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Letter

# Fe-Catalyzed Selective Cyclopropanation of Enynes under Photochemical or Thermal Conditions

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**Supporting Information** 

**ABSTRACT:** The nucleophilic Fe-complex  $Bu_4N$ [Fe-(CO)<sub>3</sub>(NO)] (TBA[Fe]) catalyzes the cyclopropanation of enynes to substituted propargyl cyclopropanes using diazoesters as carbene surrogates. The catalyst can be activated either thermally in the presence of catalytic amounts of 4nitroanisole or under photochemical conditions. Cyclopropanation occurs selectively at the enyne moiety; alternative olefinic moieties remain intact.

ropargylic acceptor-substituted cyclopropanes, accessible via cyclopropanation of enynes, are versatile electrophilic building blocks.<sup>1</sup> While a variety of transition metal catalyzed processes for enyne cyclopropanations have been developed over the years,  $^{2-5}$  and despite the progress that has been made in the field of Fe-catalyzed cyclopropanation,<sup>4,6-8</sup> thus far only some rare examples for cyclopropanation of enynes using Fecatalysts have been reported.<sup>4</sup> These processes are commonly characterized by the use of Fe-porphyrin complexes as catalysts and the use of nonisomerizable envnes, i.e. arylalkinylalkenes. Using Fe-porphyrin-based complexes offers new chances to gain new reactivities, as most of these processes are characterized by a distinct single-electron-transfer mechanism.<sup>4,7</sup> The intermediate formation of carbon-centered radicals, however, might lead to undesired side reactions. Moreover, only Cu-, Rh-, and Ag-based catalysts were shown to cyclopropanate isomerizable enynes in good yields.<sup>1d,h,5</sup>

Within recent years our group has been involved in the field of catalytic transformations using Fe–NO complexes such as  $Bu_4N[Fe(CO)_3(NO)]$  (TBA[Fe]) as catalysts.<sup>9–11</sup> In-depth spectroscopic studies revealed that this catalyst undergoes a fast ligand-centered two-electron oxidation, thus avoiding the formation of radical intermediates.<sup>12</sup> Among the catalytic transformations developed to date, carbene transfer reactions appeared particularly appealing (Scheme 1).

The coordinatively saturated ferrate proved to be active in Doyle–Kirmse or X–H insertion reactions; however, no reactivity was found for olefin insertions.<sup>10f,11</sup> We hypothesized that addition of weak oxidizing agents and/or light might facilitate ligand dissociation, liberate additional coordination sites, and hence increase the reactivity toward olefins. Herein we report the successful application of this strategy in the TBA[Fe]-catalyzed cyclopropanation of nonisomerizable as well as isomerizable enynes (Scheme 1).

We initiated our studies by employing enyne 1 to the standard carbene-transfer reaction conditions (Table 1).

While the initial conditions gave the desired product in moderate yields, addition of nitromethane as cosolvent

Scheme 1. Carbene Transfer Reactions Catalyzed by Bu<sub>4</sub>N[Fe(CO)<sub>3</sub>(NO)] (TBA[Fe]): State-of-Research and Content of This Work

⊕ NBu₄

′co

thermal

or

photochemical activation



improved the yield dramatically (entries 1 and 2, Table 1). Further investigations led to the discovery that only substoichiometric amounts of nitromethane allowed for good conversions (entry 3, Table 1). A screening of different nitroarenes indicated a strong effect of these additives on the reaction yield. *p*-Nitroanisole turned out to be the optimum choice; a catalytic amount of 0.5 mol % in the presence of only 2.5 mol % of TBA[Fe] at 40 °C led to the desired cyclopropane in a reproducible high yield (entry 6, Table 1). As the oxidative strategy was successful, we subsequently employed light irradiation under otherwise identical conditions. Previous studies on TBA[Fe]-catalyzed Cloke–Wilson rearrangements indicated that upon excitation the tetrahedral carbonyl nitrosyl ferrate in the T<sub>1</sub>-state adopts a different coordination mode, i.e. a distorted trigonal-bipyramidal

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## Table 1. Optimization of the TBA[Fe]-Catalyzed Enyne Cyclopropanation<sup>a</sup>

Ph	CO <sub>2</sub> Et N <sub>2</sub> 2 TBA[Fe] [cat.]	H H H H H H H H H H H H H H H H H H H	Et	COOEt
	1	trans-3	C	is <b>-3</b>
Entry	Solvent	Additive [mol %]	Light	Yield [%] <sup>b</sup>
1 <sup>c</sup>	1,2-DCE	_	-	66 <sup>d</sup>
2 <sup>c</sup>	1,2-DCE/MeNO <sub>2</sub> (8:2)	_	-	81 <sup>d</sup>
3 <sup>c</sup>	1,2-DCE	$MeNO_2$ (50)	_	80
4 <sup><i>c</i></sup>	1,2-DCE	nitroanisole (50)	_	88
5 <sup>c</sup>	1,2-DCE	nitroanisole (2.5)	-	81
6 <sup><i>c</i></sup>	1,2-DCE	nitroanisole (0.5)	-	82 (15) <sup>e</sup>
7 <sup>f</sup>	1,2-DCE	_	+	34 <sup>d</sup>
8 <sup>f</sup>	1,2-DCE/MeNO <sub>2</sub> (8:2)	_	+	35
9 <sup>f</sup>	1,4-dioxane/MeNO <sub>2</sub> (8:2)	-	+	51
10 <sup>g,h</sup>	1,4-dioxane/MeNO <sub>2</sub> (5:1)	-	+	65 <sup>d</sup> (traces)
11 <sup>g,i</sup>	1,4-dioxane/MeNO <sub>2</sub> (5:1)	-	+	81 <sup>d</sup>
12 <sup>g,i</sup>	1,4-dioxane/MeNO <sub>2</sub> (5:1)	-	+ <sup>j</sup>	38
13 <sup>g,i</sup>	1,4-dioxane/MeNO <sub>2</sub>	-	+ <sup>k</sup>	45

<sup>a</sup>All reactions were performed on 0.25 mmol scale in dry solvents under a nitrogen atmosphere. <sup>b</sup>Determined by <sup>1</sup>H NMR integration using mesitylene as the internal standard. <sup>c</sup>Conditions: 2.5 mol % TBA[Fe], 40 °C, 24 h. <sup>d</sup>Isolated yield. <sup>e</sup>Without TBA[Fe]. <sup>f</sup>Conditions: 2.5 mol % TBA[Fe], room temperature, 8 h, 75 W Xe-lamp. <sup>g</sup>0.5 mmol scale, 5 mol % TBA[Fe]. <sup>h</sup>16 h. <sup>i</sup>20 h. <sup>j</sup>Light source: 180 W Hg-lamp. <sup>k</sup>Light source: blue LEDs (405 nm).

configuration, in which the electron density is shifted toward the backbinding ligands.<sup>10b</sup> This "light-induced unsaturation" of the metal center translated into a significant increase in catalytic activity. While initial results on the photochemical activation were somewhat disappointing, a change in the solvent from 1,2-dichloroethane (1,2-DCE) to 1,4-dioxane led to a significant increase in the overall yield (entries 7, 8, and 9, Table 1). The addition of nitromethane as a cosolvent led to a reproducible cyclopropanation of enyne 1 in 81% yield using only 5 mol % TBA[Fe]. Importantly, independent of the reaction conditions the *trans/cis*-selectivity was in the range of about 2.8:1, indicating that the change of reaction conditions did not lead to a change in the mechanistic course.

A variety of enynes were successfully cyclopropanated using either the thermal (conditions A) or photochemical conditions (conditions B) (Scheme 2). Both electron-rich and electronpoor arylenynes reacted into the corresponding products 4-10 in good to quantitative yields. In general, the photochemical protocol (conditions B) gave significantly higher yields as compared to the thermal protocol (conditions A). While 1,2disubstituted olefins did not react, 1,1-disubstituted olefins were efficiently cyclopropanated (products 11, 12, and 19, Scheme 2). This observation points into the direction of unfavorable steric interactions between enyne and metalcarbene species in the transition state. Moreover, aliphatic enynes proved to be suitable substrates; in none of the



Scheme 2. Scope of the TBA[Fe]-Catalyzed Enyne

Cvclopropanation<sup>4</sup>

<sup>a</sup>All reactions were performed on a 0.5 mmol scale. Isolated yields; trans/cis-ratio is determined by GC-analysis on the crude mixture and given in parentheses.

investigated cases an isomerization within the  $\pi$ -bond system was observed (products 3, 13-19, Scheme 2). Even propargylic alcohols, esters, and ketones, notoriously reactive to give either  $\alpha_{\beta}$ -unsaturated ketones or rearrangement/ring-

enlargement products,<sup>13</sup> were successfully cyclopropanated to 13, 15–18, and 20, respectively. Furthermore, X–H insertions into electron-poor X–H bonds were not observed as exemplified by the successful synthesis of propargylic cyclopropanes 13 and 18. Interestingly, alternative double bonds in the substrate remained unaffected, and cyclopropane 17 was formed as the exclusive product.

The diastereoselective course of the reaction appears not to be influenced by the reaction conditions. In general, the *trans*configured propargyl cyclopropanes were formed with moderate preference.

However, the presence of coordinating groups in the propargylic position and the presence of sterically demanding substituents at the olefinic moiety had a major influence on the diastereoselectivity. While the secondary propargylic tosylamide led to an increase of the diastereomeric trans-cis ratio from approximately 2.4:1.0 in 17 to 3.2:1.0 in 18 (conditions B), an additional *tert*-butyl substituent at the olefinic moiety resulted in a highly diastereoselective formation of the *cis*-configured diastereomer 19; no *trans*-diastereomer was isolated.

A mechanistic hypothesis that eventually explains most of the observed effects in TBA[Fe]-catalyzed enyne cyclopropanation is shown in Scheme 3. Accordingly, the [Fe-





 $(CO)_3(NO)$ ]-anion reacts with the nitro group at slightly elevated temperatures with decarbonylation in the presence of ethyl diazoacetate to the reactive 16-electron Fe-carbene species III. The fact that nitrosobenzene and aniline were detected in the crude mixture when performing the reaction with nitrobenzene as an additive under thermal conditions supports this hypothesis. To test this hypothesis, the reaction was performed in the presence of *N*,*N*,*N*-trimethylamine-*N*oxide (0.5 mol %) as a decarbonylating agent.<sup>14</sup> Indeed, activation of the [Fe(CO)<sub>3</sub>(NO)]-anion is possible and cyclopropane **3** was isolated in 63% yield in a *trans/cis*-ratio of 3.1:1.

Alternatively, photochemical activation of the anion to the T<sub>1</sub>-state leads to a distorted trigonal-bipyramidal configuration, which upon reacting with ethyl diazoacetate and subsequent decarbonylation, forms III. The fact that envnes are reactive and simple olefins do not provide cyclopropanes indicates a probable coordination to the envne in an  $\eta^4$ - or more likely in an  $\eta^2$ -fashion to the alkyne in **V**. The weak but significant directing effect of the NHTs-group could be interpreted as the result of a further coordination to the metal center in V. Subsequent [2 + 2]-cycloaddition results in the formation of the diastereomeric metallacyclobutanes. The stereoselective course is influenced by the relative size of the respective olefinic substituents. For monosubstituted olefins, a slight preference for the formation of the *trans*-products is observed, reflecting the competition between moderate steric interactions between the alkyne moiety and the incoming metalcarbene species (favoring the trans-product) and alkynecoordination to the metal-carbene (favoring the formation of cis-products). Hence, in the case of 1,1-disubstituted olefins, substituents with moderate size (e.g., methyl or even cyclopropyl groups (substrates 11 and 12, Scheme 2)) lead to a slight decrease of *trans/cis* selectivity while a sterically demanding tert-butyl group results in excellent cis-selectivity, most likely due to a match situation in which the metalcarbene species is coordinated to the alkyne and avoids steric interactions with the *tert*-butyl group (product 19, Scheme 2). Formation of radicals can be excluded at this point, as the cyclopropane moiety in 12 remained intact and addition of TEMPO did not inhibit the catalytic activity. Reductive elimination provides the cyclopropane moiety, and product dissociation is favored after reaction with the incoming ethyl diazoacetate.

Although transition metal catalyzed cyclopropanations of enynes using acceptor–acceptor substituted diazo compounds are literature known, we finally became interested in benchmarking our system to previously established catalytic protocols using ethyl diazoacetate as a case of an acceptor substituted diazo compound for cyclopropanation of enynes (eq 1, Scheme 4).

Indeed, the catalysts employed did not provide satisfactory yields toward product 3 (entries 1-8, eq 1, Scheme 4). Instead, varying amounts of diethyl-maleate or -fumarate as a result of the homodimerization of ethyl diazoacetate, and/or cyclopropenation of the alkyne moiety, were observed. In sharp contrast to previous studies on TBA[Fe]-catalyzed X-H insertions, the use of highly reactive monosubstituted diazocompounds (either isolated or generated in situ) did not work under the given conditions.<sup>15</sup> These observations support our hypothesis of two different mechanisms in TBA[Fe]-catalyzed carbene transfer reactions being operative. While indications of a proton-transfer mechanism for X–H insertion reactions were obtained,<sup>10f</sup> cyclopropanations of enynes seem to rely on a preactivation of the ferrate anion via decarbonylation. Finally, the obtained propargylic cyclopropanes were used as starting materials in various follow-up reactions, such as ester reduction (eq 2, Scheme 4) or heterocycle synthesis (eq 3, Scheme 4). Both transformations gave rise to interesting building blocks without affecting the cyclopropane motif.

The nucleophilic Fe-complex  $Bu_4N[Fe(CO)_3(NO)]$  (TBA-[Fe]) catalyzes the cyclopropanation of enynes with high chemoselectivity under either thermal or photochemical

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Scheme 4. Catalyst Benchmarking and Follow-up Chemistry



conditions. Good functional group tolerance and up to quantitative yields were observed. In general the photochemical activation provided the propargylic cyclopropanes in higher yields. Alternative double bonds proved unreactive. The identification of two different modes of activation for the coordinatively saturated ferrate catalyst opens up new perspectives in the field of Fe-catalysis; some of the ventures in carbene transfer catalysis are currently under investigation in our laboratories.

22

82 % (1 : 1, trans : cis)

# ASSOCIATED CONTENT

#### **S** Supporting Information

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The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.9b04521.

Experimental procedures for preparation of starting materials and products, full characterization of all reported compounds, <sup>1</sup>H NMR spectra, <sup>13</sup>C NMR spectra, IR spectra, HRMS (PDF)

## **Accession Codes**

CCDC 1913231 and 1913243–1913245 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/ cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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(15) See Supporting Information for details (Table S2).