

Article

Cobalt-Catalyzed Regiodivergent Hydrosilylation of Vinylarenes and Aliphatic Alkenes: Ligand- and Silane-Dependent Regioselectivities

Chao Wang, Wei Jie Teo, and Shaozhong Ge

ACS Catal., Just Accepted Manuscript • DOI: 10.1021/acscatal.6b02518 • Publication Date (Web): 28 Nov 2016 Downloaded from http://pubs.acs.org on November 28, 2016

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



ACS Catalysis is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Cobalt-Catalyzed Regiodivergent Hydrosilylation of Vinylarenes and Aliphatic Alkenes: Ligand- and Silane-Dependent Regioselectivities

Chao Wang, Wei Jie Teo, and Shaozhong Ge*

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore KEYWORDS: cobalt, hdyrosilylation, vinylarenes, aliphatic alkenes, regiodivergent, homogeneous catalysis

ABSTRACT: We report a regiodivergent hydrosilylation of alkenes catalyzed by catalysts generated in situ from bench-stable Co(acac)₂ and phosphine or nitrogen-based ligands. A wide range of vinylarenes and aliphatic alkenes reacted to afford either branched (45 examples) or linear (37 examples) organosilanes in high isolated yields (average: 84%) and high regioselectivities (from 91:9 to >99:1). This transformation tolerates a variety of functional groups including ether, silyloxy, thioether, epoxide, halogen, tertiary amine, ester, boronic ester, acetal, cyano, and ketone moieties. Mechanistic studies suggested that the hydrosilylation of alkenes catalyzed by the cobalt/bisphosphine system follows the Chalk-Harrod mechanism (with a Co-H intermediate) and the hydrosilylation of alkenes catalyzed by the cobalt/pyridine-2,6-diimine system follows the modified Chalk-Harrod mechanism (with a Co-Si intermediate). Systematic studies with sterically varied silanes revealed that the steric properties of silanes play a pivotal role in controlling the regioselectivity of vinylarene hydrosilylation and the chemoselectivity of the reactions of aliphatic alkenes and silanes catalyzed by the cobalt/pyridine-2,6-diimine system.

INTRODUCTION

Hydrosilylation of alkenes catalyzed by transition metals is the most straightforward and atom-economic approach to synthesize organosilanes, which can be converted to alcohols or used as monomers for the production of silicon-based polymers.¹ Platinum-catalyzed hydrosilylation of alkenes is one of the most frequently conducted catalytic processes in industry due to its effectiveness and high selectivity.² A number of other metals, such as lanthanides,³ early transition metals,⁴ iron,⁵ cobalt,⁶ nickel,⁷ rhodium,⁸ and iridium,⁹ have also been used for this transformation. The majority of these catalysts show high selectivity toward *anti*-Markovnikov hydrosilylation.

In contrast, the Markovnikov selective hydrosilylation of alkenes has been barely studied and only a limited number of transition metals (lanthanides,^{3a,3e} Zr,¹⁰ Ni^{7b} and Pd¹¹) have been used to catalyze this transformation, but with limited substrate scope or with modest regioselectivities. For example, hydrosilylation of vinylarenes can be achieved in high regioselectivity with lanthanide catalysts, but this transformation showed very limited functional group tolerance.^{3a} It is difficult to find catalysts that can combine high catalyst activity, high selectivity and broad substrate scope for Markovnikov hydrosilylation of alkenes. During the preparation of this manuscript, Huang's group reported a cobalt-catalyzed Markovnikov hydrosilylation of aliphatic alkenes,¹² but the reported cobalt catalyst was not selective for hydrosilylation of vinylarenes. For example, the hydrosilylation of styrene with PhSiH₃ catalyzed by the reported cobalt catalyst proceeded with low regioselectivity and afforded a 1:1 mixture of linear and branched organosilane products.¹² Here we report effective cobalt catalysts that can selectively catalyze either Markovnikov or *anti*-Markovnikov hydrosilylation of both vinylarenes and aliphatic alkenes. Mechanistic studies reveal a pronounced ligand- and silane-dependent regioselectivity.



Scheme 1. Expected Pathways for Co-Catalyzed Regiodivergent Hydrosilylation of Vinylarenes (A and B) and Aliphatic Alkenes (C and D)

Our rationale to develop the Co-catalyzed regiodivergent hydrosilylation of alkenes is depicted in Scheme 1. Phosphineligated cobalt hydride complexes have been well studied for hydroformylation of alkenes.¹³ Migratory insertion of alkenes into metal-hydride bonds has been shown to provide a versatile foundation for hydrofunctionalization of alkenes.¹⁴ As for migratory insertion, vinylarenes have an electronic preference for 2,1-insertion to form a secondary benzylcobalt species (I) over 1,2-insertion to form a primary alkylcobalt species (II).^{3a,15} Due to steric influence of the alkyl group on the cobalt center, the major species (I) is less reactive than the minor species (II) toward σ -bond metathesis,¹⁶ but these two intermediates are interconverted through β -H elimination and reinsertion of vinylarene into the Co-H bond. We envision that a Co-alkyl species coordinated with an appropriate ligand can selectively react with sterically differentiated hydrosilanes to produce either branched (Markovnikov selective, pathway A) or linear (anti-Markovnikov selective, pathway B) organosilanes.

In contrast, aliphatic alkenes have a steric preference for 1,2-insertion to generate a primary alkylcobalt species (III) over 2,1-insertion to generate a secondary alkylcobalt species (IV).^{3a,17} Since the major intermediate (III) is more reactive than the minor intermediate (IV) toward σ -bond metathesis, the pathway involving "Co-H" will preferentially produce linear alkylsilanes (pathway C) regardless of the hydrosilanes used. To develop a Co-catalyzed Markovnikov hydrosilylation of aliphatic alkenes, we envision that a pathway involving a Co-Si intermediate (bearing a less congested silyl group) will operate, as aliphatic alkenes have a steric preference for 1,2-insertion over 2,1-insertion. This pathway is designated as D in Scheme 1. A pathway involving a Co-Si species was previously proposed by Chirik for the Co-catalyzed dehydrogenative silylation of alkenes.¹⁸

RESULTS AND DISCUSSION

Evaluation of Ligands and Silanes for the Co-Catalyzed Regiodivergent Hydrosilylation of Styrene. We initiated our studies on the Co-catalyzed regiodivergent hydrosilylation of vinylarenes by evaluating the reactions of styrene with sterically varied hydrosilanes, such as PhSiH₃, Ph₂SiH₂, PhMe-SiH₂, Et₃SiH, (EtO)₂MeSiH, (EtO)₃SiH, and (Me₃SiO)₂MeSiH (MD'M). We examined a variety of cobalt precursors, ligands, and temperatures for these model reactions. The selected examples of these experiments are summarized in Table 1 (see the Supporting Information for the detailed evaluation).

The reactions of styrene with primary silane PhSiH₃ were carried out with 1 mol % of cobalt catalyst at room temperature or 50 °C (entries 1–5). Reactions catalyzed by the combination of Co(acac)₂ and dppf or dpephos occurred in low conversions (entries 1 and 2). Interestingly, the reaction conducted with the catalyst generated from Co(acac)₂ and xantphos at room temperature proceeded to full conversion with excellent selectivity (97%) for Markovnikov hydrosilylation (entry 3). The same reactions conducted at 50 °C proceeded to full conversion, but with slightly lower regioselectivity (entry 4). We also tested anitrogen-based ligand ^{mes}PDI (entry 5) and the reaction afforded a mixture of the branched and linear products with *b/l* of 69:31. The reactions of styrene with secondary silane Ph_2SiH_2 were conducted with 2 mol % cobalt catalysts at room temperature or 50 °C (entries 6–11). The reaction conducted with 2 mol % of Co(acac)₂ and xantphos at room temperature did not produce any hydrosilylation products (entry 6). The same reaction conducted at 50 °C proceeded to full conversion and afforded a mixture of branched and linear products with the ratio of 36:64 (entry 7). The catalyst generated in situ from Co(acac)₂ and dpephos showed very low reactivity (entry 8). Improved results were obtained for the reaction conducted with Co(acac)₂/dppf and these reactions occurred in full conversion with 98% selectivity for the linear product at room temperature or 50 °C (entries 9 and 10). In addition, the combination of Co(acac)₂ and ^{mes}PDI did not catalyze styrene hydrosilylation with Ph₂SiH₂ at 50 °C (entry 11).

 Table 1. Evaluation of Cobalt Precursors, Ligands, and
 Silanes for Hydrosilylation of Styrene^a

		Co(acac) ₂ (1–2 mol %) ligand (1–2 mol %)		ol %) %) [Si]	+[Si]	
Ph ² 🚿	+ [5]	THF	, temp, 6 h	Ph Me branched	⁺ Ph ⁻ V ¹⁰¹	
entry	ligand (r	nol %)	temp	conversion (%)	product ratio (b/l)	
[Si-H] = PhSiH ₃ , entries 1–10						
1	dppf (1)	rt	<2	-	
2	dpepho	os (1)	rt	15	76:24	
3	xantph	os (1)	rt	>98	97:3	
4	xantphos (1)		50 °C	>98	87:13	
5	^{mes} PDI	(2)	50 °C	>98	69:31	
		[Si-H] = I	Ph₂SiH₂, e	entries 10–11		
6	xantph	os (2)	rt	0	_	
7	xantph	os (2)	50 °C	>98	36:64	
8	dpepho	os (2)	50 °C	12	21:79	
9	dppf (2)	50 °C	>98	2:98	
10 ^b	dppf (2)	rt	>98	2:98	
11	^{mes} PDI	(2)	50 °C	0	-	
PPPha a A Me Me						



^aConditions: styrene (0.500 mmol), silane (0.550 mmol), cobalt precursor (5.0–10.0 μ mol), ligand (5.0–10.0 μ mol), THF (1 mL), conversions and product ratios are determined by GC analysis using dodecane as internal standard; ^b24 h.

The reactions of styrene with tertiary silanes (Ph₃SiH, PhMe₂SiH, Et₃SiH, and (EtO)₂MeSiH) did not occur in the presence of 2 mol % of Co(acac)₂ and xantphos at 50 °C. The lack of reactivity for this Co(acac)₂/xantphos-catalyzed hydrosilylation with tertiary silanes implies two possibilities: (1) Co(acac)₂ can not be activated by these tertiary silanes to generate active cobalt species; (2) the combination of Co(acac)₂ and xantphos does not catalyze the hydrosilylation of styrene with tertiary silanes under the applied conditions. To distinguish these two cases, we conducted hydrosilylation of styrene with tertiary silanes at 50 °C in the presence of 3 mol % of Co(acac)₂/xantphos and 30 mol % of PhSiH₃ (to activate the cobalt catalyst precursor). These reactions exclusively afforded the branched benzylic silane (from the reaction with

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41 42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58 59 60 PhSiH₃), without the formation of any hydrosilylation products from reactions with tertiary silanes. These results confirm the possibility (2), but can not rule out the possibility (1).

The data in Table 1 indicate that silanes have significant effects on the regioselectivity of styrene hydrosilylation. For the same catalyst system (entries 2 and 8; 3 or 4 and 7), the reaction with PhSiH₃ afforded the branched benzylic silane as the major product (entries 2, 3, and 4), but the corresponding reaction with Ph₂SiH₂ gave the linear silane as the major product (entries 7 and 8). This inverted regioselectivities were expected from the proposed pathways **A** and **B** in Scheme 1, as Ph₂SiH₂ is more congested than PhSiH₃. Reactions with more sterically varied silanes to illustrate this observed silane effects will be discussed in detail in the mechanistic consideration section.

Evaluation of Ligands and Silanes for the Co-Catalyzed Regiodivergent Hydrosilvlation of 1-Octene. After identifying the conditions for regiodivergent hydrosilylation of styrene, we evaluated the conditions for hydrosilylation of 1octene and the selected experiments are summarized in Table 2. The reactions of 1-octene with PhSiH₃ conducted with catalysts generated in situ from Co(acac)₂ and xantphos, dppf or dppe occurred in full conversion at room temperature in 3 h and afforded the linear product in high yields with only trace amounts of the branched product (entries 1-3). The same reactions with more congested Ph₂SiH₂ proceeded sluggishly and gave the linear product in low to modest yields (entries 4-6). In addition, we also conducted the 1-octene hydrosilylation at 60 °C (entry 7) and the similarly high regioselectivity was obtained compared to the reaction at room temperature (entry 1). The same regioselectivity observed for 1-octene hydrosilylation with sterically differentiated silanes PhSiH₃ and Ph₂SiH₂ can be explained by the preferential formation of more reactive primary alkyl cobalt species by the 1,2-insertion of 1-octene to the Co-H bond (pathway C in Scheme 1). Under the conditions for entries 1 and 7, 1-octene did not undergo hydrosilylation with tertiary silanes (Ph₃SiH, PhMe₂SiH, Et₃SiH, and (EtO)₂MeSiH).

Table 2. Evaluation of Cobalt Precursors, Ligands, andSilanes for Hydrosilylation of 1-octene^a

 $\begin{array}{c} \text{Co(acac)}_2 (2-3 \text{ mol } \%)\\ n\text{-}C_6H_{13} & + [\text{H-Si]} \xrightarrow{\text{ligand } (2-3 \text{ mol } \%)} & I \end{array}$

		· · ·	,, 0 ₆ b	ranched	linez	ar
entry	ligand (mol %)	[H-Si]	temp.	time [h]	yield [' branched	%] linear
1	xantphos (2)	PhSiH₃	r.t.	3	<2	95
2	dppf (2)	PhSiH ₃	r.t.	3	<2	91
3	dppe (2)	PhSiH ₃	r.t.	3	<2	87
4	xantphos (2)	Ph_2SiH_2	r.t.	3	<2	26
5	dppf (2)	Ph_2SiH_2	r.t.	3	<2	<2
6	dppe (2)	Ph_2SiH_2	r.t.	3	<2	62
7	xantphos (2)	PhSiH ₃	60 °C	3	<2	93
8	^{mes} PDI (3)	PhSiH ₃	60 °C	24	55	<2
9	^{iPr} PDI (3)	PhSiH ₃	60 °C	24	37	<2
10 ^b	^{mes} PDI (3)	PhSiH ₃	60 °C	24	84	<2
11°	^{mes} PDI (3)	PhSiH ₃	60 °C	24	96	<2
12°	^{mes} PDI (3)	PhSiH ₃	rt	24	<5	-

^aConditions: 1-octene (0.500 mmol), silane (0.550 mmol), cobalt precursor (10.0–15.0 μ mol), ligand (10.0–15.0 μ mol), THF (1 mL), yields are determined by GC analysis using dodecane as internal standard; ^bhexane (1 mL); ^ctoluene (1 mL).

To develop the Co-catalyzed Markovnikov hydrosilylation of aliphatic alkenes, we studied the hydrosilylation of 1-octene with Co(acac)₂ and nitrogen-based pyridine-2,6-diimine (PDI) ligands, a class of ligand used for the Co-catalyzed dehydrogenative silylation of aliphatic alkenes.^{6i, 18} The reaction of 1-octene with PhSiH₃ catalyzed by 3 mol % of Co(acac)₂ and ^{mes}PDI in THF at 60 °C proceeded sluggishly and afforded the branched product in 55% yield (entry 8). The use of more congested ^{iPr}PDI ligand led to a decreased yield (entry 9). However, the reactions conducted in hexane and toluene occurred smoothly and afforded the branched product in high yields and high selectivity (entries 10 and 11). This observed solvent effect might stem from the coordinating ability of solvents (THF > toluene > hexane) and the solubility of the catalyst in these solvents (THF ~ toluene > hexane).¹⁹

The reaction of 1-octene with Ph_2SiH_2 in the presence of 3 mol % of Co(acac)₂ and ^{mes}PDI at 60 °C proceeded very sluggishly and afforded a mixture of branched/linear alkylsilane and *E/Z*-allylsilane products in a low yield (the total yield for the four products <10%). The detailed studies with tertiary silanes (PhMe₂SiH, Et₃SiH, and (EtO)₃SiH) to reveal the silane effects on selectivity for the Co/PDI catalysts will be discussed in the mechanistic study section.

Scope of the Co-Catalyzed Markovnikov Hydrosilylation of Vinylarenes. With an active catalyst and reliable conditions identified for the Markovnikov hydrosilvlation of styrene (entry 3 in Table 1), we studied the scope of vinylarenes that undergo this transformation. The results are summarized in Table 3. In general, a wide range of vinylarenes containing electronically and sterically varied aryl groups reacted with PhSiH₃ smoothly at room temperature in the presence of 1 mol % Co(acac)₂ and 1 mol % xantphos, yielding the corresponding secondary benzylic silanes (1a-1w) in modest to excellent isolated yields (51%-96%, average: 86%) with high to excellent regioselectivities (b/l ratio: 97:3 to >99:1). The GC-MS analysis on the crude mixtures of these reactions indicated that vinylsilanes, products derived from catalytic dehydrogenative silylation of vinylarenes, were not formed during this catalytic hydrosilylation reaction.²

The data in Table 3 show that the electronic properties of the aryl groups do not have significant influence on this Cocatalyzed hydrosilylation. Products from reactions of vinylarenes containing electron-deficient (1a-1f) and electronrich (1h-1l) aryl groups were isolated in similarly high yields as the product (1g) from the reaction of styrene.

The steric hindrance at the *meta*-position (1a, 1n, and 1u) or the *para*-position (1b, 1e, 1h-1m, 1o-1s, 1v, and 1w) of aryl groups has little influence on the regioselectivities. However, the steric hindrance at the *ortho*-position has significant influence on the regioselectivities. For example, the hydrosilylation of 2-fluorostyrene afforded the branched silane as the major product with b/l of 70:30 (1x), but the reaction of 2,4dimethylstryrene gave the linear silane as the major product with b/l of 20:80 (1y). In particular, the sterically demanding 2,4,6-trimethylstyrene reacted to afford linear products exclusively (1z).

Si

 Table 3. The Scope of Vinylarenes for the Co-Catalyzed

 Markovnikov Hydrosilylation with PhSiH₃^a



^aConditions: vinylarene (0.500 mmol), PhSiH₃ (0.550 mmol), Co(acac)₂ (5.0 μ mol), xantphos (5.0 μ mol), THF (1 mL), yields of isolated products; ^b2 mol % catalyst. Cl?

Scope of the Co-Catalyzed *anti*-Markovnikov Selective Hydrosilylation of Vinylarenes. Table 4 summarizes the scope of vinylarenes for the Co-catalyzed *anti*-Markovnikov hydrosilylation of vinylarenes. These reactions were conducted with Ph_2SiH_2 in the presence of 2 mol % of Co(acac)₂ and 2 mol % of dppf at 50 °C for 6 h. In general, a range of electronically and sterically varied vinylarenes reacted under these conditions to produce the corresponding linear organosilanes (2a-2o) in high isolated yields (70%–97%, average: 85%) and excellent regioselectivities (l/b ratio: >99:1). These reactions did not form any vinylsilanes, as indicated by the GC-MS analysis on the crude reaction mixtures.

This $Co(acac)_2/dppf$ -catalyzed *anti*-Markovnikov hydrosilylation of vinylarenes tolerates a range of functionalities, including fluoro (**2e** and **2l**), ether (**2i**), tertiary amine (**2j**), siloxy (**2k**), and acetal (**2o**) moieties. Vinylarenes containing ketone, ester, cyano, nitro, chloro, bromo, or free hydroxyl groups are not compatible with the reaction conditions. This relatively narrow scope of vinylarenes, compared with the scope of vinylarene for Markovnikov hydrosilylation (Table 3), might be due to the presence of a Co-H intermediate at a higher temperature (50 °C).

Table 4. The Scope of Vinylarenes for the Co-Catalyzed *anti*-Markovnikov Hydrosilylation with Ph₂SiH₂^a



^aConditions: vinylarene (0.500 mmol), Ph_2SiH_2 (0.550 mmol), $Co(acac)_2$ (10.0 µmol), dppf (10.0 µmol), THF (1 mL), yields of isolated products; ^b $Co(acac)_2$ (15.0 µmol) and dppf (15.0 µmol).

The Scope of Aliphatic Alkenes for the Co-Catalyzed Markovnikov Hydrosilylation. The scope of aliphatic alkenes that undergo this Co-catalyzed Markovnikov hydrosilylation is summarized Table 5. In general, a wide range of aliphatic alkenes reacted with PhSiH₃ in the presence of 3 mol % of Co(acac)₂/^{mes}PDI in toluene at 60 °C, affording the branched organosilanes (**3a–3r**) in high yields (50%–98%, average: 83%) with high to excellent regioselectivities (*b/l* ratio: 91:9 to >99:1). However, alkenes containing allylether moiety (**3s–3u**) reacted with modest regioselectivities (*b/l* ratio: 68:32 to 71:29). As these allylether substrates are not expected to have an electronic preference for 2,1-insertion into a Co-Si intermediate (a Co-Silyl species is proposed to be active for the Co/^{mes}PDI-catalyzed reaction of alkenes with silanes), the increased amount of linear products is likely to

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20 21

22 23

24

25

26 27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59 60 stem from the interaction of the substrate ether groups with the cobalt center. The GC-MS analysis on the crude mixtures of these reactions (3a-3u) indicated that vinylsilanes or allylsilanes, products derived from the Co-catalyzed dehydrogenative silylation of alkenes, were not formed.¹⁸

This transformation tolerates a wide range of functional groups, such as ether (**3g**, **3s**, **3t**), thioether (**3h**), siloxy (**3i**), chloro (**3j**), bromo (**3k**), ester (**3l**–**3n**), amide (**3o**), acetal (**3p**), ketone (**3q**), pyridine (**3r**), and epoxide (**3u**) moieties. However, internal alkenes and alkenes containing aldehyde, nitro, unprotected hydroxyl, or unprotected amine group did not react under these conditions.

Table 5. The Scope of Aliphatic Alkenes for the Co-Catalyzed Markovnikov Hydrosilylation with PhSiH3^a



^aConditions: aliphatic alkene (0.500 mmol), PhSiH₃ (0.550 mmol), Co(acac)₂ (15.0 μ mol), ^{mes}PDI (15.0 μ mol), toluene (1 mL), yields of isolated products; ^b5 mol % catalyst.

Scope of the Co-Catalyzed *anti*-Markovnikov Hydrosilylation of Aliphatic Alkenes. Table 6 summarizes the scope of alkenes for the Co-catalyzed *anti*-Markovnikov hydrosilylation. A wide range of functionalized aliphatic alkenes readily reacted with PhSiH₃ in the presence of 2 mol % of Co(acac)₂ and xantphos in THF at room temperature, providing the corresponding linear products (4a–4s) in high isolated yields (57%–93%, average: 80%) with excellent regioselectivities (*l/b* ratio >99:1). These reactions did not produce any vinylsilanes or allylsilanes, as indicated by the GC-MS analysis on the crude mixtures of these reactions.

This $Co(acac)_2/xantphos-catalyzed anti-Markovnikov hydrosilylation of aliphatic alkenes shows high functional group tolerance. A wide range of functional groups, including ether (4i), epoxide (4j), siloxy (4k-4m), chloro (4n), cyano (4o), ester (4p, 4r, and 4s), and acetal (4q) moieties, are compatible$

with the reaction conditions. However, internal alkenes and alkenes containing aldehyde, ketone, nitro, free hydroxyl, or free amine group did not react under these identified conditions.

10 mmol-Scale Reaction. As both $Co(acac)_2$ and phosphine ligands used for this transformation are bench-stable, we tested the hydrosilylation of 4-*tert*-butylstyrene with PhSiH₃ on a 10 mmol scale in the presence of 0.2 mol % of $Co(acac)_2$ /xantphos weighed on the benchtop without using a dry box (See the Supporting Information for the 10 mmol-scale reactions of other three procedures). This reaction afforded **1i** in 93% isolated yield. Benzylic silane **1i** was readily oxidized by H_2O_2 in the presence of KHCO₃, yielding the corresponding benzylic alcohol in 96% isolated yield (for procedures, see the Supporting Information). Thus, this Cocatalyzed Markovnikov hydrosilylation can be conducted on a scale that would allow practical applications in synthesis.

Table 6. The Scope of Aliphatic Alkenes for the Co-Catalyzed *anti*-Markovnikov Hydrosilylation with PhSiH₃^a

R + PhSiH ₃	Co(acac) ₂ (2 mol %) xantphos (2 mol %) THF, rt, 3 h	∽SiH₂Ph 4a–4s
$Me \underbrace{J_n}_{n} SiH_2Ph$ n = 3, 4a , 91%, <i>l/b</i> = >99:1 n = 5, 4b , 87%, <i>l/b</i> = >99:1 n = 9, 4c , 81%, <i>l/b</i> = >99:1 n = 13, 4d , 88%, <i>l/b</i> = >99:1	→ SiH₂Ph = 0, 4e , 77%, <i>l/b</i> = >99:1 = 1, 4f , 82%, <i>l/b</i> = >99:1	$\begin{tabular}{lllllllllllllllllllllllllllllllllll$
Ph $^{-0}$ $_{/3}$ SiH ₂ Ph 0 4i, 90%, <i>l/b</i> = 98:2 4j		1eO) ₃ SiSiH ₂ Ph 4k, 57%, <i>l/b</i> = >99:1
(EtO) ₃ Si SiH ₂ Ph 4I , 80%, <i>I/b</i> = >99:1	TBSO () ₄ SiH ₂ Ph 4m , 80%, <i>l/b</i> = >99:1	Cl
NC	0 MeO 4 p , 66%, <i>l/b</i> = >99:1	EtOO OSiH ₂ Ph
0 Me SiH₂Ph 4q, 85%, //b = >99:1	AcO	∪ OEt 4s , 89%, <i>l/b</i> = >99:1

^aConditions: aliphatic alkene (0.500 mmol), PhSiH₃ (0.550 mmol), Co(acac)₂ (10.0 μ mol), xantphos (10.0 μ mol), THF (1 mL), yields of isolated products.

Mechanistic Consideration. The mechanism of the Cocatalyzed alkene hydrosilylation with *anti*-Markovnikov selectivity has been studied in detail. In general, these reactions follow either the Chalk–Harrod mechanism or the Modified Chalk–Harrod mechanism.^{1e} In the Chalk–Harrod mechanism, the migratory insertion of alkene into a Co-H bond (hydrometallation) is a key step.^{6b} However, in the modified Chalk–Harrod mechanism, the migratory insertion of alkene into a Co-Si bond (silylmetallation) is a key step.²¹ To rationalize the obtained regioselectivity for these Co-catalyzed hydrosilylation of vinylarenes and aliphatic alkenes, we conducted the following mechanistic studies.

Cobalt/Phosphine Catalyst System. To study the activation of Co(acac)₂/bisphosphine in the presence of silane, we tested the reaction of Co(acac)₂ with 8 equivalents of PhSiH₃ in the presence of 2 equivalents of dppe in THF- d_8 on an NMR scale (see the Supporting Information). A diagnostic ¹H NMR resonance (quintet, $J_{PH} = 23.6$ Hz) at δ -15.1 ppm confirmed the

As proposed in Scheme 1 (pathways A and B), cobalt alkyl species generated from 1,2-insertion and 2,1-insertion of vinylarene into the Co-H bond can be interconverted through β -H elimination and re-insertion of vinylarene into the Co-H bond. To test this hypothesis, we conducted the hydrosilylation of 4-*tert*-butylstyrene- $\beta_1\beta_2$ (eqs 1 and 2). The deuterium incorporation on the α -carbon (benzylic position) and silicon atom of the products supports the formation of a Co-H intermediate. The deuterium scrambling between β - and α -carbon occurred through β -hydrogen elimination and re-insertion of olefin into the resulting Co-D bond (Scheme 2). The incorporation of deuterium on the silicon atom of the products resulted from Co-D/Si-H hydride exchange. To provide evidence for this Co-D/Si-H hydride exchange, we analyzed the isotope pattern (GC-MS) of the unreacted Ph₂SiH₂ for the reaction (eq 2) and found the incorporation of deuterium into Ph_2SiH_2 (see the Supporting Information). Furthermore, we conducted the Markovnikov hydrosilylation of 4-tert-butylstyrene with $PhSiD_3$ (eq 3) and we found similar deuterium incorporation for the product of this reaction as for the product of the reaction depicted in eq 1.



Scheme 2. Deuterium Scrambling between β - and α -Carbon of Vinylarene

We also tested the hydrosilylation of 1-dodecene- $1, 1-d_2$ with PhSiH₃ catalyzed by Co(acac)₂/xantphos (eq 4). Different

from reactions of 4-*tert*-butylstyrene- β , β - d_2 (eqs 1 and 2), the reaction of 1-dodecene-1,1- d_2 afforded the product with deuterium atoms mainly localized on the methylene carbon next to the silyl group, with only a detectable amount of deuterium incorporation onto the β -carbon and silicon atom (eq 4). This observation implies that 1-dodecene-1,1- d_2 predominantly undergoes 1,2-insertion into the Co-H intermediate to generate a Co-alkyl species with deuterium on the α -carbon of the alkyl group (eq 5). Subsequent β -hydrogen elimination from the resulting Co-alkyl species forms the Co-H intermediate.



For comparison with *anti*-Markovnikov hydrosilylation of 1-dodecene- $1, 1-d_2$ catalyzed by the Co/xantphos system, we discuss the Markovnikov hydrosilylation of this alkene with PhSiH₃ here (eq 6). This reaction afforded the branched product with deuterium localized exclusively on the β -carbon. Deuterium was not detected for the α -carbon and silicon positions by ²H NMR analysis. In addition, we tested the Markov-nikov hydrosilylation of 1-dodecene with PhSiD₃ (eq 7). This reaction afforded the product with deuterium localized exclusively on the β -carbon and silicon atoms, as indicated by ²H NMR analysis. Furthermore, ¹H NMR analysis showed that hydrogen was not incorporated onto the silicon of the product. These results stand against the formation of a Co-H species during the Co(acac)₂/^{mes}PDI-catalyzed Markovnikov hydrosilylation.



As proposed in Scheme 1 (pathway A and B), the steric properties of silanes have significant effect on the regioselectivity of vinylarene hydrosilylation. Indeed, the data in Table 1 (entries 7 and 13) showed this profound silane effect on the regioselectivity. However, reactions with more silanes are needed to consolidate the observed silane effect. Accordingly, we tested a variety of sterically varied silanes for hydrosilylation of styrene and the results are summarized in Table 7. The results indicated that increasing the steric hindrance around Si-H (from entry 1 to entry 5) favors the formation of linear products (*anti*-Markovnikov selectivity). These data support the proposed pathways **A** and **B** in Scheme 1. Compared with the b/l ratio of 97:3 for the reaction at room temperature (entry 3 in Table 1), the relatively lower b/l ratio of 85:15 (entry 1 in Table 7) is likely due to the elevated reaction temperature.

ACS Catalysis

Table 7. Hydrosilylation of Styrene with Sterically Varied Silanes Catalyzed by Co(acac)₂/xantphos^a

Ph 🔨	Co(acac) ₂ (3 mol %) xantphos (3 mol %)	SiHPh(R) +	SiHPh(R)
PhSi(R)	H ₂ THF, 50 °C, 6 h	Ph Me	FII
		branched	linear
entry	PhSi(R)H ₂	conv. (%)	product ratio (<i>b/l</i>)
1	PhSiH ₃	>99	85:15
2	PhH ₂ Si	1e >99	65:35
3	Ph_2SiH_2	>99	34:66
4	PhH ₂ Si	55	3:97
5	Me PhH ₂ Si Me	72	2:98

^aConditions: styrene (0.250 mmol), silane (0.275 mmol), Co(acac)₂ (7.5 μ mol), xantphos (7.50 μ mol), conversion of styrene and *b*/*l* ratios are determined by GC analysis with dodecane as internal standard.

Cobalt/^{mes}PDI Catalyst System. Pyridine-2,6-diimine (PDI) cobalt complexes have been studied in detail by Chirik's group for the Co-catalyzed dehydrogenative silylation of terminal alkenes.¹⁸ They found that reactions of a wide range of hydrosilanes with 2 equivalents of terminal alkenes in the presence of (^{mes}PDI)CoMe (0.5 mol %) in neat afforded allylsilanes (*E/Z* mixture) and/or *E*-vinylsilanes with the concomitant formation of an equimolar amount of alkanes. Mechanistic studies revealed rapid β -hydride elimination from a Coalkyl intermediate (formed by migratory 2,1-insertion of alkene into a Co-Si species) prior to turnover-limiting reaction with silanes as the origin of the obtained selectivity (the DHS pathway in Scheme 3).

In this study, we found that $Co(acac)_2/^{mes}PDI$ -catalyzed hydrosilylation reactions of aliphatic alkenes with primary silane PhSiH₃ readily afforded branched products in high yields with excellent selectivity when conducted with alkenes as limiting reagents in toluene (Table 5). To rationalize this obtained Markovnikov selectivity, which is different from the reported dehydrogenative silylation for the Co/^{mes}PDI system,¹⁸ we tested Co(acac)₂/^{mes}PDI catalyst for the reactions of 1-octene with a variety of silanes, such as Ph₂SiH₂, PhMe₂SiH, Et₃SiH, and (EtO)₃SiH. However, only the reaction with Ph₂SiH₂ occurred, but with very low conversions (<5%). These results indicated that these silanes are not reactive enough to activate Co(acac)₂ in the presence of ^{mes}PDI.

Subsequently, we conducted the hydrosilylation reaction of 1-octene with selected silanes using well-defined cobalt alkyl complex (^{mes}PDI)CoMe 23 and the results are summarized in Table 8. The reaction with primary silane PhSiH₃ produced the branched silane as the major product (entry 1), which is comparable to the results of the reaction catalyzed by Co(acac)₂/ ^{mes}PDI (entry 11 in Table 2). Ph₂SiH₂ and (EtO)₃SiH

reacted to give a mixture of branched/linear alkylsilanes and E/Z-allylsilanes (entries 2 and 3). In particular, tertiary silanes PhMe₂SiH and Et₃SiH reacted with complete selectivity for dehydrogenative silylation (entries 4 and 5).

Table 8. Hydrosilylation of 1-Octene with Primary, Secondary, and Tertiary Silanes^a

n-hex + [Si-H] (mesPDI)CoMe (2 mol %) toluene, 50 °C, 5 h conv. of 1-octene >98% [Si] n-hex Inear n-hex Me branched allyIsilan						[Si] near [Si] Isilane
entr	y [Si-H]	ratios branched	of produ I linear	ct distribution allyIsilane (<i>E/Z</i>)	1,2-insertion	2,1-insertion
1	$PhSiH_3$	91%	9%	0%	91%	9%
2	Ph_2SiH_2	57%	25%	18% (1:1)	57%	43%
З	(EtO) ₃ Si⊦	1 12%	36%	52% (2:1)	12%	88%
4	PhMe₂Si⊦	H 0%	0%	>99% (4:3)	0%	>99%
5	Et ₃ SiH	0%	0%	>99% (3:2)	0%	99%

^aConditions: 1-octene (0.250 mmol), silane (0.275 mmol), cobalt catalyst (5.0 μ mol), toluene (0.5 mL), conversion of 1-octene and the ratios of product distribution were determined by GC analysis with dodecane as internal standard.

The data in Table 8 indicate a pronounced silane effect on the regio- and chemoselectivity for the Co/mesPDI-catalyzed reaction of 1-octene with silanes. It is well established that these reactions proceed through a cobalt silvl intermediate.¹ As the migratory insertion of aliphatic alkenes is mainly controlled by sterics, the steric interaction between alkene and cobalt silvl species could account for the observed selectivity. Three pathways are shown in Scheme 3 for catalytic reactions of aliphatic alkenes and silanes. (1) For the cobalt species containing a small silvl group, the alkene has a preference for 1,2insertion due to the weak steric repulsion between alkene and silyl group. The resulting Co-alkyl species (with a primary alkyl group) reacts with silane to release the branched hydrosilylation product (MHS pathway). (2) When the cobalt intermediate contains a sterically demanding silvl group, the strong steric repulsion between alkene and the silvl group disfavors 1,2-insertion. Instead, 2,1-insertion occurs to generate a Coalkyl species (with a secondary alkyl group). The subsequent reaction of this Co-alkyl species with hydrosilane will afford the linear hydrosilylation product (anti-MHS pathway). (3) If the Co-alkyl species resulted from 2,1-insertion does not react with the sterically congested silane or the reaction is much slower compared with β -H elimination, the Co-alkyl complex will undergo β -H elimination to release allyl or vinyl silane product (DHS pathway). Subsequently, alkene undergoes migratory insertion into the resulting Co-H bond to form a cobalt-alkyl species, which reacts with hydrosilane to regenerate the Co-silvl intermediate with the concomitant formation of an alkane byproduct.¹⁸

1





The pathways depicted in Scheme 3 show that the branched hydrosilylation product results from 1,2-insertion of alkenes and 2,1-insertion can lead to both linear hydrosilylation and dehydrogenative silvlation products. Based on this, the silane effect on the migratory 1,2-/2,1-insertion of 1-octene for the Co/mesPDI system is quantified and the data are listed in Table 8. The reaction of 1-octene with the sterically least congested primary silane PhSiH₃ primarily follows the MHS pathway in Scheme 3, affording the branched silane as the major product (entry 1 in Table 8). The reactions of 1-octene with sterically most congested tertiary silanes (PhMe₂SiH and Et₃SiH) proceed through the DHS pathway and afford allyl or vinylsilanes exclusively (entries 4 and 5 in Table 8). All three pathways in Scheme 3 operate for reactions of 1-octene with hydrosilanes of medium steric hindrance (Ph₂SiH₂ and (EtO)₃SiH) and products from both hydrosilvlation and dehydrogenative silylation were obtained (entries 2 and 3).

CONCLUSION

We have developed convenient and efficient protocols for the Co-catalyzed regioselective hydrosilylation of alkenes. The cobalt catalysts are generated from bench-stable Co(acac)₂ and ligands, and in situ activated by hydrosilane substrates. A broad range of vinylarenes and aliphatic alkenes underwent this transformation, selectively affording either branched or linear alkylsilanes in high isolated yields.

Deuterium labelling studies support the Chalk-Harrod mechanism (the Co-H intermediate) for the cobalt/bisphosphine system and the modified Chalk-Harrod mechanism (the Co-Si intermediate) for the cobalt/pyridine-2,6-diimine system. In addition, systematic studies with sterically varied silanes revealed a silane-dependent regioselectivity for hydrosilylation of vinylarenes and a silane-dependent chemoselectivity for the reaction of aliphatic alkenes and silanes catalyzed by the cobalt/ pyridine-2,6-diimine catalyst.

Further studies to develop bench-stable cobalt precursors that can be readily activated by substrates and to develop the cobalt-catalyzed asymmetric Markovnikov hydrofunctionalization of alkenes will be the subject of future work.

ASSOCIATED CONTENT

Supporting Information

Supporting Information available: Detailed experimental procedures and compound characterization data (pdf). This material is available via the Internet at <u>http://pubs.acs.org</u>

AUTHOR INFORMATION

Corresponding Author

* chmgsh@nus.edu.sg

Note

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was supported by National University of Singapore (No. R-143-000-614-133) and the Ministry of Education (MOE) of Singapore (No. R-143-000-615-112). The authors thank Dr. Rowan D. Young and Dr. Simon Sung for conducting the HR-MS (ESI) analysis.

REFERENCES

(1) (a) Marciniec, B.; Gulinski, J.; Urbaniac, W.; Kornetka, Z. W. Comprehensive Handbook on Hydrosilylation; Pergamon: Oxford, U.K., 1992. (b) Marciniec, B. Applied Homogeneous Catalysis with Organometallic Compounds; Wiley–VCH: Weinheim, Germany, 1996. (c) Marciniec, B.; Maciejewski, H.; Pietraszuk, C.; Pawluć, P. In Hydrosilyaltion: A Comprehensive Review on Recent Advances; Marciniec, B., Ed.; Springer: Berlin, 2009; pp 3–51. (d) Nakajima, Y.; Shimada, S. RSC Adv. 2015, 5, 20603–20616. (e) Sun, J.; Deng, L. ACS Catal. 2016, 6, 290–300.

(2) (a) Karstedt, B. D. Platinum Complexes of Unsaturated Siloxanes and Platinum Containing Organopolysiloxanes. U.S. Patent 3775452A, Nov. 27, 1973. (b) Lewis, L. N.; Stein, J.; Gao, Y.; Colborn, R. E.; Hutchins, G. *Platinum. Met. Rev.* **1997**, *41*, 66–75. (c) Markó, I. E.; Stérin, S.; Buisine, O.; Mignani, G.; Branlard, P.; Tinant, B.; Declercq, J.-P. *Science* **2002**, *298*, 204–206. (d) Markó, I. E.; Stérin, S.; Buisine, O.; Michaud, G.; Tinant, B.; Declercq, J.-P. Adv. Synth. Cat. **2004**, *346*, 1429–1434. (e) Marciniec, B.; Posała, K.; Kownacki, I.; Kubicki, M.; Taylor, R. *ChemCatChem* **2012**, *4*, 1935–1937. (f) Bernhammer, J. C.; Huynh, H. V. *Organometallics* **2014**, *33*, 172–180.

(3) (a) Fu, P.-F.; Brard, L.; Li, Y.; Marks, T. J. J. Am. Chem. Soc. **1995**, 117, 7157–7168. (b) Molander, G. A.; Dowdy, E. D.; Noll, B. C. Organometallics **1998**, 17, 3754–3758. (c) Gountchev, T. I.; Tilley, T. D. Organometallics **1999**, 18, 5661–5667. (d) Ge, S.; Meetsma, A.; Hessen, B. Organometallics **2008**, 27, 3131–3135. (e) Abinet, E.; Spaniol, T. P.; Okuda, J. Chem. – Asian J. **2011**, 6, 389– 391.

(4) (a) Takahashi, T.; Hasegawa, M.; Suzuki, N.; Saburi, M.; Rousset, C. J.; Fanwick, P. E.; Negishi, E. *J. Am. Chem. Soc.* **1991**, *113*, 8564–8566. (b) Corey, J. Y.; Zhu, X. H. Organometallics **1992**, *11*, 672–683. (c) Kesti, M. R.; Waymouth, R. M. Organometallics **1992**, *11*, 1095–1103. (d) Garcia, J.; Meyer, D. J. M.; Guillaneux, D.; Moreau, J. J. E.; Wong Chi Man, M. J. Organomet. Chem. **2009**, *694*, 2427–2433.

(5) (a) Randolph, C. L.; Wrighton, M. S. J. Am. Chem. Soc. **1986**, 108, 3366–3374. (b) Bart, S. C.; Lobkovsky, E.; Chirik, P. J. J. Am. Chem. Soc. **2004**, 126, 13794–13807. (c) Hojilla Atienza, C. C.; Tondreau, A. M.; Weller, K. J.; Lewis, K. M.; Cruse, R. W.; Nye, S.

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

A.; Boyer, J. L.; Delis, J. G. P.; Chirik, P. J. ACS Catal. 2012, 2, 2169-2172. (d) Kamata, K.; Suzuki, A.; Nakai, Y.; Nakazawa, H. Organometallics 2012, 31, 3825-3828. (e) Tondreau, A. M.; Atienza, C. C. H.; Weller, K. J.; Nye, S. A.; Lewis, K. M.; Delis, J. G. P.; Chirik, P. J. Science 2012, 335, 567-570. (f) Peng, D.; Zhang, Y.; Du, X.; Zhang, L.; Leng, X.; Walter, M. D.; Huang, Z. J. Am. Chem. Soc. 2013, 135, 19154-19166. (g) Greenhalgh, M. D.; Frank, D. J.; Thomas, S. P. Adv. Synth. Cat. 2014, 356, 584-590. (6) (a) Chalk, A. J.; Harrod, J. F. J. Am. Chem. Soc. 1965, 87, 16-21. (b) Harrod, J. F.; Chalk, A. J. J. Am. Chem. Soc. 1965, 87, 1133-1135. (c) Magomedov, G. K. I.; Andrianov, K. A.; Shkolnik, O. V.; Izmailov, B. A.; Kalinin, V. N. J. Organomet. Chem. 1978, 149, 29-36. (d) Brookhart, M.; Grant, B. E. J. Am. Chem. Soc. 1993, 115, 2151-2156. (e) Mo, Z.; Liu, Y.; Deng, L. Angew. Chem., Int. Ed. 2013, 52, 10845-10849. (f) Chen, C.; Hecht, M. B.; Kavara, A.; Brennessel, W. W.; Mercado, B. Q.; Weix, D. J.; Holland, P. L. J. Am. Chem. Soc. 2015, 137, 13244-13247. (g) Ibrahim, A. D.; Entsminger, S. W.; Zhu, L.; Fout, A. R. ACS Catal. 2016, 6, 3589-3593. (h) Noda, D.; Tahara, A.; Sunada, Y.; Nagashima, H. J. Am. Chem. Soc. 2016, 138, 2480-2483. (i) Schuster, C. H.; Diao, T.; Pappas, I.; Chirik, P. J. ACS Catal. 2016, 6, 2632-2636. (7) (a) Chen, Y.; Sui-Seng, C.; Boucher, S.; Zargarian, D. Organometallics 2005, 24, 149-155. (b) Benítez Junquera, L.; Puerta, M. C.; Valerga, P. Organometallics 2012, 31, 2175-2183. (c) Kuznetsov, A.; Gevorgyan, V. Org. Lett. 2012, 14, 914-917. (d) Lipschutz, M. I.; Tilley, T. D. Chem. Commun. 2012, 7146-7148. (8) (a) Li, J.; Peng, J.; Zhang, G.; Bai, Y.; Lai, G.; Li, X. New J. Chem. 2010, 34, 1330-1334. (b) Truscott, B. J.; Slawin, A. M. Z.; Nolan, S. P. Dalton Trans. 2013, 42, 270-276. (9) (a) Igarashi, M.; Matsumoto, T.; Kobayashi, T.; Sato, K.; Ando, W.; Shimada, S.; Hara, M.; Uchida, H. J. Organomet. Chem. 2014, 752, 141-146. (b) Muchnij, J. A.; Kwaramba, F. B.; Rahaim, R. J. Org. Lett. 2014, 16, 1330-1333. (10) Ura, Y.; Gao, G.; Bao, F.; Ogasawara, M.; Takahashi, T. Organometallics 2004, 23, 4804-4806. (11) (a) Uozumi, Y.; Hayashi, T. J. Am. Chem. Soc. 1991, 113, 9887-9888. (b) Komine, N.; Abe, M.; Suda, R.; Hirano, M. Organometallics 2015, 34, 432-437. (12) Du, X.; Zhang, Y.; Peng, D.; Huang, Z. Angew. Chem., Int. Ed. 2016, 55, 6671-6675. (13) (a) Slaugh, L. H.; Mullineaux, R. D. J. Organomet. Chem. 1968, 13, 469-477. (b) Meijboom, R.; Haumann, M.; Roodt, A.; Damoense, L. Helv. Chim. Acta 2005, 88, 676-693. (14) Ananikov, V. P.; Beletskaya, I. P. In Hydrofunctionalization; Ananikov, P. V., Tanaka, M., Eds.; Springer: Berlin, Heidelberg, 2013; pp 1-19. (15) LaPointe, A. M.; Rix, F. C.; Brookhart, M. J. Am. Chem. Soc. 1997, 119, 906-917. (16) Waterman, R. Organometallics 2013, 32, 7249-7263. (17) Guram, A. S.; Jordan, R. F. Organometallics 1990, 9, 2190-2192. (18) Atienza, C. C. H.; Diao, T.; Weller, K. J.; Nye, S. A.; Lewis, K. M.; Delis, J. G. P.; Boyer, J. L.; Roy, A. K.; Chirik, P. J. J. Am. Chem. Soc. 2014, 136, 12108-12118. (19) Diaz-Torres, R.; Alvarez, S. Dalton Trans. 2011, 40, 10742-10750. (20) Jiang, Y.; Blacque, O.; Fox, T.; Frech, C. M.; Berke, H. Chem. - Eur. J. 2009, 15, 2121-2128. (21) (a) Reichel, C. L.; Wrighton, M. S. Inorg. Chem. 1980, 19, 3858-3860. (b) Seitz, F.; Wrighton, M. S. Angew. Chem., Int. Ed. 1988, 27, 289-291. (22) Ciancanelli, R.; Noll, B. C.; DuBois, D. L.; DuBois, M. R. J. Am. Chem. Soc. 2002, 124, 2984-2992. (23) Humphries, M. J.; Tellmann, K. P.; Gibson, V. C.; White, A. J. P.; Williams, D. J. Organometallics 2005, 24, 2039-2050.

ACS Catalysis

Co(acac)₂ dppf Ar SiHPh₂

regioselectivity: 91:9 to >99:1

 $= R^{+ PhSiH_3} \xrightarrow{\text{Co(acac)}_2} R^{- SiHPh_2}$

SiH₂Ph Co(acac)₂ , xantphos Ar + [Si-H] -

82 example average yield: 84%

Co(acac)₂

Ar

R^{Me}

SiH₂Ph

1 2 3	_	
4 5 6 7		
8 9 10 11		
12 13 14 15	_	
16 17 18		
19 20 21 22		
23 24 25 26		
27 28 29		
30 31 32 33		
34 35 36 37		
38 39 40		
41 42 43 44		
45 46 47 48		
49 50 51		
52 53 54 55		
56 57 58 59		

60