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

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ABSTRACT: Readily accessible (^{*i*-Pr}PDI)CoCl₂ [^{*i*-Pr}PDI = 2,6-*bis*(2,6-diisopropylphenyliminoethyl)pyridine] reacts with 2 equivalents of NaEt₃BH 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 PhSiH₃, Ph₂SiH₂ and PhSi(Me)H₂ 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 hydrosilation 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*}PrDI)CoCl₂ 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-à-vis hydrosilylation) when (EtO)₂Si(Me)H is used in the place of PhSiH₃ is explained on the basis of an alternate silane-mediated decomposition path for the linear Co(I)-alkyl intermediate.

KEYWORDS: hydrosilyaltion, cobalt, 1,3-dienes, 1,4-dienes, 1-alkenes, vinylarenes, chemoselectivity, regioselectivity

Introduction

Hydrosilylation of alkenes catalyzed by complexes of earthabundant late-transition metals as replacements for traditional platinum catalysts have attracted significant attention recently. Most notable among these are catalysts derived from iron, cobalt, and, to a limited extend, nickel.² In sharp contrast to numerous procedures that have been published for the hydrosilylation of alkenes, only a limited number of reports deal with hydrosilvlation of dienes, even though the reactions of these substrates have a long history, starting with the early studies of Lappert, who investigated nickel,^{3a,b} and cobalt^{3c} 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 1,4adducts in good yields, especially with an optimized Ziegler system using Ni(acac)₂/ R_3Al [acac = acetylacetonate]. More recently, Hilt reported the use of zinc-reduced $[(n-Bu)_3P]CoBr_2$ as a catalyst for exclusive 1,4-hydrosilylation of isoprene with (EtO)₃SiH.⁴ Ritter reported a broadly applicable 1,4hydrosilylation of 1,3-dienes with tertiary silanes [e.g., (EtO)₃SiH, Et₃SiH and (EtO)₂Si(Me)H] using Fe(0) complexes of 2-aryliminoylpyridine as catalysts.⁵ Except for an isolated example of the use of a platina-metalacycle catalyst (Scheme 1) for the 1,2-addition of (EtO)₃SiH to 1,3-dienes,⁶ practical methods for the selective 1,2-hydrosilylation of 1,3-dienes are conspicuously absent in the literature.

Scheme 1. Regioselectivity in 1,2-Hydrosilylation of Dienes

Previous work (Hydrosilylation of 1,3-dienes)



This work (1,3- and 1,4-dienes, 1-alkenes)

1,3-dienes	(PDI)CoCl ₂ (0.1-5 mol%) NaEt₂BH (–78 ºC to rt)	1 2-adduct
1,4-dienes 1-alkenes	pri- and sec- silanes	(80 – >95% yield)

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).⁷ We reasoned that chemo- and regio-selective hydrosilylation of the terminal double bonds in the hydrovinylation products without affecting the other functional groups including very sensitive silvl 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)CoCl₂ [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 the 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.⁸ These results are reported in this paper.

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



· enantiomeric excess (92-99%)

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 $4a-d^{9,10}$ and the 2,6-*bis*oxazolylpyridine ligand $4e^{2c}$ were found to show broad range of activities in a prototypical hydrosilylation of (*E*)-1,3dodecadiene (5a) using phenylsilane as the silylating agent (Eq 1 and Table 1).



Figure 1. Ligands L in precatalysts [L]CoCl₂ for hydrosilylation

Hydrosilylation of 1,3-dodecadiene (**5a**) typically gave 3 products, in addition to the unreacted starting material and a silane metathesis product, Ph_2SiH_2 . 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.¹¹ The ratios were

initially determined by gas chromatographic analysis and later confirmed by ¹H NMR after work up and purification. From these studies the ligand ^{*i*-Pr}PDI [(**4a**)] was identified as the best ligand for 1,2-hydrosilyaltion of 1,3-dodecadiene (Entries 1 and 2, Table 1). The best selectivity is obtained when the catalyst is generated at -78 °C (entry1). If the catalyst is generated at room temperature, significant amount of a reduction product (**8a**) is observed in addition to **6a** and **7a**.



Table 1. Effect of Ligands in $(L)CoCl_2$ on the Co-Catalyzed Hydrosilylation of (E)-1,3-Dodecadiene^a

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

^a See Eq 1 and Supporting Information for details. For scouting experiments, 5 mol% Co(II) complex, 10 mol% NaEt₃BH, tol., -78 °C to rt. Ratios of products determined by GC. Results from at least 2 experiments. ^b NaEt₃BH/toluene was added at room temperature. ^c Significant amounts of Ph₂SiH₂ also produced. In these low-yielding reactions significant amounts of the starting material along with several other unidentified products were detected by the GC.

A quick survey of most commonly used activators (NaEt₃BH, EtMgBr, MeLi, Me₃Al, Et₂Zn, *n*-BuLi, methyl aluminoxane) showed that NaEt₃BH is the best reagent for reduction of the [PDI]CoCl₂ complexes, especially if the reaction is carried out at low temperature (Supporting Information, Table S1, entry 1).¹²

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.¹³ 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.¹³ 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 Ph₂SiH₂. Note that none of the side products were observed in toluene. Only the (^{*i*-Pr}PDI)CoCl₂ gave a preparatively useful

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hydrosilylation reaction. Complexes from (^{*i*-Pr}PDI)CoX₂ (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 Ph₂SiH₂ when PhSiH₃ 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)CoCl₂ complexes ease of reduction (with Zn) has been found important in other cobalt-catalyzed coupling reactions such as hydrovinylation reaction.^{7a} For a dramatic effect of counter ion in hydrosilylation see ref. 2c.

In view of the extensive literature on the use of (PDI)Cocomplexes 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 [(^{i-Pr}PDI)CoCl₂ + 2 equiv NaEt₃BH at -78 °C, toluene] *at room temperature* gave a mixture of products consisting of **6a**, **7a**, **8a** and a silane metathesis product Ph₂SiH₂, 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.

Scheme 3. Effect of Temperature on Selectivity



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**)CoCl₂, (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 NaEt₃BH (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, PhSiH₃, and secondary silanes PhMeSiH₂ and PhSiH₂ gave excellent yields of the 1,2-hydrosilylation products, while the tertiary silanes Cl₃SiH and Et₃SiH are totally unreactive under the standard conditions (entries 6-7). Et₂SiH₂ 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.¹⁴

 Table 2. Effect of Silane on the Co-Catalyzed Hydrosilylation of (E)-1,3-Dodecadiene^a

ontru	cilana	prod	ucts (%) ^b	
entry	shahe	6a	7a	8a	5a
1	PhSiH ₃	94	4	0	0
2	PhMeSiH ₂	94	6	0	0
3	Ph_2SiH_2	92	4	4	0
5	Ph ₃ SiH	-	-	64	34
6	Cl ₃ SiH	0	0	0	100
7	Et ₃ SiH	0	0	0	100
8	Et_2SiH_2	0	0	0	100
9	(EtO) ₂ MeSiH	0	0	100	0
10	(MeO) ₂ MeSiH	0	0	100	0

^a See Eq 1 and Supporting Information for details. For scouting experiments, 5 mol% catalyst [**4a**]CoCl₂, 10 mol% activator, tol., -78 °C to rt., \sim 5h ^b Ratios of products determined by GC. Results from at least 2 experiments.

The selective 1.2-hydrosilvlation of 1.3-dienes using PhSiH₃ and Ph₂SiH₂ 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 PhSiH₃ under the optimized conditions (Eq 1) using $[4a]CoCl_2$ 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 regioand stereoselectivity of the silvlation 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 silvlation 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 (61-l and 61-b). This might reflect the enhanced stability of a putative η -3 Co-allyl complex and trapping of such a complex from an equilibrium mixture of intial LCo-H adducts when a sterically unencumbered silane (e. g., PhSiH₃) is used. Among the dienes we have examined isoprene gave mostly (86%) 1,4-hydrosilylation (6n) with \sim

11% 1,2-addition. β-Myrcene gave a mixture of 1,2- and 1,4addition products 60-(1,2) and 60-(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 prepartive 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, Ph₂SiH₂ and $Ph(Me)SiH_2$ 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 PhSiH₃ even though they were not explored further in this study.

Table	3. Hydrosilylation of 1,3-	-Dienes ^a
No	diene	product (yield)
1		C _e H ₁₇ SiH ₂ Ph
1.	C ₈ H ₁₇	6a (91)
		C-H
2.	C ₅ H ₁₁	6b (81)
	_	
3.		C ₃ H ₇ SiH ₂ Ph
	C ₃ H ₇	6c (87)
	~ ~	Cyclober SiH ₂ Ph
4.	Cyclohex	6d (93)
	<.	SiH ₂ Ph
5.	<i>i-</i> Pr ₃ Si	60 (02)
	I =	Ue (92)
6.		R SiH ₂ Ph
	(E)	6f (91)
_		SiH ₂ Ph
7.	$F \cdot 7 \Lambda \cdot 56$	$\mathbf{R} \sim \mathbf{V} \sim \mathbf{V}^{2}$
	[<i>L</i> . <i>L</i> 44.30]	or [E.Z 44.30] (89)
8.		SiH ₂ Ph
		6g (88)
9	R-	SiH ₂ Ph
		6h ($R = Ph, 87$)
		$61 (\mathbf{R} = t - \mathbf{Bu}, 91)$
10		
10.		
		6j $(1,2:1,4=67:33)$
11.	Ph And	Ph
	(E:Z 47:49)	6k [E:Z 47:49] (86)
		Ph SiH ₂ Ph 6l -1
12.	Ph	SiH ₂ Ph
		Ph
		6l -b [1:b 34:66] (89)
		Ph SiH ₂ Ph
	- ~ ~	6m -1
13.	Ph'	\sim \downarrow SiH ₂ Ph
		Ph
		6m -b [1:b 42:58] (84)
	Ш	SiH ₂ Ph SiH ₂ Ph
14.		+
		6n $[1, 4:1, 2 = 86:11]$
		\downarrow
15.	e muraana	R
	p-myrcene	60 [1, 4:1, 2 = 67:33] (87)
16	C-H	C ₅ H ₁₁ SiHPh ₂
10.	∪ ₅ ⊓ ₁₁ × ×	6p (81)
17		C ₈ H ₁₇ Si(Me)HPh
1/.	G ₈ H ₁₇ ✓ ×	6q (61)

^a See Eq 1 and Supporting Information for procedure.

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The new protocol for the selective hydrosilation is equally applicable to skipped 1,4-dienes⁷ 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.



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).²



(dehydrogenative silylation) (reduction)

As we were reporting the use of (PDI)CoCl₂/NaEt₃BH as catalyts of hydrosilylation⁸ and reduction¹⁴ of dienes and alkenes, Chirik reported^{2c} 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] ($Z = N_2$, 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**).^{2f} In the reactions involving **15**, most notably, *no simple hydrosilylation* was observed using this silane.^{2f, 15}



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

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(1)-complexes **15** (Z = Cl, Me) give *only dehydrogenative silylation of 1-alkenes* with several silanes including PhSiH₃ and (TMSO)₂Si(Me)H.^{2f,15} Additions of phenylsilane (PhSiH₃) and diphenyl silane (Ph₂SiH₂) to 1octene 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.

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



Initially hydrosilylation of 1-octene was carried out using a catalyst derived from (MesPDI)CoCl₂ [(4c)CoCl₂] and NaEt₃BH at rt to enable a direct comparison to the results reported in the literature^{2f} (Scheme 4, **B**, Table 4). This catalyst, generated at rt has been reported to give dehydrogenative silvlation products (19).^{2f, 15} In sharp contrast, in a similar experiment, when the reaction was carried out by generating the catalyst at -78 °C by reacting [(4c)CoCl₂] and NaEt₃BH at -78 °C, and, adding 1octene and PhSiH₃ 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).¹⁶ Similar observations were made in the reactions of 4methylstyrene.¹⁶ No contamination from the dehydrogenative silvlation 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)CoCl₂ 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)CoCl₂, 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 silvlation 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).

Table4.Hydrosilylationof1-OcteneUsing(L)CoCl₂/NaEt₃BH^{a,b}

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entry	L in (L)CoCl ₂	conv.	products (%)	
			17a	18a
1	^{Mes} PDI (4c)	>99	52	48
2	^{Et} PDI (4b)	>99	60	40
3	^{<i>i</i>-Pr} PDI (4a)	>99	99	1
4	$^{i-Pr}PDI(4a)^{c}$	>99	97	3

^a See Scheme 4 (**B**), Figure 3 and Supporting Information for details including GCs of crude reaction mixtures. ^b The complex and NaEt₃BH were mixed in toluene at -78 $^{\circ}$ C, reagents added and mixture warmed to rt. ^c Reaction done on 0.5 g using 0.01 equiv. catalyst at 40 $^{\circ}$ C, 2 h.



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

Chirik has reported that in the addition of (TMSO)₂Si(Me)H to 1-octene, [(**4c**)CoCl₂] activated by NaEt₃BH at room temperature can be used in place of [(**4c**) Co-Me] to get similar results (Scheme 5).^{2f, 15} 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).^{15,18} Clearly the low temperature generation of the catalyst leads to different reactivity/selectivity.

Scheme 5. Dehydrogenativesilylation vs Reduction in Reactions of 1-Octene and (TMSO)₂SiMeH



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 18.¹⁶ The complex (4a)CoCl₂ activated by NaEt₃BH 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.^{2a-e,8} 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, 170, 17p and the cyclooctylphenylsilane 17q.



Figure 4. Scope of hydrosilylation of 1-alkenes

Four examples of addition of secondary silanes, Ph_2SiH_2 and $Ph(Me)SiH_2$ to terminal alkenes (17t-w) are also included in the Figure 4. We expect these silanes to have the same broad

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substrate scope as PhSiH₃ even though these have not yet been explored in greater detail. We have previously reported that (TMSO)₂SiMeH, (EtO)₃SiH and, (EtO)₂Si(Me)H gave only reduction of the double bond under these conditions, with (EtO)₂Si(Me)H giving the best result in the reduction.¹⁴

The study of ligand effects also revealed unexpected changes in the regioselectivity as a function of the ligand. For example, the pybox complex, (**4e**)CoCl₂, under our protocol gives the proportion of the Markovnikov products comparable to the less hindered PDI complexes **4b** and **4c** (Eq 6).



 17b + 18b
 C₈H₁₇ (86, 67:33)
 17i + 18i 4-Cl-phenyl (85,67:33)

 17d + 18d
 cyclohexyl (88, 80:20)
 17j + 18j 3-Br-phenyl (82, 66:34)

 17f + 18f
 4-Me-phenyl (87, 70:30)
 17x + 18x phenyl (89, 72:28)

Mechanistic Observations. The notable difference between the anti-Markovnikov hydrosilylation observed under conditions described in this paper [(MesPDI)CoCl2]/NaEt3BH/-78 °C, silane, alkene, warm to rt, Scheme 4, B] and the dehydrogenative silvlation/reduction observed when (MesPDI)Co-Me (15, Z = Me) is used as a catalyst (Scheme 4, \mathbf{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 silvlation presumably involves an unstable (PDI)Co-SiR₃ intermediate that is produced by an alternate activation mode of the pre-catalyst (MesPDI)Co-Me by a silane in which methane is produced.^{2f} We propose that the lowtemperature reduction of the [(PDI)CoCl₂] with NaEt₃BH directly gives the corresponding [(PDI)CoH (21)], that reacts with the alkene 16 to give a (alkyl)-Co species 22a,¹⁷ 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)^{17a} 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 regioslectivities between the use of ^{Mes}(PDI)CoCl₂/NaB(Et)₃H/PhSiH₃ (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 (Et₃B) in the former reaction could be responsible of this remarkable result (vide infra).





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

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Scheme 6. Possible Mechanism of Low-Temperature Hydrosilylation of Alkenes Catalyzed by (PDI)CoCl₂/NaEt₃BH



Several pieces of anecdotal evidence support this mechanism. Reaction with PhSiD₃ in the presence of $\left[\binom{i-P^{T}}{PDI}CoCl_{2}\right]$ and NaEt₃BH gives exclusively 2-d₁-n-octylphenylsilane-(Si)d₂ (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 (MesPDI)Co-Me effects dehydrogenative silvlation of terminal alkenes,^{2f} we have seen no trace of this product under the low temperature conditions in which the catalyst was generated from (^{Mes}PDI)CoCl₂. 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 silvlation.^{2f,2e}



The effect of ligand on regioselectivity in the hydrosilylation of 1-octene catalyzed by complexes derived from $CoCl_2$ 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 (^{Mes}PDI)CoCl₂, [(**4c**)CoCl₂], 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*-Pr}PDI)CoCl₂, [(4a)CoCl₂], 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 °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*-Pr}PDI)CoCl, by reduction of the corresponding (^{*i*-Pr}PDI)CoCl₂ with Zn.¹⁹ The NMR spectrum of a product obtained by reduction of (ⁱ⁻ ^{Pr}PDI)CoCl₂ with 1 equivalent of NaEt₃BH closely resembles the spectrum of isolated (and purified) (^{i-Pr}PDI)CoCl.¹¹ Attempted hydrosilylation reaction of 4-methylstyrene with PhSiH₃ 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 NaEt₃BH to the above mixture results in a quantitative reaction in $\sim 2 h$ (Eq 9b). An equally facile reaction ensues when the Co(I)Cl-complex is activated by addition of a Lewis acid such as Et_3B or $(C_6F_5)_3B$ (Eq 9c, 9d). Indeed the catalyst generated from (^{*i*-Pr}PDI)CoCl and (C₆F₅)₃B has broad applications in addition of primary, secondary and tertiary silanes to wide range of alkenes and these results will be reported separately.²⁰ These experiments suggest that (^{*i*-Pr}PDI)CoH (presumably produced by the reaction of the cationic Co(I) with the silane in this instance) rather than the (^{*i*-Pr}PDI)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 PhSiH₃ is unlikely at -78 °C,²¹ since **21** would be expected to undergo faster addition to the alkene. At higher temperatures either 21 or 15 (Z =Me) could lead to 23 and this might ex-

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plain 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 PhSiH₃ as a reducing agent for (^{'-Pr}PDI)CoCl. For example, there is no time-dependent change in the NMR spectrum of a 1:1 mixture of this complex and PhSiH₃ in C₆D₆ up to 24 h. No changes were observed upon addition of 4-methylstyrene to this mixture. Specifically no signals corresponding to PhSi(Cl)H₂ is seen in these ¹H NMR spectra. However, the addition of B(C₆F₅)₃ results in a fast and exceptionally clean conversion to the product, the anti-Markovnikv adduct **17f**. In the absence of the alkene, a mixture of (^{'-Pr}PDI)CoCl, PhSiH₃ and (C₆F₅)₃B resulted in a spectrum that contained no discernable features. Recall that a hydride in (^{'-Pr}PDI)CoH has not been observed in the NMR spectrum even though other evidence including IR stretching attributed to Co-H has been reported.¹⁷.

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 (PDI)Co-H, driven by a metathesis reaction with R_3SH in which RC(O)O-SiR₃ is formed. Formation of a stable 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 (EtO)₂SiMeH instead of PhSiH₃ is currently not known and remains under investigation.¹⁴ One plausible explanation relies on an alternate path for the intermediate **22a** (Scheme 6), which undergoes a σ -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 cobaltcatalyzed 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*-Pr}PDI)CoCl₂ reacts with 2 equivalents NaEt₃BH at -78 ^oC 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 PhSiH₃, Ph₂SiH₂ and PhSi(Me)H₂ 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 hydrosilation 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 (^{iPr}PDI)CoCl₂ gives exclusively the linear silane for a wide variety of terminal alkenes. Under these conditions no trace of dehydrogenative silvlation products (allyl silanes), which have been reported in reactions catalyzed by structurally related cobalt complexes [e.g., (^{Mes}PDI)Co-X, X = Me, Cl], are observed. Hydrosilylation of 1-octene with PhSiD₃ produces the expected product with >97% incorporation of the 3 deuteriums. An in situ generated complex from (^{*i*-Pr}PDI)CoCl and NaEt₃BH, Et₃B or (C₆F₅)₃B also catalyzes the reaction giving identical distribution of hydrosilvlation products when alkenes are reacted with PhSiH₃. A mechanism that involves a metal hydride is proposed. A reactive catalyst generated from mes(PDI)Co-Me complex and hydrogen, behaves like the combination of (PDI)CoCl₂ and 2 equivalents of NaEt₃BH: in that 1-octene undergoes exclusive hydrosilylation, and no dehydrogenative silvlation, but with different regioselctivity. The origin of this selectivity is currently unknown.¹⁵ Reduction of the terminal double bond (vis-à-vis hydrosilylation) when (EtO)₂Si(Me)H is used in the place of PhSiH₃ is rationalized on the basis of an alternate decomposition path for the linear Co(I)-alkyl intermediate that involves this silane.

ASSOCIATED CONTENT

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

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Notes

The authors declare no financial interest.

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(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 hydrosilyaltion 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).

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