

Rapid, Regioconvergent, Solvent-Free Alkene Hydrosilylation with a Cobalt Catalyst

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Supporting Information

ABSTRACT: Alkene hydrosilylation is typically performed with Pt catalysts, but inexpensive base-metal catalysts would be preferred. We report a Co catalyst for anti-Markovnikov alkene hydrosilylation that can be used without added solvent at low temperatures with low loadings, and can be generated *in situ* from an air-stable precursor that is simple to synthesize from low-cost, commercially available materials. In addition, a mixture of Co catalysts performs a tandem catalytic alkene isomerization/hydrosilylation reaction that converts multiple isomers of hexene to the same terminal product. This regioconvergent reaction uses isomerization as a benefit rather than a hindrance.

Alkene hydrosilylation (eq 1) is one of the largest-scale homogeneous catalytic reactions and is used to make lubricants, adhesives, rubbers, release coatings, and stationary phases for chromatography.^{1,2}



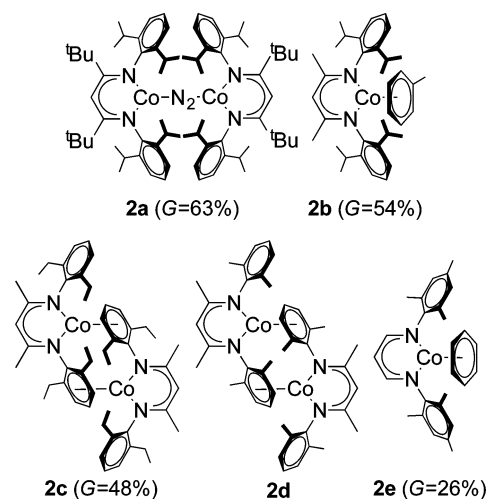
Although platinum complexes such as Speier's³ and Karstedt's⁴ catalysts are widely used because of their stability and high turnover frequencies, the precious-metal catalyst is often not recoverable (in applications such as polymer cross-linking and silicone release coatings).² Therefore, catalysts derived from more abundant metals are an area of active interest, in both academics and industry.⁵ Some current challenges for nonplatinum catalysts are limited catalyst stability, functional group compatibility, and the ability to convert mixtures of alkenes into a single, terminal silane product.

First-row transition metal catalysts for hydrosilylation have been known for decades,⁶ but traditional iron⁷ and cobalt^{8,9} carbonyl catalysts require high temperatures and suffer from side reactions such as dehydrogenative silylation and isomerization.¹⁰ More recently, iron catalysts reported by Chirik,^{11,12} Huang,¹³ Thomas,^{14,15} and Ritter¹⁶ have addressed some of these limitations, but not all in the same system. Another limitation is that these reactions use terminal alkenes to give the desired linear products. Internal alkenes, whether naturally occurring, resulting from impurities, or resulting from isomerization during hydrosilylation, are generally unreactive for alkene hydrosilylation.¹³

Cobalt catalysts for alkene hydrosilylation are rare. Brookhart reported a cyclopentadienylcobalt complex for selective anti-Markovnikov hydrosilylation with Et₃SiH.⁹ Deng reported a NHC-Co system for 1-octene + PhSiH₃.¹⁷ Hilt reported a Cophosphine catalyzed 1,4-hydrosilylation of isoprene.¹⁸ In addition, several recent patents indicate industrial interest in cobalt catalysts for hydrosilylation.^{19–21} Here, we show a very active cobalt catalyst which can use a solvent-free mixture of equimolar alkene and silane, has excellent functional group compatibility, uses an air-stable catalyst precursor, and can convert internal alkenes into terminal silanes under solvent-free conditions. This regioconvergent reaction could simplify the hydrosilylation of mixtures of alkenes using an inexpensive, easy to use catalyst.

The catalysts are β -diketiminato-supported cobalt(I)–arene complexes **2a–2e** (Chart 1), which were synthesized in three steps from commercial precursors (Scheme 1). The cobalt(II) chloride precursors **1b–1e** came from diketimines, which can be prepared on large scale from anilines.²² The cobalt(II) chloride precursors were reduced using Grignard reagents or using potassium graphite to yield cobalt(I) products that were crystallographically characterized: in **2b** and **2e**, cobalt(I) was

Chart 1. Cobalt(I) β -Diketiminato Complexes Used in This Study and Their Steric *G* Parameters

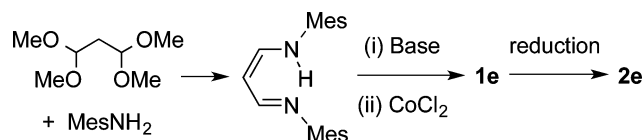


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Scheme 1. An Example of Catalyst Synthesis



bound to a solvent arene, while, in complexes **2c** and **2d**, cobalt(I) was bound to a diketiminate arene to form a dimer. The supporting ligands span a range of size from 26% to 63% of the metal overshadowed, as quantified using the *G* parameter (Chart 1 and Table S1).²³

Initial hydrosilylation experiments were conducted with a equimolar mixture of 1-hexene (1 M) and PhSiH₃ (1 M) using 1 mol % loading (10 mM) of catalysts **2a–d** in C₆D₆ solution under an atmosphere of N₂. The results were analyzed by ¹H NMR spectroscopy with mesitylene as an internal standard (Table 1, entries 1–4). The catalyst supported by the most

Table 1. Hydrosilylation of 1-Hexene with PhSiH₃

$\text{CH}_2=\text{CH}-n\text{-Bu} + \text{PhSiH}_3 \xrightarrow[\text{C}_6\text{D}_6]{\text{[Co] 1.0 M}} n\text{-Bu}-\text{CH}_2-\text{CH}_2-\text{SiH}_2\text{Ph}$		
catalyst	reaction conditions	yield (selectivity) ^a
1.0% 2a	1 M, 40 °C, 24 h	no reaction
1.0% 2b	1 M, 40 °C, 16 h	90% (>98%)
1.0% 2c	1 M, 40 °C, 2 h	91% (>98%)
1.0% 2d	1 M, 40 °C, 2 h	96% (>98%)
0.05% 2e	neat, 25 °C, 1 h	97% (>98%)

^aYields and selectivities determined by ¹H NMR analysis.

bulky ligand (**2a**) gave no hydrosilylation products, while all other reactions gave the linear (anti-Markovnikov) silane in $\geq 90\%$ yield at 40 °C. Higher reactivity was observed under the same conditions with less bulky supporting ligands.²⁴ Catalyst **2e**, with the least bulky supporting ligand, was active at low loading (0.05 mol %) at room temperature without any solvent: after 1 h, a 97% yield of hexylsilane was formed with >98% linear selectivity. 1% of Markovnikov product and <1% disubstituted silane were detected by GC-MS, and no dehydrogenated hydrosilylation products were observed. The rate and the selectivity of hydrosilylation were unchanged when a drop of Hg was added to the hydrosilylation reactions catalyzed by **2a–e**, suggesting that the reaction is not being catalyzed by solid or nanoparticulate cobalt.²⁵

Consistent with the trend observed with PhSiH₃, reactions of the bulkier, less reactive triethoxysilane^{12,26} worked best with catalyst **2e** (Table 2). Again, no vinylsilane or allylsilane was observed. Catalysts **2a–2d** with larger supporting ligands gave

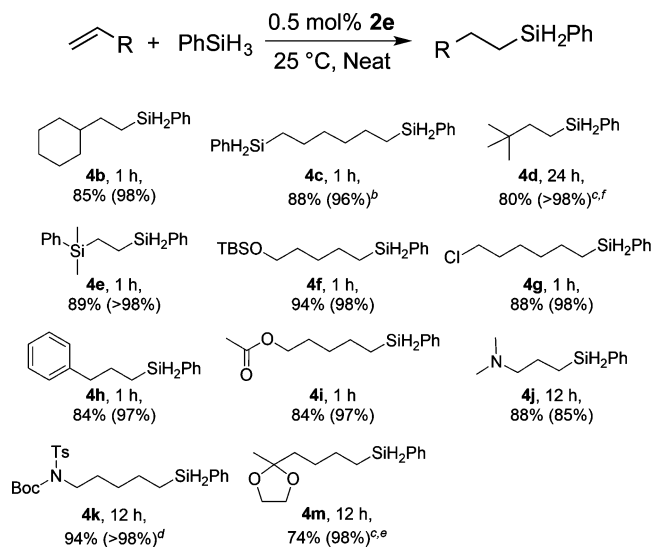
Table 2. Hydrosilylation of 1-Hexene with (EtO)₃SiH

$\text{CH}_2=\text{CH}-n\text{-Bu} + (\text{EtO})_3\text{SiH} \xrightarrow[\text{4 h}]{\text{[Co] Neat, 60 }^\circ\text{C}} n\text{-Bu}-\text{CH}_2-\text{CH}_2-\text{Si}(\text{OEt})_3$		
catalyst	internal alkene	yield (linear selectivity) ^a
2.0% 2c	63%	12% (96%)
2.0% 2d	57%	23% (>98%)
2.0% 2e	5%	89% (>98%)

^aYields and selectivities determined by GC analysis.

significant amounts of internal alkenes,²⁷ but isomerization was minor with **2e**. These studies again identify **2e** as the most reactive and selective catalyst. Therefore, subsequent studies used catalyst **2e** without added solvent.

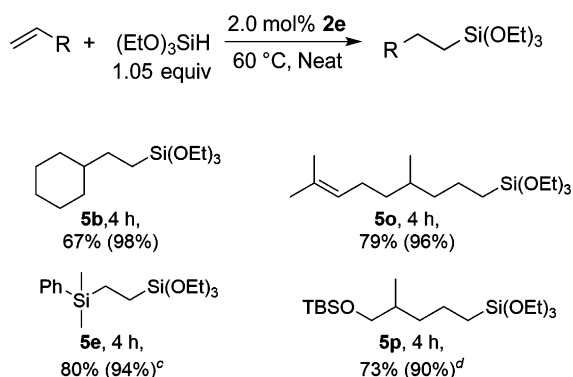
To investigate the limitations of **2e**, we examined the catalytic hydrosilylation of alkenes bearing functional groups (Scheme 2). Functionalized alkenes bearing silane, silyl ether,

Scheme 2. Functionalized Hydrosilylation Products from PhSiH₃ Using Catalyst **2e**^a

^aYields are isolated yields after purification by column chromatography. Linear selectivities were determined by ¹H NMR or GC-MS analysis and appear in parentheses. ^b2 equiv of PhSiH₃ added. ^cSmall amount of 1,1-disilylalkane was detected. ^d50 μL of THF were added to the 1.0 mmol reaction to dissolve solid alkene. ^e11% internal alkene detected by ¹H NMR spectroscopy. ^fThe reaction mixture was heated to 60 °C.

halide, arene, ester, tertiary amine, and amide substituents were hydrosilylated at room temperature by **2e**, as shown by isolation of **4e–n** in 74–94% yield with high linear selectivity. Some of the products were accompanied by a small amount (7% (**4d**), 5% (**4m**)) of a 1,1-disilylalkane product, and a longer reaction time was required for bulky substrate **3d**. Hydrosilylation of 1,5-hexadiene successfully gave **4c**, but conjugated dienes (1,3-hexadiene and 1,3-butadiene) gave no conversion. Hydrosilylation of selected terminal alkenes with (EtO)₃SiH gave a good yield and selectivity under the same conditions used in Table 2 (Scheme 3), though the rates are slower with this less-reactive silane (4 h at 60 °C, compared to 1 h at rt using PhSiH₃).

During the studies with the less-active catalyst **2b**, we noticed that it slowly catalyzed hydrosilylation of internal hexenes to give the terminal silane selectively (Table 3). This has been seen previously with certain Zr catalysts,²⁸ Pt catalysts,²⁹ and Fe catalysts.¹¹ We propose that this transformation is a tandem isomerization–hydrosilylation consisting of two steps: (1) rapid isomerization of the alkene and (2) selective hydrosilylation of the terminal alkene. In order to maximize the efficiency of this tandem process with the Co system, we took advantage of the fact that **2b** can isomerize internal hexenes into an equilibrium mixture of all isomers,²⁷ and paired it with **2e**, which is the most rapid hydrosilylation catalyst. As shown in Tables 3 and 4, a mixture of 2 mol % of **2b** and 0.5 mol % of **2e** was effective for

Scheme 3. Functionalized Hydrosilylation Products from (EtO)₃SiH Using Catalyst 2e^{a,b}


^aIsolated yields after distillation under reduced pressure. ^bLinear selectivity determined by ¹H NMR and GC-MS analysis. ^c15% ethylenecyclohexane and 7% 1-ethylcyclohex-1-ene detected by ¹H NMR spectroscopy. ^d13% internal alkene detected by ¹H NMR spectroscopy.

Table 3. Hydrosilylation of Internal Alkenes with PhSiH₃

$$\text{Hexene} + \text{PhSiH}_3 \xrightarrow[1.0 \text{ M in THF, } 60^\circ\text{C}]{[\text{Co}]} n\text{-Bu}-\text{SiH}_2\text{Ph}$$

hexene isomer	2b (mol %)	2e (mol %)	alkene remaining	yield (selectivity) ^a
cis-2-	0	0.5	83%	9% (ND) ^b
cis-2-	2.0	0	4%	83% (>98%)
cis-2-	2.0	0.5	3%	85% (>98%)
cis-3-	2.0	0.5	4%	86% (>98%)
trans-2-	4.0	0.5	33%	60% (>98%)

^aThe yield and linear selectivity was determined by ¹H NMR spectroscopy after 4 h. ^bThe linear selectivity could not be determined by ¹H NMR and GC-MS due to the low intensity.

Table 4. Hydrosilylation of Internal Alkenes with (EtO)₃SiH

$$\text{Hexene} + (\text{EtO})_3\text{SiH} \xrightarrow[\text{Neat, } 60^\circ\text{C}]{[\text{Co}]} n\text{-Bu}-\text{Si}(\text{OEt})_3$$

hexene isomer	2b (mol %)	2e (mol %)	alkene remaining	yield (selectivity) ^a
cis-2-	0	2.0	77%	4% (ND)
cis-2-	4.0	2.0	12%	71% (>98%)
cis-3-	4.0	2.0	32%	62% (95%)
trans-2-	4.0	2.0	20%	34% (96%)

^aYields and linear selectivities determined by ¹H NMR spectroscopy and GC-MS analysis after 12 h.

regioselective isomerization/hydrosilylation of *cis*-2-hexene or *cis*-3-hexene by PhSiH₃ to form the *terminal* product, 1-hexylphenylsilane. The mixture of catalysts was much more effective for these internal alkenes than catalyst 2e by itself, supporting the proposed role of 2b for isomerization. The *trans* isomers were less reactive in the tandem reaction, perhaps because they do not coordinate as well to the metal center.²⁷ We note that some silane products can be oxidized to alcohols through a Tamao–Fleming oxidation, and so this provides a potential route to linear alcohols from internal alkenes.^{14,30}

Catalytic hydrosilylation of internal hexenes with (EtO)₃SiH was also improved with the mixture of catalysts (Table 4). Since catalyst 2b is inactive toward hydrosilylation with

(EtO)₃SiH, it is particularly likely that the catalysts have different roles: 2b isomerizes the internal alkene into the terminal alkene, which is hydrosilylated with 2e.

Although catalysts 2 must be stored and handled under N₂, the cobalt(II) chloride precursor 1e is stable in dry air for days (see Supporting Information for details). This allows for the *in situ* generation of active catalyst 2e using standard air-free techniques on the benchtop without the need for a glovebox. We found that even after standing open in an air-filled desiccator for 2 days, 1e was analytically pure and could be activated with *n*BuLi or EtMgBr in high yield (or using KO^tBu in somewhat lower yield) to give catalytically active mixtures that gave alkene hydrosilylation in yields similar to those observed using isolated 2e. In the most convenient protocols (Table 5), sequential addition of 1 equiv of EtMgBr, 200 equiv

Table 5. Comparison of *in Situ* Formed Catalysts

$$\text{Hexene} + \text{PhSiH}_3 \xrightarrow[25^\circ\text{C, 1.0 M in THF}]{0.55 \text{ mol\% } 1e, 0.5 \text{ mol\% Reagent}} n\text{-Bu}-\text{SiH}_2\text{Ph}$$

silane	reagent	time	yield (selectivity) ^a
PhSiH ₃	<i>n</i> BuLi	2 h	85% (>98%)
PhSiH ₃	KO ^t Bu	2 h	85% (>98%)
PhSiH ₃	EtMgBr	1 h	91% (>98%)
PhSiH ₃	EtMgBr	2 h	84% (>98%) ^b

^aYields and linear selectivities determined by ¹H NMR spectroscopy and GC-MS analysis. ^bGram scale reaction on benchtop, which provided 1.62 g of 1-hexylphenylsilane.

of PhSiH₃, and 200 equiv of 1-hexene to 1e under N₂ gave a >90% yield of 1-hexyl-1-phenylsilane with >98% linear selectivity in 2 h at room temperature. This procedure was effective on a gram scale using standard Schlenk techniques, giving a yield that was only slightly lower than a smaller-scale reaction performed in a glovebox (last entry, Table 5).

Reaction of 1-hexene with PhSiD₃ gave the *d*₃ product with deuteration only at the Si–H and the β-carbon. No deuterium scrambling was observed, suggesting that there is no β-hydride elimination before reductive elimination of the C–Si bond. However, we cannot yet distinguish whether the catalysis uses a standard Chalk–Harrod type pathway or a radical pathway. Though the rapid rate of catalysis has so far hindered kinetic studies, mechanistic studies are underway.

Overall, these results show the utility of β-diketiminato-supported cobalt(I)–arene catalysts for catalytic alkene hydrosilylation. Future studies will address the mechanism of these reactions, the identity of the cobalt intermediates, and the development of improved catalysts.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b08611.

Crystallographic data (CIF)

Details of synthesis and characterization (PDF)

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Notes

The authors declare no competing financial interest.

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■ NOTE ADDED IN PROOF

Hu very recently described catalytic hydrosilylation with a similarly low loading of a nickel catalyst and excellent functional group compatibility. They also observe isomerization/hydro-silylation using higher loading of the catalyst.³¹