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

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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.[1] We[2] and others[3] have reported that the oxidative decomplexation of (pentenediyl)iron complexes bearing an electron-withdrawing substituent provides a novel methodology to generate vinylcyclopropanes.[4] 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**.[6] The relative stereochemistry of **1a** and **1b** were established by X-ray diffraction analysis.[6] 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 occuring with retention of stereochemistry. In comparison, oxidation of **1a** with trimethylamine *N*-oxide (TMANO, C_6H_6, 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 ^{1}H NMR spectral data.[7] 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.[8] It is important to note that vinylcyclopropane **2a** does not isomerize to **3a** or **4a** upon treatment with either TMANO or triethylamine (C_6H_6, 80 °C). Thus, the products **3a** and **4a** are not the result of rearrangement or epimerization of **2a**.
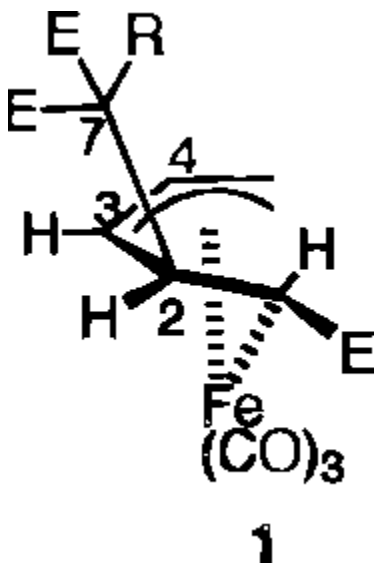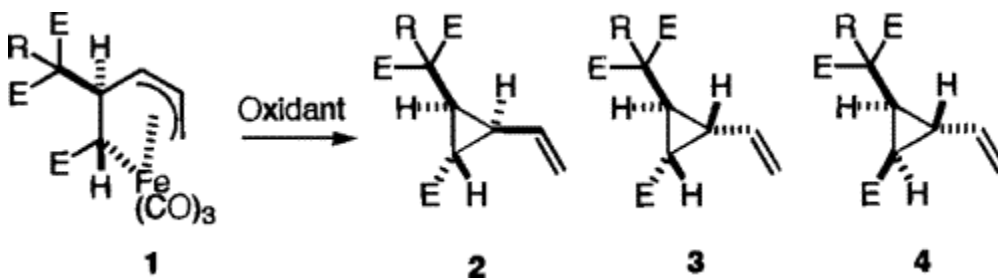

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Table 1. Oxidative Decomplexation of (Pentenediyl)iron Complexes (E = CO_2Me; **a**, R = H; **b**, R = Me; **c**, R = OMe)

| entry	R	conditions	product ratio (**2:3:4**)	total yield (%)
1	H (**a**)	CAN/DMF/23 °C	10:1:0	70
2	H (**a**)	TMANO/C_6H_6/80 °C	2:4:1	69
3	Me (**b**)	CAN/DMF/23 °C	0:1:0	55
4	Me (**b**)	TMAO/C_6H_6/80 °C	0:1:0	56
5	OMe (**c**)	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 ^{1}H NMR spectral data.[7] 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[9] 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 comparision of its ^{1}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.


$$E = CO_2Me \qquad (1)$$
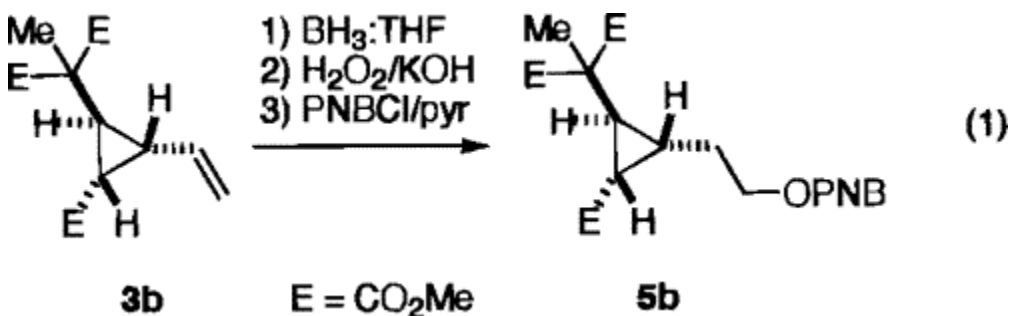
The following mechanism is proposed to rationalize these results (Scheme 1). Oxidation of pentenediyl complex **1** leads directly to the species **6**. A π−σ−π rearrangement of **6** via the metallocyclohexene intermediate **8** generates the species **7** with inversion of configuration at C3 (with respect to the configurations at C1 and C5).[10] Reductive elimination of **6**, with retention of configuration, leads to vinylcyclopropanes **2**. For products **3**, the apparent inversion of configuration results from π−σ−π rearrangement followed by reductive elimination (i.e., inversion followed by retention). For **6a** (R = H) at 23 °C, the π−σ−π 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 substitutent occupies a pseudoaxial position and the C1 ester a pseudoequatorial position in **6** (cf., the X-ray crystal structures[6] of **1a** and **1b**) while in **7** the malonate substitutent 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.[10]
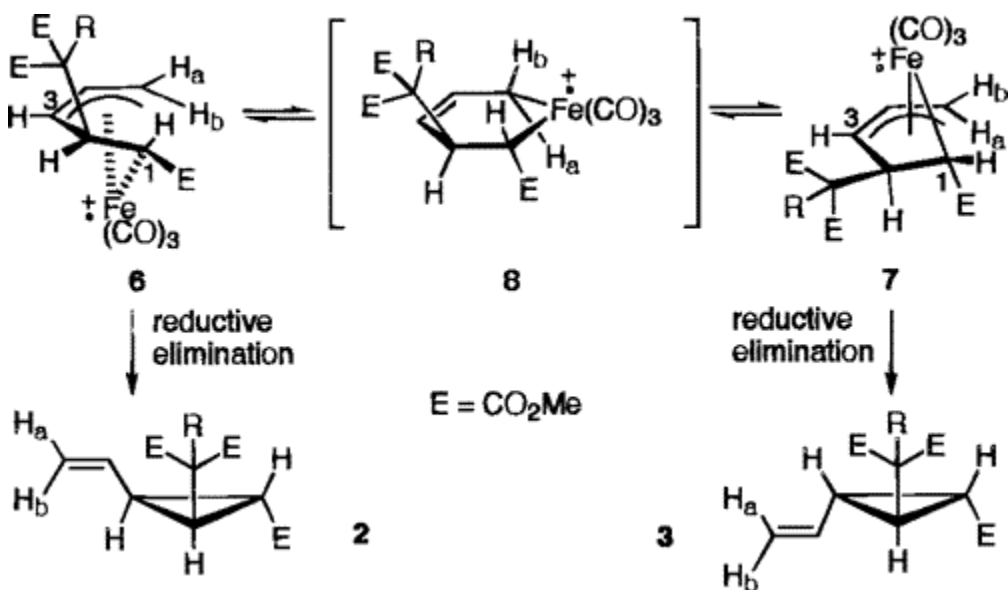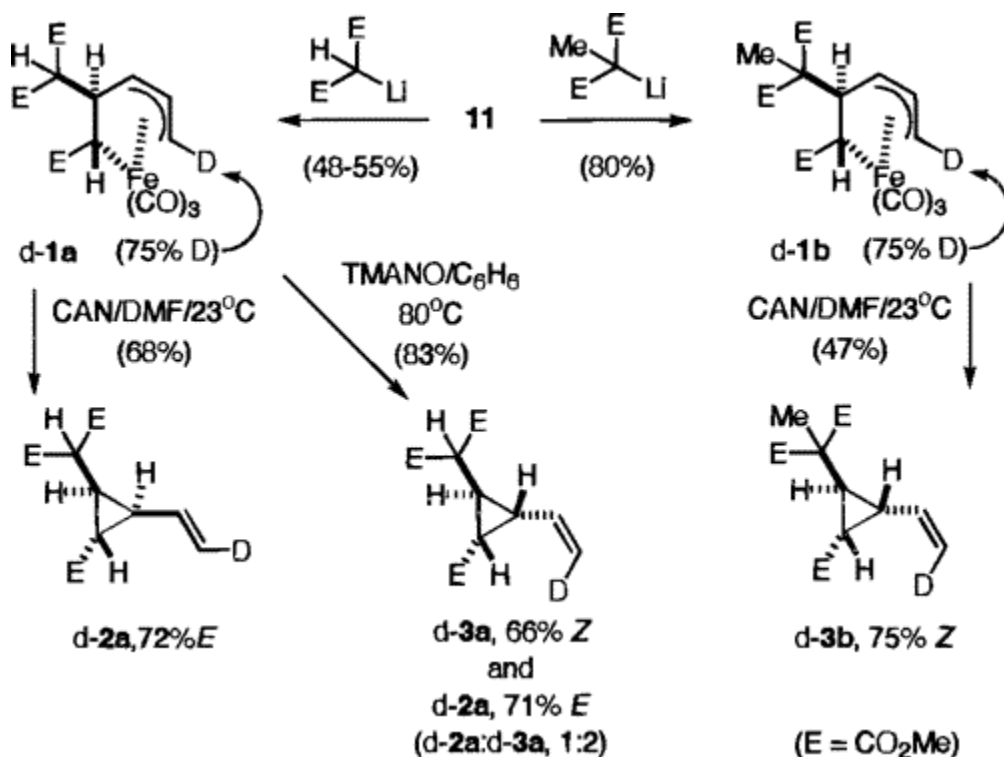

Scheme 1

It is proposed that the π−σ−π rearrangement of the pentenediyl complexes occurs readily *only for the oxidized species* **6**/**7**.[11] (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_6H_6/80 °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 π−σ−π 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_6H_6/80 °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 π−σ−π rearrangement of **6** to **7** occurs with inversion of the *exo-endo* stereochemistry at the σ-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**.[12] 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 ^{1}H NMR spectrum. Reaction of **11** with dimethyl malonate or dimethyl methylmalonate anion gave predominantly[13] the pentenediyl complexes d-**1a** and d-**1b** in which deuterium was located 75% in the *exo*-position (Scheme 3).
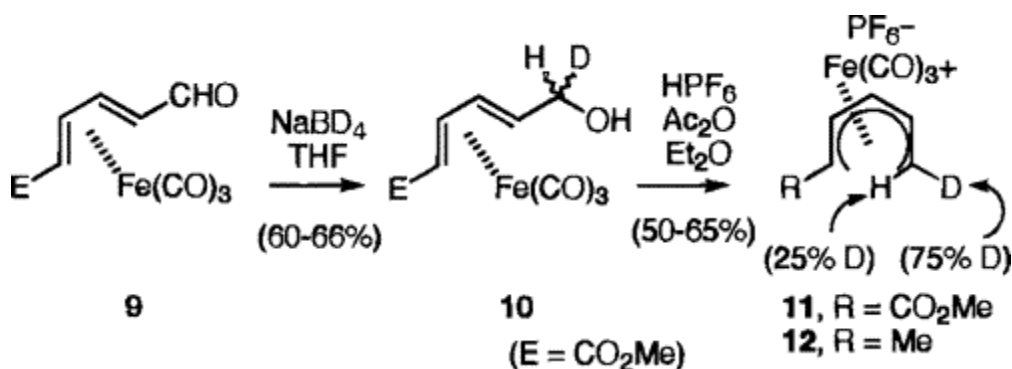
Scheme 2

Scheme 3

The oxidative decomplexation of d-**1a** (CAN/DMF/23 °C) gave d-**2a**; ^{1}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**; ^{1}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_6H_6/80 °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

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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[4]The reverse process, formation of (pentenediyl)$Fe(CO)_3$ complexes from the reaction of vinylcyclopropanes with $Fe(CO)_5$, has been reported.[5] However, since the iron species generated as a byproduct in the present case is not $Fe(CO)_5$, it can not be assumed that these reactions follow the same reversible reaction pathway.

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[7]Selected 300 MHz ^1H NMR spectral data (C_6D_6). For **2a**: δ_H 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_H 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_H 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**: δH 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).

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[10]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.[6]

[11]Notably, *syn-anti* isomerization of (π-allyl)Fe(CO)$_4^+$ cations (18-electron complexes) via a π−σ−π 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.

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[13]The reaction of lithium dimethyl malonate with (1-(methoxycarbonyl)pentadienyl)Fe(CO)$_3^+$ gave **1a** and a minor amount of diene complex *i* (20:1).[4] The reaction of **11** with lithium dimethyl malonate gave d-**1a** and d-***i*a**(6:1), while reaction of **11** with lithium dimethyl methylmalonate gave d-**1b** and d-***i*b** (8:1). This increase in the ratio of attack at C5 vs C2 is attributed to an inverse α-secondary isotope effect.

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