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# An Unusual Stereochemical Outcome in the Oxidatively Induced Reductive Elimination of (Pentenediyl)iron Complexes

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# An Unusual Stereochemical Outcome in the Oxidatively Induced Reductive Elimination of (Pentenediyl)iron Complexes

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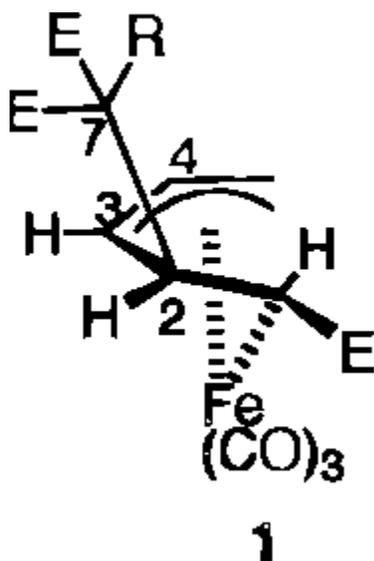
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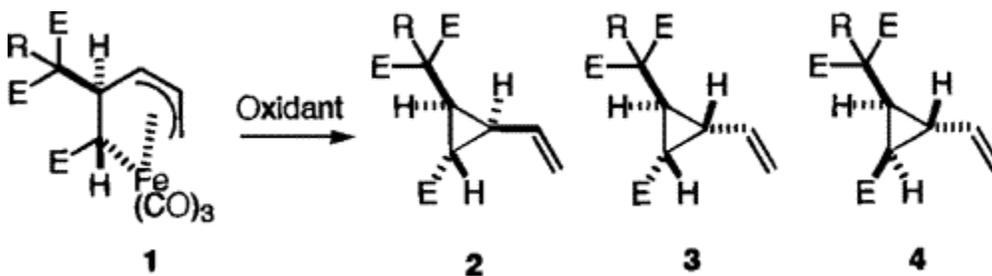
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Oxidatively induced reductive elimination is an important reaction step in numerous stoichiometric and catalytic transition metal mediated carbon–carbon bond formations. This process is well-known to occur with retention of stereochemistry.<sup>1</sup> We<sup>2</sup> and others<sup>3</sup> have reported that the oxidative decomplexation of (pentenediyl)iron complexes bearing an electron-withdrawing substituent provides a novel methodology to generate vinylcyclopropanes.<sup>4</sup> We herein report on an unexpected stereochemical outcome for certain substrates and propose a mechanism to account for these results.

We have previously reported that the reaction of tricarbonyl(1-(methoxycarbonyl)pentadienyl)iron(1+) cation with malonate anions occurs regioselectively at an internal position (C2) to give stable (pentenediyl)iron complexes **1a–c**.<sup>6</sup> The relative stereochemistry of **1a** and **1b** were established by X-ray diffraction analysis.<sup>6</sup> Oxidative decomplexation of **1a** with cerium ammonium nitrate (CAN, 10 equiv, DMF or MeOH) generates the vinylcyclopropane **2a** as the major product (Table 1; entry 1). This result is consistent with an oxidatively induced reductive elimination occurring with retention of stereochemistry. In comparison, oxidation of **1a** with trimethylamine *N*-oxide (TMANO, C<sub>6</sub>H<sub>6</sub>, reflux) gave a mixture of diastereomeric vinylcyclopropanes **2a**, **3a**, and **4a** (Table 1; entry 2). The relative stereochemistries of **2a**, **3a**, and **4a** are based on their <sup>1</sup>H NMR spectral data.<sup>7</sup> In particular, the ring protons of each with a *cis* relationship are coupled by ca. 9 Hz, while ring protons with a *trans* relationship are coupled by ca. 5–6 Hz.<sup>8</sup> It is important to note that vinylcyclopropane **2a** does not isomerize to **3a** or **4a** upon treatment with either TMANO or triethylamine (C<sub>6</sub>H<sub>6</sub>, 80 °C). Thus, the products **3a** and **4a** are not the result of rearrangement or epimerization of **2a**.

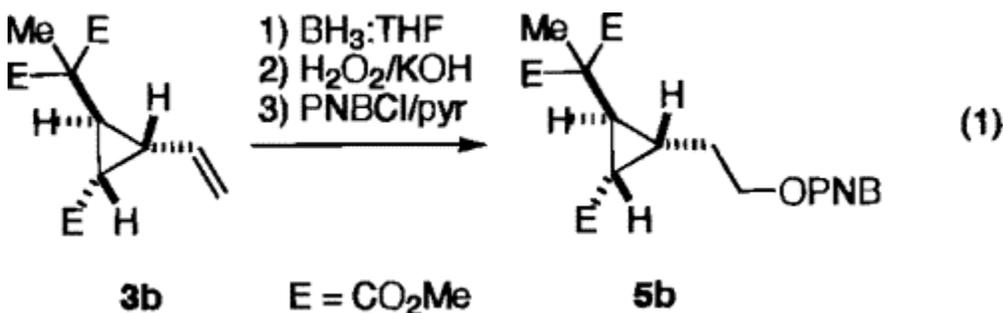


**Table 1.** Oxidative Decomplexation of (Pentenediyl)iron Complexes (E = CO<sub>2</sub>Me; **a**, R = H; **b**, R = Me; **c**, R = OMe)

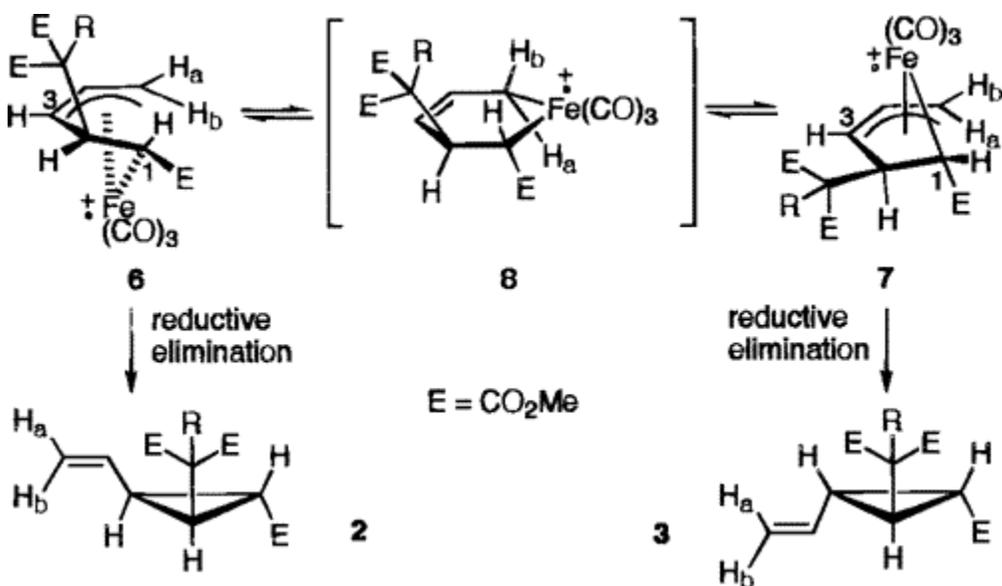


entry	R	conditions	product ratio ( <b>2</b> : <b>3</b> : <b>4</b> )	total yield (%)
1	H ( <b>a</b> )	CAN/DMF/23 °C	10:1:0	70
2	H ( <b>a</b> )	TMANO/C <sub>6</sub> H <sub>6</sub> /80 °C	2:4:1	69
3	Me ( <b>b</b> )	CAN/DMF/23 °C	0:1:0	55
4	Me ( <b>b</b> )	TMAO/C <sub>6</sub> H <sub>6</sub> /80 °C	0:1:0	56
5	OMe ( <b>c</b> )	CAN/DMF/23 °C	0:1:0	25

In sharp contrast, oxidative decomplexation of **1b** with either CAN or TMANO gave only **3b** (Table 1; entries 4 and 5). The relative stereochemistry of vinylcyclopropane **3b** was tentatively assigned on the basis of its <sup>1</sup>H NMR spectral data.<sup>7</sup> In particular, the vinylic methine proton of **3b** appears at δ 6.14 ppm, while those of vinylcyclopropanes **2a**, **3a**, and **4a** appear at δ 5.26, 6.07, and 5.13 ppm, respectively. This tentative assignment was subsequently confirmed by X-ray diffraction analysis<sup>9</sup> of a crystalline derivative (**5b**) prepared in an unambiguous fashion (eq 1). Similarly, the oxidative decomplexation of **1c** gave **3c** (25%) along with recovered starting material (25%) (Table 1; entry 5). The structure of **3c** was assigned by comparison of its <sup>1</sup>H NMR spectral data with that of **3b**. The vinylcyclopropanes **3b** and **3c** represent oxidatively induced reductive elimination of **1b** and **1c** with *apparent* inversion of configuration at C3.



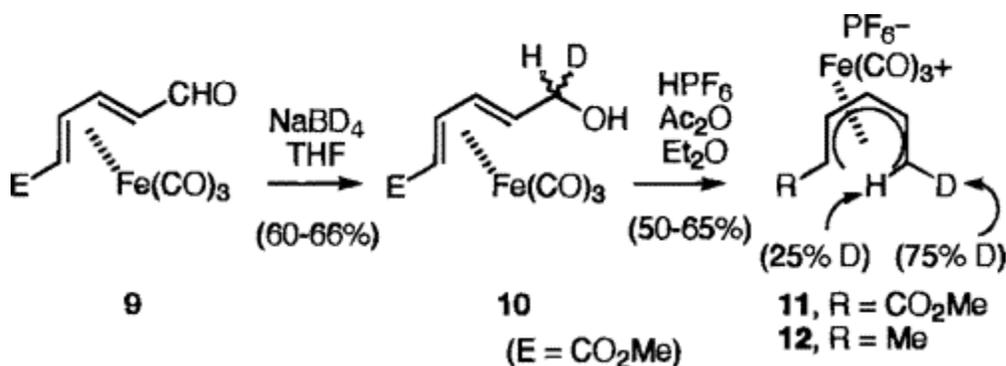
The following mechanism is proposed to rationalize these results (Scheme 1). Oxidation of pentenediyl complex **1** leads directly to the species **6**. A  $\pi$ - $\sigma$ - $\pi$  rearrangement of **6** via the metallocyclohexene intermediate **8** generates the species **7** with inversion of configuration at C3 (with respect to the configurations at C1 and C5).<sup>10</sup> Reductive elimination of **6**, with retention of configuration, leads to vinylcyclopropanes **2**. For products **3**, the apparent inversion of configuration results from  $\pi$ - $\sigma$ - $\pi$  rearrangement followed by reductive elimination (i.e., inversion followed by retention). For **6a** (R = H) at 23 °C, the  $\pi$ - $\sigma$ - $\pi$  rearrangement is slow with respect to reductive elimination; however, at higher reaction temperatures the rearrangement becomes rapid enough to allow for the formation of both **2a** and **3a**. In comparison, rearrangement of **6b** to **7b** (R = Me) is rapid compared to reductive elimination. It should be noted that the malonate substituent occupies a pseudoaxial position and the C1 ester a pseudoequatorial position in **6** (cf., the X-ray crystal structures<sup>6</sup> of **1a** and **1b**) while in **7** the malonate substituent occupies a pseudoequatorial position and the C1 ester a pseudoaxial position. The equilibrium between **6b** and **7b** lies farther in the direction of **7b** than does the equilibrium between **6a** and **7a**, due to the greater steric bulk of the dimethyl methylmalonate substituent.<sup>10</sup>



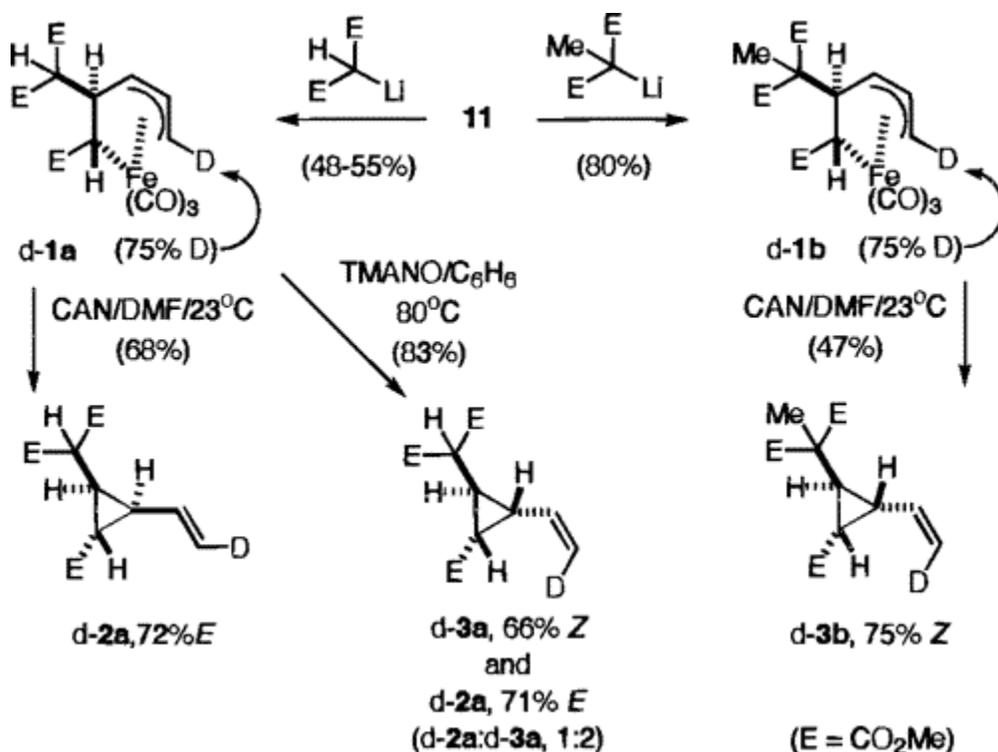
**Scheme 1**

It is proposed that the  $\pi$ - $\sigma$ - $\pi$  rearrangement of the pentenediyl complexes occurs readily *only for the oxidized species 6/7*.<sup>11</sup> (Pentenediyl)iron complex **1a** is recovered unchanged under the reaction conditions of entry 1 or 2 in the absence of oxidant (DMF/23 °C/18 h or C<sub>6</sub>H<sub>6</sub>/80 °C/4 h), and **1b** was recovered unchanged upon stirring to conditions in entry 3 in the absence of oxidant (DMF/18 h/23 °C). If the 18-electron pentenediyl complexes **1a** or **1b** undergo  $\pi$ - $\sigma$ - $\pi$  rearrangement at these conditions, these equilibria must lie far in the direction of the **1a** and **1b**, since no diastereomeric pentenediyl complexes are observed under the reaction conditions, in the absence of oxidant. Furthermore, when the oxidation of **1a** (CAN/DMF/23 °C or TMANO/C<sub>6</sub>H<sub>6</sub>/80 °C) was carried to less than completion, the unreacted **1a** was recovered *unchanged*, in addition to the vinylcyclopropane products.

It may be noted that the  $\pi$ - $\sigma$ - $\pi$  rearrangement of **6** to **7** occurs with inversion of the *exo-endo* stereochemistry at the  $\sigma$ -bound end of the allylic portion of **6**. If the proposed mechanism is valid, this inversion of stereochemistry should be reflected in the products. Toward this end, the deuterium-labeling studies were carried out. The stereoselectively deuterium-labeled cation **11** was prepared from **9** (Scheme 2) in a fashion similar to our previous preparation of the stereoselectively labeled cation **12**.<sup>12</sup> Cation **11**, prepared by this method, was found to possess the deuterium label 75% in the *exo*-position and 25% in the *endo*-position, by integration of its <sup>1</sup>H NMR spectrum. Reaction of **11** with dimethyl malonate or dimethyl methylmalonate anion gave predominantly<sup>13</sup> the pentenediyl complexes d-**1a** and d-**1b** in which deuterium was located 75% in the *exo*-position (Scheme 3).



## Scheme 2



### Scheme 3

The oxidative decomplexation of **d-1a** (CAN/DMF/23 °C) gave **d-2a**; <sup>1</sup>H NMR integration of the vinyl methylene protons indicated the product to be 72% *E* (Scheme 3). In comparison, oxidative decomplexation of **d-1b** (CAN/DMF/23 °C) gave **d-3b**; <sup>1</sup>H NMR integration of the vinyl methylene protons indicated the product to be 75% *Z* (Scheme 3). Finally, the oxidative decomplexation of **d-1a** (TMANO/C<sub>6</sub>H<sub>6</sub>/80 °C) gave a mixture of **d-2a** and **d-3a** (1:2). Analysis of the mixture indicated that **d-2a** was 71% *E* while **d-3a** was 66% *Z*. Thus, inversion of configuration at the vinylcyclopropyl carbon is accompanied by an inversion in the stereochemistry about the C=C double bond. These results are consistent with the mechanism proposed in Scheme 1.

We are currently examining the application of this methodology for the preparation of cyclopropyl-containing natural products.

## Acknowledgment

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## Supporting Information Available

Experimental details and spectroscopic data (7 pages). See any current masthead page for ordering and Internet access instructions.

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- <sup>4</sup>The reverse process, formation of (pentenediyl)Fe(CO)<sub>3</sub> complexes from the reaction of vinylcyclopropanes with Fe(CO)<sub>5</sub>, has been reported.<sup>5</sup> However, since the iron species generated as a byproduct in the present case is not Fe(CO)<sub>5</sub>, it can not be assumed that these reactions follow the same reversible reaction pathway.
- <sup>5</sup>Aumann, R. *J. Am. Chem. Soc.* **1974**, *96*, 2631–2. Schulze, M. M.; Gockel, U. *Tetrahedron Lett.* **1996**, *37*, 357–8. Schulze, M. M.; Gockel, U. *J. Organomet. Chem.* **1996**, *525*, 155–8.
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- <sup>7</sup>Selected 300 MHz <sup>1</sup>H NMR spectral data (C<sub>6</sub>D<sub>6</sub>). For **2a**: δ<sub>H</sub> 5.26 (ddd, *J* = 7.5, 9.9, 17.1 Hz, 1H), 4.93 (d, *J* = 17.1 Hz, 1H), 4.88 (d, *J* = 11.4 Hz, 1H), 3.27, 3.26, and 3.25 (3 s, 9H), 3.04 (d, *J* = 11.0 Hz, 1H), 2.57 (ddd, *J* = 4.9, 9.6, 11.1 Hz, 1H), 2.33 (dt, *J* = 4.9, 8.5 Hz, 1H), 1.76 (apparent t, *J* = 4.9 Hz, 1H). For **3a**: δ<sub>H</sub> 6.07 (ddd, *J* = 9.2, 10.2, 17.2 Hz, 1H), 5.16 (dd, *J* = 1.2, 17.1 Hz, 1H), 4.99 (dd, *J* = 1.2, 10.2 Hz, 1H), 3.26, 3.22, and 3.21 (3 s, 9H), 2.73 (d, *J* = 9.8 Hz, 1H), 2.53 (ddd, *J* = 5.4, 6.1, 9.8 Hz, 1H), 1.88 (dd, *J* = 5.3, 9.1 Hz, 1H), 1.71 (dt, *J* = 6.2, 9.1 Hz, 1H). For **4a**: δ<sub>H</sub> 5.13 (ddd, *J* = 7.6, 10.0, 17.3 Hz, 1H), 4.97 (dd, *J* = 1.7, 17.3 Hz, 1H), 4.80 (dd, *J* = 1.7, 10.0 Hz,

1H), 4.23 (d,  $J = 10.7$  Hz, 1H), 3.30, 3.25, and 3.23 (3 s, 9H), 2.18 (br q,  $J = 6.3$  Hz, 1H), 1.99 (ddd,  $J = 6.3, 8.8, 10.8$  Hz, 1H), 1.82 (dd,  $J = 5.0, 8.9$  Hz, 1H). For **3b**:  $\delta_{\text{H}}$  6.14 (ddd,  $J = 8.8, 10.2, 17.1$  Hz, 1H), 5.18 (dd,  $J = 1.8, 17.1$  Hz, 1H), 5.02 (dd,  $J = 1.8, 10.2$  Hz, 1H), 3.31, 3.22, and 3.21 (3 s, 9H), 2.61 (dd,  $J = 5.9, 6.6$  Hz, 1H), 2.18 (dd,  $J = 5.9, 9.3$  Hz, 1H), 2.00 (dt,  $J = 6.7, 9.0$  Hz, 1H), 1.23 (s, 3H).

<sup>8</sup>Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; John Wiley & Sons, Inc.: New York, 1991.

<sup>9</sup>Young, V. G., Jr.; Yun, Y. K.; Donaldson, W. A. Submitted.

<sup>10</sup>The difference in the steric sizes of the dimethyl malonate substituent present in **1a** and the dimethyl methylmalonate substituent present in **1b** is manifested in a considerably larger C4–C3–C2–C7 torsional angle for **1b** (81.3°) compared to **1a** (65.3°) in the crystal state.<sup>6</sup>

<sup>11</sup>Notably, *syn-anti* isomerization of ( $\eta$ -allyl)Fe(CO)<sub>4</sub><sup>+</sup> cations (18-electron complexes) via a  $\pi$ – $\sigma$ – $\pi$  mechanism requires heating (60 °C) for extended periods of time (36–144 h). Gibson, D. H.; Erwin, D. K. *J. Organomet. Chem.* **1975**, *86*, C31–C33. Salzer, A.; Hafner, A. *Helv. Chim. Acta* **1983**, *66*, 1774–85.

<sup>12</sup>Donaldson, W. A.; Shang, L.; Ramaswamy, M.; Droste, C. A.; Tao, C.; Bennett, D. W. *Organometallics* **1995**, *14*, 5119–26.

<sup>13</sup>The reaction of lithium dimethyl malonate with (1-(methoxycarbonyl)pentadienyl)Fe(CO)<sub>3</sub><sup>+</sup> gave **1a** and a minor amount of diene complex *i* (20:1).<sup>4</sup> The reaction of **11** with lithium dimethyl malonate gave d-**1a** and d-**ia**(6:1), while reaction of **11** with lithium dimethyl methylmalonate gave d-**1b** and d-**ib** (8:1). This increase in the ratio of attack at C5 vs C2 is attributed to an inverse  $\alpha$ -secondary isotope effect.