ACS Catalysis

Research Article

Cite This: ACS Catal. 2018, 8, 4473−4482

pubs.acs.org/acscatalysis

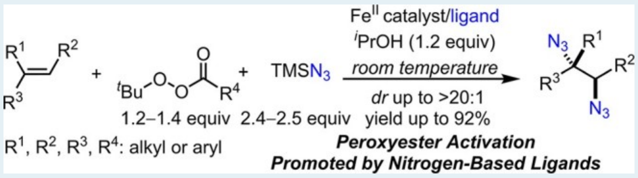
Iron-Catalyzed Direct Olefin Diazidation via Peroxyester Activation Promoted by Nitrogen-Based Ligands

Shou-Jie Shen, Cheng-Liang Zhu, Deng-Fu Lu, and Hao Xu*

Department of Chemistry, Georgia State University, 100 Piedmont Avenue Southeast, Atlanta, Georgia 30303, United States

Supporting Information

ABSTRACT: We herein report an iron-catalyzed direct diazidation method via activation of bench-stable peroxyesters promoted by nitrogen-based ligands. This method is effective for a broad range of olefins and N-heterocycles, including those that are difficult substrates for the existing olefin diamination and diazidation methods. Notably, nearly a stoichiometric amount of oxidant and $TMSN_3$ are sufficient for high-yielding diazidation for most substrates. Preliminary mechanistic studies elucidated the similarities and differences between this method and the benziodoxole-based olefin diazidation method previously developed by us. This method effectively addresses the limitations of the existing olefin diazidation methods. Most notably, previously problematic nonproductive oxidant decomposition can be minimized. Furthermore, X-ray crystallographic studies suggest that an iron−azide−ligand complex can be generated in situ from an iron acetate precatalyst and that it may facilitate peroxyester activation and the rate-determining $C-N_3$ bond formation during diazidation of unstrained olefins.



KEYWORDS: iron catalyst, peroxyesters, olefins, N-heterocycles, diazidation, diamination

INTRODUCTION

Vicinal primary diamines are incorporated in a large number of small-molecule pharmaceuticals and biological probes; therefore, extensive efforts have been devoted to the development of selective and general olefin diamination methods, and a variety of powerful methods have been invented.[1] However, there are still significant synthetic challenges that cannot be fully addressed by these methods. These challenges include the following: (a) it is still difficult to directly convert aliphatic isolated olefins, especially internal olefins, to vicinal primary diamines; (b) methods for selective diamination of highly functionalized olefins have remained underdeveloped; (c) direct diamination of N-heterocycles to afford vicinal primary diamines for complex−alkaloid synthesis has been underexplored.[2]

Alternatively, both stoichiometric[3] and catalytic[4,5] olefin diazidation methods have emerged with unique value. These methods complement the olefin diamination methods and provide a convenient approach to producing synthetically important vicinal primary diamines that are otherwise difficult to obtain. Although an array of olefin diazidation methods have been reported to date,[3−5] the vast majority of them are predominantly restricted to certain limited types of olefins.[3,4c,d] Furthermore, many of them involve the usage of a superstoichiometric amount of NaN_3 in acidic media. Additionally, selective diazidation methods for functionalized N-heterocycles have been underdeveloped.[6]

In 2015, we reported an iron-catalyzed direct diazidation method for a broad range of olefins, in which an iron catalyst activates $TMSN_3$ in the presence of bench-stable benziodoxole 1a to achieve direct olefin diazidation (Scheme 1).[4a] This reaction occurs at room temperature with low catalyst loading, and it is effective for a wide variety of olefins, including those that are incompatible with the existing methods.[3] Notably, the anti selectivity for cyclic olefins can be modulated by iron catalysts (dr up to >20:1). Coupled with facile reduction, this method readily provides an array of valuable vicinal primary diamines.

The preliminary mechanistic analysis has revealed that $TMSN_3$ may reversibly convert the insoluble benziodoxole 1a to azidoiodinane 1b and then to a transient iodine(III)−diazide species 1c, with which an iron catalyst may be oxidized to a high-valent iron−azide species that promotes the stepwise olefin diazidation (Scheme 1).[4a,b] A variety of control experiments corroborate that the iron−ligand complexes are involved in the rate- and diastereoselectivity-determining $C-N_3$ bond-forming step in diazidation of unstrained olefins.[4a]

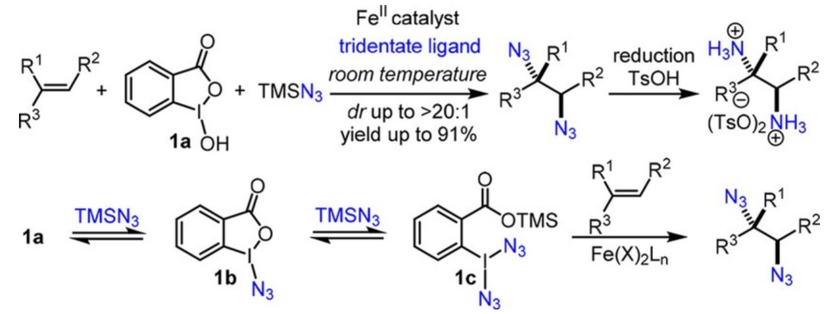
Identification of the high-valent iron−azide species as a possible reactive intermediate has inspired us to develop a new method that significantly improves upon the reported method. There are two outstanding challenges in this benziodoxole-based diazidation method.

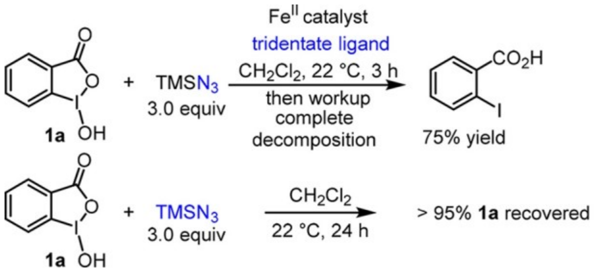
First, in the absence of an olefin, an iron catalyst completely decomposes benziodoxole 1a together with $TMSN_3$ in 3 h (eq 1a), presumably through the iron-promoted decomposition of iodine(III)−diazide species 1c.[7] In contrast, 1a is stable toward $TMSN_3$ in the absence of an iron catalyst in CH_2Cl_2 (eq 1b).[7] This competing pathway can be particularly problematic for substrates with low reactivity since an excess amount

Received: February 28, 2018
Revised: April 2, 2018
Published: April 6, 2018

DOI: 10.1021/acscatal.8b00821
ACS Catal. 2018, 8, 4473−4482

Scheme 1. Iron-Catalyzed Olefin Diazidation with Benziodoxole 1a and the Proposed Mechanistic Working Hypothesis



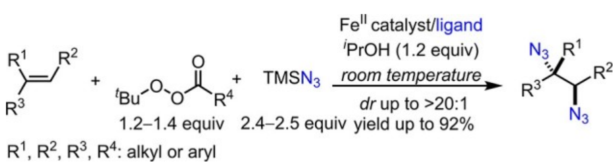

(1a)
(1b)

of oxidant 1a would be necessary to achieve a synthetically useful yield. Some of these problematic substrates include electronically deactivated allylic esters and carbamates. Therefore, a new catalytic method has yet to be developed such that this nonproductive oxidant−decomposition pathway may be suppressed or even eliminated.

Next, an excess amount of $TMSN_3$ (3.6−4.0 equiv) is often applied to achieve high yields in the aforementioned iron-catalyzed olefin diazidation in order to effectively activate benziodoxole 1a.[4a] A stoichiometric amount of $TMSN_3$ (2.0−2.5 equiv) often led to incomplete conversion for certain substrates in the aforementioned method, especially aliphatic isolated olefins. Ideally, nearly a stoichiometric amount of $TMSN_3$ should be sufficient for a more sustainable and efficient olefin diazidation method.

Herein, we report a new iron-catalyzed direct diazidation method via nitrogen-based ligand-promoted activation of bench-stable peroxyesters that effectively addresses the limitations of the previously developed method (Scheme 2). In this method,

Scheme 2. Iron-Catalyzed Olefin Diazidation via Nitrogen-Based Ligand-Promoted Peroxyester Activation



nearly a stoichiometric amount of oxidant and $TMSN_3$ are sufficient for effective diazidation of a broad range of olefins and N-heterocycles at room temperature. Notably, a variety of previously difficult substrates are compatible with this new method, some of which include allylic esters and carbamates, β-pinene, highly functionalized indoles, pyrroles that are prone to rapid rearomatization, as well as β,γ-unsaturated ketones.

Compared with the benziodoxole-based method, preliminary mechanistic studies revealed that the previously problematic nonproductive oxidant--decomposition pathway can be effectively suppressed with this new method. X-ray crystallographic studies further suggest that an iron−azide−ligand complex can be generated in situ from an iron acetate precatalyst, and it may facilitate peroxyester activation and the rate-determining $C-N_3$ bond formation during diazidation of unstrained olefins.

RESULTS AND DISCUSSION

Bench-stable tert-butyl peroxyesters have been extensively applied in a variety of oxygen-atom transfer reactions;[8] however, room-temperature olefin diazidation via ligand-promoted peroxyester activation using nearly a stoichiometric amount of azide source has not been developed.[9] To explore the possible new reactivity through iron catalysis, we select indene (2) as a model substrate in catalyst discovery for both synthetic and mechanistic considerations (Table 1). Extensive exploration of a range of iron catalysts and ligands revealed that the $Fe(OAc)_2$−bidentate ligand L1 complex effectively activates bench-stable tert-butyl peroxybenzoate 3a in the presence of $TMSN_3$ (2.4 equiv) and ^iPrOH (1.2 equiv) and that it catalyzes efficient indene diazidation with excellent dr at room temperature (Table 1).

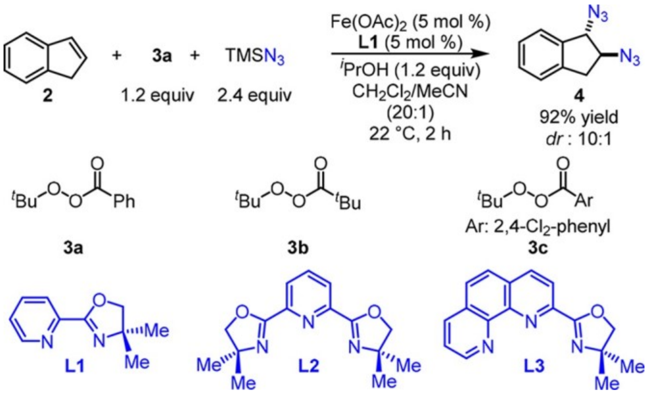
There are several key observations that are mechanistically important (Table 1). First, the iron-catalyzed peroxyester activation and olefin diazidation are enabled by nitrogen-based ligands: in the absence of a ligand, essentially no reaction was observed and both 2 and 3a were fully recovered (entry 1). Next, mild proton donors are critical for catalyst turnover and ^iPrOH leads to a more efficient reaction than H_2O (entries 2 and 3). Furthermore, the iron catalyst can activate a range of peroxyesters (entries 4 and 5): a more electron-deficient peroxyester 3c leads to a faster reaction, and distinct dr values were observed with different peroxyesters (3b vs 3c). These observations suggest that the corresponding carboxylate ligand, presumably generated through the iron-mediated O−O bond cleavage, may be involved in the dr-determining transition state.

To our surprise, the $Fe(OAc)_2$−tridentate ligand L2 complex, an effective catalyst in our previously reported benziodoxole-based olefin diazidation method,[4a] is almost inactive in this reaction: only a small amount of product was observed (entry 6, 6% yield, dr 16:1). Furthermore, another $Fe(OAc)_2$−tridentate ligand L3 complex also suffers from low reactivity (entry 7). Interestingly, both the $Fe(NTf_2)_2$−L1 and the $Fe(NTf_2)_2$−L2 complexes catalyze a rapid reaction; however, the desired indene diazide 4 was isolated in only moderate yields (entries 8 and 9). These results suggest that there may be mechanistic nuances between the $Fe(OAc)_2$- and the $Fe(NTf_2)_2$-catalyzed reactions.

Most notably, in the absence of an olefin, the vast majority of 3a is recovered under the reaction condition (eq 2),[7] which suggests that the nonproductive oxidant decomposition has been minimized with this new method.

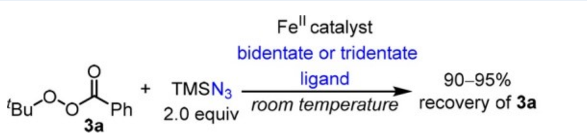
DOI: 10.1021/acscatal.8b00821
ACS Catal. 2018, 8, 4473−4482

Table 1. Catalyst Discovery for Indene Diazidation via Nitrogen-Based Ligand-Promoted Peroxyester Activation



entry[a]	variation from the standard conditions	observations[b,c]
1	in the absence of L1	<5% yield <5% conversion
2	in the absence ^{i}PrOH	48% yield dr 10:1 59% conversion
3	replace ^{i}PrOH with H_2O	52% yield dr 10:1 65% conversion in 4 h
4	replace 3a with 3b	75% yield dr 6.7:1 87% conversion in 4 h
5	replace 3a with 3c	87% yield dr 10:1 95% conversion in 1 h
6	replace L1 with L2	6% yield dr 16:1 ca. 10% conversion
7	replace L1 with L3	8% yield dr 7:1 ca. 16% conversion
8	replace $Fe(OAc)_2$ with $Fe(NTf_2)_2$ (2.5 mol %)	42% yield dr 4.2.1 68% conversion
9	replace $Fe(OAc)_2$ with $Fe(NTf_2)_2$ (2.5 mol %) and replace L1 with L2	52% yield dr 3.5.1 87% conversion

[a]Reactions were carried out under N_2 and subsequently quenched with saturated Na_2CO_3 solution. [b]Conversion was measured by ^1H NMR analysis. [c]Isolated yield. Standard safety precautions about handling $TMSN_3$ should be taken; see SI for details.

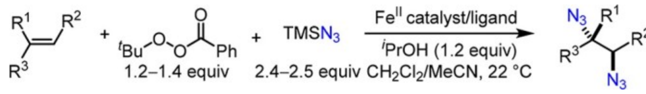


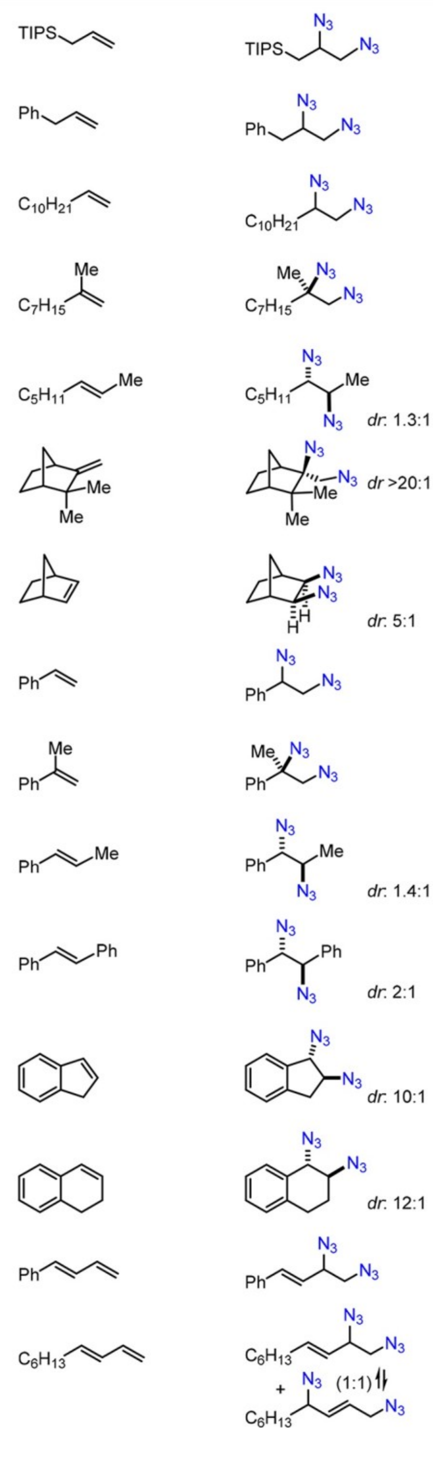
(2)

Upon the discovery of active iron catalysts, we explored this method with a range of unfunctionalized olefins (Table 2). First, we evaluated olefins with electron-rich allylic C−H bonds which tend to undergo C−H azidation.[10] We observed that both the $Fe(OAc)_2$−L1 and the $Fe(NTf_2)_2$−L2 complexes are effective for allylsilane diazidation; however, the $Fe(NTf_2)_2$−L2 catalyst promotes a more rapid reaction with low catalyst loading (entry 1). It is noteworthy that a slight excess of peroxyester 3a (1.4 equiv) is used to ensure reaction reproducibility since a strong Lewis-acidic $Fe(NTf_2)_2$ catalyst is applied. Allylbenzene, a substrate prone to undergo direct C−H azidation, is selectively converted to the corresponding diazide (entry 2). We also observed that this method is effective for isolated olefins, including monosubstituted, 1,1-disubstituted, and trans-disubstituted olefins (entries 3−5). Notably, the iron-catalyzed diazidation of (+)-camphene diastereoselectively affords the camphene diazide with excellent dr (entry 6, dr > 20:1).[11]

Since norbornane diamines are valuable synthetic building blocks and their previous syntheses are less straightforward,[12] we evaluated norbornene in this iron-catalyzed diazidation and

Table 2. Iron-Catalyzed Peroxyester Activation for Diazidation of Unfunctionalized Olefins



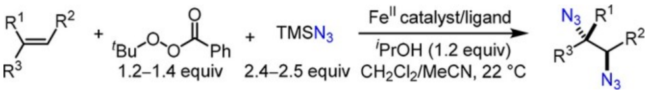


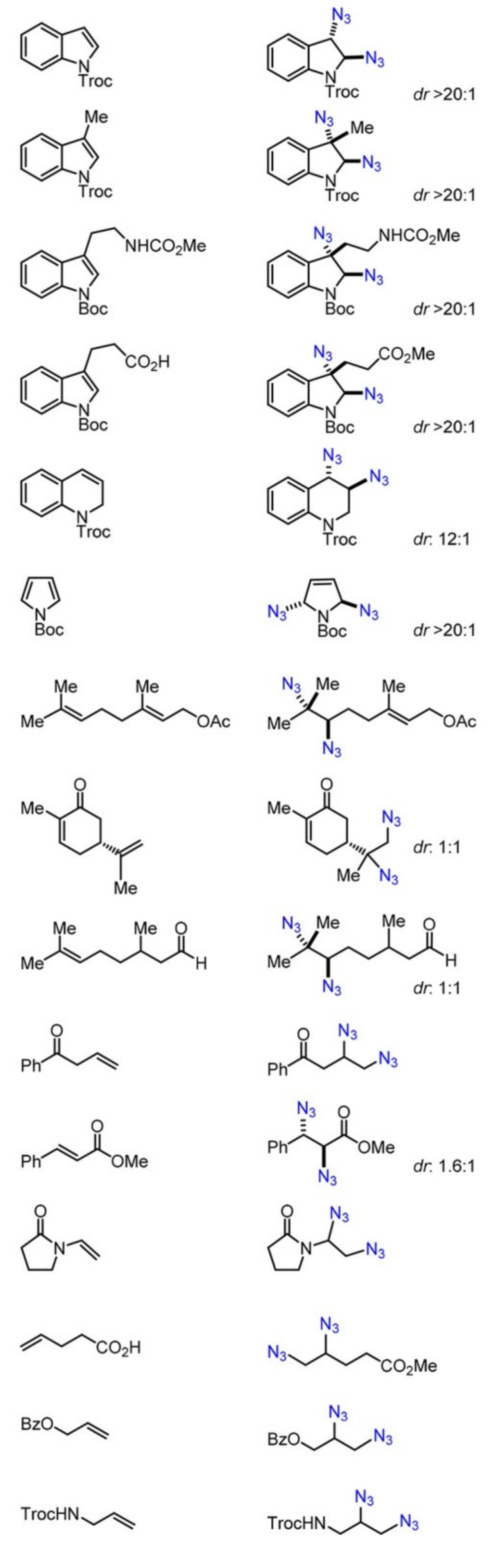
entry[a]	olefins / diazidation products	yield[b]
1[c]		81%
2[c]		70%
3[c]		83%
4[c]		86%
5[c]	dr: 1.3:1	88%
6[d]	dr >20:1	87%
7[d]	dr: 5:1	81%
8[d]		82%
9[d]		86%
10[d]	dr: 1.4:1	92%
11[d]	dr: 2:1	89%
12[d,e]	dr: 10:1	92%
13[d]	dr: 12:1	82%
14[d]		81%
15[c]	(1:1)	78%

[a]Reactions were carried out under N_2 unless stated otherwise. [b]Isolated yield. [c]$Fe(NTf_2)_2$ (5 mol %), L2 (5 mol %), ^{t}BuOOBz (1.4 equiv), $TMSN_3$ (2.5 equiv), and ^{i}PrOH (1.2 equiv). [d]$Fe(OAc)_2$ (10 mol %), L1 (10 mol %), ^{t}BuOOBz (1.2 equiv), $TMSN_3$ (2.4 equiv), and ^{i}PrOH (1.2 equiv). [e]Catalyst loading (5 mol %).

DOI: 10.1021/acscatal.8b00821
ACS Catal. 2018, 8, 4473−4482

Table 3. Iron-Catalyzed Peroxyester Activation for Diazidation of N-Heterocycles and Highly Functionalized Olefins

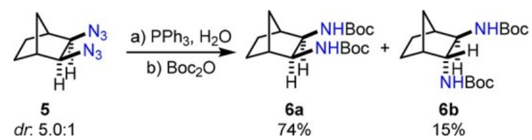




entry[a]	olefins / diazidation products	dr	yield[b]
1[c]		dr >20:1	81%
2[c]		dr >20:1	78%
3[c,d]		dr >20:1	76%
4[c,e,f]		dr >20:1	74%
5[c]		dr: 12:1	85%
6[c]		dr >20:1	82%
7[c]			72%
8[c]		dr: 1:1	67%
9[g]		dr: 1:1	76%
10[c]			84%
11[c]		dr: 1.6:1	72%
12[g]			91%
13[c,e,f]			73%
14[h]			85%
15[h]			77%

[a]Reactions were carried out under N_2 unless stated otherwise. [b]Isolated yield. [c]$Fe(NTf_2)_2$ (5 mol %), L2 (5 mol %), ${}^tBuOOBz$ (1.4 equiv), $TMSN_3$ (2.5 equiv), and ${}^iPrOH$ (1.2 equiv). [d]Ten mol % catalyst was applied. [e]Neither ${}^iPrOH$ nor other proton donor was applied. [f]MeI (5.0 equiv) and K_2CO_3 (3.0 equiv). [g]$Fe(OAc)_2$ (10 mol %), L1 (10 mol %), ${}^tBuOOBz$ (1.2 equiv), $TMSN_3$ (2.4 equiv), and ${}^iPrOH$ (1.2 equiv). [h]$Fe(NTf_2)_2$ (10 mol %), L2 (10 mol %), ${}^tBuOOBz$ (3.0 equiv), $TMSN_3$ (4.0 equiv), and ${}^iPrOH$ (0.5 equiv).

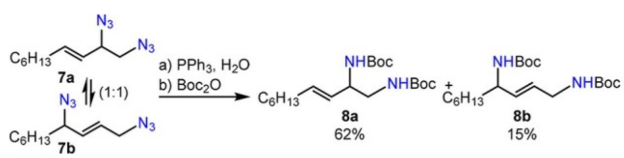
discovered that the $Fe(OAc)_2$−L1 complex catalyzes norbornene diazidation with a good overall yield, albeit in moderate dr (entry 7). Gratifyingly, a facile reduction−N-Boc protection procedure furnishes the readily separable N-Boc norbornane diamines 6a and 6b in an excellent overall yield (eq 3).



(3)

This method also proves compatible with styrenyl olefins. We observed that the $Fe(OAc)_2$−L1 complex catalyzes high-yielding diazidation of styrene, α- and β-methylstyrenes, as well as trans-stilbene (entries 8−11). Furthermore, the same catalyst also promotes diazidation of indene and dihydronaphthalene with excellent diastereoselectivity (entries 12 and 13).

Both 1,2- and 1,4-allylic primary diamines are important building blocks in synthesis; however, expedient synthesis of 1,4-allylic primary diamines through direct 1,4-diene diamination has been difficult.[13] Likewise, methods for vicinal diamination of the terminal olefin in a 1,4-diene for primary diamine synthesis have also been underdeveloped.[14] To achieve expedient synthesis of these allylic primary diamines, we explored the iron-catalyzed diazidation with 1,3-dienes (entries 14 and 15). We observed that the $Fe(OAc)_2$−L1 complex catalyzes vicinal diazidation of a phenyl-substituted 1,3-diene and that the $Fe(NTf_2)_2$−L2 complex rapidly catalyzes alkyl-substituted 1,3-diene diazidation to afford a 1:1 mixture of 1,2- and 1,4-diazides that are in equilibrium, presumably through a facile allylic azide rearrangement.[15] A standard reduction−N-Boc protection procedure can convert the diazide mixture 7a/b to readily separable 1,2- and 1,4-N-Boc-diamines 8a and 8b (eq 4).[15]



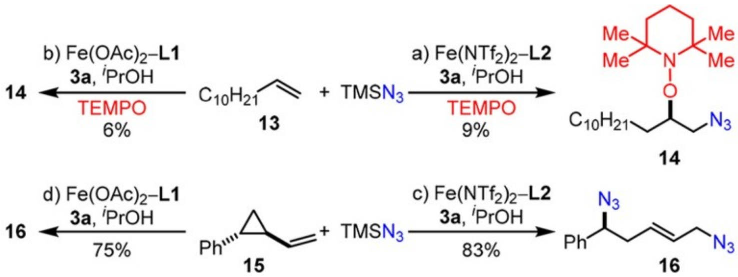
(4)

With the success of this new method for selective diazidation of unfunctionalized olefins, we subsequently evaluated a wide variety of N-heterocycles as well as highly functionalized olefins (Table 3).

We discovered that both N-Troc indole and 3-methyl N-Troc indole are excellent substrates and the corresponding trans-diazides were isolated as a single diastereomer (entries 1 and 2).[9] We further observed that the iron catalyst is sufficiently functional group tolerant such that tryptamine carbamate, indole propionic acid, and N-Troc dihydroquinoline are all readily converted to the corresponding trans-diazides with excellent dr (entries 3−5). Interestingly, the $Fe(NTf_2)_2$−L2 complex also catalyzes a previously difficult 1,4-selective N-Boc pyrrole diazidation, affording a trans-pyrrol diazide with excellent dr (entry 6, dr > 20:1).[16]

DOI: 10.1021/acscatal.8b00821
ACS Catal. 2018, 8, 4473−4482

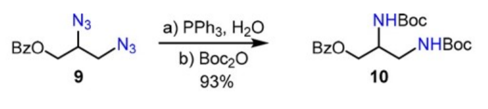
Scheme 3. Mechanistic Experiments To Probe for the Intermediacy of a Carbo−Radical Species[a]



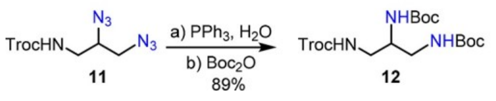
[a]$Fe(NTf_2)_2$ (10 mol %), L2 (10 mol %), 3a (1.4 equiv), $TMSN_3$ (2.5 equiv), and ${}^{i}PrOH$ (1.2 equiv), TEMPO (1.0 equiv). [b]$Fe(OAc)_2$ (10 mol %), L1 (10 mol %), 3a (1.2 equiv), $TMSN_3$ (2.4 equiv), ${}^{i}PrOH$ (1.2 equiv), and TEMPO (1.0 equiv). [c]$Fe(NTf_2)_2$ (5 mol %), L2 (5 mol %), 3a (1.4 equiv), $TMSN_3$ (2.5 equiv), and ${}^{i}PrOH$ (1.2 equiv). [d]$Fe(OAc)_2$ (10 mol %), L1 (10 mol %), 3a (1.2 equiv), $TMSN_3$ (2.4 equiv), and ${}^{i}PrOH$ (1.2 equiv).

Highly functionalized terpenes are important building blocks for organic synthesis; however, selective terpene diazidation has been difficult since redox-labile functional groups are less compatible with the vast majority of the existing diazidation methods. Therefore, we further explored this iron-catalyzed method with a range of complex terpenes. We observed that a more electron-rich olefin at the distal position in geranyl acetate can be preferentially functionalized, affording a geranyl diazide (entry 7). Likewise, two olefinic moieties within (−)-carvone can be differentiated, and the azido group is selectively transferred to the less electron-deficient olefin (entry 8). Notably, the labile aliphatic aldehyde group in (±)-citronellal is compatible with the method without detrimental aldehyde oxidation (entry 9). Furthermore, a β,γ-unsaturated ketone can readily undergo diazidation without olefin isomerization (entry 10). Moreover, this method is effective for both electron-deficient methyl cinnamate and electron-rich enamide (entries 11 and 12). It is also compatible with a carboxylic acid functional group without lactone formation (entry 13).

Multifunctional vicinal diamino alcohols and triamines are valuable building blocks for organic synthesis; however, diamination methods for allylic esters and carbamates have not been developed.[17,18] Additionally, electronically deactivated allylic esters and carbamates present low reactivity under the standard reaction condition in our previously reported method. As a result, we explored the new method with these challenging substrates and discovered that the $Fe(NTf_2)_2$−L2 complex catalyzes high-yielding diazidation of these electronically deactivated substrates (entries 14 and 15). A straightforward reduction−protection sequence can thereby afford the functionalized vicinal diamino alcohol 10 and triamine 12 (eqs 5 and 6).



(5)



(6)

The unique synthetic strength of this iron-catalyzed method has inspired us to probe for its mechanistic details with a series of control experiments and to elucidate the similarities and differences between this olefin diazidation method and the previously reported benziodoxole-based method.[4a]

First, TEMPO radical was introduced in the iron-catalyzed dodecene (13) diazidation, and a TEMPO−addition product 14 was observed when either $Fe(NTf_2)_2$ or $Fe(OAc)_2$ was used as a catalyst (Scheme 3). Next, we evaluated a substituted vinylcyclopropane 15 with this iron-catalyzed method and isolated the ring-opening product 1,5-diazide 16 in excellent yields with either iron catalyst (Scheme 3). These results suggest that azido radical is likely involved in the first C−N_3 bond-forming step, which may initiate radical addition to an olefin and afford a carbo−radical species.

After the first C−N_3 bond formation, the second C−N_3 bond-forming step can proceed through azido group transfer to either a carbo−radical or a carbocation species. In order to differentiate these two mechanistic possibilities, we explored diazidation of (−)-β-pinene 17 (Scheme 4). Notably, the exocyclic olefin of (−)-β-pinene can be selectively 1,2-difunctionalized using both iron catalysts, which exclusively affords a vicinal diazide 18 with excellent dr (Scheme 4, dr > 20:1). Facile reduction and protonation of 18 furnishes diaminium salt 19.

To our surprise, neither a ring-contraction nor a ring-fragmentation product (20a or 20b) was detected. Since ring contraction from the (−)-β-pinene scaffold has been well precedented in carbocation-mediated reactions,[19] the absence of 20a suggests that the second C−N_3 bond formation likely proceeds through a carbo−radical instead of a carbocation species. Additionally, the lack of the ring-fragmentation product 20b suggests that the rate of the second C−N_3 bond formation is faster than that of carbo−radical fragmentation.

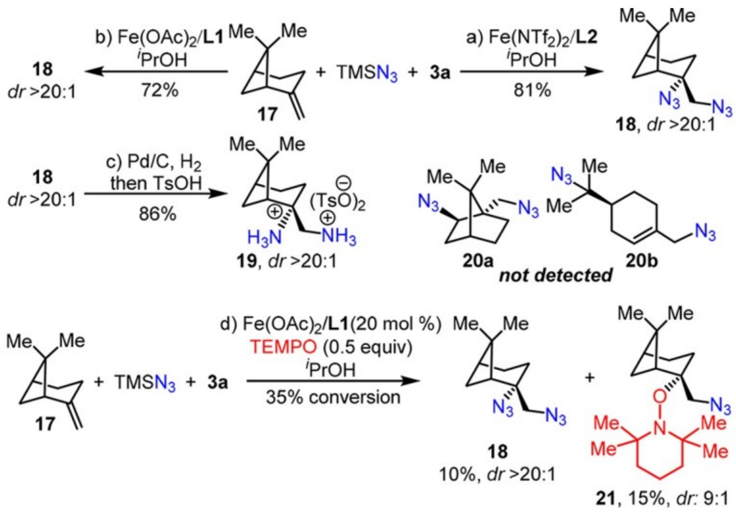
Unlike dodecene (Scheme 3), the diazidation of highly strained (−)-β-pinene in the presence of TEMPO radical affords both the TEMPO-addition product 21 and the diazidation product 18, which suggests that the second C−N_3 bond-forming step is not rate limiting for this highly strained substrate.

In order to determine which C−N_3 bond-forming step is rate limiting for unstrained olefins, we carried out a few control experiments (Scheme 5). First, we evaluated (Z)-hex-3-en-1-ol 22a in the $Fe(NTf_2)_2$-catalyzed diazidation with 3a and identified a significant amount of the isomerization product (E)-hex-3-en-1-ol 22b along with the diazide 23 within 5 min. Notably, both 22a and 22b were converted to diazide 23 in a stereoconvergent manner in 2 h. Interestingly, when the $Fe(OAc)_2$−L1 complex was used as the catalyst, only the isomerization product 22b was observed. Notably, the $Fe(OAc)_2$ catalyst promotes a faster reaction with a more electron-deficient oxidant 3c: both 22b and 23 were observed within 2 h. These results suggest that the second C−N_3 bond-forming step is rate limiting in the iron-catalyzed diazidation of unstrained olefins.

Since azido−radical is likely involved in the first C−N_3 bond-forming step, we further investigated the mechanistic details of the ligand-promoted peroxyester activation for azido−radical

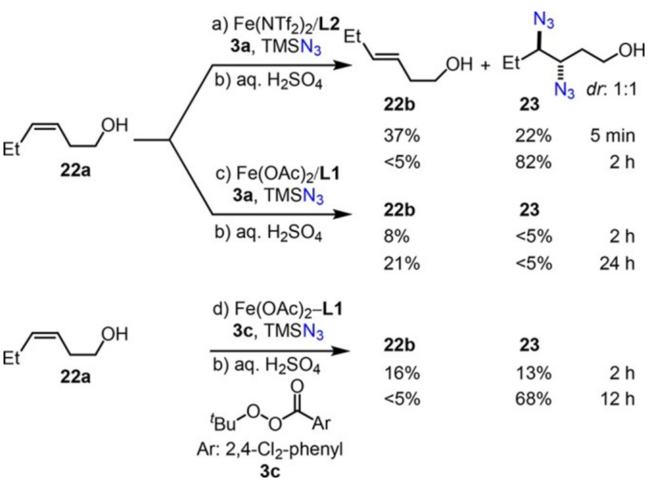
DOI: 10.1021/acscatal.8b00821
ACS Catal. 2018, 8, 4473−4482

Scheme 4. Iron-Catalyzed Diastereoselective Vicinal Diazidation of (−)-β-Pinene[a]



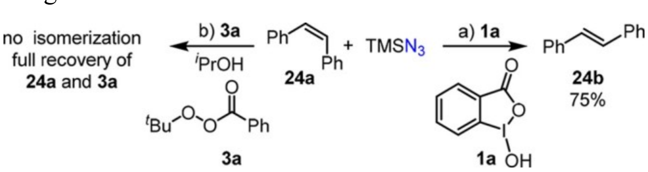
[a]$Fe(NTf_2)_2$ (5 mol %), L2 (5 mol %), 3a (1.4 equiv), $TMSN_3$ (2.5 equiv), and ^{i}PrOH (1.2 equiv). [b]$Fe(OAc)_2$ (10 mol %), L1 (10 mol %), 3a (1.2 equiv), $TMSN_3$ (2.4 equiv), and ^{i}PrOH (1.2 equiv). [c]Pd/C (10 wt %) in MeOH, 12 h, then p-TsOH·H_2O. [d]$Fe(OAc)_2$ (20 mol %), L1 (20 mol %), 3a (1.2 equiv), $TMSN_3$ (2.4 equiv), and ^{i}PrOH (1.2 equiv), TEMPO (0.5 equiv).

Scheme 5. Control Experiments To Determine the Rate-Limiting Step for Diazidation of Unstrained Olefins[a]



[a]$Fe(NTf_2)_2$ (5 mol %), L2 (5 mol %), 3a (1.4 equiv), and $TMSN_3$ (2.5 equiv). [b]One molar aqueous H_2SO_4, 15 min. [c]$Fe(OAc)_2$ (10 mol %), L1 (10 mol %), 3a (1.2 equiv), and $TMSN_3$ (2.4 equiv). [d]$Fe(OAc)_2$ (10 mol %), L1 (10 mol %), 3c (1.2 equiv), and $TMSN_3$ (2.4 equiv).

Scheme 6. Control Experiments To Probe for Mechanistic Insights of Azido-Radical Generation[a]



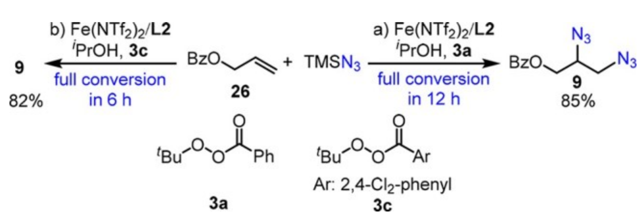
[a]1a (1.2 equiv), $TMSN_3$ (4.0 equiv), 2 h. [b]3a (1.2 equiv), $TMSN_3$ (2.4 equiv), and ^{i}PrOH (1.2 equiv).

generation (Scheme 6). We observed that benziodoxole 1a and $TMSN_3$ promote isomerization of cis-stilbene 24a to trans-stilbene 24b in the absence of an iron catalyst.[4a] However, without an iron catalyst, cis-stilbene 24a is completely unreactive toward peroxyester 3a with $TMSN_3$ and no isomerization is observed. These results suggest that, unlike the benziodoxole-based method, azido−radical generation is iron catalyst dependent in this new method.

Likewise, in the absence of an olefin, an iron catalyst completely decomposes benziodoxole 1a with $TMSN_3$, furnishing o-iodobenzoic acid 25 (eq 1a in the Introduction).[7] However, we observed that the vast majority of peroxyester 3a is recovered with either iron catalyst in the absence of an olefin using this new method (eq 2).[7] These observations suggest that the nonproductive peroxyester decomposition pathway can be suppressed in this new method.

The observed electronic effect of a peroxyester over the reaction rate in an $Fe(OAc)_2$-catalyzed diazidation (Scheme 5) has inspired us to re-evaluate the $Fe(NTf_2)_2$-catalyzed diazidation of challenging substrates, such as allyl benzoate 26. As a result, we observed an evidently faster reaction using a more electron-deficient peroxyester 3c compared with the standard oxidant 3a (Scheme 7). Since the O−O bond cleavage of

Scheme 7. Control Experiments To Corroborate the Involvement of a Carboxylate Ligand in the Rate-Determining C−N_3 Bond-Forming Step for Unstrained Olefins[a]



[a]$Fe(NTf_2)_2$ (10 mol %), L2 (10 mol %), 3a (3.0 equiv), $TMSN_3$ (4.0 equiv), and ^{i}PrOH (0.5 equiv). [b]$Fe(NTf_2)_2$ (10 mol %), L2 (10 mol %), 3c (3.0 equiv), $TMSN_3$ (4.0 equiv), ^{i}PrOH (0.5 equiv).

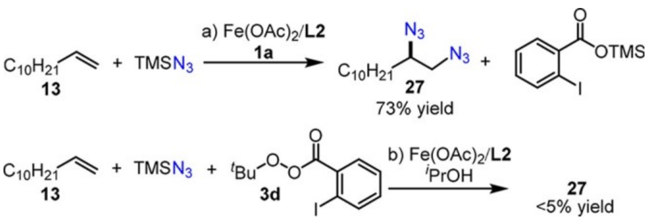
electronically distinct 3a/3c is less likely to be rate limiting (Scheme 5), this result suggests that the carboxylate ligand, presumably generated through the O−O bond cleavage, is

DOI: 10.1021/acscatal.8b00821
ACS Catal. 2018, 8, 4473−4482

likely involved in the rate-determining transition state in both $Fe(NTf_2)_2$- and $Fe(OAc)_2$-catalyzed reactions.

Not only can an oxidant affect the diazidation rate, a ligand can also evidently modulate the reactivity. In particular, the observed ligand effect in the $Fe(OAc)_2$-catalyzed olefin diazidation is mechanistically intriguing: while the $Fe(OAc)_2$−bidentate ligand L1 complex is effective for indene diazidation, the $Fe(OAc)_2$−tridentate ligand L2 complex is almost inactive (Table 1, entry 6). Since the first $C-N_3$ bond formation is reversible for diazidation of unstrained olefins, the observed rate retardation with the $Fe(OAc)_2$−L2 complex may be attributed to either ineffective peroxyester O−O bond cleavage or inefficient carbo−radical oxidation.

Scheme 8. Control Experiments To Probe for Ligand Effect[a]



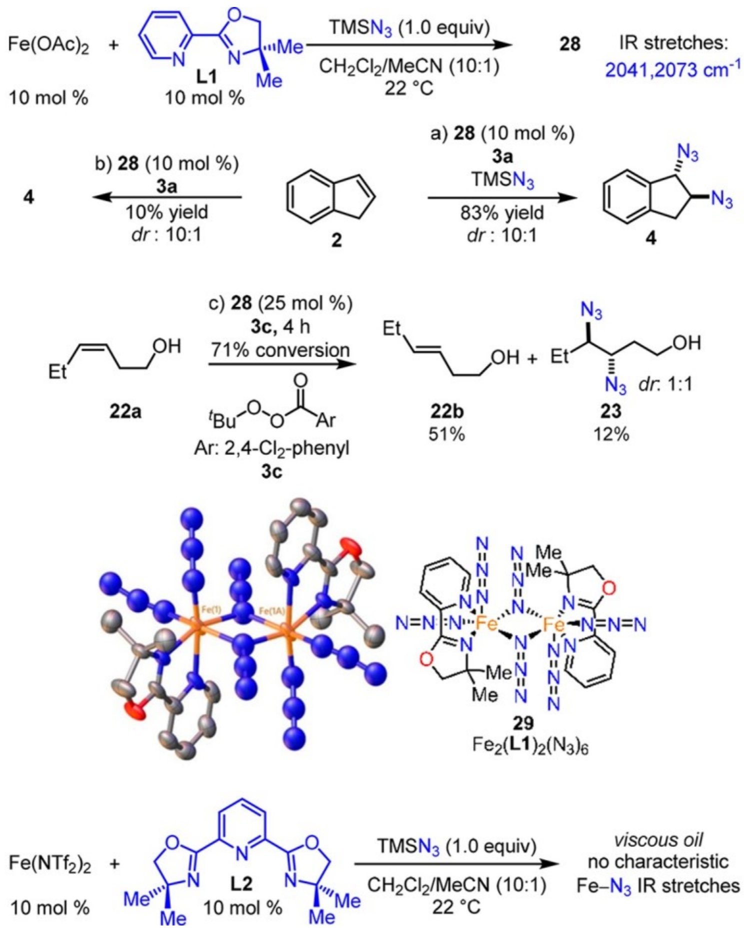
[a]$Fe(OAc)_2$ (10 mol %), L2 (10 mol %), 1a (1.2 equiv), and $TMSN_3$ (4.0 equiv). [b]$Fe(OAc)_2$ (10 mol %), L2 (10 mol %), 3d (1.2 equiv), $TMSN_3$ (2.4 equiv), and ^{i}PrOH (1.2 equiv).

To differentiate these two possibilities, we carried out a few control experiments (Scheme 8). First, we observed that the $Fe(OAc)_2$−tridentate L2 complex rapidly catalyzes dodecene diazidation using benziodoxole 1a; however, it is completely inactive when tert-butyl peroxy 2-iodobenzoate 3d is used as the oxidant. These results suggest that the inefficient O−O bond cleavage by the $Fe(OAc)_2$−L2 complex is likely the reason for the observed low reactivity.

Since the $Fe(OAc)_2$- and $Fe(NTf_2)_2$-catalyzed reactions present distinct reactivity profiles (Table 1), we suspect that different active catalytic species may be involved. Therefore, we further studied the coordination chemistry of the $Fe(OAc)_2$− and $Fe(NTf_2)_2$−ligand complexes in the presence of $TMSN_3$ (Scheme 9).

We observed that the gray solution of the $Fe(OAc)_2$−L1 complex turned dark when an excess amount of $TMSN_3$ was introduced. Subsequent ether trituration readily afforded solid 28, and IR analysis revealed strong azido group absorptions (2041 and 2073 cm^{-1}) shifted to lower energy in comparison to free azide, characteristic of iron−azide complexes (Scheme 9).[20] We discovered that 28 is catalytically active for indene diazidation. Interestingly, in the absence of $TMSN_3$, 28 also promotes the diazidation with essentially the same dr, albeit in a low yield (Scheme 9).[21] Additionally, 28 promotes diazidation of (Z)-hex-3-en-1-ol 22a in the absence of $TMSN_3$, which readily

Scheme 9. Structure−Reactivity Relationship Studies of the $Fe(OAc)_2$ and $Fe(NTf_2)_2$ Catalysts in the Presence of $TMSN_3$[a]



[a]28 (10 mol %), 3a (1.2 equiv), and ^{i}PrOH (1.2 equiv). [b]$Fe(OAc)_2$ (10 mol %), L2 (10 mol %), 3d (1.2 equiv), $TMSN_3$ (2.4 equiv), and ^{i}PrOH (1.2 equiv). [c]28 (25 mol %) and 3c (1.2 equiv).

DOI: 10.1021/acscatal.8b00821
ACS Catal. 2018, 8, 4473−4482

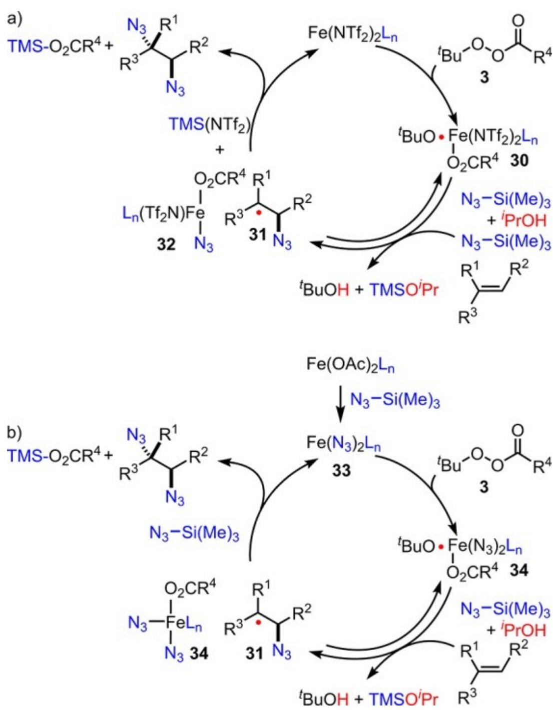
affords both the diazidation product 23 and the olefin isomerization product 22b (Scheme 9).

Extensive exploration of crystallization conditions of 28 afforded solid 29 that is suitable for X-ray crystallographic analysis, which revealed the bridged dimeric structure of solid 29 as $Fe^{III}_2(L1)_2(N_3)_6$ (Scheme 9). We suspect that 28 may be oxidized to afford 29 during crystal growth.[22] These experiments suggest that the $Fe(OAc)_2$ catalysts are converted to iron−azide complexes in their resting state by $TMSN_3$ and that the iron−azide bond may be involved in the rate-limiting azido group transfer during diazidation of unstrained olefins.

Interestingly, we did not observe the solid formation of the $Fe(NTf_2)_2$−L2 complex under the analogous condition, and IR analysis of the resulting viscous oil revealed a lack of characteristic azido group absorptions (Scheme 9). This experiment suggests that the $Fe(NTf_2)_2$ catalysts may not be converted to the corresponding iron−azide complexes by $TMSN_3$ in their resting state.

Upon the basis of a variety of collected mechanistic insights, we propose the mechanistic working hypotheses for the $Fe(NTf_2)_2$- and $Fe(OAc)_2$-catalyzed olefin diazidation (Scheme 10).

Scheme 10. Mechanistic Working Hypotheses of the $Fe(NTf_2)_2$- and $Fe(OAc)_2$-Catalyzed Olefin Diazidation via Ligand-Promoted Activation of Peroxyesters



In an $Fe(NTf_2)_2$-catalyzed reaction (Scheme 10a), an $Fe(NTf_2)_2$−ligand complex may reductively cleave the O−O bond in a peroxyester 3 to generate a tert-butoxyl radical which is associated with a high-valent iron complex 30 with a carboxylate ligand. ^{i}PrOH presumably facilitates gradual release of HN_3 from $TMSN_3$, and tert-butoxyl radical may thereby be rapidly sequestered by HN_3 to liberate azido radical. The azido radical may readily add to an olefin to afford carbo−radical species 31. Since the carboxylate ligand is involved in the rate-determining transition state in the $Fe(NTf_2)_2$-catalyzed diazidation, we propose that $TMSN_3$ may reversibly convert the iron(III) species 30 to a high-valent iron−azide species 32, which presumably mediates the rate-determining azido group transfer to the carbo−radical species 31 and afford the diazidation product.[23] Notably, the $Fe(NTf_2)_2$−ligand complex can be readily regenerated by the transiently generated $TMSNTf_2$.

In an $Fe(OAc)_2$-catalyzed reaction (Scheme 10b), an iron−azide−ligand complex 33 can be generated in situ, which may facilitate the O−O bond cleavage and azido−radical generation in an analogous way. However, the high-valent iron−azide species 34 may directly mediate the rate-limiting azido group transfer to the carbo−radical species 31 and furnish the diazidation product. Subsequently, $TMSN_3$ may readily convert the iron(II)−carboxylate complex back to the catalytically active iron−azide complex 33 via anion metathesis.

CONCLUSIONS

In conclusion, we have reported an iron-catalyzed direct diazidation method via nitrogen-based ligand-promoted activation of bench-stable peroxyesters. This method significantly improves upon our previously reported, benziodoxole-based method, and it is effective for a broad range of olefins and N-heterocycles, including those that are difficult substrates for the existing olefin diamination and diazidation methods. Most notably, nearly a stoichiometric amount of oxidant and $TMSN_3$ are sufficient for high-yielding diazidation for most substrates. Furthermore, preliminary mechanistic studies were carried out to elucidate the similarities and differences between this new method and the benziodoxole-based diazidation method. It was revealed that, unlike the benziodoxole-based method, azido−radical generation is iron catalyst dependent and the nonproductive oxidant−decomposition pathway can be effectively suppressed using this new method. X-ray crystallographic studies further suggest that an iron−azide−ligand complex can be generated in situ from an iron acetate precatalyst, and it may facilitate peroxyester activation and the rate-determining $C-N_3$ bond formation for diazidation of unstrained olefins. Our current efforts focus on synthetic applications of this new method for complex molecule synthesis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.8b00821.

Experimental procedure, characterization data for all new compounds, and selected NMR spectra (PDF)

Crystallographic information (CIF)

checkCIF/PLATON report (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: hxu@gsu.edu.

ORCID

Deng-Fu Lu: 0000-0003-1931-9559

Hao Xu: 0000-0001-5029-8392

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was supported by the National Institutes of Health (GM110382) and Alfred P. Sloan Foundation (FG-2015-65240). H.X. is an Alfred P. Sloan Research Fellow. We thank Prof. Caleb D. Martin and Ms. Sam Yruegas for X-ray

DOI: 10.1021/acscatal.8b00821
ACS Catal. 2018, 8, 4473−4482

crystallographic analysis of an iron–azide complex 29. We also thank a referee for the insightful critiques.

REFERENCES

(1) For selected references of olefin diamination methods, see: (a) Chong, A. O.; Oshima, K.; Sharpless, K. B. Synthesis of Dioxobis(tert-alkylimido)osmium(VIII) and Oxotris(tert-alkylimido)-osmium(VIII) Complexes. Stereospecific Vicinal Diamination of Olefins. J. Am. Chem. Soc. 1977, 99, 3420−3426. (b) Backvall, J.-E. Stereospecific Palladium-Promoted Vicinal Diamination of Olefins. Tetrahedron Lett. 1978, 19, 163−166. (c) Becker, P. N.; White, M. A.; Bergman, R. G. A New Method for 1,2-Diamination of Alkenes Using Cyclopentadienylnitrosylcobalt Dimer/NO/$LiAlH_4$. J. Am. Chem. Soc. 1980, 102, 5676−5677. (d) Bar, G. L. J.; Lloyd-Jones, G. C.; Booker-Milburn, K. I. Pd(II)-Catalyzed Intermolecular 1,2-Diamination of Conjugated Dienes. J. Am. Chem. Soc. 2005, 127, 7308−7309. (e) Streuff, J.; Hövelmann, C. H.; Nieger, M.; Muñiz, K. Palladium-(II)-Catalyzed Intramolecular Diamination of Unfunctionalized Alkenes. J. Am. Chem. Soc. 2005, 127, 14586−14587. (f) Zabawa, T. P.; Kasi, D.; Chemler, S. R. Copper(II) Acetate Promoted Intra-molecular Diamination of Unactivated Olefins. J. Am. Chem. Soc. 2005, 127, 11250−11251. (g) Du, H.; Yuan, W.; Zhao, B.; Shi, Y. Catalytic Asymmetric Diamination of Conjugated Dienes and Triene. J. Am. Chem. Soc. 2007, 129, 11688−11689. (h) Zhao, B. G.; Peng, X. G.; Cui, S. L.; Shi, Y. Cu(I)-Catalyzed Regioselective Diamination of Conjugated Dienes via Dual Mechanistic Pathways. J. Am. Chem. Soc. 2010, 132, 11009−11011. (i) Sibbald, P. A.; Rosewall, C. F.; Swartz, R. D.; Michael, F. E. Mechanism of N-Fluorobenzenesulfonimide Promoted Diamination and Carboamination Reactions: Divergent Reactivity of a Pd(IV) Species. J. Am. Chem. Soc. 2009, 131, 15945−15951. (j) Iglesias, A.; Perez, E. G.; Muñiz, K. An Intermolecular Palladium-Catalyzed Diamination of Unactivated Alkenes. Angew. Chem., Int. Ed. 2010, 49, 8109−8111. (k) Olson, D. E.; Su, J. Y.; Roberts, D. A.; Du Bois, J. Vicinal Diamination of Alkenes under Rh-Catalysis. J. Am. Chem. Soc. 2014, 136, 13506−13509. (l) Conway, J. H.; Rovis, T. Regiodivergent Iridium(III)-Catalyzed Diamination of Alkenyl Amides with Secondary Amines: Complementary Access to γ- or δ-Lactams. J. Am. Chem. Soc. 2018, 140, 135−138. For selected references of enantioselective olefin diamination methods, see ref 1g and (m) Muñiz, K.; Barreiro, L.; Romero, R. M.; Martínez, C. Catalytic Asymmetric Diamination of Styrenes. J. Am. Chem. Soc. 2017, 139 (139), 4354−4357. (n) Ingalls, E. L.; Sibbald, P. A.; Kaminsky, W.; Michael, F. E. Enantioselective Palladium-Catalyzed Diamination of Alkenes Using N-Fluorobenzenesulfonimide. J. Am. Chem. Soc. 2013, 135, 8854−8856.

(2) For selected recent syntheses of complex alkaloids with 1,2-diaminated N-heterocyles, see: (a) Seiple, I. B.; Su, S.; Young, I. S.; Lewis, C. A.; Yamaguchi, J.; Baran, P. S. Total Synthesis of Palau'amine. Angew. Chem., Int. Ed. 2010, 49, 1095−1098. (b) Fleming, J. J.; Du Bois, J. A Synthesis of (+)-Saxitoxin. J. Am. Chem. Soc. 2006, 128, 3926−3927. (c) Ma, Z.; Wang, X.; Ma, Y.; Chen, C. Asymmetric Synthesis of Axinellamines A and B. Angew. Chem., Int. Ed. 2016, 55, 4763−4766.

(3) For early studies of an iron(II)−iron(III)-mediated stoichio-metric olefin diazidation approach using either peroxydisulfate or hydrogen peroxide with NaN_3, see: (a) Minisci, F.; Galli, R. Influence of the Electrophilic Character on the Reactivity of Free Radicals in Solution Reactivity of Alkoxy, Hydroxy, Alkyl and Azido Radicals in Presence of Olefins. Tetrahedron Lett. 1962, 3, 533−538. (b) Minisci, F. Free-Radical Additions to Olefins in the Presence of Redox Systems. Acc. Chem. Res. 1975, 8, 165−171. This stoichiometric approach provides good yield for styrene diazidation; however, it provide modest to moderate yields for diazidation of unfunctionalized aliphatic olefins. For selected references of other stoichiometric diazidation methods for limited types of olefins, see: (c) Fristad, W. E.; Brandvold, T. A.; Peterson, J. R.; Thompson, S. R. Conversion of Alkenes to 1,2-Diazides and 1,2-Diamines. J. Org. Chem. 1985, 50, 3647−3649. (d) Snider, B. B.; Lin, H. An Improved Procedure for the Conversion of Alkenes and Glycals to 1,2-Diazides Using $Mn(OAc)_3{\cdot}2H_2O$ in Acetonitrile Containing Trifluoroacetic Acid. Synth. Commun. 1998, 28, 1913−1922. (e) Moriarty, R. M.; Khosrowshahi, J. S. A Versatile Synthesis of Vicinal Diazides Using Hypervalent Iodine. Tetrahedron Lett. 1986, 27, 2809−2812. (f) Arimoto, M.; Yamaguchi, H.; Fujita, E.; Nagao, Y.; Ochiai, M. Diazidation of Allylsilanes with a Combination of Iodosylbenzene and Trimethylsilyl Azide, and Synthesis of Allyl Azides. Chem. Pharm. Bull. 1989, 37, 3221−3224. (g) Magnus, P.; Lacour, J. New Trialkylsilyl Enol Ether Chemistry. Direct β-Azido Functionalization of Triisopropylsilyl Enol Ethers. J. Am. Chem. Soc. 1992, 114, 767−769. (h) Chung, R.; Yu, E.; Incarvito, C. D.; Austin, D. J. Hypervalent Iodine-Mediated Vicinal Syn Diazidation: Application to the Total Synthesis of (±)-Dibromophakellstatin. Org. Lett. 2004, 6, 3881−3884. (i) Sasaki, T.; Kanematsu, K.; Yukimoto, Y. Heteroaromaticity. LX. Reactions of Medium-Mem-bered-Ring Unsaturated Compounds with Iodine Azide. J. Org. Chem. 1972, 37, 890−894. (j) Nocquet-Thibault, S.; Rayar, A.; Retailleau, P.; Cariou, K.; Dodd, R. H. Iodine(III)-Mediated Diazidation and Azido-oxyamination of Enamides. Chem. - Eur. J. 2015, 21, 14205−14210. (k) Kamble, D. A.; Karabal, P. U.; Chouthaiwale, P. V.; Sudalai, A. $NaIO_4$−NaN_3-Mediated Diazidation of Styrenes, Alkenes, Benzylic alcohols, and Aryl Ketones. Tetrahedron Lett. 2012, 53, 4195−4198.

(4) For selected references of catalytic olefin diazidation methods, see: (a) Yuan, Y.-A.; Lu, D.-F.; Chen, Y.-R.; Xu, H. Iron-Catalyzed Direct Diazidation for a Broad Range of Olefins. Angew. Chem., Int. Ed. 2016, 55, 534−538. (b) Zhu, H.-T.; Arosio, L.; Villa, R.; Nebuloni, M.; Xu, H. Process Safety Assessment of the Iron-Catalyzed Direct Olefin Diazidation for the Expedient Synthesis of Vicinal Primary Diamines. Org. Process Res. Dev. 2017, 21, 2068−2072. For selected catalytic methods for styrene diazidation, see: (c) Fumagalli, G.; Rabet, P. T. G.; Boyd, S.; Greaney, M. F. Three-Component Azidation of Styrene-Type Double Bonds: Light-Switchable Behavior of a Copper Photoredox Catalyst. Angew. Chem., Int. Ed. 2015, 54, 11481−11484. (d) Lu, M.-Z.; Wang, C.-Q.; Loh, T.-P. Copper-Catalyzed Vicinal Oxyazidation and Diazidation of Styrenes under Mild Conditions: Access to Alkyl Azides. Org. Lett. 2015, 17, 6110−6113. For more recent examples, see: (e) Peng, H.; Yuan, Z.; Chen, P.; Liu, G. Palladium-Catalyzed Intermolecular Oxidative Diazidation of Alkenes. Chin. J. Chem. 2017, 35, 876−880. (f) Zhou, H.; Jian, W.; Qian, B.; Ye, C.; Li, D.; Zhou, J.; Bao, H. Copper-Catalyzed Ligand-Free Diazidation of Olefins with $TMSN_3$ in CH_3CN or in H_2O. Org. Lett. 2017, 19, 6120−6123. For selected examples of catalytic intramolecular olefin azidation, see: (g) Shen, K.; Wang, Q. Copper-Catalyzed Alkene Aminoazidation as a Rapid Entry to 1,2-Diamines and Installation of an Azide Reporter onto Azaheterocycles. J. Am. Chem. Soc. 2017, 139, 13110−13116. (h) Zhu, R.; Buchwald, S. L. Versatile Enantioselective Synthesis of Functionalized Lactones via Copper-Catalyzed Radical Oxyfunctionalization of Alkenes. J. Am. Chem. Soc. 2015, 137, 8069−8077. For a selected review for olefin azidation, see: (i) Wu, K.; Liang, Y.; Jiao, N. Azidation in the Difunctionalization of Olefins. Molecules 2016, 21, 352.

(5) For an electrochemical diazidation method, see: (a) Fu, N.; Sauer, G. S.; Saha, A.; Loo, A.; Lin, S. Metal-Catalyzed Electrochemical Diazidation of Alkenes. Science 2017, 357, 575−579. See also: (b) Schafer, H. Oxidative Addition of the Azide Ion to Olefins. A Simple Route to Diamines. Angew. Chem., Int. Ed. Engl. 1970, 9, 158−159.

(6) For N-heterocycle diazidation, see: refs 3h,4a,b, and 5a.

(7) For detailed studies of the iron-catalyzed nonproductive decomposition of 1a, see Supporting Information.

(8) For selected references of oxygen atom transfer with peroxyesters, see: (a) Kharasch, M. S.; Sosnovsky, G. The Reactions of tert-Butyl Perbenzoate and Olefins - A Stereospecific Reaction. J. Am. Chem. Soc. 1958, 80, 756−756. (b) Gokhale, A. S.; Minidis, A. B. E.; Pfaltz, A. Enantioselective Allylic Oxidation Catalyzed by Chiral Bisoxazoline-Copper Complexes. Tetrahedron Lett. 1995, 36, 1831−1834. (c) Kawasaki, K.; Katsuki, T. Enantioselective Allylic Oxidation of Cycloalkenes by Using Cu(II)-Tris(oxazoline) Complex as a Catalyst. Tetrahedron 1997, 53, 6337−6350. (d) Sekar, G.; DattaGupta, A.; Singh, V. K. Asymmetric Kharasch Reaction: Catalytic

DOI: 10.1021/acscatal.8b00821
ACS Catal. 2018, 8, 4473−4482

Enantioselective Allylic Oxidation of Olefins Using Chiral Pyridine Bis(diphenyloxazoline)−Copper Complexes and tert-Butyl Perbenzoate. J. Org. Chem. 1998, 63, 2961−2967. (e) Sharma, A.; Hartwig, J. F. Enantioselective Functionalization of Allylic C−H Bonds Following a Strategy of Functionalization and Diversification. J. Am. Chem. Soc. 2013, 135, 17983−17989.

(9) For selected references of ligand-accelerated or ligand-promoted catalysis, see: (a) Jacobsen, E. N.; Marko, I.; Mungall, W. S.; Schroeder, G.; Sharpless, K. B. Asymmetric Dihydroxylation via Ligand-Accelerated Catalysis. J. Am. Chem. Soc. 1988, 110, 1968−1970. (b) Berrisford, D. J.; Bolm, C.; Sharpless, K. B. Ligand-Accelerated Catalysis. Angew. Chem., Int. Ed. Engl. 1995, 34, 1059−1070. (c) Wang, D.-H.; Engle, K. M.; Shi, B.-F.; Yu, J.-Q. Ligand-Enabled Reactivity and Selectivity in a Synthetically Versatile Aryl C−H Olefination. Science 2010, 327, 315−319. For a recent report of ligand-free, high-temperature diazidation in water, see 4f.

(10) For selected references of the iron-catalyzed C−H azidation of electron-rich C−H bonds, see: (a) Sharma, A.; Hartwig, J. F. Metal-catalysed azidation of tertiary C-H bonds suitable for late-stage functionalization. Nature 2015, 517, 600−604. (b) Karimov, R. R.; Sharma, A.; Hartwig, J. F. Late Stage Azidation of Complex Molecules. ACS Cent. Sci. 2016, 2, 715−724.

(11) For stereochemistry determination, see details in the Supporting Information.

(12) For selected references of previous norbornane primary diamine synthesis, see: (a) Bolm, C.; Schiffers, I.; Atodiresei, I.; Ozcubukcu, S.; Raabe, G. A Novel Asymmetric Synthesis of Highly Enantiomerically Enriched Norbornane-Type Diamine Derivatives. New J. Chem. 2003, 27, 14−17. (b) Maisonial, A.; Traikia, M.; Gautier, A.; Aitken, D. J. Control of the Platinum(II) Ligating Properties of Rigid 1,2-Diamines: the Case of trans-2,3-Diaminonorbornane. Tetrahedron Lett. 2006, 47, 8091−8093.

(13) For selected references of both catalytic (ref. 13a) and stoichiometric (refs 13b−c) 1,4-diene diamination to afford building blocks other than 1,4-allylic primary diamines, see: (a) Wu, Z.; Zhang, J.; Li, Y.; Zhang, W. Pd(II)-Catalyzed Aerobic Intermolecular 1,4-Diamination of Conjugated Dienes: A Regioselective [4 + 4] Annulation for the Construction of Medium-Ring 1,6-Benzodiazocine Derivatives. Tetrahedron Lett. 2017, 58, 2640−2643. (b) Akermark, B.; Backvall, J.-E.; Löwenborg, A.; Zetterberg, K. Palladium(II)-Promoted 1,4-Diamination of 1,3-Dienes. Stereochemistry of Amination of a π-Allylpalladium Complex. J. Organomet. Chem. 1979, 166, C33−36. (c) Martínez, C.; Martínez, L.; Kirsch, J.; Escudero-Adan, E. C.; Martin, E.; Muñiz, K. Copper-Mediated 1,4-Diamination of 1,3-Butadienes. Eur. J. Org. Chem. 2014, 2014, 2017−2021.

(14) For palladium-catalyzed vicinal diamination of a more substituted olefin moiety in a 1,3-diene, see: Du, H.; Zhao, B.; Shi, Y. A Facile Pd(0)-Catalyzed Regio- and Stereoselective Diamination of Conjugated Dienes and Trienes. J. Am. Chem. Soc. 2007, 129, 762−763. For copper catalyst-controlled regioselective vicinal diene diamination of either a more or a less substituted olefin moiety, see ref 1h.

(15) For allylic azide rearrangement, see: Feldman, A. K.; Colasson, B.; Sharpless, K. B.; Fokin, V. V. The Allylic Azide Rearrangement: Achieving Selectivity. J. Am. Chem. Soc. 2005, 127, 13444−13445. The ratio of 8a/8b does not match that of 7a/7b, which is presumably due to the different reactivity of 7a/7b under the reduction condition controlled by the Curtin−Hammett principle.

(16) There are four NMR signals in the ^{13}C NMR spectrum in addition to the ones from N-Boc group; therefore, we assign its relative stereochemistry as trans.

(17) For selected references of synthesis of vicinal diamino alcohols, see: (a) Khayer, K.; Jenn, T.; Akhtar, M.; John, R.; Gani, D. Synthesis of (R)- and (S)-2,3-Diaminopropyl Sulfate: Mechanism Based Inhibition of Glutamate 1-Semialdehyde Aminomutase. Tetrahedron Lett. 2000, 41, 1637−1641. (b) Biannic, B.; Bozell, J. J.; Elder, T. Steric Effects in the Design of Co-Schiff Base Complexes for the Catalytic Oxidation of Lignin Models to para-Benzoquinones. Green Chem. 2014, 16, 3635−3642.

(18) For selected references of synthesis of vicinal triamines, see: (a) Busto, E.; Gotor-Fernandez, V.; Montejo-Bernardo, J.; García-Granda, S.; Gotor, V. Development of a Chemoenzymatic Strategy for the Synthesis of Optically Active and Orthogonally Protected Polyamines. Tetrahedron 2009, 65, 8393−8401. (b) Mitra, R.; Ganesh, K. N. Aminomethylene Peptide Nucleic Acid (am-PNA): Synthesis, Regio-/Stereospecific DNA Binding, And Differential Cell Uptake of (α/γ,R/S)am-PNA Analogues. J. Org. Chem. 2012, 77, 5696−5704.

(19) For selected references of carbocation rearrangements from the β-pinene scaffold, see: (a) Winstein, S.; Holness, N. J. Neighboring Carbon and Hydrogen. XVIII. Solvolysis of the Nopinyl p-Bromobenzenesulfonates. J. Am. Chem. Soc. 1955, 77, 3054−3061. (b) Prakash, G. K. S.; Reddy, V. P.; Rasul, G.; Casanova, J.; Olah, G. A. The Search for Persistent Cyclobutylmethyl Cations in Superacidic Media and Observation of the Cyclobutyldicyclopropylmethyl Cation. J. Am. Chem. Soc. 1998, 120, 13362−13365.

(20) For a selected reference of characterized monomeric iron−azide complexes and their IR measurements, see: Grove, L. E.; Hallman, J. K.; Emerson, J. P.; Halfen, J. A.; Brunold, T. C. Synthesis, X-Ray Crystallographic Characterization, and Electronic Structure Studies of a Di-Azide Iron(III) Complex: Implications for the Azide Adducts of Iron(III) Superoxide Dismutase. Inorg. Chem. 2008, 47, 5762−5774.

(21) For experimental details, see the Supporting Information.

(22) Complex 29 is inactive for olefin diazidation with peroxyesters (3a−d); however, it is active for olefin diazidation using benziodoxole 1a, in which azido−radical generation is non-iron catalyst dependent.

(23) For selected references of metal-mediated radical oxidation, see ref 8a and (a) Kharasch, M. S.; Sosnovsky, G.; Yang, N. C. Reactions of tert-Butyl Peresters. I. The Reaction of Peresters with Olefins. J. Am. Chem. Soc. 1959, 81, 5819−5824. (b) Kochi, J. K. Mechanisms of Organic Oxidation and Reduction by Metal Complexes. Science 1967, 155, 415−424.

DOI: 10.1021/acscatal.8b00821
ACS Catal. 2018, 8, 4473−4482