

# Chiral-Auxiliary-Directed Asymmetric Tricarbonyliron Complexation of Dienes

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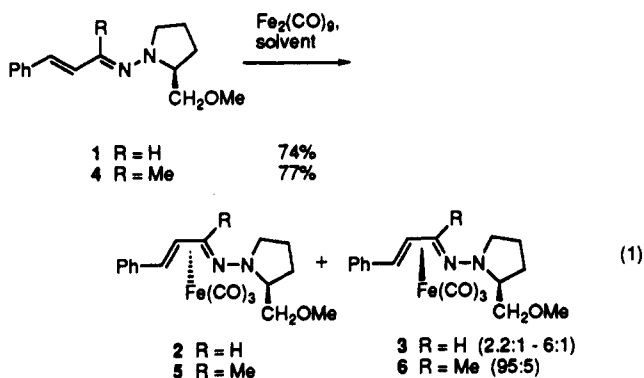
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**Summary:** Reactions of two azadienes and four dienamides, carrying chiral substituents, with nonacarbonyl diiron are reported to proceed in good to excellent yields and diastereoselectivity, the degree of selectivity depending on the nature of the chiral auxiliary that is used. The highest selectivity for azadiene reactions was 95:5, while complete selectivity was observed for the dienamide prepared from (*S*)-2-(diphenylhydroxymethyl)pyrrolidine and sorbic acid, leading to chiral nonracemic diene-Fe(CO)<sub>3</sub> complex **9d**. The stereochemistry of the product from the latter reaction was determined by single-crystal X-ray methods. This represents the first reported efficient preparation of an optically pure all-carbon-diene-Fe(CO)<sub>3</sub> complex via asymmetric induction methods.

Stereocontrolled bond constructions based on a transition-metal template effect have been increasingly studied in recent years, due to the ability of the metal to exert steric or stereoelectronic control over reactions of complexed or uncomplexed double bonds. Work in our laboratory is focused on exploring these effects in complexes of cyclic olefinic compounds,<sup>1</sup> while others<sup>2</sup> have studied acyclic systems. In the latter context, Grée and co-workers<sup>2a</sup> have developed the known<sup>3</sup> ability of an Fe(CO)<sub>3</sub> group to protect a butadiene moiety during functionalization of a neighboring uncomplexed carbon-carbon double bond, a process which usually occurs with a high degree of stereoselectivity due to the bulky organometallic group. This chemistry may be used to effect the synthesis of optically pure chiral substances, but the requisite iron complexes have been accessible only by optical resolution of the racemic materials. A few attempts to achieve asymmetric synthesis of chiral diene-Fe(CO)<sub>3</sub> complexes have been recorded in the literature, with variable success.<sup>4</sup> We report herein a study on complexation of dienes having chiral auxiliaries, which demonstrates for the first time

the feasibility of efficient asymmetric synthesis of diene-Fe(CO)<sub>3</sub> complexes.

A number of chiral amines and hydrazines were prepared using the literature methods.<sup>5</sup> Our initial studies utilized the aza diene **1**, prepared from cinnamaldehyde. Reaction



of **1** with Fe<sub>2</sub>(CO)<sub>9</sub> in toluene at 50–60 °C gave an equimolar mixture of diastereomeric complexes **2** and **3** in 86% yield. The use of acetone as solvent at room temperature gave a 2.2:1 ratio in favor of **2** in 77% combined yield, while a 6:1 ratio was obtained in refluxing ether. The stereochemistry of the major product was assigned by comparison with the results of an X-ray crystal structure determination (see later), assuming the preferred conformation indicated for **1**. The methyl-substituted hydrazone **4**, prepared from benzylideneacetone, gave a 95:5 ratio of complexes **5** and **6** in 74% yield, presumably reflecting a greater conformational bias in the hydrazone due to the methyl substituent. Encouraged by these results, we proceeded to examine the complexation reactions of a series of dienamides in which the chiral center is further removed from the coordinating ligand.

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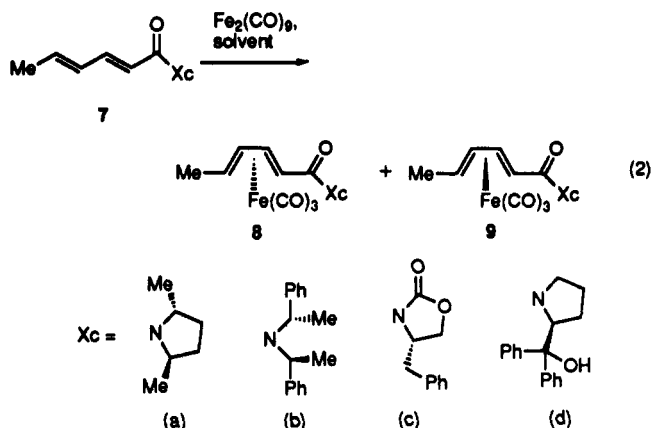
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**Table 1. Diastereoselective Complexation of Dienamides 7a-d**

dienamide	reacn conditions <sup>a</sup>	combined yield (%)	major product <sup>b</sup>	diastereomer <sup>c</sup> ratio
7a	Et <sub>2</sub> O, reflux	95	8a	4.6:1
7a	BDA-Fe(CO) <sub>3</sub> , Et <sub>2</sub> O, reflux	74	8a	2.2:1
7b	Et <sub>2</sub> O, reflux	46		1.5:1
7c	Et <sub>2</sub> O reflux	78	8c	2:1
7d	Et <sub>2</sub> O, CH <sub>2</sub> Cl <sub>2</sub> , reflux	84 <sup>d</sup>	9d	>99:1

<sup>a</sup> All reactions used Fe<sub>2</sub>(CO)<sub>9</sub>, unless otherwise noted. <sup>b</sup> Stereochemistry of major product assigned tentatively, except for 9d. <sup>c</sup> Estimated by integration of <sup>1</sup>H NMR spectrum. <sup>d</sup> Based on diene consumed at ~50% conversion; 48% yield of pure diene was recovered, but attempts to increase conversion did not lead to an improvement in mass balance, due to decomposition of the complex during extended reaction time.

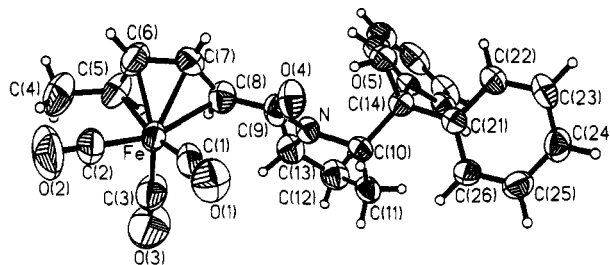
The results of the dienamide complexation study are summarized in eq 2 and Table 1. The substrates were all



prepared in high yield from sorbic acid and the chiral amine or oxazolidinone, using standard coupling methods (acid chloride, mixed anhydride, or dicyclohexylcarbodiimide). Complexation reactions were found to proceed best using Fe<sub>2</sub>(CO)<sub>9</sub> in diethyl ether at reflux or, in cases where solubility of the amide was problematic, using diethyl ether/methylene chloride as solvent. A trial experiment, in which 7a was treated with benzylideneacetone-Fe(CO)<sub>3</sub> (BDA-Fe(CO)<sub>3</sub>) as the complexing reagent,<sup>6</sup> gave lower yield and poorer diastereoselectivity. In all cases the diastereomeric complexes could be separated by crystallization and/or chromatography but diastereomer ratios were determined by integration of the <sup>1</sup>H NMR spectrum of the mixture.

The stereochemistry of the major products from the complexation of 7a and 7b are tentatively assigned on the

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**Figure 1.** X-ray Structure of complex 9d, showing thermal ellipsoids (atom numbering is arbitrary). Selected bond lengths (Å): Fe-C(2), 1.761(8); Fe-C(5), 2.144(7); Fe-C(6), 2.023(8); Fe-C(7), 2.035(8); Fe-C(8), 2.141(7); C(5)-C(6), 1.387(12); C(6)-C(7), 1.413(9); C(7)-C(8), 1.410(10). Selected bond angles: C(2)-Fe-C(6), 92.4(4); C(6)-Fe-C(7), 40.8(3); C(7)-C(8)-C(9), 119.9(5); C(6)-C(7)-C(8), 118.0(7); C(7)-C(6)-C(5), 120.7(7).

basis of known reactions of the related acrylamide derivatives with, for example, organic free radicals.<sup>7</sup> The stereochemistry of the single diastereomer obtained from 7d was established by a single-crystal X-ray structure determination,<sup>8</sup> shown in Figure 1, and presumably arises from reaction of the olefinic group with Fe(CO)<sub>4</sub> (the electron-deficient reactive intermediate from dissociation of Fe<sub>2</sub>(CO)<sub>9</sub>) at the less sterically hindered face, the preferred conformation of which can be deduced from inspection of Figure 1 (except that the diene will be (*S*)-*trans*). The stereocontrol during these reactions is exerted by a somewhat remote chiral center, and this explains the requirement for a sterically demanding (Ph<sub>2</sub>COH) directing group.

In conclusion, we have demonstrated the feasibility of asymmetric complexation of substituted butadienes and azadienes in good yields using readily available chiral auxiliaries as directing groups.

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**Supplementary Material Available:** Full details of the X-ray structure of complex 9d, including tables of atomic coordinates, bond lengths, bond angles, and anisotropic displacement coefficients (8 pages). Ordering information is given on any current masthead page.

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(8) Crystallographic data were collected using a Syntex P2<sub>1</sub> diffractometer with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The SHELXTL PLUS program set was used for structure solution and refinement. C<sub>26</sub>H<sub>25</sub>FeNO<sub>5</sub>: orthorhombic, P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>,  $a = 8.816(2)$  Å,  $b = 9.817(2)$  Å,  $c = 27.283(5)$  Å,  $V = 2361.3(8)$  Å<sup>3</sup>,  $Z = 4$ . The intensity data were collected using an  $\omega$  scan over the range  $3.5 \leq 2\theta \leq 50^\circ$  at room temperature. Hydrogen atoms were placed in ideal positions. Refinement to convergence of the 297 parameters on 2167 unique data with  $|F_o| > 4.0\sigma(F_o)$  confirmed the absolute configuration  $\eta = 0.89(9)$ ,  $R_F = 5.10\%$ ,  $R_w = 5.53\%$ , and GOF = 1.55; all unique data (2902 reflections) gave  $R_F = 7.31\%$  and  $R_w = 5.86\%$ .