SELECTIVE TRANSFORMATION OF CARBONYL LIGANDS TO ORGANIC MOLECULES

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Outline

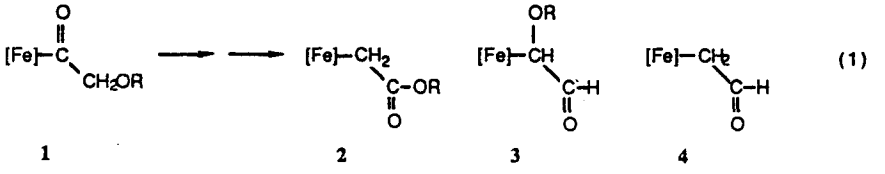
Abstract

Studies on anionic phosphido alkyl and acetyl complexes $Cp(CO)(PPh_2)Fe\text{-}R^-$ (**1**) and $In(CO)(PPh_2)Fe\text{-}R^-$ (**2**) [R=CH_3 (**a**), $COCH_3$ (**b**); In=η^5-indenyl] and their neutral phosphine derivatives $Cp(CO)(PPh_2H)Fe\text{-}R$ (**3**) and $In(CO)(PPh_2H)Fe\text{-}R$ (**4**) are complete. Attempts to carbonylate **1a** and **2a** to **1b** and **2b** failed; also, **3a** and **4a** resist carbonylation. Reacting **1b** with MeI affords a neutral PPh_2Me acetyl compound **5**, whereas $MeOSO_2CF_3$ gives the Fischer carbene complex $Cp(PPh_2)(CO)Fe{=}C(OMe)CH_3$ (**6**). Carbene **6** isomerizes to **5** at room temperature. Reaction conditions have been optimized for generating vinylidene compounds $In_2(CO)_3Fe_2\mu\text{-}(C{=}CHR)$ from $InFe(CO)_2^-$ and $In(CO)_2Fe\text{-}CH_2R$ (R=H, Me, OMe). The bimetallic carbonylation procedure for converting $Fp^-(Li^+, Na^+, PPN^+)$ and $In(CO)_2Fe\text{-}CH_3$ to $InCp(CO)_3Fe_2(COCH_3^-)$ and then regioselectively to $FpCOCH_3$ (1 atm. CO) has been optimized. Studies are finished on the diastereofacial selectivity observed during reduction of the alkoxycarbenes $Cp[P(OR)_3](CO)Fe{=}C(OCH_3)CH_3^+$ (R=Me, Ph) with borohydride reagents R_3BH^- (Li^+, Na^+, K^+) and with $(PPh_3CuH)_6$. A survey of the Rh(I)-catalyzed hydrosilation of a variety of iron acyl complexes has been concluded. FpCOR thus adds R'_2SiH_2 to give α-siloxyalkyl complexes $FpCH(OSiHR'_2)R$ (R=CH_3, Et, n-Pr, i-Pr, i-Bu, Ph; R'_2=Et_2, Ph_2, PhMe). With $PhSiH_3$, catalytic hydrosilation produces fully reduced $FpCH_2R$ (R-Me, Ph). Hydrosilation of $Mn(CO)_5COR$ gives $(CO)_5Mn\text{-}CH(OSiR'_2H)R$ (R=Me, Ph) without a Rh catalyst. Thus, for $Co_2(CO)_8$ and $(CO)_5MnCOR$ also act as efficient hydrosilation catalysts for FpCOR.

I. Introduction: Past-Present-Future Endeavors

A. C_2 Chemistry: Oxygenated C_2 Ligands Originating from Carbon Monoxide Synthesis Reactions

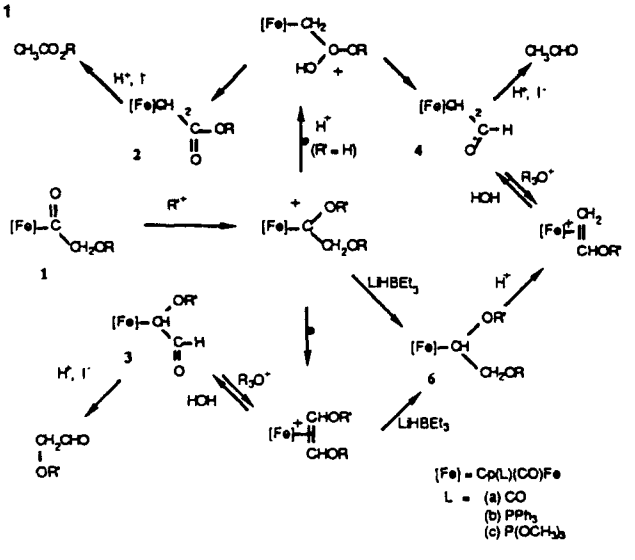
During the beginning of this grant period we finished our organoiron chemistry studies that concerned using the alkoxyacetyl ligand on Cp(L)(CO)Fe-$COCH_2OR$ (**1**, L=CO, PPh_3, $P(OMe)_3$; R=Me, Et) as a template for generating other C_2 oxygenated ligands (eq.1). Under the appropriate reaction conditions, **1** isomerizes



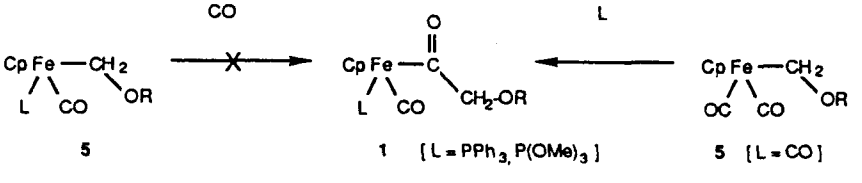
(1)

either to carbalkoxymethyl **2** or to alkoxyformylmethyl **3** and reduces to formylmethyl **4**. The coordinated ligand reactions that interconvert these C_2 oxygenated ligands and transform them selectively into acetic acid ester, glycolaldehyde ether, and acetaldehyde are summarized in Figure 1. All organoiron compounds illustrated were characterized as reported in several recent papers[1] and a review.[2]

Figure 1



Three conclusions from these studies serve as a basis for our ongoing and planned research. First, the alkoxyacetyl compounds **1** are not available by carbonylating alkoxymethyl complexes **5** (eq.2); even phosphine-promoted



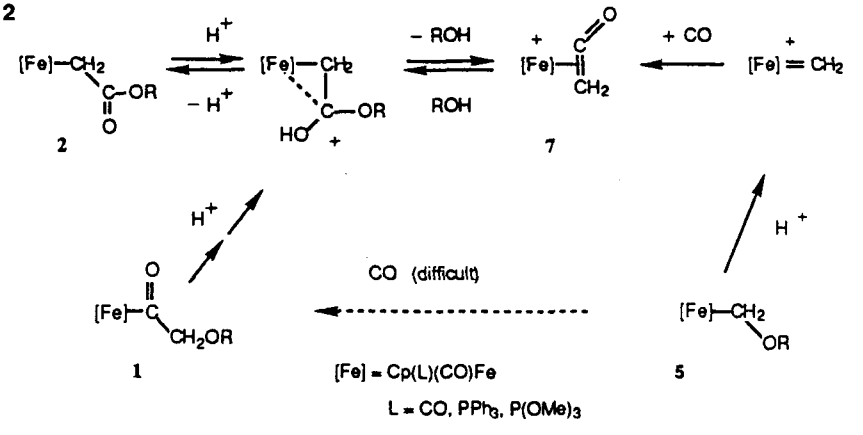
(2)

alkoxymethyl-CO migration amounts to a sluggish reaction. This resistance to CO insertion exhibited by **5** contrasts the relative ease of carbonylating analogous methyl complexes,[3] but substantiates earlier observations on the difficulty of carbonylating alkoxymethyl complexes in general.[4] In recent studies, we have overcome this resistance of alkoxymethyl ligands to undergo CO migratory insertion by: (1) designing a bimetallic carbonylation route using (indenyl)iron complexes, (Section IIC2), and (2) switching to (indenyl)ruthenium compounds (Section IID).

The second conclusion is that α,β-dialkoxyethyl complexes $Cp(CO)_2Fe\text{-}CH(OEt)\text{-}CH_2OR$ (**6**) (Figure 1) are surprisingly stable and do not isomerize to β,β-dialkoxyethyl compounds, $Fp\text{-}CH_2CH(OR)_2$, for example. Although examples of **6** are sensitive to electrophiles, once isolated they are as stable as related complexes bearing oxygenated alkyl ligands such as $Fp\text{-}CH(OR)CH_3$, $Fp\text{-}CH_2CH_2OR$, and $Fp\text{-}CH_2CH(OR)_2$. Therefore congeners of **5** should be viable intermediates in our ongoing carbonylation studies (Section I of proposal).

The third conclusion concerns the surprising versatility of carbalkoxymethyl compounds **2**. They are readily accessible by acid-catalyzed isomerization of **1** or by treating the (η^2-C,C) ketene complex $Fp(CH_2CO)^+$ (**7**) with alcohol (Figure 2).

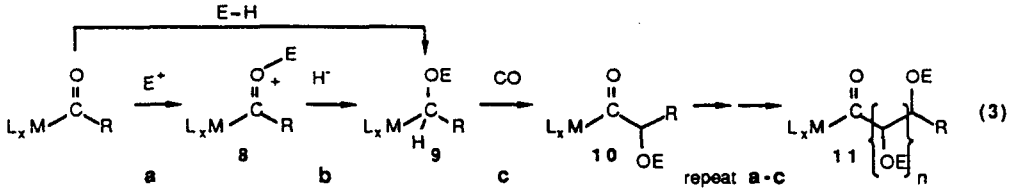
Figure 2



Interestingly, examples of **2** are more readily available from alkoxymethyl complexes **5** via the ligated ketene route than from the corresponding alkoxyacetyl compounds **1**. Since alkoxyacetyl and hydroxyacetyl compounds are plausible intermediates during homogeneous catalysis of CO reduction,[5] analogous carbalkoxymethyl compounds, their chemistry modeled by **2**, also may prove to be useful intermediates under the appropriate conditions.[6,7] In Section IIIC of the proposal, we address the synthesis of α-carbalkoxyalkyl compounds from the required substituted ketene compounds.

B. Poly(alkoxymethylene)acyl Complexes: Acyl Ligand Reduction then Carbonylation

We have initiated studies on synthesizing poly(alkoxymethylene)acyl ligands **7** that derive from carbon monoxide and retain an oxygen functionality at each carbon center (eq.3). These transition organometallic acyl complexes result from repeating a three-step sequence of ligand reactions (eq. 3): (a) electrophilic activation of an acyl ligand, (b) hydride transfer to its oxycarbenoid derivative **8**,[2,8] and (c) carbonylation of the resulting alkoxyalkyl group on **9**. The net result amounts to sequentially



incorporating carbon monoxide into a lengthening poly(alkoxymethylene) ligand.[9] We emphasize characterizing the acyl products **10** (**11**) since they often are more stable than their corresponding alkoxycarbene and alkoxyalkyl precursors.

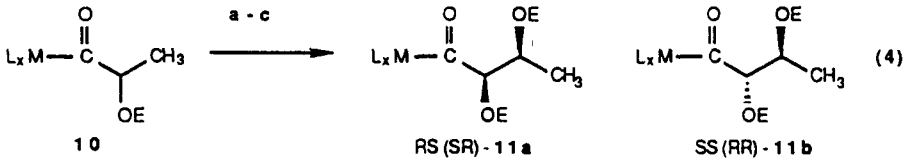
This project involves two overlapping objectives. First, appropriate organometallic systems and procedures for achieving the noted ligand skeletal construction reactions (eq.3) must be developed. Second, the stereochemistry of each emerging chiral center (step **b**, eq. 3) must be controlled.

Selecting an organometallic system that facilitates these ligand construction reactions, however, is complicated by their antithetical requirements. The first two ligand reactions **a** and **b**, resulting in net reduction of the acyl ligand, require a coordinatively saturated, nonlabile metal center in order to contain the chemistry at the acyl ligand. The third ligand reaction **c**, carbonylation of an α-alkoxyalkyl complex, on the other hand, requires a relatively labile metal center, especially considering the anticipated difficulty of this alkyl-CO migratory-insertion step.

Stereochemical control resides in step **b** (reduction of an alkoxycarbene **8** to its α-alkoxyalkyl derivative **9**, et seq.), since the carbonylation step **c** should go with retention of configuration at the α-carbon.[10] This report summarizes our ongoing research into the diasteroselectivity of acyl ligand reduction. We separately address the use of a chiral metal center L_XM on **8** and a chiral alkoxymethylene center on **10** (expressed as its carbenoid homolog of **8**) as sterochemical control elements. The proposal document builds upon these results and also introduces our approaches to enantioselection.

Creating two or more stereogenic centers on **11** engenders diastereoselectivity if either the alkoxyacyl ligand or the organometallic moiety ML_X preferentially controls the approach of the achiral reductant in step **b**. This diastereoselectivity is evident during the 1,2-asymmetric induction involved in converting alkoxypropionyl

10 into *threo*(syn)- and *erythro*(anti)- α,β-dialkoxybutyryl complexes **11a** and **11b**(eq. 4).[11] We envisage two approaches for achieving this 1,2-asymmetric induction: (1) The asymmetric center on **10** adjacent to the acyl (or alkoxy-carbene) π-system causes



(4)

the diastereofacial selectivity (Section IIA). (2) Diastereoselectivity originates through the stereoelectronic influence of a chiral metal center on L_x*M-COR[12] or its alkoxycarbene derivative **8** directing the transition state for each emerging chiral center (Section IIB).

Another approach to reducing the acyl ligand involves combining steps a and b and adding E-H across the acyl ligand in one step (eq. 3). Catalytic hydrosilation (E-H = R_3Si-H) accordingly is being developed (Section II-D). These studies will be extended to enantioselective hydrosilation of acyl complexes using homochiral hydrosilation catalysts.

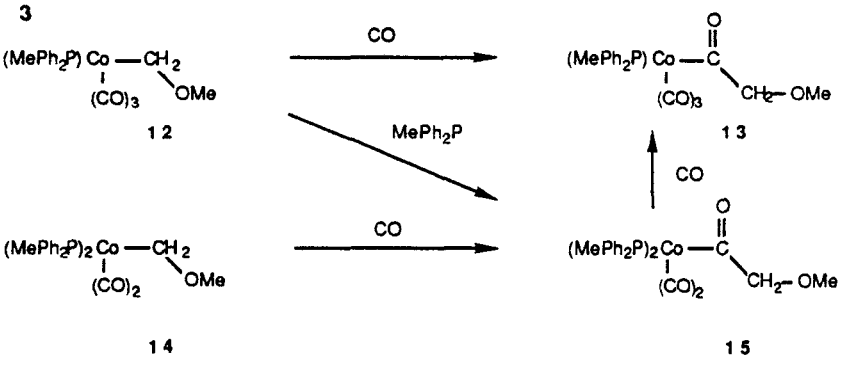
II. Carbonylation Chemistry: Acyl Ligand Reduction - then - Carbonylation

A. (Phosphinecarbonyl)Cobalt-Acetyl Chemistry

We initiated studies with (phosphinecarbonyl)cobalt alkyl and acyl complexes in the belief that these compounds nicely balance our previously mentioned prerequisites for: (1) a "robust" organometallic system forming stable acyl, carbene, and alkyl complexes that react at the ligand, and (2) an organometallic system that is sufficiently labile to permit carbonylating alkoxymethyl and α-alkoxyalkyl complexes. In our surveys of three (phosphinecarbonyl)cobalt systems[13] using PPh_3, $PMePh_2$, and $Ph_2PCH_2CH_2PPh_2$ (dppe), we observed the mildest conditions yet used in carbonylating alkoxymethyl compounds[14] (1 atm CO) and the diastereoselective synthesis of a α,β-diethoxybutyryl ligand (**11a**, eq. 4) via stepwise incorporation and reduction of two carbonyl groups.

We synthesized and fully characterized (^1H, ^{13}C, ^{31}P NMR and IR spectroscopy) the $MePh_2P$-containing cobalt complexes illustrated in Figure 3.[15] The methoxymethyl compound **12** quantitatively adds CO (1 atm; 2 h in THF solution) and affords its stable methoxyacetyl derivative **13**. The bis-phosphine cobalt methoxymethyl complex **14** likewise adds CO, but mixtures of **13** and bis-phosphine methoxyacetyl **15** inevitably

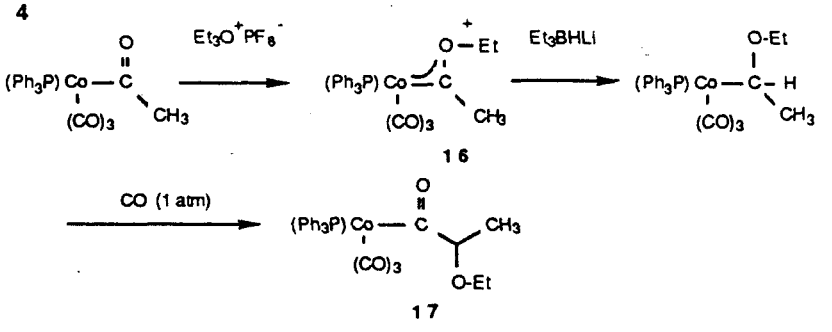
Figure 3



form. Under conditions of this reaction, **15** dissociates phosphine and incorporates CO (as established from the results of independent experiments). Working with $MePh_2P$-substituted cobalt carbonyl complexes, however, proved to be tedious as most alkyl and some acyl compounds formed unstable gums.

The (PPh_3)cobalt carbonyl α-alkoxy-alkyl and acyl complexes that we worked with are exhibited in Figure 4.[16] (All compounds are characterized fully.) Alkylation of the cobalt acetyl affords the ethoxycarbene complex **16** (81% yield) (a rare

Figure 4

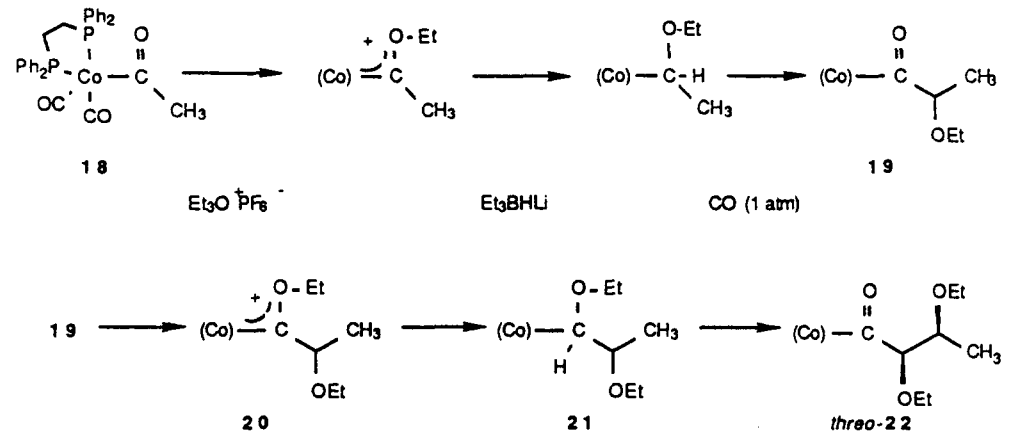


example of a cobalt Fischer-carbene compound)[16], which was converted to the α-ethoxypropionyl **17** (85%). Attempts to further chain extend **17** to its next alkoxyalkyl homolog $(PPh_3)(CO)_3Co\text{-}COCH(OEt)CH(OEt)CH_3$ stalled at the alkylation / activation step of **17** (a in eq. 3), not at the carbonylation step. Treating **17** with $Et_3O^+PF_6^-$ or other carbocationic alkylating agents decomposes it to $(PPh_3)_2Co(CO)_3^+$ as the major soluble cobalt species.

The dppe-substituted moiety,[18] $(dppe)(CO)_2Co$, proved to be the ideal substrate for reducing and then carbonylating an acyl ligand. The two phosphine centers render the cobalt acyls sufficiently basic that electrophilic alkylating agents convert them to alkoxycarbene compounds, and the presence of the dppe chelate ring prevents loss of a phosphine ligating center during carbonylation. All compounds depicted in Figure 5 typically are isolated as yellow solids that are often crystalline.

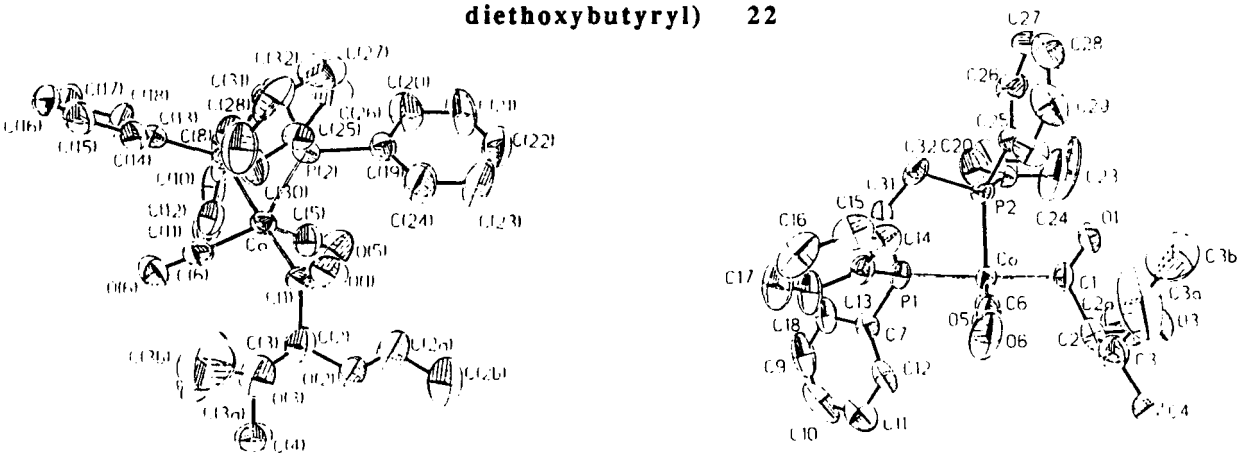
We converted the $(dppe)(CO)_2Co$ acetyl **18** to α-ethoxypropionyl **19** (81%),which underwent a second sequence of acyl ligand reduction and carbonylation and gave its homologous α,β-diethoxybutyryl **22** (74% from **19**). This forms exclusively as its threo-

Figure 5

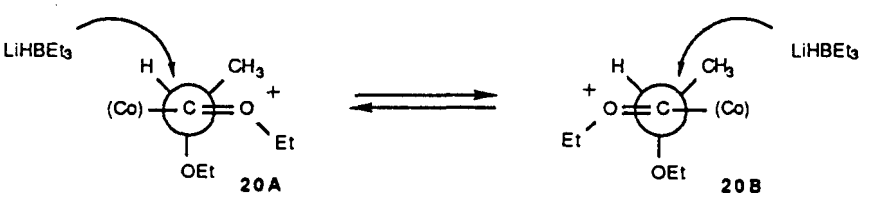


(syn) diastereomer; this assignment rests on its ^1H NMR spectrum ($^3J_{H-H}$ = 5.7 Hz for α,β-methine positions) and on the results of its single-crystal X-ray structure determination (Figure 6; single enantiomer only is illustrated).

Figure 6 X-Ray Structure Determination of (dppe)$(CO)_2$Co-*threo*(a,b-diethoxybutyryl) 22



The syn-diastereoselectivity observed in reducing **20** to **21** (*erythro*-**21**, but *threo*-**22**) is consistent with a Felkin-Anh transition-state argument.[19] In the absence of chelation effects,[20] 1,2-asymmetric induction arises from differential interactions of the attacking hydride donor with the hydrogen and methyl substituents on the equilibrating conformers **20A** and **20B**. Both conformers retain the β-ethoxy group,



the carbon substituent bearing the lowest lying σ* orbital, perpendicular to the cobalt-ethoxycarbene plane depicted (rather than the most sterically demanding group). Since the hydride donor follows a Burgi-Dunitz trajectory in attacking

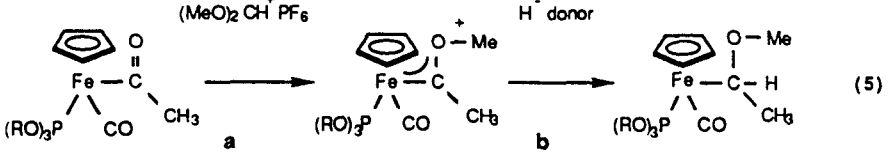
antiperiplanar to the alkyl ethoxy substituent, conformer **20A** should preferentally react. This transition-state argument parallels that used to rationalize the diastereoselectivity observed in adding nucleophiles (e.g., enolates) to α-alkoxyaldehydes.[19d] The β-ethoxyalkyl asymmetric center on **20** (not the cobalt-phosphine system) similarly controls the stereochemistry in forming **21**.

One conclusion that emerges from the structure determination of **22** is that the phenyl rings on the equatorial phosphine P(2) of the dppe chelate (spanning axial-equatorial positions of the trigonal bipyramidal structure) evidently do not shield the proximate face of the acyl carbonyl, C(1)-C(19) = 3.68 Å and C(1)-C(25)=3.73 Å. We can not envision a phenyl ring sterically limiting reagent access to one face of the acyl carbon, which would correspond to the diastereofacial selectivity argument developed by Davies[21] for PPh_3-containing pseudooctahedral Cp iron acyl complexes.

We believe that this interpretation is valid, even though a structure determination of ethoxycarbene **20** would be more appropriate. NMR spectral NOE measurements on **20** are planned that will probe the spatial relationship of the phenyl rings to the carbene ligand. It is worth noting that straightforward application of a Davies argument for the stereochemical outcome of reducing **20** -- diastereofacial selectivity due to a phenyl ring shielding one face of the carbene ligand from approach of the hydride donor -- predicts the erythro(anti) diastereomer (cf. **11b**, eq. 4 and Section IIB).

B. Diastereoselective Reduction of $Cp(P(OR)_3)(CO)Fe{=}C(OMe)CH_3{+}$

We investigated the stereochemistry involved in reducing the phosphite-substituted alkoxycarbene compounds **24** and **27** (eq.5). Our experience in generating the triphenylphosphite alkoxyethyl complex **25** (as a 1:1 mixture of diastereomers) and its subsequent conversion into ethylidene and vinyl compounds previously had been communicated.[22] The present goal is to determine under what conditions the alkoxycarbene reduction depicted (step **b**, eq.5) will be diastereoselective.



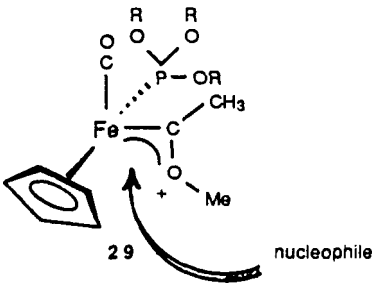
(5)

23 R=Me **24** **25**

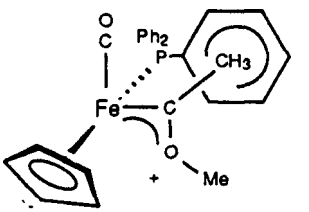
26 R=Ph **27** **28**

The central question is whether the phosphite ligand, acting analogously to ligated triphenylphosphine, sterically blocks reagent access to one face of the

carbene ligand. Davies had demonstrated that one phenyl ring of ligated PPh_3 lies in a plane parallel and close (3-4Å) to the plane containing the $Fe\text{-}CO_{terminal}\text{-}C_\alpha$ centers of the acyl, acyl enolate, or alkoxycarbene (e.g., **30** below), thus shielding the "underside" of this sp^2 ligated carbon. Selective addition of the appropriate nucleophile to the "topside" of either **29** or **30**, diastereofacial selectivity, generates a second chiral center and one of two possible diastereomerically related pairs of enantiomers.

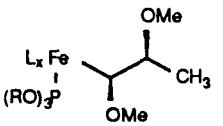


29 nucleophile



30

The origin of this putative stereoselectivity is critical to furthering our synthetic goals. We project that repeating the acyl reduction (reactions **a** and **b** in eq.5) and carbonylation (reaction **c**, eq.3) steps soon will be feasible (perhaps with analogous (indenyl)ruthenium complexes, vide infra). The first iteration accordingly would provide either erythro or threo diastereomers (**31** and **32**, respectively). If the



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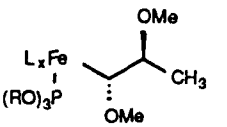


32

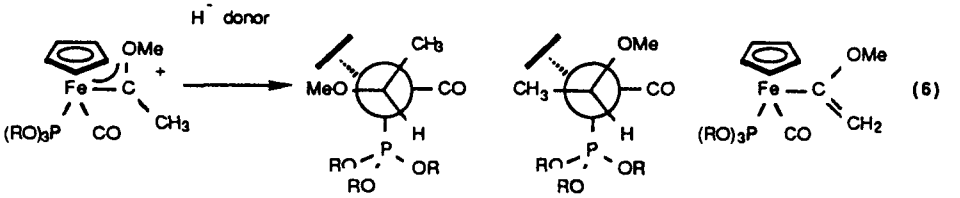
phosphite ligand plays no role in controlling the stereochemistry of the alkoxycarbene ligand reduction, then *erythro*-**31** will form. This assumes that the Felkin-Anh transition-state argument observed in our (dppe)Co carbonyl work pertains: the chiral carbene ligand controls the stereochemistry. If, on the other hand, presence of the phosphite ligand is responsible for the diastereofacial selectivity (according to the Davies argument as applied to related PPh_3-containing systems), then *threo*-**32** will emerge: the chiral metal system controls the stereochemistry.

An intriguing possibility is that for a given phosphite on compounds related to **24** and **27** *either* **31** or **32** could result by carefully choosing the hydride donor and reaction conditions in the two sequential alkoxycarbene reduction steps. Conceivably only larger hydride donors might exhibit diastereofacial selectivity due to the phosphite ligand restricting their access to the alkoxycarbene center. Under these conditions, using a bulky hydride donor could ultimately give *threo*-**32**, whereas a relatively small hydride donor would favor *erythro*-**31**. Our immediate objective, therefore, is to determine if varying the size of the hydride donor will permit selec-

tively reducing **24** (or **27**) either to a 1:1 mixture of diastereomers for **25** (eq.5) (conditions where ligated phosphite on **24** is not sterically dominating) or to a single diastereomer of **25** (conditions of high diastereofacial selectivity).

We base this premise on the smaller relative size of ligated phosphite vs phosphine, as indicated by their relative cone angles: $P(OMe)_3$ (107°), $P(OPh)_3$ (128°), PEt_3 (132°), and PPh_3 (145°).[23] Efficacy of a phosphine or phosphite in sterically shielding an alkoxycarbene ligand also could depend partially upon an attractive interaction between the electron deficient carbene center and one of the phosphine or phosphite substituents (vide infra). $Cp(P(OR)_3)(CO)Fe$ acyl complexes have not been used in stereochemical studies, one deterrent being the instability of their acyl enolate complexes.[24]

In the present study,[25] we treated the alkoxycarbene complexes **24** and **27** with a series of trialkylborohydride reagents $R_3BH^-M^+$ (M=Li, Na, K) in which varying the alkyl group alters the size of the hydride donor. The phosphine copper (I) hydride cluster, $(PPh_3CuH)_6$,[26] which was introduced by Nelson[27] for reducing alkoxymethylene ligands, served as our extremely bulky hydride donor. These hydride donors converted **24** (or **27**) into mixtures of α-methoxyethyl compounds **25** (or **28**) and the α-methoxyvinyl compounds **33** (or **34**) (eq.6), the latter resulting from deprotonation of the methoxycarbene ligand.[22,28]



24 (R=Me) **27** (R=Ph) | (RS)-**25A** (RS)-**28A** | (RS)-**25B** (RS)-**28B** | **33** **34**

All six products were characterized by ^1H, ^{13}C, and ^{31}P NMR spectral data. The α-methoxyethyl compounds typically exist as diastereomeric mixtures: for **28**, (RS, SR)-**28A** and (RR, SS)-**28B**. (Only one of each pair of enantiomers for diastereomeric **28A** and **28B** are depicted.) We could not separate these diastereomeric mixtures by fractional crystallization (they deposit from solution as unchanged gums or resins upon cooling) nor by column chromatography. They degrade on alumina or silica gel (flash chromatography) even at -50°C. Acceptable elemental analyses are available for **33**, **34**, and diastereomeric mixtures **25A,B** and **28A,B**.

The α-methoxyethyl conformers **28A** and **28B** (or **25A** and **25B**) depicted (eq.6) are expected to be the only rotamers in solution at ambient temperatures. For each of these rotamers the unique C_α methine hydrogen resides in the sterically most hindered site between CO and the phosphite ligands. This analysis is in accord with

Davies conformational model,[29] as applied to the pseudooctahedral iron alkyl complexes $Cp(PPh_3)(CO)Fe\text{-}CHR^1R^2$ and more recently[30] the triethylphosphine analogs $Cp(PEt_3)(CO)Fe\text{-}CHR^1R^2$. Results of our NOESY studies on **28** also are consistent with the rotamer assignments for **28A** and **28B**.

Assigning structures **28A** and **28B** (and **25A** and **25B**) to our product mixtures follows from examining the C-methyl absorptions (δ 2.2-1.7 in C_6D_6) in their ^1H NMR spectra. The (RR, SS) enantiomers exhibit a downfield doublet (for **28B**, δ 2.16, $^3J_{HH}$ = 6.1Hz), whereas their diastereomers (RS, SR) present a distinctive doublet of doublets[29c,30a] (for **28A**, δ = 1.93, $^3J_{HH}$ = 6.3, $^4J_{PH}$ = 2.0Hz). The extra $^4J_{PH}$ W-coupling that exists for the RS(SR) diastereomers of **25A** and **28A** (eq.6) indicates an anti-periplanar array of methyl and phosphite centers, consistent with the assigned structures.

Table 1 summarizes the product ratios observed for reducing the triphenylphosphite-substituted methoxycarbene compound **27** with one equivalent of the hydride donor in THF at the stated temperature. These ratios, which were determined by ^1H NMR spectroscopy after replacing the THF by C_6D_6, represent the kinetic products. In separate experiments, direct ^1H and ^{31}P NMR spectral monitoring at low temperatures (immediately after thawing) afforded similar product ratios. Results of a parallel set of reduction reactions of the trimethyl-phosphite-substituted methoxycarbene **24** also are available. We find that using either $P(OPh)_3$ or $P(OMe)_3$ as the phosphite ligand in these methoxycarbene ligand reductions affords essentially identical product distributions.

Table 1 Reduction of $Cp[P(OPh)_3](CO)Fe{=}C(OMe)CH_3{}^+PF_6{}^-$ (27)

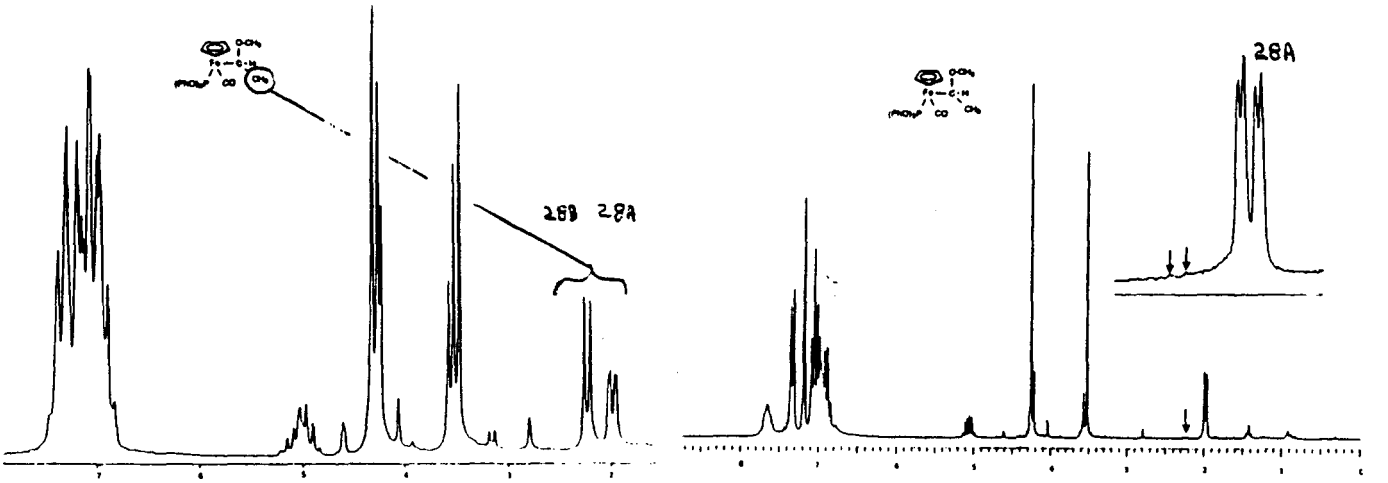
Entry	Hydride Donor[a]	T(°C)	(RS,SR)-28A	(RR,SS)-28B	34
1.	$KHBEt_3$	-78°	0.8	1.0	0.45
2.	$LiHBEt_3$	-98°	0.5	1.0	trace
3.		-78°	0.6	1.0	0.1
4.		-52°	0.9	1.0	0.2
5.		0°	0.9	1.0	0.3
6.	$KHB(sec\text{-}Bu)_3$	-78°	3.2	1.0	1.8
7.		-52°	3.7	1.0	3.5
8.		+25°	1.5	1.0	10.0
9.	$LiHB(sec\text{-}Bu)_3$	-98°	6.3	1.0	1.0
10.		-78°	3.5	1.0	0.2
11.		-52°	3.0	1.0	10
12.		+25°	trace	trace	1
13.	$NaHB(sec\text{-}Bu)_3$	-78°	3.5	1.0	24
14.	$(Cu(PPh_3)H)_6$	-78°	1.0	trace	0.2
15.	$LiHB(CHMeCHMe_2)_3$	-78°	0	0	1

a. One equivalent of hydride donor added to THF solution of 27 at indicated temperature. Relative yields of $Cp(P(OPh)_3)(CO)Fe\text{-}CH(OMe)CH_3$ (28A and 28B) and $Cp(P(OPh)_3)(CO)Fe\text{-}C(OMe){=}CH_2$ (34) are determined by ^1H NMR spectroscopy.

Three results emerge from this study. First, $(PPh_3CuH)_6$ reduces **24** (**27**) to (RS,SR)-**25A** (**28A**) with a diastereoselectivity in excess of 100:1 (RR, SS) **25B** (**28B**) (entry 14). With careful temperature control, samples of **25B** or **28B** are isolated that

contain essentially no **25A** or **28A** and less than 10% of the contaminating α-methoxyvinyl complexes. Figure 7 illustrates two ^1H NMR spectra of such reaction mixtures. The left spectrum corresponds to a $LiHBEt_3$ run (-60°C), and the right scans correspond to $(PPh_3CuH)_6$ experiments.

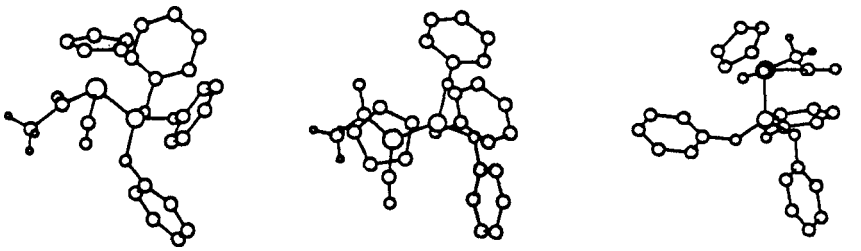
Figure. 7 ^1H NMR Spectra of 28A/28B



The second result concerns the tremendous range in reactivity exhibited by trialkylborohydride reagents. For example, $LiHBEt_3$ favors **28B** over **28A** by 2:1 (-98°C), whereas $LiH(sec\text{-}Bu)_3$ reverses this selectivity, **28A** to **28B** by 6:1 (-98°C). The even more hindered $LiHB(CHMeCHMe_2)_3$ only deprotonates **27** to give the methoxyvinyl compound **34** (entry 15). The final result, is that temperature control is critical: Selectivity for either **28B** or **28A** drops and the proportion of **34** increases with the temperature. As a dramatic example, entry 12 indicates that $LiHB(sec\text{-}Bu)_3$ reduction of **27** at room temperature affords only the deprotonation product **34**.

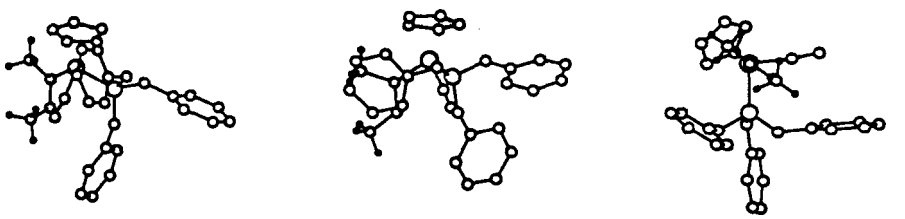
Interpretation of the observations in Table 1 (as well as for the analogous data for reducing **24**) requires an appreciation of the starting methoxycarbene structures **24** and **27**. When planning this work, we assumed that the ligated phosphite would not sterically shield one face of an acetyl (**23, 26**) or a carbene ligand (**24, 27**). Reger had published X-ray crystallographic data for two triphenylphosphite iron alkenylacyl complexes $Cp(P(Ph)_3)(CO)Fe\text{-}C(O)CR{=}CR_2R_3$ that showed the three phenyl rings splayed away from the acyl group.[31] Since one could argue that the vinyl substituent (methyl or methoxymethyl groups) cis to the acyl carbonyl in his structures pushes one phosphite phenyl ring away, we did an X-ray structure determination of the parent acetyl complex **26**. Figure 8 represents this data and indicates that the phosphite phenyl groups clearly are not in the vicinity of the acyl group. Other salient data are an iron-carbon (acetyl) bond length of 1.92Å and a CH_3-C(acetyl)-Fe-CO dihedral angle of 23.4°.

Figure 8 X-Ray Structure Determination of $Cp(P(Ph)_3(CO)Fe\text{-}COCH_3$ (26)



We also carried out an X-ray crystallographic structure determination of a starting methoxycarbene complex, as it is the conformation of this carbene ligand during the hydride transfer step **b** (eqs. 3 and 5) that is involved in creating the new chiral center. Figure 9 illustrates this data for the triphenylphosphite-containing compound **27** (PF_6^-), apparently the first example of a structure determination for this important

Figure 9 X-Ray Structure Determination $Cp(POPh)_3(CO)Fe=C(CH_3)OMe^+PF_6^-$ (27)



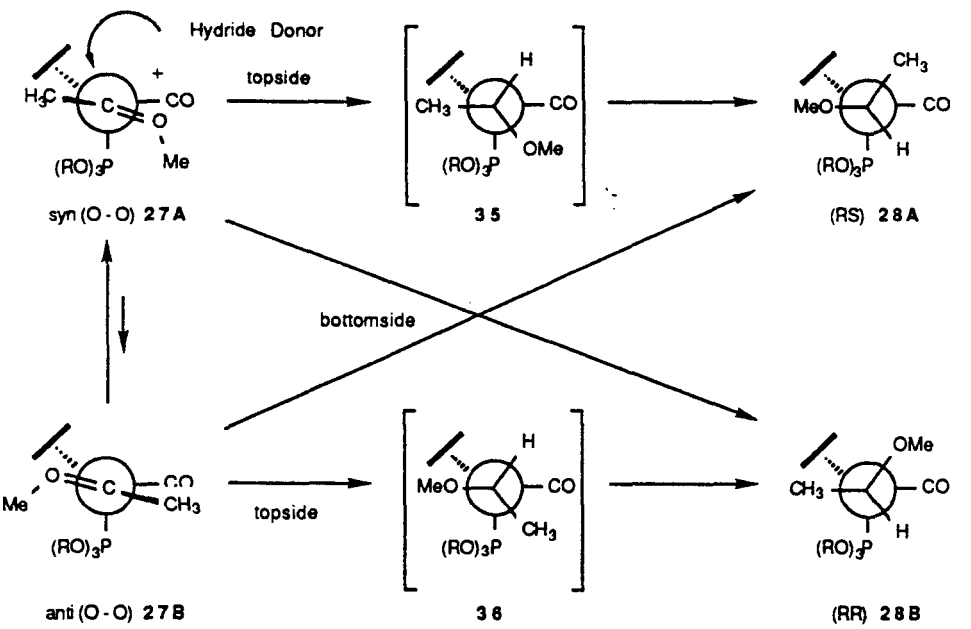
class of CpFe(alkoxycarbene) compounds.[32] Two useful observations obtain: (1) the $CH_3\text{-}C_\alpha\text{-}OCH_3$ carbene plane is oriented syn (O-O) and aligned orthogonal to the Cp ligand (MeO-C_α-Fe-CO dihedral angle = 44.5°); (2) the phosphite group is disposed such that a phenyl ring (actually the ipso and two ortho-carbon centers) is within 3.3Å of the carbene center and evidently shields its lower face. The Fe-C_α bond length is 1.87Å.

The structure of $Cp(P(OPh)_3)(CO)Fe=C(OMe)CH_3^{(+)}$ (**27**) is noteworthy for the vertical orientation of the carbene $H_3C\text{-}C_\alpha\text{-}OMe$ plane. This geometry is anticipated for analogous $CpFe(CO)_2$ (Fp) complexes based upon theoretical studies,[33] results of an X-ray structure determination of $Fp=CH(SPh)^{(+)}$[34], and solution NMR spectral studies of $Cp(dppe)Fe=CH_2^{(+)}$[35] and $Cp^*(CO)_2Fe=CH(OMe)^{(+)}$[36]. Both heteroatom-substituted carbene compounds also maintain anticlinal conformations. (A structure determination of $Fp=C(SMe)CH_3^+$ by Helquist,[34] however, established a horizontal orientation for the carbene ligand plane.) In contrast, phosphine (and presumably phosphite[23b]) iron carbene complexes $Cp(L)(CO)Fe=CR^1R^{2(+)}$ are expected to have the carbene plane aligned with the Fe-CO axis,[33] in accord with observations advanced by Gladysz[37] for isolobal rhenium complexes $Cp(PPh_3)(NO)Re=CR^1R^{2(+)}$.

The solution structure of **27**, however, is not obvious. Its ^1H and ^{31}P NMR spectra in d^8-THF exhibited neither significant line broadening nor variation in chemical

shift for individual absorptions upon cooling to -90°C. NOESY experiments (still in progress) are consistent with syn(O-O) **27A** (Figure 10) as the only detectable carbene rotamer (although the presence of very low concentrations of anti (O-O) **27B** obviously can't be ruled out.[38]) Therefore, either only **27A** is present in solution or **27A** rapidly equilibrates with **27B** (rotational barrier < 8 kcal/mol) and exhibits a large equilibrium quotient, [**27A**]/[**27B**] > 15.

Figure 10



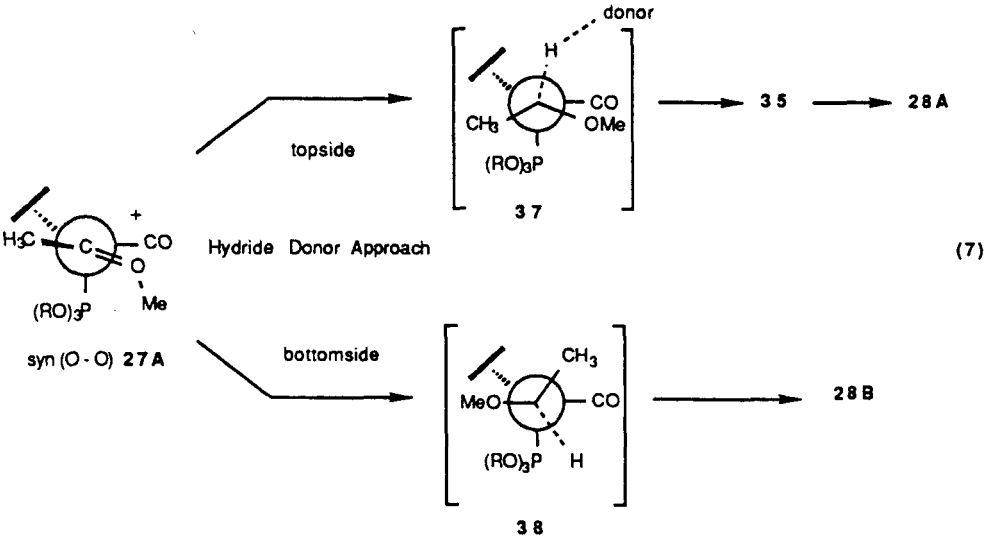
Low rotational barriers of the same magnitude have been measured for ethylidene compounds $Cp(L)(CO)Fe{=}CHCH_3^+$ (L=PMe_3, PPh_3[30]) and for $Cp(dppe)Fe{=}CH_2^{(+)}$[35]. The prevalent observation is that *presumed* iron-carbene rotation remains rapid (i.e., it is not detected) for $Fp{=}CHPh^{(+)}$[39], $Fp{=}CHSMe^{(+)}$[34], and $Fp^*{=}CHOMe^{(+)}$[36] at or below -90°C. Related rhenium complexes $Cp(PPh_3)(NO)Re{=}C(OMe)R^+$ (R=H, CH_3) studied by Gladysz[37] evidently exist in solution at room temperature as mixtures of anticlinal and synclinal isomers, which align the carbene ligand parallel to the Re-NO axis and have the anti (O-O) isomer greatly predominating. The consensus is that rotational barriers for $Cp(L)(CO)Fe{=}CHR^+$ complexes are very low (ca. 8 kcal/mol), in contrast to much higher observed barriers for analogous $Cp(PPh_3)(NO)Re(carbene)^+$ compounds (15-21 kcal/mol)

We find it suprising that **27** with both methyl and methoxy groups at the carbene center could rotate (**27A** ⇄ **27B**) with such a low barrier. Both molecular mechanics calculations and further NMR spectral studies are in progress to examine rotational barriers for the acetyl complexes **23** and **26**, and for their methoxycarbene derivatives **24** and **27**.

The reaction scheme in Figure 10 accounts for the diastereoselectivity observed in reducing **27**.[40] Syn (O-O) **27A** predominately adds hydride topside (the unhindered si-face) from $LiHB(sec\text{-}Bu)_3$ and $(PPh_3CuH)_6$ to give (RS,SR)-**28A**. Diastereomer **28B** that does form (especially when using $LiHBEt_3$) originates from bottomside hydride addition. Intuitively one expects **28B** to derive from topside addition to anticlinal **27B**, especially since the rotomers **35** and **36** that initially form (from **27A** and **27B**, respectively) should have similar energies.[30b] (Rotamer **35** should be slightly favored because a methyl group is somewhat bulkier than a methoxy substituent.[41]) The observation that the copper hydride cluster produces almost no **28B** suggests that either **27B** is not present or it is unreactive: We see no reason why **27B** would be less susceptible to topside nucleophilic attack than **27A**.

A similar selectivity occurs during the reactions or iron enolates $Cp(PPh_3)(CO)Fe\text{-}C(O)=CHR^-$ with electrophiles.[21] Although their synclinal (O-O) and anticlinal (O-O) isomers (analogous to **27A** and **27B**, respectively) equilibrate,[21c,d,h] only the latter reacts. The stereoselectivity of these alkylation reactions moreover increases with the steric bulk of the attacking electrophile.

The slight preference of $LiHBEt_3$, a smaller hydride donor, towards forming **28B** during the reduction of **27** can be explained from an analysis of the transition states for the initially generated product conformations (eq.7). Topside hydride addition to synclinal (O-O) **27A** goes through a transition state **37** that forces the methoxy-group into the sterically most demanding site between CO and phosphite. This highly crowded transition state then gives the unstable rotamer **35** which undergoes a hindered rotation to the observed **28A**.



Bottomside attack of the hydride donor engenders a less crowded transition state **38** which forms the C_α-H bond as C_α rehybridizes from sp^2 to sp^3; **28B** directly forms. On balance, a bulkier hydride will prefer topside attack to **27A**, a favorable steric

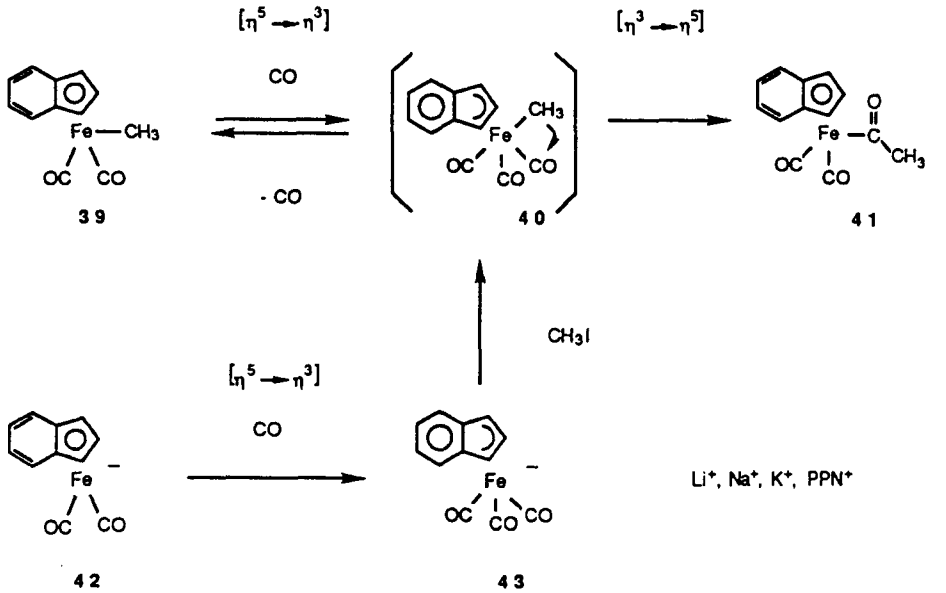
approach nevertheless generating a crowded transition state **37**, whereas a smaller hydride donor will competitively go through a hindered steric approach (due to the phosphite) but a less crowded transition state **38**.

C. Indenyl Ligands and Carbonylation Reactions: Bimetallic Carbonylation Procedure

The objective of these studies is to use the η^5-indenyl ligand (In) in place of the Cp group to promote carbonylation of alkyl complexes, particularly InFe(CO)(L)(α-alkoxyalkyl) compounds. Switching to InFe(CO)(L) compounds retains the synthetic versatility and presumably the stereochemical control associated with the more established Fp and related CpFe systems, but the presence of the indenyl ligand enhances reactivity at the iron center.

We believe that enhanced carbonylation reactivity of indenyl complexes originates from reversible η^5-η^3 indenyl ring slippage that successively fosters CO association at the metal and then alkyl-CO migration (e.g., **39-40-41** in Figure 11). (In contrast, (η^3-*Cp*)Fe intermediates analogous to **40** are disfavored energetically,[42,43]

Figure 11



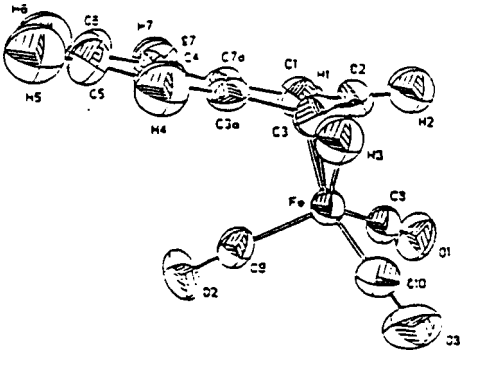
and carbonylating (η^5-Cp) iron alkyl complexes typically requires the Calderazzo mechanism[3] in which alkyl-CO migratory insertion proceeds prior to or concomitant with CO association). This η^5-η^3 indenyl ring shift[44] and its attendant facile ligand association at the metal has been termed the "indenyl effect" by Basolo.[45] The indenyl effect has been extensively studied as it applies to ligand displacement reactions (e.g., phosphine for coordinated CO) that occur under unusually mild conditions for indenyl complexes.[44] The only study previous to our work that links the indenyl effect with

alkyl-CO migration is that by Mawby[43b] for the reaction of phosphine with $In(CO)_3MoCH_3$, which gives $In(PPh_3)(CO)_2MoCOCH_3$ under mild conditions.

We established in earlier studies that (η^5-In)iron methyl complexes $In(L)(CO)FeCH_3$ (L=CO (**39**), PPh_3) carbonylate to give their acetyl compounds (**41**, for L = CO) under incredibly mild conditions of 1 atm. CO in dichloromethane.[46] This enhanced reactivity does not extend to the methoxymethyl compounds, however. $In(PPh_3)(CO)FeCH_2OMe$ when treated with 80 atm. of CO replaces ligated phosphine by CO. (The anticipated product, $In(PPh_3)(CO)FeCOCH_2OCH_3$, had been synthesized independently and is stable.) We also had attempted to promote carbonylation of $In(L)(CO)FeCH_2OMe$ and $Cp(L)(CO)FeCH_2OMe$ by adding Lewis acids,[47] by hydrogen bonding,[46] and by incorporating oxidative electron-transfer catalysis,[48] all to no avail.

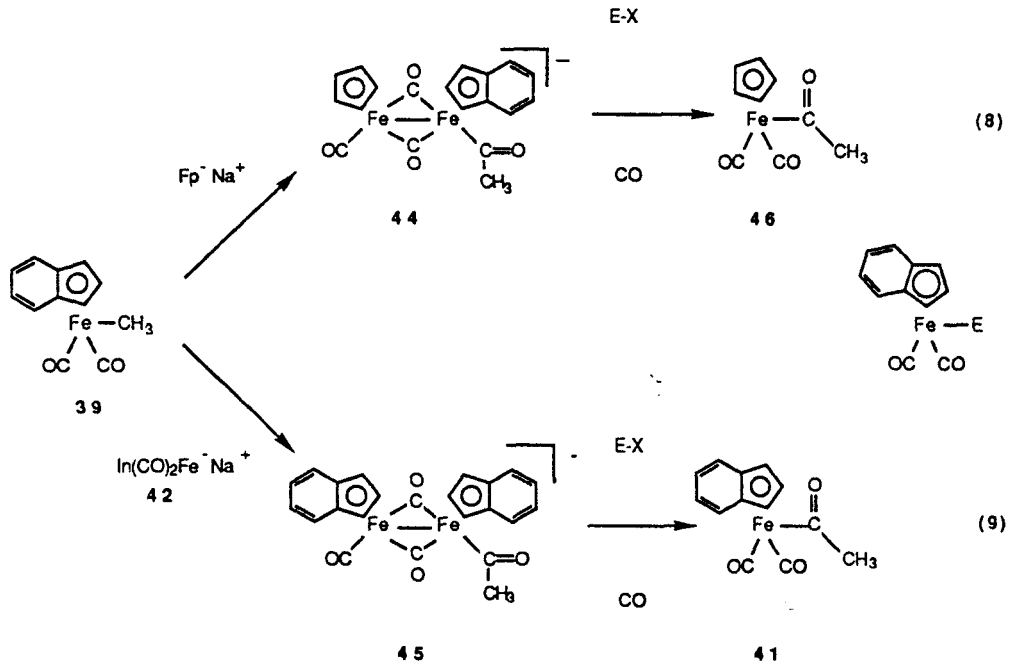
During the present grant period we finished our preliminary studies that linked CO association at iron, reversible η^5/η^3 indenyl ligand shifts, and methyl-CO migration. We now summarize evidence for associative reactions of (η^5-In)Fe complexes. Nucleophilic $InFe(CO)_2^-Na^+$ (**42**) immediately and irreversibly incorporates CO (at 1 atm.) and generates (η^3-In)$Fe(CO)_3^-Na^+$ (**43**) (Figure 11), which was characterized fully as its PPN^+ salt.[49] The noteworthy conclusion from an X-ray crystallographic structure determination (Figure 12) is the 21° dihedral or fold angle between its η^3-allyl and benzenoid fragments. Structure determinations for two other η^3-indenyl complexes have been reported.[50]

Figure 12 **X-Ray Structure Determination of (η^3-In)$Fe(CO)_3^-$ PPN^+** (**43**)



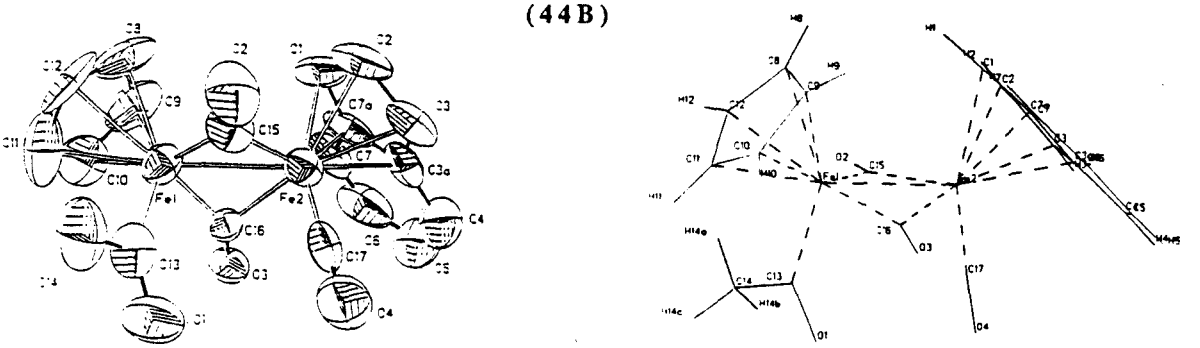
Treatment of **43** PPN^+ with methyl iodide and 1 atm. of CO gives a 1:3 mixture of iron acetyl **41** and methyl **39** complexes. The (η^3-In) iron methyl intermediate **40** again presumably couples its η^3-η^5 indenyl tautomerization with competing methyl-CO migration (giving **41**) and CO dissociation (giving **39**) steps. Yields of **41** increase at the expense of **39** with increasing CO pressure: 13% **41** (1 atm. N_2), 25% (1 atm. CO), and 38% (85psi CO).

Reversible η^5/η^3 indenyl ring slippage is the driving force in a newly developed two-step, metalate-promoted carbonylation procedure involving $In(CO)_2Fe$-alkyl complexes (eqs. 8, 9).[51] Treating $In(CO)_2Fe\text{-}CH_3$ (**39**) in THF first with 1 mol.



equiv. of metalate Fp^-Na^+ or $InFe(CO)_2{}^-Na^+$ (**42**) and then with an electrophile E-X in the presence of 1 atm. of CO produces an acetyl complex **46** or **41** in 75-95% yields. With Fp^- as the metalate, the acetyl ligand regioselectively ends up on the Fp moiety as **46**. Alkylating agents EX that have been used include MeI, EtI, and Ph_3SnCl.

Figure 13 X-Ray Structure Determination $Cp(COCH_3)Fe(\mu\text{-}CO)_2Fe(CO)In^-PPN^+$ (44B)

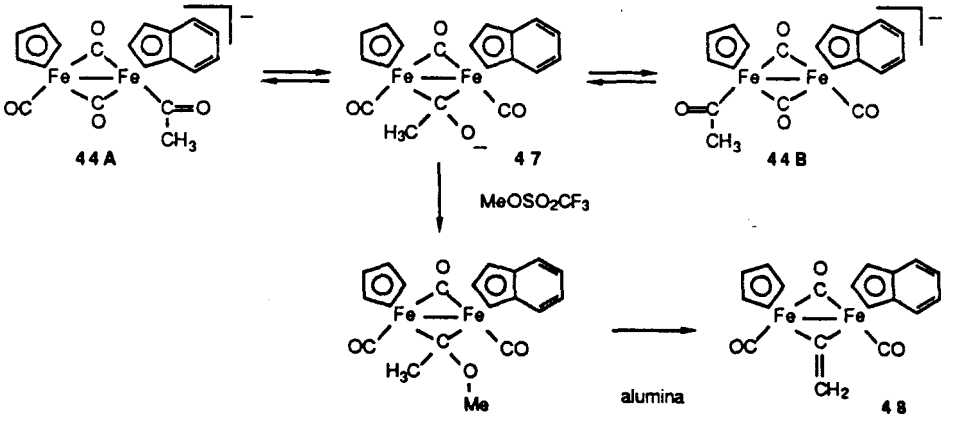


Bimetallic acetyl compounds **44** and **45**, key intermediates in this carbonylation procedure, are isolated as their PPN^+ salts in 78% and 52% yields, respectively. An X-ray structure determination of the mixed CpIn dimer **44** (Figure 13) establishes that it crystallizes with the terminal acetyl ligand on the CpFe end (**44B**, Figure 14), and that the overall structure has a cis array of the Cp and planar η^5-In groups. In solution, **44** exists as a 1:1 mixture of regioisomers **44A** and **44B** (^1H and ^{13}C NMR spectra are fully

assigned). The acetyl ligand shuttle between these iron centers was studied by ^1H NMR magnetization (spin saturation) transfer: $k_1=0.33$ sec^{-1} (22°C).

Interconverting **44A** and **44B** requires intermediacy of a μ-oxycarbene complex **47**, which we detect by IR and NMR spectroscopy. Stone[52] postulated a similar intermediate in the reaction between CH_3Li and the μ-CO on $Cp_2Fe_2(CO)_4$. In the presence of Na^+ and PPN^+ counterions, **47** is barely detected at 3-7% of the **44A / 44B** mixture, whereas the Li^+ counterion sequesters a higher concentration of **47** (35%). Note that treating **44A / 44B / 47** mixtures as their Li^+, Na^+, or PPN^+ salts with MeI / CO regio-selectively affords the same yield of $FpCOCH_3$ (**46**) (eq. 8). Studies concerned with further characterization of **47Li$^+$** are still in progress.

Figure 14



We intercept the μ-oxycarbene intermediate **47** by treating **44 PPN$^+$** with methyl iodide in dichloromethane or with methyl triflate in THF, with or without CO present. This gives the μ-vinylidene compound **48** in over 50% yield after chromatography as 15-18 to 1 mixtures of *cis* and *trans* isomers. We are separately publishing optimal procedures for synthesizing bimetallic μ-alkenylidene compounds **48** and $In_3(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}C{=}CHR)$ (R-H, CH_3, OCH_3) from the requisite starting alkyl complexes $In(CO)_2Fe\text{-}CH_2R$ and Fp^-Na^+ or **42**.[53]

Several examples of nucleophilic metal carbonylates promoting alkyl-CO migration are documented.[54] The resulting bimetallic acyl compounds typically alkylate at the acyl-O to give bimetallic complexes bearing terminal alkoxycarbene ligands, however. We believe that the presence of at least one indenyl ligand -- and its accessible η^5/η^3 ring slippage -- on our bimetallic acetyl compounds **44** and **45** is critical both for their formation and for their cleavage with EX / CO. (Fp^-Na^+ does not react with $FpCH_3$ other than to exchange the methyl group between the two iron centers.[55]) Overall, the two-step carbonylation procedure involving (i) metalate-promoted alkyl migration, (ii) a bimetallic intermediate that cleaves and gives the

mononuclear acyl product, and (iii) indenyl ligand ring slippage represents a conceptually new carbonylation procedure.

In Figure 15 we outline a proposed mechanism for the two-step carbonylation of $In(CO)_2Fe\text{-}CH_3$, (i.e., treatment with Fp^-Na^+ then with CH_3I / CO) that accounts for the observed regioselectivity. Carbonylation of **44B** and **49** at the indenyl Fe produces the $(\eta^3\text{-In})Fe\text{-}CO$ adduct **50**, analogous to $(\eta^3\text{-In})Fe(CO)_3^-$ (**43**), that adds the electrophile E-X at iron and gives **51**. (The sequence **49-50-51**, in fact, closely resembles the **42-43-40** transformation presented in Figure 11.) A reverse $\eta^3\text{-}\eta^5$ indenyl ring shift on **51** degrades it to the observed mononuclear products. More work of course is needed to further establish this hypothesized mechanism, especially the precise timing of the carbonylation, the indenyl ring slippage, and the alkylation (with EX) steps.

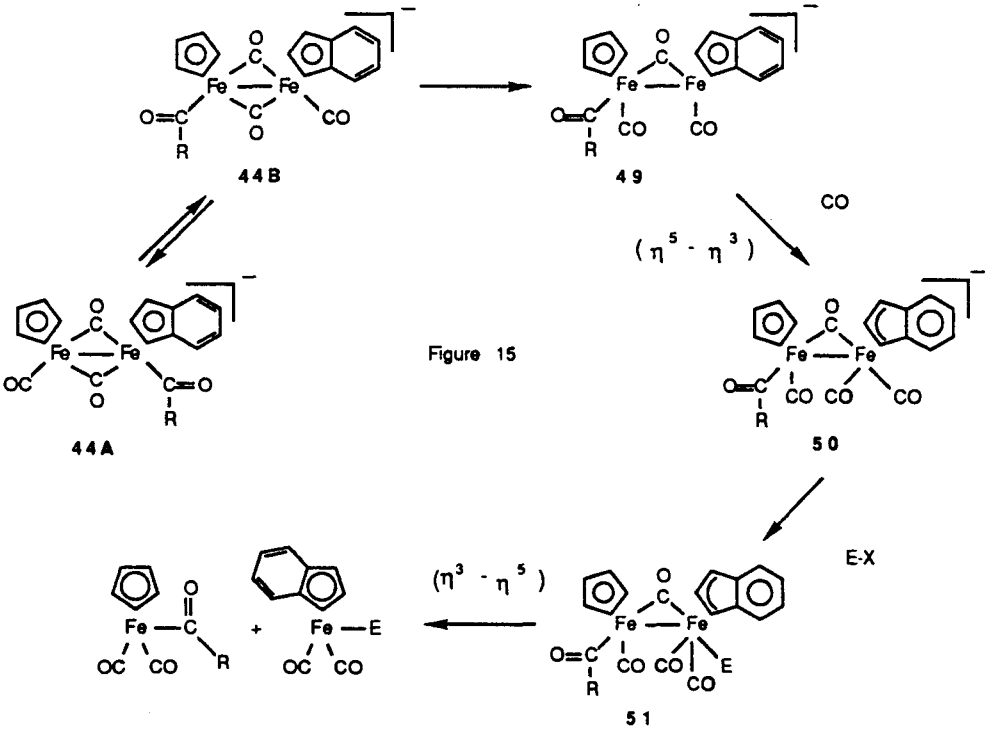
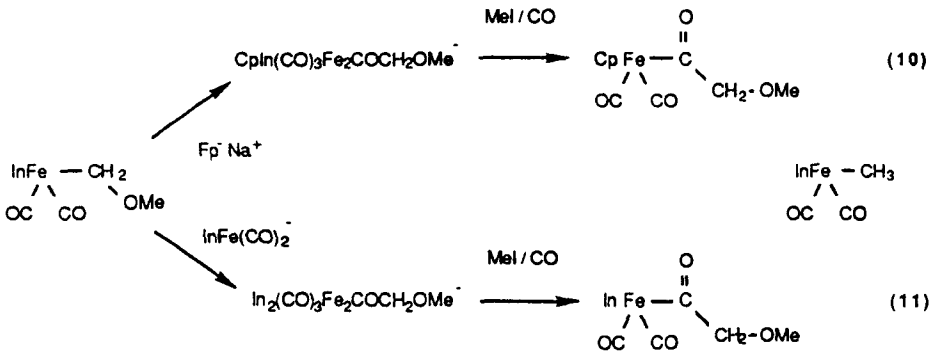
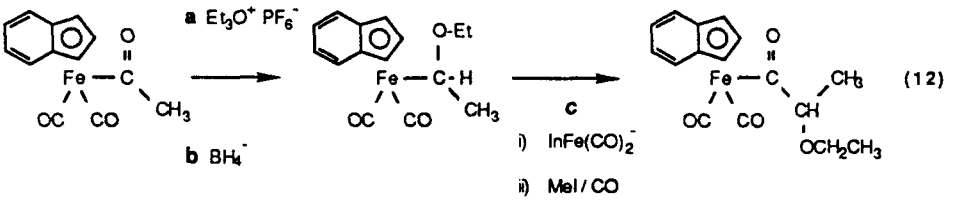


Figure 15

A gratifying outcome of our studies on this two-step carbonylation procedure is the successful carbonylation of iron α-alkoxyalkyl complexes with *1 atm. of carbon monoxide*. Treatment of the methoxymethyl complex $In(CO)_2Fe\text{-}CH_2OCH_3$ either with Fp^-Na^+ or with $InFe(CO)_2^-$ (**42**) followed by methyl iodide and CO affords methoxyacetyl compounds (eqs. 10, 11) in 43%[51] and 60%[56] yields, respectively. By starting with indenyl ligands on both the metalate nucleophile and the starting alkyl complex (eq. 11), we obtain the acyl product retaining an indenyl ligand and formally corresponding to net carbonylation of the starting alkoxymethyl compound.



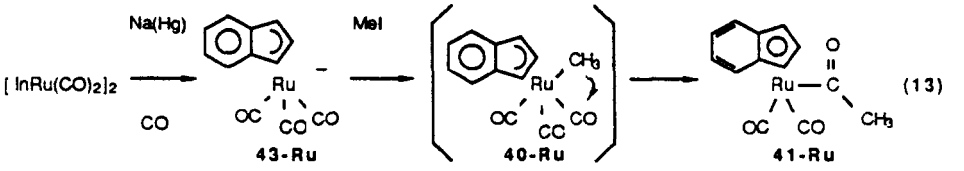
We used the two-step carbonylation procedure in one cycle of (a) activating, (b) reducing, and (c) carbonylating an acetyl ligand (cf. eq. 3). Treating the InFe acetyl complex **39** successively with (a) $Et_3O^+PF_6^-$, (b) $NaBH_4$ / NaOMe in methanol, and (c) $InFe(CO)_2^-Na^+$ (**42**) then CO / MeI affords the α-ethoxypropionyl iron complex (eq. 12) in 47% overall yield.[56] This reaction sequence is carried out as a one-pot operation



with a solvent change (CH_2Cl_2 to THF) for step **c** and isolation of the final product by column chromatography. The intermediate ethoxycarbene and α-ethoxyethyl compounds also have been individually isolated (87% and 92% yields, respectively) and fully characterized. We attribute the moderate yields of the α-alkoxyacyl complexes (59% for $In(CO)_2Fe\text{-}COCH(OEt)CH_3$) to the inherent resistance of these α-oxygenated alkyl ligands to migrate to a carbonyl ligand. We are nevertheless confident that these procedures can be optimized, that the yields can be improved, and that the procedure can be used for further lengthening the acyl ligand chain by incorporating CO.

D. Indenyl Ruthenium Chemistry

We have since found that indenyl ruthenium alkyl complexes are especially prone to carbonylate. Developing this chemistry was hampered initially by the inaccessibility of $InRu(CO)_2^-$ (**42-Ru**), since Na(K) and Na(Hg) decompose $In_2Ru(CO)_4$ into insoluble residues while producing low yields of **42-Ru**. (Similar observations apply to a lesser degree to reductive cleavage of $Cp_2Ru_2(CO)_4$, although we recently found that using sodium metal in conjunction with an ultrasonic bath alleviates this problem.[57]) Sodium amalgam cleavage of $In_2Ru_2(CO)_4$ in the presence of carbon monoxide (1 atm., THF), however, gives the stable $(\eta^3\text{-In})Ru(CO)_3^-$ (**43-Ru**)[49]. In contrast to the behavior of its iron congener (**43** in Figure 11) methylation of **43-Ru**

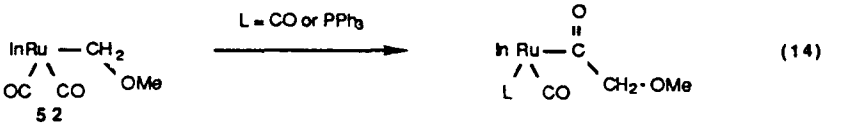


selectively affords the acetyl complex **41-Ru** (eq. 13) with less than 2% $In(CO)_2Ru\text{-}CH_3$ detected.

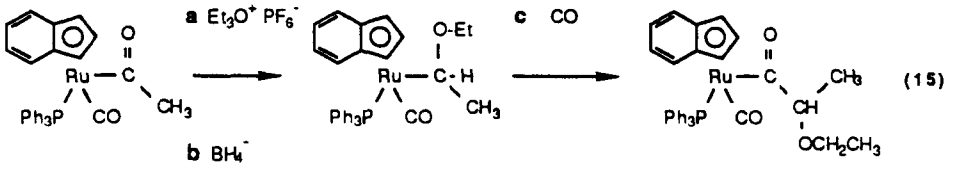
Reductive cleavage of $In_2Ru(CO)_4$ by $KHBEt_3$ in THF emerges as a dependable albeit inefficient procedure for generating solutions of $InRu(CO)_2^-K^+$ (**42-Ru**). We have been unsuccessful at isolating it as a pure solid. Treating solutions of **42-Ru** with the appropriate alkyl halides affords $In(CO)_2RuCH_3$, $In(CO)_2RuCO\ CH_3$ (**41-Ru**), and $In(CO)_2RuCH_2OCH_3$ in moderate (40-60%) yields after a workup involving column chronatography.

The truly astounding development is that direct carbonylation of the alkyl complexes $In(CO)_2RuR$ is possible under extremely mild conditions.[58] $In(CO)_2Ru\text{-}CH_3$, for example, quantitative converts to its acetyl derivative **41-Ru** when exposed to 1 atm. of CO in dichloromethane (8 h.), which dramatically contrasts the inertness of $Cp(CO)_2RuCH_3$ in nitromethane to 80 atm. of CO. Of all the methyl complexes, congeners of $Fp\text{-}CH_3$, that we have studied the carbonylation chemistry of, $In(CO)_2RuCH_3$ is by far the most reactive and $Cp(CO)_2RuCH_3$ the least. More importantly, this InRu systems lends itself to carbonylating methoxymethyl **52** and presumably other α-alkoxyalkyl complexes.

Treatment of $In(CO)_2RuCH_2OCH_3$ (**52**) with 85psi CO in nitromethane affords its methoxyacetyl derivative (eq. 14) in 66% yield after 12h. THF also can be used as the solvent, but higher pressures (800 psig, 8 h) for similar conversion. This enhanced



reactivity also extends to phosphine-promoted alkyl migration: at room temperature, PPh_3 in benzene transforms **52** quantitatively (6 h) into the phosphine-substituted methoxyacetyl compound. In contrast, the analogous $Cp(CO)_2RuCH_2OMe$ remains unchanged after 7 days in refluxing acetonitrile with PPh_3. Within the remaining time of this grant period, we will finish the three-step sequence outlined in eq 15 for converting $In(PPh_3)(CO)Ru\text{-}COCH_3$ into its α-ethoxypropionyl homolog illustrated. The phospine-substituted $In(PPh_3)(CO)Ru$ system should be even more susceptible to incorporating CO into its alkyl complexes, based upon our experience with analogous InFe systems.

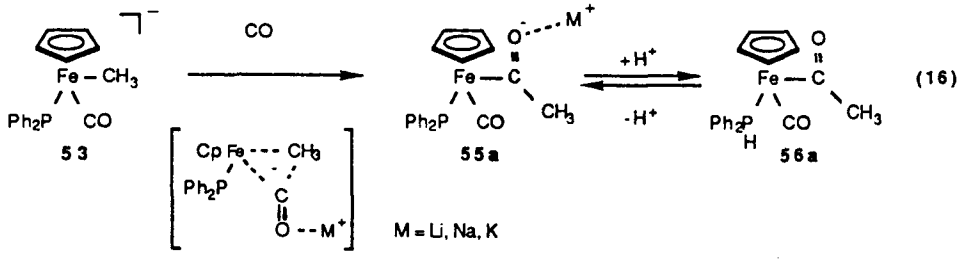


The enhanced susceptibility of InRu alkyl complexes over their iron homologs to undergo carbonylation reactions contravenes the prevailing belief that this reactivity should diminish with descent in the periodic group of the central metal for a homologous series of alkyl complexes.[3] The carbonylation of iron and ruthenium complexes $(PR_3)_2(CO)_2M(X)R$ may represent a possible exception to this trend, however, since both metals apparently sustain equally facile carbonylation reactions.[59]

Our working hypothesis for the increased carbonylation reactivity of InRu alkyl complexes over their iron counterparts is illustrated in Figure 11. Both iron and ruthenium methyl complexes **39** and **39-Ru** evidently associate CO to give putative η^3-indenyl intermediates $(\eta^3\text{-In})(CO)_3M\text{-}CH_3$ (**40**, M = Fe; **40-Ru**); the reversible η^3 to η^5 indenyl ring slippage then couples either with CO dissociation or with methyl-CO migratory insertion. CO dissociation regenerates the methyl complexes **39** and **39-Ru**, and methyl-CO insertion provides the acetyl compounds **41** and **41-Ru**. For iron **40**, CO dissociation kinetically predominates, whereas for the less labile **40-Ru**, methyl-CO migration prevails. If this hypothesis is correct (labeling and kinetic studies are contemplated), then the thermodynamically more stable η^3-indenyl intermediate **40-Ru** (with respect to CO dissociation) also may be more reactive because of the η^3 to h^5 indenyl shift perhaps driving the alkyl-CO migration step.

E. Phosphide Iron Acyl Chemistry

Results of our study on the synthesis and characterization of anionic (phosphido)iron methyl and acetyl complexes[60] are complete.[61] Our premise, as illustrated for the CpFe systems in eq. 16, is that the anionic methyl complex **53a** could carbonylate to give its acetyl derivative **55a** under even milder conditions than those



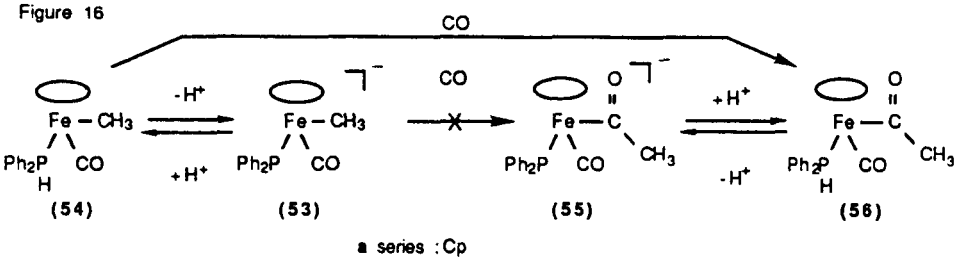
observed for its neutral analog $Cp(PPh_3)(CO)Fe\text{-}CH_3$. Lewis acid counterions (e.g., Li^+) should efficiently promote the alkyl-CO migration by forming ion pairs with the

developing (anionic) acetyl ligand.[62] Our goal was to extend this approach to carbonylating analogous methoxymethyl compounds.

Another motivation for this study centers on the interconvertibility of the anionic and neutral acetyl complexes **55a** and **56a**[63], and the possibility that each could engender differant stereochemistry (diastereoselectivity) during reduction of the acetyl ligand (steps **a / b** in eq. 3). Davies had demonstrated that reduction of $Cp(PPh_3)(CO)FeCOCH_3$ (actually its methoxycarbene derivative) is highly diastereoselective,[40] and the same should apply to **56a**. [We assume that the often noted[21c,d,h] electronic attraction between the acyl/carbene α-carbon and one phenyl ring that situates this phosphine substituent so as to shield one face of the acyl ligand (c.f. **30**) applies to **56a**.] The stereoelectronic interactions of the phosphide ligand on **55a** surely differ from those of the phosphine on **56a**. Therefore, reducing **55a** (or a derivative retaining the integrity of the phosphide ligand (Section IC of the proposal) could afford a different stereochemical outcome. The possibility then would exist that interconverting the phosphide-phosphine ligand as noted could act as a molecular "switch" for controlling the stereochemistry of the acyl reduction step.

The anionic (phosphido)iron methyl and acetyl complexes, separately prepared containing Cp and indenyl ligands, that we worked with are noted in Figure 16. All neutral compounds noted in this report are characterized by IR and ^1H, ^{13}C, and ^{31}P NMR spectroscopy and by acceptable elemental analyses. Deprotonation of the neutral acetyl compounds **56a** and **56b** using n-BuLi, NaH, or KH in THF or acetonitrile (or using MEt_3BH, M = Li, Na, K, in THF) at room termperature quantitatively generates dark red solutions containing the (phosphido)iron acetyl salts **55a** and **55b**. These are

Figure 16

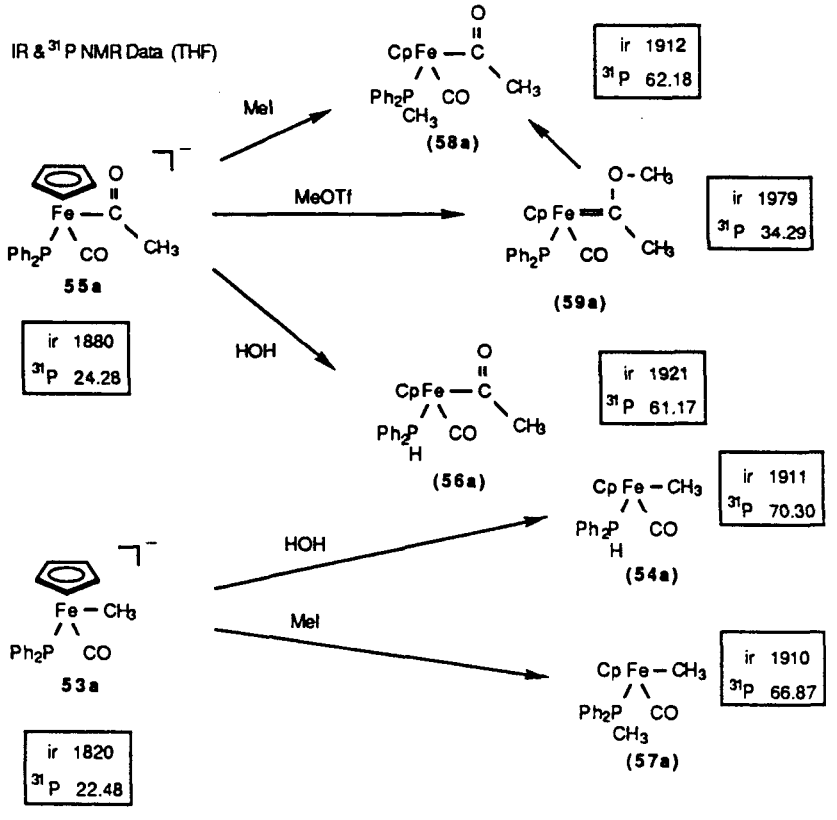


isolated as solids with the K^+ counterion, but their instability precluded elemental analyses. Full spectral data and the results of derivatization reactions (Figure 17) are in full accord with the indicated (phosphido)iron acetyl structures **55**. Because the (phosphido)iron methyl complexes **53a** and **53b** are even less stable, we restricted our preparative work to generating and immediately using the red-purple potassium salts. They are characterized by their IR and ^{31}P NMR spectral data and by their derivatives.

Extremely reactive (phosphido)iron methyl and acetyl complexes **53a,b** and **55a,b** undergo the reactions illustrated in Figure 17 for the CpFe series. Yields of isolated products typically exceed 85%, although they are somewhat lower (70-78%) for their η^5-indenyl Fe analogs. Particularly noteworthy is the methylation of (phosphido)iron acetyl **55a** with methyl triflate, which affords the Fischer carbene **59** [^{13}C NMR(CD_3CN) **59** δ 250.1 (d, J_{PC}=30Hz, carbene C) vs. **58** δ 339.5 (d, J_{PC}=30Hz, acetyl C)].[64] This carbene complex **59** smoothly isomerizes to its tautomer **58** ($t_{1/2}$=6h), a reaction that needs further study.

The most significant finding of this study is that the (phosphido)iron methyl compounds **53a** and **53b** do not carbonylate (85 psig CO in THF, with or without 10% $Cp_2Fe^+PF_6^-$ present) to give their acetyl derivatives. Under comparable conditions, the neutral methyl complexes $Cp(PPh_2Me)(CO)FeCH_3$ (**57**) and $In(PPh_2H)(CO)FeCH_3$ (**54b**), for example, give their acetyl compounds **58** and **56b**.

Figure 17 IR & ^{31}P NMR Data (THF)

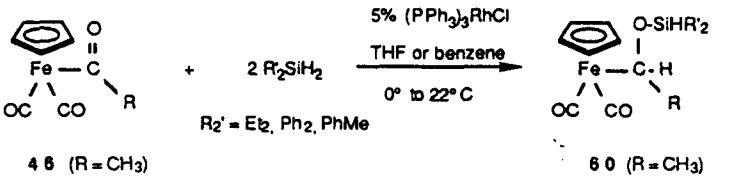


Our inability to carbonylate **53a** and **53b** is surprising. Certainly other anionic metal carbonyls convert to their acyl counterparts when treated with CO, as exemplified in Collman's classic studies[65] with $(CO)_4FeR^-$. One possible explanation is that the Cp (or In) ligand acting as a π-donor ligand conveys electron density to the iron center, in contrast with the ability of the carbonyls to more efficiently delocalize excess charge density. Indeed, results of recent studies are consistent with the rates of alkyl-

CO migration increasing with the electrophilicity of the metal center.[3d] Therefore, combination of a Cp or indenyl ligand, fewer carbonyls, and the charge could render the iron centers on **53a** and **53b** less susceptible to alkyl-CO migration.

F. Hydrosilation of Metal Acyl Complexes

We have established the catalytic hydrosilation of Fp acetyl (**46**) and related acyl complexes under mild conditions.[66] These reactions (eq. 18) typically are run



46 (R = CH_3) **60** (R = CH_3) (18)

in benzene or THF (0° to 22°C) using 5 mol % $(PPh_3)_3RhCl$ and 2 equiv. of dihydrosilane: see Table 2. (The $(PPh_3)_3RhCl$ decarbonylates Fp acetyl (**46**)[67] in the absence of silane, and **46** is inert to excess dihydrosilane in the absence of catalyst.) A number of (α-diethylsiloxyalkyl)Fp complexes have been isolated after rapid chromatography on a short column of deactivated silica gel and have been fully characterized.

Table 2 $(PPh_3)_3RhCl$-Catalyzed Hydrosilation of Organoiron Acyl Complexes.

Acyl Complex[a]	Reaction[b]	Product	Isolated Yield	^1H NMR (C_6D_6) δ Fe-CH
Fp-C(O)CH_3	100% (10m)	Fp-CH(OSiHEt$_2$)CH_3	83%[c]	5.68 (q, J=5.9 Hz)
Fp-C(O)CH_2CH_3	68% (1.0h)	Fp-CH(OSiHEt$_2$)CH_2CH_3	59%[c]	5.43 (dd, J=3.3, 8.4)
Fp-C(O)$CH(CH_3)_2$	50% (14h)[d]	Fp-CH(OSiHEt$_2$)$CH(CH_3)_2$	41%[c]	5.41 (d, J=5.1)
Fp-C(O)$CH_2CH_2CH_3$	55% (1.0h)	Fp-CH(OSiHEt$_2$)$CH_2CH_2CH_3$	45%[c]	5.57 (dd, J=2.4, 9.1)
Fp-C(O)$CH_2CH(CH_3)_2$	30% (4.5h)[d]	Fp-CH(OSiHEt$_2$)$CH_2CH(CH_3)_2$	21%[c]	5.73 (dd, J=2.1, 9.5)
$(C_5Me_5)(CO)_2$Fe-C(O)CH_3	100% (0.25h)	$(C_5Me_5)(CO)_2$Fe-CH(OSiHEt$_2$)CH_3	88%[c]	5.19 (q, J=6.0)
$(C_9H_7)(CO)_2$Fe-C(O)CH_3	100% (0.75h)	$(C_9H_7)(CO)_2$Fe-CH(OSiHEt$_2$)CH_3	91%[c]	5.14 (q, J=5.8)
Fp-C(O)Ph	60% (1.0h)[d]	Fp-CH(OSiHEt$_2$)Ph	51%[c]	6.62 (s)
Fp-C(O)CH_3	60% (0.5h)[f]	Fp-CH(OSiHPh$_2$)CH_3	46%[c]	5.91 (q, J=6.0)
Fp-C(O)CH_3	100% (0.25h)[g]	Fp-CH(OSiHMePh)CH_3	59%[c]	5.50 (q, J=6.0)
Cp[P(OMe)$_3$](CO)Fe-C(O)CH_3	100% (0.50h)	Cp[P(OMe)$_3$](CO)Fe-CH(OSiHEt$_2$)CH_3		5.35 (dq, $J_{PH}=J_{CH}=6.2$)

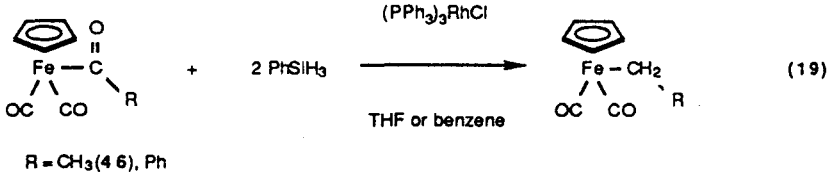
(a) Fp=(η^5-C_5H_5)Fe(CO)$_2$. Cp[P(OMe)$_3$]=(η^5-C_5H_4)Fe(CO)[P(OMe)$_3$]. C$_9$H$_7$=η^5-indenyl. (b) Reaction conditions: 5% (mol) $(PPh_3)_3RhCl$, 2.0 mol equiv Et_2SiH_2 in benzene or THF at 0°C, and 0.67 molar in iron acyl. Extent of reaction is ascertained by IR spectral monitoring. (c) IR, ^1H, and ^{13}C NMR spectral assignments and results of acceptable elemental analysis are available. (d) 10% $(PPh_3)_3RhCl$ is used. (e) Yield is ascertained by ^1H NMR spectroscopy using Cp_2Fe or C_6Me_6 as an internal standard, since the product retains small amounts of unidentified polysilane residues. IR, ^1H, and ^{13}C NMR spectral assignments are assigned. (f) Identical reaction conditions, but Ph_2SiH_2 is used. (g) Identical reaction conditions, but $PhMeSiH_2$ is used; product obtained as 1:1 mixture of diastereomers.

A major problem is that the rhodium catalyst also consumes the dihydrosilanes via competing silane redistribution and dehydrogenative coupling pathways that give disilanes and Si-Si oligomers.[68] The presence of small amounts of these residues (5-10%) inevitably contaminate the hydrosilation products **60** when using Ph_2SiH_2 and $PhMeSiH_2$. Analogous byproducts that form when using Et_2SiH_2 with $(Ph_3P)_3RhCl$ are volatile and are easily removed.

Hydrosilation of these iron acyl complexes affords stable α-siloxyalkyl products **60**. Other examples of α-siloxyalkyl complexes have been postulated as intermediates

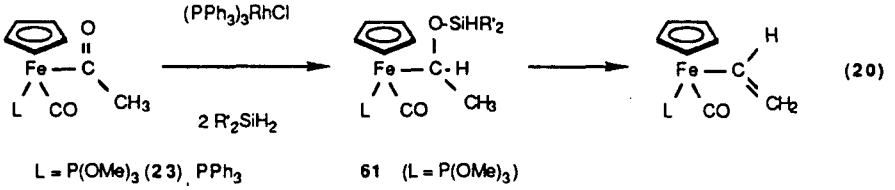
in several reactions. Cobalt[69] and manganese[70] carbonyl trialkysilyl compounds $(CO)\chi M\text{-}SiR'_3$ (χ=4,5) incorporate aldehydes to generate unstable a-siloxyalkyl compounds $(CO)\chi M\text{-}CH(OSiR'_3)R$. (A few α-siloxybenzyl manganese and rhenium compounds have been isolated and characterized by Gladysz.[71]) Similar chemistry occurs during $(PPh_3)_3RhCl$ - catalysed hydrosilation of organic aldehydes and ketones;[72,73] a 1,2-silatropic rearrangement of a silyl-η^2-ketone intermediate $(PPh_3)_2Cl(H)(R'_3Si)Rh(O{=}CR_2)$ gives its transient (α-siloxyalkyl)Rh(III) hydride, $(PPh_3)_2Cl(H)Rh\text{-}CR_2(OSiR'_3)$, before releasing its silylether product $HCR_2OSiR'_3$.[74]

A significant difference between the rhodium-catalyzed hydrosilation of ketones and of the iron acyl compounds (eq. 18) is that the latter α-siloxalkyl products **60** continue reacting with additional silane / rhodium catalyst under the appropriate conditions. Treatment of Fp acetyl (**46**) or Fp benzoyl with phenylsilane cleanly affords the fully reduced ethyl and benzyl complexes (eq. 19) in moderate 45-70%yields.[75]



(19)

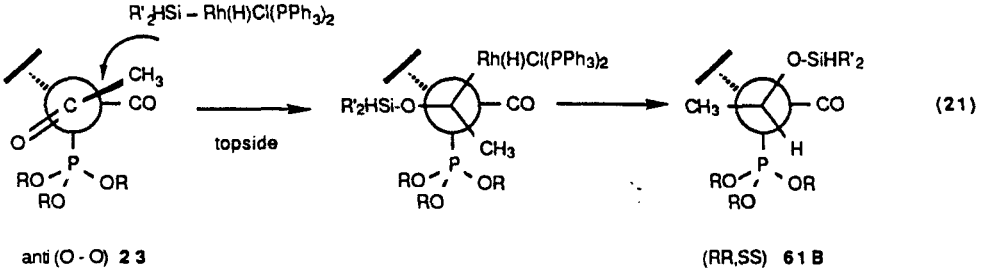
Phosphite (**23**) and phosphine-substituted acetyl compounds upon reacting with dihydrosilane and catalyst convert to their vinyl compounds as the final products (eq. 20). No α-siloxyvinyl complexes $Cp(L)(CO)Fe\text{-}C(OSiHR'_2){=}CH_2$ were detected[76] even though analogous α-alkoxyvinyl compounds are well known.[22,28] ^1H NMR spectral monitoring of the reactions between **23** and Ph_2SiH_2 or Et_2SiH_2 indicate the intermediacy of α-siloxyalkyl complexes. Quenching these reactions and removing the rhodium catalyst (by evaporation, extraction with pentane, and filtration through celite) leaves mixtures of varying ratios of vinyl and α-siloxyalkyl complexes (typically 3:1). Thus far, we have only ^1H and ^{13}C NMR spectral data for **61**, R'=Et, Ph.



(20)

Preliminary results from ^1H NMR spectral monitoring the reactions involving **23** and R'_2SiH_2 indicate that **61** forms as a 4:1 mixture of two diastereomers. The minor diastereomer **61A** was assigned the RS(SR) structure (cf. **25A**) in agreement with the observed doublet of doublets for the β-methyl absorption; **61B** corresponds to the RR(SS) structure that exhibits the corresponding slightly downfield methyl doublet. Rotamer **61B** could predominate through topside interaction of the acetyl ligand in its

anti (O-O) conformation with the hydridorhodium silyl intermediate (eq. 21). Although nearly unhindered rotation about the Fe-C(acetyl) bond of **23** is expected, selective reactions through its anti(O-O) rotamer is precedented with its PPh_3-analog[21c,d,h]. We are presently unsure of the extent of diastereoselectivity in these hydrosilation reactions because the kinetic product(s) (**61A** and/or **61B**) are not evident. Current studies focus on generating potentially less reactive (ruthenium) analogs to **61** and on finding more selective hydrosilation catalysts.

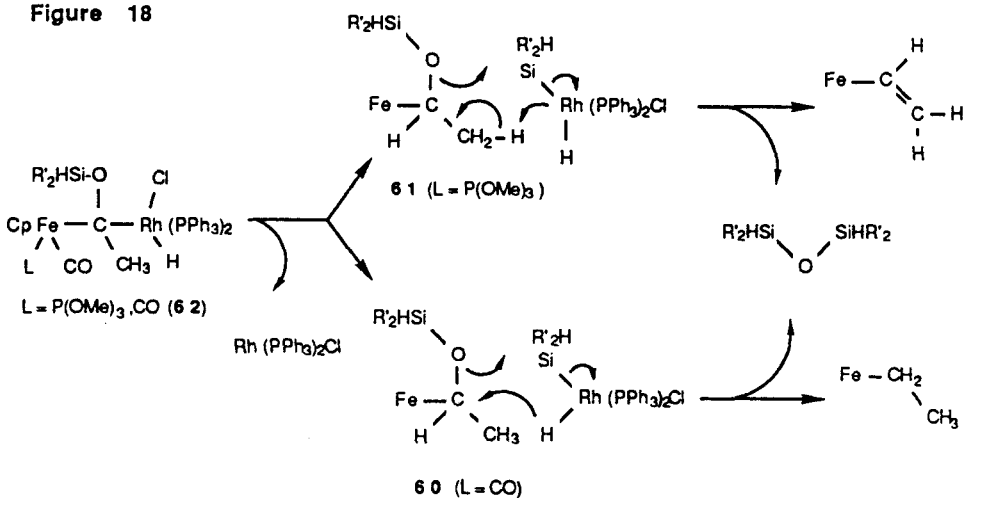


(21)

If the diastereofacial selectivity postulated in eq. 21 is accurate, then hydrosilation of **23** has the opposite diastereoselectivity of the alkylation-reduction (using copper hydride) sequence discussed in Section IIB.

We suggest as a working hypothesis that the mechanism of catalytic hydrosilation of iron acetyl complexes $Cp(L)(CO)Fe\text{-}COCH_3$ resembles the catalytic hydrosilation of ketones.[73] An iron μ-(α-siloxyalkylidene) rhodium hydride intermediate $Cp(L)(CO)Fe\text{-}CR(OSiHR'_2)\text{-}Rh(H)Cl(PPh_3)_2$ (**62**) reductively eliminates the observed iron (α-siloxyalkyl) product **60** (L = CO) or **61** (L = $P(OMe)_3$ and regenerates the presumed active catalyst $(PPh_3)_2RhCl$ (Figure 18). Subsequent reactions of **60** and **61**,

Figure 18



however, entail the hydrido Rh(III) silyl intermediate either deprotonating the α-siloxyethyl ligand on **61** to give the benzyl product or transferring hydride to the α-carbon on **60** and releasing the fully reduced ethyl product. Both sets of reactions would have in common as driving forces the capability of the iron centers to stabilize

a developing positive charge on the α-carbon of **60/61**, commensurate with release of the siloxy group and formation of the thermodynamically favored disiloxane byproduct.[77]

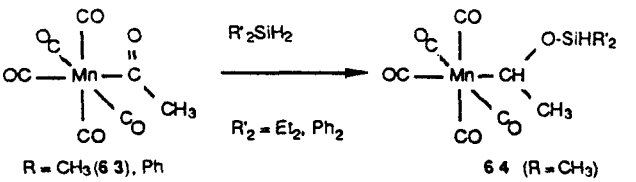
I must emphasize that the arrow-pushing exercises in Figure 18, although consistent with all of our observations, are merely suggestive. Detailed mechanistic studies clearly are required and will be an outgrowth of our immediate studies as they focus on four issues:

1. Establish the synthetic methodology and the scope of rhodium-catalysed acyl ligand hydrosilation. Studies that vary the silane, the Rh(I) catalysts, and the metal acyl complexes are in progress.
2. Survey other potential metal complexes as pre-catalysts for hydrosilation of Cp(L)(CO)FeCOCH3 (L=CO, $P(OMe)_3$, etc.). Immediate objectives are to minimize the competing silane redistribution and oligomerization reactions and to further investigate the subsequent reactions of the α-siloxyalkyl ligand that are noted in Figure 18.
3. Find appropriate organometallic systems that support both hydrosilation of their acyl complexes and subsequent carbonylation of their α-siloxyalkyl derivatives.
4. Probe (and eventually control) the stereochemistry implicit in hydrosilation (reduction) of the acyl ligand. Both diastereofacial selectivity during hydrosilation of a chiral acyl complex and enantiofacial selectivity when using a homochiral Rh(I) catalyst are anticipated.

We are currently finishing separate studies on using labile manganese and cobalt carbonyl complexes as extremely efficient pre-catalysts for hydrosilation of Cp iron acyl compounds. Several manganese complexes -- $(CO)_5MnY$: Y = $SiMe_3$, CH_3, and $COCH_3$ -- promote hydrosilation of $FpCOCH_3$ (**46**) with R_2SiH_2 for example. Particularly noteworthy is that 1 equiv. of dihydrosilane suffices (5% $(CO)_5Mn\text{-}SiMe_3$ in benzene at 25°C) to give $FpCH(OSiHR_2)CH_3$ selectively, although increasing concentrations of dihydrosilane or of manganese pre-catalyst competitively produce fully reduced $FpCH_2CH_3$. The deleterious silane redistribution and reductive coupling side reactions that impeded our Rh-catalysis studies, however, are not evident.

The importance of using dihydrosilane in these manganese-catalyzed reactions is illustrated by the reaction chemistry of $(CO)_5MnCOCH_3$ (**63**). Triethylsilane neither reacts with **63** (benzene, 22°C) nor adds to **46** with any of the manganese (or cobalt, vide infra) complexes noted, as expected. Treatment of **63** with either Ph_2SiH_2 or Et_2SiH_2 (1-3 equiv. in C_6D_6 or C_7D_8, 0° to 25°C) quantitatively affords the α-siloxyethyl

complexes **64**, as identified by ^{1}H and ^{13}C NMR spetroscopy, in a few minutes (eq. 22). These reaction products also efficiently catalyze the hydrosilation of **46**.



(22)

We note that the reactions summarized by eq. 22 represent the first examples in which a silane converts an acyl complex directly to its unambiguously characterized α-siloxyalkyl derivative. Other groups previously established that silanes (R'_3SiH) oxidatively add to labile metal acyl complexes and reductively eliminate aldehyde and presumably a metal silyl compound;[69,70,78] under other conditions, metal silyl compounds slowly add aldehydes and produce largely uncharacterized α-siloxyalkyl compounds. A forthcoming manuscript outlines mechanistic alternatives extant in eq. 22, presents results of our experimental controls related to these alternatives, and documents the use of these manganese complexes $(CO)_5MnY$ as hydrosilation catalysts.[79]

Cobalt carbonyl dimer, $Co_2(CO)_8$, is perhaps the most active hydrosilation pre-catalyst that we have found.[80] One-half of one percent of the dimer and one equiv. of Ph_2SiH_2 or Et_2SiH_2 transform either **46** or its benzoyl analog FpCOPh into their α-siloxyalkyl derivatives in over 70% yields. Reactions are very slow under these conditions (80% conversion in 48h); using 3 equiv. of dihydrosilane under otherwise identical conditions consumes **46a** in a few hours. Although increasing the dimer concentration (up to 13%) also dramatically increases the reaction rates, approximately 1:1 mixtures of **60** and fully reduced $FpCH_2CH_3$ form. The hydrosilation of FpCOPh under such mild conditions is particularly significant since we regard it to be a difficult hydrosilation substrate. Full characterization of diphenylsiloxyalkyl compelxes, e.g., Fp-$CH(OSiHPh_2)CH_3$ also is in progress since these compounds now are available without contaminants that plagued our rhodium studies.

The cobalt dimer apparently reacts rapidly with 2 or more equiv. of R_2SiH_2 to give $(CO)_4CO\text{-}SiHR_2$. It is tempting to ascribe the catalytic activity to $CO_2(CO)_8$ to these silyl complexes, particularly since independently prepared $CO(CO)_4SiEt_3$ also catalyzes these hydrosilation reactions. We must reserve our judgment; $CO_2(CO)_8$ when treated with 2 equiv. of R'_2SiH_2 forms at least two uncharacterized cobalt silyl species. Further mechanistic studies clearly are required.

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.

Recent Publications (DOE Supported Work) 9/1/86 - 8/31/89

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1. "Transition Organometallic-Mediated Synthesis of C_3 Malonic Ester from Carbon Monoxide", T. W. Bodnar, E. J. Crawford, and A. R. Cutler, *Organometallics* **1986**, ***5***, 947.

2. "Copper(I) as a Phosphine Abstractor from $(\eta^5\text{-}C_5H_5)(CO)(PPh_3)FeCOCH_3$", S. Levitre, C. Tso, and A. Cutler, *J. Organomet. Chem.* **1986**, ***308***, 253.

3. "Alkyl-CO Insertion Reactions of $(PMePh_2)(CO)_3Co\text{-}\eta^1$-Methyl, Methoxymethyl, and Carbomethoxymethyl Complexes", C. C. Tso and A. R. Cutler, *Organometallics* **1986**, ***5***, 1834.

4. "Dialkoxyethylidene and η^2-1,2-Dialkoxyethylene Iron Compounds as Templates in the Selective Syntheses of Acetaldehyde and Glycoaldehyde Ether from Two CO Ligands", T. Bodnar, E. Crawford, and A. Cutler, *J. Am. Chem. Soc.* **1986**, ***108***, 6202.

5. "Characterization of a Stable $(\eta^3$-Indenyl)iron Metalate $(\eta^3\text{-}C_9H_7)Fe(CO)_3^-$. A Role for $\eta^3\text{-}\eta^5$ Indenyl Ligand Tautomerization During Alkyl-CO Insertion Reactions", T. C. Forschner, A. R. Cutler, and R. K. Kullnig, *Organometallics* **1987**, ***6***, 889.

6. "Incorporating CO into Poly(alkoxymethylene)acyl Ligands. Converting $(PPh_2CH_2CH_2PPh_2)(CO)_2Co\text{-}COCH_3$ into *threo*-$(DPPE)(CO)_2Co\text{-}COCH(OEt)CH(OEt)CH_3$", C. C. Tso, A. R. Cutler, and R. K. Kullnig, *J. Am. Chem. Soc.* **1987**, ***109***, 5844.

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8. "Bimetallic Acetyl Complexes $(\eta^5$-Indenyl$)_2(CO)_3Fe_2COCH_3^-$ and $(\eta^5$-Indenyl$)(\eta^5$-Cp$)(CO)_3Fe_2COCH_3^-$: Their Role in a Novel Carbonylation Reaction", T. C. Forschner, A. R. Cutler, and R. K. Kullnig, *J. Organomet. Chem.* **1988**, ***356***, C12..

9. "Carbon Monoxide and Carbon Dioxide Fixation: Relevant C_1 and C_2 Ligand Reactions

Recent Publications (DOE Supported Work)

Emphasizing (η^5-C_5H_5)Fe-Containing Complexes", A. R. Cutler, P. K. Hanna, and J. C. Vites, *Chem. Rev.* **1988**, ***88***, 1363 (Invited).

10. "Interconversion of Acetyl-and Terminal- Carbonyl Groups on Labeled (η^5-Indenyl)$(CO)_2$ Fe-$^{13}C(O)CH_3$", T. C. Forschner and A. R. Cutler, *J. Organomet. Chem.* **1989**, ***361***, C41.

11. "Carbonylation of (η^5-Indenyl)$(CO)_2$Fe-α-Alkoxyalkyl Complexes Using Bimetallic α-Alkoxyacyl Intermediates", S. A. Levitre, A. R. Cutler, and T. C. Forschner, *Organometallics* **1989**, in press (April).

12. "Preparation of Some Bimetallic μ-(η^1-C,O) Acetyl Complexes", T. Forschner and A. Cutler, *Inorganic Synthesis*, ***26***, in press (Invited).

13. "$RhCl(PPh_3)_3$- Catalyzed Hydrosilation of Organoiron Acyl Complexes", E. J. Crawford, P. K. Hanna, and A. R. Cutler, *J. Am. Chem. Soc.* **1989**, accepted for publication.

14. "(η^5-C_5H_5)$(CO)Fe(CH_3CN)_2^+$ as a Synthetic Intermediate in Preparing Disubstituted Compounds (η^5-C_5H_5)$(CO)Fe(L_1)(L_2)$", A. B. Todaro, L. D. Tarazano, A. R. Cutler, and J. J. Benoit, **1989**, manuscript submitted.

15. "Electrophilic Activation, Reduction, and Carbonylation of the Acetyl Ligand On $(PPh_3)(CO)_3CoCOCH_3$", C. C. Tso and A. R. Cutler, **1989**, manuscript submitted.

Manuscripts in Preparation

16. "Manganese Carbonyl Complexes as Hydrosilation Catalysts towards Organoiron Acyl Compounds", P. K. Hanna and A. R. Cutler.

17. "Non-Catalyzed Hydrosilation of Manganese Acyls $(CO)_5MnCOR$ (R = CH_3, Ph) with Dihydrosilanes," P. K. Hanna, E. J. Crawford, and A. R. Cutler.

18. "Diastereofacial Selective Reduction of Phosphite-Substituted Alkoxycarbene Complexes (η^5-C_5H_5)$(P(OR)_3)(CO)Fe{=}C(OCH_3)CH_3^+PF_6^-$", P. K. Hanna, G. A. O'Doherty, E. J. Crawford, and A. R. Cutler.

Recent Publications (DOE Supported Work)

19. "Synthesis and Reactions of the Organometallic Lewis Acids $(\eta^5\text{-}C_5H_5)_2WH^+SbF_6^-$ and PF_6^-", A. B. Todaro and A. R. Cutler.

20. "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.

21. "Bridging Phosphide Complexes Derived from $Cp(CO)_2Fe\text{-}PPh_2\text{-}Fe(CO)_2Cp^+$ and Their Reactions with $Cp(CO)_2Fe\text{-}PPh_2$", M. E. Giuseppetti-Dery, A. R. Cutler, and T. C. Forschner.

22. "Synthesis of μ-Alkenylidene Complexes $(\eta^5\text{-}C_9H_7)_2(CO)_3Fe_2(C{=}CHR)$ Using $(\eta^5\text{-}C_9H_7)(CO)_2Fe^-$-Promoted CO Insertion on $(\eta^5\text{-}C_9H_7)(CO)_2Fe\text{-}CH_2R$ (R=H, CH_3, OCH_3, and Ph)", P. K. Hanna, and A. R. Cutler.

23. "Bimetallic $\mu(\eta^1\text{-}C{:}\eta^1\text{-}O)$ Acetyl Complexes $Cp(L)(CO)Fe\text{-}C(CH_3)O\text{-}M^+$ {M= $Cp(CO)_2Fe$, $Cp(CO)_3Mo$, $Cp(CO)_3W$, and $Cp(NO)(CO)Re$} and {L=CO, PPh_3}, Their Characterization, Lability, and Reactions with Hydride Donors", A. B. Todaro, T. C. Forschner, C. C. Tso and A. R. Cutler.

24. "Synthesis and Solution Dynamics of $[Cp(CO)_2Fe]_2(CH{=}CH_2)^+PF_6^-$, a $\mu\text{-}(\eta^1{:}\eta^2)$ Vinyl Complex Not Containing a Metal-Metal Bond", L. Tarazano, T.W. Bodnar, T.C. Forschner, and A. R. Cutler.