

Non-Precious-Metal Catalytic Systems Involving Iron or Cobalt Carboxylates and Alkyl Isocyanides for Hydrosilylation of Alkenes with Hydrosiloxanes

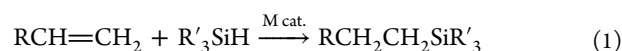
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S Supporting Information

ABSTRACT: A mixture of an iron or a cobalt carboxylate and an isocyanide ligand catalyzed the hydrosilylation of alkenes with hydrosiloxanes with high efficiency (TON >10³) and high selectivity. The Fe catalyst showed excellent activity for hydrosilylation of styrene derivatives, whereas the Co catalyst was widely effective in reaction of alkenes. Both of them catalyzed the reaction with allylic ethers. Chemical modification and cross-linking of silicones were achieved by choosing the right catalyst and reaction conditions.

Hydrosilylation of alkenes (eq 1), involving the addition of organosilicon hydrides to a C=C bond, is an important reaction for producing organosilicon compounds.¹ Catalysts are commonly used to activate the Si–H bond of hydrosilanes, and soluble platinum compounds are used in a homogeneous phase. In particular, hydrosilylation of alkenes with hydrosiloxanes is important for the industrial production of silicone fluids and resins via chemical modification and cross-linking of silicone polymers containing Si–H groups.¹ As a consequence of the rapid growth in the global silicone market, a large quantity of Pt is consumed annually by the silicone industry (5.6 metric tons per year).² Most of this Pt is not recoverable. The scarcity of natural resources like precious metals offers challenges to find replacements for precious-metal catalysts such as Pt.³ Development of new non-precious-metal catalysts, e.g., those including Fe and Co, that can promote efficient hydrosilylation of alkenes is a challenging target in homogeneous catalysis.^{2,4–11}



Although Fe,^{2,4–7} Co,^{4,8–10} and Ni¹¹ complexes have been studied for the catalytic hydrosilylation of alkenes, the reaction usually also included PhSiH₃ or Ph₂SiH₂ as the hydrosilane; only a few studies reported hydrosilylation with hydroalkoxysilanes and hydrosiloxanes. Catalysts useful for PhSiH₃ and Ph₂SiH₂ often are inactive or less efficient for hydrosilylation using hydrosiloxanes. A typical example involves Fe(0) complexes containing bis(imino)pyridine with two 2,6-diisopropylphenyl groups on the imino nitrogen, as reported by Chirik et al, which are very reactive catalysts for hydrosilylation of alkenes with PhSiH₃ but not for tertiary hydrosilanes, including hydrosiloxanes.^{5b} The discovery of modified catalysts bearing less sterically hindered N-substituents allowed the highly efficient hydrosilylation of alkenes

with hydrosiloxanes. A possible industrial application was suggested, cross-linking the silicone fluids by reacting a vinyl group containing silicone and a polymethylhydrosiloxane.² In addition, Holland et al. recently reported that cobalt β-diketiminato complexes acted as good catalysts for adding PhSiH₃ to alkenes; they were less reactive than Chirik's catalysts but could be used under solvent-free conditions.¹⁰ Hydrosilylation of alkenes was achieved using (EtO)₃SiH, which is useful for industrial production of silane coupling reagents. Reaction with hydrosiloxanes was not performed.

Although these reported complexes possessed good catalytic ability in the hydrosilylation of alkenes, they were limited by their high sensitivity toward air and moisture, which necessitates careful preparation and usage. To improve the procedure, *in situ* generation of catalytically active species was examined by treating stable Fe(II) or Co(II) precursors with an organometallic co-catalyst like EtMgBr, BuLi, or NaEt₃BH.^{12,13} However, these activators are moisture sensitive, the strong nucleophilic nature of the activator could potentially cleave the Si–O bonds in the alkoxy silanes and siloxanes, and the Li, Mg, or B metal from the activator can contaminate the product. These are problems, especially when the catalyst system is applied to the synthesis of silicone polymers. A desirable catalyst should contain stable and easily handled metal salts and ligands that are active without requiring strong co-catalysts. The present report describes a new catalyst system that involves iron or cobalt carboxylates associated with an isocyanide ligand. This new catalyst system was useful for the hydrosilylation of alkenes with hydrosiloxanes and could modify and cross-link silicone polymers.

A previous report described a catalyst system composed of Fe(0) and Fe(II) organometallic precursors with isocyanide ligands, which achieved hydrosilylation of styrene derivatives with hydrosiloxanes.^{14a} Improvement of this catalyst system required replacement of air-sensitive catalyst precursors, e.g., Fe(COT)₂ and open ferrocenes, with easy-to-handle metal compounds, and expansion of the substrate scope from styrene derivatives to various alkenes. Nishiyama et al. reported that Fe(OAc)₂ could be activated by a hydrosilane in the presence of a tridentate nitrogen ligand to generate active species for Fe-catalyzed hydrosilylation of ketones.¹⁵ For catalyst screening, styrene or α-methylstyrene was reacted with 1,1,3,3,3-pentamethyldisiloxane (PMDs, Me₃SiOSiHMe₂) as the hydrosiloxane (1.3 equiv to the C=C

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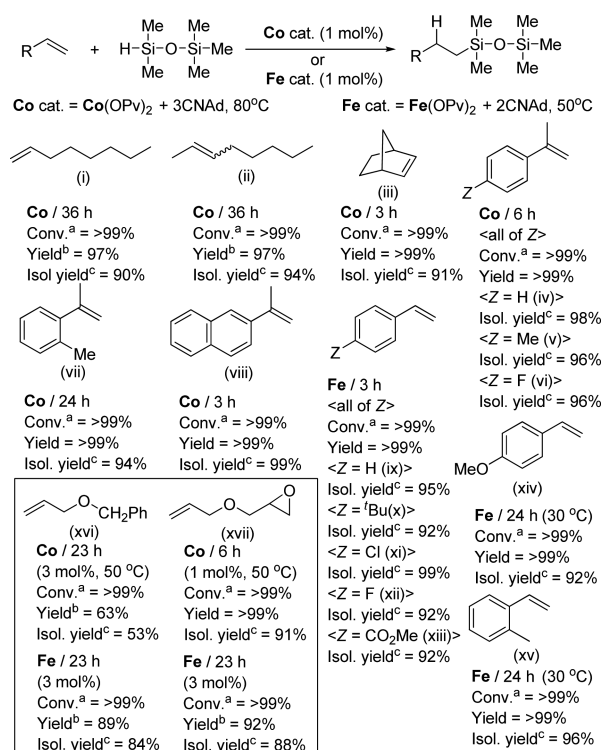
Table 1. Hydrosilylation of Styrene or α -Methylstyrene Catalyzed by $\text{Fe}(\text{OPv})_2$ or $\text{Co}(\text{OPv})_2$

Entry	Catalyst	H-SiY ₃	Yield (%) ^a
1	$\text{Fe}(\text{OPv})_2$	PMDS	83
2	$\text{Fe}(\text{OPv})_2$	PhMe_2SiH	99
3	$\text{Fe}(\text{OPv})_2$	$\text{Me}(\text{EtO})_2\text{SiH}$	16
4	$\text{Co}(\text{OPv})_2$	PMDS	> 99
5	$\text{Co}(\text{OPv})_2$	MD'M	> 99
6	$\text{Co}(\text{OPv})_2$	PhMe_2SiH	> 99
7	$\text{Co}(\text{OPv})_2$	$(\text{EtO})_2\text{Me SiH}$	> 99
8	$\text{Co}(\text{OPv})_2$	$(\text{EtO})_3\text{SiH}$	53

^aDetermined by ¹H NMR.

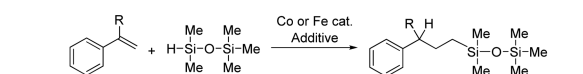
bond) under solvent-free conditions. Among the combinations of metal salt (3 mol%) and isocyanide (2–3 equiv to the metal salt) examined, two commercially available metal salts, $\text{Fe}(\text{OAc})_2$ and $\text{Co}(\text{OAc})_2$, were identified as appropriate metal precursors and catalyzed the reaction in the presence of 1-adamantyl isocyanide (CNAd). Further optimization of metal salts and isocyanides resulted in the discovery of $\text{Fe}(\text{OPv})_2$ or $\text{Co}(\text{OPv})_2$ (Pv = pivaloyl) and CNAd (see Supporting Information (SI), Tables S1–S4). Interestingly, $\text{Fe}(\text{OPv})_2$ and $\text{Co}(\text{OPv})_2$ were complementarily useful in the reactions of styrene and α -methylstyrene, respectively. Treating styrene with PMDS in the presence of a 1:2 mixture of $\text{Fe}(\text{OPv})_2$ (3 mol%) and CNAd at 80 °C for 3 h afforded the corresponding adduct **1a** as the major product in 83% yield (Table 1, entry 1). In contrast, reacting α -methylstyrene with PMDS in the presence of a 1:3 mixture of $\text{Co}(\text{OPv})_2$ (3 mol%) and CNAd at 80 °C for 3 h provided adduct **2a** in quantitative yield as the sole product (entry 4). Reaction of styrene using the Co catalyst, or reaction of α -methylstyrene using the Fe catalyst, resulted in smooth consumption of the starting material but also concomitant dehydrogenative silylation as a side reaction. Screening of hydrosilanes under the same reaction conditions using Co catalysis indicated that the hydrosilylation of α -methylstyrene with various trisubstituted hydrosilanes, e.g., 1,1,1,3,5,5,5-heptamethyltrisiloxane (MD'M), Me_2PhSiH , and $(\text{EtO})_2\text{MeSiH}$, formed the corresponding hydrosilylated products in high yields (entries 5–7). Although the conversion of α -methylstyrene was moderate, the trialkoxysilane $(\text{EtO})_3\text{SiH}$ also was applicable in this catalysis (entry 8). With Fe catalysis, the scope of applicable hydrosilanes was relatively narrow; reaction of styrene with PhMe_2SiH proceeded efficiently to afford the corresponding product in quantitative yield (entry 2). With both catalysts, reactions with PhSiH_3 and Ph_2SiH_2 were slower than those with PMDS, and the Markovnikov adduct was obtained as a byproduct from reaction with the Fe catalyst (Tables S5 and S6).

Scheme 1 shows the hydrosilylation of various alkenes with PMDS catalyzed by the $\text{Co}(\text{OPv})_2$ or $\text{Fe}(\text{OPv})_2/\text{CNAd}$ system. Results show that the $\text{Co}(\text{OPv})_2/\text{CNAd}$ catalyst was applicable to a wide variety of alkenes, except for styrene derivatives, although the reaction required a higher temperature (80 °C). In the presence of 1 mol% of the $\text{Co}(\text{OPv})_2/\text{CNAd}$ catalyst, α -methylstyrene derivatives underwent hydrosilylation at 80 °C to give the corresponding adduct in >96% isolated yields. In contrast, the $\text{Fe}(\text{OPv})_2/\text{CNAd}$ catalyst was more useful than the Co catalyst for a limited number of substrates that had greater activity at 50 °C. Reaction of styrene derivatives using the $\text{Fe}(\text{OPv})_2/\text{CNAd}$ catalyst provided the corresponding hydro-

Scheme 1. Hydrosilylation of Various Alkenes Catalyzed by $\text{Fe}(\text{OPv})_2$ or $\text{Co}(\text{OPv})_2$ ^aDetermined by ¹H NMR. ^bSmall amounts of internal alkenes were also formed. ^cIsolated yield.

silylated product in >91% isolated yield with >99% selectivity at 50 °C. Isomerization of the C=C bond is a serious side reaction in the conventional Pt-catalyzed hydrosilylation of terminal alkenes, and addition of excess amounts of the alkene is necessary due to the low reactivity of the internal alkenes formed.¹⁶ Treatment of 1-octene with the $\text{Co}(\text{OPv})_2/\text{CNAd}$ catalyst led to rapid alkene migration to a mixture of 2-, 3-, and 4-octenes, which subsequently reacted with PMDS to afford 1-silylated octane as a sole product in 90% yield. Hydrosilylation of 2-octene proceeded with a rate similar to that of the reaction with 1-octene, giving the 1-silylated octane in high yield. Co-catalyzed reaction of 2-norbornene with PMDS gave 2-silylated norbornane with exo:endo = 9:1. Functional group compatibility revealed that both of the catalysts were tolerant to ester and halogen groups in styrene or α -methylstyrene derivatives. Interestingly, allylic ethers were the substrates that worked well with the Fe and Co catalyst systems. Two allylic compounds, allyl glycidyl ether and allyl benzyl ether, were hydrosilylated successfully with both the Co and Fe catalyst systems to form the corresponding product in medium to high yields. The catalyst was tolerant even toward the oxirane ring in allyl glycidyl ether, which is susceptible to ring-opening reactions. Hydrosilylation of 1-octene, 2-norbornene, and α -methylstyrene derivatives with MD'M as the sterically hindered hydrosiloxane, using the $\text{Co}(\text{OPv})_2$ (1 mol%)/CNAd (3 mol%) catalytic system, also was successful at 80 °C for 6–48 h, to afford the corresponding hydrosilylated products in 80–99% isolated yields with desired selectivity (see details in Table S9). No Markovnikov products were formed in all cases.

Investigations suggested that the $\text{Co}(\text{OPv})_2$ or $\text{Fe}(\text{OPv})_2/\text{CNAd}$ system possessed catalytic performance to achieve turnover numbers (TON, moles of product per mole of catalyst)

Table 2. Effect of Additives in the Hydrosilylation of α -Methylstyrene or Styrene with PMDS


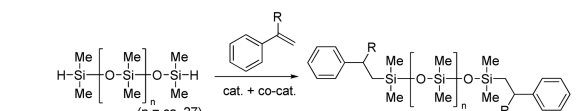
Entry	R	Catalyst (mol%; ppm/M)	Additive (eq. to cat.)	Temp (°C)	Time (h)	Yield (%) ^a
1	Me	Co(OPv) ₂ (0.05; 94)	none	80	24	88
2	Me	Co(OPv) ₂ (0.1; 188)	(EtO) ₃ SiH (4)	50	3	83
3 ^b	H	Fe(OPv) ₂ (0.01; 22)	none	50	24	86
4	H	Fe(OPv) ₂ (0.02; 37)	HBpin (8)	50	3	95
5	H	Fe(OPv) ₂ (0.02; 37)	(EtO) ₂ MeSiH (10)	50	3	96

^aIsolated yield. ^b8 equiv of CNAd to Fe(OPv)₂ was used.

>1000. Treatment of α -methylstyrene (10 mmol) with PMDS (13 mmol) at 80 °C for 24 h in the presence of the Co(OPv)₂/CNAd catalyst (0.05 mol%) gave the hydrosilylated product as a single product quantitatively (isolated yield after distillation = 88%) (Table 2, entry 1). The TON value reached 1885. A higher TON (9700) was achieved in hydrosilylation of styrene (200 mmol) with PMDS (200 mmol) catalyzed by Fe(OPv)₂/CNAd (0.01 mol%) at 50 °C for 24 h (isolated yield after distillation = 86%) (Table 2, entry 3).

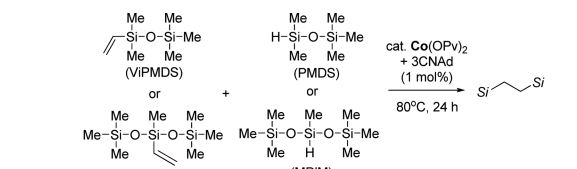
In the catalyst systems described, the hydrosiloxanes behaved as both an activator of the metal carboxylates and the reactant for hydrosilylation. We found that strong organometallic reagents like HBpin and EtMgBr behaved as a co-catalyst to activate the metal carboxylates, but stable and easy-to-handle co-catalysts are desirable for actual applications.¹⁷ Hydroalkoxysilanes, e.g., (EtO)₃SiH, (MeO)₃SiH, (EtO)₂MeSiH, and (MeO)₂MeSiH, were less reactive reactants for hydrosilylation, but behaved as good co-catalysts to generate catalytically active species. Thus, preactivating metal carboxylates with a hydroalkoxysilane at room temperature for 1 h helped to accelerate subsequent hydrosilylation of alkenes with hydrosiloxanes. Table 2 shows typical results for Co-catalyzed hydrosilylation of α -methylstyrene with PMDS, in which catalyst preactivation with (EtO)₃SiH lowered reaction temperature and shortened reaction time. In the Fe-catalyzed reaction of styrene, the time required to complete the reaction was one-eighth of that without preactivation. Catalyst preactivation allowed effective hydrosilylation of several functionalized alkenes. First, the reaction temperature for the hydrosilylation of allyl glycidyl ether with PMDS catalyzed by Co(OPv)₂ (1 mol%)/CNAd (3 mol%) could be reduced using an activator; reaction proceeded at 50 °C in the absence of activator, whereas complete conversion was confirmed at room temperature with the aid of additional (EtO)₂MeSiH (4 mol%). Second, two substrates, 3-(2-methoxyethoxy)prop-1-ene and CH₂=CHCH₂(OCH₂CH₂)_nOMe (*n* = 8), were difficult to hydrosilylate under standard reaction conditions in the absence of (EtO)₂MeSiH. However, a hydrosilylated product was obtained in 42% yield by reacting 3-(2-methoxyethoxy)prop-1-ene with PMDS catalyzed by Fe(OPv)₂ (3 mol%)/CNAd (6 mol%)/(EtO)₂MeSiH (8 mol%). Hydrosilylation of allyl polyether, CH₂=CHCH₂(OCH₂CH₂)_nOMe (*n* = 8), under the same reaction conditions gave the desired product in 62% yield.

Important applications of hydrosilylations to commercial products in the silicone industry include production of modified silicone fluids and cross-linking of silicone polymers containing

Table 3. Modification of HMe₂SiO(SiMe₂O)_nSiMe₂H


Entry	R	Catalyst (mol%; ppm/M) ^a	Additive (eq. to cat.)	Temp (°C)	Time (h)	Yield (%) ^b
1	Me	Co(OPv) ₂ (1;491)	none	80	24	77
2	Me	Co(OPv) ₂ (1;491)	(EtO) ₃ SiH (4)	50	24	99
3	H	Fe(OPv) ₂ (1;478)	none	80	24	81 ^c
4	H	Fe(OPv) ₂ (1;478)	(EtO) ₂ MeSiH (8)	25	18	96

^aCorresponding to 1 mol% per Si-H group. ^bIsolated yield. ^cDehydrogenative hydrosilylation occurred as a side reaction to lower the product yield (see the SI).

Table 4. Hydrosilylation of Vinylsiloxanes with PMDS or MD'M Catalyzed by Co(OPv)₂


Entry	H-Si	alkene	Conv. (%) ^a	Selectivity (%) ^a	Yield (%) ^b
1	PMDS	ViPMDS	>99	>99 ^d	79
2 ^c	MD'M	ViPMDS	>99	>99 ^d	84
3	PMDS	ViHMTS	>99	>99 ^d	97
4 ^c	MD'M	ViHMTS	>99	>99 ^d	80

^aConversion and selectivity determined by ¹H NMR. ^bIsolated yield. ^c3 mol% of Co(OPv)₂ was used. ^dNo byproduct was detected.

vinyl groups with polymethylhydrosiloxanes. Table 3 presents two examples of silicone polymer modifications, hydrosilylation of Me₂HSiO(SiMe₂O)_nSiHMe₂ (*n* ≈ 27, as determined by ¹H NMR) with α -methylstyrene or styrene, for which using an alkoxysilane as the co-catalyst was effective. Reaction of α -methylstyrene was catalyzed by the Co(OPv)₂/CNAd/(EtO)₃SiH catalyst system, whereas that of styrene was promoted by Fe(OPv)₂/CNAd/(EtO)₂MeSiH. With ~500 ppm of the metal catalyst, modification resulted in quantitative yield of the desired product. The metal residue was removed easily by passing the solution through a short pad of alumina; metal content in the modified silicone was <3 ppm (2.5 ppm for the Fe-catalyzed reaction, 0.1 ppm for the Co-catalyzed reaction).

Cross-linking of polydimethylsiloxanes having terminal and/or internal vinyl groups, and polymethylhydrosiloxanes containing terminal Me₂Si-H groups and/or internal MeSi-H moieties was performed to produce silicone resins. Model reactions, shown in Table 4, used 1-vinyl-1,1,3,3,3-tetramethyltrisiloxane (ViPMDS) or 3-vinyl-1,1,1,3,5,5,5-heptamethyltrisiloxane (ViHMTS) as the alkene, and PMDS or MD'M as the hydrosilane. All four of these combinations were hydrosilylated successfully with a 1:3 mixture of Co(OPv)₂ (1–3 mol%) and CNAd in 79–97% isolated yields with the desired selectivity. These model reactions indicated that cross-linking was possible, and a preliminary study was performed: reaction of CH₂=CHSiMe₂O(SiMe₂O)_nSiMe₂-CH=CH₂ (*n* ≈ 47, determined by ¹H NMR and ²⁹Si NMR) and Me₃SiO(Si(H)MeO)_mSiMe₃ (*m* ≈ 8, determined by ¹H

NMR and ^{29}Si NMR) with $\text{Co}(\text{OPv})_2/\text{CNAd}$ catalyst (195 ppm based on Co) at 120 °C for 15 min gave an insoluble silicone gel. Solid-state ^1H quantitative and ^{29}Si DD NMR suggested that the degree of cross-linkage was 70–80%, which was supported by IR spectroscopy. The Co residues were likely to cause coloring of the silicone gel formed, which was found to be true. The brown color of the reaction mixture due to the catalytically active Co species was maintained even when the product was kept under an atmosphere of inert gas. Surprisingly, the brown color of the silicone gel faded upon exposure to air and turned slightly pale blue to almost colorless after 12 h at room temperature, presumably due to oxidation of the catalytically active species to Co(III).

A clue to understanding the possible intermediates may be the well-known analogy of isocyanides ($\text{C}\equiv\text{NR}$) to carbon monoxide ($\text{C}\equiv\text{O}$) as a π -acceptor ligand to the metal. Similar to iron and cobalt carbonyls, isocyanide complexes of Fe(0) and Co(I) are prepared from the Fe(II) and Co(II) precursors in the presence of reducing agents. Earlier studies on the hydrosilylation of alkenes with Et_3SiH proposed involvement of $\text{Fe}(\text{CO})_3$,^{4a,c} $\text{R}_3\text{SiCo}(\text{CO})_3$,^{4d,e} and $\text{HCo}(\text{CO})_3$.^{4b} These suggest that similar coordinatively unsaturated Fe(0) or Co(I) species stabilized by $\text{C}\equiv\text{NR}$ ligands generated from Fe(II) or Co(II) carboxylates may be responsible for the present hydrosilylation. Strong affinity of silicon to oxygen contributes to generating the active species from the carboxylate precursor by hydrosilanes.

In summary, this new catalyst system consisting of cobalt or iron carboxylates and isocyanide ligands provides new non-precious-metal-based catalysts for hydrosilylation of hydro-siloxanes, which are active enough to be used in industrially important processes to modify silicone fluids and cross-link silicone polymers to silicone gels. An important feature of these multi-component catalyst systems is that all of the components (metal carboxylates, isocyanide ligands, and hydrosilanes) are stable and easily handled.¹⁸ We are now actively investigating the hydrosilylation and the further improvement of catalyst efficiency and functional group compatibility¹⁹ by combinatorial methods of catalyst screening, systematically changing the hydrosilane, alkene, metal carboxylate, isocyanide ligand, and activator with the aid of mechanistic studies.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b11311.

Experimental details and spectral data (PDF)

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Notes

The authors declare no competing financial interest.

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(17) Selected results using strong organometallic reagents, e.g., HBpin, Et_3Al , and EtMgBr , are described in the SI. With these co-catalysts, metal halides can be used instead of metal carboxylates when strong alkyl and hydride reagents are used as activators.

(18) Among the catalyst component, cobalt and iron pivalates are somewhat sensitive toward air, and storage under an inert gas atmosphere is recommended. It is notable that the iron and cobalt pivalates, after exposure to air for 72 h, possessed catalytic activity similar to that of samples maintained under an inert gas atmosphere, though the induction period was observed (for details see the SI).

(19) Functional group compatibility is a recent topic in the non-precious-metal-catalyzed hydrosilylation of alkenes. Chirik's catalyst is useful for alkenes having ether and amines,² whereas several reactions with Ph_2SiH_2 or PhSiH_3 are tolerant to carbonyl groups.^{10,11b,12} At the present stage, hydrosilylation with hydrosiloxanes is tolerant to ethers, amines, esters, and amides, but not to aldehydes and ketones.