Cobalt- and Iron-Catalyzed Regiodivergent Alkene Hydrosilylations

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Cobalt- and Iron-Catalyzed Regiodivergent Alkene Hydrosilylations

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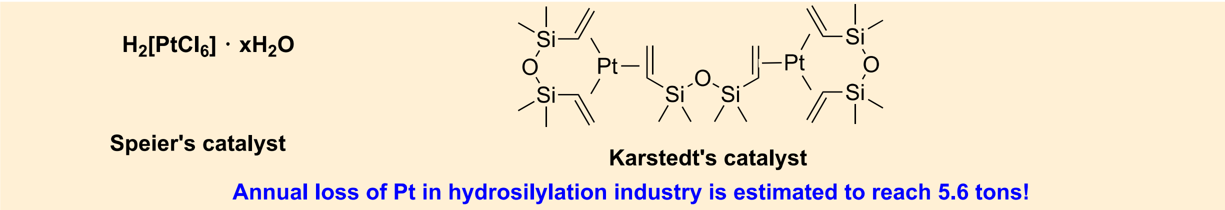
ABSTRACT: A complementary set of base metal catalysts has been developed for regiodivergent alkene hydrosilylations: iron complexes of amine-iminopyridine ligands are selective for Markovnikov hydrosilylations (branched/linear up to >99:1), while the cobalt complexes bearing the same type of ligands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

Introduction

Transition metal catalyzed hydrosilylation[1-5] is one of the most widely studied and applied transformations for the upgrading of commodity alkenes and alkynes. Alkene hydrosilylation is most commonly used in the industrial production of commodity silicones, which are important feedstock for silicon-based polymers and versatile building blocks in organic synthesis. The majority of catalysts capable of alkene hydrosilylation are based upon precious metals,[1-2, 6] and in particular, Pt-based complexes have been explored extensively (Scheme 1a).[7-10] However, platinum is a rare metal with an abundance of only 0.005 ppm in the earth's crust. Furthermore, these homogeneous precious metal catalysts are difficult to recover and are often left behind as residual impurities in the organosilicon products; the annual loss of Pt resulting from industrial hydrosilylation is estimated to reach 5.6 tons.[11] Given these facts, the ideal catalyst in hydrosilylation should be based upon an earth-abundant metal complex. In the past decades, tremendous progress in homogeneous base-metal catalysis has been witnessed, particularly in Fe and Co catalysis (Scheme 1b).[3-5, 12-22] With rational design of ligands, excellent reactivity, regioselectivity and even enantioselectivity can be readily achieved. In particular, Huang and coworkers also demonstrated that regiodivergent olefin hydrosilylation was possible within a single ligand class through variation of the metal center.[18]

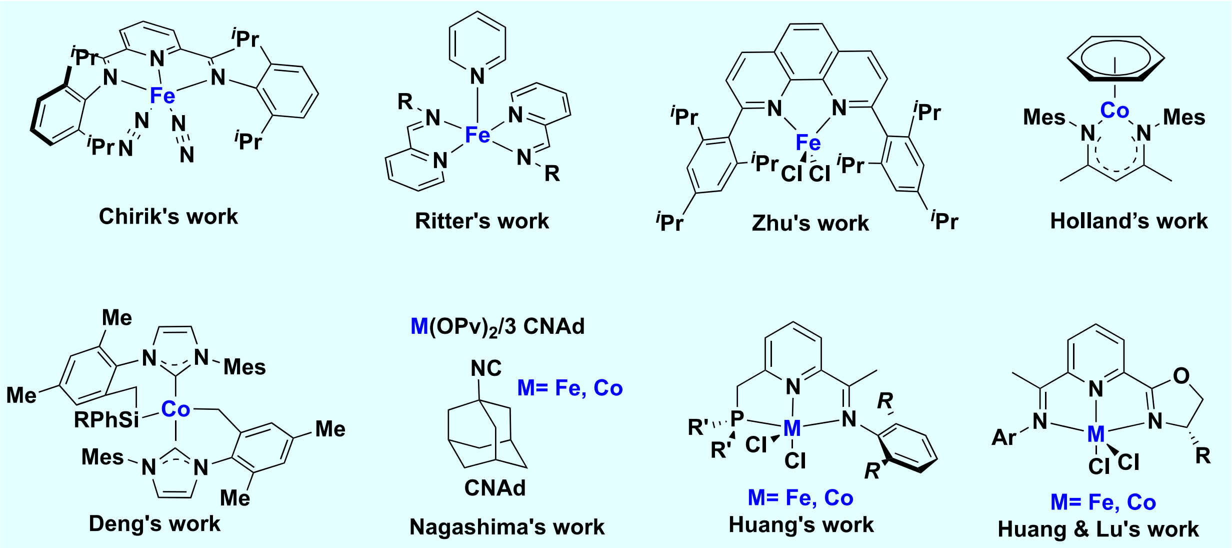
Scheme 1. The development of hydrosilylation of alkenes (in industry and academia) and challenging issues.

a. Platinum catalysts in hydrosilylation industry



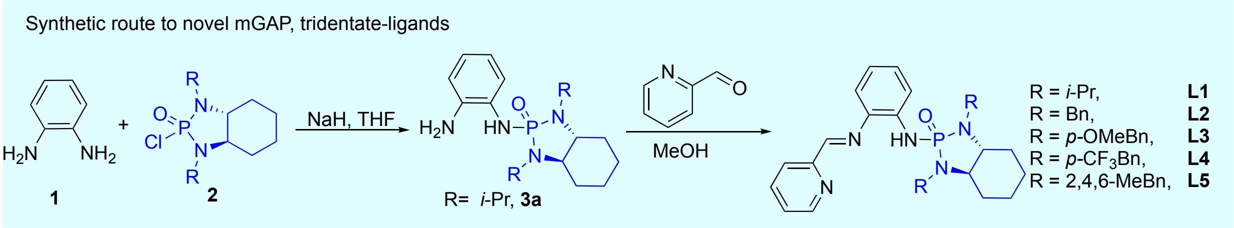
Annual loss of Pt in hydrosilylation industry is estimated to reach 5.6 tons!

b. Selected examples of cobalt and iron catalysts in hydrosilylation of alkenes



Inspired by group-assisted purification (GAP) chemistry,[23-28] we hypothesized that incorporating the phosphoramide group into a ligand platform (metalla-GAP) might be an effective strategy to generate a novel and highly selective homogeneous catalyst.[29] Thus, in three synthetic steps, a series of tunable tridentate ligands are readily accessed (Scheme 2). Upon complexation with either Co(II) or Fe(II) salts, highly active systems were produced which proved capable of catalyzing the hydrosilylation of olefins. Both Co and Fe systems feature excellent substrate generality and chemoselectivity and, remarkably, regiodivergent outcomes are obtained within the same ligand class which appears to be metal-dependent. The iron catalysts reported are highly selective for Markovnikov hydrosilylations, whereas the analogous cobalt catalysts afford the opposite anti-Markovnikov regiochemistry.

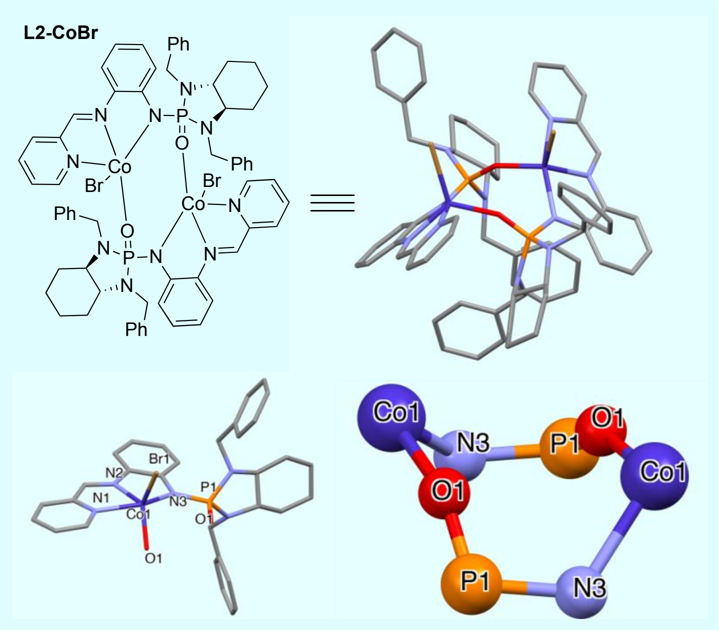
Scheme 2. Synthesis of amine-iminopyridine ligands.



Results and Discussion

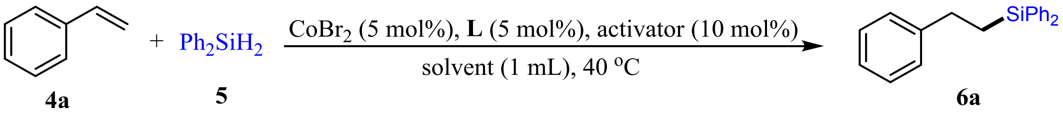
Preparation of catalysts. To effect olefin hydrosilylation, catalysts were typically generated *in-situ* via addition of an activator $NaHBEt_3$ or NaOtBu to a mixture of GAP ligand (**L1-L4**) and $CoBr_2$ (1:1) in THF. It proved possible to isolate X-ray quality crystals of both **L2-CoBr** and **L2-FeBr** from concentrated DCM solutions layered with toluene. The solid-state structures of **L2-CoBr** and **L2-FeBr** are isostructural and exhibit monoclinic structures in which each metal center is coordinated with only one **L2** ligand in a tridentate fashion (**L2-CoBr** shown in **Figure 1**). A dimeric structure is revealed in the solid-state and is held together by P=O•••M interactions which result in an eight-membered ring. We believe in solution and under catalytic conditions, it is likely that the dimer-structure must dissociate to afford a catalytically active monomer which can facilitate hydrosilylation of olefin substrates.

Figure 1. Solid-state structure of **L2-CoBr** obtained using X-ray diffraction experiments.



Cobalt-catalyzed hydrosilylation of alkenes. We chose styrene (**4a**) as a model substrate and performed catalytic hydrosilylation reactions employing diphenylsilane (**5**) (Table 1). As an activator, we tested both $NaHBEt_3$ and NaO*t*Bu, which are proposed to produce cobalt (II) hydride complexes.[30] Recent work from Thomas and coworkers have also implicated an 'ate' species forming from NaO*t*Bu and silanes serves as the real activator in the reaction.[30] Combination of Co(II) centers with **L1-5** in the presence of NaO*t*Bu revealed moderate to good yields of hydrosilylation product (Entries 1-5, Table 1); **L2** afforded both the highest yield and regioselectivity (87 % and 11 : 1) (Entry 2, Table 1). Switching reaction solvent from THF to either toluene or 1,4-dioxane had no effect on regioselectivity and in the case of 1,4-dioxane a substantial decrease in overall yield was observed (Entries 6-7, Table 1). Upon switching activator from NaO*t*Bu to $NaHBEt_3$ no noticeable difference in yield (85 %) was found, however a substantially enhanced regioselectivity (23 : 1) was achieved (Entry 8, Table 1). Initial attempts at exploring the effects of the silane reductant were unsuccessful, both Ph_3SiH and $PhSiH_3$ afforded no hydrosilylation products and thus further studies of the scope of the reaction were pursued using Ph_2SiH_2.

Table 1. Cobalt catalyzed *anti*-Markovnikov hydrosilylation[a]



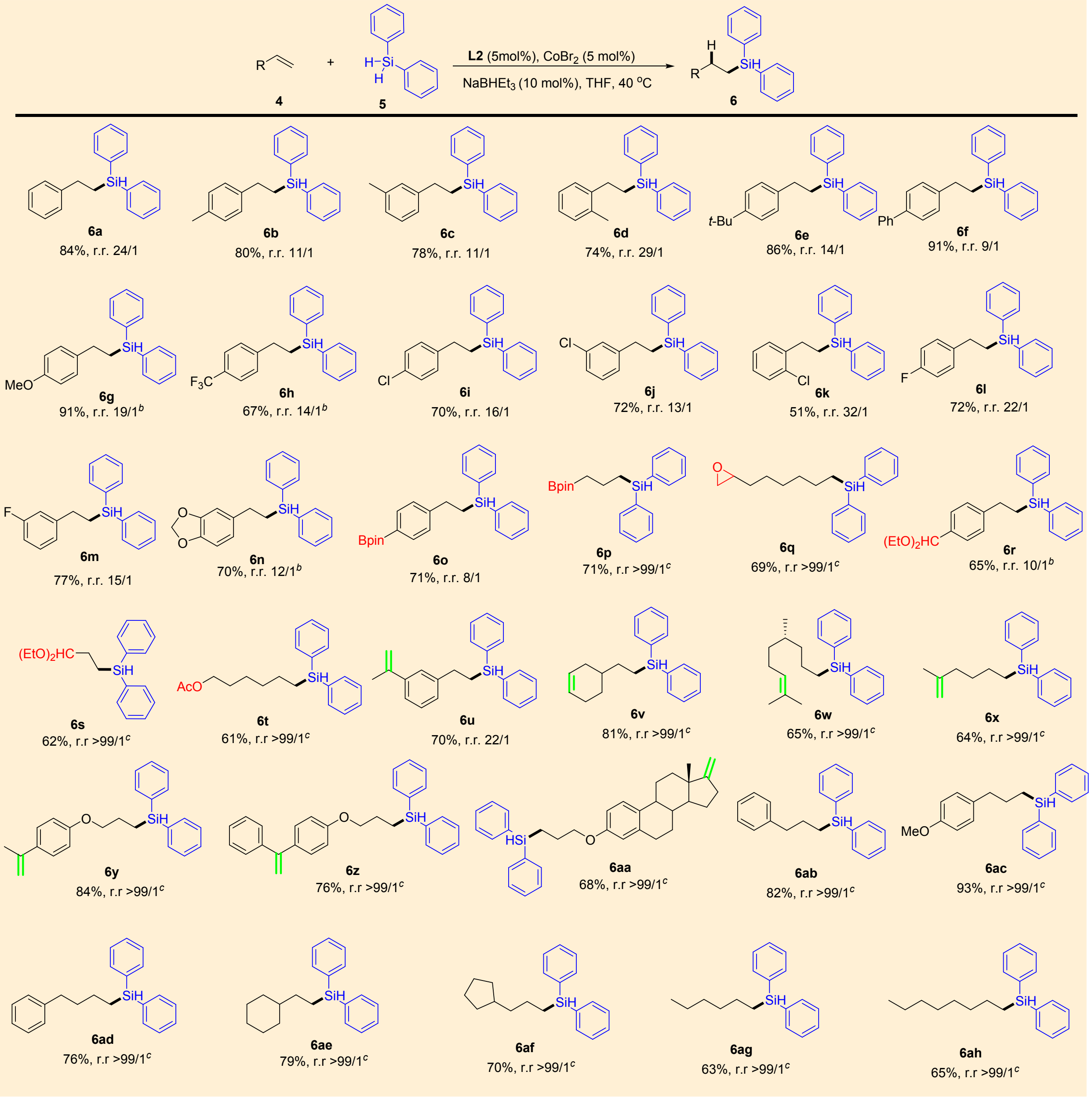
Entry	Ligand	Solvent	Activator	Yield (%)[b]	r.r (*l*/*b*)[c]
1	**L1**	THF	NaO*t*Bu	52	5/1
2	**L2**	THF	NaO*t*Bu	87	11/1
3	**L3**	THF	NaO*t*Bu	76	7/1
4	**L4**	THF	NaO*t*Bu	64	4/1
5	**L5**	THF	NaO*t*Bu	56	4/1
6	**L2**	Toluene	NaO*t*Bu	82	10/1
7	**L2**	1,4-dioxane	NaO*t*Bu	69	10/1
8	**L2**	THF	$NaHBEt_3$	85	23/1

[a] The reaction of **4a** (0.2 mmol) with **5** (0.3 mmol) was performed in the presence of $CoBr_2$ (5 mol%), **L** (5 mol%) and activator (10 mol%) in solvent (1 mL) at 40 ºC under argon for 24 h . [b] Yield of isolated product. [c] The regioisomer ratio (r.r) of the product **6a** was determined by ^1H NMR.

With these optimized reaction conditions in hand, we decided to probe the scope of substrate amenable to our reaction conditions (Scheme 3). The cobalt catalyst mediates hydrosilylation of a diverse array of alkenes with Ph_2SiH_2, furnishing linear products in high isolated yield with excellent regioselectivities. In total, 34 substrates were shown to undergo hydrosilylation in good to excellent yield (61 – 99 %) with superb regioselectivity in most cases (from 8 : 1 to >99 : 1 of *anti*-Markovnikov : Markovnikov product). Initially, styrene derivatives were evaluated with the optimal conditions (**6a-6o, 6r** and **6u**). The electronic effect of the substituents was explored by varying *para*-substituents of styrene (**6b, 6e-6i, 6l, 6o** and **6r**). In general, electron-rich styrenes seems to be superior substrates (**6b, 6e-6g**), which produce the hydrosilylation products with higher yields comparing with the electron-deficient ones (**6h, 6i, 6l, 6o** and **6r**). The regioselectivity of reaction was largely independent of electronic properties, and most of the products were observed with >10:1 regioselectivity, although some specific substrates gave the products with lower selectivities (**6f, 6o, 6r**). *Meta*-substitutions were well-tolerated in the transformation and maintained the reaction performances (**6c, 6j, 6m, 6u**). In contrast, changing from *para*- to *ortho*-substitution resulted in lower yields but higher *anti*-Markovnikov selectivity, presumably due to the steric effects imparted by an *ortho*-substituent (**6d, 6k**). A substrate bearing a fused aromatic ring (**6n**) also proved to be amenable to these reaction conditions and affords the corresponding product with satisfactory results. Next, a broad range of aliphatic alkenes were examined with modified conditions (**6p, 6q, 6s, 6t** and **6v-6ah**). Regardless of the nature of functional groups in the substrates, a uniformly excellent regioselectivity was obtained. Specifically, a series of synthetically useful functionalities, such as, borate, epoxy, acetal and ester groups, showed good tolerance to the reaction conditions (**6o-6t**). It is noteworthy that chemoselective hydrosilylation was possible (**6u-6aa**) and silylated products were readily obtained without affecting the internal alkene groups.

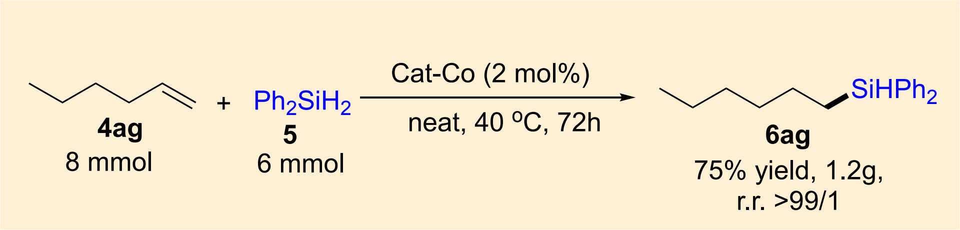
To further demonstrate the robustness of the catalyst, a gram-scale reaction was conducted with 2% catalyst loading under air and higher yield (1.2 g, 75%) was observed comparing the aforementioned reaction (Figure 2).

Scheme 3. Cobalt-catalyzed, anti-Markovnikov-selective, hydrosilylation of olefins[a]



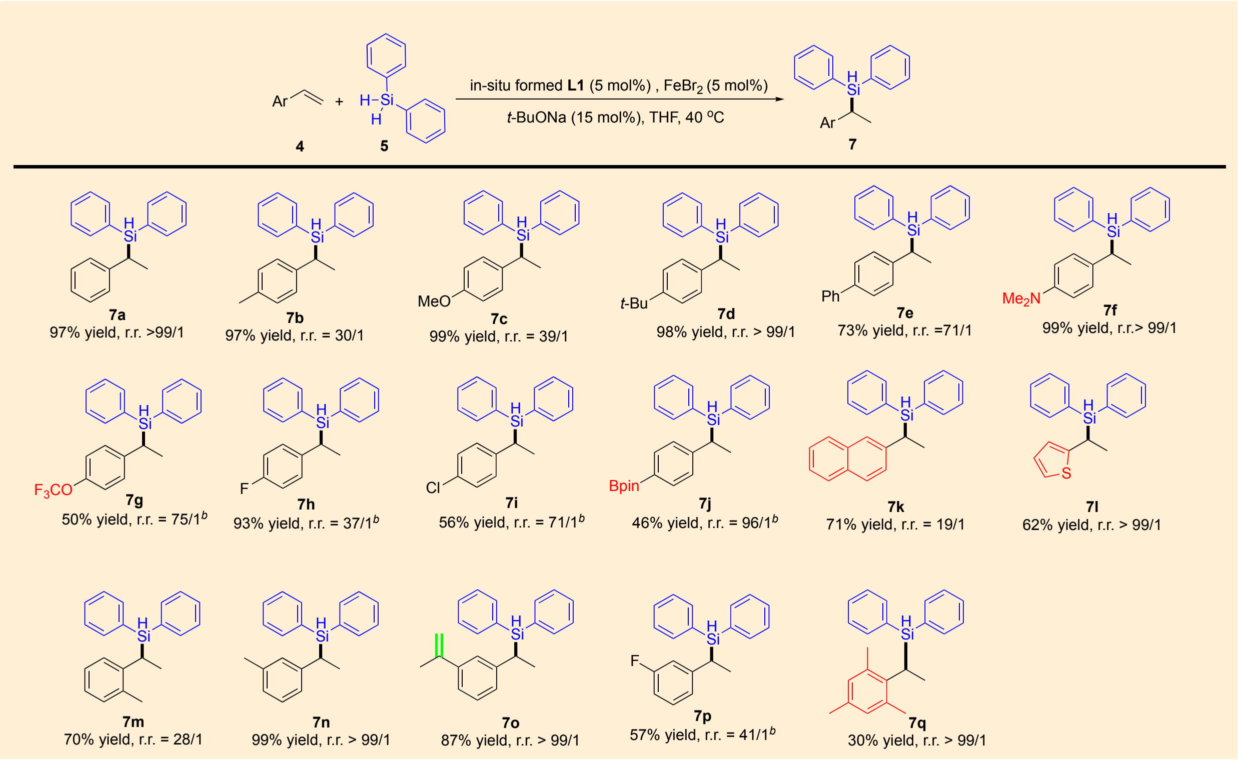
[a] The reaction of **4** (0.3 mmol) with **5** (0.45 mmol) was performed in the presence of $CoBr_2$ (5 mol%), **L2** (5 mol%) and $NaBHEt_3$ (10 mol%) in THF (1 mL) at 40 °C under argon for 24 h (Condition I, for details see supporting information). [b] **L3** was used as a ligand (Condition II, for details see supporting information). [c] NaO*t*Bu was used as an activator (Condition III, for details see supporting information).

Figure 2. Gram-scale reaction of **4ag** with **5**.



Iron-catalyzed hydrosilylation of alkenes. We commenced the optimization by using styrene (**4a**) and diphenylsilane (**5**) as pilot substrates. After screening various ligands and solvents, the iron catalyst (**L1-FeBr$_2$**) in combination with activator NaO^{t}Bu was identified as the optimal conditions. Remarkably, regioselectivity could be reversed when the iron analog was employed;[18] Markovnikov product **7a** was obtained in 97% yield and > 99:1 regioselectivity (for details see Entry 10, Table S2 in supporting information). Subsequently, we investigated the substrate scope of iron-catalyzed Markovnikov hydrosilylation with the optimal conditions (Scheme 4).[18, 31] Consistent with the results of cobalt-catalyzed hydrosilylation, higher efficiency (73-99% yields) was observed in the cases of electron-rich styrenes (**7b-7f**) comparing with electron-deficient ones (**7g-7j**). Remarkably, this novel protocol was well compatible with the highly electron-donating NMe_2 group (**7f**), which might disturb the coordination of iron catalyst as a coordinate site. This method was also extended to fused ring and heterocycle (**7k, 7l**), producing the corresponding products with moderate yields and good regioselectivities. As well as *para*-substitution, *meta*- and *ortho*-substituted styrenes could proceed smoothly in the reaction and provided the hydrosilylation products with relative satisfactory results (**7m-7p**). It is important to underline the high chemoselectivity of the hydrosilylation as internal alkene was not altered in the reaction (**7o**). Gratifyingly, sterically bulky substrate vinylmesitylene was amenable to the Markovnikov hydrosilylation, albeit with a diminished yield (**7q**). However, aliphatic alkenes failed in the reaction, which could only furnish traces of *anti*-Markovnikov products.

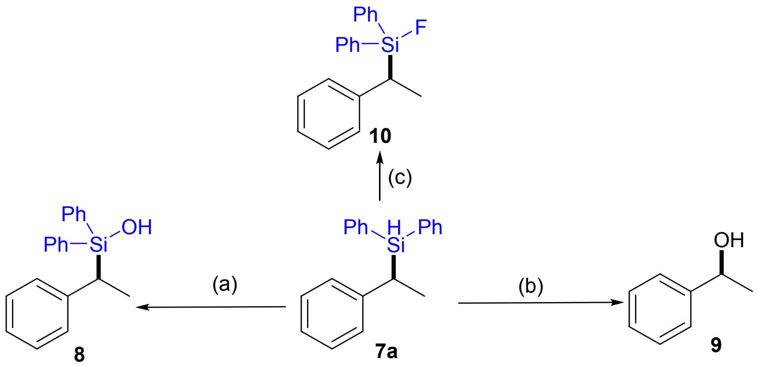
Scheme 4. Iron-catalyzed, Markovnikov-selective, hydrosilylation of olefins



[a] The reaction of **4** (0.3 mmol) with **5** (0.9 mmol) was performed in the presence of $FeBr_2$ (5 mol%), in-stiu formed **L1** (5 mol%) and NaO*t*Bu (15 mol%) in THF (1 mL) at 40 ºC for 24 h (Condition IV, for details see supporting information). [b] **L2** was used as a ligand**,** NaO*t*Bu (25 mol%) was used as an activator, 1,4-dioxane was used as solvent (Condition V, for details see supporting information).

The elaboration of Markovnikov product (**7a**) was then conducted to demonstrate its synthetic utility (Scheme 5).[31] Potential applications of Markovnikov-selective olefin hydrosilylations include the conversion of readily available olefin substrates into synthetically important secondary alcohols. Thus, we decided to explore the Fleming-Tamao oxidation as a classical route to oxidize silanes to alcohols; by varying equivalents of reagents and reaction temperature the extent of oxidation could be controlled. At lower equivalents of KF and $KHCO_3$ a silanol product (**8**) could be obtained at room temperature, while the full oxidative hydrolysis product 1-phenylethan-1-ol (**9**) could be accessed via use of increased equivalents KF and $KHCO_3$ and at an elevated temperature. Finally, a transition-metal-free fluorination of silane was exploited, which provides mild route to fluorosilane (**10**).

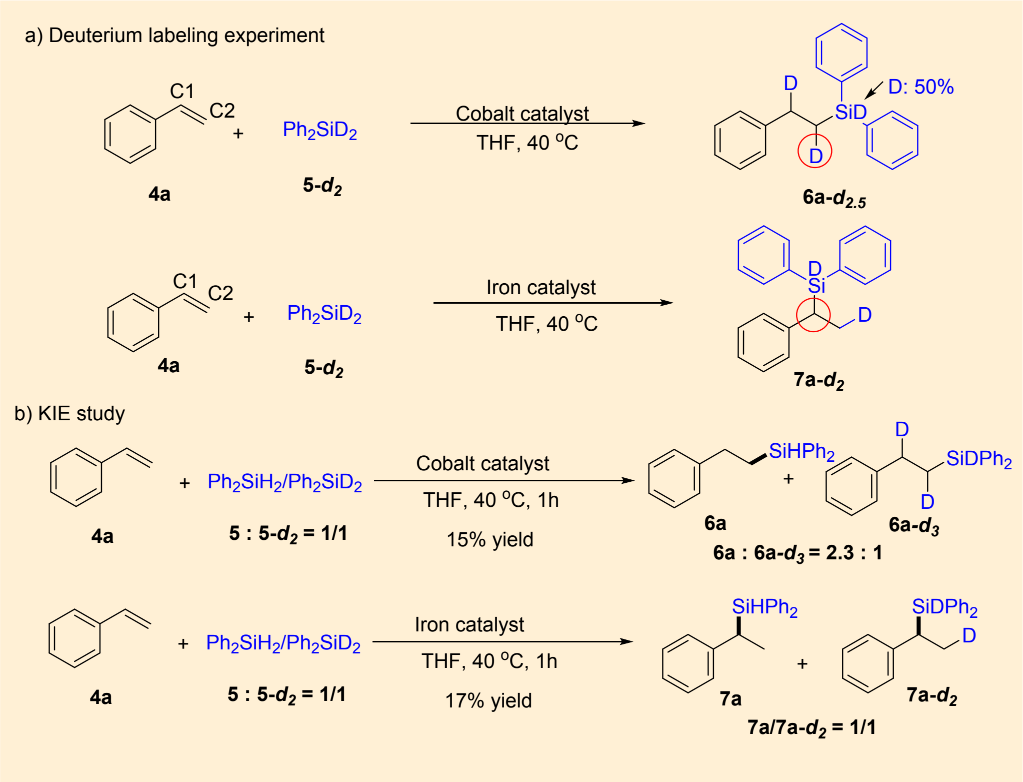
Scheme 5. Elaboration of Markovnikov product (**7a**)



(a) H_2O_2 (30% aq), $KHCO_3$ (4 equiv.), KF (4 equiv.), MeOH/THF, rt
(b) H_2O_2 (30% aq), $KHCO_3$ (8 equiv.), KF (5 equiv.), MeOH/THF, 50 ^oC
(c) Selectfluor (2.4 equiv.), K_2CO_3 (1.2 equiv.), CH_3CN, 50 ^oC

Preliminary Mechanistic Study. The extensive study of the mechanism of these transformations using both experimental and computational techniques are ongoing in our laboratory, our preliminary experiments have provided interesting results. To gain insight into the hydrosilylation mechanism, deuterium labeling and kinetic isotope effect (KIE) experiments were conducted (Scheme 6). As shown in the deuterium labeling experiments, extensive deuterium incorporation (100 %) at the C2 position was detected in the *anti*-Markovnikov product **6a**-$d_{2.5}$ (Scheme 6a). Iron-catalyzed hydrosilylation of **4a** with deuterated diphenylsilane **5**-d_2 was also explored. In contrast to the results of cobalt-catalyzed hydrosilylation, product **7a**-d_2 was obtained without deuterium incorporation at the C1 position. These observations strongly argue for the formation of a cobalt deuteride / hydride and against a similar species in the case of iron in the catalytic cycle. The presence of such intermediates would lead to facile H/D exchange between M-D and C-H bonds through reversible olefin insertion into the M-D bond.[18, 32-33] The KIE study of the cobalt- and iron-catalyzed hydrosilylation showed sharp differences in the ratio of k_H/k_D (2.3/1 *vs* 1/1). This result further illustrates that distinct pathways are involved in the regioselectively-divergent transformations.

Scheme 6. Deuterium labeling experiment and KIE studies.



On the basis of the KIE and deuterium labeling experiments and related mechanistic studies,[18,21,31] divergent catalytic pathways were proposed to rationalize the complementary regioselectivity (Figure 3). As depicted in Figure 3a, cobalt catalyst is transformed *in-situ* into a Co-H species (**I**) in the presence of $NaHBEt_3$. Styrene undergoes 1,2-insertion into the Co-H bond of **I**, which is the origin of the *anti*-Markovnikov regioselectivity. The resulting intermediate **Int-Co** proceeds via the rate-determining Si-migration step to regenerate the active Co-H catalyst. In contrast, iron-catalyzed hydrosilylation is initiated by an Fe-Si intermediate (**II**), and styrene inserts into an Fe-Si bond via a 1,2-insertion process giving **Int-Fe** (Figure 3b). The same insertion mode in both catalytic cycles might be attributed to the similar catalyst structure shown in the Figure 1. Finally, diphenylsilane reacts with the intermediate species **Int-Fe** affording the Markovnikov product **7a** via hydride insertion and regeneration of **II**.

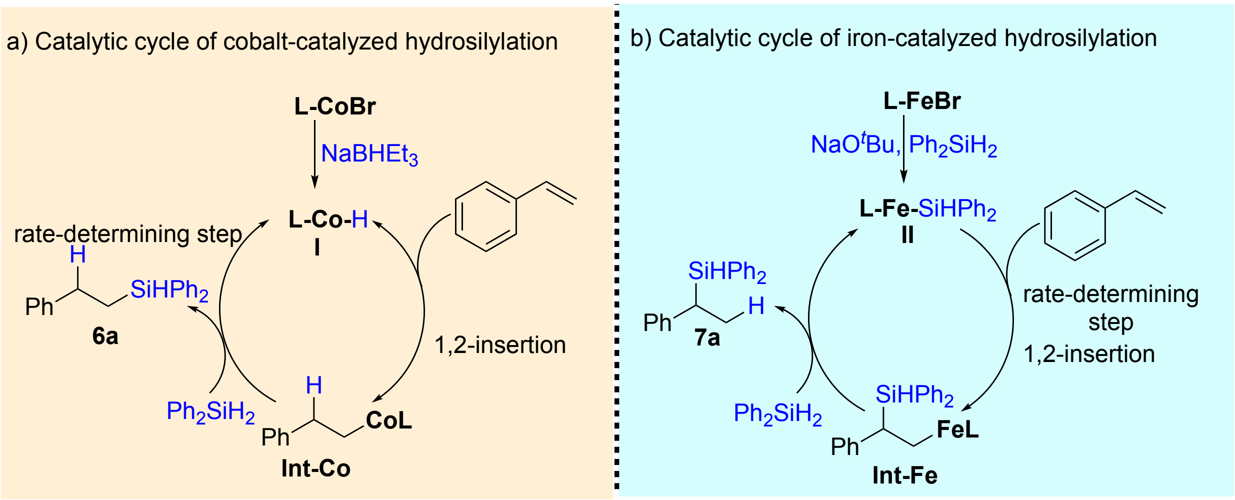


Figure 3. a) Catalytic cycle of cobalt-catalyzed hydrosilylation. b) Catalytic cycle of iron-catalyzed hydrosilylation.

Conclusions

In summary, we have prepared a series of iron and cobalt alkene hydrosilylation catalysts bearing amine-iminopyridine ligands which incorporate a phosphoramide (GAP) group. It proved possible to switch the regioselectivity of olefin hydrosilylations from >99:1 to <1:99 by simply changing the metal center from cobalt to iron. Non-precious metal-based catalysts such as these deliver a number of advantages over traditional (precious metal) systems: highly efficient, mild reaction conditions, and broad functional group tolerance with a divergent and high level of regioselectivity.

Methods

General. Full experimental procedures for the preparation and purification of all new compounds, complete spectroscopic characterization data for substrates and products and a description of the NMR can be found in the Supporting Information.

General procedure for cobalt-catalyzed hydrosilylation. Inside an argon-atmosphere glovebox, a borosilicate glass vial was charged with $CoBr_2$ (3.2 mg, 0.015 mmol) and **L2** (8.1 mg, 0.015 mmol), with anhydrous THF (1 mL) as solvent. Subsequently, $NaBHEt_3$

(30 μL) (1 mol/L in THF) was added as activator. The resulting mixture was stirred at room temperature for 5 hours to form the active catalyst. Subsequently, diphenylsilane **5** (84 μL, 0.45 mmol, 1.5 equiv.) was added and the mixture was stirred for 30 min before adding styrene **4a** (34 μL, 0.3 mmol). The reaction mixture was removed from the glovebox and stirred at 40 °C under an argon atmosphere for 24 hours. The reaction solvent was evaporated in vacuum and the resulting residue was purified by silica gel column chromatography (hexane followed by diethyl ether/hexane = 1/200) affording 73 mg (84% yield) product **6a** as colorless oil.

General procedure for iron-catalyzed hydrosilylation Inside an argon-atmosphere glovebox, a borosilicate glass vial was charged with $FeBr_2$ (3.2 mg, 0.015 mmol), **3a** (5.3 mg, 0.015 mmol), picolinaldehyde (1.4 μL, 0.015 mmol) and ^{t}BuONa (4.3 mg, 0.045 mmol), with anhydrous THF (1mL) as solvent. The resulting mixture was stirred at room temperature for 5 hours to form the active catalyst. Subsequently, diphenylsilane **5** (167 μL, 0.9 mmol, 3.0 equiv.) was added and the mixture was stirred for 30 min before adding styrene **4a** (34 μL, 0.3 mmol). The reaction mixture was removed from the glovebox and stirred at 40 ºC under an argon atmosphere for 24 hours. Then the reaction solvent was evaporated in vacuum and the resulting residue was purified by silica gel column chromatography (hexane followed by diethyl ether/hexane = 1/200) affording 84 mg (97% yield) product **7a** as colorless oil.

Data Availability

All data supporting the findings of this study, including experimental details, spectroscopic characterization data for all compounds are available within the paper and its SI Appendix.

Acknowledgements

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Author Contributions

M.F., S.Z. and G.L. conceived the project, designed the experiments and wrote the manuscript. S.Z. and J.-S.L. performed the experimental work. All authors discussed the results and commented on the manuscript.

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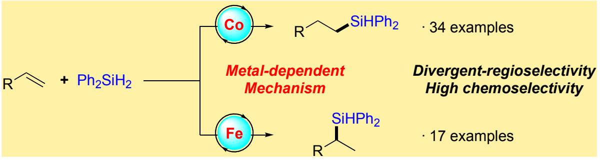

Choose your regiochemical adventure; regiodivergent olefin hydrosilylation products can be accessed through a simple change in metal center within a single ligand class. Linear products (anti-Markovnikov) are obtained employing cobalt-based catalysts whereas branched (Markovnikov) products result from an iron-based analogue.