Stereochemistry and Mechanism of Cyclopropane Formation from Ionization of $C_5H_5(CO)_2Fe(CH_2)_3X$

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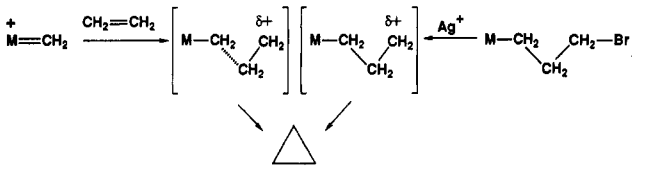
Cyclopropane was produced efficiently both in the Ag^+-assisted dissociation of bromide from $C_5H_5(CO)_2Fe(CH_2)_3Br$ (1) and in the dissociation of phenyl methyl sulfide from $C_5H_5(CO)_2Fe(CH_2)_3S(CH_3)C_6H_5{}^+CF_3SO_3^-$ (8). Clean inversion of stereochemistry at the carbon bound to iron was seen in the formation of *cis*-1,2-dideuteriocyclopropane from the threo sulfonium salt $C_5H_5(CO)_2FeCHDCHDCH_2S(CH_3)C_6H_5{}^+CF_3SO_3^-$ (*threo*-8-d_2). This stereochemical result is consistent with a W-shaped transition state for cyclopropane formation and rules out a mechanism involving a metallacyclobutane intermediate. A new explanation for the selective formation of cis cyclopropanes from the reaction of alkenes with $(CO)_5W{=}CHC_6H_5$ is proposed in light of the results reported here.

Introduction

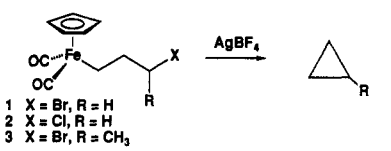
Electrophilic transition-metal carbene complexes react with alkenes to form cyclopropanes in high yield.[1,2] The transition state for cyclopropanation has been proposed to involve electrophilic attack of the carbene carbon on the less substituted alkene carbon and build up of substantial positive charge on the more substituted alkene carbon γ to the metal center.[3-6] The effect of electron donor substituents on alkene reactivity is consistent with this proposed transition state for cyclopropanation. For example, the relative rates of cyclopropane formation in the reactions of alkenes with $(CO)_5W{=}CHC_6H_5$ are $(CH_3)_2C{=}CH_2$ (3500) > $(CH_3)HC{=}CH_2$ (11) ≫ $CH_2{=}CH_2$ (0).[3] To test for the importance of an electrophilic carbon γ to a transition metal in cyclopropanation, we sought to develop an alternative route to such a species and initiated studies of the reaction of $C_5H_5(CO)_2Fe(CH_2)_3Br$ (1) with silver ion.[7]



Here we report that generation of an electrophilic site γ to iron by silver-assisted halide dissociation or by thermal dissociation of $C_6H_5SCH_3$ from a sulfonium salt leads to cyclopropane formation. We have also determined that cyclopropane formation from *threo*-$C_5H_5(CO)_2FeCHDCHDCH_2S(CH_3)C_6H_5{}^+CF_3SO_3^-$ occurs with inversion of stereochemistry at the carbon bound to iron.[8] Brookhart's related study of cyclopropane formation in the reaction of *threo*-$C_5H_5(CO)_2FeCHDCHDCH(C_6H_5)OCH_3$ with TMSOTf led to the same conclusion.[9] The implications of this stereochemical result for cyclopropane formation from metal carbene complexes will be discussed.

Results

Cyclopropane Formation from $C_5H_5(CO)_2FeCH_2CH_2CHRX$. A series of ($\omega$-haloalkyl)iron compounds first synthesized by Moss[10] provided attractive starting materials for generation of electrophilic centers in the neighborhood of carbon–metal bonds. An immediate reaction ($t_{1/2} \leq 10$ min) took place when a suspension of $AgBF_4$ was shaken with a solution of $C_5H_5(CO)_2Fe(CH_2)_3Br$ (1) in benzene-d_6. Visually, the reaction produced a cream-colored precipitate, a red, sticky, insoluble iron species, and a colorless solution. ^1H NMR analysis of the solution using hexamethylbenzene as a quantitative internal standard indicated that cyclopropane (δ 0.13) was formed in 73% yield as the only detectable organic product. The identity of cyclopropane was confirmed by comparison of its GC–MS spectrum with that of an authentic sample. Similarly, the reaction of the chloro compound, $C_5H_5(CO)_2Fe(CH_2)_3Cl$ (2), with a suspension of $AgBF_4$ in benzene-d_6 led to the formation of cyclopropane in 68% yield.



The secondary (3-bromobutyl)iron complex, $C_5H_5(CO)_2Fe(CH_2)_2CHCH_3Br$ (3) was prepared in 43% yield from the reaction of $Na^+C_5H_5(CO)_2Fe^-$ with 1,3-dibromobutane. Complex 3 is very thermally labile and decomposed within 12 h in the dark at room temperature under nitrogen. Reaction of a suspension of $AgBF_4$ with a solution of 3 in benzene-d_6 produced methylcyclopropane in 70% yield. The identity of methylcyclopropane was confirmed by comparison of its GC–MS spectrum with that of an authentic sample.

In contrast to the rapid conversion of (γ-halopropyl)iron complexes 1–3 to cyclopropane, the reactions of (δ-bromoalkyl)- and (ϵ-bromoalkyl)iron compounds with

(1) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411.
(2) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919.
(3) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282.
(4) Brookhart, M.; Humphrey, M. B.; Kratzer, H. J.; Nelson, G. O. *J. Am. Chem. Soc.* **1980**, *102*, 7802.
(5) (a) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258. (b) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1981**, *103*, 979.
(6) Brookhart, M.; Liu, Y.; Goldman, E. W.; Timmers, D. A.; Williams, G. D. *J. Am. Chem. Soc.* **1991**, *113*, 927.
(7) A preliminary communication has appeared: Casey, C. P.; Smith, L. J. *Organometallics* **1988**, *7*, 2419.
(8) A preliminary communication has appeared: Casey, C. P.; Smith, L. J. *Organometallics* **1989**, *8*, 2288.
(9) (a) Brookhart, M.; Liu, Y. *Organometallics* **1989**, *8*, 1569. (b) Brookhart, M.; Liu, Y. *J. Am. Chem. Soc.* **1991**, *113*, 939.
(10) Moss, J. R. *J. Organomet. Chem.* **1982**, *231*, 229.

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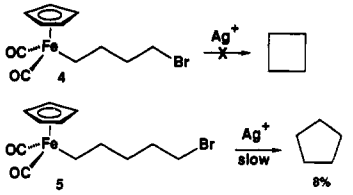
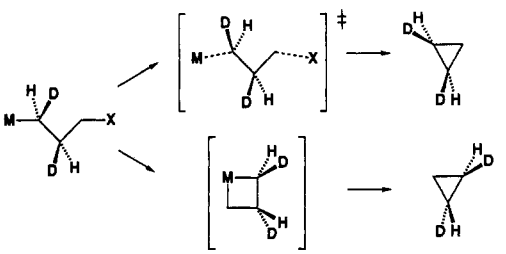
$AgBF_4$ were very slow. Reaction of a suspension of $AgBF_4$ with a solution of $C_5H_5(CO)_2Fe(CH_2)_4Br$ (**4**)[10] in benzene-d_6



proceeded very slowly (50% decomposition of **4** after 2.5 h and 78% decomposition after 2 days). No cyclobutane (<1%) was detected by ^1H NMR analysis. The only benzene-soluble product observed by ^1H NMR spectroscopy was a small amount (8%) of 1-bromobutane. Reaction of a suspension of $AgBF_4$ with a benzene-d_6 solution of the (5-bromopentyl)iron complex, $C_5H_5(CO)_2Fe(CH_2)_5Br$ (**5**),[10] occurred slowly with a time for half-reaction of 1 day. ^1H NMR spectra indicated that cyclopentane was produced in 8% yield in addition to small amounts of pentenes. The formation of cyclopentane was confirmed by GC–MS.

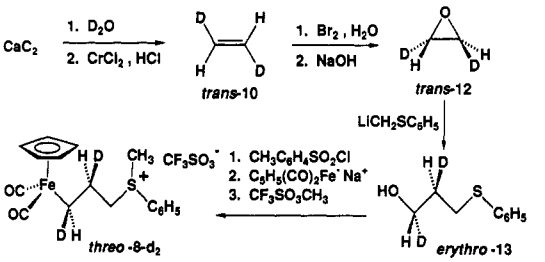
Cyclopropane Formation from $C_5H_5(CO)_2Fe(CH_2)_3S(CH_3)C_6H_5^+CF_3SO_3^-$. The observation of facile cyclopropane formation in the reactions of (γ-haloalkyl)iron compounds **1–3** with Ag^+ provided support for the postulate that generation of an electrophilic site γ to a metal center is important in cyclopropane formation. Two possible mechanisms were considered for cyclopropane formation from the reaction of **1** with Ag^+. The first involves formation of a metallacyclobutane intermediate which subsequently reductively eliminates cyclopropane. The second involves a W-shaped transition state in which the back lobe of the Fe–C σ bond attacks the developing electrophilic center at the γ-carbon of **1**. The first mechanism requires retention of stereochemistry at the carbon bound to iron, while the second mechanism requires inversion at this center. Because of the importance of these reactions in relation to cyclopropane formation from electrophilic metal carbene complexes and alkenes, we considered it crucial to determine the stereochemistry of cyclopropane formation.

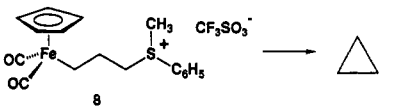


To determine the stereochemistry of cyclopropane formation at the carbon bound to iron, it is necessary to synthesize a precursor with known relative stereochemistry at C_α and C_β. Since we were unable to devise a synthesis of an appropriately labeled (γ-haloalkyl)iron compound, we explored the use of other leaving groups γ to iron and found that loss of $C_6H_5SCH_3$ from a sulfonium salt provided an alternative route to cyclopropane formation. Helquist has previously used a similar strategy for generation of cationic carbene complexes from $C_5H_5(CO)_2FeCH_2S(CH_3)_2^+$.[11]

Reaction of $Na^+C_5H_5(CO)_2Fe^-$ with p-$CH_3C_6H_4SO_3(CH_2)_3SC_6H_5$ (**6**) led to the isolation of $C_5H_5(CO)_2Fe(CH_2)_3SC_6H_5$ (**7**) in 63% yield as a low-melting solid. **7** is thermally stable at 65 °C for 5 h. Reaction of **7** with 2 equiv of methyl triflate at room temperature led to the isolation of the sulfonium salt, $C_5H_5(CO)_2Fe(CH_2)_3S(CH_3)C_6H_5^+CF_3SO_3^-$ (**8**), in 44% yield as a thick red oil that resisted all attempts at crystallization.

Scheme I





Cyclopropane formation occurred readily upon thermolysis of the isolated sulfonium salt. When a solution of **8** in CD_2Cl_2 was heated at 62 °C, cyclopropane was formed in 63% yield with a half-life of about 2 h. Pyrolysis of the neat salt **8** at 64 °C for 2 h also led to cyclopropane in 58% yield.

Synthesis of *threo*-$C_5H_5(CO)_2FeCHDCHDCH_2S(CH_3)C_6H_5^+CF_3SO_3^-$. In order to determine the stereochemistry of cyclopropane formation, we needed to synthesize *threo*-$C_5H_5(CO)_2FeCHDCHDCH_2S(CH_3)C_6H_5^+CF_3SO_3$ (*threo*-**8**-d_2) and to differentiate between *cis*- and *trans*-1,2-dideuteriocyclopropane (*cis*- and *trans*-**9**). Fortunately, the gas-phase infrared analysis of cyclopropane isomers had been rigorously worked out by Berson.[12] In particular, *cis*-**9** has characteristic bands at 2279, 1038, and 846 cm^{-1}, while *trans*-**9** has bands at 2271, 1041, 1024, and 849 cm^{-1}.

threo-**8**-d_2 was prepared stereospecifically in eight steps from calcium carbide (Scheme I). The reaction of CaC_2 with D_2O afforded dideuterioacetylene, which was reduced with a solution of chromium(II) chloride in aqueous HCl to give pure *trans*-CHD=CHD (*trans*-**10**) containing no infrared-detectable *cis*-CHD=CHD or CHD=CH_2.[13] Major bands for *trans*-**10** appear at 1298, 987, and 726 cm^{-1} in the gas-phase FT-IR spectrum, while *cis*-**10** has bands at 1342 and 842 cm^{-1} and CHD=CH_2 has major bands at 1402, 1000, 943, and 808 cm^{-1}.[14] The peak width at half-height of the 1298-cm^{-1} peak of *trans*-**10** was only 2 cm^{-1}. Anti addition[15] of Br_2 in H_2O to *trans*-**10** gave *erythro*-BrCHDCHDOH (*erythro*-**11**), which was converted to *trans*-1,2-dideuteriooxirane[16,17] (*trans*-**12**) by treatment with aqueous NaOH.

(11) O'Connor, E. J.; Brandt, S.; Helquist, P. *J. Am. Chem. Soc.* **1987**, *109*, 3739.

(12) (a) Berson, J. A.; Pedersen, L. D.; Carpenter, B. K. *J. Am. Chem. Soc.* **1976**, *98*, 122. (b) Pedersen, L. D. Ph.D. Thesis, Yale University, 1975.

(13) (a) Nicholas, P. P.; Carroll, R. T. *J. Org. Chem.* **1968**, *33*, 2345. (b) Price, C. P.; Spector, R. *J. Am. Chem. Soc.* **1966**, *88*, 4171.

(14) (a) Brondsema, P. Ph.D. Thesis, University of Wisconsin—Madison, 1984. (b) Pinchas, L.; Laulicht, I. *Infrared Spectra of Labelled Compounds*; Academic Press: New York, 1971; p 84.

(15) (a) March, J. *Advanced Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1977; p 741. (b) Boguslavskaya, L. S. *Russ. Chem. Rev.* **1972**, *41*, 740.

(16) The procedure of Price[13b] was modified as suggested by Brookhart.

(17) Reaction of *trans*-CHD=CHD with *m*-chloroperoxybenzoic acid according to the procedure described by Vollhardt was extremely slow and gave very low yields in our hands. (a) Aalbersberg, W. G. L.; Vollhardt, K. P. C. *Isr. J. Chem.* **1981**, *21*, 145. (b) Aalbersberg, W. G. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1977**, *99*, 2792.

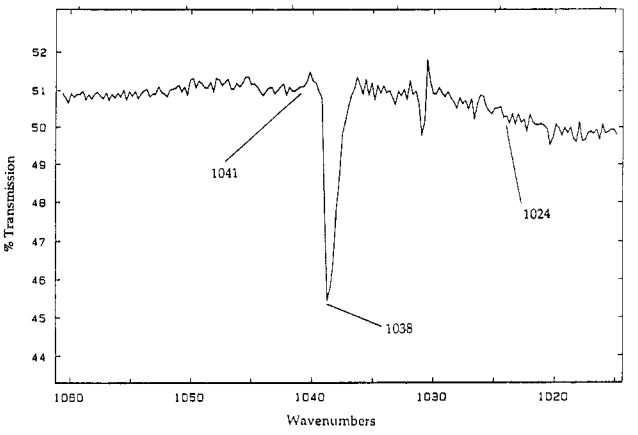


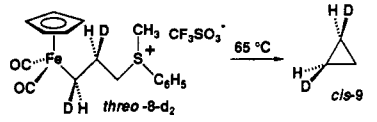
Figure 1. FT-IR spectrum of *cis*-1,2-dideuteriocyclopropane (*cis*-**9**) from pyrolysis of *threo*-**8**-d_2.

Nucleophilic ring opening of *trans*-**12** with ((phenylthio)methyl)lithium in THF gave *erythro*-$HOCHDCHDCH_2SC_6H_5$ (*erythro*-**13**) in 57% yield. Closely related ring openings are known to occur with inversion of stereochemistry.[18] The alcohol *erythro*-**13** was readily converted to the tosylate *erythro*-**6**-d_2 in 92% yield by treatment with 2 equiv of tosyl chloride in pyridine.

Addition of a THF solution of $Na^+C_5H_5(CO)_2Fe^-$ to a THF solution of tosylate *erythro*-**6**-d_2 at 0 °C gave *threo*-$C_5H_5(CO)_2FeCHDCHDCH_2SC_6H_5$ (*threo*-**7**-d_2) as a bright yellow, low-melting oil (mp 15–20 °C) in 82% yield after column chromatography. The ^1H NMR spectrum of *threo*-**7**-d_2 confirmed the presence of deuterium at C_α and C_β. While we have no direct spectroscopic evidence for the stereochemistry of *threo*-**7**-d_2, Whitesides has shown that reaction of $Na^+C_5H_5(CO)_2Fe^-$ with *erythro*-(*p*-BrC_6H_4)-$SO_3CHDCHDC(CH_3)_3$ occurred with complete inversion of stereochemistry at C_α.[19] A solution of *threo*-**7**-d_2 and methyl triflate (2 equiv) in CH_2Cl_2 was stirred for 2 h at room temperature to give the sulfonium salt, *threo*-$C_5H_5(CO)_2FeCHDCHDCH_2S(CH_3)C_6H_5^+CF_3SO_3^-$ (*threo*-**8**-d_2) in 83% yield as a thick, red oil.

The synthesis of *threo*-**8**-d_2 outlined in Scheme I was designed to be highly stereospecific and employed only reactions of known stereochemistry. While we had no direct measure of the isomeric purity of sulfonium salt *threo*-**8**-d_2, the observation to be described below that *threo*-**8**-d_2 is converted to >95% isomerically pure *cis*-1,2-dideuteriocyclopropane requires that *threo*-**8**-d_2 be >95% isomerically pure.

Stereochemistry of Cyclopropane Formation. When neat *threo*-**8**-d_2 was heated at 65 °C for 4.5 h, *cis*-1,2-dideuteriocyclopropane (*cis*-**9**) was formed in 35% yield as the only volatile product. 1,2-Dideuteriocyclopropane was



identified by ^1H NMR analysis (δ 0.12) and GC–MS, which established that the product was >97% deuterated form. The stereochemistry of the cyclopropane was shown to be cis by observation of its gas-phase FT-IR spectrum which had bands at 2279, 1038, and 846 cm^{-1} that are characteristic of *cis*-**9**. Bands characteristic of the *trans*-**9** isomer at 2271, 1041, 1024, and 849 cm^{-1} were absent.

Berson's IR spectrum of a 1:1 equilibrium mixture of *cis*-**9** and *trans*-**9** has equal intensity peaks at 1038 cm^{-1} for *cis*-**9** and 1041 cm^{-1} for *trans*-**9**.[12] In our spectrum shown in Figure 1, there is an intense absorption (20 × noise level) at 1038 cm^{-1} for *cis*-**9** and no absorption above noise level at 1041 cm^{-1} where *trans*-**9** absorbs. Therefore, the ratio of *cis*-**9**:*trans*-**9** must be greater than 20:1. The formation of *cis*-**9** establishes that cyclopropane formation occurs with inversion of stereochemistry at the carbon bound to iron.

threo-**8**-d_2 was also generated and pyrolyzed in situ. Reaction of sulfide *threo*-**7**-d_2 with neat methyl triflate (2 equiv) at 65 °C for 6 h produced *cis*-1,2-dideuteriocyclopropane in 45% yield as the only detectable volatile product.

Discussion

Cyclopropane was produced efficiently from both the silver-assisted dissociation of bromide from (γ-bromopropyl)iron (**1**) and the dissociation of phenyl methyl sulfide from (γ-sulfoniumpropyl)iron (**8**). This establishes that generation of an electrophilic center γ to iron can lead to cyclopropane formation. These results are consistent with the proposed importance of an electrophilic γ-carbon in the cyclopropane-forming reactions of metal–carbene complexes with alkenes.

A comparison of the relative rates of reaction of Ag^+ with 1 and simple organic bromides demonstrates that the iron center accelerates the loss of bromide. The reactions of **1–3** with $AgBF_4$ in benzene-d_6 at room temperature were complete within 15 min after mixing. In contrast, 1-bromopropane reacted only very slowly (33% reaction after 4 days) with $AgBF_4$ in benzene-d_6 to form the rearrangement product 2-bromopropane. Similarly, the thermal conversion of iron-substituted sulfonium salt **8** to cyclopropane occurred at a temperature much lower than that required for thermal decomposition of ordinary sulfonium salts. This is consistent with iron-assisted loss of C_6H_5S-CH_3 from **8**.

Three-membered ring formation from complexes **1–3** occurred much more rapidly than four- and five-membered ring formation from complexes **4** and **5**, respectively. A qualitative comparison of the relative rates of reaction of $AgBF_4$ with the (3-halopropyl)iron complexes versus the (4-bromobutyl)- and (5-bromopentyl)iron complexes shows that reaction of the propyl species occurs at least 100 times faster than the longer four- and five-carbon chain species. The fact that the reaction of the (4-bromobutyl)iron complex (**4**) did not give any cyclobutane, but instead small amounts of 1-bromobutane, along with the fact that the reaction of the (5-bromopentyl)iron complex (**5**) gave only a very low yield of cyclopentane suggests that these longer chain complexes react via a different route than the (3-halopropyl)iron complexes.

Clean inversion of stereochemistry at the carbon bound to iron was seen in the formation of *cis*-1,2-dideuteriocyclopropane from the threo sulfonium salt *threo*-**8**-d_2. Brookhart also found that cyclopropane formation occurred with inversion of stereochemistry at the carbon bound to iron in the reactions of *erythro*- and *threo*-$C_5H_5(CO)_2FeCHDCHDCH(C_6H_5)OCH_3$ with TMSOTf.[9] These stereochemical results clearly rule out a metallacyclobutane intermediate in cyclopropane formation. Inversion of stereochemistry can be explained in terms of a

(18) (a) Williams, D. R.; Phillips, J. G.; White, F. H.; Huffman, J. C. *Tetrahedron* **1986**, *42*, 3003. (b) Williams, D. R.; Phillips, J. G. *Tetrahedron* **1986**, *42*, 3012.

(19) (a) Bock, P. L.; Boschetto, D. J.; Rasmussen, J. R.; Demers, J. P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 2814. (b) Whitesides, G. M.; Boschetto, D. J. *J. Am. Chem. Soc.* **1971**, *93*, 1529.

W-shaped transition state in which the back lobe of the carbon–iron σ bond attacks the developing electrophilic site at the carbon γ to iron.

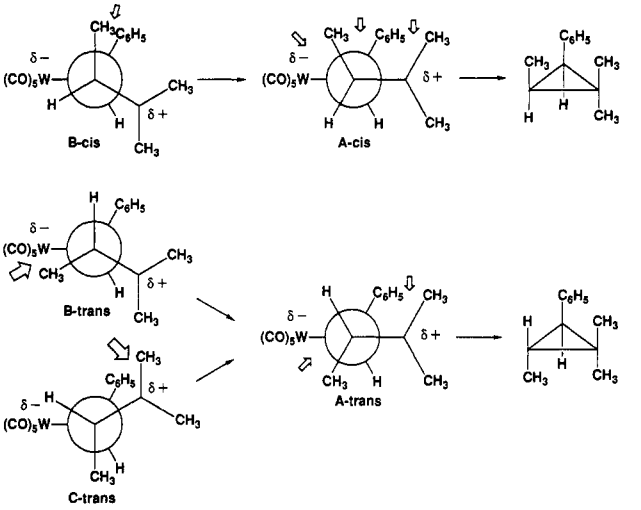
Similar Behavior of $R_3Sn(CH_2)_nX$ Systems. W-Shaped transition states have been proposed to explain cyclopropane formation from organotin compounds possessing a sulfonate leaving group γ to tin.[20] Inversion of stereochemistry at the carbon bound to the metal was also seen in these reactions. As in the case of our iron compounds, Kuivila found that the fastest rates of reaction occurred when the leaving group was γ to tin.[21] For the series of [ω-(tosyloxy)alkyl]trimethyltins, $(CH_3)_3Sn(CH_2)_nOTs$ (n = 3–5), he found that thermolysis of the [3-(tosyloxy)propyl]trimethyltin compound occurred at a rate >700 times faster than the [4-(tosyloxy)butyl]- and [5-(tosyloxy)pentyl]tin compounds. Moreover, the [3-(tosyloxy)propyl]tin compound produced cyclopropane in 82% yield while the [4-(tosyloxy)butyl]- and [5-(tosyloxy)pentyl]tin compounds produced mainly alkenes.

Since tin has no available d electrons to assist in loss of tosylate, the rapid rate of cyclopropane formation was explained in terms of donation of electrons from the back lobe of the tin–carbon σ bond to the developing electrophilic center. Because of the similar behavior of our iron compounds, we believe that d electrons are not involved and that the back lobe of the iron–carbon σ bond is responsible for accelerating the reaction of 1 to give cyclopropane.

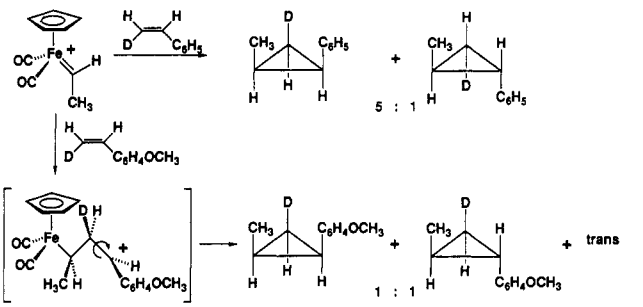
Relationship between Cyclopropane Formation from $Cp(CO)_2Fe(CH_2)_3X$ and from Metal–Carbene Complexes. There appears to be a close relationship between the reaction of alkenes with metal–carbene complexes and the dissociation of bromide or sulfide from γ-substituted iron compounds 1 and 8. Both reaction types produce cyclopropane and both involve an electrophilic carbon γ to iron. The rate of reaction of metal–carbene complexes with alkenes is accelerated by electron-donor substituents on one carbon of the alkene.[3-6] In all but one case, the reaction of metal–carbene complexes with alkenes to form cyclopropanes occurs with retention of the alkene stereochemistry. For example, reaction of $C_5H_5(CO)_2Fe{=}CHCH_3^+$ with *cis*-CHD=CHPh leads to the formation of a 5:1 mixture of *cis*:*trans*-1-phenyl-2-methylcyclopropane with complete retention of stereochemistry of the former alkene.[22] This indicates that a long-lived γ-carbocation intermediate cannot be involved in formation of this cyclopropane since rotation about C_β–C_γ would have resulted in some loss of stereochemistry. Therefore, the transition state for cyclopropane formation must involve partial formation of each of the two new carbon–carbon bonds of the cyclopropane.

For the more electron-rich alkene *p*-methoxystyrene, Brookhart found extensive loss of stereochemistry in the reaction of $C_5H_5(CO)_2Fe{=}CHCH_3^+$ with *cis*-CHD=CHC_6H_4-*p*-OCH_3 in the formation of a 0.9:1 *cis*:*trans*-1-(*p*-methoxyphenyl)-2-methylcyclopropane.[23] In this case, the *p*-methoxy substituent was proposed to stabilize the

Scheme II



electrophilic γ-carbon to such an extent that a carbocation intermediate is generated and lives long enough to partially scramble the stereochemistry prior to cyclopropane formation.



We believe that the stereochemistry of cyclopropane formation from *threo*-8-d_2 is relevant to the reaction of metal carbene complexes with alkenes and that this information must be incorporated into the detailed mechanism of cyclopropane formation from metal–carbene complexes and alkenes. Brookhart has described the reaction of $C_5H_5(CO)(L)Fe{=}CHR^+$ with alkenes as beginning with an attack of the electrophilic carbene carbon on the alkene which generates an electrophilic center at C_γ. The developing γ-carbocation then attacks the backside of the Fe–C_α bond to form cyclopropane with inversion of stereochemistry at C_α. With the added postulate that the reactions proceed through the less stable but more reactive synclinal rotamer of $C_5H_5(CO)(L)Fe{=}CHR^+$, Brookhart has satisfactorily explained the absolute stereochemistry and high enantiomeric excesses of cyclopropane products from enantiomerically pure iron systems.[6,24]

New Explanation of the Stereochemistry of Cyclopropane Formation from $(CO)_5W{=}CHC_6H_5$. Earlier we had attempted to explain the formation of cis cyclopropanes from $(CO)_5W{=}CHPh$ and *cis*-$CH_3CH{=}CHCH_3$ or $(CH_3)_2C{=}CHCH_3$ by a mechanism involving interaction of the ipso carbon of the aryl ring on C_α with the more substituted alkene carbon followed by conversion to a metallacycle and reductive elimination.[3] The results reported here demonstrating inversion of stereochemistry at the α-carbon strongly suggest that this explanation is incorrect. In spite of the fact that we have now retracted

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(22) Brookhart, M.; Timmers, D.; Tucker, J. R.; Williams, G. D.; Husk, G. R.; Brunner, H.; Hammer, B. *J. Am. Chem. Soc.* **1983**, *105*, 6721.

(23) Brookhart, M.; Kegley, S. E.; Husk, G. R. *Organometallics* **1984**, *3*, 650.

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two different explanations for the stereochemistry of cyclopropane formation, we have overcome our reluctance to offer a third explanation of the stereochemistry of cyclopropane formation from $(CO)_5W{=}CHC_6H_5$.

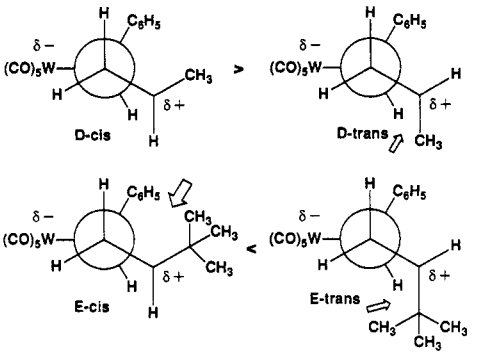
Some key features of the stereochemistry of cyclopropane formation from $(CO)_5W{=}CHC_6H_5$ that need to be explained are (1) the preferred formation of cis cyclopropanes from $CH_2{=}CHCH_3$ (1.8:1 cis:trans) and $CH_2{=}CHC_6H_5$ (9.7:1 cis:trans), (2) the high stereochemical influence of the substituent on the less substituted alkene carbon of $CH_3CH{=}C(CH_3)_2$ (94:1 cis:trans), (3) the higher preference for cis cyclopropanes from *cis*-$CH_3CH{=}CHCH_3$ (41:1 syn:anti) than from $CH_2{=}CHCH_3$ (1.8:1 cis:trans), and (4) a shift from cis to trans selectivity as the size of the alkyl group on $CH_2{=}CHR$ increases from R = CH_3 (1.8:1 cis:trans) to R = CH_2CH_3 (1:1.1 cis:trans) to R = $CHMe_2$ (1:2.8 cis:trans) to R = CMe_3 (1:99 cis:trans).[3]

The stereochemistry of cyclopropane formation from $(CO)_5W{=}CHC_6H_5$ will be discussed using the important example of cis cyclopropane formation from $CH_3CH{=}C(CH_3)_2$ (Scheme II). A mechanism that involves inversion of stereochemistry at C_α and a W-shaped conformation immediately prior to cyclopropane formation cannot, by itself, explain selective formation of cis cyclopropanes. Comparison of the two possible W-shaped geometries indicates that A-cis which leads to cis cyclopropane is destabilized relative to A-trans by a gauche interaction between the phenyl group on C_α and the methyl group on C_β; A-trans which leads to trans cyclopropane has a more stable anti relationship between these groups. Therefore, the product determining approach of the alkene and the carbene complex must be somewhat different from the W-shaped geometries A-cis and A-trans.

It should be noted that there are two major destabilizing interactions common to both A-cis and A-trans: (1) a steric interaction between $W(CO)_5$ and a methyl group on C_β and (2) a steric interaction between the phenyl group and C_γ and its attached methyl group. More favorable approach geometries might decrease these interactions and need to be considered for the product-determining transition states. We have therefore considered other approach geometries that differ by rotation about the C_α–C_β axis but that are similar enough to the W-shaped geometry to allow facile rotation to A-cis or A-trans without allowing formation of a carbocation intermediate that could lose alkene stereochemistry by rotation about the C_β–C_γ bond before cyclopropane formation. Approach geometries similar to B-cis, B-trans, and C-trans in which the dihedral angle between the W–C bond and the alkene double bond is 120° (±30°) can explain the preference for cis cyclopropane formation. In approach geometry B-cis, the γ-carbon is rotated away from the phenyl group. This rotation relieves both the interaction between the phenyl group and C_γ and its attached methyl group and the interaction between $W(CO)_5$ and the methyl group on C_β while increasing the interaction between the phenyl group and the methyl group on C_β. Overall this should stabilize B-cis relative to A-cis.

Rotation of C_γ away from the phenyl group in A-trans leads to geometry B-trans in which the interaction between the phenyl group and C_γ and its attached methyl group is relieved but the interaction between the $W(CO)_5$ and the methyl group on C_β is greatly increased. Alternatively, rotation of C_γ toward the phenyl group in A-trans leads to geometry C-trans in which the interaction between the $W(CO)_5$ and the methyl group on C_β is relieved but the interaction between the phenyl group and C_γ and its attached methyl group is significantly increased. The preference for formation of cis cyclopropane is explained by the greater stability of B-cis compared with either A-, B-, or C-trans.

Scheme III



Transition states similar to B-cis and B-trans underscore the important role of substituents on C_β, the less substituted alkene carbon, in determining product stereochemistry. The key role of β-substituents explains the greater cis stereoselectivity seen for *cis*-2-butene (41:1 cis:trans) compared to propene (1.8:1 cis:trans).

Alkyl substituents at C_γ, the most substituted alkene carbon, also play a role in controlling the stereochemistry of cyclopropane formation. This role is difficult to explain since a smooth change from cis selectivity to trans selectivity is seen as the size of the alkyl substituent is increased from methyl to *tert*-butyl. The slight preference for formation of cis cyclopropane from propene might be explained in terms of the greater stability of D-cis compared with D-trans, which is destabilized by an interaction between the methyl group and a hydrogen on C_α (Scheme III). In contrast, the strong preference for trans cyclopropane formation from *tert*-butylethylene is explained by the greater stability of E-trans compared with E-cis which is greatly destabilized by interaction of the *tert*-butyl group with the phenyl ring.

Experimental Section

General Considerations. All reactions and manipulations of air-sensitive materials were carried out using standard high-vacuum-line techniques or in an inert-atmosphere glovebox. Benzene-d_6 was distilled from a purple solution of sodium and benzophenone. CD_2Cl_2 was dried over P_2O_5. Column chromatography of organometallic species was conducted on activity 0 alumina in an inert-atmosphere drybox.

^1H NMR spectra were obtained on Bruker WP200, WP270, and AM500 spectrometers. ^{13}C NMR spectra were obtained on Bruker WP270 (68 MHz) and AM500 (126 MHz) spectrometers. Infrared spectra were measured on a Mattson Polaris FT-IR infrared spectrometer. Gas-phase spectra were taken using a high-vacuum cell with NaCl windows and a path length of 1 dm. Mass spectra were determined on a Kratos MS-80 spectrometer and GC-MS was performed on a Carlo-Erba gas chromatograph using a phenylmethylsilicone fused-silica capillary column interfaced to a Kratos MS-25 mass spectrometer. Ionization at 20–25 eV was used for low molecular weight, gaseous samples. Analytical gas chromatography was performed using a Hewlett-Packard 5890A gas chromatograph with a cryogenic cooling system (liquid CO_2).

$C_5H_5(CO)_2Fe(CH_2)_3Br$ (1). 1 was prepared by a modification of the method of Moss.[10] A solution of $Na^+[C_5H_5(CO)_2Fe]^-$ (2.8 mmol) in THF (20 mL) was added dropwise to neat 1,3-dibromopropane (0.20 mL, 2.0 mmol) with stirring at −20 °C. Solvent was evaporated under vacuum to give a brownish green residue which was extracted with hexane. The extract was filtered, concentrated, and chromatographed (alumina, hexane) to give 1 as a bright yellow oil (0.56 g, 96%). The yellow oil was crystallized from hexane by slow cooling (over 2–5 h) to give 1 (mp 22–24 °C) free of 1,3-dibromopropane. ^1H NMR (200 MHz, C_6D_6):

δ 3.90 (C_5H_5), 3.06 (t, J = 8 Hz, CH_2Br), 1.82 (m, CH_2), 1.09 (m, $FeCH_2$). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ 217.5 (CO), 85.2 (C_5H_5), 41.6 (CH_2Br), 35.8 (CH_2), −0.2 ($FeCH_2$). IR (hexane): 2018 (s), 1960 (s), 1935 (sh) cm^{-1}.

$C_5H_5(CO)_2Fe(CH_2)_3Cl$ (2). 2 was prepared by addition of a solution of $Na^+[C_5H_5(CO)_2Fe]^-$ (2.8 mmol) in THF (20 mL) to neat 1-bromo-3-chloropropane (0.30 g, 1.9 mmol) at −20 °C. Chromatography (alumina, hexane) gave 3 (0.39 g, 81%) as a bright yellow oil. ^1H NMR (200 MHz, C_6D_6): δ 3.92 (C_5H_5), 3.21 (t, J = 7.0 Hz, CH_2Cl), 1.75 (m, CH_2), 1.15 (m, $FeCH_2$). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ 217.6 (CO), 85.3 (C_5H_5), 47.3 (CH_2Cl), 41.4 (CH_2), −1.4 ($FeCH_2$). IR (hexane): 2009 (s), 1957 (s), 1931 (sh) cm^{-1}. HRMS calcd for $C_{10}H_{11}ClFeO_2$: 253.9797. Found: 253.9787.

$C_5H_5(CO)_2Fe(CH_2)_2CHCH_3Br$ (3). A solution of $Na^+[C_5H_5(CO)_2Fe]^-$ (12.5 mmol) in THF (25 mL) was added dropwise to neat 1,3-dibromobutane (2.7 g, 12.5 mmol) at −20 °C. Chromatography (alumina, hexane) gave 3 as a bright yellow oil (1.7 g, 43%) which was thermally sensitive. ^1H NMR (200 MHz, C_6D_6): δ 3.98 (C_5H_5), 3.85 (m, $CHCH_3$), 1.86 (m, CH_2), 1.52 (d, J = 6.6 Hz, CH_3), 1.17 (m, $FeCH_2$). ^{13}C NMR (126 MHz, C_6D_6): δ 217.6 (CO), 85.3 (C_5H_5), 55.2 (d, J_{CH} = 64 Hz, CHBr), 49.5 (t, J_{CH} = 54 Hz, CH_2), 25.8 (q, J_{CH} = 55 Hz, CH_3), −0.8 (t, J_{CH} = 57 Hz, $FeCH_2$). IR (hexane): 2011 (s), 1964 (sh), 1968 (s) cm^{-1}.

Reactions of (ω-Haloalkyl)iron Complexes with $AgBF_4$. A benzene-d_6 solution of the iron alkyl halide complex and hexamethylbenzene as an internal NMR standard was prepared in a 1-mL volumetric flask in the drybox. One 0.25-mL portion of this solution was syringed into an NMR tube and sealed under vacuum for use as a standard. A second 0.25-mL portion was syringed into an NMR tube containing a frozen suspension of $AgBF_4$ (ca. 2 equiv) in benzene-d_6 at liquid nitrogen temperature. The tube was sealed under vacuum, warmed to room temperature, and shaken. A ^1H NMR spectrum of the tube containing $AgBF_4$ was taken within 15 min. The reaction progress was then monitored by ^1H NMR spectroscopy, and the product yields were calculated by comparison of NMR integrations of the reaction mixture and the standard solution using hexamethylbenzene as a standard.

Reaction of $C_5H_5(CO)_2Fe(CH_2)_3Br$ (1) with $AgBF_4$. A 0.25-mL aliquot of a standard solution of 1 (54 mg, 0.181 mmol) and hexamethylbenzene (3 mg) was added to $AgBF_4$ (15 mg, 0.077 mmol). Complete conversion of 1 occurred within 15 min. Cyclopropane was formed as the only product detectable by ^1H NMR spectroscopy (δ 0.13) in 73% yield. The identity of cyclopropane was confirmed by GC–MS.

Reaction of $C_5H_5(CO)_2Fe(CH_2)_3Cl$ (2) with $AgBF_4$. A 0.25-mL aliquot of a standard solution of 2 (62 mg, 0.24 mmol) and hexamethylbenzene (4 mg) was added to $AgBF_4$ (23 mg, 0.12 mmol). Complete conversion of 2 occurred within 15 min. Cyclopropane was formed as the only product detectable by ^1H NMR spectroscopy in 68% yield. The identity of cyclopropane was confirmed by GC–MS.

Reaction of $C_5H_5(CO)_2Fe(CH_2)_2CH(CH_3)Br$ (3) with $AgBF_4$. A 0.25-mL aliquot of a standard solution of 3 (74 mg, 0.24 mmol) and hexamethylbenzene (2 mg) was added to $AgBF_4$ (24 mg, 0.12 mmol). Complete conversion of 3 occurred within 15 min. Methylcyclopropane [δ 0.94 (d, J = 5.7 Hz, CH_3), 0.58 (m, CH), 0.37 (m, 2 H), −0.06 (m, 2 H)] was formed as the only product detectable by ^1H NMR spectroscopy in 70% yield. The identity of methylcyclopropane was confirmed by GC–MS.

Reaction of $C_5H_5(CO)_2Fe(CH_2)_4Br$ (4) with $AgBF_4$. A 0.25-mL aliquot of a standard solution of 4 (65 mg, 0.21 mmol) and hexamethylbenzene (4 mg) was added to $AgBF_4$ (17 mg, 0.087 mmol). ^1H NMR analysis showed 25% decomposition of 4 after 15 min and 50% decomposition after 2.4 h; however, no new product peaks were apparent. After 14 days, decomposition of 4 was complete and 8% 1-bromobutane was seen by NMR spectroscopy. The ^1H NMR spectrum of the volatile materials showed only 1-bromobutane and benzene-d_6. ^1H NMR spectrum of the nonvolatile products dissolved in acetone-d_6 showed signals for $C_5H_5(CO)_3Fe^+$ (δ 6.11), $C_5H_5(CO)_2Fe(\eta^2\text{-}CH_2{=}CH_2)^+$ (δ 5.89, 3.95), $C_5H_5(CO)_2FeBr$ (δ 5.24) and $[C_5H_5(CO)_2Fe]_2$ (δ 4.93) along with the major C_5H_5 peak at δ 5.57, which was not identified.

Reaction of $C_5H_5(CO)_2Fe(CH_2)_5Br$ (5) with $AgBF_4$. A 0.25-mL aliquot of a standard solution of 5 (54 mg, 0.16 mmol) and hexamethylbenzene (3 mg) was added to $AgBF_4$ (15 mg, 0.077 mmol). After 1 day, 50% decomposition of 5 was seen. After 14 days, decomposition was complete and a small amount of cyclopentane (δ 1.45, 8%) was seen by NMR spectroscopy. The identity of cyclopentane was confirmed by GC–MS.

$HO(CH_2)_3SC_6H_5$. A solution of ethylene oxide (11 mmol) in 50 mL of benzene was vacuum-transferred into a THF solution of $LiCH_2SC_6H_5$[25] (10.6 mmol) at −196 °C. The reaction mixture was stirred for 30 min at room temperature and quenched with 10 mL of saturated aqueous ammonium chloride. The product alcohol was extracted into ether, dried ($MgSO_4$), and distilled to give $HO(CH_2)_3SC_6H_5$ as a clear liquid (0.98 g, 55%), bp 120 °C (1 mmHg). ^1H NMR (200 MHz, $CDCl_3$): δ 7.38–7.17 (m, C_6H_5), 3.76 (t, J = 6.1 Hz, CH_2O), 3.03 (t, J = 7.1 Hz, CH_2S), 1.90 (m, CH_2), 1.69 (br s, OH). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 136.1 (C_{ipso}), 129.1 and 128.8 (C_{ortho}, C_{meta}), 125.9 (C_{para}), 61.2 (CH_2O), 31.7 (CH_2S), 30.2 (CH_2). IR (neat film): 3500 cm^{-1} (OH, str). HRMS calcd for $C_9H_{12}OS$: 168.0609. Found: 168.0612.

$p\text{-}CH_3C_6H_4SO_3(CH_2)_3SC_6H_5$ (6). Reaction of p-toluenesulfonyl chloride (1.33 g, 7.0 mmol) with $HO(CH_2)_3SC_6H_5$ (0.68 g, 4.0 mmol) in pyridine (5 mL) at 0 °C overnight followed by aqueous workup, ether extraction, acid washing, and drying over $MgSO_4$ led to the isolation of 6 (1.19 g, 92%) as a light orange oil. ^1H NMR (200 MHz, $CDCl_3$): δ 7.77–7.13 (m, aryl), 4.12 (t, J = 6.0 Hz, CH_2O), 2.89 (t, J = 7.0 Hz, CH_2S), 2.40 (s, CH_3), 1.90 (m, CH_2). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$), δ: 144.8, 135.1, 132.6, 129.8, 129.0, 128.6, 127.7, 126.1 (aryl); 68.5 (CH_2O); 29.3 (CH_2S); 28.1 (CH_2); 21.4 (CH_3).

$C_5H_5(CO)_2Fe(CH_2)_3SC_6H_5$ (7). A solution of $Na^+[C_5H_5(CO)_2Fe]^-$ (2.3 mmol) in 20 mL of THF was added to a stirred solution of $p\text{-}CH_3C_6H_4SO_3(CH_2)_3SC_6H_5$ (0.61 g, 1.9 mmol) in THF (2 mL) at −20 °C. Evaporation of solvent under vacuum gave a reddish brown residue which was extracted with hexane. The extract was filtered, concentrated, and chromatographed (alumina, 1:1 hexane:ether) to give 7 as a dark yellow oil (0.39 g, 63%). ^1H NMR (200 MHz, acetone-d_6): δ 7.33–7.11 (m, C_6H_5), 4.90 (s, C_5H_5), 2.92 (t, J = 7 Hz, CH_2S), 1.75 (m, CH_2), 1.45 (m, $FeCH_2$). $^{13}C\{^1H\}$ NMR (126 MHz, acetone-d_6): δ 218.7 (CO), 138.4 (C_{ipso}), 129.6 and 128.8 ($C_{ortho,\,meta}$), 125.9 (C_{para}), 86.5 (C_5H_5), 38.2 (CH_2), 37.1 (CH_2S), 1.95 ($FeCH_2$). IR (hexane): 2011 (s), 1957 (s), 1927 (w) cm^{-1}. HRMS calcd for $(M-2CO)^+$, $C_{14}H_{16}FeS$: 272.0322. Found: 272.0316. Because 7 is a viscous air-sensitive oil, elemental analysis was not obtained; ^1H and ^{13}C NMR data indicated that 7 was >95% pure.

$C_5H_5(CO)_2Fe(CH_2)_3S(CH_3)C_6H_5{}^+CF_3SO_3{}^-$ (8). Methyl triflate (0.92 mmol) and 7 (0.15 g, 0.46 mmol) in CH_2Cl_2 (1.5 mL) were stirred in the dark at room temperature for 12 h. All volatile material was evaporated under high vacuum to give a thick red oil which was washed with hexane (3 × 10 mL) and dried under vacuum to give thermally sensitive 8 (0.10 g, 44%). ^1H NMR (500 MHz, acetone-d_6): δ 8.20–7.73 (m, C_6H_5), 4.92 (s, C_5H_5), 3.20 (m, CH_2S), 3.47 (s, CH_3), 1.82 (m, $-CH_2-$), 1.40 (m, $FeCH_2$). $^{13}C\{^1H\}$ NMR (126 MHz, acetone-d_6): δ 218.9 (CO), 138.1 (C_{ipso}), 132.2 and 129.0 ($C_{ortho,meta}$), 124.1 (C_{para}), 86.7 (C_5H_5), 49.5 (CH_2S), 32.3 (CH_2), 26.4 (CH_3), −1.0 ($FeCH_2$). IR (hexane): 2005 (w), 2001 (s), 1950 (s) cm^{-1}. Because 8 is thermally sensitive, elemental analysis was not obtained; ^1H and ^{13}C NMR data indicated that 8 was >90% pure.

Thermolysis of 8 in CD_2Cl_2. 8 (25 mg, mmol) and hexamethylbenzene (5 mg) were weighed into a 5-mm NMR tube. CD_2Cl_2 was distilled into the tube. The tube was sealed under vacuum and heated at 62 °C. ^1H NMR spectroscopy showed that after 6.5 h 98% of the 8 had reacted and cyclopropane was formed in 63% yield.

Pyrolysis of Neat 8. Sulfonium salt 8 (60 mg, 0.122 mmol) was heated at 64 °C for 2 h in a small Schlenk tube equipped with a high-vacuum stopcock. Volatile materials was transferred on a vacuum line to a gas-phase IR cell. The FT-IR spectrum exhibited bands at 3100.6, 3023.2, 1027.2, and 866.6 cm^{-1}, characteristic of cyclopropane. The yield of cyclopropane (0.072 mmol, 59%) was measured from the pressure in a known volume.

***trans*-1,2-Dideuterioethylene (*trans*-10)** (0.0312 mol) was prepared in 41% yield by the method of Nicholas and Carroll.[13a]

(25) Corey, E. J.; Seebach, D. *J. Org. Chem.* **1966**, *31*, 4097.

Infrared analysis indicated that the product was completely free of any d_0, d_1, or d_2 isomers. Partial FT-IR (gas phase): 1298.6, 987.2, 726.1 cm^{-1}. Reported: 1300, 988, 727 cm^{-1}.[14]

***erythro*-BrCHDCHDOH (*erythro*-11).** A modification of the procedure of Price and Spector was used.[13b,16] A solution of bromine (1.5 mL, 29 mmol) in water (150 mL) was stirred at room temperature until all of the bromine had dissolved (1 h). This solution was added via cannula to a 500-mL Schlenk flask containing *trans*-**10** (22.5 mmol). After 2 h, excess bromine was quenched by dropwise addition of aqueous sodium thiosulfate. The aqueous mixture was extracted with CH_2Cl_2 (24 × 50 mL) and the combined organic layers were dried ($MgSO_4$) and concentrated to give *erythro*-**11** (1.50 g, 52%) as a yellow liquid. ^1H NMR (200 MHz, $CDCl_3$): δ 3.86 (br s, C*H*DOH), 3.49 (m, CHDBr), 2.32 (br s, OH). IR (film): 3330, 2930, 2050, 1420, 1305 cm^{-1}.

***trans*-1,2-Dideuterioethylene Oxide (*trans*-12).** According to the procedure of Price and Spector[13b] aqueous sodium hydroxide (10 mL, 1 M) was added to *erythro*-**11** (1.24 g, 9.8 mmol). *trans*-**12** (4.0 mmol, 41%) was isolated and purified by trap to trap distillation. ^1H NMR (200 MHz, C_6D_6): δ 0.54. FT-IR (gas): 3023, 2241, 1742, 1227, 1110, 916, 889, 878, 817, 750 cm^{-1}.

***erythro*-HOCHDCHDCH$_2$SC$_6$H$_5$ (*erythro*-13).** *trans*-**12** (4.3 mmol) was vacuum-transferred into a degassed solution of LiCH$_2$SC$_6$H$_5$ (4.3 mmol)[25] in THF. After 20 min, the reaction mixture was quenched with saturated aqueous ammonium chloride (10 mL). The layers were separated, and the aqueous layer was extracted with ether. The combined organic layers were dried ($MgSO_4$), and volatile material was evaporated under high vacuum to leave *erythro*-**13** (0.42 g, 57%) as a clear liquid. ^1H NMR (200 MHz, $CDCl_3$): δ 7.36–7.10 (m, C_6H_5), 3.68 (br d, J = 6 Hz, CHDO), 2.97 (br d, J = 8 Hz, CH_2S), 1.80 (br q, J = 8 Hz, CHD), 1.50 (br s, OH). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 136.2 (C_{ipso}), 129.1 and 128.9 ($C_{ortho,meta}$), 125.9 (C_{para}), 60.9 (t, J_{CD} = 21 Hz, CHDO), 31.2 (t, J_{CD} = 19 Hz, CHD), 30.1 (CH_2S). IR (film): 3352, 2922 cm^{-1}. HRMS calcd for $C_9H_{10}D_2OS$: 170.0734. Found: 170.0730.

***erythro*-*p*-CH$_3$C$_6$H$_4$SO$_3$CHDCHDCH$_2$SC$_6$H$_5$ (*erythro*-6-*d*$_2$).** Addition of *p*-toluenesulfonyl chloride (0.40 g, 2.0 mmol) to *erythro*-**13** (0.23 g, 1.0 mmol) in pyridine (3.5 mL) at 0 °C led to the isolation of *erythro*-**6**-d_2 (0.30 g, 92%). ^1H NMR (200 MHz, $CDCl_3$): δ 7.8–7.2 (m, aryl), 4.13 (br d, J = 6 Hz, CHDO), 2.91 (br d, J = 8 Hz, CH_2S), 2.44 (s, CH_3), 1.90 (br q, J = 8 Hz, CHD). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$), δ: 144.8, 135.4, 133.0, 129.8, 129.6, 129.0, 127.8, 126.3 (C_{aryl}); 68.2 (t, J_{CD} = 23 Hz, CHDO); 29.6 (CH_2S); 28.0 (t, J_{CD} = 20 Hz, CHD); 21.6 (CH_3). IR (film): 3062, 2925, 1363, 1180 cm^{-1}. HRMS calcd for $C_{16}H_{16}D_2O_3S_2$: 324.0822. Found: 324.0823.

***threo*-C$_5$H$_5$(CO)$_2$FeCHDCHDCH$_2$SC$_6$H$_5$ (*threo*-7-*d*$_2$).** A solution of $Na^+[C_5H_5(CO)_2Fe]^-$ (**2**) (1.2 mmol) in THF (20 mL) was added to a stirred solution of *erythro*-**6**-d_2 (0.30 g, 0.92 mmol) in THF (3 mL) at −20 °C. Chromatography (alumina, hexane) gave *threo*-**7**-d_2 (0.25 g, 82%) as a bright yellow oil. ^1H NMR (200 MHz, acetone-d_6): δ 7.32–7.14 (m, aryl), 4.91 (s, C_5H_5), 2.91 (br d, J = 6 Hz, CH_2S), 1.73 (m, CHD), 1.43 (m, FeCHD). $^{13}C\{^1H\}$ NMR (126 MHz, acetone-d_6): δ 218.8 (CO), 138.5 (C_{ipso}), 129.6 and 128.9 ($C_{ortho,meta}$), 126.0 (C_{para}), 86.6 (C_5H_5), 37.8 (t, J_{CD} = 18 Hz, CHD), 37.1 (CH_2S), 1.54 (t, J_{CD} = 19 Hz, FeCHD). IR (hexane): 2010 (s), 1967 (s) cm^{-1}. HRMS calcd for $C_{15}H_{14}D_2FeOS$, $(M - CO)^+$: 302.0396. Found: 302.0398.

***threo*-C$_5$H$_5$(CO)$_2$FeCHDCHDCH$_2$S(CH$_3$)C$_6$H$_5^+$CF$_3$SO$_3^-$ (*threo*-8-*d*$_2$).** Methyl triflate (0.28 mmol) was vacuum-transferred into a solution of $C_5H_5(CO)_2FeCHDCHDCH_2SC_6H_5$ (*threo*-**7**-d_2) (40 mg, 0.121 mmol) in CH_2Cl_2 (1 mL). After 5 h, all volatile material was evaporated under vacuum and the resulting red oil was washed with hexane (5 mL) and dried to give *threo*-**8**-d_2 (50 mg, 83%) as a red oil. ^1H NMR (200 MHz, CD_2Cl_2): δ 7.65–7.95 (m, C_6H_5), 4.77 (s, C_5H_5), 3.67 (m, CH_2S), 3.25 (s, CH_3), 1.65 (m, CHD), 1.31 (m, FeCHD). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ 217.4 (CO), 135.3 (C_{ipso}), 131.7 and 130.8 (C_{ortho}, C_{meta}), 123.4 (C_{para}), 85.9 (C_5H_5), 49.8 (CH_2S), 30.0 (CHD), 25.1 (CH_3), −1.7 (FeCHD). IR (hexane): 2005 (w), 2001 (s), 1950 (s) cm^{-1}.

Pyrolysis of Neat *threo*-8-*d*$_2$. *threo*-**8**-d_2 (50 mg, 0.10 mmol) was heated in an evacuated Schlenk tube at 65 °C for 4.5 h (until no more volatile product was formed). The FT-IR spectrum of the gaseous product showed bands at 2279, 1038, and 846 cm^{-1}, characteristic of *cis*-1,2-dideuteriocyclopropane.[12] No bands for the trans isomer (2271, 1041, 1024, and 849 cm^{-1}) were present. The yield of *cis*-1,2-dideuteriocyclopropane (0.036 mmol, 35%) was determined by measurement of the pressure in a known volume.

Thermolysis of *threo*-8-*d*$_2$ in CD$_2$Cl$_2$. A sealed NMR tube containing *threo*-**8**-d_2 (20 mg) and hexamethylbenzene (5 mg) was prepared. The ratio of hexamethylbenzene (δ 2.13) to *threo*-**8**-d_2 (δ 3.6) was measured by ^1H NMR integration. The thermolysis at 62 °C was monitored by ^1H NMR spectroscopy. After 2 h, *threo*-**8**-d_2 was 50% decomposed; after 4.5 h, *threo*-**8**-d_2 was 90% decomposed and 1,2-dideuteriocyclopropane (**9**) was formed in 33% yield (37% based on unreacted *threo*-**8**-d_2). Thioanisole (δ 2.6) was formed in 78% yield.

Pyrolysis of *threo*-7-*d*$_2$ in Neat CF$_3$SO$_3$CH$_3$. *threo*-**7**-d_2 (120 mg, 0.36 mmol) and methyl triflate (0.32 mmol) were heated in a sealed evacuated tube at 65 °C for 6.5 h total. Volatiles were collected at 1.75, 2.75, 4.25, and 6.5 h. **9** (0.14 mmol, 45%) was isolated by trap to trap distillation on a high-vacuum line. Only *cis*-1,2-dideuteriocyclopropane (*cis*-**9**) was observed by FT-IR: 2279, 1038, 846 cm^{-1}.

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