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Catalytic Olefin Cyclopropanation Using μ-Oxo−bis[(salen)iron(III)] Complexes

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A series of μ-oxo−bis[(salen)iron(III)] complexes was prepared from the reaction of the corresponding salen ligands with $FeCl_3 \cdot 6H_2O$ in the presence of NEt_3, and characterized by elemental analysis, infrared spectroscopy, and mass spectrometry. These air-stable complexes catalyzed the cyclopropanation of olefins with ethyl diazoacetate in good yields. The catalytic activity of these μ-oxo dimers, in the cyclopropanation of styrene, was examined as a function of the diamine backbone and the substituents in the 3,3′- and 5,5′-positions of the phenyl rings on the ligands. Solvent variation, catalyst loading, and styrene concentration were investigated to determine the optimal reaction conditions. The complex [Fe(3,3′,5,5′-^{t}Bu$_4$-salen)]$_2$O (**1d**) was identified as the most efficient catalyst in the series, which successfully catalyzed the cyclopropanation not only of styrene but also of less reactive substrates such as α-methylstyrene, α-(trifluoromethyl)styrene, 1,1-diphenylethylene, methylenecyclohexane, and *n*-butyl vinyl ether and internal olefins such as *trans*- and *cis*-β-methylstyrene and ethylidenecyclohexane.

Introduction

The great importance of the cyclopropyl moiety in chemistry and biochemistry can be gauged by its frequent occurrence in natural products, insecticides, modern pharmaceuticals, and critical synthetic intermediates.[1−3] Synthetically, cyclopropanes can best be made from the metal-mediated cycloaddition of a carbene fragment to an olefin in the so-called olefin cyclopropanation reaction. Metal complexes which facilitate such reactions range from stoichiometric metal carbene transfer reagents[4] to catalysts.[2,5] Iron is rather unique among the transition metals capable of cyclopropanation, because iron complexes have been used extensively in both stoichiometric[4,6−15] as well as catalytic[16−19] reactions.

Hossain and co-workers reported the use of [CpFe(CO)$_2$(THF)](BF$_4$) as the catalyst in the cyclopropanation of a variety of olefins, with either ethyl diazoacetate (EDA) or phenyl diazoacetate as the carbene source, to synthesize cyclopropanes in good yields and with high cis selectivity.[16,20,21] Optimal conditions for these reactions included a nitrogen atmosphere with dichloromethane as the solvent at 40 °C. In 1995, Woo, Kodadek, and co-workers reported the use of several iron(II) and iron(III) porphyrins as cyclopropanation catalysts to yield mainly *trans*-cyclopropanes from various terminal alkenes and EDA.[17] Before most of the iron(III) porphyrins could be used as efficient catalysts, they had to be reduced to iron(II), either by the use of cobaltocene[17] or by heating with EDA, which can act as a mild reducing agent.[22] An exception to this was chloro[*meso*-tetrakis(pentafluorophenyl)porphyrin]iron(III), which functioned as a catalyst at room temperature. Although iron(III) porphyrins were air-stable, the reduced iron(II) species generated in situ were not and had to be handled under argon. Some other iron(II) porphyrins and iron(II) tetramethyldibenzotetraaza[14]annulene (tmtaa) have been used as cyclopropanation catalysts as well.[18] This latter study also reported the ability of a putative Fe(Saldach) complex

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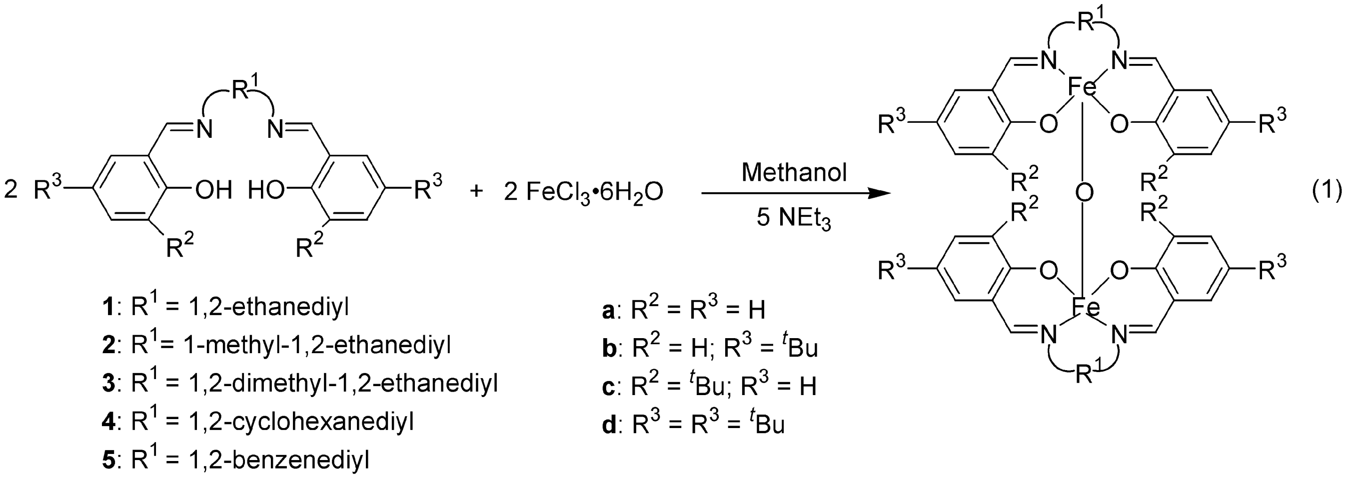
Scheme 1



(Saldach = dianion of *trans*-1,2-cyclohexanediamino-*N*,*N′*-salicylidene) to catalyze the cyclopropanation of styrene, albeit with less efficiency (the combined cyclopropane and carbene dimer yields were less than 30% with EDA as the carbene source). Iron(III) and iron(IV) corroles, including binuclear (*μ*-oxo)iron(IV) corrole, were also shown to catalyze various cyclopropanation reactions.[19,23] Usually cyclopropanation reactions with iron-based catalysts had to be carried out under an inert atmosphere.

Recent work in our laboratory has shown that ruthenium(II) salen complexes are very efficient and selective cyclopropanation catalysts.[24] This discovery prompted us to investigate the use of (salen)iron complexes[25] as an inexpensive alternative metal compound for cyclopropanation catalysis. On the basis of precedents in the iron porphyrin literature[17,18] and similar tetradentate nature of both porphyrin and salen ligands, iron(II) salen complexes were reasonable targets as active cyclopropanation catalysts. However, since iron(II) salen complexes are known to be readily contaminated with (*μ*-oxo)iron(III) dimers (due to their penchant to undergo oxidation in air to give the latter species),[26−28] we decided instead to explore the (*μ*-oxo)iron(III) dimers as catalyst precursors. On the basis of the aforementioned work by Kochi, Woo, Kodadek, and co-workers, we hypothesized that EDA can reduce these Fe(III) precursor complexes to generate the active (salen)iron(II) cyclopropanation catalyst in situ at high temperature. In this paper, we report the use of a series of air-stable *μ*-oxo−bis[(salen)iron(III)] complexes as effective EDA-based cyclopropanation catalysts. Unlike other iron-based cyclopropanation catalysis, our system does not require an inert atmosphere during the reaction. Further, in contrast to many existing catalytic systems where olefin formation from the dimerization of the diazo ester carbene source is a major side reaction, this nonproductive coupling was not observed for our system when terminal olefins were used. We were also able to successfully cyclopropanate internal olefins with EDA as the carbene source. Hence, the use of an inexpensive, abundant metal such as iron, the ease of synthesis of *μ*-oxo−bis[(salen)iron(III)] catalysts, and the facile tunability of the salen ligand environment make these cyclopropanation catalysts potentially quite attractive to synthetic chemists.

Results and Discussion

μ-Oxo−bis[(salen)iron(III)] compounds were prepared in moderate to excellent yields from a variety of salen ligands by following the literature procedure for the synthesis of [Fe(3,3′,5,5′-^{t}Bu$_4$Salcen)]$_2$O (Salcen = 1,2-cyclohexanediamino-*N*,*N′*-bis(salicylidene))[29] (Scheme 1). Refluxing the reaction mixture and increasing the reaction time did not affect the yields significantly. However, it was found that the use of Mg(OMe)$_2$-dried and distilled methanol was important, as unpurified methanol often led to the formation of products, which gave irreproducible cyclopropanation results. These *μ*-oxo−bis[(salen)iron(III)] complexes were characterized by mass spectrometry, elemental analysis, and infrared spectroscopy. The asymmetric Fe−O−Fe stretching band in the IR spectrum appears roughly in the 820−860 cm^{-1} region, as has been observed previously.[28,30]

Optimization of the cyclopropanation reaction was carried out using styrene as the test substrate and EDA as the carbene source under reflux conditions (Scheme 2). The EDA addition time was varied to find the optimal rate of addition to the reaction mixture (Table 1). The reaction shown in Scheme 2 was carried out in distilled toluene, and the EDA−undecane solution (in toluene) was added slowly via a syringe pump (except for Table 1, entry 1). We observed that the slow addition of the EDA−undecane solution over 30 min gave the best result, about an 8% increase in yield relative to that for a one-shot addition (Table 1; cf. entries 1 and 3). Hence, in all subsequent reactions a slow addition time of 30 min was used.

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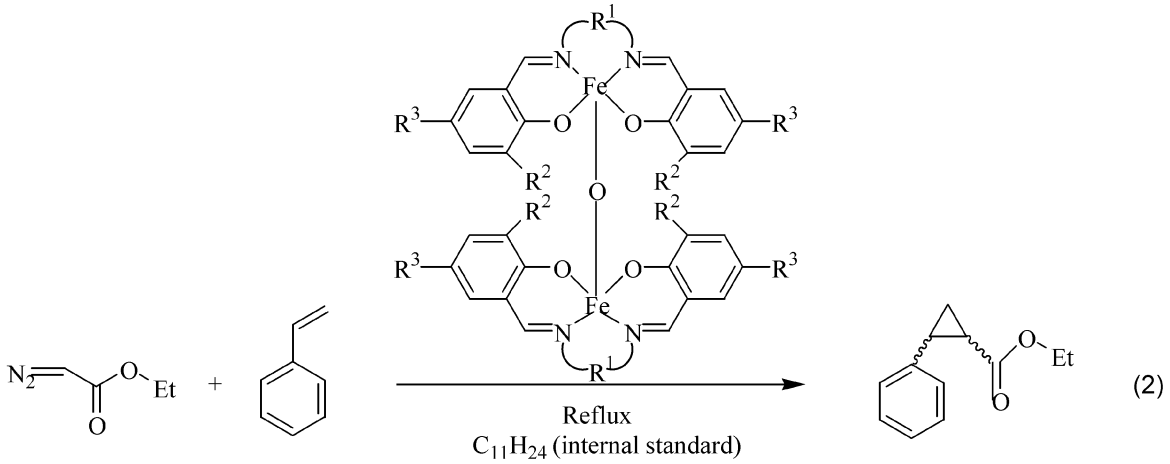
Scheme 2



1: R^1 = 1,2-ethanediyl
2: R^1 = 1-methyl-1,2-ethanediyl
3: R^1 = 1,2-dimethyl-1,2-ethanediyl
4: R^1 = 1,2-cyclohexanediyl
5: R^1 = 1,2-benzenediyl

a: $R^2 = R^3 = H$
b: $R^2 = H$; $R^3 = {}^t$Bu
c: $R^2 = {}^t$Bu; $R^3 = H$
d: $R^2 = R^3 = {}^t$Bu

Table 1. Effect of Varying EDA−Undecane Solution Addition Time Using [Fe(3,3′,5,5′-^{t}Bu$_4$Salen)]$_2$O as the Catalyst[a]

entry	addition time (min)[b]	yield (%)[c]	cis:trans
1	0	66	1:1.8
2	15	71	1:1.8
3	30	74	1:1.8
4	60	69	1:1.8
5	80	69	1:1.6

[a] Conditions: [Fe(3,3′,5,5′-^{t}Bu$_4$salen)]$_2$O as catalyst (5 mol %), EDA (1 equiv), styrene (5 equiv), undecane (1 equiv) as the internal standard, in refluxing distilled toluene for 20 h. [b] Addition time of EDA−undecane solution to the reaction mixture. [c] Determined by GC analysis.

Table 2. Solvent Effect on Cyclopropanation Using [Fe(3,3′,5,5′-^{t}Bu$_4$Salen)]$_2$O as the Catalyst[a]

		with cat.[b]		without cat.	
entry	solvent	yield (%)[c]	cis:trans	yield (%)[c]	cis:trans
1	benzene[d]	85(8)[e]	1:2.5	25(1)	1:1.8
2	toluene	74(3)	1:2.2	47(4)	1:1.7
3	THF	20(4)	1:2.4	8(0)	1:2.1
4	hexanes	53(0)	1:2.8	11(0)	1:1.7
5	methanol	7(1)	1:2.5	0	0
6	ethanol[d]	47(2)	1:2.8	4(0)	1:2

[a] Conditions: EDA (1 equiv), styrene (5 equiv), undecane (1 equiv) as the internal standard, under reflux conditions for 15 h. [b] Catalyst (5 mol %). [c] Determined by GC analysis. [d] Not distilled. [e] Values in parentheses are standard deviations based on a minimum of two runs.

The reaction shown in Scheme 2 was carried out in various solvents to determine the ideal medium (Table 2). With [Fe(3,3′,5,5′-^{t}Bu$_4$salen)]$_2$O (**1d**) as the catalyst, it was found that polar or protic solvents such as THF and methanol did not give high cyclopropane yields (Table 2, entries 3 and 5). The low yields are most likely due to the ligation of the coordinating solvent to the metal center, which in turn could decrease catalytic activity. Although ethanol was a better reaction solvent than methanol (Table 2, cf. entries 5 and 6), probably due to its higher boiling point, ether formation (from O−H insertion with EDA)[3] became a competitive side reaction. Interestingly, no reaction was observed when either dichloromethane or tetrachloroethane was used as the solvent. This is in stark contrast to the Woo−Kodadek iron porphyrin catalyst system, where dichloromethane is the solvent of choice.[17] Benzene and toluene were both effective solvents, even though the background thermal cyclopropanation rate[31] increased significantly with rising reaction temperature (refluxing in toluene for 15 h in the absence of the catalyst lead to yields of up to 47%) (Table 2, entry 2). However, since the background reaction in refluxing benzene was lower than that for refluxing toluene, all subsequent reactions were carried out in refluxing benzene. In general, our catalytic reaction gave a modestly higher trans:cis ratio than the background thermal reaction. Our moderate trans:cis selectivity is consistent with that observed by Hamaker et al. for Fe(II) porphyrin catalysts, where higher temperature often leads to a decrease in the diastereoselective ratio.[18] Since our catalytic reactions were performed at moderately high temperatures in refluxing solvents, varying the nature of the solvent did not have a significant effect on the diastereomeric ratios of the cyclopropanation products.

Varying catalyst loading relative to EDA did not significantly affect the product yield over a 16-h period (Table 3), although 5 mol % of the catalyst was moderately better than the lower loadings (Table 3, entry 3). Increasing the styrene concentration did speed up the

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(31) EDA is known to thermally add to ethylenic linkages to form five-membered pyrazoline carboxylic esters via 1,3-dipolar cycloadditions. (See: Drake, N. L.; Sweeney, T. R. *J. Org. Chem.* **1946**, *11*, 67−74. *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; Vol. 1.) At higher temperatures, these pyrazoline rings lose nitrogen to form cyclopropanes. The high yields of some of the thermal background reactions could be attributed to this process (Table 2, entries 1 and 2). The different yields of the thermal background reactions could be explained by the different boiling points of the solvents used under reflux conditions (Table 2).

Table 3. Effect of Catalyst Loading on Reaction Rate and Yield Using $[Fe(3,3',5,5'\text{-}^tBu_4Salen)]_2O$[a]

		4 h		8 h		12 h		16 h	
entry	cat. (mol %)	yield (%)[b]	cis:trans	yield (%)	cis:trans	yield (%)	cis:trans	yield (%)	cis:trans
1	0.5	34(3)[c]	1:2.4	67(4)	1:2.5	80(1)	1:2.5	80(0)	1:2.5
2	1	39(6)	1:2.5	67(5)	1:2.6	81(4)	1:2.5	83(1)	1:2.5
3	5	40(10)	1:2.4	72(5)	1:2.5	85(8)	1:2.5	85(6)	1:2.5
4	none	9(0)	1:1.9	17(1)	1:1.9	25(1)	1:2.0	28(1)	1:1.9

[a] Conditions: $[Fe(3,3',5,5'\text{-}^tBu_4salen)]_2O$ as catalyst, EDA (1 equiv), styrene (5 equiv), undecane (1 equiv) as the internal standard, in refluxing undistilled benzene. [b] Determined by GC analysis. [c] Values in parentheses are standard deviations in the yields based on at least two runs.

catalyzed reaction, but the background activity was also much higher (Table 4).[32] Thus, subsequent reactions were carried out under the optimal conditions of 5 molar equiv of the olefin and 5 mol % catalyst loading relative to EDA.

Increasing the steric bulk of the diamine backbone only had a modest effect on the reaction rate and the cis:trans ratio (Table 5). Catalyst **1d**, with the least sterically hindered ethanediyl backbone, reacted the fastest (85% yield for styrene cyclopropanation after 15 h), while catalyst **3d** with the bulkier 1,2-dimethyl-1,2-ethanediyl backbone reacted the slowest (73% yield for styrene cyclopropanation after 15 h). Catalyst **5d** with the rigid 1,2-benzyldiyl backbone gave better yield (Table 5, entry 5) than catalysts **3d** and **4d**, which have less rigid backbones. Generally, having bulky *tert*-butyl groups at the 3,3′- and 5,5′-positions of the ligand phenyl rings led to higher yields (Table 6). Further, the presence of bulky substituents at the 3- and 3′-positions was more influential in increasing the reaction yield than those at the 5- and 5′-positions (Table 6, entries 2 and 3), although this effect was minor.[33]

We found that the reaction shown in Scheme 2 gave comparable results both in air and under an inert nitrogen atmosphere. Consequently, most of our experiments were performed under benchtop conditions.[34] According to Woo et al.,[17] analogous air-stable iron(III) porphyrins could be reduced to the catalytically active, air-sensitive iron(II) species under an argon atmosphere, either with cobaltocene or by refluxing the reaction mixture with EDA acting as a mild reducing agent. Assuming that the same catalyst activation mechanism operates for our μ-oxo−bis[(salen)iron(III)] complexes, the air stability of our catalyst system is rather remarkable.

We tested the cyclopropanation of a variety of olefin substrates with EDA as the carbene source and $(Fe(3,3',5,5'\text{-}^tBu_4salen))_2O$ (**1d**) as the catalyst (Table 7). These substrates included mono- and disubstituted terminal alkenes, internal olefins, and olefins having ether and ester functionalities. It was found that 1,1-disubstituted olefins, such as 1,1-diphenylethylene, gave the highest yields (Table 7, entry 4). Even electron-rich alkenes, such as *n*-butyl vinyl ether, could be cyclopropanated in reasonably good yields (Table 7, entry 6). However, we were not successful in using our catalyst to cyclopropanate olefins containing ester functionalities, such as methacrylate, methyl methacrylate, and vinyl benzoate. Other alkenes that were not successfully cyclopropanated by our system included difficult substrates such as cyclohexene, 1-methylcyclohexene, α-bromostyrene, and 3-chloro-2-chloromethyl-1-propene.

Hossain et al. found that, with $[CpFe(CO)_2(THF)](BF_4)$ as the catalyst, internal olefins such as cyclopentene and 2-methyl-2-butene could be cyclopropanated, albeit in moderate yields (∼25%), only when phenyldiazomethane was used as the carbene source instead of EDA.[21] Woo and co-workers obtained similar results using iron porphyrins, whereby *trans*-β-methylstyrene could be cyclopropanated in roughly 35% yield using the bulky mesityldiazomethane as the carbene source.[18] However, when they used EDA as the diazo compound, less than 5% yields were obtained when a variety of internal olefins were cyclopropanated.[17] In most cases the major products were the carbene dimers. Unlike these systems, our catalyst was able to cyclopropanate internal olefins, such as β-methylstyrene, in moderate yields using EDA as the carbene source (Table 7, entries 7 and 8). We noted that *trans*-β-methylstyrene gave a slightly higher yield than the cis analogue. However, for both cases the cyclopropane yield of the background reaction was very low and only the *trans*-cyclopropane product was formed. Even trisubstituted internal olefins such as ethylidenecyclohexane were cyclopropanated with EDA in modest yields (Table 7, entry 9).

In contrast to other known iron-based catalysts,[16,17] no carbene dimers were observed in the cyclopropanation of mono- and disubstituted terminal olefins using our μ-oxo−bis[(salen)iron(III)] catalyst. This is quite remarkable considering the high temperature of our reaction, especially in the case of refluxing toluene, which suggests that the trapping of the postulated metal carbene intermediate by the styrene substrate is quite efficient. Dimerization was only observed when internal olefins were cyclopropanated. Interestingly, in all cases only the diethyl maleate (cis) dimer was formed. When *trans*- and *cis*-β-methylstyrene were cyclopropanated, ∼16% of diethylmaleate was formed after 23 h, while in the case of ethylidenecyclohexane ∼20% of the cis dimer was obtained after 19 h. No dimer was detected in the background thermal reaction.

To test the catalyst lifetime, an additional 1 equiv of EDA was added every 12 h to a reaction mixture of styrene and EDA with **1d** as the catalyst. Before each addition the cyclopropane yield was monitored. It was noted that over a period of 60 h the turnover number increased linearly versus each additional 1 equiv of EDA, suggesting that the catalyst was stable and maintained a consistent activity over this period (Figure 1). A large-scale styrene cyclopropanation was also carried out with catalyst **1d** under the optimal reaction conditions where the yield at 15 h and the cis:trans ratio of the isolated product were comparable to our GC data from lower-scale runs.

We propose a mechanistic model where the μ-oxo−bis[(salen)iron(III)] dimer is first reduced by EDA at high temperature to a monomeric (salen)iron(II) inter-

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[32] It is known that styrene and EDA react at high temperatures to give the respective cyclopropane products when neat styrene is used (68% yield relative to EDA). See: Burger, A.; Yost, W. L. *J. Am. Chem. Soc.* **1948**, *70*, 2198−2201.

[33] We note that Mukherjee and co-workers have observed that increasing the steric bulk at the 3- and 3′-positions causes the Fe−O−Fe moiety to be more linear but does not change the individual Fe−O bond length. See: Mukherjee, R. N.; Stack, T. D. P.; Holm, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 1850−1861.

[34] However, for catalyst **3d** consistent, reproducible results could only be obtained under nitrogen.

Table 4. Effect of Styrene Loading on Reaction Rate and Yield Using [Fe(3,3′,5,5′-^{t}Bu$_4$Salen)]$_2$O as the Catalyst[a]

			4 h		8 h		12 h		16 h	
entry	styrene (equiv)[b]	cat.	yield (%)[c]	cis:trans	yield (%)	cis:trans	yield (%)	cis:trans	yield (%)	cis:trans
1	1	yes	6(1)[d]	1:2.5	15(4)	1:2.5	22(3)	1:2.5	24(1)	1:2.5
2	1	no	0	0	5(1)	1:2.7	6(1)	1:1.9	7(1)	1:1.8
3	5	yes	40(10)	1:2.4	72(5)	1:2.5	85(8)	1:2.5	85(6)	1:2.5
4	5	no	9(0)	1:1.9	17(1)	1:1.9	25(1)	1:2.0	28(1)	1:1.9
5	10	yes	69(1)	1:2.5	87(4)	1:2.5	89(1)	1:2.5	90(1)	1:2.5
6	10	no	15(0)	1:1.9	26(2)	1:1.8	37(3)	1:1.9	43(1)	1:1.8

[a] Conditions: [Fe(3,3′,5,5′-^{t}Bu$_4$salen)]$_2$O as catalyst (5 mol %), EDA (1 equiv), undecane (1 equiv) as the internal standard, in refluxing undistilled benzene. [b] Relative to EDA. [c] Determined by GC analysis. [d] Values in parentheses are standard deviations in the yields based on at least two runs.

Table 5. Effect of Catalyst Backbone on Reaction Yield Using [Fe(3,3′,5,5′-^{t}Bu$_4$(bis(salicylaldimine)))]$_2$O Complexes as Catalysts[a]

entry	diamine backbone	yield (%)[b]	cis:trans
1	1,2-ethanediyl	85(8)[c]	1:2.5
2	1-methyl-1,2-ethanediyl	81(3)	1:2.5
3	1,2-dimethylethanediyl[d]	73(1)	1:2.3
4	1,2-cyclohexanediyl	79(2)	1:2.6
5	1,2-benzenediyl	83(1)	1:2.0
6	no catalyst	25(1)	1:1.8

[a] Conditions: EDA (1 equiv), styrene (5 equiv), catalyst (5 mol %), undecane (1 equiv) as the internal standard, in refluxing undistilled benzene for 15 h. [b] Determined by GC analysis. [c] Values in parentheses are standard deviations in the yields based on at least two runs. [d] Under nitrogen.

Table 6. Effect of Catalyst Substituents on Reaction Rate and Yield for [Fe(1,2-ethanediamino-*N*,*N*′-bis(salicylaldimine))]$_2$O Complexes as Catalysts[a]

entry	3,3′-position	5,5′-position	yield (%)[b]	cis:trans
1	H	H	75(3)[c]	1:2.6
2	H	^{t}Bu	79(2)	1:2.6
3	^{t}Bu	H	84(2)	1:2.5
4	^{t}Bu	^{t}Bu	85(8)	1:2.5

[a] Conditions: EDA (1 equiv), styrene (5 equiv), 1,2-ethanediyl backbone catalyst (5 mol %), undecane (1 equiv) as the internal standard, in refluxing undistilled benzene for 15 h. [b] Determined by GC analysis. [c] Values in parentheses are standard deviations in the yields based on at least two runs.

Table 7. Substrate Scope of the Cyclopropanation Reaction Catalyzed by [Fe(3,3′,5,5′-^{t}Bu$_4$Salen)]$_2$O[a]

			with cat.[b]		without cat.	
entry	substrate	time (h)	yield (%)[c]	cis: trans	yield (%)	cis: trans
1	styrene	12	85(8)[d]	1:2.5	25(1)	1:1.8
2	α-methylstyrene	46	93(5)	1:2.3	21(0)	1:1.5
3	α-(trifluoromethyl)styrene	24	84(1)	1:1.7	28(1)	1:1
4	1,1-diphenylethylene	8	97(1)		5(1)	
5	methylenecyclohexane	24	88(1)		12(1)	
6	*n*-butyl vinyl ether[e]	24	72(4)	1:2.2	6(1)	1:0.9
7	*trans*-*β*-methylstyrene	23	28(0)	1:2.8	2(2)	0:1
8	*cis*-*β*-methylstyrene	23	19(1)	1:1.9	5(2)	0:1
9	ethylidenecyclohexane[f]	19	27(1)	(1:1.7)[g]	0	0

[a] Conditions: EDA (1 equiv), olefin substrate (5 equiv), undecane (1 equiv) as the internal standard, in refluxing undistilled benzene. [b] 5 mol % of [Fe(3,3′,5,5′-^{t}Bu$_4$salen)]$_2$O relative to EDA. [c] Determined by GC analysis. [d] Values in parentheses are standard deviations in the yields based on at least two runs. [e] Dodecane used as the internal standard. [f] 10 equiv of olefin used. [g] The identity of cis and trans isomers not determined.

mediate, which then reacts with another 1 equiv of EDA to generate an iron(II) carbene complex (Scheme 3). This carbene intermediate can then react with the olefin to give the final cyclopropane product. Our mechanism follows the precedent set by Woo et al.[17] that showed analogous air-stable iron(III) porphyrins could be reduced to the catalytically active iron(II) species under an argon atmosphere, either with cobaltocene or by refluxing the reaction with EDA, which acts as a mild reducing agent.

The mechanism in Scheme 3 suggests the presence of ethyl glyoxylate, which is formed when EDA reduces *μ*-oxo−bis[(salen)iron(III)], in our reaction. Commercial ethyl glyoxylate exists as a mixture of oligomers and can be “cracked”[35] to give a mixture of monomers and trimers.[36] This mixture is stable at room temperature for a short time[35] and can be analyzed by IR and GC. The solution IR spectrum of freshly distilled ethyl glyoxylate in toluene has two characteristic peaks in the carbonyl stretching region at 1728 and 1757 cm^{-1}. However, taking an IR spectrum of this same solution after about 1 h at room temperature shows a broad band at 1752 cm^{-1} with a small shoulder at 1728 cm^{-1}. This pattern closely resembles that of the original commercial sample (1753 cm^{-1}), suggesting that the distilled sample has oligomerized quickly back into the oligomeric state. On the basis of these observations, we assign the peak at 1728 cm^{-1} to the monomeric species, while the 1757 cm^{-1} peak may correspond to that of the trimer. These distinctive peaks suggested that the formation of ethyl glyoxylate in reaction 2 could be detected by IR in the carbonyl region. However, the IR spectra of the various starting materials and reaction products also exhibited many bands in that same region which could potentially interfere with an absolute identification of ethyl glyoxylate: EDA has a band at 1705 cm^{-1}, diethyl fumarate at 1726 cm^{-1}, and diethyl maleate at around 1732 cm^{-1}, while the EDA−styrene cyclopropane product has a characteristic band at 1727 cm^{-1}. Unfortunately, this was indeed the case. Only a broad band in the carbonyl region was observed when EDA and our catalyst were reacted together under air in an attempt to generate ethyl glyoxylate catalytically. This same broad band was observed in another experiment where EDA, styrene, and catalyst were combined in toluene under our typical cyclopropanation reaction conditions and monitored over time. Monitoring the disappearance of the characteristic *μ*-oxo stretch was also not possible, as the solution IR of **1d** in that region did not show a distinctive stretch.

Ethyl glyoxylate monomer and trimer can also be detected by GC. However, we did not observe their

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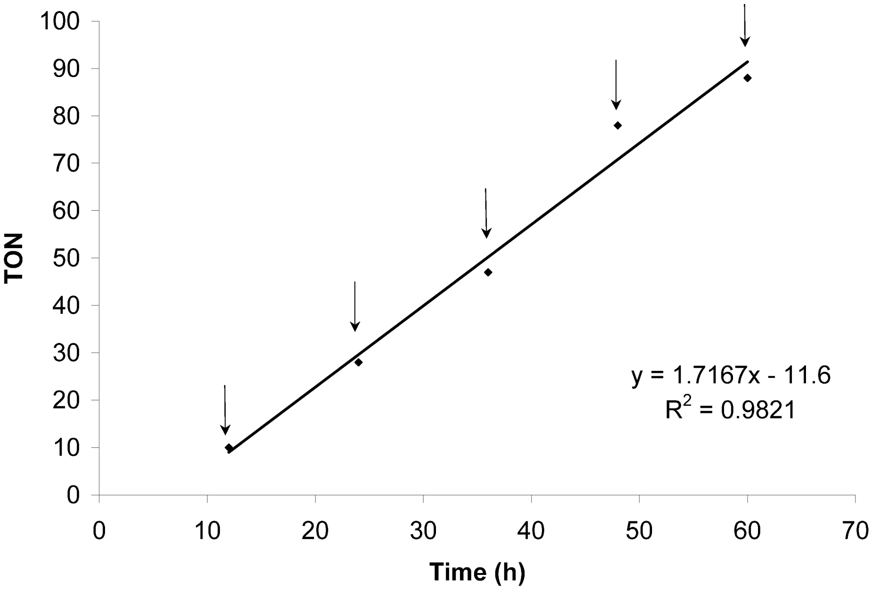
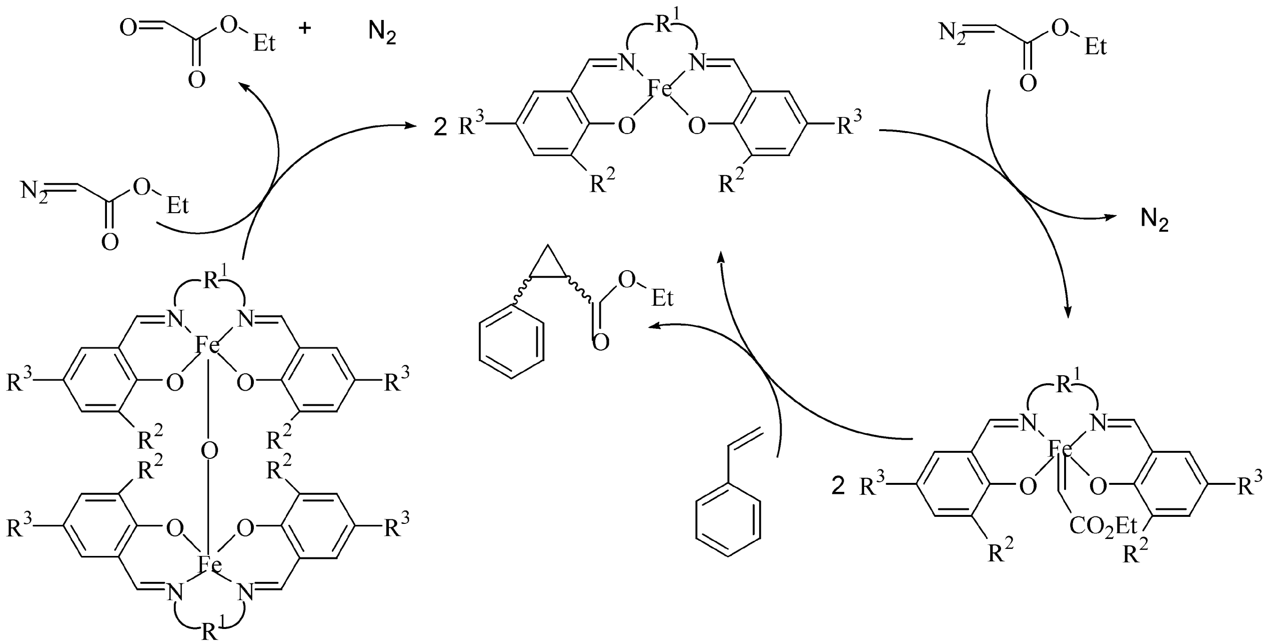


Figure 1. Continuous catalytic turnover behavior in the cyclopropanation of styrene catalyzed by **1d** upon repeated addition of EDA every 12 h. TON = total turnover number. Arrows indicate the additions of 1 equiv of EDA.

Scheme 3. Proposed Mechanism for Cyclopropanation Catalyzed by μ-Oxo–bis[(salen)iron(III)]



characteristic GC signals in our typical cyclopropanation reaction. This can be explained, as neither of these species could be eluted through either silica gel or alumina. As we used silica gel to remove the catalyst residue before analyzing the reaction mixture via GC, no ethyl glyoxylate product could come through in the eluent. Hence, we must inject reaction samples directly onto the GC column if we are to identify the glyoxylate-derived species. A stoichiometric reaction between EDA and the μ-oxo–bis[(salen)iron(III)] complex **1d** was carried out under our typical cyclopropanation reaction conditions in toluene and monitored via GC. Peaks indicative of the ethyl glyoxylate monomer and the carbene dimers were observed to increase in intensity over time at the expense of the EDA peak. In another experiment, EDA, styrene, and the catalyst were combined under our typical reaction conditions in toluene and this reaction was monitored every 20 min. Again, the GC traces for these reaction mixture aliquots showed the presence of the ethyl glyoxylate monomer. These findings support our proposed mechanism. However, we note that, for both of these cases, when reactions were carried out under identical conditions but without the presence of **1d**, ethyl glyoxylate and carbene dimers were also formed but more slowly than that in the presence of the catalyst. Experiments to quantify the rate of these background reactions are underway and will be reported in due course.

Also consistent with our model is the fact that iron(II) carbene complexes are well-known and have been used in stoichiometric cyclopropanation reactions.[4] We note that a related (diimine)iron(II) carbene complex, (tmtaa)Fe=CPh_2, has been structurally characterized.[37] The underlying assumption for the mechanism depicted in Scheme 3 is that the formation of the (salen)iron(II) carbene complex, from the (salen)iron(II) intermediate and EDA, is competitive against the reoxidation by air to the μ-oxo−bis[(salen)iron(III)] dimer. This is reasonable, considering that the reaction between (salen)iron(II) and dry oxygen is reasonably slow[27] and that there is an excess of EDA in our reaction. It is possible that a stable salen iron carbene complex can be isolated by using a less reactive, bulkier diazo reagent such as (trimethylsilyl)diazomethane or diphenyldiazomethane, and we are currently pursuing these lines of investigations.

In conclusion, air-stable μ-oxo−bis[(salen)iron(III)] compounds with a wide range of ligand environments can be easily synthesized from inexpensive, readily available, nontoxic starting materials. The use of commercially available EDA as the carbene source and the ease of handling of these μ-oxo−bis[(salen)iron(III)] complexes makes them an attractive class of catalysts for the olefin cyclopropanation reactions. Not only can a variety of mono- and disubstituted internal olefins be cyclopropanated in high yields but also unreactive internal alkenes, such as β-methylstyrene and ethylidenecyclohexane, can be successfully converted to the respective cyclopropanes. Unlike previously reported iron-catalyzed cyclopropanations, our system does not require air-free conditions. Further, no carbene dimer production was observed when terminal olefins were cyclopropanated.

Experimental Section

General Information. High-resolution mass spectra were obtained using a Micromass Quattro II ES triple-quadrupole high-resolution mass spectrometer and the atmospheric-pressure chemical ionization (APCI) technique. FAB mass spectroscopy was performed by JEOL USA, Inc. (Peabody, MA) on a JEOL JMS-SX102 instrument with MStation software. GC analyses of the cyclopropanation reactions were carried out on a Hewlett-Packard 5890A gas chromatograph equipped with an FID detector. For the determination of the trans:cis ratios and the yields of the cyclopropanes, a 30 m HP-5 capillary column with 0.32 mm inner diameter and 0.25 mm film thickness was used (method: initial temperature 50 °C, rate 10 °C/min, final temperature 250 °C, final time 0 min). Calibration curves for yield determination were produced using analytically pure samples prepared and characterized by literature methods.[38−44] Elemental analyses were provided by Atlantic Microlab, Inc. (Norcross, GA). IR data were collected on a Nicolet 5PC FT-IR with PC-IR software using a solution cell equipped with NaCl plates. All flash chromatography was carried out using a 64-mm inner diameter column containing 230−400 mesh silica gel purchased from Merck.

Materials. Salen ligands were synthesized by combining the substituted aldehyde (2 equiv) with the corresponding diamine (1 equiv) in refluxing ethanol, according to literature procedures (Scheme 2).[45,46] Dichloromethane and triethylamine were distilled over calcium hydride, and methanol was distilled over $Mg(OMe)_2$, while tetrahydrofuran (THF), toluene, and hexanes were distilled over sodium/benzophenone ketyl. All solvents were distilled under nitrogen, collected in Strauss flasks, and degassed before use. Dehydrated 200-proof ethanol (Pharmco) and benzene (Fisher Chemicals) were used without further purification. Styrene (Aldrich) was distilled over calcium hydride and stored cold. All other olefins, except *cis*-β-methylstyrene (TCI America), were obtained from Aldrich and purified with *tert*-butylcatechol inhibitor remover (Aldrich) when appropriate. Ethyl diazoacetate (Aldrich, containing ~10% CH_2Cl_2) and iron(III) chloride hexahydrate (Mallinckrodt) were used as received. Ethyl glyoxylate, which exists as an oligomeric mixture in toluene, was purchased from TCI and distilled according to literature procedures.[35]

General Procedure for the Synthesis of Iron(III) Complexes. These compounds were prepared by following a modification of the literature synthesis of $[Fe(3,3',5,5'\text{-}^tBu_4\text{-}Salcen)]_2O$.[29] The corresponding salen ligand was dissolved in $Mg(OMe)_2$-distilled methanol to which $FeCl_3\cdot 6H_2O$ and triethylamine were added. The use of $Mg(OMe)_2$-distilled methanol was important, as unpurified methanol often gave irreproducible cyclopropanation results. The literature workup procedure was followed in all cases. Variations such as longer reaction times or higher reaction temperature did not affect yields significantly.

(μ-Oxo)bis[(1,2-ethanediamino-*N,N′*-bis(salicylidene))-iron(III)] (1a). Yield: 73.0%. APCIMS (CH_2Cl_2): found, *m/z* 678.9; calcd, *m/z* 678.3 ($[M\cdot H_2O]^+$). Anal. Calcd for $C_{22}H_{28}Fe_2N_4O_3$: C, 58.21; H, 4.27; N, 8.49; O, 12.12. Found: C, 57.92; H, 4.31; N, 8.39; O, 11.97. IR (NaCl): $\nu_{Fe-O-Fe}$ 822 cm^{-1}.

(μ-Oxo)bis[(1,2-ethanediamino-*N,N′*-bis(5-*tert*-butylsalicylidene))iron(III)] (1b). Yield: 38.3%. FABMS (NPOE matrix): found, *m/z* 885.4; calcd, *m/z* 884.7 (M^+). Anal. Calcd for $C_{96}H_{126}Fe_4N_8O_{13}$ ($[Fe(5,5'\text{-}^tBu_2Salen)]_2O\cdot 1.5H_2O$): C, 63.23; H, 6.96; N, 6.15. Found: C, 63.56; H, 6.89; N, 5.82. IR (NaCl): $\nu_{Fe-O-Fe}$ 832 cm^{-1}.

(μ-Oxo)bis[(1,2-ethanediamino-*N,N′*-bis(3-*tert*-butylsalicylidene))iron(III)] (1c). Yield: 33.48%. APCIMS (CH_2Cl_2): found, *m/z*: 913.0; calcd, *m/z* 911.7 ($[M\cdot 1.5H_2O]^+$). Anal. Calcd for $C_{48}H_{62}Fe_2N_4O_6$ ($[Fe(5,5'\text{-}^tBu_2Salen)]_2O\cdot H_2O$): C, 63.86; H, 6.92; N, 6.21. Found: C, 63.99; H, 6.81; N, 6.14. IR (NaCl): $\nu_{Fe-O-Fe}$ 862 cm^{-1}.

(μ-Oxo)bis[(1,2-ethanediamino-*N,N′*-bis(3,5-di-*tert*-butylsalicylidene))iron(III)] (1d). Yield: 78.0%. APCIMS (CH_2Cl_2): found, *m/z* 546.3; calcd, *m/z* 546.6 ($[Fe(3,3',5,5'\text{-}^tBu_4\text{-}Salen)]^+$). Anal. Calcd for $C_{64}H_{92}Fe_2N_4O_5$: C, 69.31; H, 8.36; N, 5.05. Found: C, 69.38; H, 8.38; N, 5.17. IR (NaCl): $\nu_{Fe-O-Fe}$ 832 cm^{-1}.

(μ-Oxo)bis[(1-methyl-1,2-ethanediamino-*N,N′*-bis(3,5-di-*tert*-butylsalicylidene))iron(III)] (2d). Yield: 75.2%. APCIMS (CH_2Cl_2): found, *m/z* 560.2; calcd, *m/z* 560.6 ($[Fe(3,3',5,5'\text{-}^tBu_4\text{-}1,2\text{-}Me_2Salen)]^+$). Anal. Calcd for $C_{66}H_{96}Fe_2N_4O_5$: C, 69.71; H, 8.51; N, 4.93. Found: C, 69.31; H, 8.51; N, 4.88. IR (NaCl): $\nu_{Fe-O-Fe}$ 836 cm^{-1}.

(μ-Oxo)bis[(1,2-dimethyl-1,2-ethanediamino-*N,N′*-bis-(3,5-di-*tert*-butylsalicylidene))iron(III)] (3d). Yield: 42.3%. APCIMS (CH_2Cl_2): found, *m/z* 1165.7; calcd, *m/z* 1165.3 (M^+). Anal. Calcd for $C_{68}H_{104}Fe_2N_4O_5$: C, 70.09; H, 8.65; N, 4.81. Found: C, 69.83; H, 8.54; N, 4.83. IR (NaCl): $\nu_{Fe-O-Fe}$ 837 cm^{-1}.

(μ-Oxo)bis[(1,2-cyclohexanediamino-*N,N′*-bis(3,5-di-*tert*-butylsalicylidene))iron(III)] (4d). Yield: 71.7%. APCIMS (CH_2Cl_2): found, *m/z* 1235.4; calcd, *m/z* 1235.3 ($[M\cdot H_2O]^+$). Anal. Calcd for $C_{72}H_{104}Fe_2N_4O_5$: C, 71.04; H, 8.61; N, 4.60. Found: C, 70.04; H, 8.73; N, 4.47. IR (NaCl): $\nu_{Fe-O-Fe}$ 837 cm^{-1}.

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(μ-Oxo)bis[(1,2-benzenediamino-*N*,*N'*-bis(3,5-di-*tert*-butylsalicylidene))iron(III)] (5d). Yield: 38.1%. APCIMS (CH_2Cl_2): found, *m*/*z* 1205.5; calcd, *m*/*z* 1205.2 (M^+). Anal. Calcd for $C_{72}H_{92}Fe_2N_4O_5$: C, 71.75; H, 7.69; N, 4.65. Found: C, 71.26; H, 7.73; N, 4.61. IR (NaCl): $\nu_{Fe-O-Fe}$ 835 cm^{-1}.

General Procedure for Cyclopropanation. In a typical reaction, the iron(III) catalyst (5.6×10^{-6} mol, 5 mol %) was mixed with the olefin (2.8×10^{-3} mol) and dissolved in an organic solvent (5 mL) in a 25-mL two-neck round-bottom flask equipped with a magnetic stir bar and a water-cooled reflux condenser capped with a rubber septum and a venting needle. In a separate flask, ethyl diazoacetate (5.6×10^{-4} mol) and undecane as the internal standard (5.6×10^{-4} mol; for *n*-butyl vinyl ether, dodecane was used as the internal standard) were diluted in the same solvent (2 mL) and taken up in a 2.5-mL gastight syringe. The solution was then added slowly to the catalyst solution over 30 min using a syringe pump. Once the addition was complete, the flask was lowered into an oil bath that had been preheated to a temperature that was slightly higher than the boiling temperature of the solvent and allowed to reflux. (Depending on the reaction components, the reaction mixture may not be completely homogeneous at room temperature. However, it would become homogeneous under refluxing conditions.) Aliquots (0.2 mL) of the reaction mixture were taken subsequently and passed through a plug of silica gel (2.5 cm × 0.8 cm) and rinsed with dichloromethane (20 mL). Samples were then analyzed by GC.

When the reactions were carried out under nitrogen, standard Schlenk line techniques were used. The catalyst was placed into a 25-mL two-neck round-bottom flask equipped with a magnetic stir bar and a reflux condenser that was connected to a Schlenk line. The whole apparatus was evacuated and then placed under a nitrogen bubbler. In a separate Schlenk flask, the olefin was dissolved in an organic solvent (5 mL) and degassed via three freeze−pump−thaw cycles before being transferred into the flask containing the catalyst via a gastight syringe. In a third Schlenk flask, ethyl diazoacetate (5.6×10^{-4} mol) and undecane as the internal standard (5.6×10^{-4} mol) were diluted in the same solvent (2 mL) and degassed via three freeze−pump−thaw cycles before being taken up in a 2.5-mL gastight syringe. This solution was then added slowly to the catalyst solution over 30 min using a syringe pump. Once the addition was complete, the flask was lowered into an oil bath that had been preheated to a temperature that was slightly higher than the boiling temperature of the solvent and allowed to reflux under a slow flow of nitrogen. Analysis was carried via GC using the same procedure as described above.

Catalyst Lifetime. The general procedure for cyclopropanation (mentioned above) was followed. After 12 h an aliquot (0.2 mL) of the reaction mixture was taken and passed through a plug of silica gel (2.5 cm × 0.8 cm) and rinsed with dichloromethane (20 mL). The sample was then analyzed via GC. Simultaneously, an additional 1 equiv of EDA (5.6×10^{-4} mol) was diluted in 1 mL of benzene, taken up in an airtight syringe, and added to the refluxing reaction mixture through the septum on top of the condenser. Subsequently, samples (0.2 mL) were taken for GC analysis every 12 h followed by the addition of 1 equiv of EDA (in 1 mL of benzene). The reaction was allowed to proceed for a total of 60 h.

Scaled-Up Cyclopropanation. Catalyst **1d** (0.0624 g, 5.6×10^{-5} mol, 5 mol %) was mixed with styrene (0.5844 g, 5.6×10^{-3} mol) and benzene (10 mL) to form an orange suspension in a 50-mL two-neck round-bottom flask equipped with a magnetic stir bar and a reflux condenser capped with a rubber septum and a venting needle. In a separate flask, ethyl diazoacetate (0.1283 g, 1.1×10^{-3} mol) was diluted in benzene (4 mL) and taken up in a 5-mL gastight syringe. The solution was then added slowly to the catalyst solution over 30 min using a syringe pump. Once the addition was complete, the flask was lowered into an oil bath that had been preheated to a temperature that was slightly higher than the boiling temperature of the solvent and the mixture was refluxed. After 15 h the reaction mixture was cooled to room temperature and the products were separated by flash chromatography on a silica gel packed column (15 cm × 5 cm) using 1% ethyl acetate/99% hexane solution as the eluent. Yield: 0.1838 g (86.3%). The products were then analyzed by GC (cis:trans = 1:2.3).

IR Data for Ethyl Glyoxylate. Ethyl glyoxylate was distilled according to a literature procedure using a short-path distillation apparatus.[35] Commercial ethyl glyoxylate (in toluene) was first warmed to 110 °C for 1 h before being heated to 140−150 °C (head temperature 110−118 °C) to remove most of the toluene. Next the temperature was raised to 160−170 °C and a concentrated solution of ethyl glyoxylate in toluene was collected (head temperature 120−130 °C). The solution IR spectrum of the sample in toluene was taken immediately. IR: $\nu_{C=O}$ 1728 and 1757 cm^{-1}.

Reaction between EDA and 0.05 Equiv of 1d. Catalyst **1d** (0.0309 g, 2.8×10^{-5} mol) was dissolved in distilled toluene (5 mL) in a 25-mL two-neck round-bottom flask equipped with a magnetic stir bar and a water-cooled reflux condenser capped with a rubber septum and a venting needle. In a separate flask, ethyl diazoacetate (0.0640 g, 5.6×10^{-4} mol) was diluted in distilled toluene (2 mL) and taken up in a 2.5-mL gastight syringe. This solution was then added slowly to the catalyst solution over 30 min using a syringe pump. Once the addition was complete, the flask was lowered into an oil bath that had been preheated and the mixture refluxed. An aliquot (0.1 mL) of the reaction mixture was taken subsequently every 1 h for the next 4 h and analyzed by IR and GC. The IR results were inconclusive, as there were overlapping peaks from the EDA and carbene dimers in the characteristic carbonyl region. The sample was analyzed by GC by direct injection onto the GC column. The GC trace of the reaction aliquots showed peaks for ethyl glyoxylate and the carbene dimers after 1 h. Over time the peak for EDA decreased and disappeared completely after 2 h.

Reaction between EDA, Styrene, and 1d. Catalyst **1d** (0.0310 g, 2.8×10^{-5} mol) was mixed with styrene (0.2924 g, 2.81×10^{-3}) and dissolved in distilled toluene (5 mL) in a 25-mL two-neck round-bottom flask equipped with a magnetic stir bar and a water-cooled reflux condenser capped with a rubber septum and a venting needle. In a separate flask, ethyl diazoacetate (0.0641 g, 5.6×10^{-4} mol) was diluted in distilled toluene (2 mL) and taken up in a 2.5-mL gastight syringe. The solution was then added slowly to the catalyst solution over 30 min using a syringe pump. Once the addition was complete, the flask was lowered into an oil bath that had been preheated and allowed to reflux. An aliquot (0.1 mL) of the reaction mixture was subsequently taken every 20 min for the next 4 h and analyzed by IR and GC. The IR results were inconclusive, as there were overlapping peaks corresponding to EDA, carbene dimers, and the EDA−styrene cyclopropanation in the characteristic carbonyl region. The sample was analyzed by GC by direct injection onto the GC column. As soon as all the EDA was added and before the flask was lowered into the oil bath ($t = 0$), the GC trace of the reaction mixture showed a peak for ethyl glyoxylate which increased over time at the expense of EDA. The cyclopropanation products formed after 20 min of heating, while the carbene dimers started appearing after 1 h.

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