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Distinct Catalytic Performance of Cobalt(I)-NHC Complexes in Promoting the Reaction of Alkene with Diphenylsilane: Selective 2,1-Hydrosilylation, 1,2-Hydrosilylation, and Hydrogenation of Alkene

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ABSTRACT: Selectivity control on the reaction of alkene with hydrosilane is a challenging task in the development of nonprecious metal-based hydrosilylation catalysts. While the traditional way of selectivity control relies on the use of different ligandtype and/or different metals, we report herein that cobalt(I) complexes bearing different *N*-heterocyclic carbene ligands (NHCs) exhibit distinct selectivity in catalyzing the reaction of alkene with Ph₂SiH₂. [(IAd)(PPh₃)CoCl] (IAd = 1,3-diadamantylimidazol-2ylidene) is an efficient catalyst for *anti*-Markovnikov hydrosilylation of mono-substituted alkenes. [(IMes)₂CoCl] (IMes = 1,3dimesitylimidazol-2-ylidene) shows Markovnikov-addition selectivity in promoting the hydrosilylation of aryl-substituted alkenes. [(IMe₂Me₂)₄Co][BPh₄] (IMe₂Me₂ = 1,3-dimethyl-4,5-dimethylimidazol-2-ylidene) can catalyze hydrogenation of alkenes with Ph₂SiH₂ as the terminal hydrogen source. Mechanistic studies in combination with the knowledge on the steric nature of cobalt-NHC species suggest that (NHC)cobalt(I) silyl species and bis(NHC)cobalt(I) hydride species are the probable key intermediates for these hydrosilylation and hydrogenation reactions, respectively. The different steric nature of IAd *versus* IMes and the potential of IMes incurring $\pi \cdots \pi$ interaction with aryl-substituted alkenes are thought the causes for the observed 1,2- and 2,1-additionselectivity.

KEYWORDS: N-heterocyclic carbene, cobalt, alkenes, hydrosilylation, hydrogenation

Introduction

Transition-metal-catalyzed hydrosilylation of alkene is a useful method for the production of organo-silicon compounds, and noble metal complexes of platinum, rhodium, and palladium are the most widely used catalysts.^{1, 2} Hypothetically, the addition of a hydrosilane to a terminal alkene can give two types of alkylsilanes, *anti*-Markovnikov addition (2,1-addition) and Markovnikov addition (1,2-addition) products (Chart 1). In some cases, side reactions of dehydrogenative silylation and alkene hydrogenation, which afford vinylsilane and allylsilane, and alkanes, respectively, also exist (Chart 1). Hence, selectivity control is a great challenge in the development of useful hydrosilylation catalysts.



Chart 1. Transition-Metal-Catalyzed Reactions of Alkenes with Hydrosilanes

In the pursuit of new economical and environmentally benign catalysts for alkene hydrosilylation reaction,³⁻⁸ great recent efforts have been made to develop cobalt-based catalysts.⁹⁻²² The capability of cobalt in promoting alkene hydrosilylation has long been recognized since Chalk and Harrod's report on $\text{Co}_2(\text{CO})_8$ -catalyzed *anti*-Markovnikov addition of hydrosilanes with alkenes in the 1960s.²³ Since then, a plenty of cobalt complexes featuring phosphine,^{12,22} cyclopen-tadienyl,²⁴ *N*-heterocyclic carbene,^{9,15,19} β -diketiminato,¹⁷ 2,6-diiminopyridine,^{10,12,21} and isocyanide ligands²⁰ are found effective in promoting alkene hydrosilylation. In terms of selectivity, the majority of these known cobalt catalysts facilitate the addition reaction in an anti-Markovnikov addition manner. Cobalt complexes promoting Markovnikov hydrosilylation are rarely known. The pincer system (^{i-Pr}PNN^{Me})CoCl₂¹³ (ⁱ⁻ $P^{r}PNN^{Me} = 2 - (Pr_2PCH_2) - 6 - (2^{\circ}, 6^{\circ} - Me_2C_6H_3 - N = CMe)C_5H_3N)$ and $Co(acac)_2/MesPDI^{12}/(MesPDI = 2,6-(2',4',6'-Me_3C_6H_2-$ N=CMe)₂C₅H₃N), which are used in the Markovnikov hydrosilylation of alkyl-substituted alkenes with PhSiH₃, the $Co(acac)_2$ /Xantphos¹² system that catalyzes the reactions of aryl-substituted alkenes with PhSiH₃, and the $(OIP)CoCl_2/KO^tBu^{18}$ (OIP = chiral oxazoline iminopyridine ligand) system that promotes the Markovnikov addition of ArSiH₃ with both aryl- and alkyl-substituted alkenes, are among the rare examples. Interestingly, all these Markovnikov hydrosilylation systems utilize the primary hydrosilane PhSiH₃ as the silane source. Cobalt complexes that can catalyze selective dehydrogenative silvlation of alkene are also scarce. $Co_2(CO)_8$ was known to catalyze the reactions of acrylates with tertiary hydrosilanes to form (*E*)-3-silvl acrylates.²⁵ The cobalt methyl complex (MesPDI)Co(CH₃) proved an efficient catalyst for the reaction of alkyl-substituted alkenes with tertiary silanes to produce allyl silanes in good yields.²⁶ As the only known example of cobalt-catalyzed hydrogenation of alkene using hydrosilane as hydrogen source, Rajanbabu and his coworkers showed that $(^{Dipp}PDI)CoCl_2$ $(^{Dipp}PDI = 2,6 (2^{\circ}, 6^{\circ}- Pr_2C_6H_3-N=CMe)_2C_5H_3N)$ in combination with Na-

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BEt₃H catalyzes the reaction of alkenes with (EtO)₂SiMeH to form alkane.²⁷ In this reaction, polymeric silicon compounds were observed as byproduct and hydrosilylation product was hardly observed.

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As the aforementioned results point out the viability of selectivity control upon selection of suitable catalysts, we are curious whether the use of different cobalt-NHC complexes could render selectivity control on the reaction of alkene with hydrosilane. Previously, we found low-coordinate cobalt(II) complex (NHC)Co(N(SiMe₃)₂)₂ can catalyze the hydrosilylation of alkyl-substituted alkenes with HSi(OEt)3, affording selectively anti-Markovnikov addition products.¹⁹ The catalytic competence of the cobalt(I) complex [(IPr)Co(N(SiMe₃)₂)] (IPr = 1,3-di(2',6'-diisopropylphenyl)imidazol-2-ylidene) as $(IPr)Co(N(SiMe_3)_2)_2$ indicated that cobalt(I) species could be the genuine catalytic species for the alkene hydrosilylation reaction. In addition. cobalt(I)-NHC complexes [(IAd)(PPh₃)Co(CH₂SiMe₃)] and [(IAd)(PPh₃)Co(SiHPh₂)] were also found effective in catalyzing the hydrosilylation of alkynes with Ph₂SiH₂ to give alkenylsilanes.²⁸ The success thus prompted exploration on different cobalt(I)-NHC complexes with the aim of achieving selectivity control on the reaction of alkene with hydrosilane. Pertinent to this goal, we report herein cobalt(I) complexes featuring different NHC ligands can indeed promote the reaction of alkene with Ph₂SiH₂ in different manner: [(IAd)(PPh₃)CoCl] is an effective catalyst for anti-Markovnikov hydrosilylation of monosubstituted alkenes, [(IMes)2CoCl] catalyzes Markovnikov hydrosilylation of aryl-substituted alkenes. and [(IMe₂Me₂)₄Co][BPh₄] shows selectivity in catalyzing the hydrogenation of alkenes with Ph₂SiH₂ as the terminal hydrogen source. Mechanistic study in combination with the knowledge on the steric nature of cobalt-NHC species led to the proposals that cobalt(I) silyl and cobalt(I) hydride species with NHC ligation, presumably (NHC)Co(SiHPh₂) and (NHC)₂CoH, are the key active species for the hydrosilylation and hydrogenation reactions, respectively, and that the different reaction outcome is controlled by the electro-steric nature of the low-coordinate cobalt(I)-NHC species.

Results and Discussion

Catalytic performance of the Cobalt(I)-NHC Complexes. Our previous synthetic study showed that monodentate NHCs can support cobalt(I) species in diverse coordination geometries, including trigonal planar, diagonal, tetrahedral, and square planar. Chart 2 lists some examples of isolable cobalt(I)-NHC complexes. The ratio of NHC-to-cobalt in these complexes varies from 4 to 3 to 2 and to 1 as the NHC ligand changes from IR₂Me₂ (1,3-dialkyl-4,5-dimethylimidazol-2-ylidene)²⁹ to ICy (1,3-dicyclohexylimidazol-2-ylidene)³⁰ to IMes^{31,32} and IAd²⁸, which parallels with the increased steric demanding nature of these NHC ligands. Examining the catalytic performance of these cobalt complexes in the reaction of styrene with Ph₂SiH₂ revealed their different catalytic performance.

As shown in Table 1, using the mono(NHC)cobalt complex [(IAd)(PPh₃)CoCl] (2 mol%) as catalyst, the reaction of styrene with Ph₂SiH₂ (1.2 equiv.) at 70 °C for 10 hours gave the *anti*-Markovnikov hydrosilylation product **2a** in 92% GC yield along with small amount of the Markovnikov hydrosilylation product 3a (5%) and the hydrogenation product ethyl benzene



Chart 2. Cobalt(I)-NHC Complexes Examined in This Study

Table 1. Hydrosilylation of Styrene Using Cobalt Complexes with Ph₂SiH₂

+ Ph ₂ (1.2 e	1a 2 mol% Cat. SiH ₂ 70 °C, time		∕Si⊢ 2a ∕_ 4a	IPh ₂	SiHI 3a 5a	²h₂ ∕SiHPh₂	
	.			yield ^b (%)			
entry "	Cat.	time (h)	2a	3a	4a	5a	
1	(IAd)(PPh ₃)CoCI	10	92	5	2	trace	
2	(IMes) ₂ CoCl	48	3	66	2	trace	
3	(slMes) ₂ CoCl	48	4	58	4	trace	
4 ^c	(IMes) ₂ CoCI	16	3	93	3	trace	
5 ^{c,d}	[(IMes) ₂ Co][BPh ₄]	8	4	94	2	trace	
6	(ICy)₃ <mark>Co</mark> Cl	2	23	trace	44	30	
7 ^d	[(ICy) ₃ Co][BF ₄]	2	15	trace	48	22	
8 ^d	[(IPr ₂ Me ₂) ₄ Co][BPh ₄]	48	43	trace	24	10	
9 ^d	[(IEt ₂ Me ₂) ₄ Co][BPh ₄]	48	13	trace	40	5	
10 ^d	[(IMe ₂ Me ₂) ₄ Co][BPh ₄]	48	4	trace	53	2	
11 ^{c,d,e}	[(IMe ₂ Me ₂) ₄ Co][BPh ₄]	4	3	trace	70	trace	
12	(PPh ₃) ₃ CoCl	48	10	2	4	0	
13	(IAd)(PPh ₃)Co(SiHPh ₂)	8	92	3	4	trace	
14 ^{d,f}	[(IAd) <mark>Co</mark> (SiHPh ₂)] ₂	10	33	9	26	0	

^{*a*} Concentration of styrene: 1.0 mol/L in toluene or THF; ^{*b*} GC yield based on styrene with *n*-dodecane as an internal standard; ^{*c*} 5 mol% catalyst loading; ^{*d*} Solvent: THF; ^{*e*} 1.5 equiv. of Ph₂SiH₂ were used; ^{*f*} 1 mol% of [(IAd)Co(SiHPh₂)]₂ *in-situ* generated from the reaction of [(IAd)Co(vtms)₂] with Ph₂SiH₂ based on the reported procedure of ref. 41.

4a (2%) (entry 1). In stark contrast, the reactions using bis(NHC)cobalt complexes [(IMes)₂CoCl] and [(sIMes)₂CoCl] as catalysts showed different regio-selectivity, wherein the Markovnikov hydrosilylation product 3a was formed as the major product (66% and 58% GC yields, respectively, entries 2 and 3). When increasing the catalyst loading of [(IMes)₂CoCl] to 5 mol%, the yield of **3a** could reach 93% in 16 h (entry 4). The ionic complex [(IMes)₂Co][BPh₄] shows similar catalytic activity and selectivity as [(IMes)₂CoCl] (entry 5). On the other hand, reactions employing tris(NHC)cobalt complexes [(ICy)₃CoCl] and [(ICy)₃Co][BF₄] as catalysts gave mixtures of 2a (23% and 15%), 4a (44% and 48%), and 5a (30% and 22%) (entries 6 and 7). Testing the complexes performance of tetra(NHC)cobalt(I) $[(IR_2Me_2)_4Co][BPh_4]$ (R = ^{*i*}Pr, Et, Me) revealed that the reactions using [(IPr₂Me₂)₄Co][BPh₄] and [(IEt₂Me₂)₄Co][BPh₄]

as catalysts also afforded a mixture of **2a**, **4a**, and **5a** (entries 8 and 9). However, the one using $[(IMe_2Me_2)_4Co][BPh_4]$ could produce the hydrogenation product **4a** selectively (entry 10). In the case with a higher catalyst loading of 5 mol%, the yield of **4a** could reach 70% (entry 11), and the amount of the hydrosilylation and dehydrogenative silylation products are trace. In contrast, the cobalt(I) phosphine complex $[(PPh_3)_3CoCI]$ was found a poor catalyst in promoting the reaction of styrene with Ph₂SiH₂ as the reaction at 70 °C for 48 hours only produced **2a**, **3a** and **4a** in 10%, 2%, and 4%, respectively (entry 12).

Table2.HydrosilylationofAlkenesUsing(IAd)(PPh_3)CoCl as the Catalyst

		▶ ∧	PhaSiHa	2 mol	I% (IAd)(PF	Ph ₃)CoCl	CiUDE	SIHPn ₂	
		1	1.2 equiv	to	oluene, 70 °	°C, t	R	2' R	
-							2 (1)	3 (D)	
_	entry ^a	Substra	te	t (h)	conv. ^b (%	%) maj	or product	selectivity ^b (I:b)	yield ° (%)
	1	\bigcirc	∕~1a	10	>99	\bigcirc	SiHPh ₂	19:1	92
	2	F	1b	10	>99	F	SiHPh ₂ 2b	27:1	95
	3	F	1c	10	>99	F	SiHPh ₂	27:1	95
	4	ci Ci	nd 1d	10	>99		SiHPh ₂	20:1 ^d	94
	5	Ph	1e	10	>99		SiHPh ₂	9:1	85
	6	\square	1f	10	>99		SiHPh ₂	16:1	92
	7	Ŷ	1g	10	>99	\bigcirc	SiHPh ₂	13:1	90
	8	MeO	∽ 1h	10	>99		SiHPh ₂	13:1	91
	9		∕~1i	10	>99		SiHPh ₂	11:1	85
	10 ^e		 1j 	12	NR	50	-	-	-
	11	$^{\rm Ph} \sim$	1k	10	>99	Ph	SiHPh ₂	84:1	89
	12	\bigcirc	∕1I	30	>99	\bigcirc	SiHPh ₂	>99:1	87
	13	\bigcirc	∕~ 1m	30	>99	\bigcirc	SiHPh ₂	>99:1	89
	14	<i>n</i> -C ₆ H ₁₃	1n	12	>99	n-C ₆ H ₁₃	SiHPh ₂	>99:1	95
	15	Ph´	Ĭ.	48	NR		-	-	-
	16	~~	~ /	48	NR		-	-	-

^{*a*} Concentration of alkenes: 1.0 mol/L in toluene; ^{*b*} Determined by GC based on alkenes with *n*-dodecane as an internal standard; ^{*c*} Isolated yield; ^{*d*} Determined by NMR; ^{*e*} Temperature: 80 °C.

Encouraged by the distinct selectivity of [(IAd)(PPh₃)CoCl], [(IMes)₂CoCl], and [(IMe₂Me₂)₄Co][BPh₄] in promoting the reaction of styrene with Ph₂SiH₂, we further examined the scope of alkene for these catalytic systems. [(IAd)(PPh₃)CoCl] proved an efficient catalyst in catalyzing *anti*-Markovnikov hydrosilylation of Ph₂SiH₂ with both alkyl- and arylsubstituted alkenes in good yields and high selectivity. As shown in Table 2, styrenes bearing either electronwithdrawing or electron-donating groups (fluoro, chloro, methyl, phenyl, *tert*-butyl, methoxy) at *para*- or *meta*-position could undergo hydrosilylation to produce alkyl diphenylsilanes in the yields of 85-95% with high linear/branch ratio of 9:1 to 27:1 (entries 1-9). The reaction of *ortho*-substituted styrene 1-methyl-2-vinylbenzene didn't produce product even at 80 °C for 12 hours, indicating the sensitivity of the catalytic system to steric nature of C=C double bond (entry 10). [(IAd)(PPh₃)CoCl] catalyzes the hydrosilylation of alkyl-substituted alkenes with Ph₂SiH₂ to give exclusively *anti*-Markovnikov hydrosilylation products in high yields (entries 11-14). The exclusive hydrosilylation of the terminal C=C double bond of 4-vinyl-cyclohexene instead of the internal one hints the site-selectivity of the catalytic system (entry 12). This selectivity should come from the different steric nature of the two C=C double bonds in 4-vinyl-cyclohexene. Accordingly, the catalytic trials using di-substituted alkenes 1,1-diphenylethylene and (*E*)-3-octene did not produce any hydrosilylation product (entries 15 and 16).

Table 3. Hydrosilylation of Alkenes Using (IMes)₂CoCl as the Catalyst

R		5 mol	% (IMes) ₂ Co	R SiHPh2	+ J	
1	1.2 equiv.	toit	10110, 70 0, 1	2 (/)	3 (b)	
entry ^a	substrate	t (h)	conv. ^b (%)	major product	selectivity ^b (l:b)	yield ^c (%)
1	1a	16	>99	SiHPh ₂ SiHPh ₂ 3a	1:31	91
2	F ^{1b}	16	>99	F SiHPh ₂	1:23	93
3	F1c	16	>99	F SiHPh2 3c	1:10	90
4 P	h 1e	16	>99	Ph SiHPho	1:44	92
5 ^d	If	32	>99	SiHPh ₂	1:21	83
6 ^d	۲ ۱g	40	>99	3g	1:12	91
7 ^d Me		48	>99		1:10	68
8 ^d B	J 1i	60	>99		1:22	84
9 ^d	۲) ا	60	NR	-	-	-
10 ^e	Ph 1 k	40	>99	Ph SiHPh ₂ 3k*	1:1.4	40
11	11	36	57	SiHPh ₂	>99:1	26 ^f
12	1m	36	46	SiHPh ₂ SiHPh ₂ 2m	>99:1	24 ^f
13	<i>n</i> -C ₆ H ₁₃ 1n	36	65 <i>n</i> -C	SiHPh ₂	>99:1	20 ^{<i>f</i>}
14 ^{d,e}	S 10	18	>99	SiHPh ₂ 30	1:44	43
15 🜔	1p	16	>99 [SHPh	1:37	95
16	1q	16	>99	3q	1:57	86
17	Ph Ph	48	NR	-	-	-
18	\sim	48	NR	-	-	-

^{*a*} Concentration of alkenes: 1.0 mol/L in toluene; ^{*b*} Determined by GC based on alkenes with *n*-dodecane as an internal standard; ^{*c*}

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Examining the reactions of alkenes with Ph₂SiH₂ (1.2 equiv.) using the bis(NHC)cobalt complex [(IMes)₂CoCl] (5 mol%) as catalyst revealed the capability of this complex in catalyzing Markovnikov hydrosilylation of aryl-substituted alkenes. As shown in entries 1-8 in Table 3, under the catalytic conditions, vinyl arenes containing either electron-withdrawing or electron-donating groups on aryl rings can undergo selective Markovnikov hydrosilylation reaction, giving alkyl diphenvlsilanes with the linear/branched ratio of 1:10 to 1:57. In addition to substituted vinylbenzenes, 2-vinylthiophene and vinylnaphthalene can also undergo selective Markovnikov hydrosilylation (entries 14-16). In contrast to the high selectivity and high yields of the Markovnikov hydrosilylation of arylsubstituted alkenes, the reactions of alkyl-substituted alkenes with Ph₂SiH₂ using [(IMes)₂CoCl] as catalyst produced hydrosilylation products in low yields (20-26%), among which anti-Markovnikov addition products are dominating (entries 11-13). An exception is the reaction of allylbenzene, which produced hydrosilylation products in 40% yield with a linear/branch ratio of 1:1.4 (entry 10). The major product (1phenylpropyl)diphenylsilane (3k') might come from the sequential alkene isomerization-hydrosilylation processes.²⁶ The divergent selectivity in the hydrosilylation reactions of aryland alkyl-substituted alkenes using [(IMes)₂CoCl] as catalyst indicates the importance of the aryl substituent on alkene for the observed Markovnikov addition selectivity. Similar to [(IAd)(PPh₃)CoCl], the bis(NHC)cobalt complex [(IMes)₂CoCl] also found ineffective in catalyzing hydrosilylation reactions of Ph2SiH2 with the di-substituted alkenes 1methyl-2-vinylbenzene, 1,1-diphenylethylene, and (E)-3octene (entries 9, 17 and 18), probably due to steric reason.

Examining the scope of alkene of the catalytic hydrogenation reaction then revealed that the tetra(NHC)cobalt(I) complex 32 [(IMe₂Me₂)₄Co][BPh₄] can catalyze the hydrogenation of both 33 alkyl- and aryl-substituted alkenes with Ph₂SiH₂ as the termi-34 nal hydrogen source (entries 1-9, Table 4). These reactions 35 generally gave hydrogenation products in moderate yields (52-36 78%), and alkene hydrosilvlation products (1-13%) were also 37 detected as byproducts. Different from the formation of poly-38 meric silicon compounds in Rajanbabu's cobalt-catalyzed 39 hydrogenation reactions using (EtO)₂SiMeH as hydrogen source,²⁷ a disilane, Ph₂HSiSiHPh₂, was observed as a byprod-40 uct in the current catalytic system. Noting that these reactions generally have quantitative conversion of alkenes, but the 42 combined vield for the hydrogenation and hydrosilvlation 43 products are less than 100%, there should be other unknown 44 side reactions that consume alkenes. Considering the probable 45 formation of cobalt hydride species in these reactions, we 46 speculate that oligomerization or polymerization of alkenes might be the side reaction.³³⁻³⁸ The validation of this specula-48 tion, however, needs further study. In addition to mono-49 substituted alkenes, hydrogenation of di-substituted alkenes with [(IMe₂Me₂)₄Co][BPh₄] as catalyst and Ph₂SiH₂ as the 50 hydrogen source were also attempted. Unfortunately, limited success was achieved. The complex [(IMe₂Me₂)₄Co][BPh₄] 52 proved ineffective in catalyzing the hydrogenation of 1,1-53 diphenylethylene, (E)-3-octene, and (Z)-2-octene (entries 11-54 13). In the case of cyclooctene, the hydrogenation product 55

cyclooctane was obtained merely in 15% yield (entry 10). Prompted by the success with Ph₂SiH₂ as the silane and hydrogen source in the cobalt(I)-NHC-catalyzed reaction, we also examined the reactions of other silanes, e.g. Et₃SiH, Ph₃SiH, (EtO)₃SiH, and PhSiH₃ with styrene using [(IAd)(PPh₃)CoCl], [(IMes)₂CoCl], and [(IMe₂Me₂)₄Co][BPh₄] as catalyst. Unfortunately, neither hydrosilylation product nor hydrogenation product were detected in appreciable yields (Table S1).

Table 4. Hydrogenation of Alkenes Using [(IMe₂Me₂)₄Co][BPh₄] as the Catalyst



^a Concentration of alkenes: 1.0 mol/L in THF; ^b Determined by GC based on alkenes with *n*-dodecane as an internal standard; ^c Alkene isomerization was observed.

Mechanistic Consideration. The cobalt(I)-NHC-catalyzed reactions disclosed above represent a unique example of selectivity control of a reaction upon tuning the steric nature of ligands, which, in return, posed questions on their mechanism and causes for the observed selectivity. Though their exact mechanisms are far from clear at this stage, certain experimental evidences in combination with the established knowledge on cobalt-NHC complexes suggest that lowcoordinate cobalt silvl and cobalt hydride species could be the genuine catalysts for the hydrosilylation and hydrogenation reactions, respectively.

The first supporting evidence for the involvement of cobalt silyl intermediate for the hydrosilylation reactions is the evidence of trace amount of dehydogenative silvlation products in

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the hydrosilylation reactions of styrene with Ph₂SiH₂ catalyzed by [(IAd)(PPh₃)CoCl] and [(IMes)₂CoCl] (entries 1 and 4 in Table 1), which should arise from β -hydride elimination of β silylalkyl cobalt species.^{39,40} Secondly, the reactions of styrene with Ph_2SiH_2 using the cobalt(I) silyl complexes $[(IAd)(PPh_3)Co(SiHPh_2)]^{28}$ and $[(IAd)Co(SiHPh_2)]_2^{41}$ as catalysts also resulted in anti-Markovnikov hydrosilylation (entries 13 and 14 in Table 1). The relatively low catalytic efficiency of [(IAd)Co(SiHPh₂)]₂ as compared to [(IAd)(PPh₃)Co(SiHPh₂)] indicates the beneficial role of PPh₃ for improving catalytic efficiency, probably due to its capability to stabilize reactive cobalt silvl species in mononuclear has manner. Similar effect been observed on [(IAd)(PPh₃)Co(SiHPh₂)]-catalyzed alkyne hydrosilylation reaction.²⁸ With the aim to prepare cobalt silyl complexes directly from cobalt(I)-NHC chlorides, the reactions of [(IAd)(PPh₃)CoCl] and [(IMes)₂CoCl] with Ph₂SiH₂ were tried. These reactions did not lead to the isolation of the desired cobalt silvl complexes, rather revealed the capability of the two complexes in mediating the conversions of Ph₂SiH₂ to Ph₃SiH and Ph₂HSiSiPh₂H (Scheme 1a-1c). Noting transitionmetal silvl species are recognized as the key intermediates in transition-metal catalyzed silane redistribution reactions, 42-45 the formation of Ph₃SiH supports the proposal that cobalt silyl species could be formed via the reaction of cobalt(I)-NHC chlorides with Ph₂SiH₂.



Scheme 1. Reactions of the Cobalt(I)-NHC Complexes with Ph₂SiH₂ or Styrene

Based on these, we propose that the reactions of the cobalt(I)-NHC chlorides with Ph_2SiH_2 might give initially cobalt(I) hydride intermediates (**A**) and silyl chloride (Scheme 2).⁴⁶ The hydride species then interact with Ph_2SiH_2 to form cobalt(I) silyl intermediates (**B**) and H_2 . Once formed, cobalt(I) silyl intermediates could interact with alkenes *via* migratory insertion to form cobalt alkyl species (**C** or **C**²) that further interact with Ph_2SiH_2 to give hydrosilylation products and regenerate cobalt(I) silyl species **B**. In supportive to the proposed migratory insertion step, the interaction of [(IAd)(PPh_3)Co(SiHPh_2)] that was generated *in-situ* from the reaction of [(IAd)(PPh_3)Co(CH_2SiMe_3)] with Ph_2SiH_2 with styrene (2 equiv.) ²⁸ was found to afford the alkenyl silane (*Z*)-PhCH=CHSiH₂Ph in 26% GC yield, which should arise from the β -hydride elimination of the migratory insertion product (Scheme 1d). The capability of cobalt(I) species to perform oxidative addition with hydrosilanes suggests that the proposed steps involving cobalt(I) species might also operate in a sequential oxidative addition-reductive elimination manner.⁴⁷⁻



Scheme 2. Simplified Activation Mode of the Cobalt Precatalysts and Possible Catalytic Cycles for the Cobalt-Catalyzed Hydrosilylation and Hydrogenation Reactions

The migratory insertion reaction of **B** with alkenes could proceed *via* either a 2,1-insertion or 1,2-insertion way that could eventually lead to the observed selectivity of *anti*-Markovnikov addition or Markovnikov addition.⁴ Considering the different selectivity of the hydrosilylation reaction of aryl-substituted alkenes catalyzed by [(IAd)(PPh₃)CoCl] and [(IMes)₂CoCl] and the ineffectiveness of [(IMes)₂CoCl] in facilitating Markovnikov hydrosilylation of alkyl-substituted alkenes, we thought that the selectivity observed in the reactions catalyzed by [(IAd)(PPh₃)CoCl] and [(IMes)₂CoCl] might be controlled by the different steric nature of the NHC ligands and also the capability of incurring $\pi \cdots \pi$ interaction between the substituents.



Figure 1. Space-filling models of (IAd)Co (top) and (IMes)Co (bottom) generated from the crystal structures of [(IAd)(PPh₃)CoCl]²⁸ and [(IMes)₂CoCl]³², respectively. Blue ball: Co; grey ball: carbon; white ball, hydrogen.

The NHC ligands IAd and IMes differ in their steric nature (Figure 1). Consequently, an alkene ligand on the cobalt center of cobalt silyl alkene intermediate with IAd ligation, presumably (IAd)Co(RCH=CH₂)(SiHPh₂), might position its substitute R in the valley between two adamantyl groups (Figure 2a) to have least steric repulsion among the silyl, R, and Ad groups,

that will give anti-Markovnikov addition products. Similar steric model has been applied to explain the selectivity of the alkyne hydrosilylation reactions catalyzed by $[(IAd)(PPh_3)Co(CH_2SiMe_3)]^{.28}$ As for the catalytic reactions using [(IMes)₂CoCl], the steric nature of IMes might force the coordinated aryl alkene ArCH=CH₂ to position its methylene group being proximal to IMes and its aryl group to mesityl to have $\pi \cdots \pi$ interaction ^{50, 51} (Figure 2b), which then induces Markovnikov addition selectivity. The proposed $\pi \cdots \pi$ interaction could explain the distinct selectivity in the hydrosilylation reactions of arvl- and alkyl-substituted alkenes catalyzed by [(IMes)₂CoCl]. Considering this, a 1:1.4 mixture of linear and branched addition products in the reaction of allylbenzene with Ph₂SiH₂ catalyzed by [(IMes)₂CoCl] might be due to the capability of all v benzene to form $\pi \cdots \pi$ interaction with the mesityl group on IMes. The validation of these proposed models need further theoretical study.

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Figure 2. Proposed steric models rendering different selectivity of the cobalt(I)-NHC complex-catalyzed hydrosilylation reactions.

For the alkene hydrogenation reactions catalyzed by $[(IMe_2Me_2)_4Co][BPh_4]$, we propose that cobalt hydride species should be responsible for the alkene insertion step.⁵²⁻⁵⁴ Upon the interaction of [(IMe₂Me₂)₄Co][BPh₄] with of Ph₂SiH₂, the cobalt(I) complex might convert into a cobalt(I) hydride species A (Scheme 2). Noting the known reaction of nucleophilic attack of NHC toward hydrosilanes,55 this precatalyst activation step might have 2-silyl imidazolium salt as the byproduct. Indeed, GC and ²⁹Si NMR analyses indicated the formation of a small amount of 2-silvl imidazolium salt in the reaction mixof Ph₂SiH₂ with $[(IMe_2Me_2)_4Co][BPh_4]$ ture or [(IAd)(PPh₃)CoCl]. The hydride species A then reacts with alkene to give an alkyl intermediate **D** that further interact with Ph₂SiH₂ to yield the hydrogenation product and cobalt silvl intermediate **B**. Species **B** interact with another equivalent of Ph₂SiH₂ to regenerate the cobalt hydride species A with Ph₂HSiSiHPh₂ as the byproduct that was observed in the catalytic reactions. As a probable alternative mechanism, the hydrogenation products might arise directly from cobaltcatalyzed hydrogenation of alkene with H₂ that could be formed from cobalt-catalyzed dehydrogenation of Ph₂SiH₂. This route, however, seems unlikely, as the cobalt complex [(IMe₂Me₂)₄Co][BPh₄] is a poor catalyst in promoting the dehydrogenation of Ph₂SiH₂ (Scheme 1a).





^{*a*} Concentration of styrene: 1.0 mol/L in THF, and 1.2 equiv. of KC_8 were used (relative to cobalt); ^{*b*} GC yield based on styrene with *n*-dodecane as an internal standard; ^{*c*} 1.5 equiv. of Ph₂SiH₂ were used.

Another important mechanistic question is the cause for the selectivity of hydrosilylation versus hydrogenation. Following the proposed mechanisms in Scheme 2, the selectivity should come from the preference of the cobalt hydride species (NHC)_mCoH (A) or cobalt silvl species (NHC)_mCo(SiHPh₂) (B) to react selectively with Ph₂SiH₂ or alkene (Scheme 2). Thus, we reason that the number of NHC ligands in these cobalt species should play a key role. As the synthesis of lowcoordinate cobalt hydride and silvl species with IMes and IMe₂Me₂ ligation proved challenging, we examined the performance of *in-situ* generated cobalt(I)-NHC catalysts that have different NHC/cobalt ratio. As shown in Table 5, with a NHC/cobalt ratio of 1:1, the catalytic systems using IAd and IMes could promote selective anti-Markovnikov and Markovnikov hydrosilylation reaction, respectively (entries 1 and 2), whereas, the catalytic systems using IMe₂Me₂ as ligand with IMe₂Me/cobalt ratios of 2:1 and 3:1 proved more effective in catalyzing hydrogenation of styrene than that with a 1:1 ratio (entries 3-5). Based on these, it can be speculated that the active cobalt silvl species **B** in the catalytic cycles of the reactions catalyzed by [(IAd)(PPh₃)CoCl] and [(IMes)₂CoCl] might have the identity of (NHC)Co(SiHPh₂), and that of the cobalt hydride species A in the reactions catalyzed by [(IMe $_{2}Me_{2}_{4}Co][BPh_{4}]$ might be (IMe $_{2}Me_{2}_{2}_{2}CoH$. The steric nature of (NHC)_nCo and π - π interactions between (NHC)_nCo and aryl substituted alkene could induce the observed selectivity.

Conclusion

We disclosed that cobalt(I)-NHC complexes [(IAd)(PPh₃)CoCl], [(IMes)₂CoCl], and [(IMe₂Me₂)₄Co][BPh₄] display distinct performance in catalyzing the reaction of alkene with Ph₂SiH₂. [(IAd)(PPh₃)CoCl] is an effective anti-Markovnikov hydrosilylation catalysts for a series of mono-substituted alkenes, [(IMes)2CoCl] is an effective Markovnikov hydrosilylation catalysts for the hydrosilylation of aryl-substituted alkenes, and [(IMe₂Me₂)₄Co][BPh₄] catalyzes hydrogenation of alkenes with Ph₂SiH₂ as hydrogen source. For the hydrosilylation reactions, cobalt(I) silyl species was proposed as the key intermediates. The different steric

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nature of IAd *versus* IMes and the potential of IMes incurring $\pi \cdots \pi$ interaction with aryl alkenes are believed the causes for the 1,2- and 2,1-addition-selectivity. On the hydrogenation reaction, bis(NHC)cobalt(I) hydride species was proposed as the key in-cycle intermediates for the cobalt(I)-NHC catalyzed hydrogenation reaction. The study points out the wide vista of cobalt-NHC complexes as non-precious metal catalysts for other hydro-functionalization reactions which is under exploration in our laboratory.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at DOI: xxxxxxxxx

Detailed experimental procedures, characterization data, NMR, and GC-MS spectra (PDF)

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Notes

The authors declare no competing financial interests.

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REFERENCES

(1) Marciniec, B.; Gulinski, J.; Urbaniac, W.; Kornetka, Z. W. Comprehensive Handbook on Hydrosilylation; Pergamon: Oxford, U.K., 1992.

Oxford, U.K., 1992.
(2) Marciniec, B.; Maciejewski, H.; Pietraszuk, C.; Pawluć, P. *Hydrosilylation: A Comprehensive Review on Recent Advances*; Springer: Berlin, 2009.

34 (3) Du, X.; Huang, Z. Advances in Base-Metal-Catalyzed Alkene Hydrosilylation. *ACS Catal.* 2017, 7, 1227-1243.

36 (4) Sun, J.; Deng, L. Cobalt Complex-Catalyzed Hydrosilylation
37 of Alkenes and Alkynes. *ACS Catal.* 2015, *6*, 290-300.

38 (5) Buslov, I.; Becouse, J.; Mazza, S.; Montandon-Clerc, M.; Hu,

X. Chemoselective Alkene Hydrosilylation Catalyzed by Nickel
Pincer Complexes. Angew. Chem., Int. Ed. 2015, 54, 14523-14526.

(6) Lipschutz, M. I.; Tilley, T. D. Synthesis and Reactivity of a
 Conveniently Prepared Two-Coordinate Bis(amido) Nickel(II)

43 Complex. *Chem. Commun.* **2012**, *48*, 7146-7148.

(7) Greenhalgh, M. D.; Jones, A. S.; Thomas, S. P. Iron-Catalysed
Hydrofunctionalisation of Alkenes and Alkynes. *ChemCatChem*2015, 7, 190-222.

46 (8) Obligacion, J. V.; Chirik, P. J. Earth-Abundant Transition
47 Metal Catalysts for Alkene Hydrosilylation and Hydroboration.
48 Nat. Rev. Chem. 2018, 2, 15-34.

(9) Ibrahim, A. D.; Entsminger, S. W.; Zhu, L.; Fout, A. R. A
Highly Chemoselective Cobalt Catalyst for the Hydrosilylation of
Alkenes using Tertiary Silanes and Hydrosiloxanes. ACS Catal.
2016, 6, 3589-3593.

(10) Raya, B.; Jing, S.; RajanBabu, T. V. Control of Selectivity
through Synergy between Catalysts, Silanes and Reaction
Conditions in Cobalt-Catalyzed Hydrosilylation of Dienes and
Terminal Alkenes. ACS Catal. 2017, 7, 2275-2283.

(11) Schuster, C. H.; Diao, T.; Pappas, I.; Chirik, P. J. Bench-Stable, Substrate-Activated Cobalt Carboxylate Pre-Catalysts for Alkene Hydrosilylation with Tertiary Silanes. *ACS Catal.* **2016**, *6*, 2632-2636.

(12) Wang, C.; Teo, W. J.; Ge, S. Cobalt-Catalyzed Regiodivergent Hydrosilylation of Vinylarenes and Aliphatic Alkenes: Ligand- and Silane-Dependent Regioselectivities. *ACS Catal.* **2017**, *7*, 855-863.

(13) Du, X.; Zhang, Y.; Peng, D.; Huang, Z. Base-Metal-Catalyzed Regiodivergent Alkene Hydrosilylations. *Angew. Chem.*, *Int. Ed.* **2016**, *55*, 6671-6675.

(14) Lee, K. L. (Aminomethyl)pyridine Complexes for the Cobalt-Catalyzed Anti-Markovnikov Hydrosilylation of Alkoxyor Siloxy(vinyl)silanes with Alkoxy- or Siloxyhydrosilanes. *Angew. Chem., Int. Ed.* **2017**, *56*, 3665-3669.

(15) Mo, Z.; Liu, Y.; Deng, L. Anchoring of Silyl Donors on a Nheterocyclic Carbene through the Cobalt-Mediated Silylation of Benzylic C-H Bonds. *Angew. Chem., Int. Ed.* **2013**, *52*, 10845-10849.

(16) Sang, H.; Yu, S.; Ge, S. Cobalt-Catalyzed Regioselective Stereoconvergent Markovnikov 1,2-Hydrosilylation of Conjugated Dienes. *Chem. Sci.* **2018**, *9*, 973-978.

(17) Chen, C.; Hecht, M. B.; Kavara, A.; Brennessel, W. W.; Mercado, B. Q.; Weix, D. J.; Holland, P. L. Rapid, Regioconvergent, Solvent-Free Alkene Hydrosilylation with a Cobalt Catalyst. J. Am. Chem. Soc. **2015**, *137*, 13244-13247.

(18) Cheng, B.; Lu, P.; Zhang, H.; Cheng, X.; Lu, Z. Highly Enantioselective Cobalt-Catalyzed Hydrosilylation of Alkenes. J. Am. Chem. Soc. **2017**, *139*, 9439-9442.

(19) Liu, Y.; Deng, L. Mode of Activation of Cobalt(II) Amides for Catalytic Hydrosilylation of Alkenes with Tertiary Silanes. *J. Am. Chem. Soc.* **2017**, *139*, 1798-1801.

(20) Noda, D.; Tahara, A.; Sunada, Y.; Nagashima, H. Non-Precious-Metal Catalytic Systems Involving Iron or Cobalt Carboxylates and Alkyl Isocyanides for Hydrosilylation of Alkenes with Hydrosiloxanes. *J. Am. Chem. Soc.* **2016**, *138*, 2480-2483.

(21) Docherty, J. H.; Peng, J.; Dominey, A. P.; Thomas, S. P. Activation and Discovery of Earth-Abundant Metal Catalysts Using Sodium Tert-Butoxide. *Nat. Chem.* **2017**, *9*, 595-600.

(22) Chu, W.-Y.; Gilbert-Wilson, R.; Rauchfuss, T. B. Cobalt Phosphino-α-Iminopyridine-Catalyzed Hydrofunctionalization of Alkenes: Catalyst Development and Mechanistic Analysis. *Organometallics* **2016**, *35*, 2900-2914.

(23) Harrod, J. F.; Chalk, A. J. Dicobalt Octacarbonyl as a Catalyst for Hydrosilylation of Olefins. *J. Am. Chem. Soc.* **1965**, *87*, 1133-1134.

(24) Brookhart, M.; Grant, B. E. Mechanism of a Cobalt(III)-Catalyzed Olefin Hydrosilylation Reaction: Direct Evidence for a Silyl Migration Pathway. *J. Am. Chem. Soc.* **1993**, *115*, 2151-2156.

(25) Takeshita, K.; Seki, Y.; Kawamoto, K.; Murai, S.; Sonoda, N. The Catalyzed Reaction of α,β -Unsaturated Esters with Various Hydrosilanes. *J. Org. Chem.* **1987**, *52*, 4864-4868.

(26) Atienza, C. C.; Diao, T.; Weller, K. J.; Nye, S. A.; Lewis, K. M.; Delis, J. G.; Boyer, J. L.; Roy, A. K.; Chirik, P. J. Bis(imino)pyridine Cobalt-Catalyzed Dehydrogenative Silylation of Alkenes: Scope, Mechanism, and Origins of Selective Allylsilane Formation. *J. Am. Chem. Soc.* **2014**, *136*, 12108-18.

(27) Raya, B.; Biswas, S.; RajanBabu, T. V. Selective Cobalt-Catalyzed Reduction of Terminal Alkenes and Alkynes Using (EtO)₂Si(Me)H as a Stoichiometric Reductant. *ACS Catal.* **2016**, *6*, 6318-6323.

(28) Mo, Z.; Xiao, J.; Gao, Y.; Deng, L. Regio- and Stereoselective Hydrosilylation of Alkynes Catalyzed by Three-Coordinate Cobalt(I) Alkyl and Silyl Complexes. *J. Am. Chem. Soc.* **2014**, *136*, 17414-17417.

(29) Mo, Z.; Li, Y.; Lee, H.; Deng, L. Square-Planar Cobalt Complexes with Monodentate N-Heterocyclic Carbene Ligation: Synthesis, Structure, and Catalytic Application. *Organometallics* **2011**, *30*, 4687-4694.

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2

3

4

5

6

7

60

(30) Gao, Y.; Li, G.; Deng, L. Bis(dinitrogen)cobalt(-1)

8 Complexes with NHC Ligation: Synthesis, Characterization, and 9 Their Dinitrogen Functionalization Reactions Affording Side-on

Bound Diazene Complexes. J. Am. Chem. Soc. 2018, 140, 2239-2250.

 Meng, Y.; Mo, Z.; Wang, B.; Zhang, Y.; Deng, L.; Gao, S.
 Observation of the Single-Ion Magnet Behavior of d(8) Ions on Two-Coordinate Co(I)-NHC Complexes. *Chem. Sci.* 2015, *6*, 7156-7162.

(32) Mo, Z.; Chen, D.; Leng, X.; Deng, L. Intramolecular C(sp³)–
H Bond Activation Reactions of Low-Valent Cobalt Complexes with Coordination Unsaturation. *Organometallics* 2012, *31*, 7040-7043.

(33) Fryzuk, M. D.; Ng, J. B.; Rettig, S. J.; Huffman, J. C. Nature of the Catalytically Inactive Cobalt Hydride Formed Upon Hydrogenation of Aromatic Substrates. Structure and Characterization of the Binuclear Cobalt Hydride [{Prⁱ₂P(CH₂)₃PPrⁱ₂}Co]₂(H)(u-H)₃. *Inorg. Chem.* **1991**, *30*, 2437-2441.

(34) Chen, C.; Dugan, T. R.; Brennessel, W. W.; Weix, D. J.;
Holland, P. L. Z-Selective Alkene Isomerization by High-Spin Cobalt(II) Complexes. J. Am. Chem. Soc. 2014, 136, 945-955.

26 (35) Pu, L. S.; Yamamoto, A.; Ikeda, S. Catalytic Dimerization of
27 Ethylene and Propylene by
28 Nitrogentris(triphenylphosphine)cobalt Hydride. J. Am. Chem.
20 Soc. 1968, 90, 7170-7171.

Soc. 1966, 20, 1116-111.
(36) Bianchini, C.; Giambastiani, G.; Rios, I. G.; Meli, A.; Segarra, A. M.; Toti, A.; Vizza, F. Regioselective Propylene Dimerization by Tetrahedral (imino)Pyridine Co^{II} Dichloride Complexes Activated by MAO. J. Mol. Catal. A: Chem. 2007, 277, 40-46.

(37) Field, L. D.; Ward, A. J. Catalytic Hydrosilylation of
Acetylenes Mediated by Phosphine Complexes of Cobalt(I),
Rhodium(I), and Iridium(I). J. Organomet. Chem. 2003, 681, 9197.

(38) Bhattacharjee, A.; Weiss, A. K.; Artero, V.; Field, M. J.;
Hofer, T. S. Electronic Structure and Hydration of Tetramine
Cobalt Hydride Complexes. J. Phys. Chem. B 2014, 118, 55515561.

(39) Seitz, F.; Wrighton, M. S. Photochemical Reaction of [(CO)₄Co(SiEt₃)] with Ethylene: Implications for Cobaltcarbonyl-Catalyzed Hydrosilation of Alkenes. *Angew. Chem., Int. Ed.* 1988, 27, 289-291.

44 (40) Reichel, C. L.; Wrighton, M. S. Photochemistry of Cobalt
45 Carbonyl Complexes Having a Cobalt-Silicon Bond and Its 46 Importance in Activation of Catalysis. *Inorg. Chem.* 1980, *19*, 3858-3860.

(41) Sun, J.; Gao, Y.; Deng, L. Low-Coordinate NHC-Cobalt(0)-Olefin Complexes: Synthesis, Structure, and Their Reactions with Hydrosilanes. *Inorg. Chem.* 2017, 56, 10775-10784.

50 (42) Tilley, T. D. The Coordination Polymerization of Silanes to
51 Polysilanes by a "σ-Bond Metathesis" Mechanism. Implications
52 for Linear Chain Growth. Acc. Chem. Res. 1993, 26, 22-29.

53 (43) Park, S.; Kim, B. G.; Göttker-Schnetmann, I.; Brookhart, M.

Redistribution of Trialkyl Silanes Catalyzed by Iridium Silyl
Complexes. ACS Catal. 2012, 2, 307-316.

(44) Hashimoto, H.; Komura, K.; Ishizaki, T.; Odagiri, Y.; Tobita, H. Hydrogen-Bridged Bis(silylene) Complexes of Ruthenium and Iron: Synthesis, Structures and Multi-Centre Bonding Interactions at the M-Si-H-Si Four-Membered Ring. *Dalton Trans.* **2017**, *46*, 8701-8704.

(45) Okazaki, M.; Tobita, H.; Ogino, H. Reactivity of Silylene Complexes. *Dalton Trans.* **2003**, *2003*, 493-506.

(46) Chen, Y.; Sui-Seng, C.; Boucher, S.; Zargarian, D. Influence of SiMe3 Substituents on Structures and Hydrosilylation Activities of ((SiMe₃)_{1 or 2}-Indenyl)Ni(PPh₃)Cl. *Organometallics* **2005**, *24*, 149-155.

(47) Brookhart, M.; Grant, B. E.; Lenges, C. P.; Prosenc, M. H.; White, P. S. High Oxidation State Organocobalt Complexes: Synthesis and Characterization of Dihydridodisilyl Cobalt(V) Species. *Angew. Chem., Int. Ed.* **2000**, *39*, 1676-1679.

(48) Whited, M. T.; Mankad, N. P.; Lee, Y.; Oblad, P. F.; Peters, J. C. Dinitrogen Complexes Supported by Tris(phosphino)silyl Ligands. *Inorg. Chem.* **2009**, *48*, 2507-2517.

(49) Yong, L.; Hofer, E.; Wartchow, R.; Butenschön, H. Oxidative Addition of Hydrosilanes, Hydrogermane, and Hydrostannane to Cyclopentadienylcobalt(I) Bearing a Pendant Phosphane Ligand: Cyclopentadienylhydridocobalt(III) Chelate Complexes with Silyl, Germyl, and Stannyl Ligands. *Organometallics* **2003**, *22*, 5463-5467.

(50) Belger, C.; Plietker, B. Aryl-Aryl Interactions as Directing Motifs in the Stereodivergent Iron-Catalyzed Hydrosilylation of Internal Alkynes. *Chem. Commun.* **2012**, *48*, 5419-5421.

(51) Hu, M.; He, Q.; Fan, S.; Wang, Z.; Liu, L.; Mu, Y.; Peng, Q.; Zhu, S. Ligands with 1,10-Phenanthroline Scaffold for Highly Regioselective Iron-Catalyzed Alkene Hydrosilylation. *Nat. Commun.* **2018**, *9*, 221.

(52) Chirik, P. J. Iron- and Cobalt-Catalyzed Alkene Hydrogenation: Catalysis with Both Redox-Active and Strong Field Ligands. *Acc. Chem. Res.* **2015**, *48*, 1687-1695.

(53) Friedfeld, M. R.; Zhong, H.; Ruck, R. T.; Shevlin, M.; Chirik, P. J. Cobalt-Catalyzed Asymmetric Hydrogenation of Enamides Enabled by Single-Electron Reduction. *Science* **2018**, *360*, 888-893.

(54) Korstanje, T. J.; van der Vlugt, J. I.; Elsevier, C. J.; de Bruin, B. Hydrogenation of Carboxylic Acids with a Homogeneous Cobalt Catalyst. *Science* **2015**, *350*, 298-302.

(55) Frey, G. D.; Masuda, J. D.; Donnadieu, B.; Bertrand, G. Activation of Si-H, B-H, and P-H Bonds at a Single Nonmetal Center. *Angew. Chem., Int. Ed.* **2010**, *49*, 9444-9447.

SYNOPSIS TOC

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cat. NHC: (NHC)(PPh3)CoCI SiHPh₂ - R' anti-Markovnikov (R = aryl, alkyl) hydrosilylation cat. R SiHPh₂ (NHC)2CoCI ~ + Markovnikov hydrosilylation R (R = aryl) Ph₂SiH₂ cat. [(NHC)4Co][BPh4] R hydrogenation (R = aryl, alkyl)