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Iron-Catalyzed Regiodivergent Alkyne Hydrosilylation

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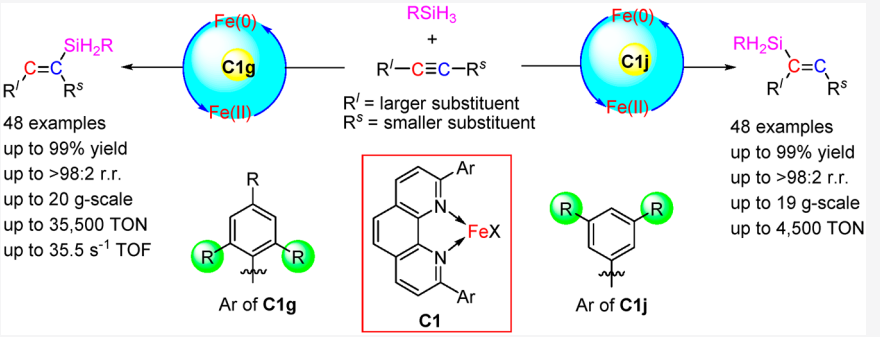

ABSTRACT: Although tremendous effort has been devoted to the development of methods for iron catalysis, few of the catalysts reported to date exhibit clear superiority to other metal catalysts, and the mechanisms of most iron catalysis remain unclear. Herein, we report that iron complexes bearing 2,9-diaryl-1,10-phenanthroline ligands exhibit not only unprecedented catalytic activity but also unusual ligand-controlled divergent regioselectivity in hydrosilylation reactions of various alkynes. The hydrosilylation protocol described herein provides a highly efficient method for preparing useful di- and trisubstituted olefins on a relatively large scale under mild conditions, and its use markedly improved the synthetic efficiency of a number of bioactive compounds. Mechanistic studies based on control experiments and density functional theory calculations were performed to understand the catalytic pathway and the observed regioselectivity.

INTRODUCTION

Because iron, which is abundant in the earth's crust, is inexpensive, readily available, and biocompatible, the development of iron-catalyzed reactions has been attracting increasing attention, and considerable progress has been made in recent decades.[1] However, few of the iron catalysts reported to date exhibit activity or selectivity superior to those of the well-established noble metal catalysts. Moreover, because of the magnetism of iron, its numerous oxidation states, and the poor stability of iron catalysts, studying the mechanisms of iron-catalyzed reactions is challenging. Specifically, the effects of spin state on activity and selectivity remain poorly understood, and this lack of information has hampered progress in this area.

The development of iron catalysts for regio- and stereoselective synthesis of alkenes would be particularly useful because alkenes are widely used in organic chemistry. Although several powerful methods, including the Wittig reaction and the alkene metathesis reaction, have been established for this purpose, their utility for stereoselective synthesis of multisubstituted internal alkenes is unsatisfactory.[2] Alkyne hydrosilylation is an alternative for preparing functionalized or unfunctionalized alkenes because the silyl groups of alkenyl silanes readily undergo a diverse array of transformations.[3,4] However, achieving regioselectivity in the hydrosilylation of unsymmetrical alkynes—that is, alkynes with different substituents at the ends of the triple bond—is difficult unless the two substituents have markedly different electronic or steric properties that can be easily identified by the catalyst. Although some catalysts have been shown to give a certain regioselectivity, achieving the opposite regioselectivity is difficult.[5] For example, the known catalysts for hydrosilylation of dialkyl acetylenes usually give products with the silyl group at the smaller alkyl end of the alkyne,[6] but the opposite regioselectivity remains unsuccessful.[7]

Herein, we report that iron complexes bearing 2,9-diaryl-1,10-phenanthroline ligands[8] efficiently catalyze the hydrosilylation of terminal and internal alkynes with primary silanes. Specifically, turnover numbers (TONs) up to 35 500 and turnover frequencies up to 35.5 s^{-1} were observed in the reactions with terminal alkynes, which are the highest values for such reactions reported to date.[3] More interestingly, simply

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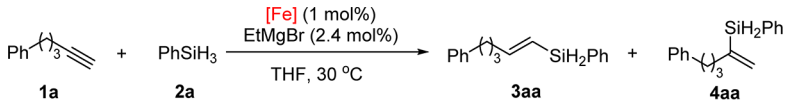
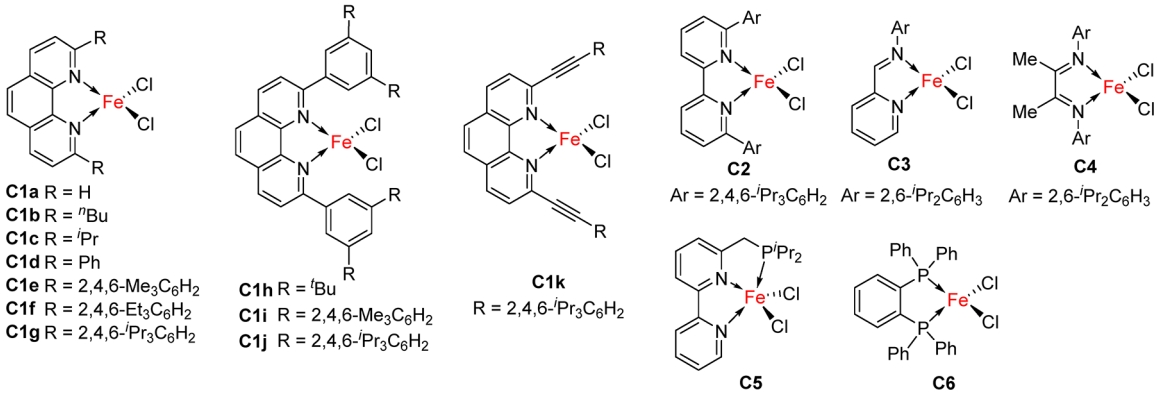
Table 1. Evaluation of Ligands for Iron-Catalyzed Hydrosilylation of Alkyne 1a with Phenylsilane (2a)[a]





entry	[Fe]	time (min)	conv. (%)[b]	yield (%)[b]	3aa/4aa[b]
1	**C1a**	120	<5	ND	NA
2	**C1b**	10	38	35	55:45
3	**C1c**	10	45	43	7:35
4	**C1d**	10	60	55	62:38
5	**C1e**	10	>95	85	>98:2
6	**C1f**	10	>95	86	>98:2
7	**C1g**	10	>95	95	>98:2
8	**C1h**	10	>95	88	23:77
9	**C1i**	10	>95	89	3:97
10	**C1j**	10	>95	92	<2:98
11	**C1k**	10	>95	88	95:5
12	**C2**	120	<5	ND	NA
13	**C3**	10	80	74	58:42
14	**C4**	20	15	10	NA
15	**C5**	10	>95	51[c]	79:21
16	**C6**	120	<5	ND	NA

[a]Reaction conditions: **1a** (0.35 mmol), **2a** (0.4 mmol), iron catalyst (1 mol %), EtMgBr (2.4 mol %) in THF (1 mL) at 30 °C. [b]Conversions, yields, and product ratios were determined by ^{1}H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard. ND, not detected. NA, not applicable. [c]Along with (*E*)-**3aa** and **4aa**, (*Z*)-**3aa** was obtained in 39% yield.

changing the 2,9-aryl substituents on the ligands completely reversed the regioselectivity of the reaction even for dialkyl acetylenes. To our knowledge, this phenomenon has not previously been observed for other iron catalysts. The remarkable ligand-induced regiodivergence of this iron-catalyzed alkyne hydrosilylation enabled us to study its mechanism by means of control experiments and density functional theory (DFT) calculations.

RESULTS AND DISCUSSION

We initiated our study by exploring conditions for the iron-catalyzed alkyne hydrosilylation reaction of aliphatic terminal alkyne (**1a**) and phenylsilane (**2a**) using EtMgBr as the reductant[4c] in tetrahydrofuran at 30 °C (Table 1). First, we systematically investigated the effects of various 1,10-phenanthroline ligands (entries 1−11). The X-ray diffraction analyses of single crystals of **C1g** and **C1h** are included in Tables S1 and S2). Iron catalysts with bulky 2,4,6-trialkylsubstituted phenyl groups at the 2- and 9-positions of the ligands (**C1e**−**C1g**) smoothly promoted the hydrosilylation reaction; conversion was complete within 10 min, and a single anti-Markovnikov addition product **3aa** was obtained (entries 5−7). To our surprise, catalysts with 3,5-disubstituted phenyl groups (**C1h**−**C1j**) gave Markovnikov addition product α-vinyl silane **4aa** as the major product (entries 8−10). Impressively, catalyst **C1j** showed >98% Markovnikov selectivity (entry 10). To the best of our knowledge, this is the first iron catalyst to show high Markovnikov selectivity in alkyne hydrosilylation.[4]

We also evaluated several typical iron catalysts bearing nitrogen- or phosphine-containing ligands (Table 1, entries 12−16); however, none of these catalysts afforded satisfactory yields or selectivities. According to the literature, an iron complex with a pyridine diimine ligand[4a] gives β-(*Z*)-vinyl silane under the similar conditions.[4c] We found that complexes prepared in situ from phenanthroline ligand **L1g** or **L1j** and other metals exhibited much lower activity or poor selectivity compared with those of the corresponding iron catalysts under our standard conditions (Tables S3−S6). The above-described results clearly show that the 1,10-phenanthroline skeleton of the ligands and the iron played important roles in the activity and selectivity of these catalysts.

Using the optimal reaction conditions (Table 1, entry 7 or 10), we investigated the substrate scope of this iron-catalyzed

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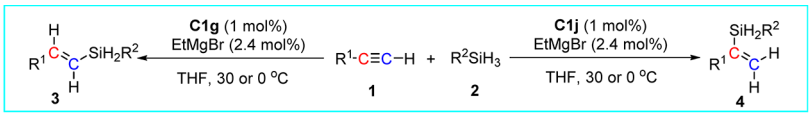
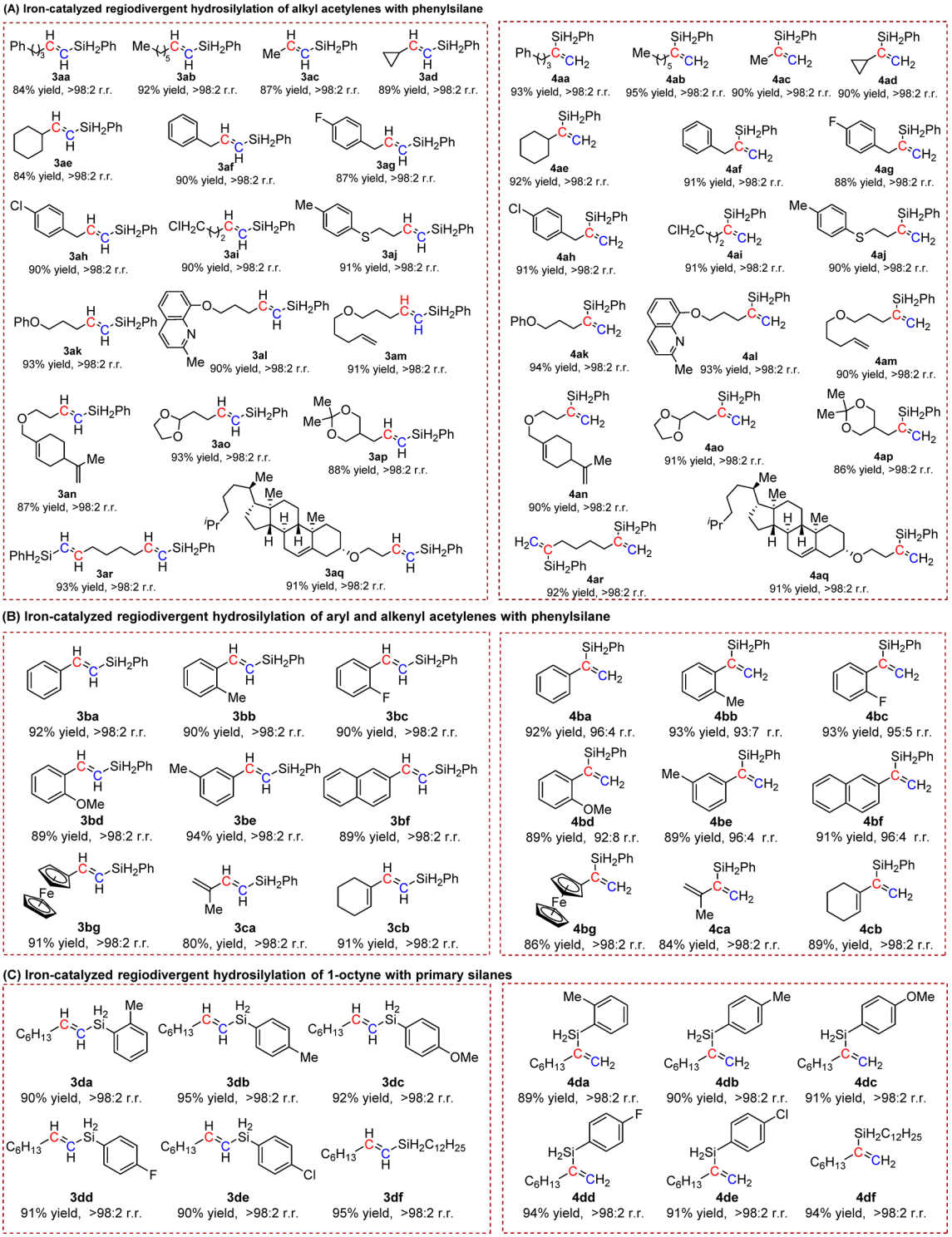
J. Am. Chem. Soc. XXXX, XXX, XXX−XXX

Scheme 1. Substrate Scope of Iron-Catalyzed Regiodivergent Hydrosilylation of Terminal Alkynes[a]





[a]Condition A (left equation): alkyne/silane/**C1g**/EtMgBr = 0.5:0.55:0.005:0.012 (mmol). Condition B (right equation): alkyne/silane/**C1j**/EtMgBr = 0.5:0.55:0.005:0.012 (mmol), in 1 mL of THF, at 30 °C (for **A**, **C**) or 0 °C (for **B**), 10 min to 1 h. Isolated yields were given. The regioisomeric ratios (r.r.) were determined by ^{1}H NMR.

alkyne hydrosilylation, starting with alkyl acetylenes and phenylsilane (Scheme 1A). With **C1g** and **C1j** as the catalysts, all the reactions went to completion in 10 min to afford high yields (84–95%) of anti-Markovnikov products **3aa**–**3ar** and

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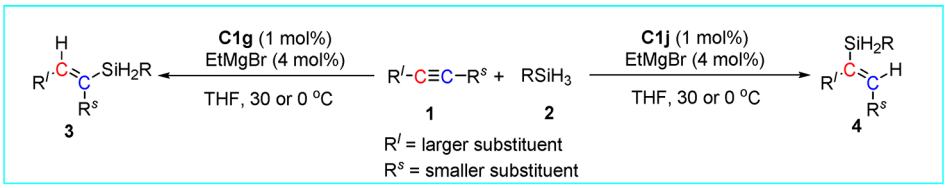
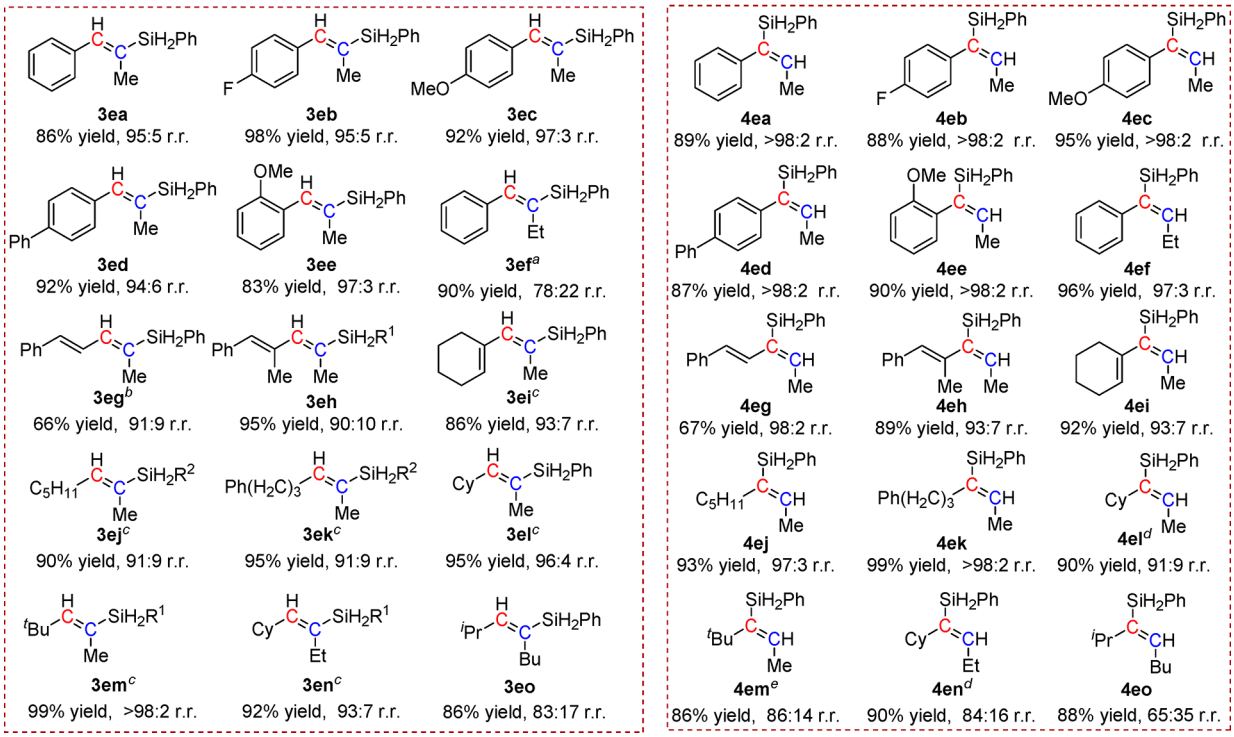
Scheme 2. Substrate Scope of Iron-Catalyzed Regiodivergent Hydrosilylation of Internal Alkynes[a]





[a]Reaction conditions: alkyne/silane/catalyst/EtMgBr = 0.5:0.55:0.005:0.02 (mmol). R^1 = n-$C_{12}H_{25}$, R^2 = p-tolylmethyl. For compounds with italic superscript numbers after, the following catalysts were used: *a*, 5mol % **C1g**; *b*, **C1k**; *c*, **C1e** (with toluene as solvent); *d*, **C1i**; *e*, **C1h**.

Markovnikov products **4aa**−**4ar**, respectively, with excellent regioisomeric ratios (r.r. > 98:2 in all cases). The chain length and steric bulk of the alkylacetylene had little effect on the yield or regioselectivity (**3ab**−**3af** and **4ab**−**4af**). The system tolerated a variety of functional groups: halogens (**3ag**−**3ai** and **4ag**−**4ai**), a thioether (**3aj** and **4aj**), quinoline (**3al** and **4al**), ethers (**3ak**−**3an** and **4ak**−**4an**), alkenes (**3am**, **3an**, **4am**, and **4an**), and ketals (**3ao**, **3ap**, **4ao**, and **4ap**). In addition, a dialkyne and an alkyne derived from structurally complex natural product were smoothly hydrosilylated in good yields with high regioselectivities (**3aq**, **3ar**, **4aq**, and **4ar**).

Our catalytic system was also successfully used for hydrosilylation of aryl acetylenes and alkenyl acetylenes with phenylsilane (Scheme 1B). Both anti-Markovnikov and Markovnikov addition products could be obtained in good yields (80−94%) with excellent regioselectivities (92−>98%) by using catalysts **C1g** and **C1j**, respectively. Generally, **C1g** showed better regioselectivity than **C1j**. It is worth mentioning that hydrosilylation reactions of alkenyl acetylenes gave useful silylated conjugated dienes (**3ca**, **3cb**, **4ca**, and **4cb**) in high yields with excellent regio- and stereoselectivities.

Hydrosilylation reactions of 1-octyne and various monosubstituted silanes with catalysis by **C1g** or **C1j** also afforded the corresponding products (**3da**−**3df** or **4da**−**4df**, respectively) in high yields (89−95%) with regioselectivities of >98% (Scheme 1C), and the steric and electronic properties of the primary silanes had a negligible effect on the reaction outcome. Because secondary and tertiary silanes were less reactive toward **C1g** and **C1j**, these alkyne hydrosilylation reactions also exhibited excellent chemoselectivity.

To our delight, our iron complexes with 1,10-phenanthroline ligands catalyzed hydrosilylation of various internal alkynes, which remains a considerable challenge in literature, with excellent regioselectivity (Scheme 2). Brief exploration of reaction conditions revealed that catalyst **C1g** afforded hydrosilylation products **3** with the silyl group at the less-hindered end of the alkynes, whereas **C1j** catalyzed hydrosilylation at the more more-hindered end to afford products **4**. Aryl methyl acetylenes generally gave the corresponding products (**3ea**−**3ee** and **4ea**−**4ee**) in high yields (83−98%) with high regioselectivities (94−>98%). Phenyl ethyl acetylene was also a suitable substrate: **C1g** afforded **3ef** in good yield with 78% regioselectivity, whereas **C1j** gave **4ef** in good yield with excellent regioselectivity. In addition, **C1j**-catalyzed hydrosilylation of alkenyl alkyl alkynes with phenylsilane smoothly afforded vinylsilanes with the silyl group on the alkenyl side (**4eg**−**4ei**), and addition of the silyl group to the alkyl side to afford **3eg**−**3ei** could be also achieved by varying the 1,10-phenanthroline ligand or the silane. We were also able to add a silyl group to either end of dialkyl alkynes with good to high regioselectivity. Varying the ligands allowed us to control the regioselectivity even for highly symmetric internal

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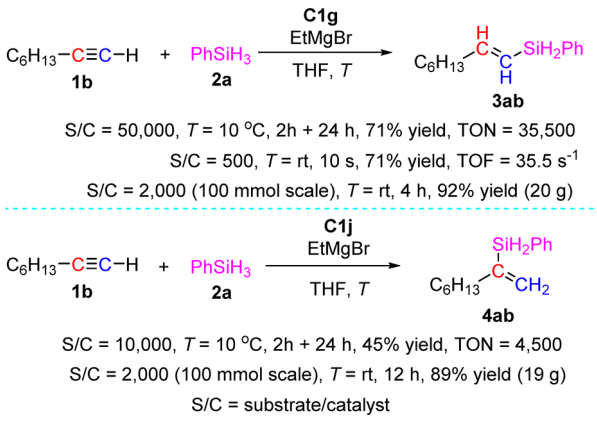
J. Am. Chem. Soc. XXXX, XXX, XXX−XXX

alkynes (**3ej** and **3ek**; **4ej** and **4ek**) and could force addition of a large silyl group to the sterically hindered end of unsymmetrical internal aliphatic alkynes to afford (**4el**–**4en**), which has not previously been achieved with any other catalyst. The hydrosilylation of 2-methyl-3-octyne having more similar sized terminal groups (^{i}Pr and Bu) afforded modest regioselectivity under standard reaction conditions (**3eo** and **4eo**).

This iron-catalyzed regiodivergent alkyne hydrosilylation showed a high TON and turnover frequency and was easy to scale up (Scheme 3). The initial turnover frequency of the

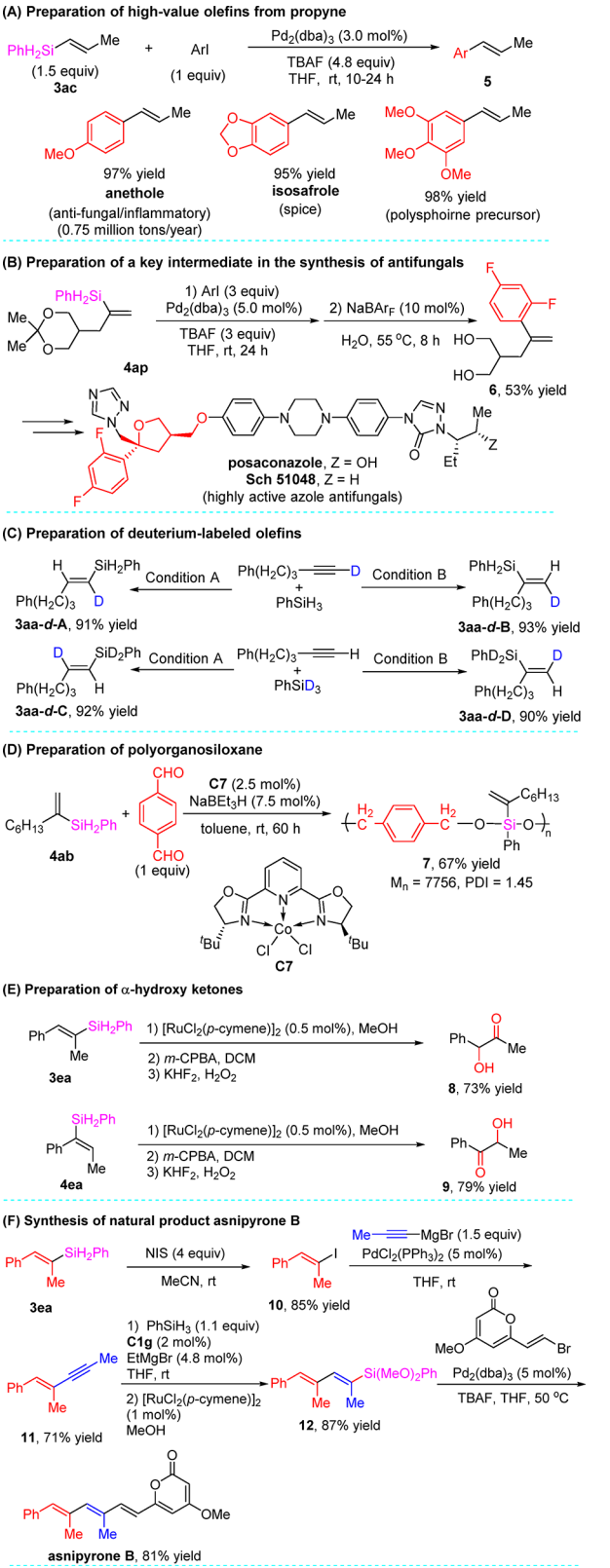
Scheme 3. Efficiency Evaluation of the Iron-Catalyzed Regiodivergent Alkyne Hydrosilylation



reaction of 1-octyne with phenylsilane in the presence of 0.2 mol % **C1g** was 35.5 s^{-1}, and TONs as high as 35 500 were obtained when 0.002 mol % of **C1g** was used. Moreover, the Markovnikov hydrosilylation reaction catalyzed by **C1j** also showed a satisfactory TON (4 500). The reaction could easily be scaled up to 100 mmol using a catalyst loading of 0.05 mol % with full conversion, and high yields of pure products **3ab** (20 g, 92%) and **4ab** (19 g, 89%) were obtained by vacuum distillation.

Because the C–Si bonds of the products can be converted to C–C bonds by means of a Hiyama–Denmark coupling reaction,[9] the hydrosilylation reaction provides an efficient route for olefin synthesis. For example, we synthesized a series of high-value olefins[10] in high overall yields with excellent regio- and stereoselectivities from propyne, a feedstock alkyne, by means of iron-catalyzed anti-Markovnikov hydrosilylation (**3ac**) followed by Hiyama–Denmark cross-coupling (Scheme 4A). Similarly, Markovnikov hydrosilylation product **4ap** could be used to prepare a key intermediate in the synthesis of posaconazole, a second-generation triazole antifungal drug (Scheme 4B).[11] Deuterated alkynes and deuterated silanes could be used to synthesize olefins with deuterium labels at various positions (Scheme 4C), which demonstrates the potential utility of this reaction for the preparation of deuterated pharmaceuticals.[12] Alkenyl silane **4ab** was easily converted to polyorganicsiloxane **7** by means of a cobalt-catalyzed hydrosilylation reaction with terephthalaldehyde (Scheme 4D). This result suggests that the current protocol may find applications in materials science. In addition, alkenyl silanes **3ea** and **4ea** could be converted to α-hydroxy ketones, versatile synthons,[13] by means of two consecutive oxidations in a single pot (Scheme 4E). Finally, we accomplished the total synthesis of the natural product asnipyrone B,[14] which has a

Scheme 4. Applications of the Hydrosilylation Protocol and Transformations of the Products



conjugated multisubstituted polyolefin moiety, starting from **3ea**, the product of hydrosilylation of phenyl methyl acetylene (Scheme 4F); a second iron-catalyzed hydrosilylation, of alkenyl alkyne **11**, was a key step in the synthesis.

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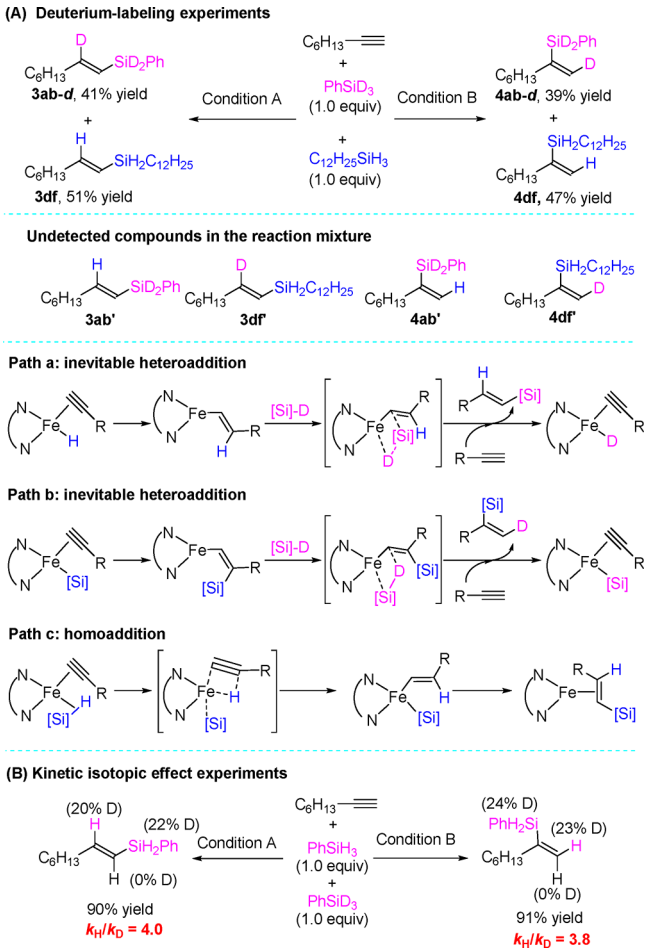
J. Am. Chem. Soc. XXXX, XXX, XXX–XXX

MECHANISTIC STUDIES

This ligand-controlled iron-catalyzed regiodivergent hydrosilylation provides an ideal model for understanding the behavior of iron catalysts. To this end, we performed some control experiments and DFT calculations. We began with deuterium-labeling experiments (Scheme 5A). When hydrosilylation reactions of 1-octyne with a 1:1 mixture of $PhSiD_3$ (98% D) and $C_{12}H_{25}SiH_3$ were carried out with catalysis by **C1g** (condition A) or **C1j** (condition B), only homoaddition products (**3ab**-*d* and **3df** with **C1g**; **4ab**-*d* and **4df** with **C1j**) were obtained; the fact that heteroaddition products **3ab′**, **4ab′**, **3df′**, and **4df′** were not generated indicates that the H/D atom and the silyl group that added to the 1-octyne came from a single silane molecule. The results of the mixed-silane experiments exclude a catalytic cycle that starts from an Fe−H (Scheme 5, Path a) or Fe−Si (Scheme 5, Path b) species but support a Chalk−Harrod-type catalytic cycle[15] (Scheme 5, Path c) because the redox-neutral process involving Fe−Si or Fe−H species would inevitably lead to heteroaddition products. According to the literature, the precursor of the iron catalyst can be reduced to active Fe(0) species by EtMgBr.[16] A kinetic isotope effect experiment involving competitive hydrosilylation reactions between 1-octyne and phenylsilane/$PhSiD_3$ with catalysis by **C1g** (condition A) or **C1j** (condition B) showed first-order kinetic isotope effects (k_H/k_D = 4.0 and 3.8, respectively; Scheme 5B). These data indicate that hydrogen transfer might be a rate-limiting step.[17]

Scheme 5. Control Experiments



The kinetic isotopic effect experiment for parallel reactions failed to be performed because of the extremely fast reaction rate.

To obtain detailed information about this unusual divergent regioselectivity, we carried out DFT calculations on the transition-state of ligand to ligand hydrogen transfer (LLHT, **Ts-1a**) at all three possible spin states (singlet, triplet, and quintet) of the iron catalysts (Figure 1a). Gaussian 09 was used for calculations at the (dispersion-corrected) unrestricted ωB97XD/6-31G*/TZVP level of theory with CPCM-UωB97XD/def2-TZVPP single-point energy calculations. Our calculation revealed that the LLHT at triplet state has the lowest energy (^{3}**Ts-1a**, Figure 1a). Next, we calculated the energies of ^{3}**Ts-1** with iron catalysts **C1e** and **C1i**, which gave opposite regioselectivities under the identical conditions (Figure 1b and Table S7). When **C1e** was used, the energy of anti-Markovnikov addition transition state **Ts-1a** was about 3.5 kcal mol^{-1} lower than that of Markovnikov transition state **Ts-1a′**, which is consistent with the experimentally observed high anti-Markovnikov selectivity. In contrast, the calculations indicated that anti-Markovnikov addition transition state **Ts-1b** was 1.8 kcal mol^{-1} higher in energy than Markovnikov addition transition state **Ts-1b′** when **C1i** was used as the catalyst, which is again consistent with the observed high Markovnikov selectivity. The calculation results exhibited good accordance with the experimental outcomes of **C1b** and **C1d** as well (Figure S1).

To gain a better understanding of the parameters responsible for the regiodivergence of the reaction, we performed additional calculations by using 1,10-phenanthroline-modified iron catalyst **C1a** as a reference (Figure 1b). When this catalyst was used, the energy difference between transition states **Ts-1c** and **Ts-1c′**, which lead to anti-Markovnikov and Markovnikov selectivity, respectively, was very small (0.13 kcal mol^{-1}), indicating poor regioselectivity. Because coordination of the triple bond with the iron center was almost completely unaffected by the ligand, the overlap between the alkyne and iron center orbitals in this transition state was larger than that in any of the other transition states. Because of the directionality of molecular orbitals, addition of substituents to the 2- and 9-positions of the 1,10-phenanthroline ligand resulted in steric hindrance between the substituents, which decreased the overlap between the alkyne and iron orbitals and thus increased the transition state energy. To quantify the degree of orbital overlap, we chose the plane defined by the iron atom and the nitrogen atoms of the 1,10-phenanthroline ligand (Fe−N−N) as the reference and the dihedral angle (θ) between this plane and the plane defined by the iron atom and the carbon atoms of the alkyne triple bond (Fe−C−C) as an index to measure the orbital overlap. These calculations showed that the difference in dihedral angle ($\Delta\theta$) between anti-Markovnikov transition state **Ts-1a** and reference transition state **Ts-1c** ($\Delta\theta$ = 76.75° − 77.64° = −0.89°) was considerably lower than the difference for Markovnikov transition state **Ts-1a′** and **Ts-1c′** ($\Delta\theta$ = 78.40° − 80.92° = −2.52°); these results are consistent with the experimentally observed anti-Markovnikov selectivity exhibited by **C1e**. In contrast, when catalyst **C1i**, which has 3,5-disubstituted aryl groups, was used, the difference in dihedral angle between anti-Markovnikov transition state **Ts-1b** and reference transition state **Ts-1c** ($\Delta\theta$ = 81.51° − 77.64° = 3.87°) is greater than the difference between Markovnikov transition state **Ts-1b′** and **Ts-1c′** ($\Delta\theta$ = 83.10° − 80.92° = 2.18°), which is consistent

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J. Am. Chem. Soc. XXXX, XXX, XXX−XXX

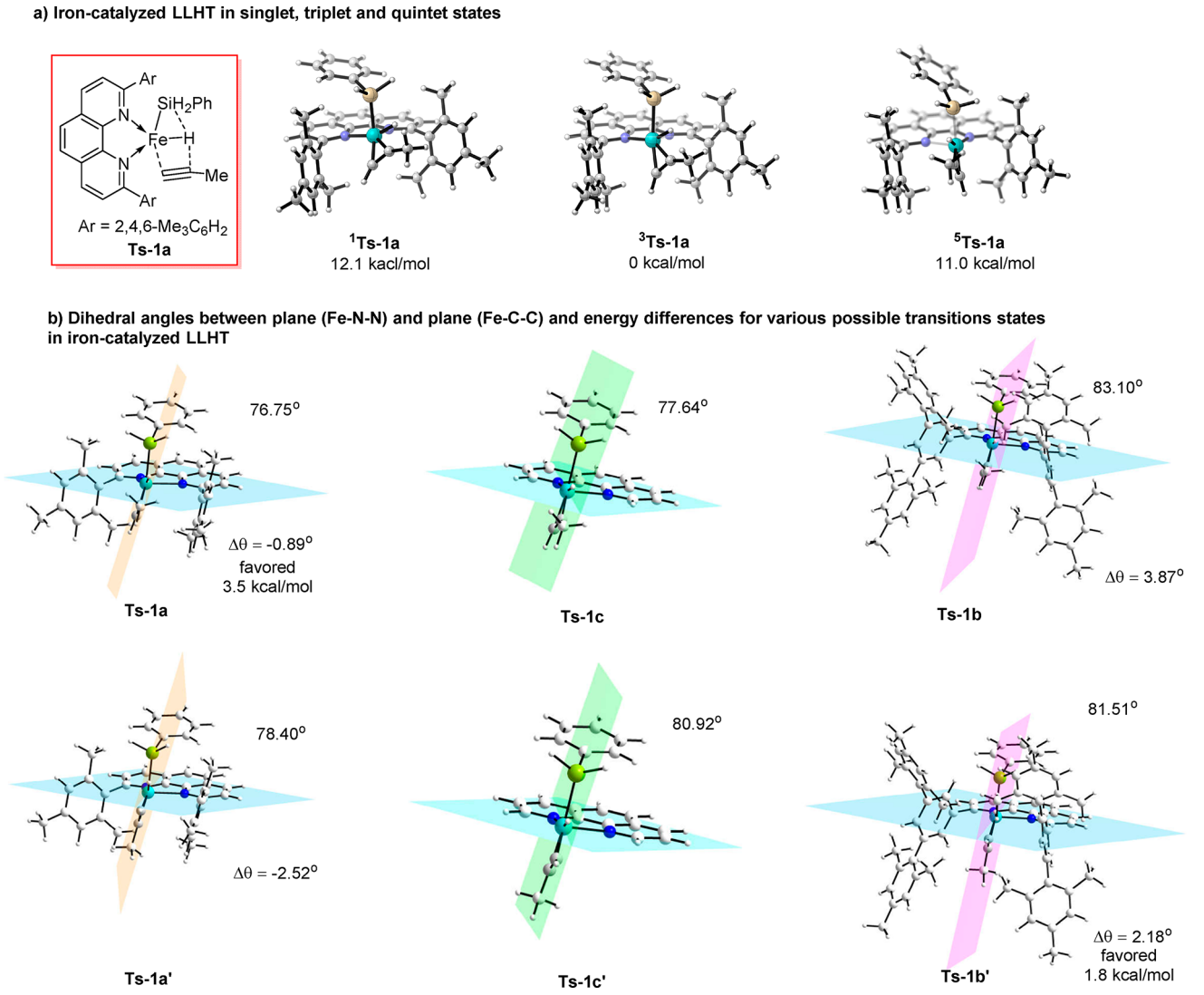

Figure 1. (a) Iron-catalyzed LLHT in singlet, triplet, and quintet states; (b) dihedral angles between plane (Fe−N−N) and plane (Fe−C−C) and energy differences for various possible transitions states in iron-catalyzed LLHT. Although the above calculations are helpful for understanding the activity and selectivity of iron catalysts, the other mechanisms and regioselective control models cannot be ruled out at the current stage. The isolation and determination of proposed intermediates are still undergoing in our laboratory.

with Markovnikov selectivity. These results indicate that the fundamental reason for the selectivity we observed is that the substituents on the sterically bulky 2,9-aryl groups of the 1,10-phenanthroline ligand deflected the alkyne during hydrogen migration and thus decreased the degree of overlap between the iron and alkyne molecular orbitals, which in turn permitted regiodifferentiation of the two ends of the alkyne. That is, the electronic structure of the triplet-state iron catalyst enabled fine discrimination of the steric differences between the two ends of the alkynes and thus allowed for the regiodivergent hydrosilylation.

SUMMARY

In summary, we have developed a protocol for stereospecific, regiodivergent hydrosilylation reactions of terminal and internal alkynes with primary silanes catalyzed by iron complexes bearing 2,9-diaryl-1,10-phenanthroline ligands. The catalytic system described herein can completely reverse the regioselectivity of various alkynes by simply changing the substitution pattern on the ligands and exhibits excellent activity (TONs up to 35 500). This protocol facilitated the preparation of vinyl silanes containing two Si−H bonds, which could therefore be used for highly selective synthesis of disubstituted and trisubstituted olefins, as well as for the potential of organosilicon materials. Mechanistic studies suggested that the iron catalysts might promoted the hydrosilylation by means of $2e^-$ redox cycle and maximization of the overlap between the iron and alkyne orbitals might be the driving force for the observed regioselectivity. The above-described findings have deepened our understanding of iron-catalyzed reactions and can be expected to facilitate the development of new iron catalysts and iron-catalyzed reactions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c09083.

Geometrical parameters for the structure of reagents (PDF)

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Crystallographic information file for **C1g**; this information is also available from the Cambridge Crystallographic Data Centre (https://www.ccdc.cam.ac.uk/) under reference number CCDC 1974110 (CIF)

Crystallographic information file for **C1h**; this information is also available from the Cambridge Crystallographic Data Centre (https://www.ccdc.cam.ac.uk/) under reference number CCDC 1960979 (CIF)

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Notes

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