

Bis(imino)pyridine Cobalt-Catalyzed Dehydrogenative Silylation of Alkenes: Scope, Mechanism, and Origins of Selective Allylsilane Formation

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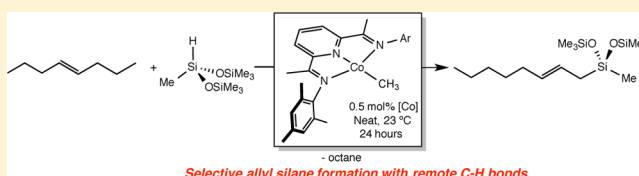
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S Supporting Information

ABSTRACT: The aryl-substituted bis(imino)pyridine cobalt methyl complex, (^{Mes}PDI)CoCH₃ (^{Mes}PDI = 2,6-(2,4,6-Me₃C₆H₂-N=CMe)₂C₅H₃N), promotes the catalytic dehydrogenative silylation of linear α -olefins to selectively form the corresponding allylsilanes with commercially relevant tertiary silanes such as (Me₃SiO)₂MeSiH and (EtO)₃SiH. Dehydrogenative silylation of internal olefins such as *cis*- and *trans*-4-octene also exclusively produces the allylsilane with the silicon located at the terminus of the hydrocarbon chain, resulting in a highly selective base-metal-catalyzed method for the remote functionalization of C–H bonds with retention of unsaturation. The cobalt-catalyzed reactions also enable inexpensive α -olefins to serve as functional equivalents of the more valuable α, ω -dienes and offer a unique method for the cross-linking of silicone fluids with well-defined carbon spacers. Stoichiometric experiments and deuterium labeling studies support activation of the cobalt alkyl precursor to form a putative cobalt silyl, which undergoes 2,1-insertion of the alkene followed by selective β -hydrogen elimination from the carbon distal from the large tertiary silyl group and accounts for the observed selectivity for allylsilane formation.

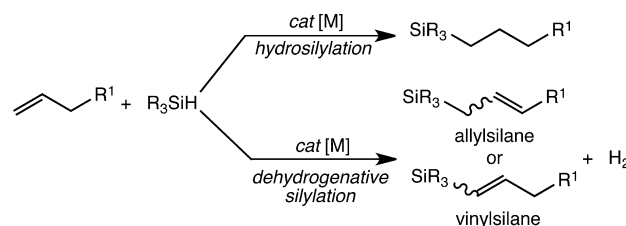


INTRODUCTION

The anti-Markovnikov hydrosilylation of terminal alkenes with precious metal catalysts is well-established and widely practiced for the commercial manufacture of adhesives, surfactants, fluids, and molding products.¹ Base-metal alternatives, particularly iron catalysts with higher activity, have been reported and often operate without solvent with high selectivity for anti-Markovnikov addition.^{2–6} An alternative and related catalytic process is dehydrogenative silylation where carbon–silicon bond formation occurs but the unsaturation of the alkene substrate is retained (Scheme 1). Formal loss of dihydrogen accompanies C–Si bond formation, and both vinyl- and allylsilanes are possible products.

Dehydrogenative silylation was first identified as an undesired side pathway that is competitive with metal-catalyzed hydrosilylation, and catalysts that selectively furnish either vinyl- or allylsilanes remain rare.^{1,7–9} Most catalysts for alkene dehydrogenative silylation rely on precious metals such as rhodium,^{10–12} iridium,^{13,14} ruthenium,¹⁵ platinum,¹⁶ and palladium.¹⁷ Examples with alternative metals including titanium,¹⁸ nickel,¹⁹ rhenium,²⁰ and iron²¹ have been reported, although regioselectivity (vinyl- versus allylsilane) and stereo-selectivity are often poor. Nakazawa and co-workers recently

Scheme 1. Metal-Catalyzed Hydrosilylation and Dehydrogenative Silylation



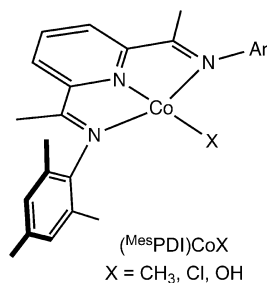
described an iron-catalyzed variant of this reaction whereby diene substrates lacking allylic hydrogens undergo C–Si bond formation to yield a vinylsilane with the other olefin serving as an internal H₂ acceptor.²² Given the utility of allylsilanes in synthesis,²³ base-metal-catalyzed dehydrogenative silylation is a potentially attractive route to these valuable products. Other precious-metal-catalyzed routes to allyl- and vinylsilanes include silyl-Heck-type reactions^{24–26} and selective alkyne hydrosilylations.^{27,28}

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Unlike with iron, cobalt-catalyzed carbon–silicon bond forming reactions remain rare. Seminal examples include cobalt carbonyl and phosphine complexes that produced low

Chart 1. (^{Mes}PDI)CoX Complexes Evaluated for the Dehydrogenative Silylation of Alkenes



hydrosilylation activity for terminal alkenes with olefin isomerization and nonselective dehydrogenative silylation as significant side reactions.^{29–33} Grant and Brookhart have reported a cyclopentadienyl cobalt complex for the selective anti-Markovnikov hydrosilylation of 1-hexene with Et₃SiH.³⁴ Isotopic labeling studies established alkene insertion into a cobalt silyl followed by chain running and ligand substitution as key steps. Experimental³⁵ and computational studies³⁶ on various cyclopentadienyl cobalt complexes with neutral ligands (L = CO, ethylene, phosphine) have been conducted to gain fundamental insight into the transformations such as Si–H oxidative addition that are likely relevant to catalytic turnover. Deng and co-workers have since described cobalt complexes supported by N-heterocyclic carbene with pendant silyl donors that are active for the hydrosilylation of 1-octene with PhSiH₃.³⁷ Although high turnover numbers were observed, the scope of the cobalt-catalyzed reaction beyond these two silane substrates has not been reported. Here we describe bis(imino)pyridine cobalt-catalyzed methods for the dehydrogenative silylation of alkenes to selectively form allylsilanes with the silyl substituent located exclusively at the terminus of the hydrocarbon chain. The method has been extended to internal olefins and provides a functionalization sequence for remote C–H bonds where unsaturation is maintained in the final product. This methodology allows

readily available olefins to function as synthetic equivalents of more valuable α,ω -dienes and provides a unique method of tethering polysiloxane fluids with defined hydrocarbon chain lengths. The origin of the high selectivity of these reactions and activation modes of the base-metal catalyst has been elucidated.

RESULTS AND DISCUSSION

Evaluation of Various Bis(imino)pyridine Cobalt Precatalysts: Dehydrogenative Silylation of 1-Octene.

Aryl-substituted bis(imino)pyridine cobalt alkyl complexes were studied for catalytic C–Si bond forming chemistry given their relative ease of preparation,³⁸ synthetic modularity, and established performance in catalytic alkene hydrogenation^{39,40} and tandem isomerization–hydroboration reactions.⁴¹ The readily available mesityl-substituted variant, (^{Mes}PDI)CoCH₃ (Chart 1), was chosen for initial evaluation using 1-octene and the commercially relevant tertiary silane, (Me₃SiO)₂MeSiH. In neat substrate and in the presence of 2 mol % of the cobalt complex, selective formation of the anti-Markovnikov allylsilane was observed as a 3:1 ratio of *E/Z* isomers. An equivalent of octane was also formed and accounts for the balance of the dihydrogen (Table 1). The reported conversions are based on consumption of silane to the allylsilane product.

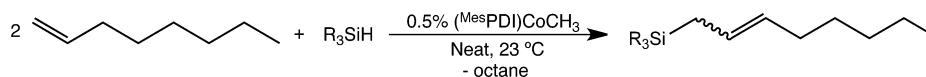
Other bis(imino)pyridine cobalt precursors were also evaluated, and the results of these studies are presented in Table 1. Both cobalt dinitrogen, (^{Ar}PDI)CoN₂,⁴² and methyl complexes are effective precursors, and as is often observed,² the catalytic activity increases with smaller 2,6-aryl substituents. Notably, both (^{Mes}PDI)CoOH and (^{Mes}PDI)CoCl are also effective precatalysts, suggesting that catalytic dehydrogenative silylation reactions may be tolerant to small quantities of water or halide impurities. Because of the ease of preparing (^{Mes}PDI)CoCH₃ and its relatively high activity in catalytic dehydrogenative silylation, subsequent experiments were conducted using this cobalt precursor. We also note that similar catalytic performance was obtained by in situ activation of the more readily accessible cobalt dihalide, (^{Mes}PDI)CoCl₂, with 2 equiv of NaBEt₃H, LiCH₃, DIBAL-H (diisobutylaluminum hydride) or LiN(SiMe₃)₂.⁴³

Table 1. Evaluation of Bis(imino)pyridine Cobalt Compounds for Catalytic Carbon–Silicon Bond Formation

entry	cobalt precursor	% conversion (1 h) ^a	% conversion (24 h) ^a
1	(^{iPr} PDI)CoN ₂	<2	39 (10:1)
2	(^{Et} PDI)CoN ₂	87	>98 (5:1)
3	(^{Mes} PDI)CoN ₂	>98 (3:1)	
4	(^{iPr} PDI)CoCH ₃	<2	38
5	(^{Mes} PDI)CoCH ₃	>98 (3:1)	
6	(^{Mes} PDI)CoOH	65	>98 (3:1)
7	(^{Mes} PDI)CoCl	18	>98 (3:1)
8	[(^{Mes} PDI)CoCH ₃][BAR ₄ ^F] ^b	<2	32

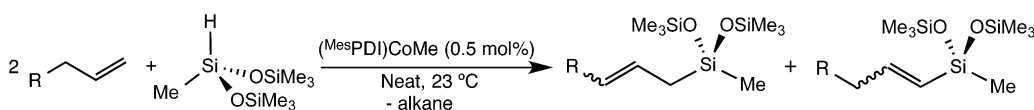
^aDetermined by GC-FID. In all cases, the % conversion was based on consumption of silane. In all cases, a 1:1 molar ratio of octane to allylsilane was observed. Values in parentheses are *E/Z* ratios. ^bBAR₄^F = B(3,5-(CF₃)₂-C₆H₃)₄. The cobalt dinitrogen complexes were prepared as described previously.⁴²

Table 2. Evaluation of Silanes in the Bis(imino)pyridine-Catalyzed Dehydrogenative Silylation of 1-Octene



silane	time	% conversion	E/Z ratio
(Me ₃ SiO) ₂ MeSiH	15 min	>98	3:1
(EtO) ₃ SiH	15 min	>98	3:1
Et ₃ SiH	24 h	>98	3:1
Ph ₂ SiH ₂	15 min	>98 ^a	2:1
PhSiH ₃ ^b	15 min	>98	2:1 ^c

^aWith 45% of the Markovnikov hydrosilylation product observed. ^bThe stoichiometry was 1:4 PhSiH₃/1-octene. ^cOverall E/Z ratio of the two octyl substituents.

Table 3. Silylation of Alkenes Using (Me₃SiO)₂MeSiH in the Presence of 0.5 mol % of (^{Mes}PDI)CoCH₃

Entry	Substrate	Time (h)	Conversion(%) ^a	Allylsilane(%)	Vinylsilane(%)
1		1	>98	82 (18) ^b	0
2		1	>98	100	0
3		1	>98	100	0
4		1	>98	100	0
5		1	>98	78 ^c	22 ^c
6		1	>98	84 ^c	16 ^c
7		1	>98	N/A	98 ^c
8		24 ^c	>98	15	85
9		24	>98	14 ^d	0
10		1	>98	100 ^e	0
11		1	>98	100 ^e	0

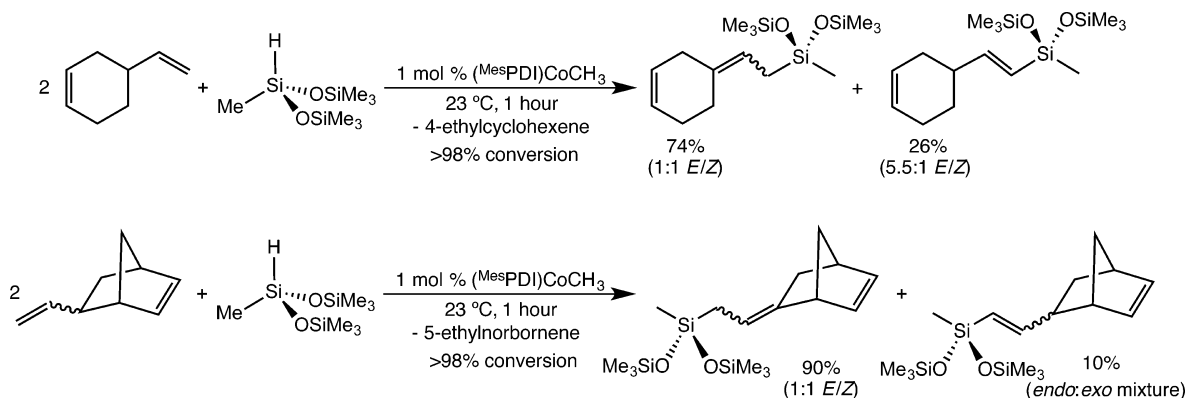
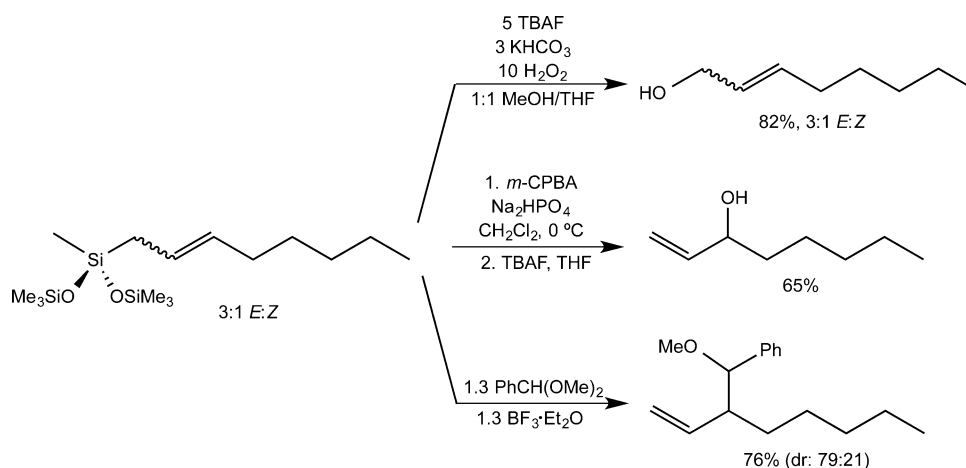
^aBased on consumption of the silane and determined by GC-FID. Unless stated otherwise, all product mixtures contain an equimolar quantity of alkane. ^bPercentage in parenthesis corresponds to propylsilane. ^cReaction performed at 65 °C. ^dCyclohexene (5 equiv) was used relative to silane, and 86% of the hydrosilylated product was observed. ^eE isomer only.

The silane substrate scope of the cobalt-catalyzed dehydrogenative silylation was also explored. Initial emphasis was on tertiary silanes due to their commercial relevance. Because of the high activity and selectivity observed with 1-octene and (Me₃SiO)₂MeSiH, each of the subsequent silane evaluation experiments was conducted with 0.5 mol % of (^{Mes}PDI)CoCH₃. As reported in Table 2, (EtO)₃SiH was also effective for dehydrogenative silylation, reaching complete conversion in approximately 15 min at 23 °C. Reduced activity was observed with Et₃SiH requiring 24 h for complete formation of the allylsilane product. In both cases, a 3:1 ratio of E/Z isomers of terminally functionalized allylsilanes were observed. Primary and secondary silanes also participated in the cobalt-catalyzed dehydrogenative silylation of 1-octene (Table 2). Ph₂SiH₂ underwent silylation to afford a mixture of 2-octyldiphenylsilane and 2-octenyldiphenylsilane with the E and Z products in a 2:1 ratio. With PhSiH₃, multiple dehydrogenative silylations occurred per silane and principally

yielded PhSi(2-octenyl)₂H as a 2:1 mixture of E and Z isomers.

The alkene scope of the bis(imino)pyridine cobalt-catalyzed dehydrogenative silylation was also explored and is presented in Table 3. Entries 1–6 demonstrate that simple, unactivated α-olefins underwent rapid and selective conversion to the corresponding anti-Markovnikov allylsilanes. In all cases, 1 equiv of the corresponding alkane accompanied the catalytic dehydrogenative silylation reactions. The reported yield of products is based on silane. The functional group tolerance of the reaction was briefly evaluated, and introduction of an allylic N,N-dimethylamino substituent (entry 10) or an allyl polyether (entry 11) had little impact on the activity or selectivity of catalytic turnover as complete conversion of silane to allylsilane was observed in less than 1 h at 23 °C. In cases where mixtures of E and Z isomers are observed, the ratios remained constant throughout the reaction and in

Scheme 2. Cobalt-Catalyzed Dehydrogenative Silylation of Dienes

Scheme 3. Application of 1-(TMSO)₂MeSi-2-octene to Synthetic Transformations

subsequent chemistry. As such, we are unable to distinguish whether the mixture is kinetic or thermodynamic in origin.

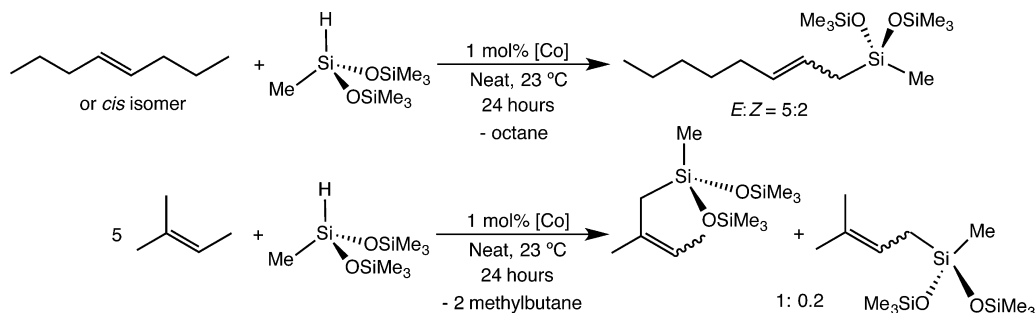
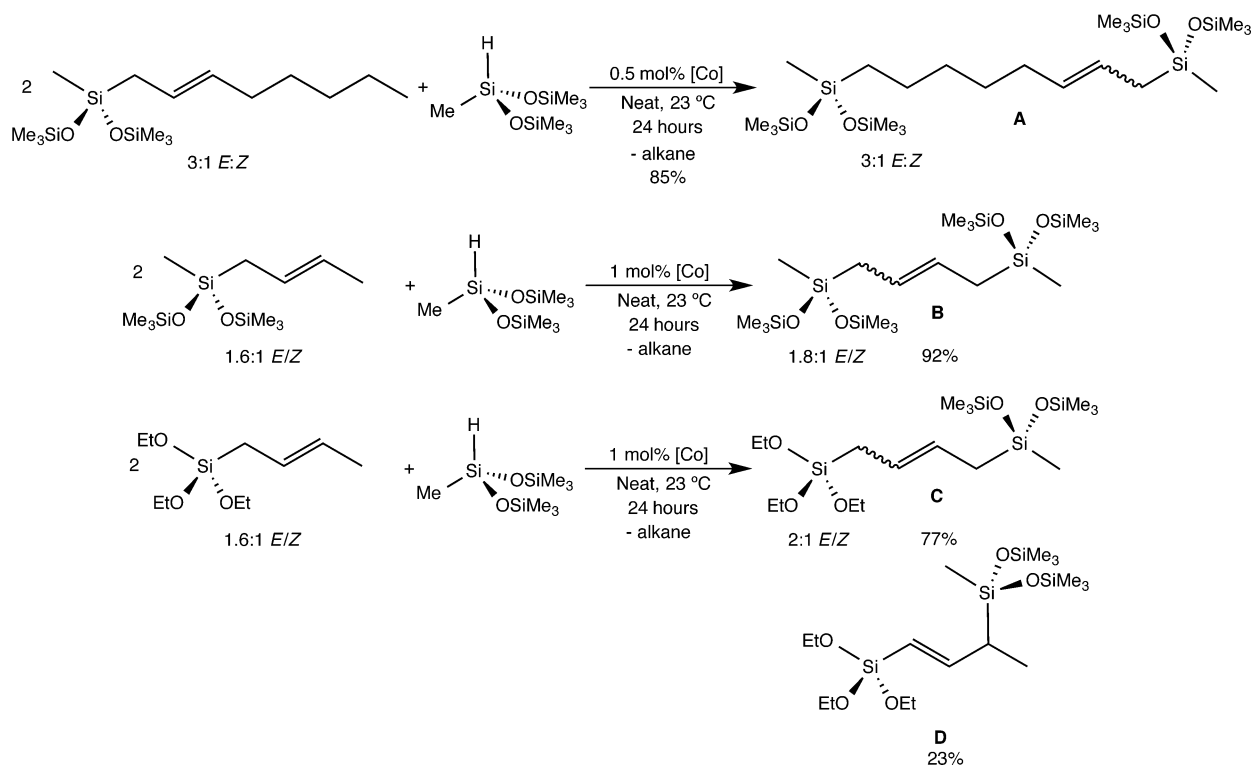
Substrates lacking allylic hydrogens were examined to probe the possibility of alternative outcomes of the dehydrogenative silylation process. For 3,3-dimethylbutene (entry 7), the *E* isomer of the vinylsilane was observed exclusively along with the requisite quantity of 2,2-dimethylbutane. The geminal olefin isobutene (entry 8) produced poor selectivity for allylsilane, yielding only 15% of the product after 24 h. Conversion, however, was complete with the remainder of the product being identified as vinylsilane. Reduced selectivity was obtained with cyclohexene (entry 9), as significant quantities (86%) of the hydrosilylation product were observed.

Because the catalytic reactions consume 1 equiv of the alkene substrate, performing the dehydrogenative silylation in the presence of sacrificial olefins as hydrogen acceptors was explored. One strategy, pioneered by Nakazawa and co-workers using cyclopentadienyl iron carbonyl precatalysts,²² relies on diene substrates where one olefin undergoes dehydrogenative silylation and the other undergoes hydrogenation. With a neat mixture of 1,5-hexadiene and (Me₃SiO)₂MeSiH in the presence of 1 mol % of (MesPDI)-CoCH₃, a complex mixture of silylated products was observed. The desired 1-silylhex-2-ene product was observed along with 1-silyl-2,5-hexadiene, 1,6-disilyl-2,4-hexadiene, 1-hexene, and hexane, suggesting that an internal hydrogen acceptor is not selective. Likewise, stirring 2:1 mixtures of either 4-vinylcyclohexene or 5-vinyl-2-norbornene with (Me₃SiO)₂MeSiH and 1

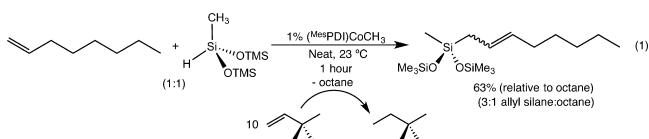
mol % of (MesPDI)CoCH₃ resulted in complete (>98%) conversion of the silane to silylated products over the course 1 h at 23 °C (Scheme 2). With 4-vinylcyclohexene, a 3:1 mixture of the allyl- and vinylsilanes was obtained. For the vinylsilanes, the *E* isomer was formed, whereas no preference for either isomer was observed with the allylsilane. In the case of 5-vinyl-2-norbornene, the allylsilane product was obtained as a 1:1 *E/Z* mixture in 90% yield. Importantly, no products featured hydrogenation of the internal alkene.

Addition of a sacrificial alkene as the hydrogen acceptor was also studied. The dehydrogenative silylation of 1-octene with (Me₃SiO)₂MeSiH was conducted with 1 mol % of (MesPDI)-CoCH₃ in the presence of 10 equiv of cyclohexene, cyclooctene, 1,5-cyclo-octadiene, or norbornene and produced no perturbation to the product mixture. By contrast, with the addition of 10 equiv of *tert*-butyl ethylene (TBE) as the H₂ acceptor, 63% of the 1-octene was converted to a 3:1 mixture of allylsilane to octane (eq 1). Small amounts, approximately 5% of the vinylsilane, were observed from dehydrogenative silylation of the TBE. Attempts to perform “acceptorless” dehydrogenative silylation by increasing the amount of silane relative to olefin were conducted with the goal of intercepting the putative cobalt hydride, (MesPDI)CoH, to liberate H₂. No perturbation to the product mixture of octane and silyloctene was observed when performing the catalytic dehydrogenative silylation with a 10:1 ratio of (Me₃SiO)₂MeSiH to 1-octene.

Scheme 4. Cobalt-Catalyzed Dehydrogenative Silylation of Internal Olefins To Yield Terminally Functionalized Allylsilanes

Scheme 5. Cobalt-Catalyzed Tandem Isomerization–Dehydrogenative Silylation of Allylsilanes^a

^aAlkane byproduct denotes alkyl silane.

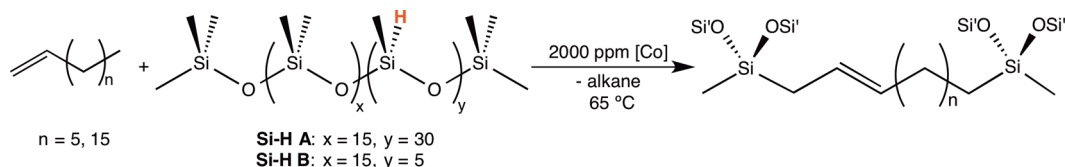


With a base-metal-catalyzed method for the synthesis of allylsilanes in hand, the utility of the products in additional synthetic transformations was briefly assayed. Using 1-(TMSO)₂MeSi-2-octene as a representative example, Tamao-Fleming oxidation (Scheme 3)⁴⁴ yielded the corresponding alcohol in 82% isolated yield while treatment with *meta*-chloroperbenzoic acid (*m*-CPBA) followed by tetrabutylammonium fluoride (TBAF) furnished 1-octen-3-ol in 65% yield (Scheme 3). An allyl transfer reaction was also explored as addition of benzaldehyde dimethylacetal to 1-(TMSO)₂MeSi-2-octene in the presence of BF₃·Et₂O as Lewis acid generated the methyl ether, 3-((methoxyphenylmethyl)-1-octene, in 76% yield (Scheme 3). Analysis of the

product by ¹H NMR spectroscopy established a 79:21 mixture of diastereomers.

Cobalt-Catalyzed Dehydrogenative Silylation of Internal Olefins: Application to Remote C–H Functionalization. The dehydrogenative silylation of linear, internal alkenes was also studied with (MesPDI)CoCH₃ to explore the selectivity of the process and potential for remote C–H bond functionalization. Our laboratory recently reported that bis(imino)pyridine iron⁴⁵ and cobalt⁴¹ precatalysts are effective for the tandem isomerization–hydroboration of internal alkenes, providing a convenient method for remote hydrofunctionalization of terminal methyl groups. If successful, cobalt-catalyzed dehydrogenative silylation would provide a similar strategy for remote terminal functionalization but maintain the unsaturation of the substrate. Controlling the selectivity of the reaction is potentially more challenging given the number of possible regioisomers of the alkene and the silyl group.

Stirring a 2:1 mixture of *cis*-4-octene and (Me₃SiO)₂MeSiH in the presence of 1 mol % of (MesPDI)CoCH₃ resulted in

Table 4. Cross-Linking of Polymeric Silylhydrides with α -Olefins in the Presence of 2000 ppm (Mes PDI)CoCH₃

siloxane	α -olefin	product label	yield of polymer
Si-H A (0.500 g)	1-octene (0.750 g)	Si-H A/C8	0.860 g (98%)
Si-H A (0.285 g)	1-octadecene (0.965 g)	Si-H A/C18	0.733 g (96%)
Si-H B (0.825 g)	1-octene (0.485 g)	Si-H B/C8	0.985 g (95%)
Si-H B (0.580 g)	1-octadecene (0.672 g)	Si-H B/C18	0.868 g (95%)

quantitative conversion to the terminal allylsilane (Scheme 4). The same outcome was observed with *trans*-4-octene. With both alkene isomers, the dehydrogenative silylation was slower than that with terminal alkenes requiring 24 h to reach complete conversion. Monitoring the course of the reaction by ¹³C NMR spectroscopy established the intermediacy of 2- and 3-octene isomers. Performing the dehydrogenative silylation with (EtO)₃SiH produced a mixture of silane redistribution products as well as octyl and octenylsilanes, suggesting that the more reactive silane intercepts cobalt internal alkyl intermediates. With Et₃SiH, however, the allylsilane was obtained in good yields (70–75%).⁴⁶ Excess olefin was used to push the reaction to completion.

The facile and selective dehydrogenative silylation of internal olefins prompted the study of allylsilanes as a means of introducing a second silyl group and accomplishing a net, remote C–H functionalization reaction. Stirring a neat 2:1 molar mixture of 1-(Me₃SiO)₂MeSi-2-octene and (Me₃SiO)₂MeSiH at 23 °C in the presence of 0.5 mol % of (Mes PDI)CoCH₃ produced an equimolar mixture of the desired doubly silylated product along with the corresponding alkane (Scheme 5). Notably, the silyl groups were located exclusively at the termini of the hydrocarbon chain, establishing a useful method for the selective, remote hydrofunctionalization of sp³ C–H bonds with retention of the allylsilane functionality in the starting material. The major isomer of the doubly silylated product, **A**, was identified and constituted 85% (relative to silane) of the product mixture as a 3:1 mixture of *E/Z* isomers, the same ratio found in starting allylsilanes. The remaining 15% of the material was also doubly silylated and is a mixture of other regioisomers. The doubly silylated product, **A**, was also obtained directly from 1-octene. Complete conversion was achieved in 24 h using 0.3 mol % of (Mes PDI)CoCH₃ (Scheme 5). In all cases, removal of the alkane byproduct was accomplished by fractional distillation.

The double silylation method was also studied with 1-butene as the shorter carbon chain facilitates product characterization by NMR spectroscopy and GC-MS methods. Addition of (Me₃SiO)₂MeSiH to neat 1-(Me₃SiO)₂MeSi-2-butene in the presence of 1 mol % of (Mes PDI)CoCH₃ resulted in complete consumption of the silane over the course of 24 h at 23 °C and furnished the 1,4-disilylated compound, **B**, as a 1.8:1 ratio of *E* and *Z* isomers in 92% yield. The remainder of the material was identified as a 1:1 mixture of linear and branched vinylsilanes. Using (EtO)₃SiH as the silane allowed introduction of two different silyl groups into the hydrocarbon chain and furnished the expected disilyl-2-butene, **C**, in 77% yield (*E/Z* = 2:1) with the remainder of

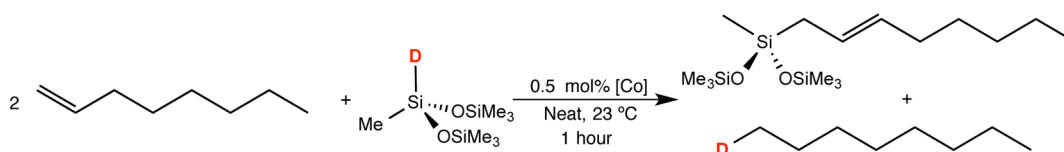
the product as the vinylsilane, **D**, arising from Markovnikov Si–H addition and olefin isomerization. Such products may prove valuable to exploit the differential reactivity of the silanes. In all dehydrogenative silylation reactions, regardless of the identity of the silane, terminal olefins such as 1-octene and 1-butene have proven to be much more reactive than the corresponding allylsilane product.

Application to Silicone Cross-Linking. The cobalt-catalyzed dehydrogenative silylation method allows readily available and inexpensive α -olefins to serve as functional equivalents of α,ω -dienes. In most cases, the dienes are expensive and, for many longer chain lengths, not commercially available. We sought to apply the remote C–H functionalization chemistry to the cross-linking of silicone fluids as tethering two poly(dimethyl)–poly(methylhydrogen) siloxanes by a defined carbon tether would provide access to new materials with potentially unique physical properties. In a typical experiment, a mixture of a poly(dimethyl)–poly(methylhydrogen) siloxane containing [Si–H] functionality was stirred with an α -olefin in the presence of 2000 ppm (0.5 mol %) of (Mes PDI)CoCH₃ (mg Co/kg reaction mixture) at 65 °C for 4 h. Two poly(dimethyl)–poly(methylhydrogen) siloxanes, **Si-H A** and **Si-H B**, that differ by the amount of [Si–H] content were examined, while both 1-octene and 1-octadecene were evaluated to determine the influence of hydrocarbon tether length on the resulting polymer properties. The results of these experiments are reported in Table 4. Each reaction initially yielded a hard gel which, following grinding and washing with hexane to remove the alkane byproduct, furnished white powders.

The degree of double silylation in the silicone polymers was determined to be between 46 and 92%, depending on the starting silane. These determinations were made using a combination of IR-ATR spectroscopy, solid-state NMR spectroscopy, and chemical degradation experiments. Representative spectra and results of Toepler pump experiments are reported in the Supporting Information. In general, use of longer chain α -olefins resulted in higher degrees of double silylation, likely due to the lower volatility of the alkene and the resulting alkane product that maintains a fluid reaction mixture. Higher degrees of double silylation were observed with decreasing amount of [Si–H] groups in the polysiloxanes. This again is likely a result of the lower viscosity of the partially silylated material, allowing the catalyst to mix with the polymer and promote additional reactivity.

A final set of control experiments was conducted to definitively confirm formation of cross-linked material derived from cobalt-catalyzed dehydrogenative silylation. The cross-linking of **Si-H A** was conducted with 1,7-octadiene in the

Scheme 6. Deuterium Labeling Studies in Bis(imino)pyridine Cobalt-Catalyzed Dehydrogenative Silylation of 1-Butene and 1-Octene



presence of 2000 ppm Karstedt's catalyst, a known hydro-silylation catalyst. Immediate gel formation and an exothermic reaction were observed. Analysis of the product using the ethanolic KOH degradation experiments established $65 \pm 4\%$ double silylation. It should be noted that in this material the hydrocarbon tether is completely unsaturated. The morphology of this material and that prepared from the cobalt-catalyzed method were indistinguishable.

Stepwise cross-linking experiments were conducted using bis(imino)pyridine cobalt-catalyzed dehydrogenative silylation. Addition of 1-octene (3 equiv per Si-H group) to Si-H A in the presence of 2000 ppm of $(^{\text{Mes}}\text{PDI})\text{CoCH}_3$ followed by analysis of the resulting material by ^1H and ^{13}C NMR spectroscopy established formation of octenyl side chains in a 2:1 E/Z ratio. No remaining silyl hydrides were detected by ^1H NMR or IR spectroscopies or by degradation with ethanolic KOH. Fresh Si-H A was then added to the octenylated polymer in the presence of 2000 ppm of $(^{\text{Mes}}\text{PDI})\text{CoCH}_3$. A significantly lower degree ($24 \pm 4\%$) of disilylation was observed in the stepwise process, likely due to more rapid gel formation and difficult diffusion in the absence of solvent.

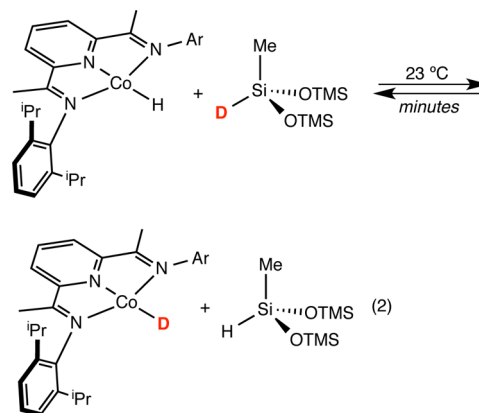
Exploring the Mechanism of Bis(imino)pyridine Cobalt-Catalyzed Alkene Dehydrogenative Silylation.

The observation of bis(imino)pyridine cobalt-catalyzed dehydrogenative silylation to selectively form allylsilanes prompted studies into the mechanism of the transformation. Questions under consideration included: (i) why do bis(imino)pyridine cobalt complexes promote dehydrogenative silylation while hydroboration selectivity was observed with the same catalyst? (ii) How is the mechanism different from Brookhart's cyclopentadienyl cobalt(III) catalyst, which is selective for alkene hydrosilylation? (iii) Why are the cobalt catalysts selective for allylsilane relative to vinylsilane? To answer these questions, the mechanism of catalytic turnover was investigated.

Stoichiometric Experiments. Our investigations were initiated by examining the activation mode of $(^{\text{Mes}}\text{PDI})\text{CoCH}_3$ under catalytic conditions. Addition of 1 equiv of 1-octene to a benzene- d_6 solution of $(^{\text{Mes}}\text{PDI})\text{CoCH}_3$ produced no change over the course of hours at 23 °C. In contrast, addition of 1 equiv of 1- $(\text{Me}_3\text{SiO})_2\text{MeSiH}$ to $(^{\text{Mes}}\text{PDI})\text{CoCH}_3$ resulted in immediate liberation of a stoichiometric quantity of methane as determined by a Toepler pump experiment. Analysis of the cobalt product by ^1H and ^{13}C NMR spectroscopy established a mixture of unidentified products, suggesting that the putative bis(imino)pyridine cobalt silyl is too reactive for observation under these conditions. Performing the reaction at lower temperatures also did not result in observation of the cobalt silyl. Addition of 1 equiv of $(\text{Me}_3\text{SiO})_2\text{MeSiD}$ to a benzene- d_6 solution of $(^{\text{Mes}}\text{PDI})\text{CoCH}_3$ resulted in formation of both CH_4 and CH_3D . Hydrolysis of the resulting mixture of cobalt complexes and analysis of the free bis(imino)pyridine ligand by ^2H NMR spectroscopy established

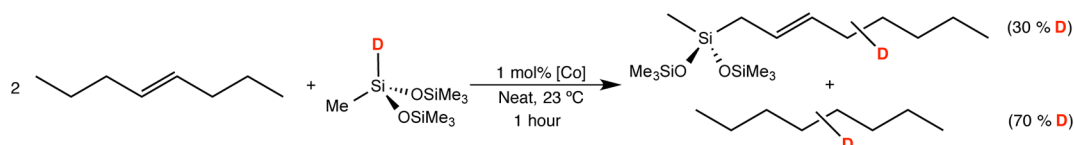
deuterium incorporation into the 2,6-methyl groups of the aryl ring, a result of reversible C-H cyclometalation. This process likely accounts for formation of CH_4 and the instability of the putative cobalt silyl.

The synthesis of another likely catalytic intermediate, $(^{\text{Mes}}\text{PDI})\text{CoH}$, was also explored. Attempts to synthesize this compound by hydrogenation of $(^{\text{Mes}}\text{PDI})\text{CoCH}_3$ have been unsuccessful. The more sterically hindered example, $(^{\text{iPr}}\text{PDI})\text{CoH}$, has been established to be observable in solution but known to convert to the corresponding dinitrogen complex, $(^{\text{iPr}}\text{PDI})\text{CoN}_2$, upon exposure to 1 atm of N_2 .^{48,49} This specific cobalt hydride compound was used as a surrogate for the mesityl variant for understanding olefin insertion chemistry. Addition of 1 equiv of 1-butene to a benzene- d_6 solution of $(^{\text{iPr}}\text{PDI})\text{CoH}$ afforded $(^{\text{iPr}}\text{PDI})\text{Co}(n\text{-butyl})$, the identity of which was confirmed by independent synthesis from addition of *n*-butyllithium to $(^{\text{iPr}}\text{PDI})\text{CoCl}$.⁴⁸ A deuterium labeling experiment was also performed. Addition of $(\text{Me}_3\text{SiO})_2\text{MeSiD}$ ⁵⁰ to the solution of $(^{\text{iPr}}\text{PDI})\text{CoH}$ in benzene- d_6 resulted in appearance of the $(\text{Me}_3\text{SiO})_2\text{MeSi-H}$ resonance, indicating rapid H/D exchange between the Si-D and Co-H (eq 2). Importantly, this experiment establishes a different activation mode for bis(imino)pyridine cobalt alkyls versus hydrides. For the former, treatment with silane generates the corresponding cobalt silyl, while for the latter, degenerate exchange occurs. While the origin of this difference is currently under investigation, these results have profound implications for cobalt-catalyzed dehydrogenative silylation as attempts to intercept the putative cobalt hydride following $\beta\text{-H}$ elimination with excess silane to regenerate the cobalt-silyl and H_2 will not occur due to these reactivity preferences.

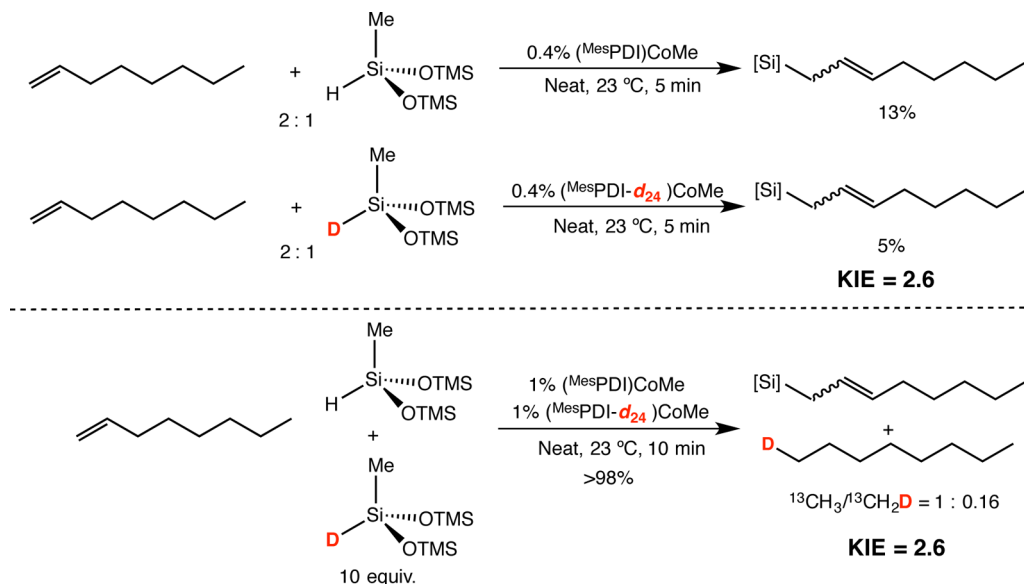


Catalytic Reactions with $(\text{Me}_3\text{SiO})_2\text{MeSiH}$. To gain insight into the catalyst resting state and possibly the turnover-limiting step of the cycle, the catalytic reaction using $(^{\text{Mes}}\text{PDI})\text{CoCH}_3$ was monitored in benzene- d_6 solution by ^1H NMR spectroscopy. At approximately 10% conversion, a mixture of two bis(imino)pyridine cobalt alkyl complexes, $(^{\text{Mes}}\text{PDI})\text{Co}(n\text{-Oct})$ and $(^{\text{Mes}}\text{PDI})\text{CoCH}_3$, was observed by ^1H

Scheme 7. Deuterium Labeling Studies in Bis(imino)pyridine Cobalt-Catalyzed Dehydrogenative Silylation of 4-Octene



Scheme 8. Determination of Deuterium Kinetic Isotope Effects in Bis(imino)pyridine Cobalt-Catalyzed Dehydrogenative Silylation of 1-Octene



NMR spectroscopy. While $(^{Mes}\text{PDI})\text{Co}(n\text{-Oct})$ is the catalyst resting state, the slow activation of $(^{Mes}\text{PDI})\text{CoCH}_3$ by the tertiary silane complicates more detailed kinetic measurements. We do note that, at longer reaction times, quantitative formation of methane was observed (vide supra) and corroborated by a Toepler pump experiment.

Catalytic dehydrogenative silylation experiments were also conducted with deuterated silane. The neat dehydrogenative silylation of 1-octene with $(\text{Me}_3\text{SiO})_2\text{SiMeD}$ in the presence of 1 mol % of $(^{Mes}\text{PDI})\text{CoCH}_3$ and analysis of the organic products by ^2H NMR spectroscopy after 1 h at 23 °C established exclusive incorporation of the isotopic label in the terminal position of the alkane byproduct (Scheme 6). Deuterium incorporation was lower than expected, likely a result of competing cyclometalation chemistry within the cobalt complex. Performing a similar isotopic labeling experiment with a 2:1 mixture of neat 1-octene and $(\text{EtO})_3\text{SiD}$ in the presence of 1 mol % of $(^{Mes}\text{PDI})\text{CoCH}_3$ also yielded octane-1- d_1 along with the expected allylsilane.

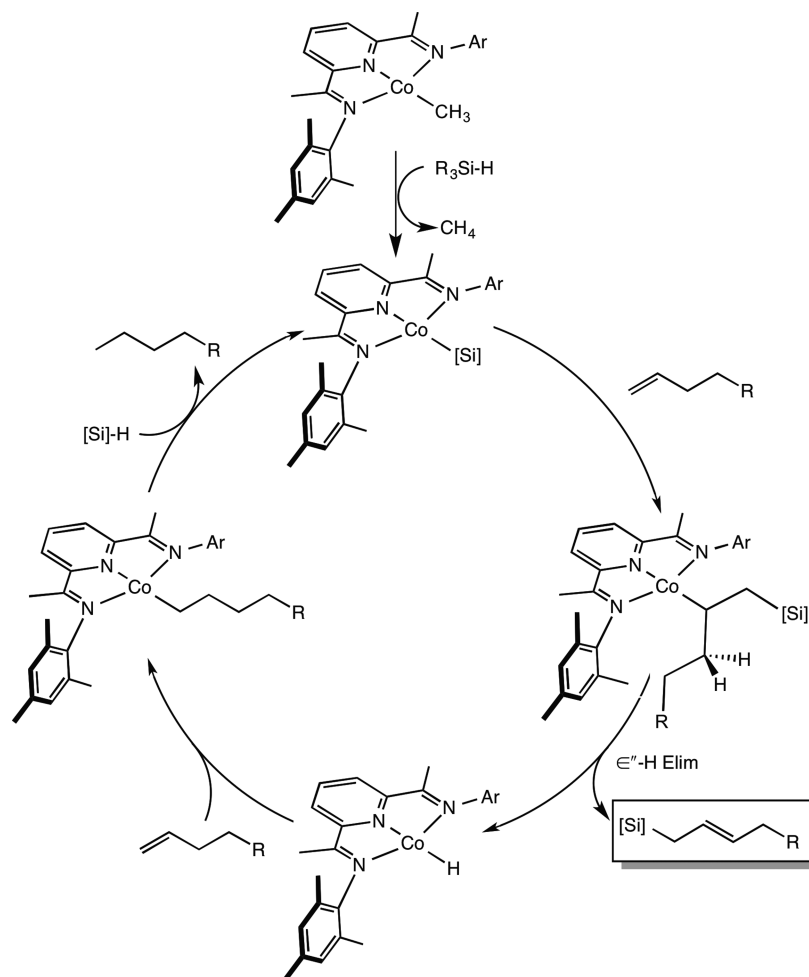
Deuterium labeling experiments were also conducted with *trans*-4-octene and $(\text{TMSO})_2\text{SiMeD}$ in the presence of 1 mol % of $(^{Mes}\text{PDI})\text{CoCH}_3$ (Scheme 7). Analysis of the organic products by ^2H and ^{13}C NMR spectroscopies established 70% incorporation of the deuterium label into octane with the remaining 30% distributed statistically throughout the allylsilane. The observation of deuterium incorporation into the allylsilane product is likely a result of reversible insertion of the starting alkene into a cobalt hydride (vide infra).

Determination of Deuterium Kinetic Isotope Effect for Dehydrogenative Silylation. To determine the deuterium kinetic isotopic effect for cobalt-catalyzed dehydrogenative silylation, two parallel catalytic reactions with

$(\text{Me}_3\text{SiO})_2\text{SiMeH}$ and $(\text{Me}_3\text{SiO})_2\text{SiMeD}$ were conducted in the presence of 0.4 mol % of $(^{Mes}\text{PDI})\text{CoCH}_3$ and $(^{Mes-d_{24}}\text{PDI})\text{CoCH}_3$, respectively. In the deuterated cobalt compound, the methyl groups on the mesityl substituent of the imine ligands were also labeled with deuterium to avoid complications with cyclometalation. After 5 min, the reactions were quenched and the products analyzed by gas chromatography. The natural abundance reaction produced 13% yield of allylsilane, whereas the reaction with $(\text{Me}_3\text{SiO})_2\text{SiMeD}$ furnished the allylsilane in 5% yield. Comparison of these values established a deuterium KIE of 2.6 at 23 °C (Scheme 8).

The deuterium kinetic isotope effect was also determined by internal competition. In this experiment, a mixture of 1-octene with 10 total equiv of silane was prepared. The composition of the silane was an equimolar mixture of $(\text{Me}_3\text{SiO})_2\text{SiMeH}$ and $(\text{Me}_3\text{SiO})_2\text{SiMeD}$. Addition of 1 mol % each of $(^{Mes}\text{PDI})\text{CoCH}_3$ and $(^{Mes-d_{24}}\text{PDI})\text{CoCH}_3$ to this mixture followed by quenching after 10 min resulted in complete conversion of the alkene. Analysis of the octane by quantitative ^{13}C NMR spectroscopy established a 1.0:0.16 ratio of octane to 1- d_1 -octane (Scheme 8). Notably, this measurement also produced a deuterium KIE of 2.6, consistent with the independent rate measurements.

Proposed Mechanism. A mechanism consistent with the experimental observations for bis(imino)pyridine cobalt-catalyzed dehydrogenative silylation is presented in Scheme 9. The sequence begins with activation of $(^{Mes}\text{PDI})\text{CoCH}_3$ with the tertiary silane to form methane and the putative cobalt silyl. This activation mode contrasts with alkene hydroboration where cobalt hydride is formed upon treatment of the corresponding alkyl complex with HBPIn.⁴¹ Following

Scheme 9. Proposed Mechanism for Bis(imino)pyridine Cobalt-Catalyzed Dehydrogenative Silylation of α -Olefins

generation of the cobalt silyl, the first equivalent of the terminal alkene undergoes 2,1-insertion, forming a secondary bis(imino)pyridine cobalt alkyl complex, accounting for the anti-Markovnikov selectivity in the dehydrogenative silylation. Subsequent fast β -hydrogen elimination furnishes the observed allylsilane. The selective formation of allyl- rather than vinylsilane is derived from preferential β -hydrogen elimination away from the large tertiary silane substituent and forms the cobalt hydride, $(^{\text{Mes}}\text{PDI})\text{CoH}$. The stoichiometric experiments and those previously reported by Gibson⁴⁸ suggest that the insertion of a second equivalent of olefin is fast to furnish the bis(imino)pyridine cobalt alkyl intermediate. When internal alkenes such as 4-octene are used as substrates, either the cobalt hydride or the silyl alkyl complex can promote chain-running processes through reversible β -H elimination and olefin insertion events, evident from the observation of 2- and 3-octenes during the dehydrogenative silylation process. The observation of 2- and 3-octenes during the dehydrogenative silylation process suggests that isomerization from the hydride can occur in the absence of C–Si bond formation. The reaction of bis(imino)pyridine cobalt alkyl with silane is the turnover-limiting step, liberating the corresponding alkane and regenerating the cobalt silyl, consistent with the observation of bis(imino)pyridine cobalt alkyl as the resting state. This proposal is also in agreement with the primary deuterium kinetic isotope effects determined

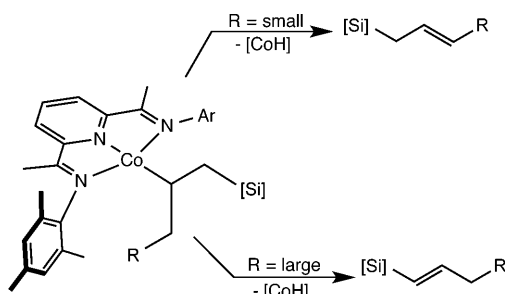
from both independent rate measurement and intermolecular competition.⁵¹

A similar mechanistic proposal has been offered by Grant and Brookhart for the *hydrosilylation* of 1-hexene by cyclopentadienyl cobalt(III) complexes with Et_3SiH .³⁴ Notably, isotopic labeling studies with Et_3SiD placed deuterium in the 6-position of the hexyl silane, consistent with rapid chain running prior to C–Si bond formation. Activation of the cobalt alkyl by Et_3SiH was proposed to form a cobalt silyl which undergoes 2,1-insertion of 1-hexene to furnish the silyl alkyl. Chain running without olefin dissociation forms a terminal cobalt hexyl complex that upon reaction with additional Et_3SiH releases the observed product and regenerates the active silyl complex. The difference between the cyclopentadienyl complex of Brookhart and bis(imino)pyridine derivative reported here is that the former does not dissociate olefin following β -hydrogen elimination while the latter does. The origin of this discrepancy is likely due to the presence of an electrophilic and relatively substitutionally inert Co(III) complex in the cyclopentadienyl case versus a more reducing and labile Co(II) center in the bis(imino)pyridine derivative.^{39,42}

The selective formation of allyl- rather than vinylsilane is derived from preferential β -hydrogen elimination away from the large tertiary silane substituent and forms the cobalt hydride. Support for sterically induced selectivity for allylsilane formation is derived from variation of the alkene substrates

reported in Table 3. For relatively small α -olefins, such as propene and 1-octene, the steric profile of the tertiary silane is dominant and directs β -hydrogenation elimination away from the large substituent, resulting in exclusive formation of allylsilane. Introduction of a $[\text{CMe}_3]$ (Table 3, entry 5) or $[\text{SiMe}_3]$ (Table 3, entry 6) along the hydrocarbon chain increases the steric profile along the alkyl and results in formation, albeit in minor amounts, of vinylsilane co-product. A model for these observations is presented in Scheme 10. Similar control of allyl- versus vinylsilane selectivity using

Scheme 10. Model for Altering the Selectivity for Selective Allylsilane Formation in Bis(imino)pyridine Cobalt-Catalyzed Dehydrogenative Silylation



ligand control has been reported by Watson and co-workers in palladium-catalyzed silyl Heck chemistry.²⁶

CONCLUDING REMARKS

A cobalt-catalyzed method for the dehydrogenative silylation of alkenes has been discovered. With α -olefins and tertiary silanes, the catalytic process is highly selective for formation of allylsilane with the silyl group located exclusively at the terminus of the hydrocarbon chain. Notably, this selectivity has been extended to internal alkenes such as *cis*- and *trans*-4-octene, providing a method for the remote silylation of unactivated C–H bonds with retention of unsaturation. This method has also been extended to the cross-linking of silicone fluids where commercially available α -olefins serve as synthetic equivalents of α,ω -dienes. An additional application of this method has been made to the synthesis of unsaturated silahydrocarbons.⁵² Deuterium labeling experiments in conjunction with substrate scope and in situ monitoring experiments support a mechanism involving initial formation of a cobalt silyl complex followed by 2,1-olefin insertion and selective β -hydrogen elimination to form a cobalt hydride and the allylsilane. Insertion of a second equivalent of alkene followed by turnover-limiting reaction with silane completes the catalytic cycle. The selectivity for cobalt silyl rather than cobalt hydride formation as the mode of catalyst activation is likely the origin of dehydrogenative silylation reactivity.

EXPERIMENTAL SECTION⁵³

Synthesis of $(^{\text{Mes}}\text{PDI})\text{CoOH}$. A 20 mL scintillation vial was charged with 0.100 g (0.203 mmol) of $(^{\text{Mes}}\text{PDI})\text{CoCl}$, 0.012 g (0.30 mmol, 1.5 equiv) of NaOH, and approximately 10 mL of THF. The reaction mixture was stirred for 2 days, and a color change from dark pink to red was observed. The volatiles were removed in vacuo, and the residue was dissolved in approximately 20 mL of toluene. The resulting solution was filtered through Celite, and the solvent was removed from the filtrate in vacuo. Recrystallization of the crude product from 3:1 pentane/toluene yielded 0.087 g (90%) of dark pink crystals identified as $(^{\text{Mes}}\text{PDI})\text{CoOH}$. The compound is

dichroic, exhibiting a pink color with a green hue. ^1H NMR (500 MHz, C_6D_6): δ = 0.26 (s, 6H, $\text{C}(\text{CH}_3)$), 1.07 (s, 1H, CoOH), 2.10 (s, 12H, *o*- CH_3), 2.16 (s, 6H, *p*- CH_3), 6.85 (s, 4H, *m*-aryl), 7.49 (d, 2H, 3-pyridine), 8.78 (t, 1H, 4-pyridine). ^{13}C $\{^1\text{H}\}$ NMR (125 MHz, C_6D_6): δ = 19.13 (*o*- CH_3), 19.42 ($\text{C}(\text{CH}_3)$), 21.20 (*p*- CH_3), 114.74 (4-pyridine), 121.96 (3-pyridine), 129.22 (*m*-aryl), 130.71 (*o*-aryl), 134.78 (*p*-aryl), 149.14 (*i*-aryl), 153.55 (2-pyridine), 160.78 ($\text{C}=\text{N}$). IR (C_6H_6): ν_{OH} = 3582 cm^{-1} . Anal. Calcd for $\text{C}_{27}\text{H}_{32}\text{CoN}_3\text{O}$: C, 68.49; H, 6.81; N, 8.87. Found: C, 68.40; H, 7.04; N, 8.77.

General Procedure for the Dehydrogenative Silylation of 1-Octene with Different Silanes Using $(^{\text{Mes}}\text{PDI})\text{CoCH}_3$. A scintillation vial was charged with 0.100 g (0.891 mmol) of 1-octene and 0.449 mmol (0.5 equiv) of the desired silane (0.100 g of $(\text{Me}_3\text{SiO})_2\text{MeSiH}$, 0.075 g of $(\text{EtO})_3\text{SiH}$, or 0.052 g of Et_2SiH), and 0.001 g (0.002 mmol, 0.5 mol %) of $(^{\text{Mes}}\text{PDI})\text{CoCH}_3$ was then added to the mixture. The reaction was stirred at room temperature for the desired amount of time and then quenched by exposure to air. The product mixture was analyzed by gas chromatography and NMR spectroscopy (see Table S3). The allylsilane was purified by passing the mixture through a silica gel column with hexane followed by removal of the volatiles in vacuo. The reaction of 1-octene and $(\text{Me}_3\text{SiO})_2\text{MeSiH}$ was further optimized using 1.000 g (8.912 mmol) of 1-octene, 1.000 g (4.494 mmol, 0.504 equiv) of $(\text{Me}_3\text{SiO})_2\text{MeSiH}$, and 0.003 g (0.006 mmol, 0.14 mol %) of $(^{\text{Mes}}\text{PDI})\text{CoCH}_3$, and 1.413 g (94%) of the allylsilane product was obtained after filtration through a silica plug.

Silylation of 1-Bis(trimethylsilyloxy)methylsilyl-2-octene with $(\text{Me}_3\text{SiO})_2\text{MeSiH}$ Using $(^{\text{Mes}}\text{PDI})\text{CoCH}_3$. This experiment was performed in a manner similar to the silylation of 1-octene using 0.100 g (0.301 mmol) of 1-bis(trimethylsilyloxy)methylsilyl-2-octene, 0.034 g (0.152 mmol, 0.51 equiv) of $(\text{Me}_3\text{SiO})_2\text{MeSiH}$, and 0.001 g (0.002 mmol, 1 mol %) of $(^{\text{Mes}}\text{PDI})\text{CoCH}_3$. The reaction was stirred at room temperature for 24 h and quenched by exposure to air. Analysis of the mixture by GC-FID, GC-MS, and NMR spectroscopy showed an approximately 1:0.85 mixture of 1-bis(trimethylsilyloxy)methylsilyloctane and 1,8-bis(bis(trimethylsilyloxy)methylsilyl)-2-octene (0.15 equiv are regioisomers). The disilylated product was determined to be a 3:1 *E/Z* mixture by NMR spectroscopy. Similar results were obtained when the vinylsilane, (*E*)-1-bis(trimethylsilyloxy)methylsilyl-1-octene, was used.

Alternative Procedure for the Double Silylation of 1-Octene with $(\text{Me}_3\text{SiO})_2\text{MeSiH}$ Using $(^{\text{Mes}}\text{PDI})\text{CoCH}_3$. This experiment was performed in a manner similar to the silylation of 1-octene using 1.000 g (8.912 mmol) of 1-octene, 1.500 g (6.742 mmol, 0.756 equiv) of $(\text{Me}_3\text{SiO})_2\text{MeSiH}$, and 0.010 g (0.021 mmol, 0.3 mol %) of $(^{\text{Mes}}\text{PDI})\text{CoCH}_3$. The reaction was stirred at room temperature for 24 h and quenched by exposure to air. Analysis of the crude mixture by GC-FID showed an approximately 2:1:1 mixture of octane, 1-bis(trimethylsilyloxy)methylsilyloctane and 1,8-bis(bis(trimethylsilyloxy)methylsilyl)-2-octene (major isomer, 85%). The mixture was passed through silica gel using hexane, and the volatiles were removed in vacuo. The mono- and disilylated products were separated by vacuum distillation. 1-Bis(trimethylsilyloxy)methylsilyloctane was isolated as the fraction that boiled at 45 $^{\circ}\text{C}$ (5 mmHg), and the disilylated product was collected as the residue (1.126 g, 92%).

ASSOCIATED CONTENT

Supporting Information

Additional experimental details, including general considerations, complete characterization data for allylsilanes and polymeric silanes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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