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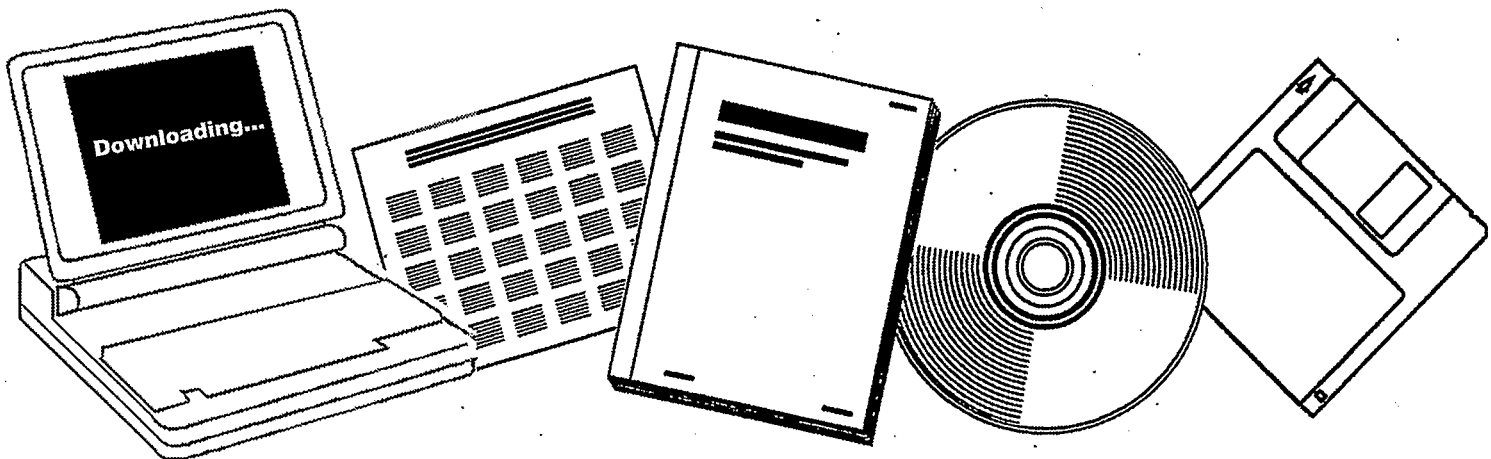
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MECHANISTIC STUDIES OF CARBON MONOXIDE REDUCTION. PROGRESS REPORT, JANUARY 1, 1988-DECEMBER 31, 1990

PENNSYLVANIA STATE UNIV., UNIVERSITY
PARK. DEPT. OF CHEMISTRY

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FOR SUPPORT OF RESEARCH ENTITLED:

MECHANISTIC STUDIES OF CARBON MONOXIDE REDUCTION

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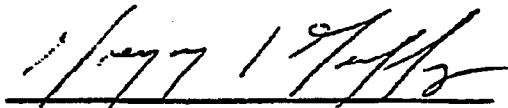
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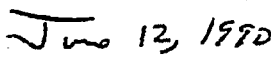
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Publications Resulting from this DOE Grant

- Geoffroy, G. L.; Bassner, S. L. "Interaction of ketenes with Organometallic Compounds. Ketene, Ketenyl, and Ketenylidene Complexes". *Adv. Organomet. Chem.*, 1988, 28, 1.
- Bassner, S. L.; Geoffroy, G. L.; Rheingold, A. L. "Generation and Reactivity of Ketene Ligands on Triosmium Clusters". *Polyhedron* 1988, 7, 791.

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11. Bassner, S. L.; Sheridan, J. B.; Kelley, C.; Geoffroy, G. L. "Reactivity of the α -Ketoacyl Ligand in $\text{Cp}^*(\text{L})(\text{NO})\text{Mn-C}(\text{O})\text{C}(\text{O})\text{Tol}$ with Electrophiles, Nucleophiles, and Alkynes" *Organometallics* 1989, **8**, 2121-2126.
12. Mirkin, C. A.; Lu, K.-L.; Geoffroy, G. L.; Rheingold, A. L. "Fluorine-Substituted Ferracyclopentadiene Complexes with an Unprecedented Fluorine Bridge between Boron and Carbon" *J. Am. Chem. Soc.* 1990, **112**, 461-462.
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14. Lugan, N.; Kelley, C.; Terry, M. R.; Geoffroy, G. L.; Rheingold, A. L. "Conjugate-Addition of a Chiral Manganese Acetylide Complex to Epoxides, Vinylketones, and Heterocumulenes" *J. Am. Chem. Soc.*, 1990, **112**, 3220.
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18. Stufkens, D. J.; Sheridan, J. B.; Geoffroy, G. L. "IR Evidence for the Formation of an $\eta^2(\text{C},\text{O})$ - α -ketoacyl Complex Upon Low Temperature Photolysis of $(\eta\text{-C}_5\text{H}_4\text{Me})(\text{CO})(\text{NO})\text{Mn-C}\{\text{O}\}\text{C}\{\text{O}\}\text{Tol}$ " Inorg. Chem., submitted for publication.

PROGRESS REPORT

(Jan 1, 1988 - Apr 1, 1990)

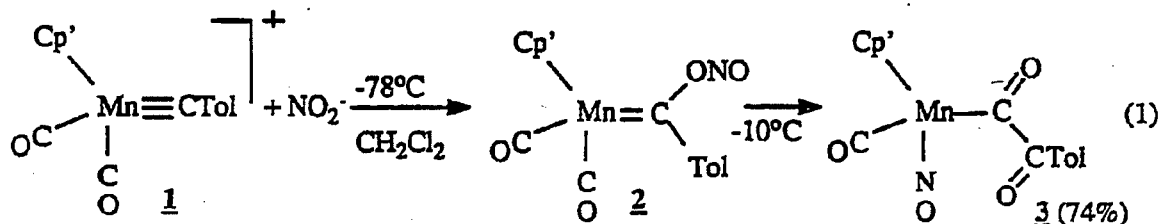
The research supported by this grant has focussed on three themes:

1. Oxidatively-induced double carbonylation reactions to form α -ketoacyl complexes and studies of the reactivity of the resulting compounds.
2. Mechanistic studies of the carbonylation of nitroaromatics to form isocyanates, carbamates, and ureas.
3. Studies of the formation and reactivity of unusual metallacycles and alkylidene ligands supported on binuclear iron carbonyl fragments.

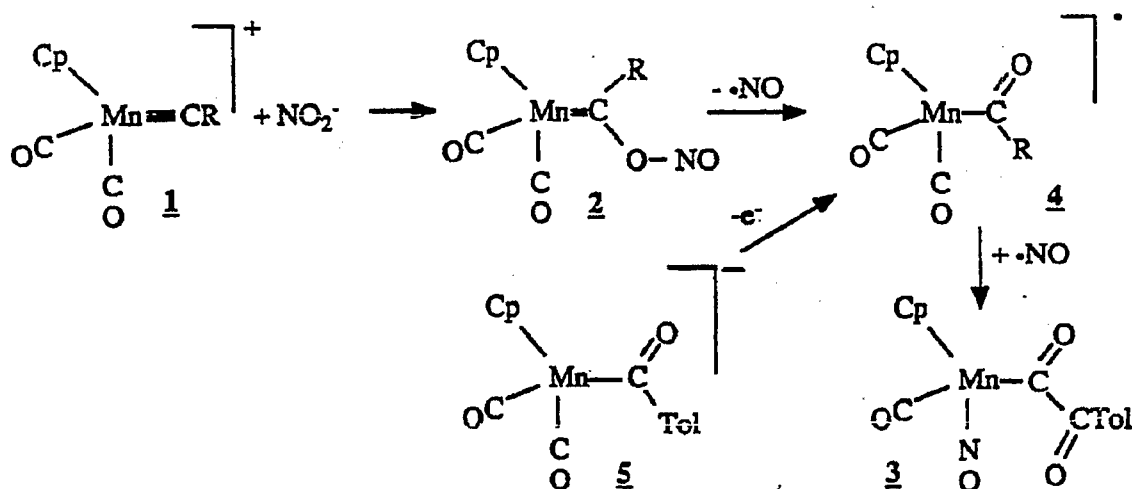
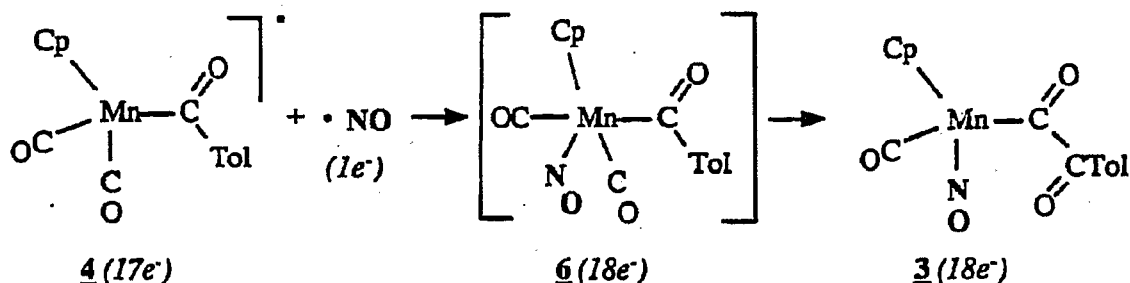
The progress made in each of these areas during the current grant period is summarized in the following paragraphs.

I. Oxidatively-Induced Double Carbonylation Reactions. Migratory insertion of CO into metal-alkyl bonds is a well established reaction of fundamental importance in organometallic chemistry and is an essential step in many catalytic and stoichiometric reactions. In contrast, migratory-insertion of CO into metal-acyl bonds to form α -ketoacyl ligands has long been recognized as an unfavorable reaction¹ and one with no definitive examples until the work summarized below was first reported.^{2,3}

In late 1987 we discovered an example of the migratory-insertion of CO into a metal acyl bond induced by a unique oxidation/NO addition reaction sequence.^{2,3} This work initially began while we were investigating aspects of the chemistry of the carbyne complex **1**. Upon treating this species with [PPN][NO₂] at low temperature, we observed the formation of carbene complex **2** through the addition of NO₂⁻ to the electrophilic carbyne carbon, analogous to the many other nucleophiles known to add to this carbon.⁴ However, upon warming above -10°C this species decayed to form the α -ketoacyl complex **3** (eq. 1) which was isolated in high yield and was spectroscopically and crystallographically characterized, Figure 1.² While investigating the

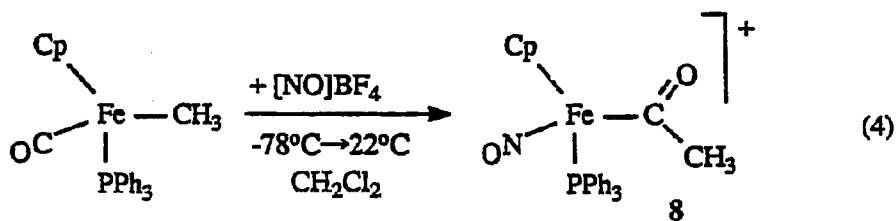
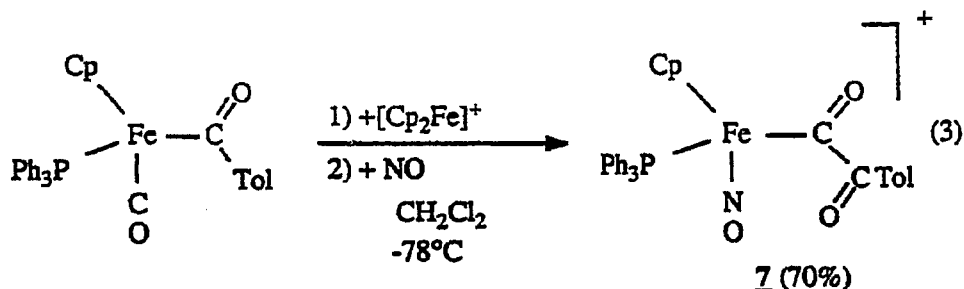


mechanism of the latter transformation, we considered the possibility that carbene complex **2** could decay to give free NO and the 17e⁻ acyl complex Cp'(CO)₂Mn-C[O]Tol, **4**, which could then recombine with NO to yield the α -ketoacyl complex **3** (see below). To test this possibility, complex **4** was independently generated by oxidation of the known acyl complex

Scheme 1Scheme 2

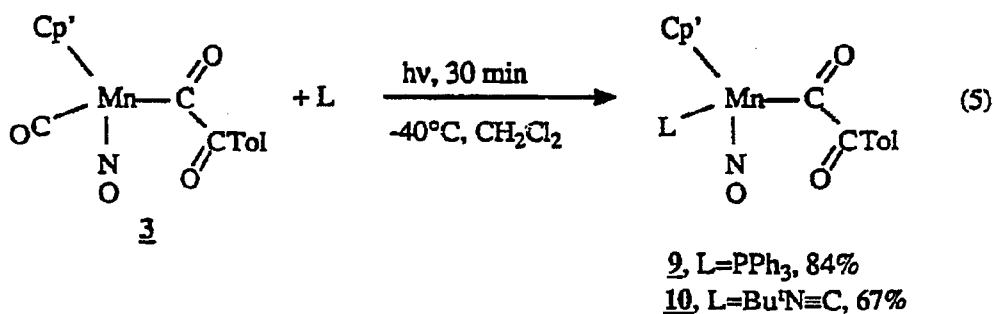
The migratory-insertion of CO into the metal-acyl bond is not confined to manganese nor to anionic acyl complexes since the neutral iron acyl complex $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}-\text{C}(\text{O})\text{Me}$ undergoes a similar transformation to give the corresponding cationic α -ketoacyl complex **7**, eq. 3.² Likewise, insertion of CO into the iron-methyl bond of $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}-\text{Me}$ has been found to be promoted by a similar oxidation/NO addition reaction sequence, eq. 4. Complex **8** is an unusual example of a cationic acyl complex. The iron center is chiral and the complex is isoelectronic with the neutral chiral acyl complex $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}-\text{C}(\text{O})\text{Me}$ which has been shown to be a useful reagent for stereospecific syntheses of organic compounds.⁵ Compound **8**, as well as **7**, may find similar applications, but modified by the cationic character of the complex.

The most important aspect of the work described above is the demonstration that α -ketoacyl ligands can be formed by the migratory-insertion of CO into metal-acyl bonds. Although it was



necessary to use the unusual oxidation/NO addition reaction sequence to accomplish this transformation, the results described herein clearly show that this is a viable reaction step and one that must be considered in discussions of "double carbonylation" reactions.

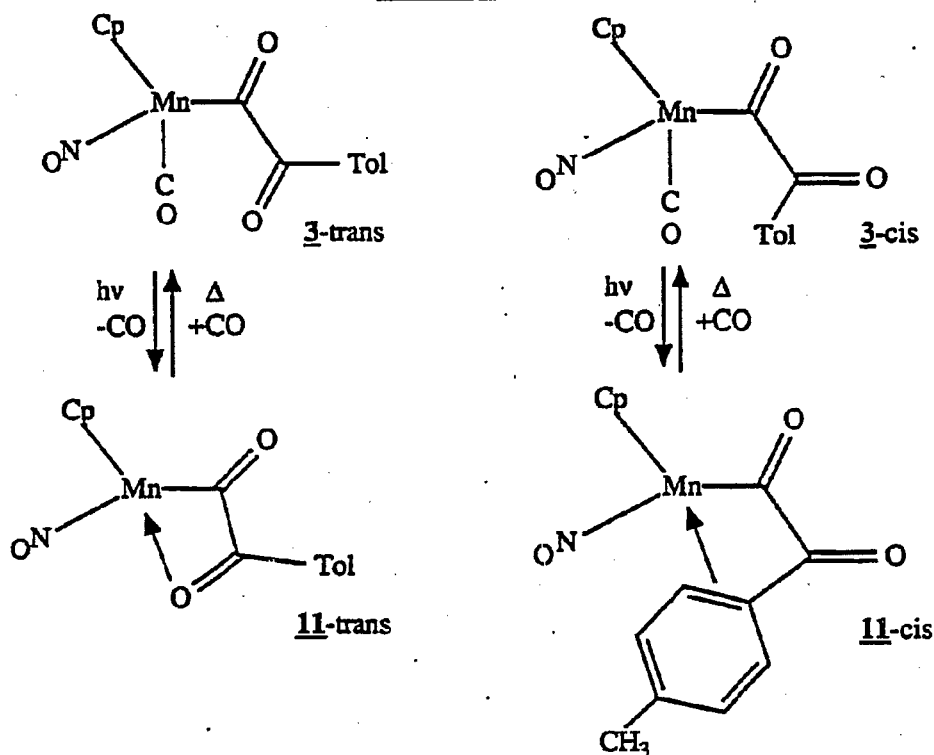
II. Reactivity of the α -Ketoacyl Ligand in $\text{Cp}'(\text{L})(\text{NO})\text{Mn}-\text{C}(\text{O})\text{C}(\text{O})\text{Tol}$. After preparing the above-described α -ketoacyl complexes, we recognized that relatively little was known about the chemical properties of α -ketoacyl ligands. We thus undertook an exploration of the reactivity of α -ketoacyl complex 3.^{6,7} The first observation was that when heated in toluene (66° , 12h) in the presence of ~ 1 equivalent of PPh_3 , complex 3 gave the phosphine substituted complex 9. This species was more conveniently prepared by photolyzing 3 with excess PPh_3 , eq. 5. The $\text{Bu}^t\text{N}\equiv\text{C}$



substituted derivative 10 was similarly prepared. A surprising feature of the chemistry of the α -ketoacyl complex 3 is its resistance to CO deinsertion to form an acyl complex when either heated or irradiated in the *absence* of added ligand.^{3a} Under these conditions, only slow decomposition occurred as evidenced by the gradual disappearance of all IR bands in the

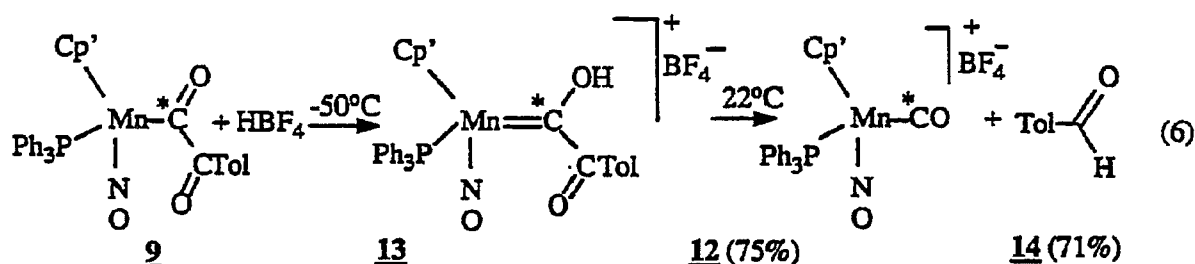
1600-2000 cm^{-1} region. To explore the basis for this surprising result, we recently completed a low-temperature photochemical study of the complex with the assistance of Derk Stufkens of the University of Amsterdam.⁸ IR monitoring showed that irradiation at -140°C in 2-MeTHF and at -100°C in CH_2Cl_2 gave spectral changes consistent with formation of the 11-cis and 11-trans products shown in Scheme 3 which derive from photoinduced CO loss from the S-cis and S-trans isomers of 3. Particularly indicative of this proposal is the loss of the metal carbonyl stretch, the

Scheme 3

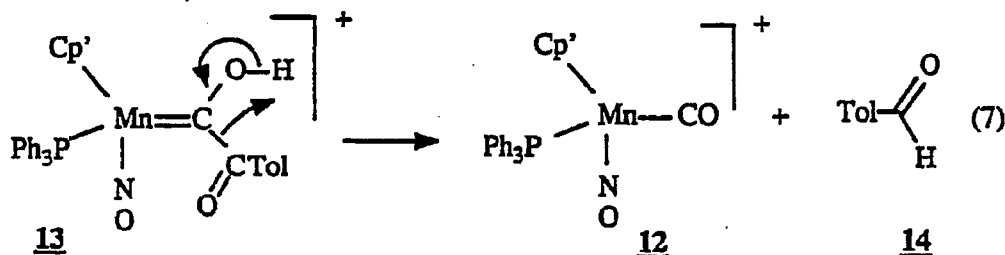


appearance of the ν_{CO} band of free CO, and the 50 cm^{-1} shift of the IR band assigned to the β -carbonyl of the S-trans isomer upon photolysis as compared to the smaller 15 cm^{-1} shift of the analogous band of the S-cis isomer.

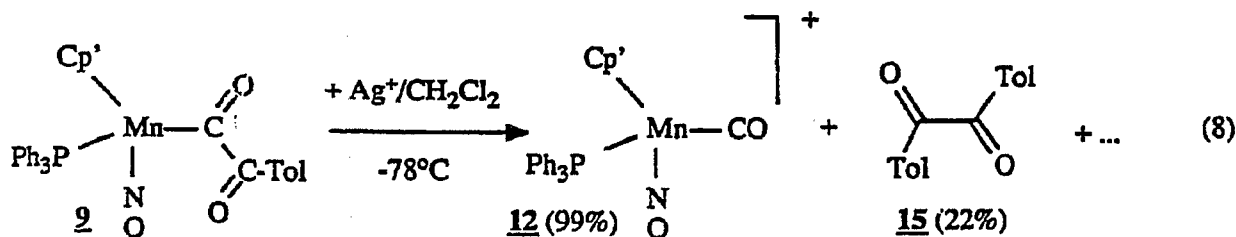
An intriguing reaction occurred when the PPh_3 substituted α -ketoacyl complex was protonated. When this species was treated with one equiv of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ at room temperature, the known complex $[\text{Cp}'\text{Mn}(\text{CO})(\text{NO})(\text{PPh}_3)]^+$, 12,⁹ and 4-methylbenzaldehyde rapidly formed, eq. 6.⁶ As indicated in the equation, a ^{13}C labeling study using 9 exclusively enriched in ^{13}C at the α -carbonyl carbon led to 12 with a ^{13}C enriched CO ligand. This demonstrates that the metal coordinated CO in 12 derives from the α -carbonyl of the α -ketoacyl ligand, and thus protonation induces cleavage of the α -ketoacyl carbon-carbon bond. When reaction 6 was conducted at -78°C and monitored by IR, an intermediate (13) formed ($\nu_{\text{NO}} = 1771\text{ cm}^{-1}$) which then gave 12 upon



warmup. Similar ^{13}C NMR monitoring of the -50°C protonation of **9**, enriched at the α -carbon of the α -ketoacyl ligand, showed a resonance at δ 335.4 (d, $J_{\text{C-P}} = 23$ Hz) due to the intermediate species. Upon warming to 0°C , the δ 335.4 resonance decreased in intensity as the δ 223.6 resonance of **12** grew in. These intermediate spectroscopic features are attributed to the hydroxycarbene complex **13** illustrated in eq. 6. This is the logical product of protonation since many acyl complexes have been shown to undergo protonation at the acyl carbonyl oxygen to give hydroxycarbene derivatives.¹⁰ The most likely mechanism for the **13**→**12**+**14** conversion is one involving an intramolecular hydrogen shift concomitant with cleavage of the carbon-carbon bond in the α -ketoacyl ligand, as outlined in eq. 7.



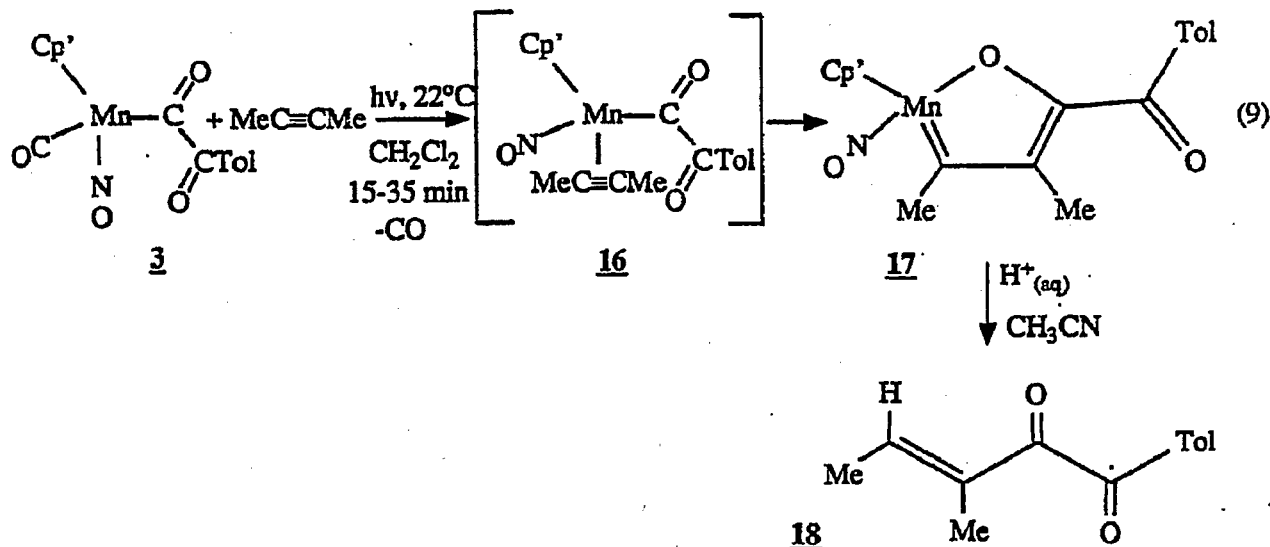
Cleavage of the α -ketoacyl carbon-carbon bond also occurred when complex **9** was oxidized. Treatment of a CH_2Cl_2 solution of **9** at -78°C with one equivalent of $[\text{Cp}_2\text{Fe}]^+$ or Ag^+ resulted in near instantaneous and quantitative conversion to the known cation **12**, along with a complex mixture of organic products, eq. 8. The only organic formed in substantial yield and the



only one confidently identified was TolC(O)-C(O)Tol , **15**. The stoichiometry of this reaction indicates that oxidation induces cleavage of the carbon-carbon bond of the α -ketoacyl ligand to form **12** and $\text{Tol-C(O)^\bullet}$ radicals. A substantial fraction of the latter must couple to form the observed **15**, with the remainder decaying to other unidentified organic products.

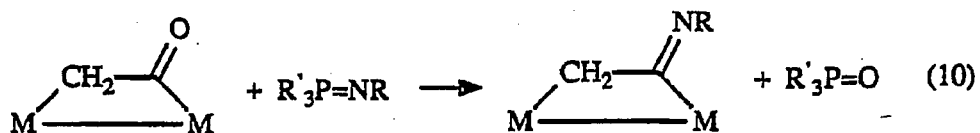
To explore the possibility of coordination and then interaction of small organic molecules with the α -ketoacyl ligand in complex **3**, this species was irradiated in the presence of alkynes in

anticipation of photosubstitution of alkyne for CO. Rapid reaction occurred with small electron-rich alkynes to form metallacycles of the type **17** depicted in eq. 9 for $\text{MeC}\equiv\text{CMe}$.⁶ The



intermediate alkyne complex **16** was not detected, but it is the logical species that would result upon photoinduced CO loss and coordination of alkyne. Similar metallacycles were observed to form upon reaction of **3** with $\text{Bu}^t\text{C}\equiv\text{CH}$, $\text{MeC}\equiv\text{CEt}$, and $\text{MeC}\equiv\text{CPh}$ under photochemical conditions. The metallacycle produced in the above reaction is extremely susceptible to hydrolysis, and the complex can easily be demetallated by addition of aqueous HCl to a CH_3CN solution of the complex and also to a large extent upon chromatographic work-up, to form the vinyl α -dione **18**, eq. 9.

III. New Transformations of Binuclear Iron Carbonyl Complexes. In the course of our studies of ketene ligands, we sought ways to transform these ligands into other types of organics. Particularly interesting was their conversion into ketenimine ligands via deoxygenation with phosphinimines, eq. 10. One such attempt this past year with the potential ketene precursor



$\text{Fe}_2(\mu\text{-CH}_2)(\text{CO})_8$, **19**, gave instead a remarkable and unprecedented series of transformations which are summarized in Scheme 4 on the next page.¹¹ The initial products isolated from the reactions of **19** with $\text{Bu}_3\text{P}=\text{NBu}^t$ and $\text{Ph}_3\text{P}=\text{NPh}$ were the 3-ferra-4-pyrrolin-2-one complexes **20a** and **20b**. This type of metallacycle had not been previously reported, although these complexes are isomeric with several known ferra-pyrrolinones in which the carbonyl and imido groups have

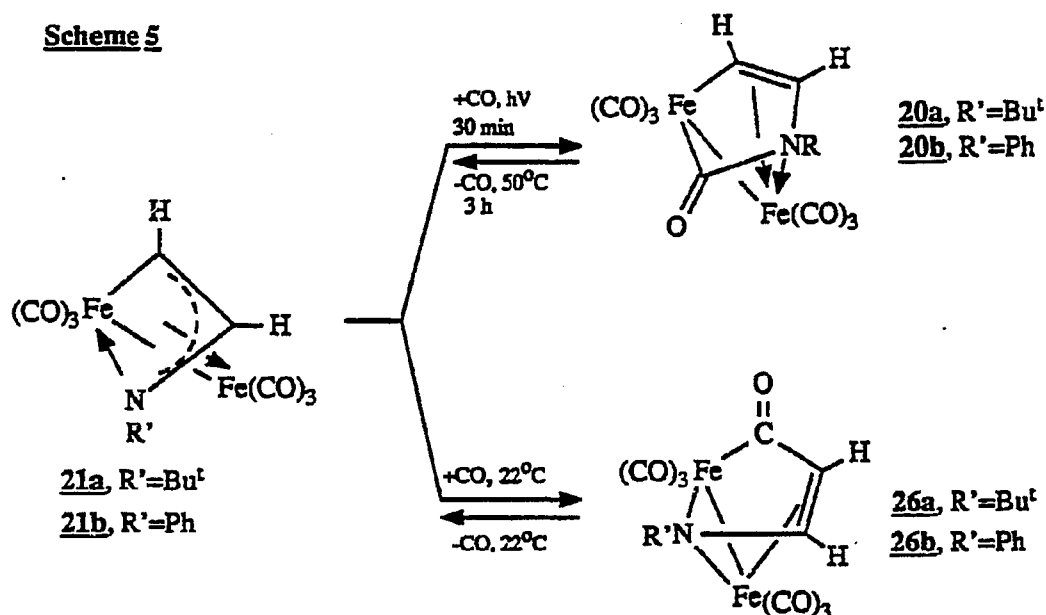
exchanged positions.¹² However, unlike those isomers, complexes 20a,b slowly de-insert CO to form the 2-ferra-3-azetine complexes 21a,b which are also new types of metallacycles. In addition to spectroscopic characterization, the new complexes 20b and 21a have been crystallographically defined, Figures 2 and 3.

The likely mechanism by which the ferri-pyrrolinone complexes 20a,b derive from 19 is shown in Scheme 4. Evidence for initial addition of the phosphinimine to a carbonyl carbon to form 23 comes from the observation that the μ -CMe₂ analog of 19 reacts with BuⁿN=P(Buⁿ)₃ to form a similar complex which has been isolated and spectroscopically characterized [$\nu_{\text{CO}}=1752$ cm⁻¹; ¹³C NMR: δ 231.7 (C[O]NBuⁿ)]. Phosphinimines have been previously proposed to deoxygenate carbonyl ligands via this type of intermediate, and species like this form from the reactions of ylides with metal carbonyls.¹³ Elimination of R₃P=O from 23 would form the ketenimine complex 24 which must then rearrange to the formimido carbene complex 25, similar to rearrangements previously observed by Pettit in related compounds.¹⁴ Nucleophilic attack of the imine nitrogen of 25 on a CO ligand would yield the ferri-pyrrolinone ring. Evidence for this step comes from observation that treatment of the protonated azaallylidene complexes 22a,b (Scheme 4) with base leads to quantitative formation of the ferri-pyrrolinone complexes 20a,b, presumably by attack of the imine nitrogen on a CO ligand concomitant with CO loss from the metal framework. The 23 to 24 conversion does not likely proceed via decay of 23 into O=PR₃ and a C $\equiv$ NR ligand which could insert into the metal carbonyl bond to form 24, since reaction of 19 with BuⁿN $\equiv$ C does not yield any of the products described above.

As illustrated in Scheme 5, the ferri-azetine complexes 21a,b have also been found to undergo reversible carbonylation to give *isomeric* ferri-pyrrolinone complexes, depending upon whether thermal or photochemical conditions are used. Under photochemical conditions in the presence of 1 atm CO, the 3-ferri-4-pyrrolin-2-one complexes 20a and 20b were formed in near quantitative yield. However, when complexes 21a,b were stirred at room temperature under 1 atm CO, carbonylation occurred at the other end of the metallacycle to give the 2-ferri-4-pyrrolin-3-one complexes 26a and 26b, which are also completely new types of metallacycles, but with no trace of 20a or 20b. For complex 21b, this latter reaction was rapid (1h), and 26b was isolated in 72% yield by slow evaporation of solvent under a CO atm. However, with complex 21a, ¹H NMR analysis showed formation of an equilibrium mixture of 26a (18%) and 21a (82%), and we were unable to isolate 26a because of its facile conversion back to 21a when the CO atm was removed. Similarly, complex 26b reformed 21b when solutions were stirred under an N₂ atm.

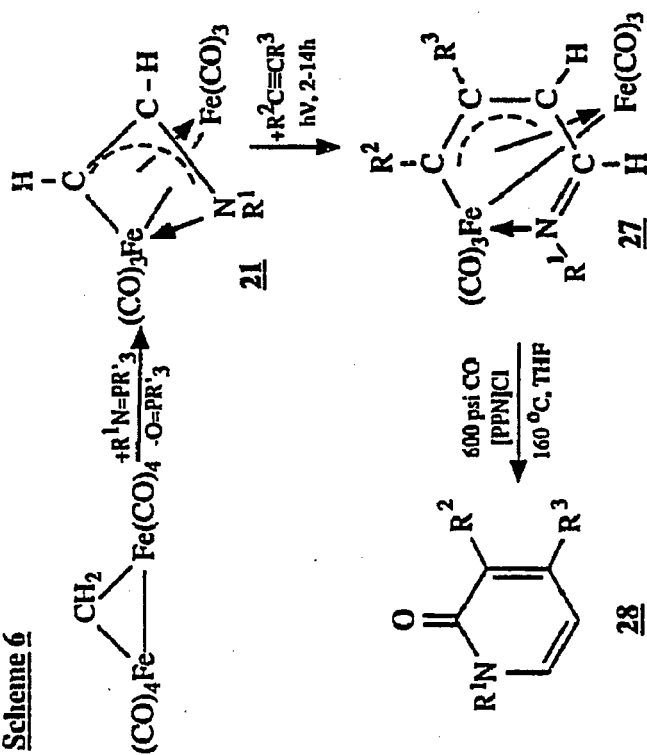
In the course of the studies described in the above sections, we discovered a metal-assisted route to mono-, di-, and tri-substituted 2-pyridinones based on the reaction of phosphinimines

Scheme 5



with $\text{Fe}_2(\mu\text{-CH}_2)(\text{CO})_8$. The binuclear ferra-azetene complex **21a,b** were found to readily insert alkynes into the Fe-carbon bond under photochemical conditions to give the ferra-pyridine complexes **27a-g** shown in Scheme 6.¹⁵ These latter species were isolated in 72-87% yields as microcrystalline solids and have been spectroscopically characterized, with complex **27e** ($R^1, R^2, R^3 = \text{Ph}$) fully defined by an X-ray diffraction study, Figure 4. NMR data indicate that terminal alkynes insert regiospecifically to give only the isomer with the substituted carbon adjacent to the iron center.¹⁵ As illustrated in Scheme 6, free 2-pyridinones were readily released when complex **27** was either heated under 600 psi CO in the presence of 1 eq of $[\text{PPN}]\text{Cl}$ or when refluxed in CH_3CN solution. The 2-pyridinones **28a-g** were isolated by silica gel chromatography and were spectroscopically characterized. The overall reaction occurs with high regiospecificity due to the selectivity of the alkyne insertion step to form the ferra-pyridines. In the case of mono-substituted alkynes, the substituted carbon atom is always adjacent to the iron center in the ferra-pyridine ring and hence adjacent to the nitrogen atom in the pyridinone.

As shown in Table I, this synthetic method allows for strong substituent control at the 1- and 3-positions by varying the phosphinimine and the alkynes employed. Significantly, the Bu^t -N substituted 2-pyridinones can be converted into N-H 2-pyridinones by refluxing in $\text{CF}_3\text{CO}_2\text{H}$ followed by $\text{K}_2\text{CO}_3(\text{aq})$ workup as illustrated by entries **28h** and **28i** in Table I. The N-H pyridinones are an important class of biologically active molecules, with **28i** being a patented anti-inflammatory agent. Further, N-H 2-pyridinones give wide potential substituent variability at this position by employing many of the known methods for alkyl and aryl substitution. Entry **28g** is particularly attractive since it not only demonstrates the versatility in choice of alkyne, but also

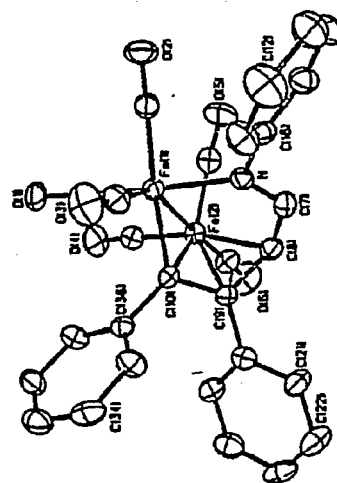
Scheme 6Table I.

entry	R ¹	R ²	R ³	(%) ^a	(%) ^b
28a	Ph	Bu ^t	H	87	57
28b	Bu ^t	Bu ^t	H	86	66
28c	Bu ^t	Ph	H	79	57
28d	Bu ^t	Ph	D	79	57
28e	Ph	Ph	Ph	34	16
28f	Bu ^t	Et	Et	76	61
28g	Bu ^t	SiMe ₃	H	79	73
28h^c	H	Bu ^t	H	81	62
28i^c	H	Ph	H	68	49

^aIsolated yields based on conversion from **27**

^bIsolated yields based on conversion from Fe₂(μ-CH₂)(CO)₈

^c**28h** and **28i** were synthesized using the same methodology to produce **28b** and **28c** followed by a 48 h reflux in CF₃CO₂H

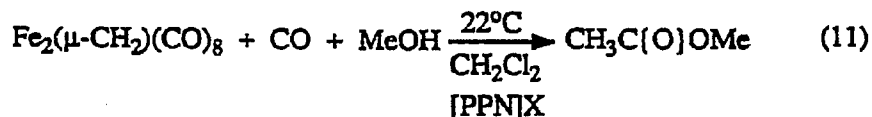
Figure 4. Complex 27e.

the added SiMe₃ functionality allows for further manipulation at the 3-position by known organic methods.

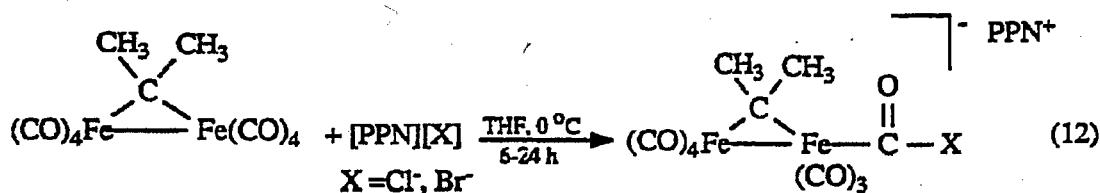
This synthetic route for pyridinones offers a convenient step-wise synthesis of substituted pyridinones from readily available starting materials – alkynes, phosphinimines, and Fe₂(μ-CH₂)(CO)₈. It also has many advantages over conventional methods of pyridinone synthesis. First of all, it employs simple, inexpensive, and readily available starting materials. Secondly, it appears to have wide substituent variability, both on the nitrogen atom and the alkyne. Finally, the starting complex Fe₂(μ-CH₂)(CO)₈ and the intermediate metallacycles are not particularly air-sensitive, and the reactions can be readily conducted under tank N₂. Its limitation is that presently only tri-substituted pyridinones can be formed as the substituents in the 5 and 6 positions of the pyridinone ring are limited to hydrogen atoms. Current efforts are aimed at developing methodology to synthesize 5-substituted pyridinones as well as the 4-substituted isomer not observed in this reaction.

IV. Halide-Promoted Insertion of Carbon Monoxide into Iron-μ-Carbene Bonds. A long-standing research theme in our DOE supported research has involved studies of the halide-promoted insertion of carbon monoxide into metal-carbene and metal-nitrene bonds. We recently investigated the reactivity of halides with methylene complex Fe₂(CO)₈(μ-CH₂) which has been shown by Keim to require extreme conditions (40 atm; 70°C, 24h) for carbonylation to occur in the absence of a nucleophile.¹⁶ Keim also showed that in the presence of methoxide ion, carbonylation readily occurred under 1 atm CO to form methylacetate, but in the absence of methoxide the complex did not react with methanol at room temperature under 1 atm CO.

We have found that halides and cyanide dramatically promote the carbonylation of Fe₂(CO)₈(μ-CH₂) in CH₂Cl₂ solution containing a few equivalents of methanol (1 atm CO; 22°C; minutes) to form near quantitative yields of methylacetate, but without the detection of organometallic intermediates, eq. 11. The halides Cl⁻, Br⁻, and I⁻ and cyanide are all effective in

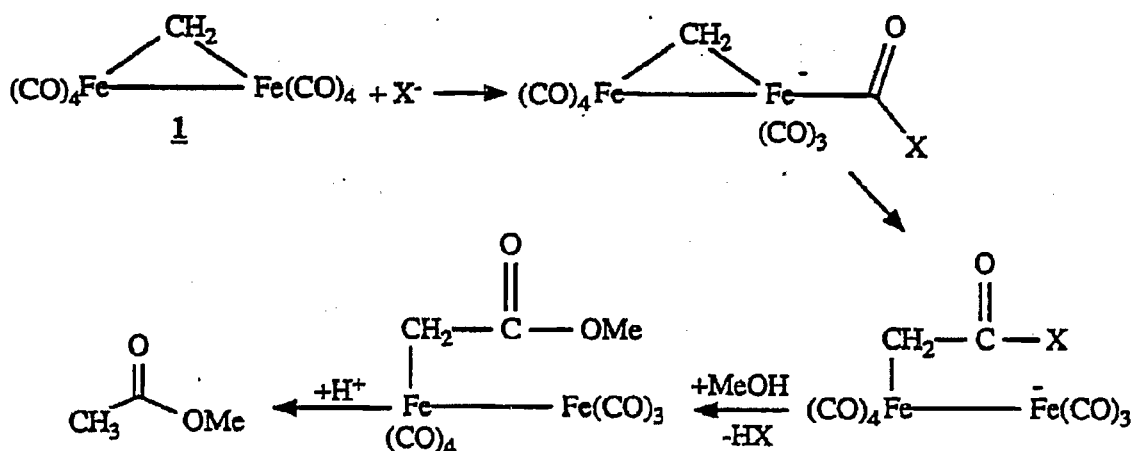


inducing this transformation, but in the absence of halide no reaction occurs. The key question concerns exactly how halides promote this and related carbonylation reactions. We have gained insight into this process by studying the substituted carbene complex Fe₂(CO)₈(μ-CMe₂). Spectroscopic data indicate that this latter species reacts with halides to form the halocarbonyl complexes shown in eq. 12. Haloacyl complexes have often been suggested as important



intermediates in a number of halide promoted reactions¹⁷ but have never been directly observed, except for one serendipitous preparation of the fluoroacyl complex $[\text{F}(\text{CO})_2(\text{PEt}_3)_2\text{Ir-C}(\text{O})\text{F}]^+$ which was sufficiently stable to isolate and structurally characterize.¹⁸ The haloacyl complexes shown in eq. 12 are relatively stable compounds and have been isolated and spectroscopically characterized, but they do not further transform into products involving carbonylation of the carbene ligand. Their formation in eq. 12 suggest that halides promote the carbonylation of $\text{Fe}_2(\mu\text{-CH}_2)(\text{CO})_8$ by a similar process involving initial halide addition to a carbonyl ligand, Scheme 7. Subsequent migration of this ligand to the methylene ligand followed by solvation

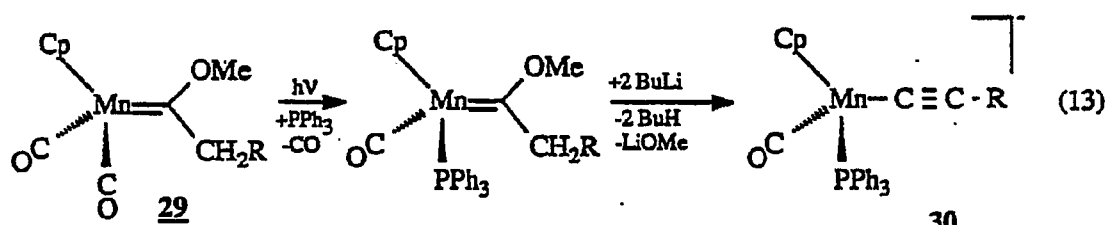
Scheme 7



with methanol would give the observed methylacetate product. This proposal, which is in line with the mechanism suggested by Keim for the methoxide induced carbonylation,¹⁶ relies on the assumption that a haloacyl ligand will rapidly couple with the methylene ligand whereas a CO ligand does not easily undergo this migration. The function of the halide is then to activate the CO for the coupling step, and once this step has occurred, the halide is solvated by the methanol solvent.

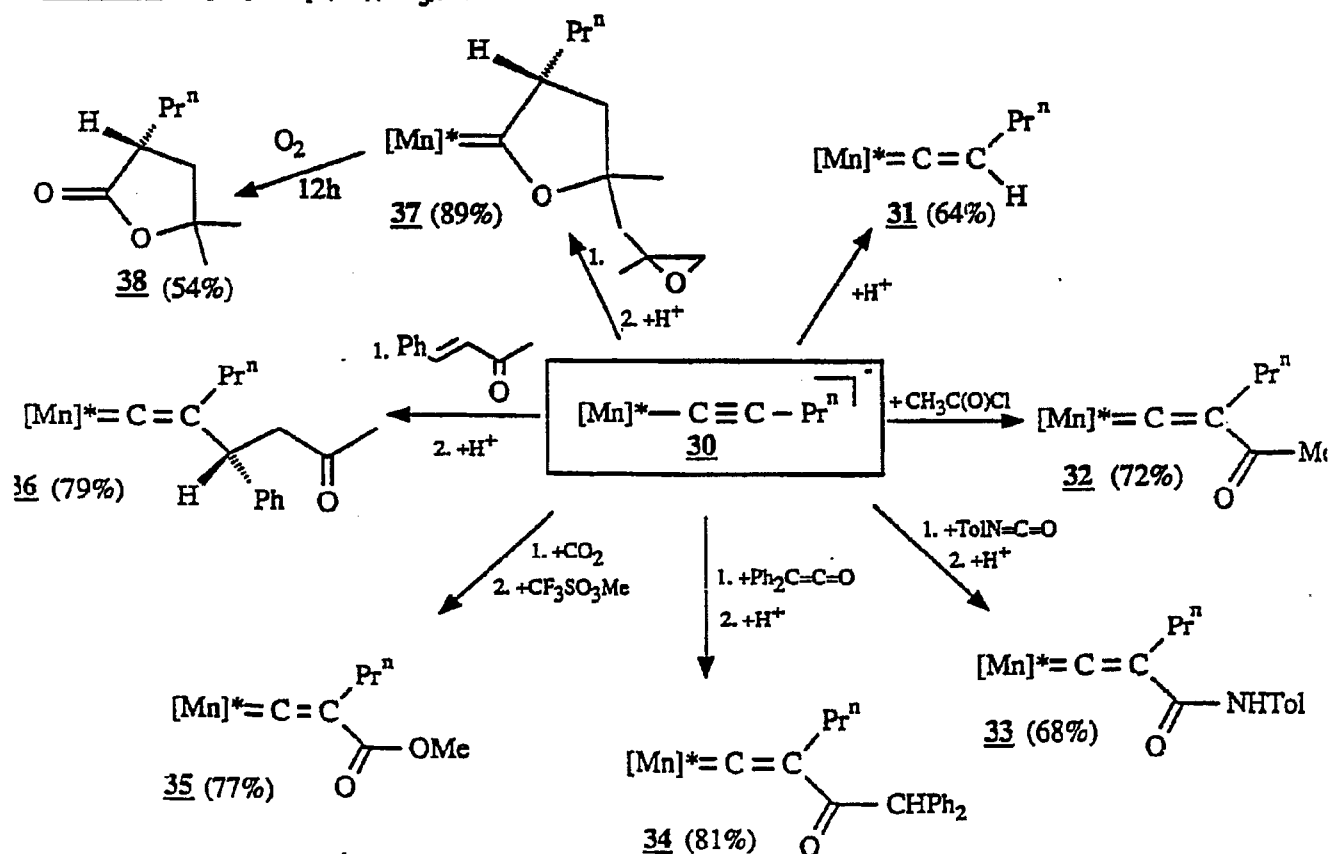
V. New Addition and Cycloaddition Reactions with Highly Nucleophilic and Chiral Manganese Acetylide Complexes. In an extension of the acyl to CO migratory-insertion reaction discussed in Section I of this report, we sought to induce a similar migration of a carbene

ligand by oxidizing the complex $\text{Cp}(\text{CO})_2\text{Mn}=\text{C}(\text{OMe})\text{Me}$. This did not work, but in the course of these studies we prepared and investigated the PPh_3 substituted complexes $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Mn}=\text{C}(\text{OMe})\text{CH}_2\text{R}$, **29**, eq. 13. This led to the discovery of a remarkable set of Mn-acetylide and -vinylidene complexes that promise to have considerable potential for use in stereospecific organic and organometallic syntheses.¹⁹ Complex **29** was found to react with two equivalents of *n*-BuLi to form the anionic acetylide complex **30** shown in eq. 13 ($\text{R}=\text{H}$, CH_3 , Pr^i).



These latter complexes are highly reactive and readily undergo nucleophilic addition to $\text{PhN}=\text{C}=\text{O}$, $\text{Ph}_2\text{C}=\text{C}=\text{O}$, CO_2 , vinylketones, and epoxides to give the products illustrated in Scheme 8. All of the products shown in the scheme were isolated as spectroscopically

Scheme 8 $[\text{Mn}]^* = \text{Cp}^*(\text{CO})(\text{PPh}_3)\text{Mn}$



characterized solids, and complexes **36** ($R=PR^n$) and **37** (with CH_3 instead of Pr^n) were also characterized by X-ray diffraction studies. Acetylide complex **30** readily undergoes protonation and acylation to give the vinylidene complexes **31** and **32**, and it adds to the heterocummulenes $TolN=C=O$, $Ph_2C=C=O$, and CO_2 to give, after protonation or alkylation, the vinylidene complexes **33-35**. These latter complexes likely form via the intermediacy of species **39**. A similar conjugate addition occurs with *trans*-4-phenyl-3-buten-2-one to initially form **40** which gives the vinylidene complex **36** upon protonation. A significant finding is that complex **36** is



produced as a 9:1 mixture of the two possible diastereomers, implying that the chiral Mn center induces a high degree of stereospecificity during the nucleophilic addition step. The crystallographically characterized RR,SS diastereomer of **36** is the one expected to form if protonation occurred from the least sterically hindered side of the intermediate vinylidene complex and is presumably the diastereomer which is formed in excess.

One of the most surprising reactions observed for the acetylide complex **30** was its cycloaddition with isobutylene oxide to give the carbene complex **37**. Significantly, NMR data indicate that only a single pair (RR/SS *or* RS/SR) of diastereomers of **37** is produced in this reaction, implying that the stereochemical configuration at Mn dictates the configuration adopted at the chiral carbon of the cyclic carbene ligand. The methyl analogue of **37** prepared from $[Cp'(CO)(PPh_3)Mn-C\equiv CCH_3]^+$, was similarly shown by 1H NMR to form as a single diastereomeric pair, and this species was crystallographically characterized. The ORTEP drawing shown in Figure 5 indicates that it is the RS/SR pair that has formed, with the CH_3 substituent and the bulky PPh_3 ligand located on opposite sides of the planar metallacycle. As indicated in Scheme 8, oxidation of carbene complex **37** with $O_2(g)$ in dry CH_2Cl_2 releases the free lactone **38** which was isolated in modest yield. The stereochemical selectivity in the formation of **37** implies that lactone **38** would be produced as a single enantiomer if enantiomerically pure **29** were used in the initial reaction.

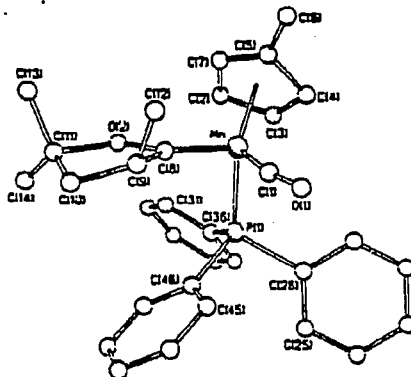
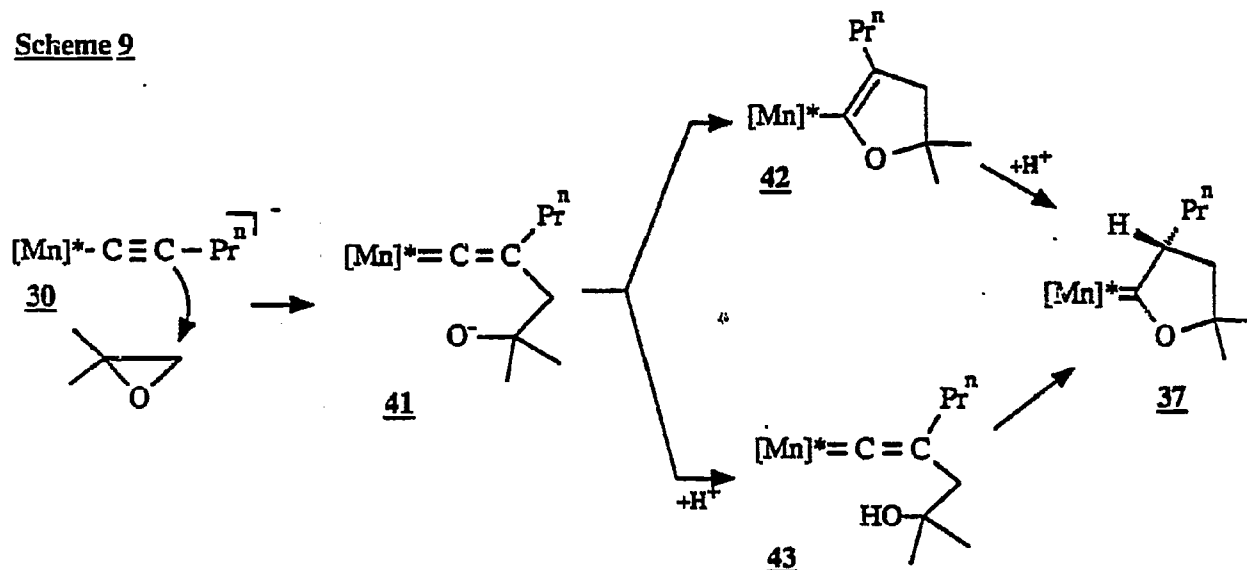


Figure 5

The formation of 37 and its methyl analogue likely proceeds via one of the mechanistic paths shown in Scheme 9 involving initial ring opening of the epoxide to give vinylidene

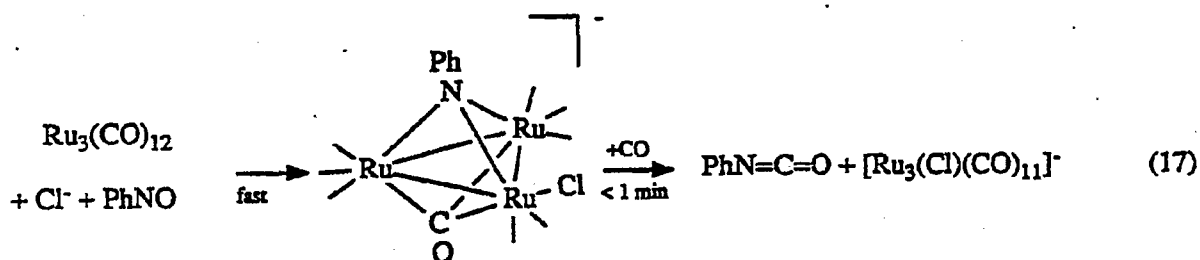
Scheme 9



complex 41. Carbene complex 37 could then form by ring closure to give the vinyl complex 42 followed by protonation at the β -carbon. Alternatively, protonation of 41 could occur prior to ring closure to yield the vinylidene complex 43 from which 37 would result by addition of the OH bond across the $\text{C}=\text{C}$ bond of the vinylidene ligand, a characteristic reaction of vinylidene complexes. In this latter path, the chiral Mn center would dictate the stereochemistry of the final product by sterically controlling the transition state in the ring closure step. However, if the former path were operative, the stereochemistry of 37 would be dictated by the protonation step, which could occur directly at the β carbon or at the metal followed by hydride migration to the β -carbon.

The conjugate addition reactions summarized above for acetylide complex 30 are similar to transformations previously demonstrated for the conjugate bases of metal carbene complexes.²⁰ The ability of the chiral manganese center in 30 to effectively dictate the chirality of the emerging stereocenter in the organic ligands of 36 and 37 imply that transformations like these may have potential use in stereospecific organic syntheses and could complement the many stereospecific transformations observed by Davies and co-workers for the related acyl complexes $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}-\text{C}(\text{O})\text{CR}'\text{R}]$.⁵ Current efforts are focused on resolving carbene complex 29 into its separate enantiomers and on extending the addition and cycloaddition reactions reported herein to other organic substrates.

VI. Halide-Promoted Carbonylation Reactions of Nitro- and Nitrosoaromatics. We have been interested in the metal catalyzed carbonylation of nitro- and nitrosoaromatics for some years because of the commercial interest in finding ways not involving the use of phosgene for the conversion of these chemicals into isocyanates and isocyanate derived products. There has been considerable speculation that cluster bound imido (nitrene) ligands are important in these reactions, and thus part of our studies have focussed on the carbonylation behavior of model organometallic compounds. In earlier work we showed that halides dramatically promote both the CO induced deoxygenation of nitroso reagents to form imido ligands on Ru_3 clusters and the carbonylation of these ligands to form isocyanates, eq. 14.²¹ These reactions were suggested to



model some of the transformations which occur in Chini's $\text{Ru}_3(\text{CO})_{12}$ catalyzed and chloride-promoted carbonylation of PhNO_2 in the presence of methanol to form N-phenyl methylcarbamate.²² As a continuation of these studies, and in a collaborative effort with Duane Dombek at Union Carbide, we filled in several of the missing pieces of the puzzle of the reactions which occur when halides are added to solutions of the clusters $\text{Ru}_3(\text{CO})_{12}$ and $\text{Fe}_3(\text{CO})_{12}$. That work is described in ref 23.

Also, as part of these studies we had prepared the heteronuclear imido clusters $\text{FeRu}_2(\mu_3\text{-NPh})(\text{CO})_{10}$ and $\text{Fe}_2\text{Ru}(\mu_3\text{-NPh})(\text{CO})_{10}$ ²¹ and observed that they showed a greatly enhanced reactivity towards CO than did the homonuclear species $\text{Ru}_3(\mu_3\text{-NPh})(\text{CO})_{10}$. This led us to examine mixed $\text{Fe}_3(\text{CO})_{12}/\text{Ru}_3(\text{CO})_{12}$ catalysts for nitroaromatic reactions, and *in the presence of chloride* we found that $\text{Fe}_3(\text{CO})_{12}$ significantly increases the catalytic activity of $\text{Ru}_3(\text{CO})_{12}$ in the carbonylation of nitrobenzene to form methyl N-phenylcarbamate, even though $\text{Fe}_3(\text{CO})_{12}$ alone is inactive under the conditions used. At a constant catalyst concentration of 0.093M, optimum activity was observed for an Fe/Ru molar ratio of 2:1. A similar synergistic Fe/Ru behavior was observed for the chloride promoted reduction of nitrobenzene to aniline using $\text{CO}/\text{H}_2\text{O}$ mixtures and for the water-gas shift reaction. The latter Fe/Ru synergistic effect is known from the studies of Peter Ford, although the effect of chloride had not been previously observed. We have proposed a unified series of mechanisms for these three different but related catalytic reactions and an explanation for the Fe/Ru synergistic effect which will be detailed in the complete paper on this work which is about to be submitted.

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