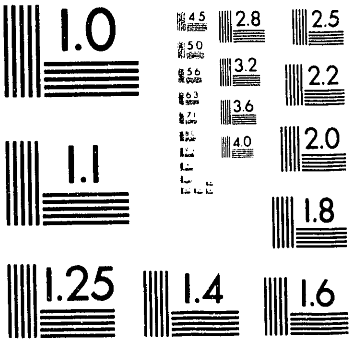
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SELECTIVE TRANSFORMATION OF CARBONYL LIGANDS TO ORGANIC MOLECULES

Progress Report

for Period 11/15/92 - 11/14/93

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Selective Transformation of Carbonyl Ligands to Organic Molecules

Outline

PROGRESS REPORT (11/15/92-11/14/93)

PROPOSED RESEARCH (11/15/93 - 11/14/94)

Fiscal Year-1993 Abstract

Carbonylation of α-alkoxyethyl ruthenium complexes (η^5-indenyl)(L)(CO)Ru-CH(OR)CH_3 [L = PPh_3, PEt_3, $P(OMe)_3$; R = Me, Et] gave isomerized α-alkoxypropionyl derivatives, (η^5-Ind)(L)(CO)Ru-C(O)CH_2CH_2OR. Treatment of (η^5-Ind)$(CO)_2$Ru-CH(OR)CH_3 with PEt_3 (room temperature) provided the same products. These CO insertion/isomerization studies have been extended to (η^5-Ind)$(CO)_2$Ru-*n*-/*i*-propyl complexes. Obtaining the necessary alkyl complexes entailed synthesizing and characterizing η^2-alkene complexes, (η^5-Ind)(L)(CO)Ru(η^2-CH_2=CHR)$^+$. Diastereoselective, $Mn(CO)_5C(O)Ph$-catalyzed hydrosilation of Cp(L)(CO)Fe-C(O)CH_3 [L = PPh_3, PEt_3, $P(OMe)_3$, $P(OPh)_3$] has been established. Examples of RR, SS and RS, SR diastereomers of Cp(L)(CO)Fe-CH(OY)CH_3 [Y = $SiHPh_2$, $SiHEt_2$, Me, Et] were prepared; the alkoxyethyl complexes were obtained through alcoholysis of the siloxyethyl systems. With a variety of Rh catalysts, Cp(L)(CO)Fe-C(O)CH_3 and dihydrosilanes transform directly to their vinyl derivatives, Cp(L)(CO)Fe-CH=CH_2. Rh-catalyzed $PhSiH_3$ reduction of Fe acyl complexes efficiently affords alkyl derivatives, Cp(L)(CO)FeCH_2R [R = Me, Et, t-Bu, Ph]. This silane with Mn-catalysis (e g., $Mn(CO)_5C(O)Ph$) quantitatively convert esters RC(O)OR' to ethers RCH_2OR', an unprecedented reaction. These reactions, often exothermic, can be carried out on a preparative scale with a wide range of ester substrates, including unsaturated and lactones. A kinetics study on the $Mn(CO)_5$(p-toluoyl)-catalyzed SiH/SiD exchange between $DSiMe_2Ph$ and $HSiMe_2Et$ (room temperature in C_6D_6) has been completed. Preequilibrium kinetics were consistent with second-order isotope exchange reaction. Plots of initial velocities υ_0 against $(HSiMe_2Et)_i$ are consistent with saturation kinetics; Graphical analysis of double reciprocal or Lineweaver-Burk plots (linear) is in accord with a ping-pong Bi Bi mechanism that operates under rapid equilibrium conditions and involves coordinatively unsaturated manganese silyls, $(CO)_4Mn$-SiR_3, as active catalysts. These manganese silyls interconvert by sequentially adding one substrate silane and then releasing a product silane. A related mechanism apparently operates during $[Mn(CO)_4Br]_2$-catalyzed alcoholysis of $HSiMe_2Ph$, N_t = 11,200 h^{-1} for 2-butanol. Tertiary and unsaturated alcohols (1:1 with silane) work with 0.08% precatalyst.

A. *Manganese Acyl Complexes as Hydrosilation Substrates and Precatalysts*

Objectives:

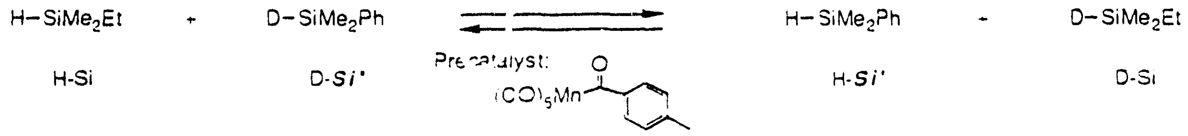
(1) Elucidate the different pathways that are available for reactions between manganese acyl complexes $L(CO)_4MnC(O)R$ and hydrosilanes. Several novel ligand reactions already have been described that appear unrelated to similar reactions involving other reductants such as H_2, metal hydrides, or stannanes?

(2) Study the reactivity of manganese alkyl, halide, and pseudohalide complexes $L(CO)_4MnY$ with hydrosilanes. Many of these reactions afford extremely reactive hydrosilation catalysts. We need to understand the reactions that generate the active catalyst(s) and optimize the catalysis.

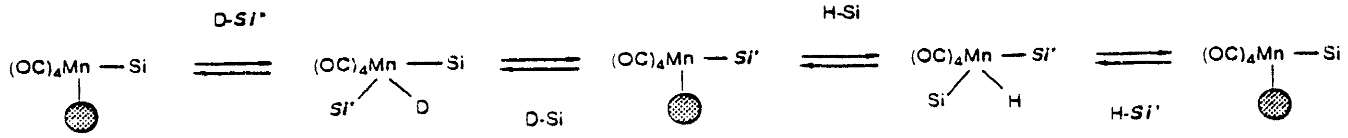
(3) Definitively relate this hydrosilation catalysis with the reaction chemistry of coordinatively unsaturated manganese silyls $L(CO)_3MnSiR_3$.

1. SiH/SiD Exchange Kinetics Study.[5]

The manganese p-toluoyl complex $(OC)_5MnC(O)\text{-p-}C_6H_4CH_3$ (as little as 0.5%) catalyzes SiH/SiD exchange between $DSiMe_2Ph$ (*Si'D*) and $HSiMe_2Et$ (SiH) at room temperature in C_6D_6. This silane exchange is the simplest catalytic reaction that we can study once the excess silanes transform the precatalyst, $(OC)_5MnC(O)\text{-p-}C_6H_4CH_3$, into the active catalyst. By doing a complete mechanistic study, we determined the active catalyst and probed its reactions with hydrosilanes. This study afforded the working hypothesis for much of our current research: manganese acyl-hydrosilane mixtures ultimately generate unsaturated silyl complexes, $(OC)_4MnSiR_3$, and these are plausible active catalysts for hydrosilation reactions with a variety of substrates.



The preequilibrium kinetics of the SiH/SiD exchange are consistent with second-order isotope exchange reaction: plots of initial velocities υ_0 against $(HSiMe_2Et)_i$ further established saturation kinetics. Lineweaver-Burk double reciprocal plots of $1/\upsilon_0$ vs. $1/(SiH)_i$ are in accord with a ping-pong Bi Bi mechanism that operates under rapid equilibrium conditions and involves coordinatively unsaturated manganese silyls, $(OC)_4MnSiMe_2R$, as active catalysts. These manganese silyls interconvert by sequentially adding one substrate silane and then releasing a product silane. The derived kinetic



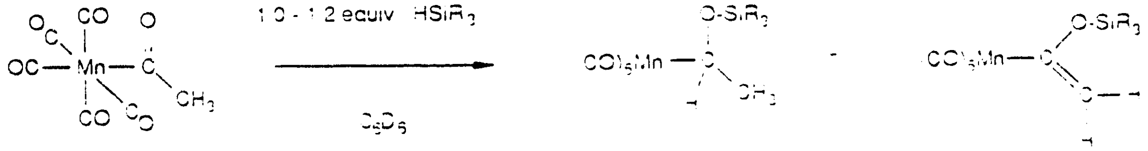
expression for this exchange reaction uniquely accounts for the appearance of these Lineweaver-Burk plots.

Although the kinetics were well behaved and reproducible, doing the appropriate controls and fitting the kinetics data to the unusual mechanism was extremely time consuming. The graphical analysis of the Lineweaver-Burk plots, however, definitively ruled out other bireactant-biproduct (Bi Bi) mechanisms, including the ping-pong version under steady-state conditions that is commonly found in enzymatic systems.

During the reproducible induction period, the hydrosilanes transform the precatalyst to p-toluoyl silyl ethers (verified on a preparative scale) plus the active catalyst. Maximum catalytic efficacy for this isotope exchange required pretreating the manganese aroyl complex with excess hydrosilane for 0.75 h (until all starting precatalyst had been consumed) and then adding the other silane reagent. This pretreatment procedure is now our standard procedure that we use in other manganese-catalyzed hydrosilation reactions.

2. Hydrosilation of Manganese Acetyl $(OC)_5MnC(O)CH_3$ with Monohydrosilanes, an Autocatalytic Reaction.[7]

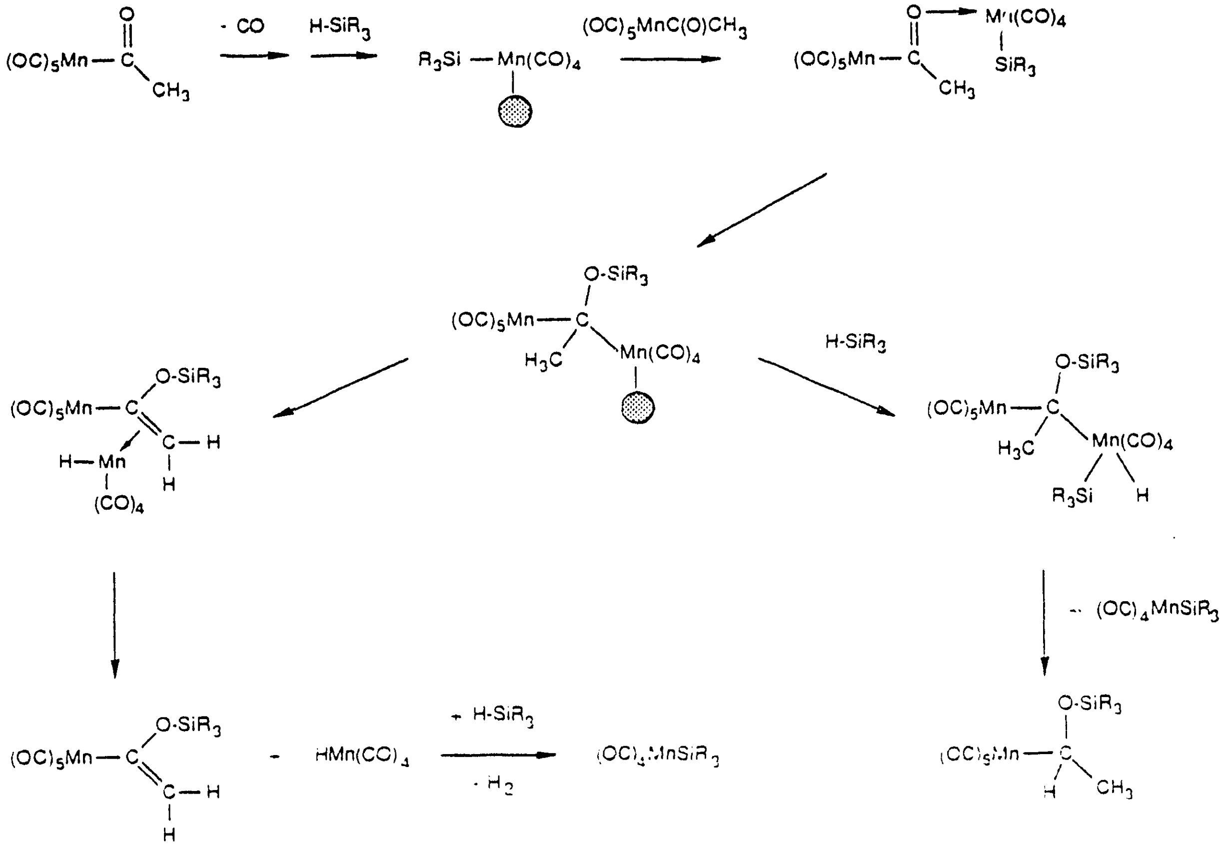
Studies have been completed on the hydrosilation chemistry involving twelve monohydrosilanes and $(CO)_5MnC(O)CH_3$. Of the 9 α-siloxyethyl complexes $(CO)_5MnCH(OSiR'_3)CH_3$ that formed, 7 were isolated in 46-70% yields after column chromatography. Five then were further characterized as their stable α-siloxypropionyl derivatives $(CO)_5Mn\text{-}C(O)CH(OSiR'_3)CH_3$ after carbonylation at 80 psig. Spectral data also are reported for five α-siloxyvinyl byproducts $(CO)_5MnC(OSiR'_3)=CH_2$, their yields depending on the silane.



SiR_3 = a) $SiMe_2Ph$, b) $SiMePh_2$, c) $SiMe_2OEt$, d) $SiMe_2OSiMe_3$, e) $SiMe_2Et$, f) $SiMeEt_2$, g) $SiMe(OSiMe_3)_2$, h) $SiMe(OMe)_2$, i) $SiMe_2Cl$

We demonstrated that these hydrosilation reactions are autocatalytic, with silane-induced degradation of the α-siloxyethyl complexes $(CO)_5MnCH(OSiR'_3)CH_3$ providing the coordinatively unsaturated manganese silyl $(CO)_4MnSiR'_3$ as the active catalyst. Consistent with this intermolecular process, pretreatment of catalytic quantities of $(CO)_5MnC(O)CH_3$ or $(CO)_5MnC(O)C_6H_4CH_3$ with excess silane, systems known to generate $(CO)_4MnSiR'_3$, before adding the substrate $(CO)_5MnC(O)CH_3$ dramatically enhanced hydrosilation rates.

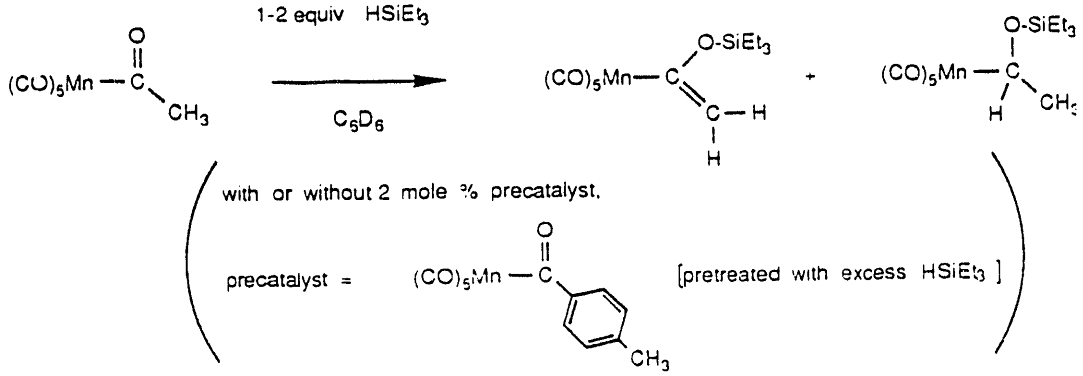
All observations can be accomodated by an intermolecular pathway in which the active catalyst $(CO)_4MnSiR'_3$ binds the substrate $(CO)_5MnC(O)CH_3$ and rearranges to the unsaturated μ-siloxyethylidene $(CO)_5MnC(CH_3)(OSiMe_2Ph)Mn(CO)_4$ as the key catalysis intermediate. Silane addition then affords $(CO)_5MnCH(OSiR'_3)CH_3$ whereas β-deinsertion



produces $(CO)_5MnC(OSiR'_3)=CH_2$. Both reactions regenerate the active catalyst, which evidently is unstable and is replenished continuously through the silane-induced decomposition of $(CO)_5MnCH(OSiR'_3)CH_3$. We believe that this mechanism may be generalized to hydrosilation reactions involving manganese acyl complexes as precatalysts and other organometallic or organic acyl substrates.

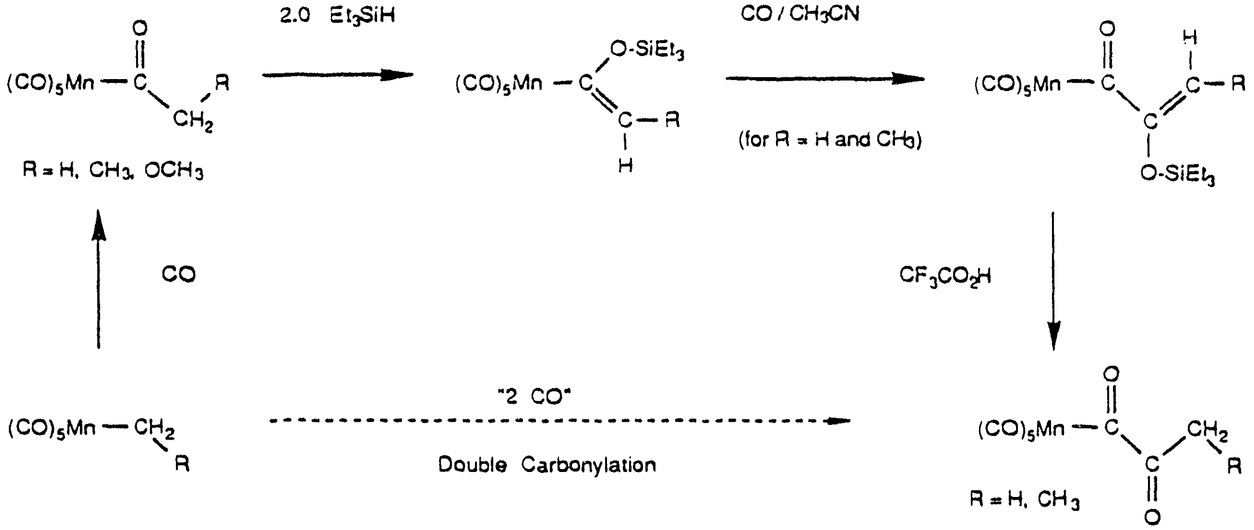
3. Triethylsilane Hydrosilation of Manganese Acyls $(CO)_5MnC(O)CH_2R$ (R = H, CH_3, OCH_3). The role of the Siloxyvinyl Products $(CO)_5MnC(OSiEt_3)=CHR$ to Double Carbonylation of Manganese Alkyl Complexes $(CO)_5MnCH_2R$.[8]

Of all the monohydrosilanes that we examined, triethylsilane 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, but the α-siloxyethyl compound (characterized by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy) promptly decomposed via the silane-induced degradation under the reaction conditions. 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 $(CO)_5MnC(OSiEt_3)=CH_2$.



Additional mechanistic studies are consistent with the same autocatalytic hydrosilation mechanism (above) with $(CO)_4MnSiEt_3$ as the active catalyst. For example, pretreating catalytic quantities of the manganese toluoyl $(CO)_5MnC(O)\text{-}p\text{-}C_6H_4CH_3$ 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.

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. 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



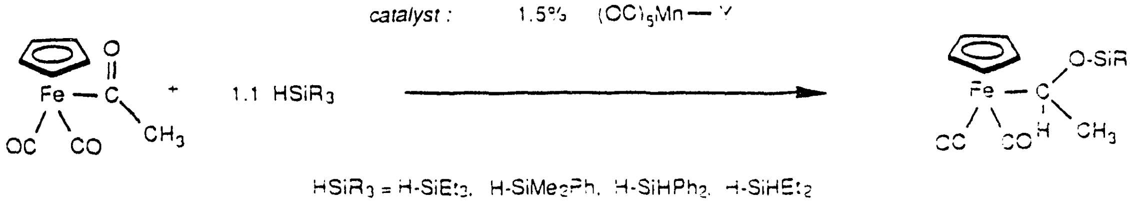
α-ketoacyl derivatives, represents a novel double-carbonylation sequence.

4. Catalytic Hydrosilation of Iron Acyls $Cp(CO)_2FeC(O)R$ using Manganese Carbonyl Catalyst Precursors $(CO)_5MnY$ (Y = Alkyl, Acyl, Halide).[10]

Recently completed mechanistic studies on the manganese-catalyzed hydrosilation of the iron acyls $Cp(CO)_2FeC(O)CH_3$ ($FpCOCH_3$) and FpC(O)Ph satisified three objectives.

(1) These reactions represent the catalytic hydrosilation of nonlabile metal acyl complexes. The substrate iron acyls accordingly do not function also as catalyst precursors, and are unreactive towards hydrosilanes in the absence of a catalyst. With an appropriate catalyst, these reactions afford easily isolated and stable α-siloxyalkyl iron complexes, $FpCH(OSiR'_3)R$ (R = CH_3, Ph), with a variety of mono- and dihydrosilanes.

(2) A variety of manganese complexes $L(CO)_4MnY$ have been tested as precatalysts,



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)* >

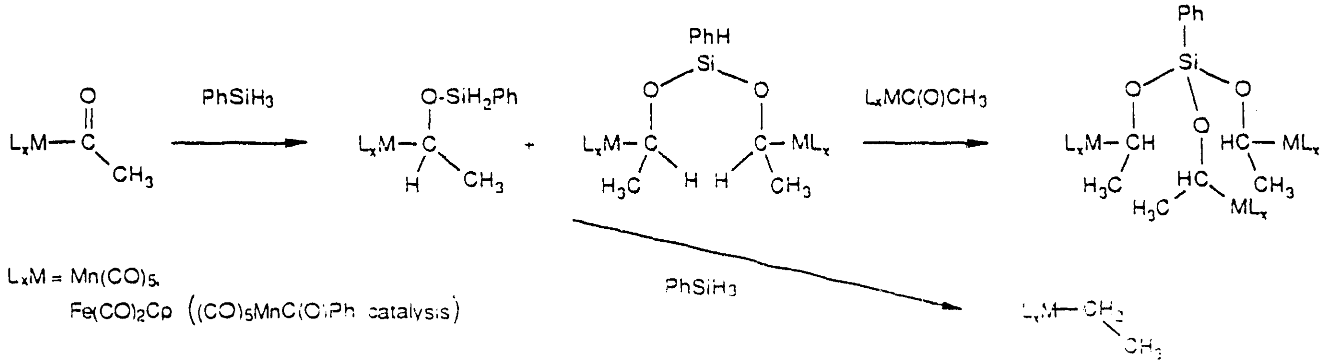
$(CO)_5Mn\text{-}COCH_3$ *(12 h)* >> $(PPh_3)(CO)_4Mn\text{-}COCH_3$, $(CO)_5Mn\text{-}SiMe_2Ph$, $Mn_2(CO)_{10}$

and reaction conditions have been optimized. These manganese catalytic systems typically are far more active and selective than are the rhodium catalysts that we examined.

(3) Results of mechanistic studies on using manganese acyl precatalysts $(CO)_5Mn-C(O)R$ ($R = CH_3$, Ph) are consistent with our autocatalysis pathway. First these precatalysts must hydrosilate and then degrade to manganese silyl active catalysts, reactions that the iron acyl substrates competitively inhibit. Thus, the reaction time for $(CO)_5MnC(O)Ph$-catalyzed hydrosilation ($HSiMe_2Ph$) of $FpCOCH_3$ decreases from three hours to twenty minutes when the manganese precatalyst is treated with the excess silane (45 min) before adding the $FpCOCH_3$ substrate.

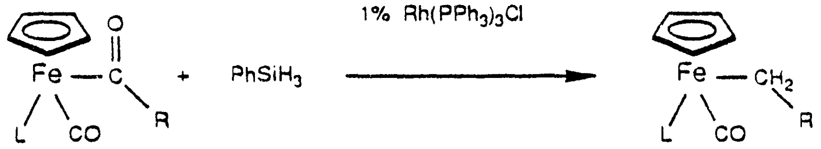
5. $PhSiH_3$ Hydrosilation of Iron and Manganese Acyls $(CO)_5MnC(O)CH_3$ and $Cp(L)(CO)FeC(O)R$; $Rh(Cl)(PPh_3)_3$ and $(CO)_5MnC(O)R$ Catalysis.[12]

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, an unusual development. With other hydrosilanes, these manganese acyls are much more reactive hydrosilation catalysts than Wilkinson's compound, although both types typically provided the same products.



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 transpired upon treating

$(CO)_5MnC(O)CH_3$, the substrate, with $PhSiH_3$.



R = CH3; L = CO, PPh3, PEt3, P(OMe)3, P(OPh)3

R = CHMe2, CMe3, Ph; L = CO

$Rh(Cl)(PPh_3)_3$ 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.

B. Manganese Carbonyl-Catalyzed Hydrosilation of Organic Compounds

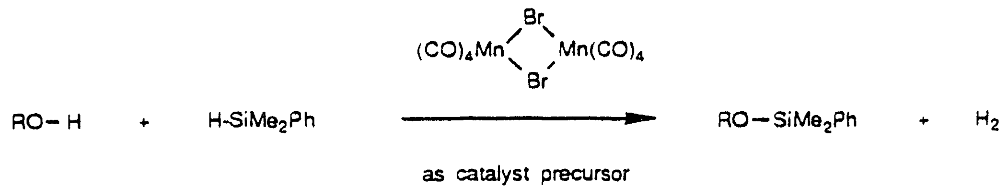
General Observations:

1. *Manganese complexes, particularly $(CO)_5MnBr$, $(CO)_5MnC(O)Ph$, and $PPh_3(CO)_4Mn$-$C(O)CH_3$, selectively catalyze a variety of reactions between hydrosilanes and C-O bonds on organic molecules. Carbon-carbon double bonds are unreactive.*
2. *The manganese catalysts usually are much more reactive, than $RhCl(PPh_3)_3$ and even catalyze a number of reactions that $RhCl(PPh_3)_3$ will not.*
3. *During these hydrosilation reactions most of the manganese precatalyst (typically added at 1-5%) is unaltered, at least until the substrate gets consumed. Pretreatment of a manganese acyl with the excess silane (until the former is consumed) before adding the substrate rapidly generates the active catalyst and subsequently accelerates the catalysis. Timing this pretreatment procedure is difficult since the active catalyst has a limited lifetime.*

1. Manganese Carbonyl Bromide-Catalyzed Alcoholysis of the Monohydrosilane $HSiMe_2Ph$.[6]

Dimeric manganese carbonyl bromide $[Mn(CO)_4Br]_2$ 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 $[Mn(CO)_4Br]_2$ (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.

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.



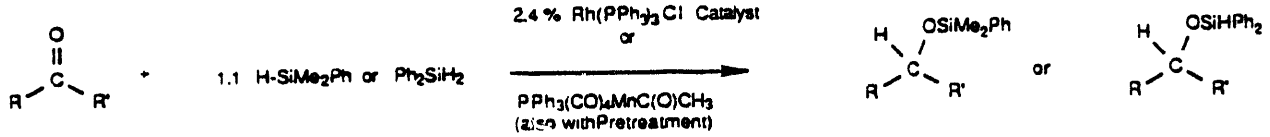
^1H NMR spectral monitoring of catalyzed reactions between methanol or *sec*-butanol with $HSiMe_2Ph$ was used in screening other manganese carbonyl complexes as potential $HSiMe_2Ph$ alcoholysis catalysts. Their reaction times varied: $[Mn(CO)_4Br]_2 > Mn(CO)_5Br >> Mn(CO)_5CH_3 = Mn(CO)_5C(O)Ph > Mn(PPh_3)(CO)_4Br > Mn(PPh_3)(CO)_4C(O)CH_3 >> Mn(CO)_5(SiMe_2Ph) >> Mn_2(CO)_{10} = Rh(PPh_3)_3Cl$ (no reaction).

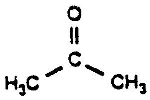
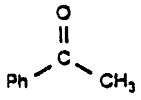
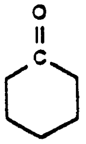
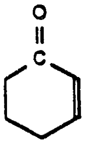
Solvent-dependent turnover frequencies were determined for the $[Mn(CO)_4Br]_2$ (1.4 mol %) -catalyzed dehydrocoupling of *sec*-butanol and $HSiMe_2Ph$ (0.289 M): N_t = 2183 (THF), 2728 (C_6H_6), and 5457 h^{-1} (CH_2Cl_2). In a second procedure, a preparative scale reaction (3.12 M for each reactant) in CH_2Cl_2 containing only 0.084 mol % precatalyst afforded a much higher turnover frequency of 11,217 h^{-1}.

2. Manganese Acyl-Catalyzed Hydrosilation of Ketones. Work in progress: M. DiBiase and B. T. Gregg

The manganese acetyl $PPh_3(CO)_4MnC(O)CH_3$ is an extremely effective precatalyst for hydrosilating the ketones in the accompanying chart. (Reaction times were determined by ^1H NMR spectral monitoring under comparable conditions.) Interestingly, $RhCl(PPh_3)_3$ does not catalyze hydrosilation reactions involving the monohydrosilane. With diphenylsilane, the manganese and rhodium exhibit similar activities. Pretreatment of $PPh_3(CO)_4MnC(O)CH_3$ with the silane (20 min) prior to adding the ketone dramatically enhances the hydrosilation rate.

Isolated yields of the silyl ethers for most of these reactions are over 90%. We also



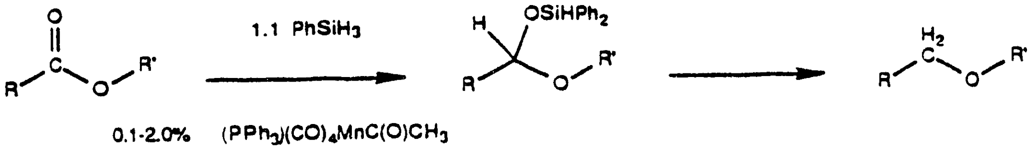
Reaction Times (min)					
H-SiMe$_2$Ph	Rh(Cl)(PPh$_3$)$_3$	11	NR	NR	NR
	PPh$_3$(CO)$_4$MnC(O)CH$_3$	50	35	120	NR
	Pretreatment	≤5	≤5	≤5	NR
H-SiHPh$_2$	Rh(Cl)(PPh$_3$)$_3$	≤5	≤5	≤5	35
	PPh$_3$(CO)$_4$MnC(O)CH$_3$	32	40	90	155
	Pretreatment	≤5	≤5	≤5	240

noted that PPh$_3$(CO)$_4$MnC(O)CH$_3$ is a much more active ketone hydrosilation catalyst than (CO)$_5$MnC(O)CH$_3$, (CO)$_5$MnC(O)C$_6$H$_4$CH$_3$ (even with pretreatment), (CO)$_5$MnBr, and others. Work remaining entails accurately measuring some turnover frequencies in order to quantify the unusually high catalyst activity.

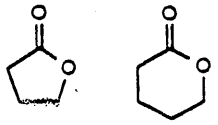
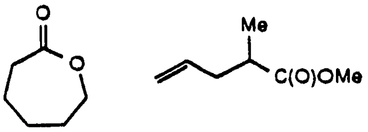
3. Manganese Acyl-Catalyzed Hydrosilation of Esters. Work in progress: Z. Mao and B. T. Gregg

Last year, we announced that several manganese complexes catalytically reduce organic esters with hydrosilanes. Thus PhSiH$_3$ and ≤ 2% PPh$_3$(CO)$_4$MnC(O)CH$_3$, the most effective precatalyst, *quantitatively* reduce a number of esters to their ethers. These exothermic reactions are complete in < 45 min, with no other organic products detected by ^{1}H and ^{13}C NMR spectroscopy.

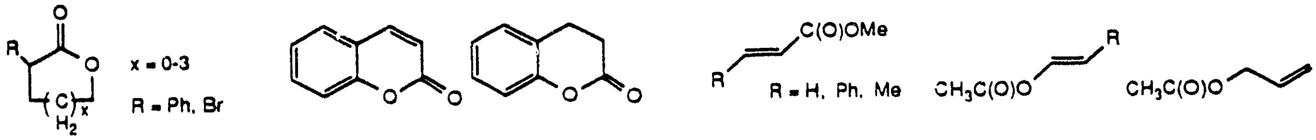
Other esters upon catalytic PhSiH$_3$ hydrosilation give mixtures of silyl acetals and the fully reduced ethers (see above). Varying the ester, precatalyst, and other reaction conditions alters the proportion of silyl acetal, which forms as mono-, bis-, and tris-silyl



Results

	Mixtures of silyl acetal and ether	*Ether quantitatively formed*
Starting esters	$R = CH_3$; $R' = Ph$	$R = CH_3$; $R' = Me, Et, i\text{-}Pr$
	$R' = CH_3, CH_2CH_3$; $R = H, i\text{-}Pr, t\text{-}Bu, Ph, BrCH_2$	$R' = CH_3, CH_2CH_3$; $R = PhCH_2, C_6H_{11}, CH_3(CH_2)_4, Br(CH_2)_3, EtO_2C(CH_2)_2$
		

Currently under study



acetal adducts of $PhSiH_3$, $PhSiH_n[OCHR(OR')]_{3-n}$. Fortunately, several analogous mono- and bis-silyl acetal adducts of Ph_2SiH_2, $Ph_2SiH_n[OCHR(OR')]_{2-n}$ (fully characterized), serve as spectroscopic models for their $PhSiH_3$ analogs. These Ph_2SiH_2-derived silyl acetals are the sole products our manganese-catalyzed ester hydrosilation reactions.

Very little precedent exists for directly reducing esters to ethers! This hydrosilation represents an extremely efficient homogeneous catalytic procedure for carrying out an otherwise difficult organic reduction. Remaining work on our ester reduction centers on understanding the precatalyst / $PhSiH_3$ / active catalyst chemistry and includes:

(1) Optimizing the reaction conditions for converting esters to ethers and the purification procedures for separating the ether products from contaminating silyl acetals.

(2) Selectively reducing esters to silyl acetals with Ph_2SiH_2 represents a potentially convenient synthesis of aldehydes (after hydrolysis of the silyl acetals).

(3) Extending the synthetic scope of ester hydrosilation to carboxylic acid anhydrides, amides/lactams, and perhaps even CO_2 may be possible.

(4) Manganese-catalyzed hydrosilation (e.g., with $HSiMe_2Ph$) of carboxylic acids RCO_2H

quickly and quantitatively gives silyl esters, $RCO_2SiR'_3$. Their further catalytic hydrosilation with $PhSiH_3$ will be examined.

(5) Silane, SiH_4, should be an even more potent reductant in these catalytic hydrosilations.

C. Indenyl Ruthenium Carbonylation Chemistry

Objectives:

(1) *Indenyl ruthenium alkyl complexes $(\eta^5\text{-}C_9H_7)(L)(CO)RuR$ exhibit incredibly facile carbonylation reactivity. Our immediate goal is to use the "indenyl effect" to drive otherwise infeasible carbonylation reactions.*

(2) *Establish that reversible η^5/η^3 indenyl ring slippage is the driving force in the carbonylation reactions of (η^5-indenyl) iron and ruthenium alkyl complexes. This reactivity engenders a novel associative pathway in organometallic chemistry.*

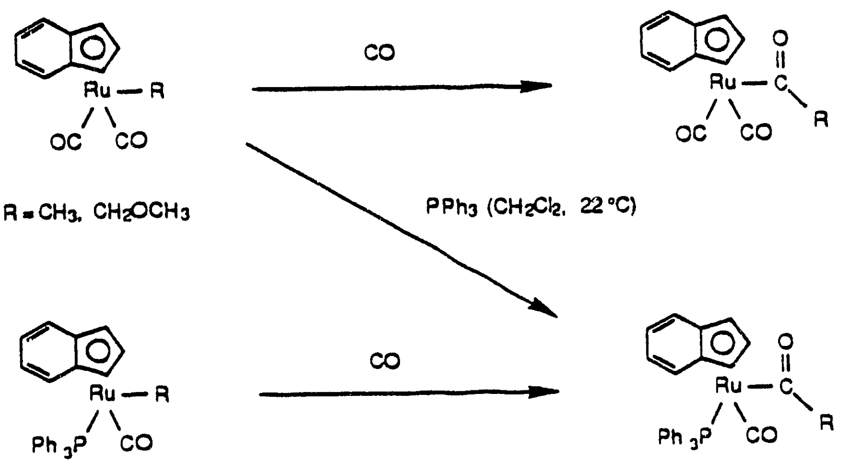
(3) *Determine if indenyl ruthenium alkyl complexes undergo alkyl ligand reactions under unusually mild conditions. Ligand reactions of interest include alkyl-alkene migratory insertion, alkyl ligand isomerization, and the reactions of hydrosilanes with the alkyl complexes.*

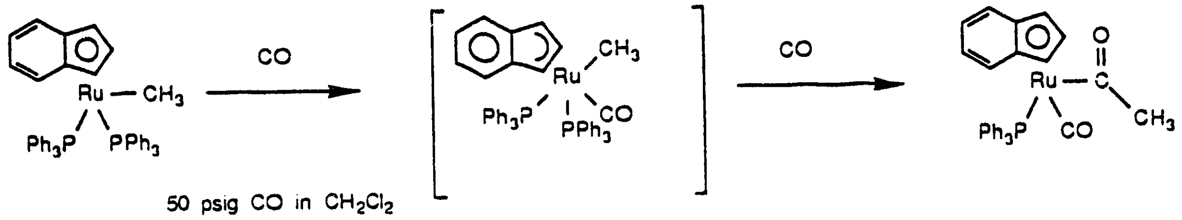
(4) *Ascertain if ruthenium hydride and silyl complexes $(\eta^5\text{-}C_9H_7)(L)(CO)RuR$ (R = H, SiR'_3) associate and incorporate (migratory insertion) CO, CO_2, alkenes, and ketones.*

1. Unusually Facile Carbonylation of (η^5-Indenyl)ruthenium Methyl and Methoxymethyl Complexes.[9]

We established the unusually mild carbonylation chemistry of η^5-indenyl ruthenium alkyl complexes involving the ten methyl / acetyl and methoxymethyl / methoxyacetyl complexes depicted. 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 $Cp(CO)_2RuCH_3$ in nitromethane.)

Of the iron and ruthenium methyl complexes $(\eta^5\text{-dienyl})(L)(CO)M\text{-}CH_3$ complexes that we have studied, $Ind(PPh_3)(CO)RuCH_3$ represents the most and $Cp(CO)_2RuCH_3$ the least reactive. According to our working hypothesis, reversible η^5/η^3 indenyl ring slippage couples first with association of CO and then with alkyl migration to give the product acyl. Support for IndRu alkyl complexes associating CO (commensurate with η^5/η^3-indenyl ring



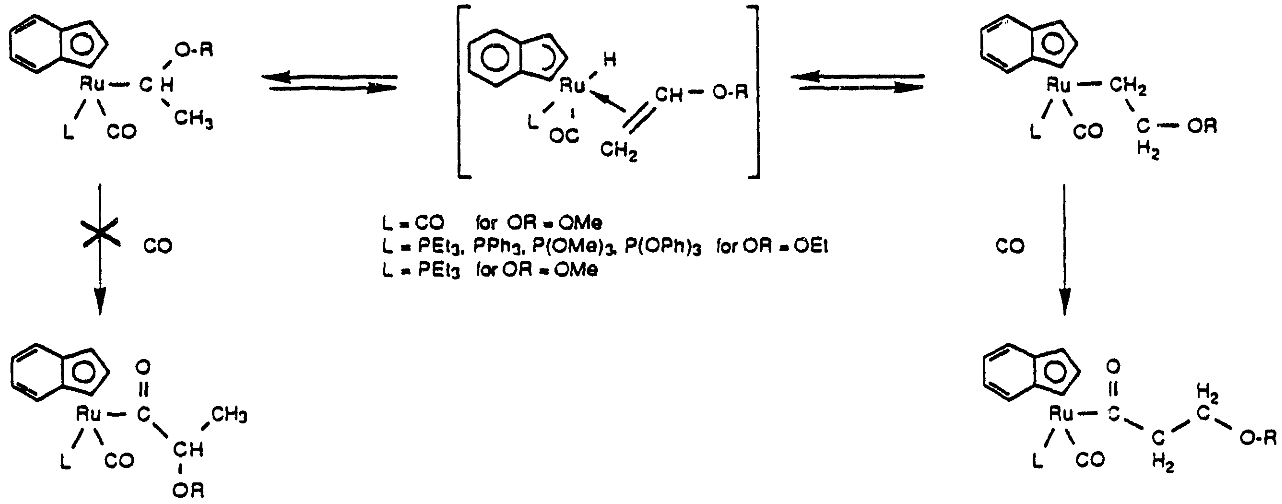


slippage) during their carbonylation reactions derives from the results of carbonylating Ind(PPh$_3$)$_2$RuCH$_3$. This complex efficiently incorporates CO ($\leq$ 50 psig, 22°C in CH$_2$Cl$_2$) and gives an acetyl complex in which a phosphine ligand also has been replaced by CO. The Cp analog, Cp(PPh$_3$)$_2$Ru-CH$_3$, does not interact with CO (80 psig).

The significant result is that now we can directly carbonylate these α-alkoxymethyl complexes under conditions where CpFe, IndFe, and CpRu congeners are inert towards CO. Much of our present efforts are directed towards extending the unusually high carbonylation reactivity of these IndRu alkyl complexes to other ligand reactions.

2. Isomerization and Carbonylation of (η^5-Indenyl)ruthenium α-Alkoxyethyl Complexes.[13]

We also are in the process of publishing results on the unprecedented α-alkoxyethyl ligand isomerization-then-carbonylation. Either treating Ind(CO)$_2$RuCH(OMe)CH$_3$ with PPh$_3$ or carbonylating Ind(L)(CO)RuCH(OR)CH$_3$ affords the same β-alkoxypropionyl products. No intermediates were detected. These products are accounted for by sequential β-hydrogen migratory deinsertion / reinsertion that isomerizes the alkyl ligand prior to carbonylation. The facility of this isomerization is consistent with coupling reversible η^5/η^3 indenyl ring slippage and the deinsertion / reinsertion steps as illustrated.



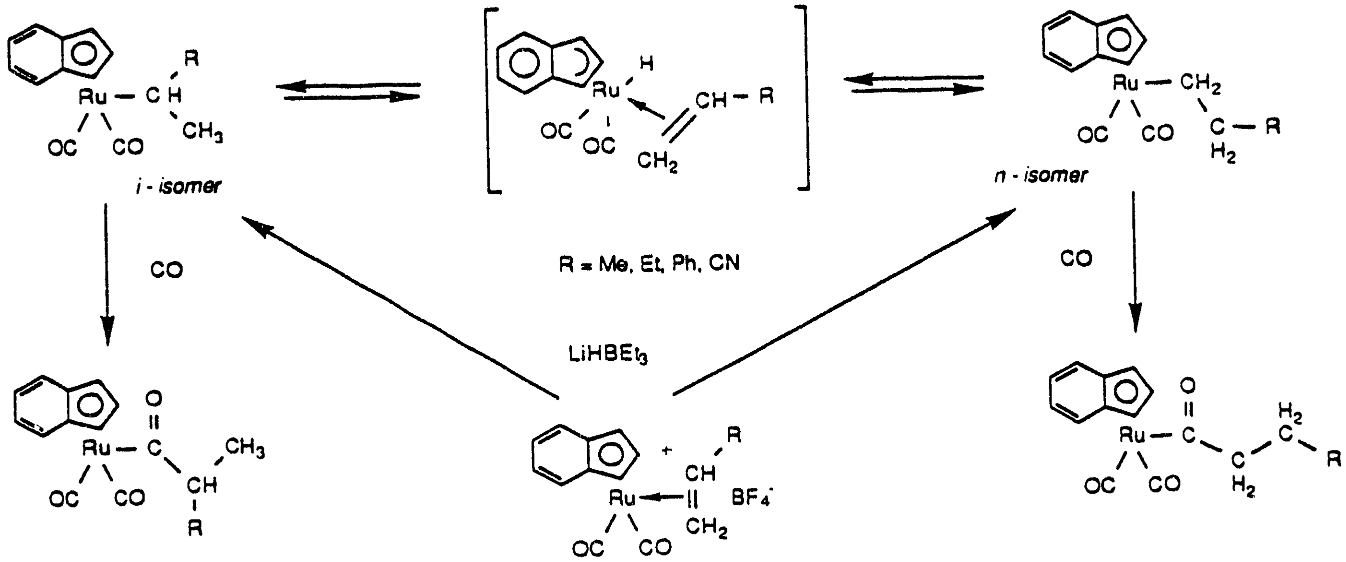
L = CO for OR = OMe
L = PEt$_3$, PPh$_3$, P(OMe)$_3$, P(OPh)$_3$ for OR = OEt
L = PEt$_3$ for OR = OMe

An intriguing observation on this IndRu α-alkoxyethyl chemistry is that the carbonylation step drives the α-alkoxyethyl ligand isomerization. The IndRu α-alkoxyethyl complexes do not rearrange to their β-alkoxyethyl isomers in the absence of CO. Presumably low concentrations of this β-alkoxyethyl isomer do form and preferentially carbonylate, thus shifting the α- / β-alkoxyethyl ligand equilibrium to the right.

3. Carbonylation Driven Isomerization of (η^5-Indenyl)ruthenium Alkyl Complexes.

Work in progress: R. J. Chiulli

The following scheme outlines synthetic chemistry in progress concerning phosphine-promoted CO insertion reactions on Ind(CO)$_2$Ru alkyl complexes. Our approach entails generating mixtures of *iso-* and *normal-* alkyl ligand isomers and assess the extent of their isomerization in the absence and presence of phosphine. Thus far, we generated 45/55 mixtures of the isopropyl and n-propyl complexes (R = Me), which on the laboratory time frame did not isomerize. Carbonylating these methylene chloride solutions, however, transformed these mixtures into a 10/90 ratio of isobutyryl and n-butyryl complexes. Apparently, the alkyl ligand isomerization is linked to the carbonylation.



TIME AND EFFORT COMMITMENT TO PROJECT

The principal investigator has devoted approximetely 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.

PROPOSED STUDY

Since this next year is the last year in this DOE grant, every effort will be made to consolidate the ongoing research. Accordingly, research plans for next year are noted in the Progress Report and in the Technical Scope document.

PUBLICATIONS

Appearing During Granting Period 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* **1993**, in press.

7. "Hydrosilation of Manganese Acetyl $(CO)_5MnC(O)CH_3$ With Monohydrosilanes", B. T. Gregg and A. R. Cutler, manuscript submitted.

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, manuscript submitted.

9. "Unusually Facile Carbonylation of (η^5-Indenyl)ruthenium Methyl and Methoxymethyl Complexes $(\eta^5\text{-}C_9H_7)(L_1)(L_2)RuR$ (L_1, L_2 = CO, PPh_3)", R. J. Chiulli, D. L. Tarazano, M. E. Dery, and A. R. Cutler, manuscript to be submitted.

Manuscripts in Preparation

10. "Catalytic Hydrosilation of Iron Acyls $Cp(CO)_2FeC(O)R$ using Manganese Carbonyl

Catalyst Precursors $(CO)_5MnY$ (Y = Alkyl, Acyl, Halide)", B. T. Gregg and A. R. Cutler.

11. "Carbonylation Driven Isomerization of (η^5-Indenyl)ruthenium α-Alkoxyethyl Complexes", R. J. Chiulli, D. L. Tarazano, and A. R. Cutler.

12. "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.

13. "Diastereoselective Hydrosilation of Iron Acetyl Complexes $Cp(L)(CO)FeCOCH_3$ (L = PPh_3, PEt_3, $P(OMe)_3$, $P(OPh)_3$) using Rhodium Catalysis", J. R. Pinkes and A. R. Cutler.

14. "Organoiron Phosphido-Acetyl and -Methyl Complexes $(\eta^5\text{-}C_5H_5)(CO)(PPh_2)Fe\text{-}X^-$ and $(\eta^5\text{-}C_9H_7)(CO)(PPh_2)Fe\text{-}X^-$ (X = $COCH_3$ and CH_3), their Synthesis, Interconversion, and Reactions with Electrophiles", A. B. Todaro and A. R. Cutler.

I anticipate finishing and submitting the above 5 manuscripts by the end of the year.

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10/12/93

END