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Abstract

Iron(II) *meso*-tetraphenylporphyrin is an efficient catalyst for the selective olefination of a variety of aromatic and aliphatic aldehydes with use of ethyl diazoacetate in the presence of triphenylphosphine. These reactions gave olefin products in excellent yields (>85%) with high selectivity for the *E*-isomer (>90%). For the olefination of ketones, the reactions were generally slow and the selectivities were low compared with those observed with aldehydes. Iron(III) *meso*-tetraphenylporphyrin chloride, reduced in situ, could be used as an olefination precatalyst to produce similar yields and selectivities. The olefination mechanism was investigated and the likely pathways are discussed.

Disciplines

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Iron Porphyrin-Catalyzed Olefination of Carbonyl Compounds with Ethyl Diazoacetate

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Iron(II) *meso*-tetraphenylporphyrin is an efficient catalyst for the selective olefination of a variety of aromatic and aliphatic aldehydes with use of ethyl diazoacetate in the presence of triphenylphosphine. These reactions gave olefin products in excellent yields (>85%) with high selectivity for the *E*-isomer (>90%). For the olefination of ketones, the reactions were generally slow and the selectivities were low compared with those observed with aldehydes. Iron(III) *meso*-tetraphenylporphyrin chloride, reduced in situ, could be used as an olefination precatalyst to produce similar yields and selectivities. The olefination mechanism was investigated and the likely pathways are discussed.

Introduction

Transition metal complexes have been used extensively by this group¹ and others² to catalyze the cyclopropanation of alkenes with ethyl diazoacetate and other suitable diazo reagents. In this paper, we describe an extension of the catalytic activity of metalloporphyrins and its applications with the first use of an iron(II) metalloporphyrin complex as a catalyst for an efficient olefination of carbonyl compounds. The generation of a carbon–carbon double bond is one of the important synthetic transformations in organic chemistry, especially in the areas of natural products and polymer synthesis. Commonly used procedures include the Wittig reaction and its modified versions, the Peterson reaction, and the Julia reaction.³ Organometallic variants for this transformation have also been

investigated in the past two decades and some achieved great success.⁴ Another alternative is the olefination of carbonyl compounds by suitable diazo reagents in the presence of transition metal catalysts and reducing agents such as triphenylphosphine or trialkylstibines.⁵ In contrast to the conventional Wittig method, the metal-mediated syntheses are streamlined into one simple reaction. However, several drawbacks are apparent. These include (a) high reaction temperatures that increase safety hazards when diazo compounds are used,^{5a,b} (b) high catalyst loading (>5 mol %),^{5a–c} (c) stereoselectivities^{5c} that often depend strongly on the choice of the aldehydes, and (d) low yields.^{5a,c} In 1998, Fujimura reported a one-pot olefination method using a ruthenium(II) complex as the catalyst.⁶ In this methodology, the amount of catalyst was reduced to 2.5 mol % and a temperature of 50 °C was employed. For some aldehyde substrates, the isolated yields were not particularly high.

We recently reported an olefination process using iron(II) *meso*-tetratolylporphyrin, Fe(TTP), as the catalyst.⁷ Compared to the observations described above, high stereoselectivities and high yields of olefins are generally produced from a variety of aldehydes with this new method. Our reaction conditions are the mildest among all the catalytic olefination methods reported. The *meso*-tetraphenylporphyrin analogue, Fe(TPP), pro-

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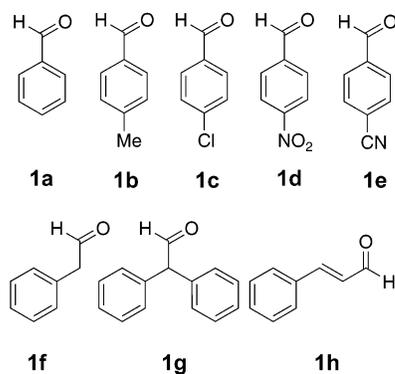
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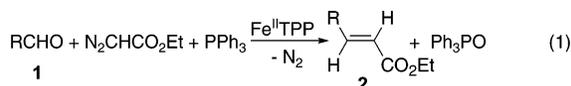
Chart 1



duces similar results. More details and additional mechanistic studies are reported here.

Results and Discussion

Catalytic Olefination of Aldehydes. A one-pot approach for the synthesis of α,β -unsaturated esters was developed with use of aldehydes, ethyl diazoacetate (EDA), and triphenylphosphine, Ph_3P , in the presence of catalytic amounts of iron(II) *meso*-tetraphenylporphyrin (0.1–2 mol %), in toluene at 22 °C (eq 1).



Reactions were generally run in an inert-atmosphere glovebox, but could also be conveniently performed on a benchtop with Schlenk techniques. The ratio of reagents was qualitatively optimized by examining reactions at short times (3 min). With 1.1 equiv of EDA per benzaldehyde, a 54% conversion of substrate was observed by GC. Ethyl maleate and fumarate were also formed and their production decreased the availability of EDA to participate in the desired reaction. A reaction run with 2 equiv of EDA resulted in a 71% conversion under the same conditions. In addition to better yields, the higher amount of EDA helps to keep $\text{Fe}(\text{TPP})$ in its reduced state.^{1c} However, extreme excesses of EDA only served to increase the production of maleates and fumarates over longer times. Consequently, 2 equiv of EDA was used in all subsequent reactions.

The ratio of triphenylphosphine was also examined in a similar manner at early reaction times. With 1.1 equiv of triphenylphosphine, the conversion of benzaldehyde was 57% after 3 min. Increasing the Ph_3P amount to 2 equiv increased the conversion to 71% in the same reaction time. With 5 and 10 equiv of Ph_3P , the conversion dropped to 60% and 54%, respectively, after 3 min. Because excess Ph_3P also made the product separation more difficult, 1.1 equiv of Ph_3P was used in our typical reaction conditions.

A variety of aromatic and aliphatic aldehydes (Chart 1) were olefinated and the results are listed in Table 1. In a typical reaction with benzaldehyde, 100% conversion was achieved within 3 h and purification of reaction mixture gave a 94% isolated yield of the cinnamate with an *E/Z* ratio of 24. Very similar results were reported with $\text{O}=\text{ReCl}_3(\text{PPh}_3)_2$ as a catalyst.^{5f} Ethyl maleate and ethyl fumarate were also produced in a combined yield

Table 1. Olefination of Aldehydes with EDA/ $\text{Ph}_3\text{P}/\text{Fe}^{\text{II}}(\text{TPP})$

aldehyde	reaction time (h)	turnover no.	product	isolated yield (%)	<i>E/Z</i> selectivity
1a	3	128	2a	94	24:1
1b	6	119	2b	91	28:1
1c	2	98	2c	95	18:1
1d	0.2	80	2d	90	15:1
1e	0.5	103	2e	95	18:1
1f	24	95	2f	85	10:1
1g	2	64	2g	93	40:1
1h	2	103	2h	95	10:1

of 15% (GC), but were readily removed by column chromatography. The reaction is catalytic as no cinnamates were produced without $\text{Fe}^{\text{II}}(\text{TPP})$. In the absence of the catalyst, the azine, $\text{PhCH}=\text{N}-\text{N}=\text{CHCO}_2\text{Et}$, was produced in 40% yield when the reaction mixture was allowed to stir for a period of 4 days.

The reaction in the absence of triphenylphosphine also produced no olefination product. We found that this reaction required a stoichiometric amount of triphenylphosphine relative to that of the aldehydes to give a high conversion to olefination products. Triphenylphosphine serves as an oxygen atom acceptor, producing 1 equiv of triphenylphosphine oxide. GC and GC-MS analysis confirmed the formation of $\text{Ph}_3\text{P}=\text{O}$ (*m/z* 278).

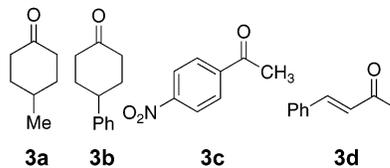
The catalyst has a reasonably long lifetime in the absence of oxygen. $\text{Fe}(\text{TPP})$ survived three generations of reagent addition over a period of 15 h with little or no sign of deactivation. In addition, the catalyst does not serve to isomerize the product after its formation. In control experiments, treatment of authentic samples of ethyl cinnamate (*E/Z* 6:1) in toluene with $\text{Fe}(\text{TPP})$, with or without EDA, resulted in no change in the *E/Z* ratio over a period of 4 days. Thus, olefin isomerization does not occur under catalytic conditions.

With an electron-donating group on the substrate, the 4-tolualdehyde reaction required a longer reaction time of 6 h to achieve a 95% conversion. On the other hand, aromatic aldehydes with electron-withdrawing groups, such as 4-chlorobenzaldehyde, 4-nitrobenzaldehyde, and 4-cyanobenzaldehyde, reacted much faster than benzaldehyde. It only took 4-chlorobenzaldehyde 2 h to completely convert to the corresponding olefin. The reaction time for 4-nitrobenzaldehyde is 10 min, and 30 min for 4-cyanobenzaldehyde.

Two aliphatic aldehyde substrates, phenylacetaldehyde and diphenylacetaldehyde, were also examined. Olefination of phenylacetaldehyde was slow and required 24 h of reaction time for a 91% conversion. However, the reaction of diphenylacetaldehyde was substantially faster and after 2 h, a 95% conversion was achieved with an *E/Z* selectivity of 40:1.

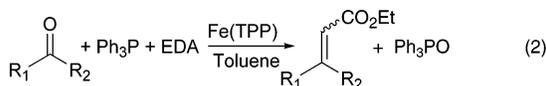
Olefination of *E*-cinnamaldehyde was also a facile reaction. A 100% conversion was achieved after 2 h of stirring. Purification of the reaction mixture by column chromatography afforded a 95% isolated yield with an *E/Z* selectivity of 10:1.

Solvent Effects. Olefination reactions were also performed in coordinating and noncoordinating solvents. In THF with standard conditions of 1 equiv of benzaldehyde, 2 equiv of EDA, 1.1 equiv of Ph_3P , and 1 mol % of $\text{Fe}(\text{TPP})$, the reaction reached a 73% conversion in 3 h. The corresponding reaction in toluene achieved a 100% conversion in the same time.

Table 2. Olefination of Ketones with EDA/Ph₃P/Fe^{II}(TPP)


ketone	reaction time (days)	product	isolated yield (%) (vs EDA)	<i>Z/E</i> selectivity
3a	3	4a	64	none
3b	3	4b	75	none
3c	4	4c	80	2:1
3d	2	4d	66	2.8:1

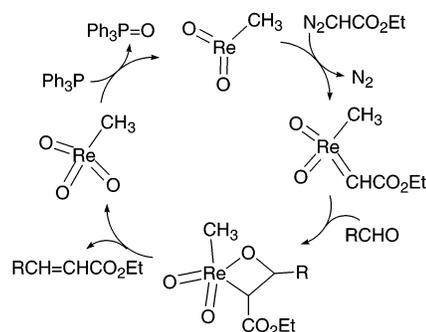
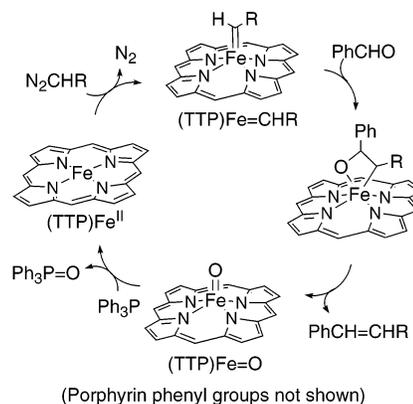
Catalytic Olefination of Ketones. Reactions of ketones were substantially slower than the aldehyde reactions. With 4-methylcyclohexanone and similar reaction ratios as in the analogous aldehyde reactions, no ethyl 1-(4-methylcyclohexylidene)acetate was observed after 2 days of stirring. EDA dimerization was the only reaction observed (30% GC yield). Higher temperatures (50 °C) still only produced maleates and fumarates (60% GC yield, 2 days). Large excesses of ketone were necessary to produce acceptable yields of olefination products. Typical reaction conditions (eq 2)



were 10 equiv of ketone, 1.1 equiv of triphenylphosphine, and 1 equiv of ethyl diazoacetate, with 5 mg of Fe^{II}(TPP) catalyst (1 mol % versus ethyl diazoacetate). Isomer assignments were determined by 2D-NOSY. For *Z*-isomers, a through-space interaction was observed between the vinyl hydrogen and the methyl protons on the double bond. Results for ketone reactions are summarized in Table 2.

Effect of Catalyst Loading. A lower catalytic loading (0.1 mol % of catalyst) was examined for three aldehydes and one ketone. For benzaldehyde (**1a**), the reaction was slightly slower than when 1.0 mol % of catalyst was used. A 2 h reaction time was required for reaction to achieve 95% conversion compared to 1 h when 1 mol % of catalyst was used. For 4-nitrobenzaldehyde (**1d**), qualitative estimates were insufficient to detect rate differences as a function of catalyst amounts. Within 3 min, an 85% conversion was achieved for 0.1 mol % of catalyst, compared to an 81% conversion with 1 mol % of catalyst. Interestingly, the *E/Z* selectivity of this reaction increased substantially from 15:1 to 24:1 with the lower catalyst loading (vide infra). The same trend was observed for 4-cyanobenzaldehyde (**1e**). Within half an hour, 100% conversions of the electron-deficient aldehydes were achieved for both 1 and 0.1 mol % of catalyst loadings. The *E/Z* selectivity for **1e** was 18:1 with 1 mol % of catalyst, compared to 26:1 with 0.1 mol % of catalyst. Higher catalyst loadings (10 mol %) were applied to the 4-nitrobenzaldehyde and 4-cyanobenzaldehyde reactions. The *E/Z* selectivities in these cases were 4:1 (4-nitrobenzaldehyde) and 6:1 (4-cyanobenzaldehyde).

With less reactive substrates such as 4-methylcyclohexanone (**3a**), lowering the catalyst had a different

Scheme 1**Scheme 2**

effect. When 0.1 mol % of catalyst was used, the azine, CH₃C₆H₉=N=N=CHCO₂Et, became the major product.

Fe^{III}(TPP)Cl as the Precatalyst. For practical applications, the possibility of using Fe^{III}(TPP)Cl as a catalyst was examined. EDA is known to be a mild reducing agent⁸ and is effective at reducing Fe(TTP)Cl in situ.^{1c} The olefination of benzaldehyde with Fe^{III}(TPP)Cl was slower than that with Fe^{II}(TPP). When 1 mol % of Fe^{III}(TPP)Cl was used under N₂ at 22 °C, a 4-h reaction time was required to achieve 95% conversion as compared to 1 h for Fe^{II}(TPP). The *E/Z* selectivity remained the same as with Fe^{II}(TPP).

Mechanistic Studies. Herrmann et al. reported a methyltrioxorhenium (MTO)-catalyzed olefination method in 1991.^{5c} To account for the mechanism of this reaction, a catalytic cycle (Scheme 1) was proposed. In the first step, an oxygen atom was abstracted from MTO by triphenylphosphine. The resultant Re(V) dioxo complex then reacted with a diazo reagent to produce a carbene complex that subsequently formed a metallaoxetane species in the presence of aldehydes. Fragmentation of the metallaoxetane produced the new olefin and regenerates MTO.

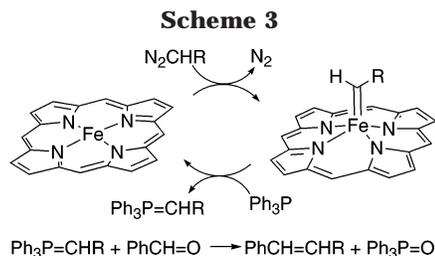
In analogy to the MTO system, a similar catalytic cycle for the iron(II) porphyrin is shown in Scheme 2. A likely active species in the iron porphyrin-catalyzed reactions is an iron-carbene complex formed by reaction of the iron(II) porphyrin with EDA. Even though (TTP)-Fe=CHCO₂Et is very reactive and has never been isolated or detected spectroscopically, related complexes prepared from mesityl diazomethane and trimethylsilyl diazomethane are readily observed by ¹H NMR spectroscopy.^{1c,d} The more electron rich analogue, (TTP)-

$\text{Os}=\text{CHCO}_2\text{Et}$, has been isolated and well characterized.^{1a,b} The iron-carbene complex may serve as a nucleophile⁹ that attacks the carbonyl functional group of the aldehydes and ketones to produce a metallaoxetane intermediate. This is consistent with the higher reactivity of electron poor aldehydes. Subsequent ring cleavage of the metallaoxetane would produce an olefin and an oxoiron porphyrin complex. Regeneration of the Fe(TPP) would occur by oxidation of triphenylphosphine to triphenylphosphine oxide.

For this mechanism to be viable, the inner sphere reaction between unencumbered oxoiron(IV) and iron(II) porphyrins, producing a μ -oxo Fe(III) dimer,¹⁰ must be minimal. Formation of the Fe(III) dimer would serve to quickly inactivate the catalyst. In a control experiment, catalyst Fe(TPP) was tested for three generations of substrate addition (benzaldehyde, triphenylphosphine, and EDA) over a 15-h period. The catalyst showed no significant deactivation.

Attempts were then made to test for the presence of the oxoiron(IV) with other oxygen atom acceptors. Olefins were chosen since oxoiron(IV) porphyrin complexes can epoxidize the double bond.¹¹ To examine this possibility, an experiment was run with benzaldehyde, ethyl diazoacetate, 1.0 mol % of Fe(TPP), and styrene as the reductant in place of triphenylphosphine. After the reaction, no ethyl cinnamate was observed. The only product was ethyl 2-phenylcyclopropylcarboxylate (100%), indicating that styrene was much more efficient in reacting with the carbene complex than was the aldehyde. An alternative oxygen acceptor, cyclohexene, was subsequently employed. 1,2-Disubstituted olefins are poor cyclopropanation substrates,^{1c} but readily undergo epoxidation.¹¹ However, using cyclohexene in place of triphenylphosphine under catalytic conditions resulted in neither olefination of the aldehyde nor epoxidation of the alkene. The organic products were ethyl maleate and fumarate produced by carbene dimerization. These studies indicated that an iron-carbene complex was involved but that the oxoiron(IV) species was an unlikely intermediate. Moreover, metallaoxetane intermediates were proposed as key product forming species in metalloporphyrin-catalyzed epoxidations,¹² but no direct evidence for such intermediates has been reported.¹³

The reactivity profile of the Fe(TPP)-catalyzed olefination reaction differs significantly from that of the $\text{MoO}(\text{S}_2\text{CNET}_2)_2$ -mediated process. The catalytic cycle for the Mo system purportedly involves metalloazines,^{5a} $(\text{Et}_2\text{NCS}_2)_2\text{OMo}=\text{N}=\text{N}=\text{CHCO}_2\text{Et}$, and phosphazines, $\text{Ph}_3\text{P}=\text{N}=\text{N}=\text{CHCO}_2\text{Et}$.¹⁴ The phosphazine is presum-



ably responsible for the formation of large amounts of azines with electron-poor aldehydes in this system.

An alternative mechanism for the Fe(TPP) olefination reaction is shown in Scheme 3. In this process, Fe(TPP) serves to catalytically convert the diazo reagent and phosphine to phosphorane. The phosphorane in turn produces a new olefin and phosphine oxide on reaction with the aldehyde. An experiment set up with Ph_3P , EDA, and Fe(TPP) (1 mol %) was consistent with this. After 30 min of stirring, phosphorane, $\text{Ph}_3\text{P}=\text{CHCO}_2\text{Et}$, was detected by ^1H and ^{31}P NMR spectroscopy as the major product along with a combined 5% yield of Ph_3P and Ph_3PO . Purification of the reaction mixture afforded pure phosphorane in 60% yield. Key ^1H NMR signals identifying the phosphorane are the methine signals at 2.94 (cisoid isomer) and 2.76 ppm (transoid isomer). In addition, the ^{31}P NMR spectrum contained resonances for the cisoid isomer at δ 18.8 ppm and the transoid isomer at δ 17.3 ppm. These spectral data were experimentally identical with reported values.¹⁵ Particularly diagnostic is the coupling constant $J = 21$ Hz between the phosphorus and the methine proton.^{12a}

For comparison with the catalytic process, a stoichiometric reaction of 100 mg of benzaldehyde with 1 equiv of $\text{Ph}_3\text{P}=\text{CHCO}_2\text{Et}$ was run at room temperature. The formation of ethyl cinnamate was complete within 4 h, producing an *E/Z* ratio of 23:1. This ratio matches values reported previously.¹⁶ The time scale of the stoichiometric reaction also was consistent with published rate constants¹⁷ and is comparable to the time necessary for the analogous catalytic process.

The proposed catalytic cycle in Scheme 3 suggests that an increased phosphine concentration should enhance the rate of reaction. However, phosphine can bind to Fe(TPP)¹⁸ and may inhibit the formation of the carbene complex. These competitive factors were observed. Qualitatively, the rate of reaction with 2 equiv of Ph_3P was faster than when 1 equiv was used, with no noticeable change in yields. Above 2 equiv of Ph_3P , the rate appeared to saturate.

A set of experiments was then set up to test the olefination selectivities under three different conditions as shown in reactions 3–5. The results are listed in Table 3. For ketones and electron-rich aldehydes, little or no differences in reaction rates or yields were observed as a function of conditions. These data give

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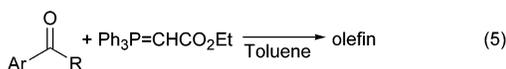
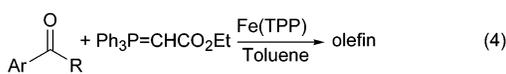
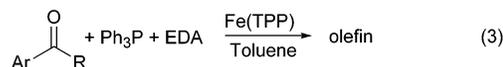
Table 3. Product Selectivities

substrate	<i>E/Z</i> ratio		
	reaction 3	reaction 4	reaction 5
benzaldehyde	24:1	23:1	23:1
4-tolualdehyde	28:1	28:1	28:1
4-nitroacetophenone	1:2	1:2.7	1:2.8
4-nitrobenzaldehyde	15:1	17:1	31:1
4-cyanobenzaldehyde	18:1	19:1	33:1

Table 4. 4-Nitrobenzaldehyde Olefination Results

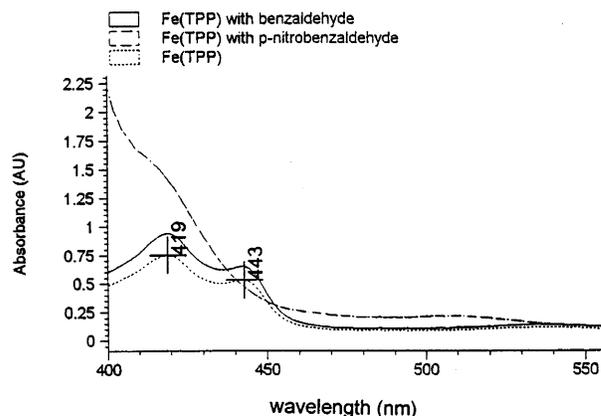
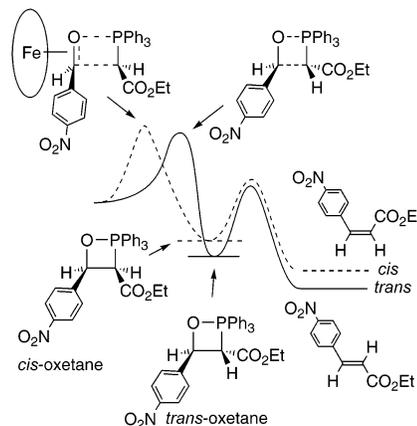
reactants	<i>E/Z</i> product selectivity vs catalyst loadings			
	10 mol %	1 mol %	0.1 mol %	0 mol %
4-nitrobenzaldehyde + Ph ₃ P + EDA	4.1:1	15:1	24:1	none
4-nitrobenzaldehyde + Ph ₃ P=CHCO ₂ Et	6.0:1	17:1	24:1	31:1

strong support for the mechanism shown in Scheme 3 for benzaldehyde and less reactive aldehydes and ketones.



For more reactive aldehydes such as 4-nitrobenzaldehyde and 4-cyanobenzaldehyde, the mechanism seems to be more complicated than that shown in Scheme 3. More detailed results illustrating the effects of catalyst loading with 4-nitrobenzaldehyde are listed in Table 4. The trend is consistent for either the catalytic olefination reaction or the stoichiometric reaction. The key finding is that the larger the catalyst loading, the higher the amount of *cis* olefin produced from electron-poor aldehydes. This trend is not consistent with a Lewis acid promoted retro-Wittig process. The Lewis acidic Fe(III)(TPP) would be less likely to interact with an oxaphosphetane bearing strongly electron withdrawing nitro or cyano substituents. Moreover, carbonyl-stabilized ylides exhibit little tendency for loss of stereochemistry through reversibility of the Wittig reaction.¹⁹ Alternatively, Fe(II)(TPP) must perturb the oxetane formation with electron-poor aldehydes.

UV-Vis Studies. An UV-vis study was undertaken to probe the interaction between iron(II) porphyrin and aldehydes. The Soret region for Fe^{II}(TPP) exhibits distinct peaks at 422 and 440 nm in toluene.²⁰ Addition of benzaldehyde (greater than 10³-fold excess) resulted in no change to the spectrum. However, addition of a similar amount of 4-nitrobenzaldehyde to the iron(II) porphyrin solution resulted in the disappearance of the peak at 440 nm. These observations are illustrated in Figure 1. It is clear that 4-nitrobenzaldehyde forms a complex with Fe(III)(TPP). On the basis of previous work on π -coordinated electron-poor aldehydes,²¹ it is likely that a π -interaction occurs between iron(II) porphyrin

**Figure 1.** UV studies of Fe(III)(TPP) in the presence of benzaldehyde and 4-nitrobenzaldehyde.**Scheme 4**

and electron-poor aromatic aldehydes. Complexation of unsaturated organic molecules to transition metals is well-known to activate multiple bonds toward attacks by nucleophiles.²²

Formation of the π -complex between Fe(II)(TPP) and 4-nitrobenzaldehyde is consistent with the change in *trans/cis* selectivity on increasing the amount of Fe(II)(TPP) in both catalytic and stoichiometric reaction as shown in Scheme 4. Without iron(II) porphyrin, steric effects play an important role in the formation of the *trans*-oxetane with stabilized ylides.²³ In this case, the transition state for the formation of the oxetane is likely to be late in the reaction coordinate and is presumably product-like, favoring the formation of the *trans* product. When Fe(II)(TPP) is present, the π -interaction between the aldehyde carbonyl and the Lewis acidic iron(II) porphyrin will activate the carbonyl group toward nucleophilic attack by the phosphorane. Consequently, the transition state for oxetane formation occurs earlier than without the metal complex. In the earlier transition state, steric factors are not as important as in the

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late transition state and a larger fraction of *cis*-oxetane will be produced.

The proposed mechanism in Scheme 4 suggests that changing the electronic nature of the iron(II) porphyrin will modify the stability of the π -complex and alter the *trans/cis* selectivities. This effect was observed with the electron-deficient iron(II) tetra(pentafluorophenyl)porphyrin and the more electron-rich iron(II) tetra(4-methoxyphenyl)porphyrin. When 1.0 mol % of iron(II) tetra(pentafluorophenyl)porphyrin was used in the 4-nitrobenzaldehyde olefination reaction, a *trans/cis* ratio of 23:1 was observed, compared to the *trans/cis* ratio of 15:1 when 1.0 mol % of Fe(TPP) was used. This is due to the reduced π -back-bonding from iron(II) tetra(pentafluorophenyl)porphyrin to 4-nitrobenzaldehyde, which makes the π -complex less accessible. The opposite effect was observed when a more electron-rich complex was used in the 4-nitrobenzaldehyde olefination reaction. With 1.0 mol % of iron(II) tetra(4-methoxyphenyl)porphyrin as catalyst, a *trans/cis* ratio of 13:1 was observed.

Conclusion

We have reported the first application of iron porphyrins for the convenient and efficient catalytic olefination of carbonyl compounds with EDA in the presence of Ph₃P. Both aromatic and aliphatic aldehydes were efficiently converted to olefin products in excellent yield (>85%) with high selectivity for the *E*-olefin isomer (>90%). Ketones react slowly but are also converted to olefins with this method. The reaction mechanism involves the formation of a free ylide through catalytic transfer of a carbene ligand from iron(II) to phosphine. The highest diastereoselectivities are achieved with a stoichiometric reaction between the isolated ylide and aldehyde. However, a convenient one-pot synthesis can be run with a lower catalyst loading of 0.1% Fe(TPP) with only a small drop in diastereoselectivity. Prereduction of the iron porphyrin to Fe(II) is also unnecessary. Commercially available Fe(III) porphyrin complexes can be reduced in situ to achieve useful and simple catalytic processes.

Experimental Section

General Methods. All reactions involving Fe(TPP) were carried out under dry nitrogen in a Vacuum Atmosphere glovebox equipped with a MO40H DriTrain gas purification system. THF was distilled from blue solutions of sodium benzophenone ketyl. Toluene was passed through a column of catalytic copper and alumina as described by Grubbs et al.²⁴ All aldehydes and ethyl diazoacetate were purchased from Aldrich and degassed by 3 freeze-pump-thaw cycles prior to use. Iron(III) *meso*-tetraphenylporphyrin, iron(III) *meso*-tetra(pentafluorophenyl)porphyrin chloride, iron(III) *meso*-tetra(4-methoxyphenyl)porphyrin, and 200–425 mesh Silica were purchased from Aldrich and used as received. Iron(II) *meso*-tetraphenylporphyrin was synthesized following the procedure of Reed by reducing iron(III) *meso*-tetraphenylporphyrin with Zn/Hg amalgam in toluene for 6 h.²⁵ The UV/vis spectrum for iron(II) tetraphenylporphyrin was analogous to that reported

in the literature.²⁰ Iron(II) *meso*-tetra(pentafluorophenyl)porphyrin and iron(II) *meso*-tetra(4-methoxyphenyl)porphyrin were synthesized from the corresponding Fe(III) complexes by a similar method used for the preparation of iron(II) *meso*-tetraphenylporphyrin.

¹H NMR and ¹³C spectra were recorded on Varian VXR300 or Bruker DRX400 spectrometers. ¹H NMR peak positions were referenced against residual proton resonances of deuterated solvent (δ (ppm): CHCl₃, 7.26). ¹³C NMR peak positions were referenced against the center line of the deuterated solvent resonance (δ (ppm): CDCl₃, 77). ³¹P NMR spectra were recorded on a Varian VXR400 spectrometer and peak positions were referenced against the internal standard of Ph₃P (δ (ppm): -4.71).²⁶ Gas chromatography was performed with a HP 5890 Series II instrument²⁷ and GC/MS data were obtained from a Finnegan Magnum GC-MS.²⁸ High-resolution mass spectrometry for exact mass determination was performed on a Kratos MS50 spectrometer with electron impact (EI) ionization.

Synthetic details and ¹H NMR data for compounds that have appeared in the literature are provided in the Supporting Information (2a–2d, 2f–2h, 4a–4b, and 4d). The stereochemistry of the aldehyde olefination products was assigned by ¹H NMR spectroscopy, using coupling constants of the vinyl protons. The stereochemistry of the ketone olefination products was assigned by ¹H NMR and 2D-NOSY. Once the major isomer was assigned, product ratios were determined by GC.

Aldehyde Olefination Reactions with Fe(TPP) (Procedure A). In a typical experiment, 0.943 mmol (1 equiv) of aldehyde, 272 mg (1.04 mmol, 1.1 equiv) of triphenylphosphine, and 5 mg (1 mol % versus aldehyde) of Fe^{II}(TPP) were placed into a round-bottom flask and dissolved in 10 mL of toluene at 22 °C. A solution of 215 mg (1.88 mmol, 2 equiv) of ethyl diazoacetate in 3 mL of toluene was added dropwise over approximately 2 min to the reaction mixture with vigorous stirring. After the addition was finished, the progress of the reaction was monitored by GC. When the reaction reached maximum conversion, the reaction flask was removed from the glovebox and the solvent was removed in vacuo. The residue was then purified by flash column chromatography (SiO₂, 1.5 cm × 25 cm), using 20:1 hexane/EtOAc. The olefin was isolated by evaporation of the solvent. The *E/Z* selectivity was determined by GC and ¹H NMR. ¹H NMR analysis showed a ³J_{HH} of 15.9 Hz for *trans*-hydrogens and a ³J_{HH} of 12.6 Hz for *cis*-hydrogens. In GC analyses, the *E* isomer appeared at a shorter retention time relative to that of the *Z* isomer.

Ketone Olefination Reactions with Fe(TPP) (Procedure B). In a typical experiment, 8.74 mmol (10.0 equiv) of ketone, 253 mg (0.961 mmol, 1.10 equiv) of triphenylphosphine, and 5 mg (1 mol % versus ethyl diazoacetate) Fe^{II}(TPP) were placed in a round-bottom flask and dissolved in 10 mL of toluene at 22 °C. A solution of 99.7 mg (0.874 mmol, 1.00 equiv) of ethyl diazoacetate in 3 mL of toluene was added dropwise over approximately 2 min to the reaction mixture with vigorous stirring. After the addition was finished, the progress of the reaction was monitored by GC as described above. On completion of the reaction, the flask was removed from the glovebox and the solvent was removed in vacuo. The residue was then purified by flash column chromatography (SiO₂, 1.5 cm × 25 cm), using 20:1 hexane/EtOAc. The olefin was isolated by evaporation of the solvent.

Control Reaction without Catalyst. As in procedure A except with no catalyst, a control reaction was set up with 0.100 g (0.943 mmol, 1.00 equiv) of benzaldehyde, 272 mg (1.04

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(27) DB-5 capillary column (30 m, 0.32-mm i.d., 0.25 μ m film thickness).

(28) 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 μ m film thickness]).

mmol, 1.10 equiv) of triphenylphosphine, and 215 mg (1.88 mmol, 2.00 equiv) of ethyl diazoacetate. After the addition of the diazo reagent was finished, the reaction was monitored by GC over a period of 4 days. The reaction mixture was taken subsequently out of the box and the solvent was removed in vacuo. The residue was purified by flash column chromatography (SiO₂, 1.5 cm × 25 cm), using 20:1 hexane/EtOAc. Evaporation of the solvent afforded a yellowish oil that proved to be the azine, PhCH=N-N=CHCO₂Et (77 mg, 40%). ¹H NMR (CDCl₃, 300 MHz): δ 1.38 (t, 3H, -CH₃), 4.39 (q, 2H, -CH₂), 7.41–7.53 (m, 3H, 3,4-phenyl), 7.79–7.84 (m, 2H, 2-phenyl), 7.90 (s, 1H, =CHCO₂Et), 8.59 (s, 1H, =CHPh). MS (EI): *m/z* 204 [M]⁺, 131 [M - CO₂Et]⁺, 104, 77. Spectral data were experimentally identical with the reported value.^{5a}

Control Reaction without Triphenylphosphine. By using procedure A except with no triphenylphosphine, a control reaction was set up with 0.100 g (0.943 mmol, 1.00 equiv) of benzaldehyde, 5 mg (1 mol % versus aldehyde) of Fe^{II}(TPP), and 215 mg (1.88 mmol, 2.00 equiv) of ethyl diazoacetate. After the addition of the diazo reagent was finished, the reaction was monitored by GC over a period of 4 days. No consumption of benzaldehyde was observed.

4-NC-C₆H₄CH=CHCO₂Et (2e).²⁹ Procedure A was used with 0.100 g (0.763 mmol, 1.00 equiv) of 4-cyanobenzaldehyde, 0.220 g (0.840 mmol, 1.10 equiv) of triphenylphosphine, 5 mg (1 mol % versus 4-nitrobenzaldehyde) of Fe^{II}(TPP), and 174 mg (1.53 mmol, 2.00 equiv) of ethyl diazoacetate. In half an hour, a 100% conversion was achieved. After column chromatography (SiO₂, 1.5 cm × 25 cm), using 200 mL of pure hexane then hexane/EtOAc (2/1 v/v), a colorless solid was obtained upon evaporation of the solvent. Yield: 146 mg, 95%. The *Z* isomer was produced in a small amount and could not be cleanly separated from the *E* isomer. Only the *E* isomer was cleanly isolated. IR (CH₂Cl₂, cm⁻¹): ν 3052.08, 2985.30, 2230.03, 1716.95, 1639.67, 1411.61, 1368.27, 1313.34, 1266.11, 1204.77, 1181.27, 1031.1, 982.42, 832.28, 739.23. ¹H NMR (CDCl₃, 300 MHz): δ 1.33 (t, 3H, -CH₃), 4.27 (q, 2H, -CH₂), 6.50 (d, 1H, *J* = 16.2 Hz, =CHCO₂Et), 7.59 (d, 2H, *J* = 8.1 Hz, 2-phenyl), 7.64 (d, 1H, *J* = 16.2 Hz, =CHC₆H₄CN), 7.67 (d, 2H, *J* = 8.4 Hz, 3-phenyl). ¹³C NMR (CDCl₃, 75 MHz): δ 14.4, 61.1, 113.5, 118.5, 122.0, 128.5, 132.8, 138.9, 142.3, 166.3. MS (EI): *m/z* 201 [M]⁺, 173, 156 (base), 128, 101. HRMS calcd

for C₁₂H₁₁NO₂ 201.07898, found 201.07915. GC chromatograms indicated the product had an *E/Z* ratio of 18.

Ethyl 3-(4-Nitrophenyl)crotonate (4c).³⁰ Procedure B was used with 1.45 g (8.80 mmol, 10.0 equiv) of 4-nitroacetophenone, 253 mg (0.967 mmol, 1.10 equiv) of triphenylphosphine, and 5 mg (1 mol % versus ethyl diazoacetate) of Fe^{II}(TPP) placed in a round-bottom flask and dissolved in 10 mL of toluene at 22 °C. A solution of 0.100 g (0.879 mmol, 1.00 equiv) of ethyl diazoacetate in 3 mL of toluene was added dropwise over approximately 2 min to the reaction mixture with vigorous stirring. After the addition was finished, the progress of the reaction was monitored by GC as described above. After 4 days, the flask was removed from the glovebox and the solvent was removed in vacuo. The residue was then purified by flash column chromatography (SiO₂, 1.5 cm × 25 cm), using hexane/EtOAc (20/1 v/v). The olefin was isolated by evaporation of the solvent to afford a colorless solid. Yield: 165 mg, 80%. The *Z* and *E* isomers were identified by 2D-NOSY. Only the *Z* isomer was cleanly isolated. IR (CH₂-Cl₂, cm⁻¹): ν 3052.08, 2980.72, 1714.14, 1627.78, 1598.09, 1522.36, 1346.86, 1265.66, 1178.57, 1043.14, 909.54, 854.43, 738.42. ¹H NMR (CDCl₃, 300 MHz) for the *Z* isomer: δ 1.11 (t, 3H, -CH₂CH₃), 2.19 (d, 3H, *J* = 1.5 Hz, =CPhCH₃), 4.01 (q, -CH₂CH₃), 6.00 (q, *J* = 1.5 Hz, 1H, =CH), 7.35 (d, 2H, *J* = 8.7 Hz, 2-phenyl), 8.22 (d, 2H, *J* = 8.7 Hz, 3-phenyl). ¹³C NMR (CDCl₃, 75 MHz): δ 14.5, 18.1, 60.5, 119.6, 120.3, 124.0, 127.5, 184.8, 152.9, 166.3. The MS(ED): *m/z* 235 [M]⁺, 218, 190 (base), 160, 144, 115. HRMS calcd for C₁₂H₁₃NO₄ 235.08446, found 235.08490. GC chromatograms indicated the product had a *Z/E* ratio of 2:1.

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Supporting Information Available: Experimental details and characterization of products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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