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Iron-Catalyzed Intermolecular [2π + 2π] Cycloaddition

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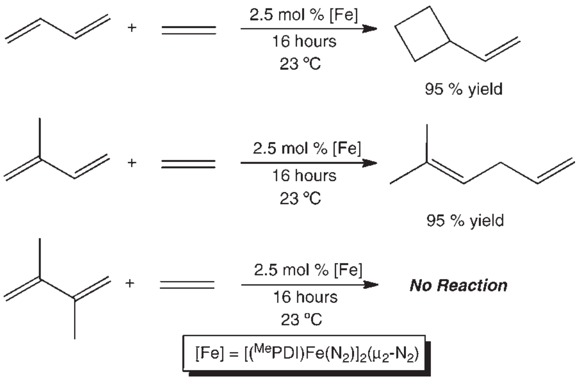
Supporting Information

ABSTRACT: The bis(imino)pyridine iron dinitrogen compounds, $(^{iPr}PDI)Fe(N_2)_2$ and $[(^{Me}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ ($^{R}PDI = 2,6\text{-}(2,6\text{-}R_2\text{-}C_6H_3N{=}CMe)_2C_5H_3N$; R = ^{i}Pr, Me), promote the catalytic intermolecular [2π + 2π] cycloaddition of ethylene and butadiene to form vinylcyclobutane. Stoichiometric experiments resulted in isolation of a catalytically competent iron metallocycle intermediate, which was shown to undergo diene-induced C−C reductive elimination. Deuterium labeling experiments establish competitive cyclometalation of the bis(imino)pyridine aryl substituents during catalytic turnover.

Cycloaddition reactions are powerful and broadly applied methods for the construction of cyclic compounds. The prototypical example is the Diels−Alder reaction, a symmetry-allowed [4π + 2π] transformation[1] between an alkene and a diene to yield a six-membered ring. By contrast, the corresponding [2π + 2π] cycloaddition to form cyclobutane derivatives, while thermodynamically favorable, is thermally forbidden,[1] and alternative synthetic routes such as photochemistry,[2] use of highly strained substrates[3] and activated π-systems,[4] and metal catalysis[5] have all been used to overcome the orbital symmetry constraint. Our laboratory has reported a facile iron-catalyzed method for the intramolecular [2π + 2π] cyclization of α,ω-dienes to the corresponding cyclobutane-containing bicycles.[6] One notable feature of the base metal-catalyzed method is the ability to rapidly cyclize unactivated dienes such as 1,6-heptadiene to [0.2.3]bicycloheptane as well as various allyl amines to the corresponding disubstituted fused pyrrolidines in the absence of chromophores.[6] Extension of the [2π + 2π] cyclization to intermolecular examples is necessary if a general base metal-catalyzed process for the synthesis of substituted cyclobutanes is to be realized. Here we describe progress toward this objective with the synthesis of vinyl cyclobutane from the intermolecular cycloaddition of ethylene and butadiene. Investigations into the mechanism of this unusual reaction and isolation and characterization of a catalytically-competent intermediate are also described.

The reaction of ethylene and butadiene is often cited as a pedagogical example of the [4π + 2π] Diels−Alder reaction,[7] although in practice high temperatures (175 °C) and pressures (6000 psi) are required to promote cycloaddition.[8] Addition of metal catalysts facilitates the addition, but linear hexadienes are the major products.[9] Ritter and co-workers[10] have reported an iron-catalyzed version of this reaction for the selective 1,4-addition of various styrene derivatives to dienes such as isoprene and myrcene, an interesting variant of established cobalt-catalyzed hydrovinylation reactions.[11] Cannell has reported observation of vinylcyclobutane as a component of the product mixture obtained from addition of ethylene to butadiene in the presence of organotitanium catalysts at high temperature (T = 135−150 °C) and pressure (1200 psi).[12] A related iron-catalyzed [2π + 2π] cycloaddition of norbornadiene and butadiene has also been described, but the selectivity for the cyclobutane product was relatively low (~20%). Codimerization of ethylene with butadiene or isopropene has also been reported with $Fe(acac)_3/AlR_3$ mixtures to yield predominantly linear products.[13]

Scheme 1



Our laboratory has recently reported the straightforward synthesis and catalytic utility of bis(imino)pyridine iron butadiene compounds, $(^{R}PDI)Fe(\eta^4\text{-}C_4H_6)$ ($^{R}PDI = 2,6\text{-}(2,6\text{-}R_2\text{-}C_6H_3N{=}CMe)_2C_5H_3N$; R = ^{i}Pr, Me).[6,14] The potential intermediacy of these species in an intermolecular [2π + 2π] cycloaddition with ethylene prompted additional studies. Exposure of an equimolar mixture of ethylene and butadiene to a benzene-d_6 solution containing 5 mol % (total [Fe]) of either $(^{iPr}PDI)Fe(N_2)_2$[15] or $[(^{Me}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$[16] at 23 °C furnished vinylcyclobutane in 95% yield over the course of 24 and 16 h, respectively (Scheme 1). Only the product from iron-catalyzed intermolecular [2π + 2π] cycloaddition was observed; no hydrovinylation products were detected by ^{1}H NMR spectroscopy. The reaction was also performed on a preparative scale with both iron compounds in decane solvent and exclusively furnished vinylcyclobutane in >95% yield.

Introduction of a methyl group into the diene substrate altered the outcome of the catalytic reaction, favoring 1,4-addition over [2π + 2π] cycloaddition. A benzene-d_6 solution containing an equimolar mixture of ethylene and isoprene exclusively furnished 5-methylhexa-1,4-diene in the presence of 2.5 mol % of

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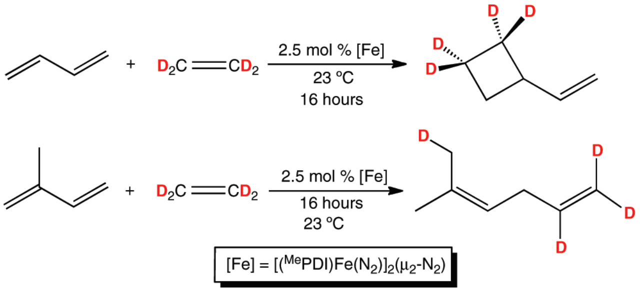
$[(^{Me}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ after 16 h at 23 °C. Performing the same reaction with 5 mol % of $(^{iPr}PDI)Fe(N_2)_2$ also resulted in 1,4-addition chemistry, with (*E*)-2-methylhexa-2,4-diene identified as the sole product. This diene likely arises from alkene isomerization of initially formed 5-methylhexa-1,4-diene to form the conjugated diene, as $(^{iPr}PDI)Fe(N_2)_2$ has been shown to be an effective iron-based olefin isomerization catalyst.[15] The most substituted diene examined, 2,3-dimethylbuta-1,3-diene, produced no reaction with ethylene in the presence of either $(^{iPr}PDI)Fe(N_2)_2$ or $[(^{Me}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ (Scheme 1). The observation of hydrovinylation with ethylene and isoprene expands the scope of this iron-catalyzed carbon−carbon bond-forming reaction, as the previous example was effective only with substituted styrenes.[10]

The mechanisms of the iron-catalyzed intermolecular $[2\pi + 2\pi]$ cycloaddition and 1,4-addition were probed with a series of deuterium labeling experiments (Scheme 2). Performing the catalytic cyclization of butadiene with $CD_2{=}CD_2$ in the presence of 2.5 mol % of $[(^{Me}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ exclusively furnished vinylcyclobutane-d_4, with the deuterium atoms solely in the 2 and 3 positions of the four-membered ring (Scheme 2). With isoprene as the diene substrate, 1,4-addition of $CD_2{=}CD_2$ in the presence of 2.5 mol % of $[(^{Me}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ furnished 5-methylhexa-1,4-diene-d_4, with isotopic labels in the 1 and 2 positions of the diene as well as the in the methyl group (Scheme 2). Other unidentified minor products accompanied formation of 5-methylhexa-1,4-diene-d_4 and were observed only when $CD_2{=}CD_2$ was used.

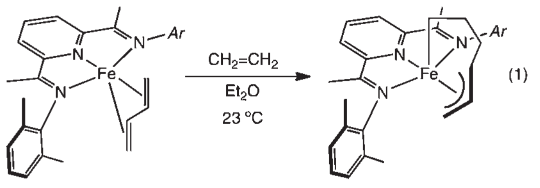
One possibility is that the catalytic formation of vinylcyclobutane proceeds via initial hydrovinylation to form 1,4-hexadiene, followed by cyclization to yield the observed $[2\pi + 2\pi]$ product. Addition of excess 1,4-hexadiene to a benzene-d_6 solution of $[(^{Me}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ produced no reaction, arguing against hydrovinylation as a precursor to overall $[2\pi + 2\pi]$ cycloaddition. Likewise, performing the cyclization in presence of 1,4-hexadiene did not consume the diene. These results are consistent with the deuterium labeling experiments, which also support exclusive cycloaddition.

Scheme 2



Stoichiometric experiments were also conducted in an attempt to observe and characterize catalytically competent intermediates. Our laboratory has previously reported that addition of 1,3-butadiene to the iron dinitrogen compound, $(^{iPr}PDI)Fe(N_2)_2$, yielded the corresponding *trans*-butadiene derivative, $(^{iPr}PDI)Fe(\eta^4\text{-}C_4H_6)$.[6] The methyl analogue, $(^{Me}PDI)Fe(\eta^4\text{-}C_4H_6)$, was prepared in a similar manner. An analogous isoprene compound was also spectroscopically characterized using the same synthetic route. In a related experiment, addition of ethylene to a benzene-d_6 solution of $[(^{Me}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ initially yielded a yellow solution, tentatively assigned as the iron ethylene complex, $(^{Me}PDI)Fe(\eta^2\text{-}C_2H_4)$, which is significantly less stable than $(^{Me}PDI)Fe(\eta^4\text{-}C_4H_6)$ and readily forms the latter compound when treated with butadiene.

Treatment of a diethyl ether solution of $(^{Me}PDI)Fe(\eta^4\text{-}C_4H_6)$ with a slight excess of ethylene (~3 equiv) furnished a new diamagnetic product, identified as the bis(imino)pyridine iron metallocycle, containing an allyl and an alkyl ligand, arising from ethylene insertion into the coordinated diene (eq 1).



(1)

$(^{Me}PDI)Fe(\eta^4\text{-}C_4H_6)$ $(^{Me}PDI)Fe((CH_2)_3(CH)_2CH_2)$

The iron metallocycle, $(^{Me}PDI)Fe((CH_2)_3(CH)_2CH_2)$, was also cleanly prepared from addition of vinylcyclobutane to a benzene-d_6 solution of $[(^{Me}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$, demonstrating the reversibility of the C−C bond-forming reaction. This reaction also represents a rare observation of $sp^3{-}sp^3$ C−C bond activation under mild conditions by an iron compound.[17]

The diamagnetic bis(imino)pyridine iron metallocycle was characterized by ^1H and ^{13}C NMR spectroscopy, Mössbauer spectroscopy, combustion analysis, and single-crystal X-ray diffraction. Representations of the solid-state structure of the molecule are presented in Figure 1, along with selected metric parameters. The iron−carbon distances are consistent with an η^3-allyl ligand tethered to a metal alkyl, giving rise to a rare example of a six-coordinate bis(imino)pyridine iron compound.[18]

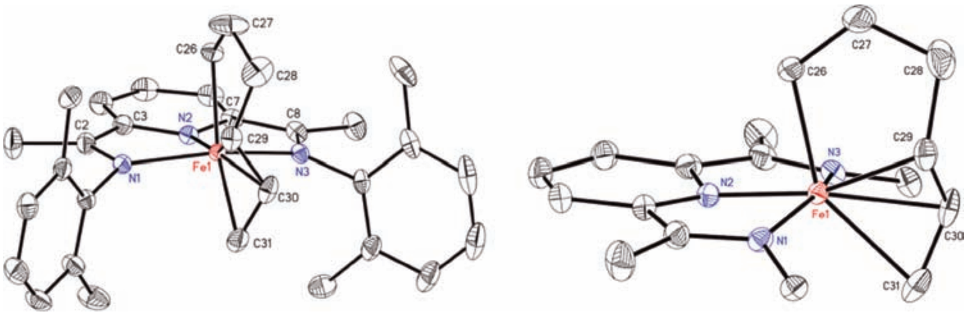
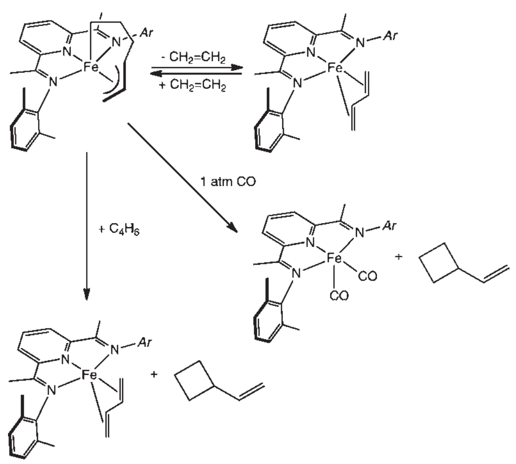
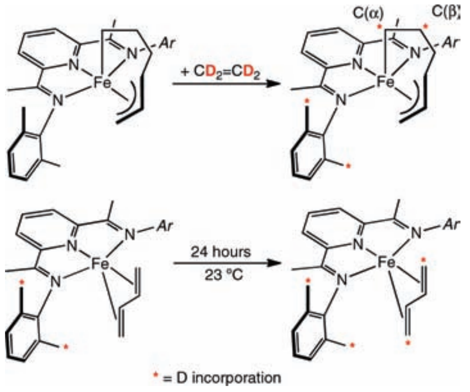


Figure 1. Representation of the solid-state structure of $(^{Me}PDI)Fe((CH_2)_3(CH)_2CH_2)$ at 30% probability ellipsoids. Bond distances (Å): C(26)−C(27), 1.505(3); C(27)−C(28), 1.453(4); C(28)−C(29), 1.524(7); C(29)−C(30), 1.341(6); Fe(1)−C(26), 2.0797(19); Fe(1)−C(29), 2.155(5); Fe(1)−C(30), 2.096(4); Fe(1)−C(31), 2.149(2). Angles (deg): N(2)−Fe(1)−C(26), 84.13(7); N(2)−Fe(1)−C(30), 164.03(17); C(26)−Fe(1)−C(30), 107.00(17).

Scheme 3



Scheme 4



The competency of (^{Me}PDI)Fe((CH_2)$_3$(CH)$_2$$CH_2$) in the catalytic [$2\pi + 2\pi$] cycloaddition process was also evaluated to gain insight into the mechanism of turnover. Allowing a benzene-d_6 solution of (^{Me}PDI)Fe((CH_2)$_3$(CH)$_2$$CH_2$) to stand for 24 h at 23 °C resulted in dissociation of ethylene, with reconstitution of (^{Me}PDI)Fe(η^4-C_4H_6). Under the experimental conditions employed, a 2:1 mixture of (^{Me}PDI)Fe((CH_2)$_3$(CH)$_2$$CH_2$) and (^{Me}PDI)Fe($\eta^4$-$C_4H_6$) was obtained after 24 h (Scheme 3). This reaction was suppressed by addition of excess ethylene to the solution. Attempts to promote C−C reductive elimination by warming a benzene-d_6 solution of (^{Me}PDI)Fe((CH_2)$_3$(CH)$_2$$CH_2$) to 65 °C were unsuccessful, as decomposition of the iron compound predominated. No vinylcyclobutane was observed, establishing that C−C reductive elimination does not proceed directly from (^{Me}PDI)Fe((CH_2)$_3$(CH)$_2$$CH_2$).[19]

The lack of thermal reductive elimination from (^{Me}PDI)Fe((CH_2)$_3$(CH)$_2$$CH_2$) prompted exploration of alternative ligand-induced pathways.[20] Addition of 4 atm of CO to a benzene-d_6 solution of (^{Me}PDI)Fe((CH_2)$_3$(CH)$_2$$CH_2$) at 23 °C cleanly and quantitatively induced C−C bond formation and generated vinylcyclobutane along with the iron dicarbonyl derivative, (^{Me}PDI)Fe(CO)$_2$.[16] Hydrogenation (1 atm, 16 h, 23 °C) of (^{Me}PDI)Fe((CH_2)$_3$(CH)$_2$$CH_2$) produced a similar outcome, as ethylcyclobutane was observed, consistent with the initial formation of vinylcyclobutane, followed by rapid alkene hydrogenation.[16] In chemistry more relevant to catalytic turnover, treatment of (^{Me}PDI)Fe((CH_2)$_3$(CH)$_2$$CH_2$) with excess butadiene also liberated vinylcyclobutane, with concomitant formation of the iron butadiene compound, (^{Me}PDI)Fe(η^4-C_4H_6). Notably, addition of isoprene to the same iron compound did not induce C−C bond formation. All of the above experiments are consistent with a ligand-induced reductive elimination process; however, it is noteworthy that ethylene and isoprene are not sufficiently potent ligands to promote C−C bond formation and vinylcyclobutane dissociation.

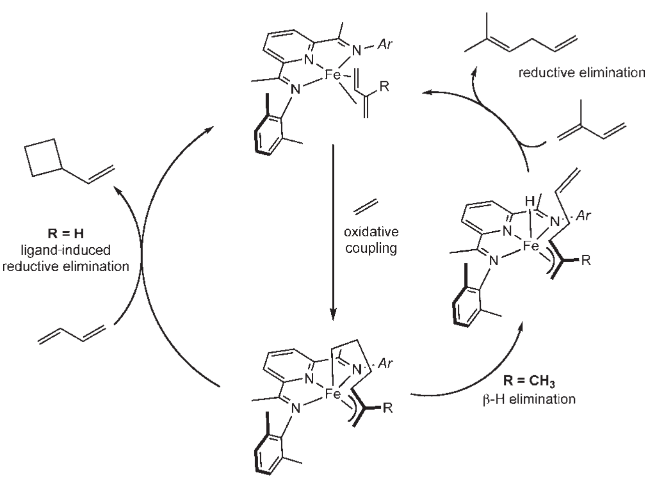
The observation of ethylene loss from (^{Me}PDI)Fe((CH_2)$_3$(CH)$_2$$CH_2$) established the reversibility of olefin insertion. To further explore this phenomenon, a benzene solution of (^{Me}PDI)Fe((CH_2)$_3$(CH)$_2$$CH_2$) was treated with 3 equiv of CD_2=CD_2 (Scheme 4). Monitoring the reaction by ^{2}H NMR spectroscopy established deuterium incorporation into the expected C(α) and C(β) positions of the alkyl portion of the metallocycle. Notably, deuterium incorporation was also observed in the aryl methyl groups of the bis(imino)pyridine ligand, suggesting that cyclometalation[21] is also competitive with the insertion−deinsertion reaction. Analysis of the isotopically labeled product by ^{1}H NMR spectroscopy in benzene-d_6 revealed proton incorporation into both the C(α) and C(β) positions. In a control experiment, CD_2=CD_2 was added to a benzene solution of [(^{Me}PDI)Fe(N_2)]$_2$(μ_2-N_2) at 23 °C, and rapid deuterium incorporation into the bis(imino)pyridine aryl methyl groups was observed, demonstrating reversible cyclometalation from the putative iron ethylene compound as well.[21]

Converse experiments were also conducted with bis(imino)pyridine iron compounds with deuterated methyl groups on the aryl substituents. These compounds will be denoted with an asterisk. Monitoring a benzene solution of (^{Me*}PDI)Fe(η^4-C_4H_6) by ^{2}H NMR spectroscopy established deuterium incorporation into the terminal positions of the butadiene ligand. No isotopic label was observed in the internal positions of coordinated diene over the course of 16 h. The relevance of the isotopic exchange process to catalytic cyclization was also examined by monitoring the isotopic composition of the [(^{Me}PDI)Fe] species by ^{2}H NMR spectroscopy during turnover. At both 20 and 50% conversion to vinylcyclobutane-d_4 using CD_2=CD_2, deuterium incorporation into the aryl methyl groups was observed, demonstrating that aryl substituent cyclometalation occurs during catalytic turnover.

On the basis of all of the experimental observations, a mechanism for the bis(imino)pyridine iron-catalyzed intermolecular [$2\pi + 2\pi$] cyclization and 1,4-addition[10] is proposed (Scheme 5). Catalytic turnover initiates with displacement of the dinitrogen ligands by butadiene to form the iron η^4-butadiene complex. Insertion of ethylene forms the observed and characterized iron metallocycle, and turnover-limiting butadiene-induced reductive elimination furnishes vinylcyclobutane and regenerates the propagating iron butadiene compound. With isoprene as the substrate, it is likely the analogous intermediate is formed, as proposed by Ritter.[10] The more sterically hindered diene is a less potent ligand and, as a consequence, decreases the rate of ligand-induced reductive elimination, allowing β-hydrogen elimination from the metallocycle to become competitive. Subsequent C−H reductive elimination furnishes the observed 1,4-addition product. In both pathways, deuterium labeling experiments establish cyclometalation from both methyl and isopropyl aryl substituents during turnover.

In summary, an iron-catalyzed intermolecular [$2\pi + 2\pi$] cycloaddition between butadiene and ethylene to form vinylcyclobutane has been discovered. Isolation of a catalytically competent

Scheme 5



iron metallocyclic intermediate established turnover limiting diene-induced reductive elimination as a key component of the catalytic cycle. Such mechanistic insight may ultimately prove valuable in catalyst development efforts aimed at expanding the scope of the reaction.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Complete experimental procedures, characterization, and crystallographic data for $(^{\mathrm{Me}}\mathrm{PDI})\mathrm{Fe}((\mathrm{CH}_2)_3(\mathrm{CH})_2\mathrm{CH}_2)$. This material is available free of charge via the Internet at http://pubs.acs.org.

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