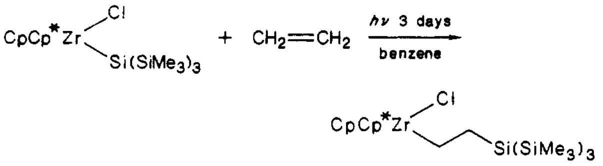

(3)

2

only ca. 10 h. This reaction is relatively clean (by ^{1}H NMR in benzene-d_6), and pure **2** can be isolated in ca. 50% yield as yellow crystals from pentane.[12] In the absence of light no product is formed after 5 days, indicating that insertion requires photochemical activation of CpCp*Zr[Si(SiMe$_3$)$_3$]Cl. The UV–vis spectrum of CpCp*Zr[Si(SiMe$_3$)$_3$]Cl exhibits an absorption at 461 nm (ϵ = 500 L mol^{-1} cm^{-1}), and use of cutoff filters has determined that the corresponding electronic transition gives rise to the observed photochemistry. The quantum yield for this reaction (λ = 380–470 nm, benzene-d_6) in the presence of excess ethylene is 2.5, suggesting a radical chain mechanism initiated by homolytic cleavage of a M–Si bond.[13]

Compound **1** is remarkably stable for an alkyl complex with β-hydrogens, very little decomposition being observed after 3 days at 80 °C (by ^{1}H NMR in benzene-d_6). Future work will involve further development and study of this insertion chemistry. Preliminary experiments show that Cp*Cl$_2$ZrSi(SiMe$_3$)$_3$ is unreactive toward styrene, propene, and Me$_3$SiCH=CH$_2$ and that Cp*Cl$_2$HfSi(SiMe$_3$)$_3$ is inert toward diphenylacetylene and 1-hexene.

Acknowledgment is made to the Air Force Office of Scientific Research, Air Force Systems Command, USAF, for support of this work under Grant No. AFOSR-88-0273 and to the DoD University Research Instrumentation Program (Grant DAAL03-87-G-0071) for funds to purchase an X-ray diffractometer. The U.S. Government is authorized to reproduce and distribute reprints for Governmental purposes. T.D.T. thanks the Alfred P. Sloan Foundation for a research fellowship (1988–1990).

Supplementary Material Available: A listing of crystal, data collection, and refinement parameters and tables of positional and thermal parameters, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates for **1a** (9 pages); a table of observed and calculated structure factors for **1a** (21 pages). Ordering information is given on any current masthead page.

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[12] For **2**: Anal. C, H. ^{1}H NMR (benzene-d_6, 22 °C, 300 MHz): δ 0.34 (s, 27 H, SiMe$_3$), 1.08 (m, 2 H, CH$_2$Si), 1.40 (m, 2 H, ZrCH$_2$), 1.71 (s, 15 H, Cp*), 5.90 (s, 5 H, Cp). UV–vis (pentane, nm): 225 (ϵ = 6000 M^{-1} cm^{-1}), 329 (ϵ = 1000 M^{-1} cm^{-1}).

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A Palladadigermetane: Palladium-Catalyzed Insertion Reactions of Digermiranes

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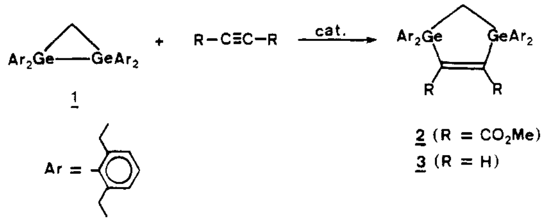
Received May 1, 1989

Summary: The palladium-catalyzed reactions of digermirane **1** with dimethyl acetylenedicarboxylate and acetylene give the ring expansion products **2** and **3**. Reaction with methyl acrylate gives the rearranged product **4**. In the stoichiometric reaction of **1** with Pd(PPh$_3$)$_4$, palladadigermetane **6** is isolated as a stable compound. **6** reacts with dimethyl acetylenedicarboxylate, acetylene, and methyl acrylate to yield **2**, **3**, and **4**, respectively. The similar palladium-catalyzed reactions of thia- and selenadigermiranes **9** and **10** with acetylene give the ring expansion products **11** and **12**, respectively.

One of the most interesting reactions of the Si–Si bond of the reactive disilanes is the transition-metal-catalyzed insertion of unsaturated hydrocarbons, and numerous papers have been published so far.[1–7] In spite of these studies, no interest has been shown in the transition-metal-catalyzed insertion of unsaturated compounds into the Ge–Ge bond.[8] Recently, we reported the preparation and chemical properties of a digermirane and its heterocyclic analogues.[9,10] We report here the novel palladium-catalyzed ring-expansion reactions of a digermirane and thia- and selenadigermiranes. We also report the stoichiometric reaction of the digermirane with Pd(PPh$_3$)$_4$ to yield a palladadigermetane as stable red crystals.

When a benzene solution of digermirane **1**,[9c] dimethyl acetylenedicarboxylate, and Pd(PPh$_3$)$_4$ (10 mol %) was heated to reflux for 45 h under an argon atmosphere, a crystalline product identified as digermacyclopentene **2**,[11] a insertion product of the acetylene into the Ge–Ge bond, was obtained in 51% yield (eq 1). It was also found that



(1)

1

2 (R = CO$_2$Me)
3 (R = H)

Pd(II) complexes such as PdCl$_2$(PPh$_3$)$_2$ and PdCl$_2$(PhCN)$_2$ and NiCl$_2$(PPh$_3$)$_2$ catalyzed the insertion of the acetylene into the Ge–Ge bond of the digermirane **1** equally, giving the adduct **2**. Unsubstituted acetylene also reacted with

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[11] Compound **2**: colorless crystals; mp 173–174 °C; ^{1}H NMR (60 MHz, CDCl$_3$) δ 0.87 (t, J = 7 Hz, 24 H, CH$_3$), 1.30 (s, 2 H, GeCH$_2$Ge), 2.50 (q, J = 7 Hz, 16 H, CH$_2$), 3.53 (s, 6 H, OMe), 6.9–7.4 (m, 12 H, Ar); ^{13}C NMR (25 MHz, CDCl$_3$) δ 11.5 (t, GeCH$_2$Ge), 15.1 (q, CH$_3$), 30.3 (t, CH$_2$), 51.8 (q, OMe), 125.9 (d, Ar), 128.8 (d, Ar), 141.2 (s, Ar), 147.8 (s, Ar), 157.9 (s, Ar), 169.9 (s, C=C).

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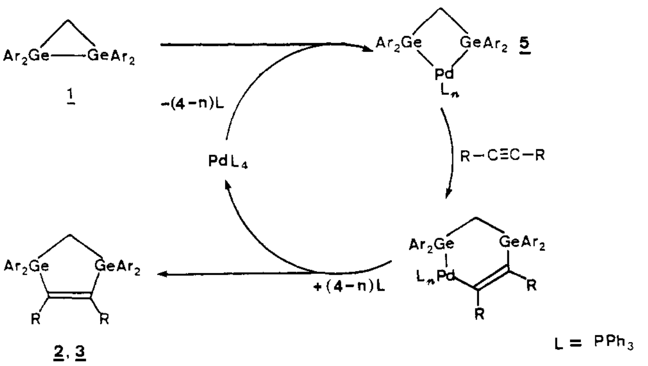
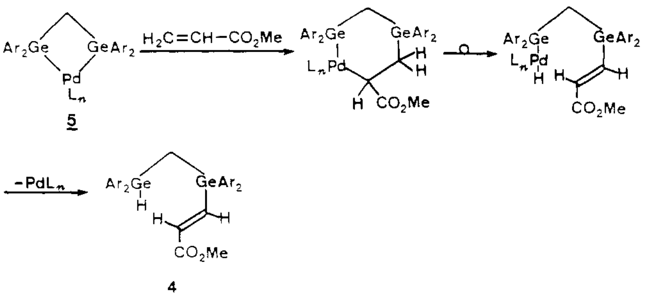
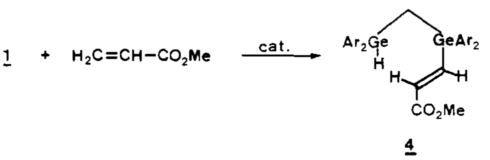
Scheme I



Scheme II



1 to yield an adduct, 3,[12] in 20–25% yield when acetylene was bubbled into a toluene solution of 1 in the presence of a Pd(0) or Pd(II) catalyst at 80 °C (eq 1). The reaction of 1 with methyl acrylate under similar conditions (refluxed in benzene for 18 h) gave a ring-opened type product, 4,[13] in 20% yield (eq 2).



(2)

A reasonable pathway for the formation of the products obtained is shown in Scheme I. We propose that a palladadigermetane intermediate 5 is involved in the formation of compounds 2 and 3. The formation of 4 may be explained by the participation of the same intermediate followed by β-elimination (Scheme II).

To confirm the mechanism, we next tried to isolate a palladadigermetane in a stoichiometric reaction. When a toluene solution of 1 and Pd(PPh$_3$)$_4$ was heated at 90 °C for 20 h, palladadigermetane 6 was obtained as a red crystalline solid in 45% yield (eq 3).[14] The fact that the ^{1}H-decoupled ^{13}C NMR spectrum of 6 shows a doublet at δ 30.0 ppm ($J_{\text{C-P}}$ = 16.8 Hz) clearly indicates this resonance can be assigned to the ring carbon atom of palladadigermetane 6 and that only one molecule of PPh$_3$ is coordinated to palladium. In the ^{1}H NMR spectrum one doublet was observed at δ 2.68 ppm ($J_{\text{P-H}}$ = 2.7 Hz) which was assigned to methylene protons in the ring. The crystals of palladadigermetane 6 are air-sensitive, but much less than in solution, and can be handled in air for a short time (mp 182–185 °C dec).[15]

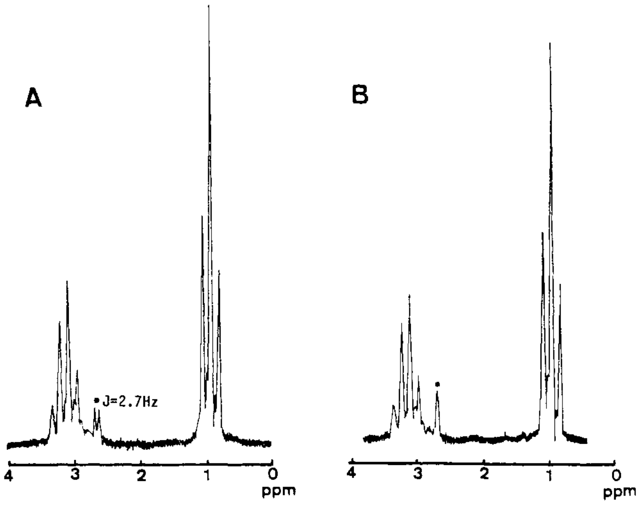
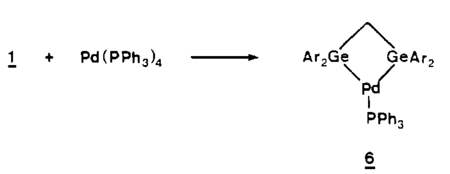
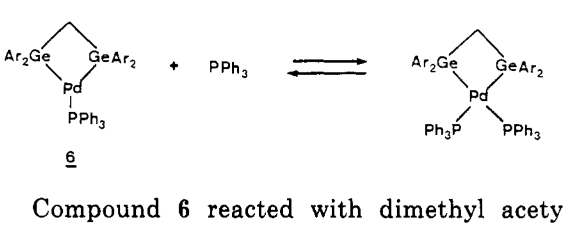


Figure 1. (A) ^{1}H NMR spectrum of compound 6 in C$_6$D$_6$ (60 MHz). (B) After the addition of PPh$_3$ to a C$_6$D$_6$ solution of compound 6 (60 MHz). Asterisks indicate the resonances assigned to methylene protons of the palladadigermetane.



(3)

When PPh$_3$ was added to the benzene-d_6 solution of 6, a doublet at δ 2.68 ppm in the ^{1}H NMR spectrum was changed to a singlet at δ 2.68 ppm as shown in Figure 1.[16] The changes can be interpreted in terms of the rapid equilibrium between the mono(triphenylphosphine)palladium complex and the bis(triphenylphosphine)palladium complex (eq 4).



(4)

Compound 6 reacted with dimethyl acetylenedicarboxylate, acetylene, and methyl acrylate to form the corresponding addition products 2, 3, and 4 in 100%, 96%, and 45% yields, respectively (Scheme III).[17] These results indicate that the four-membered palladacycle is involved in the catalytic reactions of 1.[18]

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(12) Compound 3: colorless crystals; mp 124–125 °C; ^{1}H NMR (60 MHz, CDCl$_3$) δ 0.80 (t, J = 7 Hz, 24 H, CH$_3$), 1.20 (s, 2 H, GeCH$_2$Ge), 2.55 (q, J = 7 Hz, 16 H, CH$_2$), 6.8–7.2 (m, 12 H, Ar), 7.63 (s, 2 H, CH=CH); ^{13}C NMR (125 MHz, CDCl$_3$) δ 8.6 (t, GeCH$_2$Ge), 15.4 (q, CH$_3$), 29.9 (t, CH$_2$), 125.9 (d, Ar), 128.5 (d, Ar), 141.2 (s, Ar), 148.5 (s, Ar), 150.4 (d, C=C).

(13) Only one of the two possible isomers was isolated and was identified as trans isomer. Compound 4: colorless crystals; mp 76–81 °C; ^{1}H NMR (100 MHz, CDCl$_3$) δ 0.86 (t, J = 7 Hz, 12 H, CH$_3$), 0.96 (t, J = 7 Hz, 12 H, CH$_3$), 1.59 (d, J = 4 Hz, 2 H, GeCH$_2$Ge), 2.53 (q, J = 7 Hz, 8 H, CH$_2$), 2.60 (q, J = 7 Hz, 8 H, CH$_2$), 3.61 (s, 3 H, OMe), 5.42 (t, J = 4 Hz, 1 H, GeH), 6.88 (AB, J_{AB} = 18 Hz, $\Delta\nu_{AB}$ = 189 Hz, 2 H, CH=CH), 6.9–7.3 (m, 12 H, Ar); ^{13}C NMR (22.5 MHz, CDCl$_3$) δ 11.0 (t, GeCH$_2$Ge), 15.3 (q, CH$_3$), 29.6 (t, CH$_2$), 30.0 (t, CH$_2$), 51.5 (q, OMe), 125.7 (d, Ar), 126.2 (d, Ar), 128.9 (d, Ar), 129.0 (d, Ar), 132.6 (d, C=C), 138.1 (s, Ar), 138.2 (s, Ar), 148.8 (s, Ar), 149.1 (s, Ar), 152.7 (d, C=C).

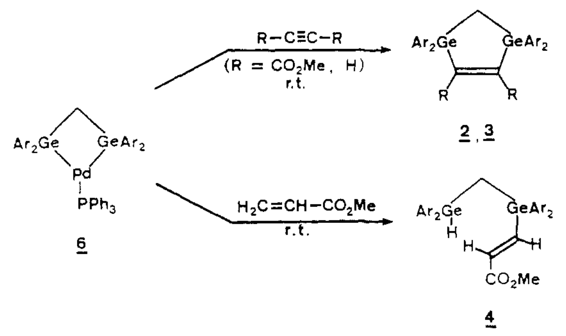
(14) Compound 6: ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 0.93 (t, J = 7.4 Hz, 24 H, CH$_3$), 2.68 (d, $J_{\text{P-H}}$ = 2.7 Hz, 2 H, GeCH$_2$Ge), 3.11 (dq, J = 7.4, 14.8 Hz, 8 H, CH$_2$), 3.21 (dq, J = 7.4, 14.8 Hz, 8 H, CH$_2$), 7.0–7.4 (m, 27 H, Ar); ^{13}C NMR (125 MHz, C$_6$D$_6$, ^{1}H-decoupled) δ 15.6 (s, CH$_3$), 30.0 (d, $J_{\text{P-C}}$ = 16.8 Hz, GeCH$_2$Ge), 32.1 (s, CH$_2$), 125.8–148.9 (aromatic C); ^{31}P NMR (C$_6$D$_6$, 85% phosphoric acid as external standard) δ 7.8 (s).

(15) We attempted an X-ray structure analysis of compound 6, but, because of the decomposition in the X-ray beam, sufficient data could not be obtained. Preliminary results indicate that the four-membered ring system in compound 6 is almost planar.

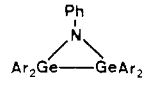
(16) Also, in the ^{1}H-decoupled ^{13}C NMR spectrum a doublet at δ 30.0 ppm was changed to a singlet, and in the ^{31}P NMR spectrum a singlet at δ 7.8 ppm was shifted to δ −4.2 ppm (br). The changes in the spectra were observed even when 6 was treated with a small amount of PPh$_3$.

(17) In the presence of PPh$_3$ 6 reacted with the unsaturated compounds similarly.

Scheme III

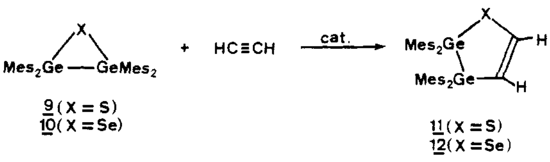


Under similar conditions azadigermiridine **8**[9c] did not react with dimethyl acetylenedicarboxylate or acetylene in the presence of $Pd(PPh_3)_4$ or $PdCl_2(PPh_3)_2$. But,

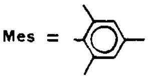


8

thiadigermirane **9**[9a,b] reacted with acetylene in the presence of a catalytic amount of $Pd(PPh_3)_4$ or $PdCl_2(PPh_3)_2$ at 80 °C cleanly to produce the adduct **11**[19] in 44-54% yield (eq 5). In contrast to the reactions of digermirane **1** the adduct **11** obtained is the insertion product of acetylene into the Ge-S bond. No products of the insertion into the Ge-Ge bond were obtained. The reaction of selenadigermirane **10**[9a,b] with acetylene under similar conditions gave the corresponding addition product **12** (eq 5).[20] A simple

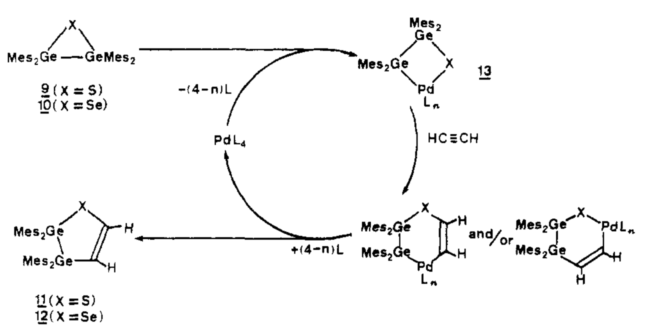


(5)



catalytic scheme can be proposed for the formation of adducts **11** and **12** (Scheme IV). We tried to proof the intervention of an intermediate such as **13**. However, attempts to isolate Pd-containing intermediates in stoichiometric reactions were not successful, so the chemistry in Scheme IV is only a suggestion.

Scheme IV



Acknowledgment. This research was supported by a Grant-in-Aid for Scientific Research (No. 63106003) from the Ministry of Education, Science, and Culture of Japan. We thank T. Kawai and Y. Nagai, Eisai Co., Ltd., for the X-ray analysis of compound **6**.

Supplementary Material Available: Detailed information concerning IR, MS, and analytical data of new compounds (3 pages). Ordering information is given on any current masthead page.

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(18) The mechanism of the palladium(II)-catalyzed insertions of acetylenes into the Ge-Ge bond of **1** is of some interest. As reported earlier (see ref 5) there is the possibility that a Pd(II) compound is reduced to a Pd(0) species. An experiment in which **1** was treated with a stoichiometric amount of $PdCl_2(PPh_3)_2$ confirmed that this was the case. The reaction produced two products, palladadigermetane and $ClAr_2Ge-CH_2-GeAr_2Cl$ (**7**), *in about a 1:1 ratio. It would appear that an initial* reaction of **1** with $PdCl_2(PPh_3)_2$ reduces the latter to $Pd(PPh_3)_2$ and forms **7**. The coordinatively unsaturated $Pd(PPh_3)_2$ then inserts into the Ge-Ge bond of **1**. Compound **7**: colorless crystals, mp 119-121 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 0.92 (t, $J = 7.4$ Hz, 24 H, CH_3), 2.51 (dq, $J = 7.4$, 14.8 Hz, 8 H, CH_2), 2.56 (s, 2 H, $GeCH_2Ge$), 2.77 (dq, $J = 7.4$, 14.8 Hz, 8 H, CH_2), 6.97 (d, $J = 7.7$ Hz, 8 H, Ar), 7.22 (t, $J = 7.7$ Hz, 4 H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.2 (q, CH_3), 28.0 (t, $GeCH_2Ge$), 29.1 (t, CH_2), 126.7 (d, Ar), 129.8 (d, Ar), 139.4 (s, Ar), 148.1 (s, Ar).

(19) Compound **11**: colorless crystals; mp 174-175 °C; ^1H NMR (60 MHz, $CDCl_3$) δ 2.10 (s, 12 H, CH_3), 2.21 (br s, 24 H, CH_3), 6.62 (br s, 8 H, Mes), 6.95 (AB, $J_{AB} = 8.4$ Hz, $\Delta\nu_{AB} = 30$ Hz, 2 H, HC=CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.8 (q, CH_3), 25.1 (q, CH_3), 25.2 (q, CH_3), 128.8 (d, Mes), 128.9 (d, Mes), 129.2 (d, C=C), 135.8 (s, Mes), 138.0 (s, Mes), 138.2 (s, Mes), 140.2 (d, C=C), 143.3 (s, Mes), 143.9 (s, Mes).

(20) Compound **12**: colorless crystals, mp 114-120 °C; ^1H NMR (60 MHz, $CDCl_3$) δ 2.13 (s, 12 H, CH_3), 2.21 (s, 24 H, CH_3), 6.63 (br s, 8 H, Mes), 7.41 (AB, $J_{AB} = 10.2$ Hz, $\Delta\nu_{AB} = 25.0$ Hz, 2 H, CH=CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.8 (q, CH_3), 20.9 (q, CH_3), 25.3 (q, CH_3), 25.5 (q, CH_3), 128.8 (d, Mes), 128.9 (d, Mes), 134.3 (d, C=C), 136.1 (s, Mes), 136.2 (d, C=C), 137.9 (s, Mes), 138.2 (s, Mes), 143.2 (s, Mes), 143.8 (s, Mes).

Inversion of Stereochemistry at the Carbon Bound to Iron in Cyclopropane Formation from *threo*-$C_5H_5(CO)_2FeCHDCHDCH_2S(CH_3)C_6H_5^+$

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Received June 5, 1989

Summary: Upon heating at 65 °C, *threo*-$C_5H_5(CO)_2FeCHDCHDCH_2S(CH_3)C_6H_5^+CF_3SO_3^-$ is converted to *cis*-1,2-dideuteriocyclopropane with inversion of stereochemistry at the carbon bound to iron.

The reaction of electrophilic carbene complexes with alkenes leads to the formation of cyclopropanes[1] with complete retention of alkene stereochemistry.[2] Since electron-rich alkenes have enhanced reactivity, electrophilic addition of the carbene carbon to the least substituted alkene carbon has been proposed to lead to a transition state with substantial positive charge at the carbon γ to the metal center. Cyclopropane formation can then be completed by carbon-carbon bond formation between C_α and C_γ by one of two stereochemically differentiated modes of ring closure (Scheme I). Net retention of stereochemistry at C_α could occur by nucleophilic attack of iron at the electrophilic γ-carbon to produce a cationic metallacyclobutane which then reductively eliminates cyclopropane.[3] Net inversion of stereochemistry at C_α could occur via a W-shaped transition state in which the electrophilic γ-carbon attacks the backside of the C_α-Fe bond.

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