was stirred for 2h at -78°C with color change from orange to green; cooling bath was removed and stirring was continued at room temperature for 1h. Work-up as above yielded a colorless oily mixture of two inseparable products **19** and **20** (12%) together with another mixture of more polar diastereomeric products **21a** and **21b** (29 mg, 38%) in a proportion of 1.4:1.0.

Mixture of **21a** and **21b**: IR (film): no C=O signal; MS (m/z): 216 and 214[(M+2):M=1:1](31%), 170 and 172(1:1), 91(100%), 43; **21a:** ^{1}H-NMR (δ): 7.35-7.46(m, 5H, Ph), 4.86(d, 1H, J 8.1 Hz, Br-CH<), 4.20(dq, 1H, O-C<u>H</u><), 1.11(d, 3H, J 6.3 Hz, Me); **22b:** ^{1}H-NMR (δ): 7.35-7.46(m, 5H, Ph), 4.88(d, 1H, J 6.3 Hz, Br-CH<), 4.23(dq, 1H, O-C<u>H</u><), 1.35(d, 3H, J 6.2 Hz, Me).

Among the degradation products of **11** with both procedures, another product **22** was also observed by TLC. The ^{1}H-NMR spectrum of this product showed only one diastereomer.

22: ^{1}H-NMR (δ): 7.2-7.4(m, 5H, Ph), 4.37(dq, 1H, J 6.2 and 6.7 Hz, HOC<u>H</u><), 4.19(dq, 1H, J_{AB} 10.8 Hz, OC<u>H</u>$_A$<u>H</u>$_B$Me), 4.11(dq, 1H, OCH$_A$<u>H</u>$_B$Me), 3.52(d, 1H, J 6.7 Hz, -CH<), 1.21(d, 1H, J 6.2 Hz, Me), 1.22(t, 1H, J 7.1 Hz, CH$_2$<u>Me</u>).

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