

Asymmetric synthesis of C_2 -symmetric 5,6-bis(benzyloxy)-cyclohexa-1,3-diene and a tricarbonyliron complex

Akiko Watanabe, Takao Kamahori, Mariko Aso and Hiroshi Suemune*

Graduate School of Pharmaceutical Sciences, Kyushu University, Fukuoka 812-8582, Japan

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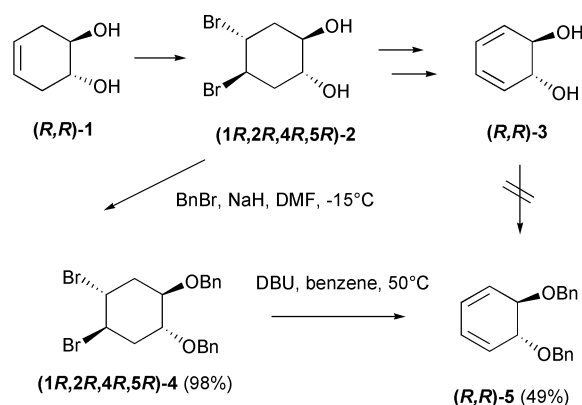
The C_2 -symmetric 5,6-bis(benzyloxy)cyclohexa-1,3-diene and the corresponding tricarbonyliron complex have been synthesized in enantiomerically pure form. Reaction of the complex with trialkylaluminium gave a mono-alkylated product accompanied by racemization.

Introduction

In the course of our studies on the development of asymmetric reactions using a metal catalyst with novel diene compounds as chiral ligands,¹ we describe the asymmetric synthesis of C_2 -symmetric 5,6-bis(benzyloxy)cyclohexa-1,3-diene **5** and its tricarbonyliron complex **6**. Previously, we reported the enantioselective synthesis of cyclohexa-3,5-diene-1,2-diol **3**, starting from optically active cyclohex-4-ene-1,2-diol **1** prepared by kinetic resolution using an enzymatic process. In this work, we designed the corresponding benzyl ether **5** as a key compound for the construction of the tricarbonyliron complex **6**.

Results and discussion

A preliminary synthetic approach to **5** by direct *O*-benzylation of cyclohexa-3,5-diene-1,2-diol **3** gave a complex mixture. Next, *O*-benzylation of C_2 -symmetric (1*R*,2*R*,4*R*,5*R*)-4,5-dibromocyclohexane-1,2-diol **2** under usual conditions gave the desired product **4** in 98% yield. Reaction of **4** with DBU in benzene at 50 °C gave the corresponding diene **5** in 49% yield accompanied by an aromatized product, (phenylmethoxy)benzene, in 8% yield. The structure of **5** was confirmed by spectroscopic analyses. In the ¹H-NMR spectrum, C1-H and C2-H were observed at δ 4.44 (2H, s), and the olefinic protons (C3–6)-H at δ 5.92–6.00 (4H). In the ¹³C-NMR spectrum, eight carbon signals were observed for the C_2 -symmetric structure (Scheme 1).

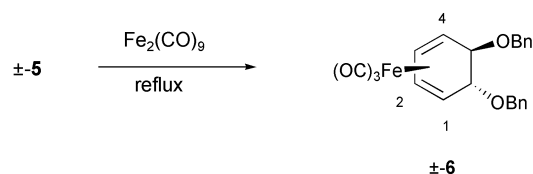


Next, syntheses of tricarbonyliron complexes of cyclohexa-1,3-diene derivatives³ were studied by using (\pm)-**3**, (\pm)-**5** and *cis*-cyclohexa-3,5-diene-1,2-diol **9**. At first, complex formation of (\pm)-**5** with $Fe_2(CO)_9$ was investigated.⁴ The results are

Table 1 Synthesis of tricarbonyliron–diene complex **6**

| Entry | Solvent | $Fe_2(CO)_9$ /eq. | Time/h | Yield (%) |
|-------|--------------------------------|-------------------|--------|----------------|
| 1 | | 2 | 1 | 42 |
| 2 | | 2 | 4 | 58 |
| 3 | THF | 2 | 6 | 42 |
| 4 | | 3 | 2 | 64 |
| 5 | Et ₂ O | 2 | 4 | — ^a |
| 6 | (<i>i</i> -Pr) ₂ O | 2 | 4 | 25 |
| 7 | dioxane | 2 | 4 | 7 ^b |

^a The (\pm)-**5** was recovered. ^b Reaction gave a complex mixture.

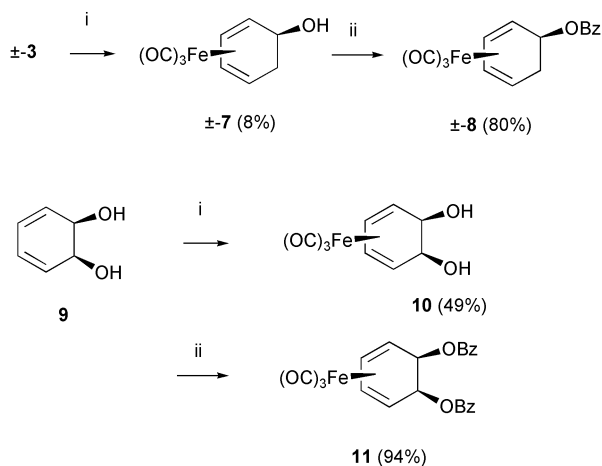
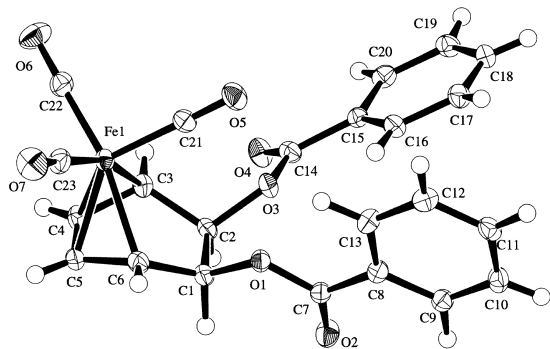


summarized in Table 1 and (Scheme 2). It was found that the reaction was highly affected by the solvent used. Among the solvents such as Et₂O, (*i*-Pr)₂O, dioxane and tetrahydrofuran (THF), only THF gave reasonable results affording the desired product (\pm)-**6** in 42–64% yield (entries 1–4 in Table 1), although the reproducibility of this reaction was somewhat poor. On the other hand, reaction in Et₂O did not afford (\pm)-**6** at all.

In the ¹H-NMR spectrum of (\pm)-**6**, olefinic protons were observed at δ 5.4–5.5 (C2,3-H, 2H), δ 3.10 (C4-H, 1H) and δ 3.01 (C1-H, 1H). A pair of benzylic methylene protons was observed at δ 4.53 (C6-*exo*-OCH₂, 2H, s) and another pair at δ 4.50 and 4.38 (1H each, *endo*-C6-OCH₂, d, J = 11.6 Hz). The protons at the C5,6-positions were also observed at δ 3.84 and 3.53, respectively.^{3a} Reaction of *trans*-diol (\pm)-**3** under the same conditions in THF gave a complex mixture, and the isolable product was a reduced derivative (\pm)-**7** (8% yield). Compound (\pm)-**7** was converted into the corresponding benzoate (\pm)-**8** in 80% yield. The structures of **7** and **8** were determined by spectroscopic analyses. The reaction of prochiral *cis*-diol **9** with $Fe_2(CO)_9$ gave a complex **10** in 49% yield, which was not stable for purification by silica-gel column chromatography.^{3b} The crude complex **10** was converted into the corresponding dibenzoate **11** in 94% yield, which was sufficiently stable for purification (Scheme 3). The stereochemical structure of complex **11** was determined by X-ray crystallographic analysis as shown in Fig. 1 and Table 2. It was interesting that the relative stereochemistry between the iron and the bis(benzyloxy) group was *endo*, which suggested that chelation control between

Table 2 Crystal and diffraction parameters of **11**

| 11 | |
|---|--|
| Empirical formula | C ₂₃ H ₁₆ O ₇ Fe ₁ |
| <i>M_r</i> | 460.22 |
| Crystal dimensions/mm | 0.50 × 0.30 × 0.20 |
| Data collection temp. | −150 °C |
| Crystal system | Orthorhombic |
| Lattice parameters: | |
| <i>a</i> , <i>b</i> , <i>c</i> /Å | 11.2695(7), 17.0311(8), 10.3072(6) |
| <i>a</i> , <i>β</i> , <i>γ</i> /° | 90, 90, 90 |
| <i>V</i> /Å ³ | 1978.3 |
| Space group | <i>P</i> 2 ₁ 2 ₁ 2 ₁ |
| <i>Z</i> value | 4 |
| <i>D</i> _{calc} /g/cm ³ | 1.545 |
| <i>μ</i> (Mo- <i>Kα</i>)/cm ^{−1} | 8.06 |
| No. of observations | 2583(<i>I</i> > −10.0σ(<i>I</i>)) |
| No. of variables | 346 |
| <i>R</i> , <i>R_w</i> | 0.047, 0.070 |
| No. of reflections of calc. <i>R</i> ₁ | 2360(<i>I</i> > 2.0σ(<i>I</i>)) |
| <i>R</i> ₁ | 0.028 |
| Solvent of crystallization | EtOH |

**Scheme 3** Reagents: i. Fe₂(CO)₉; ii. BzCl, pyridine.**Fig. 1** ORTEP drawing of the crystal structure of **11** with atom numbering (ellipsoids at 50% probability).

the iron and oxygen atoms of the hydroxy groups might preferentially act on diastereomeric face selection.⁵

Synthesis of the optically active complex

These results prompted us to synthesize the corresponding complex in optically active form and to study its application as a chiral source. Reaction of (*R,R*)-**5** (97% ee) with Fe₂(CO)₉ (1 equiv.) in refluxing THF for 2 h gave optically active (*R,R*)-**6** in 95% ee and 40% yield. To our knowledge, this is the first example of the preparation of an optically active tricarbonyl-iron complex without diastereoface selectivity because of its

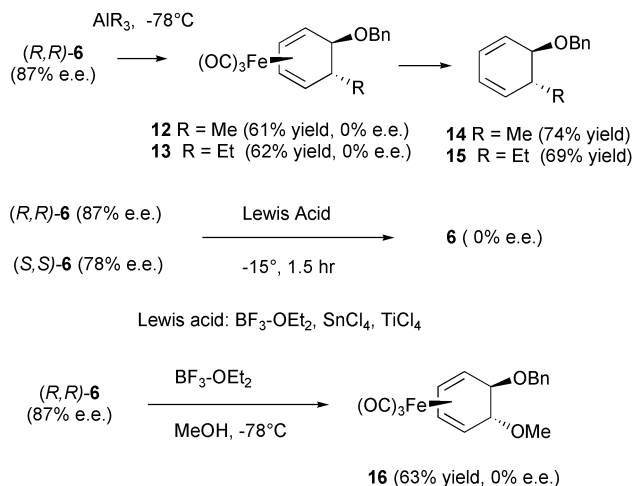
Table 3 Complexation of (*R,R*)-**5**

| $\begin{matrix} (R,R)\text{-5} & \xrightarrow[\text{THF, reflux}]{\text{Fe}_2(\text{CO})_9} & (R,R)\text{-6} \\ (97\% \text{ ee}) & & \end{matrix}$ | |
|---|----------------------------------|
| Reaction duration/h | % Ee of (<i>R,R</i>)- 6 |
| 2 | 95 |
| 4 | 89 |
| 6 | 80 |
| 9 | 44 |

C₂-symmetry. The optical purity of complex **6** was determined by high performance liquid chromatography with a CHIRAL-PAK AD column detected using UV radiation at 260 nm.⁶ To our surprise, prolonging the reaction decreased the ee of the complex as shown in Table 3. On the other hand, the ee of the isolated complex **6** (95% ee) was not decreased by the 5 h reaction with Fe₂(CO)₉. This racemization during the formation of the complex might be caused by some species with weak Lewis acidity derived from Fe₂(CO)₉.

Synthetic approach to cyclohexadiene derivatives

In order to study the synthetic applications of complex **6**, substitution reactions of optically active complex **6** and trialkyl-aluminium were studied. The results are shown in Scheme 4.

**Scheme 4**

Reaction of (*R,R*)-**6** (87% ee) with trimethylaluminium gave monomethylated product **12** in 61% yield, and that with triethylaluminium gave monoethylated **13** in 62% yield. The relative stereochemistry between the benzyloxy and alkyl groups was determined to be *trans* after conversion into the corresponding compounds **14** and **15**. In the NOESY spectrum of compound **14**, correlation between C5-H and C6-Me was observed, and a similar relationship was also observed in that of compound **15**. In addition, both products **12** and **13** were optically inactive, which means that complete racemization took place during the reaction. These results prompted us to study the reaction of optically active **6** (78% ee) with several Lewis acids such as BF₃·OEt₂, SnCl₄ and TiCl₄ at −15 °C in CH₂Cl₂ for 1.5 h. In all cases, the recovered substrate in 80–95% yield was completely racemized into 0% ee.

These results led us to consider the reaction mechanisms as shown in Fig. 2. At first, the Lewis acid coordinated the ether oxygen opposite the Fe atom because of steric effects, then elimination of the benzyloxy group afforded a prochiral dienyl cation (A) as an intermediate. Finally, regeneration of the C–(O-benzyl) bond opposite the Fe atom at the C4 or C6 position of (A) gave completely racemic **6**. These reaction

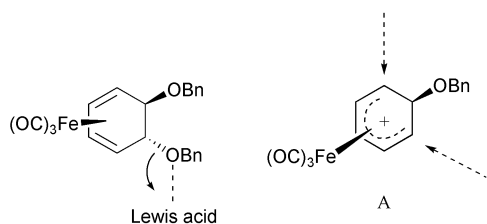


Fig. 2

mechanisms were also supported by the reaction of (*R,R*)-**6** (87% ee) with $\text{BF}_3 \cdot \text{OEt}_2$ in the presence of MeOH to afford the racemic **16** in 63% yield. In this reaction, formation of a bis(methoxy) product was not observed. For the formation of the cationic intermediate A, the *exo*-benzyloxy group at the C6-position was considered necessary based on the fact that the bis-*endo*-(benzyloxy) complex (**11**) did not react with trialkylaluminium and/or Lewis acid. These obtained results using optically active complex **6** might be important evidence of the formation of the dienyl cation intermediate (A).

Experimental

IR spectra were measured with a JASCO A-202 spectrometer or a Thermo Nicolet Avator 320 KYD spectrometer. ^1H NMR and ^{13}C NMR spectra were measured by a JEOL JNM-GX 270 or JNM-GX 500 spectrometer using CDCl_3 as a solvent and tetramethylsilane (TMS) as an internal standard. Coupling constants (*J*) are given in Hz. Mass spectra were measured on a JEOL JMS-600H or JMS-SX/SX102A spectrometer. Optical rotations were measured on a JASCO DIP-360 polarimeter in units of $10^{-1} \text{ deg cm}^2 \text{ g}^{-1}$. HPLC were performed using a HITACHI L-7100F with UV-detection, and Chiralpak AD was used as a chiral column. For column chromatography, silica gel (Nakarai Tesque, Silica Gel 60, 230–400 mesh) was used. All organic solvent extracts were dried over anhydrous MgSO_4 .

(–)-(1*R*,2*R*,4*R*,5*R*)-4,5-Bis(phenylmethoxy)-1,2-dibromocyclohexane (–)-**4**

A solution of (1*R*,2*R*,4*R*,5*R*)-4,5-dibromocyclohexane-1,2-diol (**2**, 2.74 g, 10 mmol) in DMF (10 ml) was added to a stirred mixture of 60% sodium hydride (1.3 g, 30 mmol, 3 eq.) in DMF (50 ml) at -15°C under an Ar atmosphere. Benzyl bromide (4.5 ml, 70 mmol) was then added dropwise at the same temperature. The mixture was stirred for 5 h at room temperature. The reaction was quenched by addition of sat. aqueous NH_4Cl and was extracted with ether. The organic layer was washed with brine and dried. After removal of the solvent, the residue was purified by silica-gel column chromatography (hexane–ethyl acetate = 30 : 1) to afford (–)-**4** (4.4 g, 98% yield) as a colorless oil. $[\alpha]_{\text{D}}^{24} = 44.9$ ($c = 1.09$, CHCl_3). δ_{H} (270 MHz, CDCl_3) 7.39–7.27 (10H, m, Ph), 4.60 (4H, s), 4.45 (2H, t, $J = 3.47$), 3.79 (2H, t, $J = 2.64$), 2.60–2.50 (2H, m), 2.41–2.32 (2H, m); δ_{C} (68 MHz, CDCl_3) 138.1 (s), 128.4 (d), 127.7 (d), 127.5 (d), 76.17 (d), 71.83 (t), 52.30 (d), 36.02 (t); $\nu_{\text{max}}/\text{cm}^{-1}$ (neat) 3020, 2850, 1440, 1170, 1080, 1060, 1020, 720, 680; m/z (FAB) 453 ($[\text{M} + \text{H}]^+$ 33.3), 181 (100) [Calcd For $\text{C}_{20}\text{H}_{23}\text{O}_2\text{Br}_2$: $\text{M} + \text{H}$ 453.0065. Found: $(\text{M} + \text{H})^+$ 453.0036 (FAB)]. For (+)-(1*S*,2*S*,4*S*,5*S*)-4,5-bis(benzyloxy)-1,2-dibromocyclohexane (+)-**4** $[\alpha]_{\text{D}}^{22} = +44.4$ ($c = 1.20$, CHCl_3).

(–)-(5*R*,6*R*)-5,6-Bis(benzyloxy)cyclohexa-1,3-diene (–)-**5**

To a solution of (–)-**4** (2.27 g, 5 mmol) in benzene (20 ml), DBU (3 ml, 20 mmol) was added at room temperature. The reaction was warmed to 50°C and stirred for 5 h. After addition of water to the reaction mixture, it was extracted with benzene. The organic layer was dried and concentrated *in vacuo*. The residue was purified by silica-gel column chromatography

(hexane–ethyl acetate = 20 : 1) to give (–)-**5** (715 mg, 49% yield) as a colorless oil. $[\alpha]_{\text{D}}^{24} = -270.7$ ($c = 1.00$, CHCl_3) 97% ee. δ_{H} (270 MHz, CDCl_3) 7.38–7.26 (10H, m, Ph), 6.00–5.91 (4H, m), 4.65 (4H, s), 4.44 (2H, d, $J = 1.0$); δ_{C} (68 MHz, CDCl_3) 138.5 (s), 128.4 (d), 127.8 (d), 127.6 (d), 124.5 (d), 78.22 (d), 70.85 (t); $\nu_{\text{max}}/\text{cm}^{-1}$ (neat) 3040, 2850, 1490, 1440, 1080, 1060, 720, 680; m/z (FAB) 292 (M^+ , 7.0), 91 (Bn, 100) [Calcd For $\text{C}_{20}\text{H}_{20}\text{O}_2$: M 292.1463. Found: M^+ 292.1481 (EI)]. For (+)-(5*S*,6*S*)-5,6-bis(benzyloxy)cyclohexa-1,3-diene ((+)-**5**); $[\alpha]_{\text{D}}^{18} = +263.0$ ($c = 1.04$, CHCl_3), 96% ee.

Typical procedure for complex formation

(–)-(5*R*,6*R*)-[5,6-Bis(benzyloxy)cyclohexa-1,3-dienyl]-tricarbonyliron (–)-**6**

To a solution of (–)-**5** (300 mg, 1.0 mmol) in THF (25 ml), iron nonacarbonyl (730 mg, 2 mmol) was added portionwise at room temperature. The reaction was refluxed for 2 h after which time it was passed through a short silica-gel column (ether), and concentrated *in vacuo*. The residue was purified by silica-gel column chromatography (hexane–ethyl acetate = 15 : 1) to give (–)-**6** (250 mg, 58% yield) of 95% ee as a yellowish oil; $[\alpha]_{\text{D}}^{20} = -71.9$ ($c = 0.91$, CHCl_3); δ_{H} (270 MHz, CDCl_3) 7.35–7.23 (10H, m, Ph), 5.49–5.41 (2H, m), 4.54 (2H, s), 4.51 (1H, d, $J = 11.7$), 4.37 (1H, d, $J = 11.7$), 3.84 (1H, dd, $J = 3.63, 0.99$), 3.53 (1H, dd, $J = 3.63, 0.99$), 3.10 (1H, m), 3.02 (1H, d, $J = 6.27$); δ_{C} (68 MHz, CDCl_3) 210.6 (s), 138.4 (s), 138.3 (s), 128.4 (d), 128.3 (d), 127.7 (d), 127.6 (d), 127.5 (d), 85.0 (d), 84.4 (d), 84.3 (d), 78.4 (d), 71.0 (t), 70.2 (t), 58.97 (d), 58.40 (d); $\nu_{\text{max}}/\text{cm}^{-1}$ (neat) 3025, 2850, 2920, 2045, 1970 (br), 1440, 1340, 1080, 1060, 730, 690; m/z (FAB) 431.1 ($[\text{M} - \text{H}]^+$, 1.6), 241.1 ($[\text{M} - \text{OBn} - (\text{CO})_3]^+$, 100) [Calcd for $\text{C}_{23}\text{H}_{19}\text{O}_5\text{Fe}$: $\text{M} - \text{H}$ 431.0582. Found: $(\text{M} - \text{H})^+$ 431.0543 (FAB)]; For (+)-**6** of 95% ee; $[\alpha]_{\text{D}}^{20} = +72.1$ ($c = 0.90$, CHCl_3).

(1*R*,2*S*,5*R*)-(1-Hydroxycyclohexa-2,4-dienyl)tricarbonyliron (±)-**7**

Yellow solid; δ_{H} (270 MHz, CDCl_3) 5.31–5.24 (2H, m), 3.80 (1H, m), 3.22 (1H, m), 3.14 (1H, ddd, $J = 2.31, 3.62, 11.87$), 2.07 (1H, ddd, $J = 2.31, 6.39, 15.84$), 1.56–1.48 (1H, m); $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr) 3256, 2943, 2895, 2038, 1942 (br), 1455, 1424, 1378, 1326, 1292, 1256, 1078, 1059, 1026, 935, 902, 622, 560; m/z (FAB) 235 ($[\text{M} - \text{H}]^+$).

(1*S*,2*R*,3*R*,6*S*)-(1,2-Dihydroxycyclohexa-3,5-dienyl)-tricarbonyliron **10**

Compound **10** was obtained as a crude yellow solid; δ_{H} (270 MHz, CDCl_3) 5.29 (2H, dd, $J = 2.64, 5.28$), 3.84 (2H, s), 3.15 (2H, t, $J = 3.29$), 2.64 (2H, br s); $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr) 3250, 2030, 1970, 1940, 1320, 1285, 1220, 1070, 1040; m/z (FAB) 252.0 (M^+).

(1*R*,2*S*,5*R*)-(1-Benzoyloxycyclohexa-2,4-dienyl)tricarbonyliron (±)-**8**

To a stirred solution of (±)-**7** (126 mg, 0.53 mmol) and pyridine (0.1 ml) in CH_2Cl_2 (0.5 ml) was added benzoyl chloride (0.15 ml, 1.25 mmol) at 0°C . The reaction was stirred at room temperature for 1 h. After addition of water, the reaction was extracted with ether. The organic layer was dried and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (hexane–ethyl acetate = 10 : 1) to afford (±)-**8** (169 mg, 91% yield) as yellowish needles; mp 113.4 – 114.4°C (acetone); δ_{H} (270 MHz, CDCl_3) 8.10 (2H, m), 7.57 (1H, m), 7.46 (2H, m), 5.38 (1H, m), 4.99 (1H, m), 3.33 (1H, m), 3.19 (1H, m), 2.23 (1H, ddd, $J = 2.31, 6.93, 15.84$), 1.81 (1H, dt, $J = 2.64, 15.84$); $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr) 3059, 3032, 2923, 2939, 2833, 2049, 1958, (br), 1704, 1488, 1448, 1283, 1263, 1111, 711, 620,

558; m/z (FAB) 354 (M^+); Anal. calcd for $C_{16}H_{12}FeO_5$: C, 56.50; H, 3.56. Found: C, 56.56; H, 3.52%.

(1RS,2SR,3RS,6SR)-[1,2-Bis(benzoyloxy)cyclohexa-3,5-dienyl]tricarboyliron **11**

By a similar manner to that described for the preparation of **8**, compound **10** was converted into bis-benzoate **11** in 94% yield; yellow prisms; mp 156.5–157.5 °C (EtOH); δ_H (270 MHz, $CDCl_3$) 7.94 (4H, dd, $J = 1.32, 8.58$), 7.47 (2H, tt, $J = 1.65, 7.59$), 7.26 (4H, t, $J = 7.59$), 5.45 (2H, dd, $J = 3.30, 5.28$), 5.28 (2H, s), 3.26 (2H, s), 2.64 (2H, tt, $J = 1.32, 3.96$); ν_{max}/cm^{-1} (KBr) 3380, 3330, 2020, 1980, 1950, 1710, 1250, 1100, 1060, 1010, 920, 930, 880, 795, 695; m/z (FAB) 458.9 ($(M - H)^+$, 0.9); Anal. calcd for $C_{23}H_{16}FeO_7$: C, 60.30; H, 3.50. Found: C, 60.08; H, 3.50%.

X-Ray analysis†: The yellow prisms of **11** were grown from acetone–EtOH. Data collection was performed on a Rigaku-RAXIS-RAPID Imaging Plate diffractometer, graphite monochromated Mo- $K\alpha$ radiation. Crystal and collection parameters are listed in Table 2. The crystal remained stable during the X-ray data collection. The structure was solved by direct methods with SIR92⁶ and expanded by Fourier techniques.⁷ All non-H-atoms were given anisotropic thermal parameters, and H-atoms were refined isotropically. The final cycle of full-matrix least-squares refinement of **11** gave an R factor of 0.047 ($R_w = 0.070$) based on 2583 ($I > -10.00 \sigma(I)$) reflections and R_I factor of 0.028 based on 2360 ($I > 2.0 \sigma(I)$) reflections, and the largest peak and hole in the final difference Fourier map were 0.36 and $-0.36 e\text{\AA}^{-3}$. All calculations were performed by means of the teXsan⁸ crystallographic package. The absolute configuration could not be determined from the refinement.

Reaction of **6** with trialkylaluminium

To a solution of (*R,R*)-**6** of 87% ee (432 mg, 1 mmol) in CH_2Cl_2 (10 ml), 1.0 M trialkylaluminium (2 ml, 2 mmol) was added at -78 °C under an Ar atmosphere. After being stirred for 2 h at the same temperature, the reaction was warmed slowly to room temperature. The reaction was quenched by addition of 1% aqueous HCl, and the reaction mixture was extracted with ether. The organic layer was washed with saturated aqueous $NaHCO_3$, brine and dried. After removal of the solvent *in vacuo*, the residue was purified by silica-gel column chromatography (hexane–ethyl acetate = 50 : 1) to give (\pm)-**12** or **-13**.

(1RS,4SR,5SR,6RS)-5-Benzyloxy-6-methylcyclohexa-1,3-dienyltricarboyliron (\pm)-**12**

Yield: 54%; yellow oil; δ_H (270 MHz, $CDCl_3$) 7.38–7.25 (5H, m, Ph), 5.32 (1H, m), 5.26 (1H, m), 4.54 (1H, d, $J = 11.9$), 4.49 (1H, d, $J = 11.9$), 3.15 (1H, d, $J = 6.6$), 3.10 (1H, s), 3.05 (1H, m), 2.08 (1H, m), 0.95 (3H, d, $J = 7.26$); δ_C (68 MHz, $CDCl_3$) 211.5 (s), 138.7 (s), 128.3 (d), 127.5 (d), 127.4 (d), 84.18 (d), 83.06 (d), 80.38 (d), 69.90 (t), 67.28 (d), 63.23 (d), 42.74 (d), 23.97 (q); ν_{max}/cm^{-1} (neat) 3040, 2960, 2925, 2860, 2050, 1990–1940 (br), 1450, 1335, 1260, 1090, 1060, 1020, 860, 730, 690; m/z (FAB) 340.1 (M^+ , 8.2) [Calcd for $C_{17}H_{16}O_4Fe$: M 340.0398. Found: $M - H^+$ 340.0392 (FAB)].

(1RS,4SR,5SR,6RS)-5-Benzyloxy-6-ethylcyclohexa-1,3-dienyltricarboyliron (\pm)-**13**

Yield: 82%; yellow oil; δ_H (270 MHz, $CDCl_3$) 7.35 (5H, br, Ph), 5.29 (2H, br), 4.52 (2H, br), 3.16 (2H, br), 3.09 (1H, br), 1.89 (1H, br, C2–H), 1.22 (2H, m, $-CH_2-$ Me), 0.85 (3H, br, $-CH_2-$

CH_3); ν_{max}/cm^{-1} (neat) 3035, 2970, 2920, 2850, 2045, 1980–1950 (br), 1445, 1335, 1280, 1090, 1070, 1020, 855, 730; m/z (FAB) 354.1 (M^+) [Calcd for $C_{18}H_{18}O_4Fe$: M 354.0555. Found: M^+ 354.0564 (FAB)].

(5RS,6SR)-5-Benzyloxy-6-methylcyclohexa-1,3-diene (\pm)-**14**

To a stirred solution of NaOH (200 mg, 6 mmol) and 30% H_2O_2 (0.7 ml, 6 mmol) in MeOH (8 ml), a solution of (\pm)-**12** (340 mg, 1 mmol) in MeOH (2 ml) was added at 0 °C. After being stirred for 1 h, the reaction was diluted with ether, and washed with 1% aqueous HCl, saturated aqueous $NaHCO_3$ and brine, and dried. After removal of the solvent *in vacuo*, the residue was purified by silica-gel column chromatography (hexane–ethyl acetate = 20 : 1) to give (\pm)-**14** (148 mg, 74% yield). Colorless oil; δ_H (270 MHz, $CDCl_3$) 7.37–7.26 (5H, m, Ph), 6.05 (1H, dd, $J = 9.61, 5.03$), 5.91–5.80 (3H, m), 4.59 (1H, d, $J = 11.9$), 4.52 (1H, d, $J = 11.9$), 3.88 (1H, m), 2.62 (1H, m), 1.02 (3H, d, $J = 7.26$); δ_C (68 MHz, $CDCl_3$) 138.9 (s), 133.3 (d), 128.3 (d), 127.7 (d), 127.4 (d), 125.7 (d), 124.4 (d), 121.6 (d), 77.47 (d), 69.38 (t), 34.43 (d), 17.79 (q); ν_{max}/cm^{-1} (neat) 3060, 3040, 2960, 2925, 2870, 1495, 1450, 1380, 1025, 1060, 730, 1020, 690; m/z (FAB) 200 (M^+ , 16), 91 (Bn, 100); [Calcd for $C_{14}H_{16}O$: M 200.1201. Found: M^+ 200.1166 (FAB)].

(5RS,6SR)-5-Benzyloxy-6-ethylcyclohexa-1,3-diene (\pm)-**15**

A similar reaction of (\pm)-**13** gave (\pm)-**15** in 69% yield; colorless oil; δ_H (500 MHz, $CDCl_3$) 7.38–7.30 (4H, m, Ph), 7.28–7.24 (1H, m, Ph), 6.06 (1H, ddd, $J = 0.91, 5.03, 8.69$), 5.94 (1H, dt, $J = 1.14, 5.03$), 5.90–5.86 (2H, m), 4.57 (1H, d, $J = 11.89$, O– CH_2 –Ph), 4.52 (1H, d, $J = 11.89$, O– CH_2 –Ph), 3.96 (1H, t, $J = 5.03$, C1–H), 2.47 (1H, m, C2–H), 1.50–1.35 (2H, m, $-CH_2-$ Me), 0.93 (3H, t, $J = 7.55$, $-CH_2-CH_3$); ν_{max}/cm^{-1} (neat) 3060, 3040, 2960, 2925, 2870, 1495, 1450, 1380, 1025, 1060, 730, 1020, 690; m/z (FAB) 214.2 (M^+) [Calcd for $C_{15}H_{18}O$: M 214.1358. Found: M^+ 214.1319 (FAB)].

(1RS,4SR,5RS,6RS)-5-Benzyloxy-6-methoxycyclohexa-1,3-dienyltricarboyliron **16**

To a stirred solution of (\pm)-**6** (432 mg, 1 mmol) and MeOH (0.2 ml) in CH_2Cl_2 (10 ml), $BF_3 \cdot OEt_2$ (0.2 ml, 2 mmol) was added at 0 °C. The reaction was stirred at the same temperature for 1 h. The reaction mixture was poured into aqueous saturated $NaHCO_3$, and extracted with ether. The combined extracts were dried and concentrated *in vacuo*. The residue was purified by silica-gel column chromatography (hexane–ethyl acetate = 50 : 1) gave (\pm)-**16** (157 mg, 63% yield as a yellow oil. ν_{max}/cm^{-1} (neat) 3025, 2930, 2870, 2050, 1970, 1170, 1025, 1000, 940, 930, 905, 860, 735, 695; δ_H (500 MHz, $CDCl_3$) 7.39–7.25 (5H, m, Ph), 5.43 (2H, C5,6–H), 4.56 (2H, s, O– CH_2 –Ph), 3.61, 3.43, 3.08, 3.00 (1H each, olefinic H), 3.25 (3H, s, OMe); m/z (FAB) 355 ($M^+ - H$).

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