

1,3-Asymmetric induction by planar chiral (η^4 -diene)Fe(CO)₃ complexes in Diels–Alder reaction

Saburo Nakanishi ^{*}, Katsuhisa Kumeta, Yasuhiro Sawai, Toshikazu Takata

Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, 1-1 Gakuen-cho, Sakai, Osaka 593, Japan

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Abstract

The Diels–Alder reaction of 1,3-dienes with α,β -unsaturated ketones adjacent to planar chiral (η^4 -1,3-diene)Fe(CO)₃ complexes in the presence of Lewis acid proceeded diastereoselectively. The dienophiles reacted with cyclopentadiene to give the endo adducts stereoselectively. The Lewis acid affected remarkably the diastereoselectivity in the reaction.

Keywords: Iron; Carbonyl; Diene; Diolefin; Ketone; Planar chiral; Diels–Alder reaction

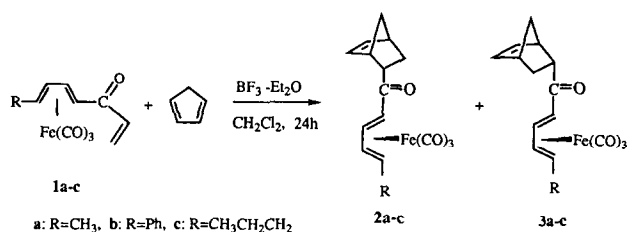
Planar chiral (η^4 -1,3-diene)Fe(CO)₃ complexes have received considerable attention as useful reagents for organic synthesis [1]. They can serve as chiral auxiliaries for asymmetric induction, and also as reagents introducing 1,3-diene groups into organic compounds. One of the attractive applications of the (η^4 -1,3-diene)Fe(CO)₃ complexes is the asymmetric Diels–Alder reaction owing to their planar chirality [2,3]. Although a variety of asymmetric syntheses has been reported by use of the planar chiral (η^4 -1,3-diene)Fe(CO)₃ complexes, most of them have been confined to 1,2-asymmetric induction and little is known about more remote asymmetric induction. The only exceptional case is 1,4-asymmetric induction in the aldol condensation reaction by chiral (η^4 -1,3-diene)Fe(CO)₃ complexes [4], however, its diastereoselectivity is poor. In this paper, we wish to report an example of 1,3-asymmetric induction based on the planar chiral (η^4 -1,3-diene)Fe(CO)₃ complexes in the Diels–Alder reaction of α,β -unsaturated ketones adjacent to planar chiral (η^4 -1,3-diene)Fe(CO)₃ complexes.

α,β -Unsaturated ketones (**1**) were prepared by reaction of (η^4 -1,3-dienecarboxylic acid chloride)Fe(CO)₃ and vinyltrimethylsilane [5]. The Diels–Alder reaction of **1** with cyclopentadiene was carried out in dichloromethane in the presence of boron trifluoride

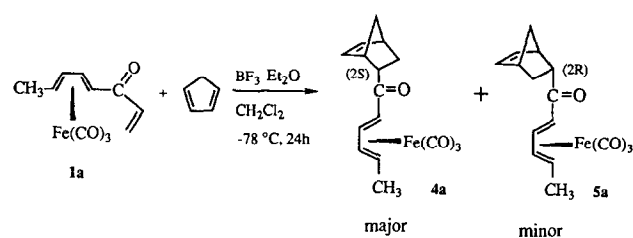
etherate to give only endo norbornene derivatives, which consist of a mixture of the diastereomers (**2** and **3**) [6] in good yields. The diastereomers were separated by column chromatography on silica gel. The ratio of the diastereomers was determined by HPLC. The results are shown in Table 1. Regardless of the presence or absence of the Lewis acid, the reaction proceeded stereoselectively to give the endo adducts. However, the Lewis acid not only accelerated the reaction rate but also enhanced the diastereoselectivity. Furthermore, the diastereomeric ratio of the products increased with decreasing temperature. The best selectivity was attained when the reaction was carried out at -78°C in the presence of the Lewis acid, while a reversed ratio of diastereomers was observed when the reaction took place at room temperature in the absence of the Lewis acid.

To further investigate the stereochemistry the reaction of enantiomerically pure (2*R*,5*S*)-**1a** [7] with cyclopentadiene was carried out, giving **4a** as a major product (**4a**:**5a** 92:8). The structure of **4a** was unambiguously determined by X-ray analysis [8] and is illustrated in Fig. 1. **4a** has the (2*S*)-configuration of the norbornene fragment. The above results suggest that a probable transition state is depicted by assembly **6**, as shown in Fig. 2. Cyclopentadiene approaches the dienophile from the opposite side of the Fe(CO)₃ fragment. BF₃ coordinates to the carbonyl oxygen from the opposite side of the Fe(CO)₃ fragment and stabilizes the *s-trans* conformation of the α,β -unsaturated ketones.

^{*} Corresponding author.



Scheme 1.



Scheme 2.

Table 1

Diels-Alder reaction of α,β -unsaturated ketones adjacent to $(\eta^4\text{-diene})\text{Fe}(\text{CO})_3$ complexes with Cyclopentadiene^a

Complex	R	Temperature (°C)	Lewis acid	Yield ^b (%)	2/3 (de (%))
2a, 3a	CH ₃	-78	BF ₃	95	92/8 (84)
	CH ₃	room temp.	BF ₃	92	65/35 (30)
	CH ₃	-78	none	24	70/30 (40)
	CH ₃	-78	none	90 ^c	71/29 (42)
	CH ₃	room temp.	none	96	40/60 (20)
2b, 3b	Ph	-78	BF ₃	95	89/11 (78)
2c, 3c	C ₃ H ₇	-78	BF ₃	94	86/14 (72)

^a A mixture of **1** (2.0 mmol), cyclopentadiene (3.0 mmol) and Lewis acid (2.0 mmol) in dichloromethane (10 ml) stirred for 24 h.

^b Isolated yields based on **1**.

^c Reaction time 60 h.

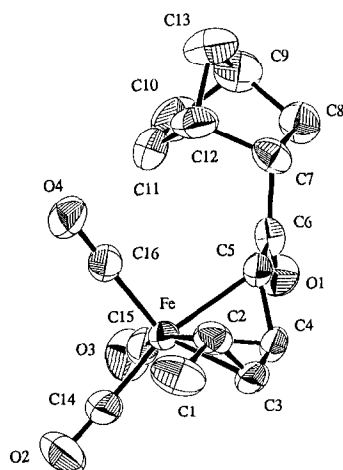


Fig. 1. Molecular structure of **4a**. Selected bond lengths (Å) and angles (°): Fe-C2 2.160(5), Fe-C3 2.058(4), Fe-C4 2.035(4), Fe-C5 2.138(4), Fe-C14 1.763(5), Fe-C15 1.795(5), Fe-C16 1.798(5), C5-C6 1.482(6), O1-C6 1.216(5), C6-C7 1.495(6); Fe-C2-C3 66.6(2), C1-C2-C3 120.7(4), C2-C3-C4 119.3(4), C3-C4-C5 119.7(4), C4-C5-C6 119.4(4), O1-C6-C5 121.0(4), C6-C7-C8 116.5(4).

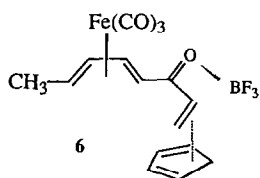
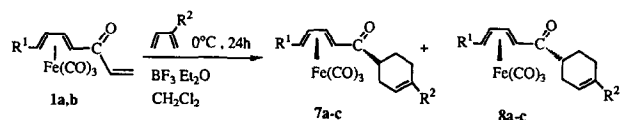


Fig. 2.



Scheme 3.

Table 2

Diels-Alder reaction of α,β -unsaturated ketones adjacent to $(\eta^4\text{-diene})\text{Fe}(\text{CO})_3$ complexes with 1,3-dienes^a

Complex	R ¹	R ²	Yield ^b (%)	de (%)
7a, 8a	CH ₃	CH ₃	73	86
7b, 8b	CH ₃	CH ₂ CH ₂ CH=C(CH ₃) ₂	53	81
7c, 8c	Ph	CH ₃	61	83

^a A mixture of **1** (2.0 mmol), cyclopentadiene (3.0 mmol) and boron trifluoride etherate (2.0 mmol) in dichloromethane (10 ml) stirred for 24 h at 0°C.

^b Isolated yields based on **1**.

The high degree of 1,3-asymmetric induction is provably due to such a stereochemical assembly between the $\text{Fe}(\text{CO})_3$ fragment, Lewis acid, dienophile and 1,3-diene.

Other 1,3-dienes reacted with **1a,b** to give the cycloadducts with good diastereoselectivity as shown in Scheme 3 and Table 2; but the reaction rate of **1a,b** with the dienes was slow compared with cyclopentadiene.

References and notes

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- [6] All new compounds were characterized by their spectral data. Selected data for **2a**. Yellow solids, m.p. 109–111°C. IR (KBr): 2052, 1986 (CO), 1667 (C=O) cm⁻¹. ¹H NMR (270 MHz,

CDCl_3): δ 1.24 (1H, d, $J = 7.2$ Hz, CH=), 1.28–1.33 (1H, m, CH_2), 1.43–1.69 (5H, m, CH_3 , CH_2), 1.72 (1H, dd, $J = 3.3$, 5.2 Hz, CH_2), 2.85–2.91 (1H, m, CH), 3.00–3.06 (1H, m, CH), 3.27–3.32 (1H, m, CH), 5.24 (1H, dd, $J = 4.8$, 7.2 Hz, CH=), 5.70–5.75 (1H, m, CH=), 5.92 (1H, dd, $J = 2.8$, 5.6 Hz, CH=), 6.19 (1H, dd, $J = 2.8$, 5.6 Hz, CH=). ^{13}C NMR (67.5 MHz, CDCl_3): δ 19.07 (CH_3), 27.73, 50.24 (CH_2), 42.62, 47.07, 51.30 (CH), 53.56, 59.08, 81.84, 88.38, 131.41, 137.84 (C=), 206.12 (C=O), 220.12 (CO). For **3a**. Yellow solids, m.p. 84–86°C. IR (KBr): 2052, 1986 (CO), 1669 (C=O) cm^{-1} . ^1H NMR (270 MHz, CDCl_3): δ 1.24 (1H, d, $J = 7.2$ Hz, CH=), 1.28–1.33 (1H, m, CH_2), 1.43–1.69 (5H, m, CH_3 , CH_2), 1.72 (1H, dd, $J = 3.3$, 5.2 Hz, CH_2), 2.88 (1H, s, CH), 2.92–3.00 (1H, m, CH), 3.14–3.18 (1H, m, CH), 5.24 (1H, dd, $J = 4.8$, 7.2 Hz, CH=), 5.70–5.75 (1H, m, CH=), 5.82 (1H, dd, $J = 2.8$, 5.6 Hz, CH=), 6.15 (1H, dd, $J = 2.8$, 5.6 Hz, CH=). ^{13}C NMR (67.5 MHz, CDCl_3): δ 19.07 (CH_3), 28.40, 48.82 (CH_2), 42.81, 46.05, 48.83

(CH), 53.32, 59.00, 81.77, 88.45, 131.50 (C=), 205.90 (C=O), 220.33 (CO).

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- [8] Crystallographic details For **4a**. $\text{C}_{16}\text{H}_{16}\text{O}_4\text{Fe}$, FW 328.15. **4a** was crystallized in space group $P2_1/c$ (No. 14) with lattice parameters $a = 6.196(4)$, $b = 11.198(6)$, $c = 21.975(4)$ Å, $V = 1511(1)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.442$ g cm⁻³. From a crystal of dimensions $0.250 \times 0.250 \times 0.150$ mm³, 3672 independent reflections were measured over a 2θ range of 6–55.1° using Mo K α radiation ($\lambda = 0.71069$ Å) at 23°C. The Fe atom was found from a three-dimensional Patterson map, and the non-hydrogen atoms were located by subsequent difference Fourier syntheses. All hydrogen atoms were included at calculated positions. Full-matrix least-squares refinement using 1543 reflections with $I > 5.00$ $\sigma(I)$ converged to final agreement factors $R = 0.034$ and $R_w = 0.035$ with GOF 2.25.