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SELECTIVE TRANSFORMATION OF CARBONYL LIGANDS TO ORGANIC MOLECULES

Final Report

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Abstract (11/15/92 - 11/14/95)

Selective Transformation of Carbonyl Ligands to Organic Molecules

The hydrosilation chemistry involving manganese acyl complexes $(L)(CO)_4MnC(O)R$ (L = CO, PPh_3; R = CH_3, Ph) as substrates and as precatalysts has been developed. Results of a kinetics study on the $(CO)_5Mn$(p-toluoyl)-catalyzed SiH/SiD exchange between $DSiMe_2Ph$ and $HSiMe_2Et$ established that coordinatively unsaturated $(CO)_4MnSiR_3$, the active catalyst, sequentially adds one substrate silane and then releases a product silane. Results of this mechanistic study afforded the working hypothesis for much of our current research: manganese acyl-hydrosilane mixtures generate unsaturated silyl complexes, which are active catalysts for the hydrosilation of a variety of substrates. These active catalysts, $(CO)_4MnSiR_3$, also were generated through photolysis of $(CO)_5MnSiR_3$.

The same active catalyst evidently operates during autocatalytic hydrosilation of $(CO)_5MnC(O)CH_3$ with $HSiR_3$: the resulting mixtures of $(CO)_5MnCH(OSiR_3)CH_3$ and $(CO)_5MnC(OSiR_3)=CH_2$ are accomodated by an intermolecular mechanism in which the active catalyst and substrate afford $(CO)_5MnC(CH_3)(OSiMe_2Ph)$-$Mn(CO)_4$ as the key intermediate. Silane addition affords the former product whereas β-deinsertion produces the latter. The active catalyst originates via independently studied silane-induced degradation of manganese complexes. A similar mechanism operates when $(CO)_5Mn$-Y [Y = C(O)R, R, Br - but not $SiMe_3$ or $Mn(CO)_5$] are used as efficient hydrosilation precatalysts for nonlabile iron acyls $Cp(CO)(L)FeC(O)R$. These reactions gave $FpCH(OSiR_3)CH_3$ under conditions where typical Rh(I) hydrosilation catalysts are inactive.

These manganese complexes and hydrosilanes also afford extremely active catalysts for hydrosilane alcoholysis, silation of carboxylic acids, hydrosilation of organic aldehydes and ketones, and hydrosilation-then-reduction of organic esters. $(L)(CO)_4MnC(O)CH_3$-catalyzed H_3SiPh reactions with esters RC(=O)OR' promptly afford silyl acetal intermediates $RCH(OSiR_3)OR'$ that transform to the ethers RCH_2OR' and in some cases to alkoxysilane products RCH_2OSiR_3 and $R'OSiR_3$. Less reactive H_2SiPh_2 and $HSiMe_2Ph$ have been used mainly to procure the silyl acetals for spectroscopic and mechanistic studies.

Results of carbonylation studies on (η^5-indenyl)(L)(CO)Ru-alkyl complexes show: (1) that the (Ind)Ru alkyl moiety promotes otherwise infeasible carbonylation reactions, as compared to CpFe or Ru or even (Ind)Fe congeners; (2) that this carbonylation engenders a novel alkyl ligand isomerization process. Carbonylation of (Ind)(L)(CO)Ru-$CH(OR)CH_3$, for example, gave only (Ind)(L)(CO)Ru$C(O)CH_2CH_2OR$; neither [Ru]-CH_2CH_2OR intermediates nor [Ru]-$C(O)CH(OR)CH_3$ were detected. These carbonylation-assisted isomerization reactions apparently involve the sequential coupling of reversible η^5/η^3 Ind ring slippage with carbonylation and then η^3/η^1 Ind ring slippage with alkyl ligand isomerization steps. Carbonylation of $(Ind)(PPh_3)(^{13}CO)FeCH_3$ exclusively gave $(Ind)(PPh_3)(CO)Fe^{13}C(O)CH_3$, which corresponds to a stereoselective CO association coupled with an η^5/η^3 Ind ring shift.

PROGRESS REPORT

Prologue

My DOE-sponsored research program has undergone an extensive restructuring with regards to research objectives. The starting point for this restructuring was our work on carbonylation chemistry as it related to generating and transforming organotransition metal acyl complexes plus CO to poly(alkoxymethylene)acyl compounds, L_xM-$C(O)[CH(OR)]_nCH_2(OR)$.[1,2]

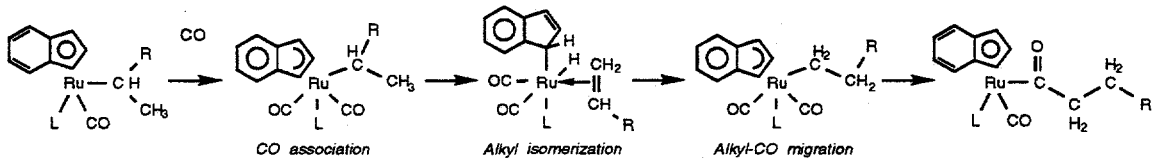
During these studies, we reported (a) procedures using the "indenyl effect" to drive otherwise infeasible carbonylation reactions[3] and (b) the hydrosilation chemistry involving acyl complexes.[4] Just prior to stopping this work, we had developed the catalytic conditions for carrying out these acyl ligand hydrosilation reactions with high diastereofacial selectivity — this work will be published in the near future. However, finding a metal system L_xM that couples the preparation of the acyl ligand (carbonylation) with its reduction (hydrosilation) was becoming an exercise in synthesis.

In restructuring this program, we focused on two of our recent developments that engender particularly promising novel coordinated ligand reactions *and* applied catalysis:

(1) Carbonylation-assisted alkyl ligand isomerization on (η^5-indenyl)ruthenium complexes, (Ind)(L)(CO)RuR, and its application to hydroformylation catalysis. (25% effort)

(2) The reactions of manganese carbonyl complexes with hydrosilanes, and characterization of these systems as unusually powerful hydrosilation and dehydrogenative silation catalysts towards a variety of organic substrates. (75% effort)

We withheld publishing our work on the (Ind)Ru alkyl carbonylation chemistry until recently[5,6] — we suspected that more was involved than just unusually high carbonylation reactivity due to the indenyl effect. That something more turns out to be an unprecedented alkyl ligand isomerization that requires a carbonylation step. Work in

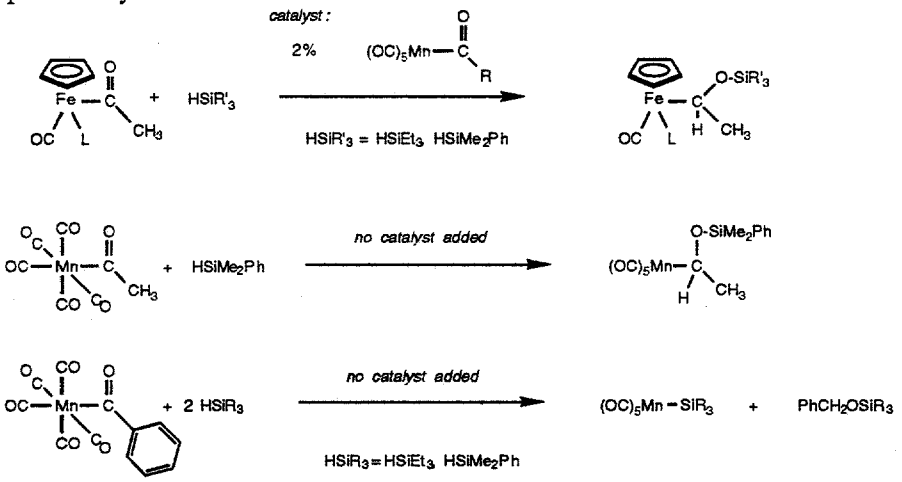


progress includes kinetics and other mechanistic studies that relate reversible η^5/η^3 Ind ring slippage to the alkyl-CO migration and η^3/η^1 Ind ring slippage to the alkyl ligand isomerization. We will continue to use indenyl ligand haptomerization to promote otherwise infeasible (for related Cp-metal compounds) carbonylation then migratory insertion sequences that are catalytically relevant.

The manganese carbonyl-hydrosilane chemistry has evolved from our studies on the autocatalytic hydrosilation of manganese acyl compounds[4,7,8] and on the use of these reaction mixtures as hydrosilation catalysts for other organometallic and organic acyl

compounds. The present catalysis work builds upon the results of our recently published kinetics study on the manganese acyl-catalyzed SiH/SiD isotope exchange.[9]

These current studies arose from observing three types of reactions between hydrosilanes and the organometallic acyl complexes illustrated. Nonlabile metal systems such as $Cp(CO)_2FeC(O)R$ (FpCOR) require catalysts in order to hydrosilate the acyl ligand to α-siloxyalkyl derivatives.[10,11] Labile acyl complexes $L(CO)_4MnC(O)R$[7,8,12] and $L(CO)_3Co$-$C(O)R$[13] add hydrosilanes in the absence of a catalyst and form either α-siloxyalkyl complexes or alkoxysilane / metal silyl mixtures. For example, hydrosilanes $HSiR_3$ convert the labile Mn acetyl and benzoyl complexes illustrated into Mn α-siloxyethyl and silyl compounds, respectively.



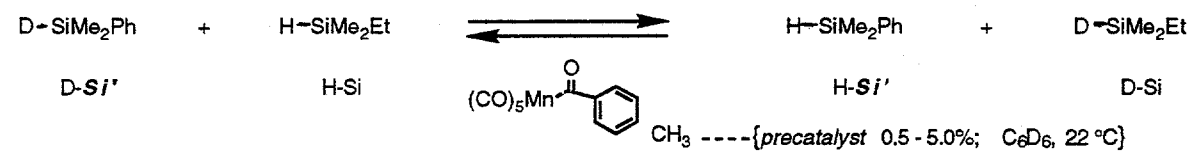
Both of the above manganese acyl-hydrosilane reaction mixtures function as superb hydrosilation catalysts towards FpCOR.[11] Indeed, the Mn precatalysts are far more active and selective than is $Rh(PPh_3)_3Cl$. In order to understand the Mn acyl / hydrosilane chemistry, we expanded these studies to encompass the reactions of other labile Mn and Co alkyl and acyl complexes with hydrosilanes.

Hydrosilation reactions involving the manganese acyl complexes are of interest for three reasons. (1) Hydrosilane reactions with labile metal acyls (as substrates) resemble similar reactions involving other reductants such as H_2[14] or metal hydride[15] complexes. (2) Acyl ligand hydrosilation engenders other novel ligand reactions. Examples include transforming acetyl ligands L_xM-$C(=O)CH_3$ plus hydrosilane to α-siloxyvinyl L_xM-$C(OSiR_3)=CH_2$,[8] vinyl L_xM-$CH=CH_2$,[10] and fully reduced alkyl L_xM-CH_2CH_3 groups.[10,16,17] (3) These manganese acyl / hydrosilane systems afford extremely active catalysts for, thus far, SiH/SiD isotope exchange,[9] hydrosilane alcoholysis,[18] silation of carboxylic acids, hydrosilation of aldehydes and ketones,[19] and hydrosilation then further reduction of esters.[20]

A. Hydrosilation Chemistry Involving Manganese Carbonyl Complexes as Catalysts and as Substrates

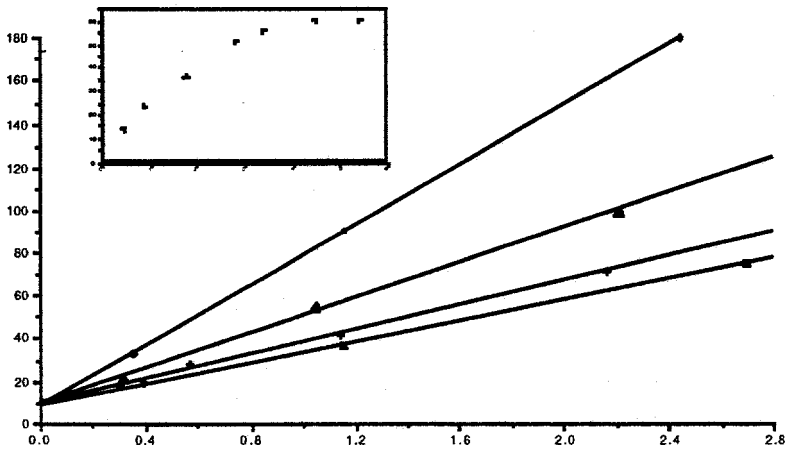
1. SiH/SiD Exchange Kinetics Study and Implications.[9]

The manganese, p-toluoyl $(CO)_5MnC(O)$-p-$C_6H_4CH_3$, serves as a precatalyst for SiH/SiD exchange between Me_2PhSiD (*Si'D*) and Me_2EtSiH (SiH). This isotope exchange is of interest as it addresses the reactivity of the active catalyst with silane alone. By doing a complete mechanistic study, we developed the working hypothesis for much of our current research: manganese acyl-hydrosilane mixtures generate unsaturated silyl complexes, $(CO)_4MnSiR_3$, which are active catalysts for the hydrosilation of a variety of substrates.[21,22]



With as little as 0.5% precatalyst, these redistribution reactions afford reproducible induction, preequilibrium, and final equilibrium periods. During the induction period, the silanes transform the precatalyst to the active catalyst plus the alkoxysilanes p-$CH_3(C_6H_4)CH_2OSiMe_2R$ (verified on a preparative scale). The preequilibrium kinetics are consistent with second-order isotope exchange reaction: plots of $-\ln[1-(Si'H)/(Si'H)_{eq}]$ vs. time are linear.

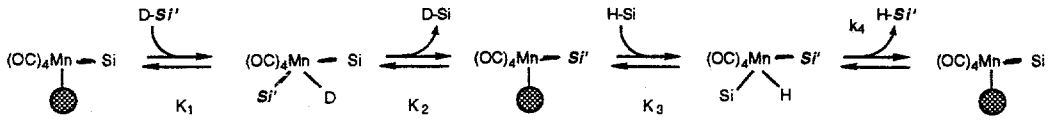
In further studies on the preequilibrium kinetics of SiH/SiD exchange, initial velocities, υ_0, were determined for constant $(\text{precatalyst})_i$ and $(Si'D)_i$ and varying $(SiH)_i$. Plots of υ_0 against $(SiH)_i$ are consistent with saturation kinetics; double reciprocal or Lineweaver-Burk plots of $1/\upsilon_0$ vs. $1/(SiH)_i$ remained linear over wide changes in $(SiH)_i$. The kinetics of this bireactant-biproduct (bi bi) reaction are linear or 'pure', as judged by the appearance of the 2° plot: slope/(SiH) vs $1/(Si'D)$ is linear ($R^2 = 0.992$).[23]



Plots of Initial Velocities υ_0 vs. Initial Concentrations of Varied Substrate $HSiMe_2Et$

Conditions: initial concentrations of $(CO)_5MnC(O)$-p-$C_6H_4CH_3$ (10 mg, 0.050 M), $DSiMe_2Ph$ (*Si'D*) (101 mg, 1.143 M), $HSiMe_2Et$ (SiH) (25-300 mg, 0.462-5.409 M) in C_6D_6 (22 °C). Line in double reciprocal plot with smallest slope is for illustration only; it is defined only by two points. Intercept for double reciprocal plots = 8.99 ± 0.75 (2σ).

Graphical analysis of these Lineweaver-Burk plots is in accord with a ping-pong bi bi mechanism that operates under rapid equilibrium conditions and involves unsaturated manganese silyls, $(CO)_4MnSiMe_2R$, as active catalysts. These intermediates interconvert by sequentially adding one substrate silane and then releasing a product silane.



The kinetic expression that we derived for this exchange reaction has the coordinatively unsaturated silyl $(CO)_4MnSiMe_2Ph$ (*MnSi'*) as the initiating active catalyst.[22] If the initial forward velocity in the absence of the second product is considered, the final kinetic expression is,

$$\upsilon_o = k_4\,(MnSi^{t}SiH) = \frac{k_4\,(MnSi)_T\,(SiH)}{K_3\left\{\frac{(SiD)}{K_2}\left(1+\frac{K_1}{(Si^{t}D)}\right)+1\right\}+(SiH)}$$

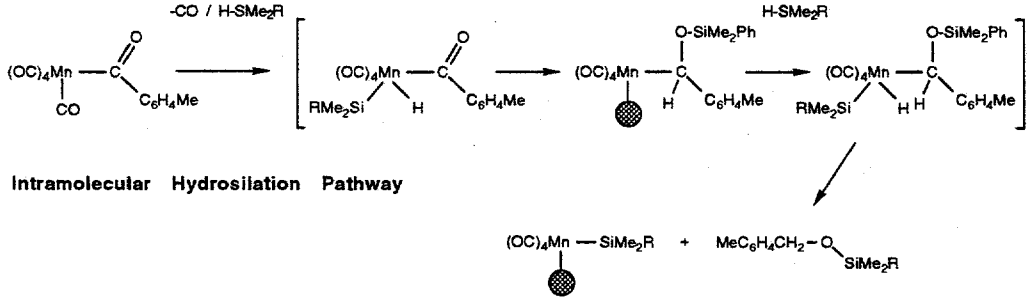
$$\frac{1}{\upsilon_o} = \frac{K_3}{k_4\,(MnSi)_T}\left\{\frac{(SiD)}{K_2}\left(1+\frac{K_1}{(Si^{t}D)}\right)+1\right\}\left[\frac{1}{(SiH)}\right] + \frac{1}{k_4\,(MnSi)_T}$$

This kinetic expression agrees with the graphical analysis: (a) the intercept factor of this equation, $1/[k_4(MnSi)_T]$, accounts for the Lineweaver-Burk plots intersecting on the vertical axis and (b) the competitive activation term, $[1 + K_1/(Si'D)]$, verifies that the multiple plots should pivot clockwise about the intersection point with increasing $(Si'D)_i$.

Other bi bi mechanisms are incompatible with our results. For example, the ping-pong version under steady-state conditions, which commonly occurs in enzymatic systems, also has a single active site and an obligate order of adding substrate 1, ejecting product 1 and adding substrate 2, ejecting product 2.[23] The resulting kinetic expression however defines multiple Lineweaver-Burk plots with parallel lines and uncompetitive activation.

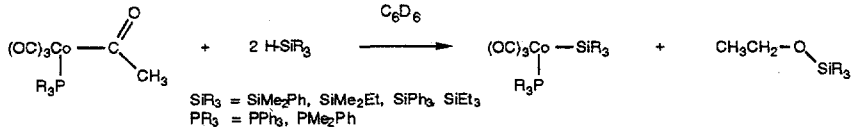
Two results from this mechanistic study are directly applicable to our ongoing effort using manganese carbonyl complexes as hydrosilation catalysts. First, the coordinatively saturated $(CO)_5MnSiMe_2Ph$ and $(CO)_5MnSiPh_2H$ are not catalyst precursors for SiH/SiD exchange (nor is $Mn_2(CO)_{10}$). However, photolysis of these silyl complexes in the presence of our silane mixtures engenders efficient isotope exchange.

Second, pretreating the manganese aroyl complex with excess Me_2EtSiH for 0.75 h (until all of the starting precatalyst had been consumed) before adding Me_2PhSiD eliminates the induction period. Although this pretreatment step maximizes catalytic efficacy for this isotope exchange, the timing is critical. The active catalyst is short lived, and productive catalysis of the silane exchange ceases within 1.25 h. This pretreatment



procedure now is used routinely in other manganese-catalyzed hydrosilation reactions.

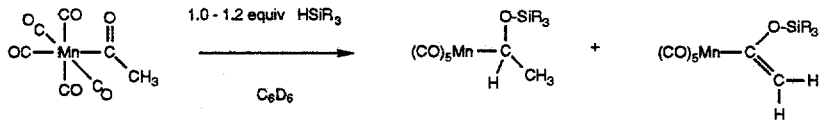
The remaining mechanistic question concerning the catalytic SiH/SiD exchange is the origin of the active catalysts, $(OC)_4MnSiMe_2R$.[22] We proposed that they originate via the illustrated intramolecular pathway.[24] Independent studies confirmed that this reaction quantitatively affords the benzyloxysilane; the manganese materials balance consisted of $Mn_2(CO)_{10}$ and moderate yields of $(CO)_5MnSiMe_2R$ (a maximum of 58% with 1 atm. CO present). We previously documented the operation of this pathway during the hydrosilation of cobalt acetyl complexes, reactions which had proved to be exceptionally clean.[13]



2. Autocatalytic Hydrosilation of $(CO)_5MnC(O)CH_3$ with Monohydrosilanes.[7,8]

The hydrosilation chemistry of $(CO)_5MnC(O)CH_3$ with 12 monohydrosilanes is being published.[7] Of the 10 α-siloxyethyl complexes $(CO)_5MnCH(OSiR_3)CH_3$ that formed, 7 were isolated in 46-70% yields after column chromatography.[25] Once isolated, α-siloxyethyl products **a-d** are stable in benzene solution for at least six hours. Five of these α-siloxyethyl complexes also were carbonylated (80 psig) and characterized as their α-siloxypropionyl derivatives, $(CO)_5MnC(O)CH(OSiR'_3)CH_3$.

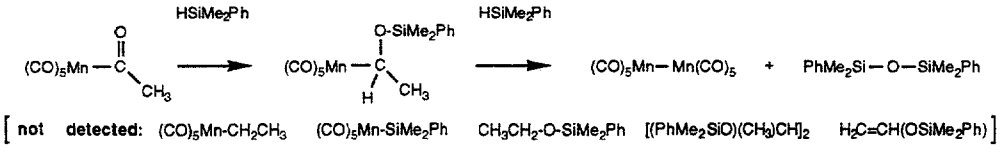
Also reported are six α-siloxyvinyl byproducts $(CO)_5MnC(OSiR_3)=CH_2$. Of these, only the α-siloxyvinyl complexes containing at least one SiEt group formed in substantial yields: $SiEtMe_2$ (12%), $SiEt_2Me$ (22%), and $SiEt_3$ (60%). We summarize their reaction chemistry in the next section. Although much of the synthetic chemistry in these two sections was done prior to this grant period, we delayed publishing this work until the kinetics study in the previous section and the mechanistic work outlined in these two sections was finished.

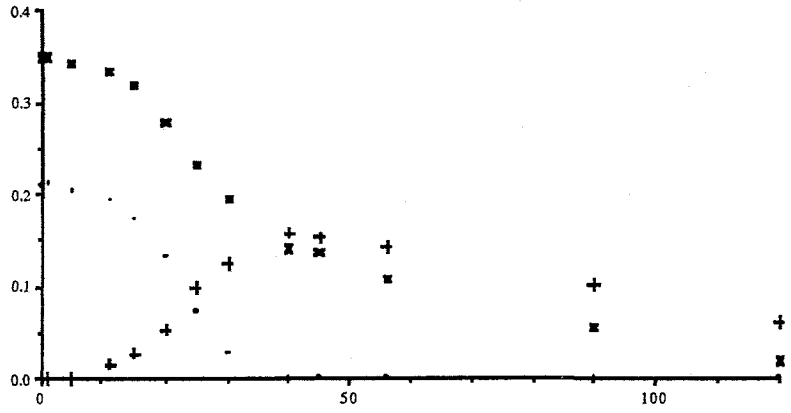


SiR_3 = (a) $SiMe_2Ph$, (b) $SiMePh_2$, (c) $SiMe_2OEt$, (d) $SiMe_2OSiMe_3$,
(e) Me_2Et, (f) $SiMeEt_2$, (g) $SiEt_3$, (h) $Me(OSiMe_3)_2$, (i) $SiMe(OMe)_2$, (j) $SiMe_2Cl$

Reaction profiles of these hydrosilations demonstrate two mechanistic points: (1) the siloxyethyl and siloxyvinyl complexes form independently and the former does not transform into the latter, and (2) the siloxyethyl complexes subsequently react with hydrosilanes. The last point was noted in studies using $HSiMe_2Ph$ under conditions that afforded < 5% $(CO)_5MnC(OSiMe_2Ph)=CH_2$. The accompanying reaction profile illustrates the sensitivity of $(CO)_5MnCH(OSiMe_2Ph)CH_3$ (our most stable manganese siloxyethyl complex) towards $HSiMe_2Ph$.

In the presence of excess silane, $(CO)_5MnCH(OSiMe_2Ph)CH_3$ degrades to $O[SiMe_2Ph]_2$, $Mn_2(CO)_{10}$, and a complex mixture of organics. Even more noteworthy is the absence of





Reaction Profile:

$(CO)_5MnC(O)CH_3$ and $HSiMe_2Ph$

(0.21 mmol) (1.75 equiv)

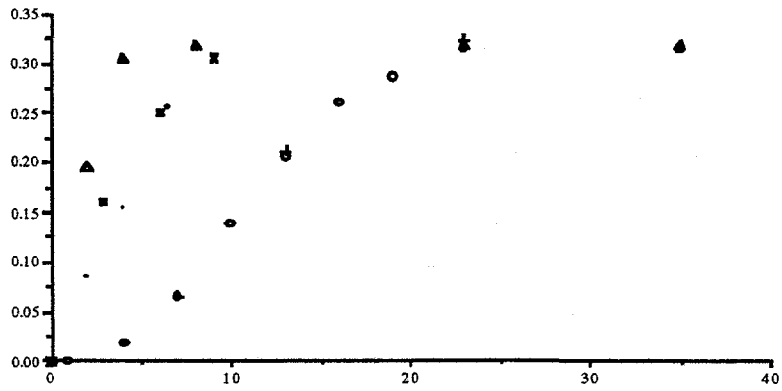
- • $(CO)_5MnC(O)CH_3$
- \+ $(CO)_5MnCH(OSiMe_2Ph)CH_3$
- x $HSiMe_2Ph$

concentration (M) vs. time (min)

several potential byproducts. The absence of the ethoxysilane, siloxyvinyl ether, and $(CO)_5MnSiMe_2Ph$ is inconsistent with the intermediacy of the unsaturated $(CO)_4Mn-CH(OSiMe_2Ph)CH_3$ and with the operation of the intramolecular hydrosilation pathway.

Somewhat different results were communicated by Akita, Moro-oka, and coworkers[16] for treating $(CO)_5MnC(O)CH_3$ with excess H_2SiPh_2. Their reactions produced complex mixtures of alkanes and alkenes, with the presence of CO (1 atm) favoring higher alkenes. These products presumably originated from the initially formed $(CO)_5MnCH(OSiHPh_2)CH_3$, although the fates of the manganese and silicon moieties were not reported.

We further demonstrated that the $HSiMe_2Ph$ hydrosilation of $(CO)_5MnC(O)CH_3$ is pseudo autocatalytic, with silane-induced degradation of $(CO)_5MnCH(OSiMe_2Ph)CH_3$ providing the coordinatively unsaturated $(CO)_4MnSiMe_2Ph$ as the active catalyst.[22] As illustrated in the following reaction profiles, pretreatment of catalytic quantities (1%) of



Reaction Profiles: $HSiMe_2Ph$ / $(CO)_5MnC(O)CH_3$ Autocatalysis

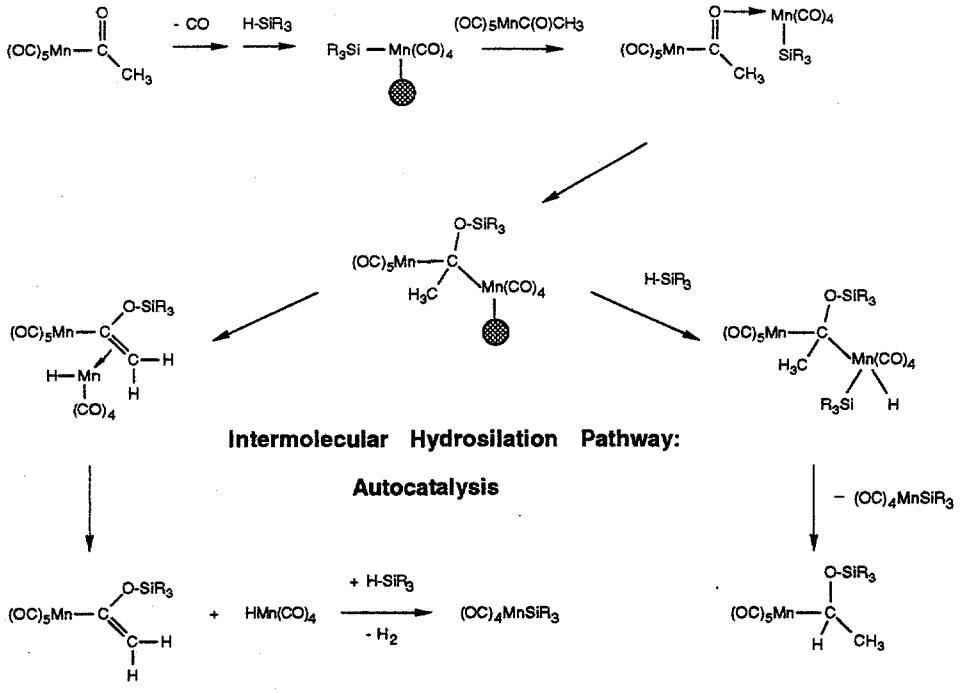
- o $(CO)_5MnC(O)CH_3$ autocatalysis
- \+ $(CO)_5MnSiMe_2Ph$
- • $(CO)_5MnC(O)CH_3$ + $HSiMe_2Ph$ Premix
- X $(CO)_5MnCH(OSiMe_2Ph)CH_3$
- Δ $(CO)_5MnC(O)$-p-$C_6H_4CH_3$ + $HSiMe_2Ph$ Premix

concentration (M) vs. time (min)

$(CO)_5MnC(O)CH_3$ or $(CO)_5MnC(O)C_6H_4CH_3$ with excess silane, systems known to generate $(CO)_4MnSiMe_2Ph$, before adding the substrate $(CO)_5MnC(O)CH_3$ dramatically enhanced hydrosilation rates. Also note that the presence of $(CO)_5MnSiMe_2Ph$ had no effect.

All observations, including the results of inhibition experiments, agree with an intermolecular pathway in which the active catalyst $(CO)_4MnSiR_3$ binds $(CO)_5MnC(O)CH_3$ and rearranges to the unsaturated μ-siloxyethylidene $(CO)_5MnC(CH_3)(OSiR_3)Mn(CO)_4$ as the key catalytic intermediate. Silane addition then affords $(CO)_5MnCH(OSiR_3)CH_3$ whereas β-deinsertion produces $(CO)_5MnC(OSiR_3)=CH_2$. Both intermolecular hydrosilation reactions regenerate the active catalyst, which evidently is unstable and is replenished continuously through the silane-induced decomposition of $(CO)_5MnCH(OSiR_3)CH_3$.

The silane oxidative-addition and reductive-elimination steps evident in this pro-



posed mechanism, although precedented,[26] could be replaced by η^2-(H-Si) complexation[27] and σ-metathesis[28] steps. It is the β-deinsertion step, however, that is noteworthy. Assigning the β-elimination step to $(CO)_5MnC(CH_3)(OSiR_3)Mn(CO)_4$ nicely accounts for generating $(CO)_5MnC(OSiR_3)=CH_2$, as opposed to forming vinyl silyl ether $CH_2=CH(OSiR_3)$ via β-elimination from a mononuclear $(CO)_4MnCH(OSiR_3)CH_3$.[29]

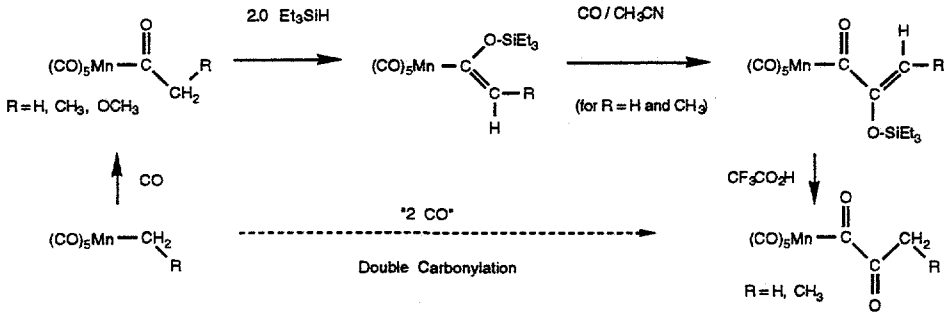
In summary, reactions of hydrosilanes with $(CO)_5MnC(O)CH_3$ evidently involve an intermolecular (pseudo-autocatalytic) pathway in which $(CO)_4MnSiR_3$ serves as the active catalyst that produces $(CO)_5MnCH(OSiR_3)CH_3$. In contrast, reactions of hydrosilanes with $(CO)_5MnC(O)Ph$ illustrate the intramolecular pathway in which alkoxysilanes and varying yields of $(CO)_5MnSiR_3$ are the primary products.

3. Siloxyvinyl Derivatives $(CO)_5MnC(OSiEt_3)=CHR$ (R = H, CH_3, OCH_3); An Approach to Double Carbonylation of $(CO)_5MnCH_2R$.[8]

Of all the monohydrosilanes examined, $HSiEt_3$ hydrosilation of $(CO)_5MnC(O)CH_3$ afforded the greatest concentration of an α-siloxyvinyl complex, $(CO)_5MnC(OSiEt_3)=CH_2$, as a 2:1 mixture with $(CO)_5MnCH(OSiEt_3)CH_3$. The α-siloxyvinyl complex was isolated (55-64%) and fully characterized. Materials balance plots for this hydrosilation reaction further indicate that both products form via independent pathways: $(CO)_5MnCH(OSiEt_3)CH_3$ does not convert to $(CO)_5MnC(OSiEt_3)=CH_2$. Pretreating catalytic quantities of $(CO)_5MnC(O)$-p-$C_6H_4CH_3$ with excess $HSiEt_3$ prior to adding the substrate $(CO)_5MnC(O)CH_3$ dramatically increased the hydrosilation rates without significantly altering the product distribution.

As discussed for the intermolecular (autocatalytic) hydrosilation pathway, $(CO)_5Mn$-$C(OSiEt_3)=CH_2$ originates from a rate-determining β-deinsertion on $(CO)_5MnC(CH_3)(OSiEt_3)$-$Mn(CO)_4$.[30] Hydrosilation of $(CO)_5MnC(O)CD_3$ with $HSiEt_3$ thus furnished a 1:2 mixture of $(CO)_5MnC(OSiEt_3)=CD_2$ and $(CO)_5MnCH(OSiEt_3)CD_3$. Thus $(CO)_5MnC(CD_3)(OSiR_3)Mn(CO)_4$ preferentially adds silane, releasing $(CO)_5MnCH(OSiEt_3)CD_3$, as opposed to breaking a C-D bond in reductively eliminating $(CO)_5MnC(OSiEt_3)=CD_2$.

Triethylsilane hydrosilation of $(CO)_5MnC(O)CH_2R$ (R = CH_3, OCH_3) provided only the α-siloxyvinyl complexes (*Z*)-$(CO)_5MnC(OSiEt_3)=CHR$ in 55-80% isolated yields. The vinyl configurations were assigned from the results of NOE difference spectroscopy experiments.



Carbonylation of two α-siloxyvinyl complexes gave their acyl derivatives (E)-$(CO)_5MnC(O)C(OSiEt_3)=CHR$ (>80% isolated yields); subsequent protonolysis (CF_3CO_2H) generated the α-ketoacyl complexes $(CO)_5MnC(O)C(O)CH_2R$ (R = H, CH_3) (86-89% after chromatography). This set of ligand reactions, the net conversion of the manganese methyl and ethyl complexes to their α-ketoacyl derivatives, represents a novel double-carbonylation sequence.[32]

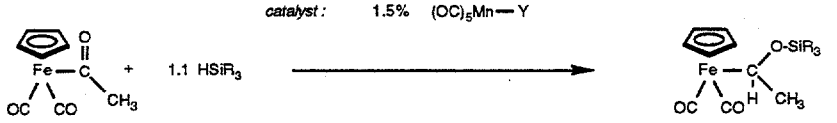
4. Catalytic Hydrosilation of Iron Acyls $Cp(CO)_2FeC(O)R$ using Manganese Carbonyl Precatalysts $(CO)_5MnY$ (Y = Alkyl, Acyl, Halide).[11]

We prefer to use Fp acyl compounds in exploratory studies for developing new hydrosilation catalysts, since the resulting stable products, $FpCH(OSiR_3)R$, are easily isolated or quantified spectroscopically. $FpC(O)CH_3$ is particularly convenient for mechanistic studies and FpC(O)Ph is our choice for a "difficult" substrate.[4,11] Chiral iron acetyl substrates, $Cp(PR_3)(CO)FeC(O)CH_3$, have been used in assessing diastereofacial selectivity in forming a

new stereogenic center during hydrosilation. Both types of iron acetyl complexes have proven useful for elucidating subsequent hydrosilane-induced reactions of alkyl ligands coordinated to nonlabile metal systems.[10]

A variety of manganese alkyl, acyl, and bromide complexes function as extremely efficient hydrosilation precatalysts towards $FpC(O)R$. We illustrate the enhanced activity of these catalytic systems over $RhCl(PPh_3)_3$ (and other rhodium catalysts that we examined) by noting that $(CO)_5MnC(O)Ph$ catalytically adds *monohydrosilanes* to $FpCOCH_3$. In contrast, $RhCl(PPh_3)_3$ only catalyzes $FpC(O)R$ hydrosilation with more reactive dihydrosilanes, H_2SiR_2. Not all manganese carbonyl complexes are hydrosilation catalysts, however: $(CO)_5MnSiMe_2Ph$, $(CO)_5MnSiHPh_2$, $Cp(CO)_2Mn(H\text{-}SiHPh_2)$, and $Mn_2(CO)_{10}$ are inactive towards $FpC(O)R$ hydrosilation with either monohydro- or dihydrosilanes.

We established that the choice of manganese catalyst *and* silane controls the hydrosilation reactivity of $FpC(O)CH_3$ and $FpC(O)Ph$. A portion of this data appears below for the qualitative ranking of hydrosilation reactivity of 1.5% Mn precatalyst towards $FpC(O)CH_3$ and 1.1 equiv. of $PhMe_2SiH$ (as relative reaction times to consume starting $FpC(O)CH_3$):



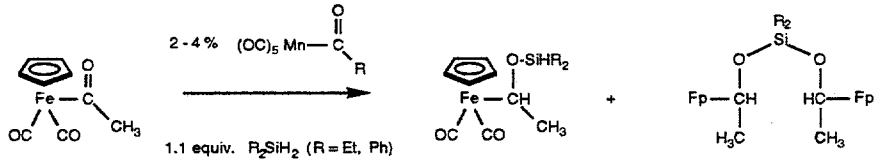
For H-SiMe$_2$Ph:

$[(CO)_4Mn\text{-}Br]_2$ *(10 min)* >> $(CO)_5Mn\text{-}Br$ *(45 min)* >> $(CO)_5Mn\text{-}COPh$ *(3 h)* >

$(CO)_5Mn\text{-}CH_3$ *(4 h)* > $(CO)_5Mn\text{-}Ph$ *(6 h)* > $(CO)_5Mn\text{-}CH_2Ph$ *(9 h)* > $(PPh_3)(CO)_4Mn\text{-}COPh$ *(12 h)* >

$(CO)_5Mn\text{-}COCH_3$ *(12 h)* >> $(PPh_3)(CO)_4Mn\text{-}COCH_3$, $(CO)_5Mn\text{-}SiMe_2Ph$, $Mn_2(CO)_{10}$

This ranking however varies somewhat with the choice of hydrosilane. With the dihydrosilanes, $(PPh_3)(CO)_4MnCH_3$ and $(PPh_3)(CO)_4MnC(O)CH_3$ now are the most reactive precatalysts (< 35 min.), although such obvious candidates as $(CO)_5MnSiMe_2Ph$, $(CO)_5Mn\text{-}SiMe_3$, $(CO)_5MnH$, and $Mn_2(CO)_{10}$ still are inactive. Moreover, these PPh_3-substituted Mn complexes selectively afford mono-Fp(siloxyethyl) products, whereas the remaining cata



lysts generate 0.8-1.2 mixtures of mono- and bis-Fp(siloxyethyl) compounds. Analytically pure samples of all four products were procured by size-exclusion chromatography.

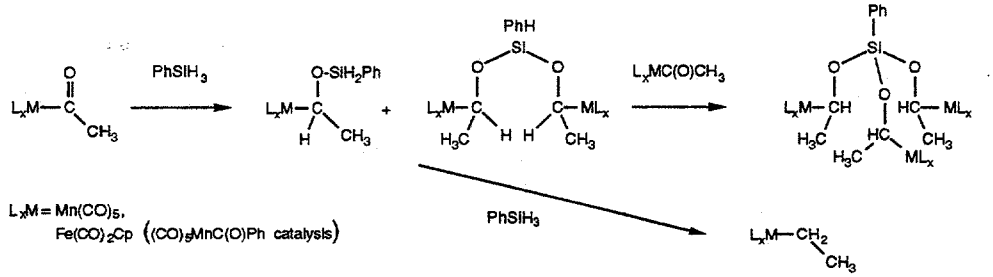
Results of mechanistic studies on using the precatalysts $(CO)_5MnC(O)R$ (R = CH_3, Ph) for the hydrosilation of $FpCOCH_3$ are consistent with our intermolecular pathway (p. 7). After the precatalysts transform to $(CO)_4MnSiR_3$,[22] these active catalysts then bind $FpC(O)CH_3$ and finish the catalytic cycle as was illustrated for the $(CO)_5MnC(O)CH_3$ substrate. The reaction time for $(CO)_5MnC(O)Ph$-catalyzed hydrosilation (1.1 equiv. of $HSiMe_2Ph$) of

$FpC(O)CH_3$ accordingly decreases from 3 h. to 20 min. when the manganese precatalyst is treated with the excess silane (45 min) before adding the iron substrate.

Other results pertaining to the mechanistic studies include: (1) Van't Hoff plots for the $(CO)_5MnC(O)Ph$-catalyzed hydrosilation (1.0-6.8 equiv. of $HSiMe_2Ph$) of $FpC(O)CH_3$ indicate a first-order dependency in $HSiMe_2Ph$ and in $(CO)_5MnC(O)Ph$. (2) A minimal isotope effect, k_H/k_D = 1.2, was determined for this reaction using 5 equiv. each of $HSiMe_2Ph$ and $DSiMe_2Ph$. (3) Crossover experiments using 1:1 $DSiMe_2Ph$ / $HSiMe_2Et$ mixtures were carried out for the manganese-catalyzed hydrosilation of $FpC(O)CH_3$. The four (independently characterized) products $FpCX(OSiMe_2Y)CH_3$ (X = H, D; Y = Ph, Et) that formed were assayed by 500 MHz ^1H NMR spectroscopy. Although these results are consistent with the proposed hydrosilation mechanism, we have been unable to minimize competing SiH/SiD exchange.

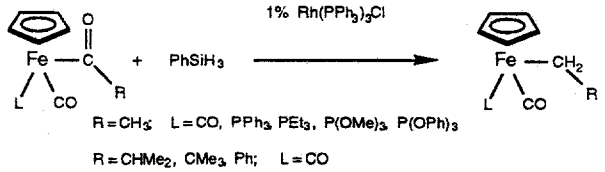
5. $PhSiH_3$ Hydrosilation of Iron and Manganese Acyls $Cp(L)(CO)FeC(O)R$ and $(CO)_5MnC(O)CH_3$ Using $Rh(Cl)(PPh_3)_3$ and $(CO)_5MnC(O)R$ Catalysis.[17]

By using the more reactive phenylsilane, we catalytically hydrosilated and reduced organometallic acyls. The products of these reactions depended on whether $Rh(Cl)(PPh_3)_3$ or $(CO)_5MnC(O)R$ (R = CH_3, Ph) was used as a catalyst.



With the manganese acyl precatalysts, $PhSiH_3$ and $FpC(O)CH_3$ transformed to the depicted mono-, bis-, and tris-α-siloxyethyl complexes. The mono-iron and bis-iron adducts formed first, then they competitively transformed into the tris-iron compound and the fully reduced iron ethyl complex, $FpCH_2CH_3$. After 12 hours, only the latter compounds remained. The fully characterized tris-iron compound did not convert into $FpCH_2CH_3$ under the original reaction conditions. Essentially the same reactions occurred upon treating $(CO)_5MnC(O)CH_3$ with $PhSiH_3$.

$Rh(Cl)(PPh_3)_3$ also catalyzes phenylsilane hydrosilation of $FpC(O)CH_3$ and the other CpFe acyl complexes depicted. These reactions produced only their fully reduced alkyl derivatives, with no detectable intermediates. The 65-90% isolated yields of the indicated iron alkyl complexes categorizes this $Rh(Cl)(PPh_3)_3$-catalyzed phenylsilane hydrosilation as a useful synthetic method for reducing (iron) acyl complexes.[33]



B. Manganese Carbonyl-Catalyzed Hydrosilation of Organic Compounds.

General Observations:

(1) Thus far, three types of manganese hydrosilation precatalysts are available,
   (a) Manganese bromides, $[(CO)_4MnBr]_2$ or $(CO)_5MnBr$
   (b) Mn alkyl, acyl complexes, $(L)(CO)_4MnR$ (R = CH_3, $C(O)CH_3$, C(O)Ph; L = CO, PPh_3)
   (c) Manganese silyl complexes, $(CO)_5MnSiMe_2Ph$, $(CO)_5MnSiHPh_2$, under photochemical conditions. These compounds and $Mn_2(CO)_{10}$ are otherwise inert as catalysts.

(2) The manganese bromide precatalysts are not consumed by excess silane, whereas the manganese alkyl and acyl precatalysts are transformed by silane to putative unsaturated manganese silyl compounds as the active catalysts.

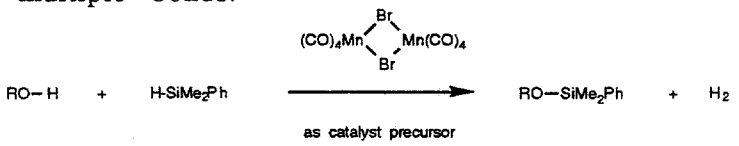
(3) Pretreatment of a manganese acyl with the excess silane (until the former is consumed) before adding the substrate generates the active catalyst and subsequently accelerates the catalysis. Timing this pretreatment procedure must be done carefully since the active catalyst has a limited lifetime.

(4) These Mn complexes, particularly $(CO)_5MnBr$, $(CO)_5MnC(O)Ph$, and $PPh_3(CO)_4MnC(O)CH_3$, selectively catalyze a variety of reactions between hydrosilanes and C=O or O-H bonds on organic molecules. Carbon-carbon double bonds are unreactive.[31]

(5) The manganese catalysts usually are much more reactive than $RhCl(PPh_3)_3$ and frequently catalyze a number of reactions that $RhCl(PPh_3)_3$ will not.

1. Manganese-Catalyzed Alcoholysis of $HSiMe_2Ph$.[18]

Dimeric $[(CO)_4MnBr]_2$ is extremely effective at catalyzing the alcoholysis of dimethylphenylsilane in benzene at room temperature. Preparative scale procedures using 1200 : 1200 : 1 mixtures of alcohol, $HSiMe_2Ph$, and $[(CO)_4MnBr]_2$ (0.084 mol %) afforded analytically pure alkoxysilanes in good yields. t-Butanol, for example, gave $(CH_3)_3COSiMe_2Ph$ in 82% yield after a 35 min reaction time, and allyl and propargyl alcohols quantitatively transformed to their alkoxysilane derivitives, with no evidence of competing hydrosilation of the carbon-carbon multiple bonds.[34]



Competitive reactions involving 1 : 1 : 1 mixtures of *sec*-butanol-acetone-$HSiMe_2Ph$ and $[Mn(CO)_4Br]_2$ as catalyst exhibited chemoselective alcoholysis of dimethylphenylsilane. ^1H NMR spectral monitoring of manganese-catalyzed reactions between methanol or *sec*-butanol with $HSiMe_2Ph$ was used in screening manganese carbonyl complexes as potential $HSiMe_2Ph$ alcoholysis catalysts. Their reaction times varied:

$[(CO)_4MnBr]_2 > (CO)_5MnBr >> (CO)_5MnCH_3 \approx (CO)_5MnC(O)Ph > (PPh_3)(CO)_4MnBr > (PPh_3)(CO)_4MnC(O)CH_3 >> (CO)_5MnSiMe_2Ph >> Mn_2(CO)_{10} \approx Rh(PPh_3)_3Cl$ (no reaction).

Turnover frequencies were determined for the dehydrocoupling of *sec*-butanol and $HSiMe_2Ph$ (0.289 M) catalyzed by $[(CO)_4MnBr]_2$ (1.4 mol %). We used the initial velocities for H_2 evolution to yield turnover frequencies that varied with the solvent: N_t = 2183 (THF), 2728 (C_6H_6), and 5457 h^{-1} (CH_2Cl_2). In a second procedure, a preparative scale reaction (3.12 M for each reactant) in CH_2Cl_2 containing only 0.084 mol % precatalyst afforded a much higher turnover frequency of 11,217 h^{-1}. The unusually high activity and selectivity, as well as easy accessibility and low cost, of the manganese carbonyl bromides make them attractive catalysts for the alcoholysis of hydrosilanes.[34]

2. Manganese Acyl-Catalyzed Hydrosilation of Ketones.[19]

We studied the manganese-catalyzed hydrosilation of ketones[31] in order to probe the fundamental ligand reactions that are extant for the (pre)catalyst-hydrosilane-substrate. Specific issues that we addressed include: (a) the extent to which manganese-catalyzed hydrosilation of ketones resembles the catalytic hydrosilation of metal acyl compounds, (b) whether aldehydes or ketones inhibit the catalytic hydrosilation of metal acyl compounds, and (c) the facility with which Mn carbonyl-hydrosilane mixtures could hydrosilate aldehydes that may be released during the catalytic hydrosilation of metal acyl complexes.

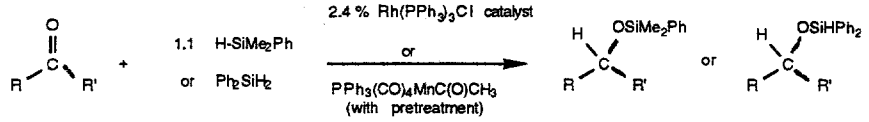
The relative activity of several manganese precatalysts (2.4%) was determined for the hydrosilation of acetone with 1.10 equiv. of $HSiMe_2Ph$:

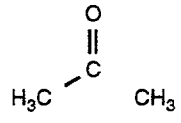
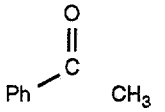
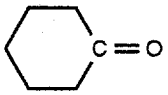
$(PPh_3)(CO)_4MnC(O)CH_3$ (< 5 min) >> $(CO)_5MnBr$ > $(CO)_5MnC(O)Ph$ > $(CO)_5MnCH_3$ > $(CO)_5MnC(O)CH_3$ (4.5 h) >> $Mn_2(CO)_{10} \approx (PPh_3)(CO)_4MnBr \approx (CO)_5MnSiMe_2Ph$.

As a result of this survey, $(PPh_3)(CO)_4MnC(O)CH_3$ was used in subsequent ketone hydrosilation studies. Our procedure entailed treating this precatalyst with the full amount of $HSiMe_2Ph$ (1.0-2.4% and 1.1 equiv., respectively) for 20 min before adding the ketone. This pretreatment procedure maximized the catalyst performance: reaction times jumped from 50 min without pretreatment to < 4 min after adopting the pretreatment procedure.

An interesting observation that will be pursued is that ketone hydrosilation using $(CO)_5Mn(SiMe_2Ph)$ as the precatalyst progresses during photolysis.

The following table compares reaction times for the hydrosilation of acetone, acetophenone, and cyclohexanone using $Rh(PPh_3)_3Cl$ (the standard ketone hydrosilation catalyst)[31] and $(PPh_3)(CO)_4MnC(O)CH_3$ as precatalysts. Although $PPh_3(CO)_4MnC(O)CH_3$ is a much more active than $RhCl(PPh_3)_3$ as a precatalyst for ketone hydrosilation with $HSiMe_2Ph$, both catalysts exhibit similar activity with H_2SiPh_2. For acetone hydrosilation in benzene (0.15 M) using 1% Mn acetyl precatalyst, we measured turnover numbers, N_t = 3200 h^{-1}, from initial velocities (IR spectral monitoring). Although we have not attained the optimal precatalyst or catalysis conditions involving these manganese hydrosilation systems, those already available greatly eclipse the activity of the standard $Co_2(CO)_8$ / $(CO)_4CoSiR_3$ and $RhCl(PPh_3)_3$ catalytic systems.[30,31]

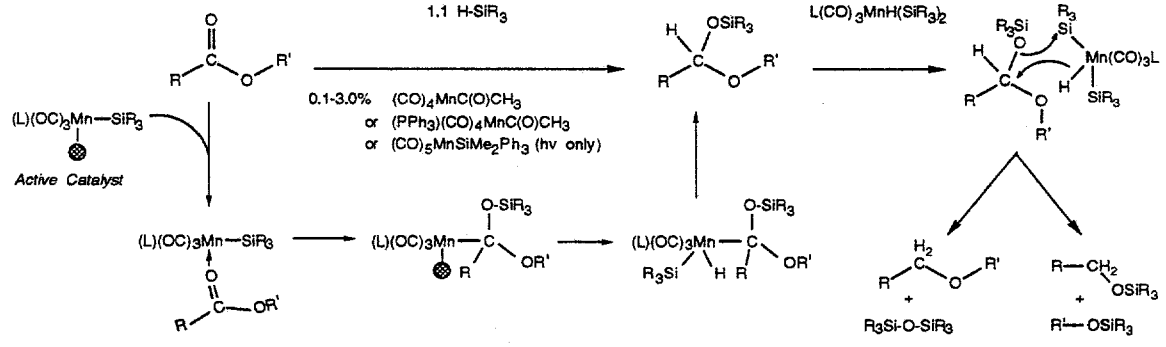


Ketone	Silane	Precatalyst	Reaction Time (min)	NMR Yield	Isolated Yield
	$HSiMe_2Ph$	$(L)(CO)_4MnC(O)CH_3$	<4 min	>95%	89%
		$Rh(PPh_3)_3Cl$	11 min	>90%	
	H_2SiPh_2	$(L)(CO)_4MnC(O)CH_3$	<4 min	>95%	
		$Rh(PPh_3)_3Cl$	<4 min	>90%	
	$HSiMe_2Ph$	$(L)(CO)_4MnC(O)CH_3$	<4 min	>95%	95%
		$Rh(PPh_3)_3Cl$	>5 hours	27%	
	H_2SiPh_2	$(L)(CO)_4MnC(O)CH_3$	<4 min	>95%	
		$Rh(PPh_3)_3Cl$	<4 min	>90%	
	$HSiMe_2Ph$	$(L)(CO)_4MnC(O)CH_3$	<4 min	>94%	92%
		$Rh(PPh_3)_3Cl$	no reaction		
	H_2SiPh_2	$(L)(CO)_4MnC(O)CH_3$	<4 min	91%	
		$Rh(PPh_3)_3Cl$	<4 min	>90%	

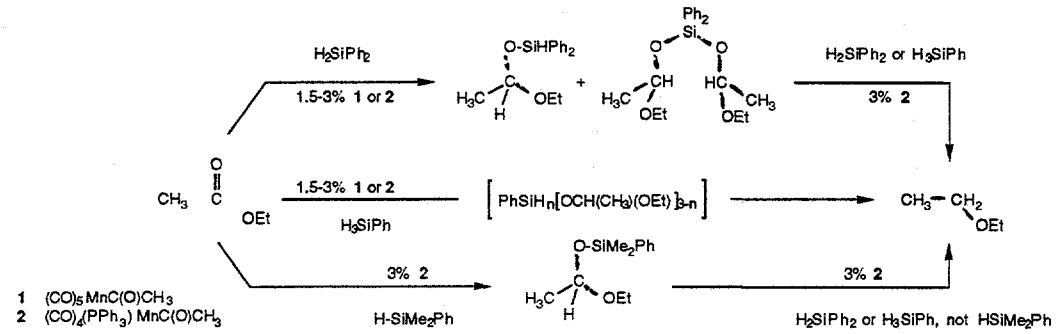
3. Manganese Acyl Catalyzed Hydrosilation-then-Reduction of Esters.[20]

The manganese acetyl complexes $(L)(CO)_4MnC(O)CH_3$ (L = PPh_3, CO) catalyze the H_3SiPh hydrosilation-then-reduction of esters RC(=O)OR' to ethers RCH_2OR' and in some cases to alkoxysilane products. By also using H_2SiPh_2 and $HSiMe_2Ph$, we demonstrated that catalytic ester hydrosilation first forms a silyl acetal $RCH(OSiR_3)OR'$. This silyl acetal then undergoes further manganese-catalyzed reduction (with H_3SiPh or even H_2SiPh_2) that partitions the silyl acetal between ether and alkoxysilanes (RCH_2OSiR_3 and $R'OSiR_3$).

Treatment of ethyl acetate, for example, with H_3SiPh (1.2 equiv) and $(PPh_3)(CO)_4Mn$-$C(O)CH_3$ (1.5%) initiated an exothermic reaction that yielded 85% Et_2O [and $PhSiH(OEt)_2$] within 15 min; a slower reaction (1.5 h) using $(CO)_5MnC(O)CH_3$ quantitatively provided



Et_2O. Analogous reactions using H_2SiPh_2 and $HSiMe_2Ph$ afforded silyl acetals (80-90% isolated yields), which underwent further $(PPh_3)(CO)_4MnC(O)CH_3$-catalyzed reduction to ether with H_3SiPh or even H_2SiPh_2.



The results of reducing a series of 14 esters with $(PPh_3)(CO)_4MnC(O)CH_3$ (1.5%) and H_3SiPh (1.2 equiv) appear in Table II. Ten of these esters produced the expected ether in moderate to high yields via detectable silyl acetal intermediates $PhSiH_{3-x}[OCH(R)OR']_x$ (x = 1,2). [Several mono- and bis-silyl acetal adducts of H_2SiPh_2, $Ph_2SiH_n[OCHR(OR')]_{2-n}$ (fully characterized), serve as spectroscopic models for their H_3SiPh analogs.] Entries 9 and 10 represent esters that are difficult to reduce, due either to steric encumbrance of the ester or to the presence of aromatic residues or other C-C unsaturation. Nevertheless, even these esters undergo rapid catalytic hydrosilation, but their silyl acetals slowly reduce to alkoxysilanes as the favored products.

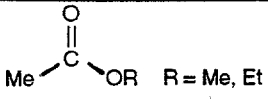
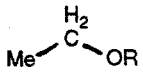
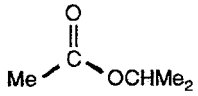
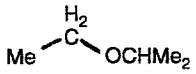
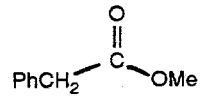
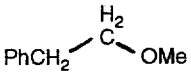
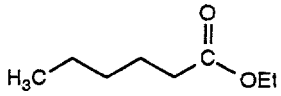
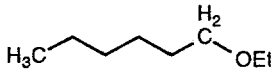
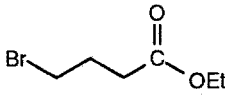
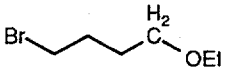
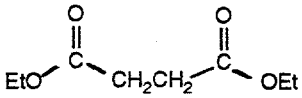
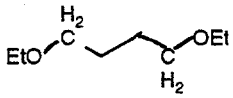
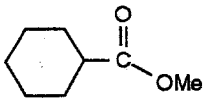
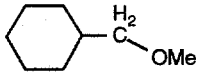
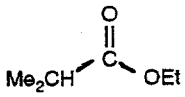
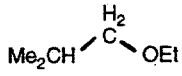
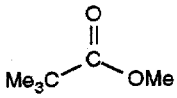
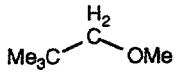
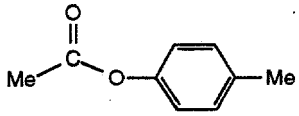
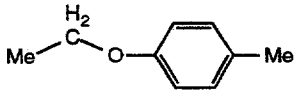
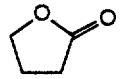
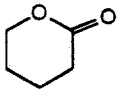
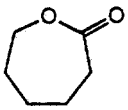
The 5-7 membered ring lactones, entries 11-13, represent special cases. Catalytic reduction with H_3SiPh rapidly consumes the lactone, but now silyl acetal intermediates break down to their ethers plus small to moderate amounts of ring-opened (alkoxysilane) polymers. These polymers, which predominate in concentrated solutions, will be discussed further in the research plan.

We propose that the coordinatively unsaturated manganese silyl $(L)(CO)_3MnSiR_3$[22] serves as the active catalyst for the ester hydrosilation and perhaps the subsequent silyl acetal reduction step. For the ester hydrosilation step, the active catalyst ligates the ester, rearranges via a 1,3-silatropic shift to give $(L)(CO)_3Mn[CR(OSiR_3)(OR')]$,[35] coordinates $HSiR_3$, and reductively eliminates the silyl acetal. This is essentially the same mechanism that we advanced for the hydrosilation of $(CO)_5MnC(O)CH_3$, $FpC(O)CH_3$, and ketones.

For the silyl acetal reduction step, $(L)(CO)_3MnH(SiR_3)_2$ (i.e., the active catalyst plus $HSiR_3$)[26] could function as the key intermediate. This bis(silyl)Mn hydride intermediate would transfer hydride to the silyl acetal commensurate with disiloxane, $R_3SiOSiR_3$, formation. A similar pathway evidently operates during the $RhCl(PPh_3)_3$-catalyzed reduction of $Cp(L)(CO)FeC(O)CH_3$ to $Cp(L)(CO)FeCH_2CH_3$ with Ph_2SiH_2 or $PhSiH_3$.[10,17] In these reactions, hydride transfer from $(PPh_3)_2(Cl)RhH(SiR_3)$ to $Cp(L)(CO)FeCH(OSiR_3)CH_3$ is presumed to be concerted with respect to disiloxane loss.

Interestingly, this active catalyst also can be generated and efficient ester

Table II. $(PPh_3)(CO)_4MnC(O)CH_3$ - Catalyzed Ester Hydrosilation with $PhSiH_3$

Entry	Ester	Consume Ester (min)[a]	Ether	NMR yield (%)[a]	isolated yield (%)[a]
1.	 R = Me, Et	15		85[b]	
2.		≤ 30		95	
3.		25		92[b]	83[c]
4.		30		96	81[d]
5.		35		92	72[c]
6.		20		83	68[d]
7.		≤ 25		81	70[c]
8.		≤ 30		69	61[d]
9.		30 12 hr		10[b,e] 34[f]	
10.		15 10 hr		5[b,g] 12[h]	
11.		30		50[i]	35[d]
12.		30		74[i]	64[d]
13.		≤ 30		80[i]	65[d]

a) Reaction times: ester replaced by mixtures of silyl acetal, ether, and in some reactions alkoxysilanes. NMR yields obtained after 1 h; isolated yields for 20 mmol scale reactions after 2 h. (b) Analogous silyl acetals $Ph_2HSi[OCH(OR')R]$ were independently synthesized from RC(O)OR'. (c) 2.0 mmol scale reaction in 2.0 g C_6H_6; product was isolated by flash chromatography. (d) 20.0 mmol scale in 10 mL C_6H_6; product was distilled. (e) 40% silyl acetals, mostly $PhSiH[OCH(OMe)CMe_3]_2$, and 46% alkoxysilanes, mostly $PhSiH[OCH_2CMe_3]_2$ and $PhSiH[OMe]_2$. (f) Silyl acetals and alkoxysilanes: 16% and 50%, respectively. (g) Silyl acetals, $PhSiH[OCH(CH_3)(p\text{-}OC_6H_4Me)]_2$ (49%), and alkoxysilanes, $PhSiH[p\text{-}OCH_2C_6H_4Me]_2$ / $PhSiH[OEt]_2$ (46%). (h) Silyl acetals and alkoxysilanes: 8% and 76%, respectively. (i) Integrations approximate - partial overlap with broadened absorptions due to ring-opening polymerization.

hydrosilation-then-reduction can be carried out by photolysis of $(CO)_5MnSiMe_2Ph$ (3%) in the C_6D_6-H_3SiPh (1.2 equiv) solution.

Very little precedent exists for directly reducing esters to ethers.[36] In recent reports, Buchwald and coworkers established that $(EtO)_3SiH$ reduces esters to alcohols (after aqueous workup) in the presence of catalytic quantities of the titanium complexes Cp_2TiCl_2/*n*-BuLi and Ti(O-*i*-Pr)$_4$.[37] This titanium work differs from ours both in the type of products that form and in the precatalyst and presumed reaction pathway. Certainly the use of readily available manganese acetyl (or other metal carbonyl) complexes as such powerful ester hydrosilation and reduction catalysts was unexpected.

Our hydrosilation-reduction results with a limited collection of esters clearly indicate that this procedure holds great promise for directly reducing at least simple esters. Since we have as yet to optimize the choice of precatalyst and reaction conditions, the ester hydrosilation reaction scope and selectivity, however, remains to be defined. Our current interest lies in coupling new information on the accessibility of unsaturated manganese silyl complexes $(L)(CO)_3MnSiR_3$ with the design and testing of even more powerful hydrosilation-reduction catalysts.

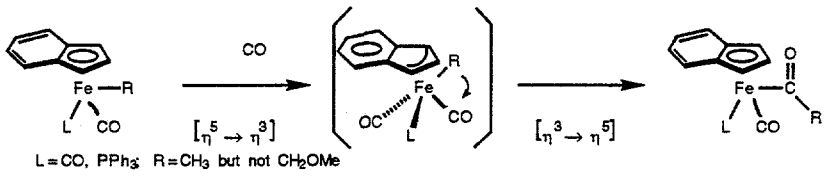
C. Indenyl Ruthenium Carbonylation Chemistry and New Directions

Studies using Cp(carbonyl)metal alkyl complexes have been instrumental in elucidating organometallic transformations that are germane to homogeneous catalysis. The $Cp(CO)_2Fe$ or Fp moiety, for example, and more recently its isolobal $Cp(PPh_3)(CO)Fe$ and $Cp(PPh_3)(NO)Re$ systems have been used to establish the stereoelectronic constraints of their coordinated ligand reactions.[38] These alkyl complexes, although generally quite stable, also are relatively nonlabile and do not readily undergo carbonylation.[39]

Our premise is that replacing the Cp ligand by the η^5-indenyl group (Ind) may promote carbonylation of these metal alkyl compounds. The presence of the Ind ligand thus retains the thermodynamic stability of these alkyl compounds while building in kinetic lability. This lability towards carbonylation involves the operation of the kinetic indenyl effect: reversible η^5/η^3 Ind ring slippage[41] couples with CO association at the metal and then alkyl-CO migration. Availability of this alternative pathway involving the indenyl ligand evidently enhances the carbonylation rates.[41] Although the indenyl effect has been established for associative ligand substitution reactions, we have been the first to use it in carbonylation chemistry.[1,42]

Our objective is not limited to just building in carbonylation activity by switching from the Cp to the Ind ligand. We will design and establish (Ind)metal systems that carry out truly difficult carbonylation reactions, the longer range goal being to adapt this associative reactivity of (Ind)metal complexes to homogeneous catalysis.

In early studies, we noted that (Ind)Fe methyl complexes carbonylate under conditions ($\leq$ 80 psig) that their Cp analogs are inert.[41a,b] This enhanced carbonylation

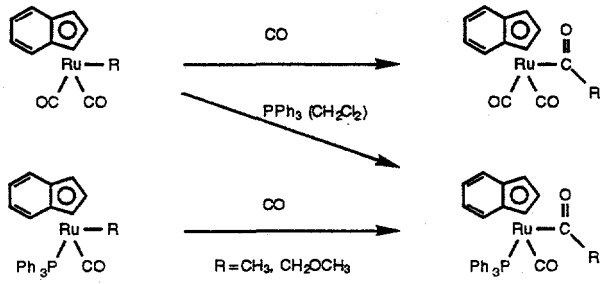


reactivity unfortunately does not extend to similar methoxymethyl complexes. Their treatment with 80 *atm* of CO only replaced ligated phosphine by CO,[41a] even though the corresponding stable methoxyacetyl products are independently available.

One initial objective has been to develop Ind Fe/Ru methoxymethyl complexes Ind(L)(CO)M-CH_2OMe that would carbonylate. Although this transformation is central to CO fixation schemes, few alkoxymethyl complexes have been carbonylated, and of these none were (η^5-dienyl)metal derivatives.[2,43] By switching to (Ind)Ru alkyl complexes, we now can drive these otherwise infeasible carbonylation reactions. As the following sections will demonstrate, this extraordinary reactivity of the (Ind)Ru alkyl complexes towards CO has progressed to the stage that we now are addressing other catalytically relevant reactions that also may be accelerated with (Ind)Ru alkyl systems.

1. Facile Carbonylation of (η^5-Ind)Ru Methyl and Methoxymethyl Complexes.

We established the unusually mild carbonylation chemistry of the (Ind)Ru alkyl system involving the 8 methyl/acetyl and methoxymethyl/methoxyacetyl complexes depicted.[5] The methyl-to-acetyl carbonylations take place under incredibly mild conditions, 15-50 psig CO in CH_2Cl_2 (22 °C). (Carbonylation reactions involving CpRu congeners require considerably more vigorous conditions, e.g., 100 *atm* CO for $Cp(CO)_2RuCH_3$.) The most dramatic carbonylation is that of (Ind)(PPh_3)(CO)$RuCH_2OMe$ at 80 psig CO.



The following order of methyl-to-acetyl carbonylation activity for (η^5-dienyl)(L)(CO)M-CH_3 complexes was established:

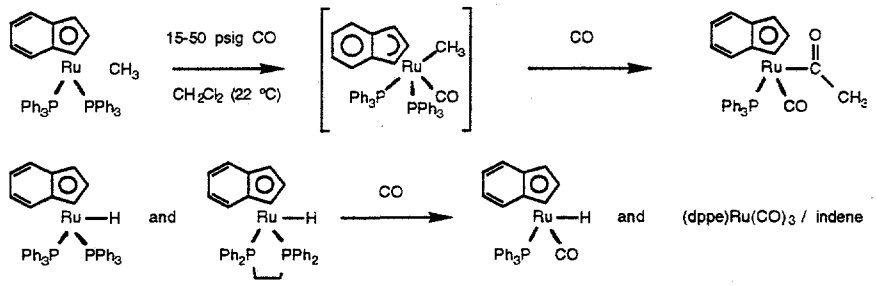
(Ind)((PPh_3)CO)Ru >> (Ind)$(CO)_2$Ru > (Ind)(L)(CO)Fe >> Cp(L)(CO)Fe >> $Cp(CO)_2$Ru

(Ind)Ru methyl complexes may be the most reactive, but their CpRu congeners are the least susceptible to carbonylation.

The dramatic *increase* in carbonylation activity of the (Ind)Ru vs. (Ind)Fe systems resembles the increase in reactivity (Ind)$Re(CO)_3$ vs. (Ind)$Mn(CO)_3$[44] for the phosphine displacement of CO. These displacement reactions involve an associative pathway that evidently couples ligand association-dissociation with reversible η^5/η^3 indenyl ring slippage.

The much higher reactivity of Re vs. Mn, however, is inverted from that observed for phosphine reactions with $CpM(CO)_3$ and with $(CO)_5MX$ (Mn > Re). Basolo and coworkers[44c] attributed the enhanced reactivity of $(Ind)Re(CO)_3$ to the increased size of Re over Mn, which could facilitate the phosphine association (commensurate with Ind ligand shifting).

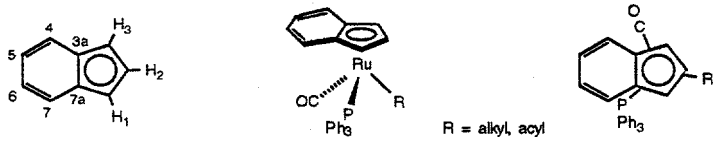
Our Ind-enhanced carbonylation reactions also take place without benefit of ancillary CO ligands present on the ruthenium. Carbonylation of $Ind(PPh_3)_2RuCH_3$ cleanly affords $(Ind)(PPh_3)(CO)RuC(O)CH_3$ with no detectable intermediates.[45] In contrast, both the CpRu and (Ind)Fe analogs, $Cp(PPh_3)_2RuCH_3$ and $(Ind)(PPh_3)_2FeCH_3$, are inert to 80 psig CO.



Attempts to generate the corresponding formyl complexes $(Ind)(L)(CO)RuC(O)H$ were unsuccessful. Carbonylating the depicted (Ind)Ru hydrides gave only $(Ind)(PPh_3)(CO)RuH$ (80% isolated yields) and ultimately indene/ruthenium carbonyls. Using a variety of reaction conditions, we did not detect any formyl intermediates. Such intermediates if present should have been detected, since stable analogs $Cp^*(PR_3)(CO)RuC(O)H$ had been described.[46]

The main value of this work is the advance in synthetic chemistry[47] due to the ease of converting the readily accessible $Ind(PPh_3)_2RuCl$ (from $RuCl_3$) to $Ind(PPh_3)_2RuR$ (R = H, CH_3) and finally to the observed carbonylation products. These can be converted to $(Ind)(PPh_3)(CO)RuI$ after I_2 treatment. Alternative synthetic routes are ultimately limited by the capricious preparation of $(Ind)_2Ru_2(CO)_4$ from $Ru_3(CO)_{12}$.

The PPh_3-containing complexes $(Ind)(PPh_3)(CO)RuR$ and $(Ind)(PPh_3)(CO)RuC(O)R$ (R = CH_2OCH_3, CH_3) evidently populate a preferred conformation in solution. Results of difference NMR NOE experiments on these complexes are consistent with conformers that situate the PPh_3 on the H1,7 side of the indenyl ligand and align the Ru-R or Ru-C(O)R bond under H2, perhaps rotated a little towards H1. Thus the stronger trans-influence alkyl or acyl ligand is oriented anti to the Ind C_{3a}-C_{7a} bond, which is optimally situated to facilitate Ind ring slippage.[48] These results turn out to be important for interpreting our labeling studies, vide infra.

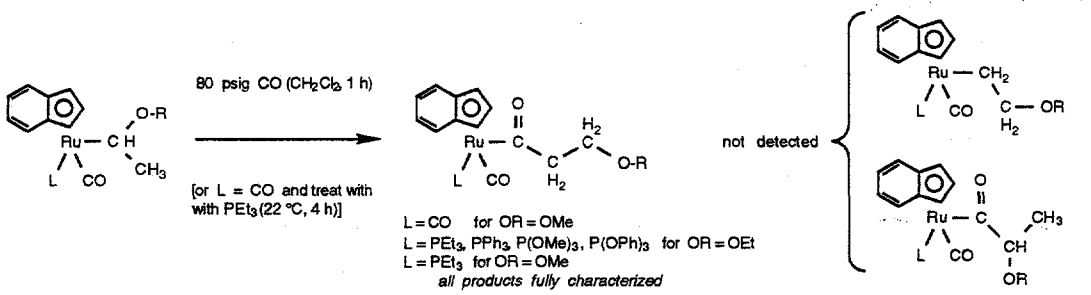


The preferred conformation that we arrive at agrees with those established for a number of chiral Co and Fe complexes having the general formula $(Ind)(L)(PR_3)M\text{-}Y$. Jablonski and Zhou studied a series of Co perfluoroalkyl complexes $(Ind)(I)(PR_3)Co\text{-}R_f$[49a]

using NMR NOE difference spectroscopy, and Pannell's group performed X-ray crystallographic structure determinations on three Fe silyl complexes (Ind)(CO)(PPh_3)Fe-SiR'_3.[49b] Bassetti and coworkers and Davies et. al. also carried out X-ray structure determinations on the Fe acyl complexes (η^5-Ind)(CO)(PPh_3)FeC(O)R [R = CH_3,[49c] $CHMe_2$[42e]].

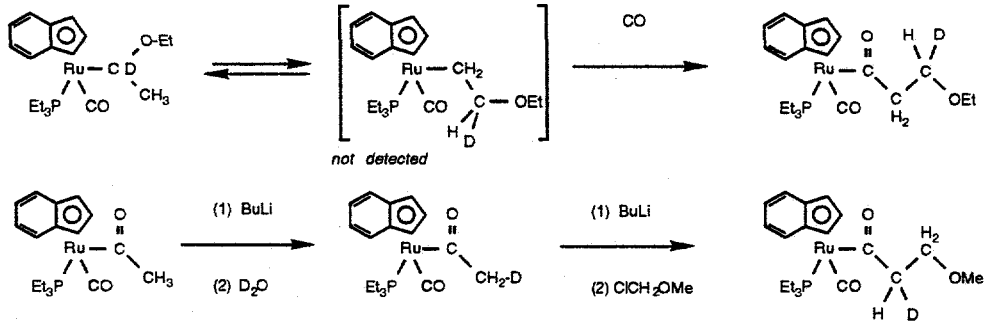
2. Carbonylation-assisted Alkyl Isomerization: Carbonylation of (Ind)Ru α-Alkoxyethyl Complexes.

We are in the process of publishing details on the unprecedented carbonylation-assisted isomerization of the α-alkoxyethyl ligand.[6] Either treating $Ind(CO)_2RuCH(OMe)CH_3$

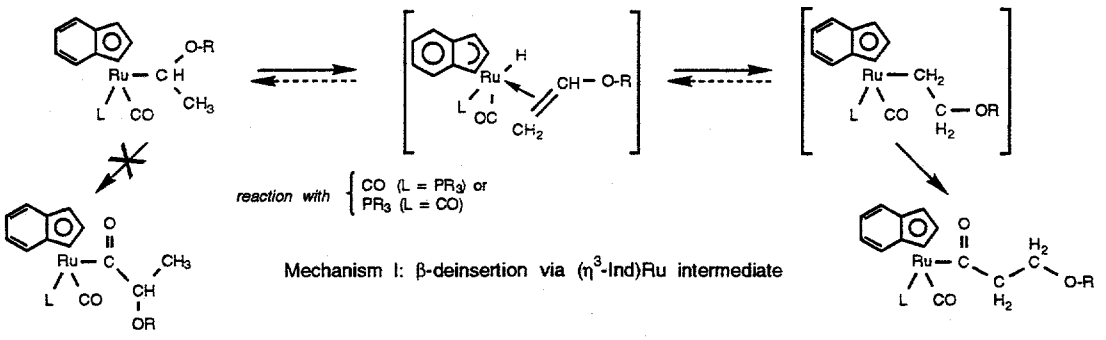


with PPh_3 or carbonylating $Ind(L)(CO)RuCH(OR)CH_3$ (80 psig CO, < 1 h) quantitatively affords β-alkoxypropionyl products. Neither intermediates nor regioisomeric α-alkoxypropionyl products were detected, although we previously had synthesized the congeneric $Ind(CO)_2FeC(O)CH(OEt)CH_3$ via our two-step carbonylation procedure.[3]

Two labeling experiments helped us interpret these carbonylation results. First, (Ind)(PEt_3)(CO)$RuCD(OEt)CH_3$ [synthesized by $LiDBEt_3$ reduction of (Ind)(PEt_3)(CO)Ru=$C(OEt)CH_3^+$] was unchanged in refluxing CH_2Cl_2 (6 h); it neither shuttled the D label within the α-alkoxyethyl ligand nor converted to its β-alkoxyethyl isomer. Carbonylation, however, rapidly yielded (Ind)(PEt_3)(CO)$RuC(O)CH_2CHD(OEt)$. The second labeling experiment was required in order to unambiguously assign the methylene NMR resonances of the β-alkoxypropionyl products. Using established ligand reactions (for CpFe chemistry),[38a] we prepared the α-labeled β-methoxypropionyl complex depicted and used it for spectral assignments.



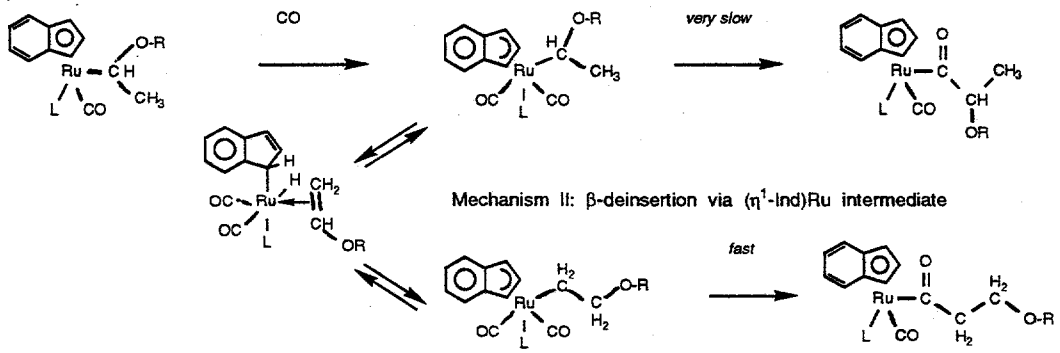
We envisage two plausible mechanisms for the carbonylation-assisted isomerization of the α-alkoxyethyl ligand, depending on whether reversible η^5/η^3 or η^3/η^1 Ind ring shifts couple to the alkoxyethyl ligand β-H deinsertion/reinsertion steps. According to the



first mechanism, the α- to β-alkoxyethyl ligand isomerization occurs simultaneously with η^5/η^3 Ind ring slippage. Although rare, the overall α- to β-alkoxyethyl ligand rearrangement is precedented: CpFe or Ru α-alkoxyalkyl compounds engage in similar isomerization reactions depending on the availability of coordinatively unsaturated intermediates.[50]

A potential driving force for mechanism I is that carbonylation of the β-alkoxyethyl complex will be greatly preferred over its α- isomer.[39] The (Ind)Ru α-alkoxyethyl complexes thus either equilibrate with or irreversibly transform very slowly to their β-isomers, which rapidly carbonylate. These β-alkoxyethyl compounds, however, were *never* detected even during incomplete carbonylation reactions. Moreover, we found that independently synthesized $(Ind)(CO)_2RuCH_2CH_2OMe$ does not convert to its α-methoxyethyl isomer, thus ruling out an equilibrium between α- and β-alkoxyethyl compounds that favors the former.

Mechanism II on the other hand links η^3/η^1 Ind ring tautomerization to the alkoxyethyl ligand isomerization steps. This isomerization evidently takes place after carbonylation provides an η^3-(Ind)Ru intermediate; subsequent alkyl-CO migratory insertion, mediated by η^3 to η^5 Ind ring shifting, preferentially occurs for the β-alkoxyethyl complex. By invoking the (undetected) η^1-(Ind)Ru intermediate for the β-H deinsertion step, we account for (a) the absence of the β-alkoxyethyl compounds and (b) the required carbonylation step.



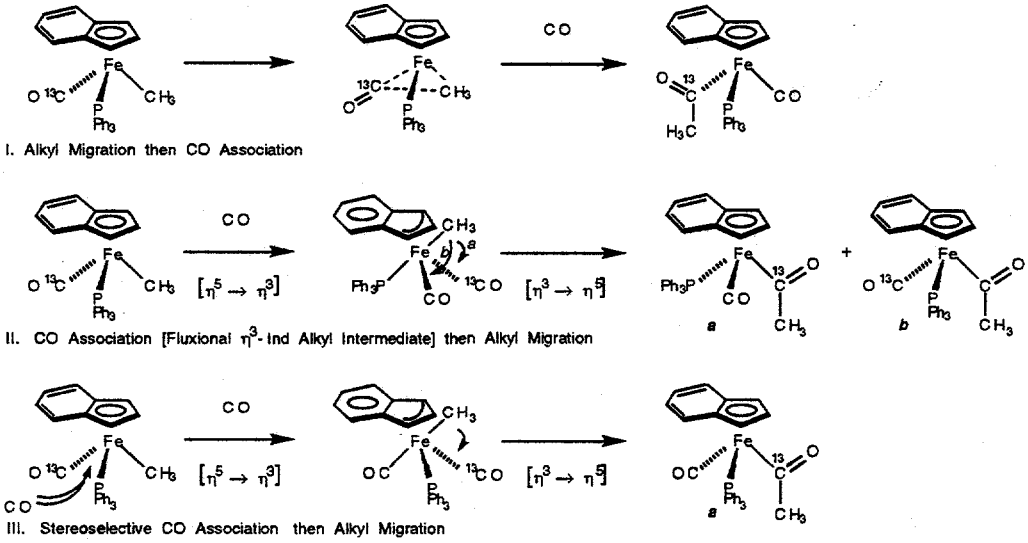
Mechanism II is distinguished by the intermediacy of η^1-(Ind) complexes, which has precedent. Ligand association reactions on (Ind)metal complexes often involve η^1-Ind intermediates; the presence of potential donor ligands determine whether η^1- or η^5-Ind bonding is thermodynamically preferred over η^3-Ind complexation.[44b,c,51] A recent example is the Foo and Bergman carbonylation study of $(Ind)(PMe_3)Ir(R)(R')$. This chemistry afforded $(\eta^1\text{-Ind})(PMe_3)(CO)_2Ir(R)_2$ even though a desired product, $(\eta^5\text{-Ind})(PMe_3)(R)Ir$-

$C(O)CH_3$, was prepared independently.[51e]

Of the alternative reaction pathways that we considered for this α-alkoxyethyl isomerization / carbonylation reaction, the most attractive required ionization of the alkoxide to generate an ethylidene ligand. Subsequent ethylidene to ethylene rearrangement via hydride transfer,[52] nucleophilic addition of alkoxide to the η^2-ethylene compounds,[53] and carbonylation accounts for the observed β-alkoxypropionyl products. We discount this mechanism with two additional observations. (1) Carbonylation of $(Ind)(PEt_3)(CO)Ru-CH(OEt)CH_3$ in benzene-MeOH yielded only the β-ethoxypropionyl derivative, not the β-methoxy analog.[54] (2) (Ind)Ru alkyl complexes not bearing alkoxy groups also undergo carbonylation-assisted isomerization reactions - see the research plan.

3. Carbonylation of Labeled $(Ind)(PPh_3)(^{13}CO)FeCH_3$ (and its CpFe analog).

We carbonylated the labeled iron methyl compounds $Cp(^{13}CO)(PPh_3)FeCH_3$ and $(Ind)(^{13}CO)(PPh_3)FeCH_3$ (50-60% ^{13}C-label). Both were prepared from their 99% labeled acetyl compounds $(dienyl)(CO)_2Fe^{13}C(O)CH_3$ after photolysis and treatment with PPh_3.[41c] [Our inability to extend this photolysis step to (Ind)Ru analogs precluded us from doing this study with the more reactive Ru compounds.] Carbonylation of $(Ind)(^{13}CO)(PPh_3)FeCH_3$ in CH_2Cl_2 or CH_3NO_2 and $Cp(^{13}CO)(PPh_3)FeCH_3$ in CH_3NO_2 at 80 psig gave identical results: *all of the terminal carbonyl label transformed into acetyl carbonyl.* It is also important to note that all of the label was retained.



This transfer of all of the ^{13}C label from both labeled CpFe and (Ind)Fe methyl complexes to their product acetyl sites is at first sight perplexing. We expect this labeling result for the CpFe system, since alkyl migration followed by CO incorporation (route I, above) had been established.[55] The (Ind)Fe methyl complex, however, could afford a 1:1 mixture of **a** and **b** (route II), the result of CO association preceding alkyl migration. This assumes either nonstereospecific CO association or stereochemical nonrigidity of an η^3-Ind intermediate.

The results of the labeling experiments can be accommodated by a stereoselective CO

association during the operation of the indenyl effect, as outlined in route III. Reversible η^5/η^3 indenyl ring slippage, commensurate with both the initial CO association and subsequent alkyl migration steps, remains the mechanism by which the $FeCH_3$ carbonylation avoids higher energy coordinatively unsaturated intermediates. According to our new hypothesis, the (Ind)Fe methyl stereoselectively adds CO to its preferred conformation in which the methyl ligand resides anti to the Ind C_{3a}-C_{7a} bond (cf. p 18). The incoming CO is trans to the methyl ligand, thus facilitating $\eta^5 \rightarrow \eta^3$ indenyl ring slippage, and methyl migration must take place to the labeled CO. Our approach for testing this working hypothesis appears in the research plan.

PUBLICATIONS

Appearing During Grant Period (11/15/92 - 11/14/95) and Acknowledging DOE Support

1. "Catalyzed and Noncatalyzed Hydrosilation of Organotransition Metal Acyl Complexes", P. K. Hanna, B. T. Gregg, D. L. Tarazano J. R. Pinkes, and A. R. Cutler, In *Homogeneous Transition Metal Catalyzed Reactions*; Advances in Chemistry 230; **1992**, p. 491.

2. "Reactivity of Cobalt Acetyl Complexes $(PR_3)(CO)_3CoCOCH_3$ toward Monohydrosilanes", B. T. Gregg and A. R. Cutler, *Organometallics* **1992**, *11*, 4276.

3. "Synthesis and Solution Dynamics of $[Cp(CO)_2Fe]_2(CH{=}CH_2)^+BF_4^-$, a μ-(η^1:η^2) Vinyl Complex Not Containing a Metal-Metal Bond", D. L. Tarazano, T.W. Bodnar, and A. R. Cutler, *J. Organomet. Chem.* **1993**, *448*, 139.

4. "Synthesis and Carbonylation of Some α- Alkoxyalkyl Cobalt Complexes, $[RCH(OR')Co(CO)_3PPh_3]$ (R = H, CH_3; R' = Me, Et)", C. C. Tso and A. R. Cutler, *Polyhedron* **1993**, *12*, 149.

5. "$Mn(CO)_5C(O)$-*p*-$C_6H_4CH_3$ - Catalyzed Monohydrosilane SiH/SiD Exchange: Evidence from a Kinetics Study Implicating Coordinatively Unsaturated Manganese Silyl Intermediates", B. T. Gregg and A. R. Cutler, *Organometallics* **1993**, *12*, 2006.

6. "Manganese Carbonyl Bromide - Catalyzed Alcoholysis of the Monohydrosilane $HSiMe_2Ph$", B. T. Gregg and A. R. Cutler, *Organometallics* **1994**, *13*, 1039.

7. "Hydrosilation of Manganese Acetyl $(CO)_5MnC(O)CH_3$ With Monohydrosilanes", B. T. Gregg and A. R. Cutler, *J. Am. Chem. Soc.*, accepted for publication.

8. "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.

9. "Unusually Facile Carbonylation of (η^5-Indenyl)ruthenium Methyl and

Methoxymethyl Complexes (η^5-C_9H_7)(CO)(L)RuR (L = CO, PPh_3)", R. J. Chiulli, D. L. Tarazano, M. E. Dery, and A. R. Cutler, *Organometallics*, manuscript submitted.

10. "Transformation of Manganese Acyls $(CO)_5MnC(O)CH_2R$ (R = H, CH_3, OCH_3) into their Siloxyvinyl 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*, manuscript submitted.

11. "$(PPh_3)(CO)MnC(O)CH_3$-Catalyzed Hydrosilation of the Alkoxycarbonyl Complexes $Cp(L)(CO)M\text{-}C(O)OCH_3$ (M = Fe, Ru; L = CO, PPh_3) and $M'(CO)_x(L)C(O)OCH_3$ (M = Co (x = 3), Mn, (x = 4); L = CO, PPh_3)", B. T. Gregg, R. J. Chiulli, M. DiBiase, and A. R. Cutler, *J. Organomet. Chem*, manuscript submitted.

12. "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*, manuscript accepted

13. "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, *J. Organomet. Chem.*, manuscript submitted.

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5. "Unusually Facile Carbonylation of (η^5-Indenyl)ruthenium Methyl and Methoxymethyl Complexes (η^5-C_9H_7)(CO)(L)RuR (L = CO, PPh_3)", Chiulli, R. J.; Tarazano, D. L.; Dery, M. E.; Cutler, A. R. *Organometallics*, manuscript submitted.
6. "Carbonylation-assisted Alkyl Isomerization: Carbonylation of (η^5-Indenyl)Ru α-Alkoxyethyl Complexes", R. J. Chiulli, D. L. Tarazano, M. E. Dery, and A. R. Cutler, *Organometallics*, manuscript submitted.
7. "Hydrosilation of Manganese Acetyl $(CO)_5MnC(O)CH_3$ With Monohydrosilanes", B. T. Gregg and A. R. Cutler, *J. Am. Chem. Soc.*, accepted for publication.
8. "Transformation of Manganese Acyls $(CO)_5MnC(O)CH_2R$ (R = H, CH_3, OCH_3) into their Siloxyvinyl 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*, manuscript submitted.
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17. "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)", Mao, Z.; Gregg, B. T.; Cutler, A. R., manuscript in preparation.
18. Gregg, B. T.; Cutler, A. R. *Organometallics* **1994**, *13*, 1039.
19. "Manganese Carbonyl Complexes as Catalysts for the Hydrosilation of Ketones, A Comparison with $RhCl(PPh_3)_3$", DiBiase, M.; Gregg, B. T.; Cutler, A. R., manuscript in preparation.
20. "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.*, manuscript submitted.
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DISCLAIMER

PRINCIPAL INVESTIGATOR

A. Biographical Sketch

Name	Title	Date of Birth
Alan Richard Cutler	Professor of Chemistry	[redacted]

Education

Clark University, Worcester, MA	B.A.	1968	Chemistry (Honors)
Brandeis University, Waltham, MA	Ph.D.	1974	Organometallic Chemist
Harvard University, Cambridge, MA	Postdoc.	1973-74	Bioinorganic and Organometallic Chemist
University of British Columbia Vancouver, BC	Postdoc.	1974-76	Bioinorganic and Organometallic Chemist
Standard University Palo Alto, CA	Postdoc.	1976-77	Bioinorganic

Professional Experience

Professor; Department of Chemistry, Renssealer Polytechnic Institute, Troy, NY; August 1989-present.

Associate Professor; Department of Chemistry, Renssealer Polytechnic Institute, Troy, NY; August 1982-1989.

Assistant Professor of Chemistry; Wesleyan University, Middletown, CT; July 1977-August 1982

Postdoctoral Fellowship; Stanford University, Palo Alto, CA; 1976-1977 (Research Advisor, Professor Richard Holm)

Postdoctoral Fellowship; The University of British Columbia, Vancouver, BC; 1974-1976 (Research Advisor, Professor David Dolphin)

Postdoctoral Fellowship; Harvard University, Cambridge, MA; 1973-1974 (Research Advisor, Professor David Dolphin)

Research Program

Synthetic and Mechanistic Transition Organometallic Chemistry: Reactions of coordinated ligands that selectively convert carbon monoxide and carbon dioxide to oxygenated organic molecules.

Mechanistic details of these coordinated ligand reactions facilitate rational design of homogeneous catalysts that effect the same transformations. We are particularly interested in developing coordinated ligand reactions that engender stereoselective organic transformations of synthetic utility and that generate novel organometallic oligomeric materials having unusual electronic or structural properties.