ACCOUNTS of chemical research

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1,4-Functionalization of 1,3-Dienes With Low-Valent Iron Catalysts

Published as part of the Accounts of Chemical Research special issue "Earth Abundant Metals in Homogeneous Catalysis".

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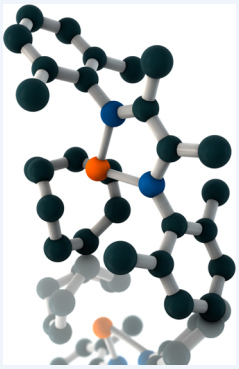
CONSPECTUS: Iron-catalyzed or -mediated transformations of organic substrates have been important throughout the development of organic chemistry due to iron's abundance, low cost, and favorable toxicity profile. Highly reduced iron species, although difficult to isolate and characterize, have proven valuable as catalysts for a variety of C−C and C−heteroatom bond forming processes, as well as cyclization and cycloisomerization reactions.



We have developed iminopyridine-ligated low-valent iron catalysts that facilitate selective 1,4-hydrovinylation, hydoboration, hydrosilylation, and polymerization of 1,3-dienes. The catalysts are generated in situ from iron(II) precursors in the presence of activated magnesium metal or trialkylaluminum reductants. The 1,4-addition processes provide access to valuable products such as 1,4-dienes, allylboronic esters, allylsilanes, and highly regioregular polyisoprene. In these transformations, addition is stereoselective, providing (*E*)-alkene isomers selectively, and (1,2)-addition products are generally not observed. Moreover, modification of steric bulk on the iminopyridine ligand can be used to change selectivity for (1,4)- versus (4,1)-addition to dienes with nonsymmetric substitution.

Access to low-valent iron precursor complexes is limited, and we have developed a diaryliron(II) precursor that undergoes smooth reductive elimination in the presence of iminopyridine ligands to provide easy access to low-valent iron catalysts without the use of heterogeneous reductants, which complicate the isolation and study of low-valent iron complexes. We obtained crystal structures of our iron(II) catalyst precursor and an iminopyridine-ligated reduced iron species generated from it. Spectroscopic analysis suggests that although this species is formally iron(0), the redox-active iminopyridine ligands accept electron density from the metal and the complex is more properly formulated as iron(II) coordinated by two radical-anion ligands.

We believe that a closely-related set of reaction manifolds is responsible for the 1,4-functionalization reactivity displayed by the iron(iminopyridine) complexes (see text). Kinetics experiments and deuterium-labeling studies provide evidence for the proposed catalytic cycle. The geometry of the double bond remaining after 1,4-addition is set by the requirement that the diene bind to the iron center in an *s-cis* geometry, and the regioselectivity of addition can be rationalized by the location of steric bulk on the iminopyridine ligand.

The transformations presented in this Account utilize iron catalysts to provide access to valuable diene 1,4-addition products such as 1,4-dienes, allylboronate esters, and allylsilanes, as well as highly regioregular polyisoprene. The development of a stable diaryliron(II) precatalyst, structural characterization of an iminopyridine-ligated iron(0) complex, and mechanistic insights into the selective nature of this transformation provide a window into the reactivity profile of low-valent iron.

1. INTRODUCTION

Iron and other first-row metals can perform both one-and two-electron elementary reactions. This reactivity profile provides the opportunity for development of reactions that are not known to proceed with second- or third-row metal catalysts, which often rely on two-electron elementary steps. Careful consideration of how to use and control the redox behavior and ligand exchange rates at the metal is challenging but important for the design of selective, high-yielding reactions catalyzed by first-row metals. Despite the challenges, the discovery and development of iron catalysts in both homogeneous and heterogeneous catalysis, show the promise and importance of iron catalysis, as exemplified by the Haber−Bosch process, C−H oxidation, and cross-coupling chemistry.

Low-valent iron can show strong, but fluxional, interactions with carbon−carbon π bonds. We hypothesized that the activation of 1,3-dienes by the electron-rich iron center could be channeled into selective catalytic transformations by appropriate choice of ancillary ligand. We found that the redox-active iminopyridine family of ligands allows for 1,4-selective catalytic additions to 1,3-dienes. The use of iminopyridines rather than the more widely used redox-active diiminopyridines[1] leaves an additional coordination site vacant, for subsequent diene and reagent binding. Hydrovinylation,[2] hydroboration,[3] hydrosilylation,[4] and polymerization of 1,3-dienes[5] are all catalyzed with high degrees of regio- and stereoselectivity for the products.[6] These transformations complement known 1,2-selective transformations of 1,3-dienes.[7]

In our experience, the development of low-valent iron catalysis has been hampered by a lack of suitable but stable iron precursor complexes. Although there are several readily available, stable iron(0) sources, including iron carbonyl species, they all contain strongly π-accepting ligands. Strongly

Received: January 30, 2015
Published: July 27, 2015

DOI: 10.1021/acs.accounts.5b00050
Acc. Chem. Res. 2015, 48, 2330−2343

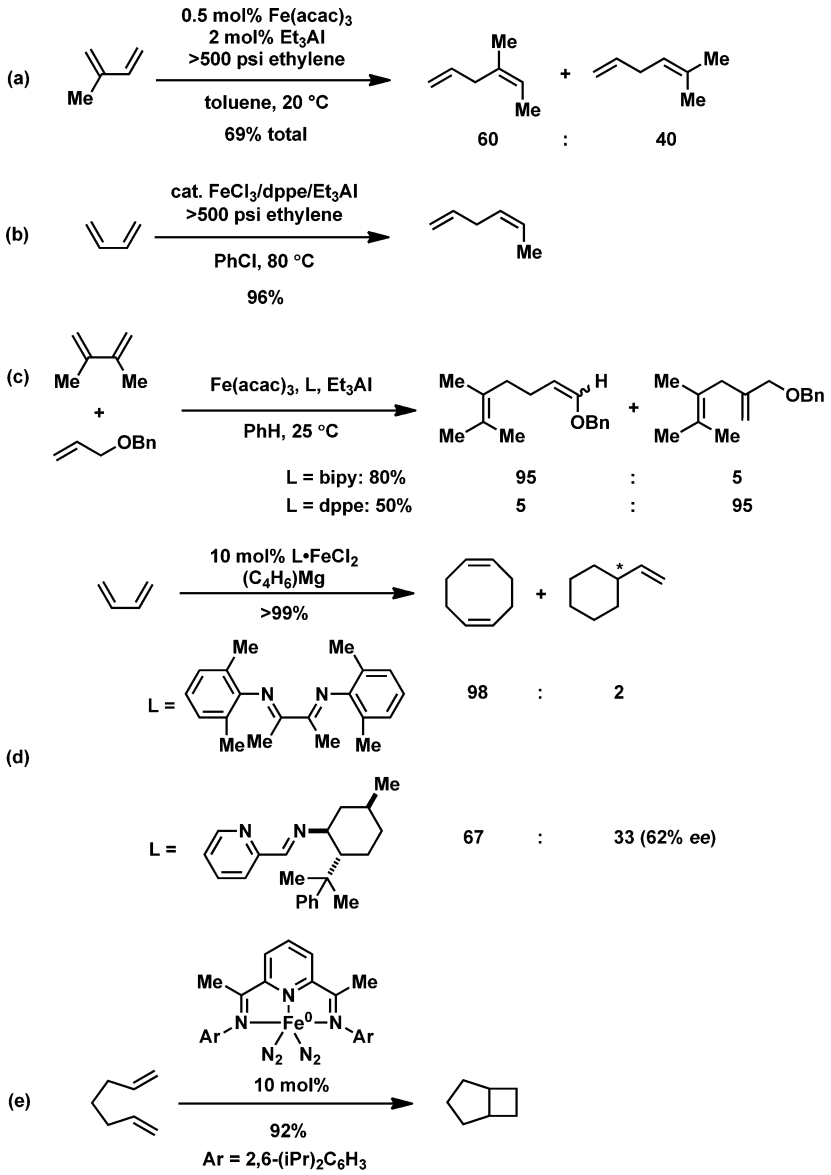


Figure 1. Known reactions of dienes with low-valent iron catalysts, from the work of (a) Hata, (b) Iwamoto, (c) Takacs, (d) tom Dieck, and (e) Chirik.

π-accepting ligands decrease the available electron density at the iron center, which weakens π-backbonding interactions with substrates and can result in inefficient catalysts. In situ reduction of higher-valent iron species is possible but often leads to ill-defined mixtures that are difficult to study. We have developed a broadly applicable diaryliron(II) precatalyst that readily undergoes reductive elimination in the presence of exogenous ligand to form well-defined formal iron(0) species that are catalytically active for 1,4-functionalization of 1,3-dienes.

2. LOW-VALENT IRON IN CATALYSIS

Iron can adopt a wide range of formal oxidation states, from −II to +VI. Low-valent iron complexes are capable of catalyzing a variety of reactions, including cross-coupling, cycloisomerization, and cycloaddition reactions.[8] The electron-rich nature of low-valent iron allows for π-activation of bound alkenes, in particular 1,3-dienes. The large number of stable oxidation states of iron allows for many possible reaction manifolds. Ligation of iron with carefully selected redox-active ligands can channel reactivity into selective pathways.

To put our work in context, we give a brief summary of previous iron-catalyzed transformations of 1,3-dienes: In the 1960s, Hata and Iwamoto reported the reaction of 1,3-dienes with simple olefins using iron catalysts to afford 1,4-diene products.[9] Initially, iron(III) acetylacetonate and triethylaluminum were used to catalyze the reaction of 1,3-dienes with ethylene and propylene (Figure 1a). These reactions gave exclusively the *cis* isomer of the 1,4-diene products, but some isomerization (for example, to 1,5-diene products) was observed. When unsymmetrically substituted dienes were used as substrates, mixtures of isomeric products were obtained. Further exploration showed that the zerovalent iron complex Fe(dppe)(C_2H_4) catalyzed the addition of ethylene to butadiene.[10] Addition of Lewis acids, in particular diethylaluminum chloride, was found to increase the efficiency and selectivity of the process. Iwamoto and Yuguchi showed that mixtures of $FeCl_3$, Et_3Al, and tertiary phosphines catalyzed the addition of

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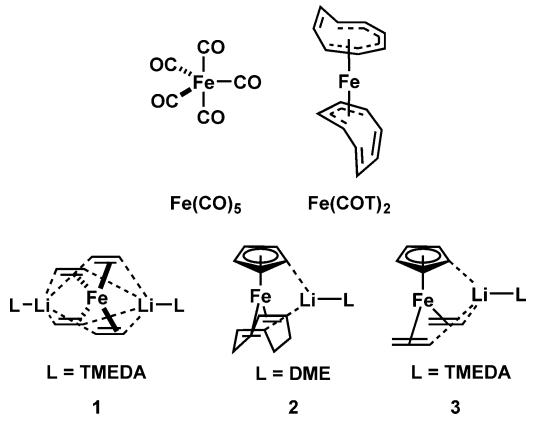


Figure 2. Known low-valent iron complexes used in catalysis.

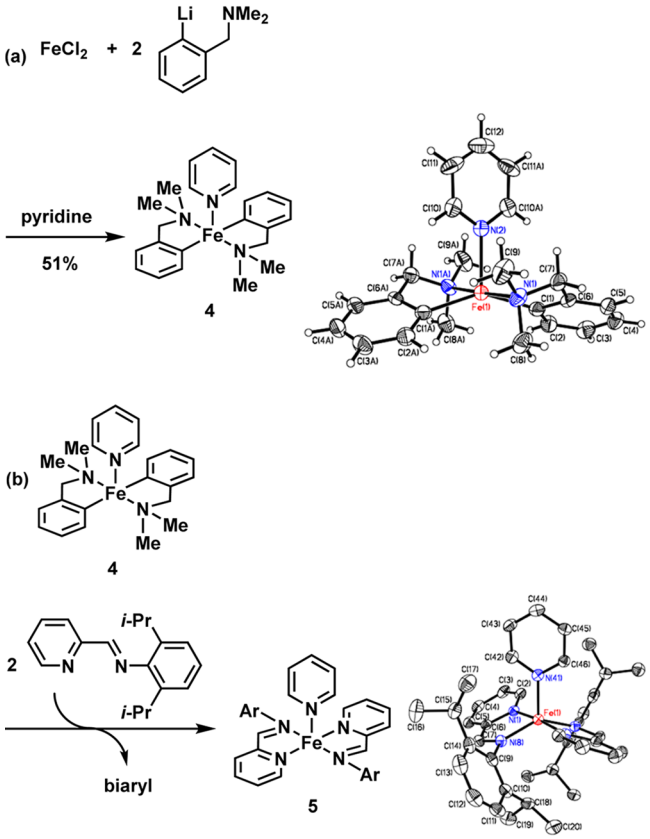


Figure 3. (a) Synthesis of Fe(II) precatalyst **4** with X-ray crystal structure and (b) reductive elimination in the presence of iminopyridine ligand to give Fe(0) complex **5**.

ethylene to butadiene to give a mixture of 1,3- and 1,4-diene products.[11] Further experimentation showed that bidentate phosphines such as dppp or dppe provided improved results relative to monodentate phosphines (Figure 1b).[12]

During the 1980s, Takacs et al. reported iron-catalyzed formal [4 + 4] ene reactions of 1,3-dienes with allylic ethers.[13] Importantly, they found selectivity in this reaction was profoundly affected by ligand changes, with bipyridine providing primarily linear 1,5-dienes, while diphosphines such as dppe gave primarily branched 1,4-dienes (Figure 1c). Use of pyridine rather than bidentate ligands resulted in the formation of much more 1,2-addition product rather than 1,4-addition.

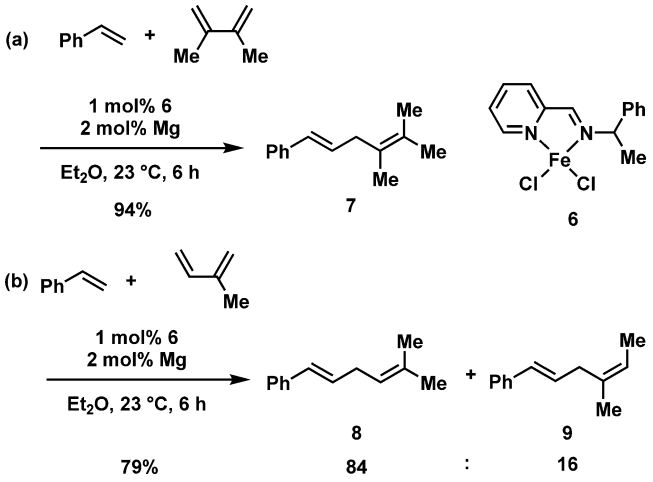


Figure 4. Iron-catalyzed addition of styrene to (a) 2,3-dimethylbutadiene and (b) isoprene.

tom Dieck and Dietrich have shown that diimine and iminopyridine ligands allow for dimerization of butadiene to give cyclooctadiene and vinylcyclohexene products (Figure 1d).[14] The ratio of cyclooctadiene to vinylcyclohexene could be varied by changing the ligand, and moderate enantioselectivity could be obtained for the vinylcyclohexene product by use of enantiopure ligands. Fürstner and co-workers showed that well-defined low-valent iron complexes can catalyze cycloisomerization and cycloaddition reactions of enyne substrates.[15] Chirik et al. found that iron complexes with redox-active bis(imino)pyridine ligands catalyzed the formal $[2\pi + 2\pi]$ cycloaddition of α,ω-dienes to give bicyclic cyclobutane products (Figure 1e).[16] The redox-active nature of the ligand was proposed to be crucial in the putative catalytic cycle, allowing iron to remain in the ferrous oxidation state and preventing precipitation of iron(0).

3. DEVELOPMENT OF A WELL-DEFINED IRON CATALYST

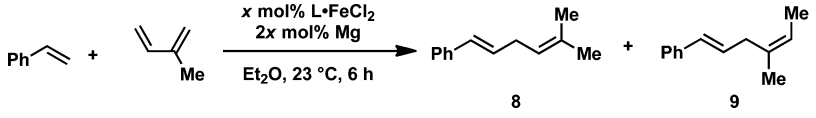
The development of catalysis with late transition metals has been greatly advanced by the availability of low-valent precatalyst complexes such as $Pd_2(dba)_3$, $Ni(cod)_2$, or $RhCl(PPh_3)_3$ (Wilkinson's catalyst). In contrast to these readily available and stable compounds, low-valent iron complexes suitable for catalytic applications are scarce. This has led to the in situ generation of low-valent iron by reduction of ferrous precursors by organomagnesium or organolithium reagents, or by $NaBHEt_3$ or zinc metal.[17] These processes typically lead to ill-defined and often heterogeneous mixtures, making characterization of the active catalytic species most challenging.

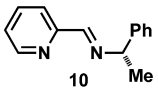
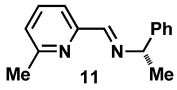
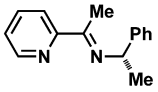
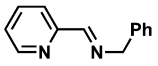
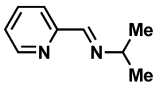
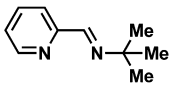
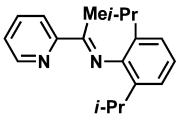
Many of the commonly available low-valent iron complexes (Figure 2a) are unsuitable as catalyst precursors. Although carbon monoxide-ligated complexes of iron(0) such as $Fe(CO)_5$ and $Fe_2(CO)_9$ are inexpensive and straightforward to handle, the π-acidic character of the CO ligands drastically decreases the electron density at the iron center, and hence the complex's ability to catalyze reactions that rely on electron-rich metal centers. The cyclooctatetraene-ligated complex $Fe(COT)_2$ suffers from tight binding of the COT ligands, restricting available coordination sites as well as removing electron density from the metal center through π-backbonding.

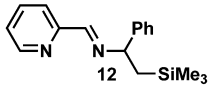
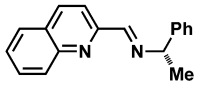
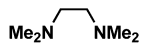
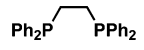
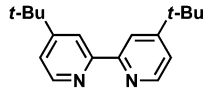
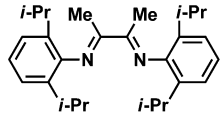
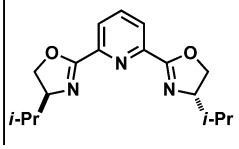
Other low-valent iron complexes, more suitable to act as catalyst precursors, have been developed in recent years.

DOI: 10.1021/acs.accounts.5b00050
Acc. Chem. Res. 2015, 48, 2330−2343

Table 1. Effect of Ligand Structure on Iron-Catalyzed Coupling of Styrene and Isoprene



Ligand	Loading (mol%)	Styrene Conversion (%)	Regioselectivity (8:9)
 10	2	100	84:16
 11	2	35	16:84
	10	<5	nd
	5	80	76:24
	10	100	complex mixture
	10	0	nd
	10	0	nd

Ligand	Loading (mol%)	Styrene Conversion (%)	Regioselectivity (8:9)
 12	20	60	90:10
	10	0	nd
	20	20	25:75
	20	<5	nd
	10	50	complex mixture
	10	0	nd
	20	35	25:75

Pioneering work by Jonas showed that one or both cyclopentadienyl ligands of ferrocene could be removed under reductive conditions and replaced with ethylene or cyclooctadiene ligands, yielding complexes **1**−**3** (Figure 2).[18] The Fürstner group has used these complexes as catalysts for cross-coupling and cyloisomerization of enynes.[8d]

Due to the dearth of readily available low-valent iron precatalyst complexes and the difficulty of performing mechanistic studies on reactions where iron is reduced in situ, we sought a stable precursor to low-valent iron complexes that would generate the iron(0) species without addition of external reductants and allow for variation of the coordination sphere of iron.[4] One potential path to generating iron(0) species is by reductive elimination from a ferrous precursor. Initial experiments with known diaryliron(II) species such as tetramesityldiiron[19] either resulted in unstable complexes or showed no evidence of reductive elimination to form zerovalent iron. We designed diaryliron(II) complex **4** (Figure 3a). Complex **4** is readily synthesized by mixing two equivalents of aryllithium with ferrous chloride in the presence of 4 equiv of pyridine. The chelating 2-(dimethylaminomethyl)phenyl ligands stabilize the complex and prevent it from undergoing spontaneous reductive elimination possibly due to the *trans* disposition of the two aryl groups. However, upon addition of an exogenous ligand such as an iminopyridine, clean reductive elimination occurs to give complex **5** (Figure 3b). Although **5** is formally iron(0), examination of bond lengths in the ligand reveals that it is more accurately described as iron(II), with each redox-active iminopyridine ligand reduced by one electron.[20] The ligand-induced reductive elimination from **4** is likely due to geometric reorganization of the aryl ligands induced by iminopyridine binding, placing the two aryl ligands *cis* to one another and allowing reductive elimination to take place. The reductive elimination to form iron(0) can be followed by NMR and has proven useful in mechanistic studies of iron-catalyzed 1,4-hydrosilylation of 1,3-dienes (vide infra).

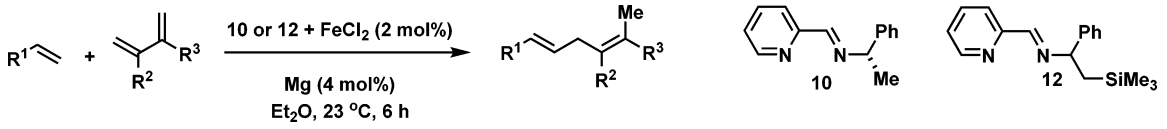
4. IRON-CATALYZED 1,4-FUNCTIONALIZATION OF DIENES

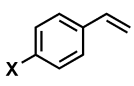
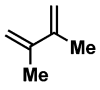
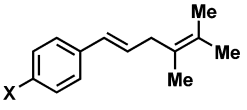
4.1. 1,4-Hydrovinylation

Our first successful iron-catalyzed reaction was 1,4-addition of α-olefins to 1,3-dienes.[2] We found that iminopyridine-ligated iron(II) complex **6**, when treated with activated magnesium metal in diethyl ether, formed a mixture that efficiently catalyzed the 1,4-addition of styrene to 2,3-dimethylbutadiene. The 1,4-diene product, **7**, was formed in 94% isolated yield after 6 h at 23 °C (Figure 4a). When a nonsymmetric 1,3-diene such as isoprene was used instead of 2,3-dimethylbutadiene, two isomeric products **8** and **9** were formed in an 84:16 ratio, in 79% total yield (Figure 4b). The structure of the iminopyridine ligand supporting the iron center was found to influence both the yield and the regioselectivity of the reaction, while other ligand classes such as diamines, bisphosphines, bipyridines, diimines, and pyridinebisoxazolines provided poor conversions or low regioselectivities (Table 1). Ligand **12** was found to improve the ratio of **8**:**9** to 90:10, while methyl substitution at

DOI: 10.1021/acs.accounts.5b00050
Acc. Chem. Res. 2015, 48, 2330−2343

Table 2. Iron-Catalyzed 1,4-Addition of Olefins to 1,3-Dienes



Alkene	Diene	Product	X	Ligand	Yield	Regioselectivity[a]
			H	10	94[b]	-
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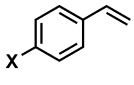
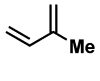
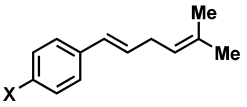
			Cl		78	-
			OAc		85	-
			CF		90	-
			t-Bu		92	-
			H	12	60[c]	90:10
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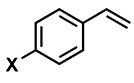
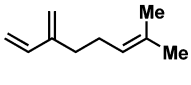
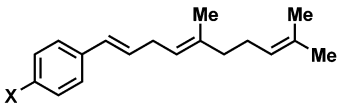
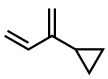
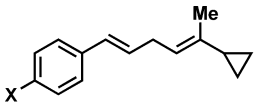
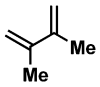
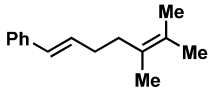
			H	12	66[d]	93:7
			OMe		51[d]	96:4
			-	10	77	98:2
			-	10	79[e]	-

[a]Regioisomeric ratio as described in Figure 4. All products were formed with >99:1 *E*/*Z* selectivity. [b]1 mol % **10**·$FeCl_2$ used. [c]20 mol % **12**·$FeCl_2$ used. [d]10 mol % **12**·$FeCl_2$ used. [e]5 mol % **10**·$FeCl_2$ used.

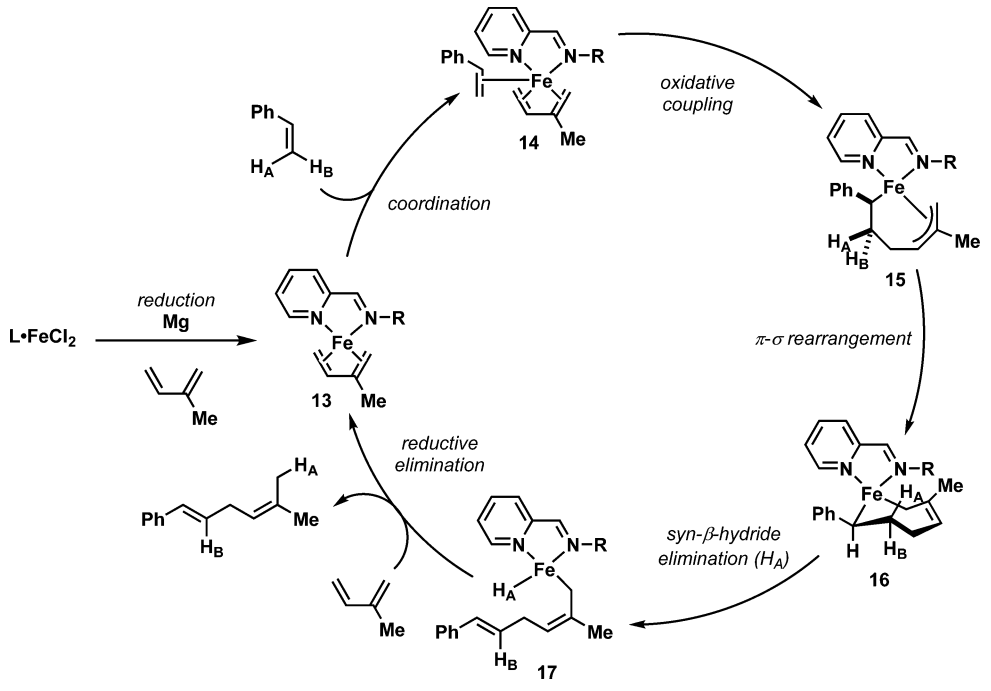


Figure 5. Proposed catalytic cycle for 1,4-addition of styrene to 1,3-dienes.

the 6-position of the pyridine (ligand **11**) inverted the ratio to 16:84.

Both the 1,3-diene and styrene components of the reaction could be varied; results are shown in Table 2. Importantly, in all cases, the stereochemistry of both double bonds was controlled, and only a single double-bond isomer (*E*/*Z* ratio > 99:1 for all applicable cases) was observed for each addition product. Synthesis of stereodefined trisubstituted double bonds is challenging to achieve through other methods.[21] Olefins other than styrenes typically gave mixtures of branched and linear 1,4-dienes, as well as products resulting from double-bond migration. High yields of a single product were only

DOI: 10.1021/acs.accounts.5b00050
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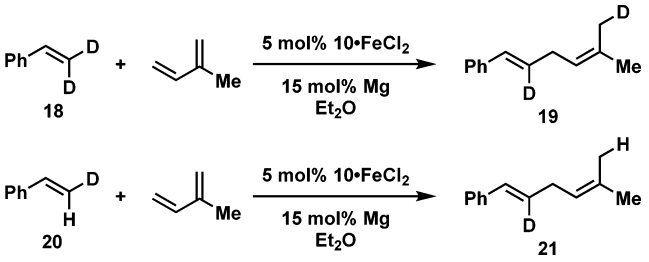


Figure 6. Deuterium labeling experiments are consistent with the proposed mechanism for iron-catalyzed 1,4-hydrovinylation of 1,3-dienes.

achieved for styrenes and select other olefins such as allylbenzene.

Our mechanistic hypothesis for the 1,4-hydrovinylation of 1,3-dienes is shown in Figure 5. Reduction of the Fe(II) precatalyst by activated magnesium metal in the presence of diene gives diene-ligated Fe(0) complex **13**. Coordination of styrene and oxidative coupling gives alkyl π-allyl iron(II) complex **15**. Following $\pi-\sigma$ rearrangement of the allyl moiety, only one of the two protons derived from the β-position of styrene (H_A) is positioned *syn* to iron in complex **16**, accounting for the stereoselective formation of the *E* double bond. C−H reductive elimination from intermediate **17** with concomitant diene binding to iron provides 1,4-diene product and turns over the catalytic cycle. To substantiate our mechanistic hypothesis, we performed substrate deuterium-labeling experiments. When β,β-dideuterostyrene **18** and (*E*)-β-deuterostyrene **20** were coupled with isoprene under our standard conditions, deuterium labeling was found in the products (**19** and **21**, respectively) exclusively at the positions indicated, consistent with our proposed mechanism (Figure 6).

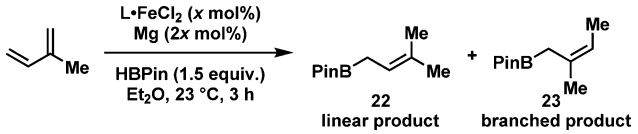
4.2. 1,4-Hydroboration

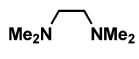
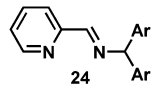
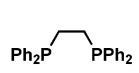
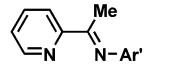
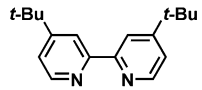
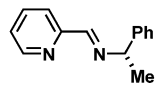
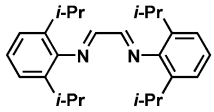
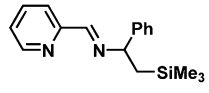
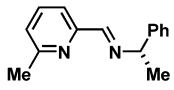
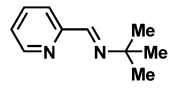
Successful 1,4-hydrovinylation of 1,3-dienes led us to hypothesize that other reagents might also add to 1,3-dienes in a 1,4-fashion under low-valent iron catalysis. The synthetic utility of allylboranes as precursors to allylic alcohols and as organometallic reagents for addition to carbonyl compounds led us to develop 1,4-hydroboration chemistry to access these valuable building blocks in an efficient, functional-group tolerant, and stereodefined fashion.[3] 1,4-Hydroboration of 1,3-dienes has limited precedence in the literature,[22] and synthesis of stereodefined trisubstituted allylboron reagents is challenging.

As a starting point, we tested several types of ligands for 1,4-hydroboration of isoprene using pinacolborane. We again found that iminopyridine ligands were optimal for the selective 1,4-functionalization reaction (Table 3). Other ligand types, such as diamines, diimines, bipyridines, and bisphosphines, gave inferior yields or poor selectivities. We identified ligand **24** as capable of providing good selectivity for product **22** over **23** Notably, no 1,2-hydroboration was observed.

A variety of 1,3-dienes proved to be amenable to 1,4-hydroboration (Table 4). For 1,4-hydroboration of 2-(dimethylphenylsilyl)butadiene, we found that ligand **24** provided the optimal yield of linear product (entry 6), while ligand **25** shifted the selectivity to favor the branched product (entry 7). Ligand **25** also proved more effective for 2,3-disubstituted dienes (entries 1 and 2) Using ligand **24**, higher linear:-branched selectivities were observed for unsymmetrical dienes

Table 3. Evaluation of Ligands for 1,4-Hydroboration of Isoprene with Pinacolborane[a]

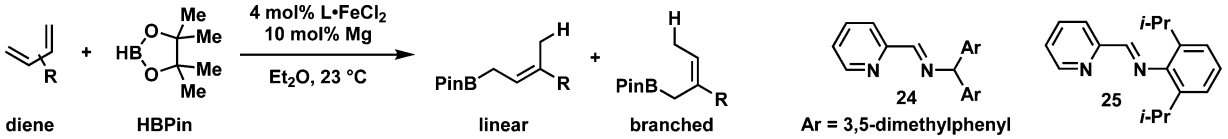


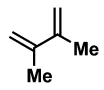
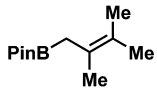
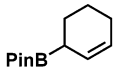
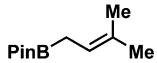
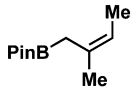
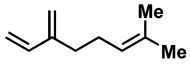
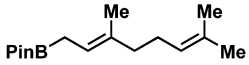
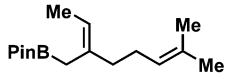
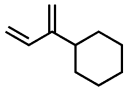
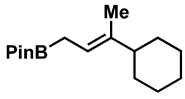
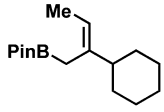
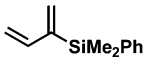
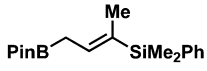
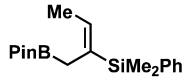
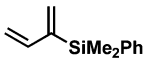
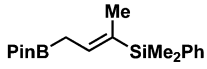
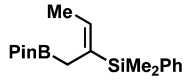
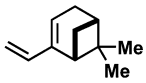
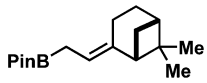
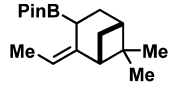
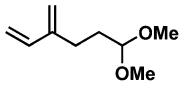
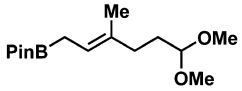
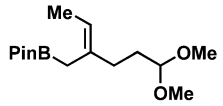
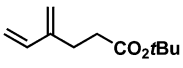
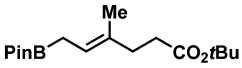
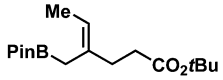
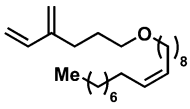
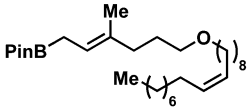
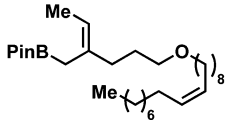
Ligand	Loading (mol%)	Yield (%)	Regioselectivity (22:23)	Ligand	Loading (mol%)	Yield (%)	Regioselectivity (22:23)
	5	28	68:32	 24 Ar = 3,5-dimethylphenyl	4	92	90:10
	5	<10	nd	 Ar' = 2,6-diisopropylphenyl	10	88	15:85
	5	68	57:43		10	92	73:27
	5	30	50:50		5	68	77:23
	10	<10	nd		10	99	66:34

[a]Yields and regioselectivity determined relative to trimethoxybenzene external standard.

DOI: 10.1021/acs.accounts.5b00050
Acc. Chem. Res. 2015, 48, 2330−2343

Table 4. Scope of Iron-Catalyzed 1,4-Hydroboration of 1,3-Dienes Using Pinacolborane



Entry	Diene	Linear Product	Branched Product	L	Yield (%)	Linear:Branched
1			--	25[a]	91	--
2			--	25[a]	83[b]	--
3				24	92[c]	90:10
4				24	89	93:7
5				24	68[b,d]	94:6
6				24	91[b]	99:1
7				25[a]	73[b]	<1:99
8				24	91[b]	98:2
9				24	71[b]	94:6
10				24	66[b,d]	94:6
11				24	68[b,d]	93:7

[a]Using 5 mol % 25·$FeCl_2$. [b]Using 15 mol % 2,3-dimethyl-1,3-butadiene as an additive to stabilize low-valent iron. [c]Using 1.5 equiv of HBPin. [d]Product degradation was observed upon purification by chromatography on silica gel; the yield can be higher if used in situ.

with bulky substituents. In all cases, the (*E*) isomer of the product was formed exclusively. Unlike the hydrovinylation reaction, substitution at the terminal positions of the 1,3-diene was tolerated (entries 2 and 8). Interestingly, the reaction is selective for hydroboration of 1,3-dienes in the presence of isolated alkenes (entry 11). With respect to the borane component of the reaction, pinacolborane was found to be optimal. Other boronic esters such as catecholborane resulted in products that were unstable to hydrolysis or chromatography; bulky alkylboranes such as 9-BBN and diisopinylcamphenylborane did not provide hydroboration products under these conditions.

We have shown that the stereodefined allylboronic esters produced by our 1,4-hydroboration reaction undergo known reactions of allylboranes to provide stereodefined products. Oxidation with basic peroxide gives rise to stereodefined (*E*)-trisubstituted allylic alcohols such as **27** and **29** (Figure 7a,b), useful in Noyori hydrogenation,[23] isomerization to chiral aldehydes,[24] and Sharpless asymmetric epoxidation.[25] Hydroboration products can also be used to allylate aldehydes (Figure 7c). In this case, a 93:7 mixture of regioisomers resulting from hydroboration was used directly in the addition to benzaldehyde. Acid-catalyzed cyclization gave lactone **31** as a single diastereomer in 65% yield over three steps.

DOI: 10.1021/acs.accounts.5b00050
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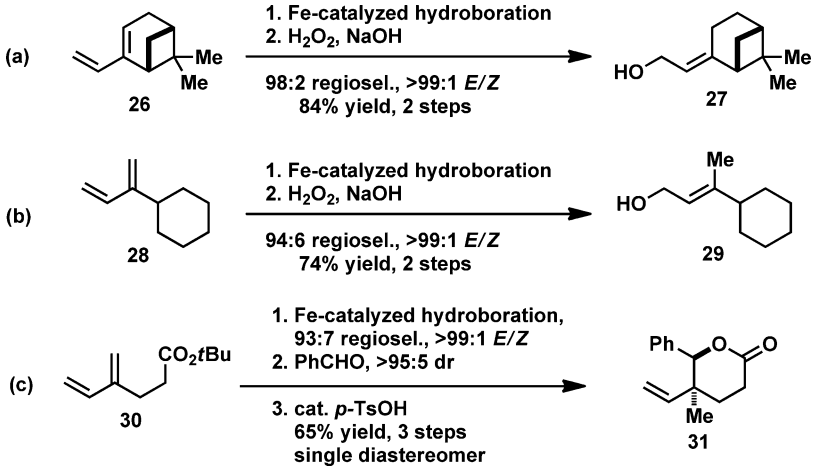

Figure 7. Synthetic applications of allylboronic esters resulting from Fe-catalyzed 1,4-hydroboration. (a, b) Oxidation provides stereodefined allylic alcohols. (c) Allylborane intermediates can be treated directly with aldehydes to afford addition products.

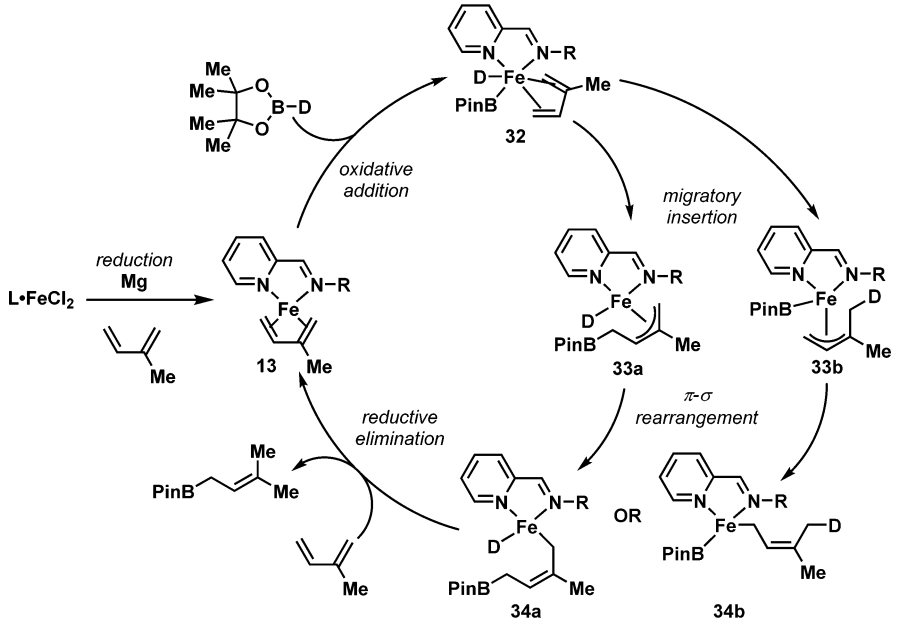

Figure 8. Proposed mechanism for iron-catalyzed 1,4-hydroboration of 1,3-dienes. Either C−B migratory insertion or C−H(D) migratory insertion may be the operative pathway.

Our mechanistic hypothesis for this transformation is shown in Figure 8. As in the hydrovinylation reaction, a ferrous precatalyst is reduced to iron(0) by activated magnesium metal in the presence of 1,3-diene to give compound **13**. Oxidative addition of pinacolborane gives an iron(II) boryl hydride complex **32**. Migratory insertion then occurs, with either the boryl or the hydride ligand undergoing migration, to give **33a** or **33b**, respectively. $\pi-\sigma$ rearrangement gives η^1-allyl species **34a** or **34b**, which undergoes reductive elimination to provide allylboronic ester product. Deuteration experiments show that the hydrogen atom from pinacolborane is incorporated at the opposite terminus of the 1,3-diene from the boron moiety, but at this time it is uncertain whether insertion into the Fe−H bond or the Fe−B bond is the preferred pathway.

4.3. 1,4-Hydrosilylation

We became interested in 1,4-hydrosilylation of 1,3-dienes due to the synthetic utility of the allylsilane products. Allylsilanes are often produced by allylmetal additions to chlorosilanes, conditions that are incompatible with electrophilic or protic functionality.[26] Other transition metal-catalyzed methods for allylsilane synthesis from dienes are known but regioselectivity is often problematic.[27] Rhodium(I) catalysts typically give branched allylsilane products, where C−Si bond formation occurs at the more sterically hindered diene terminus.[28] Palladium-catalyzed 1,4-hydrosilylation gives exclusively branched allylsilanes in low yield.[29] A highly linear-selective 1,4-hydrosilylation of 1,3-dienes would thus be a valuable addition to the synthetic chemist's toolkit.

We found that iminopyridine-complexed iron species catalyze a highly regio- and stereoselective 1,4-hydrosilylation of 1,3-dienes.[4] This research was greatly aided by the availability of the well-defined precatalyst **4** described in section 3. When precatalyst **4** was mixed with iminopyridine ligands, clean reductive elimination took place to provide Fe(0) catalytic species. Evaluation of a range of iminopyridine ligands in the hydrosilylation of myrcene showed that ligand **37** gave high

DOI: 10.1021/acs.accounts.5b00050
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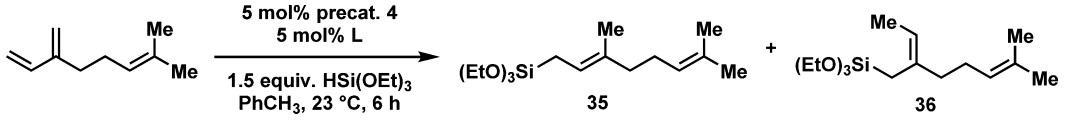
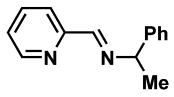
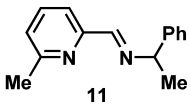
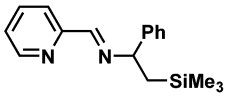
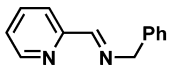
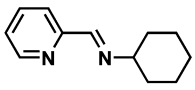
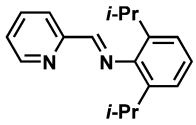
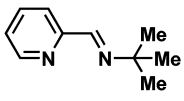
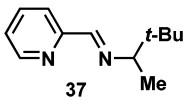
Table 5. Evaluation of Iminopyridine Ligands for 1,4-Hydrosilylation of Myrcene



Ligand	Conversion (%)	Regioselectivity 35:36	Ligand	Conversion (%)	Regioselectivity 35:36
	100	81:19	 11	100	85:15
	100	77:23		100	68:32
	100	80:20		32	45:55
	100	90:10	 37	100	95:5

yields of predominantly (95:5) linear hydrosilylation product (Table 5). As with hydrovinylation and hydroboration, no 1,2-addition product was observed and only the (*E*) isomer of the olefin was observed.

The hydrosilylation is compatible with a variety of polar functional groups, including esters, ethers, epoxides, and amines (Table 6). Moreover, a variety of silanes could be incorporated, including trialkylsilanes, trialkoxysilanes, and mixed alkyl-(dialkoxy)silanes. It was found that ligand **11**, utilized above for diene hydrovinylation, gave the best linear/branched selectivity when triethylsilane was used as the hydrosilane component (entry 2). The functional group compatibility of this method, combined with the ready availability of dienes and hydrosilane coupling partners, should make this chemistry a valuable addition to the methods available for accessing useful allylsilane building blocks.

A proposed mechanism for the 1,4-hydrosilylation reaction is shown in Figure 9. Mechanistic studies were conducted with the isolable Fe(0) complex **5** because the reaction mixtures were homogeneous and kinetic analysis could be readily conducted by NMR or GC. Initial dissociation of pyridine and displacement of one equivalent of iminopyridine by diene gives complex **13**. Oxidative addition of hydrosilane gives Fe(II) silyl hydride complex **38**. Migratory insertion, $\pi-\sigma$ rearrangement, and reductive elimination generates the hydrosilylated product with full control of double bond geometry.

The mechanism in Figure 9 shows migratory insertion of the 1,4-diene into the Fe−Si bond to give (π-allyl)iron hydride complex **39**. The reaction could conceivably also proceed through an alternative pathway in which migratory insertion occurs into the Fe−H bond to give a (π-allyl)iron silyl complex. However, previous studies have shown that for iron-catalyzed hydrosilylation with $Cp^*(CO)_2Fe-SiMe_3$, ethylene insertion into the Fe−Si bond is facile and reversible, and C−H reductive elimination is preferred over C−Si reductive elimination at iron centers.[30] Therefore, we propose C−Si migratory insertion followed by C−H reductive elimination for the 1,4-hydrosilylation reaction.

Kinetic studies using precatalyst **5** showed that the addition of exogenous pyridine or iminopyridine slowed the reaction rate considerably, consistent with the requirement for dissociation of pyridine and 1 equiv of iminopyridine prior to the onset of catalysis. We found that use of Fe(II) precatalyst **4** and 1 equiv of ligand led to faster reaction rates than when **5** was used, and hence, we employed those conditions for synthetic reactions. We were unable to isolate any iron complex generated from **4** and one equivalent of ligand, presumably due to the lability of such coordinatively unsaturated species. Nevertheless, kinetic data support the 1:1 Fe:iminopyridine ratio in the active catalyst.

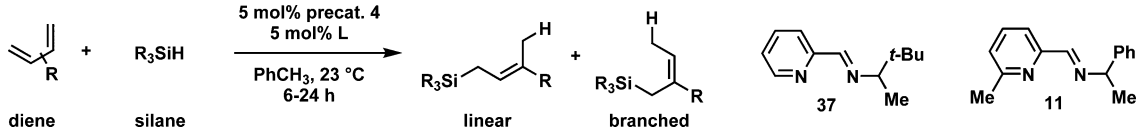
4.4. Polymerization

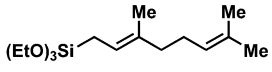
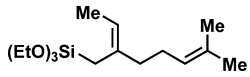
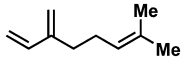
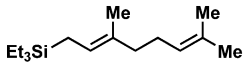
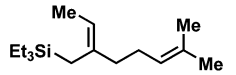
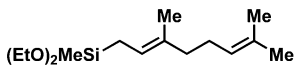
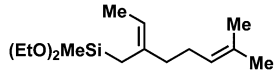
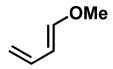
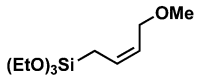
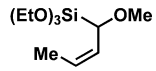
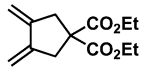
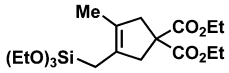
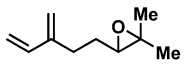
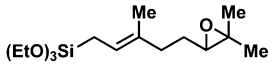
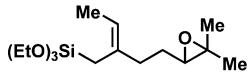
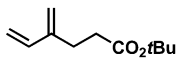
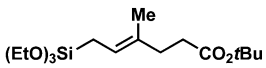
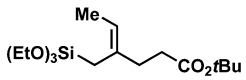
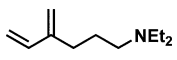
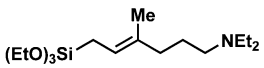
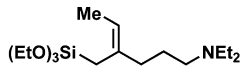
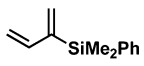
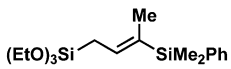
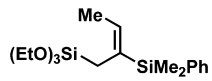
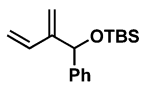
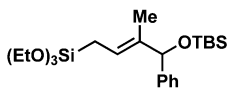
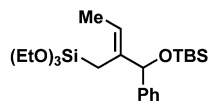
Rubber is perhaps the most-familiar natural polymer. Found in nature in the sap of tropical trees such as *Hevea braziliensis* or *Gutta percha*, rubber is composed largely of polymerized isoprene. Natural rubber is produced in quantities of over 10 million tons per year, and artificial polyisoprene ("synthetic rubber") is produced in even greater quantities.[31] Polymerization of isoprene can potentially result in several different microstructures (Figure 10). The double bond resulting from 1,4-insertion can be either *cis* or *trans*, and 1,4-insertion must compete with 1,2- or 3,4-insertion pathways. Natural rubber derived from *Hevea braziliensis* contains >99.9% *cis*-1,4-polyisoprene, while *Gutta-percha* rubber is >99.9% *trans*-1,4-polyisoprene. Synthetically produced polyisoprene is typically a mixture of *cis*- and *trans*-1,4-polyisoprene, often with significant quantities of 1,2- or 3,4-insertion observed. This lack of stereocontrol in synthetic polyisoprene means that natural rubber has high-performance mechanical properties superior to the synthetic version.

Our success in iron-catalyzed 1,4-hydrofunctionalization of 1,3-dienes, combined with the high degree of stereocontrol observed in the resulting olefins (>99:1 in all cases) led us to consider the possibility of using iron as a catalyst for the polymerization of isoprene.[5] Iron-catalyzed polymerization is well-known for ethylene,[32] but polymerization of 1,3-dienes is considerably less explored, and selective

DOI: 10.1021/acs.accounts.5b00050
Acc. Chem. Res. 2015, 48, 2330−2343

Table 6. Scope of Iron-Catalyzed 1,4-Hydrosilylation of 1,3-Dienes



Entry	Diene	Linear Product	Branched Product	L	Yield (%)[a]	Linear:Branched
1		 35	 36	37	91	95:5
2				11	76	95:5
3				37	91	95:5
4				37	89	>99:1
5			--	37	66[b]	--
6				37	86	97:3
7				37	76[c]	94:6
8				37	83[c]	94:6
9				37	89[c]	99:1
10				37	80[b]	99:1

[a]Isolated yield, average of two runs. [b]15 mol % precatalyst **4** and 15 mol % ligand **37**. [c]10 mol % precatalyst **4** and 10 mol % ligand **37**.

control over polymer microstructure has proven difficult to achieve.[33]

Building on our experience with other diene functionalization reactions, we chose iminopyridines as appropriate ligands for diene polymerization. Bisiminopyridines have been used as ligands for iron-catalyzed olefin polymerization;[32] iminopyridines should retain the redox-active behavior of bisiminopyridines while leaving an additional coordination site open to facilitate binding of dienes rather than olefins. We identified ferrous complexes **41** and **42** as suitable catalysts (Table 7). In combination with an alkylating reagent (trialkylaluminum) and a dealkylating reagent ($Ph_3C^+B(C_6F_5)_4^-$), these complexes catalyzed efficient polymerization of isoprene in an aprotic solvent, leading to polymer molar masses $>10^5$ g/mol and with >99:1 selectivity for double bond geometry (*cis* for complex **42**, *trans* for complex **41**, Table 7). Selectivity for 1,4-addition over 3,4-addition was modest, ranging from 2:1 to 12:1. The side chain olefins resulting from 3,4-addition (present in 7−15% yield for the polymers generated in this study) can increase the toughness of the polymer after selective cross-linking, a potentially desirable property for some applications.

In addition to isoprene, complexes **41** and **42** also proved to be effective for polymerization of myrcene and farnesene. The *cis*/*trans* and 1,4/3,4 ratios are similar to those seen for isoprene polymerization for both **41** and **42**. The polymerization is selective for the β isomers of myrcene and farnesene; the α isomers could be removed as monomers after polymerization. The materials obtained from iron-catalyzed polymerization of myrcene and farnesene provide access to new elastomers with regular incorporation of pendant olefins.

A proposed mechanism for the iron-catalyzed polymerization of isoprene is given in Figure 11. Initial reaction of iron dichloride complex **41** with 3 equiv of AlR_3 and 1 equiv of $Ph_3C^+B(C_6F_5)_4^-$ gives mixed iron−aluminum species **43**. Reversible dissociation of AlR_3 gives coordinatively unsaturated iron alkyl complex **44**. Coordination of isoprene in either the s-*cis* or s-*trans* configurations, followed by migratory insertion, gives either *cis*- or *trans*-olefin incorporation into the growing polymer chain. Further coordination of monomer,

DOI: 10.1021/acs.accounts.5b00050
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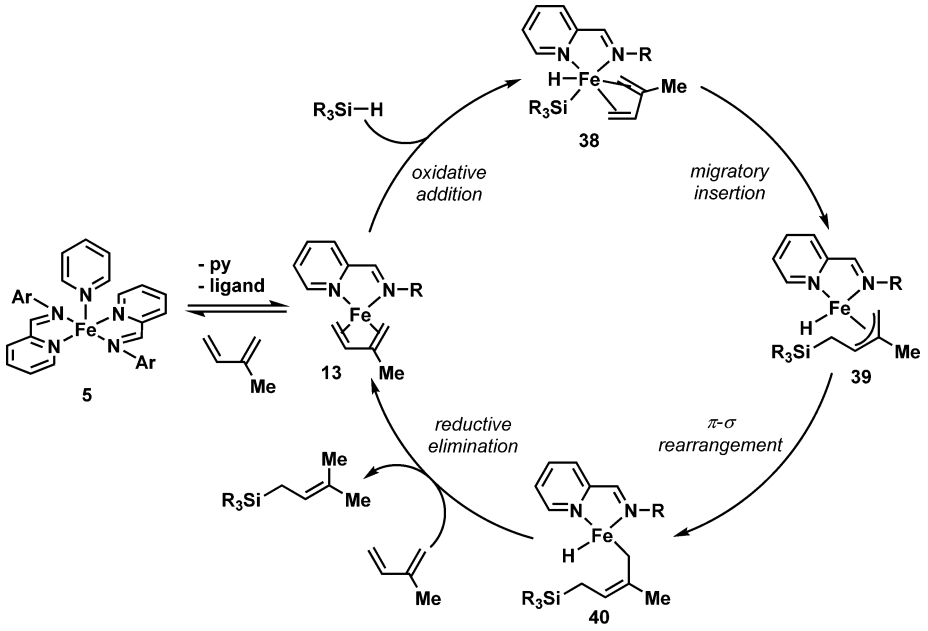


Figure 9. Proposed mechanism for iron-catalyzed 1,4-hydrosilylation of 1,3-dienes, beginning with precatalyst **5**.

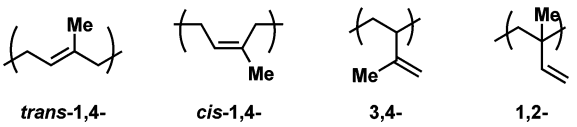
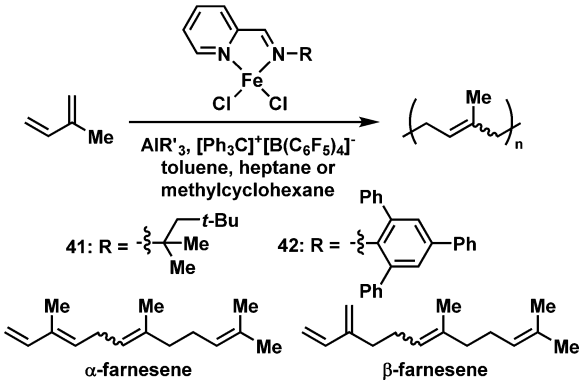


Figure 10. Possible microstructures resulting from the polymerization of isoprene.

and migratory insertion elongates the chain. The factors responsible for control over *cis*- vs *trans*-selectivity are not clear at this point, especially given the similarity of the ligands involved. The high *cis*/*trans* selectivity of this polymerization and the ability to access new elastomers from polymerization of myrcene and farnesene make this reaction manifold

Table 7. Stereoselective Polymerization of Isoprene, Myrcene, and Farnesene with Iminopyridine-Ligated Iron



conditions	[Fe]/[Al]/[Ph_3C^+][dience]	polymer M_w/D[a]j	selectivity 1,4/3,4 *trans*/*cis*[b]	yield (%)[c]
41/Al*i*Bu_3, 2 h, 23 °C	1:3:1:1000	125 000/2.0	12:1, >99:1	99
41/Al*i*Bu_3, 5 h, 23 °C	1:3:1:5000	650 000/3.9	12:1, >99:1	>99
42/$AlEt_3$, 1 h, 23 °C	1:3:1:1000	150 000/1.9	2:1, 1:>99	>99
42/$AlEt_3$, 4 h, −78 °C	1:3:1:1000	140 000/1.7	6:1, 1:>99	>99
42/$AlEt_3$, 4 h, −78 °C	1:3:1:5000	800 000/3.5	5:1, 1:>99	>99
myrcene				
41/Al*i*Bu_3, 12 h, 23 °C	1:5:1:2000	250 000/2.1	12:1, >20:1	91
42/$AlEt_3$, 12 h, 23 °C	1:5:1:2000	230 000/2.2	4:1, 1:>20	87
farnesene				
41/Al*i*Bu_3, 24 h, 23 °C	1:30[d]:1:2000	110 000/1.5	11:1, >20:1	90[e]
42/$AlEt_3$, 24 h, 23 °C	1:30[d]:1:2000	100 000/1.4	3:1, 1:>20	84[e]

[a]Determined by size-exclusion chromatographic analysis in THF using a refractive index detector and a UV detector (λ = 212 nm). [b]Determined by ^1H and ^{13}C NMR spectroscopy. [c]Determined gravimetrically. [d]More trialkylaluminum reagent was necessary to act as drying agent in addition to acting as alkylation agent. [e]Yields based on the β-farnesene content (both 6*Z* and 6*E* isomers) of commercially available farnesene (mixture of α and β isomers).

DOI: 10.1021/acs.accounts.5b00050
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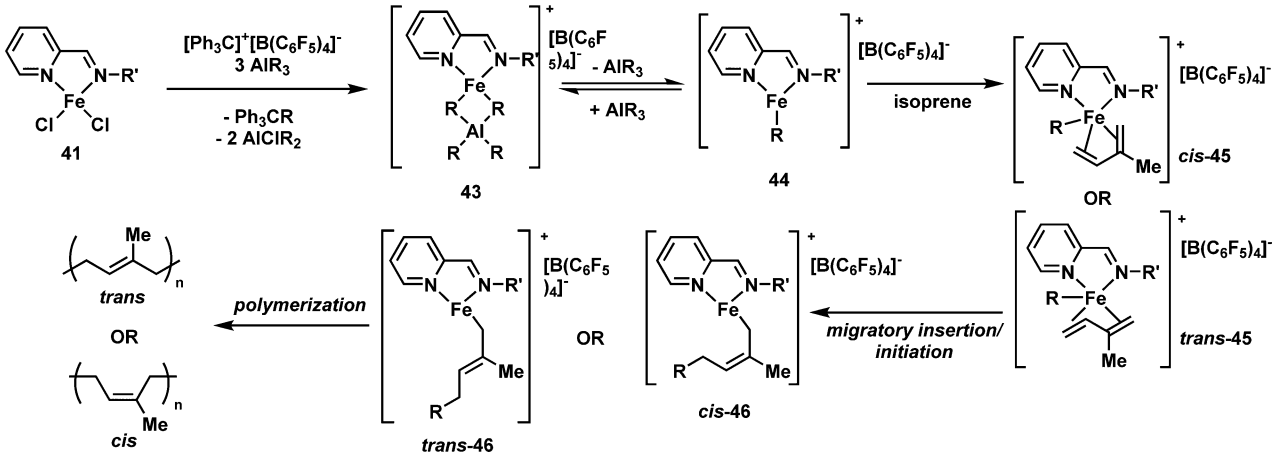

Figure 11. Potential mechanism for the stereoselective iron-catalyzed polymerization of isoprene.

an intriguing platform for the development of new polymer chemistry.

5. CONCLUSION

The promise of low-valent iron catalysis is high, but logical design is difficult due to iron's rich redox behavior and the lack of sufficient well-defined complexes. We have contributed a few iron-catalyzed reactions of 1,3-dienes, to provide useful products. Beyond the synthetic utility, our work may be relevant to increase the understanding of low-valent iron catalysis because we were able to isolate, characterize, and evaluate a few well-defined, catalytically active iron complexes. In our opinion, the development of well-defined, isolable, and characterizable, but catalytically reactive iron complexes will help to increase the utility, understanding, and ability to rationally design the field of iron catalysis.

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Notes

The authors declare no competing financial interest.

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