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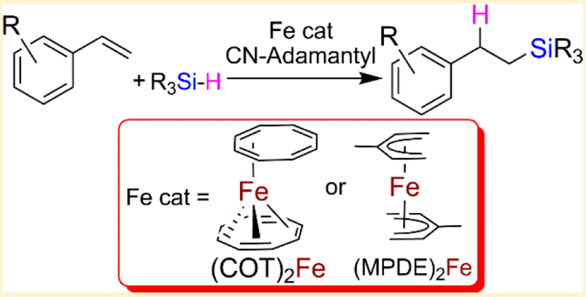
Combinatorial Approach to the Catalytic Hydrosilylation of Styrene Derivatives: Catalyst Systems Composed of Organoiron(0) or (II) Precursors and Isocyanides

Yusuke Sunada, Daisuke Noda, Hiroe Soejima, Hironori Tsutsumi, and Hideo Nagashima*

Institute for Materials Chemistry and Engineering and Graduate School of Engineering Sciences, Kyushu University, and CREST, Japan Science and Technology Agency (JST), Kasuga, Fukuoka 816-8580, Japan

Supporting Information

ABSTRACT: $(COT)_2Fe$ and the open ferrocenes $(MPDE)_2Fe$ (MPDE = η^5-3-methylpentadienyl) and $(DMPDE)_2Fe$ (DMPDE = η^5-2,4-dimethylpentadienyl) were found to function as catalyst precursors for the hydrosilylation of alkenes in the presence of auxiliary ligands. Screening trials determined that the optimal catalyst system was composed of $(COT)_2Fe$ and adamantyl isocyanide, allowing the selective hydrosilylation of styrene derivatives with trisubstituted hydrosiloxanes and a polydimethylsiloxane bearing Me_2SiH moieties as the end groups. Under the appropriate conditions, the dehydrogenative silylation side reaction was completely suppressed, and the reaction TON exceeded 5000.



INTRODUCTION

The transition metal-promoted homogeneous catalytic hydrosilylation of alkenes is one of the most useful reactions for producing organosilicon compounds.[1] In general, salts and complexes of second and third row transition metals, including Pt, Pd, Rh Ir, and Ru, have been applied as effective catalysts for this reaction,[1] and Pt catalysts are especially useful for synthesizing a variety of organosilicon compounds and silicones on both laboratory and industrial scales.[1c] However, there are increasing demands for the development of more environmentally benign as well as more cost-effective synthetic processes, in which precious metal catalysts are replaced by less toxic and more abundant metals.[2] In this context, Fe-based hydrosilylation catalysts and catalyst systems have recently received considerable attention.[3]

Several iron complexes have been reported to be active for the hydrosilylation of alkenes.[3−7] The well-defined Fe(0)-dinitrogen complexes bearing bis(imino)pyridine ligands reported by Chirik and co-workers are an example of successful hydrosilylation catalysts exhibiting high catalytic activity and good selectivity to generate anti-Markovnikov adducts from 1-alkenes.[4] In earlier work with hydrosilanes intended for hydrosilylation, the available compounds were limited to Ph_2SiH_2 and $PhSiH_3$;[4a] however, the appropriate choice of substituents on the bis(imino)pyridine ligands led to the successful hydrosilylation of alkenes with trisubstituted hydrosilanes and hydrosiloxanes.[4b] A drawback of these bis(imino)pyridine Fe(0) complexes is their significant instability in contact with air and moisture. To mitigate this, Fe(II) complexes bearing bis(imino)pyridine, terpyridine, or related tridentate ligands have been reported that generate various active species including Fe hydrides or alkyliron compounds when treated with strong organometallic activators.[8,9] Fe carbonyls, such as $Fe(CO)_5$ and $Fe_3(CO)_{12}$, are conventional Fe-based catalysts and may possibly function in the hydrosilylation reaction of $RCH{=}CH_2$ and $H\text{-}SiR'_3$ to give the desired product $RCH_2CH_2SiR'_3$.[3,6a−c] Fe carbonyls are generally stable and easy to handle but have the unfortunate tendency to promote the simultaneous dehydrogenative silylation reaction, giving a 1:1 mixture of $RCH{=}CHSiR'_3$ and RCH_2CH_3. In response to this shortcoming, our group has previously developed an Fe(II) carbonyl compound having a disilaferracyclic structure, $[1,2\text{-}(SiMe_2)_2C_6H_4]Fe(CO)_2[1,2\text{-}\{\eta^2\text{-}(H\text{-}SiMe_2)_2\}C_6H_4]$. This compound represents a unique Fe catalyst that is moderately stable in response to air and moisture, and selectively affords the hydrosilylation product without contamination with byproducts derived from dehydrogenative silylation.[7a]

In these previous studies, the Fe complexes were isolated and subsequently applied to the catalytic reactions. In our continuous efforts to develop new Fe catalysts for the hydrosilylation of alkenes, we were interested in developing a convenient means of synthesizing catalytically active species from isolable Fe precursors and auxiliary ligands. If the appropriate Fe precursors can be determined, screening of the ligand should be readily performed, making it possible to apply a combinatorial-type approach to the search for new catalyst systems. The catalysts reported in the literature suggest that Fe(0) complexes capable of reacting with the desired ligands to form catalytically active species represent one possible series of candidates for the catalyst precursor. An

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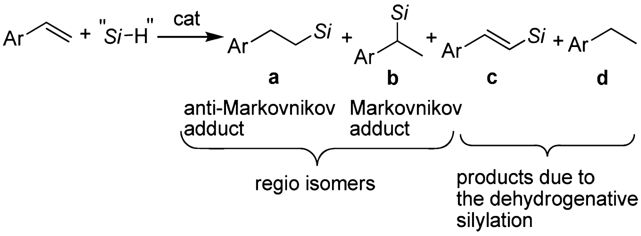
organoiron(II) precursor containing an Fe−H or Fe−C moiety that generates an active species when in contact with the ligand is another possibility. In this article, we report an Fe(0) complex, $(COT)_2Fe$ (COT = 1,3,5,7-cyclotetraene),[10] and Fe(II) complexes consisting of two open ferrocenes, $(MPDE)_2Fe$ (MPDE = η^5-3-methylpentadienyl) and $(DMPDE)_2Fe$ (DMPDE = η^5-2,4-dimethylpentadienyl),[11] as effective catalyst precursors that allow ligand screening. As noted above, the catalytic hydrosilylation of alkenes is sometimes accompanied by products representing Markovnikov addition and dehydrogenative silylation. We selected styrene derivatives as the alkene substrates for use in catalyst screening because it is well-known that the hydrosilylation of styrene tends to give a mixture of regioisomers (**a** and **b**)[12] in addition to products resulting from dehydrogenative silylation (**c** and **d**)[6] (Scheme 1). It is also known that dehydrogenative silylation is a serious side reaction in the Fe-catalyzed hydrosilylation of styrene and that this reaction occurs to the exclusion of other reactions in extreme cases.[6a] In the screening aimed at the selective formation of **a**, we found that isocyanides worked as effective ligands for the catalyst systems when combined with the Fe precursors, thus producing a catalytic system that has never before been applied to the Fe-catalyzed hydrosilylation of alkenes.

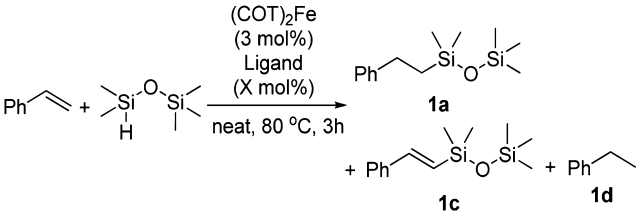
Scheme 1. General Scheme for Hydrosilylation of Styrene to Form a−d



■ RESULTS AND DISCUSSION

Search for Ligands Using $(COT)_2Fe$ as the Fe Catalyst Precursor. As a catalyst precursor, $(COT)_2Fe$, in which cyclooctatetraene ligands bound to the Fe center in an η^4- or η^6-fashion, was chosen since the COT ligands are known to participate in substitution reactions.[13,14] As noted, Fe(0) dinitrogen complexes supported by Me_2PDI (Me_2PDI = 2,6-$(2,6\text{-}Me_2\text{-}C_6H_3N{=}CMe)_2C_5H_3N$) or Et_2PDI (Et_2PDI = 2,6-$(2,6\text{-}Et_2\text{-}C_6H_3N{=}CMe)_2C_5H_3N$) exhibited excellent catalytic activity during the hydrosilylation of alkenes.[4b] We therefore examined the potential generation of catalytically active species from a mixture of $(COT)_2Fe$ and Me_2PDI during the reaction of styrene with $HMe_2SiOSiMe_3$ (PMDS). In a typical experiment, a 1:1 mixture of $(COT)_2Fe$ and Me_2PDI was treated with styrene (1 mmol) and PMDS (1.3 mmol) at 80 °C for 3 h. The reaction of styrene with PMDS in the presence of $(COT)_2Fe$ and Me_2PDI was successful, affording the corresponding hydrosilylated compound **1a** as the single product in 75% yield (Table 1, entry 2). Other possible byproducts, such as **1b**, **1c**, and **1d**, were not evident in the ^1H NMR spectrum of the crude product. It was also determined that, in the absence of Me_2PDI, no reaction took place (entry 1).

Table 1. Hydrosilylation of Styrene with PMDS Catalyzed by $(COT)_2Fe$ in the Presence of the Ligands

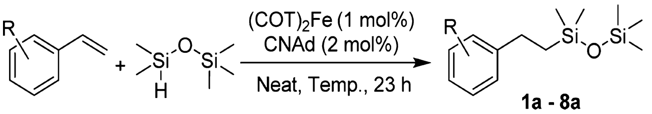


entry	ligand	ligand loading (mol %)	conv. (%)[a]	yield (%)[a] 1a	1c	1d
1	none		0	0	0	0
2	Me_2PDI	3	75	75	0	0
3	2,2′:6′,6″-terpyridine	3	0	0	0	0
4	IPr[b]	6	0	0	0	0
5	NEt_3	6	0	0	0	0
6	TMEDA[c]	3	0	0	0	0
7	PMDETA[d]	3	0	0	0	0
8	PPh_3	6	0	0	0	0
9	P^tBu_3	6	0	0	0	0
10	$P(OCH_2)_3CEt$	6	0	0	0	0
11	Me_2S	6	0	0	0	0
12	$MeSCH_2CH_2CH_2SMe$	3	0	0	0	0
13	CNAd	6	>99	74	12	14
14	CNAd	3	72	56	9	7
15	CNAd	9	90	66	12	12
16	CN^tBu	6	>99	73	19	17
17	CNCy	6	>99	75	11	14
18	CNMes	6	>99	0	49	51

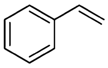
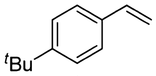
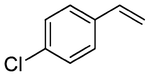
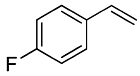
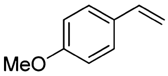
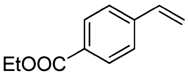
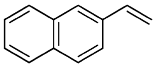
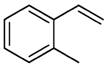
[a] Determined by ^1H NMR. [b] IPr = 1,3-Bis(2,6-diisopropylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene. [c] TMEDA = *N*,*N*,*N*′,*N*′-tertramethylethylenediamine. [d] PMDETA = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine.

Additional results indicated that catalytically active species could be formed from a mixture of $(COT)_2Fe$ and ligands other than Me_2PDI. As shown in entries 3−12 of Table 1, mono-, di-, and tridentate nitrogen, phosphorus, and sulfur ligands were examined, along with an NHC ligand, and none were found to generate a hydrosilylation catalyst under the present conditions. However, we did determine that isocyanides (RNC) were effective for the reaction in combination with $(COT)_2Fe$. Isocyanides are isoelectronic with CO but have advantages over CO in that their electronic and structural environments can be finely tuned by changing the substituent (R) on the nitrogen atom. Entries 13−18 showed the results using adamantyl, *t*-butyl, cyclohexyl, and mesityl isocyanides. In all cases, styrene was completely consumed within 3 h. As shown in entry 13, the combination of $(COT)_2Fe$ (3 mol %) and CNAd (6 mol %) generated the hydrosilylated product **1a** in 74% yield. The optimal ratio of $(COT)_2Fe$ to CNAd in terms of obtaining the highest conversion of styrene was 1:2 (entries 14 and 15). It should be noted, however, that, although the regio-isomer **1b** was not formed, the simultaneous formation of **1c** (12%) and **1d** (14%) was not suppressed under these reaction conditions (entry 13). Two other alkylisocyanides, *tert*-butyl isocyanide and cyclohexyl isocyanide, were effective (entries 16 and 17), but gave the same byproducts as in entry 13. When mesityl isocyanide was used as a means of assessing the utility of an arylisocyanide ligand, only a 1:1 mixture of **1c** and **1d** was formed (entry 18).

Table 2. Hydrosilylation of Styrene Derivatives with PMDS Catalyzed by $(COT)_2Fe$ with CNAd



1a - 8a

Entry	Substrate	Product	$(COT)_2Fe$ loading (mol%)	CNAd loading (mol%)	Temp. (°C)	Conv.[a] (%)	Selectivity[a] (%)	Isolated yield[b] (%)
1			1	2	50	>99	>99	94
2		**1a**	1	2	25	>99	>99	95
3			0.02	0.04	50	>99	96	89
4		**2a**	1	2	50	>99	>99	93
5		**3a**	1	2	50	>99	>99	97
6		**4a**	1	2	50	>99	>99	95
7		**5a**	1	2	40	>99	97[c]	96[c]
8		**6a**	1	2	50	>99	>99	99
9		**7a**	3	6	50	>99	>99	98
10		**8a**	3	6	50	>99	88[d]	84[d]

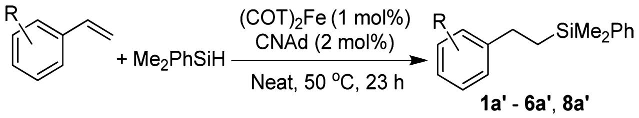
[a] The conversion and product selectivity were determined by ^1H NMR of the crude products. [b] The products **1a**−**8a** were isolated by distillation. [c] ^1H NMR revealed that the crude product contained **5a** and two byproducts, 1,1,1,3,3-pentamethyl-3-[(1*E*)-2-(*p*-methoxy)-phenylethenyl]-disiloxane (**5c**) and 1-ethyl-4-methoxybenzene (**5d**) in a ratio of 98:1:1. The product **5a** was isolated as a single product by distillation (6 Pa, 70−75 °C). [d] ^1H NMR revealed that crude product contained **8a** and two byproducts, 1,1,1,3,3-pentamethyl-3-[(1*E*)-2-(*o*-methyl)-phenylethenyl]-disiloxane (**8c**) and 1-ethyl-2-methylbenzene (**8d**), in a ratio of 92:4:4. The product **8a** was isolated as a single product by distillation (3 Pa, 120−125 °C).

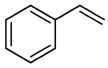
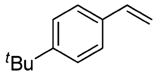
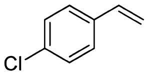
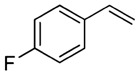
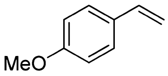
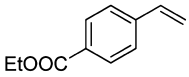
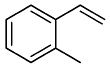
We carried out further studies by using CNAd as a representative of the three alkyl isocyanides described above. Performing the reaction at temperatures below 80 °C represented a breakthrough in terms of increasing the selectivity for **1a**, such that the selective synthesis of **1a** was achieved either at 50 °C or at room temperature. Under these conditions, **1a** was isolated in 94 or 95% yield after 23 h of reaction time via distillation (Table 2, entries 1 and 2), with no evidence for the formation of either vinylsilane or ethylbenzene. The high catalytic efficiency of this system was demonstrated by the reaction of styrene with PMDS at lower catalyst loadings; a reaction using only 0.02 mol % $(COT)_2Fe$ and 0.04 mol % CNAd was found to provide **1a** in high yields (TON = 5000) (entry 3). It should be noted that no reaction took place when CN^tBu or CNCy was used as the ligand under the same conditions. In this context, CNAd is the best ligand among the isocyanides we examined. In addition, the reaction of a series of substituted styrenes by the $Fe(COT)_2$/CNAd catalyst system showed that the present catalyst system is able to function in the presence of several functional groups, including ^tBu, F, Cl, and CO_2Et. Styrenes bearing these substituents at the *para* position underwent the reaction smoothly under the same reaction conditions as those used for the hydrosilylation of styrene, and the corresponding hydrosilylated products **2a**, **3a**, **4a**, and **6a** were obtained in high yields (entries 4−6, 8). Although the selectivity was slightly decreased (97%), the hydrosilylation of *p*-methoxystyrene proceeded at a lower temperature (40 °C) to afford **5a** in 96% yield (entry 7). The hydrosilylation reactions of 2-vinylnaphthalene and sterically hindered *o*-methylstyrene required slightly higher catalyst loadings (3 mol %) but still gave the corresponding products **7a** and **8a**, respectively, in high yields (entries 9 and 10). In the case of *o*-methylstyrene, some amounts of the byproducts **8c** and **8d** were also formed.

The screening of several hydrosilanes under the conditions indicated that the hydrosilylation of styrene with trialkylsilanes such as PMDS, Me_2PhSiH, and $EtMe_2SiH$ resulted in the formation of the corresponding hydrosilylated products with good selectivity (details are given in the Supporting Information). Concomitant dehydrogenative silylation remains a significant side reaction in the reaction with sterically hindered hydrosilanes such as Et_3SiH and 1,1,1,3,5,5,5-heptamethyltrisiloxane (MD'M) to give a mixture of the homologues of **1a** and **1b**, as well as ethylbenzene (**1d**) as shown in Table S-1 in Supporting Information.

Table 3 summarizes the reactions of styrene derivatives with dimethylphenylsilane, all of which afford the corresponding products in high yields with high selectivity under the same

Table 3. Hydrosilylation of Styrene with Dimethylphenylsilane Catalyzed by $(COT)_2Fe$ with CNAd



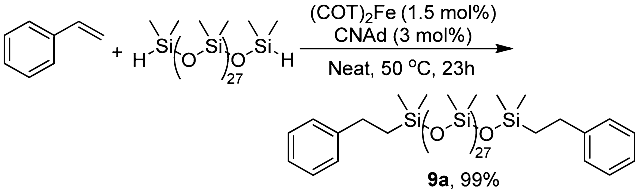
Entry	substrate	product	Conv.[a] (%)	Selectivity[a] (%)	Isolated yield[b] (%)
1		1a’	>99	>99	85
2		2a’	>99	>99	95
3		3a’	>99	97[c]	91[c]
4		4a’	>99	>99	98
5		5a’	>99	>99	82
6		6a’	>99	>99	99
7		8a’	>99	>99	96

[a] The conversion and product selectivity were determined by ^1H NMR of the crude products. [b] The products 1a′–8a′ were isolated by distillation. [c] ^1H NMR revealed that crude product contained 3a′ and two byproducts, 1-chloro-4-(dimethylphenylsilyl)-benzene (3c′), and 1-chloro-4-ethylbenzene (3d) in a ratio of 98:1:1. The product 3a′ was isolated as a single product by distillation (14 Pa, 80–85 °C).

reaction conditions previously applied when using PMDS (Table 2).

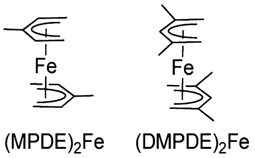
As briefly noted in the introduction, the hydrosilylation of polysiloxanes bearing Si–H groups with alkenes is an important reaction with regard to industrial applications.[1] It is thus worth noting that the reaction of styrene with polydimethylsiloxane having Si–H end groups also proceeded at 50 °C to give the corresponding polydimethylsiloxane bearing *β*-phenethyl groups at the polymer ends, in quantitative yield (Scheme 2).

Scheme 2. Hydrosilylation of Styrene with Polymeric Hydrosiloxane



Open Ferrocenes as Fe(II) Catalyst Precursors in the Presence of CNAd. As discussed, it is known that the Fe(II)-alkyl complex $[bis(imino)pyridine]Fe(CH_2SiMe_3)_2$ is able to act as an alternative catalyst in place of the Fe(0) catalyst $[bis(imino)pyridine]Fe(N_2)_2$ for the hydrosilylation of alkenes.[4d] This prompted us to examine several homoleptic organoiron complexes during the present study.[15] Although ferrocenes represent potential candidates for Fe(II) catalyst precursors, they were found to be too stable to react with isocyanides. We thus considered that the open ferrocenes (Chart 1) previously reported by Ernst and co-workers[11] could be more reactive than ferrocenes and possibly generate catalytically active species in contact with CNAd.

Chart 1. Structures of Two Open Ferrocenes, $(MPDE)_2Fe$ and $(DMPDE)_2Fe$

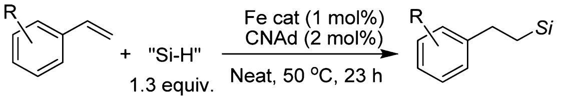


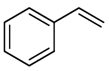
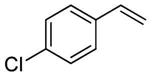
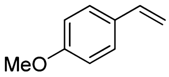
In fact, $(MPDE)_2Fe$ (MPDE = η^5-3-methylpentadienyl)[11a] showed catalytic activity comparable to that of $(COT)_2Fe$ for the reaction of styrene with PMDS and $PhMe_2SiH$ to give **1a** as the sole product in good yields (entries 1 and 3, Table 4). Another open ferrocene, $(DMPDE)_2Fe$ (DMPDE = η^5-2,4-dimethylpentadienyl),[11] also exhibited catalytic activity, although somewhat lower than that of $(MPDE)_2Fe$. $(COT)_2Fe$ is moderately thermally stable but sensitive to air and so must be handled in a glovebox. In contrast, the open ferrocenes are sufficiently stable in air such that they can be weighed out under ambient atmosphere in a short time without decomposing. Selected substituted styrenes were applied to the hydrosilylation reaction with either PMDS or $PhMe_2SiH$, and both *p*-chlorostyrene and *p*-methoxystyrene were found to convert to the corresponding hydrosilylated products in high yields and selectivities (entries 4–7).

Mechanistic Considerations. $(COT)_2Fe$ and open ferrocenes are useful as catalyst precursors and generate active species in contact with CNR because of facile changes in the hapticity of the conjugated *π*-ligands. The carbon–carbon double bonds in these hydrocarbon ligands assist in stabilizing the catalyst precursors to keep them in a coordinatively saturated state. Under the reaction conditions employed in the present study, these ligands dissociated from the Fe center and generated open coordination sites for isocyanides, hydrosilanes, and styrene.

When employing $(COT)_2Fe$ as the catalyst precursor, it is apparent that both of the COT ligands are eliminated during the catalytic reactions. In fact, when the crude product obtained by the hydrosilylation of styrene with PMDS mediated by a combination of $(COT)_2Fe$ and CNAd was assessed by ^1H NMR, the spectrum indicated the formation of 2 equiv (based on Fe) of 1,3,5,7-cyclooctatetraene. It should be mentioned that hydrosilylation of 1,3,5,7-cyclooctatetraene did not take place in the course of this reaction. To gain further insight into the reaction mechanism, stoichiometric reactions of $(COT)_2Fe$ with 1 or 3 equiv of CNAd in toluene were performed at room temperature for 1 h, from which two types of Fe(0)-isocyanide complexes, $(\eta^4\text{-COT})_2Fe(CNAd)$ (**10**) and $(\eta^4\text{-COT})Fe(CNAd)_3$ (**11**), were isolated in 62 and 63% yields, respectively. The reaction of $(COT)_2Fe$ with 2 equiv of CNAd gave a 1:1 mixture of **10** and **11**. ^1H NMR spectrum of **10** and **11** at room temperature exhibited only one singlet attributed to the COT ligands at 4.52 and 5.46 ppm, respectively. No spectral changes were observed from room temperature to −90 °C. This indicates the COT ligand to be fluxional. The IR spectra of **10**

Table 4. Hydrosilylation of Styrene Derivatives with PMDS or Dimethylphenylsilane Catalyzed by $(MPDE)_2Fe$ or$(DMPDE)_2Fe$ with CNAd



Entry	Substrate	Product	"Fe cat"	"Si-H"	Conv.[a] (%)	Selectivity[a] (%)	Isolated yield[b] (%)
1		**1a**	$(MPDE)_2Fe$	PMDS	>99	>99	81
2		**1a**	$(DMPDE)_2Fe$	PMDS	13	>99	-
3		**1a'**	$(MPDE)_2Fe$	$PhMe_2SiH$	>99	>99	95
4		**3a**	$(MPDE)_2Fe$	PMDS	>99	>99	74
5		**3a'**	$(MPDE)_2Fe$	$PhMe_2SiH$	>99	>99	95
6		**5a**	$(MPDE)_2Fe$	PMDS	>99	97[c]	81[c]
7		**5a'**	$(MPDE)_2Fe$	$PhMe_2SiH$	>99	>99	99

[a] The conversion and product selectivity were determined by ^1H NMR of the crude products. [b] The products were isolated by distillation. [c] ^1H NMR revealed that crude product contained **5a** and two byproducts, 1,1,1,3,3-pentamethyl-3-[(1*E*)-2-(*p*-methoxy)-phenylethenyl]-disiloxane (**5c**) and 1-ethyl-4-methoxybenzene (**5d**), in a ratio of 98:1:1. Product **5a** was isolated as a single product by distillation (6 Pa, 70–75 °C).

and **11** exhibited characteristic C≡N stretching bands at 2119 cm^{-1} for **10** and 2104, 2041, and 1937 cm^{-1} for **11**. The spectral features of **11** are consistent with those reported for an analogous complex bearing the CN^tBu ligand, $(\eta^4\text{-COT})Fe(CN^tBu)_3$.[17]

The molecular structures of **10** and **11** were determined by X-ray diffraction and are depicted in Figure 1. The associated bond distances and angles are summarized in the Supporting Information. Complex **10** evidently consisted of two η^4-coordinated COT ligands and one CNAd ligand, and its overall molecular geometry can be regarded as a bent-sandwich structure together with a CNAd ligand. The bond distances between Fe and the η^4-coordinated carbon atoms ranged from 2.031(6) to 2.195(6) Å, while the CN bond distance was 1.166(7) Å. The C=C bond distances bound to the iron center in an η^4-fashion are in the range of 1.381(9)−1.415(9) Å, which are considerably longer compared with those of noncoordinated C=C (1.312(9)−1.363(9) Å). The Fe center of **11** adopted a three-legged piano stool coordination geometry with one η^4-coordinated COT ligand as the seat and three CNAd ligand as the legs. The bond distances between Fe and the η^4-coordinated C atoms as well as the C≡N distance in **11** were comparable to those reported for $(\eta^4\text{-}C_6H_8)Fe(CO)_2(CNEt)$ and $(\eta^4\text{-}C_7H_8)Fe(CO)_2(CNMe)$ (Fe−C = 2.041(3) to 2.202(3) Å, C≡N = 1.168(3) to 1.192(3) Å).[18] The C−C bond distances of η^4-coordinated C=C moieties (C(1)−C(2) = 1.431(4) and C(3)−C(4) =1.432(4) Å) are significantly lengthened relative to those of the noncoordinated C=C moieties (C(5)−C(6) = 1.355(4) and C(7)−C(8) = 1.352(4) Å). Although the variable temperature ^1H NMR studies of **10** indicated rapid exchange of the coordination sites of the iron species on the COT ligand in the solution state, X-ray diffraction analysis revealed that the four carbon atoms (C(1)−C(4) and C(9)−C(12)) of the COT ligand in **10** coordinated to the iron center in an η^4-fashion in the solid state. The other four carbon atoms, C(5)−C(8) and C(13)−C(16), did not coordinate to the iron center. Similarly, COT ligand in **11** coordinated to the iron center in an η^4-manner with four carbon atoms (C(1)−C(4)) in the solid state.

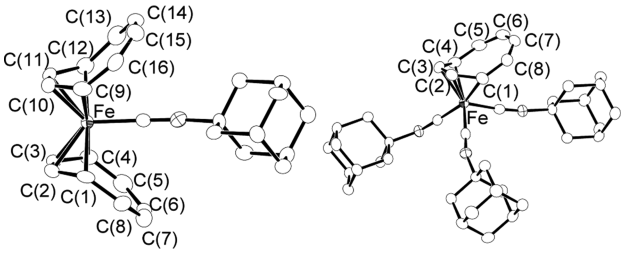
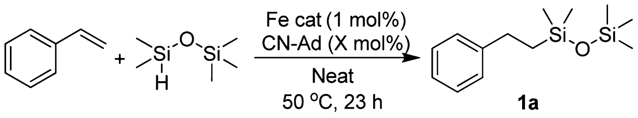


Figure 1. Molecular structures of complexes **10** and **11**. With 50% probability ellipsoids. Hydrogen atoms were omitted for clarity.

Table 5. Hydrosilylation of Styrene with PMDS Catalyzed by $(COT)_2Fe$, 10, and 11



entry	Fe catalyst	CNAd loading (mol %)	CNAd/Fe ratio	conv.[a] (%)	selectivity[a] (%)	isolated yield[b] (%)
1	$(COT)_2Fe$	2	2	>99	>99	98
2	$(\eta^4\text{-COT})_2Fe(CNAd)$ (**10**)	0	1	67	>99	63
3	$(\eta^4\text{-COT})_2Fe(CNAd)$ (**10**)	1	2	>99	>99	97
4	$(\eta^4\text{-COT})Fe(CNAd)_3$ (**11**)	0	3	82	>99	80

[a] The conversion and product selectivity were determined by ^1H NMR of the crude products. [b] Product **1a** was isolated by distillation.

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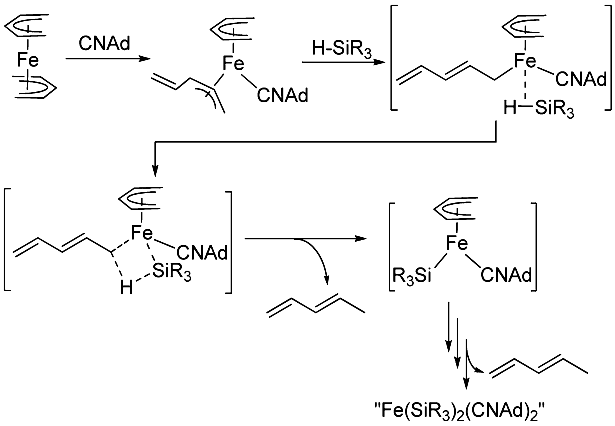
As stated, a $(COT)_2Fe$ to CNAd ratio of 1:2 was found to be optimal for the effective hydrosilylation of styrene with PMDS (Table 5, entry 1) under conditions consisting of 1 mol % of the Fe complex at 50 °C for 23 h. Reactions employing **10** (Fe/CNAd = 1:1) or **11** (Fe/CNAd = 1:3) as the catalyst under the same conditions demonstrated that both **10** and **11** exhibited somewhat lower catalytic performance, generating yields of **1a** below 85% under the same reaction conditions (entries 2 and 4). Importantly, this catalytic activity was comparable to that reported in entry 1, the case for which 1 equiv of CNAd was added to **10** (entry 3). These results indicate that two molecules of CNAd were bound to the catalytically active Fe species. In other words, "(η^4-COT)Fe$(CNAd)_2$L (L = alkene, η^2-(H-SiR_3), or a vacant coordination site)" may be a primary intermediate in this reaction, followed by the generation of coordinatively unsaturated iron species "Fe$(CNAd)_2$" via the dissociation of the η^4-COT moiety to create the coordination sites for both alkene and the "H−Si" bond of hydrosilane. Oxidative addition of the Si−H bond to an iron center gives the "H−Fe−Si" species followed by insertion of C═C, then reductive elimination took place to afford the hydrosilylated product. This is consistent with our previous observation that the "Fe$(CO)_2$" species was responsible for the efficient catalytic hydrosilylation of amides and alkenes.[7a,19]

Studies aimed at generating active species from (η^5-DMDPE)$_2$Fe provided the following results. First, the reaction of styrene with PMDS was performed in the presence of $(DMDPE)_2Fe$ (10 mol %) and CNAd (20 mol %). The crude product was passed through a pad of alumina, from which the formation of 2,4-dimethyl-1,3-pentadiene was confirmed based on assessments by ^1H NMR and gas chromatography−mass spectrometry (GC-MS). This indicates that the DMDPE ligands were converted to 2,4-dimethyl-1,3-pentadiene. It should be mentioned that hydrosilylation of 2,4-dimethyl-1,3-pentadiene did not take place in the course of this reaction, suggesting that hydrosilylation of styrene preferentially proceeded over that of 2,4-dimethyl-1,3-pentadiene. Unfortunately, attempts to identify the iron species by monitoring the reaction of styrene with PMDS in the presence of $(COT)_2Fe$ (10 mol %) and CNAd (20 mol %) by ^1H NMR spectroscopy were hampered due to the formation of paramagnetic species. Second, the coordination mode of one of the DMDPE ligands transitioned from η^5 to η^3 when CNAd was added to a solution of (η^5-DMDPE)$_2$Fe. ^1H NMR data suggested that the resulting Fe species was (η^5-DMDPE)(η^3-DMDPE)Fe(CNAd) since four signals due to the H_2C═CMe- group of the η^5-DMDPE moiety were detected with a 1:1:1:1 integral ratio at 0.12, 0.17, 2.66, and 4.38 ppm, demonstrating their nonequivalency. Three protons derived from the η^3-coordinated moiety appeared at 1.73, 1.87, and 2.90 ppm, respectively, while two signals were observed at 4.32 and 4.34 ppm, attributed to the terminal MeC═CH_2 group. These data indicated a change in the hapticity of the two η^5-DMPE ligands, generating open coordination sites for the two CNAd ligands, the hydrosilane and the styrene. Coordination of the hydrosilane was followed by reaction of the Si−H bond with the Fe−C bond to produce 2,4-dimethyl-1,3-pentadiene. We have previously reported the reaction of 1,2-bis(dimethylsilyl)benzene with [Fe(mesityl)$_2$]$_2$, in which the Si−H bond reacts with the Fe−C(mesityl) moiety to form Fe−Si and C−H bonds.[20] In an analogous manner, compounds with the general formula "$(R_3Si)_2Fe(CNR)_2$" are expected to be formed during the present catalytic reaction (Scheme 3). Only very broad peaks were observed by monitoring the ^1H NMR spectrum of the reaction of styrene with PMDS in the presence of $(COT)_2Fe$ (10 mol %) and CNAd (20 mol %), thus intermediary iron species were not characterized by spectroscopy. This mechanism is similar to that which generates active species in the reactions of [bis(imino)pyridine]Fe-dialkyl catalysts, compounds that exhibit catalytic activity for the hydrosilylation of alkenes similar to those of Fe(0) bis(imino)pyridine compounds. It has been reported that the reaction of these compounds likely generates active species by homolysis of Fe−C bonds, although a detailed mechanism has not been determined.[4d] Further investigations including the theoretical calculations are required to elucidate the reaction mechanism and the possible active iron species generated during hydrosilylation.

Scheme 3. Proposed Reaction Mechanism for the Generation of Catalytically Active Species from the Reaction of (η^5-Pentadienyl)$_2$Fe with CNAd and Hydrosilane



Hydrosilylation of Aliphatic Alkenes. Although iron catalysts other than Chirik's bis(imino)pyridine complexes usually results in dehydrogenative silylation of styrene as a major reaction pathway,[6a−c] the $(COT)_2Fe$/CNAd catalyst system demonstrated high activity and selectivity for the hydrosilylation of styrene derivatives with trisubstituted hydrosilanes. The next challenge should be applications of this catalyst system to hydrosilylation of aliphatic alkenes. Use of the Fe$(COT)_2$ (3 mol %)/CNAd (6 mol %) catalyst system for the reaction of 1-octene with PMDS gave rise to the complete consumption of 1-octene within 3 h at 80 °C. However, the products were a mixture of desired 1,1,3,3,3-petamethyl-1-octyldisiloxane and three byproducts, a vinylsilane, an allylic silane, and *n*-octane in a ratio of 13:9:38:40. Similarly, dehydrogenative hydrosilylation predominantly proceeded in the reaction of methyl 10-undecenoate with PMDS (see Supporting Information).[21] The selectivity was not improved by lowering the reaction temperature to 40 °C. 1,1-Disubstituted alkenes like (±)-limonene and cyclic alkenes such as cyclopentene and cyclohexene did not undergo the reaction. In contrast, aliphatic alkenes such as 1-octene and cyclopentene were successfully hydrosilylated by the iron carbonyl complex [1,2-$(SiMe_2)_2C_6H_4$]Fe$(CO)_2$[1,2-{η^2-(H-$SiMe_2$)$_2$}C_6H_4] in good yields with high selectivity as reported in our previous paper.[7a] Since isocyanides are isoelectronic to CO, we consider that further search for new isocyanide ligands, which have electronic properties similar to those of CO, could solve the problem.

■ CONCLUSIONS

The above results clearly demonstrate that both $(COT)_2Fe$ and various open ferrocenes function as useful Fe(0) and Fe(II) precursors for combinatorial-type surveys of appropriate ligands for the Fe-catalyzed hydrosilylation of styrene derivatives. Experimental trials using a series of auxiliary ligands confirmed that the bis(imino)pyridine ligand Me_2PDI[21] was suitable for use with Fe(0) and Fe(II) species during catalytic hydrosilylation and that isocyanides are also effective ligands. To the best of our knowledge, isocyanides have rarely been used as ligands for Fe-catalyzed reactions,[2] and the present report is the first example of Fe-isocyanide species catalyzing the hydrosilylation of alkenes. Alkylisocyanides such as CNAd are also effective ligands in combination with $(COT)_2Fe$ or $(MPDE)_2Fe$ for the hydrosilylation of styrene derivatives with PMDS or $PhMe_2SiH$ with high selectivity between ambient temperature and 50 °C to give the desired hydrosilylated products without dehydrogenative silylation byproducts and produced only the anti-Markovnikov adducts. Under the optimized conditions, the TON value typically exceeded 100 and, in the most successful example, reached 5000. These findings solve the general problem of the hydrosilylation of styrene derivatives, which is often accompanied by the formation of byproducts and, in some cases, the polymerization of styrene. The Fe(0) and Fe(II) precursors presented in this article should allow further screening of ligands to solve the problems remaining unsolved, e.g., selective hydrosilylation of aliphatic or cyclic alkenes, and active studies including a survey of appropriate isocyanide ligands having appropriate electronic and/or steric properties for highly efficient selective hydrosilylations are under way.

■ 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. ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded on a JEOL Lambda 400 or a Lambda 600 spectrometer at ambient temperature. ^1H, ^{13}C, ^{19}F, and ^{29}Si NMR chemical shifts (δ values) were given in ppm relative to the solvent signal (^1H 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. $(COT)_2Fe$,[10] bis(η^5-3-methylpentadienyl)Fe,[11] bis(η^5-2,4-dimethylpentadienyl)Fe,[11] and ethyl 4-vinylbenzoate,[22] mesitylisocyanide,[23] and 2,6-(2,6-Me_2-$C_6H_3N{=}CMe)_2C_5H_3N$[24] were synthesized by the method reported in the literature. Isocyanides (CNAd, CN^tBu, and CNCy) were purchased from Tokyo Chemical Industries Co., Ltd., and were used without further purification. Hydrosilanes, $PhMe_2SiH$, Et_3SiH, $(EtO)_3SiH$, Ph_2SiH_2, and $PhSiH_3$, were purchased from Tokyo Chemical Industries Co., Ltd., and $EtMe_2SiH$ was purchased from Sigma-Aldrich and was used after distillation. PMDS, MD'M, and the polymeric hydrosiloxane were obtained from Shin-Etsu Chemical Co. Ltd.

General Procedure for the Hydrosilylation of Styrene with 1,1−3,3,3-Pentamethyldisiloxane (PMDS) Catalyzed by $(COT)_2Fe$ and Various Ligands (Table 1). $(COT)_2Fe$ (7.9 mg, 0.03 mmol) and the ligand (0.03 or 0.06 or 0.09 mmol) were placed in a 4 mL glass vial, then the mixture of styrene (115 μL, 1.0 mmol) and 1,1,3,3,3-pentamethyldisiloxane (PMDS) (254 μL, 1.3 mmol) was added. The resulting mixture was stirred at 80 °C for 3 h. After the reaction, the mixture was cooled to room temperature, then anisole (108 mg, 1.0 mmol) was added into the mixture as an internal standard. The conversion of styrene and the yields of the products were analyzed by ^1H NMR spectroscopy.

Hydrosilylation of Styrene with PMDS Catalyzed by $(COT)_2Fe$ with CNAd (Table 2, Entries 1 and 2). $(COT)_2Fe$ (2.6 mg, 0.01 mmol) and 1-isocyanoadamantane (3.2 mg, 0.02 mmol) were placed in a 4 mL glass vial, then the mixture of styrene (115 μL 1.0 mmol) and PMDS (254 μL 1.3 mmol) was added. The resulting mixture was stirred at 50 °C (entry 1) or at room temperature (entry 2) for 23 h. After the reaction, the mixture was cooled to room temperature, then anisole (108 mg, 1.0 mmol) was added into the mixture as an internal standard. The conversion of styrene was determined by ^1H NMR spectroscopy, and the product **1a** was isolated by distillation (8 Pa, 65−70 °C). Isolated yield (entry 1), 237 mg (0.94 mmol, 94%); (entry 2), 245 mg (0.95 mmol, 95%). ^1H NMR (400 MHz, $CDCl_3$) δ: 0.07 (s, 6H, -$SiMe_2$-), 0.08 (s, 9H, -$SiMe_3$), 0.86−0.92 (m, 2H, −CH_2Si), 2.61−2.68 (m, 2H, −CH_2−), 7.13−7.22 (m, 3H, Ar−H), 7.24−7.29 (m, 2H, Ar−H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 0.3, 2.0, 20.4, 29.4, 125.5, 127.8, 128.3, 145.2. ^{29}Si NMR (119 MHz, $CDCl_3$) δ: 7.09, 7.52. HRMS (EI) calcd for [$C_{13}H_{24}OSi_2$]: 252.1366. Found: 252.1369.

Hydrosilylation of Styrene with PMDS Catalyzed by $(COT)_2Fe$ with CNAd (Table 2, Entry 3). $(COT)_2Fe$ (5.4 mg, 0.02 mmol) and 1-isocyanoadamantane (6.8 mg, 0.04 mmol) were placed in a 20 mL Schlenk tube, then the mixture of styrene (10.42 g, 100 mmol) and PMDS (14.84 g, 100 mmol) was added. The resulting mixture was stirred at 50 °C for 23 h. Product **1a** was isolated by distillation (8 Pa, 65−70 °C). Isolated yield: 22.41 g (88.7 mmol, 89%).

Hydrosilylation of 4-*t*-Butylstyrene with PMDS Catalyzed by $(COT)_2Fe$ with CNAd (Table 2, Entry 4). $(COT)_2Fe$ (2.6 mg, 0.01 mmol) and 1-isocyanoadamantane (3.2 mg, 0.02 mmol) were placed in a 4 mL glass vial, then the mixture of 4-*t*-butylstyrene (180 μL 1.0 mmol) and PMDS (254 μL 1.3 mmol) was added. The resulting mixture was stirred at 50 °C for 23 h. After the reaction, the mixture was cooled to room temperature, then anisole (108 mg, 1.0 mmol) was added into the mixture as an internal standard. The conversion of 4-*t*-butylstyrene was determined by ^1H NMR spectroscopy, and the product **2a** was isolated by distillation (6 Pa, 70−75 °C). Isolated yield: 293 mg (0.93 mmol, 93%).^1H NMR (400 MHz, $CDCl_3$) δ: 0.08 (s, 9H, -$SiMe_3$), 0.08 (s, 6H, -$SiMe_2$-), 0.85−0.92 (m, 2H, −CH_2Si), 1.31 (s, 9H, -CMe_3), 2.58−2.65 (m, 2H, −CH_2−), 7.14 (d, *J* = 7.7 Hz, 2H, Ar−H), 7.30 (d, *J* = 7.7 Hz, 2H, Ar−H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 0.3, 2.0, 20.2, 28.8, 31.4, 34.3, 125.1, 127.4, 142.1, 148.3. ^{29}Si NMR (119 MHz, $CDCl_3$) δ: 7.13, 7.44. HRMS (EI) calcd for [$C_{17}H_{32}OSi_2$]: 308.1992. Found: 308.1989.

Hydrosilylation of 4-Chlorostyrene with PMDS Catalyzed by $(COT)_2Fe$ with CNAd (Table 2, Entry 5). $(COT)_2Fe$ (2.6 mg, 0.01 mmol) and 1-isocyanoadamantane (3.2 mg, 0.02 mmol) were placed in a 4 mL glass vial, then the mixture of 4-chlorostyrene (127 μL 1.0 mmol) and PMDS (254 μL 1.3 mmol) was added. The resulting mixture was stirred at 50 °C for 23 h. After the reaction, the mixture was cooled to room temperature, then anisole (108 mg, 1.0 mmol) was added into the mixture as an internal standard. The conversion of 4-chlorostyrene was determined by ^1H NMR spectroscopy, and the product **3a** was isolated by distillation (8 Pa, 80−85 °C). Isolated yield: 277 mg (0.97 mmol, 97%).^1H NMR (400 MHz, $CDCl_3$) δ: 0.07 (s, 6H, -$SiMe_2$-), 0.08 (s, 9H, -$SiMe_3$), 0.82−0.88 (m, 2H, −CH_2Si), 2.58−2.64 (m, 2H, −CH_2−), 7.12 (d, *J* = 8.2 Hz, 2H, Ar−H), 7.23 (d, *J* = 8.2 Hz, 2H, Ar−H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 0.3, 2.0, 20.3, 28.8, 128.3, 129.2, 131.1, 143.6. ^{29}Si NMR (119 MHz, $CDCl_3$) δ: 6.90, 7.71. HRMS (EI) calcd for [$C_{13}H_{23}ClOSi_2$]: 286.0976. Found: 286.0963.

Hydrosilylation of 4-Fluorostyrene with PMDS Catalyzed by $(COT)_2Fe$ with CNAd (Table 2, Entry 6). $(COT)_2Fe$ (2.6 mg, 0.01 mmol) and 1-isocyanoadamantane (3.2 mg, 0.02 mmol) were placed in a 4 mL glass vial, then the mixture of 4-fluorostyrene (154 μL 1.0 mmol) and PMDS (254 μL 1.3 mmol) was added. The resulting mixture was stirred at 50 °C for 23 h. After the reaction, the mixture was cooled to room temperature, then anisole (108 mg, 1.0 mmol) was added into the mixture as an internal standard. The conversion of

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4-fluorostyrene was determined by ^{1}H NMR spectroscopy, and the product **4a** was isolated by distillation (8 Pa, 65−70 °C). Isolated yield: 257 mg (0.95 mmol, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.07 (s, 6H, -$SiMe_2$-), 0.08 (s, 9H, -$SiMe_3$), 0.83−0.89 (m, 2H, −CH_2Si), 2.58−2.65 (m, 2H, −CH_2−), 6.92−6.98 (m, 2H, Ar−H), 7.12−7.17 (m, 2H, Ar−H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 0.3, 2.0, 20.5, 28.7, 114.9 (d, J_{C-F} = 21.3 Hz), 129.1 (d, J_{C-F} = 8.2), 140.7 (d, J_{C-F} = 3.3 Hz), 161.0 (d, J_{C-F} = 242.8 Hz). ^{19}F-NMR (565 MHz, $CDCl_3$) δ: −119.27. ^{29}Si NMR (119 MHz, $CDCl_3$) δ: 6.94, 7.63. HRMS (EI) calcd for [$C_{13}H_{23}FOSi_2$]: 270.1272. Found: 270.1255.

Hydrosilylation of 4-Methoxystyrene Derivatives with PMDS Catalyzed by (COT)$_2$Fe with CNAd (Table 2, Entry 7). (COT)$_2$Fe (2.6 mg, 0.01 mmol) and 1-isocyanoadamantane (3.2 mg, 0.02 mmol) were placed in a 4 mL glass vial, then the mixture of 4-methoxystyrene (134 μL 1.0 mmol) and PMDS (254 μL 1.3 mmol) was added. The resulting mixture was stirred at 40 °C for 23 h. After the reaction, the mixture was cooled to room temperature, then anisole (108 mg, 1.0 mmol) was added into the mixture as an internal standard. The conversion of 4-methoxystyrene was determined by ^{1}H NMR spectroscopy, and the product **5a** was isolated by distillation (6 Pa, 70−75 °C). Isolated yield: 271 mg (0.96 mmol, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.07 (s, 6H, -$SiMe_2$-), 0.08 (s, 9H, -$SiMe_3$), 0.83−0.89 (m, 2H, −CH_2Si), 2.56−2.62 (m, 2H, −CH_2−), 3.79 (s, 3H, O−CH_3), 6.82 (d, J = 8.7 Hz, 2H, Ar−H), 7.12 (d, J = 8.7 Hz, 2H, Ar−H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 0.3, 2.0, 20.6, 28.5, 55.3, 113.7, 128.6, 137.3, 157.6. ^{29}Si NMR (119 MHz, $CDCl_3$) δ: 7.09, 7.48. HRMS (EI) calcd for [$C_{14}H_{26}O_2Si_2$]: 282.1471. Found: 282.1460.

Hydrosilylation of Ethyl 4-Vinylbenzoate with PMDS Catalyzed by (COT)$_2$Fe with CNAd (Table 2, Entry 8). (COT)$_2$Fe (2.6 mg, 0.01 mmol) and 1-isocyanoadamantane (3.2 mg, 0.02 mmol) were placed in a 4 mL glass vial, then the mixture of ethyl 4-vinylbenzoate (176 mg 1.0 mmol) and PMDS (254 μL 1.3 mmol) was added. The resulting mixture was stirred at 50 °C for 23 h. After the reaction, the mixture was cooled to room temperature, then anisole (108 mg, 1.0 mmol) was added into the mixture as an internal standard. The conversion of 4-vinylbenzoate was determined by ^{1}H NMR spectroscopy, and the product **6a** was isolated by distillation (6 Pa, 135−140 °C). Isolated yield: 324 mg (0.99 mmol, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.08 (s, 6H, -$SiMe_2$-), 0.09 (s, 9H, -$SiMe_3$), 0.86−0.92 (m, 2H, −CH_2Si), 1.39 (t, J = 7.2 Hz, 3H, −CH_3), 2.66−2.72 (m, 2H, −CH_2−), 4.36 (q, J = 7.2 Hz, 2H, O−CH_2−), 7.26 (d, J = 8.2 Hz, 2H, Ar−H), 7.95 (d, J = 8.2 Hz, 2H, Ar−H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 0.3, 2.0, 14.3, 20.1, 29.6, 60.7, 127.8, 127.9, 129.6, 150.7, 166.7. ^{29}Si NMR (119 MHz, $CDCl_3$) δ: 6.90, 7.79. HRMS (EI) calcd for [$C_{16}H_{28}O_3Si_2$]: 324.1577. Found: 324.1566.

Hydrosilylation of 4-Vinylnaphthalene with PMDS Catalyzed by (COT)$_2$Fe with CNAd (Table 2, Entry 9). (COT)$_2$Fe (7.9 mg, 0.03 mmol) and 1-isocyanoadamantane (9.7 mg, 0.06 mmol) were placed in a 4 mL glass vial, then the mixture of 4-vinylnaphthalene (154 mg 1.0 mmol) and PMDS (254 μL 1.3 mmol) was added. The resulting mixture was stirred at 50 °C for 23 h. After the reaction, the mixture was cooled to room temperature, then anisole (108 mg, 1.0 mmol) was added into the mixture as an internal standard. The conversion of 4-vinylnaphthalene was determined by ^{1}H NMR spectroscopy, and the product **7a** was isolated by distillation (6 Pa, 120−125 °C). Isolated yield: 297 mg (0.98 mmol, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.08 (s, 6H, -$SiMe_2$-), 0.08 (s, 9H, -$SiMe_3$), 0.85−0.92 (m, 2H, −CH_2Si), 1.39 (t, J = 7.2 Hz, 3H, −CH_3), 2.66−2.72 (m, 2H, −CH_2−), 4.36 (q, J = 7.2 Hz, 2H, O−CH_2−), 7.26 (d, J = 8.2 Hz, 2H, Ar−H), 7.95 (d, J = 8.2 Hz, 2H, Ar−H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 0.3, 2.0, 20.3, 29.6, 124.9, 125.4, 125.8, 127.1, 127.4, 127.6, 127.8, 131.9, 133.7, 142.7. ^{29}Si NMR (119 MHz, $CDCl_3$) δ: 7.13, 7.63. HRMS (EI) calcd for [$C_{17}H_{26}OSi_2$]: 302.1522. Found: 302.1517.

Hydrosilylation of 2-Methylstyrene with PMDS Catalyzed by (COT)$_2$Fe with CNAd (Table 2, Entry 10). (COT)$_2$Fe (7.9 mg, 0.03 mmol) and 1-isocyanoadamantane (9.7 mg, 0.06 mmol) were placed in a 4 mL glass vial, then the mixture of 2-methylstyrene (129 μL 1.0 mmol) and PMDS (254 μL 1.3 mmol) was added. The resulting mixture was stirred at 50 °C for 23 h. After the reaction, the mixture was cooled to room temperature, then anisole (108 mg, 1.0 mmol) was added into the mixture as an internal standard. The conversion of styrene was determined by ^{1}H NMR spectroscopy, and the product **8a** was isolated by distillation (3 Pa, 120−125 °C). Isolated yield: 224 mg (0.84 mmol, 84%). ^{1}H NMR (395 MHz, $CDCl_3$) δ: 0.09 (s, 9H, -$SiMe_3$), 0.10 (s, 6H, -$SiMe_2$-), 0.80−0.85 (m, 2H, −CH_2Si), 2.30 (s, 3H, -Me), 2.58−2.62 (m, 2H, −CH_2−), 7.06−7.17 (m, 4H, Ar−H). ^{13}C NMR (99 MHz, $CDCl_3$) δ: 0.4, 2.2, 19.3 (two peaks due to the *o*-*Me*-$C_6H_4MeCH_2$ and *o*-Me-$C_6H_4MeCH_2$ are overlapped), 26.9, 125.8, 126.2, 128.1, 130.3, 135.6, 143.5. ^{29}Si NMR (119 MHz, $CDCl_3$) δ: 7.09, 7.59. HRMS (EI) calcd for [$C_{14}H_{26}OSi_2$]: 266.1522. Found: 266.1521.

Hydrosilylation of Styrene Derivatives with PhMe$_2$SiH Catalyzed by (COT)$_2$Fe with CNAd (Table 3, Entry 1). (COT)$_2$Fe (26 mg, 0.1 mmol) and 1-isocyanoadamantane (32 mg, 0.2 mmol) were placed in a 20 mL Schlenk tube, then the mixture of styrene (1.04 g 10.0 mmol) and $PhMe_2SiH$ (1.77 g 13.0 mmol) was added. The resulting mixture was stirred at 50 °C for 23 h. After the reaction, the mixture was cooled to room temperature, then anisole (108 mg, 1.0 mmol) was added into the mixture as an internal standard. The conversion of styrene was determined by ^{1}H NMR spectroscopy, and the product **1a′** was isolated by distillation (14 Pa, 75−80 °C). Isolated yield: 2.03 g (8.5 mmol, 85%). ^{1}H NMR (395 MHz, $CDCl_3$) δ: 0.30 (s, 6H, -$SiMe_2$), 1.11−1.18 (m, 2H, −CH_2Si), 2.62−2.68 (m, 2H, −CH_2−), 7.14−7.20 (m, 3H, Ar−H), 7.24−7.30 (m, 2H, Ar−H), 7.36−7.40 (m, 3H, Ar−H), 7.53−7.57 (m, 2H, Ar−H). ^{13}C NMR (99 MHz, $CDCl_3$) δ: −3.0, 17.7, 30.0, 125.5, 127.8, 127.8, 128.3, 128.9, 133.6, 139.0, 145.0. ^{29}Si NMR (119 MHz, $CDCl_3$) δ: −2.89. HRMS (EI) calcd for [$C_{16}H_{20}Si$]: 240.1334. Found: 240.1336.

Hydrosilylation of 4-*t*-Butylstyrene with PhMe$_2$SiH Catalyzed by (COT)$_2$Fe with CNAd (Table 3, Entry 2). (COT)$_2$Fe (2.6 mg, 0.01 mmol) and 1-isocyanoadamantane (3.2 mg, 0.02 mmol) were placed in a 4 mL glass vial, then the mixture of 4-*t*-butylstyrene (180 μL 1.0 mmol) and $PhMe_2SiH$ (202 μL 1.3 mmol) was added. The resulting mixture was stirred at 50 °C for 23 h. After the reaction, the mixture was cooled to room temperature, then anisole (108 mg, 1.0 mmol) was added into the mixture as an internal standard. The conversion of 4-*t*-butylstyrene was determined by ^{1}H NMR spectroscopy, and the product **2a′** was isolated by distillation (8 Pa, 125−130 °C). Isolated yield: 281 mg (0.95 mmol, 95%). ^{1}H NMR (395 MHz, $CDCl_3$) δ: 0.29 (s, 6H, -$SiMe_2$), 1.10−1.16 (m, 2H, −CH_2Si), 1.31 (s, 9H, -CMe_3), 2.58−2.65 (m, 2H, −CH_2−), 7.12 (d, J = 8.7 Hz, 2H, Ar−H), 7.28 (d, J = 8.2 Hz, 2H, Ar−H), 7.29−7.39 (m, 3H, Ar−H), 7.51−7.55 (m, 2H, Ar−H). ^{13}C NMR (99 MHz, $CDCl_3$) δ: −3.1, 17.5, 29.3, 31.4, 34.3, 125.1, 127.4, 127.8, 128.9, 133.6, 139.1, 141.9, 148.3. ^{29}Si NMR (119 MHz, $CDCl_3$) δ: −2.89. HRMS (EI) calcd for [$C_{20}H_{28}Si$]: 296.1960. Found: 296.1961.

Hydrosilylation of 4-Chlorostyrene Derivatives with PhMe$_2$SiH Catalyzed by (COT)$_2$Fe with CNAd (Table 3, Entry 3). (COT)$_2$Fe (26 mg, 0.1 mmol) and 1-isocyanoadamantane (32 mg, 0.2 mmol) were placed in a 20 mL Schlenk tube, then the mixture of 4-chlorostyrene (1.39 g 10.0 mmol) and $PhMe_2SiH$ (1.77 g 13.0 mmol) was added. The resulting mixture was stirred at 50 °C for 23 h. After the reaction, the mixture was cooled to room temperature, then anisole (108 mg, 1.0 mmol) was added into the mixture as an internal standard. The conversion of 4-chlorostyrene was determined by ^{1}H NMR spectroscopy, and the product **3a′** was isolated by distillation (14 Pa, 80−85 °C). Isolated yield: 2.505 g (9.1 mmol, 91%). ^{1}H NMR (395 MHz, $CDCl_3$) δ: 0.32 (s, 6H, -$SiMe_2$), 1.08−1.15 (m, 2H, −CH_2Si), 2.59−2.65 (m, 2H, −CH_2−), 7.09−7.13 (m, 2H, Ar−H), 7.21−7.25 (m, 2H, Ar−H), 7.37−7.41 (m, 3H, Ar−H), 7.52−7.57 (m, 2H, Ar−H). ^{13}C NMR (99 MHz, $CDCl_3$) δ: −3.1, 17.7, 29.4, 127.8, 128.3, 129.0, 129.1, 131.2, 133.5, 138.8, 143.4. ^{29}Si NMR (119 MHz, $CDCl_3$) δ: −2.89. HRMS (EI) calcd for [$C_{16}H_{19}ClSi$]: 274.0945. Found: 274.0938.

Hydrosilylation of 4-Fluorostyrene with PhMe$_2$SiH Catalyzed by (COT)$_2$Fe with CNAd (Table 3, Entry 4). (COT)$_2$Fe (2.6 mg, 0.01 mmol) and 1-isocyanoadamantane (3.2 mg, 0.02 mmol) were placed in a 4 mL glass vial, then the mixture of 4-fluorostyrene (154

μL 1.0 mmol) and $PhMe_2SiH$ (202 μL 1.3 mmol) was added. The resulting mixture was stirred at 50 °C for 23 h. After the reaction, the mixture was cooled to room temperature, then anisole (108 mg, 1.0 mmol) was added into the mixture as an internal standard. The conversion of 4-fluorostyrene was determined by ^{1}H NMR spectroscopy, and the product **4a**′ was isolated by distillation (8 Pa, 95−100 °C). Isolated yield: 252 mg (0.98 mmol, 98%) ^{1}H NMR (395 MHz, $CDCl_3$) δ: 0.29 (s, 6H, -$SiMe_2$), 1.07−1.13 (m, 2H, −CH_2Si), 2.57−2.64 (m, 2H, −CH_2−), 6.93 (t, J = 8.7 Hz, 2H, Ar−H), 7.08−7.13 (m, 2H, Ar−H), 7.35−7.38 (m, 3H, Ar−H), 7.50−7.54 (m, 2H, Ar−H). ^{13}C NMR (99 MHz, $CDCl_3$) δ: −3.1, 17.9, 29.2, 114.9 (d, J_{C-F} = 20.5 Hz), 127.8, 129.0, 129.0 (d, J_{C-F} = 8.2 Hz), 133.6, 138.9, 140.5 (d, J_{C-F} = 3.3 Hz), 161.1 (d, J_{C-F} = 242.0 Hz). ^{19}F-NMR (565 MHz, $CDCl_3$) δ: −119.11. ^{29}Si NMR (119 MHz, $CDCl_3$) δ: −2.93. HRMS (EI) calcd for [$C_{16}H_{19}FSi$]: 258.1240. Found: 258.1241.

Hydrosilylation of 4-Methoxystyrene with $PhMe_2SiH$ Catalyzed by $(COT)_2Fe$ with CNAd (Table 3, Entry 5). $(COT)_2Fe$ (26 mg, 0.1 mmol) and 1-isocyanoadamantane (32 mg, 0.2 mmol) were placed in a 20 mL Schlenk tube, then the mixture of 4-methoxystyrene (1.34 g 10.0 mmol) and $PhMe_2SiH$ (1.77 g 13.0 mmol) was added. The resulting mixture was stirred at 50 °C for 23 h. After the reaction, the mixture was cooled to room temperature, then anisole (108 mg, 1.0 mmol) was added into the mixture as an internal standard. The conversion of 4-methoxystyrene was determined by ^{1}H NMR spectroscopy, and the product **5a**′ was isolated by distillation (14 Pa, 85−90 °C). Isolated yield: 2.20 g (8.2 mmol, 82%). ^{1}H NMR (395 MHz, $CDCl_3$) δ: 0.30 (s, 6H, -$SiMe_2$), 1.09−1.15 (m, 2H, −CH_2Si), 2.58−2.64 (m, 2H, −CH_2−), 3.80 (s, 3H, O−CH_3), 6.81−6.84 (m, 2H, Ar−H), 7.09−7.12 (m, 2H, Ar−H), 7.36−7.40 (m, 3H, Ar−H), 7.53−7.57 (m, 2H, Ar−H). ^{13}C NMR (99 MHz, $CDCl_3$) δ: −3.1, 17.9, 29.0, 55.3, 113.7, 127.8, 128.6, 128.9, 133.6, 137.1, 139.1, 157.6. ^{29}Si NMR (119 MHz, $CDCl_3$) δ: −3.01. HRMS (EI) calcd for [$C_{17}H_{22}OSi$]: 270.1440. Found: 270.1441.

Hydrosilylation of 4-Vinylbenzoate with $PhMe_2SiH$ Catalyzed by $(COT)_2Fe$ with CNAd (Table 3, Entry 6). $(COT)_2Fe$ (2.6 mg, 0.01 mmol) and 1-isocyanoadamantane (3.2 mg, 0.02 mmol) were placed in a 4 mL glass vial, then the mixture of ethyl 4-vinylbenzoate (176 mg 1.0 mmol) and $PhMe_2SiH$ (202 μL 1.3 mmol) was added. The resulting mixture was stirred at 50 °C for 23 h. After the reaction, the mixture was cooled to room temperature, then anisole (108 mg, 1.0 mmol) was added into the mixture as an internal standard. The conversion of 4-vinylbenzoate was determined by ^{1}H NMR spectroscopy, and the product **6a**′ was isolated by distillation (4 Pa, 130−135 °C). Isolated yield: 312 mg (0.99 mmol, 99%). ^{1}H NMR (395 MHz, $CDCl_3$) δ: 0.30 (s, 6H, -$SiMe_2$), 1.09−1.16 (m, 2H, −CH_2Si), 1.38 (t, J = 7.2 Hz, 3H, −CH_3), 2.64−2.71 (m, 2H, −CH_2−), 4.36 (q, J = 7.2 Hz, 2H, O−CH_2−), 7.22 (d, J = 8.2 Hz, 2H, Ar−H), 7.35−7.39 (m, 3H, Ar−H), 7.50−7.55 (m, 2H, Ar−H), 7.93 (d, J = 8.2 Hz, 2H, Ar−H). ^{13}C NMR (99 MHz, $CDCl_3$) δ: −3.2, 14.3, 17.5, 30.1, 60.7, 127.7, 127.8, 127.9, 129.0, 129.6, 133.5, 138.6, 150.3, 166.6. ^{29}Si NMR (119 MHz, $CDCl_3$) δ: −2.78. HRMS (EI) calcd for [$C_{19}H_{24}O_2Si$]: 312.1546. Found: 312.1548.

Hydrosilylation of 2-Methylstyrene with PMDS Catalyzed by $(COT)_2Fe$ with CNAd (Table 3, Entry 7). $(COT)_2Fe$ (2.6 mg, 0.01 mmol) and 1-isocyanoadamantane (3.2 mg, 0.02 mmol) were placed in a 4 mL glass vial, then the mixture of 2-methylstyrene (129 μL 1.0 mmol) and $PhMe_2SiH$ (202 μL 1.3 mmol) was added. The resulting mixture was stirred at 50 °C for 23 h. After the reaction, the mixture was cooled to room temperature, then anisole (108 mg, 1.0 mmol) was added into the mixture as an internal standard. The conversion of 2-methylstyrene was determined by ^{1}H NMR spectroscopy, and the product **8a**′ was purified by distillation (8 Pa, 115−120 °C). Isolated yield: 244 mg (0.96 mmol, 96%). ^{1}H NMR (395 MHz, $CDCl_3$) δ: 0.33 (s, 6H, -$SiMe_2$), 1.04−1.10 (m, 2H, −CH_2Si), 2.25 (s, 3H, −CH_3), 2.57−2.63 (m, 2H, −CH_2−), 7.09−7.15 (m, 4H, Ar−H), 7.36−7.40 (m, 3H, Ar−H), 7.54−7.58 (m, 2H, Ar−H). ^{13}C NMR (99 MHz, $CDCl_3$) δ: −3.2, 16.6, 19.0, 27.3, 125.6, 126.0, 127.8, 127.9, 128.9, 130.1, 133.6, 135.3, 139.0, 143.2. ^{29}Si NMR (119 MHz, $CDCl_3$) δ: −2.78. HRMS (EI) calcd for [$C_{17}H_{22}Si$]: 254.1491. Found: 254.1482.

Hydrosilylation of Styrene with Polymeric Hydrosiloxane Catalyzed by $(COT)_2Fe$ with 1-Isocyanoadamantane. $(COT)_2Fe$ (7.2 mg, 0.03 mmol) and 1-isocyanoadamantane (9.7 mg, 0.06 mmol) were placed in a 4 mL glass vial, then the mixture of styrene (299 μL, 2.6 mmol) and polymeric hydrosilanes, $Me_2Si(H)O(SiMe_2O)_nSi(H)Me_2$ (n = ca. 27, determined by ^{1}H NMR) (2.14 g, ca. 2.0 mmol for Si−H) was added. The resulting mixture was stirred at 50 °C for 23 h. After the reaction, the mixture was cooled to room temperature, then anisole (108 mg, 1.0 mmol) was added into the mixture as an internal standard. The conversion of styrene (>99%) and the yield of the product (>99%) were determined by ^{1}H NMR spectroscopy. The crude product was stirred for 3 h under air to decompose the iron residue, then the resulting mixture was passed through a pad of Al_2O_3. The filtrate was dried under vacuum, then the product **9a** was obtained in 99% yield (2.32 g). ^{1}H NMR (395 MHz, $CDCl_3$) δ: 0.09 (s, 156H, -$SiMe_2$-), 0.11 (s, 18H, -$SiMe_2$-), 0.87−0.98 (m, 4H, −CH_2Si), 2.61−2.73 (m, 4H, −CH_2−), 7.13−7.31 (m, 10H, C_6H_5). ^{13}C NMR (99 MHz, $CDCl_3$) δ: 0.29, 0.81, 1.18, 1.24, 1.34, 1.56, 20.4, 29.5, 125.6, 127.9, 128.4, 145.3. ^{29}Si NMR (119 MHz, $CDCl_3$) δ: 7.09, −20.70, −21.28, −21.86.

General Procedure for Hydrosilylation of Styrene Derivatives with PMDS or $PhMe_2SiH$ Catalyzed by $(MPDE)_2Fe$ with 1-Isocyanoadamantane (Table 4, Entries 1 and 3−7). $(MPDE)_2Fe$ (1.9 mg, 0.01 mmol) and 1-isocyanoadamantane (3.2 mg, 0.02 mmol) were placed in a 4 mL glass vial, then the mixture of styrene derivatives (1 mmol) and hydrosilanes (PMDS or $PhMe_2SiH$) (1.3 mmol) was added. The resulting mixture was stirred at 50 °C for 23 h. After the reaction, the mixture was cooled to room temperature, then anisole (108 mg, 1.0 mmol) was added into the mixture. The conversion of styrene derivatives and the yield of the product were determined by ^{1}H NMR spectroscopy. The product was isolated by distillation under reduced pressure.

Hydrosilylation of Styrene with PMDS Catalyzed by $(DMPDE)_2Fe$ with 1-Isocyanoadamantane (Table 4, Entry 2). $(DMPDE)_2Fe$ (2.5 mg, 0.01 mmol) and 1-isocyanoadamantane (3.2 mg, 0.02 mmol) were placed in a 4 mL glass vial, then the mixture of styrene (115 μL 1.0 mmol) and PMDS (254 μL, 1.3 mmol) was added. The resulting mixture was stirred at 50 °C for 23 h. After the reaction, the mixture was cooled to room temperature, then anisole (108 mg, 1.0 mmol) was added into the mixture. The conversion of styrene and the yield of the product were determined by ^{1}H NMR spectroscopy.

Synthesis of Bis(cyclooctatetraene)(1-isocyanoadamantane)iron (10). $COT)_2Fe$ (50 mg, 0.19 mmol) and toluene (2 mL) were placed in a 20 mL Schlenk tube, then 1-isocyanoadamantane (33 mg, 0.21 mmol) was added to this solution at room temperature. The solution was stirred at room temperature for 1 h, then the resulting mixture was passed through a short pad of Celite. The mother liquid was collected, and pentane (10 mL) was added. Complex **10** was obtained as black crystals by recrystallization at −35 °C (50 mg, 0.12 mmol, 62%). ^{1}H NMR (600 MHz, C_6D_6) δ: 1.37 (br, 6H), 1.79 (s, 3H), 1.97 (s, 6H), 4.52 (br, 16H). ^{13}C NMR (151 MHz, C_6D_6) δ: 29.3, 35.8, 44.4, 55.7, 101.0 (br), 166.6. FT-IR (KBr, pellet): ν_{C-N} = 2119 cm^{-1} Anal. calcd for $C_{27}H_{31}NFe$; C 76.23, H 7.35, N 3.29; found, C 76.18, H 7.85, N 3.10.

Synthesis of (Cyclooctatetraene)tris(1-isocyanoadamantane)iron (11). In a 20 mL Schlenk tube were placed $(COT)_2Fe$ (100 mg, 0.38 mmol), 1-isocyanoadamantane (185 mg, 1.15 mmol), and toluene (4 mL). The solution was stirred at room temperature for 1 h, then the resulting mixture was passed through a short pad of Celite. The mother liquid was collected, and pentane (40 mL) was added. Complex **11** was obtained as red crystals by recrystallization at −35 °C (168 mg, 0.24 mmol, 63%). ^{1}H NMR (600 MHz, C_6D_6) δ: 1.32 (br, 18H), 1.72 (s, 9H), 1.86 (s, 18H), 5.46 (br, 8H). ^{13}C NMR (151 MHz, C_6D_6) δ: 29.5, 35.8, 45.1, 56.4, 97.1 (br), 183.8. FT-IR (KBr, pellet): ν_{C-N} = 2104, 2041, 1937 cm^{-1} Anal. calcd for $C_{41}H_{53}N_3Fe$; C 76.50, H 8.30 N 6.53; found, C 76.48, H 8.74, N 6.48.

Hydrosilylation of Styrene with PMDS Catalyzed by $(COT)_2Fe(CNAd)$ (10) (Table 5, Entry 2). $(COT)_2Fe(CNAd)$ (**10**)

(4.3 mg, 0.01 mmol) were placed in a 4 mL glass vial, then the mixture of styrene (115 μL 1.0 mmol) and PMDS (254 μL 1.3 mmol) was added. The resulting mixture was stirred at 50 °C for 23 h. After the reaction, the mixture was cooled to room temperature, then anisole (108 mg, 1.0 mmol) was added. The conversion of styrene (67%) and the yield of the product (67%) were determined by ^{1}H NMR spectroscopy. The product was isolated by distillation under reduced pressure (8 Pa, 65−70 °C). Isolated yield: 159 mg (0.63 mmol, 63%).

Hydrosilylation of Styrene with PMDS Catalyzed by (COT)$_2$Fe(CNAd) (10) in the Presence of CNAd (Table 5, Entry 3). (COT)$_2$Fe(CNAd) (**10**) (4.3 mg, 0.01 mmol) and CNAd (1.6 mg, 0.01 mmol) were placed in a 4 mL glass vial, then the mixture of styrene (115 μL 1.0 mmol) and PMDS (254 μL 1.3 mmol) was added. The resulting mixture was stirred at 50 °C for 23 h. After the reaction, the mixture was cooled to room temperature, then anisole (108 mg, 1.0 mmol) was added. The conversion of styrene (>99%) and the yield of the product (>99%) were determined by ^{1}H NMR spectroscopy. The product was isolated by distillation under reduced pressure (8 Pa, 65−70 °C). Isolated yield: 245 mg (0.97 mmol, 97%).

Hydrosilylation of Styrene with PMDS Catalyzed by (COT)Fe(CNAd)$_3$ (11) (Table 5, Entry 4). (COT)Fe(CNAd)$_3$ (**11**) (6.4 mg, 0.01 mmol) was placed in a 4 mL glass vial, then the mixture of styrene (115 μL 1.0 mmol) and PMDS (254 μL 1.3 mmol) was added. The resulting mixture was stirred at 50 °C for 23 h. After the reaction, the mixture was cooled to room temperature, then anisole (108 mg, 1.0 mmol) was added into the mixture. The conversion of styrene (82%) and the yield of the product (82%) were determined by ^{1}H NMR spectroscopy. The product was isolated by distillation under reduced pressure (8 Pa, 65−70 °C). Isolated yield: 202 mg (0.80 mmol, 80%).

X-ray Data Collection and Reduction. X-ray crystallography was performed on a Rigaku Saturn CCD area detector with graphite monochromated Mo−Kα radiation (λ = 0.71075 Å). The data were collected at 123(2) K using ω scan in the θ range of $2.77 \leq \theta \leq 30.81°$ (**10**) and $2.45 \leq \theta \leq 30.74°$ (**11**). The data obtained were processed using Crystal-Clear (Rigaku) on a Pentium computer and were corrected for Lorentz and polarization effects. The structures were solved by direct methods[25] and expanded using Fourier techniques.[26] Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 4586 observed reflections and 262 variable parameters for **10**, and 7618 observed reflections and 406 variable parameters for **11**. Neutral atom scattering factors were taken from Cromer and Waber.[27] All calculations were performed using SHELXL-97.[28] Details of the final refinement as well as the bond lengths and angle are summarized in Tables S2 and S3 (Supporting Information), and the numbering scheme employed is also shown in Figures S1 and S2 in the Supporting Information, which were drawn with ORTEP at a 50% probability ellipsoid.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of additional experiments, the molecular structures of **10** and **11**, and details of crystallographic studies, and the copy of the actual NMR chart for all products. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00201.

■ AUTHOR INFORMATION

Corresponding Author

*Tel: +81-92-583-7819. Fax: +81-92-583-7819. E-mail: nagasima@cm.kyushu-u.ac.jp.

Notes

The authors declare no competing financial interest.

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(15) A homoleptic [Fe(mesityl)$_2$]$_2$ complex also behaved as a catalyst for the hydrosilylation of styrene in the presence of CNAd. In this case, CNAd was possibly inserted between the Fe-C bond of the complex, and the resulting imidoyliron species may have been responsible for the catalysis.[16]

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(21) Use of a bis(imino)pyridine ligand instead of CNAd provided a partial solution to this drawback, giving the hydrosilylated product 1-silyl-octane selectively in 55% isolated yield (60% conversion of 1-octene) during the reaction mediated by (COT)$_2$Fe (3 mol%) and Me$_2$PDI (3 mol%) under the same reaction conditions. The low conversion of alkenes in these reactions may be attributed to the insufficient generation of the active (Me$_2$PDI)Fe species as a result of the relatively strong coordination of the COT ligand to the iron center. However, a prolonged reaction time (23 h) at 80 °C gave the desired product in 88% isolated yield with full conversion of the 1-octene. Another deficit associated with the disclosed catalysis system arises from the fact that only dehydrogenative silylation took place in the reaction of styrene with sterically hindered hydrosilanes such as MD'M. This could be mitigated by using Me$_2$PDI as the ligand, and selective hydrosilylation of styrene with MD'M was achieved following a reaction at 80 °C over 23 h in the presence of (COT)$_2$Fe (3 mol%) and Me$_2$PDI (3 mol%) to afford the desired product in 92% isolated yield. The combination of (MPDE)$_2$Fe (3 mol%) with Me$_2$PDI (3 mol %) also gave satisfactory results; hydrosilylation of 1-octene with PMDS or styrene with MD'M at 80 °C for 23 h afforded the expected hydrosilylated product selectively in quantitative yield.

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