Markovnikov Hydrosilylation

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Base–Metal-Catalyzed Regiodivergent Alkene Hydrosilylations

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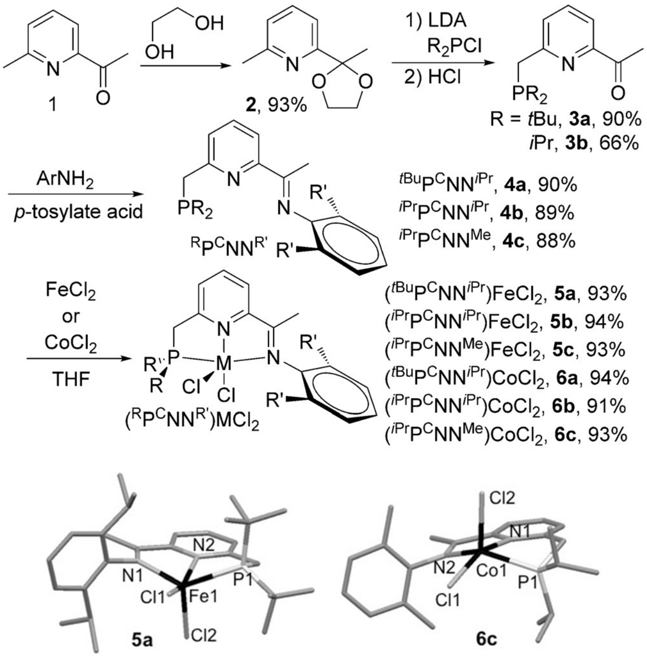
Abstract: *A complementary set of base metal catalysts has been developed for regiodivergent alkene hydrosilylations: iron complexes of phosphine-iminopyridine are selective for anti-Markovnikov hydrosilylations (linear/branched up to >99:1), while the cobalt complexes bearing the same type of ligands provide an unprecedented high level of Markovnikov selectivity (branched/linear up to >99:1). Both systems exhibit high efficiency and wide functional group tolerance.*

Alkene hydrosilylation is one of the largest volume reactions conducted with homogeneous catalysts.[1] Platinum-based Speier and Karstedt's complexes are the most widely used hydrosilylation catalysts because of their high activities and ease of handling.[2] However, over the last decade the low abundance, high cost, and environmental concerns associated with precious metals have spurred extensive study toward developing earth-abundant base metal alternatives.[3] To date, a few iron,[4] cobalt,[4j,5] and nickel[6] catalysts have been developed for *anti*-Markovnikov alkene hydrosilylations.

While *anti*-Markovnikov alkene hydrosilylations are well-established, reactions demonstrating Markovnikov selectivity are rare. Several lanthanum metal catalysts are known for Markovnikov hydrosilylation of activated alkenes, such as styrene and acrylonitrile.[7] Markovnikov hydrosilylation of unactivated alkenes using nickel[8] and palladium[9] catalysts have been reported, but the existing systems suffer from moderate to low regioselectivities and limited substrate scope. Thus, a general method for selective Markovnikov alkene hydrosilylation requires development. Driven by our interest in developing base metal catalysts for alkene functionalizations,[4e,10] herein we report the synthesis of iron and cobalt complexes of phosphine-iminopyridine (P^{C}NN) ligands. The iron catalysts described are highly selective for *anti*-Markovnikov hydrosilylations, whereas the corresponding cobalt catalysts offer the opposite regioselectivity.

During the course of our earlier studies on the phosphinite-iminopyridine (P^{O}NN) iron catalysts for chemoselective *anti*-Markovnikov alkene hydrosilylations,[4e] we found that the P^{O}NN ligands are prone to degradation by O−P bond cleavage. To this end, we sought to prepare more robust phosphine-iminopyridine (P^{C}NN) ligands by replacing the O-linker connecting the phosphorus atom and the pyridyl backbone with a methene (CH_2) unit.[11] The synthesis of the P^{C}NN ligands is outlined in Scheme 1.[12] The acetyl group of 1-(6-methylpyridin-2-yl)ethanone (**1**) was first protected with ethylene glycol. Deprotonation of the Me group at the 2-pyridyl position in **2** with LDA, followed by addition of $t\mathrm{Bu}_2\mathrm{PCl}$ or $i\mathrm{Pr}_2\mathrm{PCl}$ and subsequent deprotection of the acetyl group with HCl, generated phosphine-acetylpyridines (**3a**, **3b**). Condensations of **3a** and **3b** with arylamines bearing *i*Pr or Me substituents at the 2,6-aryl positions gave the P^{C}NN ligands **4a**–**4c** in 88–90 % yield. The Fe^{II} and Co^{II} dichloride complexes **5a**–**c** and **6a**–**c** were formed in high yields by reaction of **4a**–**c** with $FeCl_2$ or $CoCl_2$. Single-crystal X-ray diffraction studies of complexes **5a** and **6c** revealed distorted square pyramidal geometries around the metal centers (Scheme 1).[13]



Scheme 1. Synthesis of phosphine-iminopyridine (P^{C}NN) ligands and iron and cobalt complexes, and the ORTEP structures for **5a** and **6c**.

Initial studies of the catalytic activities of these new iron and cobalt complexes focused on the hydrosilylation of a simple aliphatic alkene, 1-octene, with $PhSiH_3$. The results are summarized in Table 1. In situ activation of iron and cobalt dihalides with $NaBHEt_3$ has been reported for catalytic alkene hydrofunctionalizations.[4e,10c,14] Using $NaBHEt_3$ (2 mol %) as the activator, the most sterically hindered iron complex (^{tBu}P^{C}NN^{iPr})$FeCl_2$ (**5a**; 1 mol %) is active for *anti*-Markovnikov hydrosilylation. The reaction of 1-octene with $PhSiH_3$ in THF at 25 °C formed the linear product **8a** in 98 % yield with excellent regioselectivity (entry 1). Reducing the

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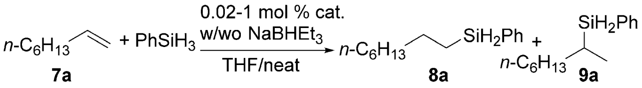
Table 1: Iron- and cobalt-catalyzed 1-octene hydrosilylation with $PhSiH_3$.[a]



Entry	Cat. [mol %]	$NaBHEt_3$ [mol %]	T [°C]	*t* [h]	Yield [%] **8a**	Yield [%] **9a**
1	**5a** (1)	2	25	3	98	1
2[b]	**5b** (1)	2	25	3	72	1
3[c]	**5c** (1)	2	25	3	50	6
4	**5a** (1)	0	60	3	0	0
5	**5a** (0.1)	0.2	25	24	96	1
6[d,e]	**5a** (0.1)	0.2	25	24	93	<1
7[d,f]	**5a** (0.02)	0.08	25	24	79	<1
8	**6a** (1)	2	25	3	3	23
9	**6b** (1)	2	25	3	6	49
10	**6c** (1)	2	25	3	2	98
11	**6c** (1)	0	25	3	<1	62
12	**6c** (1)	0	25	12	<1	98
13[d,e]	**6c** (0.05)	0	60	6	<1	>99
14[g]	$CoCl_2$ (0.35)/^{Mes}PDI (1.1)	0	60	6	4	5
15[d,e]	**6c** (0.05)/**4c** (0.5)	0	60	6	<1	78
16	$CoCl_2$/**4c** (1)	0	60	24	<1	79

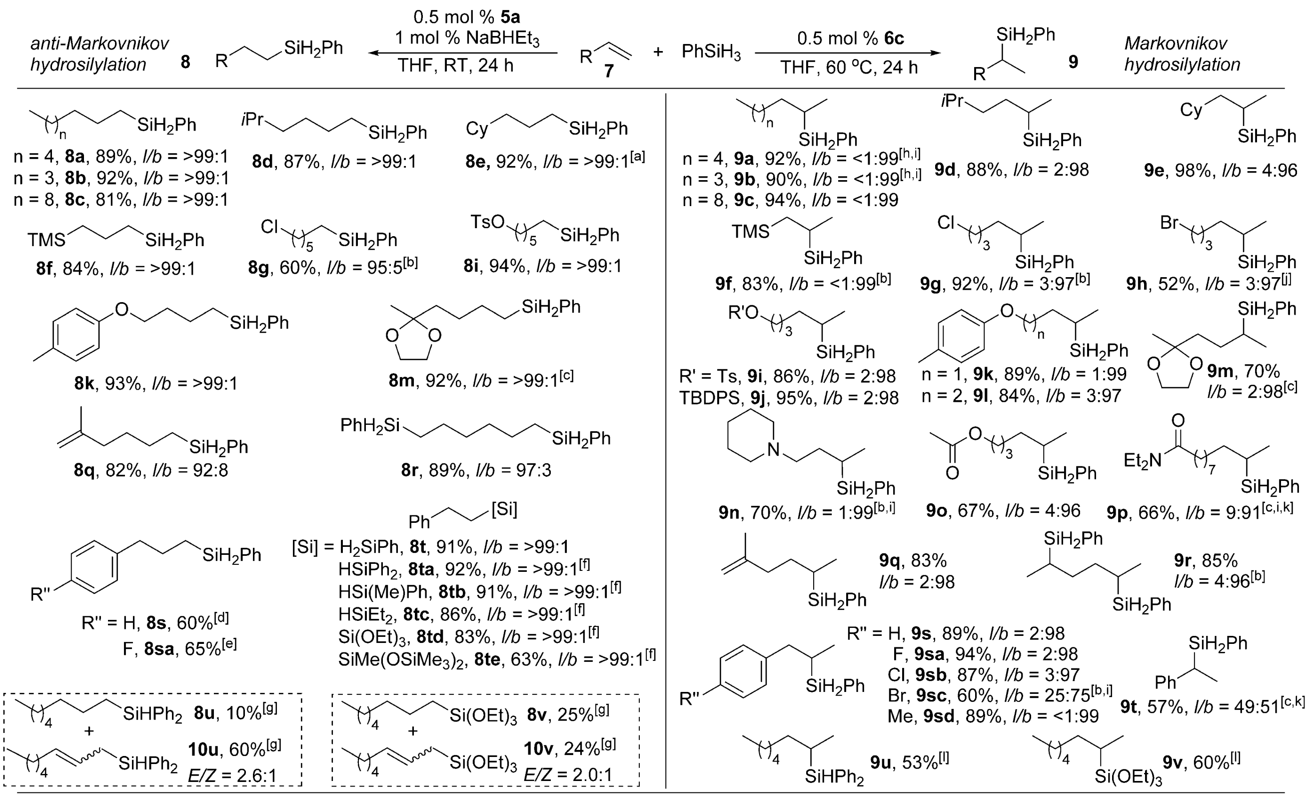
[a] Conditions: **7a** (0.6 mmol), $PhSiH_3$ (0.6 mmol) in THF (1 mL). The yields were determined by GC with mesitylene as an internal standard. [b] 2% (*E*)-allylsilane was detected. [c] 7% (*E*)-allylsilane was detected. [d] In neat conditions. [e] 3 mmol scale. [f] 10 mmol scale. [g] **7a** (1.6 mmol), $PhSiH_3$ (1.6 mmol) in THF (1 mL).

steric hindrance of the P^{C}NN ligands resulted in inferior activity and selectivity (entries 2, 3). A control experiment in the absence of $NaBHEt_3$ revealed that the activator is necessary to achieve catalytic conversion with the iron complex **5a** (entry 4). The reactions using 0.1 mol % **5a**, with or without solvent, gave **8a** in nearly quantitative yield after 24 h (entries 5, 6). In the presence of 0.02 mol % of **5a** (51 ppm iron metal), the reaction in neat conditions gave **8a** in 79% yield (TON = 3950, entry 7). The results indicate that complex (^{tBu}P^{C}NN^{iPr})$FeCl_2$ **5a** is significantly more active than the precatalyst (^{tBu}P^{O}NN^{iPr})$FeCl_2$ bearing an O-linker; the hydrosilylation reaction using the latter required 1 mol % of catalyst to attain good conversion.[4e] The selective formation of the *anti*-Markovnikov product is consistent with earlier reports using iron catalyst systems.[4]

Remarkably, regioselectivity could be reversed when cobalt analogues were employed. All cobalt complexes **6a–c** gave the Markovnikov product **9a** as the major product (entries 8–10). In particular, the least crowded precatalyst (^{iPr}P^{C}NN^{Me})$CoCl_2$ **6c** was very effective for Markovnikov hydrosilylation. The reaction in the presence of 1 mol % of **6c** and 2 mol % of $NaBHEt_3$ at 25 °C formed **9a** in 98% yield after 3 h (entry 10). Surprisingly, control experiments with **6c** in the absence of $NaBHEt_3$, afforded the branched product **9a** in 62 and 98% yield after 3 and 12 h, respectively (entries 11, 12). These runs gave regioselectivity similar to that observed in the reaction using a combination of **6c** and $NaBHEt_3$, albeit with a relatively slow reaction rate (entries 11 vs. 10). At elevated temperature (60 °C), in the presence of 1100 ppm of **6c** (0.05 mol %, 130 ppm cobalt metal), the reaction in neat 1-octene and $PhSiH_3$ gave **9a** in quantitative yield after 6 h (TON = 2000, entry 13). Thus, an additional additive is not required for activation of the catalyst in the cobalt-catalyzed hydrosilylation reactions.[15] In a recent patent, Boyer et al. reported that a combination of bis(imino)pyridine $(2,4,6\text{-}Me_3C_6H_2N{=}CMe)_2C_5H_3N$ (^{Mes}PDI; 3 equiv) and $CoCl_2$ catalyzes Markovnikov alkene hydrosilylation with $PhSiH_3$. It was proposed that ^{Mes}PDI acts as a promoter for catalyst activation.[16] However, using the conditions described in the patent, the reaction gave only 5% of **9a** and 4% of **8a** (entry 14) in the presence of $CoCl_2$ (0.35 mol %) and ^{Mes}PDI (1.1 mol %). To explore the role of our ^{iPr}P^{C}NN^{Me} ligand **4c** in the hydrosilylation process, an experiment in the presence of additional ligand was conducted. The reaction with **6c** (0.05 mol %) and **4c** (10 equiv relative to **6c**) was less effective than the reaction without **4c**, implying that there is an inhibitory effect of the additional ligand on the catalysis (entries 15 vs. 13). Finally, a simple combination of **4c** and $CoCl_2$ (1 mol % each) was effective for Markovnikov hydrosilylation (entry 16), albeit with reduced catalytic efficiency in comparison with the reaction employing **6c**.

Utilizing the base metal catalysts, we examined the substrate scope with respect to alkenes for regiodivergent hydrosilylations (Scheme 2). The iron catalyst mediates hydrosilylation of a diverse array of alkenes with $PhSiH_3$, furnishing linear products in high isolated yield with excellent regioselectivities. Most reactions employed 0.5 mol % of **5a** and 1 mol % $NaBHEt_3$. Functional groups including chloride (**8g**), protected alcohol (**8i**), ether (**8k**), acetal (**8m**), and *gem*-disubstituted olefin (**8q**) were tolerated. Hydrosilylation of 1,5-hexadiene with 2 equiv of $PhSiH_3$ produced 1,6-disilylhexane (**8r**) in high yield. Allylarenes gave the desired products in moderate yields (**8s**, 60%; **8sa**, 65%) with the formation of a small amount of dehydrogenative silylation products, (*E*)-allylsilanes (ca. 20%). Styrene was hydrosilylated in high yield (**8t**). Furthermore, using the least crowded complex **5c** (1 mol %) as the precatalyst, hydrosilylations of styrene with various secondary and tertiary silanes in neat conditions occurred smoothly (**8ta–8te**). Notably, reaction of 1-octene with $(EtO)_3SiH$[17] or Ph_2SiH_2 gave a mixture of the hydrosilylation (**8u** or **8v**) and the dehydrogenative silylation products (allylsilane, **10u** or **10v**).[18]

A wide variety of functionalized alkenes were subjected to selective cobalt-catalyzed Markovnikov hydrosilylation (**9f–q**). Most reactions were performed at 60 °C with very low catalyst loadings (0.05–0.5 mol % **6c**). Reactions of substrates bearing bromide (**9h**, **9sc**), ester (**9o**), amide (**9p**), and 1,1-disubstituted olefin (**9q**) functional groups proceeded in a chemo- and regioselective manner. Markovnikov additions to the two terminal double bonds in 1,5-hexadiene formed the branched disilyl product (**9r**). Allylbenzene and its derivatives, which bear both electron-donating and withdrawing groups, were efficiently hydrosilylated (**9s–9sd**). An exception was the reaction of styrene (**9t**), which gave the branched and linear products in an approximately 1:1 ratio. Markovnikov hydrosilylations with secondary and tertiary silanes are more difficult than that with primary silane. The catalyst generated from **6b** and $NaBHEt_3$ was identified as the optimal system for Markovnikov hydro-



Scheme 2. Iron-catalyzed *anti*-Markovnikov and cobalt-catalyzed Markovnikov hydrosilylation of various alkenes. General conditions: **7** (1.2 mmol), $PhSiH_3$ (1.2 mmol) in THF (0.5–1 mL). Yield of isolated products, unless noted otherwise. Product ratios were determined by ^1H NMR spectroscopy. [a] With cat. (0.1 mol %). [b] With cat. (1 mol %). [c] With cat. (2 mol %). [d] 25 % (*E*)-allylsilane detected. [e] 23 % (*E*)-allylsilane detected. [f] With **5c** (1 mol %) and $NaBHEt_3$ (2 mol %), 1.8 mmol scale, in neat conditions. [g] With **5c** (2 mol %) and $NaBHEt_3$ (4 mol %), yield determined by NMR. [h] With **6c** (0.05 mol %). [i] Neat conditions. [j] With **6c** (2 mol %) and $NaBHEt_3$ (4 mol %). [k] Yield determined by NMR. [l] With **6b** (1 mol %) and $NaBHEt_3$ (2 mol %) in toluene (1 mL), yield determined by NMR. **10u** (18 %) and **10v** (15 %) detected.

silylations of 1-octene with Ph_2SiH_2 (**9u**, 53 %) and $(EtO)_3SiH$ (**9v**, 60 %), though a small amount of allylsilanes (**10u**, 18 %; **10v**, 15 %) was also detected.

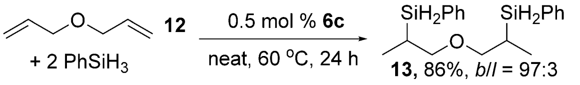
Potential applications of Markovnikov hydrosilylations include the conversion of readily available α-olefins into synthetically versatile secondary alcohols. Satisfactorily, treatment of various Markovnikov hydrosilylation products with $HBF_4{\cdot}Et_2O$, followed by oxidation with H_2O_2 under basic conditions, produced secondary alcohols **11** in useful yields (Supporting Information, Scheme S1).

For iron-catalyzed *anti*-Markovnikov alkene hydrosilylations, mechanistic proposals involving oxidative addition of silane, followed by olefin insertion and reductive elimination of linear alkylsilane, have previously been elucidated.[4b] Although additional experimental and theoretical studies are ongoing in an attempt to gain a full understanding of the mechanism of cobalt-catalyzed Markovnikov hydrosilylations, our preliminary experiments provide interesting results. A radical mechanism is not very likely, as the reactions of dienes **7q** and **7r** did not form any cyclized products (Scheme 2). More importantly, a diallylether (**12**) known to undergo rapid radical cyclization under conditions that allow the generation of a radical,[19] reacted with 2 equiv of $PhSiH_3$ to form a dual hydrosilylation product **13** in 86 % yield; no cyclized products were detected during the catalysis [Eq. (1)]. Lastly, addition of 10 mol % of TEMPO (10 equiv relative to cobalt) as a radical trap imposed no detrimental effects, although increasing the amount of TEMPO further to 100 mol %, led to complete inhibition of catalysis (see the Supporting Information).[20]

To provide insight into the catalyst activation mode and the nature of the cobalt intermediacy, stoichiometric and deuterium-labeling experiments were conducted. Treatment of $(^{iPr}P^{C}NN^{Me})CoCl_2$ (**6c**) with 1 equiv of $PhSiH_3$ in $[D_6]$benzene at 60 °C for 4 h formed a diamagnetic, putative Co^I monochloride $(^{iPr}P^{C}NN^{Me})CoCl$ (**14**) in 49 % yield, along with $PhSiH_2Cl$ in 27 % yield [Eq. (2)].[21] To conclusively determine the identity of the Co^I species, **14** was independently prepared using a procedure known for transforming Co^{II} dichloride into Co^I monochloride.[22] The reaction of **6c** with 1 equiv of LiMe in C_6D_6 at room temperature gave 54 % of the monochloride (**14**) and another diamagnetic species **15** in 10 % yield. Further addition of 1.5 equiv of LiMe to the mixture resulted in the disappearance of **14** and build-up of **15**, which was identified as $(^{iPr}P^{C}NN^{Me})CoMe$ (71 %; [Eq. (3)]). The NMR spectra of **15** display a diagnostic ^1H doublet at −0.62 ppm and a ^{13}C doublet at −58.1 ppm corresponding to the Co-*Me* moiety. Importantly, both Co^I complexes **14** and **15** were active for catalytic Markovnikov hydrosilylation [Eq. (4)]. The data indicates that the Co^{II}

dichloride can be reduced/activated with $PhSiH_3$ to form a catalytically active Co^I species.

The reaction of 1-dodecene-d_2 with $PhSiH_3$ in the presence of **6c** (1 mol %) gave **9c**-d_2 selectively [Eq. (5)]. Additionally, the reaction of 1-octene with the deuterated silane $PhSiD_3$ yielded **9a**-d_3 [Eq. (6)]. No deuterium incorporation into the α-carbon of the products was observed in either case. These results argue strongly against the formation of a cobalt deuteride or hydride intermediate in the catalytic cycle, because facile H/D exchange between Co-D and C_α-H would otherwise occur through reversible olefin insertion into the Co−D bond.[10d,18]



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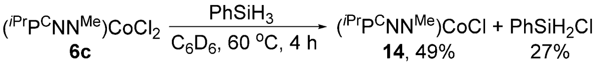
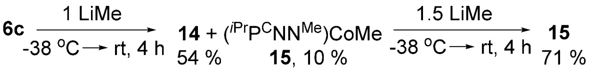
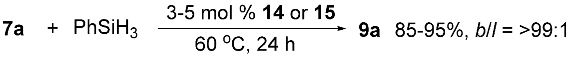


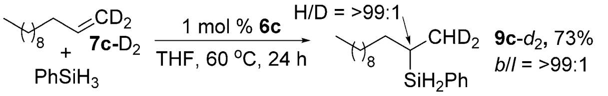
$$\underset{\mathbf{6c}}{(^{iPr}P^{C}NN^{Me})CoCl_2} \xrightarrow[C_6D_6,\ 60\ ^{\circ}C,\ 4\ h]{PhSiH_3} \underset{\mathbf{14},\ 49\%}{(^{iPr}P^{C}NN^{Me})CoCl} + \underset{27\%}{PhSiH_2Cl} \qquad (2)$$



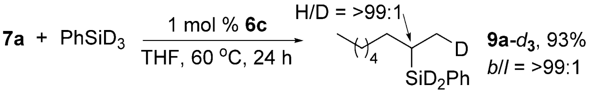
$$\mathbf{6c} \xrightarrow[-38\ ^{\circ}C \rightarrow \text{rt},\ 4\ h]{1\ LiMe} \underset{54\ \%}{\mathbf{14}} + \underset{\mathbf{15},\ 10\ \%}{(^{iPr}P^{C}NN^{Me})CoMe} \xrightarrow[-38\ ^{\circ}C \rightarrow \text{rt},\ 4\ h]{1.5\ LiMe} \underset{71\ \%}{\mathbf{15}} \qquad (3)$$



$$\mathbf{7a} + PhSiH_3 \xrightarrow[60\ ^{\circ}C,\ 24\ h]{3\text{-}5\ mol\ \%\ \mathbf{14}\ or\ \mathbf{15}} \mathbf{9a}\ \ 85\text{-}95\%,\ b/l = >99{:}1 \qquad (4)$$



(5)



(6)

On the basis of our preliminary results and reported precedent regarding cobalt-catalyzed alkene functionalization,[10d,18] we propose a silyl migration pathway involving a Co^I silyl intermediate (Supporting Information, Scheme S4).[23] For apolar olefins, 1,2-insertion of the C=C double bond into the Co−Si bond prevails (presumably because of steric effects),[24] furnishing the Markovnikov product. An alternative, but less likely pathway, involves 2,1-insertion of the olefin, which leads to formation of the *anti*-Markovnikov product. For vinylarenes, 2,1-insertion may compete with the 1,2-insertion pathway because there is marked electronic discrimination between the two olefinic carbon atoms. This proposal is consistent with the data obtained from the hydrosilylation of styrene (**9t**; Scheme 2).

In summary, we have prepared a series of iron and cobalt alkene hydrosilylation catalysts bearing phosphine-iminopyridine ligands. The regioselectivity of alkene hydrosilylations can be inverted from > 99:1 to < 1:99 by changing the metal center of the catalyst from iron to cobalt. The advantages these non-precious metal catalysts offer include, high efficiency, mild conditions, and broad functional group compatibility combined with a divergent and high level of regiochemistry.

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