Silylformylation of Carbonyl Compounds: A Study of Substrate, Catalyst, and Reaction Conditions

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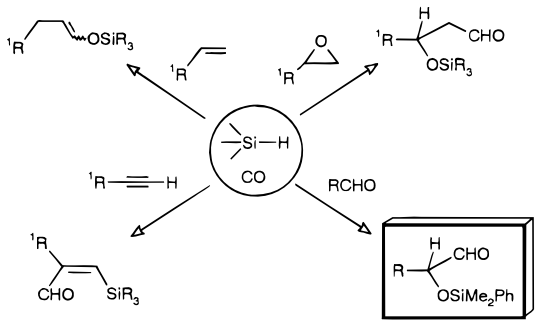
This paper presents a study of the rhodium-catalyzed silylformylation [Rh(I) precatalyst, $PhMe_2SiH$, THF, carbon monoxide (15−1500 psig), 23 °C] of aldehydes. This new catalytic homologation reaction produces α-(silyloxy) aldehydes in a highly efficient manner. Rhodium-(I) appears to be the optimum transition metal for the catalytic process. The reaction is optimized at carbon monoxide pressures over 50 psig. It appears that $PhMe_2SiH$ is the silane reagent of choice. The silylformylation of carbonyl compounds is very general for aldehyde substrates (aromatic, heterocyclic, alkyl, and ferrocenyl: 16 examples presented) and can tolerate the presence of internal alkene and alkyne, ester, and acyclic ketone functional groups. Aldehydes with α-substituents show moderately good diastereoselectivity, producing the *syn*-α-(silyloxy) aldehyde (10 to 20:1, *syn*:*anti*) as the major product. Ketone substrates possessing *β*-hydrogens yield only silyl enol ether without concomitant hydrosilylation coproducts. Imine substrates are found unreactive under normal silylformylation conditions. The rhodium-catalyzed silylformylation is a concentration- and solvent-dependent catalytic process. THF is the optimum solvent. Performing the reaction in acetonitrile or neat leads to reduced yields, and dichloromethane and benzene afford no silylformylation product. Dioxane can be used only if employed in conjunction with an auxiliary ligand (pyridine or *N*-methylpyrazole). Phosphine and phosphite ligands, both mono and bidentate, inhibit the rhodium-catalyzed silylformylation, whereas nitrogen-based ligands like 2,2′-bipyridine can be used at high ligand to metal ratios (*e.g.* ligand/rhodium, 10/1, respectively).

Introduction

Transformations involving the aldehyde functional group, both in a catalytic[1] and stoichiometric[2] fashion, have been the center piece of many elegant synthetic reports. There exist several well-known reaction sequences which produce formal homologation (*e.g.* addition of TMSCN (trimethylsilyl cyanide) followed by reduction) of aldehydes;[3] however, a single catalytic process for the homologation of aldehydes has not been discovered. The transition metal catalyzed hydroformylation of aldehydes produces only a product arising from formylation of the oxygen.[4] Following a report by Murai and co-workers[5] on the cobalt-catalyzed "silylcarbonylation" of aldehydes, we recently communicated the rhodium-catalyzed silylformylation of aldehydes and demonstrated the latter to be an excellent catalytic route for the homologation of aldehydes.[6]

Scheme 1



A variety of reactions have been reported covering treatment of a substrate with a silane reagent in the presence of carbon monoxide (Scheme 1).[7] A common theme found in the reactions is a thermodynamically driven step where an oxygen−silicon bond is formed.[7] It is apparent in the case of the rhodium-catalyzed silylformylation this facilitates formation of the new carbon−carbon bond and averts formation of a formate ester. We are continuing to find the rhodium-catalyzed silylformylation of carbonyl compounds to be an unique

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(2) *The Chemistry of the Carbonyl Group*; Patai, S., Ed.; Interscience: New York, 1966−70. *Methods of Organic Chemistry*; Houben-Weyl; G. Thieme: Stuttgart, New York, 1983; Vol. E3. For stereoselective transformations of the aldehyde group, see: Evans, D. *Aldrichim. Acta* **1982**, *15*, 23. Heathcock, C. H. *Aldrichim. Acta* **1990**, *23*, 99. Heathcock, C. H. *Science* **1981**, *214*, 395.

(3) For formation of cyanohydrins from aldehydes using trimethylsilyl cyanide see: Hayashi, M.; Miyamoto, Y.; Inoue, T.; Oguni, N. *J. Org. Chem.* **1993**, *58*, 1515. Semmelhack, M. F.; Appapillai, Y.; Sato, T. *J. Am. Chem. Soc.* **1985**, *107*, 4577.

(4) Marko, L. *Proc. Chem. Soc.* **1962**, *67*. Marko, L.; Szabo, P. *Chem. Technol. (Berlin)* **1961**, *13*, 482; *Chem. Abstr.* **1962**, *56*, 7102. Harrod, J. F.; Chalk, A. J.; Wender, I.; Pino, P. *Organic Synthesis via Metal Carbonyls*; Wiley: New York, 1977; Vol. 2, pp 12, 84.

(5) Murai, S.; Kato, T.; Sonoda, N.; Seki, Y.; Kawamoto, K. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 393. Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 837 and references cited therein.

(6) Wright, M. E.; Cochran, B. B. *J. Am. Chem. Soc.* **1993**, *115*, 2059.

(7) For a general treatment of silane/carbon monoxide reactions see: *Silicon Chemistry*; Corey, J. Y., Corey, E. R., Gasper, P. P., Eds.; Halstead Press: New York, 1988; Chapter 32. Scheme 1, alkene reaction: Chatani, N.; Ikeda, S.; Ohe, K.; Murai, S. *J. Am. Chem. Soc.* **1992**, *114*, 9710. Epoxide ring opening reaction: Fukumoto, Y.; Chatani, N.; Murai, S. *J. Org. Chem.* **1993**, *58*, 4187.

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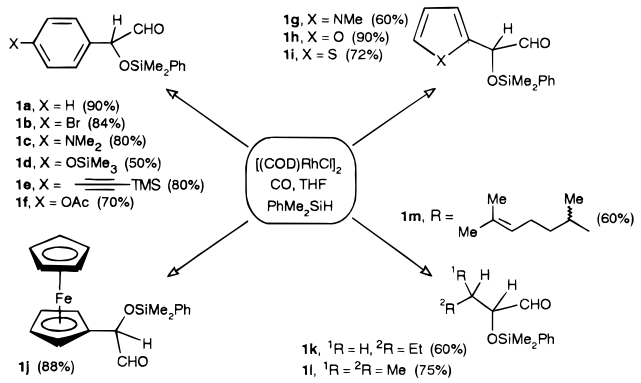
Scheme 2



and thus extremely interesting reaction from both a mechanistic and synthetic point of view.

The research groups of Ojima,[8a] Matsuda,[8b] and Doyle[8c] have made significant advances in the area of alkyne silylformylation. The change in substrate from alkyne to aldehyde introduces a variety of puzzling restrictions on silane reagent, ligand, and solvent suitability. Our investigation of this intriguing rhodium-catalyzed carbonylation reaction continues, and herein we present a comprehensive study of carbonyl and imine substrates, catalyst, and ligand and a preliminary discussion of possible mechanisms.

Results and Discussion

Substrate Survey. Carbonyl substrates for the rhodium-catalyzed silylformylation have been examined for a wide variety of aldehydes and ketones. It is apparent from the examples and yields in Scheme 2 the reaction is quite general for aldehyde substrates. The reaction can be performed in the presence of internal alkyne and alkene, an ester, and heterocyclic functional groups. In most cases analytically pure product was isolated; however, for certain samples (such as **1m**) minor byproducts (*e.g.* hydrosilylation) contaminated the sample. Use of α,*β*-unsaturated alkenes leads to a complicated array of products. We believe this indicates that 1,4-addition[9] and other more complex reactions are taking place. Electron deficient aldehydes are also poor substrates affording only partial conversion and varying amounts of hydrosilylation byproducts. This may indicate that *σ*-bonding of the carbonyl group to the metal is an important factor for binding of the aldehyde substrate. Gladysz and co-workers recently described effects on aldehyde coordination to cationic rhenium complexes.[10] The study produced strong evidence that *π*-coordination is favored in aldehydes with electron-withdrawing groups. Stereoelectronic factors may also play an important role in the migratory amplitude[11] of the (α-silyloxy)alkyl intermediate in the catalytic cycle.

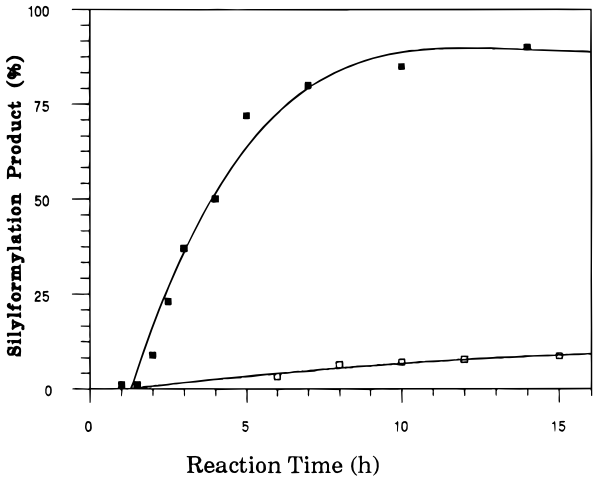
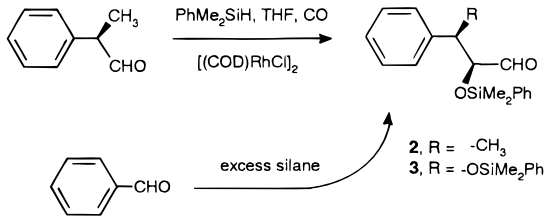


Figure 1. Relative rate study for the reaction of benzaldehyde (■) and **1a** (□) with dimethylphenylsilane, carbon monoxide, and $[(COD)RhCl]_2$.

Scheme 3



Treatment of α-substituted aldehydes under the conditions of silylformylation affords predominately the *syn*-isomer (J = 4.4 Hz for the *syn*-isomer versus J = 6.4 Hz for the *anti*-isomer) with moderately good diastereoselectivity for *syn*-isomer (*syn*/*anti* ratios varying from 10 to 20) (Scheme 3). The stereoselectivity can be modeled by applying Cram's rule[12] to coordination (reversible) of the catalyst to the least hindered carbonyl face, followed by a stereospecific and irreversible migratory-insertion step.[13]

The success found in the rhodium-catalyzed silylformylation lies in the ability of the catalyst to differentiate between substrate−aldehyde and the newly formed α-(silyloxy) aldehyde. We have determined the relative rates of reaction for benzaldehyde and **1a** under similar reaction conditions. A plot of the relative rate data is presented in Figure 1. Modeling of **3** by molecular mechanics indicates the carbonyl group is severely congested at both the *re*- and *si*-faces.[14]

Taking optimum silylformylation conditions {*i.e.* THF, $PhMe_2SiH$, CO (500 psig), $[(COD)RhCl]_2$} and introduc-

(8) (a) Ojima, I.; Tzamarioudaki, M.; Tsai, C. *J. Am. Chem. Soc.* **1994**, *116*, 3643. Ojima, I.; Donovan, R. J.; Eguchi, M.; Shay, W. R.; Ingallina, P.; Korda, A.; Zeng, Q. *Tetrahedron* **1993**, *49*, 5431. Ojima, I.; Donovan, R. J.; Ingallina, P.; Clos, N.; Shay, W. R.; Eguchi, M.; Zeng, Q.; Korda, A. *J. Cluster Sci.* **1992**, *3*, 423. Ojima, I.; Ingallina, P.; Donovan, R. J.; Clos, N. *Organometallics* **1991**, *10*, 38. (b) Matsuda, I.; Sakakibara, J.; Inoue, H.; Nagashima, H. *Tetrahedron Lett.* **1992**, 5799. Matsuda, I.; Ogiso, A.; Sato, S. *J. Am. Chem. Soc.* **1990**, *112*, 6120. Matsuda, I.; Ogiso, A.; Sato, S.; Izumi, Y. *J. Am. Chem. Soc.* **1989**, *111*, 2332. (c) Doyle, M. P.; Shanklin, M. S. *Organometallics* **1993**, *12*, 11. (d) For an additional and important contribution, see: Zhou, J. Q.; Alper, H. *Organometallics* **1994**, *13*, 1586.

(9) Ojima, I.; Kogure, T.; Nagai, Y. *Tetrahedron Lett.* **1972**, 5035. Ojima, I.; Tetsou, K. *Organometallics* **1982**, *1*, 1390. Sadykh-Zade, S. I.; Petrov, A. D. *Zh. Obshch. Khim.* **1959**, *29*, 3194.

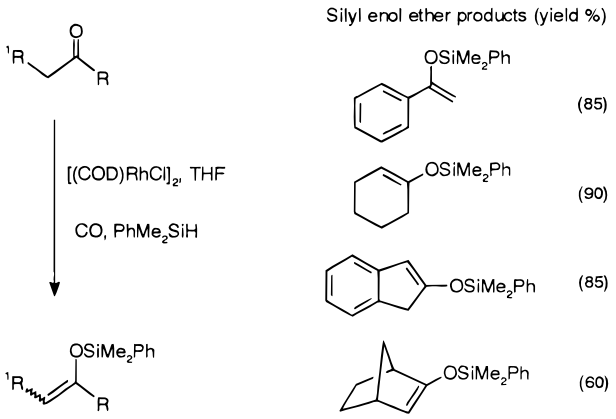
(10) Gladysz, J. A.; Klein, D. P. *J. Am. Chem. Soc.* **1992**, *114*, 8710. Gladysz, J. A.; Mendez, N. Q.; Arif, A. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *12*, 1473. Gladysz, J. A.; Mendez, N. Q.; Arif, A. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *12*, 1475. Gladysz, J. A.; Huang, Y.-H. *J. Chem. Educ.* **1988**, *65*, 298.

(11) Gladysz, J. A.; Selover, J. C.; Strouse, C. E. *J. Am. Chem. Soc.* **1978**, *100*, 6766.

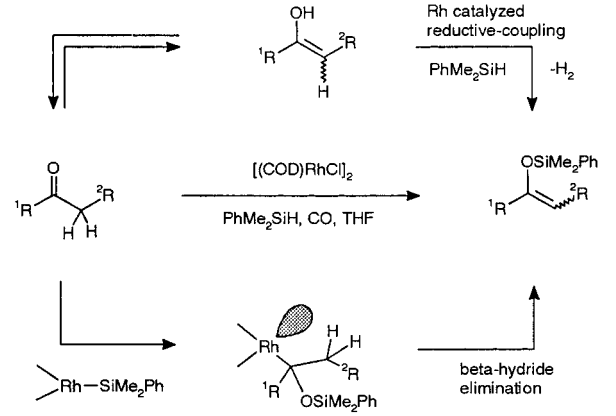
(12) Cram, D. J.; Elhafez, F. A. *J. Am. Chem. Soc.* **1952**, *74*, 5828. Cram, D. J.; Kopecky, K. R. *J. Am. Chem. Soc.* **1959**, *81*, 2748. Leitereg, T. J.; Cram, D. J. *J. Am. Chem. Soc.* **1968**, *90*, 4019.

(13) Ojima, I.; Kogure, T.; Kumagai, M.; Horiuchi, S.; Sato, T. *J. Organomet. Chem.* **1976**, *122*, 83. Hayashi, T.; Yamamoto, K.; Kasuga, K.; Omizu, H.; Kumada, M. *J. Organomet. Chem.* **1976**, *113*, 127. Yamamoto, K.; Hayashi, T.; Kumada, M. *J. Organomet. Chem.* **1973**, *54*, C45.

Scheme 4

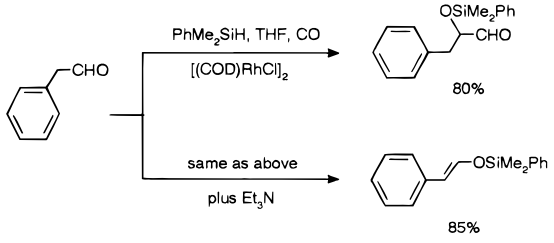


Scheme 5



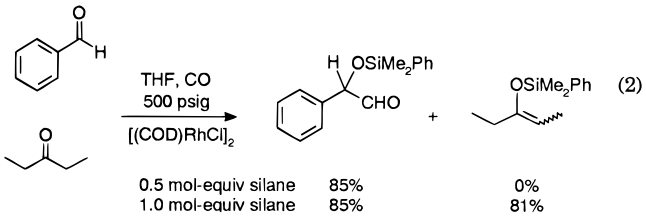
ing a ketone substrate with β-hydrogens leads to an efficient production of the silyl enol ether with no competitive hydrosilylation (Scheme 4).[15] The regio- and diastereoselectivity of the silyl enol formation for 3-pentanone and 2-butanone is very similar to that seen earlier by Sakurai *et al.* in a cobalt-catalyzed reaction.[16] However, the present catalytic system produces only silyl enol ether with no concomitant hydrosilylation observed (*e.g.* with acetophenone).

Even when we use 2-norbornanone, where silyl enol ether formation introduces significant ring strain,[17] we still observe only formation of the silyl enol ether (**4**) in 60% isolated yield. Only in the case of cyclobutanone do we observe what we believe is silylformylation; however, the product aldehyde apparently undergoes a ring-opening reaction before it can be isolated.[18] The readily enolizable aldehyde phenylacetaldehyde undergoes silylformylation under standard silylformylation conditions but yields silyl enol ether exclusively when 1 equiv of triethylamine is present (eq 1).



(1)

We have tested the compatibility of ketone and aldehyde functional groups by performing competition reaction studies involving the two substrates (eq 2).

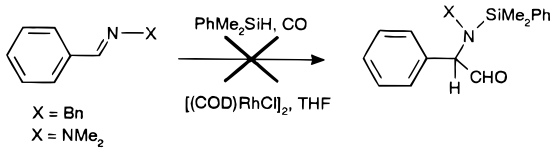


(2)

Reactions are carried out with various ratios of silane reagent using an equal molar ratio of aldehyde and ketone. With limited silane reagent we observe excellent selecitivity for the aldehyde and recovery of the ketone (acyclic). On the other hand, we observe that "cyclohexanone" (or the enol ether) is a better substrate than benzaldehyde and silyl enol ether formation is dominant.

There are two likely pathways for silyl enol ether formation as shown in Scheme 5, and to our knowledge, neither pathway should be discounted since both appear to have ample precedence in the literature. Aldehydes are in general known to exist in the enol tautomeric form at higher concentrations compared to related ketones.[19] A ketone will coordinate to a transition metal much weaker than a related aldehyde based on steric considerations.[20] Even though the enol tautomers exist at very low steady state concentrations, the rhodium-catalyzed reductive-coupling[21] of the silane with the enol may be relatively fast for ketones when compared to a pathway requiring π-coordination of the ketone and a subsequent migratory-insertion step. In the case of a readily enolizable aldehyde, like phenylacetaldehyde, we can "tip the balance" and go from clean silylformylation to that of only silyl enol ether formation by simply adding triethylamine (5 mol %). β-Hydride elimination prior to migratory-insertion of the α-(silyloxy)alkyl species to carbon monoxide is certainly a possibility which must also be considered.

We have briefly explored the use of imine substrates[22] and find in general they are not suitable for silylformylation (eq 3). For the case of an imine possessing a



(3)

coordinating group (*i.e.* NMe_2) on the nitrogen we observe silylformylation; however, it appears to be the

(14) Calculations were performed using MMX (contained in Alingers PCM4).
(15) Ojima, I.; Yamamoto, K.; Kumada, M. In *Aspects of Homogenous Catalysis*; Reidel: Dordrecht, The Netherlands, 1977; Vol. 3, p 186.
(16) Sakurai, H.; Miyoshi, K.; Nakadaira, Y. *Tetrahedron Lett.* **1977**, 2671.
(17) Máksić, Z. B.; Kovaćevic, K.; Eckert-Maksić, M. *Tetrahedron Lett.* **1975**, *2*, 101.
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(19) Gero, J. *J. Org. Chem.* **1954**, *19*, 469.
(20) Ojima, I.; Nagai, Y. *J. Organomet. Chem.* **1973**, *57*, C42.
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(22) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 7562. Burk, M. J.; Feaster, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 6266. Kang, G. J.; Cullen, W. R.; Fryzuk, M. D.; James, B. R.; Kutney, J. P. *J. Chem. Soc. Commun.* **1988**, 1466.

Scheme 6

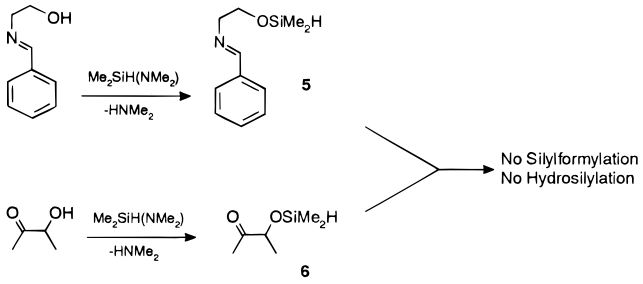

Table 1. Catalyst Survey[a]

catalyst	silylformylation (%)	hydrosilylation (%)
$[Rh(COD)Cl]_2$	92	0
$[Rh(CO)_2Cl]_2$	90	0
$[Ru(COD)Cl]_n$	0	0
$PdCl_2/SnCl_2$	0	0
$(PPh_3)_2PtCl_2/SnCl_2$	0	50

[a] Catalyst at 10 mol %, 1000 psig carbon monoxide, 1.0 equiv of Me_2PhSiH.

silylformylation of benzaldehyde which is produced by hydrolysis of the imine.

We prepared an imine (**5**) and a ketone (**6**) each containing a tethered silyloxy−hydride group poised to carry out an *intramolecular-silylformylation* (Scheme 6).[23] We found each substrate to be unreactive under silylformylation conditions. In the absence of carbon monoxide we also found the intramolecular-hydrosilylation chemistry to be extremely slow using the $[(COD)RhCl]_2$ precatalyst.

Catalyst, Carbon Monoxide Pressure, and Ligand Survey. We have explored the use of other rhodium complexes and different transition metal as potential catalysts for the silylformylation (Table 1). The results to date show $[(COD)RhCl]_2$ to be the most convenient and efficient precatalyst and the ruthenium system catalytically inactive.[24] Notably, the platinum−tin complex mixture, which is known to be an effective hydroformylation catalyst,[25] affords only hydrosilylation chemistry.

We have also tried the reaction in a variety of solvents and have discovered a remarkable solvent dependence (Table 2). THF is clearly the solvent of choice, yielding 90% silylformylation in ∼8 h under the very low carbon monoxide pressures. Surprisingly, the $[(COD)RhCl]_2$ catalyst in dioxane produced no silylformylation unless specific nitrogen ligands (*i.e. N*-methylpyrazole, pyridine) are used and this is discussed below. This "ligand-assisted" silylformylation proceeds cleanly but at a relative rate that is much slower than the reactions in THF.[26]

We initially speculated that the presence of a strongly coordinating solvent (*i.e.* THF) is vital for the success

Table 2. Solvent Survey for Rhodium-Catalyzed Silylformylation of Benzaldehyde

solvent	silylformylation (%)	hydrosilylation (%)
neat[a]	55	15
THF	95	0
acetonitrile[b]	40	0
benzene	0	95
dichloromethane	0	15
dioxane	0	0
diethyl ether	0	0
pyridine	0	50

[a] 10 mol % $[(COD)RhCl]_2$ used. [b] These conditions result in only 65% silylformylation after 48 h (100% silane is consumed).

Table 3. Dependence on THF for the Rhodium-Catalyzed Silylformylation of Benzaldehyde[a]

solvent THF/benzene	silylformylation (%)	hydrosilylation (%)
10/90	0	10
20/80	15	4
30/70	16	3
40/60	71	0
80/20	80	0

[a] 2 mol % $[(COD)RhCl]_2$ and 500 psig carbon monoxide.

of silylformylation. We used 2,5-dimethylfuran which is known to slow reactions which utilize the nucleophilicity of THF; however, in the present case (*i.e.* silylformylation) we see no reaction.[27] Furthermore, solvent mixtures containing THF (*e.g.* 10% THF in benzene, CH_2Cl_2, and dioxane) do not work. For each of these mixtures no trace of silylformylation is observed. Then at what point is there sufficient THF to "promote" silylformylation?

We have carried out a series of experiments systematically varying the percentage of THF from 10 to 90%, and the results are summarized in Table 3. At a low percentage of THF we observe *inhibition of both silylformylation and hydrosilylation!* When ∼40% THF is present, the silylformylation catalytic process "kicks in" and we observe almost exclusively the product of silylformylation. It is possible that some catalytic species in the reaction sequence is trapped or formed very slowly in the mixtures containing less than ∼40% THF. Another possibility is that the THF is activating the silane reagent through complexation in some manner, hence promoting a crucial step in the catalytic sequence.

The effects of varying carbon monoxide on the reaction are presented in Figure 2. Benzaldehyde undergoes clean silylformylation at 50 psig of carbon monoxide and at a rate comparable to that observed at 1500 psig of carbon monoxide.[28] For aliphatic aldehydes we see a noticeable decrease in rate at the lower pressure. We observe at 15 psig of carbon monoxide pressure that hydrosilylation and silylformylation are occurring at approximately the same rate for benzaldehyde. This is coupled with a very poor substrate conversion (combined ∼30% in 24 h). We also find that the carbonyl substrate must be extremely dry and pure when using lower carbon monoxide pressures. Silylformylation is inhibited by trace amounts of water whereas the rhodium-catalyzed hydrosilylation of the substrate proceeds at a relatively unaffected rate. A catalytic species involved for silylformylation might be destroyed by trace amounts

(23) Bergens, S. H.; Noheda, P.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 2121. Bergens, S. H.; Noheda, P.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 2128.

(24) For examples of ruthenium hydroformylation catalysts, see: Strohmeier, W.; Weigelt, L. *J. Organomet. Chem.* **1979**, *171*, 121. Sanchez-Delgado, R. A.; Bradley, J. S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 399. Evans, D.; Osborn, J. A.; Jardine, F. H.; Wilkinson, G. *Nature* **1965**, *208*, 1203.

(25) Schwager, I.; Knifton, J. F. *J. Catal.* **1976**, *45*, 256. Parrinello, G.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 7122. Clark, H. C.; Davies, J. A. *J. Organomet. Chem.* **1981**, *213*, 503. Scrivanti, A.; Paganelli, S.; Mateoli, U.; Botteghi, C. *J. Organomet. Chem.* **1990**, *385*, 439.

(26) The reaction takes 48 h for completion.

(27) Wax, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 7028.

(28) Reaction complete in 8 h under optimum conditions.

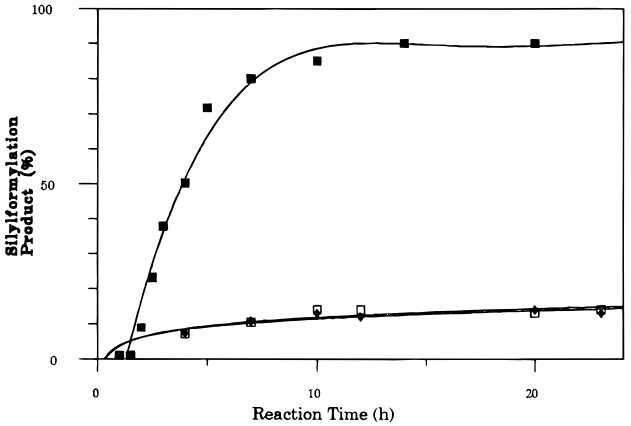

Figure 2. Rhodium-catalyzed silylformylation of benzaldehyde at 50 psig (■) and 15 psig (□, silylformylation product; ♦, hydrosilylation byproduct) of carbon monoxide pressure.

Table 4. Phosphine and Phosphite Ligand Survey Using [(COD)RhCl]$_2$

ligand	solvent	*T* (°C)	silylformylation (%)	hydrosilylation (%)
Ph_3P	THF	25	0	0
Ph_3P	AN	25	0	0
Ph_3P	THF	50	0	0
$(PhO)_3P$	THF	25	0	0
$(PhO)_3P$	THF	50	0	0
DIPHOS	THF	25	0	0
DIPHOS-F_{20}[a]	THF	25	20	0

[a] DIPHOS-F_{20} = $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$.

Table 5. Phosphine Ligands Using Cationic Rhodium(I)

catalyst	silylformylation (%)	hydrosilylation (%)
{(COD)Rh(PPh_3)$_2$}[ClO_4]	0	50
{(COD)Rh[$P(OPh)_3$]$_2$}[ClO_4]	0	50
{(COD)Rh(diphos)}[ClO_4]	0	5

of water whereas the catalytic pathway for hydrosilylation is unaffected.

A number of different ligands have been tried in conjunction with the precatalyst, [(COD)RhCl]$_2$, in order to assess the potential of developing an asymmetric version of silylformylation. The use of chiral phosphine ligands in asymmetric catalysis is well-established.[29] We find that addition (1 mol equiv/Rh, either chelating or monodentate) of typical phosphine and phosphite ligands leads to a total loss of catalyst activity (Tables 4 and 5). The silane and starting aldehyde are usually recovered intact, although in some cases we observe decomposition of silane reagent (reductive-coupling). Moderate heating (~50 °C) only leads to decomposition of the silane. Perchlorate salts of phosphine and phosphite cationic rhodium(I) precatalysts produce the product of hydrosilylation or exhibit no catalytic activity. The only phosphine to show catalytic activity was DIPHOS-F_{20}. It is very possible that because this ligand possesses diminished σ-donating capabilities it might be dissociating and in fact the silylformylation chemistry is carried out by a phosphine-free rhodium complex.[30]

Table 6. Nitrogen Ligands for the Rhodium-Catalyzed Silylformylation[a]

ligand	solvent	silylformylation (%)	hydrosilylation (%)
bipyridine	THF	93	0
N-Mepyr	dioxane	85	0
pyridine	dioxane	80	0
bipyridine	dioxane	0	0
N-Mepyr	benzene	0	<5
N-Mepyr	CH_2Cl_2	0	<5

[a] 2 mol % [(COD)RhCl]$_2$ and 500 psig carbon monoxide. Ligands were all employed at a ligand/rhodium ratio of 10.

Chiral nitrogen ligands have been shown to excel in the asymmetric hydrosilylation of ketones, and so we explored their compatibility in silylformylation chemistry.[31] It is gratifying to find that nitrogen ligands do not inhibit silylformylation even at relatively high ligand/rhodium ratios (Table 6). As noted earlier, *N*-methylpyrazole and pyridine are in fact essential for silylformylation to occur in dioxane. The addition of 2,2′-bipyridine is found to significantly diminish the formation of poly(THF), which is seen in silylformylation reactions requiring reaction times greater than 24 h.[32]

Silane Reagent Survey. One of our most intriguing observations is that only $PhMe_2SiH$ will carry out the silylformylation of aldehydes. We find that alkoxy, phenyl, or alkyl substitution leads to a complete shut down of silylformylation chemistry. In some cases the silane reagents are recovered intact, and in other examples they are consumed (*e.g.* reductive coupling). It is noteworthy to point out that in the silylformylation of alkynes a variety of silane reagents can be used.[8]

Comments on the Mechanism of Silylformylation. We have gathered a considerable amount of information on experimental factors which have a direct effect on the performance and outcome of the rhodium-catalyzed silylformylation of carbonyl compounds. The mechanism for the hydrosilylation of alkynes has recently been independently investigated by the groups of Crabtree[33] and Ojima.[34] There is quite uniform agreement concerning the mechanism of hydrosilylation for the key step of migratory-insertion. However, the implication of a bimetallic catalytic step(s) has not been considered for rhodium-catalyzed hydrosilylation chemistry. With recent evidence suggesting this is important for rhodium-catalyzed hydroformylation catalysts,[35] we believe it should also be considered for silylformylation. With this in mind, we propose the mechanistic pathways for the rhodium-catalyzed silylformylation of carbonyl compounds shown in Scheme 7.

Our results illustrate that silylformylation and hydrosilylation have some very distinct and important differences, the specificity for the silane reagent $PhMe_2SiH$ being one. Second, there is the tremendous solvent dependency for our silylformylation reaction which is

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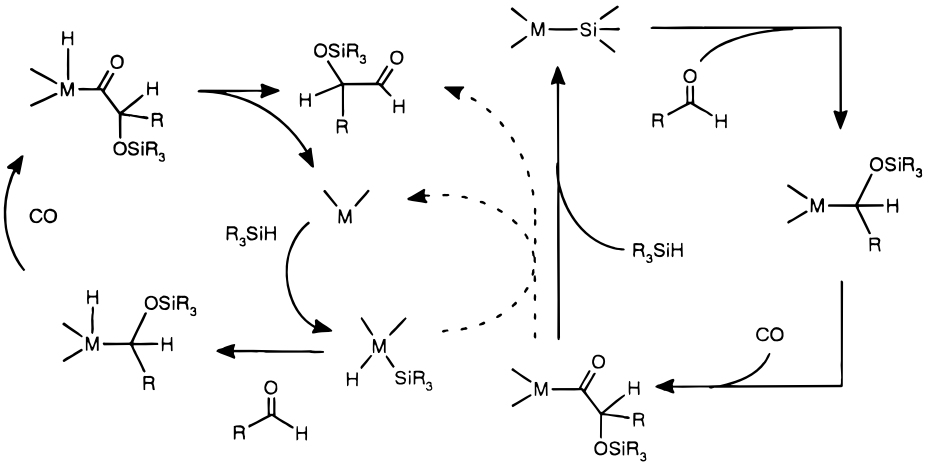
Scheme 7



not seen in hydrosilylation chemistry or for that matter in the silylformylation of alkynes. The outstanding performance of aldehydes relative to ketones is also unique to silylformylation. These differences suggest that the silylformylation of carbonyl compounds involves a very unique and intriguing mechanistic pathway.

The mechanism for the silylformylation of carbonyl compounds invokes an intriguing set of questions varying from the fundamental aspects carbonyl coordination chemistry to the possible involvement of bimetallic reaction steps. A more detailed analysis of each proposed catalytic step is needed in order to better understand the catalytic cycle leading to a strategy to optimize and further exploit the silylformylation of carbonyl-like substrates.

Experimental Section

Methods. All manipulations of compounds and solvents were carried out using standard Schlenk techniques. Solvents were degassed and purified by distillation under nitrogen from standard drying agents. Spectroscopic measurements utilized the following instrumentation: ^{1}H NMR, Varian XL 300; ^{13}C NMR, JOEL-270, Varian XL 300 (at 75.4 MHz); infrared, Perkin-Elmer 1750 FT-IR. NMR chemical shifts are reported in δ versus Me_4Si in ^{1}H NMR and with assignment of the $CDCl_3$ resonance at 77.0 ppm in ^{13}C spectra. All aldehyde and ketone substrates, phosphorus ligands, $[(C_2H_4)_2RhCl]_2$, and $[(COD)RuCl]_n$ were purchased from Aldrich Chemical Co. The $PtCl_2$, $PdCl_2$, and $RhCl_3$ (hydrate) were purchased from Alpha Chemical Co. $[(CO)_2RhCl]_2$ and $(CO)_2RuCl_2(PPh_3)_2$ were purchased from Strem Chemicals. The $[(COD)RhCl]_2$,[36] $(PPh_3)_2PtCl_2$,[37] and rhodium cationic complexes[38] were prepared from the literature methods. All silane reagents were purchased from Huls America.

General Procedure for Silylformylation of Aldehydes. A round-bottom flask (50 mL) was charged with the appropriate aldehyde (1.5 mmol), dimethylphenylsilane (0.20 g, 1.5 mmol), and THF (8 mL). The mixture was degassed by three consecutive freeze−pump−thaw cycles and then cannulated into a nitrogen-purged glass vessel containing $[(COD)RhCl]_2$ (1.9 mg, 3.8×10^{-3} mmol, 0.5 mol %). The glass vessel was placed in a stainless steel bomb and purged three times with carbon monoxide {50 ⇔ 500 psig}. The bomb was brought to the desired reaction pressure and stirred at room temperature for 24 h. The glass vessel was removed from the bomb, and the solvent removed under reduced pressure. The reaction mixture was analyzed by ^{1}H NMR using 1,1,1-trichloroethane as an internal standard to obtain the NMR yields. Purification of the α-(silyloxy) aldehyde was achieved through distillation at 0.1 mmHg.

$C_6H_5CH(OSiMe_2Ph)CHO$ (1a): 90%, bp 130−140 °C at 0.1 mmHg; ^{1}H NMR ($CDCl_3$) δ 9.52 (s, 1 H, CHO), 7.55−7.28 (m, 10 H, Ar H), 4.99 (s, 1 H, C*H*CHO), 0.43, 0.37, 0.33 (s's, 6 H, Si CH_3's); ^{13}C NMR ($CDCl_3$) δ 198.4 (CHO), 139.4 (Ar C), 136.3 (Ar C), 135.9 (Ar C), 133.3 (Ar CH), 132.8 (Ar CH), 132.7 (Ar CH), 130.0 (Ar CH), 129.7 (Ar CH), 129.0 (Ar CH), 128.5 (Ar CH), 128.3 (Ar CH), 128.2 (Ar CH), 128.1 (Ar CH), 128.0 (Ar CH), 127.8 (Ar CH), 127.5 (Ar CH), 126.5 (Ar CH), 126.2 (Ar CH), 79.9 (*C*HCHO), 0.6, −1.4, −1.6, (Si CH_3's); IR (CH_2Cl_2) $\nu_{C=O}$ 1736 cm^{-1}. Anal. Calcd for $C_{16}H_{18}O_2Si$: C, 71.06; H, 6.72. Found: C, 71.12; H, 6.94.

{4-BrC_6H_4}CH(OSiMe$_2$Ph)CHO (1b): 84%, bp 130−140 °C at 0.1 mmHg; ^{1}H NMR ($CDCl_3$) δ 9.49 (s, 1 H, CHO), 7.54−7.20 (m, 9 H, Ar CH), 4.92 (s, 1 H, C*H*CHO), 0.44, 0.38 (s's, 6 H, Si CH_3's); ^{13}C NMR ($CDCl_3$) δ 198.7 (CHO), 136.1 (Ar C), 135.2 (Ar C), 133.4 (Ar CH), 132.9 (Ar CH), 131.8 (Ar CH), 131.7 (Ar CH), 130.1 (Ar CH), 129.2 (Ar CH), 128.2 (Ar CH), 128.0 (Ar CH), 127.8 (Ar CH), 127.6 (Ar CH), 122.5 (Ar C), 79.4 (*C*HCHO), −1.3, −1.4 (Si CH_3's); IR (CH_2Cl_2) $\nu_{C=O}$ 1731 cm^{-1}. Anal. Calcd for $C_{16}H_{17}O_2BrSi$: C, 55.01; H, 4.91. Found: C, 54.91: H, 4.95.

{4-(Me$_2$N)C_6H_4}CH(OSiMe$_2$Ph)CHO (1c): 80%, bp 130−140 °C at 0.1 mmHg; ^{1}H NMR ($CDCl_3$) δ 9.48 (s, 1 H, CHO), 7.56−7.53 (m, 2 H, Ar CH), 7.40−7.33 (m, 3 H, Ar CH), 7.18−7.16 (m, 2 H, Ar CH), 6.71−6.68 (m, 2 H, Ar CH), 4.91 (s, 1 H, C*H*CHO), 2.92 (s, 6 H, $N(CH_3)_2$), 0.40, 0.34, 0.33 (s's, 6 H, Si CH_3's); ^{13}C NMR ($CDCl_3$) δ 198.3 (CHO), 150.4 (Ar C), 136.7 (Ar C), 133.3 (Ar CH), 132.8 (Ar CH), 132.7 (Ar CH), 129.6 (Ar CH), 129.0 (Ar CH), 128.0 (Ar CH), 127.8 (Ar CH), 127.7 (Ar CH), 127.5 (Ar CH), 123.0 (Ar C), 112.3 (Ar CH), 79.8 (*C*HCHO), 40.1 (NCH_3), 0.7, −1.2, −1.5 (Si CH_3's); IR (CH_2Cl_2) $\nu_{C=O}$ 1733 cm^{-1}. Anal. Calcd for $C_{18}H_{23}NO_2Si$: C, 68.96; H, 7.41. Found: C, 68.96; H, 7.49.

{4-(Me$_3$SiO)C_6H_4}CH(OSiMe$_2$Ph)CHO (1d): 50%, bp 130−140 °C at 0.1 mmHg; ^{1}NMR ($CDCl_3$) δ 9.50 (s, 1 H, CHO), 7.54−7.49 (m, 2 H, Ar CH), 7.43−7.29 (m, 3 H, Ar CH), 7.20−7.17 (m, 2 H, Ar CH), 6.86−6.81 (m, 2 H, Ar CH), 4.93 (s, 1 H, C*H*CHO), 0.41, 0.35, 0.26 (3 s, 15 H, Si CH_3's); ^{13}C NMR ($CDCl_3$) δ 199.0 (CHO), 155.5 (Ar C), 136.6 (Ar C), 133.5 (Ar CH), 129.9 (Ar CH), 128.9 (Ar C), 128.1 (Ar CH), 127.9 (Ar CH), 127.6 (Ar CH), 120.3 (Ar CH), 79.8 (*C*HCHO), 0.2, −1.2, −1.4 (Si CH_3's); IR (CH_2Cl_2) $\nu_{C=O}$ 1733 cm^{-1}. Anal. Calcd for $C_{19}H_{26}O_3Si_2$: C, 63.63; H, 7.32. Found: C, 63.84; H, 7.09.

{4-(2-(trimethylsilyl)ethynyl)C_6H_4}CH(OSiMe$_2$Ph)-CHO (1e). 1e was purified by flash chromatography on deactivated alumina (elution with 40% ethyl acetate/hexanes).

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The sample could not be obtained in analytically pure form. ^{1}H NMR ($CDCl_3$): δ 9.50 (s, 1 H, CHO), 7.55−7.27 (m, 9 H, Ar CH), 4.95 (s, 1 H, C*H*CHO), 0.43, 0.37, 0.33 (3 s, 6 H, Si CH_3's), 0.27 (s, 9 H, Si CH_3's). Selected ^{13}C NMR ($CDCl_3$) data: δ 198.5 (CHO), 133.4 (Ar CH), 132.2 (Ar CH), 129.7 (Ar CH), 126.4 (Ar CH), 104.5 (Ar*C*≡C), 94.8 (ArC≡*C*), 79.7 (*C*HCHO), 0.8, −0.2, −1.4 (Si CH_3's); IR (CH_2Cl_2) $\nu_{C=O}$ 1736 cm^{-1}.

{(4-acetoxy)C$_6$H$_4$}CH(OSiMe$_2$Ph)CHO (1f): 90%, bp 140−150 °C at 0.1 mmHg; ^{1}H NMR ($CDCl_3$) δ 9.49 (s, 1 H, C*H*O), 7.54 (d, J = 1.8 Hz, 2 H, Ar H), 7.40−7.34 (m, 5 H, Ar CH), 7.10 (d, J = 1.8 Hz, 2 H, Ar CH), 4.98 (s, 1 H, C*H*CHO), 2.27 (s, 3 H, CH_3), 0.44, 0.39, 0.33 (s's, 6 H, Si CH_3's); ^{13}C NMR ($CDCl_3$) δ 198.5 (CHO), 169.0 (CO_2), 150.6 (Ar C), 133.5 (Ar C), 133.3 (Ar CH), 132.8 (Ar CH), 129.9 (Ar CH), 127.9 (Ar CH), 127.5 (Ar CH), 121.8 (Ar CH), 79.3 (*C*HCHO), 20.8 (CH_3), −1.4, −1.5 (Si CH_3's); IR (CH_2Cl_2) $\nu_{C=O}$ 1736 cm^{-1}.

{2-(*N*-methylpyrroyl)}CH(OSiMe$_2$Ph)CHO (1g): 60%, bp 110−120 °C at 0.1 mmHg; ^{1}H NMR ($CDCl_3$) δ 9.60 (s, 1 H, CHO), 7.61−7.32 (m, 5 H, Ar H), 6.58−6.55 (m, 1 H, pyrrole CH), 6.07 (m, 2 H, pyrrole CH's), 5.09 (s, 1 H, C*H*CHO), 3.41 (s, 3 H, NCH_3), 0.38, 0.33, 0.30 (s's, 6 H, Si CH_3's); ^{13}C NMR δ 197.1 (CHO), 136.4 (Ar C), 133.4 (Ar CH), 133.3 (Ar CH), 129.6 (Ar CH), 129.4 (Ar CH), 127.7 (Ar CH), 127.6 (pyrrole C), 126.8 (pyrrole C), 124.4 (pyrrole CH), 110.9 (pyrrole CH), 107.3 (pyrrole CH), 74.5 (*C*HCHO), 35.6 (NCH_3), 0.7, −1.5, −1.8 (Si CH_3's); IR (CH_2Cl_2) $\nu_{C=O}$ 1738 cm^{-1}. Anal. Calcd for $C_{15}H_{19}NO_2Si$: C, 65.66; H, 7.14. Found: C, 65.88; H, 7.02.

{2-furyl}CH(OSiMe$_2$Ph)CHO (1h): 90%, bp 90−100 °C at 0.1 mmHg; ^{1}H NMR ($CDCl_3$) δ 9.63 (s, 1 H, CHO), 7.60−7.52 (m, 2 H, Ar CH), 7.43−7.32 (m, 4 H, Ar CH and furyl CH), 6.34−6.32 (m, 1 H, furan CH), 6.28−6.26 (m, 1 H, furyl CH), 5.02 (s, 1 H, C*H*CHO), 0.40, 0.35, 0.33 (s's, 6 H, Si CH_3's); ^{13}C NMR ($CDCl_3$) δ 196.8 (CHO), 149.3 (furyl C), 143.3 (furyl CH), 136.2 (Ar C), 133.4 (Ar CH), 132.8 (Ar CH), 129.8 (Ar CH), 129.1 (Ar CH), 127.8 (Ar CH), 127.5 (Ar CH), 110.4 (furyl CH), 109.7 (furyl CH), 73.8 (*C*HCHO), 0.7, −1.5, −1.9 (Si CH_3's); IR (CH_2Cl_2) $\nu_{C=O}$ 1736 cm^{-1}. Anal. Calcd for $C_{14}H_{16}O_3Si$: C, 64.57; H, 6.21. Found: C, 64.41; H, 6.24.

{2-thiophenyl}CH(OSiMe$_2$Ph)CHO (1i): 72%, bp 90−100 °C at 0.1 mmHg; ^{1}H NMR ($CDCl_3$) δ 9.52 (s, 1 H, CHO), 7.57−7.27 (m, 7 H, Ar CH/thiophene CH), 7.01−6.95 (m, 1 H, thiophene CH), 5.19 (s, 1 H, C*H*CHO), 0.44, 0.40, 0.33 (3 s, 6 H, Si CH_3's); ^{13}C NMR ($CDCl_3$) δ 196.9 (CHO), 139.4 (Ar C), 136.1 (Ar C), 133.5, 132.9, 130.0, 129.2, 127.5, 127.6, 127.2, 126.3, 125.3 (Ar and thiophene CH's), 76.2 (*C*HCHO), 0.8, −1.3, −1.6 (Si CH_3's); IR (CH_2Cl_2) $\nu_{C=O}$ 1737 cm^{-1}. Anal. Calcd for $C_{14}H_{16}O_2SSi$: C, 60.84; H, 5.83. Found: C, 60.40; H, 6.10.

{η^5-C$_5$H$_5$}Fe{η^5-C$_5$H$_4$CH(OSiMe$_2$Ph)CHO} (1j): 88%, purified by flash chromatography through deactivated fluorosil; ^{1}H NMR ($CDCl_3$) δ 9.61, 9.62 (s's, 1 H, CHO), 7.59−7.34 (m, 5 H, phenyl CH's), 4.74 (s, 1 H, C*H*CHO), 4.21−4.17 (m, 3 H, Cp CH's), 4.11 (s, 5 H, Cp), 4.04−4.03 (m, 1 H, Cp CH), 0.40, 0.38, 0.33 (3s, 6 H, Si CH_3's); ^{13}C NMR ($CDCl_3$) δ 196.9 (CHO), 136.9 (Ar C), 133.5 (Ar CH), 132.9 (Ar CH), 129.8 (Ar CH), 129.2 (Ar CH), 127.9 (Ar CH), 127.6 (Ar CH), 82.1 (Cp C), 75.6 (Cp CH), 68.8 (*C*HCHO), 68.6 (Cp CH), 68.4 (Cp CH), 68.3 (Cp CH), 67.5 (Cp CH), 66.6 (Cp CH), 0.8, −1.0, −1.1 (Si CH_3's); IR (CH_2Cl_2) $\nu_{C=O}$ 1734 cm^{-1}. Anal. Calcd for $C_{20}H_{22}O_2SiFe$: C, 63.49; H, 5.86. Found: C, 63.26; H, 6.10.

CH$_3$(CH$_2$)$_2$CH(OSiMe$_2$Ph)CHO (1k): 60%, bp 90−100 °C at 0.1 mmHg; ^{1}H NMR ($CDCl_3$) δ 9.55 (s, 1 H, CHO), 7.59−7.31 (m, 5 H, Ar CH), 3.97 (dt, J = 6.5, 1.2 Hz, 1 H, C*H*CHO), 1.81−1.30 (m, 4 H, CH_2's), 0.86 (t, J = 7.3 Hz, 3 H, CH_3), 0.43, 0.42, 0.33 (s's, 6 H, Si CH_3's); ^{13}C NMR ($CDCl_3$) δ 203.5 (CHO), 136.8 (Ar C), 133.4 (Ar CH), 133.3 (Ar CH), 132.9 (Ar CH), 129.9 (Ar CH), 129.8 (Ar CH), 129.2 (Ar CH), 127.9 (Ar CH), 127.8 (Ar CH), 127.6 (Ar CH), 78.9 (*C*HCHO), 34.3 (*C*H$_2$CH(OSiMe$_2$Ph)CHO), 17.9 (*C*H$_2$CH$_3$), 13.8 (CH$_2$*C*H$_3$), 0.8, −1.4, −1.50 (Si CH_3's); IR (CH_2Cl_2) $\nu_{C=O}$ 1734 cm^{-1}. Anal. Calcd for $C_{13}H_{20}O_2Si$: C, 66.04; H, 8.54. Found: C, 65.82; H, 8.56.

(CH$_3$)$_2$CHCH(OSiMe$_2$Ph)CHO (1l): 75%, bp 90−100 °C at 0.1 mmHg; ^{1}H NMR ($CDCl_3$) δ 9.55 (s, 1 H, CHO), 7.64−7.31 (m, 5 H, Ar CH), 3.75 (dd, J = 4.9, 1.9 Hz, 1 H, C*H*CHO), 2.06−1.99 (m, 1 H, C*H*(CH$_3$)$_2$), 0.93 (d, J = 6.0 Hz, 3 H, CHC*H*$_3$), 0.91 (d, J = 6.0 Hz, 3 H, CHC*H*$_3$), 0.41 (s, 6 H, Si CH_3's); ^{13}C NMR ($CDCl_3$) δ 203.9 (CHO), 136.9 (Ar C), 133.4 (Ar CH), 133.3 (Ar CH), 132.9 (Ar CH), 129.8 (Ar CH), 129.6 (Ar CH), 129.2 (Ar CH), 127.8 (Ar CH), 127.6 (Ar CH), 82.0 (*C*HCHO), 31.1 (*C*H(CH$_3$)$_2$), 19.2 (*C*H(CH$_3$)$_2$), 18.8 (*C*H(CH$_3$)$_2$), 18.5 (*C*H(CH$_3$)$_2$), 16.8 (*C*H(CH$_3$)$_2$), 14.8 (*C*H(CH$_3$)$_2$), 0.8, −1.46, −1.51, (Si CH_3's); IR (CH_2Cl_2) $\nu_{C=O}$ 1734 cm^{-1}. Anal. Calcd for $C_{13}H_{20}O_2Si$: C, 66.04; H, 8.54. Found: C, 66.15; H, 8.52.

Me$_2$C=CH(CH$_2$)$_2$CH(CH$_3$)CH$_2$CH(OSiMe$_2$Ph)CHO (1m): 60%, bp 160−170 °C at 0.1 mmHg. Selected NMR data: ^{1}H NMR ($CDCl_3$) δ 9.55 (s, 1 H, C*H*O), 7.60−7.53 (m, 2 H, Ar H), 7.41−7.35 (m, 3 H, Ar CH), 5.09−5.05 (m, 1 H, vinyl CH), 4.06−4.03 (m, 1 H, C*H*CHO−), 1.69 (s, 3 H, vinyl CH_3), 1.60 (s, 3 H, vinyl CH_3), 0.89 (d, 3 H, J = 3.4 Hz, alkyl CH_3), 0.34, 0.36 (2s, 6 H, Si CH_3's). IR (CH_2Cl_2): $\nu_{C=O}$ 1733 cm^{-1}.

Compound 2: 80%, bp 140−150 °C at 0.1 mmHg; ^{1}H NMR ($CDCl_3$) (major isomer) δ 9.53 (s, 1 H, C*H*O), 7.39−7.19 (m, 10 H, Ar H), 4.05 (d, J = 4.4 Hz, 1 H, C*H*CHO), 3.25−3.18 (m, 1 H, C$_6$H$_5$C*H*), 1.29 (d, J = 7.0 Hz, 3 H, CHC*H*$_3$), 0.33, 0.27, 0.24, 0.18 (4 s, 6 H, Si CH_3's); ^{13}C NMR ($CDCl_3$) (major and minor isomers) δ 203.5, 203.2 (CHO), 149.1 (Ar C), 142.3 (Ar C), 136.9 (Ar C), 136.6 (Ar C), 133.7 (Ar C), 132.9 (Ar C), 129.8, 128.3, 128.2, 128.0, 127.8, 127.6, 126.8 (Ar CH), 125.1, 123.7, 121.1 (Ar CH), 82.1, 81.8 (*C*HCHO), 42.3, 42.1 (C$_6$H$_5$*C*H), 14.5, 14.3 (CH*C*H$_3$), 0.8, −0.4, −1.4, −1.7, −1.9 (Si CH_3's); IR (CH_2Cl_2) $\nu_{C=O}$ 1733 cm^{-1}. Anal. Calcd for $C_{18}H_{22}O_2Si$: C, 72.43; H, 7.44. Found: C, 72.30; H, 7.50.

C$_6$H$_5$CH(OSiMe$_2$Ph)CH(OSiMe$_2$Ph)CHO (3). The compound was found to decompose upon distillation at reduced pressure and on chromatographic supports. Selected ^{1}H NMR ($CDCl_3$) data: δ 9.53 (s, 1 H, C*H*O), 7.62−7.16 (m, 15 H, Ar H), 4.93 (d, J = 3.9 Hz, 1 H, C$_6$H$_5$C*H*−), 4.01 (d, J = 3.9 Hz, 1 H, C*H*CHO), 0.4 − 0.1 (m, 12 H, Si CH_3's); IR (CH_2Cl_2) $\nu_{C=O}$ 1734 cm^{-1}.

Relative Rate Study for Benzaldehyde and C$_6$H$_5$CH(OSiMe$_2$Ph)CHO. THF solutions (200 mL) of benzaldehyde (6.0 g, 0.28 M), dimethylphenylsilane (7.7 g, 0.28 M), and C$_6$H$_5$CH(OSiMe$_2$Ph)CHO (15 g, 0.28 M) were prepared, degassed by three consecutive freeze−pump−thaw cycles, and stored under nitrogen at −30 °C for the duration of the study. A THF (20 mL) solution of [(COD)RhCl]$_2$ (79 mg, 7.1 × 10^{-3} M THF) was prepared and degassed. For each run, an aliquot of the aldehyde/silane solution (5.0 mL) and catalyst solution (0.50 mL) was transferred via a gas tight syringe into a nitrogen-purged glass vessel and then placed in stainless steel bomb. The bomb was purged three times with carbon monoxide (50−500 psig) and brought to reaction pressure of 1000 psig. The reaction was carried out at ambient temperature with stirring. For each data point the glass vessel was removed from the bomb and the solvent removed under reduced pressure. The reaction mixture was analyzed by ^{1}H NMR using 1,1,1-trichloroethane as an internal standard to obtain the NMR yields.

General Procedure for Silyl Enol Ether Synthesis. A THF (5 mL) solution of ketone (1.4 mmol) and dimethylphenylsilane (0.19 g, 1.4 mmol) was prepared in a small round bottom flask (50 mL) and then degassed by three consecutive freeze−pump−thaw cycles. A glass vessel was purged with nitrogen and charged with 2 mol % [(COD)RhCl]$_2$ (6.8 mg, 1.4 × 10^{-2} mmol). The THF solution was cannulated into the catalyst-containing glass vessel, and the vessel was placed into a stainless steel bomb. The bomb was purged with carbon monoxide three times and brought to a final pressure of 1000 psig CO. It was stirred at room temperature for 24 h and the solvent removed under reduced pressure. The silyl enol ether product(s) were purified by bulb-to-bulb distillation.

Silyl Enol Ether from 2-Norbornanone (4): 60%, bp 115−120 °C at 0.1 mmHg; ^{1}H NMR ($CDCl_3$) δ 7.58−7.52 (m, 2 H, Ar H), 7.39−7.31 (m, 3 H, Ar H), 4.61 (d, J = 2.97 Hz, 1 H, vinyl CH), 2.70 (m, 1 H, aliphatic CH), 2.54 (m, 1 H,

aliphatic CH), 1.67−1.54 (m, 2 H, aliphatic CH_2's), 1.43−1.41 (m, 1 H, aliphatic CH_2's), 1.21−1.16 (m, 1 H, aliphatic CH_2's), 1.08−1.04 (m, 1 H, aliphatic CH_2's), 0.99−0.97 (m, 1 H, aliphatic CH_2's), 0.44, 0.33 (s's, 6 H, Si CH_3's); ^{13}C NMR ($CDCl_3$) δ 160.7 (vinyl C), 139.8 (Ar C), 137.2 (Ar C), 133.3 (Ar CH), 133.0 (Ar CH), 129.7 (Ar CH), 129.2 (Ar CH), 127.8 (Ar CH), 127.7 (Ar CH), 106.1 (vinyl CH), 46.9, 45.3, 40.9, 27.5, 24.4 (aliphatic CH_2's), 0.8, −1.4 (Si CH_3's). Anal. Calcd for $C_{15}H_{20}OSi$: C, 73.72; H, 8.25. Found: C, 73.30; H, 7.98.

Phenacetaldehyde Silylformylation Product: 80%, bp 135−145 °C at 0.1 mmHg; ^{1}H NMR ($CDCl_3$) δ 9.61 (s, 1 H, C*H*O), 7.54 (d, J = 7.0 Hz, 2 H, Ar CH), 7.37−7.24 (m, 6 H, Ar CH), 7.16 (d, J = 7.2 Hz, 2 H, Ar CH), 4.12 (dd, J = 9.0, 4.1 Hz, 1 H, C*H*CHO), 2.99 (dd, J = 13.7, 4.0 Hz, 1 H, benzylic CH_2), 2.78 (dd, J = 13.7, 9.0 Hz, 1 H, benzylic CH_2), 0.3, 0.2 (3 s, 6 H, Si CH_3's); ^{13}C NMR ($CDCl_3$) δ 203.0 (*C*HO), 139.8 (Ar C), 136.8 (Ar C), 136.5 (Ar C), 133.4 (Ar CH), 133.0 (Ar CH), 129.9 (Ar CH), 129.8 (Ar CH), 129.2 (Ar CH), 128.5 (Ar CH), 127.9 (Ar CH), 127.7 (Ar CH), 126.7 (Ar CH), 79.0 (*C*HCHO), 38.8 (benzylic CH_2), 0.8, −1.7, −2.0 (Si CH_3's).

Silyl Enol Ether from Phenacetaldehyde: 80%, bp 155.165 °C at 0.1 mmHg; ^{1}H NMR ($CDCl_3$) δ 7.66−7.60 (m, 3 H, Ar H), 7.44−7.41 (m, 3 H, Ar H), 7.66−7.60 (m, 4 H, Ar CH), 6.96 (d, J = 12.2 Hz, 1 H, vinyl CH), 6.08 (d, J = 12.2 Hz, 1 H, vinyl CH), 0.53, 0.52, 0.33 (3s, 6 H, Si CH_3's); ^{13}C NMR ($CDCl_3$) δ 141.5, 139.8, 136.2, 136.0, 133.5, 133.0, 130.1, 129.2, 128.5, 128.3, 128.1, 128.0, 127.7, 125.9, 125.2 (Ar C or CH), 113.6, 109.7 (vinyl CH), 0.8, −1.7 (Si CH_3's). Anal. Calcd for $C_{16}H_{18}OSi$: C, 75.54; H, 7.13. Found: C, 75.38; H, 7.26.

Preparation of $C_6H_5CHNCH_2CH_2OSiMe_2H$ (5). A Schlenk flask was charged with benzaldehyde (1.0 g, 9.4 mmol), THF (20 mL), molecular sieves, and ethanolamine (0.57 g, 9.4 mmol) and allowed to react with stirring at ambient temperature for 2 h. The mixture was cannulated into a Schlenk flask, chilled in an ice bath, and then treated with (dimethylamino)-dimethylsilane (1.2 g, 10 mmol). The ice bath was removed and the mixture allowed to react for an additional 2 h with stirring. The solvent and excess silane reagent were removed under reduced pressure to afford *spectroscopically pure* **5** (80%): ^{1}H NMR ($CDCl_3$) δ 8.28 (s, 1 H, CHN), 7.74−7.71 (m, 2 H, Ar CH), 7.42−7.39 (m, 3 H, Ar CH), 4.65−4.61 (m, 1 H, SiH), 3.95 (t, J = 5.6 Hz, 2 H, CH_2O), 3.26 (t, J = 5.6 Hz, 2 H, CH_2N), 0.18 (s, 6 H, Si CH_3's); ^{13}C NMR ($CDCl_3$) δ 162.6 (*C*HN), 135.9 (Ar C), 130.4 (ArCH), 128.3 (ArCH), 127.9 (ArCH), 63.5 (CH_2N), 63.1 (CH_2O), −1.7 (Si CH_3's); IR (CH_2Cl_2) $\nu_{C=N}$ 1647 cm^{-1}.

Preparation of Compound 6. A THF solution of the 3-hydroxy-2-butanone (0.88 g, 10 mmol) was chilled to 0 °C and then treated with (dimethylamino)dimethylsilane (1.3 g, 12 mmol), and then the cooling bath was removed and the mixture allowed to reach ambient temperature and stir for an additional 4 h. The solvent and dimethylamine were removed under reduced pressure to afford analytically pure **6** (80%): ^{1}H NMR ($CDCl_3$) δ 4.80−4.75 (m, 1 H, SiH), 3.79 (q, 1 H, J = 6.6 Hz, C*H*CH_3), 1.35 (s, 3 H, CH_3), 1.07 (d, 3 H, J = 6.6 Hz, CH_3), 0.24 (s, 6 H, Si CH_3's); ^{13}C NMR ($CDCl_3$) δ 96.4 (CO), 70.1 (CH), 24.7 (*C*H_3C=O), 15.2 (*C*H_3CH), −0.36 (Si CH_3's); IR (CH_2Cl_2) ν_{Si-H} 2132 cm^{-1}. Anal. Calcd for $C_6H_{14}O_2Si$: C, 49.26; H, 9.67. Found: C, 49.20; H, 9.69.

Solvent Survey. A round-bottom flask (50 mL) was charged with benzaldehyde (50 mg, 0.47 mmol), dimethylphenylsilane (64 mg, 0.47 mmol), and the appropriate solvent (5 mL). The mixture was degassed by three consecutive freeze−pump−thaw cycles and then cannulated into a nitrogen-purged glass vessel containing $[(COD)RhCl]_2$ (9 mg, 2 mol %). The glass vessel was placed in a stainless steel bomb and purged three times with carbon monoxide {50−500 psig}. The bomb was stirred at the appropriate carbon monoxide pressure at room temperature for 8 h. The glass vessel was removed from the bomb and the solvent removed under reduced pressure. The reaction mixture was analyzed by ^{1}H NMR using 1,1,1-trichloroethane as an internal standard to obtain the NMR yields.

Competition Study Involving Aldehydes and Ketones. A round-bottom flask (50 mL) was charged with aldehyde (0.47 mmol), ketone (0.47 mmol), dimethylphenylsilane (64 mg, 0.47 mmol), and THF (5 mL). The mixture was degassed by three consecutive freeze−pump−thaw cycles and then cannulated into a nitrogen-purged glass vessel containing $[(COD)RhCl]_2$ (9 mg, 2 mol %). The glass vessel was placed in a stainless steel bomb and purged three times with carbon monoxide {50−500 psig}. The bomb was stirred at 1000 psig of carbon monoxide pressure at room temperature for 8 h and then worked up in the usual manner.

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Supporting Information Available: Figures displaying NMR spectra (10 pages). Ordering information is given on any current masthead page.

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