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Mode of Activation of Cobalt(II) Amides for Catalytic Hydrosilylation of Alkenes with Tertiary Silanes

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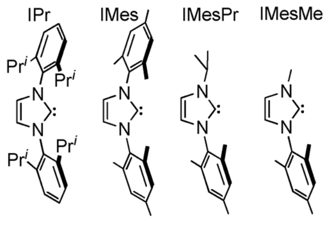
Supporting Information

ABSTRACT: Cobalt(II) complexes capable of catalyzing alkene hydrosilylation in the absence of external activators are rarely known, and their activation mode has remained poorly understood. We present here that cobalt(II) amide complexes, $[Co(N(SiMe_3)_2)_2]$ and its NHC adducts $[(NHC)Co(N(SiMe_3)_2)_2]$ (NHC = *N*-heterocyclic carbene), are effective catalysts for the hydrosilylation of alkenes with tertiary silanes. Mechanistic studies revealed that cobalt(II) amides can react with hydrosilane to form cobalt(I) species, silylamide, and hydrogen, which serves as the entry to the genuine catalytically active species, presumably cobalt(I) species, for the cobalt-catalyzed hydrosilylation reaction.

There has been great interest in the development of iron- and cobalt-based hydrosilylation catalysts as alternatives for the applied noble metal catalysts.[1] As the traditional design of the alkene hydrosilylation catalysts has focused on low-valent iron and cobalt complexes,[2] a new development in the field is the direct use of iron(II) and cobalt(II) complexes as precatalysts.[3,4] Initially, this type of divalent metal catalyst was restricted to the alkyl complexes, e.g., $(PDI)Fe(CH_2SiMe_3)_2$ (PDI = 2,6-diiminopyridine),[4a] $(tpy)Fe(CH_2SiMe_3)_2$ (tpy = terpyridine),[4a] and $Co(IMes')_2$ (IMes′ = cyclometalated IMes ligand, Chart 1),[4b] that promote the hydrosilylation of alkenes with primary and secondary silanes. Very recently, Nagashima, Chirik, and their co-workers found that the carboxylate complexes $M(Opiv)_2/CNBu^t$ (M = Fe, Co; Opiv = pivalate)[4c] and $(PDI)Co(2\text{-}EH)_2$ (EH = 2-ethylhexanonate)[4d] are also effective, effecting the hydrosilylation of alkenes with tertiary silanes. The divalent metal complex-based catalysts obviate the use of external reducing reagents, e.g., $NaBHEt_3$ and alkyl lithium reagents, to generate active species, which is highly desired from the view of catalyst's practical usage. The new development also brings fundamental mechanistic questions as to the activation mode of the precatalysts and the nature of the genuine catalytic species, which are unsolved yet. In this study, we report a new type of cobalt(II) complex-based hydrosilylation catalyst, the simple binary complex $[Co(N(SiMe_3)_2)_2]$ and its NHC adducts (Chart 1), which does not require the use of external activator. These cobalt(II) amides can catalyze the *anti*-Markovnikov hydrosilylation of alkenes with tertiary silanes. Intriguingly, the system allows the establishment of the activation mode of the precatalyst that entails the reaction of cobalt(II) bis(amide) with hydrosilane to form cobalt(I) amide, silylamide, and hydrogen. The resulting cobalt(I) amide further reacts with hydrosilane to form cobalt(I) hydride. The comparable catalytic activity of the isolated cobalt(I) amide complex to its cobalt(II) precursor suggests that cobalt(I) species could be the genuine catalytically active species in the cobalt-catalyzed hydrosilylation reaction.

Chart 1. Cobalt(II) Amide Catalysts

$[Co^{II}(N(SiMe_3)_2)_2]$ (**1**)
$[(IPr)Co^{II}(N(SiMe_3)_2)_2]$ (**2**)
$[(IMes)Co^{II}(N(SiMe_3)_2)_2]$ (**3**)
$[(IMesPr)Co^{II}(N(SiMe_3)_2)_2]$ (**4**)
$[(IMesMe)Co^{II}(N(SiMe_3)_2)_2]$ (**5**)



Inspired by Tilley's recent report of $Fe(N(SiMe_3)_2)_2$-catalyzed hydrosilylation of ketones with H_2SiPh_2,[5] we perceived the capability of $[Co(N(SiMe_3)_2)_2]$ (**1**) in promoting alkene hydrosilylation. The speculation was verified by the reaction of 1-octene with $HSi(OEt)_3$ (1.2 equiv). Using **1** (5 mol %, Chart 1) as the catalyst, the reaction could furnish the hydrosilylation product $n\text{-}C_8H_{17}Si(OEt)_3$ (HS) in 26% and 79% GC yields in 0.5 and 24 h, respectively. Interestingly, in addition to the hydrosilylation product, the alkene isomers of 1-C_8H_{16} and the dehydrogenative silylation product $n\text{-}C_6H_{13}CH{=}CHSi(OEt)_3$ (DS) were also formed at the early stage of the reaction. At the late stage of the reaction, these side products, however, fully converted into $n\text{-}C_8H_{17}Si(OEt)_3$ and *n*-octane (entry 1 in Table 1). The change of product distribution over time suggests that, under the reaction conditions, **1** serves as an effective precatalyst not only for alkene hydrosilylation but also for alkene isomerization and hydrogenation.[6] In pursuit for a more selective hydrosilylation catalyst, *N*-heterocyclic carbene (NHC) ligands were applied to tune the reaction selectivity. As shown in Table 1, the reactions employing 5 mol % $[(IPr)Co(N(SiMe_3)_2)_2]$[7] (**2**, Chart 1) and $[(IMes)Co(N(SiMe_3)_2)_2]$[7] (**3**, Chart 1) have similar outcome with that of **1**, giving the hydrosilylation product in 68% and 76% yields in 24 and 36 h, respectively (entries 2 and 3). On the other hand, decreasing the steric bulk of the NHC ligand by using $[(IMesPr)Co(N(SiMe_3)_2)_2]$[8] (**4**, Chart 1) as the

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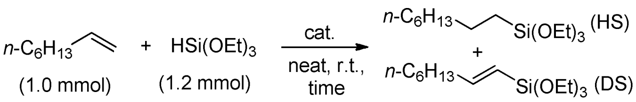
Table 1. Catalytic Performance of Cobalt(II) Amide Complexes in the Reaction of 1-Octene with $HSi(OEt)_3$



entry	cat.	time (h)	conv. (%)	GC yield (%)[a]			
				HS	DS	C_8H_{16}[b]	n-C_8H_{18}
1	5.0 mol % **1**	0.5	>99	26	10	52	12
		24	>99	79	3	<1	18
2	5.0 mol % **2**	0.5	>99	5	1	90	4
		24	>99	68	0	<1	32
3	5.0 mol % **3**	0.5	93	11	1	75	6
		36	>99	76	3	<1	21
4	0.1 mol % **4**	24	>99	86	0	10	3
5	0.1 mol % **5**	0.5	>99	99	0	1	0

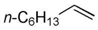
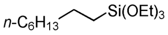
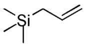
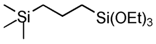
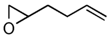
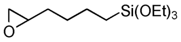
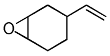
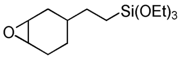
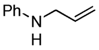
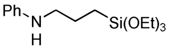
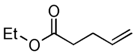
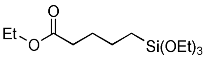
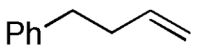
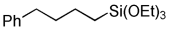
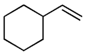
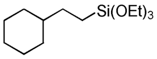
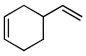
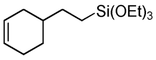
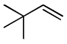
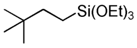
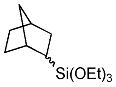
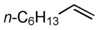
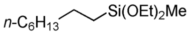
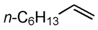
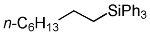
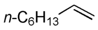
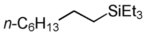
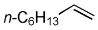
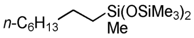
[a]Yields were based on the alkene. [b]Isomers of 1-octene.

precatalyst, the yield of n-$C_8H_{17}Si(OEt)_3$ could be increased to 86% (entry 4). In a marked contrast, the reaction utilizing $[(IMesMe)Co(N(SiMe_3)_2)_2]$[8] (**5**, Chart 1) has nearly full conversion to the hydrosilylation product in 0.5 h even with a 0.1 mol % catalyst loading (entry 5). Notably, further adding 1-octene and $HSi(OEt)_3$ to the mixture can trigger the catalytic hydrosilylation reaction though with slightly decreased conversion (Figure S11), demonstrating the high activity of the catalytic system.

Using **5** (1 mol %) as the catalyst and $HSi(OEt)_3$ as the silane source, a preliminary substrate scope study on the cobalt-catalyzed alkene hydrosilylation reaction was performed. The cobalt(II) amide catalyst can effectively promote the hydrosilylation of monosubstituted aliphatic alkenes to selectively give *anti*-Markovnikov addition products in moderate to excellent yields (Table 2).[8] High chemo-selectivity was observed in the reactions of the aliphatic alkenes bearing ester, epoxide, and secondary amine functional groups, wherein the hydrosilylation reaction took place selectively on the C–C double bonds (entries 3–6 in Table 2). The catalytic system is sensitive to the steric properties of alkenes, as the hydrosilylation of 4-vinyl-cyclohexene took place exclusively on the vinyl group (entry 9), the reaction with the *tert*-butyl substituted alkene afforded the hydrosilylation product in a decreased yield (entry 10) than that with 1-octene, and the reaction of norbornene required elevated temperature (60 °C, entry 11). Probably due to the coordination effect of arene toward the in situ generated low-coordinate cobalt species (vide infra), the cobalt(II) amide catalyst is incapable in promoting the hydrosilylation of styrene. The cobalt-catalyzed hydrosilylation reaction is also sensitive to the steric properties of hydrosilanes. The reactions with the tertiary hydrosilanes $HSiMe(OEt)_2$ and $HSiPh_3$ gave the corresponding hydrosilylation products in lower yields (entries 12 and 13) and the sterically hindered hydrosilanes $HSiEt_3$ and MD′M (MD′M = 1,1,1,3,5,5,5-heptamethyltrisiloxane) are inapplicable for the cobalt-catalyzed hydrosilylation reaction (entries 14 and 15). It should be noted that, in addition to the steric effect, the different electronic property of the Si–H bonds in these hydrosilanes might also exert influence.

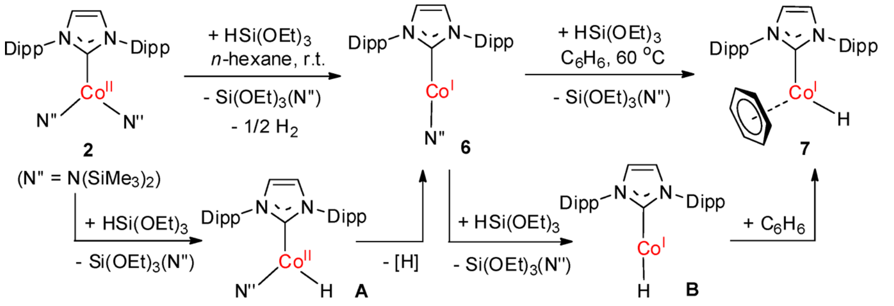
The cobalt(II) amide complexes **1**–**5** represent a new category of cobalt catalyst for alkene hydrosilylation obviating the use of external activator after the aforementioned alkyl and carboxylate complexes.[4] Noting the very limited knowledge on the activation mode of these divalent metal complex-based precatalysts, the stoichiometric reactions of cobalt(II) amide complexes with hydrosilanes and alkenes were studied. These cobalt(II) amide complexes are inert toward 1-octene under ambient conditions, but they can readily react with $HSi(OEt)_3$. Although the attempts to access reactive cobalt species from the reaction of $[(IMesMe)Co(N(SiMe_3)_2)_2]$ (**5**) with $HSi(OEt)_3$ were unsuccessful. The interaction of $HSi(OEt)_3$ with $[(IPr)Co(N(SiMe_3)_2)_2]$ (**2**) that has a more bulky NHC ligand in n-hexane at room temperature led to the clean formation of the two-coordinate cobalt(I) amide complex $[(IPr)Co(N(SiMe_3)_2)]$ (**6**)[9] that can further react with $HSi(OEt)_3$ at 60 °C in benzene to furnish the cobalt(I) hydride complex $[(IPr)Co(\eta^6\text{-}C_6H_6)H]$ (7) in high yield (Scheme 1).[8] Notably,

Table 2. Hydrosilylation of Various Alkenes with Tertiary Silanes[a]

entry	Alkene	Silane	Product	Yield[b]
1[c]		$HSi(OEt)_3$		98%
2		$HSi(OEt)_3$		88%
3		$HSi(OEt)_3$		92%
4		$HSi(OEt)_3$		94%
5		$HSi(OEt)_3$		93%
6[d,e]		$HSi(OEt)_3$		79%
7		$HSi(OEt)_3$		76%
8		$HSi(OEt)_3$		86%
9		$HSi(OEt)_3$		42%
10[d]		$HSi(OEt)_3$		47%
11[d]		$HSi(OEt)_3$		87%
12		$HSi(OEt)_2Me$		76%
13[d]		$HSiPh_3$		28%[f]
14[d]		$HSiEt_3$		0[f]
15[d]		MD'M		1%[f]

[a]Conditions: alkene (1.0 mmol), silane (1.2 mmol), complex **5** (1 mol %) at room temperature in neat conditions. [b]Isolated yields. [c]0.1 mol % catalyst loading. [d]At 60 °C. [e]1.05 mmol $HSi(OEt)_3$ were used. [f]GC yield, and alkene isomers were observed.

Scheme 1. Reactions of Cobalt Amide Complexes with HSi(OEt)$_3$



the latter reaction could also take place at room temperature though with decreased rate (Figure S14). Along with the cobalt complexes, the silylamide Si(OEt)$_3$(N(SiMe$_3$)$_2$) was also formed in both reactions.[8] Complexes **6** and **7** have been characterized by NMR spectroscopic methods, elemental analyses, and X-ray crystallographic studies (Figures S2 and S3). Complex **6** is a rare example of heteroleptic two-coordinate cobalt(I) complex after Jones' [(IPr$_2$Me$_2$)Co(NSiPh$_3$Ar*)].[10] Complex **7** is diamagnetic. The characteristic signal at −21.6 ppm in its ^{1}H NMR spectrum supports the presence of the metal-bounded hydride ligand.

The reaction of HSi(OEt)$_3$ with **2** results in the reduction of the cobalt(II) species to cobalt(I), which is different from the known oxidative addition or σ-bond metathesis reaction of hydrosilanes with cobalt species,[11] and also differs from the existing cobalt(II)-to-cobalt(I) reduction reactions that generally employ strong reducing reagents, e.g., alkali metals, alkali earth metals, and boron hydrides.[12] The formation of **6** might result from the homolytic Co−H bond cleavage reaction of a cobalt(II) hydride[13] intermediate (IPr)Co(H)(N(SiMe$_3$)$_2$) (**A**) that can be formed from the σ-bond metathesis reaction of **2** with HSi(OEt)$_3$ (Scheme 1). In support of this proposal, the byproducts Si(OEt)$_3$(N(SiMe$_3$)$_2$) and H$_2$ were detected in NMR-scale reactions (Figures S6−S9). The formation of **7** implies the production of the low-coordinate cobalt(I) hydride (IPr)Co(H) (**B**) in the reaction of **6** with HSi(OEt)$_3$ (Scheme 1). This reaction outcome is distinct from that of the cobalt(I) alkyl complex [(IAd)Co(PPh$_3$) (CH$_2$SiMe$_3$)] with HSiPh$_3$, wherein cobalt(I) silyl complex [(IAd)Co(PPh$_3$) (SiPh$_3$)], rather than a cobalt(I) hydride, was formed.[14] The difference might root in the selectivity of the cobalt(III) intermediate (NHC)Co(H) (SiR$_3$)(X) (X = CH$_2$SiMe$_3$, N(SiMe$_3$)$_2$), which can be formed from the oxidative addition of cobalt(I) species with hydrosilanes, to perform either H−X or R$_3$Si−X bond-forming reductive elimination. The large Si−N bond enthalpy[15] could drive the Si−N bond-forming reductive elimination, giving the hydride species.

The attainment of these cobalt(I) complexes prompted further studies on their catalytic performance in the reaction of 1-octene with HSi(OEt)$_3$. The reaction using **6** as the catalyst shows similar selectivity as that using **2**, wherein alkene hydrosilylation took place after alkene isomerization, but both reactions have faster rates. As depicted in Figure 1, the reaction using 5 mol % **6** merely requires 4 h to reach the plateau, whereas that with **2** needs 14 h (Figure 1). Despite this, the reaction still shows a short induction period, implying that **6** is an intermediate complex en route to in-cycle catalytic species. Complex **7** can effectively catalyze alkene isomerization, but is an inefficient catalyst for alkene hydrosilylation (blue lines in Figure 1). The fine performance of **7** in catalyzing alkene isomerization implies that low-coordinate cobalt(I) hydride species formed from the reaction of **6** with HSi(OEt)$_3$, presumably (IPr)Co(H), should be responsible for the alkene isomerization process in the cobalt(II) amide-catalyzed reaction. The poor performance of **7** in promoting alkene hydrosilylation might be due to the coordinative saturation of its metal center, which renders the coordination of the hydrosilane and its subsequent activation difficult. To a certain degree, it also provides explanation for the observations that benzene is not a suitable solvent and styrene is not applicable for the cobalt(II) amide complex-catalyzed hydrosilylation reaction, because in these cases the in situ formed reactive low-valent cobalt species could be readily trapped by these aromatic molecules. On the other hand, the successful hydrosilylation of *N*-allyl aniline and 4-phenylbutene (entries 5 and 7 in Table 1) might benefit from their electron-rich arene fragments that might have weaker affinity toward cobalt(I) center as compared to benzene.

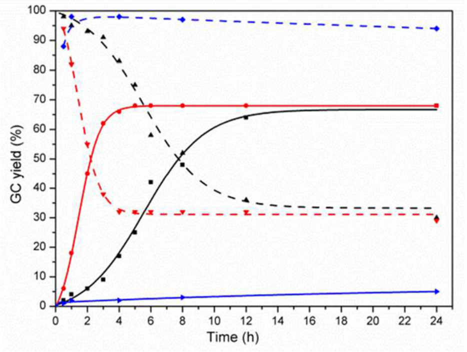


Figure 1. Reaction profiles of the reaction of 1-octene (1 mmol) with HSi(OEt)$_3$ (1.2 mmol) using 5 mol % of **2** (black), **6** (red), and **7** (blue) as the precatalysts. Solid lines show the change of the total yield of the HS and DS products versus time. The dashed lines show the change of the net yield of the mixture of alkene isomers and *n*-octane.

As the results have pointed out that the genuine catalytic species for the hydrosilylation reactions might be produced from the reaction of cobalt(I) amide species with one (or more) equivalent of HSi(OEt)$_3$, one could speculate its identity as a low-coordinate cobalt(I) hydride or a cobalt(I) silyl species. The latter could be formed from the reaction of cobalt(I) hydride with one equivalent of HSi(OEt)$_3$ after eliminating H$_2$.[16] At this stage, the exact identity of the genuine catalytically active species is difficult to confirm. However, the observation of the dehydrogenative silylation product *n*-C$_6$H$_{13}$CH═CHSi(OEt)$_3$ in these cobalt-catalyzed reactions (Table 1, entries 1−3) implies the involvement of cobalt silyl intermediates,[1] whose interaction with *n*-octene could give β-

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silylalkyl cobalt species that could further undergo *β*-H elimination to give the dehydrogenative silylation product. On the other hand, it is noted that the low-coordinate cobalt(0) complex $[(IPr)Co(\eta^2\text{-vtms})_2]$ (**8**) (vtms = vinyltrimethylsilane)[17] is ineffective in promoting the hydrosilylation reaction, which excludes the involvement of cobalt(0) species as the genuine catalytically active species.

In summary, we found that cobalt(II) amide complexes can serve as catalysts for the hydrosilylation of alkenes with tertiary silanes, obviating the use of external activator. Mechanistic studies disclosed that hydrosilane can react with cobalt(II) bis(amide) complex to form cobalt(I) amide and cobalt(I) hydride species, and that low-coordinate cobalt(I) species could be the genuine catalysts for the alkene hydrosilylation reaction. New catalyst design for alkene hydrosilyation employing the unique catalyst-activation mode is ongoing.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b12938.

Experimental procedures, characterization data of the compounds, and NMR spectra (PDF)

Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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