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A Strategy for the Synthesis of Well-Defined Iron Catalysts and Application to Regioselective Diene Hydrosilylation

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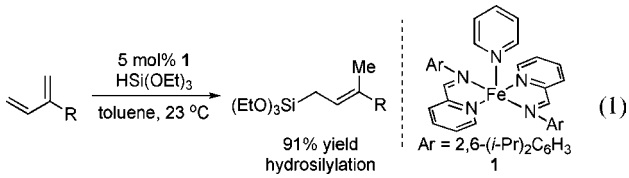
Abstract: We report the development of a well-defined Fe catalyst and its application to the regio- and stereoselective 1,4-hydrosilylation of 1,3-dienes. To the best of our knowledge, this is the first example of accessing a characterized low-valent Fe catalyst by controlled reductive elimination from a readily accessible Fe precatalyst.

Iron catalysis for organic synthesis has experienced intermittent development since work by Kharasch in 1941.[1,2] Many Fe-catalyzed reactions use simple Fe compounds such as $FeCl_3$ and $Fe(CO)_5$,[2] which is advantageous for simplicity but rarely offers the opportunity to rationally improve reactivity or selectivity, because the identities of the active catalysts are typically unknown, ill-defined, or cannot be rationally altered. Purified and well-characterized low-valent Fe catalysts are rare and typically challenging to prepare but, when available, can be used for rational reaction improvement.[3,4] Herein we report the development of a well-defined Fe catalyst and its application to regio- and stereoselective hydrosilylation of 1,3-dienes (eq 1). This report describes the first example of accessing a characterized low-valent Fe catalyst by controlled reductive elimination from a readily accessible Fe precatalyst. Our strategy allowed us to quickly and reliably identify suitable ligands to control regio- and stereoselectivity for the hydrosilylation reaction at previously unreported levels.

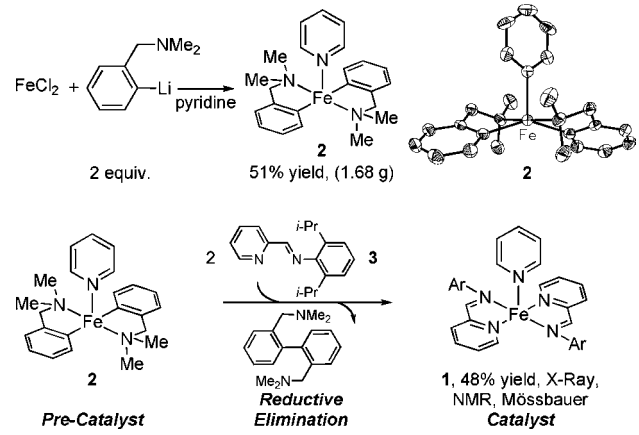


(1)

Catalysis development with low-valent late transition metals benefits from the availability of useful precatalysts such as Pd_2dba_3 and $Ni(cod)_2$; no analogous complex has been available for Fe. $Fe(0)(CO)_n$ and $Fe(0)(cyclooctatetraene)_2$ complexes are accessible; however, the increasing difficulty to displace all CO or COT ligands only allows access to CO- or COT-containing Fe catalysts.[5] Previously, we used magnesium metal to reduce Fe(II) complexes to afford ill-defined catalysts.[6] Reduction of Fe(II) complexes is an established method to access low-valent Fe complexes but requires optimization of reaction conditions for every individual complex.[7] The strategy reported here demonstrates access to low-valent Fe catalysts by controlled reductive elimination from a single Fe(II) bis(aryl) precatalyst upon exogenous ligand coordination. Well-defined two-electron reductive elimination reactions, well-known for other late transition metals such as Pd or Ni, are uncommon for Fe.

When our evaluation of known bis(aryl) Fe complexes[8] for reductive elimination resulted in complexes that either were unstable or did not afford low-valent Fe complexes, we designed the new bis(aryl) Fe(II) complex **2**, readily prepared from $FeCl_2$, pyridine, *n*-BuLi, and *N*,*N*-dimethylbenzylamine (Scheme 1).

Scheme 1. Synthesis of Well-Defined Fe Catalyst **1**



Complex **2** is sufficiently stable for isolation, likely due to the chelating amino aryl ligands that position both carbon-based ligands mutually pseudo-*trans* and therefore prevent reductive elimination. Upon coordination of an exogenous ligand, however, ligand rearrangement can take place, possibly by nitrogen dissociation, and reductive elimination can occur. Addition of 2 equiv of iminopyridine ligand **3** to **2** produced the bis(iminopyridine)Fe pyridine complex **1**, which could be purified and characterized.

For catalysis, we selected redox-active ligands on Fe,[9] such as the iminopyridine **3**, to potentially lower activation barriers due to metal−ligand redox chemistry. Redox-active ligands may function as electron reservoirs and compensate the electronic demand of the Fe at different stages of the catalytic cycle, similar to metal−metal cooperation in bimetallic catalysis.[10] Evidence for metal−ligand redox participation in **1** was obtained spectroscopically (see Supporting Information) and suggests that Fe complex **1** should be more correctly represented as Fe(II), coordinated by two radical anion ligands, as previously observed for related complexes.[9]

Complex **1** is a precatalyst for the 1,4-hydrosilylation of 1,3-dienes (eq 1). A proposed catalytic cycle for the Fe-catalyzed hydrosilylation is shown in Scheme 2. In contrast to our previous work with ill-defined Fe species in heterogeneous reactions,[6] reaction with **1** is homogeneous, is well behaved, and can be followed kinetically. From the kinetic profiles shown in the insert of Scheme 2, we identified that addition of exogenous pyridine and

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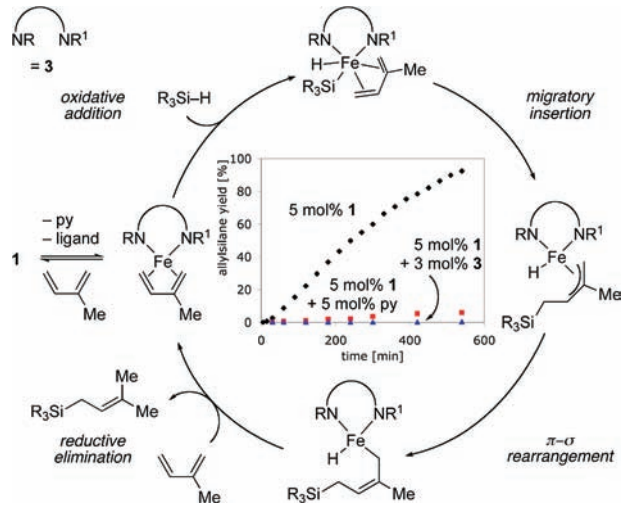
Scheme 2. Proposed Fe-Catalyzed Hydrosilylation Mechanism[a]



[a] Graph shows kinetic profiles for hydrosilylation catalyzed by **1**, with no added ligand (top), with added pyridine (middle), and with added **3** (bottom).

iminopyridine ligand **3** retarded the rate of hydrosilylation. Addition of only 1 equiv of iminopyridine ligand to **2** generated a catalyst more active than when 2 equiv of iminopyridine were added. While no complex could be isolated and characterized, presumably due to instability of a catalytically active, coordinatively unsaturated Fe center, hydrosilylation efficiency increased. This procedure had the added advantage that **2** could be used directly, without conversion to and purification of **1**.

Allylsilane synthesis by hydrosilylation can avoid allylmetal addition to chlorosilanes, which is not compatible with several electrophilic functional groups. Several regioselective diene hydrosilylation reactions catalyzed by various transition metals have been reported.[11] None, however, has been shown to generally afford the allylsilane products in as high regioselectivity as we report here, and often other constitutional isomers are observed as major products.

Availability of the Fe precatalyst **2** allowed us to readily evaluate different ligands to control regioselectivity. Catalyst **1** affords allylsilanes as a 1:2 mixture of constitutional isomers (linear/branched, see Supporting Information), but we identified iminopyridine ligands **4** and **5** that controlled regioselectivity to afford the linear product predominantly, typically in a ratio of 94:6 or greater (Table 1). Hydrosilylation proceeded for 1-, 2-, and 2,3-substituted dienes. Double bond geometry was controlled in all cases with >99:1 selectivity, possibly a consequence of the stereospecific mechanism suggested in Scheme 2, without double bond isomerization. Several functional groups, including epoxides, esters, and amines, are tolerated, and different silanes can be used (**7**, **8**, **9**).

In conclusion, we report the synthesis and use of a well-defined Fe complex as a precatalyst for 1,4-hydrosilylation of 1,3-dienes to afford allylsilanes in high selectivities that have not been reported with other methods. Reductive elimination from **2** can generate several Fe catalysts that control the regio- and stereoselectivity of hydrosilylation. Access to a low-valent Fe precatalyst can support the development of Fe catalysis.

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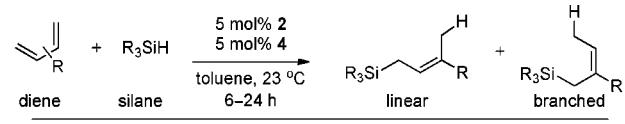
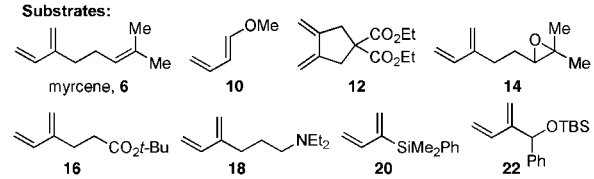
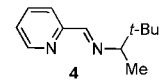
Table 1. Regio- and Stereoselective Fe-Catalyzed Hydrosilylation

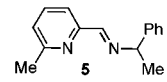


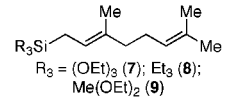
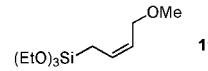
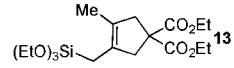
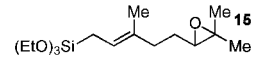
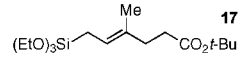
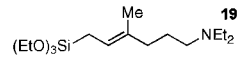
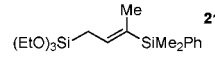
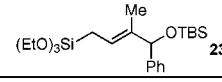
Substrates:



Ligands:





Diene	Linear Product	Linear: Branched	*E*:*Z*	Yield[a]
6	 R_3 = $(OEt)_3$ (**7**); Et_3 (**8**); $Me(OEt)_2$ (**9**)	95:5 (**7**) 95:5 (**8**) 93:7 (**9**)	> 99:1 > 99:1 > 99:1	91% 76%[b] 91%
10	 **11**	> 99:1	< 1:99	89%
12	 **13**	--	> 99:1	66%[c]
14	 **15**	97:3	> 99:1	86%
16	 **17**	94:6	> 99:1	76%[d]
18	 **19**	94:6	> 99:1	83%[d]
20	 **21**	99:1	> 99:1	89%[d]
22	 **23**	99:1	> 99:1	80%[c]

[a] Isolated yield; average of two runs. [b] 5 mol % ligand **5**. [c] 15 mol % **2** and 15 mol % **4**. [d] 10 mol % **2** and 10 mol % **4**.

Supporting Information Available: Detailed experimental procedures and spectroscopic data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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