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Catalytic Cyclopropanation with Iron(II) Complexes

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Iron(II) complexes of *meso*-tetra-*p*-tolylporphyrin (TTP), tetramethyldibenzotetraaza[14]-annulene (tmtaa), and *trans*-1,2-*bis*(salicylidene)cyclohexanediamine (saldach) catalyzed the cyclopropanation of styrene with aryldiazomethanes. When *p*-tolyldiazomethane was used as the carbene source, *trans*-cyclopropanes were the major products. *Trans/cis* ratios of up to 17:1 were obtained. However, using mesityldiazomethane resulted in a reversal of stereoselectivity, giving *cis*-cyclopropanes as the major product (*cis/trans* ratios of up to 2.9:1). The stereoselectivity of iron(II) porphyrin-catalyzed cyclopropanation reactions was enhanced by performing the reactions at low temperature or by using bulky porphyrin ligands. Using trimethylsilyldiazomethane as the carbene source, trimethylsilylcyclopropanes were produced in excellent yields with (TTP)Fe. On treatment of (TTP)Fe with diazoreagents, carbene complexes were observed spectroscopically. These complexes transferred their carbene ligand to styrene to produce cyclopropanes stoichiometrically.

Introduction

Transition-metal-mediated cyclopropanation has received much attention recently.[1] The majority of catalytic studies employ diazocarbonyl compounds as the carbene source. Despite numerous reports of *stoichiometric* cyclopropanation with transition metal benzylidene complexes,[2] few reports exist on transition-metal-catalyzed cyclopropanation using aryldiazomethanes.[3,4] Moreover, production of arylcyclopropanes from mixtures of aryldiazomethanes and olefins is typically achieved by treatment with zinc halides[5] or by photolysis.[6]

Arylcyclopropanes are reactive molecules and valuable synthetic intermediates. For example, they have been used as starting materials in the synthesis of 1,3-dihalo-1,3-diarylpropanes,[7] 1,3-dimethoxy-1,3-diarylpropanes,[8] 3,5-diaryl-1,2-dioxolanes,[9] 3,5-diaryl-2-isoxazolines,[10] and cyclopropanecarboxylic acids.[11] In addition, arylcyclopropanes also possess useful photochemical properties.[12] Thus the catalytic production of arylcyclopropanes is an important synthetic goal.

Although silylcyclopropanes are also versatile synthetic intermediates,[13] very few reports exist on cyclopropanation reactions employing trimethylsilyldiazomethane as the carbene source.[3e,14] Trimethylsilyldiazomethane is one of the most robust diazo compounds known.[15] In addition, its commercial availability[16] makes it an attractive reagent.

We recently reported that iron(II) porphyrin complexes are efficient catalysts for the formation of cyclopropyl esters.[17] Related complexes containing the readily derivatized salen[18] and tmtaa ligand systems (Figure

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(18) Abbreviations used: salen = dianion of a generic bis(salicylidene)diamine; saldach = dianion of *trans*-1,2-bis(salicylidene)-cyclohexanediamine; tmtaa = dianion of tetramethyldibenzotetraaza-[14]annulene; TTP = dianion of *meso*-tetra-*p*-tolylporphyrin; TPP = dianion of *meso*-tetraphenylporphyrin; TMP = dianion of *meso*-tetramesitylporphyrin; TDMPP = dianion of *meso*-tetrakis(2,6-dimethoxyphenyl) porphyrin; EDA = ethyl diazoacetate; THF = tetrahydrofuran; TMS = trimethylsilyl.

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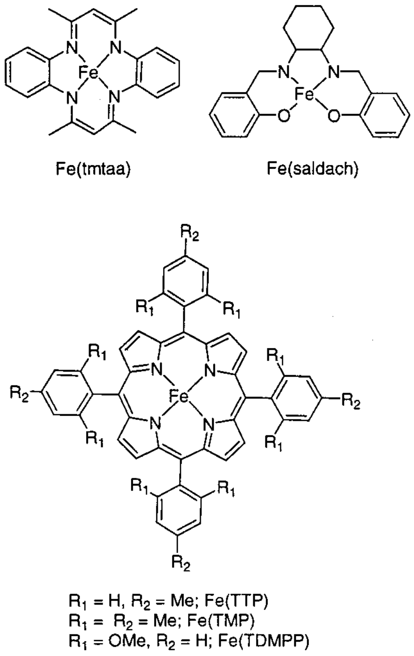


R_1 = H, R_2 = Me; Fe(TTP)
R_1 = R_2 = Me; Fe(TMP)
R_1 = OMe, R_2 = H; Fe(TDMPP)

Figure 1. Iron complexes used in this study.[18]

1) seemed like a logical extension to our cyclopropanation studies. Jacobsen and others have used (salen)Mn(III) complexes extensively as epoxidation catalysts.[19] Moreover, chiral salen ligands have been used in highly enantioselective Mn(III)-catalyzed epoxidation[19] and in Co(III)-catalyzed cyclopropanation reactions.[20] While no reports exist, to our knowledge, on reactions between (salen)Fe(II) complexes and diazo reagents, Floriani and co-workers recently reported the isolation of (tmtaa)Fe=CPh_2 by treatment of (tmtaa)Fe(II) with diphenyldiazomethane.[21] Floriani also demonstrated that (tmtaa)Fe reacts with phenyldiazomethane to yield a carbene complex which is only observable at low temperature. At room temperature, the benzylidene complex decomposed to give (tmtaa)Fe and a mixture of cis- and *trans*-stilbene.

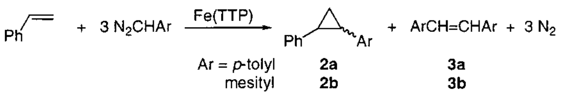
Results

Catalytic Production of Arylcyclopropanes Using (TTP)Fe. Since iron(II) porphyrins are efficient catalysts for the production of cyclopropyl esters from ethyl diazoacetate and olefins,[17] an investigation of the catalytic production of diarylcyclopropanes using (TTP)Fe was undertaken. Indeed, (TTP)Fe, **1**, was an excellent catalyst for the cyclopropanation of olefins with aryldiazomethanes. Dropwise addition of a hexanes solution of *p*-tolyldiazomethane to a THF solution containing styrene (14 equiv) and (TTP)Fe (<1 mol %) produced 1-(4-methylphenyl)-2-phenylcyclopropane, **2a**, in 79% yield (*trans/cis* = 14 ± 1) as shown in eq 1. A side product, 4,4′-dimethylstilbene, **3a**, was obtained in 21% yield (Table 1). When the *p*-tolyldiazomethane was added as a solution in diethyl ether, the *trans/cis* ratio for cyclopropane **2a** increased slightly to 17:1. This solvent-dependent *trans/cis* ratio is consistent with previous observations.[17]

Table 1. Synthesis of 1-*p*-Tolyl-2-phenylcyclopropane from Styrene and N_2CH(*p*-tolyl)

entry	catalyst	addition time	4,4-dimethylstilbene yield,[a] %	cyclopropane yield,[a] %	*trans*/*cis*[a]
1	(saldach)$Fe^{II\,b}$	50 min	33(4)[c]	18(4)[c]	4.0(4)[c]
2	(tmtaa)$Fe^{II\,b}$	2 h	84(7)	16(7)	1.9(4)
3	(TTP)$Fe^{II\,d}$	25 min	21(5)	79(4)	14(1)

[a] Determined by GC analysis. [b] 1.5−1.7 mol % catalyst. [c] Values in parentheses are standard deviations in the last digit based on at least three catalytic runs. [d] 0.8−0.9 mol % catalyst.



(1)

Interestingly, when mesityldiazomethane was used as the carbene source, the *cis*-cyclopropane isomer became the major product (*cis/trans* = 2.0 ± 0.2). The yield of 1-mesityl-2-phenylcyclopropane, **2b**, was 60% and the yield of 2,2′,4,4′,6,6′-hexamethylstilbene, **3b**, was 40% using a 30 min slow addition of a 48 mM hexanes solution of mesityldiazomethane. Additionally, *trans*-β-methylstyrene was converted to 1-mesityl-2-methyl-3-phenylcyclopropane, **2c**, in the presence of (TTP)Fe and mesityldiazomethane. Compound **2c** was obtained in ca. 35% yield (unoptimized) and was detected by GC/MS (m/z = 250 $[M]^+$). Using other diazo reagents such as ethyl diazoacetate (EDA) and trimethylsilyldiazomethane, *trans*-β-methylstyrene was not converted to cyclopropane when (TTP)Fe was used as the catalyst.

Catalytic Cyclopropanation with (tmtaa)Fe. The scope of cyclopropanation with catalytic amounts of (tmtaa)Fe, **4**, was also examined. Results using EDA as the carbene source were poor. Generally, less than 20% of EDA was converted to products in the presence of complex **4** and an excess of styrene. However, complex **4** was an efficient catalyst for the decomposition of aryldiazomethanes. Dropwise addition of a 39 mM pentane/THF solution of *p*-tolyldiazomethane over 2 h to a solution containing 14 equiv (relative to the diazo reagent) of styrene and (tmtaa)Fe (1.5 mol %) in THF produced cyclopropane **2a** in 16% yield. The remaining *p*-tolyldiazomethane was converted to olefin **3a** (84% yield). However, the *trans/cis* ratio for cyclopropane **2a** was 1.9 ± 0.4, significantly lower than the 14:1 ratio obtained using (TTP)Fe as the catalyst. When mesityldiazomethane was used as the diazoalkane, the yield of cyclopropane **2b** was 43% and the yield of olefin **3b** was 57% using a 60 min slow addition of diazo reagent. As with (TTP)Fe, the major cyclopropane isomer was *cis*-**2b** (*cis/trans* = 2.9 ± 0.3).

Catalytic Cyclopropanation Using (saldach)Fe. An iron(II) salen complex, (saldach)Fe, **5**, was also investigated as a cyclopropanation catalyst. Cyclopropanation of styrene using EDA and catalytic amounts of **5** gave less than 30% yield of diethyl maleate, diethyl fumarate, and ethyl-2-phenylcyclopropane carboxylate, **6**, combined. Unlike (tmtaa)Fe, changing the diazo reagent to *p*-tolyldiazomethane did not improve product yields. Only about 50% of the *p*-tolyldiazomethane was

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Table 2. Effect of Porphyrin Structure in the Cyclopropanation of Styrene with EDA

entry	catalyst	solvent	*trans/cis*	ref
1	(TTP)Fe	toluene	8.0:1	17
2	(TTP)Fe	THF	13:1	17
3	(TMP)Fe	toluene	13:1	*a*
4	(TDMPP)Fe	toluene	15:1	*a*
5	(TDMPP)Fe	THF	21:1	*a*

[a] This work.

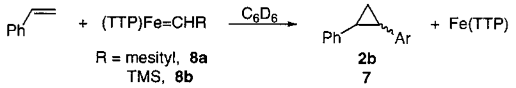
converted to cyclopropane **2a** and olefin **3a** in the presence of excess styrene.

Temperature Effects in the Cyclopropanation of Styrene with EDA Catalyzed by (TTP)Fe. In our studies of catalytic cyclopropanation reactions, it was possible to vary slightly the stereoselectivity by changing the solvent. Additionally, the reaction temperature had a dramatic effect on the *trans/cis* ratio. When a dichloromethane solution of (TTP)Fe and excess styrene was treated with EDA at −78 °C for 3 h, cyclopropane **6** was obtained in 92 ± 7% yield with a *trans/cis* ratio of 29 ± 2. This is significantly greater than the 8.8:1 ratio for the same reaction in dichloromethane at 25 °C.[17]

Effect of Porphyrin Structure in Iron(II) Porphyrin-Catalyzed Cyclopropanation. The structure of the porphyrin also had an effect on the diastereoselectivity of iron(II) porphyrin-catalyzed cyclopropanation reactions. At ambient temperature in toluene, the cyclopropanation of styrene with EDA produced primarily *trans*-**6**. When the porphyrin was TTP, the *trans/cis* ratio was 8.0:1. With TMP, methyl groups occupy all of the ortho positions of the aryl substituents, and the *trans/cis* ratio increased to 13:1. Moreover, using the bulky TDMPP ligand with *o*-methoxy substituents increased the *trans/cis* ratio to 15:1 (Table 2).

Catalytic Synthesis of 1-Phenyl-2-Trimethylsilylcyclopropane, 7. Since trimethylsilyl diazomethane is commercially available, its use as a carbene source in catalytic cyclopropanation reactions was also investigated. Using 0.6 mol % of (TTP)Fe and approximately a 10-fold excess (relative to N_2CHTMS) of styrene, 1-phenyl-2-trimethylsilylcyclopropane, **7**, was obtained in 89 ± 4% yield with trimethylsilyl diazomethane as the carbene source. Unlike previously reported cyclopropanation reactions using (trimethylsilyl)diazomethane, no evidence for formation of 1,2-*bis*(trimethylsilyl)ethene byproducts from carbene coupling was observed. The *trans/cis* ratio for cyclopropane **7** was 10 ± 1 when the reaction was performed in toluene and 13 ± 1 when the reaction was performed in THF. Neither (tmtaa)Fe nor (saldach)Fe produced any detectable quantities of cyclopropane **7** under similar conditions.

Spectroscopic Identification of Carbene Complexes of (TTP)Fe. Treatment of a solution of (TTP)Fe with a solution of N_2CHR (R = mesityl, trimethylsilyl) led to the formation of carbene complexes (TTP)Fe=CHR (R = mesityl, **8a**; R = trimethylsilyl, **8b**). Samples of the carbene complexes were usually contaminated with ca. 5% of unreacted (TTP)Fe as evidenced by ^1H NMR. Unlike (TTP)Fe, the iron carbene complexes are diamagnetic and have NMR spectra that are similar to the known osmium(II) complexes, (TTP)Os=CHR.[22] The α-protons of the carbene ligands show large downfield shifts (δ = 19.71 ppm for **8a** and δ = 24.86 ppm for **8b** in C_6D_6), while the protons on the R groups show large upfield shifts, consistent with their position above the porphyrin ligand. Complexes **8a** and **8b** slowly decomposed during recrystallization, preventing isolation of pure samples. However, both complexes generated cyclopropanes from a *stoichiometric* reaction in the presence of excess styrene (eq 2).



(2)

The stoichiometric reaction between (TTP)Fe=CH(mesityl) and styrene was followed by ^1H NMR spectroscopy. The reaction was monitored by following the disappearance of the β-pyrrole signal of the porphyrin and the *o*-methyl signal of the mesityl group. In the presence of excess styrene, the reaction followed pseudo-first-order kinetics (Supporting Information Figure S1). The half-life at 25 °C was approximately 41 min in the presence of 12 equiv of styrene and approximately 17 min in the presence of 18 equiv of styrene.

Discussion

Ligand Effects in Iron(II)-Catalyzed Cyclopropanation. Given the efficiency of iron(II) porphyrins as cyclopropanation catalysts, iron(II) complexes of the related saldach and tmtaa ligand systems were investigated. Both (TTP)Fe and (tmtaa)Fe were efficient catalysts for the catalytic cyclopropanation of olefins with aryldiazomethanes. The cyclopropane stereoselectivities derived from (TTP)Fe were greater than those obtained using (tmtaa)Fe, when using *p*-tolyldiazomethane. Steric differences in the metal complexes may influence these observed stereoselectivities. The iron atom in complex **4** is displaced 0.114 Å above the N_4 plane of the tmtaa ligand,[23] while the iron atom in (TPP)Fe lies within the N_4 plane of the porphyrin ligand.[24] Moreover, in the structurally characterized complex (tmtaa)Fe=CPh_2, the iron atom lies 0.355(1) Å above the N_4 plane toward the carbene ligand.[21] As a result, the carbene ligand encounters little steric encumbrance from the benzo rings of the tmtaa ligand. Presumably, the carbene carbon in (tmtaa)Fe=CHR is more accessible compared to the carbene carbon of (TTP)Fe=CHR. Thus, the less crowded environment at the active site in (tmtaa)Fe=CHR leads to lower stereoselectivities compared to that of (TTP)Fe=CHR. Further evidence for the steric influence of the macrocyclic ligand on diastereoselectivities was derived from studies in which the size of the ortho-substituents of the tetraarylporphyrin was varied. This served to modify the size of the pocket around the active site. As the ortho-group increased in steric bulk [R = H (TTP), Me (TMP), and OMe (TDMPP)], the *trans/cis* ratio for cyclopropane **6** increased sequentially from 8.0:1, to 13:1, and to 15:1, respectively (Table 2).

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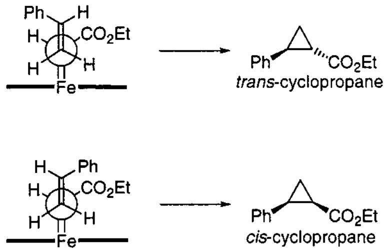

Figure 2. Olefin approach to the iron carbene intermediate when the carbene substituent is small. The trans/cis ratio of the product cyclopropane is determined by the approach of the styrene molecule and a late transition state along the reaction path.

The complex (saldach)Fe was not an efficient catalyst for cyclopropanation. This may be due to activation of the imine bonds of the salen ligand[25] and complications arising from side reactions involving these functional groups.

Effect of Diazo Reagent Structure on Cyclopropane Stereoselectivity. Catalytic production of *cis*-substituted cyclopropanes is rare. Rhodium(III) porphyrins give slight excesses of *cis*-substituted cyclopropanes using diazo esters as the carbene source.[26] Doyle and co-workers showed that catalysis using rhodium(II) acetate gave primarily *cis*-substituted cyclopropanes when phenyldiazomethane was used as the carbene source (*cis/trans* = 3.3 for 1,2-diphenylcyclopropane), but the yields are often low (38% for 1,2-diphenylcyclopropane).[3b] Additionally, Seitz and Hossain reported that 10 mol % of the iron complex [(η^5-C_5H_5)Fe$(CO)_2$(THF)][BF_4] catalyzed the production of *cis*-substituted cyclopropanes (*cis/trans* ≥ 24:1) using phenyl diazomethane as the carbene source.[3c]

Using either ca. 0.8 mol % (TTP)Fe or ca. 1.8 mol % (tmtaa)Fe and *p*-tolyldiazomethane, primarily *trans*-cyclopropanes were obtained with styrene (*trans/cis* = 14:1 for **1** and 1.9:1 for **4**). However, by changing the diazo reagent to mesityldiazomethane, *cis*-cyclopropanes became the major product. A mechanistic analysis rationalizes these phenomena. As proposed previously for (TTP)Fe,[17] the preferred olefin approach for cyclopropanation arises from a parallel, side-on orientation of the C=C−C alkene plane relative to the Fe=CHC$_\alpha$ plane (Figure 2). When the substituent on the carbene ligand is 2,4,6-mesityl, this side-on approach is impeded by the methyls in the 2,6-positions of the mesityl group (Figure 3). Consequently, the only available product-forming olefin approach with the mesitylmethylidene intermediate is from above the iron mesitylmethylidene complex. The preference for the cis-product is presumably due to a $\pi-\pi$ interaction between the arenes in the transition state (Figure 4).

The change in olefin approach with the mesityldiazomethane system is supported by the observation that *trans*-β-methylstyrene was converted to cyclopropane **2c** using mesityldiazomethane as the carbene source and (TTP)Fe as the catalyst. In comparison, *trans*-β-methylstyrene was not cyclopropanated when EDA, *p*-tolyldiazomethane, or trimethylsilyldiazomethane were used as the carbene source. The side-on approach shown in Figure 2 is not available to 1,2-substituted olefins due to unfavorable steric interactions with the porphyrin (or tmtaa) ligand.

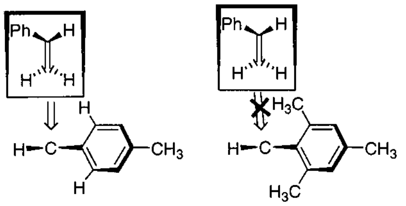

Figure 3. Olefin approach to the iron carbene intermediate as viewed down the C=Fe bond (Fe atom not shown beneath the carbene carbon). The plane of the olefin is parallel to the plane defined by the Fe=CH fragment. When the carbene substituent is mesityl (right), the *o*-methyl groups prevent the olefin from approaching from the same direction as when the substituent is *p*-tolyl (left).

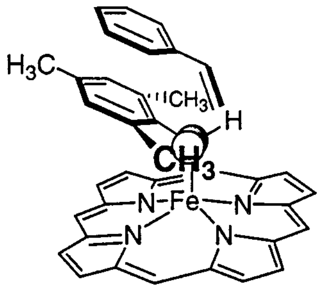

Figure 4. Illustration of styrene approach toward (TTP)Fe=CH(mesityl). Arene $\pi-\pi$ interactions presumably promote formation of the *cis*-cyclopropane.

Use of Low-Temperature To Improve Stereoselectivity in (TTP)Fe-Catalyzed Cyclopropanation Reactions. A common method used to increase the *trans/cis* ratio for catalytic cyclopropanation of olefins with diazo esters is to increase the size of the alkyl group on the diazo ester.[27] However, most of these diazo reagents are not commercially available. Consequently, it would be synthetically useful to improve diastereoselectivities with commercially available reagents. At ambient temperature in methylene chloride solvent, catalytic amounts of (TTP)Fe produce cyclopropane from EDA and styrene with a *trans/cis* ratio of 8.8:1.[17] By lowering the reaction temperature to −78 °C, the *trans/cis* ratio for cyclopropane **6** was dramatically increased to 29 ± 2 when methylene chloride was used as the solvent. This increase in stereoselectivity is consistent with the late transition state for (TTP)Fe-catalyzed cyclopropanation reactions proposed previously.[17]

Cyclopropanation with Trimethylsilyldiazomethane. In the few documented cases of cyclopropanation using trimethylsilyldiazomethane as the carbene source, yields were generally low. A 46% yield of cyclopropane **7** with a *trans/cis* ratio of 4.8 was obtained using catalytic amounts of copper(I) chloride,[14c] and only a 2% yield of cyclopropane **7** was obtained using a ruthenium(II) carbene complex as the catalyst.[3e] Also, significant amounts of *bis*(trimethylsilyl)ethene were produced. When (TTP)Fe was used as the catalyst, styrene was

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converted to cyclopropane **7** in 89 ± 4% yield with no bis(trimethylsilyl)ethene production. Additionally, the stereoselectivity for the reaction was excellent, providing up to a 13-fold excess of *trans*-**7**.

Conclusions

Iron(II) porphyrins are among the most efficient catalysts reported for the catalytic cyclopropanation of olefins with diazo reagents. Using iron(II) complexes of tmtaa and porphyrins, the stereochemistry of product cyclopropanes can be controlled by varying the reaction temperature, solvent, macrocyclic substituents, or diazo reagent. For example, at −78 °C, *trans/cis* ratios of up to 29:1 were possible in the cyclopropanation of styrene with EDA using (TTP)Fe. The complex (TDMPP)Fe gave higher *trans/cis* ratios than (TTP)Fe. Additionally, (TTP)Fe and (tmtaa)Fe were efficient catalysts for the production of diarylcyclopropanes from aryldiazomethanes and styrene. Significantly, a reversal of stereoselectivity was observed with mesityldiazomethane. Cyclopropane *cis/trans* ratios of 2.9:1 were achieved using mesityldiazomethane and (tmtaa)Fe. The complex (TTP)-Fe was also an excellent catalyst for the production of silylcyclopropanes using (trimethylsilyl)diazomethane as the carbene source. When styrene was employed as the olefin, 1-phenyl-2-trimethylsilylcyclopropane was obtained in 89% yield.

Experimental Section

General Method. All reactions were carried out under dry nitrogen or argon using a Vacuum/Atmospheres glovebox equipped with a MO40H DriTrain gas purification system or on a vacuum line using standard Schlenk techniques. All solvents were dried using standard methods.[28] Olefins were dried over activated 4 Å molecular sieves and degassed prior to use. All slow additions were performed with a dropping funnel. ^1H NMR spectra were recorded on Varian VXR300 or Bruker DRX400 spectrometers. ^1H NMR peak positions were referenced against residual proton resonances of deuterated solvents (δ, ppm: $CDCl_3$, 7.24; C_6D_6, 7.15). Gas chromatography was performed using a HP 5890 Series II[29] and GC/MS data was obtained from a Finnegan Magnum GC-MS.[30] Electrospray mass data was obtained on a Finnigan TSQ 700 in the positive ion mode. Elemental analyses (C, H, N) were performed by Iowa State University Instrument Services. Hexamethylbenzene (aryldiazomethane reactions) or dodecane (EDA or N_2CHTMS reactions) were used as the internal standard for GC yield determinations. Aryldiazomethanes were prepared from the corresponding tosylhydrazones according to a literature procedure,[31] except that diethlyene glycol methyl ether was used rather than triethylene glycol as the solvent. The tetraazaannulene ligand, H_2tmtaa, was synthesized using a literature procedure.[32] The ligand H_2-(saldach) was synthesized by treating 2 equiv of salicylaldehyde with *trans*-1,2-diaminocyclohexane in refluxing ethanol for 1 h.[33] The disodium salt, Na_2(saldach) was synthesized according to a literature procedure.[32] A procedure published by Reed on the reduction of either (TTP)FeCl or $[(TTP)Fe]_2$-(μ-O) with Zn/Hg amalgam was used to synthesize (TTP)Fe.[34] Modified procedures as described below were used for the preparation of (tmtaa)Fe[35] and (saldach)Fe.[36]

Synthesis of (tmtaa)Fe, 4. In a round-bottom flask, 271 mg (0.790 mmol) of H_2tmtaa and 474 mg (2.20 mmol) of $FeBr_2$ were dissolved in ca. 5 mL of 2:1 (v/v) toluene/THF. To the stirred reaction was added approximately 1 mL of triethylamine, and the reaction mixture changed from orange to red-purple in color. After 19 h, the solvent was removed in vacuo and the product dissolved in 5 mL of toluene. The mixture was filtered through a pad of Celite to remove excess $FeBr_2$ and triethylammonium bromide. Recrystallization at −25 °C from toluene/hexanes (1:5 (v/v)) afforded 213 mg (68%) of complex **4** as a purple solid in two crops. The complex (tmtaa)Fe was paramagnetic with no observable signals in the ^1H NMR. However, sharp signals for the complex $(tmtaa)Fe(py)_2$ were observed upon addition of an excess of pyridine. ^1H (C_6D_6, 300 MHz): 7.03 (m, 12 H, $H_{Ar} + H_{py-3,5}$); 6.56 (d, 4H, $H_{py-2,6}$); 4.27 (s, 2H, methine); 2.42 (s, 12H, H_{Me}). The pyridine H-4 triplet was not observed. These data match the literature values in which (tmtaa)Fe was synthesized from H_2tmtaa and $Fe(py)_4$-$(NCS)_2$.

Synthesis of (saldach)Fe, 5. A round-bottom flask was charged with Na_2(saldach) (440 mg, 1.20 mmol), $FeBr_2$ (270 mg, 1.25 mmol), and 12 mL of toluene. THF (3 mL) was added to the brown-orange slurry which immediately changed color to a bright purple. The reaction was stirred for 10 min and then passed through a pad of Celite. The solvent was removed from the filtrate in vacuo, the residue was dissolved in a minimum of toluene and diluted with hexanes (4:1 (v/v) toluene/hexanes). Cooling to −25 °C produced microcrystalline **6** on filtration and washing with hexanes (230 mg, 51%). The complex (saldach)Fe was paramagnetic with no observable signals in the ^1H NMR spectrum. Addition of pyridine or *tert*-butyisocyanide did not yield any species observable by ^1H NMR. The UV/vis data were similar to those reported for the complex (salen)Fe which was synthesized from either H_2salen and iron(II) sulfate or iron(II) acetate in DMF or ethanol or from H_2(salen) and $Fe_3(CO)_{12}$ in DMF. UV/vis (toluene): 350, 533 nm. Anal. Calcd (found) for $C_{20}H_{20}FeN_2O_2$: C, 63.85 (63.40); H, 5.36 (5.65); N, 7.45 (6.59). MS{ESI}: $m/z = 376\ [M]^+$.

Catalytic Cyclopropanation Reactions Using Aryldiazomethanes. To a round-bottom flask was added 1.0 mL (8.7 mmol) of styrene, a known amount (typically on the order of 30 mg) of hexamethylbenzene (internal standard for GC), the appropriate iron catalyst, and 5 mL of THF. To the stirred reaction mixture was slowly added a solution of aryldiazomethane in 15 mL of 2:1 (v/v) petroleum ether/THF (ca. 580 μmol for reactions using *p*-tolyldiazomethane and ca. 600 μmol for reactions using mesityldiazomethane). The reaction was analyzed by GC to determine product yields. Products were identified by co-injection with authentic samples.

Independent Synthesis of 1-Mesityl-2-phenylcyclopropane, 2b. An authentic sample of compound **2b** was synthesized using the method of Applequist and Gdanski from mesitaldehyde and acetophenone.[7] The yield was 900 mg (12.2%) of a tan, viscous oil having a *trans/cis* ratio of 1.5:1. ^1H NMR ($CDCl_3$, 400 MHz) of *cis*-isomer, **5c**: 7.02 (m, 3H, C_6H_5), 6.72 (s, 2H, $C_6H_2(CH_3)_2$), 6.44 (m, 2H, C_6H_5), 2.21 (s, 6H, CH_3), 2.19 (s, 3H, CH_3), 2.02 (m, 1H, C_3H_4), 1.97 (m, 1H, C_3H_4), 1.40 (m, 1H, C_3H_4), 1.04 (m, 1H, C_3H_4). ^1H NMR ($CDCl_3$). ^1H NMR ($CDCl_3$, 400 MHz) of *trans*-isomer, **5c**: 7.32 (t, 2H, C_6H_5, $J_{HH} = 7.6$ Hz), 7.20 (m, 3H, C_6H_5), 6.86 (s, 2H,

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[29] DB-5 capillary column (30 m, 0.32 mm i.d., 0.25 μm film thickness).

[30] Varian gas chromatograph coupled to an ITS 40 ion trap mass spectrometer (capillary column DB-5MS (30 m, 0.25 mm i.d., 0.25 μm film thickness)).

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$C_6H_2(CH_3)_2$), 2.37 (s, 3H, CH_3), 2.27 (s, 6H, CH_3), 1.84 (m, 1H, C_3H_4), 1.76 (m, 1H, C_3H_4), 1.17 (m, 1H, C_3H_4), 1.02 (m, 1H, C_3H_4). ^{13}C NMR ($CDCl_3$, 100.8 MHz) *trans*- and *cis*-isomers: 143.23, 141.03, 138.95, 138.62, 135.85, 135.52, 135.28, 130.78, 128.72, 128.70, 128.34, 127.29, 126.31, 125.53, 125.42, 124.93, 25.85, 24.86, 23.42, 22.90, 20.82, 20.81, 20.79, 20.67, 19.50, 17.77.[37] MS{EI} *m/z* (rel intens): 236 $[M]^+$ (100), 222 (24), 133 (24), 117 (20), 63 (70), 53 (31).

Low-Temperature Preparation of Ethyl-2-phenylcyclopropanecarboxylate, 3. In a glovebox, 18 mg (25 μmol) of (TTP)Fe, 22 μL of dodecane (GC standard), and 9.13 mmol of styrene were placed into a round-bottom flask and dissolved in 15 mL of dichloromethane. The flask was capped with a rubber septum and removed from the glovebox. The flask was cooled to −78 °C with a dry ice/acetone bath, and EDA (108 μmol) was added via syringe. The reaction was stirred at −78 °C for 3 h and then allowed to warm to room temperature. The reaction was analyzed by gas chromatography. The yield of cyclopropane was 92 ± 7% with a *trans/cis* ratio of 29:1.

1-Phenyl-2-(trimethylsilyl)cyclopropane, 7. In a typical reaction, 8.5 mmol of styrene, 3.5 mg of (TTP)Fe (4.8 μmol, 0.6 mol %), and 20 μL of dodecane (GC standard) were dissolved in 3 mL of solvent. Trimethylsilyldiazomethane (400 μL of a 2.0 *M* solution in hexanes, 800 μmol) in 12 mL of solvent was added dropwise over approximately 1 h. The reaction mixture was stirred vigorously and analyzed by GC after ca. 18 h. Unlike cyclopropanation with other diazo reagents, the slow addition was not necessary, as no carbene dimer, 1,2-*bis*(trimethylsilyl)ethene, was ever detected in the reactions performed using (TTP)Fe as a catalyst. Therefore, subsequent reactions were performed by adding all of the trimethylsilyldiazomethane at once, rather than dropwise. The yield of cyclopropane was 89 ± 4%. The *trans/cis* ratio was 10 ± 1 using toluene as the solvent and 13 ± 1 using THF as the solvent. The cyclopropane could be isolated by removing all of the solvent and excess styrene in vacuo, dissolving the residue in hexanes, passing the solution through a plug of neutral alumina (2 × 5 cm), and eluting with hexanes. The cyclopropane was isolated after removal of the hexane from the combined filtrate and washings by rotary evaporation. ^1H (C_6D_6, 300 MHz) of the *trans*-isomer: 7.13 (m, 2H, C_6H_5), 7.03 (m, 3H, C_6H_5), 1.74 (m, 1H, C_3H_4), 0.89 (m, 1H, C_3H_4), 0.77 (m, 1H, C_3H_4), −0.03 (m, 10H, $C_3H_4 + Si(CH_3)_3$). ^1H (C_6D_6, 300 MHz) of the *cis*-isomer: 0.85 (m, 1H, C_3H_4), −0.19 (s, 9H, $Si(CH_3)_3$). All other signals for the *cis*-cyclopropane were obscured by those of the *trans*-isomer.

(TTP)Fe═CH(mesityl), 8a. A round-bottom flask was charged with 9 mg (13 μmol) of (TTP)Fe and ca. 2 mL of THF. To this solution was added 120 μL of a 136 mM solution of N_2CH(mesityl) (16.3 μmol) in pentane. The reaction mixture was stirred vigorously for 3 min, and then the solvent was removed in vacuo. The resulting complex was dissolved in C_6D_6, and its ^1H NMR spectrum was recorded. ^1H (C_6D_6, 400 MHz): 19.71 (s, 1H, ═CHAr), 8.72 (s, 8H, β-H), 7.84 (br, 8H, $C_6H_4CH_3$), 7.23 (d, 8H, $C_6H_4CH_3$, $J_{HH} = 7.6$ Hz), 5.54 (s, 2H, $C_6H_2(CH_3)_3$), 2.34 (s, 12H, $C_6H_4CH_3$), 1.70 (s, 3H, p-$C_6H_2(CH_3)_3$), −1.12 (s, 6H, o-$C_6H_2(CH_3)_3$). Contamination of the sample with ca. 5% (TTP)Fe precluded the isolation of pure material for elemental analysis.

(TTP)Fe═CH(TMS), 8b. To a solution of 24 mg (TTP)Fe (33 μmol) in 5 mL of toluene was added 51.5 μL of a 2.0 M solution of N_2CH(TMS) (1.0×10^2 μmol) in hexanes. The mixture was stirred for 3 h, and the solvent was removed at reduced pressure. The residue was dissolved in C_6D_6, and its ^1H NMR spectrum was recorded. ^1H (C_6D_6, 300 MHz): 24.86 (s, 1H, ═CHTMS), 8.69 (s, 8H, β-H), 7.92 (d, 8H, $C_6H_4CH_3$, $J_{HH} = 7.8$ Hz), 7.17 (d, 8H, $C_6H_4CH_3$, partially obscured by C_6D_6), 2.31 (s, 12H, $C_6H_4CH_3$), −1.80 (s, 9H, $Si(CH_3)_3$). Contamination of the sample with ca. 5% (TTP)Fe precluded the isolation of pure material for elemental analysis.

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Supporting Information Available: Plot of kinetic data for the reaction between (TTP)Fe═CH(mesityl) and styrene. This information is available free of charge via the Internet at http://pubs.acs.org.

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