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LETTERS

Asymmetric olefination of metallic arene or diene complexes to form planar chiral complexes

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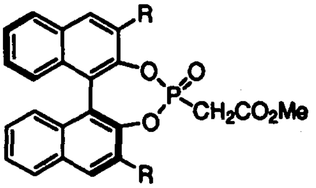
Abstract

The chiral phosphonoacetate (*S*)-**1** can discriminate between the enantiotopic dicarbonyls of η^6-arene Cr and η^4-diene Fe complexes to afford optically active olefins with planar chirality in high enantiomeric excess and good yield. An analogous reagent (*S*)-**2** was used for kinetic resolution of a racemic mixture of the aldehyde of the Fe η^4-diene, which resulted in formation of the corresponding olefin together with the recovered aldehyde in high enantiomeric excess. The absolute stereostructures of these adducts were determined by X-ray analysis with anomalous dispersion of metals. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: asymmetric reaction; olefination; kinetic resolution.

Recently we reported an efficient asymmetric Horner–Wadsworth–Emmons (HWE) reaction with optically active phosphonate reagent (*S*)-**1** or (*S*)-**2**, which each possesses an axially chiral 1,1′-binaphthalene-2,2′-diol (2,2′-BINOL) as an auxiliary at the phosphate moiety.[1] Since the cyclic phosphonate of 2,2′-BINOL may act as a good leaving group in addition to being an excellent stereocontroller,[1a] it is expected that an asymmetric HWE reaction[2] using the anion of this type of chiral reagent would directly result in optically active olefins with high enantiomeric bias.



(*S*)-1; R = H
(*S*)-2; R = Me

As an extension of our research on asymmetric olefination, we report here asymmetrization of the *meso*-dicarbonyls of η^6-arene Cr(0) or η^4-diene Fe(0) complex as well as kinetic resolution of a racemic

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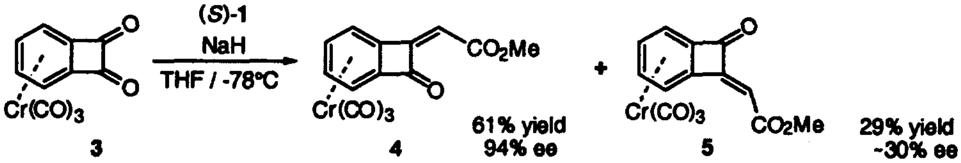
mixture of the aldehyde of the η^4-diene Fe(0) complex, to the respective optically active enoate with planar chirality.

Chromium complex **3**, which was prepared according to the Butenshön's method,[3] was treated with the anion of (*S*)-**1** at −78°C in THF for 1 h to give the Z-olefin **4** (reddish prisms, $[\alpha]_D^{20}$ −59.3 ($CHCl_3$, *c* 0.51)) with 94% ee (HPLC analysis on a chiral column) in 61% yield, together with the minor *E*-isomer **5** of 29% yield whose ee was as high as 30% (Scheme 1). The relative stereostructures of **4** and **5** were deduced from comparison of the chemical shift of the olefinic protons[4] on ^{1}H NMR (δ 5.80 for **4**, 5.98 for **5**). The absolute structure of **4** (recrystallized from benzene) was unambiguously determined by X-ray diffraction analysis using anomalous dispersion of the chromium atom[5,12] (Fig. 1).



Scheme 1.

The stereochemical outcome of this reaction can be explained in terms of a previously proposed mechanism.[1b,c] The anion of (*S*)-**1** reacts with an alternative carbonyl group of *meso*-compound to yield a non-racemic *E*- and *Z*-olefin, respectively. Therefore, the absolute structure of the minor product **5** can be tentatively drawn as shown in Scheme 1.

The asymmetric reaction of tricarbonyl (η^4-2,4-hexadiene) dialdehyde Fe(0) complex **6** with the anion of (*S*)-**1** was next examined under the same reaction conditions as above (Scheme 2). Recently, efficient and successful discrimination of aldehydes on this type of substrate with zinc reagent has been reported.[6]

E-olefin **7** ($[\alpha]_D^{16}$ −14.4 ($CHCl_3$, *c* 0.77) was obtained as a major product in 56% yield with 63% ee, while the *Z*-olefin **8** was a minor product (14% yield and 36% ee). Detailed ^{1}H NMR analysis of the major product **7** including the NOE experiment proved that shift isomerization and racemization[7] had not occurred in the η^4–Fe complex of the product. The absolute stereostructure of the major product **7** (recrystallized from benzene/hexane)[8,12] was also determined by X-ray diffraction analysis of anomalous dispersion of the iron atom (Fig. 2).

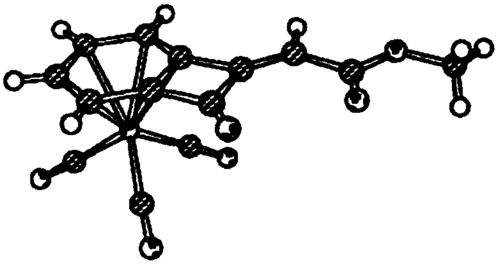
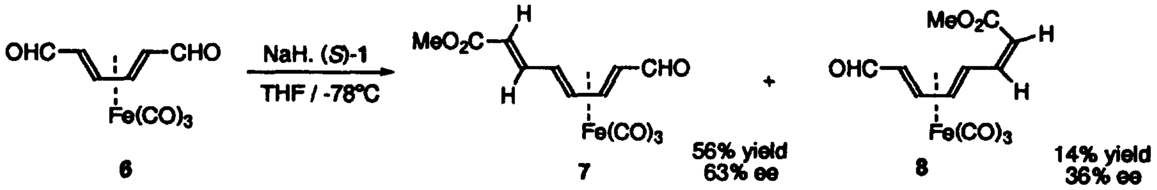
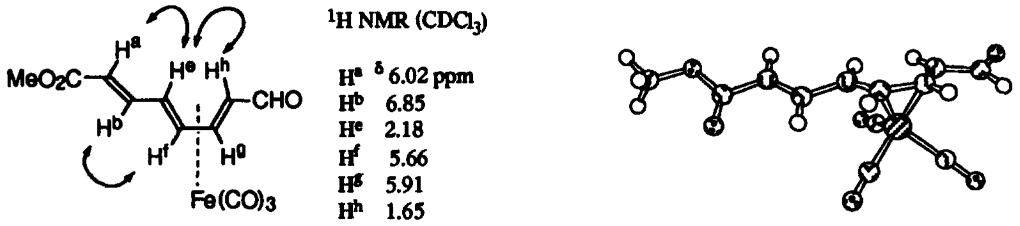


Figure 1. Crystal structure of 4



Scheme 2.

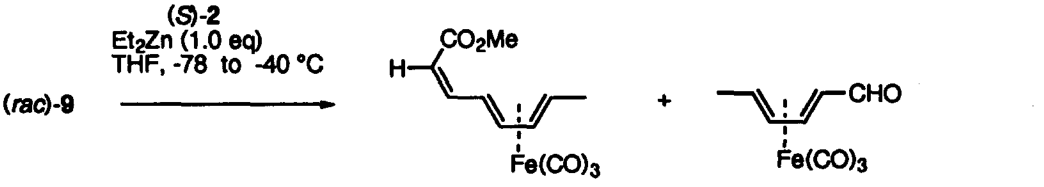


^{1}H NMR ($CDCl_3$)

Ha	δ 6.02 ppm
Hb	6.85
He	2.18
Hf	5.66
Hg	5.91
Hh	1.65

Figure 2. Chemical shift and observed NOE in ^{1}H NMR of **7** (left) and crystal structure of **7** (right)

Kinetic resolution of a racemic mixture of carbonyl compounds is an alternate approach to asymmetric olefination.[2,9] In order to increase the efficiency of this type of reagent, the anion of (*S*)-**2** was reacted with a racemic mixture of the aldehyde of metallic complex **9**. In this case, each 1.0 equiv. of reagent (*S*)-**2** and Et_2Zn (1.0 M in hexane) was used as the reagent and base, respectively, in THF at −20°C.[10] The reaction was carried out at −78 to −40°C for 20 h to afford **10** (34% yield, 88% ee), recovered **9** (37% yield, 86% ee) and a trace amount of the *E*-adduct (5% yield, 32% ee). The absolute stereostructure and ee of the recovered **9** were determined by comparison with the reported sign and value[11] of the specific rotation, respectively; the recovered **9** was found to have 2*R* configuration. The ee was also confirmed by HPLC analysis on chiral stationary phase (Scheme 3).



10 34% (88% ee) (*2R*)-**9** 37% (86% ee)

Scheme 3.

The observed stereochemistry of the product of the kinetic resolution can be explained as follows. Provided that the conjugated aldehyde **9** exists in *s-trans* conformation, the nucleophilic addition, which can be regarded as a rate determining step,[1] from the *si*-face of the anion of the reagent is energetically favored. Additionally, this nucleophilic addition may occur on the less hindered *anti* side of the iron-carbonyls of the substrate.[6] Thus, the anion of (*S*)-**2** may approach the *re*-face of the aldehyde carbonyl (Approach A) rather than the *si*-face of the aldehyde carbonyl of (2*S*)-**9** (Approach B) (Fig. 3), leading to the preferential formation of **10**, because the latter approach (Approach B) imposes a severe steric repulsion between the reagent and the iron-carbonyl group.

In summary, we have examined the asymmetric HWE olefination of metallic complexes with the anion of (*S*)-**1** and (*S*)-**2**. The reagent effectively discriminated not only the enantiotopic carbonyls, but also racemic carbonyls in complexes to afford optically active compounds possessing planar chirality with satisfactory level of ee. Since complexation and decomplexation of these optically active compounds readily occur, these complexes are effective as stereocontrollers[6] due to the bulky metal tricarbonyl groups, and provide an effective way of forming optically active derivatives having central chirality. Investigations based on this concept are in progress.

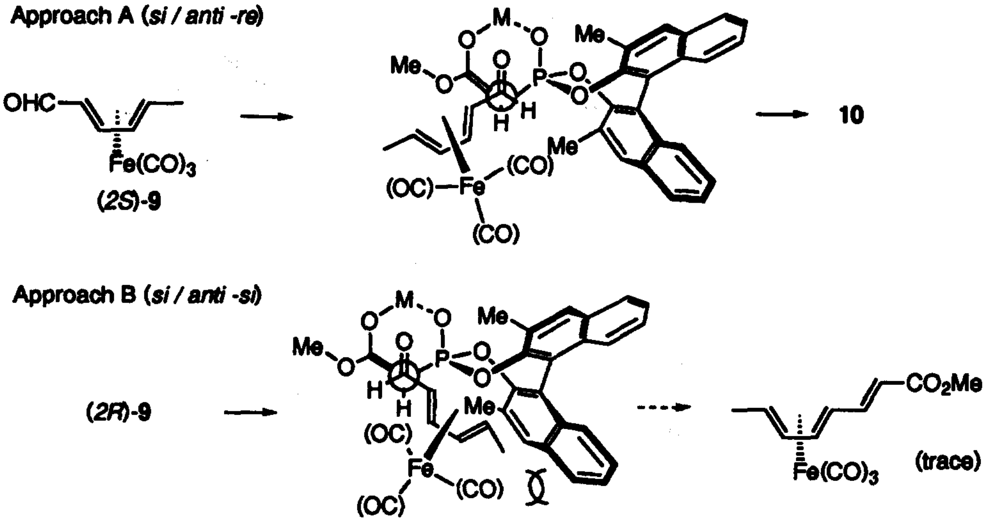


Figure 3. Possible mechanism of the kinetic resolution of (*rac*)-**9**

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4. It was suggested the olefinic proton of *E*-enoate appears in downfield shift due to anisotoropy of the carbonyl group.[1a]
5. Compound **4** was crystallized as orthorhombic, space group $P2_12_12_1$ with a=12.921 (2), b=15.720. (3), c=6.614 (2) Å, V=1343.4 (5) $Å^3$, Z=4, Dx=1.603 g/cm^3. The structure was refined to R=0.070, Rw=0.105 and S=1.77. The elucidated structure was supported by comparison of the R factor of **4** (R=0.070) and the R factor of the corresponding *ent*-**7** (R=0.115), and furthermore, by the value of the Flack parameter of **4** (x=0.0062).[12]
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8. Compound **7** was crystallized as orthorhombic, space group $P2_12_12_1$ with a=13.102 (2), b=20.078 (6), c=10.160 (2) Å, V=2672.8 (10) $Å^3$, Z=8, Dx=1.512 g/cm^3. The structure was refined to R=0.067, Rw=0.104 and S=0.91. The elucidated structure was supported by comparison of the R factor of **7** (R=0.067) and the R factor of the corresponding *ent*-**7** (R=0.104), and furthermore, by the value of the Flack parameter of **7** (x=0.0064).[12]
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