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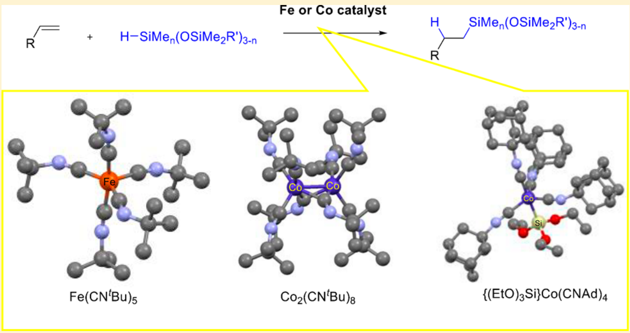
Cobalt(0) and Iron(0) Isocyanides as Catalysts for Alkene Hydrosilylation with Hydrosiloxanes

Atsushi Sanagawa and Hideo Nagashima*

Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga, Fukuoka 816-8580, Japan

Supporting Information

ABSTRACT: Iron and cobalt isocyanides, Fe(CNR)$_5$ (**1**) and Co$_2$(CNR)$_8$ (**2**), where R = *t*-butyl (^{t}Bu), adamantyl (Ad), and mesityl (Mes), were prepared by reduction of FeBr$_2$ or CoI$_2$ in the presence of CNR by C$_8$K or silica-Na. These complexes were subjected to catalytic hydrosilylation of alkenes with hydrosiloxanes, and the results are compared with those obtained by previously reported Fe(OPiv)$_2$/CNAd or Co(OPiv)$_2$/CNAd catalyst systems. Hydrosilylation of allylic ethers with 1,1,1,3,3-pentamethyldisiloxane (PMDS) catalyzed by **1** and the reaction of several alkenes with PMDS or 1,1,1,3,5,5,5-heptamethyltrisiloxane (MD′M) catalyzed by **2** exhibited greater catalytic activity than that observed for the Fe(OPiv)$_2$ or Co(OPiv)$_2$/CNR catalyst system. Complexes **1** and **2** were effective for catalytic chemical modification of silicone fluids containing Si−H groups and for two-component silicone curing. In all cases, selectivity of the reaction in terms of formation of the desired product by hydrosilylation and of byproducts due to dehydrogenative silylation did not differ between the metal isocyanide complexes and the corresponding M(OPiv)$_2$/CNR catalyst system. Catalytically active species generated from **1**, **2**, and the M(OPiv)$_2$/CNR catalyst system were also investigated.



INTRODUCTION

Hydrosilylation of alkenes is a key technology for the production of organosilicon compounds, including industrially important silicones.[1] Platinum compounds have significant advantages over other transition metal complexes or Lewis acids as practical catalysts due to their high catalytic activity and ease of handling. Several platinum catalysts,[2] such as Speier's catalysts[2a,c] and Karstedt's catalysts,[2b] have been used in the silicone industry, which utilizes 5.6 ton of platinum per year. Most of this platinum is not recovered.[3] Since platinum is an expensive precious metal and may become increasingly scarce in the future,[4] research is important[5] to find new hydrosilylation catalysts containing base metals such as iron,[6] cobalt,[7] and nickel.[8]

Base metal catalysts that are considered as substitutes for platinum catalysts in industrial production of silicone materials[1,2,5] need to possess high catalytic efficiency toward alkene hydrosilylation with hydroalkoxysilanes or hydrosiloxanes. New catalysts must demonstrate high enough catalytic activity to promote hydrosilylation at a catalyst loading on the order of a ppm [catalyst turnover numbers (TON) > 10^3−10^6].[3,9] Hydroalkoxysilanes, such as HSi(OR)$_3$, HMeSi(OR)$_2$, and HMe$_2$Si(OR), where R = Me or Et, are useful resources for the production of silane coupling reagents, whereas polysiloxanes containing Si−H groups are starting materials for silicone fluids and resins. Hydrosilylation reactions of various alkenes with HSiMe2OSiMe$_3$ (PMDS) and HSiMe(OSiMe$_3$)$_2$ (MD′M) are model reactions. Among the base metal catalysts investigated,[10−12] few are active for hydroalkoxysilanes[11] and hydrosiloxanes.[11d−f,12]

Base metals, such as iron and cobalt, prefer one- to two-electron redox reactions, often seen in precious-metal-catalyzed reactions.[1] Similar to hydrogenation of alkenes, alkene hydrosilylation involves a sequence of two-electron redox processes. Appropriate selection of ligands which make the metal center suitable for two-electron chemistry is key to achieving efficient hydrosilylation of alkenes by base metal catalysts. One typical example involves bis(imino)pyridines ligated to iron and cobalt, which behave as noninnocent redox-active ligands.[13] Another good example involves the use of strong π-acids such as C≡O as the ligand.[6] Several iron[14] and cobalt carbonyls[15] have been reported as catalysts for hydrosilylation of alkenes.

Isocyanide ligands, C≡NR, are of interest because they are isoelectronic to the C≡O ligand and effective as a π-acid ligand to achieve two-electron chemistry in base metal catalysis.[16] A 2016 report described efficient catalyst systems consisting of cobalt or iron pivalates [Fe(OPiv)$_2$ or Co(OPiv)$_2$] and isocyanide ligands for hydrosilylation of alkenes with hydrosiloxanes.[17] One advantage of this catalyst system is that both metal pivalates and isocyanide ligands are relatively easy to handle. Catalytically active species are generated from this mixture in contact with hydrosilanes. Model reactions

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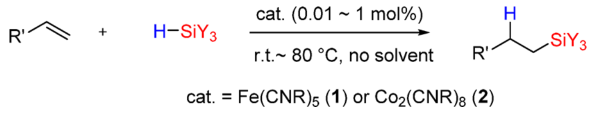
using PMDS suggested good catalytic activity of these catalyst systems that achieved TON of 10^3−10^4. The catalysts could be applied to the modification of silicone fluids using no more than 70 ppm catalyst loading. Silicone curing, i.e., cross-linking of Si−H groups containing polysiloxanes with vinyl terminated polysiloxanes, was achieved preliminary to the production of silicone rubbers and resins.

Of keen interest is catalytic species generated from a metal pivalate, isocyanide, and hydrosilane. A previous report indicated possible involvement of "Fe(0)$(CNR)_2$" and "Co(I)$(CNR)_3$" species in the reaction mechanisms.[17] In the literature,[14,15] $Fe(CO)_5$ and $Co_2(CO)_8$ are conventional base metal catalysts for alkene hydrosilylation and dehydrogenative silylation, and $Fe(CO)_3$, $R_3SiCo(CO)_4$, and $HCo(CO)_3$ have been discussed as plausible catalytic intermediates. Analogous electronic structures of C≡NR with C≡O provide possible hydrosilylation mechanisms involving "Fe(0)$(CNR)_3$" and "Co(I)$(CNR)_3$" species. This assumption regarding Fe(0)$(CNR)_3$ and Co(I)$(CNR)_3$ as possible intermediates could be verified by preparing isocyanide homologues of $Fe(CO)_5$ and $Co_2(CO)_8$ and comparing their catalytic alkene hydrosilylation performance with that of a $Fe(OPiv)_2$/CNR or $Co(OPiv)_2$/CNR catalyst system activated by hydrosilanes. The present report describes the hydrosilylation of several alkenes catalyzed by $Fe(CNR)_5$ (**1**) and $Co_2(CNR)_8$ (**2**) (Scheme 1). Catalytic activity of **1** or **2** was often greater than that of the corresponding metal carboxylates/isocyanide catalyst systems, while maintaining a similar selectivity. The results suggested that the catalytically active species generated from **1** or **2** with hydrosilanes was similar to those formed from a $Fe(OPiv)_2$/CNR or $Co(OPiv)_2$/CNR catalyst system activated by hydrosilanes.

Scheme 1. Hydrosilylation of Alkenes



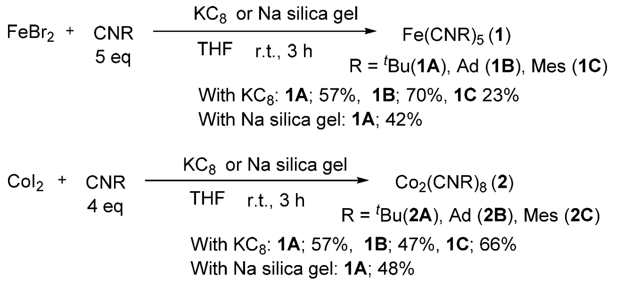
RESULTS AND DISCUSSION

Convenient Synthesis of $Fe(CNR)_5$ (1) and $Co_2(CNR)_8$ (2).

Prior to hydrosilylation studies, the synthetic methods for **1** and **2** were improved. Two isocyanide complexes, $Fe(CN^tBu)_5$ (**1a**) and $Co_2(CN^tBu)_8$ (**2a**), were synthesized by reduction of Fe(II) or Co(II) salts with Na/Hg or sodium naphthalenide in the presence of CNR as described previously.[18] However, both of these reducing reagents have problems: Na/Hg contains toxic Hg, and sodium naphthalenide produces large amounts of naphthalene, which is difficult to separate from the metal isocyanides. Two solid materials, KC_8 and commercially available sodium silica gel, were examined as reducing reagents. An advantage of these solid-state reducing reagents over conventional Na/Hg and sodium naphthalenide is the easy removal of solid wastes by filtration after the reaction. Metal isocyanides **1** and **2** could be isolated by recrystallization of the corresponding crude products.

Treatment of $FeBr_2$ with KC_8 (2 equiv to 1 equiv of $FeBr_2$) in the presence of RNC (5 equiv to 1 equiv of $FeBr_2$), where R = *tert*-butyl (^{t}Bu), adamantyl (Ad), or mesityl (Mes), at room temperature gave a suspension of bronze KC_8 in a brown solution of $FeBr_2$. The color of the solution immediately changed to dark orange, and the color of the insoluble materials turned to black. After 12 h, the solid materials were removed by filtration, and recrystallization of the residue from pentane afforded $Fe(CNR)_5$ (**1**) in 23−70% isolated yield (Scheme 2). Similar reactions of CoI_2 with KC_8 (2 equiv to 1 equiv of CoI_2) in the presence of CNR (4 equiv to 1 equiv of CoI_2) gave the corresponding $Co_2(CNR)_8$ (**2**) in 47−66% isolated yield. Commercially available sodium silica gel (stage I) could be used as a reducing reagent instead of KC_8. A typical example involved the preparation of **1** from $FeBr_2$ (1 mmol), CN^tBu (5 mmol), and sodium silica gel (ca. 5 mmol) in 42% yield, whereas **2** was synthesized from CoI_2 (1 mmol), CN^tBu (4 mmol), and silica-Na including 35 wt % Na (340 mg) in 48% yield. The products were characterized by ^{1}H and ^{13}C NMR, IR, crystallography, and elemental analysis.

Scheme 2. Synthesis of $Fe(CNR)_5$ and $Co_2(CNR)_8$



Hydrosilylation of Three Alkenes Catalyzed by 1B and 2B.

Three alkenes were selected to examine the catalytic activity of $Fe(CNAd)_5$ (**1B**) and $Co_2(CNAd)_8$ (**2B**) and the selectivity of reactions involving them. Previous studies[17] on a catalyst system composed of $Fe(OPiv)_2$ and CNAd (1:2) had the following features: (a) The catalyst system promoted hydrosilylation of styrene with PMDS to give $PhCH_2CH_2SiMe_2OSiMe_3$ (**3a**) as a single product (Scheme 3, eq 1). (b) No branched silane, $PhCH(Me)SiMe_2OSiMe_3$, was formed. (c) At temperatures higher than 50 °C, a 1:1 mixture of $PhCH{=}CHSiMe_2OSiMe_3$ (**3b**) and $PhCH_2CH_3$

Scheme 3. Hydrosilylation of Alkenes with PMDS

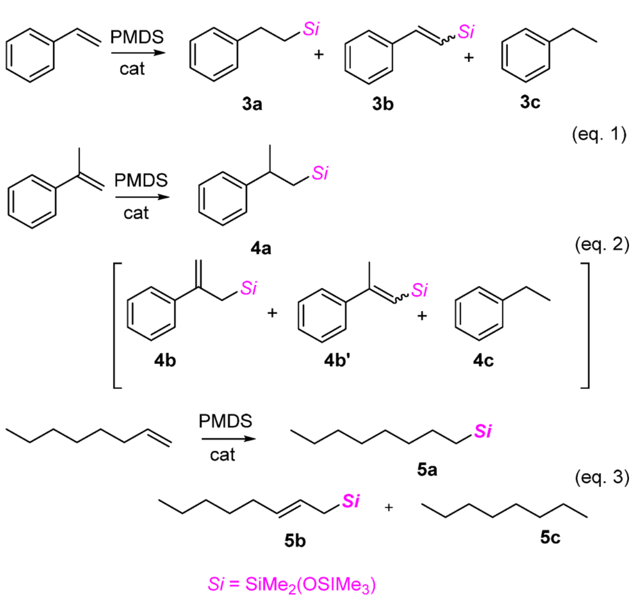


Table 1. Iron- or Cobalt-Catalyzed Reactions of Three Alkenes with PMDS

entry	cat. (mol % per metal)	temp (°C)	time (h)	conv. (%)[a]	products (% yield)[a]			
alkene = styrene (Scheme 3, eq 1)					**3a**	**3b**	**3c**	
1	**1B** (1)	80	24	>99	81	9	10	
2	**1B** (1)	50	24	>99	>99	<1	<1	
3	$Fe(OPiv)_2$ (1)/CNAd(2)/$(EtO)_3SiH$ (4)	80	24	>99	85	7	11	
4	$Fe(OPiv)_2$ (1)/CNAd(2)/$(EtO)_3SiH$ (4)	50	24	>99	>99	<1	<1	
5	**2B** (1)	50	24	>99	24	38	38	
6	$Co(OPiv)_2$ (1)/CNAd(3)/$(EtO)_3SiH$ (4)	50	24	>99	83	10	7	
alkene = α-methylstyrene (Scheme 3, eq 2)					**4a**	**4b**	**4b′**	**4c**
7	**1B** (1)	80	24	3	<1	<1	<1	<1
8	$Fe(OPiv)_2$ (1)/CNAd(2)/$(EtO)_3SiH$ (4)	80	24	5	<1	<1	<1	<1
9	**2B** (1)	50	24	>99	>99	<1	<1	<1
10	$Co(OPiv)_2$ (1)/CNAd(3)/$(EtO)_3SiH$ (4)	50	24	>99	>99	<1	<1	<1
alkene = 1-octene (Scheme 3, eq 3)					**5a**	**5b**	**5c**	
11	**1B** (1)	r.t.	24	49	16	6	21	
12	$Fe(OPiv)_2$ (1)/CNAd(2)/$(EtO)_3SiH$ (4)	r.t.	24	73	25	15	18	
13	**2B** (1)	50	24	>99	>99	<1	<1	
14	$Co(OPiv)_2$ (1)/CNAd(3)/$(EtO)_3SiH$ (4)	80	24	>99	>99	<1	<1	

[a] Conversion of the alkene and product yields were determined by ^1H NMR in the presence of internal standard.

(**3c**), due to dehydrogenative silylation, was formed as a byproduct. (d) Preactivation of the catalyst system by $HSi(OEt)_3$ accelerated the reaction, when the reaction was performed relatively high catalyst loadings (0.1−1 mol %).[19] (e) No reaction occurred under the same conditions when α-methylstyrene was used as the olefin (Scheme 3, eq 2). (f) Reaction of 1-octene with PMDS resulted in both hydrosilylation and dehydrogenative silylation concomitantly, which gave a mixture of octyl silane **5a**, allysilane **5b**, and octane **5c** (Scheme 3, eq 3).

The following results were obtained with the catalyst system composed of $Co(OPiv)_2$ and CNAd (1:3) preactivated by $HSi(OEt)_3$:[19] (a) Hydrosilylation of α-methylstyrene with PMDS gave a single product, **4a** (Scheme 3, eq 1). No byproducts, such as those due to dehydrogenative silylation and hydrogenation, were detected. (b) Reaction of styrene with PMDS under the same conditions gave a mixture of **3a**, **3b**, and **3c** derived from hydrosilylation and concomitantly occurring dehydrogenative silylation. (c) Reaction of 1-octene with PMDS resulted in rapid olefin isomerization to internal octenes, followed by hydrosilylation to give **5a** as a single product (Scheme 3, eq 3). (d) Similar to the $Fe(OPiv)_2$/CNR catalyst system, preactivation of the catalyst system by $HSi(OEt)_3$ accelerated the reaction, when the reaction was performed relatively high catalyst loadings (0.1−1 mol %).[19]

Table 1 summarizes the results of the hydrosilylation of styrene, α-methylstyrene, and 1-octene, with PMDS, with **1B** or **2B** (1 mol %) as the catalyst. Catalyst concentration and reaction time were fixed to 1 mol % and 24 h, respectively. The results are compared with those from the corresponding $M(OPiv)_2$/CNR system preactivated by $(EtO)_3SiH$. Treatment of styrene (1 mmol) with PMDS (1.3 mmol) was conducted at 80 °C for 24 h in the presence of **1B** (1 mol %) to give **3a** in 81% yield. Dehydrogenative silylation occurred concomitantly to give **3b** and **3c** in 9 and 10% yield, respectively (Table 1, entry 1). Dehydrogenative silylation was suppressed at 50 °C to afford **3a** as a single product (Table 1, entry 2). A similar temperature effect was observed in reactions with the $Fe(OPiv)_2$/CNAd catalyst preactivated by $(EtO)_3SiH$ (Table 1, entries 3 and 4). Reaction of styrene with PMDS catalyzed by **2B** and the $Co(OPiv)_2$/CNAd system did not afford **3a** as a single product. As shown in entries 5 and 6, significant amounts of **3b** and **3c** were obtained.

Entries 7−10 show the results of hydrosilylation of α-methylstyrene. Essentially no reaction occurred with **1B** or the $Fe(OPiv)_2$/CNAd catalyst system at 80 °C. In sharp contrast, both **2B** and the $Co(OPiv)_2$/CNAd catalyst system promoted hydrosilylation at 50 °C to give **4a** as a single product. Reactions of 1-octene with PMDS (entries 11−14) revealed: (a) When **1B** or the $Fe(OPiv)_2$/CNAd/$(EtO)_3SiH$ catalyst system was used as the catalyst, the reactions were faster than the hydrosilylation of styrene and occurred at room temperature to give a mixture of **5a**, **5b**, and **5c**. (b) As shown in Table 1, entries of 11 and 12, the yields of **5a**, **5b**, and **5c** were 16, 6, and 21%, respectively, in the reaction catalyzed by **1B**, whereas they were 25, 15, and 18% in the reaction catalyzed by $Fe(OPiv)_2$/CNAd/$(EtO)_3SiH$ catalyst system. The **5a**/**5b**/**5c** ratio was 37/14/49 in the former reaction, while the latter was 43/26/31. They were not significantly different. (c) Isomerization of a C═C bond of 1-octene to internal octenes occurred minimally in these iron-catalyzed reactions. (d) Both **2B** and the $Co(OPiv)_2$/CNAd catalyst system catalyzed the reaction at 50 °C to give **5a** as a single product in high yield. (e) In both cobalt-catalyzed reactions, migration of the C═C bond from terminal to internal was observed at the initial stage. (f) The resulting internal C═C bond underwent hydrosilylation involving isomerization of alkenes to form **5a** as a single product.

The selectivity of the reaction is an important outcome of this study. The desired hydrosilylation product **3a** was selectively formed by **1B** and the $Fe(OPiv)_2$/CNAd catalyst system, whereas **4a** and **5a** were obtained as a single product by **2B** and the $Co(OPiv)_2$/CNAd catalyst system. With other olefin/catalyst combinations, hydrosilylation was competitive with dehydrogenative silylation. No difference was found in selectivity of the reaction between the metal isocyanide catalyst and the $M(OPiv)_2$/CNAd catalyst system, regardless of the metal used (iron or cobalt). This selectivity outcome clearly indicates that the catalytically active species generated from $Fe(CNAd)_5$ (**1B**) should be identical to that from $Fe(OPiv)_2$/CNAd, and that the catalytically active species formed from

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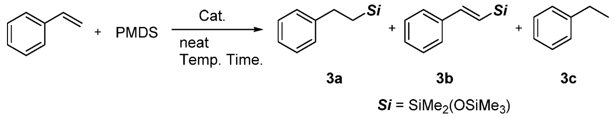
$Co_2(CNAd)_8$ (**2B**) should be similar to that from $Co(OPiv)_2$/CNAd.

Table 2. Hydrosilylation of Styrene with PMDS Catalyzed by $Fe(CNR)_5$ and the $Fe(OPiv)_2$/CNAd Catalyst System



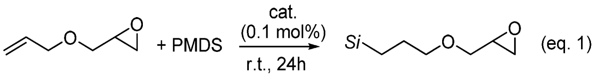
entry	cat. (mol %)	temp. (°C)	time (h)	conv. (%)	yield (%)[e]		
					3a	3b	3c
1	**1B** (1)	50	24	>99	>99	<1	<1
2	**1B** (1)	r.t.	24	7	7	<1	<1
3	**Fe-1** (1)[a]	r.t.	24	>99	>99	<1	<1
4	**Fe-2** (1)[b]	r.t.	24	2	2	<1	<1
5	**1B** (0.1)	50	24	>99	>99	<1	<1
6	**1B** (0.1)	50	3	73	73	<1	<1
7	**1A** (0.1)	50	24	>99	>99	<1	<1
8	**1A** (0.1)	50	3	19	19	<1	<1
9	**1C** (0.1)	50	24	83	5	39	38
10	**1B** (0.01)	50	24	8	3	<1	<1
11	**1A** (0.01)	50	24	11	4	<1	<1
12	**Fe-3** (0.01)[c]	50	24	8	3	<1	<1
13	**Fe-4** (0.01)[d]	50	24	91	91	<1	<1
14	**$Fe(CO)_5$** (1)	50	24	46	14	17	17

[a] **Fe-1**: $Fe(OPiv)_2$ (1 mol %)/CNAd (2 mol %) /$(EtO)_3SiH$ (4 mol %). [b] **Fe-2**: $Fe(OPiv)_2$ (1 mol %)/CNAd (2 mol %). [c] **Fe-3**: $Fe(CNAd)_5$ (0.01 mol %)/CNAd (0.03 mol %). [d] **Fe-4**: $Fe(OPiv)_2$ (0.01 mol %)/CNAd (0.08 mol %). [e] Conversion of the alkene and product yields were determined by ^1H NMR in the presence of internal standard.

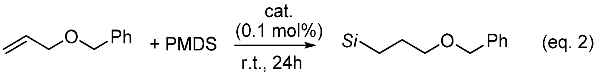
Catalytic Performance of $Fe(CNR)_5$. Table 2 summarizes the catalytic performance of **1A**, **1B**, and **1C** for hydrosilylation of styrene with PMDS. The reaction catalyzed by **1B** proceeded at 50 °C (entry 1), resulting in **3a** as a single product after 24 h. Reaction at room temperature resulted in low conversion of styrene (entry 2), which is in sharp contrast to the results from hydrosilylation of styrene catalyzed by the $Fe(OPiv)_2$ (1 mol %)/CNAd system in the presence of $(EtO)_3SiH$, which was complete under the same conditions (entry 3). Entry 4 shows the reaction in the absence of $(EtO)_3SiH$ for comparison, which was slower than the result shown in entry 3. The reaction with a lower catalyst loading (0.1 mol %) at 50 °C converted >99% styrene after 24 h and 73% after 3 h (entries 5 and 6, respectively). The results shown for entries 7 and 8 indicate that the catalytic activity of $Fe(CNtBu)_5$ (**1A**) was lower than that for **1B**. The reaction catalyzed by $Fe(CNMes)_5$ (**1C**) gave a mixture of **3a**, **3b**, and **3c** (entry 9). Competition between hydrosilylation and dehydrogenative silylation also was seen when the $Fe(OPiv)_2$/CNMes system was used as the catalyst. A previous study revealed that a mixture of $Fe(OPiv)_2$ and CNAd catalyzed the hydrosilylation of styrene to give **3a** with 0.01 mol % catalyst loading. With such low catalyst concentration, additional CNAd resulted in an increase in the yield of **3a**, and $(EtO)_3SiH$ was not necessarily useful to accelerate the reaction. The TON reached 10^4 under optimal conditions shown in entry 13. In contrast, addition of CNAd (3 equiv to **1B**) to the complex **1B** did not improve the catalytic activity (entry 12). For the experiments to lower the catalyst loadings, $Fe(OPiv)_2$/CNR catalyst system is better than $Fe(CNR)_5$. $Fe(CO)_5$ possessed inferior catalytic activity and selectivity compared to $Fe(CNR)_5$ toward the product.

The above results indicate that **1B** is a catalyst that can convert styrene and PMDS to **3a** with good selectivity, but had a lower catalytic activity than that of the $Fe(OPiv)_2$/CNAd catalyst system, especially at low catalyst loadings. An opposite trend was observed for hydrosilylation of allyl ethers with PMDS. The $Fe(OPiv)_2$/CNAd catalyst system was effective for reaction of allyl glycidyl ether, allyl benzyl ether, and allyl 2-methoxyethyl ether when 3 mol % $Fe(OPiv)_2$ was used. As shown in Scheme 4, eq 1, hydrosilylation of allyl glycidyl ether was catalyzed by **1A**, **1B**, or the $Fe(OPiv)_2$/CNAd/$(EtO)_3SiH$ catalyst system with 0.1 mol % catalyst loading at room temperature for 24 h. Catalytic activity increased in the order $Fe(OPiv)_2$/CNAd/$(EtO)_3SiH$ ≪ **1B** < **1A**. Reaction of allyl benzyl ether under similar conditions indicated **1B** possessed greater catalytic activity than did $Fe(OPiv)_2$/CNAd/$(EtO)_3SiH$ (Scheme 4, eq 2).[20] The catalytic activity of **1A** was higher than **1B**. In both cases, the corresponding hydrosilylated product, **6a** or **7a**, formed as a single product in high yield. Hydrosilylation of allyl 2-methoxyethyl ether with PMDS is also shown in Scheme 4, eq 3. With 1 mol % **1A**, **8a** was obtained as a single product in 87% yield. The activity of **1B** was lower than **1A** but greater than that of the $Fe(OPiv)_2$/CNAd catalyst system preactivated by $(EtO)_3SiH$; yield of **8a** was as low as 45%, even when using 3 mol % catalyst.

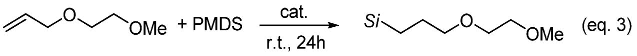
Scheme 4. Hydrosilylation of Allylic Ethers by Iron Catalysts [*Si*− = Me_3SiOMe_2Si−]



Cat.	Yield(%)
$Fe(CN^tBu)_5$(1A)	**97**
$Fe(CNAd)_5$(1B)	**43**
$Fe(OPiv)_2$/CNAd/$(EtO)_3SiH$ (1 : 2 : 4)	**4**



Cat.	Yield(%)
$Fe(CN^tBu)_5$(1A)	**99**
$Fe(CNAd)_5$(1B)	**68**
$Fe(OPiv)_2$/CNAd/$(EtO)_3SiH$ (1 : 2 : 4)	**4**

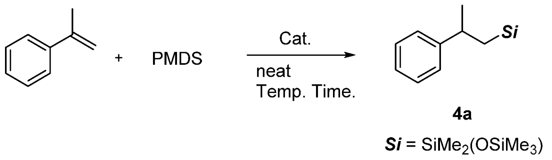


Cat. (mol%)	Yield(%)
$Fe(CN^tBu)_5$(1A) (1)	**87**
$Fe(CNAd)_5$(1B) (1)	**63**
$Fe(OPiv)_2$/CNAd/$(EtO)_3SiH$ (1 : 2 : 4) (3)	**45**

As seen for hydrosilylation of alkenes with the $Fe(OPiv)_2$/CNR catalyst system, a limited number of hydrosilanes and alkenes were effective for the $Fe(CNR)_5$-catalyzed hydrosilylation. As shown in the Table S2, hydrosilylation of styrene catalyzed by **1B** selectively afforded the desired β-phenethylsilane in good yield, when $PhMe_2SiH$, $(EtO)Me_2SiH$, or $(EtO)_2MeSiH$ was used as the hydrosilane. In contrast, reactions with $(EtO)_3SiH$ and Ph_2SiH_2 were slower, and no reaction occurred with $PhSiH_3$. Reaction with MD′M afforded a mixture of products due to hydrosilylation and dehydrogenative silylation. In all cases, no α-phenethylsilane was formed. Among the attempts of hydrosilylation of other alkenes with PMDS, norbornene was hydrosilylated to afford 2-silylnorbornane product **9a** in 68% isolated yield. A small amount of norbornane was also formed. Essentially no reaction took place with α-methylstyrene and 2-octene.

Catalytic Performance of $Co_2(CNR)_8$. Table 3 summarizes cobalt-catalyzed hydrosilylation of α-methylstyrene with PMDS (additional results in Table S3). Apparently, $Co_2(CN^tBu)_8$ (**2A**) and $Co_2(CNAd)_8$ (**2B**) possessed greater catalytic efficiency than the $Co(OCOR)_2$/CNR catalyst system. As reported earlier,[17] the same reaction was catalyzed by the corresponding $Co(OCOR)_2$ (1 mol %)/CNR catalyst system to produce desired **4a** quantitatively with 100% selectivity when the reaction was performed at 50 °C for 24 h (entry 1). However, when the reaction was performed at room temperature, the product yield decreased to 16% (entry 2). In contrast, hydrosilylation catalyzed by **2B** (1 mol %) proceeded at room temperature to give **4a** as a single product in quantitative yield after 24 h (entry 3). Experiments to reduce catalyst concentration from 1 to 0.1 mol % provided the optimum conditions at 50 °C for 24 h or 80 °C for 3 h for both **2A** and **2B** as the catalyst (entries 4–7). Interestingly, the catalytic performance of $Co_2(CNMes)_8$ (**2C**) differed from that of **2A** and **2B**. The catalytic activity of **2C** at room temperature was good enough to complete the reaction in 24 h, while **2C** was deactivated and lost activity during reaction at 50 and 80 °C (entries 8–10). Catalytic activity of $Co_2(CO)_8$ was somewhat lower than that of **2A**, **2B**, and **2C** at 80 °C for 3 h (entry 11). As reported previously, the greatest TON value achieved using the $Co(OPiv)_2$/CNAd catalyst system was 1850, although the catalyst was deactivated before conversion of α-methylstyrene reached >99%. Entries 12 and 13 demonstrate TON values of 3500–3600, achieved at 50 °C with **2B** and at room temperature with **2C**. As shown in Table S3, $Co_2(CNR)_8$ generally acted as a good catalyst for hydrosilylation of α-methylstyrene with tertiary hydrosilanes, which included MD′M, $Me_n(EtO)_{3-n}SiH$ (n = 0–2), $PhMe_2SiH$, and Et_3SiH. The $Co(OPiv)_2$/CNAd catalyst system could be applied to the hydrosilylation of various olefins with hydrosiloxanes. Table 4 shows representative examples catalyzed by **2A**. All reactions were performed using 1 mol % **2A** at 50 °C for 24 h. As described above, hydrosilylation of α-methylstyrene with PMDS gave **4a** in good yield. Reaction of α-methylstyrene with MD′M ($Me_3SiOSiMeHOSiMe_3$) also proceeded smoothly to give **10a** in high yield (entry 1). Reaction of 1-octene with PMDS gave n-octylsilane **5a** as a single product (entry 2). The same product, **5a**, was obtained by reaction of 2-octene with PMDS (entry 3), indicating that hydrosilylation was accompanied by C═C double bond migration. Norbornene was hydrosilylated with PMDS in good yield as shown in entry 4. Reactivity of

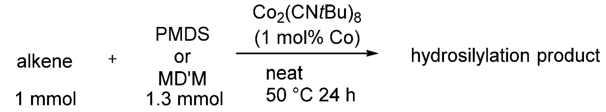
Table 3. Hydrosilylation of α-Methylstyrene with PMDS Catalyzed by $Co_2(CNR)_8$ and $Co(OPiv)_2$/CNAd Catalyst Systems

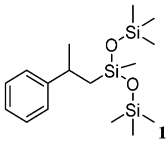
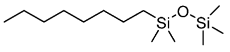
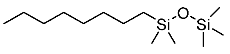
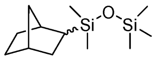
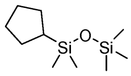
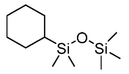
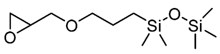


entry	cat. (mol % Co)	temp. (°C)	time (h)	conv. (%)	yield (%) 4a
1	**Co-1** (1)[a]	50	24	>99	>99
2	**Co-1** (1)[a]	r.t.	24	16	16
3	**2B** (1)	r.t.	24	>99	>99
4	**2B** (0.1)	50	24	>99	>99
5	**2B** (0.1)	80	3	>99	>99
6	**2A** (0.1)	50	24	>99	>99
7	**2A** (0.1)	80	3	>99	>99
8	**2C** (0.1)	r.t.	24	>99	>99
9	**2C** (0.1)	50	24	79	79
10	**2C** (0.1)	80	3	50	50
11	$Co_2(CO)_8$ (0.1)	80	3	88	88
12	**2B** (0.02)	80	24	70	70 (TON = 3500)
13	**2C** (0.01)	r.t.	48	36	36 (TON = 3600)
14	**Co-1** (0.02)[b]	80	24	10	10 (TON = 500)

[a] **Co-1**: $Co(OPiv)_2$ (1 mol %)/CNAd (3 mol %)/$(EtO)_3SiH$ (4 mol %). [b] **Co-2**: $Co(OPiv)_2$ (0.02 mol %)/CNAd (0.06 mol %).

Table 4. Hydrosilylation of Olefins with PMDS or MD′M Catalyzed by 2A



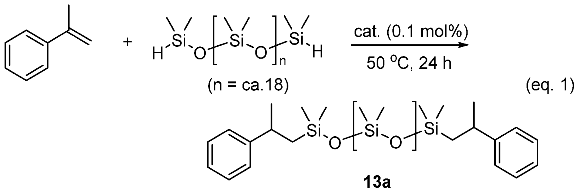
Entry	alkenes	Hydro-silane	product	Yield (%)[a]
1	α-methylstyrene	MD′M	 **10a**	97
2	1-octene	PMDS	 **5a**	96
3	2-octene	PMDS	 **5a**	97
4	norbornene	PMDS	 **10a**	91[b]
5	cyclopentene	PMDS	 **11a**	86
6	cyclohexene	PMDS	 **12a**	75
7	allyl glycidylether	PMDS	 **6a**	94

[a] Isolated yield. [b] exo/endo ratio = 9:1.

alicyclic alkenes was lower than that for linear terminal alkenes. In particular, cyclohexene is minimally hydrosilylated using a platinum catalyst.[2] The use of **2A** as the catalyst permitted the conversion of both cyclopentene and cyclohexene to the corresponding product, **11a** and **12a**, respectively, in 86 and 75% yield. Allyl glycidyl ether was hydrosilylated using **2A** as the catalyst (entry 7).

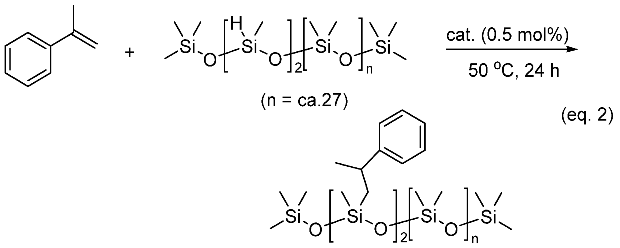
Modification of Silicone Fluids. To help develop industrially important modification processes of silicone fluids, the three reactions shown in Scheme 5 were investigated. The first two reactions involved cobalt-catalyzed hydrosilylation with α-methylstyrene, in which polydimethylsiloxane end-capped with two Me_2SiH groups and polydimethylsiloxane having two Me_3Si terminal and two −MeHSiO− units were used as the hydrosilane. The former reaction was achieved with 0.1 mol % **2B** at 50 °C to give **13a** quantitatively after 24 h (Scheme 5, eq 1). The catalyst loading of 0.1 mol % (per Co) of **2B** corresponded to 70 ppm of Co per the starting material.

Scheme 5. Iron- and Cobalt-Catalyzed Modification of Silicone Fluids with Alkenes



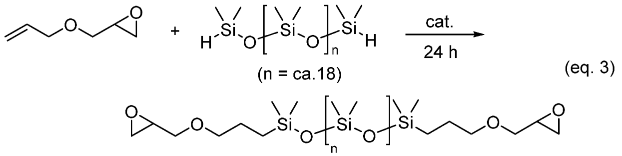
13a

Cat.	Yield(%)
$Co_2(CNAd)_8$(**2B**)	99
$Co(OPiv)_2$/CNAd/$(EtO)_3SiH$ (1 : 3 : 4)	26



14a

Cat.	Yield(%)
$Co_2(CNAd)_8$(**2B**)	99
$Co(OPiv)_2$/CNAd/$(EtO)_3SiH$ (1 : 3 : 4)	34



15a

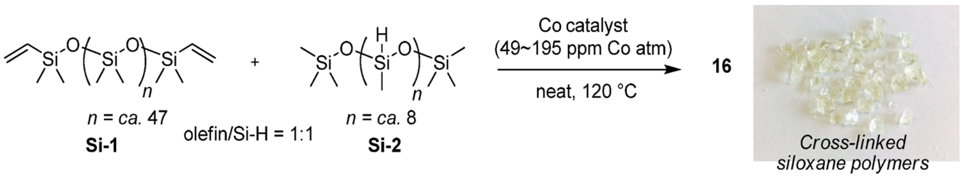
Cat. (mol%)	Temp. (°C)	Yield (%)
$Fe(CN^tBu)_5$(**1A**) (0.25)	r.t.	87
$Fe(OPiv)_2$/CNAd/$(EtO)_3SiH$ (1 : 2 : 4) (0.25)	r.t.	45
$Co_2(CNAd)_8$(**2B**) (1)	50	99
$Co(OPiv)_2$/CNAd/$(EtO)_3SiH$ (1 : 3 : 4) (1)	50	87

The reaction shown in eq 2 was complete with 0.5 mol % (per Co) of **2B** at 50 °C for 24 h, and **14a** was formed in 99% yield. In both cases, reaction using the $Co(OPiv)_2$/CNAd catalyst system activated by $(EtO)_3SiH$ provided the corresponding product in low yields. The second example involved hydrosilylation of polydimethylsiloxane end-capped with two Me_2SiH groups containing a glycidyl ether (Scheme 5, eq 3). Both $Fe(CN^tBu)_5$ (**1A**) and $Co_2(CNAd)_8$ (**2B**) catalyzed the reaction to afford **15a**. Thus, the iron catalyst showed greater catalytic activity than the cobalt catalyst; reaction with **1A** was accomplished with 0.25 mol % catalyst at room temperature in 24 h.

Two-Component Silicone Curing. Two-component silicone curing is a process used to produce silicone resins by hydrosilylation of a polydimethylsiloxane containing Si−H groups or vinyl groups.[3,11f,21] A typical example involved treatment of $(CH_2{=}CH)(Me_2SiO)(Me_2SiO)_{47}SiMe_2(CH{=}CH_2)$ (**Si-1**) and $Me_3SiO(MeHSiO)_9SiMe_3$ (**Si-2**) with **2B** or $(EtO)_3SiCo(CNAd)_4$ (**17B**) (*vide infra*). For comparison, a 1:3 mixture of $Co(OPiv)_2$ and CNAd also was examined as the catalyst. The molar ratio of **Si-1** and **Si-2** was adjusted to a 1:1 ratio of the $CH_2{=}CH$ group of **Si-1** to the Si−H moiety in **Si-2**. Table 5 summarizes the results of curing performed at 120 °C for 3−24 h. Hydrosilylation of the vinyl groups in **Si-1** with Si−H groups in **Si-2** resulted in cross-linking of two silicone chains to give insoluble silicone gel. The degree of cross-linking (DCL) was estimated by IR and solid-state NMR spectroscopy of silicone gel **16** and a 1:1 mixture of **Si-1** and **Si-2** (the standard). The IR spectra of these two samples showed ν_{Si-H} and ν_{Si-C} vibrations at 2150 and 1258 cm^{-1}, respectively. The peak integrals $I(\nu_{Si-H})$ and $I(\nu_{Si-C})$ were determined from the IR spectra of **16**, whereas $I_0(\nu_{Si-H})$ and $I_0(\nu_{Si-C})$ were estimated from the standard. DCL(IR) was defined as $\{1 - I(IR)/I_0(IR)\} \times 100$, where $I(IR) = [I(\nu_{Si-H})]/[I(\nu_{Si-C})]$ and $I_0(IR) = [I_0(\nu_{Si-H})]/[I_0(\nu_{Si-C})]$. Solid-state ^1H NMR of **16** and the standard sample showed signals due to Si−H, vinyl, and methyl groups around 4.7 ppm, 5.6−6.3 ppm, and 1.0 to −2.0 ppm, respectively. The ^{29}Si NMR spectrum contained signals at 4 to 5 ppm and −22 ppm, assigned to a Si nucleus bonded with the vinyl group and that of $SiMe_2$ moieties, respectively. As described in the Supporting Information in detail, the integral of these signals provided the basis of I and I_0 determined by NMR, from which DCL(^1H NMR)-1, DCL(^1H NMR)-2, and DCL(^{29}Si NMR) were estimated.

Table 5 shows that the time required for curing and the DCL were dependent on the catalyst and catalyst concentration. As shown in entries 1−3, curing occurred when 98−195 ppm of **2B** was used as the catalyst. With higher catalyst loadings, a shorter period was needed for gelation to occur. While only a viscous gel was obtained using 49 ppm **2B**, a solid gel was formed with **17B** (entry 5), which is more soluble in silicones than **2B**. The $Co(OPiv)_2$/CNAd catalyst system (**Co-2**) was not useful for curing at a lower catalyst loading (98 ppm). Catalytic activity for silicone curing was **17B** > **2b** > **Co-2**. The DCL was 50−60% for the experiments shown in entries 2 and 5, which produced soft gels. Gels close to a solid state were obtained from the experiments shown in entries 1 and 4, which resulted in a DCL of 66−71% and 75−93%, respectively. The color of the gel after curing was brown, which turned pale blue upon exposure to air. A similar color change was observed for the samples produced from reactions

Table 5. Cobalt-Catalyzed Silicone Curing



					degree of cross-linking (DCL)[a]			
entry	catalyst	ppm/ Co	time required for the curing	total reaction time	DCL(IR) (%)	DCL(^{1}H NMR)-1 (%)[c]	DCL(^{1}H NMR)-2 (%)[d]	DCL(^{29}Si NMR) (%)
1	**2B**	195	3 min	3 h	66	68	71	66
2	**2B**	98	30 min	3 h	50	62	59	46
3	**2B**	49	24 h (gelatinous)	24 h	39	*b*	*b*	*b*
4	**17B**	195	3 min	3 h	79	75	89	93
5	**17B**	49	3 h	24 h	50	62	64	51
6	**Co-2**[e]	195	11 min	3 h	69	59	73	60
7	**Co-2**[e]	98	no curing	24 h				

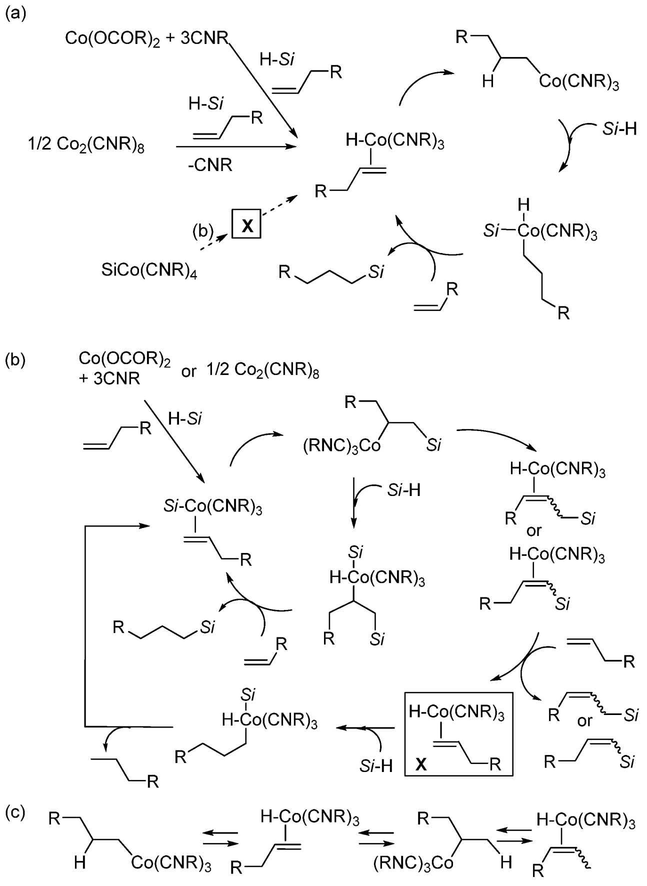
[a] Degree of cross-liking (DCL) was determined by IR and NMR spectra according to the methods described in the text and the Supporting Information. [b] Since the sample was viscous gel, we cannot measure the solid state NMR. [c] DCL(^{1}H NMR)-1 is determined by the ^{1}H signals due to the Si–H and Si–Me groups. [d] DCL(^{1}H NMR)-2 is determined by the ^{1}H signals due to the Si–vinyl and Si–Me groups. [e] **Co-2** = 1:3 mixture of $Co(OPiv)_2$ and CNAd.

using **2B** or **17b** as the catalyst. The gel formed using 49 ppm of **17b** was nearly colorless.

Mechanistic Considerations. The results presented here suggest catalytically active species generated from the $Fe(OPiv)_2$/CNR and $Co(OPiv)_2$/CNR catalyst systems were similar to those from $Fe(CNR)_5$ and $Co_2(CNR)_8$, respectively. In particular, product ratios between *n*-alkylsilane from hydrosilylation and allylsilane and alkane from dehydrogenative silylation are good supporting evidence. The geometric and electronic structures of CNR are similar to those of CO, which is useful to consider when investigating the reaction mechanism and determining the net catalyst species in the catalytic cycle. Thus, the mechanism for reactions catalyzed by $Fe(CNR)_5$ and $Co_2(CNR)_8$ would not differ from those proposed for reactions catalyzed by $Fe(CO)_5$ and $Co_2(CO)_8$.

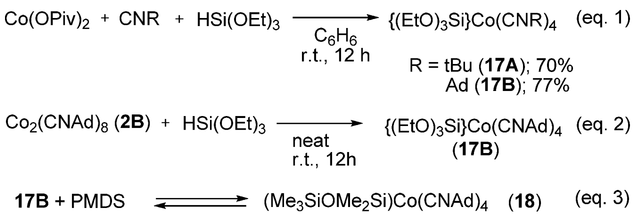
It was reported that treatment of R_3SiH with $Co_2(CO)_8$ resulted in formation of $R_3SiCo(CO)_4$ and $HCo(CO)_4$. Further reaction of $HCo(CO)_4$ with $HSiR_3$ afforded $R_3SiCo(CO)_4$ and H_2.[15a] For the $Co_2(CO)_8$-catalyzed hydrosilylation of alkenes, a Chalk–Harrod cycle was proposed in the 1960s, which involves insertion of a C=C bond into a Co–H species generated from $Co_2(CO)_8$ (Scheme 6a). Chalk and Harrod obtained no evidence for the participation of $R_3SiCo(CO)_4$ in thermal catalytic hydrosilylation of alkenes.[15b] In contrast, Wrighton and co-workers observed efficient hydrosilylation of $HSiEt_3$ with 1-pentene under photoirradiation. Detailed mechanistic studies on the photoassisted hydrosilylation of alkenes with $Co_2(CO)_8$[15c,d] supported a modified Chalk–Harrod cycle (Scheme 6b), which involved insertion of a C=C bond into a Co–Si species generated from $Co_2(CO)_8$[15e] Thus, the hydrosilylation proceeds through a Chalk–Harrod cycle thermally, possibly via a photochemically modified Chalk–Harrod cycle.

Scheme 6. (a) Chalk–Harrod Cycle, (b) Modified Chalk–Harrod Cycle for Cobalt-Catalyzed Hydrosilylation of Alkenes, (c) Possible Mechanism for Alkene Isomerization



The approach to investigate net catalytic species began with experiments to elucidate the species generated by reaction of $Co(OPiv)_2$ with $HSi(OEt)_3$ in the presence of CNR. Catalytic activity was enhanced when this treatment was performed prior to hydrosilylation of alkenes with hydrosiloxanes. Reaction of a 1:6 mixture of $Co(OPiv)_2$ and CNAd or CN^{t}Bu with excess $HSi(OEt)_3$ resulted in a color change from violet to brown and produced the corresponding silylcobalt complexes, $\{(EtO)_3Si\}Co(CNR)_4$ [R = ^{t}Bu (**17A**) or Ad (**17B**)], which were obtained as stable complexes in greater than 70% yields (Scheme 7, eq 1). The reaction was accompanied by formation of hydrogen.

Scheme 7. Synthesis of $(EtO)_3SiCo(CNR)_4$



These new silyl-cobalt complexes were characterized by NMR and IR spectroscopy, and X-ray structural determination of $\{(EtO)_3Si\}Co(CNAd)_4$ supported the spectral assignments (Figure 1). The same silyl-cobalt complexes were also formed from $Co_2(CNR)_8$ and $HSi(OEt)_3$ (Scheme 7, eq 2). For example, **2B** was treated with a large excess of $HSi(OEt)_3$ at room temperature for 12 h without solvent. Excess $HSi(OEt)_3$ was removed *in vacuo*, and the residue recrystallized from Et_2O to give **17B** in 50% yield. Evolution of hydrogen was observed. Similar to the reaction of $Co_2(CO)_8$ with R_3SiH, two reactions, formation of $HCo(CNR)_4$ and $(EtO)_3SiCo(CNR)_4$ and reaction of the resulting $HCo(CNR)_4$ with $HSi(OEt)_3$ to produce $(EtO)_3SiCo(CNR)_4$ and H_2, occurred successively. The results confirmed that the $Si(OEt)_3$ group in **17B** could be exchanged with a Me_3SiOMe_2Si group in contact with PMDS. When a 1:3 mixture of **17B** and PMDS was heated in C_6D_6 at 50 °C for 5 h, signals due to **17B** were decreased, and two new singlets appeared at δ 1.19 and 0.69 ppm, which were assigned to $SiMe_2$ and $SiMe_3$ moieties of $(Me_3SiOMe_2Si)Co(CNAd)_4$ (**18**), respectively. The ratio of **17B** to **18** was 3:7 (Scheme 7, eq 3). These experiments suggest that $(Me_3SiOMe_2Si)Co(CNR)_4$ was a precursor of net catalytic species, which was generated from either $(EtO)_3SiCo(CNR)_4$ or $Co_2(CNR)_8$ in contact with PMDS during catalysis. Compound **17B** actually acted as the catalyst for hydrosilylation of α-methylstyrene with PMDS. Comparison of two reaction profiles obtained by hydrosilylation of α-methylstyrene with PMDS catalyzed by **17B** and **2B** revealed a significantly longer induction period for the reaction with **17B**, as shown in Scheme 8. This is consistent with observations reported in the literature, in which $HCo(CO)_3$ exists inside the catalytic cycle.[22] A Chalk–Harrod cycle mediated by $HCo(CNR)_3$ is highly likely and could explain the present results from thermal hydrosilylation.[23,24]

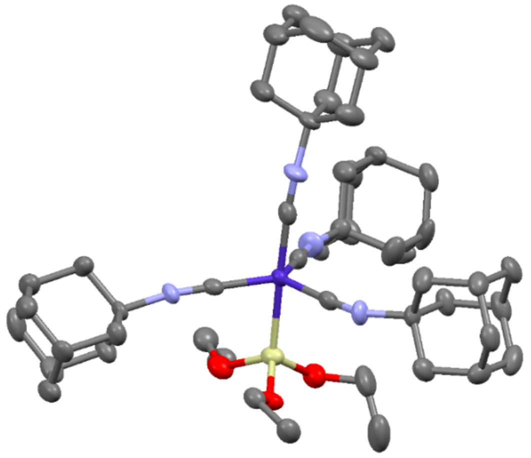
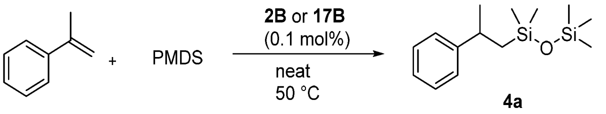


Figure 1. Molecular structure of **17B**. Hydrogen atoms and ether as a solvent molecule have been omitted for clarity.

Scheme 8. Reaction Profiles for Hydrosilylation of α-Methylstyrene with PMDS Using $Co_2(CNAd)_8$ (2B) or $(EtO)_3SiCo(CNAd)_4$ (17B) as the Catalyst[a]



Cat.	Yield of 4a (%)[a]				
	1 h	3 h	6 h	12 h	24 h
2B	6	27	68	>99	-
17B	0	0	0	8	38

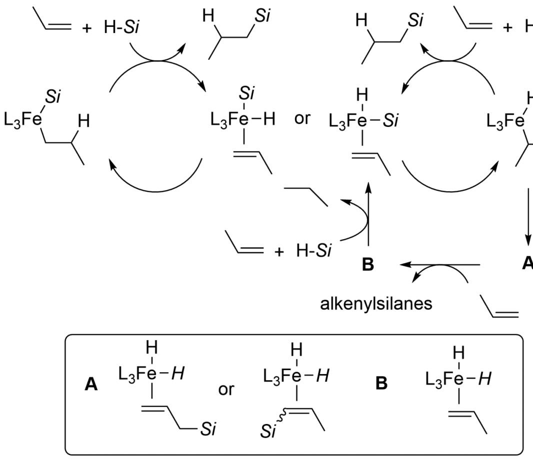
[a]The yield was determined by ^1H NMR.

The resulting mixture of 2-, 3-, and 4-octenes also are hydrosilylated to form the 1-silyloctane, which is the same product as that obtained from the hydrosilylation of 1-octene. These results can be explained by $HCo(CNR)_3$-mediated hydrosilylation. Addition of an H–Co bond to a C═C moiety followed by β-hydrogen atom elimination resulted in alkene isomerization to give internal octenes (Scheme 6c), while sequential addition–elimination reactions of a H–Co bond to a C═C moiety in internal octenes formed an *n*-octyl-Co moiety, which is susceptible to reaction with Si–Co species to form 1-silyloctane.

A recent report from the research group of Chirik suggested the involvement of a modified Chalk–Harrod mechanism in the hydrosilylation of alkenes catalyzed by bis(imino)pyridine cobalt complexes.[25] As shown in Scheme 6, the modified Chalk–Harrod cycle promoted both hydrosilylation and dehydrogenative silylation in the reaction of terminal alkenes, while dehydrogenative silylation was difficult to achieve through a Chalk–Harrod mechanism. Unlike Chirik's bis(imino)pyridine cobalt catalysts, products from dehydrogenative silylation in the reactions of terminal alkenes with hydrosilanes catalyzed by $Co_2(CNR)_8$ or $Co(OCOR)_2$/CNR have not been reported. This also supports a Chalk–Harrod mechanism for cobalt-isocyanide catalysts.

The mechanism for the hydrosilylation of alkenes catalyzed by $Fe(CNR)_5$ can be examined through analogy with $Fe(CO)_5$. However, the mechanism of $Fe(CO)_5$-catalyzed reactions has not been as thoroughly investigated as $Co_2(CO)_8$-catalyzed hydrosilylation. Hydrosilylation of alkenes catalyzed by $Fe(CO)_5$ and other iron carbonyls is competitive with dehydrogenative silylation of alkenes.[14a,26] In many cases, dehydrogenative silylation predominated over hydrosilylation. Wrighton and co-workers proposed oxidative addition of an H–Si bond to coordinatively unsaturated iron carbonyls, which was generated photochemically from $Fe(CO)_5$, an alkene, and a hydrosilane.[14b] Two reaction pathways for the resulting oxidative adduct "H–Fe–Si" were proposed: insertion of a C═C bond into the H–Fe bond that initiated a Chalk–Harrod cycle to form the hydrosilylated product or insertion into the Si–Fe bond to promote a modified Chalk–Harrod cycle that provided a mixture of the three products due to both hydrosilylation and dehydrogenative silylation. Simplified schemes for these processes are illustrated in Scheme 9. Recent DFT calculations[14c] for the possible catalytic cycles for $Fe(CO)_5$-catalyzed hydrosilylation of alkenes support the mechanisms involving $(CO)_4Fe(H)(SiR_3)$ and

Scheme 9. Chalk−Harrod and Modified Chalk−Harrod Cycles for Iron-Catalyzed Hydrosilylation of Alkenes



$(CO)_nFe(H)(SiR_3)$ (alkene), which can accommodate both the thermal and photochemical processes.

Involvement of coordinatively unsaturated $Fe(CNR)_n$ species was indicated from the significant acceleration of $Fe(CNR)_5$-catalyzed hydrosilylation by photoirradiation (Scheme S2). Similar to the photoassisted CO dissociation from $Fe(CO)_5$, photolysis induced elimination of CNR from $Fe(CNR)_5$. The mechanistic analogy to $Fe(CO)_5$ suggested that the net catalytic species would be $(RNC)_4Fe(H)(SiR_3)$ and $(RNC)_3Fe(H)(SiR_3)$(alkene). However, attempted NMR analysis of the oxidative adduct, $(RNC)_4Fe(H)(SiR_3)$, by the reaction of **1A** with PMDS was prevented due to the formation of paramagnetic species. Involvement of $(RNC)_4Fe(H)(SiR_3)$ and $(RNC)_3Fe(H)(SiR_3)$(alkene) was inconsistent with the results that the greatest catalytic activity was achieved in the $Fe(OPiv)_2$/CNR catalyst system, when the Fe:CNR ratio was adjusted to 1:2 (see, Scheme S3). The number of CNR ligands in the catalytically active species is likely to be two.

Hydrosilylation and dehydrogenative silylation catalyzed by $Fe(CO)_5$ required application of high temperatures or photoirradiation.[14b] In contrast, $Fe(CNR)_5$ catalyzed the reaction even at room temperature. Nevertheless, the catalytic activity of $Fe(CNR)_5$ was inferior to that of the $Fe(OPiv)_2$/CNR (Fe/CNR = 1:2) system when catalyst loadings were low, and photolysis accelerated the reaction. These results suggest that a significant energy barrier existed for dissociation of CNR from $Fe(CNR)_5$ to generate a catalytically active species, although the barrier was lower than that for liberation of CO from $Fe(CO)_5$. However, the better catalytic performance of $Fe(CNR)_5$ compared to that of the $Fe(OPiv)_2$/CNR system for the hydrosilylation of allylic ethers was interesting. Bidentate coordination of the oxygen atom and C═C bond in the allylic ether to the iron center would facilitate dissociation of CNR.[20]

If the $(RNC)_nFe(H)(SiR_3)$(alkene) species is assumed to be present in the reaction medium, then the next step would be insertion of the coordinated alkene between either the Fe−H or Fe−Si bond. Similar to the $Fe(CO)_5$-catalyzed hydrosilylation, these two processes are sensitive to the ratio of charged alkene and $H\text{-}SiR_3$. As shown in Table S4, reaction of 1-octene with PMDS in the presence of $Fe(CNR)_5$ and the $Fe(OPiv)_2$/CNR catalyst system resulted in hydrosilylation, especially in the presence of excess PMDS. In contrast, dehydrogenative silylation became a major reaction pathway with excess 1-octene.

An interesting feature of the $Fe(CNR)_5$ catalyst and the $Fe(OPiv)_2$/CNR catalyst system is the selectivity of the reactions involving styrene. Dehydrogenative silylation is a major reaction pathway when iron carbonyl complexes are used as the catalyst.[26] Marciniec and co-workers reported that direction of the reaction toward hydrosilylation or dehydrogenative silylation was affected not only by the hydrosilane/styrene ratio but also by the reaction temperature. Selective hydrosilylation of styrene catalyzed by (divinylsiloxane)$Fe(CO)_3$ catalysts was achieved only when using a 1:1 ratio of styrene and hydrosilane and a temperature carefully controlled at 0−10 °C.[26d] The $Fe(CNR)_5$ catalyst and the $Fe(OPiv)_2$/CNR catalyst system generally achieved selective hydrosilylation at temperatures below 50 °C. The difference in the electronic nature of CNR and CO facilitated selective hydrosilylation at relatively high temperatures.

■ CONCLUSIONS

For the hydrosilylation experiments, $Fe(CNR)_5$ and $Co_2(CNR)_8$ acted as good catalysts for hydrosilylation of alkenes with hydrosiloxanes. Similar to the corresponding $M(OPiv)_2$/CNR catalyst system, $Fe(CNR)_5$ catalyzed the hydrosilylation of styrene and allylic ethers with high selectivity, whereas $Co_2(CNR)_8$ acted as a good catalyst for hydrosilylation of α-methylstyrene, 1-octene, cycloalkenes, and allylic ethers, providing the desired siloxane as a single product. The catalyst efficiency of $Fe(CNR)_5$ was higher than that of the $Fe(OPiv)_2$/CNR catalyst system for hydrosilylation of allylic ethers, whereas $Co_2(CNR)_8$ generally had greater catalytic activity than the $Co(OPiv)_2$/CNR catalyst system. The discovery of catalysts with greater catalytic activity improved the processes of silicone modification and curing, which proceeded at a lower catalyst concentration than processes using the $M(OPiv)_2$/CNR catalyst system.

In platinum-catalyzed hydrosilylation of alkenes, Spier's catalyst, H_2PtCl_6 in ^{i}PrOH, is easy to handle and inexpensive.[2a,c] In contrast, Karstedt's catalyst, $(divinylsiloxane)_3Pt(0)_2$, is costly but possesses greater catalytic performance than Spier's catalyst.[2b] Spier's catalyst requires reduction of H_2PtCl_6 for generation of catalytically active Pt(0) species, while Karstedt's catalyst containing a Pt(0) center easily forms the active species by dissociation of divinylsiloxane. The relationship between the $M(II)(OPiv)_2$/CNR catalyst system and metal isocyanide (0 or I) catalysts was comparable to that of Spier's catalyst with Karstedt's catalyst. Thus, base-metal-catalyzed hydrosilylation of alkenes can be accomplished with the $M(OPiv)_2$/CNR catalyst system and metal isocyanide catalysts depending on the situation. The former conveniently generates the catalytically active species from stable catalyst precursors and reducing reagents, whereas the latter requires preparation of the Fe(0) or Co(I) complexes but possesses good catalytic performance. It is important from the production of silicones that discovery of new catalysts, $Fe(CNR)_5$ and $Co_2(CNR)_8$ made possible efficient modification of silicone fluids and two-component silicone curing. These are key technologies in silicone industry[1−3] and are achieved by using platinum catalysts. Lately, achievement of these processes by base-metal catalysts attracted attention, and several papers regarding two-component silicone curing appeared.[11f,21] The present report provided one of the successful examples.

In addition to these synthetic benefits, the experimental results provided clues for understanding the net catalyst species. In a previous communication, possible mechanisms involving coordinately unsaturated Fe(0) and Co(I) isocyanide species were suggested. The results presented here clearly support this hypothesis that the same catalyst species would be generated from Fe(CNR)$_5$ or from Co$_2$(CNR)$_8$. In particular, no difference was found in the selectivity of the two reaction pathways, hydrosilylation or dehydrogenative silylation, between Fe(CNR)$_5$ and the Fe(OPiv)$_2$/CNR system and between Co$_2$(CNR)$_5$ and the Co(OPiv)$_2$/CNR system. Similar to the hydrosilylation mechanism catalyzed by Co$_2$(CO)$_8$, experiments using (EtO)$_3$SiCo(CNR)$_4$ indicate that a Chalk−Harrod cycle involving insertion of a C═C bond between Co−H bond of HCo(CNR)$_3$(alkene) is reasonable. Although some mechanistic studies could not be accomplished, mechanisms analogous to those for the Fe(CO)$_5$-catalyzed hydrosilylation and dehydrogenative silylation indicate that a Chalk−Harrod pathway from the intermediary (RNC)$_n$Fe(H)(SiR$_3$) was competitive with modified Chalk−Harrod pathway.

■ EXPERIMENTAL SECTION

General. Manipulation of air- and moisture-sensitive compounds was carried out under a dry nitrogen atmosphere using Schlenk tube techniques associated with a high-vacuum line or in the glovebox, which was filled with dry nitrogen. All solvents were distilled over appropriate drying reagents prior to use. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a JEOL Lambda 400 or a Lambda 600 spectrometer at ambient temperature. ^{1}H, ^{13}C, ^{19}F, and ^{29} Si NMR chemical shifts (δ values) were given in ppm relative to the solvent signal (^{1}H and ^{13}C) or standard resonances (^{19}F, external trifluoroacetic acid; ^{29}Si, external tetramethylsilane). Elemental analyses were performed by a PerkinElmer 2400II/CHN analyzer. IR spectra were recorded on a JASCO FT/IR-550 spectrometer. Isocyanides [1-isocyanoadamantane (AdNC), *t*-butylisocyanide (^{t}BuNC)] were purchased from Tokyo Chemical Industries Co., Ltd., or Sigma-Aldrich, and were used without further purification. All of the alkenes described in the text and hydrosilanes, PhMe$_2$SiH, Et$_3$SiH, (EtO)$_3$SiH, (EtO)$_2$MeSiH, (MeO)$_3$SiH, (MeO)$_2$MeSiH, Ph$_2$SiH$_2$, and PhSiH$_3$ were purchased from Tokyo Chemical Industries Co., Ltd. Hydrosiloxanes, 1,1,3,3,3-pentamethyldisiloxane (PMDS), 1,1,1-3-5,5,5-heptamethyltrisiloxane (MD′M), a vinylsiloxane polymer [CH$_2$═CHSiMe$_2$O(SiMe$_2$O)$_n$SiMe$_2$CH═CH$_2$], and hydrosiloxane polymers [Me$_3$SiO(SiMe$_2$O)$_n$Si(H)Me$_2$ and Me$_3$SiO{Si(H)-MeO}$_m$SiMe$_3$] were donated by Shin-Etsu Chemical Co., Ltd. For the preparation of iron and cobalt isocyanides, KC$_8$, was prepared according to the literature,[27] and sodium silica gel was purchased from Ardrich.[28]

General Procedure for Synthesis of Fe(CNR)$_5$. To a solution of FeBr$_2$ (1.0 mmol) in THF (20 mL) were added RNC (5.0 mmol) and KC$_8$ (2.0 mmol) in a globe box. The solution was stirred at room temperature for 12 h, then the resulting mixture was passed through a short pad of Celite. The filtrate was concentrated *in vacuo*. When ^{t}BuNC was used as the isocyanide, the residue obtained was extracted with pentane. Complex **1A** was obtained by recrystallization from pentane. In the cases where R of RNC was Ad or Mes, toluene was used for the extraction, and recrystallization was performed from toluene/pentane. The desired product was obtained as yellow crystals.

*Fe(CN^{t}Bu)$_5$ (**1A**).* Isolated yield: 57%. Mp. 140 °C (decomp). ^{1}H NMR (600 MHz, C$_6$D$_6$) δ: 1.29 (s, 45H). ^{13}C NMR (100 MHz, C$_6$D$_6$) δ: 199.0, 55.6, 31.6. IR(ATR): ν = 2119, 2000, 1943, 1826 (C≡NR) cm^{-1}. Anal. Calcd for C$_{25}$H$_{45}$N$_5$Fe: C 63.68; H 9.62; N 14.85. Found: C 63.21; H 9.56; N 15.11.

*Fe(CNAd)$_5$ (**1B**).* Isolated yield: 70%. Mp. 200 (decomp). ^{1}H NMR (396 MHz, C$_6$D$_6$) δ: 2.15 (s, 30H), 1.88 (s, 15H), 1.50 (d, *J* = 11.5, 15H), 1.42 (d, *J* = 11.5, 15H). ^{13}C NMR (100 MHz, C$_6$D$_6$) δ: 199.9, 56.4, 45.4, 36.3, 30.0. IR(ATR): ν = 2106 (C≡NR) cm^{-1}. Anal. Calcd for C$_{55}$H$_{75}$N$_5$Fe: C 76.63; H 8.77; N 8.12. Found: C 77.10; H 8.85; N 8.34.

*Fe(CNMes)$_5$ (**1C**).* Isolated yield: 23%. Mp. 140 (decomp). ^{1}H NMR (396 MHz, C$_6$D$_6$) δ: 6.60 (s, 10H), 2.48 (s, 30H), 2.05 (s, 15H). ^{13}C NMR (100 MHz, C$_6$D$_6$) δ: 196.5, 134.4, 133.0, 129.9, 128.7, 44.5, 36.1, 21.0, 19.3. IR(ATR): ν = 1971, 1940 (C≡NR) cm^{-1}. Anal. Calcd for C$_{50}$H$_{55}$N$_5$Fe: C 76.81; H 7.09; N 8.96. Found: C 76.45; H 6.95; N 8.62.

General Procedure for Synthesis of Co$_2$(CNR)$_8$. To a solution of CoI$_2$(1.0 mmol) in THF (15 mL) was added RNC (4.0 mmol) and KC$_8$ (270 mg, 2.0 mmol) in a globe box. The solution was stirred at room temperature for 12 h, then the resulting mixture was passed through a short pad of Celite. The filtrate was concentrated under reduced pressure. When ^{t}BuNC was used as the isocyanide, the residue obtained was extracted with pentane. Complex **1A** was obtained by recrystallization from pentane. In the cases where R of RNC was Ad or Mes, toluene was used for the extraction, and recrystallization was performed from toluene/pentane. The desired product was obtained as orange crystals.

*Co$_2$(CN^{t}Bu)$_8$ (**2A**).* Isolated yield: 57%. Orange crystals. Mp. 140 °C (decomp). ^{1}H NMR (600 MHz, C$_6$D$_6$) δ: 1.44 (s, 72H). ^{13}C NMR (100 MHz, C$_6$D$_6$) δ: 54.8, 31.7. IR(ATR): ν = 1666 [C≡NR (bridge)], 2093, 1977, 1942 [C≡NR (terminal)] cm^{-1}. Anal. Calcd for C$_{40}$H$_{72}$N$_8$Co$_2$: C 61.36; H 9.27; N 14.31. Found: C 61.06; H 9.52; N 14.05.

*Co$_2$(CNAd)$_8$ (**2B**).* Isolated yield: 57%. Orange crystals. Mp. 200 °C (decomp). ^{1}H NMR (396 MHz, C$_6$D$_6$) δ: 2.32 (s, 48H), 2.06 (s, 24H), 1.71 (d, *J* = 10.3, 24H), 1.58(d, *J* = 10.3, 24H). ^{13}C NMR (100 MHz, C$_6$D$_6$) δ: 55.6, 45.0, 36.7, 30.2. IR(ATR): ν = 1647 [C≡NR (bridge)], 2101, 2000, 1954 [C≡NR (terminal)] cm^{-1}. Anal. Calcd for C$_{88}$H$_{120}$N$_8$Co$_2$: C 75.08; H 8.59; N 7.96. Found: C 75.16; H 8.62; N 7.46.

*Co$_2$(CNMes)$_8$ (**2C**).* Isolated yield, 66%. Orange crystals. Mp. 180 °C (decomp). ^{1}H NMR (396 MHz, C$_6$D$_6$) δ: 6.60 (s, 12H), 6.58 (s, 4H), 2.46 (s, 36H), 2.42 (s, 12H), 2.05 (s, 18H), 2.03(s, 6H). ^{13}C NMR (100 MHz, C$_6$D$_6$) δ: 132.5, 129.3, 128.4, 125.7 21.0, 19.3. IR(ATR): ν = 1669 [C≡NR (bridge)], 2063, 2026, 1954 [C≡NR (terminal)] cm^{-1}. Anal. Calcd for C$_{80}$H$_{88}$N$_8$Co$_2$: C 75.10; H 6.93; N 8.60. Found: C 75.21; H 6.90; N 8.60.

Preparation of 1A and 2A by Silica-Na. To a solution of FeBr$_2$(216 mg, 1.0 mmol) and THF (20 mL) were added ^{t}BuNC (415 mg, 5.0 mmol) and Na silica gel (Stage I) (340 mg, 35 wt % Na) in a globe box. The solution was stirred at room temperature for 12 h, and the resulting mixture was passed through a short pad of Celite. After removal of the solvent, the residue was dissolved in pentane (ca. 20 mL), then stored at −35 °C to give **1A** as yellow crystals (199 mg, 42%). With a similar procedure, **2A** was obtained from CoI$_2$ (1 mmol) and ^{t}BuNC (4 mmol) as orange crystals (190 mg, 48%).

Procedures for Hydrosilylation of Alkenes Catalyzed by Fe(CNR)$_5$. In general, PMDS was treated with alkene and a catalytic amount of Fe(CNR)$_5$ without solvent at r.t. to 50 °C for 3−24 h. After the reaction, the mixture was passed through a short pad of Al$_2$O$_3$ by eluting with ether to remove iron residues. After concentration, the product was isolated by distillation. Alternatively, anisole as an internal standard was added to the reaction mixture, and the product yields were determined by ^{1}H NMR. For instance, the reaction described in Scheme 3, eq 1 was performed as follows: **1A** (8.6 mg, 0.01 mmol), allyl glycidyl ether (1.14 g, 10.0 mmol), and PMDS (2.54 mL, 13 mmol) were placed in a glass vial. The resulting mixture was stirred at room temperature for 24 h. Product **6a** was isolated in 95% yield (2.45 g) by bulb-to-bulb distillation (8 Pa, 60−70 °C). In the experiment shown in Table 1, entry 2, a mixture of **1B** (8.6 mg, 0.01 mmol), styrene (115 μL, 1.0 mmol), and PMDS (254 μL, 1.3 mmol) was placed in a glass vial. The resulting solution was stirred at 50 °C for 24 h. After the reaction, anisole (108 mg, 1.0 mmol) was added to the mixture, and the product yield was determined to be >99% by comparison in the integral value of the signals due to **6a** and the peaks due to anisole as the internal standard. Detailed experimental procedures for the iron-catalyzed hydrosilylation of styrene, 1-octene, and allylic ethers are described in the Supporting Information. Characterization of the products were performed in comparison their spectral data with those reported in our previous paper.[16,17]

Procedures for Hydrosilylation of Alkenes Catalyzed by $Co_2(CNR)_8$. In general, PMDS or MD′M was treated with alkene and a catalytic amount of $Co_2(CNR)_8$ without solvent at r.t. to 80 °C for 3−24 h. After the reaction, the mixture was passed through a short pad of Al_2O_3 by eluting with ether to remove iron residues. After concentration, the product was isolated by distillation. Alternatively, anisole as an internal standard was added to the reaction mixture, and the product yields were determined by ^{1}H NMR. For instance, in the reaction shown in Table 1, entry 4, **2B** (6.4 mg, 0.0005 mmol), α-methylstyrene (1.29 mL, 10.0 mmol), and PMDS (2.54 mL, 13.0 mmol) were placed in a glass vial. The resulting mixture was stirred at 80 °C for 3 h. After the reaction, the mixture was cooled to room temperature, the product was isolated by distillation (8 Pa, 60−70 °C). Isolated yield; 2.56 g (96%). The experiment shown in Table 1, entry 13 was performed with **2B** (6.4 mg, 0.005 mmol), 1-octene (129 μL, 1.0 mmol), and PMDS (254 μL, 1.3 mmol) at 50 °C for 24 h. After the reaction, anisole (108 mg, 1.0 mmol) was added, and the product yield of >99% was determined by ^{1}H NMR spectroscopy. Detailed experimental procedures for the cobalt-catalyzed hydrosilylation of other alkenes are described in the Supporting Information. Characterization of the products were performed in comparison their spectral data with those reported in our previous paper.[16,17]

Procedure for the Hydrosilylation of Alkenes with the $M(OPiv)_2$/CNR (M = Fe, Co) Catalyst System.[16] The catalyst systems composed of $M(OPiv)_2$ and CNR were preactivated by alkoxyhydrosilanes; the resulting catalyst solution was subjected to the hydrosilylation studies. In a typical example, $Fe(OPiv)_2$ (2.6 mg 0.01 mmol) and CNAd (3.6 mg, 0.02 mmol) were dissolved in DME (0.10 mL). $(EtO)_3SiH$ (11 mg, 0.08 mmol) was added to the solution, and the mixture was stirred at room temperature for 1 h. A mixture of styrene (115 μL, 1.0 mmol) and PMDS (254 μL, 1.3 mmol) was added, and the resulting mixture was stirred at room temperature for 24 h. The yield of the product (>99%) was determined by ^{1}H NMR spectroscopy in the presence of the internal standard (anisole). The reaction of PMDS (254 μL, 1.3 mmol) with α-methylstyrene (129 μL, 1.0 mmol) was performed in similar manner as above by using $Co(OPiv)_2$ (2.6 mg 0.01 mmol) and CNAd (4.8 mg, 0.03 mmol) dissolved in DME (0.10 mL) as the catalyst and $(EtO)_3SiH$ (11 mg, 0.08 mmol) as the activator.

Procedure for the Modification of Silicone Polymer. In general, $Me_2Si(H)O(SiMe_2O)_nSi(H)Me_2$ (n = ca. 18) or $Me_3SiO(SiHMeO)_2(SiMe_2O)_nSiMe_3$ (n = ca. 27) was treated with alkene and a catalytic amount of $Fe(CNR)_5$ or $Co_2(CNR)_8$ without solvent at r.t. to 50 °C for 24 h. After the reaction, the reaction mixture was passed through a short pad of Al_2O_3 by eluting with ether to remove the iron catalysts. The filtrate was dried under vacuum to afford the product was obtained. In a typical example (Scheme 4, eq 1), $Co_2(CNAd)_8$ (6.4 mg, 0.005 mmol), α-methylstyrene (1.68 mL, 13.0 mmol), and $Me_2Si(H)O(SiMe_2O)_nSi(H)Me_2$ (n = ca. 18) (7.26 g, ca. 10.0 mmol for Si−H) were placed in a glass vial. The resulting mixture was stirred at 50 °C for 24 h. After the reaction, the mixture was cooled to room temperature, and the conversion of hydrosilane (>99%) and the yield of the product (>99%) were determined by ^{1}H NMR spectroscopy using anisole as the internal standard. The resulting mixture was passed through a pad of Al_2O_3. The filtrate was dried under vacuum. Product **13a** was obtained in 99% yield (8.40 g) as colorless oil. ^{1}H NMR (395 MHz, $CDCl_3$) δ: −0.06 (s, SiMe), −0.03 (s, SiMe), 0.04 (s, SiMe3), 0.07 (s, $SiMe_2$), 0.92−1.02 (m, 4H, CH_2Si), 1.28 (d, J = 6.8 Hz, 6H, CH_3), 2.92 (sext, J = 6.8 Hz, 2H, CH), 7.13−7.21 (m, 6H, ArH), 7.24−7.27 (m, 4H, ArH). Other results are described in the Supporting Information.

Procedure for Cross-Linking of Silicone Polymers. In general, the reaction of $CH_2{=}CHSiMe_2O(SiMe_2O)_nSiMe_2CH{=}CH_2$ (n = ca. 47; **Si-1**) with $Me_3SiO[Si(H)MeO]_mSiMe_3$ (m = ca. 8; **Si-2**) (0.13 g, ca. 1.62 mmol for Si−H) was performed in the presence of cobalt catalysts without solvent at 120 °C for 3−24 h. Meanwhile, time of gelation was measured. The cross-linked silicone gel was obtained and characterized by solid-state ^{1}H NMR and ^{29}Si DD NMR. For instance, the reaction shown in Table 4, entry 1, was performed by treatment of a mixture of **Si-1** (2.87 g, ca. 1.56 mmol for $Si\text{-}CH{=}CH_2$) and **Si-2** (0.13 g, ca. 1.62 mmol for Si−H) with $Co_2(CNAd)_8$ (6.4 mg, 0.005 mmol). The resulting mixture was stirred at 120 °C under nitrogen atmosphere. The solution set to gel after 3 min. The resulting mixture was kept at 120 °C for 3 h. After cooling, the resulting cross-linked silicone gel (**16**). Exposure to air gave **16** as a slightly green transparent solid, which was characterized by solid-state ^{1}H NMR, ^{29}Si DD NMR, IR spectroscopy. Other examples are described in the Supporting Information. Solid-state ^{1}H NMR (400 MHz) δ: −1.0−2.0 (br, SiR*Me* and SiCH_2CH_2Si), 4.9 (br, unreacted Si*H*Me), 5.8−6.4 (m, unreacted Si(*vinyl*)Me). Solid-state ^{29}Si DD NMR (119 MHz) δ: −38 to −33 (m, unreacted *Si*HMe), −23 to −20 (br, *Si*Me_2), −4.2 (m, unreacted *Si*(vinyl)Me). IR (KBr): ν = 2150 (unreacted Si−H), 1258 (Si−C) cm^{-1}.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00389.

Experimental details including the data briefly noted in the text, crystallographic data, and NMR charts of the products (PDF)

Cartesian coordinates (XYZ)

Accession Codes

CCDC 1840036 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: nagasima@cm.kyushu-u.ac.jp.

ORCID

Hideo Nagashima: 0000-0001-9495-9666

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Notes

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(19) A reviewer raised two questions. One is the fate of the OPiv group after $M(OPiv)_2$ was treated with $HSi(OEt)_3$, and another is the role of $HSi(OEt)_3$ in the $M(OPiv)_2$/CNR catalyst system, which may be more than facilitating the generation of active species. As the answer of the former question, we confirmed two products, $(EtO)_3SiOCO^tBu$ and $(EtO)_4Si$ by GC-MS and ^1H NMR (Supporting Information, page S5). As for the latter question, we performed the reactions of α-methylstyrene with PMDS catalyzed by either **1A** or **2A** (0.1 mol%) in the presence and absence of $HSi(OEt)_3$ (8 equiv to the catalyst). No difference was observed in reactivity and selectivity.

(20) A reviewer pointed out the catalyst efficiency of $Fe(CNR)_5$ is higher for allylic ethers than that of $Fe(OPiv)_2$/CNR system, and the difference of the catalytic activity between these two catalyst systems are particularly great when using allylic ethers. The reason could be ascribed to coordination of oxygen atoms in the allylic ethers to iron. In the case of $Fe(OPiv)_2$, coordination of the oxygen atoms would be disturb the coordination of CNR to the Fe(II) center. Activation of $Fe(OPiv)_2$ with hydrosilanes does not occur in the absence of CNR. In contrast, generation of active species from $Fe(CNR)_5$ needs dissociation of CNR. Coordination of the oxygen atoms in allylic ethers to the $Fe(CNR)_5$ may help the dissociation of CNR.

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(23) It should be noted that photochemical hydrosilylation catalysed by cobalt-isocyanide catalysts may proceed through the modified Chalk−Harrod mechamism. In fact, photoirradiation of **17B** provided a better result than that obtained by the thermal process (see Scheme S1).

(24) Support for the Chalk−Harrod mechanism was provided by the rapid isomerization of the terminal C═C bond of 1-octene to internal positions during hydrosilylation catalyzed by both $Co_2\ (CO)_8$ and the $Co(OPiv)_2$/CNR catalyst system. Alkene isomerization catalyzed by the $Co(OPiv)_2$/CNR catalyst system occurred through a mechanism shown in Scheme 6c involving addition and elimination of cobalt-hydride species. Although the same catalytically active species was generated from the $Co(OPiv)_2$/CNR catalyst system and $Co_2(CNR)_8$, no internal alkenes were observed in the latter catalysis. We consider that alkene isomerization occurred in the $Co_2(CNR)_8$-catalyzed hydrosilylation of 1-octene, but the resulting internal alkenes underwent rapid hydrosilylation to form 1-silyloctane.

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