



Published in final edited form as:

ACS Catal. 2017 April 7; 7(4): 2275–2283. doi:10.1021/acscatal.6b03373.

## Control of Selectivity through Synergy between Catalysts, Silanes and Reaction Conditions in Cobalt-Catalyzed Hydrosilylation of Dienes and Terminal Alkenes

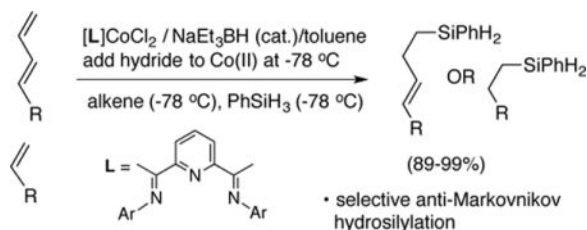
Balaram Raya, Stanley Jing, and T. V. RajanBabu\*

Department of Chemistry and Biochemistry, The Ohio State University, 100 West 18<sup>th</sup> Avenue, Columbus, OHIO 43210, USA

### Abstract

Readily accessible (*i*<sup>Pr</sup>PDI)CoCl<sub>2</sub> [*i*<sup>Pr</sup> PDI = 2,6-*bis*(2,6-diisopropylphenyliminoethyl)pyridine] reacts with 2 equivalents of NaEt<sub>3</sub>BH at -78 °C in toluene to generate a catalyst that effects highly selective anti-Markovnikov hydrosilylation of the terminal double bond in 1,3- and 1,4-dienes. Primary and secondary silanes such as PhSiH<sub>3</sub>, Ph<sub>2</sub>SiH<sub>2</sub> and PhSi(Me)H<sub>2</sub> react with a broad spectrum of terminal dienes without affecting the configuration of the other double bond. When dienes conjugated to an aromatic ring are involved, both Markovnikov and anti-Markovnikov products are formed. The reaction is tolerant of various functional groups such as an aryl bromide, aryl iodide, protected alcohol, and even a silyl enol ether. Reactions of 1-alkene under similar conditions cleanly lead to a mixture of Markovnikov and anti-Markovnikov hydrosilylation products, where ratio of the products increasingly favors the latter, as the size of the 2,6-substituents in the iminoylaryl group becomes larger. The complex (*i*<sup>Pr</sup>PDI)CoCl<sub>2</sub> gives exclusively the linear silane for a wide variety of terminal alkenes. Mechanistic studies suggest a pathway that involves a key role for an in situ generated metal hydride, (L)Co(I)-H. Exclusive reduction of the terminal double bond (*vis-a-vis* hydrosilylation) when (EtO)<sub>2</sub>Si(Me)H is used in the place of PhSiH<sub>3</sub> is explained on the basis of an alternate silane-mediated decomposition path for the linear Co(I)-alkyl intermediate.

### TOC Graphic



Corresponding Author: rajanbabu.1@osu.edu.

#### Supporting Information

Experimental procedures for the scouting experiments, syntheses and isolation of the hydrosilylation products. Spectroscopic and gas chromatographic data showing compositions of products under various reaction conditions. This material is available free of charge via the Internet at <http://pubs.acs.org>

#### Notes

The authors declare no financial interest.

## Keywords

hydrosilylation; cobalt; 1,3-dienes; 1,4-dienes; 1-alkenes; vinylarenes; chemoselectivity; regioselectivity

## Introduction

Hydrosilylation of alkenes catalyzed by complexes of earth-abundant late-transition metals as replacements for traditional platinum catalysts have attracted significant attention recently.<sup>1</sup> Most notable among these are catalysts derived from iron, cobalt, and, to a limited extent, nickel.<sup>2</sup> In sharp contrast to numerous procedures that have been published for the hydrosilylation of alkenes, only a limited number of reports deal with hydrosilylation of dienes, even though the reactions of these substrates have a long history, starting with the early studies of Lappert, who investigated nickel,<sup>3a,b</sup> and cobalt<sup>3c</sup> complexes for this reaction (Scheme 1). These early studies were largely limited to isoprene, 1,3-pentadiene, 2,3-dimethylbuta-1,3-diene and 1,3-cyclohexadiene, and, gave mixtures of 1,2- and 1,4-adducts in good yields, especially with an optimized Ziegler system using Ni(acac)<sub>2</sub>/R<sub>3</sub>Al [acac = acetylacetonate]. More recently, Hilt reported the use of zinc-reduced [(*n*-Bu)<sub>3</sub>P]CoBr<sub>2</sub> as a catalyst for exclusive 1,4-hydrosilylation of isoprene with (EtO)<sub>3</sub>SiH.<sup>4</sup> Ritter reported a broadly applicable 1,4-hydrosilylation of 1,3-dienes with tertiary silanes [e.g., (EtO)<sub>3</sub>SiH, Et<sub>3</sub>SiH and (EtO)<sub>2</sub>Si(Me)H] using Fe(0) complexes of 2-aryliminopyridine as catalysts.<sup>5</sup> Except for an isolated example of the use of a platinum-metalacycle catalyst (Scheme 1) for the 1,2-addition of (EtO)<sub>3</sub>SiH to 1,3-dienes,<sup>6</sup> practical methods for the selective 1,2-hydrosilylation of 1,3-dienes are conspicuously absent in the literature.

## Results and Discussion

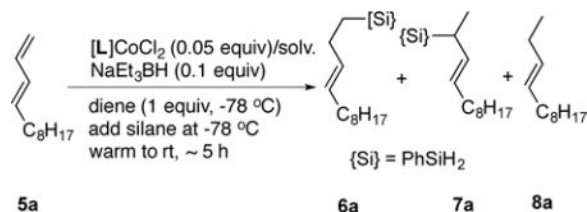
### Hydrosilylation of 1,3- and 1,4-Dienes

Our interest in this area had its origin in attempts to effect chemoselective functionalization of nearly enantiopure skipped 1,4-dienes, which were products of a recently discovered asymmetric hydrovinylation reaction (Scheme 2).<sup>7</sup> We reasoned that chemo- and regioselective hydrosilylation of the terminal double bonds in the hydrovinylation products without affecting the other functional groups including very sensitive silyl enol ethers would provide outstanding opportunities for the synthesis of other valuable enantiopure intermediates. During these studies we discovered that the reactions of 1,4-skipped dienes like **2a** or **2b** with various silane reagents in the presence of well-known (PDI)CoCl<sub>2</sub> [PDI = 2,6-*bis*(2,6-alkylphenyliminoethyl)pyridine, Figure 1] complexes are highly dependent on the nature of the silanes, the catalyst employed, and the reaction conditions. We find that by careful optimization of the reaction conditions, highly selective anti-Markovnikov hydrosilylation of not only skipped 1,4-dienes but also 1,3-dienes and terminal alkenes can be carried out.<sup>8</sup> These results are reported in this paper.

Our studies started with scouting of a series of cobalt(II) complexes of ligands (Figure 1) that have been known to be active in various hydrosilylation reactions of simple alkenes.

Among these, readily available PDI ligands **4a–d**<sup>9,10</sup> and the 2,6-bis-oxazolylpyridine ligand **4e**<sup>2c</sup> were found to show broad range of activities in a prototypical hydrosilylation of (*E*)-1,3-dodecadiene (**5a**) using phenylsilane as the silylating agent (Eq 1 and Table 1).

Hydrosilylation of 1,3-dodecadiene (**5a**) typically gave 3 products, in addition to the unreacted starting material and a silane metathesis product, Ph<sub>2</sub>SiH<sub>2</sub>. These are the linear anti-Markovnikov adduct **6a**, a branched isomer **7a**, and a reduction product **8a**, which are formed in varying amounts depending on the reaction conditions. The structures of these products, including the configuration of the double bonds in **6a** and **7a** were rigorously established by NMR methods.<sup>11</sup> The ratios were initially determined by gas chromatographic analysis and later confirmed by <sup>1</sup>H NMR after work up and purification. From these studies the ligand <sup>*i*</sup>-PrPDI [**4a**] was identified as the best ligand for 1,2-hydrosilylation of 1,3-dodecadiene (Entries 1 and 2, Table 1). The best selectivity is obtained when the catalyst is generated at -78 °C (entry 1). If the catalyst is generated at room temperature, significant amount of a reduction product (**8a**) is observed in addition to **6a** and **7a**.



(1)

A quick survey of most commonly used activators (NaEt<sub>3</sub>BH, EtMgBr, MeLi, Me<sub>3</sub>Al, Et<sub>2</sub>Zn, *n*-BuLi, methyl aluminoxane) showed that NaEt<sub>3</sub>BH is the best reagent for reduction of the [PDI]CoCl<sub>2</sub> complexes, especially if the reaction is carried out at low temperature (Supporting Information, Table S1, entry 1).<sup>12</sup>

Following the identification of the most optimal complex and activator, we examined the effect of solvents, the counter ions and experimental parameters such as temperature and order of mixing the reagents.<sup>13</sup> From these studies toluene was identified as the best solvent for the formation of the linear 1,2-hydrosilylation product, **6a**. Solvents such as THF, ether, hexane, benzene, dichloroethane and acetonitrile gave unsatisfactory results.<sup>13</sup> THF, ether and hexane gave significant amounts of the reduction product **8a** (63%, 78% and 63% respectively). Benzene gave only 13% of the hydrosilylation **6a** along with 7% of the branched isomer, **7a**. Surprisingly, benzene also gave up to 52% of the silane redistribution product Ph<sub>2</sub>SiH<sub>2</sub>. Note that none of the side products were observed in toluene. Only the (<sup>*i*</sup>-PrPDI)CoCl<sub>2</sub> gave a preparatively useful hydrosilylation reaction. Complexes from (<sup>*i*</sup>-PrPDI)CoX<sub>2</sub> (X = Br, I, OAc) gave low yields of the hydrosilylation products (<20%) under the standard conditions (See Supporting Information, Table S3). These complexes also lead to significant amounts of Ph<sub>2</sub>SiH<sub>2</sub> when PhSiH<sub>3</sub> was used as a silylating agent. We do not fully understand the role of the counter anion even though we believe that this maybe related to the reduction potential of various cobalt salts. Even within a series of

(bisphosphine)CoCl<sub>2</sub> complexes ease of reduction (with Zn) has been found important in other cobalt-catalyzed coupling reactions such as hydrovinylation reaction.<sup>7a</sup> For a dramatic effect of counter ion in hydrosilylation see ref. 2c.

In view of the extensive literature on the use of (PDI)Co-complexes for hydrosilylation reactions we were pleasantly surprised by the remarkable selectivity of this reaction (see later for other substrates such as simple alkenes), and found that the selectivity is critically dependent on the catalyst preparation and the temperature. For example, in the hydrosilylation of the prototypical diene, (*E*)-1,3-dodecadiene (**5a**) using a preformed catalyst [(<sup>i</sup>-PrPDI)CoCl<sub>2</sub> + 2 equiv NaEt<sub>3</sub>BH at -78 °C, toluene] *at room temperature* gave a mixture of products consisting of **6a**, **7a**, **8a** and a silane metathesis product Ph<sub>2</sub>SiH<sub>2</sub>, where as the same reaction carried out *at low temperature* (-78 °C – rt) gave mostly the hydrosilylation product **6a** (Scheme 3) with a trace of **7a** as analyzed by gas chromatography.

A typical procedure that evolved from these initial studies is shown in Eq 1. Thus the diene (1 equiv) and the readily accessible Co(II)-complex, (**4a**)CoCl<sub>2</sub>, (0.01–0.05 equiv) are dissolved in the appropriate solvent under argon and the mixture is cooled to -78 °C. To this solution is added a toluene solution of NaEt<sub>3</sub>BH (2 equiv. of the Co(II)-complex) followed by the silane (1.0–1.1 equiv, neat). The mixture is slowly warmed to rt while monitoring the reaction by gas chromatography (GC) and GC-mass spectrometry. There is no indication in these experiments that the reaction is reversible or the 1,4-product is formed from rearrangement of an initially formed 1,2-adduct.

Apart from the notable effects of solvents, reducing agents and counter ions, silanes also play a significant role on the course of these reactions. Table 2 summarizes these results. Thus a primary silane, PhSiH<sub>3</sub>, and secondary silanes PhMeSiH<sub>2</sub> and PhSiH<sub>2</sub> gave excellent yields of the 1,2-hydrosilylation products, while the tertiary silanes Cl<sub>3</sub>SiH and Et<sub>3</sub>SiH are totally unreactive under the standard conditions (entries 6–7). Et<sub>2</sub>SiH<sub>2</sub> is also unreactive (entry 8). Triphenylsilane gave only a low yield (64%) of the reduction product **8a** as seen in by GC-MS. Reactions with diethoxymethyl- and dimethoxymethylsilane are unique, giving quantitative yield of the reduction product **8a** (entries 9 and 10). We have examined the utility of diethoxymethylsilane as a stoichiometric reagent for quantitative and highly selective reduction of the terminal bond in a wide variety of 1,3-dienes, 1,4-dienes, terminal alkenes and alkynes, and found that the reaction can be carried out with as little as 0.001 equivalents of the catalyst. A detailed account of this remarkably tolerant reduction procedure for terminal alkenes has since been published.<sup>14</sup>

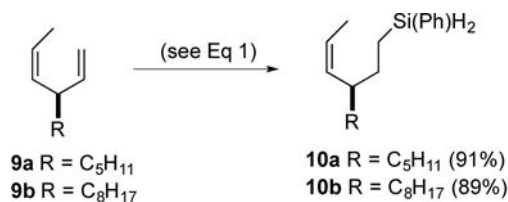
The selective 1,2-hydrosilylation of 1,3-dienes using PhSiH<sub>3</sub> and Ph<sub>2</sub>SiH<sub>2</sub> is a broadly applicable reaction giving very good to excellent yields of the anti-Markovnikov adduct (**6**), with only minor amounts (up to 6%) of other products including the branched isomer (**7**) or the reduction product (**8**). A list of products resulting from hydrosilylation of 1,3-dienes using PhSiH<sub>3</sub> under the optimized conditions (Eq 1) using [**4a**]CoCl<sub>2</sub> as catalyst along with the yield of the isolated products is shown in Table 3. As the examples illustrate, most terminal 1,3-dienes with either *E* or *Z*-geometry of the internal alkene exclusively form the anti-Markovnikov product with retention of the alkene configuration. The products **6f**(*E*) and

**6f**(E+Z) derived from the respective dienes, are illustrative of the regio- and stereoselectivity of the silylation reaction. The product **6f**(E) comes from the corresponding pure *E*-diene and **6f**(E+Z) comes from a mixture of (*E*) and (*Z*)-dienes (44:56). Similarly, **6k**(E+Z) comes from a mixture of isomers of the diene. As expected, the silylation does not affect the configuration of the internal double bond and the *E/Z*-isomeric ratio of products remains the same as that in the starting material. Dienes that are conjugated to an aromatic ring yield mixtures of 1,2-linear (l) and branched (b) products (**6l**-l and **6l**-b). This might reflect the enhanced stability of a putative  $\eta$ -3 Co-allyl complex and trapping of such a complex from an equilibrium mixture of initial LCo-H adducts when a sterically unencumbered silane (e. g., PhSiH<sub>3</sub>) is used. Among the dienes we have examined isoprene gave mostly (86%) 1,4-hydrosilylation (**6n**) with ~ 11% 1,2-addition.  $\beta$ -Myrcene gave a mixture of 1,2- and 1,4-addition products **6o**-(1,2) and **6o**-(1,4).

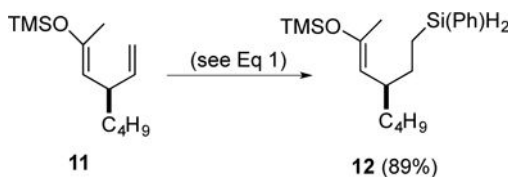
The new protocol is preparatively useful on a larger scale and even in the absence of any solvent. The 1,2-hydrosilylation product **6a** was isolated 91% yield of in >98% isomeric purity in a 0.5 g-scale reaction. Several other preparative runs were also carried out using 1 mol% catalyst at 40 °C (2 h) with no loss of yield or selectivity. Thus compounds **6d** (92%), **6f**(E) (90%), **6f**(E+Z) (88%) **6i** (93%) and **6j** (92%) were prepared under these conditions on preparative scales.

Two examples of addition of secondary silanes, Ph<sub>2</sub>SiH<sub>2</sub> and Ph(Me)SiH<sub>2</sub> to (*E*)-1,3-dienes (**6p** and **6q**) are also included in the Table (entries 16 and 17). We expect these silanes to have the same broad substrate scope as PhSiH<sub>3</sub> even though they were not explored further in this study.

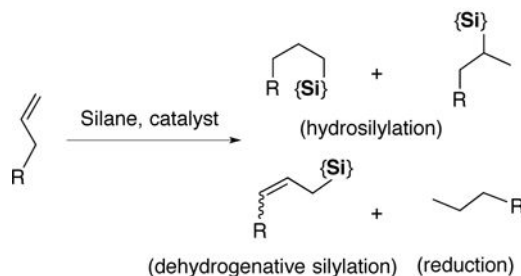
The new protocol for the selective hydrosilylation is equally applicable to skipped 1,4-dienes<sup>7</sup> as illustrated by the examples shown in Eq 2 and 3. Note that the disubstituted double bond including the one in the highly sensitive silyl enol ether (**11**) is not affected under the hydrosilylation conditions.



(2)



**Hydrosilylation of 1-Alkenes**—Hydrosilylations of terminal alkenes have been reported to give a number of products depending on the catalyst, silane and reaction conditions (Eq 4).<sup>2</sup>



(4)

As we were reporting the use of (PDI)CoCl<sub>2</sub>/NaEt<sub>3</sub>BH as catalysts of hydrosilylation<sup>8</sup> and reduction<sup>14</sup> of dienes and alkenes, Chirik reported<sup>2c</sup> the use of highly active *bis*-iminopyridine-Co(II)-ethylhexanoate complexes (**13** and **14**, Figure 2) for the hydrosilylation of alkenes with tertiary silanes, in place of 2,6-*bis*[2,6-diisopropylphenyl-iminoethyl]pyridine)Co-Z] (Z = N<sub>2</sub>, Me, OH, Cl) complexes (**15**), which had been shown to give, exclusively, a mixture of dehydrogenative silylation and reduction of alkenes with several silanes (Scheme 4, A).<sup>2f</sup> In the reactions involving **15**, most notably, *no simple hydrosilylation* was observed using this silane.

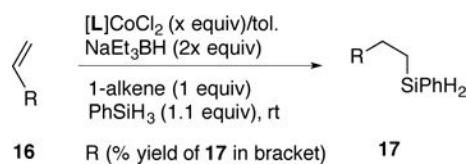
Since the exclusive 1,2-hydrosilylation of 1,3-diene that is observed in the present study appears to rely on the strict protocol reported here, we decided to explore how terminal alkenes would respond to these reaction conditions, especially since the structurally related Co(I)-complexes **15** (Z = Cl, Me) give *only dehydrogenative silylation of 1-alkenes* with several silanes including PhSiH<sub>3</sub> and (TMSO)<sub>2</sub>Si(Me)H.<sup>2f,15</sup> Additions of phenylsilane (PhSiH<sub>3</sub>) and diphenyl silane (Ph<sub>2</sub>SiH<sub>2</sub>) to 1-octene have been reported to give an unsatisfactory mixtures of products including polyalkenylated silanes and Makovnikov adducts in these reactions when excess alkene (neat, 2–4 equiv.) is used.

Initially hydrosilylation of 1-octene was carried out using a catalyst derived from (MesPDI)CoCl<sub>2</sub> [(**4c**)CoCl<sub>2</sub>] and NaEt<sub>3</sub>BH at rt to enable a direct comparison to the results reported in the literature<sup>2f</sup> (Scheme 4, B, Table 4). This catalyst, generated at rt has been reported to give dehydrogenative silylation products (**19**).<sup>2f,15</sup> In sharp contrast, in a similar experiment, when the reaction was carried out by generating the catalyst at –78 °C by reacting [(**4c**)CoCl<sub>2</sub>] and NaEt<sub>3</sub>BH at –78 °C, and, adding 1-octene and PhSiH<sub>3</sub> at the same temperature, an exceptionally clean reaction ensues giving a mixture of only the hydrosilylation products in a ratio **17a**:**18a** = 52:48 (Scheme 4, B, Figure 3).<sup>16</sup> Similar observations were made in the reactions of 4-methylstyrene.<sup>16</sup> *No contamination from the dehydrogenative silylation or reduction products* are observed (Table 4, entry 1). The 2,6-substituents on the *N*-aryl group of the PDI ligands have a huge effect on the linear (**17a**) to branched (**18a**) ratio of the products (Table 4, Figure 3). The complex (**4b**)CoCl<sub>2</sub> derived

from the 2-ethyl ligand **4b** gives 60% of the linear product **17** (entry 2), and the complex derived from the *i*-propyl derivative, (**4a**)CoCl<sub>2</sub>, gave a ratio of 99:1 (Table 3, entry 3). No reaction other than hydrosilylation was observed under these conditions as determined by gas chromatography of the crude reaction mixture (Figure 3). In none of these cases we observe any dehydrogenative silylation or reduction of the starting material as confirmed by GC and NMR. Finally, the reaction run on preparative scale using 1 mol% catalyst at 40 °C showed little loss of yield or selectivity (**17a**:**18a** = 97:3, entry 4).

Chirik has reported that in the addition of (TMSO)<sub>2</sub>Si(Me)H to 1-octene, [(**4c**)CoCl<sub>2</sub>] activated by NaEt<sub>3</sub>BH at room temperature can be used in place of [(**4c**)Co-Me] to get similar results (Scheme 5).<sup>2f, 15</sup> Only dehydrogenative silylation and reduction are observed at room temperature even when 1:1 ratio of octane and the silane is used (Supporting Information, Table S4). We have repeated these results (Scheme 5, A) and further examined the reactions of this silane under our modified conditions (-78 °C) to find *only reduction of the double bond, with no dehydrogenative silylation at low temperature* (Table S4).<sup>15,18</sup> Clearly the low temperature generation of the catalyst leads to different reactivity/selectivity.

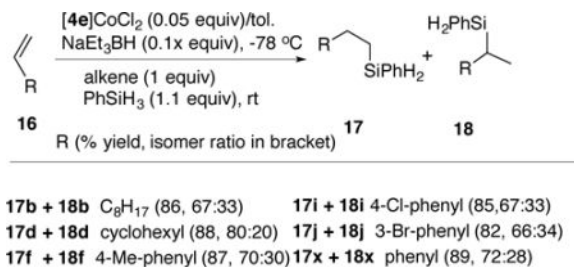
A quick survey of other ligands, activators, solvents and counter ions for Co(II) revealed that complexes with ligands **4a**, **4b**, **4c** and **4e** (Figure 1) were active in the hydrosilylation of alkenes giving excellent yields of the hydrosilylation products **17** and **18**.<sup>16</sup> The complex (**4a**)CoCl<sub>2</sub> activated by NaEt<sub>3</sub>BH produced the best results in the formation of the anti-Markovnikov product **17**. This reaction (Eq 5) which appears to have broad scope and significant functional group compatibility, is comparable to a number of other cobalt-catalyzed hydrosilylation reactions that have been reported recently.<sup>2a-e,8</sup> The scope of the substrates for this reaction is illustrated by the examples shown in Figure 4. In most cases the reactions are nearly quantitative (see the gas chromatograms of crude products that are included in the Supporting Information) even with 1.0:1.1 ratio of the alkene to the silane. Noteworthy examples for the exclusive anti-Markovnikov products are the products **17i**, **17j**, **17s**, containing Cl, Br and I, the protected alcohol derivatives **17n**, **17o**, **17p** and the cyclooctylphenylsilane **17q**.



(5)

Four examples of addition of secondary silanes, Ph<sub>2</sub>SiH<sub>2</sub> and Ph(Me)SiH<sub>2</sub> to terminal alkenes (**17t-w**) are also included in the Figure 4. We expect these silanes to have the same broad substrate scope as PhSiH<sub>3</sub> even though these have not yet been explored in greater detail. We have previously reported that (TMSO)<sub>2</sub>SiMeH, (EtO)<sub>3</sub>SiH and, (EtO)<sub>2</sub>Si(Me)H gave only reduction of the double bond under these conditions, with (EtO)<sub>2</sub>Si(Me)H giving the best result in the reduction.<sup>14</sup>

The study of ligand effects also revealed unexpected changes in the regioselectivity as a function of the ligand. For example, the pybox complex, (**4e**)CoCl<sub>2</sub>, under our protocol gives the proportion of the Markovnikov products comparable to the less hindered PDI complexes **4b** and **4c** (Eq 6).



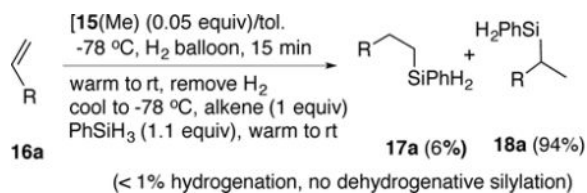
(6)

### Mechanistic Observations

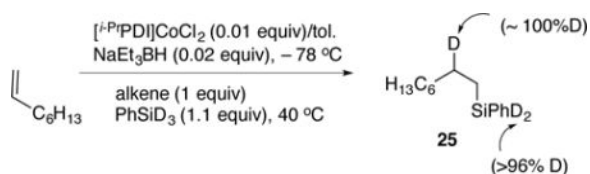
The notable difference between the anti-Markovnikov hydrosilylation observed under conditions described in this paper [<sup>Mes</sup>PDI]CoCl<sub>2</sub>/NaEt<sub>3</sub>BH/−78 °C, silane, alkene, warm to rt, Scheme 4, B) and the dehydrogenative silylation/reduction observed when (<sup>Mes</sup>PDI)Co-Me (**15**, Z = Me) is used as a catalyst (Scheme 4, A) can be explained by invoking the classical Chalk-Harrod mechanism, in which (L)Co-H is solely responsible for the former reaction (Scheme 6). Dehydrogenative silylation presumably involves an unstable (PDI)Co-SiR<sub>3</sub> intermediate that is produced by an alternate activation mode of the pre-catalyst (<sup>Mes</sup>PDI)Co-Me by a silane in which methane is produced.<sup>2f</sup> We propose that the low-temperature reduction of the [(PDI)CoCl<sub>2</sub>] with NaEt<sub>3</sub>BH directly gives the corresponding [(PDI)CoH (**21**)], that reacts with the alkene **16** to give a (alkyl)-Co species **22a**,<sup>17</sup> which upon reaction with the silane gives the linear adduct (**17a**), regenerating the metal hydride **21** (Scheme 6). A similar minor pathway is followed for the formation of the branched isomeric product, **17b**.

In an alternate mode of activation to give a reactive hydride catalyst, the complex **15** (Z = Me) was treated with hydrogen at low temperature (Eq 7, see Supporting Information for details) and the resulting product (presumably the corresponding Co-H (**15**, Z = H)<sup>17a</sup> was used for the hydrosilylation of 1-octene. A clean hydrosilylation (Figure 5) to give a mixture of **17a** and **18a** (6:94) in high yield is observed. Most strikingly *no dehydrogenative* silylation was observed under these conditions. The difference in regioselectivities between the use of <sup>Mes</sup>(PDI)CoCl<sub>2</sub>/NaB(Et)<sub>3</sub>H/PhSiH<sub>3</sub> (Table 4, entry 1) and this hydrogenative activation of **15** (Z = Me) [Eq 7] currently remains unknown. The presence of an equivalent amount of a Lewis acid (Et<sub>3</sub>B) in the former reaction could be responsible of this remarkable result (vide infra).





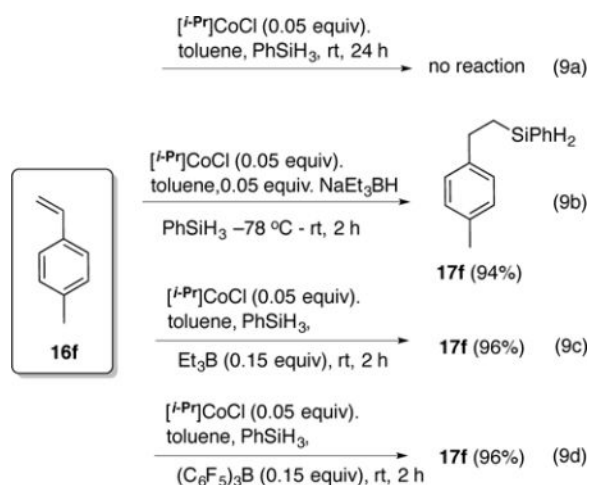
Several pieces of anecdotal evidence support this mechanism. Reaction with  $\text{PhSiD}_3$  in the presence of  $[(^i\text{PrPDI})\text{CoCl}_2]$  and  $\text{NaEt}_3\text{BH}$  gives exclusively 2-d<sub>1</sub>-*n*-octylphenylsilane- $(\text{Si})\text{d}_2$  (**25**) with > 96% incorporation of D as determined NMR and GC-MS (Eq 8). No D-incorporation was seen at other sites (D-NMR), which rules out the possibility of reversible Co-H(D) or LCo-{Si} addition to the alkene. While the catalyst prepared from  $(^{\text{Mes}}\text{PDI})\text{Co-Me}$  effects dehydrogenative silylation of terminal alkenes,<sup>2f</sup> we have seen no trace of this product under the low temperature conditions in which the catalyst was generated from  $(^{\text{Mes}}\text{PDI})\text{CoCl}_2$ . Such products are also not seen in the hydrosilylation of 1,3- or 1,4-dienes (Eq 1, 2 and 3), that initially gives an internal alkene, which, in principle, could serve as sources of allyl silanes. Recall that an internal alkenes of this kind is known to undergo Co-H mediated isomerization followed by dehydrogenative silylation.<sup>2f,2e</sup>



The effect of ligand on regioselectivity in the hydrosilylation of 1-octene catalyzed by complexes derived from  $\text{CoCl}_2$  and various PDI ligands (**4a–4c**) supports the key role of a presumed Co-H intermediate (Table 4, Figure 3). Thus the catalyst generated from  $(^{\text{Mes}}\text{PDI})\text{CoCl}_2$ ,  $[(\mathbf{4c})\text{CoCl}_2]$ , gives a quantitative yield of the anti-Markovnikov (**17a**) and the Markovnikov (**18a**) adducts in a ratio of 52:48 (Entry 1, Table 4). For the most sterically demanding complex,  $(^i\text{PrPDI})\text{CoCl}_2$ ,  $[(\mathbf{4a})\text{CoCl}_2]$ , this ratio is up to 99:1 (Entry 3, Table 4). No trace of the dehydrogenative silylation was observed in any of these reactions, carried out using the catalyst generated at  $-78\text{ }^\circ\text{C}$ .

Several experiments were conducted to examine the role of the external reducing agent on the course of this reaction. For this we first synthesized and fully characterized  $(^i\text{PrPDI})\text{CoCl}$ , by reduction of the corresponding  $(^i\text{PrPDI})\text{CoCl}_2$  with Zn.<sup>19</sup> The NMR spectrum of a product obtained by reduction of  $(^i\text{PrPDI})\text{CoCl}_2$  with 1 equivalent of  $\text{NaEt}_3\text{BH}$  closely resembles the spectrum of isolated (and purified)  $(^i\text{PrPDI})\text{CoCl}$ .<sup>11</sup> Attempted hydrosilylation reaction of 4-methylstyrene with  $\text{PhSiH}_3$  in the presence of this reagent (0.05 equiv) in toluene at room temperature gave no product (Eq 9a). Very little reaction was observed up to 24 h. However, a catalyst generated by addition of 1 equivalent

of  $\text{NaEt}_3\text{BH}$  to the above mixture results in a quantitative reaction in  $\sim 2$  h (Eq 9b). An equally facile reaction ensues when the  $\text{Co(I)Cl}$ -complex is activated by addition of a Lewis acid such as  $\text{Et}_3\text{B}$  or  $(\text{C}_6\text{F}_5)_3\text{B}$  (Eq 9c, 9d). Indeed the catalyst generated from  $(i\text{-PrPDI})\text{CoCl}$  and  $(\text{C}_6\text{F}_5)_3\text{B}$  has broad applications in addition of primary, secondary and tertiary silanes to wide range of alkenes and these results will be reported separately.<sup>20</sup> These experiments suggest that  $(i\text{-PrPDI})\text{CoH}$  (presumably produced by the reaction of the cationic  $\text{Co(I)}$  with the silane in this instance) rather than the  $(i\text{-PrPDI})\text{CoCl}$  is the active catalyst in these hydrosilylation reactions *under our conditions*. We believe that the formation of a silyl-cobalt species (**23**) from **21** and  $\text{PhSiH}_3$  is unlikely at  $-78$  °C,<sup>21</sup> since **21** would be expected to undergo faster addition to the alkene. At higher temperatures either **21** or **15** ( $Z = \text{Me}$ ) could lead to **23** and this might explain the unusual regioselectivity (major branched product, **18a**) seen in Eq 7. The subtleties of these transformations and the role of the silanes in on the regioselectivity of this transformation must await further work.



We have carried out a series of NMR experiments which further rules out the possibility of  $\text{PhSiH}_3$  as a reducing agent for  $(i\text{-PrPDI})\text{CoCl}$ . For example, there is no time-dependent change in the NMR spectrum of a 1:1 mixture of this complex and  $\text{PhSiH}_3$  in  $\text{C}_6\text{D}_6$  up to 24 h. No changes were observed upon addition of 4-methylstyrene to this mixture. Specifically no signals corresponding to  $\text{PhSi}(\text{Cl})\text{H}_2$  is seen in these  $^1\text{H}$  NMR spectra. However, the addition of  $\text{B}(\text{C}_6\text{F}_5)_3$  results in a fast and exceptionally clean conversion to the product, the anti-Markovnikov adduct **17f**. In the absence of the alkene, a mixture of  $(i\text{-PrPDI})\text{CoCl}$ ,  $\text{PhSiH}_3$  and  $(\text{C}_6\text{F}_5)_3\text{B}$  resulted in a spectrum that contained no discernable features. Recall that a hydride in  $(i\text{-PrPDI})\text{CoH}$  has not been observed in the NMR spectrum even though other evidence including IR stretching attributed to  $\text{Co-H}$  has been reported.<sup>17</sup>

We might also entertain the possibility that the enhanced hydrosilylation activity of the catalysts **13** and **14** might be related to the efficient conversion of these species to a  $(\text{PDI})\text{Co-H}$ , driven by a metathesis reaction with  $\text{R}_3\text{SiH}$  in which  $\text{RC(O)O-SiR}_3$  is formed. Formation of a stable  $\text{Si-O}$  bond might be the driving force for this reaction.

Finally, the mechanism of the highly efficient (0.001 equivalent catalyst) and *exclusive reduction* of the alkene with *no hydrosilylation* that is observed upon using  $(\text{EtO})_2\text{SiMeH}$  instead of  $\text{PhSiH}_3$  is currently not known and remains under investigation.<sup>14</sup> One plausible explanation relies on an alternate path for the intermediate **22a** (Scheme 6), which undergoes a  $\sigma$ -bond metathesis to give a cobalt(I)-silyl complex **24**. This complex returns the catalyst **21** through an as yet unknown mechanism. Circumstantial evidence for this route includes the establishment of a strict stoichiometric relation between the silane and the reduction product, and, isolation of polymeric silane byproducts that presumably arises from **24**.

## Conclusions

In spite of the prolific research activity in the hydrofunctionalization reactions of alkenes, there is dearth of reports dealing with preparatively useful, selective hydrosilylation of dienes. A study of effects of ligands, silanes, promoters, counter ions, solvents and of reaction parameters on a cobalt-catalyzed hydrosilylation of 1,3-dienes reveals a surprisingly simple procedure to effect highly selective anti-Markovnikov hydrosilylation of 1,3- and 1,4-dienes. Thus readily accessible  $(^i\text{PrPDI})\text{CoCl}_2$  reacts with 2 equivalents  $\text{NaEt}_3\text{BH}$  at  $-78^\circ\text{C}$  in toluene to generate a catalyst that effects highly selective anti-Markovnikov hydrosilylation of the terminal double bond in 1,3- and 1,4-dienes. Primary and secondary silanes such as  $\text{PhSiH}_3$ ,  $\text{Ph}_2\text{SiH}_2$  and  $\text{PhSi}(\text{Me})\text{H}_2$  react with a broad spectrum of 1,3-dienes without affecting the configuration of the second double bond. When dienes conjugated to an aromatic residue are involved, both Markovnikov and anti-Markovnikov products are formed. Reactions of 1-alkene under similar conditions cleanly lead to a mixture of Markovnikov and anti-Markovnikov hydrosilylation products, with the ratio of the products increasingly favoring the latter, as the size of the 2,6-substituents in the aryliminoyl group becomes larger. The complex  $(^p\text{PrPDI})\text{CoCl}_2$  gives exclusively the linear silane for a wide variety of terminal alkenes. Under these conditions no trace of dehydrogenative silylation products (allyl silanes), which have been reported in reactions catalyzed by structurally related cobalt complexes [e.g.,  $(^{\text{Mes}}\text{PDI})\text{Co-X}$ ,  $\text{X} = \text{Me}, \text{Cl}$ ], are observed. Hydrosilylation of 1-octene with  $\text{PhSiD}_3$  produces the expected product with  $>97\%$  incorporation of the 3 deuteriums. An in situ generated complex from  $(^i\text{PrPDI})\text{CoCl}$  and  $\text{NaEt}_3\text{BH}$ ,  $\text{Et}_3\text{B}$  or  $(\text{C}_6\text{F}_5)_3\text{B}$  also catalyzes the reaction giving identical distribution of hydrosilylation products when alkenes are reacted with  $\text{PhSiH}_3$ . A mechanism that involves a metal hydride is proposed. A reactive catalyst generated from  $^{\text{mes}}(\text{PDI})\text{Co-Me}$  complex and hydrogen, behaves like the combination of  $(\text{PDI})\text{CoCl}_2$  and 2 equivalents of  $\text{NaEt}_3\text{BH}$ : in that 1-octene undergoes exclusive hydrosilylation, and no dehydrogenative silylation, but with different regioselectivity. The origin of this selectivity is currently unknown.<sup>15</sup> Reduction of the terminal double bond (*vis-à-vis* hydrosilylation) when  $(\text{EtO})_2\text{Si}(\text{Me})\text{H}$  is used in the place of  $\text{PhSiH}_3$  is rationalized on the basis of an alternate decomposition path for the linear Co(I)-alkyl intermediate that involves this silane.

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

## Acknowledgments

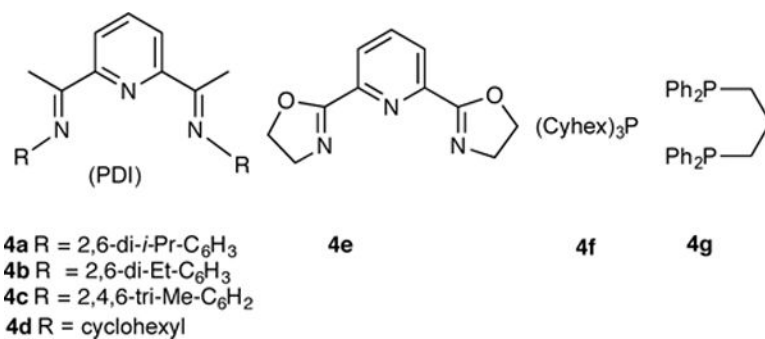
Authors thank Vagulejan Balasanthiran of this department for providing some of the (PDI)CoCl complexes and for some early NMR experiments using these complexes. Financial assistance for this research provided by US National Science Foundation CHE-1362095 and NIH (R01 GM108762).

## References

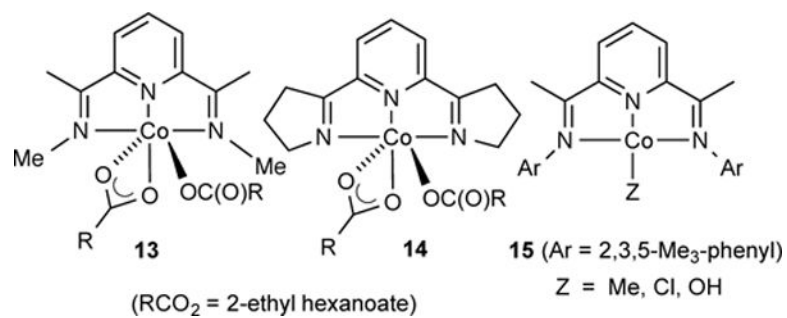
1. For recent reviews, see:(a) Sun J, Deng L. *ACS Catalysis*. 2016; 6:290–300.(b) Nakajima Y, Shimada S. *RSC Adv*. 2015; 5:20603–20616.(c) Greenhalgh MD, Jones AS, Thomas SP. *ChemCatChem*. 2015; 7:190–222.(d) Chirik, PJ. *Catalysis without Precious Metals*. Bullock, RM., editor. Wiley-VCH; Weinheim, Germany: 2010. p. 83-110.(e) Marciniak, B., editor. *Hydrosilylation: A Comprehensive Review on Recent Advances*. Springer; Berlin: 2009.
2. For representative examples of recent contributions from various research groups, see the following references and others cited there in: Cobalt-catalysis:(a) Du X, Zhang Y, Peng D, Huang Z. *Angew Chem Int Ed*. 2016; 55:6671–6675.(b) Ibrahim AD, Entsminger SW, Zhu LY, Fout AR. *ACS Catal*. 2016; 6:3589–3593.(c) Schuster CH, Diao T, Pappas I, Chirik PJ. *ACS Catal*. 2016; 6:2632–2636. (d) Noda D, Tahara A, Sunada Y, Nagashima H. *J Am Chem Soc*. 2016; 138:2480–2483. [PubMed: 26760915] (e) Chen C, Hecht MB, Kavara A, Brennessel WW, Mercado BQ, Weix DJ, Holland PL. *J Am Chem Soc*. 2015; 137:13244–13247. [PubMed: 26444496] (f) Atienza CCH, Diao T, Weller KJ, Nye SA, Lewis KM, Delis JGP, Boyer JL, Roy AK, Chirik PJ. *J Am Chem Soc*. 2014; 136:12108–12118. [PubMed: 25068530] (g) Mo Z, Liu Y, Deng L. *Angew Chem Int Ed*. 2013; 52:10845–10849.(h) Brookhart M, Grant BE. *J Am Chem Soc*. 1993; 115:2151–2156. Iron: (i) Sunada Y, Noda D, Soejima H, Tsutsumi H, Nagashima H. *Organometallics*. 2015; 34:2896–2906. (j) Nikonov GI. *ChemCatChem*. 2015; 7:1918–1919.(k) Chen J, Cheng B, Cao M, Lu Z. *Angew Chem Int Ed*. 2015; 54:4661–4664.(l) Greenhalgh MD, Frank DJ, Thomas SP. *Adv Synth Catal*. 2014; 356:584–590.(m) Peng D, Zhang Y, Du X, Zhang L, Leng X, Walter MD, Huang Z. *J Am Chem Soc*. 2013; 135:19154–19166. [PubMed: 24304467] (n) Kamata K, Suzuki A, Nakai Y, Nakazawa H. *Organometallics*. 2012; 31:3825–3828.(o) Tondreau AM, Atienza CCH, Weller KJ, Nye SA, Lewis KM, Delis JGP, Chirik PJ. *Science*. 2012; 335:567–570. Nickel: [PubMed: 22301315] (p) Srinivas V, Nakajima Y, Ando W, Sato K, Shimada S. *J Organomet Chem*. 2016; 809:57–62.(q) Buslov I, Becouse J, Mazza S, Montandon-Clerc M, Hu X. *Angew Chem Int Ed*. 2015; 54:14523–14526.(r) Miller ZD, Dorel R, Montgomery J. *Angew Chem Int Ed*. 2015; 54:9088–9091.
3. (a) Lappert MF, Nile TA, Takahashi S. *J Organomet Chem*. 1974; 72:425–439.(b) Cornish AJ, Lappert MF, Nile TA. *J Organomet Chem*. 1977; 132:133–148.(c) Cornish AJ, Lappert MF, Nile TA. *J Organomet Chem*. 1977; 136:73–85.
4. Hilt G, Lüers S, Schmidt F. *Synthesis*. 2003; 2003:634–638.
5. Wu JY, Stanzl BN, Ritter T. *J Am Chem Soc*. 2010; 132:13214–13216. [PubMed: 20809631]
6. Parker SE, Borgel J, Ritter T. *J Am Chem Soc*. 2014; 136:4857–4860. A lone example of 1,2-addition of PhSiMe<sub>2</sub>H to isoprene was published while we were preparing this manuscript. See ref. 2b. [PubMed: 24650185]
7. (a) Timsina YN, Sharma RK, RajanBabu TV. *Chem Sci*. 2015; 6:3994–4008. [PubMed: 26430505] (b) Biswas S, Page JP, Dewese KR, RajanBabu TV. *J Am Chem Soc*. 2015; 137:14268–14271. [PubMed: 26529467]
8. These results were first reported at the 251st National ACS Meeting in San Diego, March 2016, Abstract ORGN 427. Several publications dealing with Co-catalyzed hydrosilylations have since appeared (ref 2a–d).
9. PDI and related redox-active ligands have a long history in cobalt-mediated polymerization and hydrofunctionalization reactions:(a) Small BL, Brookhart M, Bennett AMA. *J Am Chem Soc*. 1998; 120:4049–4050.(b) Britovsek GJP, Bruce M, Gibson VC, Kimberley BS, Maddox PJ, Mastroianni S, McTavish SJ, Redshaw C, Solan GA, Strömberg S, White AJP, Williams DJ. *J Am Chem Soc*. 1999; 121:8728–8740.
10. For reactivity and applications of PDI ligands in hydrofunctionalization reactions, see:(a) Zhu D, Thapa I, Korobkov I, Gambarotta S, Budzelaar PHM. *Inorg Chem*. 2011; 50:9879–9887.

[PubMed: 21520927] (b) Bart SC, Chlopek K, Bill E, Bouwkamp MW, Lobkovsky E, Neese F, Wiegardt K, Chirik PJ. *J Am Chem Soc.* 2006; 128:13901–13912. [PubMed: 17044718] (c) Tondreau AM, Atienza CCH, Weller KJ, Nye SA, Lewis KM, Delis JGP, Chirik PJ. *Science.* 2012; 335:567–570. [PubMed: 22301315] (d) Obligacion JV, Chirik PJ. *J Am Chem Soc.* 2013; 135:19107–19110. See also ref <sup>2c</sup> and <sup>2f</sup>. [PubMed: 24328236]

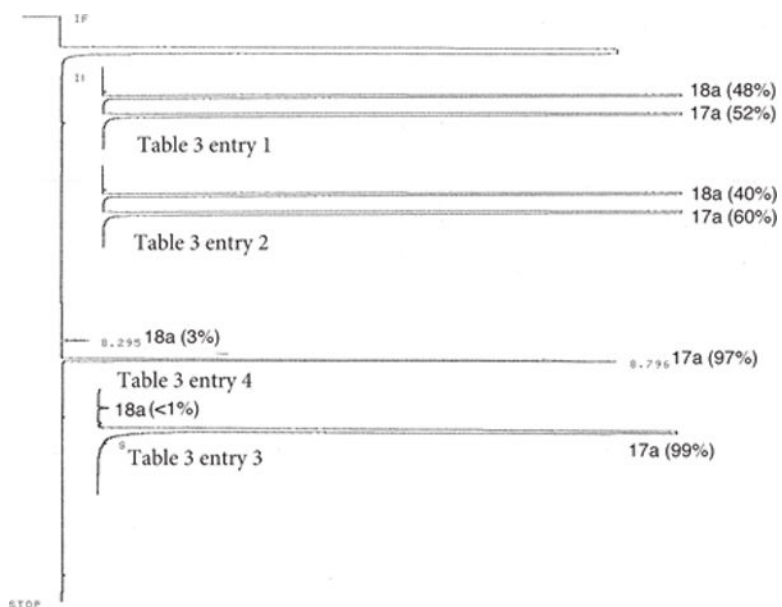
11. See Supporting Information for details. Data for full characterization of the products and gas chromatographic analysis of products of key reactions are included there.
12. See Supporting Information for the effect of various activators on the selectivity of hydrosilylation of 1,3-dienes (Table S1).
13. For the effect of solvents, the counter ions and experimental parameters, see Supporting Information for details (Tables S2 and S3).
14. Raya B, Biswas S, RajanBabu TV. *ACS Catal.* 2016; 6:6318–6323. [PubMed: 28078166]
15. See ref <sup>2f</sup>, especially, Supporting Information of this reference, p S8. We have repeated these experiments and looked at ligand effects in the reactions of (TMSO)<sub>2</sub>Si(Me)H with alkenes. As reported<sup>2f</sup> only dehydrogenative hydrosilylation and reduction were observed under these conditions. See Table S4 and pages S143–S145 in the Supporting Information for details. However, in sharp contrast, a 1:1 mixture of PhSiH<sub>3</sub> and 1-octene in toluene mixed in the presence of **15** (Z = Me) [or the corresponding *i*-Pr(PDI)Co-Me] and subsequently stirred to room temperature gives exclusive hydrosilylation giving **17a** and **18a** in a ratio of 10:90 in ~ 85% yield (See Supporting Information p S138–S142). No dehydrogenative silylation was observed under these conditions for PhSiH<sub>3</sub>. This unusual dependence on silane in these reactions on hydrosilylation vs dehydrogenative silylation, and, the reversal in regioselectivity in hydrosilylation are currently under investigation.
16. These studies were originally done with 1-octene and 4-methylstyrene as model substrates. See supporting Information for detailed Tables showing the effect of various parameters on the selectivity of this reaction.
17. (a) Tellmann KP, Humphries MJ, Rzepa HS, Gibson VC. *Organometallics.* 2004; 23:5503–5513. (b) Knijnenburg Q, Horton AD, Heijden Hvd, Kooistra TM, Hetterscheid DGH, Smits JMM, Bruin Bd, Budzelaar PHM, Gal AW. *J Mol Catal A Chem.* 2005; 232:151–159.
18. See Supporting Information (Table S5) for the effect of temperature, stoichiometry of reagents and reaction conditions on the distribution of products (dehydrogenative silylation, hydrosilylation and reduction) in the reactions of (TMSO)<sub>2</sub>Si(Me)H with 1-octene.
19. Gibson VC, Humphries MJ, Tellmann KP, Wass DF, White AJP, Williams DJ. *Chem Commun.* 2001; 2001:2252–2253.
20. This catalyst facilitates the anti-Markovnikov addition of PhSiH<sub>3</sub>, Ph(Me)SiH<sub>2</sub>, Ph<sub>2</sub>SiH<sub>2</sub> and Et<sub>3</sub>SiH to various alkenes in >95% yield. These results will be reported separately. Lewis-acid-catalyzed addition of silanes to alkenes is a well-established reaction that requires high catalysts loading and works most efficiently for tertiary silanes Rubin M, Schweir T, Gevorgyan V. *J Org Chem.* 2002; 67:1936–1940. In the present case, the addition of PhSiH<sub>3</sub> to 4-methylstyrene in the presence 5 mol% B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, gave multiple products as identified by GCMS. These included the linear hydrosilylation product **17f**, dimer of the 4-methylstyrene (mass 236) and materials with higher retention times, possibly 2:1 (16f + PhSiH<sub>3</sub>) and other similar adducts. [PubMed: 11895414]
21. Several Co(III) hydrides resulting from oxidative addition of PhSiH<sub>3</sub> to Co(I) complexes have been reported in the literature. See:(a) Scheuermann ML, Semproni SP, Pappas I, Chirik PJ. *Inorg Chem.* 2014; 53:9463. [PubMed: 25171221] (b) Rozenel SS, Padilla R, Arnold J. *Inorg Chem.* 2013; 52:11544. [PubMed: 24050728] (c) See also, ref <sup>2b</sup>.



**Figure 1.**  
Ligands L in precatalysts [L]CoCl<sub>2</sub> for hydrosilylation



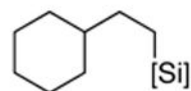
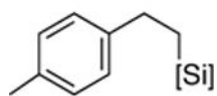
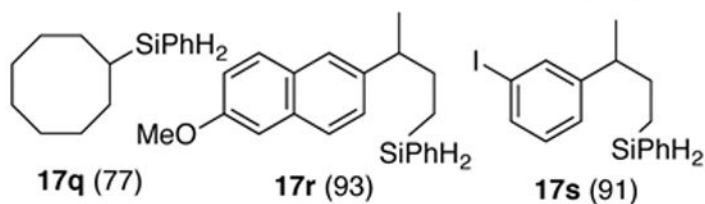
**Figure 2.** Chirik's catalysts for hydroxylation (13, 14) and dehydrogenative silylation (15) of alkenes



**Figure 3.** Ligand Effects on Markovnikov vs anti-Markovnikov Hydro-silylation of 1-Octene. GCs of crude reaction mixtures. (Table 4)



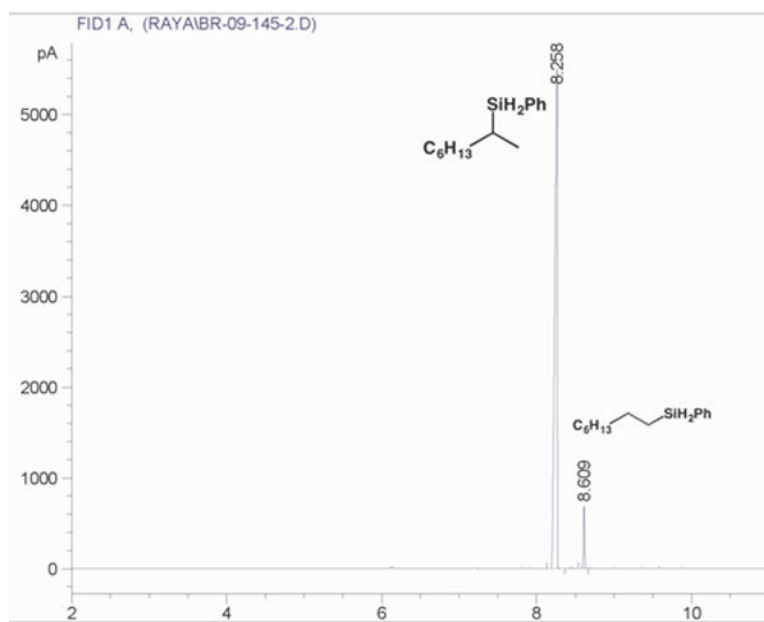
- 17a** C<sub>6</sub>H<sub>13</sub> (84)                      **17i** 4-Cl-phenyl (89)  
**17b** C<sub>8</sub>H<sub>17</sub> (86)                      **17j** 3-Br-phenyl (87)  
**17c** 2-propyl (94)                      **17k** 3-PhO-phenyl (86)  
**17d** cyclohexyl (88)                    **17l** 4-*i*-Bu-phenyl (89)  
**17e** TMS (91)                            **17m** 3-F-4-Ph-phenyl (91)  
**17f** 4-Me-phenyl (89)                  **17n** 3,4-(OCH<sub>2</sub>O)-phenyl (92)  
**17g** benzyl (91)                        **17o** 4-OAc-phenyl (91)  
**17h** CH<sub>2</sub>CH<sub>2</sub>Ph (97)                  **17p** 6-OMe-2-naphthyl (89)



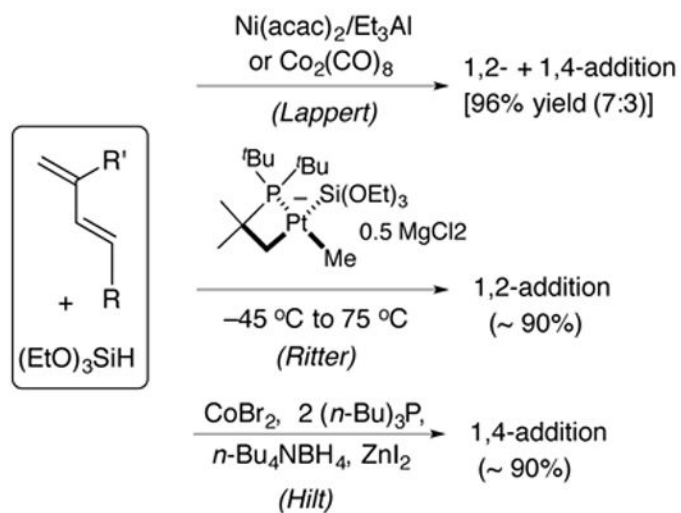
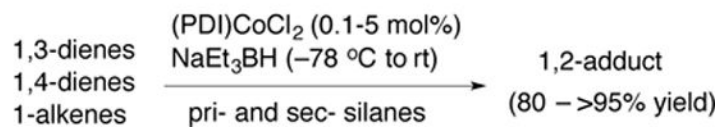
**17u** [Si] = Si(Me)(Ph)H (89)

**17w** [Si] = Si(Me)(Ph)H (87)

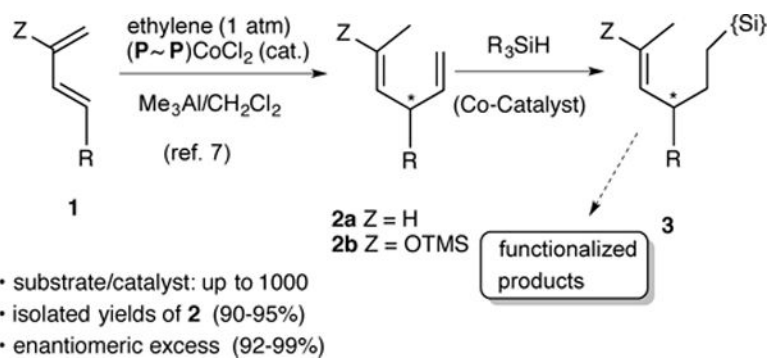
**Figure 4.**  
Scope of hydrosilylation of 1-alkenes



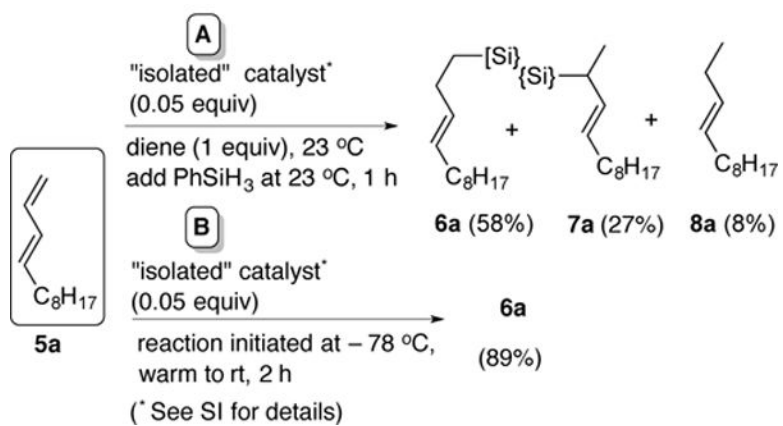
**Figure 5.**  
Gas chromatogram showing crude reaction mixture of Eq 7.

**Previous work** (Hydrosilylation of 1,3-dienes)**This work** (1,3- and 1,4-dienes, 1-alkenes)**Scheme 1.**

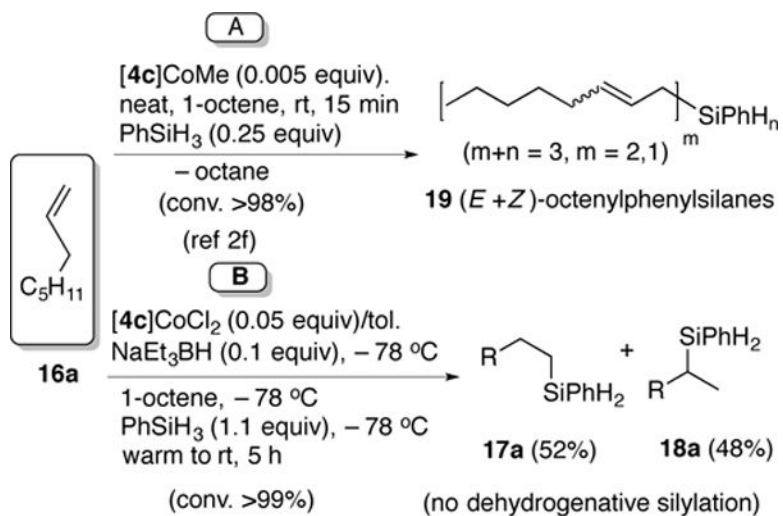
Regioselectivity in 1,2-Hydrosilylation of Dienes



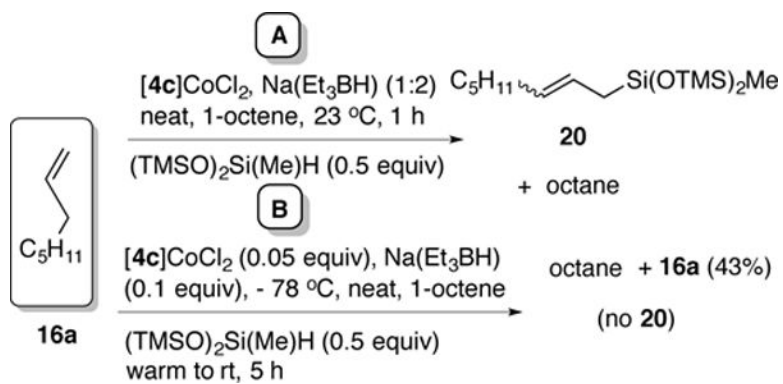
**Scheme 2.**  
Chemoselective Functionalization of Asymmetric Hydrovinylation Products of 1,3-Dienes



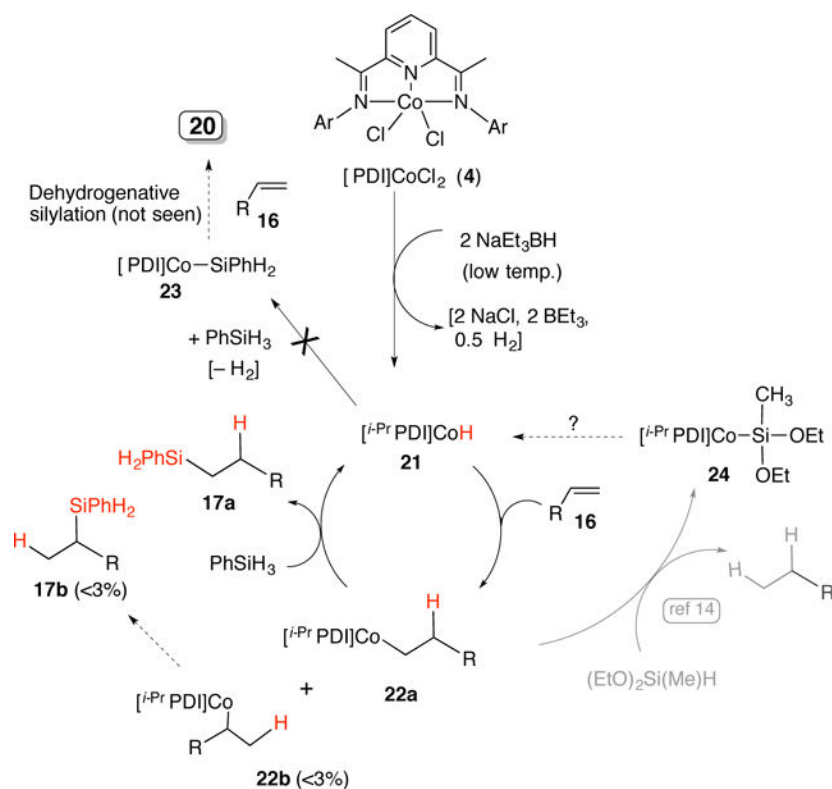
**Scheme 3.**  
Effect of Temperature on Selectivity



**Scheme 4.**  
Dehydrogenative Silylation and Hydrosilylation Using [4c]CoX Catalysts



**Scheme 5.**  
Dehydrogenativesilylation vs Reduction in Reactions of 1-Octene and  $(TMSO)_2SiMeH$



**Scheme 6.**  
Possible Mechanism of Low-Temperature Hydrosilylation of Alkenes Catalyzed by  $(PDI)CoCl_2/NaEt_3BH$



Effect of Ligands in (L)CoCl<sub>2</sub> on the Co-Catalyzed Hydroxylation of (*E*)-1,3-Dodecadiene<sup>a</sup>

Table 1

entry	L	Products (%)			
		6a	7a	8a	5a
1	<b>4a</b>	94	4	0	<2
2 <sup>b</sup>	<b>4a</b>	82	3	7	4
3	<b>4b</b>	14	6	33	0 <sup>c</sup>
4	<b>4c</b>	0	0	36	0 <sup>c</sup>
5	<b>4d</b>	2	3	0	82
6	<b>4e</b>	1	7	16	38 <sup>c</sup>
7	<b>4f</b>	9	18	14	27 <sup>c</sup>
8	<b>4g</b>	15	5	0	80

<sup>a</sup>See Eq 1 and Supporting Information for details. For scouting experiments, 5 mol% Co(II) complex, 10 mol% NaEt<sub>3</sub>BH, tol., -78 °C to rt. Ratios of products determined by GC. Results from at least 2 experiments.

<sup>b</sup>NaEt<sub>3</sub>BH/toluene was added at room temperature.

<sup>c</sup>Significant amounts of Ph<sub>2</sub>SiH<sub>2</sub> also produced. In these low-yielding reactions significant amounts of the starting material along with several other unidentified products were detected by the GC.

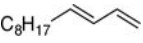
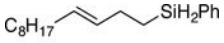
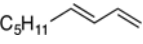
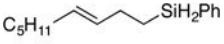
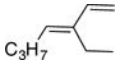
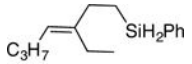
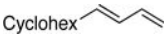
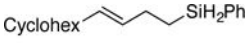
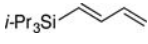
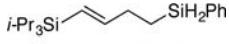
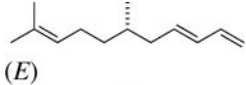
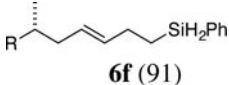
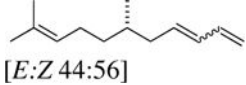
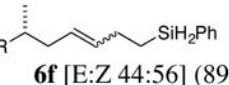
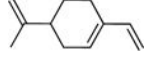
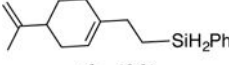
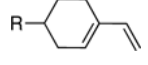
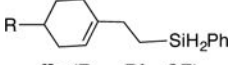
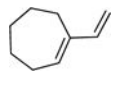
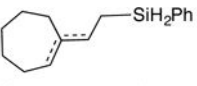
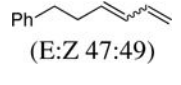
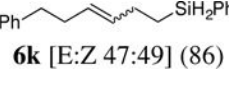
**Table 2**Effect of Silane on the Co-Catalyzed Hydrosilylation of (*E*)-1,3-Dodecadiene<sup>a</sup>

entry	silane	products (%) <sup>b</sup>			
		6a	7a	8a	5a
1	PhSiH <sub>3</sub>	94	4	0	0
2	PhMeSiH <sub>2</sub>	94	6	0	0
3	Ph <sub>2</sub> SiH <sub>2</sub>	92	4	4	0
5	Ph <sub>3</sub> SiH	-	-	64	34
6	Cl <sub>3</sub> SiH	0	0	0	100
7	Et <sub>3</sub> SiH	0	0	0	100
8	Et <sub>2</sub> SiH <sub>2</sub>	0	0	0	100
9	(EtO) <sub>2</sub> MeSiH	0	0	100	0
10	(MeO) <sub>2</sub> MeSiH	0	0	100	0

<sup>a</sup>See Eq 1 and Supporting Information for details. For scouting experiments, 5 mol% catalyst [4a]CoCl<sub>2</sub>, 10 mol% activator, toluene, -78 °C to rt., ~ 5h<sup>b</sup>Ratios of products determined by GC. Results from at least 2 experiments.

Table 3

Hydrosilylation of 1,3-Dienes<sup>a</sup>

No	diene	product (yield)
1.		 <b>6a</b> (91)
2.		 <b>6b</b> (81)
3.		 <b>6c</b> (87)
4.		 <b>6d</b> (93)
5.		 <b>6e</b> (92)
6.	 ( <i>E</i> )	 <b>6f</b> (91)
7.	 [ <i>E:Z</i> 44:56]	 <b>6f</b> [ <i>E:Z</i> 44:56] (89)
8.		 <b>6g</b> (88)
9.		 <b>6h</b> (R = Ph, 87) <b>6i</b> (R = <i>t</i> -Bu, 91)
10.		 <b>6j</b> (1,2:1,4 = 67:33)
11.	 ( <i>E:Z</i> 47:49)	 <b>6k</b> [ <i>E:Z</i> 47:49] (86)

No	diene	product (yield)
12.		<b>6l-1</b> <b>6l-b</b> [1:b 34:66] (89)
13.		<b>6m-1</b> <b>6m-b</b> [1:b 42:58] (84)
14.		+ <b>6n</b> [1, 4:1, 2 = 86:11]
15.	$\beta$ -myrcene	+ <b>6o</b> [1, 4:1, 2 = 67:33] (87)
16.		<b>6p</b> (81)
17.		<b>6q</b> (61)

<sup>a</sup>See Eq 1 and Supporting Information for procedure.

**Table 4**Hydrosilylation of 1-Octene Using (L)CoCl<sub>2</sub>/NaEt<sub>3</sub>BH<sup>a,b</sup>

entry	L in (L)CoCl <sub>2</sub>	conv.	products (%)	
			17a	18a
1	MesPDI ( <b>4c</b> )	>99	52	48
2	EtPDI ( <b>4b</b> )	>99	60	40
3	<i>i</i> -PrPDI ( <b>4a</b> )	>99	99	1
4	<i>i</i> -PrPDI ( <b>4a</b> ) <sup>c</sup>	>99	97	3

<sup>a</sup>See Scheme 4 (B), Figure 3 and Supporting Information for details including GCs of crude reaction mixtures.

<sup>b</sup>The complex and NaEt<sub>3</sub>BH were mixed in toluene at -78 °C, reagents added and mixture warmed to rt.

<sup>c</sup>Reaction done on 0.5 g using 0.01 equiv. catalyst at 40 °C, 2 h.