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Synthesis of planar chiral η^3-allyldicarbonylnitrosyliron complexes and stereochemistry of the complex forming reaction

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Abstract

Planar chiral η^3-allyldicarbonylnitrosyliron complexes were prepared by the reaction of optically active allyl tosylate and allyl bromide with tetrabutylammonium tricarbonyl nitrosylferrate. The optical purity and planar chirality of the complexes thus obtained depended on reaction solvents and leaving groups of the allylic substrates. Stereoselectivity of the complex forming reaction was also affected by the chiral auxiliary attached to the allylic substrate.

Keywords: η^3-Allyliron complexes; Nitrosyl ligand; Planar chirality; CD spectroscopy

Much attention has been focused on the chemistry of η^3-allyldicarbonylnitrosyliron complexes because of the unique reactivities [1–3]. In addition to the ambiphilic reactivity [4], the η^3-allyldicarbonylnitrosyliron complexes have planar chirality which can be utilized in asymmetric organic transformations. One of the attractive applications of such complexes is an asymmetric amination reaction of the η^3-allyldicarbonylnitrosyliron complexes yielding optically active γ-amino-α,β-unsaturated carboxylic acid derivatives [5]. However, methodology for preparation of the planar chiral η^3-allyldicarbonylnitrosyliron complexes has not been well developed yet, in contrast to planar chiral cationic η^3-allyltetracarbonyliron complexes [6]. We have recently reported a facile preparation of planar chiral η^3-allyldicarbonylnitrosyliron complexes by separation of a diastereomeric mixture of the complexes having optically active auxiliaries [7]. In this communication we wish to report another route to planar chiral η^3-allyldicarbonylnitrosyliron complexes by the reaction of optically active allyl tosylate and allyl bromide with tetrabutylammonium tricarbonylnitrosylferrate. A brief discussion is also presented about the remarkable effects of the reaction solvent and optically active substituent on the stereoselectivity of the complex forming reaction.

Optically active (*S*)-allyl tosylate **1** and (*R*)-allyl bromide **2** were prepared [8] from ethyl (*S*)-4-hydroxyl-2-pentenoate [9] derived from methyl (*S*)-lactate. The allyl tosylate **1** was allowed to react with tetrabutylammonium tricarbonylnitrosylferrate (TBAFe) to give an enantiomeric mixture of η^3-allyldicarbonylnitrosyliron

Table 1
Reaction of optically active allyl tosylate **1** with $Bu_4N[Fe(CO)_3(NO)]$

Solvent	Temperature (°C)	Yield[a] (%)	Product ratio[b] (3:4)	e.e. (%)
CH_2Cl_2	−40	83	91:9	82
CH_2Cl_2	0	81	90:10	80
CH_2Cl_2	r.t.	70	71:29	42
Toluene	0	67	97:3	94
THF	0	65	90:10	80
Acetone	0	68	80:20	60
CH_3CN	0	No reaction	—	—
CH_3CN	r.t.	58	31:69	38

[a] Isolated yield based on allyl tosylate employed.
[b] Determined by ^{1}H-NMR using a chiral NMR shift reagent Eu(hfc)$_3$ and CD spectrum.

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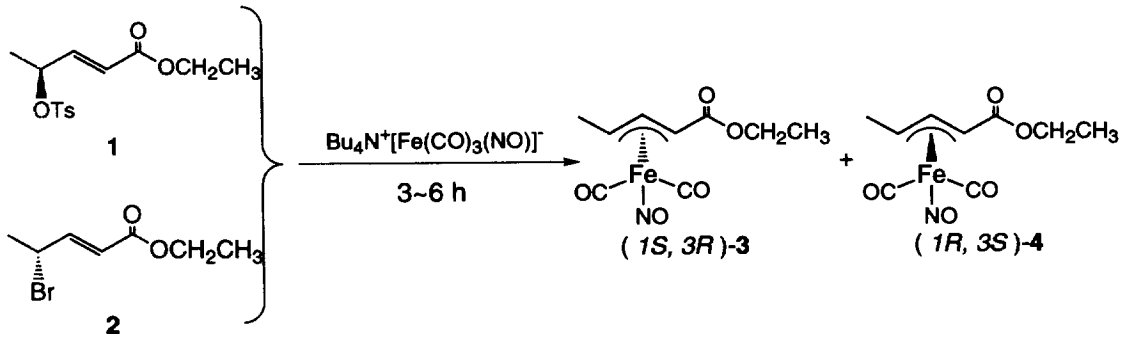
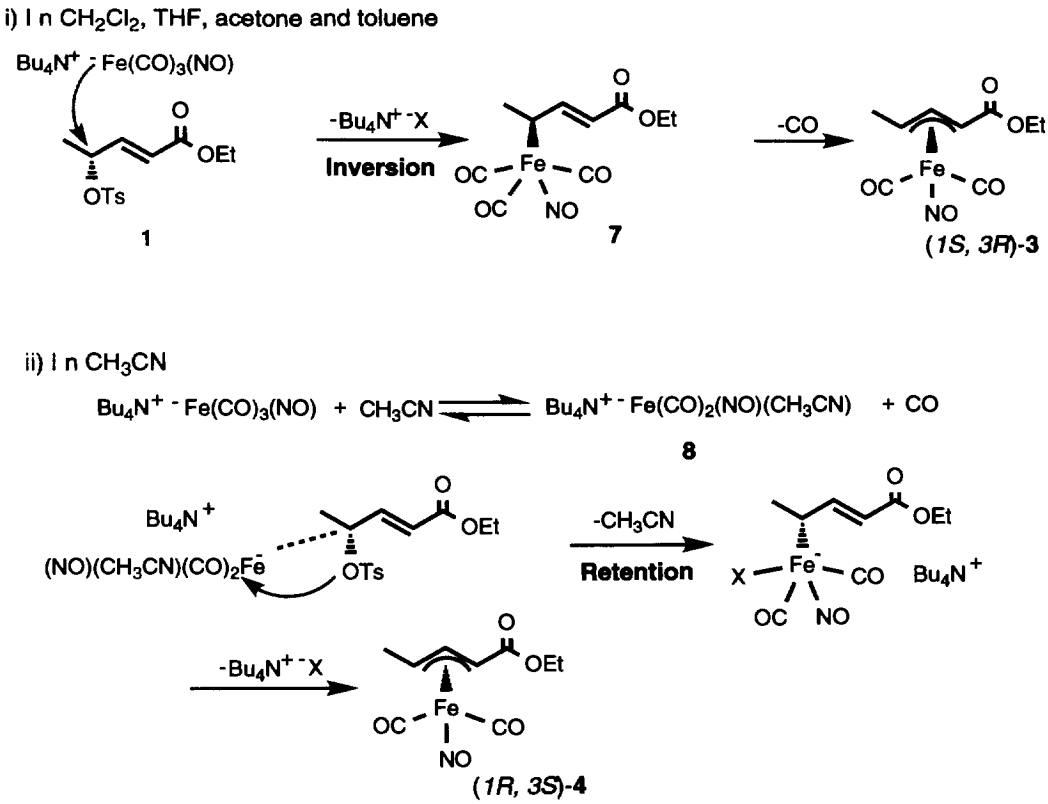


Scheme 1.



Scheme 2.

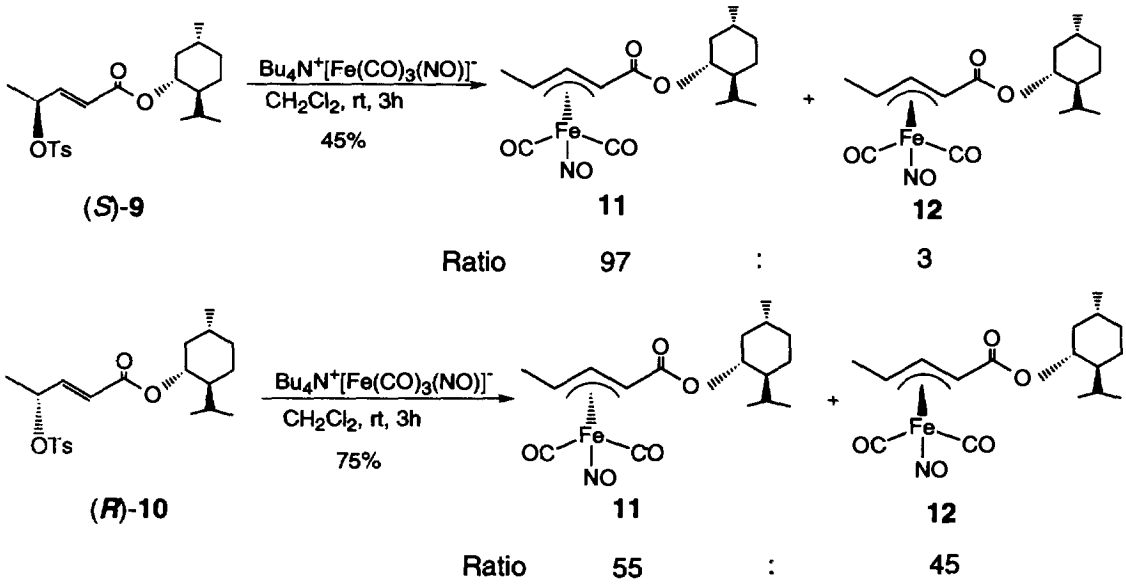
complexes (**3** and **4**) [10]. The results are summarized in Table 1.

The relationship between the planar chirality of η^3-allyldicarbonylnitrosyliron complexes and their CD spectra has been reported [7]. According to the relationship, configuration of the complexes formed from the reaction of **1** and **2** with TBAFe was determined by their CD spectra. The enantiomer's ratio (**3**: **4**) was determined by the ^{1}H-NMR spectra using a chiral shift reagent Eu(hfc)$_3$ [11]. The planar chirality and the optical purity of the complexes were remarkably affected by the solvent employed. In CH_2Cl_2, THF, acetone and toluene, (*1S*, *3R*)-**3** was preferentially yielded with inversion of the configuration of the allyl tosylate **1**. The best stereoselectivity (94% e.e.) was attained in toluene. On the other hand, (*1R*, *3S*)-**4** was a major product in CH_3CN indicating the stereochemistry with retention (Scheme 1).

Table 2
Reaction of optically active allyl bromide **2** with $Bu_4N[Fe(CO)_3(NO)]$

Solvent	Temperature (°C)	Yield[a] (%)	Product ratio[b] (3:4)	e.e. (%)
CH_2Cl_2	−40	No reaction	—	—
CH_2Cl_2	0	70	33:67	33
Toluene	0	53	31:69	38
CH_3CN	0	52	47:53	6

[a,b] See Table 1.



Scheme 3.

A possible pathway is proposed to interpret the above results as depicted in Scheme 2. In CH_2Cl_2, THF, acetone and toluene, TBAFe attacks at allylic carbon atom from the opposite site of the tosyl group via S_N2 or S_N2' mechanism to afford complex **7** which is converted to (*1S*, *3R*)-**3** through decarbonylation. Meanwhile, in the case of acetonitrile, TBAFe is first transformed into acetonitrile complex **8** with decarbonylation because of high coordinating ability of acetonitrile. CO gas was evolved by mixing TBAFe with acetonitrile, together with gradual decomposition of TBAFe. But, no CO was evolved by mixing TBAFe with the solvent other than acetonitrile. These results suggest that TBAFe may be converted to complex **8** via substitution of CO ligand by acetonitrile. *Syn* oxidative addition of the allyl tosylate to **8** leads to the formation of (*1R*,*3S*)-**4** with retention of the configuration. η^3-Allyl transition metal complex forming reaction is generally an inversion process but occasionally a retention process, although a retention process is not a common process [12]. Kurosawa et al. reported that steroselectivity of oxidative addition of allylic halides to palladium complex depends dramatically on the solvents [13]. *Syn* oxidative addition dominates in benzene, CH_2Cl_2 and THF, while *anti* addition is favored in acetonitrile. This is reverse to the results of the present reaction.

Similar treatment of allyl bromide **2** with TBAFe afforded a mixture of **3** and **4**. The results are listed in Table 2. (*1R*, *3S*)-**4** was produced as a major product in any solvent with less stereoselectivity than that of **1**. The intervention of a radical process may be conceived [14].

Further, a remarkable substituent effect on the stereoselectivity in the formation of η^3-allyl complexes was also observed. Treatment of allyl tosylates **9** and **10** [15] with TBAFe afforded a diastereomeric mixture of η^3-allyl complexes **11** and **12**, as shown in Scheme 3. (*S*)-**9** reacted with TBAFe in CH_2Cl_2 at room temperature to give **11** and **12** in a ratio of 97:3 [16]. This is a highly stereoselective process with inversion of the configuration. On the other hand, the reaction of (*R*)-**10** underwent to give a mixture of **11** and **12** in a ratio (55:45) with low stereoselectivity. The former is a matched asymmetric reaction, while the latter is mismatched one.

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[8] For **1:** colourless oil, IR(neat); 1721cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$); δ 7.79 (d, J = 7.9 Hz, 2H), 7.41–7.30 (m, 2H), 6.70 (dd, J = 15.5, 5.5 Hz, 1H), 5.89 (dd, J = 15.5, 1.2 Hz, 1H), 5.20–5.05 (m, 1H), 4.17 (q, J = 7.3 Hz, 2H), 2.44 (s, 3H), 1.40 (d, J = 6.7 Hz, 3H), 1.26 (t, J = 7.3 Hz, 3H). For **2:** colourless oil, IR (neat); 1719 cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$); δ 7.02 (dd, J = 15.3, 7.9 Hz, 1H), 5.93 (dd, J = 15.3, 1.2 Hz, 1H), 4.73–4.65 (m, 1H), 4.22 (q, J = 7.3 Hz, 2H), 1.83 (d, J = 6.7 Hz, 3H), 1.30 (t, J = 7.3 Hz, 3H).

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[10] For Complexes **3** and **4:** IR (neat); 2036, 1977 (CO), 1751 (NO), 1715 (C=O) cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$); δ 5.05 (t, J = 11.2 Hz, 1H), 4.13–4.41(m, 3H), 3.79 (d, J = 11.2 Hz, 1H), 2.03 (d, J = 6.1 Hz, 3H), 1.32 (t, J = 7.3 Hz, 3H). ^{13}C-NMR (67.5 MHz, $CDCl_3$); δ 217.0, 216.8, 172.39, 97.3, 77.9, 60.9, 56.0, 19.6, 14.2.

[11] Allylic protons of the enantiomeric complexes can be discriminated by addition of Eu(hfc)$_3$ (0.08 equivalents) to the ^{1}H-NMR sample. Thus signals (5.05 ppm) of the allylic protons were shifted to lower field (0.5 ppm) and were separated enough to determine the ratio of the enantiomers.

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[15] For **9**; colourless oil, IR(neat); 1715 (C=O), 1355, 1177 (SO_2) cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.80 (d, J = 7.9 Hz, 2H), 7.33 (d, J = 7.9 Hz, 2H), 6.71 (dd, J = 15.9, 5.5 Hz, 1H), 5.89 (d, J = 15.9, 1.8 Hz, 1H), 5.20–5.05 (m, 1H), 4.00–3.85 (m, 1H), 2.44 (s, 3H), 2.10–1.00 (m, 9H), 1.41 (d, J = 6.7 Hz, 3H), 0.91 (d, J = 6.7 Hz, 3H), 0.89 (d, J = 7.3 Hz, 3H), 0.74 (d, J = 7.3 Hz, 3H). For **10**; colourless oil, IR(neat); 1715(C=O)cm^{-1}. ^{1}H-NMR (270 MHz, CDCl3) δ 7.80 (d, J = 1.8 Hz, 2H), 7.33 (d, J = 7.9 Hz, 2H), 6.67 (dd, J = 15.9, 5.5 Hz, 1H), 5.87 (d, J = 15.9, 1.8 Hz, 1H), 5.25–5.10 (m, 1H), 4.75–4.65 (m, 1H), 2.44 (s, 3H), 1.41 (d, J = 6.7 Hz, 3H), 2.10–1.00 (m, 9H), 0.91 (d, J = 6.7 Hz, 3H), 0.89 (d, J = 7.3 Hz, 3H), 0.74 (d, J = 7.3 Hz, 3H).

[16] For **11:** red oil, IR(neat); 2044, 1988 (CO), 1750 (NO), 1715 (C=O) cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$); δ 5.22–5.11 (m, 1H), 4.82 (dt, J = 10.9 and 4.0 Hz, 1H), 4.02 (d, J = 6.8 Hz, 1H), 3.74 (d, J = 10.5 Hz, 1H), 3.11 (d, J = 12.9 Hz, 1H), 2.02 (d, J = 6.9 Hz, 3H), 2.10–1.00 (m, 9H), 0.94 (d, J = 6.9 Hz, 3H), 0.89 (d, J = 7.3 Hz, 3H), 0.81 (d, J = 6.9 Hz, 3H). For **12:** red oil, IR(neat); 2046, 1988 (CO), 1758 (NO), 1713 (C=O) cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$) δ 5.25–5.14 (m, 1H), 4.81 (dt, J = 4.4 and 10.9 Hz, 1H), 4.04 (d, J = 6.9 Hz, 1H), 3.78 (d, J = 10.9 Hz, 1H), 3.18 (d, J = 12.9 Hz, 1H), 2.02 (d, J = 6.9 Hz, 3H), 2.10–1.00 (m, 9H), 0.93 (d, J = 6.9 Hz, 3H), 0.91 (d, J = 7.3 Hz, 3H), 0.79 (d, J = 6.9 Hz, 3H). ^{13}C-NMR (67 MHz, $CDCl_3$) δ 216.21, 215.91, 172.39, 96.80, 75.13, 61.16, 55.22, 47.03, 40.65, 34.26, 31.61, 26.30, 23.47, 22.07, 20.80, 16.37.