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Iron Lewis Acid Catalyzed Cyclopropanation Reactions of Ethyl Diazoacetate and Olefins

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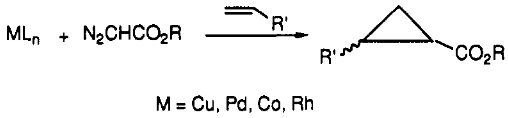
The iron Lewis acid $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(THF)]^+BF_4^-$ (1) was observed to catalyze the decomposition of ethyl diazoacetate (EDA) with olefins to form cyclopropanes. With styrene, EDA gave 68 ± 3% of cyclopropanes with very high cis selectivity (85 ± 3/15 ± 3). To determine the potential utility of the catalyst, reactions with other olefins were investigated. α-Methylstyrene gave 60% of cyclopropane products with a cis/trans ratio of 60/40, and *p*-methylstyrene gave 66% of cyclopropanes with a cis/trans ratio of 60/40. Electron-rich olefins also gave good yields of cyclopropanes with somewhat lower selectivities (ethyl vinyl ether, 68%, cis/trans 45/55; 2-methoxypropene, 66%, *Z*/*E* 55/45). The use of aliphatic olefins such as 2-methyl-2-butene and cyclohexene yielded no cyclopropanation products. Despite the unsuccessful detection of the iron carbene complex $[(\eta^5\text{-}C_5H_5)(CO)_2Fe{=}CH(CO_2Et)]^+$ (**6**) via variable-temperature ^1H NMR, the formation of carbene dimer products (diethyl fumarate and diethyl maleate) and the selectivity in the cyclopropanation reaction has led us to suggest the involvement of **6** as an intermediate for the reaction.

Introduction

Due to the importance of the cyclopropyl ring system in many naturally occurring compounds, much attention has been focused on new methods for the preparation of cyclopropanes.[1] One attractive method is the transition-metal-catalyzed decomposition of diazo compounds in the presence of olefins to yield cyclopropanes (Scheme I). Although this is a well documented procedure,[2] a resurgence has resulted from recent disclosures of many highly effective catalysts.[3] Of all the metals utilized for this transformation, rhodium carboxylates are the most efficient.[4]

The synthetic utility of catalyzed cyclopropanation reactions has been hampered by the relatively low selectivities accompanied with the catalysts used. Though most of the catalytic systems used to date preferentially provide the more stable trans cyclopropanes,[5] Doyle recently reported an increase in trans selectivities using derivatives of rhodium carboxylate catalysts.[6] More recently, Kodadek reported a rhodium porphyrin catalyst that preferentially yields the less stable cis cyclopropanes.[7] Any new catalyst which would increase the selectivities in cyclopropanation reactions could be useful complement to other known catalysts. We have recently observed[8] that the iron Lewis acid **1**, synthesized by a short and simple procedure, is an active catalyst for cyclopropanation reactions. Herein, we wish to discuss our results from the iron Lewis acid **1** catalyzed decomposition of ethyl diazoacetate (EDA) with olefins.

Scheme I



Results

The iron Lewis acid $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(THF)]^+BF_4^-$ (**1**) was synthesized in high yield by protonation of the known methyl complex $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$.[9] Normally, less than 1 equiv of $HBF_4{\cdot}OEt_2$ was used for the protonation reaction, and the acid **1** was recrystallized many times from CH_2Cl_2/THF to ensure that no HBF_4 was left as an impurity to contaminate the reaction. The olefin complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^2\text{-styrene})]^+BF_4^-$ (**2**) was prepared by stirring the Lewis acid **1** with an excess of styene in CH_2Cl_2 for 1 h, which resulted in the formation of a yellow solid. The olefin complex **2** was filtered and characterized by spectroscopic methods.[10]

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(1) (a) Wenkert, E. *Acc. Chem. Res.* **1980,** *13,* 27. (b) Danishefsky, S. *Acc. Chem. Res.* **1979,** *12,* 66. (c) Burke, S. D.; Grieco, P. A. *Org. React. (N.Y.)* **1979,** *26,* 361. (d) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1979,** *26,* 361. (e) Stevens, R. V. *Acc. Chem. Res.* **1977,** *10,* 193. (f) Conia, J. M. *Pure Appl. Chem.* **1975,** *43,* 317. (g) Reissig, H.-U. *Tetrahedron Lett.* **1981,** *22,* 2981. (h) Wenkert, E. *Heterocycles* **1980,** *14,* 1703. (i) Hudlicky, T.; Koszyk, F. F.; Kutchan, T. M.; Sheth, J. P. *J. Org. Chem.* **1980,** *45,* 5020.

(2) (a) Dave, V.; Warnhoff, E. *Org. React. (N.Y.)* **1970,** *18,* 217. (b) Marchand, A. P.; MacBrockway, N. *Chem. Rev.* **1974,** *74,* 431. (c) Doyle, M. P. In *Catalysis of Organic Reactions*; Augustine, R. L., Ed.; Marcel Dekker: New York, 1985; Chapter 4.

(3) (a) Doyle, M. P.; Van Leusen, D.; Tamblyn, W. H. *Synthesis* **1981,** 787. (b) Doyle, M. P.; Tamblyn, W. H.; Buhro, W. E.; Dorow, R. L. *Tetrahedron Lett.* **1981,** *22,* 1783. (c) Hubert, A. J.; Noels, A. F.: Anciaux, A. J.; Teyssie, P. *Synthesis* **1976,** 600. (d) Anciaux, A. J.; Hubert, A. J.; Noels, A. F.; Petiniot, N.; Teyssie, P. *J. Org. Chem.* **1980,** *45,* 695.

(4) (a) Doyle, M. P. *Chem. Rev.* **1986,** *86,* 919. (b) Doyle, M. P. *Acc. Chem. Res.* **1986,** *19,* 348.

(5) There were previously three examples of a slight cis preference when rhodium porphyrins were used as catalysts: (a) Callot, H. J.; Piechocki, C. *Tetrahedron Lett.* **1980,** *21,* 3489. (b) Callot, H. J.; Metz, F.; Piechocki, C. *Tetrahedron* **1982,** *38,* 2365. (c) Holland, D.; Milner, D. J. *J. Chem. Res., Synop.* **1979,** 317; *J. Chem. Res., Miniprint* **1979,** 3734.

(6) (a) Doyle, M. P.; Loh, K.-L.; DeVries, K. M.; Chinn, M. S. *Tetrahedron Lett.* **1987,** *28,* 833. (b) Doyle, M. P.; Bagheri, V.; Wandless, T. J.; Harn, N. K.; Brinker, D. A.; Eagle, C. T.; Loh, K. L. *J. Am. Chem. Soc.* **1990,** *112,* 1906.

(7) (a) Kodadek, T.; Brown, K. C.; O'Malley, S.; Maxwell, J. L. *Organometallics* **1992,** *11,* 645. (b) Kodadek, T.; Bartley, D. W.; Brown, D. C.; Maxwell, J. L. *Science* **1992,** *256,* 1544. (c) Brown, K. C.; Kodadek, T. *J. Am. Chem. Soc.* **1992,** *114,* 8336. (d) O'Malley, S.; Kodadek, T. *Organometallics* **1992,** *11,* 2299.

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Table I. Isolated Yields of Cyclopropanes from Reactions of Ethyl Diazoacetate with Styrene Catalyzed by 1

run no.	amt of styrene (equiv)	amt of catalyst[a] (mol %)	temp (°C)	time (h)	yield[b] (%)	cis/trans[c]
1	1	10	40	24	11	80/20
2,3	5	10	40	12	68 ± 3	85 ± 3/15 ± 3
4	5	10	room temp	12	40	84/16
5	5	10	40	24	65	80/20
6	10	10	40	12	40	90/10
7	50	10	40	12	16	90/10
8	5	5	40	12	30	84/16
9	5	25	40	12	71	85/15
10	5	10	4	24	10	97/3
11	5	10	−78	24	0	
12	5	25	−78	24	0	
13	5	0	4	24	0	
14	5	0	room temp	24	0	
15	5	0	40	24	0	
16[d]	5	10	40	12	65	84/16
17[e]	5	10	40	12	0	

[a] Based on EDA. [b] Yields were based on EDA. [c] Ratios were determined by GC. [d] Reaction was performed with 10 mol % of 2,6-di-*tert*-butylpyridine. [e] Reaction was performed with THF as solvent.

Initially, the Lewis acid was treated with EDA at 40 °C for 12 h. Isolation of the reaction mixture gave 98% of a mixture of diethyl fumarate and diethyl maleate in a 1/5 ratio. In the absence of the catalyst no diethyl fumarate or diethyl maleate formation was observed; only the starting EDA was isolated from the reaction.

Next, the reactions were performed with the catalyst 1 and EDA in the presence of styrene. These results are summarized in Table I. The first set of reactions were run to determine the optimal conditions for the reaction (mole percent of catalyst, equivalents of styrene, and temperature). From the results of runs 1–12, 10 mol % catalyst at 40 °C with 5 equiv of styrene seems to be the optimal conditions for the iron-catalyzed decomposition of EDA with styrene. The yield of cyclopropanes under these conditions is 68 ± 3% (runs 2 and 3). The interesting feature of these results is the preference for formation of the less stable cis isomer. It should be noted that all of the reactions using styrene yielded a preference for the cis isomer over the more stable trans isomer. At lower temperatures, the selectivity of the cyclopropanation was improved; for example, at 4 °C the cis/trans ratio was 97/3 (run 10). The major drawback to the enhanced selectivity is the disappointing cyclopropane yield (10%). At −78 °C there was no cyclopropane formation even with 25 mol % of catalyst; unreacted EDA was isolated from the reaction (runs 11 and 12). Data from Table I show no comparable difference for the yields if the reaction was run at 12 or 24 h (compare runs 2 and 3 with run 5); therefore, runs were subsequently conducted at 12 h.

The yield of the reaction is also dependent on the olefin concentration. With 1 equiv of styrene (run 1), only 11% of cyclopropane was obtained. A large excess of styrene (10 and 50 equiv) did not improve the yield of the product (runs 6 and 7). To further verify the catalytic activity of the Lewis acid, control reactions were run at three different temperatures, but each of these reactions yielded no cyclopropane products (runs 13–15). An additional reaction was run with the trapping agent 2,6-di-*tert*-butylpyridine (run 16). The use of this trapping agent was shown by Hersh to trap H^+ impurity which may compete with the iron for catalysis of the reaction.[11] No appreciable difference in the yield or the selectivity was observed using this trapping agent in the reaction mixture, further establishing that the iron species was the active catalyst.

Table II. Isolated Yields of Cyclopropanes from Reactions of Ethyl Diazoacetate with Other Olefins Catalyzed by 1[a]

olefin	amt of catalyst (mol %)	time (h)	yield[b] (%)	cis/trans[c] (*Z*/*E*)
α-methylstyrene	10	12	60	60/40
p-methylstyrene	10	12	66	60/40
2-methoxypropene	10	12	66	55/45
EVE	10	4	66	45/55
cyclohexene	10	12	0	
2-methyl-2-butene[d]	10	12	0	

[a] Five equivalents of olefin was used unless otherwise stated; the temperature was 40 °C. [b] Yields based upon ethyl diazoacetate. [c] Ratios were determined by GC. Cis (*Z*) and trans (*E*) isomers from the reaction mixture were isolated by column chromatography and identified by comparing their ^{1}H NMR spectra with data reported[25] and were used as authentic samples for GC. [d] Ten equivalents was used.

To determine the potential utility of the catalyst, other olefins were investigated for the catalytic cyclopropanation reactions. The results of these reactions are summarized in Table II. α-Methylstyrene yielded 60% of cyclopropane products with a cis/trans ratio of 60/40. *p*-Methylstyrene yielded 66% of cyclopropanes with a cis/trans ratio of 60/40. The use of nonaromatic olefins also gave good yields of cyclopropanes. 2-Methoxypropene yielded 66% cyclopropanes with a *Z*/*E* ratio of 55/45. Ethyl vinyl ether (EVE) yielded 68% of cyclopropanes with a cis/trans ratio of 45/55. Simple aliphatic olefins were also employed with disappointing results. For example, 2-methyl-2-butene or cyclohexene gave no cyclopropane products. Although these aliphatic olefins yielded no cyclopropanes, carbene dimers, diethyl fumarate, and diethyl maleate were isolated in >98% yield from each of these reactions.

Discussion

Despite much attention and speculation, many aspects of metal-catalyzed cyclopropanation reactions remain unclear. Although recent advances have implicated a transient metal carbene species as the active intermediate,[4] the involvement of metal carbenes has not yet been proven due to their high reactivity. The discovery of stable metal carbene complexes and their use in catalytic cyclopropanation has provided additional support for a transient metal carbene intermediate.[12] Despite the scarcity of solid evidence for the intermediacy of metal carbenes, Doyle has provided substantial indirect evidence for the intermediacy of metal carbenes in the catalytic cyclopropanation reactions involving $Rh_2(OAc)_4$. He has demonstrated a linear correlation of both reactivities and stereoselectivities for $Rh_2(OAc)_4$-catalyzed reactions of phenyldiazomethane with a variety of olefins and the stoichiometric reaction of these same olefins with the

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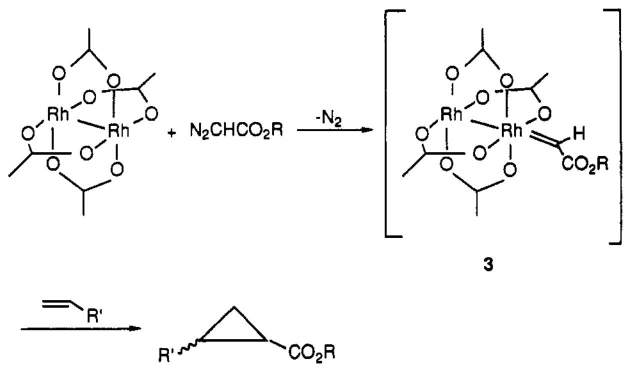
(10) Cutler, A.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.: Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1975**, *97*, 3495.

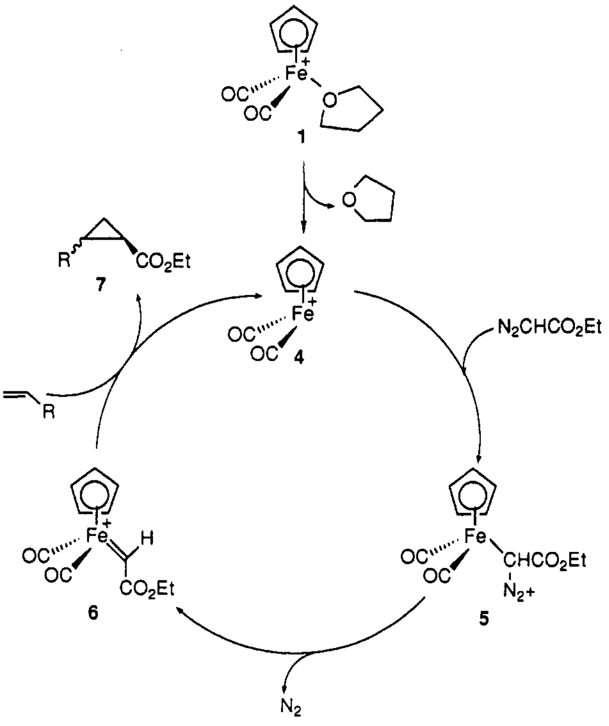
(11) Hersh, W. H.; Honeychuck, R. V.; Puckett, C. L.; Bonnesen, P. V. *J. Am. Chem. Soc.* **1989**, *111*, 6070.

(12) (a) Casey, C. P. In *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1985; Vol. 3, Chapter 4. (b) Dotz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (c) Brookhart, M.; Studabaker, W. B.; Husk, G. R. *Organometallics* **1985**, *4*, 943. (d) Kuo, G.-H.; Helquist, P.; Kerber, R. C. *Organometallics* **1984**, *3*, 806. (e) Casey, C. P.; Miles, W. H. *Organometallics* **1984**, *3*, 808.

Scheme II



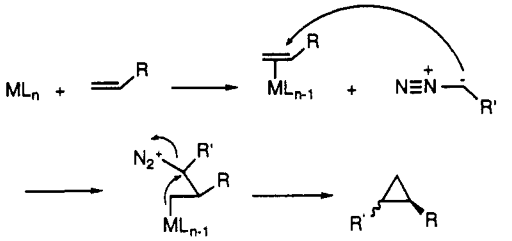
Scheme III

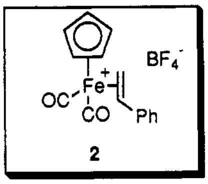


isolated tungsten carbene complex $(CO)_5W{=}CHPh$.[13] These observations have led Doyle to suggest involvement of the transient metal carbene **3** as the intermediate for the cyclopropanation reaction (Scheme II).[14]

We have studied the reaction of ethyl diazoacetate with the Lewis acid by variable-temperature ^1H NMR spectroscopy to observe any characteristic absorptions of the iron carbene complex **6** (Scheme III).[15] We observed no characteristic absorption for **6**. However, the discovery of stable iron carbene complexes and their use in stoichiometric cyclopropanation reactions with olefins strongly implicate a transient iron carbene intermediate in catalytic cyclopropanation.[16] Moreover, formation of the carbene dimers diethyl fumarate/diethyl maleate[17] and observation of cis selectivity in the cyclopropane products[18] have led us to suggest that the transient iron carbene complex **6** is an intermediate in our catalytic cyclopropanation reactions.

Scheme IV





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On the basis of our findings and experimental observations we propose a plausible catalytic cycle for the formation of cyclopropanes from the Lewis acid **1**, EDA, and olefin (Scheme III). In this proposed cycle, the iron Lewis acid **1** dissociates THF to form the active catalyst **4**. This catalyst then reacts with EDA to form the iron complex **5**,[19] followed by extrusion of nitrogen to give the highly reactive iron carbene **6**. The carbene **6** then reacts with the olefin to produce cyclopropanes **7** and regenerate the active catalyst **4**. If this mechanism is operative, then the dissociation of THF is an important step for the catalytic cycle. The absence of cyclopropane and carbene dimer formation using THF as a solvent (run 17, Table I) strongly suggests an initial dissociation of the THF ligand to form **4** as a key step in the catalytic cycle. Further, when the Lewis acid **1** was treated with EDA at −78 °C in CD_2Cl_2, we were unable to detect any free THF by ^1H NMR. The lack of THF dissociation may account for no cyclopropane formation at −78 °C. The detection of little or no cyclopropane products at lower reaction temperatues may also be attributed to the difficulty of nitrogen expulsion from complex **5** to form the carbene complex **6**. Thus, a higher reaction temperature (40 °C) and a poor coordinating solvent such as CH_2Cl_2 is needed for optimal cyclopropane formation.

Due to the propensity of the iron Lewis acid to form π complexes in the presence of an olefin,[10,20] the mechanism proposed by Wulfmann and others[21] for the metal-catalyzed cyclopropanations is also a possibility. This mechanism involves nucleophilic attack of the diazo compound on a metal alkene π-complex (Scheme IV). The mechanism was discounted since increased olefin (styrene)

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[13] Doyle, M. P.; Griffin, J. H.; Dorow, R. L.; Bagheri, V. *Organometallics* **1984**, *3*, 53.

[14] (a) Doyle, M. P.; Dorow, R. L.; Buhro, W. E.; Griffin, J. H.; Tamblyn, W. H.; Trudell, M. L. *Organometallics* **1984**, *3*, 44. (b) Anciaux, A. J.; Demonceau, A.; Noels, A. F.; Warin, R.; Hubert, A. J.; Teyssie, P. *Tetrahedron* **1983**, *39*, 2169. (d) Also see refs 3d, 4, and 13.

[15] The α-hydrogen of a known iron carbene, $Cp(CO)_2Fe^+{=}CHPh$, exhibited absorption at 16.86 ppm: Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099.

[16] Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411.

[17] (a) Shankar, B. K. R.; Shechter, H. *Tetrahedron Lett.* **1982**, *23*, 2277. (b) Also see ref 4a.

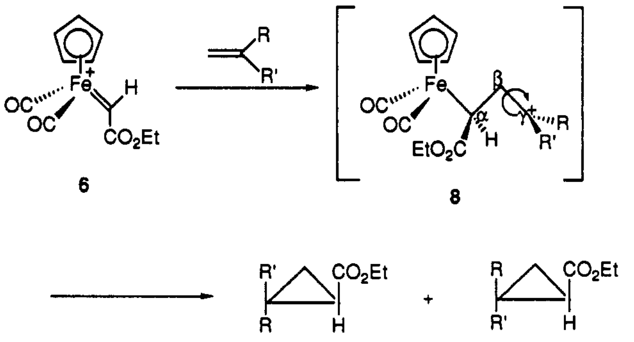
[18] (a) Vargas, R. M.; Theys, R. D.; Hossain, M. M. *J. Am. Chem. Soc.* **1992**, *114*, 777. (b) Also see ref 16.

[19] η^1(C) is the favored mode of bonding of the diazo compound to the metal for expulsion of nitrogen to form the metal carbene: (a) Nakamura, A.; Konishi, A.; Tsujitani, R.; Kudo, M.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3449. (b) Hillhouse, G. L.; Haymore, B. L. *J. Am. Chem. Soc.* **1982**, *104*, 1537.

[20] Reger, D. L.; Coleman, C. *J. Organomet. Chem.* **1977**, *131*, 153.

[21] (a) Wulfman, D. S.; McDaniel, R. S.; Peace, B. W. *Tetrahedron* **1976**, *32*, 1241. (b) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 3300. (c) Anciaux, A. J.; Hubert, J. A.; Noels, A. F.; Petiniot, N.; Teyssie, P. *Tetrahedron Lett.* **1973**, 2233. (d) Nakamura, A.; Koyama, T.; Otsuka, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 593. (e) Nakamura, A.; Konishi, A.; Tsujitani, R.; Kudo, M.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3449.

Scheme V



R	R'	Cis(Z)	Trans(E)
a, H	C_6H_5	85	15
b, H	p-$CH_3C_6H_4$	60	40
c, CH_3	OCH_3	55	45
d, H	OC_2H_5	45	55

concentration decreased the yield of cyclopropanes. At high styrene concentration, formation of olefin complex **2** would be the major pathway, which inhibits the catalytic cycle. To further support our conclusion, we carried out a reaction of EDA with styrene at 40 °C in the presence of 10 mol % of olefin complex **2** but observed no cyclopropane formation. This observation convinced us that the Wulfmann mechanism was not a possibility for these catalytic cyclopropanation reactions.

Since questions surround the mechanism of this reaction, extensive studies of olefin reactivities have not been reported. Despite this lack of data, relative reactivities of olefins are dependent upon the metal catalyst used. Given the high electrophilic nature of the proposed iron carbene species, electron-rich olefins would be expected to react preferentially with the iron carbene intermediate. This idea can be illustrated by comparing the reactivities of ethyl vinyl ether (EVE) and styrene. EVE only needs 4 h to yield optimum cyclopropane products, whereas styrene requires 12 h. The lack of cyclopropanation reactions using bulky olefins such as 2-methyl-2-butene may be linked to steric congestion around the carbene carbon due to the presence of the Cp ligand and the ester group in the carbene complex **6**. As a result, the highly reactive carbene complex **6** dimerizes or reacts with EDA to form diethyl fumarate and diethyl maleate before it reacts with the sterically hindered olefin to form cyclopropanes. The steric and electronic arguments may also explain the failure of cyclohexene to react with the iron carbene in producing cyclopropanes.

Although this is the first example of iron-catalyzed cyclopropanation reactions involving an iron carbene complex,[22] the mechanism of the formation of cyclopropanes from isolable iron carbenes has been thoroughly investigated by Brookhart and Casey.[23] Our high cis selectivity with styrene and extensive loss of stereochemistry with p-methylstyrene, 2-methoxypropene, and EVE is consistent with the mechanism of cyclopropanation proposed by Brookhart (Scheme V). The reaction of iron carbene with styrene leads to the formation of a 5.6/1 mxture of *cis*/*trans*-1-phenyl-2-carboxycyclopropane. This indicates the presence of the short-lived γ-carbocation intermediate **8a**, which collapses very rapidly before any significant rotation about the C_β–C_γ bond. For the more electron-rich olefin p-methylstyrene, the loss of stereochemistry (1.5/1 of cis/trans) indicates stabilization of the γ-carbocation intermediate **8b** by an electron-releasing substituent ($-CH_3$) and some rotation about the C_β–C_γ bond prior to cyclopropane formation. For other more electron-rich olefins such as 2-methoxypropene (1.2/1 of *Z*/*E*) and EVE (0.8/1 of cis/trans) stabilization of the γ-carbocation by oxygen lone-pair-electron participation[24] is illustrated by the extensive loss of stereochemistry.

In summary, the actual mechanism of iron Lewis acid catalyzed cyclopropanation reactions has not yet been fully established. Our results coupled with the indirect evidence cited demonstrate that the proposed catalytic cycle is a plausible route for the catalytic decomposition of EDA with olefins employing an iron Lewis acid. The discovery of iron Lewis acid catalyzed cyclopropanation is important in many regards. The iron Lewis acid is relatively inexpensive, is readily synthesized, and provides the first example of catalytic cyclopropanation involving an iron carbene. In addition, this is the first example of an iron carbene complex that produces functionalized cyclopropanes. These results raise the possibility of synthesizing an iron carbene complex with an electron-withdrawing group at a C_α position. Work is currently underway for the development of more active iron Lewis acid catalysts.

Experimental Section

General Considerations. ^1H NMR spectra were recorded on a Bruker 250-MHz spectrometer. Infrared spectra were measured on a Nicolet FTIR spectrometer. A Varian Aerograph GC, Series 1200, with a 5% SE-52, 80/100 column (8 ft × $^1/_8$ in.) was used to analyze the isomeric purity of the cyclopropanes.

All organometallic operations were performed under a dry nitrogen atmosphere using standard Schlenk techniques. All of the glass flasks were flamed under vacuum and filled with nitrogen prior to use. Column chromatography was performed using silica gel (40–140 mesh). Separation of the cyclopropane isomers was done by flash column chromatography. HPLC reagent grade CH_2Cl_2 was distilled under nitrogen from P_2O_5. HPLC reagent grade pentane was distilled from sodium under an inert atmosphere immediately prior to use. Reagent grade tetrahydrofuran was freshly distilled under a nitrogen atmosphere from sodium benzophenone ketyl. Reagent grade hexane and ethyl acetate were used directly. The iron Lewis acid $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(THF)]^+BF_4^-$ (**1**) and the olefin complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^2\text{-styrene})]^+BF_4^-$ (**2**) were prepared by literature procedures[9,10] and purities established by IR and NMR spectroscopy. Ethyl diazoacetate, styrene, α-methylstyrene, p-methylstyrene, cyclohexene, and 2-methyl-2-butene were purchased from Aldrich Chemical Co. and used directly. Ethyl vinyl ether was also purchased from Aldrich Chemical Co. and distilled prior to use. 2-Methoxypropene was purchased from Lancaster Chemical Co. and used directly.

Catalytic Cyclopropanations. All reactions were carried out in the same manner except as noted in the tables. In a typical procedure, the Lewis acid **1** (0.0308 g, 0.00917 mmol) was dissolved in 5 mL of CH_2Cl_2. To this stirred solution was added styrene (0.477 g, 0.458 mmol) followed by ethyl diazoacetate (0.105 g, 0.0917 mmol) at ambient temperature. This solution was then placed in an oil bath, maintained at 40 °C, and stirred for 12 h. The reaction mixture was worked up by concentration using rotary evaporation to yield an oil. The residual oil was then chromatographed on a column of silica gel and eluted with 1% ethyl

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[22] All known cyclopropanation reactions involving iron carbenes to date are stoichiometric reactions.[16]

[23] (a) Casey, C. P.; Vosejpka Smith, L. J. *Organometallics* **1992**, *11*, 738. (b) Brookhart, M.; Liu, Y. *J. Am. Chem. Soc.* **1991**, *113*, 939. (c) Also see ref 16.

[24] Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, 3rd ed.; Plenum Press: New York, 1990; p 276.

acetate/hexane mixture to yield excess starting material (styrene), a mixture of cyclopropane isomers, and dimethyl fumarate and diethyl maleate. The isomeric purity of the resulting cyclopropane isomers was determined by GC analysis and by comparison to known NMR spectral data.[25]

Reaction of Iron Styrene Complex 7 with Ethyl Diazoacetate and Styrene. The iron styrene complex 7 (0.0447 g, 0.122 mmol) was placed in 5 mL of CH_2Cl_2. To this solution was added, styrene (0.635 g, 6.1 mmol), along with ethyl diazoacetate (0.139 g, 1.22 mmol). The resultant solution was placed in an oil bath at 40 °C and stirred for 12 h. The usual workup gave no cyclopropanes or carbene dimers; only the starting EDA and styrene complex were isolated.

Reaction of Lewis Acid with EDA: A ^{1}H NMR Study. A sample of EDA (0.034 g, 0.030 mmol) was added to the solution of Lewis acid 1 (0.02 g, 0.060 mmol) in degassed CD_2Cl_2 (0.6 mL) in an NMR tube at −78 °C. The NMR tube was cooled in liquid N_2 and sealed under vacuum. The reaction was monitored at −78 °C by variable-temperature ^{1}H NMR every 20 min for 4 h, but no characteristic absorption at 15–50 ppm for the α-hydrogen of the carbene complex 6 was observed.[15] At this temperature no absorptions due to free THF were observed. By slow warming to room temperature, formation of carbene dimers (diethyl fumarate and diethyl maleate) and also free THF were observed, but no characteristic absorption of iron carbene complex 6.

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[25] (a) Strausz, O. P.; Kennepohl, G. J. A.; Garneau, F. X.; Do Minh, T.; Kim, B.; Valenty, S.; Skell, P. S. *J. Am. Chem. Soc.* **1974**, *96*, 5723. (b) Nakamura, A.; Konishi, A.; Tatsuno, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3443. (c) Also see refs 19, 3, and 14.