

**Metal Carbonyl-Hydrosilane Reactions and Hydrosilation
Catalysis**

Final Report

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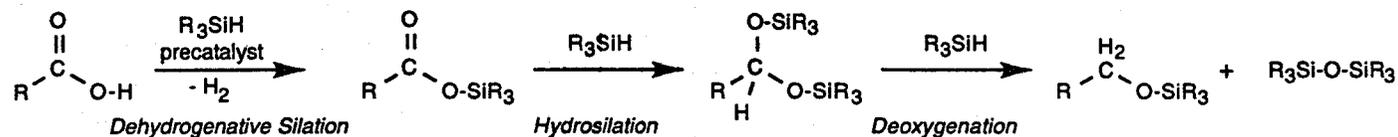
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PROJECT SUMMARY

Manganese carbonyl complexes serve as hydrosilation precatalysts for selectively transforming a carbonyl group into a siloxy methylene or a fully reduced methylene group. Substrates of interest include (1) aldehydes, ketones, carboxylic acids, silyl esters, and esters, and (2) their organometallic acyl counterparts. Three relevant catalytic reactions (illustrated for carboxylic acids) include,



Two types of manganese precatalysts have been reported: (a) alkyl and acyl complexes $(\text{L})(\text{CO})_4\text{MnR}$ [$\text{L} = \text{CO}, \text{PPh}_3$; $\text{R} = \text{COCH}_3, \text{COPh}, \text{CH}_3$] and (b) halides $(\text{CO})_5\text{MnX}$ and $[(\text{CO})_4\text{MnX}]_2$ ($\text{X} = \text{Br}, \text{I}$). The former promote hydrosilation and deoxygenation catalysis; the latter promote dehydrogenative silation of alcohols and carboxylic acids as well as hydrosilation and deoxygenation of some metallocarboxylic acid derivatives. In every case studied, these Mn precatalysts are far more reactive or selective than traditional Rh(I) precatalysts.

The reaction chemistry of the above and other Mn alkyl complexes with hydrosilanes was studied in order to probe catalysis mechanism(s). Thus, $\text{Mn}(\text{CO})_5$ methyl, benzyl, acetyl, and benzoyl (4 *p*-substituents) complexes reacted with hydrosilanes by four different mechanisms, which were established. A noteworthy development was that the methyl and benzoyl complexes gave moderate yields of a new ($\eta^2\text{-Si-H}$) silane adduct $(\text{CO})_4\text{Mn}(\text{SiMe}_2\text{Ph})(\text{H-SiMe}_2\text{Ph})$, which is stable in the presence of excess silane. This silane adduct promotes all three catalytic reactions; its extraordinary activity and potential selectivity are under study. Specific catalysis problems that have been addressed include:

- Catalytic hydrosilation-then-deoxygenation of ketones and organometallic acyls. Mn and Rh(I) precatalysts and PhSiH_3 completely reduce iron acyls $\text{Cp}(\text{CO})(\text{L})\text{FeC}(\text{O})\text{R}'$ to their alkyl derivatives, $\text{Cp}(\text{CO})(\text{L})\text{FeCH}_2\text{R}'$. Our Mn precatalysts very efficiently promote the hydrosilation of ketones.



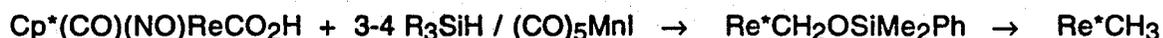
- The reactivity/selectivity of Mn precatalysts and silanes for the catalytic hydrosilation-then-deoxygenation of esters. Deoxygenation of the silyl acetal intermediates and their partitioning between ether and silyl ether deoxygenation products depends upon the choice of silane and precatalyst.



- Catalytic reactions of hydrosilanes with carboxylic acids and silyl carboxylates. Dehydrogenative silation-hydrosilation-deoxygenation of the carboxylic acids gave isolable silyl esters, disilylacetals, and silyl ethers. The catalytic formate-hydrosilane chemistry pertains to CO_2 fixation, although more work on the pyrolysis of the disilylacetals is in progress.



- Catalytic Reactions of Hydrosilanes with Metallocarboxylic Acid Derivatives. $(\text{CO})_5\text{MnI}$ catalyzes the hydrosilation-deoxygenation of $\text{Cp}^*(\text{CO})(\text{NO})\text{ReCO}_2\text{R}'$ [$\text{R}' = \text{H}$ and SiR'_3], thus providing support for our metallocarboxylic acid pathway for CO/CO_2 fixation.



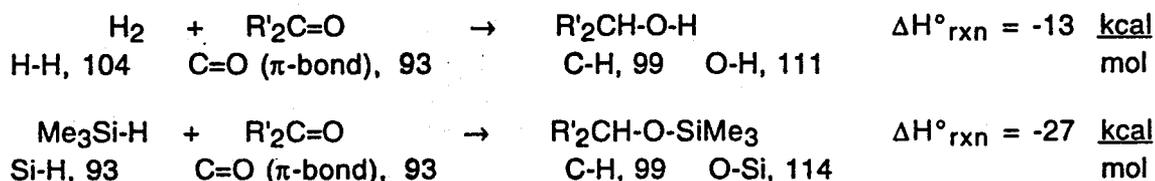
PREVIOUS RESULTS

A. Prologue

Our interest in the reactivity of hydrosilanes towards organometallic alkyl/acyl complexes - especially the reduction of acyl ligands - is an extension of our previous studies on generating and extending C₁ and C₂ ligands using (ligated) CO.¹ This chemistry entailed sequential carbonylation and reduction steps, with acyl ligand hydrogenation an obvious choice for the latter. These hydrogenation reactions instead typically release aldehydes or the corresponding alcohols.² Indeed, virtually all of the synthesis and CO fixation modeling studies of the 1970's relied on using borane, borohydride, or metal hydride reagents for reducing acyl ligands or their activated alkoxy-carbene derivatives.^{1,3}

Catalytic hydrosilation of acyl complexes became an alternative approach for reducing acyl ligands. Catalytic hydrosilation of organic aldehydes and ketones to alkoxy-silanes had been well established as an easy and dependable synthetic procedure,⁴ whereas the analogous catalytic hydrogenation of ketones to alcohols requires more effort in choice of catalyst and reaction conditions.⁵

The relative ease of hydrosilation vs. hydrogenation of a ketone is consistent with the results of thermochemical calculations using bond dissociation enthalpies (BDE's).⁶ Surprisingly, it is not the Si-O bond strength alone that favors the hydrosilation over the hydrogenation of a ketone. The relative weakness of the Si-H bond versus the H-H (by 11 kcal/mol) represents a more significant contribution to the ΔH°_{rxn} than does the strength of the Si-O versus the H-O bond (by 3 kcal/mol).



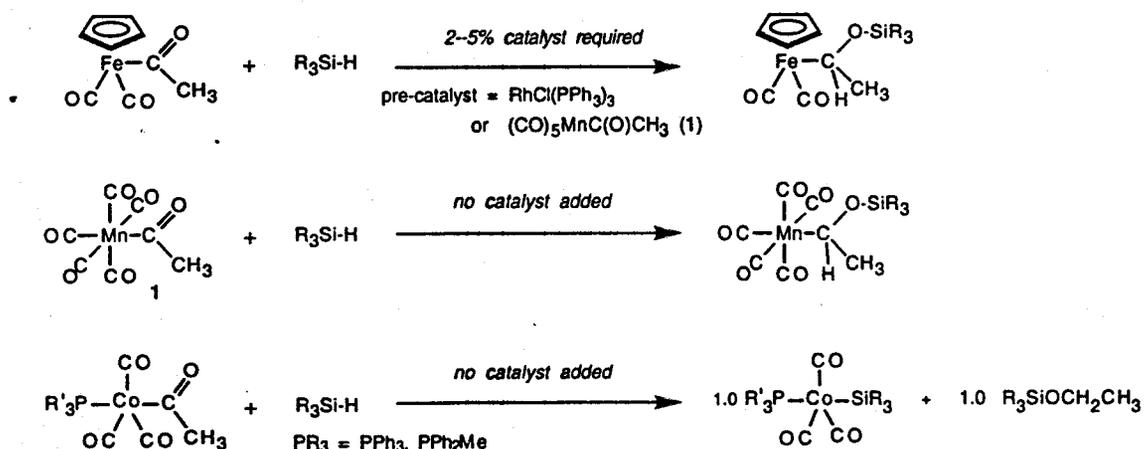
When we started our studies, very little was known about the reactions of labile metal acyl complexes with silanes.^{7,8} The expectation was that silane Si-H would add to the metal and eliminate aldehyde as the kinetic product.⁹ Alternative α -siloxyalkyl products $\text{L}_x\text{MCH}(\text{OSiR}_3)\text{R}'$ were unknown.

Cobalt α -siloxyalkyls $(\text{CO})_x\text{CoCH}(\text{OSiR}_3)\text{R}'$ had been postulated, however, in the seminal studies by Murai and co-workers¹⁰ as intermediates during the $\text{Co}_2(\text{CO})_8$ -catalyzed silylformylation of alkenes (with R_3SiH and CO). These α -siloxyalkyl precursors to the organic products presumably originate via the interaction of in situ-generated $(\text{CO})_4\text{CoSiR}_3$ with aldehyde;^{10b,c} the aldehyde in turn derived from a cobalt acyl that came from alkene, CO, and $(\text{CO})_4\text{CoH}$. The incorporation of aldehyde into the cobalt silyl has been modeled under non-catalytic conditions in studies by Gladysz and co-workers¹¹ using $(\text{CO})_5\text{MnSiMe}_3$, but again no information was forthcoming on the hydrosilation of metal acyl complexes.

A landmark paper by Markó and co-workers¹² established two important points. First, the labile $(\text{CO})_4\text{CoC}(\text{O})\text{CHMe}_2$ adds Et_3SiH and generates a transient $(\text{CO})_4\text{CoCH}(\text{OSiEt}_3)\text{CHMe}_2$, which in the presence of excess silane degrades to the detected products, $\text{Me}_2\text{CHCH}_2\text{OSiEt}_3$ and $\text{Me}_2\text{C}=\text{CHOSiEt}_3$. Second, $(\text{CO})_4\text{CoSiMe}_3$ readily incorporates an aldehyde Me_2CHCHO as a similar α -siloxy-isobutyl complex that likewise degrades to analogous organic products. In this and previous studies, all

mechanistic deduction rested solely on the identification of the organic products.

Our early studies established four points.¹³ (1) We demonstrated the first examples of catalytic hydrosilation of non-labile organometallic acyl compounds. Rhodium(I) complexes catalyze the hydrosilation of Fp acyl compounds;¹⁴ the resulting products were the first α -siloxyalkyl complexes to be isolated and fully characterized. (2) The labile manganese acetyl, $(\text{CO})_5\text{MnC}(\text{O})\text{CH}_3$ (**1**), in contrast, readily adds silanes in the absence of added catalyst, and a dozen of the resulting α -siloxyalkyl products were characterized.¹⁵ (3) Unexpectedly, **1** serves as an extraordinarily active precatalyst for the hydrosilation of FpCOCH_3 .¹⁶ For example, < 5% **1** promotes the hydrosilation of FpCOCH_3 with 2° silanes (e.g., Ph_2SiH_2) as well as with the less reactive¹⁷ 3° silanes (e.g., PhMe_2SiH),



whereas the Rh(I) precatalysts only function with the former. (4) Organotransition metal acetyl complexes, in our experience, undergo diverse reactions with silanes.¹³ In addition to the above catalytic and "apparently non-catalytic" hydrosilation of metal acyls, many metal acetyl complexes add 2 equiv. of silane and release the organic products, $\text{CH}_3\text{CH}_2\text{OSiR}_3$ and $\text{CH}_2=\text{CHOSiR}_3$.^{10,11a,12,18} Results of our study of the above cobalt acetyl compounds¹⁹ were consistent with an intramolecular pathway (*vide infra*) involving a *coordinative unsaturated* α -siloxyalkyl intermediate that adds silane and eliminates only $\text{CH}_3\text{CH}_2\text{OSiR}_3$.¹⁹

Early studies by Akita, Moro-oka, and co-workers²⁰ coincided with and generally complemented our work on the Rh(I)-catalyzed hydrosilation of Fp and $\text{Mn}(\text{CO})_5$ acyls. (The presence of a rhodium catalyst, however, is unnecessary for the hydrosilation of **1**.)^{15a} Whereas we emphasized the characterization of organometallic intermediates and products, they did a nice job on establishing the organic byproducts. For example, they demonstrated that treatment of **1** with excess Ph_2SiH_2 and 1 atm. CO with 1% $\text{RhCl}(\text{PPh}_3)_3$ produced a distribution of alkanes and alkenes reminiscent of Fischer-Tropsch (Pichler-Schulz distribution of) hydrocarbon products emanating from alternate carbonylation/reduction steps.^{20a} Subsequent studies by the same authors²¹ and others²² have focused on the hydrosilation-reduction of ligated CO, a topic that is relevant to the present proposal.

The truly unexpected dividend of this research is that these manganese carbonyl alkyl and acyl complexes function as such unusually reactive precatalysts for the reactions of silanes with organic and organometallic substrates. These well-known $\text{Mn}(\text{CO})_5$ complexes have not been used previously in

catalysis;²³ yet we find them to be far more reactive than traditional $\text{Co}(\text{CO})_4$ or even $\text{Rh}(\text{I})$ pre-catalysts for a variety of reactions between hydrosilanes and $\text{C}=\text{O}$ ²⁴ or $\text{O}-\text{H}$ ²⁵ bonds. As noted in the following Objectives summary, these catalytic reactions for organic molecules include:

- dehydrogenative silation of alcohols²⁵ and carboxylic acids,²⁶



- hydrosilation of aldehydes and ketones,²⁴ and



- hydrosilation-then-deoxygenation of esters²⁷ and silyl carboxylates,²⁶ and

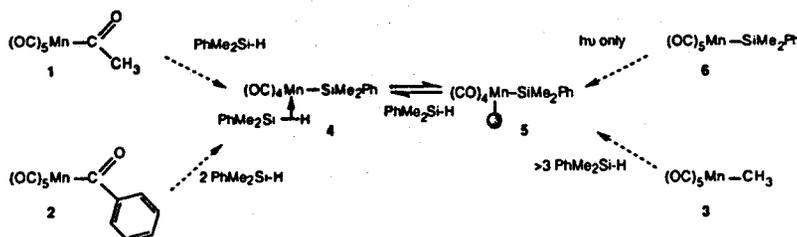


- dehydrogenative silation-then-hydrosilation-then-deoxygenation of carboxylic acids.²⁶



Organometallic substrates have included predominately iron and manganese acetyl^{25,26} and benzoyl²⁸ complexes as well as metallocarboxylic acids,²⁹ esters,³⁰ and silyl esters.³¹

In order to continuously evolve ever more active or selective hydrosilane catalysts, we are studying the reaction chemistry of silanes with manganese alkyl and acyl complexes.



During our prior grant period, we established that the manganese acetyl **1**,^{15b} benzoyl **2**,²⁸ and methyl **3**³² complexes react with PhMe_2SiH via very different mechanisms. Under the appropriate conditions all of these reaction mixtures nevertheless afford varying amounts of the same $(\eta^2\text{-Si-H})$ silane adduct **4** (which has been characterized in solution^{32b}) as the precatalyst for our hydrosilane catalysis chemistry, *vide infra*. This precatalyst **4** equilibrates with the coordinatively unsaturated manganese silyl **5**, our putative active catalyst.

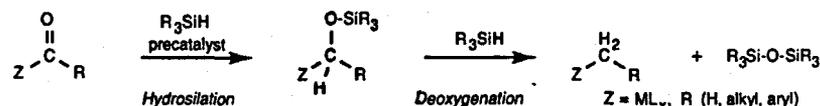
The coordinatively saturated manganese silyl **6** also provides the active catalyst **5** upon photolysis.^{24,27,28,30} A gratifying development is that the silyl intermediates **5** and **6** conform to the active catalyst and resting states, respectively, that we deduced during an earlier kinetics study^{28a} of isotope exchange between the EtMe_2SiH and PhMe_2SiD catalyzed by the three precatalysts **1-3**. With the advent of convenient and reproducible sources of **4** as precatalyst, we in the process of consolidating our understanding of the manganese carbonyl-catalyzed reactions of silanes with $\text{C}=\text{O}$ and $\text{O}-\text{H}$ bonds.

OBJECTIVES OF ONGOING AND PROPOSED RESEARCH:

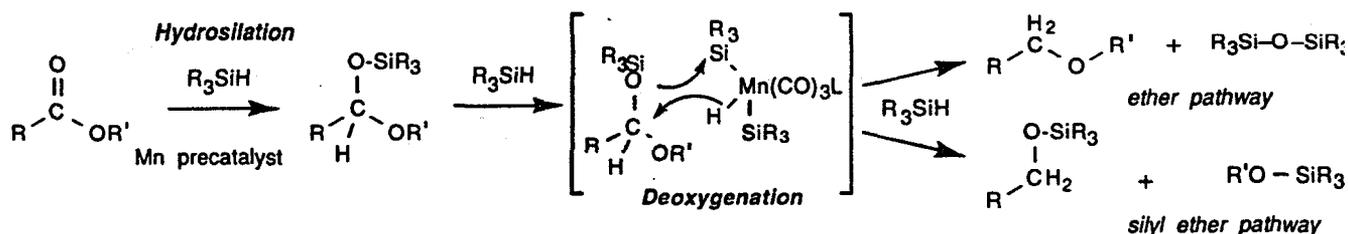
A. Study the reactions of labile $L(CO)_4Mn$ -alkyl, acyl, and halide complexes with hydrosilanes. Our studies of these novel coordinated ligand reactions are being used:

- (a) to establish these manganese carbonyl complexes as extremely reactive precatalysts for the reactions of silanes with organic and organometallic substrates, and
 (b) to determine the active catalyst and the plausible mechanisms of this catalysis.

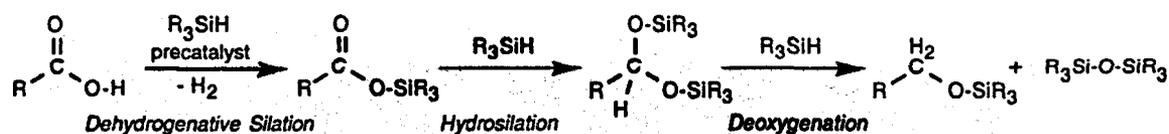
B. Establish the manganese carbonyl-catalyzed hydrosilation-then-deoxygenation of organic ketones and aldehydes and organometallic acyl carbonyl groups.



C. Finalize studies on the analogous reduction of the carbonyl group of organic esters. Here the critical issue is controlling the selectivity of the catalytic deoxygenation step to yield either ethers or silyl ethers. Resolution of this issue has depended upon our understanding of the coordinated ligand reactions of the Mn precatalysts.

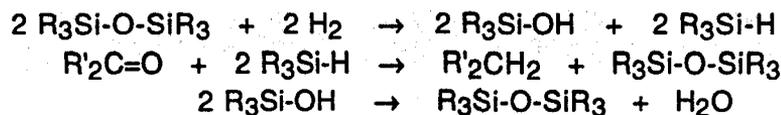


D. Establish the manganese carbonyl-catalyzed dehydrogenative silation-then-hydrosilation-then-deoxygenation of organic carboxylic acid and silyl ester derivatives. Organic formates, $R = H$, represent a special case due to their importance to both CO and CO₂ reduction.



E. Extend the Mn-hydrosilane catalysis of organic carboxylic acids to metallocarboxylic acids and derivatives $L_xMC(O)OR$ ($R = H, CH_3, SiR_3$), which are available from either ligated CO or CO₂. This models our metalloester approach to CO/CO₂ fixation: the resulting disilylacetal intermediates $L_xMCH(OSiR_3)_2$ serve as alternative C₁ templates to the usual formyl ligand.
 $L_xMCO_2H + 4 R_3Si-H \rightarrow L_xMCO_2SiR_3 \rightarrow [L_xMCH(OSiR_3)_2] \rightarrow L_xMCH_2OSiR_3 \rightarrow L_xMCH_2$

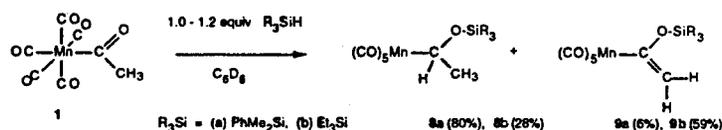
F. Explore the possibility of silane-driven hydrogenation of organic and organometallic substrates.



B. Reactions of Manganese Carbonyl Alkyl and Acyl Complexes with Hydrosilanes.

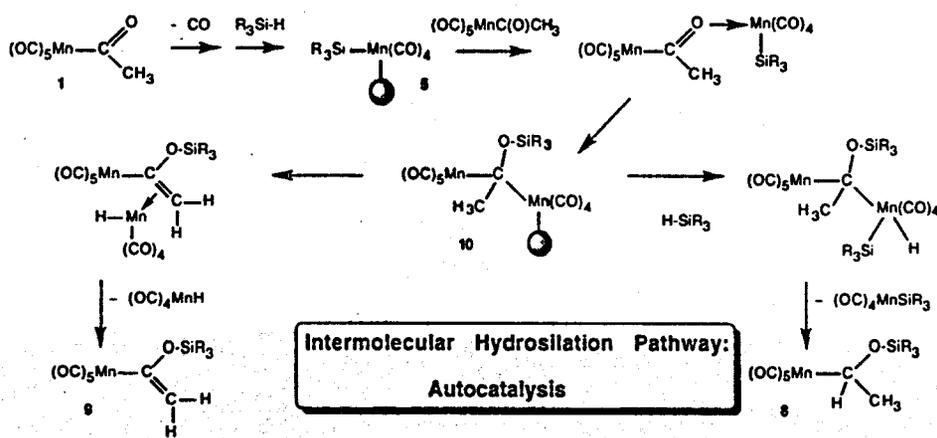
1. Manganese Carbonyl Acetyl Reactions with Hydrosilanes and Where It Led.

The thermally labile $(\text{CO})_5\text{MnC}(\text{O})\text{CH}_3$ (**1**)⁸ reacts with 1 equiv. of a monohydrosilane at room temperature in benzene to yield mixtures of α -siloxyethyl complexes $(\text{CO})_5\text{MnCH}(\text{OSiR}'_3)\text{CH}_3$ (**8**) and α -siloxyvinyl byproducts $(\text{CO})_5\text{MnC}(\text{OSiR}_3)=\text{CH}_2$ (**9**).^{15b} PhMe_2SiH and Et_3SiH were used in for mechanistic studies. Results of reaction profiles (concentration-time plots), for example, are consistent with (1) **8** and **9** forming independently, and (2) **9** subsequently reacting with hydrosilanes.



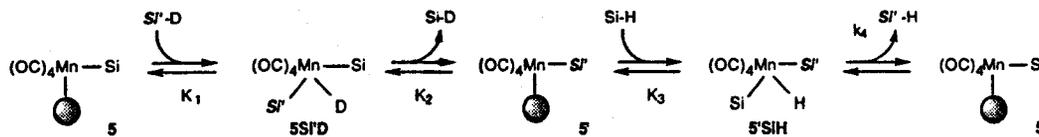
In the presence of excess silane, **8a** degrades to $(\text{PhMe}_2\text{Si})_2\text{O}$, $\text{Mn}_2(\text{CO})_{10}$, and a mixture of organics. The absence of ethoxysilane, vinyl silyl ether, and $(\text{CO})_5\text{MnSiMe}_2\text{Ph}$ (**6a**), precludes the intermediacy of the unsaturated $(\text{CO})_4\text{MnCH}(\text{OSiMe}_2\text{Ph})\text{CH}_3$ during silane-induced degradation of **8**.

An autocatalysis mechanism accounts for the formation of both **8** and **9**. Silane-induced degradation of the initially formed **8** provides the unsaturated active catalyst $(\text{CO})_4\text{MnSiR}_3$ (**5**),³³ which binds **1** and rearranges to the unsaturated μ -siloxyethylidene **10** as the key catalysis intermediate. Silane addition then affords **8** whereas β -deinsertion produces **9**.



Discerning features of this mechanism include the absence of $(\text{CO})_5\text{MnSiR}_3$, EtOSiR_3 and $\text{CH}_2=\text{CH}(\text{OSiR}_3)$, which preclude transience of unsaturated $(\text{CO})_4\text{MnCH}(\text{OSiR}_3)\text{CH}_3$ ^{11a} (the anticipated intramolecular mechanism, *vide infra*). The induction period required to generate **5** can be removed by pretreating 1% **1** or $(\text{CO})_5\text{MnC}(\text{O})\text{Ph}$ (**2**) with excess silane for 0.75 h, systems that generate **5**, before adding the substrate **1**. In a previous kinetics study^{28a} we demonstrated that the same pretreatment process (starting with either **1** or **2**) affords an active catalyst for SiH/SiD exchange between Me_2PhSiD ($\text{Si}'\text{D}$) and Me_2EtSiH (SiH).

This isotope exchange focuses on the reactivity of the active catalyst with silane alone. With as little as 0.5% precatalyst, these exchange reactions afford reproducible induction, pre-equilibrium, and final equilibrium periods. Graphical analysis of Lineweaver-Burk plots for the pre-equilibrium



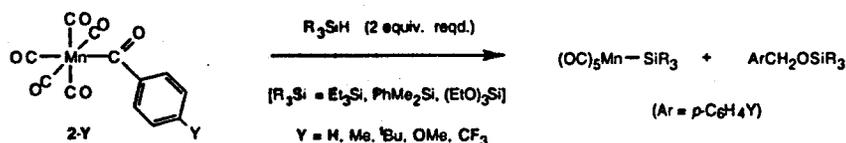
period is in accord with a ping-pong bi bi mechanism that operates under rapid equilibrium conditions and involves unsaturated $(\text{CO})_4\text{MnSiMe}_2\text{R}$ ($4'$), as active catalysts.

Although the coordinatively saturated $(\text{CO})_5\text{MnSiMe}_2\text{Ph}$ (6) and $(\text{CO})_5\text{MnSiPh}_2\text{H}$ are not catalyst precursors for SiH/SiD exchange, photolysis of these silyl complexes in the presence of silane engendered efficient isotope exchange. For reasons that will be developed, the resting state 5SiH intermediates³⁴ illustrated presumably equilibrate with $(\eta^2\text{-Si-H})$ silane Mn silyl complexes.³⁵

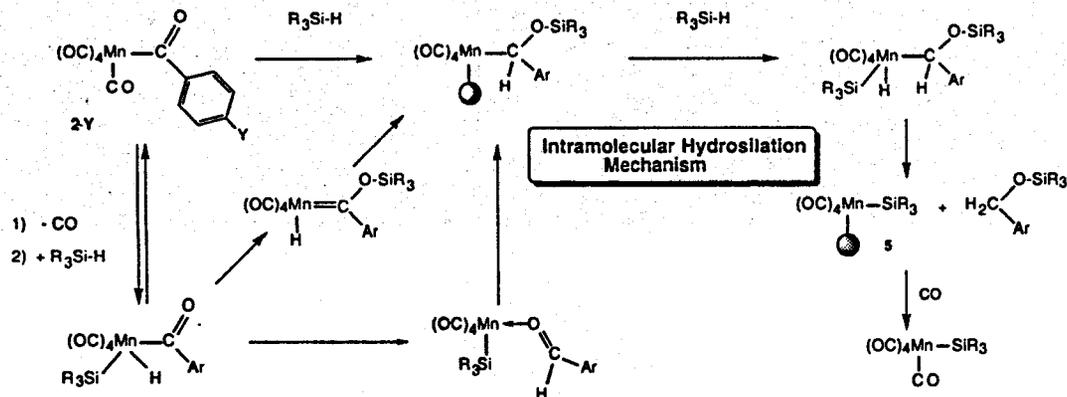
2. Hydrosilation of the Manganese Aroyl Complexes $(\text{CO})_5\text{MnC(O)-}p\text{-C}_6\text{H}_4\text{Y}$.

Our studies on the hydrosilation of $(\text{CO})_5\text{MnC(O)CH}_3$ (1) were extended to the aroyl complexes $(\text{CO})_5\text{MnC(O)C}_6\text{H}_5\text{Y}$ (2-Y ; $\text{Y} = \text{H, Me, }^t\text{Bu, OMe, CF}_3$)^{28b} for three reasons: (1) The parent benzoyl (2) is among the more active manganese precatalysts.²⁸ (2) Preliminary results indicated that 2 and 1 react with hydrosilanes via different pathways.^{28,4a} (3) Altering the para substituent Y on 2-Y alters the electronic environment on the manganese center that could provide mechanistic insight into the hydrosilation process, if not actually change the reaction pathway.

We found that the choice of the aroyl *para*-substituents had no effect on the rate or outcome of the hydrosilation reactions. All examples of 2-Y consumed 2-3 equiv. of R_3SiH within 1 hr. and gave the $\text{ArCH}_2\text{OSiR}_3$ (85-95%) plus $(\text{CO})_5\text{MnSiR}_3$ (25-30%), along with considerable $\text{Mn}_2(\text{CO})_{10}$.



We detected neither $(\text{CO})_5\text{MnCH}(\text{OSiR}_3)\text{Ar}$ nor their expected³⁶ degradation products $[\text{ArCH}(\text{OSiR}_3)]_2$ (independently prepared). Conducting these reactions with 1.0 equiv. of R_3SiH left 50% of the starting 6 and typically gave $\text{ArCH}_2\text{OSiR}_3$ in 40-45%. Taken together, these and other observations are consistent with an intramolecular hydrosilation mechanism analogous to that proposed for the reactions of silanes with $(\text{PR}_3)(\text{CO})\text{CoC(O)CH}_3$.¹⁹ Accordingly, the silane adds to and transfers sequentially from the same metal center to the aroyl ligand undergoing hydrosilation. The resulting unsaturated

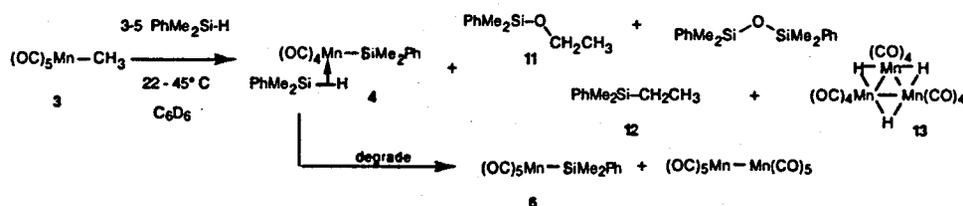


α -siloxybenzyl complex adds more silane and degrades to unsaturated **5** plus the observed $\text{ArCH}_2\text{OSiR}_3$.

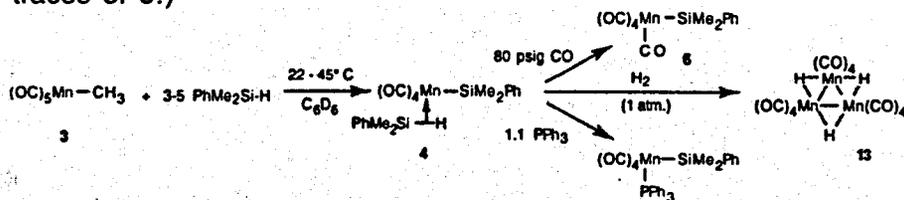
3. Hydrosilane Reactions of the Methyl Complex $(\text{CO})_5\text{MnCH}_3$ and Congeners.

This research was initiated because labile manganese alkyl complexes such as $(\text{CO})_5\text{MnCH}_3$ (**3**) and $(\text{CO})_5\text{MnCH}(\text{OSiR}_3)\text{CH}_3$ (**8**) function as viable - sometimes extremely potent - hydrosilation precatalysts.¹³ Moreover, relatively little was known concerning the reactions of silanes with alkyl complexes.^{9b,18} Related chemistry involving $(\text{CO})_5\text{MnR}$ includes hydrogenation³⁷ and their reactions with manganese hydrides $(\text{L})(\text{CO})_4\text{MnH}$.³⁸ Halpern^{38a} found that these latter reactions comprised several pathways. One particularly relevant pathway is binuclear reductive elimination, which has the manganese-hydride bond promoting alkyl-CO migratory insertion prior to releasing the aldehyde.

Heating **3** and 3-5 equiv. of PhMe_2SiH in C_6D_6 at 40°C for 3 h or at 24°C for 9-10 h furnished a red solution that contained the new silylmanganese (η^2 -Si-H) silane compound^{32a,35} $(\text{CO})_4\text{Mn}(\text{H-SiMe}_2\text{Ph})\text{SiMe}_2\text{Ph}$ (**4**). This compound, which collected in 40-55% yield, has a half life of 12 h at 22°C , although removal of the excess silane even at lower temperatures immediately decomposed it. Structure formulation for **4** rests upon the results of ^1H , ^{13}C , ^{29}Si NMR spectroscopy and derivitization experiments. The Mn-H ^1H NMR spectral resonance at δ -11.43 exhibits a $^2J_{\text{SiH}} = 40.0$ Hz ($^1\text{H}\{^{29}\text{Si}\}$ HMQC at -50°C), and EXSY experiments demonstrated silane exchange with **4**.



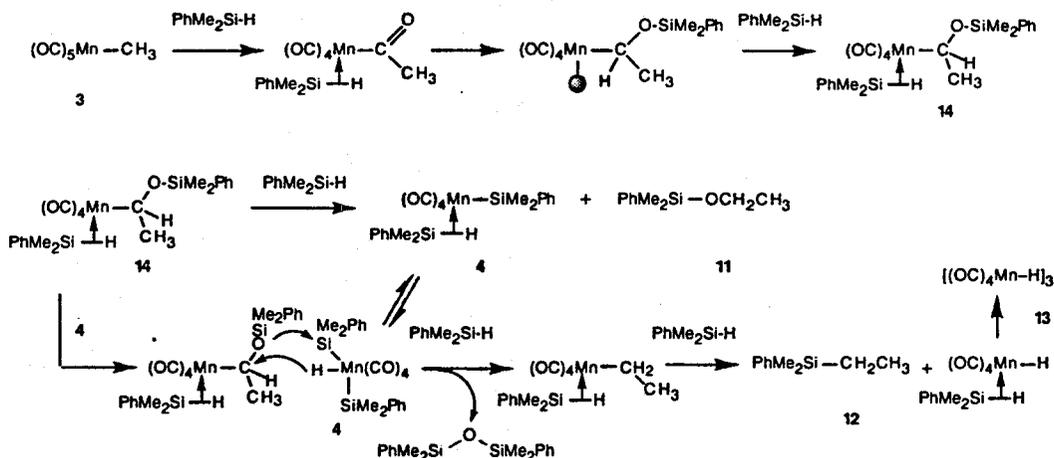
These derivitization experiments are illustrated below. Carbonylation of **4** or treatment with PPh_3 quantitatively converted it to the silyl complexes illustrated, and hydrogenation gave the requisite amount of $[(\text{CO})_4\text{MnH}]_3$ (**13**),³⁹ with quantitative release of silane. (Initially, solutions of **4** contained only traces of **6**.)



The ethoxysilane **11** and ethylsilane **12** byproducts (maximum 45 and 28% yields relative to initial **3**) that originated along with **4** clearly have incorporated and reduced one ligated carbonyl. When PhMe_2SiD was used, both **11** and **12** retained α - CD_2 groups. Concentration profiles vs. time are available (NMR spectral quantitation), in addition to IR quantitation of $\text{Mn}_2(\text{CO})_{10}$ and $[(\text{CO})_4\text{MnH}]_3$ (**13**) as a function of temperature initial silane and/or **3** concentrations, and the presence of exogenous CO (1 atm.), H_2 (70 psig), or PPh_3 .

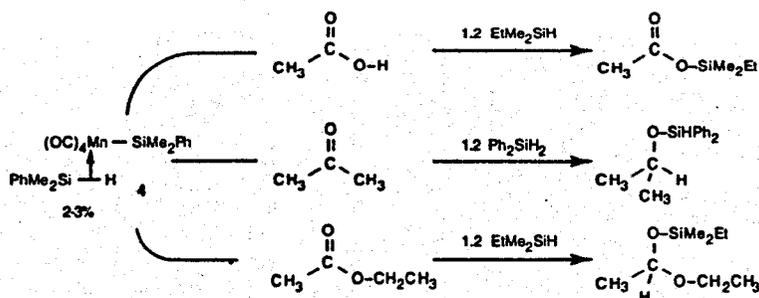
A speculative mechanism appears below that accounts for the formation of the **4** as well as the organosilanes **11** and **12**. The excess PhMe_2SiH promotes methyl-CO migratory insertion, and subsequent reduction (via the intramolecular pathway) produces the η^2 -silane adduct of α -siloxyethyl

manganese **14**, a branchpoint in the mechanism that leads to **11** and **12**. The pathway leading to **11**⁴⁰ also produces **4**, which however is consumed in the pathway leading to the ethylsilane **12**. This unusual C-Si bond formation⁴¹ could arise via a 4-mediated deoxygenation of **14** involving concurrent hydride transfer with ejection of disiloxane.⁴² Subsequent reductive elimination of **12** also releases the manganese trihydride **13**.



4. Using $(\text{CO})_4\text{Mn}(\text{H}-\text{SiMe}_2\text{Ph})\text{SiMe}_2\text{Ph}$ (**4**) as the Precatalyst with Silanes.

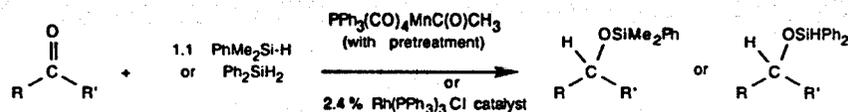
We were pleased to find that **4** serves as an extraordinarily active precatalyst for hydrosilane reactions with several substrates. The following examples illustrate successful dehydrogenative silylation (acetic acid) and hydrosilylation (acetone, ethyl acetate) runs using **4** and either EtMe_2SiH or Ph_2SiH_2 . Yields are essentially quantitative using less catalyst for significantly faster reactions (≤ 0.25 hr.). Although studies are incomplete for (successful) deoxygenation chemistry, we now have a single precatalyst that efficiently catalyzes all three of these reactions.^{32d,43,44} Studies in progress address the efficacy of using solutions containing 1-4% **4** vs. 5% **1-3** as precatalysts for the above catalytic reactions.



C. Catalytic Hydrosilylation-then-Deoxygenation of Ketones and Organometallic Acyls.

1. Manganese Acyl-Catalyzed Hydrosilylation of Ketones.

We compared the relative activity of several manganese precatalysts in C_6D_6 (2 mol%) for



$(\text{PPh}_3)(\text{CO})_4\text{MnC}(\text{O})\text{CH}_3$ (**7**) (< 5 min) \gg $(\text{CO})_5\text{MnC}(\text{O})\text{Ph}$ $>$ $(\text{CO})_5\text{MnC}(\text{O})\text{CH}_3$ $>$ $(\text{CO})_5\text{MnCH}_3$ $>$ $(\text{CO})_5\text{MnBr}$ (6.0 h) \gg $\text{Mn}_2(\text{CO})_{10}$ $=$ $(\text{PPh}_3)(\text{CO})_4\text{MnBr}$ $=$ $(\text{CO})_5\text{MnSiMe}_2\text{Ph}$ (**6**).

catalyzing the hydrosilation of acetone with 1.1 equiv. of PhMe_2SiH :²⁴ As a result of this survey, **7** was used in subsequent ketone hydrosilation studies. Pretreating 1% **7** with the full amount of PhMe_2SiH for 20 min before adding the ketone decreased the reaction times from 50 min to < 4 min. The inert **6** also turned into a moderately effective ketone hydrosilation catalyst during photolysis.

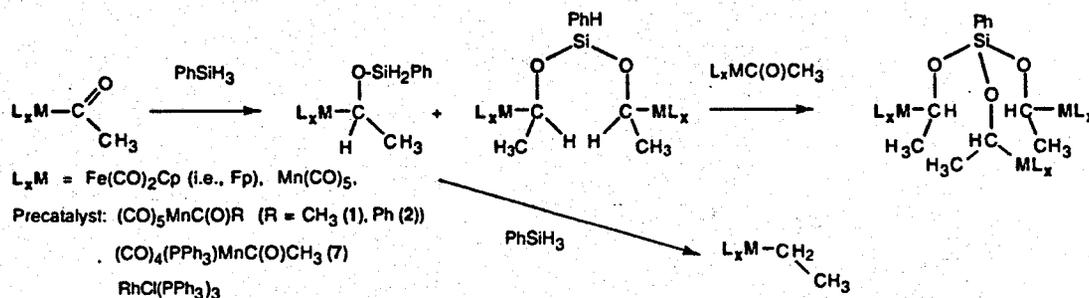
Reaction times using $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ (the standard ketone hydrosilation catalyst)⁴ and **7** as precatalysts were compared for the hydrosilation of acetone, acetophenone, and cyclohexanone. Interestingly, **7** was much more active precatalyst for ketone hydrosilation with PhMe_2SiH , although both catalysts exhibited similar activity with Ph_2SiH_2 . Isolated yields of the alkoxyasilanes exceeded 90%, with no evidence of competing dehydrogenative silation to yield vinyl silyl ethers. The manganese **7** hydrosilation systems thus greatly eclipse the ketone hydrosilation activity of the standard $\text{Co}_2(\text{CO})_8 / (\text{CO})_4\text{CoSiR}_3$ and $\text{RhCl}(\text{PPh}_3)_3$ catalytic systems in reactivity and product selectivity.^{4,45}

2. Manganese Acyl-and $\text{RhCl}(\text{PPh}_3)_3$ -Catalyzed PhSiH_3 Hydrosilation-then-Deoxygenation of Organoiron Acyl Complexes $\text{Cp}(\text{L})(\text{CO})\text{FeC}(\text{O})\text{R}$.

Prior to this study the only procedure for reducing an acyl ligand $\text{L}_x\text{MC}(=\text{O})\text{R}$ to its alkyl derivative $\text{L}_x\text{MCH}_2\text{R}$ required using excess B_2H_6 or $\text{BH}_3\cdot\text{THF}$, a messy reaction for $\text{Cp}(\text{CO})(\text{L})\text{Fe}$ acyl complexes.⁴⁶ Direct catalytic hydrogenation (e.g., with $\text{RhCl}(\text{PPh}_3)_3$)⁴⁶ of these acyl complexes has not been documented. Our objective was to find catalytic conditions for the PhSiH_3 hydrosilation-then-deoxygenation of FpCOCH_3 ($\text{L} = \text{CO}$) to FpCH_2CH_3 .^{16b} Initial observations on this reaction using $\text{RhCl}(\text{PPh}_3)_3$ catalysis were noted several years ago by Akita and Moro-Oka²⁰ and by us.^{16a} The precatalysts that we studied included $\text{RhCl}(\text{PPh}_3)_3$ and the manganese acyls **1**, **2**, and **7**.^{16b}

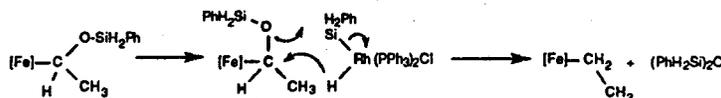
With the manganese acyl precatalysts, FpCOCH_3 and 1.1 equiv. PhSiH_3 transformed to the depicted mono-, bis-, and tris- α -siloxyethyl complexes. The initially formed mono-Fe and bis-Fe adducts transformed into the tris-Fe compound and FpCH_2CH_3 . After 12 hours, only the latter compounds remained. The tris-Fe compound did not convert into FpCH_2CH_3 under these conditions.

Two extensions of this work are worth noting. First, identical results were obtained by reacting the substrate **1** with PhSiH_3 (but without added catalyst). Second the use of $\text{RhCl}(\text{PPh}_3)_3$ (3%) and



PhSiH_3 (1.6 equiv.) is a convenient synthetic procedure for transforming $\text{Cp}(\text{L})(\text{CO})\text{FeC}(\text{O})\text{R}$ over 40-60 min. to their alkyl derivatives, $\text{Cp}(\text{L})(\text{CO})\text{FeCH}_2\text{R}$. Seven iron acyls were studied: $[\text{FpC}(\text{O})\text{R}]$, $\text{R} = \text{Me}, \text{Ph}, \text{}^i\text{Pr}, \text{}^t\text{Bu}$; $\text{Cp}(\text{L})(\text{CO})\text{FeC}(\text{O})\text{CH}_3$, $\text{L} = \text{PPh}_3, \text{P}(\text{OMe})_3$, and $\text{P}(\text{OPh})_3$.

An important outcome of this study were early examples of using silane catalysis to fully reduce an acyl group. The hydrosilation of the Fp acyls resembles Rh^4- or $\text{Mn}^{24,27}$ -catalyzed hydrosilation

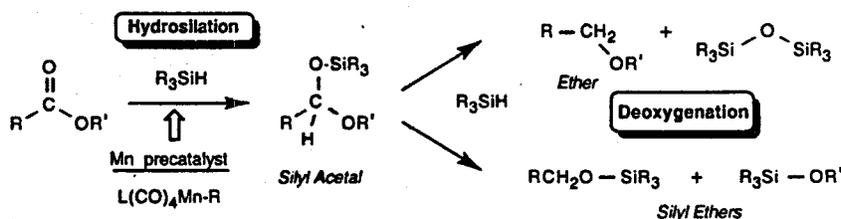


of ketones, whereas the deoxygenation step apparently entails hydride transfer from a hydrosilane adduct of the active catalyst commensurate with disiloxane, *vide infra*.

D. Manganese Acyl Catalyzed Hydrosilation-then-Deoxygenation of Esters.

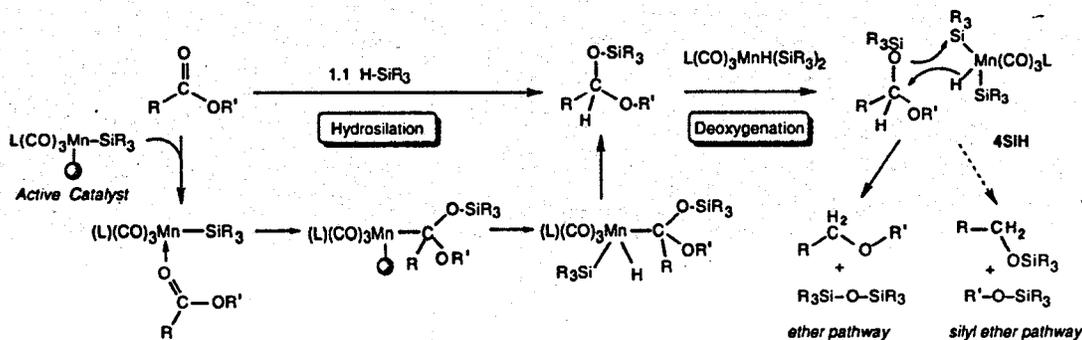
The manganese acyls $(L)(CO)_4MnC(O)CH_3$ [$L = CO$ (1), PPh_3 (7)] catalyze the $PhSiH_3$ hydrosilation-then-deoxygenation of esters $RC(=O)OR'$ to ethers and in some cases to silylether products.²⁷ By using Ph_2SiH_2 and $PhMe_2SiH$, we demonstrated that the initial ester hydrosilation step forms a silyl acetal $RCH(OSiR_3)OR'$, which upon treatment with $PhSiH_3$ or even Ph_2SiH_2 undergoes further catalytic deoxygenation. This last step yields ether and silylether (RCH_2OSiR_3 and $R'OSiR_3$) products. The following scheme illustrates these competing catalytic deoxygenation pathways.^{27,47,48}

Choice of the precatalyst affects this partitioning of deoxygenation pathways. Ethyl acetate, for example, with $PhSiH_3$ (1.2 equiv) and 7 (1.5%) underwent an exothermic reaction that yielded 85% Et_2O [and $PhSiH(OEt)_2$] within 15 min.; the same reaction but using 1 as the precatalyst went slower



(1.5 h), but quantitatively provided Et_2O . Analogous reactions using Ph_2SiH_2 and $PhMe_2SiH$ afforded silyl acetals (80-90% isolated yields), which underwent further 7-catalyzed reduction to ether with $PhSiH_3$ or even Ph_2SiH_2 .

The mechanism for this ester-hydrosilane catalysis consists of the two steps, hydrosilation and then deoxygenation. We envisage hydrosilation starting with 5 as the active catalyst and following a pathway analogous to ketone hydrosilation.^{24,4} The deoxygenation step,⁴⁹ however, with its partitioning between ether and silyl ether products remains the subject of ongoing study. Our current working hypothesis involves $5SiH$, the hydrosilane adduct of the active catalyst,³⁴ as a hydride donor to the silyl acetal commensurate with release of disiloxane (or silyl ether).^{15,16b,50}

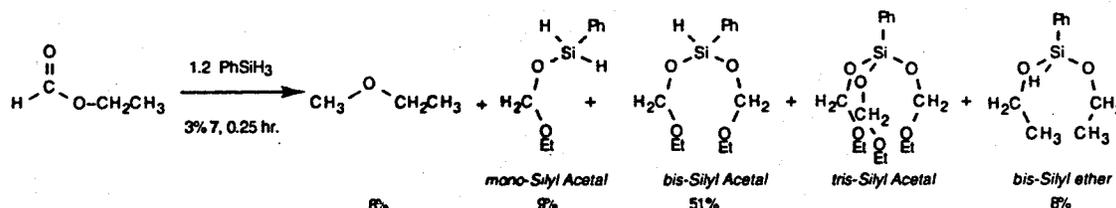


1. Catalytic Hydrosilation-then-Reduction of "Difficult" Esters.

In our initial studies, 1- and 7-catalyzed PhSiH_3 reactions with selected esters and lactones gave 40-95% yields of ethers and only minor amounts of silyl ether byproducts.²⁷ Although virtually all esters tested were consumed under our catalysis conditions, some provided complex mixtures of silyl acetals, silyl ethers, and relatively small amounts of ethers. Ethyl formate and methyl *p*-toluate are typical of these "difficult" esters that we further studied.⁵⁰

Our objective was to document the relative amounts of ester-derived ethers, silyl ethers, and silyl acetals as a function of hydrosilane, manganese precatalyst, and reaction conditions. Ultimately, this information coupled with anticipated advances in catalyst design for promoting these ester-hydrosilane reactions should permit us to transform virtually any ester selectively to its ether or silyl ether products.

A sampling of data for ethyl formate illustrates the complexity of the 7-catalyzed reaction with PhSiH_3 .⁵¹ (Under comparable conditions, $\text{CH}_3\text{CO}_2\text{Et}$ yielded 84% ether plus 8% bis-silyl ether, $\text{PhSiH}(\text{OEt})_2$.) The relative concentrations of these silyl acetals varied with the PhSiH_3 present and reaction time, but the amount of ether remained <10%. Since we could not isolate the mono- and bis-silyl acetals, analogs were synthesized using Ph_2SiH_2 and PhMeSiH_2 and used as spectroscopic models.



The apparent resistance of bis- and tris-silyl acetals towards catalytic deoxygenation by silanes¹⁶ led us to examine the reactivity of fully characterized monosilyl acetals. $\text{PhMe}_2\text{SiOCH}_2\text{OEt}$ and $\text{EtMe}_2\text{SiOCH}_2\text{OEt}$ ⁵² accordingly were treated with 1.2 equiv. of different silanes and manganese precatalysts; a sampling of this data appears below for $\text{EtMe}_2\text{SiOCH}_2\text{OEt}$. Two conclusions emerge from this data. First, the expected deoxygenation regioselectivity was confirmed with PhMe_2SiH : the mixed

$\text{H}_2\text{C}(\text{O}-\text{SiMe}_2\text{Et})-\text{O}-\text{CH}_2\text{CH}_3$ 5.5 hr., 22°C	1.2 PhMe ₂ SiH 3% 7	Silyl Acetal consumed 17%	CH ₃ OCH ₂ CH ₃ 0%	Silyl ethers (1:1) 17% CH ₃ -O-SiMe ₂ Et + CH ₃ CH ₂ -O-SiMe ₂ Ph
	1.2 Ph ₂ SiH ₂ 3% 1	62%	40%	22% CH ₃ -O-SiMe ₂ Et + CH ₃ CH ₂ -O-SiPh ₂ H
	1.2 PhSiH ₃ 3% 7	52%	52%	0%

silyl ethers $\text{CH}_3\text{OSiMe}_2\text{Ph}$ and $\text{CH}_3\text{CH}_2\text{OSiMe}_2\text{Et}$ were not detected. Second, the facility of 7-catalyzed deoxygenation of a monosilyl acetal to yield its organic ether increases: $\text{PhSiH}_3 > \text{Ph}_2\text{SiH}_2 > \text{PhMe}_2\text{SiH}$.

These conclusions can be generalized: *the choice of both the hydrosilane and the precatalyst are important in selectively converting a silyl acetal to its ether or silyl ether products.* Selectively transforming a monosilyl acetal into an ether generating the silylacetal with PhMe_2SiH and catalytically deoxygenating it with PhSiH_3 . Attempts to use just Ph_2SiH_2 or PhSiH_3 for both catalytic

steps invariably produces bis- and tris-silyl acetals, which resist subsequent deoxygenation. Although RMe_2SiH readily forms monosilyl acetals, they do not further react with monohydrosilanes.

2. Rhodium(I)-Catalyzed Hydrosilation of Organic Esters.

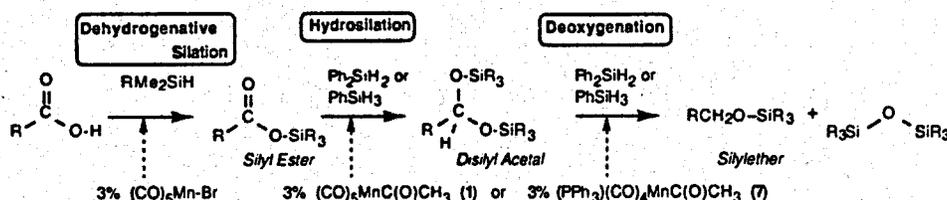
Although rhodium(I)-catalyzed hydrosilation of aldehydes and ketones represents a mature technology,⁴ similar hydrosilation of simple organic esters is unknown.^{47,48} We were therefore quite surprised to find that in "control" experiments even Wilkinson's catalyst promoted the diphenylsilane hydrosilation of ethyl acetate. The presence of 3% $\text{RhCl}(\text{PPh}_3)_3$ and 2.4 equiv. of Ph_2SiH_2 quantitatively transforms ethyl acetate to ether over 48 h, whereas $[\text{Rh}(\text{O}_2\text{CCH}_3)(\text{COD})]_2$,⁵³ stops at the monosilyl acetal stage (88%, 0.3 h).

This Rh(I) catalysis study has relied on just a few precatalysts - $\text{RhCl}(\text{PPh}_3)_3$, $[\text{RhCl}(\text{COD})]_2$, $[\text{RhCl}(\text{COD})]_2 + 2 \text{PPh}_3$, and $[\text{Rh}(\text{O}_2\text{CCH}_3)(\text{COD})]_2$,⁵³ - and ethyl acetate, ethyl formate, and methyl *p*-toluate as substrates. Under all conditions, PhMe_2SiH and Et_3SiH were unreactive, whereas Ph_2SiH_2 (and Et_2SiH_2 and PhMeSiH_2 in preliminary studies) underwent facile hydrosilation reactions.

Thus far, we only have results from ^1H , ^{13}C NMR spectral monitoring, which needs to be supplemented by GC quantitation and preparative work for selected catalytic runs. The more volatile dihydrosilanes Et_2SiH_2 , PhMeSiH_2 , and EtMeSiH_2 represent good candidates for these studies. We believe that it would be propitious to survey a few (Rh(I) for now) catalytic systems that also are promising for CO_2 hydrogenation.⁵⁴ Examples of such catalytic systems include $[(\text{dppb})\text{RhH}]_x$ and $[(\text{cod})\text{RhH}]_4$ ⁵⁵ as well as an eclectic selection of Wilkinson catalyst analogs, including replacement of the PPh_3 by PMe_3 , P^iPr_3 , etc.⁵⁶

E. Catalytic Reactions of Hydrosilanes with Carboxylic Acids and Silyl Carboxylates.

We have extended the manganese carbonyl-hydrosilane catalysis to carboxylic acids using formic, acetic, toluic, and (less extensively) phenylacetic acids as the substrates. By balancing the choice of hydrosilane and precatalyst, we selectively converted these carboxylic acids into their silyl esters, their disilyl acetals, $\text{RCH}(\text{OSiR}_3)_2$, and finally their alkoxysilanes, $\text{RCH}_2\text{OSiR}_3$.²⁶

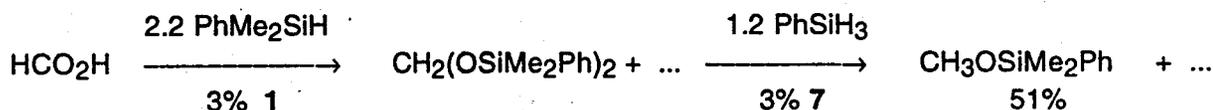


This product selectivity depends upon matching the appropriate precatalyst and silane for each of the above three catalytic steps. The dehydrogenative silylation reaction selectively forms the silyl ester⁵⁷ (even with excess RMe_2SiH , $\text{R} = \text{Et}, \text{Ph}$) with $(\text{CO})_5\text{MnBr}$ precatalyst. Formation of the disilyl acetals is best carried out using either 1 or 7 as the precatalyst with RMe_2SiH and either the acid or its silyl ester.⁵⁸ The more reactive PhSiH_3 was used in the third or deoxygenation step along with 7 as the precatalyst. By using PhSiH_3 and 7, we for example quantitatively converted $\text{CH}_3\text{CO}_2\text{SiMe}_2\text{Et}$ to a mixture of silyl ethers, $\text{EtOSiMe}_2\text{Et}$ and $\text{PhSiH}_x(\text{OCH}_2\text{CH}_3)_{3-x}$.⁵⁸

We are interested in the catalytic dehydrogenative silylation, hydrosilylation, and deoxygenation of formic acid as a novel approach to CO and CO₂ reduction. Previous work of Klinger and Rathke⁵⁹ established uncatalyzed chemistry in which the disiloxane Me₃SiOSiMe₃ and H₂ under pressure at 250 °C with CO or CO₂ yielded Me₃SiOCH₃ and HCO₂CH₃ as the final products. A silyl formate HCO₂SiMe₃ evidently mediates this chemistry and is converted to the hypothesized disilylacetal CH₂(OSiMe₃)₂ that extrudes CH₂=O. This intriguing chemistry is discussed further in the Proposed Studies.

Our immediate objective was to see if we could extend our mild catalysis conditions to convert formic acid via its uncharacterized disilylacetal to methoxysilanes. These studies then will be expanded to (a) thermal degradation of disilylacetals and (b) catalytic disiloxane hydrogenation as a silane plus silanol source coupled with (c) catalytic hydrosilylation of CO₂ and CO, respectively (*vide infra*).

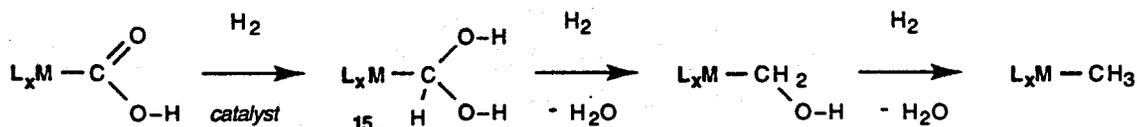
The manganese-catalyzed hydrosilylation of formic acid resembles that of ethyl formate rather than acetic acid.^{32b} We obtained the silyl formates HCO₂SiR₃ [SiR₃ = SiMe₂Et, SiEt₂Me, SiMe₂Ph, and SiHPh₂] and disilyl acetals CH₂(OSiR₃)₂ [SiR₃ = SiMe₂Et, SiMe₂Ph, and SiMe₂Et/SiHPh₂] using the above reaction chemistry. Treatment of HCO₂SiMe₂Ph with 1.2 equiv. of PhSiH₃ and 3% **7** provided < 10% CH₃OSiMe₂Ph - most of the product is the bis-disilyl acetal PhSiH(OCH₂OSiMe₂Ph)₂. Catalytic deoxygenation of preformed CH₂(OSiMe₃)₂ was more useful. The yields of CH₃OSiMe₂Ph depended on the hydrosilane used in the second step: PhSiH₃ (51%), Ph₂SiH₂ (23%), and PhMe₂SiH (9%).



F. Catalytic Reactions of Hydrosilanes with Metallocarboxylic Acid Derivatives.

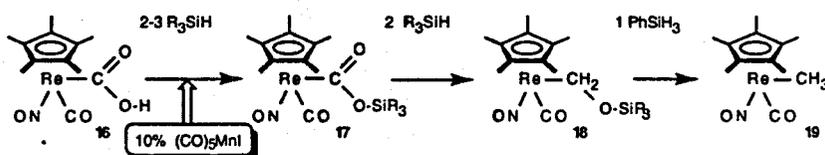
Metalloxy acids L_xMC(O)OH have an established role in catalysis, for example, the water-gas shift-reaction.⁶⁰ In this and other reactions they mediate the pH-dependent interconversion of ligated CO and CO₂. Although several metalloxy acids have been fully characterized,⁶¹ most are unstable with respect to CO₂ deinsertion and conversion to metal hydrides. (Metalloxy derivatives, alkoxy carbonyl complexes, are relatively stable and are available from ligated CO or CO₂.)⁶² Very little is known however concerning the reduction of the acyl ligand of metalloxy acids and their ester derivatives.^{63,64}

We suspect nonetheless that metalloxy acids and their derivatives could be involved in CO or CO₂ fixation.^{1a,64} Consider the hypothetical hydrogenation of a metalloxy acid to yield **15**, the hydrate of the formyl L_xMC(O)H. This acetal derivative could supplant the ubiquitous formyl ligand as a C₁ template for converting ligated CO (or CO₂) to a hydroxymethyl ligand. Although there are no examples of **15**, several acetal analogs have been reported.⁶⁵ We previously reported⁶⁴ that Cp(CO)₂FeCH(OMe)₂, which is stable at room temperature as opposed to the very unstable FpC(O)H,^{1a} could be reduced to FpCH₂OMe.



Our objective was to extend our hydrosilane catalysis to metallocarboxylic acids and their esters, thus (catalytically) transforming them to siloxymethyl complexes, $L_xMCH_2OSiR_3$.⁶⁶ Results of our initial hydrosilation survey of metallocarboxylic acid esters $L_xMCO_2CH_3$ was disappointing:³⁰ these compounds proved to be much less reactive than their acetyl analogs. Under conditions where $(CO)_5Mn(CO)CH_3$ (1) underwent hydrosilation, $(CO)_5Mn(CO)OCH_3$, for example, was *inert* towards Ph_2SiH_2 . Attempts to promote its hydrosilation using 1, 7, or Rh(I) catalysis also failed.³⁰

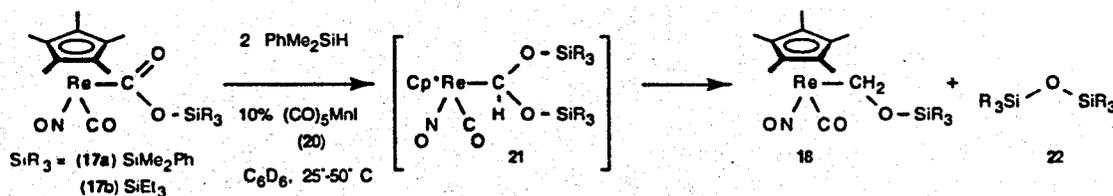
We did develop the above ligand reactions by using the nonlabile system $L_xM = Cp^*(CO)(NO)Re$ as its carboxylic acid **16**⁶⁷ and silyl ester **17**⁶⁸ complexes. Choice of a nonlabile rhenium center ensured that intermolecular hydrosilane reactions were centered on the C_1 carboxylate ligand.^{29,31}



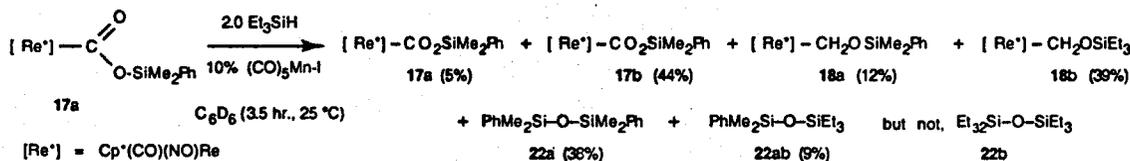
Three themes emerged from these studies. (1) $(CO)_5MnI$ (**20**) is a surprisingly effective precatalyst for hydrosilation then deoxygenation of **16** and **17**. (2) these ligand reactions differ significantly from similar catalytic reactions involving their organic carboxylic acid analogs. (3) as illustrated, either **16** or **17** can be catalytically reduced with hydrosilanes to the siloxymethyl **18** and methyl **19** complexes. This represents a rare example of using a homogeneous catalytic system to reduce carbon monoxide ligated - as its siloxycarbonyl derivative - at another metal complex.⁶⁹

1. The Catalytic Hydrosilation and Further Reduction of Rhenium Silyl Esters.

The silyl esters $Cp^*(CO)(NO)ReCO_2SiR_3$ (**17**) serve as substrates towards **20**-catalyzed hydrosilation-then-deoxygenation.³¹ With 5% **20** present, **17a** in C_6D_6 plus 2.5 equiv. of $PhMe_2SiH$ transformed within 3-4 hours to the siloxymethyl complex **18a** (89-94%) plus disiloxane **22a**. No intermediates were detected by NMR spectroscopy. The same reaction at 50° C required only 1 hr.

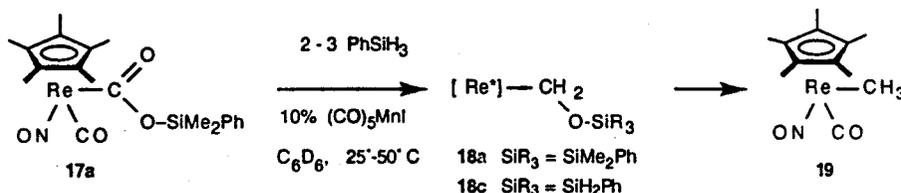


By examining concentration-time profiles for these reactions, we demonstrated that two equiv. of $PhMe_2SiH$ are required to consume **17a** and simultaneously produce **18a** plus **22a**. Although we had isolated organic disilylacetals, we did not detect **21** with the present precatalyst **20** and choices of silane. Further studies using crossover experiments - e.g., treatment of **17a** with 2.0 equiv. of Et_3SiH - uncovered an intriguing **20**-catalyzed silyl exchange reaction for silyl esters **17** (but not for **18** or



22). Yields correspond to starting 21a. Taken together, these results conform to a mechanism involving *reversible* formation of disilylacetal intermediates 21 and then subsequent deoxygenation of to yield the siloxymethyl 18^{70,71}

The use of the more reactive PhSiH₃ in 20-catalyzed reactions with 17a and 17b yielded the fully reduced methyl complex 19. Thus use of PhSiH₃ in (CO)₅MnI (10%) catalyzed reactions with 17a yielded up to 45% 19.

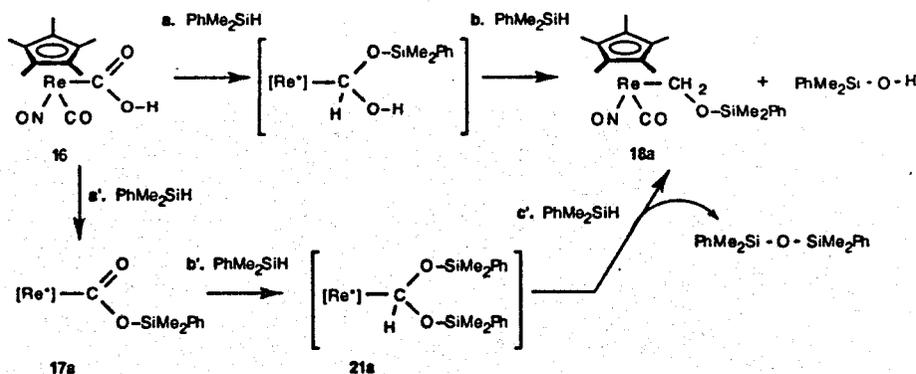


Perhaps the most important conclusion is that the putative disilylacetal complexes 21 can undergo reactions that are not available to their formyl analogs. We showed in this study that the formyl Cp*(CO)(NO)ReCHO did not undergo catalytic hydrosilation.³¹

2. The Case for the Hemisilylacetal Pathway for Catalytic Hydrosilation and Deoxygenation of a Rhenium Carboxylic Acid.

Reactions involving the rhenium acid 16⁶⁷, 2.5-3.0 equiv of PhMe₂SiH, and 5 mol% of precatalyst 20 required more than 24 hrs. at 22° C or 3-4 hrs. at 50° C to convert all of the 16 to 18a.²⁹ The relative slowness of this acid reaction vs. that of its silyl ester 17a is particularly intriguing in that 17a appeared as an intermediate during the acid reaction.

A second difference between the catalytic reactions of 16 and 17a with PhMe₂SiH is that the former reaction initially produces only the silanol PhMe₂SiOH. Formation of disiloxane 22a appeared only after most of the starting 16 had transformed into intermediate 17a or product 18a.⁷²



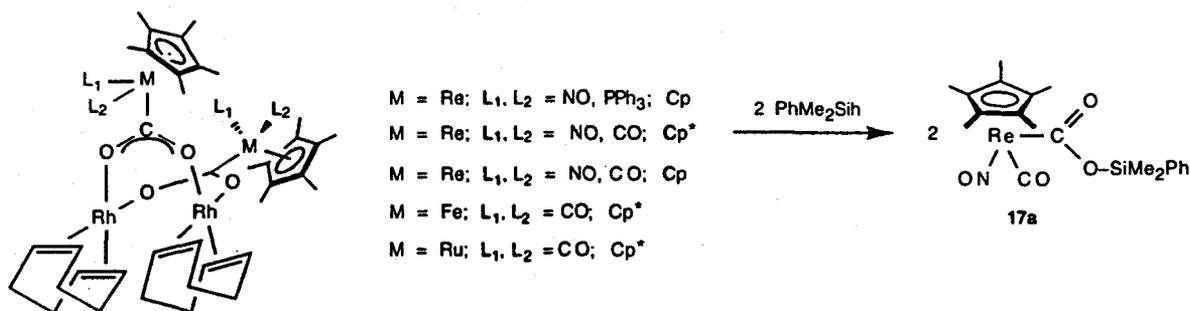
The (CO)₅MnI (20)-catalyzed PhMe₂SiH reactions with the rhenium acid 16 comprises two parallel hemisilylacetal (55%) and disilylacetal (45%) pathways. According to the former (steps a-b), starting 16 gives a hemisilylacetal intermediate 23a, which selectively releases silanol upon catalytic deoxygenation to 18a (total of 2 equiv. of PhMe₂SiH consumed). The latter pathway (steps a'-c') entails catalytic dehydrogenative silylation of 16 followed by hydrosilation to generate a disilylacetal 21a, which subsequently releases disiloxane (3 equiv. of PhMe₂SiH consumed).⁷³

A surprising outcome of this work was that the 20-catalyzed hydrosilation-then-reduction of

the rhenium acid **16** and its silyl ester **17** differ from related reactions involving organic carboxylic acids and their silyl esters, e.g., $\text{CH}_3\text{CO}_2\text{SiR}_3$.²⁶ In contrast, disilylacetals, e.g., $\text{CH}_3\text{CH}(\text{OSiR}_3)_2$, are isolable, and there is no indication of a corresponding hemisilyl acetal pathway with organic acids.

G. Postscript.

Finally, I must acknowledge an area of potential overlap of this last portion of my DOE-sponsored research and that supported by NSF. Our NSF work is concerned with heterobimetallic CO_2 complexes that have been designed to potentially facilitate (catalytic) reduction - using hydrosilanes as well as H_2 - of the ligated CO_2 . Recent efforts have been directed towards a family of Fe_2Rh_2 and Re_2Rh_2 bis-carboxylates that have been designed with catalytically active $\text{Rh}(\text{I})$ centers appended to the CO_2 .⁷⁴ Much of the exploratory work has centered on the first two Re_2Rh_2 bis- CO_2 adducts illustrated; their reactions with hydrosilanes thus far release the silyl esters, e.g., **17**.



We credit the initial synthesis and characterization of rhenium silyl esters to NSF; their catalytic hydrosilation, including current and projected mechanism studies to DOE; the details of reacting hydrosilanes with FeRh and ReRh CO_2 compounds to NSF; and development and testing of Mn and other hydrosilation catalysts to DOE. This partial overlap of DOE and NSF research programs was temporary. NSF-sponsored research now emphasizes new types of bimetallic CO_2 complexes $(L_x\text{M}-\text{CO}_2-\text{M}'L'_x)_y$ in which the labile or catalytically active metal moiety $L_x\text{M}$ [e.g., $\text{Rh}^{\text{I}}(\text{CO})(\text{PR}_3)_2$, Ir^{I} , and Ru^{II} analogs] resides on the carbon-end ($\eta^1\text{-C}$) of the CO_2 complex.

V. PUBLICATIONS

Appearing During Grant Period (5/1/95 - 4/30/99) and Acknowledging DOE Support.

(Those in italics acknowledge NSF support.)

1. "The Catalytic Hydrosilation of Organic Esters Using Manganese Carbonyl Acetyl Complexes, $(L)(CO)_4MnC(O)CH_3$ ($L = CO, PPh_3$)", Z. Mao, B. T. Gregg, and A. R. Cutler *J. Am. Chem. Soc.* **1995**, *117*, 10139.
2. "Hydrosilation of Manganese Acetyl $(CO)_5MnC(O)CH_3$ With Monohydrosilanes", B. T. Gregg and A. R. Cutler *J. Am. Chem. Soc.* **1996**, *118*, 10069.
3. "Manganese Carbonyl Complexes as Catalysts for the Hydrosilation of Ketones, A Comparison with $RhCl(PPh_3)_3$ ", M. DiBiase, B. T. Gregg, and A. R. Cutler. *Organometallics* **1996**, *15*, 2764.
4. "Carbon Dioxide Complexation: Infrared Spectroscopy of Iron and Ruthenium η^5 -Cyclopentadieny(carbonyl) Metallocarboxylates," J. R. Pinkes, C. J. Masi, R. Chiulli, B. D. Steffey, and A. R. Cutler, *Inorg. Chem.* **1997**, *36*, 70.
5. "Preparation and Characterization of the Rhenium Silyl Esters $(\eta^5-C_5Me_5)(CO)(NO)ReC(O)OSiR_3$ ($SiR_3 = SiMe_2Ph, SiEt_3$)," M. DiBiase-Cavanaugh, S. M. Tetrick, C. J. Masi, and A. R. Cutler, *J. Organomet. Chem.* **1997**, *538*, 41.
6. " $Re_2Rh_2 \mu_3-[\eta^1-C(Re):\eta^1-O(Rh):\eta^1-O'(Rh)]$ Bis-Carbon Dioxide Complexes $[(\eta^5-C_5R_5)(L)(NO)Re(CO_2)Rh(\eta^4\text{-diene})]_2$ that are Structurally Related to Rhodium(I) Carboxylate Dimers $[Rh(O_2CR)(\eta^4\text{-diene})]_2$," S. M. Tetrick, F. S. Tham, and A. R. Cutler, *J. Am. Chem. Soc.* **1997**, *119*, 6193.
7. "The Reactions of Hydrosilanes with the Methoxycarbonyl Complexes $Cp(L)(CO)MCO_2Me$ ($M = Fe, Ru$; $L = CO, PPh_3$) and $(L)(CO)_xMCO_2Me$ ($M = Co, Mn$; $L = CO, PPh_3$; $x = 3, 4$), With and Without Catalysis," B. T. Gregg, M. DiBiase-Cavanaugh, R. J. Chiulli, and A. R. Cutler, *J. Organomet. Chem.* **1997**, *547*, 173.
8. "Manganese- and Rhodium- Catalyzed Phenylsilane Hydrosilation - Reduction of Iron Acyl Complexes $Cp(L)(CO)FeC(O)R$ ($L = CO, PPh_3, PEt_3, P(OMe)_3, P(OPh)_3$; $R = CH_3, Ph, CMe_3$)," Z. Mao, B. T. Gregg, and A. R. Cutler, *Organometallics* **1998**, *17*, 1993.
9. "An Unusual Degradation of a Rhenium Silyl Ester $Cp(NO)(PPh_3)ReCO_2SiMe_2Ph$ to a Bimetallic $\mu-[\eta^1-C(Re):\eta^1-O,O'(Re)]$ Carbon Dioxide Complex $Cp(NO)(PPh_3)ReCO_2-Re(NO)(CO)(PPh_3)OSiMe_2Ph$," S. M. Tetrick, M. DiBiase-Cavanaugh, F. S. Tham, and A. R. Cutler, *Organometallics* **1998**, *17*, 1925.
10. "Synthesis of M_2Rh_2 Bis- μ_3 -Carbon Dioxide Complexes from the Reaction between $[Rh(OH)(\eta^4-COD)]_2$ and Cationic Metal Carbonyls," S. M. Tetrick, C.-Fu Xu, J. R. Pinkes, and A. R. Cutler, *Organometallics* **1998**, *17*, 1861.
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12. "The Reactivity the Metallocarboxylates $Cp(NO)(PPh_3)ReCO_2 \cdot M^+$ Towards Excess Carbon Dioxide: Degradation to a Bimetallic $\mu\text{-}[\eta^1\text{-C(Re)}:\eta^1\text{-O,O'(Re)}]$ Carbon Dioxide Complex $Cp(NO)(PPh_3)ReCO_2Re(NO)(CO)(PPh_3)(\eta^1\text{-C}_5\text{H}_5)$," S. M. Tetrick and A. R. Cutler, *Organometallics*, 1998, manuscript accepted for publication.
13. "The Catalytic Hydrosilation and Further Reduction of Some Rhenium Silyl Esters, $Cp^*(CO)(NO)ReCO_2R$, $R = SiMe_2Ph, SiEt_3$ ", M. DiBiase-Cavanaugh and A. R. Cutler, *J. Am. Chem. Soc.* 1998, submitted for publication.
14. " $(CO)_5MnI$ -Catalyzed $PhMe_2SiH$ Hydrosilation and Deoxygenation of the Rhenium Carboxylic Acid, $Cp^*(CO)(NO)ReCO_2H$; The Case for the Hemisilylacetal Pathway", M. DiBiase-Cavanaugh and A. R. Cutler, *Organometallics* 1998, submitted for publication.
15. "Transformation of Manganese Acyls $(CO)_5MnC(O)CH_2R$ ($R = H, CH_3, OCH_3$) into their Silyloxyvinyl Derivatives $(CO)_5MnC(OSiEt_3)=CHR$ with Triethylsilane; An approach to Double Carbonylation of Manganese Alkyl Complexes $(CO)_5MnCH_2R$ ", B. T. Gregg and A. R. Cutler, *Organometallics* 1998, 17, 4169.
16. "Reactions of $PhMe_2SiH$ with the Manganese Methyl Complex $(CO)_5MnC(O)CH_3$: New Reactions and a New Precatalyst, the Silylmanganese $(\eta^2\text{-Si-H})$ Silane Adduct $(CO)_4Mn(SiMe_2Ph)(H\text{-}SiMe_2Ph)$ ", C. Xu, S. M. Tetrick, S. Punia, and A. R. Cutler, *J. Am. Chem. Soc.* 1998, submitted for publication.
17. "Catalytic Hydrosilation and Deoxygenation of Ligated Carbon Dioxide on the Rhenium-Stanyl and Rhenium-Zirconocene Esters $(\eta^5\text{-C}_5\text{Me}_5)(CO)(NO)ReC(O)OML_x$ ($ML_x = SnMe_3, SnPh_3, ZrClCp_2$, and $ZrClCp^*_2$)", M. DiBiase-Cavanaugh, C. J. Masi, and A. R. Cutler, *J. Am. Chem. Soc.* 1998, manuscript to be submitted.
18. "Unusually Facile Carbonylation of $(\eta^5\text{-Indenyl})$ ruthenium Methyl and Methoxymethyl Complexes $(\eta^5\text{-C}_9\text{H}_7)(CO)(L)RuR$ ($L = CO, PPh_3$)", R. J. Chiulli, D. L. Tarazano, M. E. Dery, and A. R. Cutler, *Organometallics*, manuscript to be submitted.
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20. "Hydrosilation of the Manganese Carbonyl Aroyl Complexes $(CO)_5MnC(O)\text{-p-C}_6\text{H}_4Y$ [$Y = H, Me, ^tBu, OMe, CF_3$]", C. Xu, B. T. Gregg and A. R. Cutler, manuscript in preparation.
21. "Preparation and Characterization of $(PPh_3)(CO)_4MnSiMe_2Ph$ ", C. Xu, B. T. Gregg, M. DiBiase-Cavanaugh, and A. R. Cutler, manuscript in preparation.

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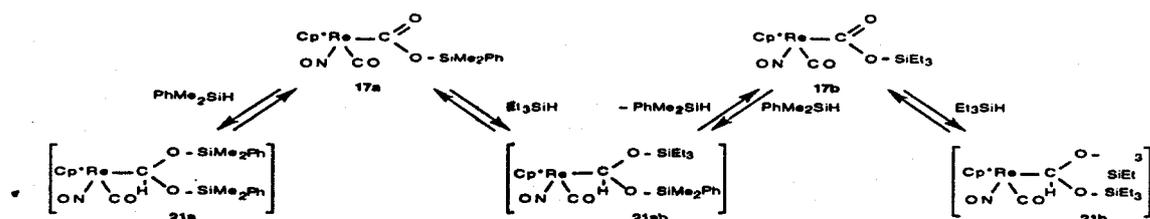
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 33. Coordinatively unsaturated (or weakly ligated) metal carbonyl silyl complexes that are isolobal with $(\text{CO})_4\text{MnSiR}_3$ have been generated thermally $[\text{CpFe}(\text{CO})\text{SiR}_3]^{18\text{a,b}}$ and photochemically $[(\text{CO})_3\text{CoSiR}_3,^{33\text{a,b}} \text{CpFe}(\text{CO})\text{SiR}_3/\text{CpFe}(\text{CO})\text{SnR}_3,^{33\text{c,d}} (\text{CO})_4\text{MnSiR}_3/(\text{CO})_4\text{MnSnR}_3^{33\text{e}}]$. (a) Reichel, C. L.; Wrighton, M. S. *Inorg. Chem.* 1980, 19, 3858. Anderson, F. R.; Wrighton, M. S. *J. Am. Chem. Soc.* 1984, 106, 995. (b) Wrighton, M. S.; Seitz, M. S. *Ang. Chem., Int. Ed. Engl.* 1988, 27, 289. (c) Randolph, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* 1986, 108, 3366. (d) Zhang, S.; Brown, T. L. *Organometallics* 1992, 11, 2122. Kawano, Y.; Tobita, H.; Ogino, H. *J. Organomet. Chem.* 1992, 428, 125. Haynes, A.; George, M. W.; Haward, M. T.; Poliakoff, M.; Turner, J. J.; Boag, N. M.; Green, M. *J. Am. Chem. Soc.* 1991, 113, 2011, and references therein. (e) Sullivan, R. J.; Brown, T. L. *J. Am. Chem. Soc.* 1991, 113, 9155.
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42. This step resembles that proposed for our catalytic deoxygenation of organic esters,²⁷ silyl esters,²⁶ and metal acyl complexes.^{16b}
43. Similarly detailed studies also have been carried out on the reactions of PhMe_2SiH with $(\text{PPh}_3)(\text{CO})_4\text{MnCH}_3$, $(\text{L})(\text{CO})_4\text{MnCH}_2\text{Ph}$ ($\text{L} = \text{CO}, \text{PPh}_3$), $(\text{L})(\text{CO})_4\text{Mn-}p\text{-C}_6\text{H}_4\text{Y}$, and $(\text{L})(\text{CO})_4\text{MnH}$.^{32d} Our standard procedure included: (1) doing reactions at room temperature and at 40°C in C_6D_6 in the presence of 2 and 4 equiv. of PhMe_2SiH (and if warranted, Ph_2SiH_2 and PhSiH_3), (2) monitoring by ^1H , ^{13}C , ^{29}Si , and ^{31}P NMR spectroscopy, (3) repeating selected reactions in the presence of H_2 , CO , and PPh_3 , (4) surveying selected reactions as precatalyst sources for (a) hydrosilation of acetone with PhMe_2SiH , (b) hydrosilation-deoxygenation of ethyl acetate with 3 equiv. of PhMe_2SiH or Ph_2SiH_2 , and (c) dehydrogenative silation-hydrosilation-deoxygenation of acetic acid with 3 equiv. of PhMe_2SiH or Ph_2SiH_2 . Only the benzyl complexes afforded truly useful hydrosilane chemistry.
44. These runs entailed adding an aliquot from a preparation of **4** to the substrate and an excess of the new hydrosilane. We are of course cognizant of the pitfalls of doing catalysis with a mixture of several components, of which one is alleged to function as the precatalyst. All other detectable components individually are ineffective catalysts. Other sources of **4** (which realize different byproducts) - including $(\text{CO})_5\text{MnC}(\text{O})\text{Ph}$ (**2**) and $(\text{CO})_5\text{MnSiR}_3$ ($h\nu$) - effect the same product distributions during silane catalysis runs. The proposal section deals with generating and characterizing stabilized but still reactive analogs of **4**.
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48. Recent examples of homogeneously catalyzed reactions of hydrosilanes with esters typically give silyl ethers or 1° alcohols after workup: (a) Berk, S. C.; Kreutzer, K. A.; Buchwald, S. L. *J. Amer. Chem. Soc.* **1991**, *113*, 5093. (b) Berk, S. C.; Buchwald, S. L. *J. Org. Chem.* **1992**, *57*, 3751. (c) Barr, K. J.; Berk, S. C.; Buchwald, S. L. *J. Org. Chem.* **1994**, *59*, 4323. (d) Breden, S. W.; Lawrence, N. J. *SYNLETT* **1994**, 833.
49. Other examples of Rh(I)-catalyzed deoxygenation of α -siloxyalkyl ligands with hydrosilanes also have been reported, see references 14, 20, 26, 29, 31.
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51. ^{13}C NMR spectral monitoring of these reactions was especially informative, since the central carbons of ester-derived ethers, silyl ethers, and silyl acetals exhibit distinctive spectral ranges. ^1H and ^{13}C NMR spectral correlations were used to discern mono-, bis-, and trisilyl ethers of PhSiH_3 , e.g., $\text{PhSiH}_x(\text{OCH}_2\text{R})_{3-x}$, as well as the corresponding silyl acetals, $\text{PhSiH}_x[\text{OCHR}(\text{OR}')]_{3-x}$. Authentic samples of these PhSiH_3 -derived silyl ethers were generated via controlled dehydrogenative silylation of the requisite alcohols and were characterized by ^1H , ^{13}C , ^{29}Si NMR spectroscopy. Small amounts of mixed silyl acetal-silyl ether and perhaps silyl acetal-siloxane compounds are sometimes detected, but not identified.
52. Products were isolated after treating HCO_2Et with 1.2 equiv. of silane and 3% 1 or 7 for 5 hr. These reactions provided 65-88% yields of the silyl acetals plus 5-15% of 1:1 methyl and ethyl silyl ether mixtures. Fully characterized silyl acetals were isolated by flash chromatography.
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 58. PhMe_2SiH and EtMe_2SiH are the most effective hydrosilanes for the first two steps. Treatment of 1.2 equiv. of the carboxylic acid substrate either with RMe_2SiH and 3% **1**, **7** or $(\text{CO})_5\text{MnBr}$ precatalyst affords 84-90% silyl ester. Treatment of acetic acid, 3.2 equiv. of RMe_2SiH , and the precatalysts **1** or **7** yielded 90-98% of the fully characterized disilyl acetals $\text{CH}_3\text{CH}(\text{OSiMe}_2\text{R})_2$ after 3 and 20 h, respectively. The $\text{PhSiH}_x(\text{OCH}_2\text{CH}_3)_{3-x}$ resulting from the **7**-catalyzed PhSiH_3 reaction with $\text{CH}_3\text{CO}_2\text{SiMe}_2\text{Et}$ was not purified. NMR spectral data for each of the three silyl ethers, however, is available from **7**-catalyzed PhSiH_3 reactions with ethanol. Treatment of $\text{CH}_3\text{CO}_2\text{SiMe}_2\text{Et}$ with Ph_2SiH_2 and **1** provided varying ratios of $\text{Ph}_2\text{Si}[\text{OCH}(\text{CH}_3)\text{OSiMe}_2\text{Et}]_2$ and $\text{Ph}_2\text{SiH}[\text{OCH}(\text{CH}_3)\text{OSiMe}_2\text{Et}]$ disilyl acetals (90-95%), which were isolated and fully characterized.
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 70. These results underscore a greater proclivity of PhMe_2SiH (even when present in much lower concentrations) than Et_3SiH to hydrosilate a silyl ester and deoxygenate its resulting silyl acetal.

The PhMe_2SiH extruded during the silyl exchange, **17a** to **17b**, is consumed selectively in their hydrosilation and in subsequent deoxygenation of their disilylacetals **21a** and $[\text{Re}^*]\text{CH}(\text{OSiMe}_2\text{Ph})(\text{OSiEt}_3)$ (**21ab**). This latter reaction preferentially transforms **21ab** to **18b** (39%) and **21a** to **18a** (12%) in order to account for the predominance of **22a** over **22ab**. The relatively large buildup of **17b** in this reaction of course confirms its relatively sluggish hydrosilation reactivity towards Et_3SiH . Similar details for the crossover reactions involving $\text{PhMe}_2\text{SiH}/\text{17b}$ and $\text{Ph}_2\text{SiH}_2/\text{17a}$ and **17b** also have been delineated.



71. This study depended upon our ability to identify and quantitate unsymmetric disiloxanes, some of which were unknown. In order to collect the necessary ^1H , ^{13}C , ^{29}Si NMR spectral data, we selectively generated these compounds in near quantitative yields via **20**-catalyzed dehydrogenative silylation of a silanol R_3SiOH with the requisite hydrosilane. All of the unsymmetric disiloxanes necessary to this study involving the four silyl groups mentioned were characterized.
72. Typical data gleaned from a reaction profile (time-concentration) for **20**-catalyzed reaction between **16** and 2.8 equiv. of PhMe_2SiH : by 100 min., < 10% **16** remained; the sum of the **17a** and **18a** accounted for 93% of the starting **16**. After 220 min., an 89% yield of **18a** corresponds to 2.4 equiv. of PhMe_2SiH consumed per **18a** formed.
73. The surprisingly low reactivity of the silyl ester **17a** during the PhMe_2SiH reactions with the rhenium acid **16** and indeed the overall sluggishness of this reaction is due to the starting **16** inhibiting the catalytic hydrosilation and reduction of **17a**. The normally rapid reaction of **17a** thus was suppressed while **16** slowly converted to **18a** plus silanol. This inhibition (as well as that of the catalytic conversion of PhMe_2SiH and PhMe_2SiOH to **22a**) was confirmed by control reactions.
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C. TIME AND EFFORT COMMITMENT TO PROJECT

The principal investigator has devoted approximately 40% of his time during the academic year and 100% during two summer months on this project. It is anticipated that about the same time and effort commitment will be maintained during the remainder of the current term.