Carbon Monoxide and Carbon Dioxide Fixation: Relevant C_1 and C_2 Ligand Reactions Emphasizing (η^5-C_5H_5)Fe-Containing Complexes

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Contents

I. Introduction

The "Fp" moiety [(η^5-Cp)$(CO)_2$Fe] and its congeners—(η^5-C_5Me_5) or Cp* and (η^5-indenyl) or In in place of Cp; phosphines or phosphites in place of CO; Ru or Os in place of Fe—are among the more versatile systems in synthetic and mechanistic transition organometallic chemistry. Coordinated ligand reactions involving Fp η^1-alkyl, η^1-acyl, η^1-carbonyl, η^1-carbene, δ^2-alkene, and alkyne complexes are commonly cited as transition organometallic precedent for reaction pathways in homogeneous catalysis and for novel synthetic organic methodology. Recent noteworthy developments involving these ligand reactions include cyclopropanation of alkenes using [Fp(carbene)]$^+$ compounds,[1] determination of the stereochemistry of reactions at a transition-metal center,[2] using Cp(CO)(PPh_3)Fe–$COCH_2^-$ as a chiral enolate equivalent,[3] conformational analysis of organoiron alkyl and acyl complexes,[4] metal-assisted cycloaddition and the reactions of electrophiles with η^1-allyl complexes,[5] use of [Fp(η^2-vinyl ether)]$^+$ compounds as vinyl cation equivalents,[5a,6] oxidatively induced migratory insertion of alkyl groups to carbonyl ligands,[7] intramolecular (1,2) migration of alkyl groups to carbene ligands,[8] organometallic photochemistry and attendant C–H bond activation of coordinatively unsaturated alkyl complexes,[9] bimetallic activation of coordinated ligands[10] [e.g., $Cp_2(CO)_3Fe_2$ systems] and hydrocarbation of olefins and alkynes,[11] regio- and stereoselective addition of nucleophiles to coordinated alkynes,[12] and reductive coupling of two adjacent acyl carbon sites on metalla-β-diketonate complexes.[13]

This review focuses on C_1 and C_2 oxygenated ligands that potentially relate to carbon monoxide and carbon dioxide fixation and their subsequent synthesis reactions. The C_1 and C_2 ligand reactions of Fp complexes—and their congeners—serve as the vehicle for this presentation. Where appropriate, results of related studies are given, especially involving the isolobal (to Fp) organometallic systems Cp(NO)(CO)Re, $Cp(CO)_3M$ (M = Mo, W), and $(CO)_5M$ (M = Mn, Re).

This paper differs from previous reviews on CO and CO_2 chemistry in that a single type of organometallic moiety is used to present a unified view of C_1 and C_2 ligand reactions. Reviews on the preparations of rele-

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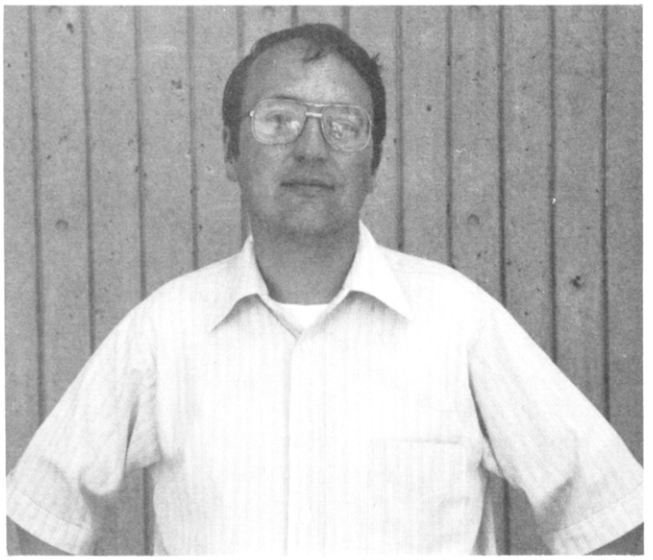


Alan R. Cutler is Associate Professor of Chemistry at Rensselaer Polytechnic Institute in Troy, NY. He was born in 1946 and received a B.A. degree in chemistry from Clark University. His Ph.D. studies in organometallic chemistry were completed in 1974 at Brandeis University under the direction of Myron Rosenblum. Postdoctoral studies with David Dolphin (Harvard University and the University of British Columbia) and with Richard Holm (Stanford University) rounded out his interests in bioinorganic and inorganic chemistry. Prior to joining the RPI chemistry faculty in 1982, he was a member of the faculty at Wesleyan University. His research interests include synthetic and mechanistic transition organometallic chemistry.

vant CpFe-[14] and CpRu-[15] containing starting materials are available.

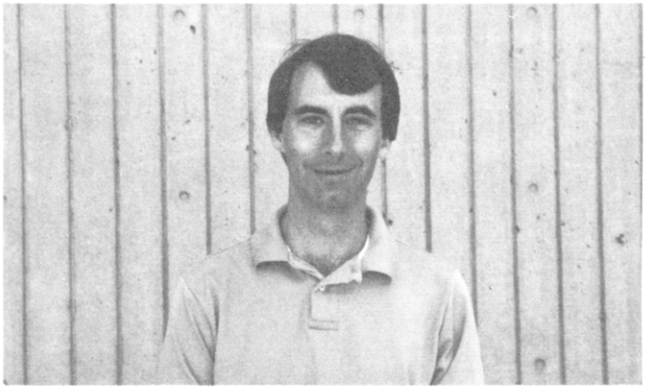
II. C_1 Chemistry: Ligands Containing the CO_2 or CS_2 Unit

A. Metallocarboxylate and Metallocarboxylate Ester Complexes

Transition organometallic complexes incorporate CO_2[16] by forming η^1-C metallocarboxylic acid esters **1** (also referred to as alkoxycarbonyl compounds[17]) or η^1-O metallocarboxylates **3**. CpFe-containing (and related)

examples of η^1-C metallocarboxylates **2** as 1:1 metal–CO_2 adducts serve as precursors to C_1 derivatives of type **1**. Corresponding η^1-O metallocarboxylates **3** also are known for Fp complexes, but these do not result from the generally useful CO_2 insertion into M–H and M–R bonds.

Evans and co-workers[18] first reported that Fp^-Na^+ in THF solution reacts with excess CO_2 at room temperature to give an unstable CO_2 adduct. Subsequent studies by Cooper[19] and by Cutler[20] established the following details: (1) The metalate Fp^- reacts rapidly with CO_2 in THF solution at −78 °C; the resulting metallocarboxylates are stable under these conditions. (2) Even in the presence of excess CO_2, solutions of Fp^-



Paul K. Hanna completed his undergraduate studies in chemistry at Santa Clara University in Santa Clara, CA. He continued his education at the University of Florida under the direction of William Jones. He is currently a postdoctoral research associate at RPI. His research interests are centered on mechanistic aspects of organic and organometallic chemistry.

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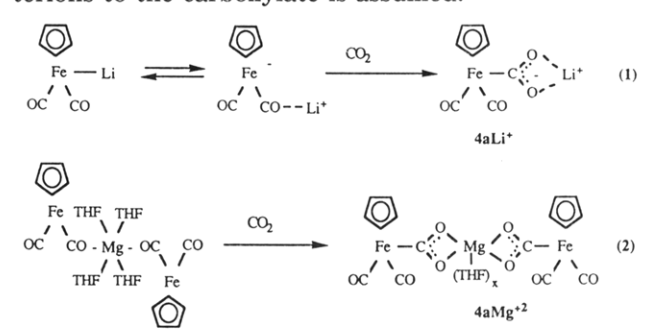
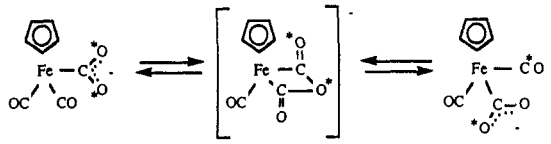
afford only 1:1 metal–CO_2 adducts; the stability of these adducts is counterion dependent and decreases in the order $Mg^{2+} > Li^+ > Na^+, K^+, NBu_4^+$. (3) The presence of excess CO_2 evidently accelerates this decomposition without incorporating itself into the products. (4) At room temperature complexes **4a** invariably degrade to Fp_2 and different amounts of FpH; reductive disproportionation[21] via a transitory 1:2 adduct Fp–C(O)OC(O)O^- collapsing to $FpCO^+$ and CO_3^{2-} does not occur. (5) Since the CO_2 adducts **4a** are too unstable to isolate, their structural assignment rests on interpretation of IR and ^{13}C NMR spectra data; chelation of the counterions to the carboxylate is assumed.



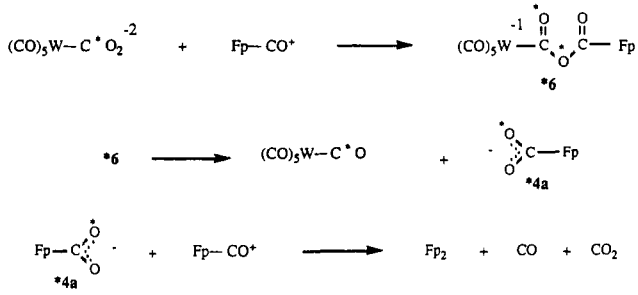
1. Metallocarboxylate Oxide Transfer

Metallocarboxylate **4aLi**$^+$ undergoes intramolecular oxide ion transfer between ligated CO_2 and CO. Using ^{13}C and ^{18}O labeling studies, Lee and Cooper[19a] demonstrated that **4aLi**$^+$ containing labeled carboxylate exchanges both ^{13}C and ^{18}O into carbonyl groups above −20 °C. The metalloanhydride **5** accordingly is a plausible intermediate.



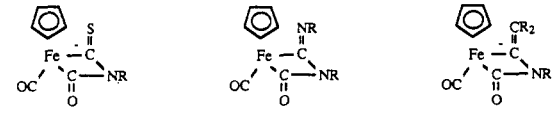
*5

Intermolecular oxide transfer between anionic η^1-C metallocarboxylates **2** and carbonyl ligands also occurs. Reacting $[(CO)_5W–C^{18}O_2]^{2-}2Li^+$[21] with $FpCO^+BF_4^-$ thus gives Fp_2 with significant label incorporation.[19b] A postulated WFe metalloanhydride species **6** accounts for the label shuttle; once the ^{18}O-carboxylate label transfers to the terminal carbonyls, the final Fp_2 product must contain label. Independently generated $FpCO_2^-$ (**4a**) reacts rapidly with the dissolving $FpCO^+$ to form Fp_2. At least three pathways can account for forming Fp_2 in the latter reaction: (1) collapse of another undetected metalloanhydride Fp–C(O)–O–C(O)–Fp and extrusion of CO_2 and CO, (2) one-electron transfer between $FpCO_2^-$ and $FpCO^+$, and finally, (3) electron transfer between Fp^- (which is in equilibrium with **4a**) and $FpCO^+$.



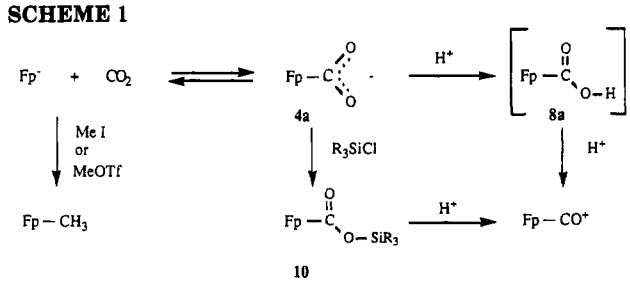
Similar intermolecular oxide transfer between the phosphine-substituted η^1-C metallocarboxylate Cp(PPh$_3$)(CO)Fe–CO_2^- (**4b**), which is prepared from Cp(PPh$_3$)(CO)Fe–$CO^+BF_4^-$ and aqueous KOH (vide infra), and $PPh_3(CO)_4Mn–CO^+BF_4^-$ has been proposed by Gibson.[33c]

Although not detected, the metalloanhydride **5** resembles other heterocumulene adducts of Fp^-. Fehlhammer reported that isothiocyanates,[22a] carbodiimides,[22b] and ketenimines[23] readily from 1:1 adducts with Fp^-. These exist as mixtures of the Fp η^1-C-coordinated heterocumulene (analogous to metallocarboxylate **4a**) and the Cp(CO)Fe [2 + 2] cycloadducts.

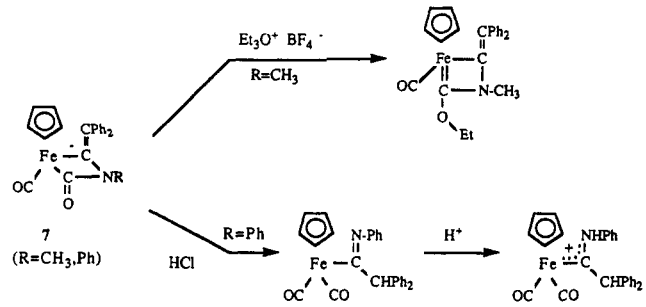


Examples of ketenimine [2 + 2] cycloadducts have been isolated, and their reactions with electrophiles have been explored. Depending on the reaction conditions,

SCHEME 1



compounds **7** either retain their ferraazetidine structures upon alkylation or acylation, or the ring opens and leaves a Fp(aminocarbene)$^+$ salt upon protonation.

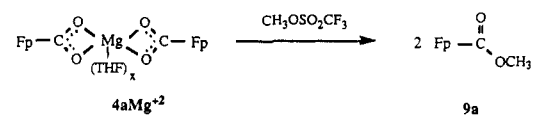


2. Metallocarboxylate Nucleophilicity

Reducing CO_2 to CO is the net result of protonating $FpCO_2^-$ (**4a**). Treating in situ generated **4aNa**$^+$[20a] or **4aMg**$^{2+}$[20b] with 2 equiv (or excess) of HBF_4 at −78 °C affords $FpCO^+BF_4^-$ in 90% isolated yield (Scheme 1). No attempt was made to detect the presumed Fp carboxylic acid intermediate **8a**. Other approaches to derivatizing **4a** are not nearly as straightforward. Attempts to alkylate the carboxylate oxygen on **4aLi**$^+$ or **4aNa**$^+$[18-20,24] to give a metallocarboxylate ester Fp–CO_2R failed. Treating **4aLi**$^+$ in THF solution (−78 to +20 °C) with methyl iodide, fluorosulfonate, or triflate (MeOTf), for example, quantitatively gives Fp–Me instead of the known[25] metalloester Fp–CO_2CH_3 (**9a**). These methylating agents apparently intercept Fp^- and drive an otherwise disfavored dissociative equilibrium (Scheme 1).

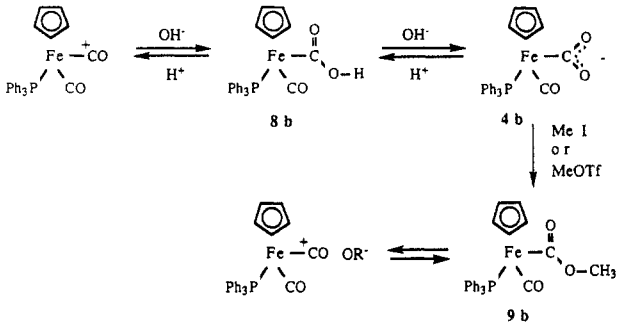
By switching to oxophilic trialkylsilyl chlorides, Giuseppetti and Cutler[24] derivatized both **4aLi**$^+$ and **4aNa**$^+$ as the metallocarboxylate trimethylsilyl and *tert*-butyldimethylsilyl esters **10** (60% isolated yields). The extremely robust Fp–$SiMe_3$ was not detected. Gladysz and co-workers[26] recently characterized [Cp(NO)(PPh$_3$)Re–CO_2]$^-$Li$^+$ as its Ph_3Sn and Ph_3Ge carboxylate esters Cp(NO)(PPh$_3$)Re–CO_2MPh_3.

The magnesium CO_2 adduct **4Mg**$^{2+}$, in contrast, alkylates at the carboxylate oxygen and gives **9a**. Treating **4aMg**$^{2+}$ with methyl triflate affords the methyl ester **9a** (70–80% yields) but only trace amounts of Fp–CH_3.[20b] Oxophilic Mg(II), by strongly bonding



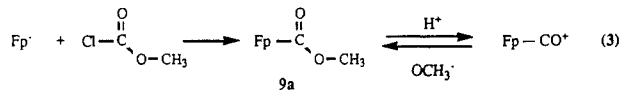
to (and presumably chelating) the carboxylate, blocks CO_2 dissociation. THF solutions of **4aMg**$^{2+}$ thus are inert to MeI at room temperature; any Fp_2Mg that would dissociate from **4aMg**$^{2+}$ would have given Fp–CH_3 immediately. An etheral solvent is required for

SCHEME 2



alkylating $\mathbf{4aMg^{2+}}$, since $\mathbf{4aMg^{2+}}$ (isolated by using THF–heptane) does not react with methyl triflate in CH_2Cl_2 solution.[27] The combination of the electron-rich Fp^- and oxophilic Mg(II) apparently serves as another example of Floriani's "bifunctional complexes" for stabilizing a transition-metal CO_2 complex.[28]

The methyl ester **9a** is a convenient starting material for preparing $Fp–CO^+$.[25c] Metalating methyl chloroformate with Fp^-Na^+ produces $Fp–CO_2CH_3$ (**9a**) (the ethyl ester is similarly available), and treating it in situ with acid gives the carbonyl salts $Fp–CO^+BF_4^-$ or $Fp–CO^+PF_6^-$ (eq 3). Silyl esters **10** likewise give $Fp–CO^+$ upon protonation (Scheme 1). Reacting $Fp–CO^+$ with methoxide regenerates **9a**, which can be isolated as a yellow solid that is stable in CH_2Cl_2 or THF solutions.[29]



3. Metallocarboxylic Acids

Examples of η^1-C metallocarboxylates **2** also are available through pH-dependent equilibria linking **2** with carbonyl and metallocarboxylic acid derivatives. Aqueous base converts $Fp–CO^+$ to mixtures of FpH and Fp_2; Pettit[30] additionally observed the unstable $Fp–CO_2H$ (**8a**)[25a,c,31] intermediate. Atton and Kane-Maguire nevertheless isolated the analogous metallocarboxylic acid $(\eta^5\text{-}C_6H_7)(CO)_2Fe–CO_2H$ in a similar reaction.[32] By using the phosphine-containing CpFe systems, Pettit[30] and Gibson[33] transformed the carbonyl salt $Cp(PPh_3)(CO)FeCO^+$ into isolable carboxylic acid **8b** and carboxylate **4b** derivatives (Scheme 2).

Metallocarboxylates $\mathbf{4bLi^+}$ and $\mathbf{4bK^+}$ are prepared by treating $Cp(PPh_3)(CO)_2Fe^+BF_4^-$ with LiOH or KOH (2 equiv) in cold aqueous acetone. Spectral data of the resulting thermally sensitive precipitates agree with the metallocarboxylate structure. (Synthesis of **4b** from CO_2 and $Cp(PPh_3)(CO)Fe^-$ has not been reported; the latter metalate is presently unknown.) Hydrolysis of $\mathbf{4bK^+}$ with aqueous HCl affords the fully characterized carboxylic acid **8b**, whereas either excess HBF_4 or 2 equiv of $Ph_3C^+BF_4^-$ (which converts to $Ph_3C–O–CPh_3$) transforms $\mathbf{4bK^+}$ to starting carbonyl salt. Partial hydrolysis alters $\mathbf{4bK^+}$ to a material Gibson[33c] tentatively formulated as the metalloanhydride $[Cp(PPh_3(CO)Fe–CO]_2O$.

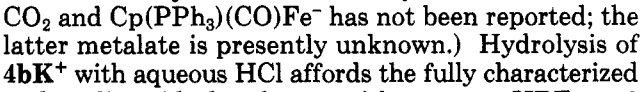
The presence of electron-releasing phosphines on the metallocarboxylate **4b** and its derivatives influences its reaction chemistry. Both methyl iodide and methyl triflate efficiently transform $\mathbf{4bK^+}$ to the methyl ester **9b** (70–85% yields).[33c] The ease with which the carboxylate oxygen on $\mathbf{4bK^+}$ alkylates, in contrast to the difficulty experienced with the Fp analogue **4a**, may be due to the more electron rich center on $\mathbf{4bK^+}$ retarding CO_2 dissociation. The phosphine on both the metallocarboxylic ester **9b** and the acid **8b** likewise facilitates their ionizing to ion pairs $Cp(PPh_3)(CO)Fe–CO^+OR^-$ in polar solvents.[30] Removing the CH_3CN or DMF solvent from **9b**, for example, and redissolving in CH_2Cl_2 reestablishes the covalent ester. This ionization accounts for the observed transesterification of esters $Cp(PPh_3)(CO)Fe–CO_2R$ by solvolysis in alcohols.[30,34]

Too much electron density on the iron center proves deleterious to forming metallocarboxylate esters. The presence of a second phosphine center on iron, $Cp(dppe)Fe–CO^+$ (dppe = $Ph_2PCH_2CH_2PPh_2$), reduces the electrophilicity of the ligand CO such that it does not react with hydroxide.[30] The same carbonyl salt also is the only product of reacting Cp(dppe)FeMgCl and CO_2.[35]

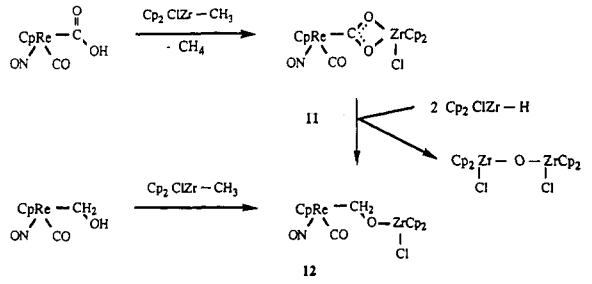
The few metallocarboxylic acids that have been characterized degrade by extruding CO_2 to leave the corresponding metal hydride complex. Ruthenium carboxylic acids $Cp^*(CO)_2Ru–CO_2H$[33d] and $Cp(PPh_3)(CO)Ru–CO_2H$[33a] and the molybdenum analogue $Cp(PPh_3)(CO)Mo–CO_2H$[33b] accordingly decarboxylate. The thermally robust $Cp(PPh_3)(CO)Ru–CO_2H$ decomposes to $Cp(PPh_3)(CO)Ru–H$ at 50–70 °C, whereas $Cp^*(CO)_2Ru–CO_2H$ and $Cp(PPh_3)(CO)Mo–CO_2H$ likewise deteriorate at room temperature. Carboxylic acid **8b**, however, decomposes at or above room temperature in benzene, THF, or acetone solutions to mixtures of $Cp(PPh_3)(CO)Fe–Fp$ and Fp_2,[33a] not to the stable hydride $Cp(PPh_3)(CO)Fe–H$.[36] Although further studies are required, these binuclear products and the results of other experiments involving **8b** can be accounted for by involvement of the 19e $Cp(PPh_3)Fe(CO)_2$ radical species.[37] Other examples of pH-dependent equilibria (cf. Scheme 2) involving characterized carbonyl salts–metallocarboxylic acids–metallocarboxylates include $Cp(PPh_3)(NO)Re–CO_2H$,[26,38] Cp(CO)(NO)Re–CO_2H,[39] and Cp- and $Cp^*(CO)(N_2Ar)Re–CO_2H$.[40]

4. Bimetallic CO_2 Complexes

Incorporating CO_2 as a bridging ligand in a bimetallic system $L_xM–CO_2–M'L_y$, a "bimetalloester", is of interest. Preliminary observations indicate that reactions between $FpCO_2^-$ ($\mathbf{4aLi^+}$, $\mathbf{4aNa^+}$) and organometallic Lewis acid precursors $Fp(THF)^+$, $Cp(CO)_3M(THF)^+$ (M = Mo, W), $Cp(NO)(CO)Re(THF)^+$, etc. provide Fp_2 as the only observed organoiron species, however.[41]

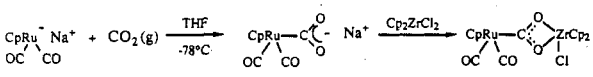


A more appealing bimetallocarboxylate synthetic target incorporates an electron-rich metal bound η^1-C and an oxophilic metal coordinating (perhaps chelating) the oxygens of CO_2. Indeed, the reactivity of heterobimetallic complexes such as $Cp(CO)_2Fe–ZrClCp_2$,[42] $Cp(CO)_2Ru–ThCl(Cp^*)_2$,[43] $Cp(CO)_2Ru–Ti(NMe_2)_3$,[44] and related species toward CO_2 should be examined. Tso and Cutler[45] did characterize the $ReZr\text{-}\mu\text{-}CO_2$ compound **11** and demonstrated its reduction to the bridging formaldehyde complex **12**.

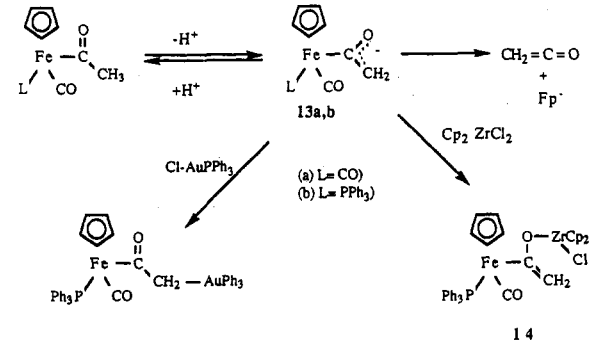


Independent syntheses of 11 and 12 depended on the sensitivity of the zirconium–methyl bond to protonolysis by the rhenium carboxylic acid and hydroxymethyl compounds, respectively. The chelating carboxylate structure illustrated for 11 is consistent also with spectral data for zirconocene carboxylates $Cp_2ClZrOC(O)R$.[45b]

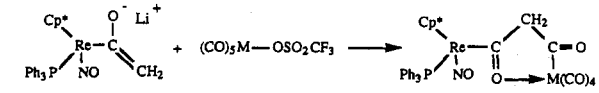
A stable heterobimetallic CO_2 complex $Cp(CO)_2Ru–CO_2–ZrClCp_2$ recently has been obtained from a CO_2-derived metallocarboxylate.[41] Treating $Cp(CO)_2Ru–CO_2^-Na^+$ with Cp_2ZrCl_2 at −78 °C affords this product in 70% yield; its spectral data are in accord with a chelating carboxylate structure analogous to 11. Under similar conditions, the less stable iron homologue $Cp(CO)_2Fe–CO_2–ZrClCp_2$ also forms.



Metalloenolates are useful models for metallocarboxylates, at least to the extent that ketene simulates the coordination chemistry of CO_2. Alkita and Kondoh[46a] deprotonated $Fp–COCH_3$ and found that the resulting enolate **13a** extrudes ketene above −50 °C. Attempts to intercept **13a** by using FpCl failed, even though the desired μ-ketene $Fp–COCH_2–Fp$ was independently prepared.[46b] The well-known (phosphine)-iron enolate **13b**[3] also decomposes above −20 °C. Floriani[47] nevertheless trapped it as the FeZr-μ-enolate **14** and as an $AuPPh_3$-substituted acetyl complex.



This synthetic approach for making bimetallic enolate (ketene) complexes is not general. O'Connor[48] reported that reacting a preformed rhenium enolate with manganese or rhenium triflates $(CO)_5M–OSO_2CF_3$ gives bimetallic μ-(η^1,η^2-malonyl) complexes, the products of enolate addition to a terminal carbonyl of the triflate species.



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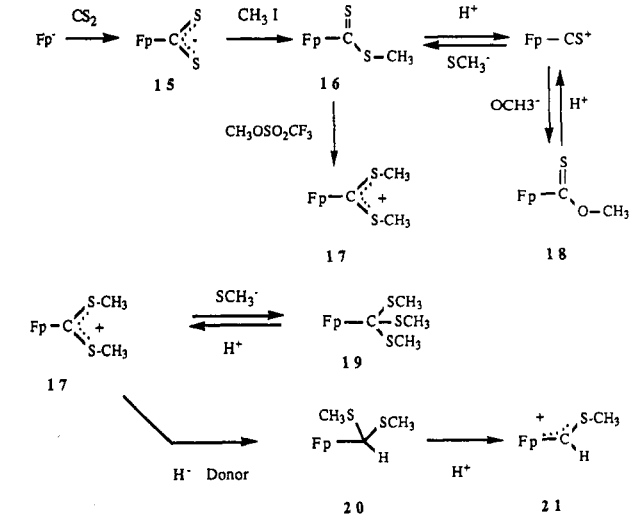

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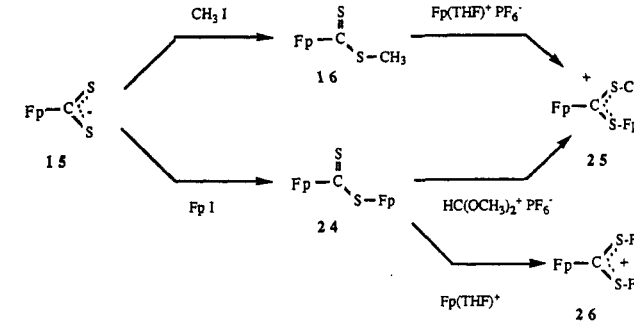


B. Dithiocarboxylate and Dithiocarbene Complexes

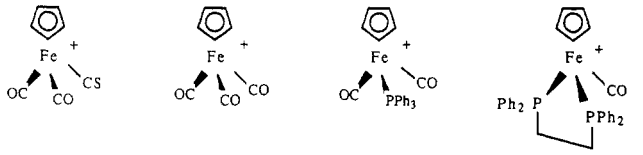
1. *Cp(CO)$_2$Fe(dithiocarboxylate)*

Information on binding (activating) and reducing CS_2[49] and CS,[50] in addition to being of intrinsic interest, may supply mechanistic details on the chemistry of ligated CO_2 and CO. Fp^- readily forms a 1:1 CS_2 adduct, $Fp–CS_2^-Na^+$ (**15**), for example, that is stable at −20 °C.[51] Although **15** has not been isolated, its spectral data and the results of derivatization studies (Schemes 3 and 4) are in accord with the η^1-C dithiocarboxylate structure.

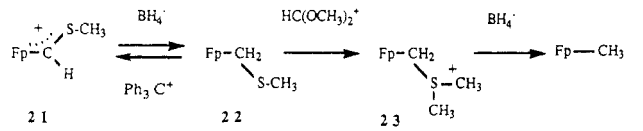
Dithiometalloester $Fp–CS_2CH_3$ (**16**) forms in THF solution after methylation of **15** with methyl iodide or methyl triflate;[51,52] it accordingly serves as a convenient starting material for other CpFe organosulfur compounds (Scheme 3). Protonating **16** affords the stable thiocarbonyl salt $FpCS^+PF_6^-$ in good yield,[52a,c] a procedure that was extended to the synthesis of the analogous ruthenium thiocarbonyl compound.[53] The thiocarbonyl ligand is quite susceptible to nucleophilic addition. Water readily hydrolyzes $FpCS^+$ to $FpCO^+$, and methoxide adds selectively to give the thioester **18**.[54,55a] Angelici further demonstrated that methylating **16** provides the dithiocarbene complex **17** (up to 87% yield) containing triflate and PF_6^- counterions.[52a,b,55] This very stable Fp(carbene)$^+$ complex is unusual in that it can be recovered intact from aqueous solution. Methyl thiolate, nevertheless, adds to **17** and gives the tris(methylthio)methyl compound **19**.[56] Hydride donors

reduce **17** to bis(methylthio)methyl complex **20**, which upon protonation affords the thiocarbene salt **21**.[55a,56b]

An X-ray crystallographic study of $FpCS^+PF_6^-$[57] completes the series of structural determinations on $Fp-CO^+PF_6^-$,[58] $Cp(PPh_3)(CO)_2Fe^+Cl^-\cdot 3H_2O$, and Cp-(dppe)$(CO)Fe^+BF_4^-$.[59] All structures adopt the ubiquitous "piano stool" array, with the iron centers approximating octahedral coordination. The CS is similar to CO as a π-acceptor ligand: the presence of CS does not measurably affect the Fe–CO bond length (1.81 Å) compared to the same bond in $Fp-CO^+$ (1.82 Å). In contrast, the Fe–CO bond length in the PPh_3- and dppe-containing carbonyl salts (1.77 and 1.74 Å, respectively) decreases substantially due to the presence of the electron-releasing phosphine centers.



The (methylthio)carbene complex **21** is a key intermediate in a study by Cutler and Menard on reducing $Fp(CS_2)^-$ (**15**) to $FpCH_3$.[60a] In an independent synthesis of $\mathbf{21}PF_6^-$, treating $FpCH_2SCH_3$ (**22**) with $Ph_3C^+PF_6^-$



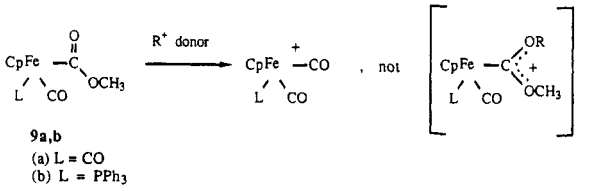
in the dark provides the CH_2Cl_2-insoluble, lemon yellow product (82% yield). Fully characterized $\mathbf{21}PF_6^-$ as previously reported,[56] is moisture sensitive, but otherwise stable at room temperature. Use of $Ph_3C^+BF_4^-$ in place of the PF_6^- trityl salt produces only very low yields of $\mathbf{21}BF_4^-$ (ca. 20%). Helquist[61] also recently reported the analogous preparation of $FpCHSPh^+PF_6^-$, as well as its X-ray structure determination. Reduction of $\mathbf{21}PF_6^-$ with $Ph_3MeP^+BH_4^-$ regenerates the (methylthio)methyl complex **22** (80% yield), which was activated as its known[62] sulfonium salt derivative $\mathbf{23}PF_6^-$ (76%).[60a] Finally, a second reduction in refluxing methylene chloride (1 h) affords $FpCH_3$ in 27% yield. Other hydride donors (e.g., $LiHBEt_3$, $KHB(O\text{-}i\text{-}Pr)_3$, and $LiAlH_4$) preferentially demethylate **23** and regenerate **22**.

2. Bimetallic μ-CS_2 Complexes

A distinctive feature of the Fp(dithiocarboxylate) system is the ease with which bimetallic derivatives form (Scheme 4). Ellis[51] first prepared the stable μ-CS_2 adduct **24** from the reaction of $FpCS_2^-$ (**15**) and FpI. A number of bimetallic and trimetallic CS_2 complexes derived from **15** and one or two other Fp, $Mn(CO)_5$, $Re(CO)_5$, or $W(CO)_5$ functionalities on the sulfur centers have since been prepared.[63] Bis-Fp **24**[51,63c] and tris-Fp **26**[63b] salts were synthesized and characterized independently by Menard and Cutler (Scheme 4)[60a] with the intent of activating the μ-CS_2 unit as a hydride acceptor. Isolated yields of **24** and **26** are in excess of 50% as yellow crystalline and black granular solids, respectively, that are light sensitive and moisture sensitive. A variety of hydride donors, including $LiHBEt_3$ (–78 °C), reduce **25** back to starting **16** (40% yield) plus $Fp-H/Fp_2$ mixtures and also degrade **26** to insoluble residues plus Fp_2 (16%).

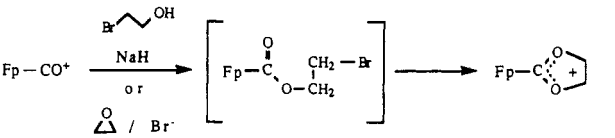
C. Dioxocarbene Complexes

Dioxocarbene complexes $Cp(L)(CO)Fe-C(OR)_2^+$, in principle, are the products of treating alkoxycarbonyl compounds with electrophilic alkylating agents. In general, electrophiles heterolytically cleave alkoxide from metalloesters $Cp(L)(CO)Fe-CO_2CH_3$ (**9a**, L = CO; **9b**, L = PPh_3). Both esters **9a** and **9b** either do not react or give their carbonyl salts upon treatment with carbocation reagents: Et_3O^+, Me_3O^+, $(MeO)_2CH^+$, $(MeO)_3C^+$, $(MeO)_2CCH_3^+PF_6^-$, $MeOSO_2F$, and $MeOSO_2CH_3$.[60b]

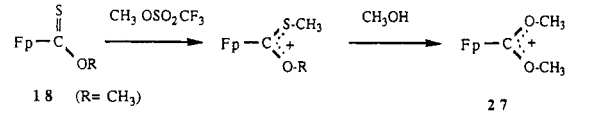


Under comparable conditions (1–2 equiv of carbocation reagent in CH_2Cl_2 at 0–22 °C), related acetyl compounds $Cp(L)(CO)Fe-COCH_3$ alkylate at the acetyl oxygen and give their established alkoxycarbene compounds $Cp(L)(CO)Fe{=}C(OR)CH_3^+PF_6^-$.[1a]

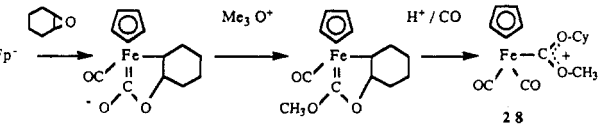
Several iron dioxocarbene complexes nevertheless are available and are actually quite stable. Neutral alkoxycarbonyl compounds do alkylate at the acyl O provided that a 2,5-dioxocyclopentylidene derivative forms.[64]



Angelici[55,65] also prepared the dimethoxycarbene compound **27** by methanolysis of mixed (methylthio)(alkoxy)carbene complexes. The desired **27** triflate salt

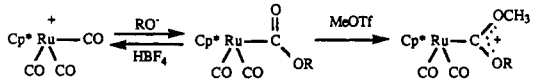


results in 89% yield as stable, pale-yellow crystals from methanol. Treating it with methoxide evidently generates the orthoester complex $Fp-C(OCH_3)_3$, which upon attempted isolation affords only $Fp-CO_2CH_3$ (**9a**) and Fp_2.[56a] Prolonged air exposure of **27** hydrolyzes it to $FpCO^+$. Rosenblum[66] prepared the iron dioxocarbene complex **28** after first reacting Fp^-Na^+ with cyclohexene oxide. The resulting β-alkoxide group then adds to an adjacent carbonyl ligand and provides the dioxocarbene ligand.



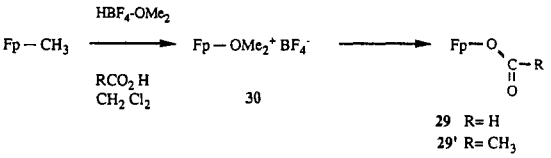
Ruthenium metalloesters recently have been reported that alkylate at the ester oxygen to give stable dialkoxycarbene complexes.[67] Treatment of $Cp^*(CO)_2Ru-CO_2R$ (R = Me, Et, *i*-Pr) with methyl triflate affords

the indicated dialkoxycarbene complexes (26–48% yields), whereas reactions with HBF_4, $Et_3O^+BF_4^-$, or Me_3SiOTf produce the starting carbonyl salt.



D. Formate and Dithioformate Complexes

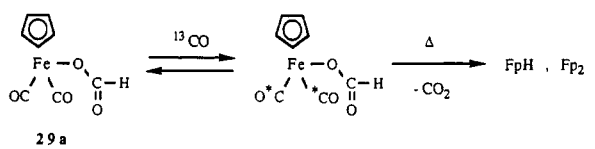
The η^1-O formate Fp complex **29** must be prepared by treating a Fp^+ source with formate ion, since CO_2 insertion using FpH is not observed.[68] Protonating $FpCH_3$ in the presence of a carboxylic acid is a reliable synthetic procedure for both **29** and its homologous η^1-O acetate compound **29′**.[69a] The resulting stable, red-



orange **29** was characterized as a covalent η^1-O formate complex also by X-ray crystallography.[68b,c] Interestingly, the Fp(dimethyl etherate)$^+$ **30** serves as the presumed intermediate in this preparative procedure. Todaro and Cutler[69b] demonstrated that protonating $FpCH_3$ with HBF_4·OR_2 in methylene chloride (−28 °C) produces the extremely labile etherate **30** and not the known[70] covalent fluoroborate $FpFBF_3$.

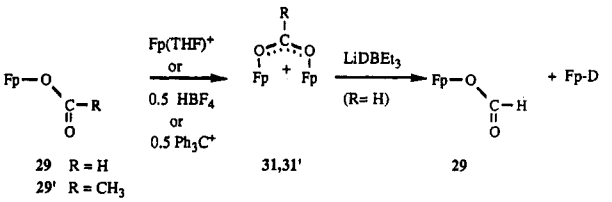
A similar procedure using HBF_4 in ether has been used by Werner and co-workers in converting molybdenum and tungsten methyl complexes, $Cp(CO)_3MCH_3$, into mixtures of acetate compounds $Cp(CO)_3M$–$OCOCH_3$ and η^2-(O,O′) $Cp(CO)_2M(O_2CCH_3)$. Warming these mixtures converts the η^1-O acetate into its chelating η^2-(O,O′) structure. An X-ray structure determination of $Cp(CO)_3W$–$OCOCH_3$ was reported.

An interesting property of the formate complex **29** is its high lability.[68b,c] Intermolecular CO exchange accordingly occurs in heptane solution at 50 °C, although the slower decarboxylation step eventually dominates.



Reversible CO dissociation from **29** evidently provides a vacant coordination site that is necessary to β-eliminate formate hydrogen to iron and extrude CO_2. Ligand dissociation from a metal center need not be a requirement for decarboxylating coordinated formate, however. The Re formate $Cp(PPh_3)(NO)Re$–OCHO, for example, decarboxylates to the hydride complex $Cp(PPh_3)(NO)Re$–H without phosphine dissociation and with retention of configuration on the rhenium center.[72]

Bimetallic μ-(η^1-O:η^1-O′)-carboxylate compounds are available by reacting a Fp^+ Lewis acid and a Fp–O–carboxylate.[69a] The resulting stable, red-orange solids, **31** and **31′**, are susceptible to bridge-cleavage reactions by iodide, PPh_3, and hydride donors. Treating bridging formate **31**, for example, with borohydride reagents furnishes **29** and FpH, whereas $LiDBEt_3$ and **31** afford only nondeuteriated Fp(formate) (**29**).



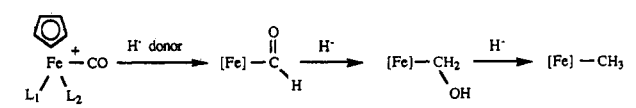
Deuteride transfer to the bridging formate and degradation (β-deinsertion of FpH/FpD) of a μ-(η^1-O:η^1-O′) *gem*-diolate Fp–OCHDO–Fp therefore can be ruled out. Hydride instead must transfer to the iron center of **31**. This transfer nevertheless transpires at the intact μ-carboxylate, because neither **31** nor **31′** reversibly dissociates in solution. Thus, redistribution of formate or acetate is not detected after **31** is mixed with **29′** (or **31′** with **29**), nor do **31** and **31′** cleave in acetonitrile solution to the nonlabile $Fp(CH_3CN)^+$ adduct.

Other homo- and heterodinuclear bridging formate complexes containing Fp, tungsten [$Cp(CO)_3W$], and rhenium [Cp(NO)(CO)Re] centers have been synthesized.[27] Reactions of the μ-carboxylates $[Cp(CO)_3W]_2$-(μ-formate)$^+$ and $[Cp(NO)(CO)Re]_2(\mu$-formate)$^+PF_6^-$ with $LiDBEt_3$ give results analogous to the reduction of **31**. It is worth noting that reduction of Cp_2ClZr–carboxylates using Cp_2ClZrH apparently generates an extremely labile μ-(η^1-O,O′) *gem*-diolate Cp_2ClZr–OCRO–$ZrClCp_2$.[45b,c]

Dithiocarboxylate analogues of the formate complexes **29** and **31** also have been characterized.[60a] Treating Fp–SC(S)H with a Fp^+ reagent gives the μ-dithiocarboxylate system Fp–SCHS–Fp^+, which upon reduction by $LiHBEt_3$ regenerates Fp–SC(S)H. The desired Fp–SCH_2S–Fp can be isolated independently as a stable product (38%) by the reduction of Fp–$CS^+PF_6^-$ with $Ph_3MeP^+BH_4^-$.[60a]

III. C_1 Chemistry: Ligands Containing the CO Unit

Carbon monoxide fixation—the reduction of ligated CO to formyl, hydroxymethyl, methyl, and related C_1 ligands[73]—has been observed with complexes of the type $CpFeL_1L_2(CO)^+$ (L_1 and L_2 = phosphine, phosphite, or CO). Experimentally, the general approach adopted involves treating an electrophilic metal carbonyl compound with a nucleophilic hydride donor, typically a borohydride or aluminohydride reagent. Depending on the precise choice of metal carbonyl substrate, hydride donor, and reaction conditions, reducing a coordinated CO then affords a formyl, hydroxymethyl, or methyl ligand. Initial hydride transfer often produces the formyl compound.



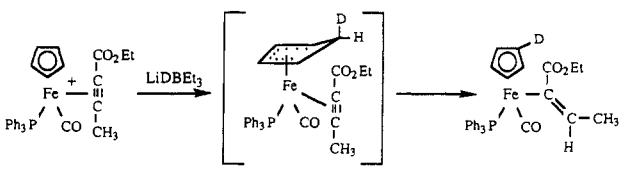
The regiochemistry of this hydride transfer in many cases varies, however, and as indicated in Table 1 hydride also adds to the Cp ring, to the metal center (with net displacement of CO), or to an unsaturated ligand L.

TABLE I

electrophilic carbonyl complex	reducing medium	products	ref
$Cp(CO)_2Fe-CO^+BPh_4^-$	$NaBH_4$/THF (−20 °C)	Fp–H, then Fp_2 (75%)	78
$Cp(CO)_2Fe-CO^+BF_4^-$	1.5 $NaBH_4$/THF (−10 °C)	Fp_2 (37%)	79
$Cp(CO)_2Fe-CO^+PF_6^-$	$NaBH_4$/acetone (−80, +22 °C)[a]	Fp–CHO, Fp–H, Fp_2	80
$Cp(CO)_2Fe-CO^+PF_6^-$	$NaBD_4$/acetone (−80, +22 °C)[a]	Fp–CDO, Fp–D, Fp_2	80
$Cp(CO)_2Fe-CO^+BF_4^-$	1.0 $NaBH_3CN$/THF (22 °C)	$(\eta^4\text{-}C_5H_6)Fe(CO)_3$ (21%)	82, 20a
	1.0 $NaBD_3CN$/THF (22 °C)	$(\eta^4\text{-}C_5H_5\text{-}exo\text{-}D)Fe(CO)_3$ (25%)	82
$Cp(CO)_2Fe-CO^+BF_4^-$	1.0 $NaBH_3CN/CH_3NO_2$ (22 °C)[a]	$(\eta^4\text{-}C_5H_6)Fe(CO)_3$ (quant)	20a
	1.0 $PPh_3Me^+BH_3CN^-/CH_2Cl_2$ (22 °C)[a]	$(\eta^4\text{-}C_5H_6)Fe(CO)_3$ (quant)	20a
$Cp(CO)_2Fe-CO^+BF_4^-$	1.0 $NaBH_3CN/CH_3OH$ (22 °C)	$Fp-CH_2OCH_3$ (40%), Fp–H	20a
	1.0 $NaBH_3CN/CH_3OH$ (0 °C)	$Fp-CH_2OH$, Fp–H	20a
$Cp(CO)_2Fe-CO^+BF_4^-$	4.0 $NaBH_3CN/CH_3OH$ (25 °C)	$Fp-CH_2OH$ (35–45%)	87
$Cp(CO)(PPh_3)Fe-CO^+(H_2O)_2Cl^-$	$NaBH_4$/THF (−10 °C)	$(\eta^4\text{-}C_5H_6)Fe(CO)_2PPh_3$ (75%)	78
$Cp(CO)(PPh_3)Fe-CO^+$	$NaBH_4(NaBD_4)$/THF[b]	$(\eta^4\text{-}C_5H_5\text{-}exo\text{-}D)Fe(CO)_2PPh_3$	106
$Cp(CO)(PPh_3)Fe-CO^+PF_6^-$	$LiAlH_4$[b]	$(\eta^4\text{-}C_5H_6)Fe(CO)_2PPh_3$ and $Cp(CO)(PPh_3)Fe-H$ (19:2)	103
$Cp(CO)(PMe_3)Fe-CO^+PF_6^-$	$LiAlH_4$[a,b]	$Cp(CO)(PMe_3)Fe-CHO$, then $Cp(CO)(PMe_3)Fe-CH_3$	103
Cp(dppe)Fe–$CO^+PF_6^-$[c]	3.0 $LiAlH_4$/1:1 THF–CH_2Cl_2 (−78 °C)[d]	Cp(dppe)Fe–CHO, then $Cp(CO)(\eta^1\text{-dppe})Fe-H$ (75%)	98, 102
	3.0 $LiAlD_4$/THF–CH_2Cl_2 (−78 °C)	$Cp(CO)(\eta^1\text{-dppe})Fe-D$ (70%)	102
	4.0 $LiAlH_4$ ($LiAlD_4$)/THF (70 °C)	$(\eta^4\text{-}C_5H_5\text{-}exo\text{-}D)Fe(dppe)(CO)$ and $Cp(dppe)Fe-CD_3$ (2:3)	102b, 104
$Cp(PPh_3)_2Fe-CO^+PF_6^-$	10.0 $LiAlH_4$ ($LiAlD_4$)/1:1 THF–CH_2Cl_2 (−78 °C)	$Cp(CO)(PPh_3)Fe-D$ (74–84%)	102b, 103
Cp(dmpe)Fe–$CO^+PF_6^-$[e]	$LiAlH_4$[b]	$Cp(dmpe)Fe-CH_3$	103
$Cp^*(CO)_2Fe-CO^+PF_6^-$[f]	$NaBH_4$/THF (20 °C)[a,b]	$Cp^*(CO)_2Fe-H$ (20%) and $Cp^*(CO)_2Fe-CH_2OH$ (80%), then $Cp^*(CO)_2Fe-CH_3$ (80%)	95
	$NaBH_4/CH_2Cl_2$ (20 °C)	$Cp^*(CO)_2Fe-CH_2OH$ (80%)	95
$Cp^*(CO)_2Fe-CO^+PF_6^-$	1.0 $Cp^*(CO)_2Fe-H$/THF (20 °C)	$Cp^*(CO)_2Fe-CH_2OH$ (10%), then $Cp^*(CO)_2Fe-CH_3$ (10%)	97
$Cp^*(CO)_2Fe-CO^+PF_6^-$	1.0 $(dppe)_2MoH_4$/THF (20 °C)	$Cp^*(CO)_2Fe-CH_2OH$ (15%)	97
$Cp^*(CO)(PMe_3)Fe-CO^+PF_6^-$	$NaBH_4$/THF (−60 to −20 °C)[a]	$Cp^*(CO)(PMe_3)Fe{=}CH(OH)$, then $Cp^*(CO)(PMe_3)Fe^+{=}CH(OBH_3^-)$, then $Cp^*(CO)(PMe_3)Fe-CH_3$	96
Cp*(dppe)Fe–$CO^+PF_6^-$	3.0 $LiAlH_4$/THF (−80 °C)[a,b]	$Cp^*(CO)(dppe)Fe^\bullet$, then $Cp^*(CO)(\eta^1\text{-dppe})Fe-H$	98
$Cp(CO)_2Ru-CO^+PF_6^-$	1.0 $K^+HB(i\text{-}Pr)_3^-$/THF (−90 °C)[a]	$Cp(CO)_2Ru-CHO$, then $Cp(CO)_2Ru-H$	99a
$Cp(CO)_2Ru-CO^+BF_4^-$	4.0 $NaBH_3CN/CH_3OH$ (25 °C)	$Cp(CO)_2Ru-CH_2OH$ (45–55%), then $Cp(CO)_2Ru-CH_2OCH_3$	87
Cp(dppe)Ru–$CO^+PF_6^-$	$LiAlH_4$/THF[a,b]	Cp(dppe)Ru–CHO, then $Cp(dppe)Ru-CH_3$	107
$Cp(PPh_3)_2Ru-CO^+PF_6^-$	$LiAlH_4$/THF (−78 °C)[a,b]	$Cp(CO)(PPh_3)Ru-H$	107
	$LiAlH_4$/THF (−30 °C)	$Cp(CO)(PPh_3)Ru-H$, $Cp(PPh_3)_2Ru-CH_3$, $(\eta^4\text{-}C_5H_6)Ru(CO)(PPh_3)_2$	107
$Cp^*(CO)_2Ru-CO^+BF_4^-$	3.0 $NaBH_3CN/CH_3OH$ (20 °C)	$Cp^*(CO)_2Ru-CHO$, then $Cp^*(CO)_2Ru-CH_2OH$ (60%) and $Cp^*(CO)_2Ru-H$	88
	1.0 $NaBH_3CN/CH_3OH$ (20 °C)	$Cp^*(CO)_2Ru-CH_2OCH_3$ (10%)	88
	1.0 $(PPh_3CuH)_6$/THF (20 °C)[g]	$Cp^*(CO)_2Ru-CHO$ and $Cp^*(CO)_2Ru-H$ (1:1)	88
	1.0 $LiHBEt_3$/THF (−78 °C)[a]	$Cp^*(CO)_2Ru^+{=}CHOBEt_3^-$, then $Cp^*(CO)_2Ru-H$ and $(Cp^*(CO)_2Ru)_2$	88
$Cp^*(CO)(PMe_2Ph)Ru-CO^+I^-$	1.0 $NaBH_4$/1:1 H_2O–THF (22 °C)[h]	$Cp^*(CO)(PMe_2Ph)Ru-CHO$ (95%)	88
$Cp^*(CO)(PEt_3)Ru-CO^+I^-$	1.0 $NaBH_4$/1:1 H_2O–THF (22 °C)	$Cp^*(CO)(PEt_3)Ru-CHO$	88
$Cp^*(CO)_2Os-CO^+BF_4^-$	2.0 $NaBH_4$/1:50 H_2O–THF (−30 °C)	$Cp^*(CO)_2Os-CH_2OH$ (86%)	91
	2.0 $NaBD_4$/1:100 D_2O–THF (−30 °C)	$Cp^*(CO)_2Os-CD_2OD$	91
$Cp^*(CO)(PMe_3)Os-CO^+I^-$	1.0 $NaBH_4$/THF (22 °C)	$Cp^*(CO)(PMe_3)Os-CH_3$ (93%)	99b

[a] Reaction monitored in situ by IR and/or ^1H spectroscopy. Stoichiometry, unless noted, was not reported. [b] Experimental details not published. [c] dppe is $PH_2PCH_2CH_2PPh_2$, η^2-ligated unless otherwise noted. [c] Diphosphines ($Ph_2PCH_2CH_2CH_2PPh_2$) and (+)-diop afford similar results. [e] dmpe is $Me_2PCH_2CH_2PMe_2$ (η^2-ligated); dppm ($Ph_2PCH_2PPh_2$) and *cis*-$Ph_2PCH{=}CHPPh_2$ afford similar results. [f] Reduction ($NaBH_4$) in aqueous THF (0 °C) quantitatively affords $Cp^*(CO)_2Fe-H$; neither $Cp^*(CO)(PPh_3)Fe-CO^+$ nor Cp*(dppe)Fe–CO^+ affords CO reduction products. [g] Quantitative yield of $Cp^*(CO)_2Ru-CHO$ in the presence of excess (9 equiv) 9,10-dihydroanthracene. [h] $(PPh_3CuH)_6$ as reductant also gives formyl.

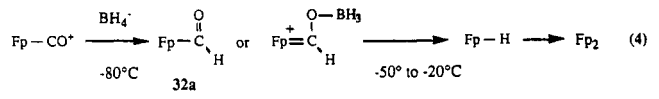
Some cationic CpFe–carbonyl compounds regioselectively reduce at ligands other than CO. Compounds $CpFeL_1L_2(CO)^+$ in which L_1 is an alkene, alkyne, or alkoxycarbene ligand and L_2 is CO, phosphine, or phosphite exclusively add hydride to L_1.[74] One pertinent observation concerning these reactions is that the kinetic product may not be apparent, at least in the absence of labeling studies.[75] In recent studies, Reger[76] demonstrated that reduction of an alkyne complex to its η^1-vinyl derivative involves hydride adding exo to the Cp ring. Subsequent internal delivery of endo hydrogen from the η^4-cyclopentadiene intermediate to the η^2-alkyne gives the observed product.



Development of preparative procedures for CO fixation on $CpFeL_1L_2(CO)^+$ compounds benefited from results of similar ongoing research with CpRe complexes. This reduction of ligated CO on Cp(L)(NO)-Re–CO^+ (L = CO, PPh_3) as well as the subsequent C_1 ligand reaction chemistry has been thoroughly documented and recently reviewed.[34b,38,77]

A. CO Fixation: Hydroxymethyl–Alkoxymethyl–Methyl Complexes

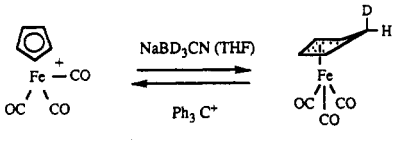
The reductive chemistry of $FpCO^+$ illustrates the interplay between choice of hydride donor and reaction conditions on the regioselectivity of hydride transfer. Treatment of $FpCO^+$ with $NaBH_4$ in THF[78,79] or methanol[20a] immediately evolves gas (CO) and forms FpH, although Fp_2 is the only organometallic product isolated at room temperature (eq 4). By conducting



(4)

this reaction in acetone at −80 °C and monitoring by ^1H NMR spectroscopy, Brown and co-workers[80] detected an absorption at δ 14.25, which is diagnostic of the formyl complex **32a** or its BH_3 adduct. Between −50 and −20 °C, the hydride resonance (δ −11.78) for Fp–H increased at the expense of the formyl absorption. Only Fp_2 was detected at room temperature, consistent with the observation that borane residues facilitate the decomposition of Fp–H to Fp_2. Fp–H nevertheless, is moderately stable in hydrocarbon and ether solvents.[84] The use of $NaBD_4$ gives Fp–C(O)D, an observation that is consistent with hydride delivery directly to the carbonyl group.

Sodium cyanoborohydride, on the other hand, transfers hydride exclusively to the Cp ring of $FpCO^+$ in THF[82] or in nitromethane[20a] solution to give the η^4-cyclopentadiene complex $(\eta^4\text{-}C_5H_6)Fe(CO)_3$ (**33**). Whitesides further demonstrated that deuteride ($NaBD_3CN$) stereoselectively adds exo to the Cp ring.[82]

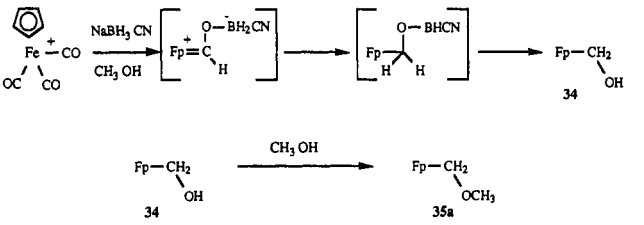


33-D

The η^4-cyclopentadiene complex **33** does not decompose to Fp–H under the aforementioned reaction conditions.[79,82] Only after heating above 80 °C does $(\eta^4\text{-}C_5H_6)Fe(CO)_3$ (**33**) degrade (to Fp_2) via an intermolecular free-radical mechanism. Under this condition, the ^2H-labeled η^4-cyclopentadiene complex **33-D** gives Fp_2 with most (85%) of the label removed. Under photolytic conditions, however, **33** converts to Fp–H via a reaction involving expulsion of a terminal carbonyl and internal delivery of the η^4-ring endo hydrogen to the iron.[83] Whitesides further established that photolyzing $(\eta^4\text{-}C_5H_5\text{-}exo\text{-}D)Fe(CO)_3$ (**33-D**) affords initially $(\eta^5\text{-}C_5H_4D)Fe(CO)_2H$ and then $[(\eta^5\text{-}C_5H_4D)Fe(CO)_2]_2$ (with 93% ^2H retention).[82]

In alcoholic media, sodium cyanoborohydride reduces ligated CO directly to the η^1-hydroxymethyl ligand. Cutler and co-workers[20a] established that $NaBH_3CN$ in

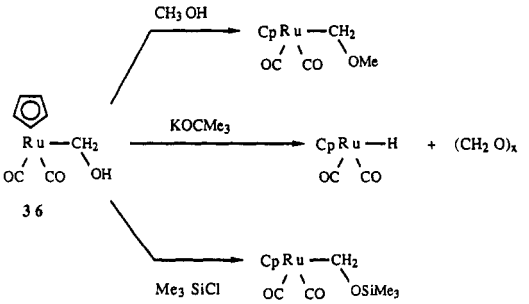
SCHEME 5



methanol converts an equimolar amount of $FpCO^+$ to the methoxymethyl complex $Fp\text{–}CH_2OCH_3$ (**35a**) (40% yield) and FpH. Neither $FpCH_3$ nor **33** was detected, although the hydroxymethyl compound $FpCH_2OH$ (**34**) appears during early stages of the reaction (Scheme 5). When conducted at 0 °C, this reaction gives primarily **34**, which was characterized by its IR and NMR spectra and by derivatization (using phenyl and ethyl isocyanate) as urethanes $Fp\text{–}CH_2OCONHR$. This reaction is useful in that quantities of **35a** (and of $Fp\text{–}CD_2OCH_3$, using $NaBD_3CN$) are readily available without recourse to metalating toxic chloromethyl methyl ether with Fp^-Na^+.[84-86]

Several stable iron and ruthenium hydroxymethyl complexes have been reported recently. Lin and coworkers[87] reacted $Fp\text{–}CO^+$ with excess $NaBH_3CN$ (4 mol equiv in methanol at 22 °C) and isolated the surprisingly stable alcohol $Fp\text{–}CH_2OH$ (**34**) as a solid (albeit contaminated with Fp_2) that decomposes slowly in solution. Its ^1H NMR spectrum in acetone-d_6 indicates coupling between the methylene group (δ 5.22, d, J = 6.8 Hz) and the hydroxyl (δ 0.91, br t, J = 6.8 Hz). The hydroxyl resonance disappears in D_2O as expected of an alcohol. The ruthenium analogue $Cp(CO)_2Ru\text{–}CH_2OH$ (**36**), which is much more stable than **34**, also was prepared. The cause of the discrepancy between using 1 equiv or excess sodium cyanoborohydride in reducing $FpCO^+$ is unclear, although Nelson[88a,c] has since made similar observations in reducing $Cp^*Ru(CO)_3^+$ to its hydroxymethyl/methoxymethyl complexes. Both $Cp^*(CO)_2Ru\text{–}CH_2OH$ and $Cp(CO)_2Ru\text{–}CH_2OH$ (**36**) are stable in solution, at least up to 60 °C in benzene.

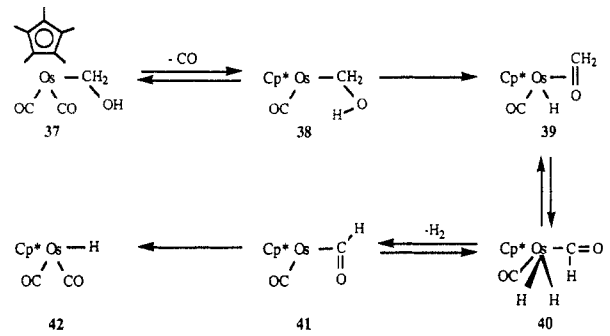
These examples of iron and ruthenium hydroxymethyl complexes undergo solvolysis in alcohols to give alkoxymethyl derivatives and they eliminate formaldehyde upon treatment with base, reactions that are observed with other transition organometallic hydroxymethyl complexes.[89]



Methanolysis of $Cp^*(CO)_2Ru\text{–}CH_2OH$ requires acid catalysis.[88a,c] This is consonant with an S_N1cA mechanism[90] in which the ruthenium-stabilized α-carbenium ion $Cp^*(CO)_2Ru\text{–}CH_2^+$ is an intermediate.

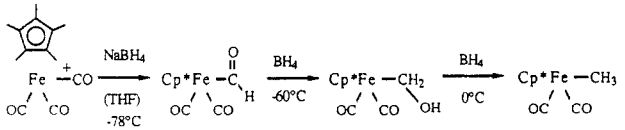
Ligand reactions of the extremely stable Os(II) hydroxymethyl compound $Cp^*(CO)_2Os\text{–}CH_2OH$ (**37**),

SCHEME 6



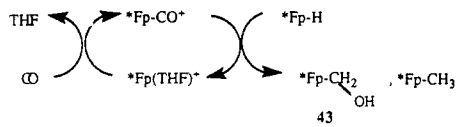
available by reducing $Cp^*Os(CO)_3^+$ with $NaBH_4$ in aqueous THF, were studied extensively by Graham.[91] Both photolysis of **37** in THF (ambient conditions) and refluxing an *n*-decane solution (bp 174 °C) cleanly eliminate CO plus H_2 and give $Cp^*(CO)_2OsH$. The thermal reaction follows first-order kinetics, and the results of a labeling study (photolysis of $Cp^*(CO)_2Os–CD_2OD$ and of $Cp^*(CO)_2Os–CD_2OH$) are consistent with the mechanism advanced in Scheme 6. Salient observations are that **37** loses CO in the rate-determining step and that the hydride ligand on **42** originates from the methylene group. The β-deinsertion step (**38** to **39**) is well-known for analogous alkyl complexes that activate a β C–H bond and extrude alkene under thermal[36a,c,92] or photochemical[9] conditions. Oxidative addition of ligated formaldehyde to give a formyl hydride complex (e.g., **39** to **40**) likewise has precedent.[93] The significance of Graham's proposed mechanism (Scheme 6) is that it corresponds to the microscopic reverse of the pathway commonly advanced for homogeneous hydrogenation of carbon monoxide using transition organometallic catalysts.[73,94]

Reduction of a carbonyl group to the methyl ligand also has been observed (Table 1). With $Cp^*Fe(CO)_3^+$, for example, 3 equiv of sodium borohydride in THF (−78 °C) affords $Cp^*(CO)_2Fe–CH_3$ in 90% yield.[95,96] By monitoring the reaction by ^1H NMR spectroscopy, Lapinte and Astruc observed the sequential buildup of formyl complex (δ 13.72), hydroxymethyl **43** (methylene doublet, δ 4.02, J = 3 Hz) above −60 °C, and methyl product (δ 0.23) above 0 °C. In contrast, the same reaction in methylene chloride stops at the hydroxymethyl **43** stage (72% yield), and $NaBH_3CN$ reduction in methanol gives just the hydride compound $Cp^*(CO)_2Fe–H$ (δ −11.74).



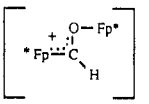
43

Reduction of $Cp^*Fe(CO)_3^+$ also is possible with $Cp^*(CO)_2Fe–H$ ($Fp^*–H$) as the hydride donor (1:1).[96b,97] In this case, the yield of $Cp^*(CO)_2Fe–CH_3$ ($Fp^*–CH_3$) decreases to 10%, and the THF adduct ($Fp^*(THF)^+$) forms as the byproduct. Lapinte and Astruc modified this reaction to give a catalytic cycle for fixing CO using $Fp^*–H$. Thus, $Fp^*(THF)^+$ (which exchanges THF for CO) and $Fp^*–H$ (1:10) interact to give the isolated hydroxymethyl **43** and methyl complexes. This reaction takes place at 40 °C under 1.2 atm of CO, and after 2 days it consumes 1.5 mol of CO per mol of $Fp^*(THF)^+$.

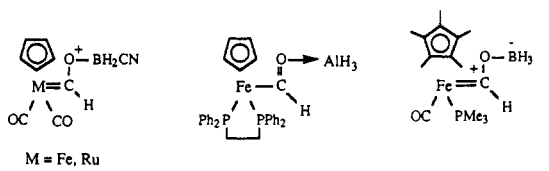


43

Further details on this interesting system are as yet unavailable, especially concerning the role of a postulated bimetallic μ-(η^1-C:η^1-O)formyl intermediate.



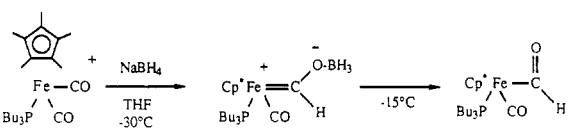
Unanswered questions remain concerning the reactions of borohydride reagents with electrophilic metal carbonyl compounds related to $CpFe(CO)_3^+$. What extent does the borane remaining after hydride transfer from a borohydride interact with the formyl complex and stabilize (or destabilize) it? The following intermediates have been formulated as examples of such adducts, albeit on the basis of limited spectral data (vide infra).



M = Fe, Ru

Precedent for these structures comes from the chemistry of the acetyl complexes $Cp(L)(CO)Fe–COCH_3$ (L = PPh_3, CO) with Lewis acids and from recent observations on the borohydride reduction of $Cp^*Fe(PBu_3)(CO)_2^+$.

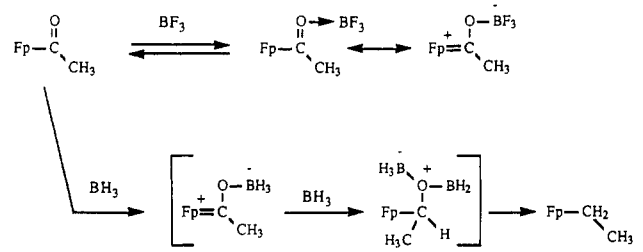
Astruc and co-workers[96] recently reported that borohydride reduction of $Cp^*(PBu_3)(CO)Fe–CO^+$ (−30 °C) initially gives mixtures of the formyl–borane adduct and the free formyl complexes. These structures are assigned by using ^1H and ^{13}C NMR spectral observations.



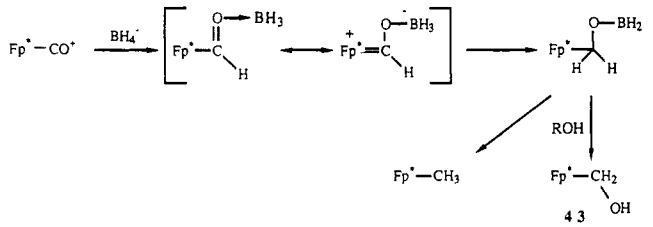
Above −15 °C, the borane adduct transfers borane to the solvent THF and leaves the free formyl compound. The presence of borane and presumably this formyl–borane adduct is required for producing methyl complex $Cp^*(PBu_3)(CO)Fe–CH_3$ as the ultimate product. Including triphenylphosphine in the reaction mixture sequesters the BH_3 byproduct and exclusively generates the hydride compound $Cp^*(PBu_3)(CO)Fe–H$. This hydride compound is the anticipated degradation product of the free formyl complex. In contrast, including excess borane (as BH_3·THF) in the reaction mixture diminishes the amount of $NaBH_4$ required to efficiently give the methyl complex to 1 equiv.

The reduction of organoiron formyl complexes by borane (BH_3) resembles analogous reactions reported for acetyl compounds. $Fp–C(O)CH_3$, although inert to $NaBH_4$ in THF at room temperature, interacts with excess borane in CH_2Cl_2 and gives the fully reduced ethyl complex. The mechanism postulated by Van Doorn, Masters, and Volger[100] (Scheme 7) assumes initial binding of BH_3 as a 1:1 adduct and involvement of a second borane molecule in deoxygenating the ligand. The Lewis basicity of organoiron acetyl complexes,

SCHEME 7



SCHEME 8



especially the formation of 1:1 adducts with boron and aluminum halides, has been documented thoroughly by Shriver's group[101] (Scheme 7).

A plausible pathway for reducing Fp*–CO^+ to the methyl complex Fp*–CH_3 with borohydride is outlined in Scheme 8. The initially formed formyl–borane adduct should function as a hydride acceptor. Either intramolecular hydride transfer (particularly in the presence of excess BH_3, Scheme 7) or intermolecular reduction by additional BH_4^- gives Fp*–CH_2OBH_2/Fp*–$CH_2OBH_3^-$. A second intermolecular or intramolecular hydride transfer, facilitated by the established (vide infra) sensitivity of this iron–methylene center of S_N1 and S_N2 displacement reactions, affords the methyl complex.

B. Formyl Complexes: Their Formation and Degradation

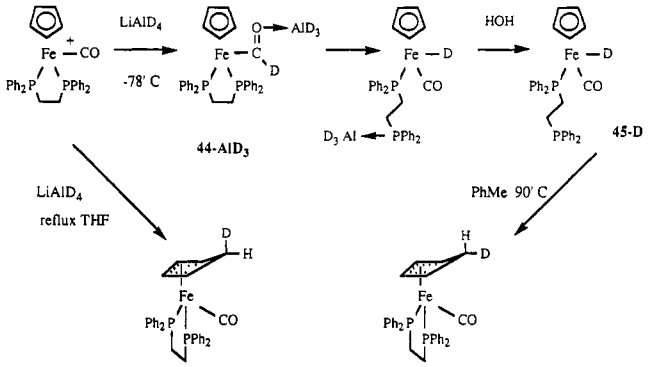
Synthesis and characterization of transition-metal formyl complexes, especially if the formyl ligand derives from CO and H_2, have been a major research topic for organometallic chemists for over a decade.[73,77a] Recent studies using CpFe and Ru systems, in fact, have played a major role in understanding the reaction chemistry of formyl complexes.

1. Hydride to Carbonyl Ligand Migratory Insertions

Davies has documented the reactivity of the unstable formyl complex Cp(η^2-dppe)Fe–CHO (**44**) (dppe = $Ph_2PCH_2CH_2PPh_2$) in an important series of papers. Treating the carbonyl salt Cp(dppe)$FeCO^+$ with excess lithium aluminum hydride at −78 °C generates the formyl·AlH_3 adduct.[102,103] Its formyl absorption in the ^1H NMR spectrum (THF-d_8) at δ 11.53 persists up to 0 °C. At higher temperatures, **44**–AlH_3 deinserts CO and gives the (η^1-dppe)iron hydride as its AlH_3 adduct. After hydrolysis, the stable product **45** is isolated in 75% yield.

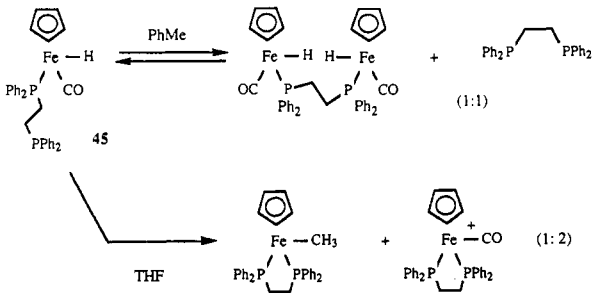
Scheme 9 depicts these transformations, but using $LiAlD_4$. The observation of iron deuteride **45**-D precludes the possibility of deuteride (hydride) adding exo to the ring, followed by the endo hydrogen transferring to the carbonyl and its subsequent decarbonylation.

SCHEME 9



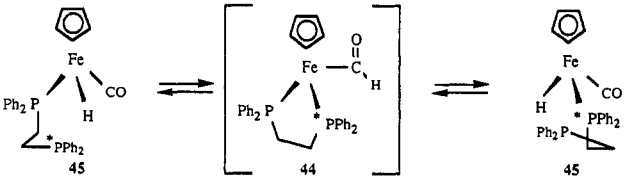
The reversible interconversion of the dppe ligand between η^1- and η^2(chelate)-bonding represents a significant driving force for reactions involving the iron hydride **45**. Heating the homologue **45**-D in toluene, for example, transfers the deuteron to the endo position of the η^4-cyclopentadiene compound, concurrent with an η^1-to-η^2 change in dppe binding. This internal delivery follows first-order kinetics and has a primary isotope effect of 1.0. For structural comparison, the fully characterized exo-D η^4-cyclopentadiene isomer is available by reducing the starting carbonyl salt with $LiAlD_4$ in refluxing THF.[104,106] Analogous carbonyl salts bearing bis(phosphine) chelates that are believed not to dissociate (e.g., $Me_2PCH_2CH_2PMe_2$) when reacting with $LiAlH_4$ give only their fully reduced methyl complexes (cf. Table 1).[103]

The iron hydride **45**, although a stable solid, is labile in solution at room temperature. In toluene, it equilibrates with the binuclear dihydride and free dppe. In THF solution, however, **45** slowly disproportionates into a mixture of methyl complex (30%) and starting carbonyl salt (60%).



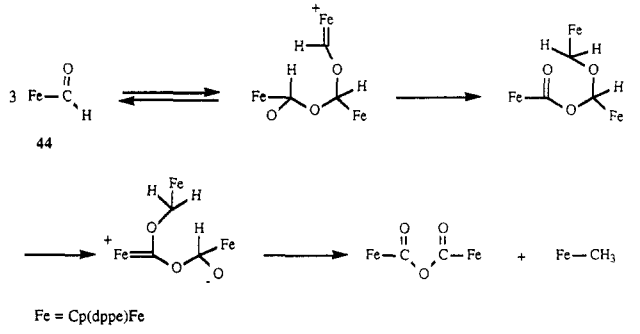
The dppe ligand again fulfills a special role, since the corresponding triphenylphosphine compound, Cp(CO)(PPh_3)Fe–H, is stable in THF solution.[102]

Davies further demonstrated that disproportionation of **45** requires its equilibration with the (η^2-dppe)iron formyl intermediate **44**.[102,105] This equilibrium best



accounts for the rapid exchange between the two phosphine centers on η^1-dppe that was observed via a $^{31}P\{^1H\}$ magnetization transfer experiment. Under the conditions of this experiment, exchange between η^1-coordinated dppe and free dppe does not occur. The

SCHEME 10

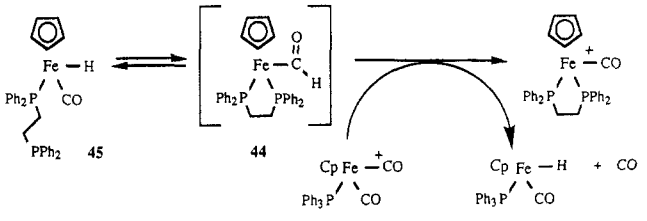


Fe = Cp(dppe)Fe

observed migratory insertion of the hydride to the carbonyl could be concerted with the η^1 to η^2 change in the dppe binding. The formyl complex **44** was not detected directly; nevertheless interconversion of **44** and **45** represents a rare example[109] of the equilibrium between a metal hydridocarbonyl and its formyl.

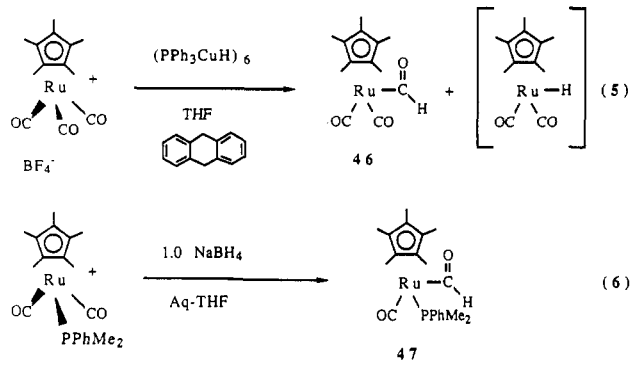
By assuming intermediacy of the formyl complex **44**, Davies postulated the mechanism outlined in Scheme 10 for disproportionating **45** to iron methyl and metallocarboxylic acid anhydride complexes. The latter produces the required 2 equiv of cationic carbonyl complex product in the presence of unidentified electrophiles. This disproportionation mechanism resembles Claisen–Tischtschenko pathways proposed for degradation of metal formyl complexes.[34b,110] Indeed, the electrophile-promoted disproportionation of $Cp(PPh_3)(NO)Re–CHO$ into a 2:1 mixture of carbonyl salt $Cp(PPh_3)(NO)Re–CO^+$ and methyl complex $Cp(PPh_3)(NO)Re–CH_3$ had been established.[38]

The iron hydride complex **45**, by reacting through its formyl isomer **44**, is a potential hydride donor.[102c] It reduces the carbonyl salt $Cp(PPh_3)(CO)_2Fe^+$ to $Cp(PPh_3)(CO)Fe–H$.



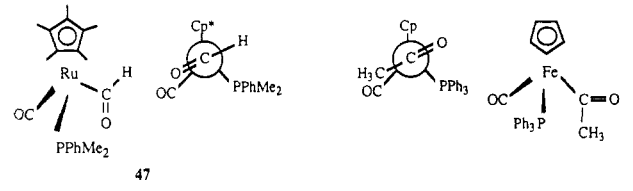
Hydride addition to a carbonyl ligand on $Cp(PPh_3)(CO)_2Fe^+$ presumably generates a transient formyl $Cp(CO)(PPh_3)Fe–CHO$[108,111] that deinserts CO and leaves the observed iron hydride. Neither (η^2-dppe)iron hydride, Cp(dppe)Fe–H, nor $Cp(PPh_3)(CO)Fe–H$ reacts with $Cp(PPh_3)(CO)_2Fe^+$. Other examples of transformylation reactions involving intermolecular hydride transfer between formyl and carbonyl ligands have been recorded.[77a,112]

Cp*Ru formyl complexes have been characterized at room temperature by Nelson and Sumner.[88] Formyl complexes **46** and **47** result from reducing the requisite cationic ruthenium carbonyl compounds with 1 equiv of copper(I) hydride $(PPh_3CuH)_6$ or of $NaBH_4$ (eq 5 and 6). The dicarbonyl formyl **46** generally contains variable concentrations of the ruthenium hydride [^{1}H NMR (C_6D_6): δ −10.2 (Ru–*H*); **46**, δ 14.0 (Ru–C*H*O)], which originates from **46** decomposing slowly in solution and especially during attempted isolation. The phosphine-containing formyl complex **47**, on the other hand, is much more stable (up to 40 °C in benzene solution);



Nelson and Sumner isolated it as pale yellow crystals in 95% yield.

Results of a recent X-ray structure determination of **47** are available.[88c] The syn conformation having a OC–Ru–CH–O torsion angle near 0° crystallizes preferentially, which may be attributed to the presence of the sterically bulky pentamethylcyclopentadienyl ligand. Other important structural features for **47** include a formyl C=O bond length (1.11 Å) that is even shorter than the terminal carbonyl C≡O (1.13 Å). These bond lengths are shorter than those reported by Cole-Hamilton[113] for the cationic ruthenium deuterioformyl compound *trans*-$(dppe)_2(CO)Ru–C(O)D^+SbF_6^-$, which has CO bond lengths of 1.19 Å (C=O) and 1.20 Å (C≡O). Both ruthenium formyl complexes retain relatively large formyl Ru–CH–O angles of 140° and 133°, respectively. Cyclopentadienyl organoiron acyl compounds $Cp(PPh_3)(CO)Fe–COR$, on the other hand, favor the anti conformation (OC–Fe–CR–O torsion angle near 180°) in the solid state, although both syn and anti conformers apparently are available in solution.[114]

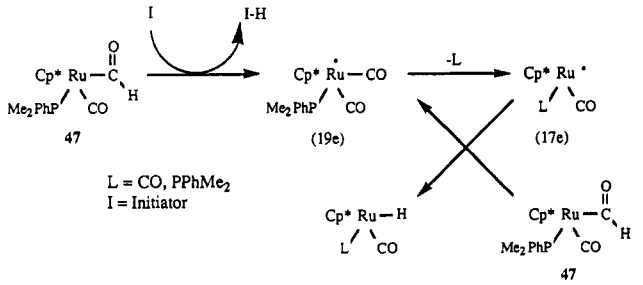


A more desirable structural comparison would be between **47** and its acetyl analogue. This information is not available, although such comparisons are available in three other cases: $[P(OPh)_3]_3(CO)_2Mn–COR$ (R = H, CH_3),[115a] $[P(OPh)_3(CO)_2Fe–COR$ (R = H, CH_3),[115b] and $Cp(PPh_3)(NO)Re–COR$ (R = H, $CHMeCH_2Ph$).[116] Two conclusions are drawn from these studies. (1) Pairs of analogous formyl and acetyl complexes exhibit similar crystal structures, with only minor geometric differences, and (2) formyl complexes studied to date all have relatively large formyl M–CH–O angles that fall between 126° and 140°. There is no apparent correlation between X-ray structure determinations of a diverse group of formyl complexes and their relative abilities to react as hydride (H^-) or hydrogen atom ($H^\bullet$) donors.

2. Formyl Complexes as Hydrogen Atom Donors: Free-Radical Chain-Transfer Reactions

Although the ruthenium formyls **46** and **47** degrade in solution to their hydride complexes, the expected deinsertion pathway (18e → 16e → 18e) involving unsaturated formyl intermediates[77a] does not prevail. The

SCHEME 11

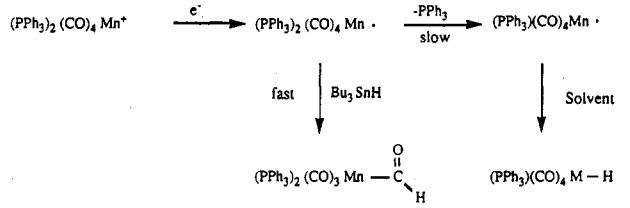


major decomposition route instead involves a free-radical chain reaction.[88b,c] Compound **47** decomposes slowly at 40 °C in benzene to a 1:1 mixture of $Cp^*(CO)_2RuH$ and $Cp^*(PMe_2Ph)(CO)RuH$. For both **46** and **47**, these degradations occur with varying and unpredictable rates. The presence of excess 9,10-dihydroanthracene (9,10-DHA), a known hydrogen atom donor, dramatically stabilizes the formyl compounds.

These observations signal a radical-initiated decomposition of a transition-metal compound.[117] Scheme 11 outlines a proposed free-radical chain pathway for the solution lability of **47**. Results of labeling studies using $Cp^*(PMe_2Ph)(CO)Ru–CDO$ (**47-D**) further establish that the 9,10-DHA does not involve itself directly in the degradative pathway: thermolysis of **47-D** in the presence of excess 9,10-DHA affords only ruthenium deuteride complexes $Cp^*(CO)(L)Ru–D$ (L = CO, PMe_2Ph).

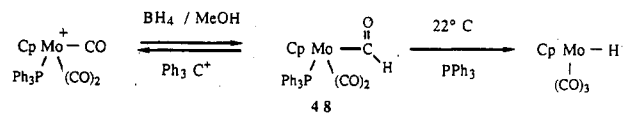
Transient 17e $Cp^*(CO)(L)Ru$ (L = CO, PMe_2Ph) and hypervalent 19e $Cp^*(CO)_2(PMe_2Ph)Ru$ free radicals[118] are proposed intermediates in the radical chain pathway of Nelson and Sumner[88b,c] (Scheme 11). The chain reaction starts with unidentified radical initiators abstracting a hydrogen atom from the starting formyl complex **47** and generating the 19e species. Nelson proposed that this labile 19e species dissociates either phosphine or CO (1:1) to give the 17e metal radicals. These chain carriers then abstract a hydrogen atom from **47** and give the observed ruthenium hydrides. Analogous hypervalent Fe(I) $Cp(CO)(L_1)(L_2)Fe$ species are proposed intermediates in several studies, a noteworthy example being work by Tyler on the photochemically induced disproportionation of Fp_2.[37b] The ruthenium formyl complexes **47** and **46** decompose primarily because they are hydrogen atom donors and the resulting 19e intermediates engage in radical chain reactions. The 9,10-DHA, also a hydrogen atom donor, thus stabilizes the formyls by trapping any radical initiators.

This radical chain pathway was proposed independently by Kochi[118a,119] for decomposition of several neutral and anionic formyl complexes to their corresponding metal hydrides. Both radical initiators (e.g., azobis(isobutyronitrile)) and photolysis dramatically promote these decarbonylation reactions whereas hydrogen atom donors (e.g., 9,10-DHA, Bu_3SnH) retard them. Kochi further demonstrated that Bu_3SnH transfers hydrogen atoms to 19e transition-metal carbonyls and generates their 18e formyl complexes.[120] For example, the 19e Mn^0 complex $(PPh_3)_2(CO)_4Mn$, generated by electrochemical procedures, affords the known[121] formyl $(PPh_3)_2(CO)_3Mn–CHO$ in the presence of Bu_3SnH. In the absence of H· donors, the degradation of the 19e system involves the 17e metal-centered Mn^0 radical $(PPh_3)(CO)_4Mn$.



Other potential hydrogen atom donors such as borohydrides, aluminohydrides,[122] and transition organometallic hydride reagents[123] may assist in forming and stabilizing metal formyl complexes. The results of a kinetics study by Halpern[124] are consonant with (porphyrin)RhH interacting as a hydrogen atom donor toward Rh(II) carbonyl adducts to give Wayland's[109a] rhodium porphyrin formyl complex. Other transition-metal hydride systems clearly transfer hydride to coordinated carbonyls.[94,125] These reactions, however, may involve one-electron reduction followed by hydrogen atom transfer to the carbonyl ligand as opposed to a direct hydride donation.

In the reduction of metal carbonyls, the choice of the reducing agent, solvent, and temperature are important considerations. The reduction of $Cp(PPh_3)Mo(CO)_3^+PF_6^-$ by borohydrides is a typical example. Treichel and Shubkin[126a] suggested in a very early study that excess sodium borohydride in THF reduces a carbonyl ligand on $Cp(PPh_3)Mo(CO)_3^+PF_6^-$ to give its methyl complex in 27% yield. For comparison, the same reaction using the analogous tungsten carbonyl gives $Cp(PPh_3)(CO)_2W–CH_3$ in 69% yield. Gladysz and co-workers[112a] found that treating $Cp(PPh_3)Mo(CO)_3^+PF_6^-$ with $LiHBEt_3$ in THF affords the formyl **48**, which according to ^1H NMR spectral evidence promptly decomposes above −40 °C. The extent to which BEt_3 (the $LiHBEt_3$ reduction byproduct) interacts with and stabilizes or destabilizes **48** is unknown.



Gibson[33b] performed the same reduction using $Et_4N^+BH_4^-$ or $Na^+BH_4^-$ in cold methanol and isolated a yellow precipitate, which was fully characterized as formyl complex **48** [87% yield; ^1H NMR (CD_2Cl_2 + $Et_4N^+BH_4^-$) δ 14.9 (d, J_{PH} = 4.0 Hz), CHO]. Although stable as a solid, **48** degrades to $Cp(CO)_3MoH$ in solution at room temperature. The presence of either excess phosphine or borohydride inhibits solution decomposition of **48**. Perhaps more importantly, BH_4^- does not further reduce isolated **48** to its methyl complex.

Once isolated, **48** is expected to react readily with BH_3 but not with BH_4^-, as is observed with its acetyl homologue.[100] Methanol as the reaction solvent of course efficiently removes the borane (BH_3) byproduct. Gibson's observation that BH_4^- stabilizes **48** is consistent with the borohydride, a hydrogen atom donor, blocking a radical chain decomposition pathway analogous to that advanced for $Cp^*(PMe_2Ph)(CO)Ru–CHO$ (**47**).

The thermal stability of the formyl complex **48** differs significantly from that of its acetyl analogue $Cp(PPh_3)(CO)_2Mo-C(O)CH_3$. This acetyl complex, which exists exclusively as the trans isomer, is stable to 70 °C in acetonitrile.[127] At this temperature, it smoothly decarbonylates to the methyl complex $Cp(PPh_3)(CO)_2Mo-CH_3$; phosphine dissociation is not evident during this thermal migratory deinsertion reaction.

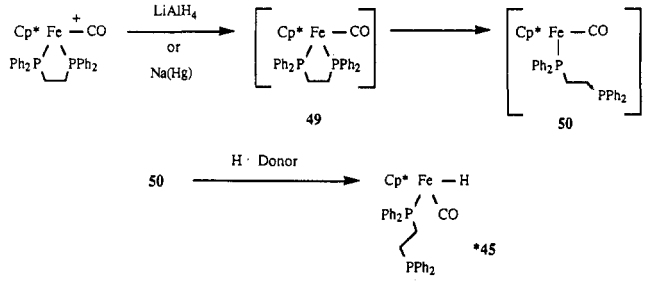
Gibson repeated the $Na^+BH_4^-$–THF reaction of $Cp(PPh_3)Mo(CO)_3^+$, as reported originally by Treichel and Shubkin,[126a] and observed only mixtures of the formyl **48** and hydride $Cp(CO)_3MoH$ complexes.[126b] Although the methyl complex was not obtained under these conditions, [48] undergoes subsequent acid-promoted disproportionation to the carbonyl cation $Cp(PPh_3)Mo(CO)_2^+$ and methyl complex $Cp(PPh_3)(CO)_2Mo-CH_3$ (2:1). It is worth noting that Treichel and Shubkin obtained this metal complex from the reaction mixture only after column chromatography on alumina. Their substantially higher yield of the analogous tungsten methyl complex (69%)[126a] indicates direct borohydride reduction of a carbonyl ligand on $Cp(PPh_3)W(CO)_3^+$ to a methyl group.

Similar observations on the stability of formyl complexes pertain to $Cp^*(PPh_3)(CO)_2Mo-CHO$[128] (**48**). Asdar and Lapinte obtained it as a 9:1 mixture of trans and cis isomers (90% yield) by $NaBH_4$ reduction of $Cp^*(PPh_3)Mo(CO)_3^+PF_6^-$ in THF. Formyl isomers trans-**48*** and *cis*-**48***, which do not interconvert in solution, were characterized spectroscopically. Both degrade to $Cp^*(CO)_3MoH$; *trans*-**48*** slowly loses PPh_3 above −20 °C, whereas *cis*-**48*** is stable to 50 °C.

The chromium formyl complex $Cp^*(P(OMe)_3)(CO)_2Cr-CHO$ recently has been reported.[128b] Treatment of $Cp^*(P(OMe)_3)Cr(CO)_3^+BF_4^-$ with $NaBH_4$ (1:1) in ethanol (−20 °C) affords this fully characterized formyl as a 1:1 mixture of cis and trans isomers. Both slowly decompose at room temperature (but at different rates) to *cis*-$Cp^*(P(OMe)_3)(CO)_2Cr-H$. The difference in hydride decomposition products observed for $Cp^*(PPh_3)(CO)_2Mo-CHO$ (**48***) and for $Cp^*(P(OMe)_3)(CO)_2Cr-CHO$ has been attributed to decreased lability of the ligated $P(OMe)_3$ vs PPh_3.

Several borohydride and aluminohydride reagents have been used in producing metal formyl complexes from their appropriate metal carbonyls. For these reactions, an initial nucleophilic bimolecular hydride transfer to the ligated carbonyl is assumed. An alternate mechanism involving one-electron reduction to the carbonyl substrate followed by hydrogen atom transfer should be also considered.[122]

This alternate pathway is evident when comparing the $LiAlH_4$ reductions of the iron carbonyl salts $Cp^*(dppe)Fe-CO^+$ and $Cp(dppe)Fe-CO^+$. With the latter, $LiAlH_4$ at −78 °C gives an orange solution containing the formyl complex Cp(dppe)Fe–CHO (**44**) or its AlH_3 adduct (Scheme 9) as the only detected organometallic species. Even though the product isolated at room temperature is the iron hydride $Cp(\eta^1\text{-dppe})(CO)Fe-H$ (**45**), direct hydride transfer to the carbonyl is favored. The Cp^* iron carbonyl salt under identical reductive conditions does not give a formyl complex.[98] Instead, a dark green solution containing paramagnetic species **49** and/or **50** results. These species afford the (η^1-dppe)iron hydride **45** at room temperature.



The same product results from sodium amalgam reduction of $Cp^*(dppe)FeCO^+$ followed by the addition of $LiAlH_4$. Compound **45** also can be obtained from the amalgam reduction of $Cp^*(dppe)FeCO^+$ in the presence of hydroxide (a hydrogen atom donor). A likely reaction pathway entails an initial electron transfer to form the 19e species **49**, followed by dissociation of a phosphine to form the 17e radical **50**. Finally, a hydrogen atom transfer to **50** gives **45**.[122] The $LiAlH_4$ reduction of $Cp(\eta^3\text{-}Ph_2PCH_2CH_2PPhCH_2CH_2PPh_2)Fe^+$ to $Cp(\eta^2\text{-triphos})Fe-H$ presumably proceeds by a similar pathway.[129]

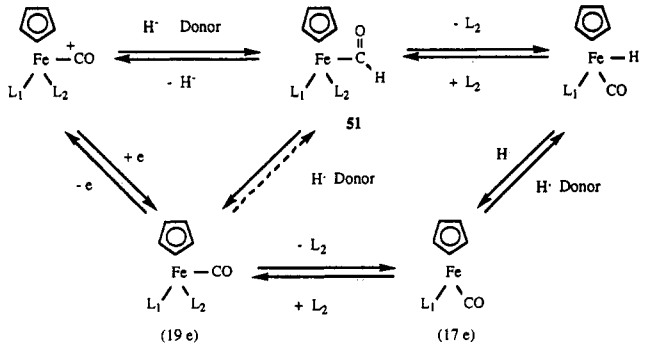
Coordinated ligand reactions noted for $Cp(L_1)(L_2)Fe$ complexes that concern the formation and degradation of formyl complexes are summarized in Scheme 12. The formyl complexes **51** typically originate from hydride transfer to an electrophilic carbonyl, from hydrogen atom transfer to a carbonyl ligated to a 19e metal radical, or from a metal hydride–CO migratory insertion. Not surprisingly, the microscopic reverse for each synthetic approach also presents a known decomposition path. The hydrogen atom decomposition pathway for **51**, for example, can be blocked by intercepting free-radical initiators with other hydrogen atom donors. Many electrophiles, including conjugate Lewis acids of main-group hydride donors, interact with formyl complexes. The extent to which these interactions inhibit CO deinsertion to give metal hydride or affect its hydrogen atom donating ability is unclear. These interactions can potentially activate the formyl ligand as a hydride acceptor (Schemes 5, 7, and 8).

C. Formyl Complexes: Miscellaneous Synthetic Approaches

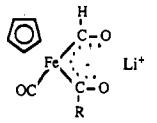
The alkoxycarbonyl ligand potentially offers a C_1 template that can be reduced to formyl or to alkoxymethyl ligands. Thorn reported that borane, BH_3, reduces the methoxycarbonyl group on $(PMe_3)_3(H)(Cl)Ir-CO_2CH_3$ to give $(PMe_3)_3(H)(Cl)Ir-CHO$.[93b] Results of preliminary studies involving reactions of the iron metalloesters $Cp(CO)_2Fe-CO_2CH_3$ (**9a**) and $Cp(PPh_3)(CO)Fe-CO_2CH_3$ (**9b**) with BH_3 and with AlH_3 have not been promising.[60b] Borane (as BH_3·THF or BH_3·SMe_2) reduces **9a** to Fp–H, whereas AlH_3 gives $Fp-CH_3$ (38% isolated yield). With either of these electrophilic hydride donors and under a variety of experimental conditions, **9b** quantitatively degrades to $CpFe(PPh_3)(CO)_2^+$.

Nucleophilic trialkylborohydride reagents have been used over many years to deliver hydride to a terminal carbonyl ligand on a neutral complex and generate an anionic formyl complex.[77a] Treating a selection of acyl complexes Fp–COR (R = CH_3, Ph, *p*-tolyl) with these

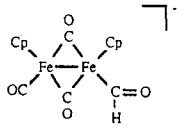
SCHEME 12



hydride donors at low temperatures affords the corresponding metallo-β-diketonate[13c] complexes.

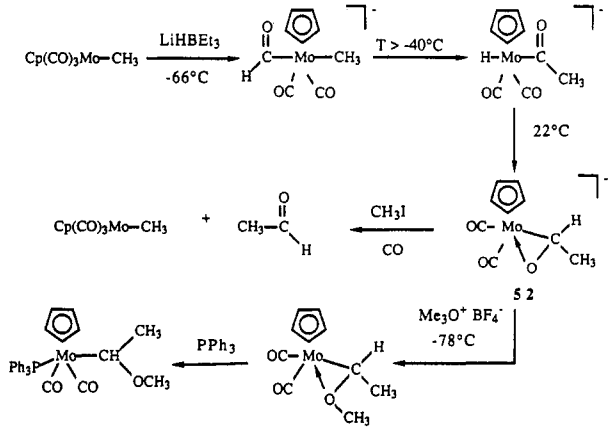


These compounds quickly decompose at room temperature, with the benzoyl derivative specifically degrading to benzyl alcohol plus Fp_2 and Fp^-.[130] The dimer Fp_2 also reacts with trialkylborohydrides (2 equiv) to ultimately generate Fp^-.[131] Although mechanistic studies are lacking, a bimetallic formyl anion is a likely intermediate.[131b]



Wong and Atwood[132] postulate a similar intermediate forming during $LiAlH_4$ destruction of Fp_2 (CH_4, C_2H_4, and C_2H_6 are the major products).

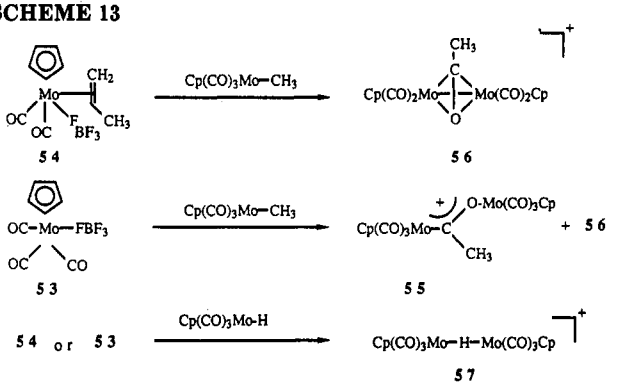
In related studies, Winter demonstrated tautomerization of a methyl formyl complex to its hydrido acetyl tautomer.[133]



The reaction between the molybdenum methyl complex $Cp(CO)_3Mo-CH_3$ and $LiHBEt_3$ initially provides its corresponding methyl formyl (^1H NMR δ 14.3, Mo–C*H*O), which tautomerizes to the hydrido acetyl (δ −5.2, Mo–*H*). At room temperature a metallaoxirane **52** prevails; methylating it under the appropriate conditions either releases acetaldehyde or delivers an α-methoxyethyl complex. The latter type of complex, an example of a reduced acetyl system, is discussed in section IVC.

Just as the interaction of electrophiles with metal alkyls facilitates their carbonylation,[134] this approach

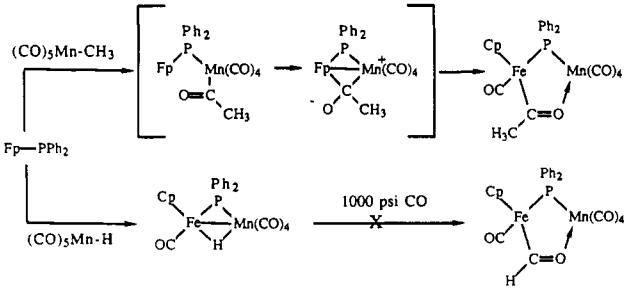
SCHEME 13



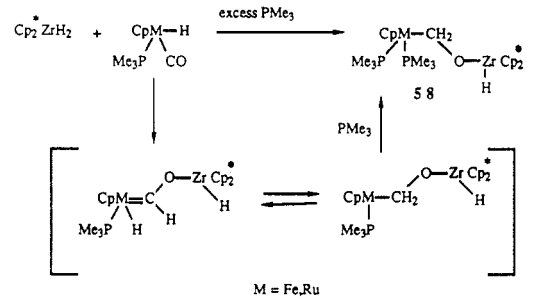
could facilitate the rearrangement of hydridocarbonyl complexes to formyl complexes. Promoting the alkyl migration to CO ligand requires that the main-group Lewis acid used (e.g., $AlBr_3$) must form an adduct with the carbonyl oxygen either on starting $L_nM(R)(CO)$ or on acyl intermediate $L_nM(CRO)$. Similar attempts at inducing analogous hydride migration, however, fail due to deleterious side reactions between the metal hydride and the necessarily strong Lewis acid.[101,135] Transition organometallic Lewis acids may yet prove to be a better choice for promoting metal hydride to CO migration, especially since the resulting bimetallic μ-formyl compounds should be more stable than corresponding mononuclear formyl complexes.[136]

Beck and Cutler have used the organomolybdenum electrophiles $Cp(CO)_3Mo^+BF_4^-$, $Cp(CO)_3Mo^+PF_6^-$ (**53**),[137-139] and $Cp(CO)_2Mo(FBF_3)(CH_2{=}CHCH_3)$ (**54**)[140] in promoting methyl to CO migration on $Cp(CO)_3Mo-CH_3$ to give μ-acetyl compounds **55** and **56** (Scheme 13). Lewis acids **53**, bearing one latent coordination site, and **54**, having two latent coordination sites, convert $Cp(CO)_3Mo-CH_3$ into either a mixture of bimetallic μ-(η^1-C:η^1-O)- and μ-(η^2-C,O)acetyl compounds (**55** and **56**) or just **56**, respectively. Interestingly, the molybdenum electrophiles stabilize the otherwise labile $Cp(CO)_3Mo-COCH_3$. In the absence of Lewis acids, this acetyl ejects CO and produces $Cp(CO)_3Mo-CH_3$.[134a,139] Reaction between $Cp(CO)_3Mo-H$ and either **53** or **54**[140,141] affords only the bridging hydride compound **57**.[142] Attempts at carbonylating **57** did not provide μ-formyl analogues of **55** and **56**.

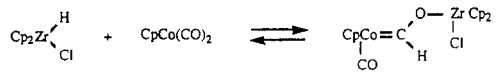
Geoffroy's[143] approach to synthesizing bimetallic acetyl and formyl compounds entails the reaction of the nucleophilic phosphide $Fp-PPh_2$ with $(CO)_5Mn-CH_3$ and $(CO)_5Mn-H$, respectively.[143a] A bimetallic μ-(η^1-C:η^1-O)acetyl compound forms in modest yield with $(CO)_5Mn-CH_3$. This structure can be accounted for by the indicated acyl ligand shift and binding of its oxygen to the more oxophilic manganese. The hydride $(CO)_5Mn-H$ under similar reaction conditions affords a μ-hydrido complex; attempted carbonylation returns unchanged μ-hydride complex.



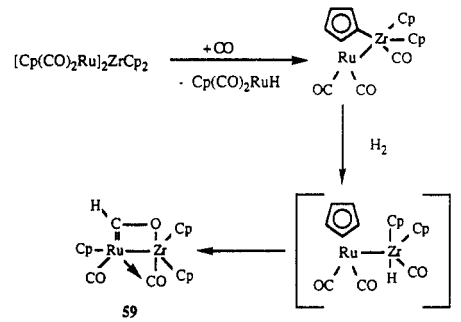
A heterobimetallic unit including an oxophilic early-transition-metal center, in addition to a CpFe or Ru group, offers greater potential for generating and possibly stabilizing bridging formyl or oxymethylene ligands. Bercaw[144] demonstrated that the zirconocene hydride $Cp^*_2ZrH_2$ reduces a ligated carbonyl on an iron or ruthenium hydride complex and gives the μ-oxymethyl compounds **58**.



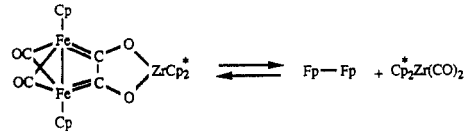
Intermediacy of a zirconoxycarbene, a μ-(η^1-C:η^1-O)-oxymethylene system, is plausible: a detectable CoZr μ-oxymethylene system results from reacting Cp_2ZrHCl with $CpCo(CO)_2$.[144]



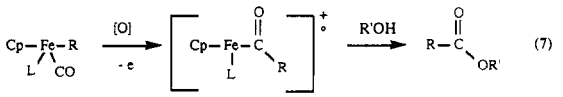
In recent studies, Casey[145] isolated a RuZr μ-zirconoxycarbene compound **59** by first carbonylating and then hydrogenating $[Cp(CO)_2Ru]_2ZrCp_2$.



Metal hydride functionalities are not required for forming zirconoxycarbenoid ligands, as evidenced by reversible complexation of $Cp^*_2Zr^{II}$ to Fp_2 as a dioxyzirconacyclopenta-3,4-diylidene unit.[146]



Another approach for generating metal formyl complexes entails promoting intramolecular hydride migration to the carbonyl ligand by one-electron oxidation. This, of course, assumes that initially formed 17e hydridocarbonyl complex does not preferentially lose a hydrogen atom.[147] Oxidatively induced alkyl to carbonyl ligand migration is well established for alkyl complexes Cp(CO)(L)Fe–R,[7] a particularly useful procedure being the carboalkoxylation reaction.[148]



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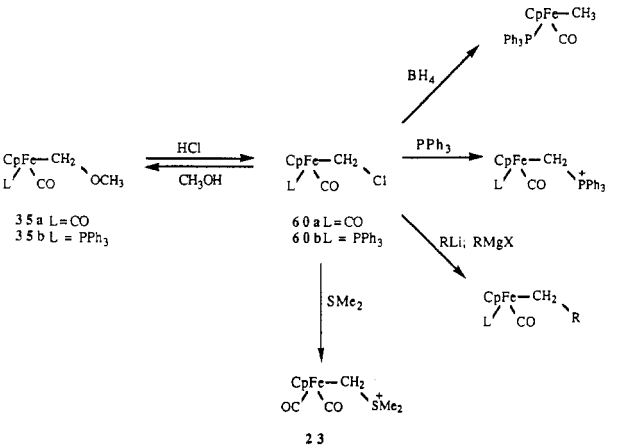
An attempt by Baird[149] to extend this reaction to Fp–H (using Cu(II) in methanol) failed to give the expected formate ester.

Some miscellaneous attempts at synthesizing Fp–CHO include reacting Fp^-Na^+ with acetic formic anhydride or with formyl fluoride.[150] In each case, only Fp_2 was detected, although the acetic formic anhydride reagent is used in generating manganese carbonyl formyl complexes.[151]

D. Alkoxymethyl-Derived Complexes

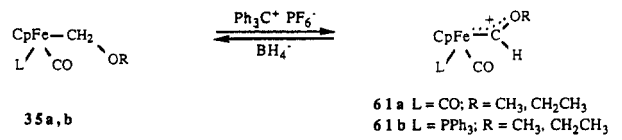
Methoxymethyl or ethoxymethyl CpFe complexes are useful substrates for a wide variety of coordinated ligand reactions. The starting PPh_3-substituted methoxymethyl complex **35b** is available from photolysis of $Fp–CH_2OCH_3$ (**35a**) in the presence of PPh_3.[90,152] Both **35a** and **35b** convert to their chloromethyl derivatives **60a**[84,153a] and **60b**,[90,152a] respectively, after brief treatment with gaseous HCl at 0 °C.



These chloromethyl complexes in turn are extremely reactive to nucleophilic displacement at the α-carbon; treatment with alcohols readily provides new alkoxymethyl complexes, for example. The acetoxymethyl complex $Fp–CH_2OC(O)CH_3$, also available from **60a**, is much less reactive than **60a** in solvolytic reactions.[154] There is no significant contribution of $Fp–CH_2^+$ ionization in ground-state configurations for $Fp–CH_2OC(O)CMe_3$, as shown by NMR studies (citing $^2J_{C-H}$ values),[155] or for the labile dimethylsulfonium salt $Fp–CH_2SMe_2^+$[156] (**23**) or $Cp(PPh_3)(CO)Fe–CH_2O$-methylate,[90b] as indicated by X-ray structure determinations. The preparative chemistry and reaction chemistry of the chloromethyl complexes $Cp(CO)_2RuCH_2Cl$,[153a,157] $Cp^*(CO)_2RuCH_2Cl$,[158] $Cp(CO)_3MCH_2Cl$,[153a,157] $Cp^*(CO)_3MCH_2Cl$ (M = Mo, W),[159] and $(CO)_5MCH_2Cl$ (M = Mn, Re)[153a,157] generally resemble that of the CpFe analogues **60a,b**.

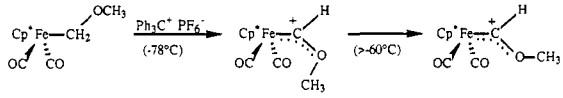
1. Alkoxymethylene Compounds

Alkoxymethylene compounds **61a,b** result in near-quantitative yield after treatment of η^1-alkoxymethyl complexes[35a,b] with trityl salts.[160] Both **61a** and **61b** are



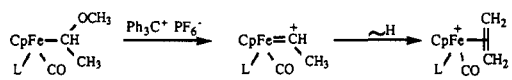
stable at room temperature, with the latter compound less susceptible to atmospheric hydrolysis. Other fully characterized methoxymethylenes prepared by similar reactions include $Cp^*(CO)_2M{=}CH(OCH_3)^+PF_6^-$ (M = Fe, Ru),[161] $Cp(PPh_3)(NO)Re{=}CH(OCH_3)^+OTf^-$,[38] and $Cp(CO)_3Mo{=}CH(OCH_3)^+PF_6^-$.[162] In contrast, $Cp(PPh_3)(CO)_2Mo{-}CH_2OCH_3$ affords the parent methylene salt under similar conditions.[163]

Lapinte and co-workers monitored the reactions between the iron and ruthenium methoxymethyl complexes $Cp^*(CO)_2M{-}CH_2OCH_3$ and $Ph_3C^+PF_6^-$.[161b] Both reactions occur instantaneously at −78 °C and produce mixtures of two geometric isomers, the anti-cis kinetic and the anti-trans thermodynamic products [in 90:10 (M = Fe) and 95:5 (M = Ru) ratios, respectively].



Upon warming, the kinetic products irreversibly isomerize to their anti-trans isomers. These geometric isomers correspond to restricted rotation about the carbene carbon–oxygen bond. The absence of syn isomers was determined by the results of NOE experiments. Both anti isomers maintain the preferred vertical or upright conformation.[175] (The dihedral angle between the Cp(center)–Fe–C(carbene) and O–C(carbene)–Fe planes approaches 0 °C.) This conformation has been defined in the solid state for $Cp(CO)_2Fe{=}CH(SPh)^+$; its X-ray structure determination further demonstrated an 80:20 mixture of anti-trans and syn-trans isomers.[61]

The observation that trityl carbocation selectively abstracts hydride instead of methoxide from methoxymethyl complexes **35a,b** does not extend to other CpFe–α-alkoxyalkyl complexes. Brookhart[164] previously demonstrated that $Ph_3C^+PF_6^-$ regioselectively abstracts methoxide from $Fp{-}CHPh(OCH_3)$. Bodnar and Cutler[165] showed that $Ph_3C^+PF_6^-$ likewise removes methoxide from CpFe–α-methoxyethyl complexes (**62**) (eq 8). Direct NMR spectral monitoring of the hydride

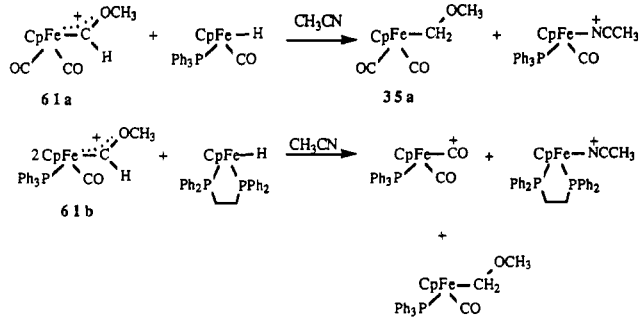


(8)

abstractions established that the ethylidene compounds **63** are kinetic products (for L = PPh_3, $P(OPh)_3$) that slowly convert to their η^2-ethylene complexes **64**. Interestingly, regioisomers $Cp(L)(CO)Fe{=}C(OCH_3)CH_3^+$ and $Cp(L)(CO)Fe(\eta^2\text{-}CH_2{=}CHOCH_3)^+$, representing formal hydride abstraction from α- and β-carbons of **62**, respectively, were not evident. The methoxycarbene complexes $Cp(L)(CO)Fe{=}C(OCH_3)CH_3^+$ (L = CO, PPh_3, and $P(OPh)_3$)[1a] and the $Fp{-}(\eta^2\text{-vinyl ether})^+$ $Cp(CO)_2Fe(CH_2{=}CHOCH_3)^+$ are well-known.[166]

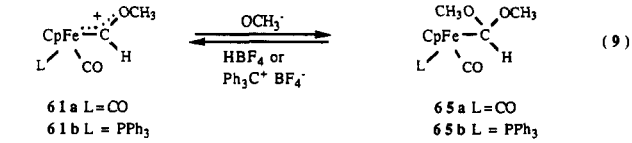
Alkoxymethylene compounds **61a,b** react like other metal alkoxycarbene complexes containing an electrophilic α-carbon;[167] they either add nucleophiles at the carbenoid α-carbon or undergo nucleophilic displacement of the *O*-alkyl group.[160,168] Thus **61a,b** readily add hydride to regenerate their alkoxymethyl complexes. Borohydride (BH_4^-) additionally provides varying amounts of the iron methyl derivatives, corresponding to borane (BH_3) reduction of initially formed alkoxymethyl complexes. This is confirmed by treating $Cp(PPh_3)(CO)Fe{-}CH_2OCH_3$ (**35b**) with $BH_3{\cdot}SMe_2$ (2 equiv) to generate $Cp(PPh_3)(CO)Fe{-}CH_3$.[160]

Transition organometallic hydride complexes are more selective in reducing **61a,b**.[169] The hydride com-



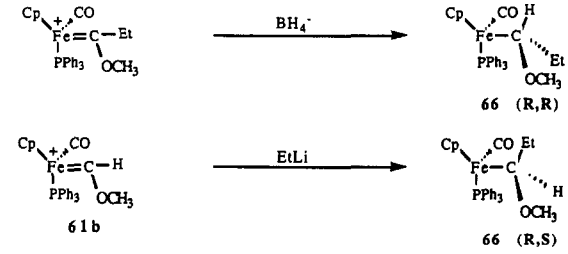
plex $Cp(PPh_3)(CO)Fe{-}H$ quantitatively reduces **61a** to its methoxymethyl derivative **35a**. In order to reduce **61b** a more nucleophilic reductant, Cp(dppe)Fe–H, is needed. This latter reaction, producing only half the expected methoxymethyl **35b**, entails nucleophilic attack at the *O*-methyl group to form Fp–CHO and methane (vide infra).

Other examples of nucleophiles adding to the methoxymethylene carbene compounds **61a,b** have been reported. In a recent study, Casey and Miles[170] established that a number of alkyllithium reagents cleanly add the carbanion to **61a** and deliver examples of α-methoxyalkyl complexes $Fp{-}CH(OCH_3)R$ (R = CH_3, *n*-Bu, Ph). Casey[171] also demonstrated that methoxide adds to both **61a** and **61b** to generate isolable formyl acetal complexes **65a** and **65b** (eq 9). Apparently methoxide does not add to $Cp(dppe)Fe{=}CHOCH_3^+$ under these conditions, undoubtedly due to dppe diminishing the electrophilicity of the carbenoid carbon.



(9)

Davies[172] documented that addition of ethyllithium to **61b** gives an α-methoxypropyl complex $Cp(PPh_3)(CO)Fe{-}CH(OCH_3)Et$ (**66**) with 30:1 diastereoselectivity

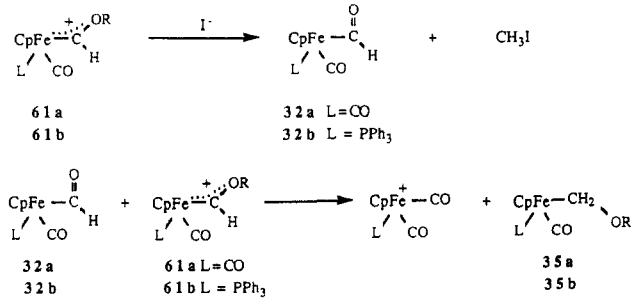


(favoring *RS* and *SR*). Their diastereomers (*RR*, *SS*), however, predominate (15:1) in the borohydride reduction of the ethylmethoxycarbene $Cp(PPh_3)(CO)Fe{=}C(OCH_3)Et^+$. The relatively high diastereofacial selectivity observed in both reactions is accounted for by the methoxycarbenes adding nucleophiles through a preferred conformation that orients the terminal carbonyl and methoxy substituents in an antiperiplanar

array. In this conformation the bottom face of the Fe=C(carbene) bond is shielded by a PPh_3 phenyl ring. Topside nucleophilic addition to the carbene ligand thus is favored.[3]

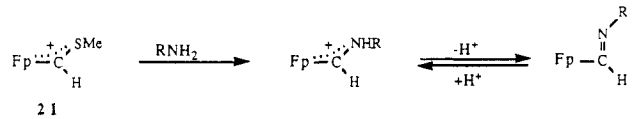
In the presence of methanol, diastereomers **66** (e.g., *RR* and *RS*) epimerize by ionizing and adding methoxide back to the transient ethylcarbene $Cp(PPh_3)(CO)Fe{=}CHEt^+$. Likewise, CD_3OH solutions of **66** incorporate the labeled methoxy group. Upon prolonged sitting, **66** in methanol eventually converts to the *trans*-methylvinyl complex $Cp(PPh_3)(CO)Fe{-}CH{=}CHCH_3$ via deprotonation of the same transient ethylcarbene complex.

Iodide dealkylates alkoxymethylene compounds **61a,b** and leaves the formyl complexes Cp(L)(CO)Fe–CHO (**32a**, L = CO; **32b**, L = PPh_3) as transient intermediates. One-half equivalent of iodide quantitatively dealkylates **61**. The resulting formyl **32** rapidly reacts with the remaining alkoxymethylene **61** to form a 1:1 mixture of the corresponding carbonyl salt and alkoxymethyl complex **35**.[160]



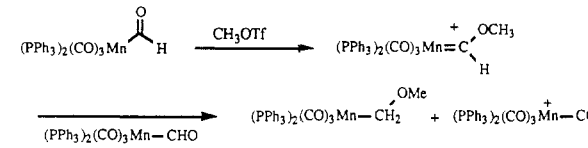
Results of control experiments are consistent with the pathway in which formyl complexes **32a,b** serve as hydride donors and starting **61a,b** are the preferred hydride acceptors.

A similar mechanism apparently operates during hydrolysis of the (methylthio)methylene salt $Fp{=}CH(SMe)^+OTf^-$ (**21**), which affords a 1:1 mixture of $Fp{-}CO^+$ and $Fp{-}CH_2SMe$ (**22**) ($Fp{-}CD_2SMe$ from $Fp{=}CD(SMe)^+$). Yu and Angelici[56b] postulated that an initial hydrolysis product, the formyl intermediate Fp–CHO (**32a**), transfers hydride to starting **21** and gives the observed products. In support of this mechanism, amines add to **21** and, depending on the reaction conditions, provide isolable aminomethylene and formimidoyl complexes.[173]



Several formyl complexes are known to alkylate at the formyl O and give isolabile methoxymethylene compounds. Lapinte[128] reported that the molybdenum formyl $Cp^*(PPh_3)(CO)_2Mo{-}CHO$ (**48***) upon treatment with $MeOSO_2F$ (−90 °C) and then PF_6^- metathesis affords $Cp^*(PPh_3)(CO)_2Mo{=}CH(OCH_3)^+PF_6^-$ containing a variable ratio of cis and trans isomers.

Gibson[121a] noted that methyl triflate converts the fully characterized formyl *mer,trans*-$(PPh_3)_2(CO)_3Mn{-}CHO$ into its methoxymethylene compound. This product reacts with 1 equiv of the starting formyl complex to give the methoxymethyl (78% yield) and cationic carbonyl (91%) compounds. The monophosphine formyl $(PPh_3)(CO)_4Mn{-}CHO$ also reacts with methyl



triflate, but the methoxymethyl complex $(PPh_3)(CO)_4Mn{-}CH_2OCH_3$ and the carbonyl salt $(PPh_3)Mn(CO)_5^+$ are the only products detected. Similar hydride transfer to a methoxymethylene ligand from a formyl complex has been postulated during the iodide cleavage of $Cp(L)(CO)Fe{=}CH(OCH_3)^+$ (**61a,b**)[160] and during the reaction of the rhenium formyl $Cp(PPh_3)(NO)Re{-}CHO$ with 0.5 equiv of $MeOSO_2F$.[38]

Cole-Hamilton[174] reported that the cationic ruthenium and osmium formyl complexes $(dppe)_2(CO)M{-}CHO^+$ undergo both protonation and methylation to generate their hydromethylene or methoxymethylene compounds, $(dppe)_2(CO)M{=}CH(OR)^{2+}(OTf^-)_2$, respectively. Reduction of these products with $(i\text{-}PrO)_3BH^-K^+$ yields hydromethyl and methoxymethyl derivatives $(dppe)_2(CO)M{-}CH_2OR^+$.

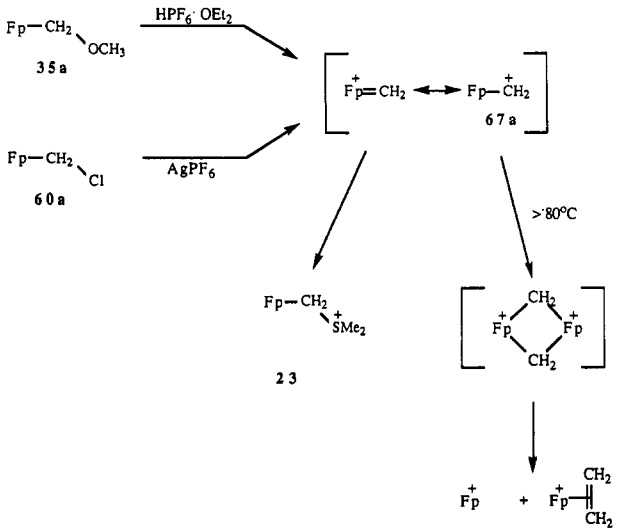
2. Methylene Compounds

The methylene complex $Fp{=}CH_2^+$ (**67a**),[84] generated from either Fp(methoxymethyl) (**35a**) or Fp(chloromethyl) (**60a**) systems (Scheme 14), is a transient intermediate that has not been detected spectroscopically.[164,175] Even at −80 °C, **67a** rapidly decomposes via an apparent disproportionation reaction[84,176] to Fp(η^2-ethylene)$^+$ and products derived from the unstable Lewis acid Fp^+, including $Fp{-}CO^+$. As deduced for the analogous disproportionation of other transition organometallic methylene complexes,[177] fragmentation of a dicationic 1,3-dimetallocyclobutane $[M{-}CH_2{-}M{-}CH_2]^{2+}$ accounts for the observed products. The $Fp{-}CH_3$ occasionally produced as **67a** degrades can be explained by **67a** abstracting hydride from starting **35a** or **60a** (vide infra) or from other sources.

The stabilizing effect of Cp* rings and phosphine ligands on electrophilic iron methylene complexes is readily apparent from the results of ^1H NMR spectroscopic studies. Although $Cp(CO)_2Fe{=}CH_2^+$ (**67a**) and apparently even $Cp(PPh_3)(CO)Fe{=}CH_2^+$ (**67b**) are quite unstable,[152,178] $Cp(dppe)Fe{=}CH_2^+$[152] in solution remains intact below 0 °C and survives brief exposure at room temperature.[179] By incorporating a Cp* group, Astruc and Lapinte were able to record ^1H NMR spectral data for $Cp^*(PPh_3)(CO)Fe{=}CH_2^+$ up to −10 °C[180a] and for $Cp^*(CO)_2Fe{=}CH_2^+$ up to −50 °C.[180b] These iron methylene systems are generated via ionization (using HBF_4 and HPF_6 etherates or trimethylsilyl triflate in CH_2Cl_2) of the requisite iron alkoxymethyl complex. They also have in common low barriers of rotation about the Fe=C bond (≤11 kcal/mol).

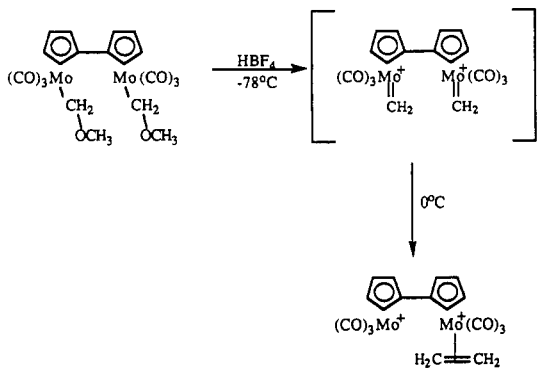
The variable-temperature ^1H NMR spectral data for $Cp^*(CO)_2Fe{=}CH_2^+$ are typical:[180b] at −90 °C the nonequivalent methylene hydrogens (δ 17.06, 16.38) correspond to the preferred vertical orientation of the methylene ligand (H–C–H plane orthogonal to the Cp* ligand plane). As the solution warms, these absorptions coalesce (T_c = −60 °C) to one time-averaged signal for the rapidly rotating methylene group. Upon further warming, $Cp^*(CO)_2Fe{=}CH_2^+$ degrades to the η^2-ethylene complex $Cp^*(CO)_2Fe(CH_2{=}CH_2)^+$;[161] the

SCHEME 14

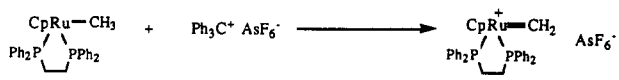


steric bulk of the Cp* ligand is not sufficient to block the bimolecular disproportionation pathway.[181]

Other electrophilic methylene compounds of note to this discussion include $Cp(CO)_3Mo{=}CH_2^+$,[84a,162,176] $Cp(CO)_3W{=}CH_2^+$,[182] and the $\eta^5{:}\eta^5$-fulvalene bis(methylene) compound.[177c]



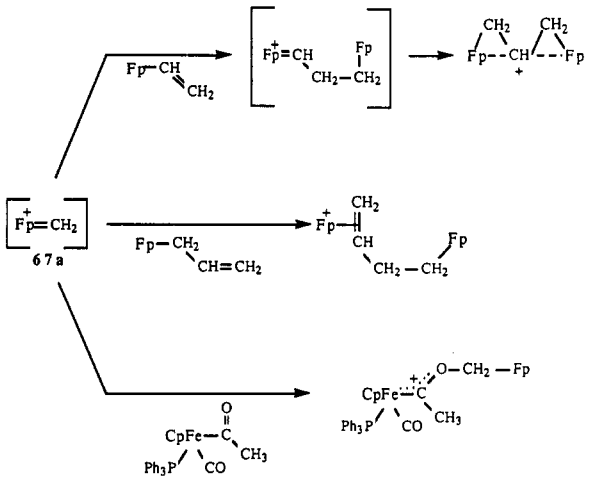
These are generated from chloro- and alkoxymethyl precursors at −78 °C and quickly treated with coreactant in order to minimize the extent of disproportionation reactions. Presence of a phosphine on the Mo or W center dramatically slows this disproportionation. Brookhart[163] accordingly reported results of variable-temperature NMR studies that followed the methylene ligand rotation on $Cp(PPh_3)(CO)_2Mo{=}CH_2^+$ (to −70 °C) and on $Cp(L)(CO)_2W{=}CH_2^+AsF_6^-$ (L = PEt_3, PPh_3) (up to −20 °C). These phosphine-substituted Mo and W methylene compounds as well as Cp(dppe)-$Ru{=}CH_2^+$, interestingly, are prepared by abstracting hydride from their methyl complexes.



Both the solution stability and the dynamics of the ruthenium–methylene rotation closely match those of the iron analogue.[179b] Gladysz also prepared Cp-$(PPh_3)(NO)Re{=}CH_2^+$ by abstracting hydride from the corresponding rhenium methyl complex; it was isolated at −23 °C and found to be stable up to 0 °C.[38,183]

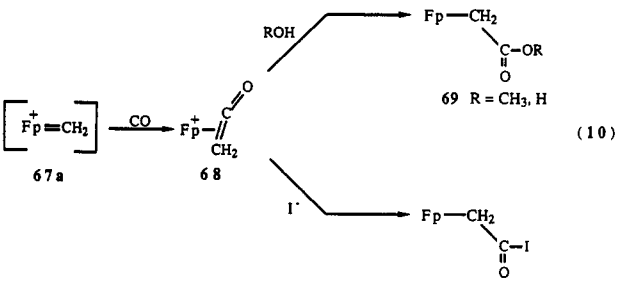
None of the cationic iron, ruthenium, molybdenum, tungsten, or rhenium methylene complexes noted thus far have been reported to degrade via electrophilic aromatic substitution of the methylene group at coordinated PPh_3[121a] or at the Cp ligand.[184]

Although $Fp{=}CH_2^+$ (**67a**) is a transient intermediate, it can be trapped and derivatized by using the appropriate nucleophiles. Dimethyl sulfide accordingly intercepts **67a** and provides adduct **23** (Scheme 14) in over 50% yield—it makes no difference whether Me_2S is added before or immediately after generating **67a** (from its chloromethyl precursor **60a** at −78 °C).[176] Under these conditions, none of the known complex $Fp{-}SMe_2^+$ (expected from complexing the disproportionation byproduct Fp^+) forms. Methylidene salt **67a** also alkylates unsaturated ligands.[176] Treating in situ generated **67a** with iron vinyl, η^1-allyl, and acetyl complexes affords the adducts indicated below in moderate yields.



This latter acetyl adduct is unstable, but the Cp-$(CO)_3Mo{=}CH_2^+$-derived analogue $[Cp(PPh_3)(CO)Fe{-}C(CH_3)O{-}CH_2Mo(CO)_3Cp]^+$ is fully characterized. Nucleophilic hydride donors reduce the acetyl adducts at the methylene carbon, generating methyl complex ($Fp{-}CH_3$ or $Cp(CO)_3Mo{-}CH_3$) plus starting acetyl compound.

Carbon monoxide (1–7 atm) also efficiently traps the methylidene compound **67a** as an isolable η^2-C,C′ ketene complex $Fp(CH_2{=}C{=}O)^+PF_6^-$ (**68**) (eq 10).[185] Spectral

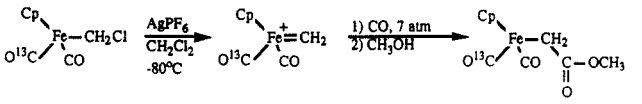


(10)

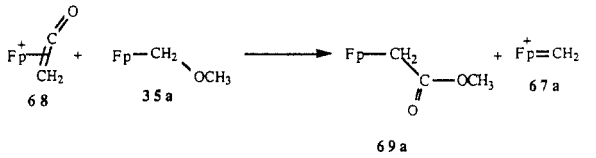
data are in accord with an unsymmetrically bound η^2-C,C′ structure, analogous to that reported for Fp-(η^2-vinyl ether)$^+$ compounds.[186] Although stable in dry nitromethane solution at room temperature, **68** is extremely reactive toward hydroxylic solvents: moisture or methanol affords the carboxylic acid or carbomethoxymethyl complexes **69**. Indeed, immediately quenching the carbonylation reaction with methanol gives **69** in over 90% isolated yields. Even iodide cleanly adds to **68** and generates the acyl iodide complex, an unexpected reaction since iodide readily dis-

places η^2-bound alkenes[187] and even vinyl ethers from their Fp^+ complexes.[188]

Exogeneous CO adds directly to this methylene center during the formation of **67**. Results of a ^{13}C-labeling study show that migration of ligated CO to this carbenoid center does not occur,[185] since none of the labeled terminal carbonyl on $Cp(^{13}CO)(CO)Fe-CH_2Cl$ ends up on the final carbomethoxymethyl ligand.

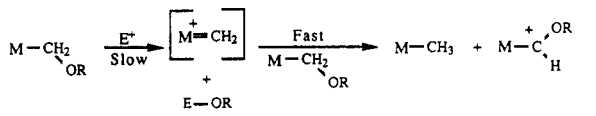


Ketene complex **68** abstracts methoxide from $Fp-CH_2OCH_3$ (**35a**) and quantitatively provides **69a**.[185]



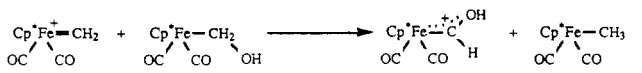
Since **68** forms from **67a** and CO, both complexes may potentially serve as chain carriers in the acid-promoted conversion of methoxymethyl complex **35a** to carboxymethyl complex **69a**, a formal carbonylation reaction.

Alkoxymethyl complexes also react with electrophilic methylene compounds. Although strongly electrophilic reagents abstract alkoxide from alkoxymethyl complexes, the resulting methylene compounds competitively abstract hydride from the starting alkoxymethyl complexes.



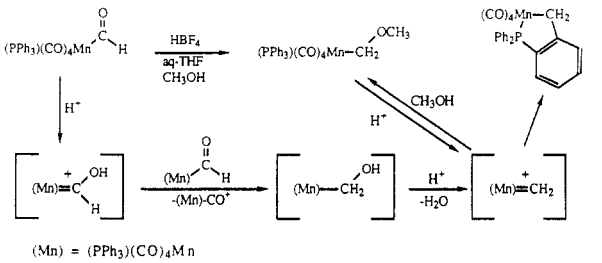
The final products, 1:1 mixtures of methyl and alkoxymethylene compounds, are the net result of alkoxymethyl disproportionation in the presence of an electrophile. Gladysz[38] first reported this disproportionation in the alkylation of $Cp(PPh_3)(NO)Re-CH_2OCH_3$ with CH_3OSO_2F. This reaction since has been extended to $Cp(PPh_3)(CO)_2Mo-CH_2OCH_3/Ph_3C^+AsF_6^-$;[163] $Cp(CO)_3Mo-CH_2OCH_3/Cp(CO)_3Mo=CH_2^+PF_6^-$;[162] $Cp(PPh_3)(CO)Fe-CH_2OCH_3/HBF_4\cdot OEt_2$;[178] $Cp^*(CO)_2Fe-CH_2OCH_3/HBF_4\cdot OEt_2$ or Me_3SiOTf;[161] $Cp(L)(CO)Fe-CH_2OCH_3$ (L = CO, PPh_3)/$Cp(CO)_3Mo^+PF_6^-$;[162] and $Cp(PPh_3)(CO)Fe-CH_2OCH_3/Fp=CH_2^+$.[189]

An analogous hydroxymethyl ligand disproportionation is involved in the synthesis of an iron hydroxymethylene complex. Guerchais and Lapinte[180b] reported that treating the hydroxymethyl $Cp^*(CO)_2Fe-CH_2OH$ with trimethylsilyl triflate (−90 °C in CD_2Cl_2) produces variable amounts of the hydroxymethylene $Cp^*(CO)_2Fe=CH(OH)^+$ and methylene $Cp^*(CO)_2Fe=CH_2^+$. This hydroxymethylene complex is independently generated by treating $Cp^*(CO)_2Fe=CH_2^+$ with the hydroxymethyl compound.



A similar pathway presumably occurs during the observed degradation of $Cp^*(CO)_2Fe-CH_2OH$ in polar solvents (CD_3OD or CD_3NO_2) to $Cp^*(CO)_2Fe-CH_3$ (50%).[161b] Other examples of hydroxymethylene complexes—$Cp(PPh_3)(NO)Re=CH(OH)^+OTf^-$,[38] *mer,trans*-$(PPh_3)_2(CO)_3Mn=CH(OH)^+BF_4^-$,[121a] $Cp^*(PPh_3)(CO)_2Mo=CH(OH)^+CF_3CO_2^-$,[128] *trans*-$(dppe)_2(CO)Ru=CH(OH)^{2+}(OTf^-)_2$,[174] and *trans*-$(dppe)_2(X)Ir=CH(OH)^{2+}(BF_4^-)_2$ (X = Cl, H)[190]—are prepared by reversible protonation of their formyl precursors.

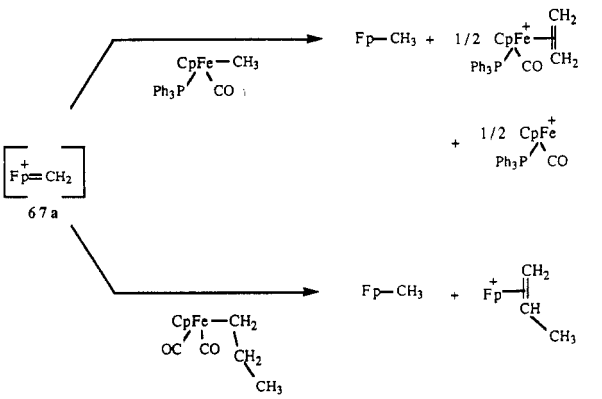
Hydroxymethyl and methoxymethyl ligand disproportionation reactions have been reported in which the transitory methylene salt undergoes intramolecular electrophilic aromatic substitution onto a PPh_3 or $P(OPh)_3$ ligand. Gibson and co-workers[121a] reported that protonating either the formyl $(PPh_3)(CO)_4Mn-CH_2OCH_3$ delivers the metallacycle $(CO)_4Mn[Ph_2P-(o-C_6H_4CH_2)]$ plus the carbonyl salt $(PPh_3)Mn(CO)_5^+$. Performing this protonation in the presence of methanol gives primarily the methoxymethyl complex. The



(Mn) = $(PPh_3)(CO)_4Mn$

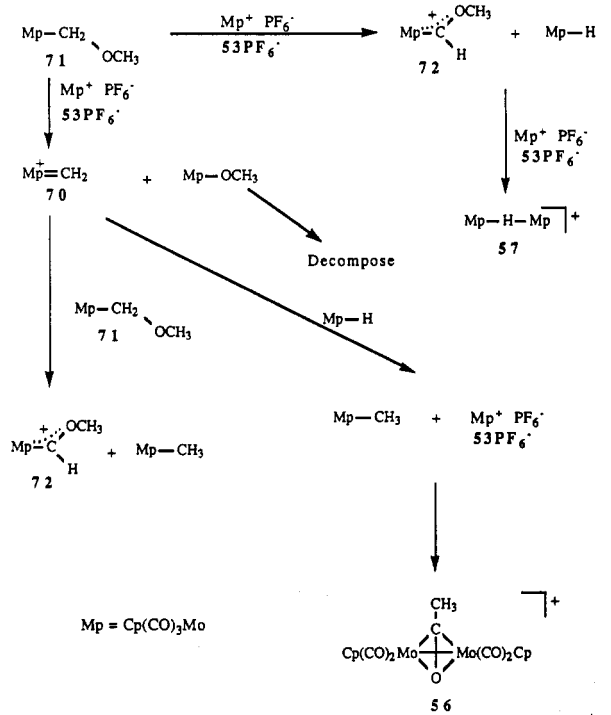
pathway advanced for these reactions entails reducing the hydroxymethylene intermediate with the starting formyl complex (which produces the carbonyl salt byproduct) and subsequently generating the reactive methylene salt $(PPh_3)(CO)_4Mn=CH_2^+$. This salt either undergoes methanolysis, or it attacks the phenyl ring of ligated PPh_3. The phosphite complexes $(P(OPh)_3)(L)(CO)_3Mn-CHO$ similarly protonate to give the metallacycles $(L)(CO)_3Mn[(PhO)_2P(o-OC_6H_4CH_2)]$ (L = CO, $P(OPh)_3$).

Other η^1-alkyl ligands react with the methylene compound **67a**. The resulting product mixtures are complex, undoubtedly due to several overlapping pathways. Both **67a** and its disproportionation product Fp^+ abstract hydride from η^1-alkyl complexes. In addition, Fp^+ can abstract the entire alkyl group from methyl and methoxymethyl iron complexes. These Fp^+ reactions were established independently by using the labile $Fp(THF)^+PF_6^-$.[189]



Reactions between **67a** and alkyl ligands are dominated by hydride abstractions. Thus $Fp=CH_2^+$ (**67a**) and $Cp(PPh_3)(CO)Fe-CH_3$ give $Fp-CH_3$ and the disproportionation products of $Cp(PPh_3)(CO)Fe=CH_2^+$, $Cp(PPh_3)(CO)Fe^+$, and $Cp(PPh_3)(CO)Fe(\eta^2$-ethylene$)^+$.

SCHEME 15

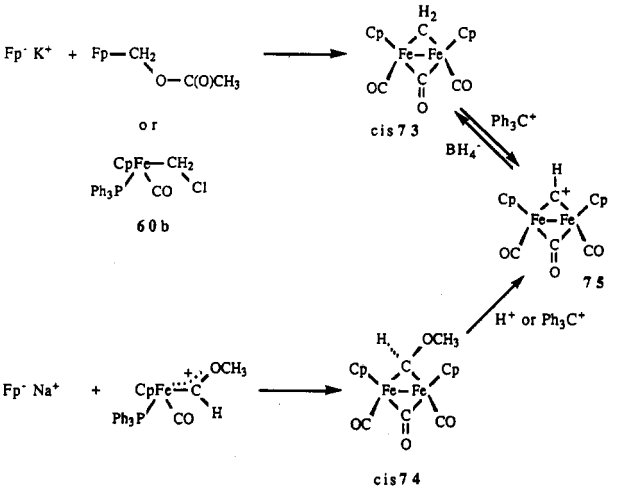


The reaction between $Fp{=}CH_2^+$ (**67a**) and Fp(*n*-propyl) affords the products of β-hydride abstraction, $Fp{-}CH_3$ and Fp(η^2-propene)$^+$ (46% conversion). Some of the $Fp{-}CH_3$ in the first reaction (54% yield) undoubtedly comes from the abstraction of a methyl group by Fp^+, a disproportionation product of $Fp{=}CH_2^+$. Fp^+ does not react with Fp(*n*-propyl) under similar conditions.

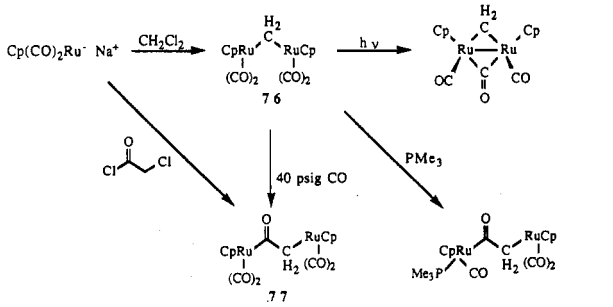
Beck's Lewis acid $Cp(CO)_3Mo^+PF_6^-$ (**53PF$_6^-$**) competitively abstracts both hydride and alkoxide from the methoxymethyl complex $Cp(CO)_3Mo{-}CH_2OCH_3$ (**71**).[162] The observed products, depicted in Scheme 15, are methoxymethylene **72**, μ-hydride **57**, and μ-(η^2-C,O)-acetyl **56**. Methoxide abstraction from **71** gives the methylene intermediate **70**, whereas hydride abstraction produces $Cp(CO)_3Mo{-}H$ and **72**. The reactions envisioned between $Cp(CO)_3Mo^+$ (**53**) and $Cp(CO)_3Mo{-}H$, between **70** and $Cp(CO)_3Mo{-}H$, and between **70** and **71**, which account for the final products, have been verified independently.

3. Bimetallic Bridging Methylene Compounds

Alkoxymethyl complexes are precursors to a number of interesting bimetallic systems. The Casey[191] and Pettit[192] research groups established that Fp^-K^+ reacts with $Fp{-}CH_2OAc$ or $Cp(PPh_3)(CO)Fe{-}CH_2Cl$ (**60b**) to give the stable μ-methylene compound **73** containing an iron–iron bond. This was isolated as a partially separable 3:1 mixture of cis and trans isomers. A convenient one-pot synthesis of **73** involves treating Fp^-K^+ with chloromethyl pivalate, $ClCH_2CO_2CMe_3$, in refluxing THF.[193] This reaction has been extended to the Fp* system. The related binuclear μ-methoxymethylene complex **74** is the product of Fp^-Na^+ and $Cp(PPh_3)(CO)Fe{=}CH(OMe)^+$ (**62b**). Both **73** and **74** convert to the bridging methylidyne compound **75** upon mixing with trityl carbocation. The μ-methylidyne compound **75** has found extensive application in hydrocarbation chemistry.[11]

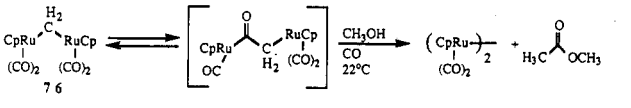


Presence of a metal–metal bond is not a structural prerequisite for obtaining bridging methylene complexes. A DuPont[194] group synthesized the diruthenium μ-methylene compound **76**. Upon photolysis this loses CO and converts to the thoroughly characterized[195] diruthenium analogue of **73**.



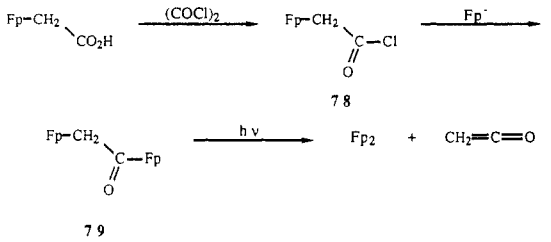
An X-ray structure determination reveals that **76** has relatively long $Ru{-}CH_2$ bonds (2.18 Å) and a wide $Ru{-}CH_2{-}Ru$ angle (123°), implying a sterically congested Ru_2CH_2 functionality that may account for its unusually high reactivity. Carbonylation under mild conditions affords the bridging ketene complex **77** (this was prepared independently by metalating chloroacetyl chloride).[194] Mononuclear ruthenium alkyl complexes, e.g., $Cp(CO)_2Ru{-}CH_3$, in contrast, carbonylate only sluggishly at higher temperatures (>50 °C) and pressures (>55 atm of CO).[194,196]

Carbon monoxide migratory insertion involving a $Ru{-}CH_2$ bond on **76** is assumed in its facile methanolysis. Lin and co-workers discovered that dissolving **76** in methanol eliminates methyl acetate and leaves dimeric $(CpRu(CO)_2)_2$, for which they postulate intermediacy of coordinatively unsaturated μ-ketene complex.[194]



In support of this mechanism, the characterized μ-ketene compound **77** only reacts with methanol after ejecting CO through photolysis. Methanolysis of $Fe_2(CO)_8(\mu\text{-}CH_2)$[197] and $Os_3(CO)_{11}(\mu\text{-}CH_2)$[198] also gives methyl acetate and may involve similar μ-ketene intermediates containing vacant sites on the metal.

The iron-containing μ-ketene analogue of **77** is available by a different synthetic route.



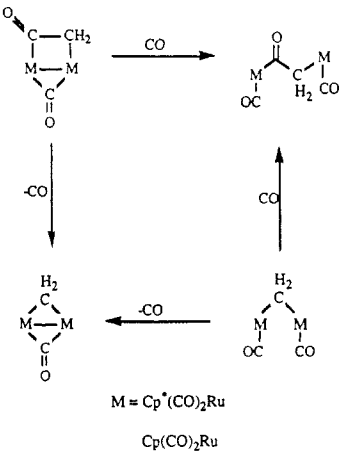
78

79

Alkita, Kondoh, and Moro-oka[46b] metalated the carboxylic acid chloride complex Fp–CH_2COCl (**78**) with nucleophilic metal carbonyl anions to afford isolable μ-(η^1-C,C′) ketene compounds, e.g., **79**. Previous attempts to prepare **79** from the metalloenolate Fp–C(O)=CH_2^- (**13a**) had given only Fp_2.[46a] Once prepared, **79** is stable at room temperature, although upon photolysis it ejects ketene and leaves Fp_2.

The chloroacetyl complex Fp–$COCH_2Cl$ (**80**), isomeric to **78**, potentially could be used in synthesizing **79** and related μ-ketene complexes. Curtis reported[199] in earlier studies that the reaction of chloroacetyl chloride, $ClCH_2COCl$, and Fp^- gives only Fp_2. Under similar conditions, metal carbonyl anions $Cp(CO)_3M^-Na^+$ (M = Mo, W) afford the molybdenum and tungsten chloroacetyl complexes $Cp(CO)_3M$–$COCH_2Cl$.[199] Cobalt chloroacetyl complexes are available through CO migration reactions with chloromethyl compounds.[200] The fully characterized cobalt chloroacetyl complex $(PPh_3)(CO)_3Co$–$COCH_2Cl$ thus is obtained either by carbonylating $(PPh_3)(CO)_3Co$–CH_2Cl (1 atm of CO) or by treating the equilibrium mixture involving $(CO)_4Co$–CH_2Cl and $(CO)_4Co$–$COCH_2Cl$ (under 1 atm of CO) with PPh_3.

Ruthenium bimetallic systems bearing μ-methylene and μ-ketene ligands, which are available through a variety of synthetic pathways, offer great potential for future study. Binuclear Cp*Ru– and CpRu– complexes containing bridging ketene ligands with and without a Ru–Ru bond have been reported recently.[201] More work is needed, but a pattern for interconverting μ-methylene and μ-ketene compounds is emerging.



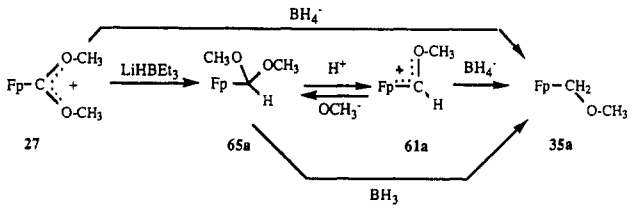
M = $Cp^*(CO)_2Ru$

$Cp(CO)_2Ru$

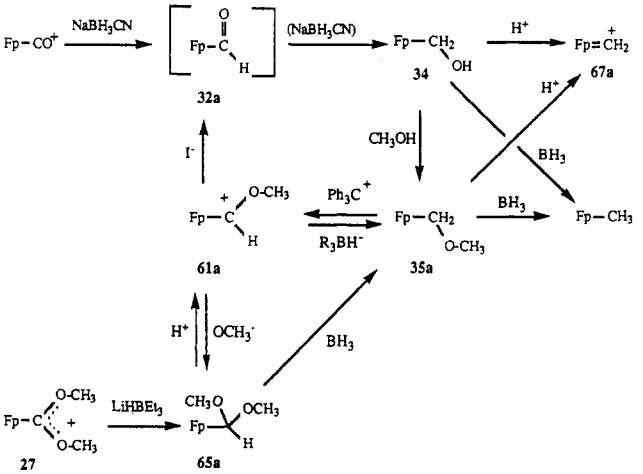
E. Formyl Acetal Complexes

Although the formyl complexes Cp(L)(CO)Fe–CHO (**32**) are reducible C_1 species, they have the disadvanage of being unstable. Formyl dimethyl acetal complexes $Cp(L)(CO)Fe–CH(OCH_3)_2$ (**65a**, L = CO; **65b**, L = PPh_3) are both stable and reducible. Casey[171] originally synthesized **65a,b** by adding methoxide to methoxymethylene salts (**61a,b** (eq 9), and Cutler[20b] prepared **65a** by $LiHBEt_3$ reduction of the dimethoxycarbene complex **27** in 82% yield (Scheme 16). Complex **65a** is a yellow oil that is stable at room temperature in CH_2Cl_2 solution for at least 12 h. One mole equivalent of BH_4^- reduces the dimethoxycarbene complex **27** directly to the mehoxymethyl compound **35a**.

SCHEME 16



SCHEME 17

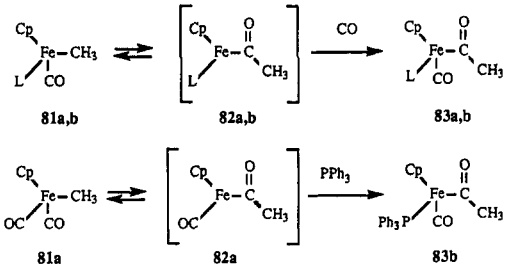


The formyl acetal **65a** reduces either directly to **35a** (93% yield) using 1.5 mol equiv of BH_3·SMe_2 or indirectly through the methoxymethylene compound **61a** and subsequent borohydride reduction.

Scheme 17 summarizes the reactions involving C_1 oxygenated ligands coordinated to the versatile $Cp(CO)_2Fe$ moiety. Hydride transfer to either Fp–CO^+ or Fp=$C(OCH_3)_2^+$ (**27**) leads into the same network of ligand reactions. Borane adducts of Fp(formyl) (**32a**) (Schemes 5 and 7) and of Fp(formyl acetal) (**65a**) further facilitate their reduction to hydroxymethyl (**34**) and methoxymethyl (**35a**). Both **34** and **35a** can be converted to either methyl complex or transient methylene **67a**.

Coordinated ligand reactions involving the formyl acetal **65a** could supplement those of the transient formyl **32a**. Two salient points regarding these ligand reactions (Scheme 17) emerge. First, converting Fp–CO^+ to the dimethoxycarbene compound **27** (and then to the formyl acetal **65a**) would permit C_1 reductive chemistry without resorting to the formyl **32a**. Such a conversion has been established for $Cp^*Ru(CO)_3^+$. Second, converting unstable formyl **32a** to its stable formyl acetal **65a** could facilitate carrying out subsequent ligand reactions. The first step, protonation or methylation of **32a** to its hydroxymethylene or methoxymethylene **61a**, has not been established. Such ligand transformations, however, are known for formyl congeners of **32a**.

SCHEME 18



IV. C_2 Chemistry: Oxygenated C_2 Ligands Originating with CO Synthesis Reactions

A. Methyl to Carbonyl Migratory Insertion

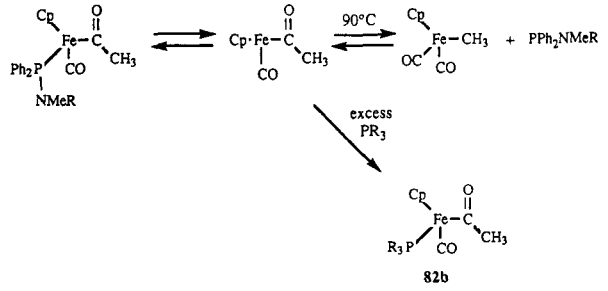
We discern between two types of CO insertion reactions, which, although mechanistically similar (Scheme 18), differ on the basis of operational details.[202] (1) Direct carbonylation of an iron methyl complex **81**, which contains at least one terminal carbonyl, produces the acetyl product **83** under CO pressure. (2) Carbon monoxide insertion in the presence of a nucleophile such as a phosphine or phosphite affords an acetyl complex incorporating the nucleophile. Steric size of the phosphine or phosphite as measured by its cone angle[203] influences the reaction rate: the smaller the phosphine, the higher the rate.[204] Electronic attributes of the phosphine are not as influential in these acetyl-forming reactions.

In the thermal phosphine-promoted carbonyl insertion, the starting methyl complex **81a** must have two terminal carbonyls. In contrast, phosphine-substituted methyl complexes $Cp(PR_3)(CO)Fe–CH_3$ (PR_3 = PPh_3 (**81b**), PPh_2NHR, PMe_3) do not react with additional phosphine to give disubstituted acetyl complexes $Cp(PR_3)_2Fe–COCH_3$. Such products are available (e.g., $Cp(PPh_2NHR)(PMe_3)Fe–COCH_3$ and $Cp(PMe_3)_2Fe–COCH_3$) through photolytic replacement of the terminal carbonyl on the monosubstituted acetyl $Cp(PR_3)(CO)Fe–COCH_3$ by PR_3.[205a]

Both types of CO insertion reactions involve the ligand migration pathway depicted in Scheme 18. Alkyl group migration to a terminal carbonyl (as opposed to the inverse) is favored for carbonylation reactions of many metal systems and for phosphine-promoted CO insertion of complexes related to **81**.[202] The carbonylation of **81** to **83** also is stereoselective, although both formal alkyl and carbonyl migration products are observed, depending on the choice of solvent.[206] Interestingly, the stereochemical outcome of those reactions that give the acyl product in high chemical yields is consistent with alkyl migration to ligated CO. For example, (*S*)-$Cp(PPh_3)(CO)Fe–Et$ in nitromethane or nitroethane and 4.4 atm of CO afford (*R*)-$Cp(PPh_3)(CO)Fe–COEt$ in 82% yield with 95% ee.[206a,c] Other solvents used such as DMSO and HMPA afford very low yields (<15%) of product of opposite configuration, the apparent result of CO migration to the ligated alkyl group. Remaining unanswered questions concerning the carbonylation of **81** include (a) the stereochemical rigidity (i.e., memory) of the unsaturated acetyl intermediate **82** in equilibrium with **81**,[205b] (b) the extent to which this intermediate is solvated, and (c) the role of η^2-acyl binding[205,206] within **82**.

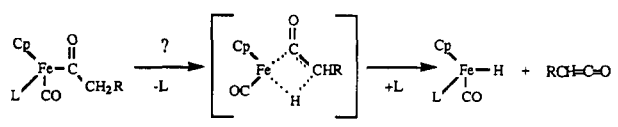
Solvent effects are significant in affecting chemical yields and rates of the alkyl–CO migration reactions. Rates of phosphine-promoted reactions involving Fp–R and cogeneric metal alkyl complexes, in particular, are enhanced greatly in more polar solvents.[207] Optimal conditions for preparing $Cp(PPh_3)(CO)Fe–COCH_3$ (**83b**) from Fp–Me, for example, involve refluxing THF or acetonitrile.[208] Gradually, a coherent mechanistic picture is emerging in which the role of the nucleophilic solvent is to catalyze the formation of the coordinatively unsaturated acyl intermediate[209] and not necessarily to stabilize it.[210]

Phosphine dissociation predominates upon warming solutions of the phosphine-substituted acetyl complexes. Brunner and Vogt[205b] thus demonstrated that heating a benzene solution of $Cp(PPh_2NMeR)(CO)Fe–COCH_3$ to 90 °C extrudes phosphine and leaves $Fp–CH_3$, the buildup of which was monitored by ^1H NMR spectroscopy.



Phosphine substitution reactions are possible under these conditions. Although phosphine dissociation is not detected at room temperature, adding the "phosphine sponge" $Cu(CH_3CN)_4^+PF_6^-$ to a methylene chloride solution of $Cp(PPh_3)(CO)Fe–COCH_3$ (**83b**) quantitatively generates $Cp(CO)_2Fe–CH_3$ over 24 h, or after a few minutes in refluxing 1,2-dichloroethane.[211] Wojcicki[36a] and Reger[36c] previously had demonstrated that PPh_3 dissociation is the initial step in the pyrolysis and subsequent deinsertion of ethylene from the η^1-ethyl complex, $Cp(PPh_3)(CO)Fe–Et$.

Other than reversible phosphine dissociation, the iron acetyl complexes $Cp(L)(CO)Fe–COCH_3$ (**83**) are thermally robust. These complexes generally decompose only after prolonged heating above ca. 150 °C. Thermal β-hydrogen migration to give ketene and the iron hydride Cp(L)(CO)Fe–H has not been recorded. This step has precedent in Baird's[212] observation that the (η^3-triphos)ruthenium acetyl, $[CH_3C(CH_2PPh_2)_3](CO)_2Ru–COCH_3^+$, immediately fragments to give ketene and $[CH_3C(CH_2PPh_2)_3](CO)_2RuH^+$. Potentially analogous examples of β-hydrogen migration releasing alkene from $Cp(PPh_3)(CO)Fe–CH_2CH_3$,[32a,c] releasing CO_2 from η^1-metallocarboxylic acids **8a,b** (section IIA3), releasing CO_2 from η^1-O formates **29** (section IID), and releasing ketene from metalloenolates $Cp(L)(CO)Fe–COCH_2^-$ **13a,b** (section IIA4) have been reported. Further work is required to find out if organoiron complexes will become precursors to substituted ketenes under convenient experimental conditions.

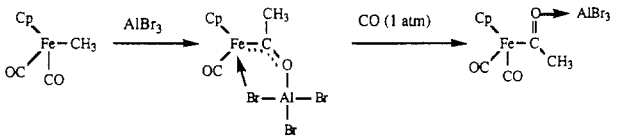


1. The Carbonylation Reaction

Until recently, relatively little was known about carbonylating $Cp(L)(CO)Fe–CH_3$ and related alkyl complexes. As recently as 1978, King[213] reported that carbonylation of $Fp–CH_3$ required high CO pressures and temperatures (325 atm, 97 °C) in tetradecane. Since then a variety of strategies have been adopted for carbonylating organoiron alkyl complexes Cp(L)(CO)-Fe–R:

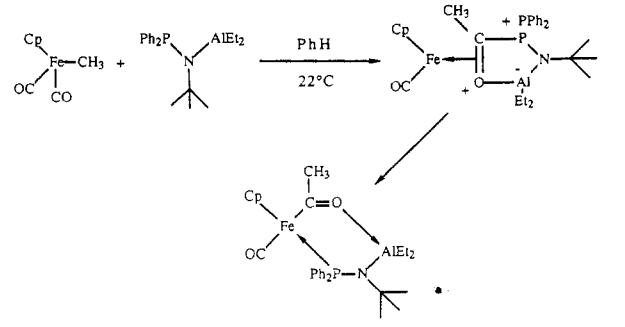
1. Lewis acid promotion
   a. Bifunctional Lewis acids ($AlBr_3$, BF_3)
   b. Organometallic Lewis acids (Fp^+, $Cp(CO)_3Mo^+BF_4^-$, PF_6^-)
2. Protonic acid promotion, including solvent effects
3. One-electron oxidative promotion
   a. Electron-transfer radical chain mechanism
   b. Carboalkoxylation
4. Indenyl ligand promotion (η^5/η^3 ring shift)

Lewis acids promote alkyl to CO migration.[134] Shriver demonstrated that group 13 halides (e.g., $AlBr_3$) are particularly effective in promoting carbonylation reactions.[134a,b] Treating $Fp–CH_3$ with $AlBr_3$, for example, immediately forms an acetyl adduct that subsequently reacts with CO (under 1 atm) to afford $Fp–COCH_3·AlBr_3$.

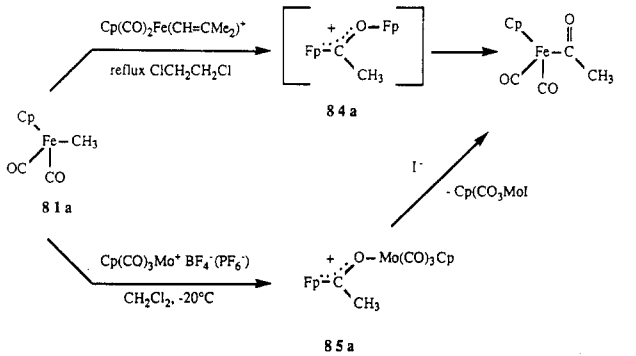


Hydrolysis then releases $Fp–COCH_3$. Boron trifluoride also promotes carbonylation of phosphine- and phosphite-substituted alkyl complexes, Cp(L)(CO)Fe–R [R = Et, L = PPh_3 and $P(OCH_2)_3CMe$;[206a,c] R = Me, L = $PPh_2NMe(CHMePh)$[206b]]. Using the ethyl complexes, Flood[206c] further demonstrated that the presence of 1–6% BF_3 (relative to ethyl complex) catalyzes their carbonylation.

Labinger and co-workers[134c] used an amphoteric aluminophosphine $Et_2AlN(t\text{-Bu})PPh_2$, which functions both as a trialkylaluminum Lewis acid to promote alkyl migration and as a nucleophilic phosphine. This aluminophosphine and $Fp–CH_3$ in benzene (22 °C) afford initially the Fe(O) ketone complex, the result of P–C bond formation, as the kinetic product. It isomerized to the chelated iron acetyl thermodynamic product having Fe–P(phosphine) binding. The analogous phosphine $Ph_2P–NH\text{-}t\text{-Bu}$ lacking the dialkylaluminum functionality, in contrast, requires harsher conditions of refluxing THF before the acetyl complex $Cp(Ph_2P–NH\text{-}t\text{-Bu})(CO)FeCOCH_3$ slowly and reversibly forms.



Transition organometallic Lewis acids also promote alkyl to carbonyl migration by forming bimetallic μ-acyl complexes. The Lewis acids $Cp(CO)_2Fe^+$ and $Cp(CO)_3Mo^+BF_4^-$, PF_6^- are available as high-energy transient intermediates through ionization of appropriate precursors;[138] they readily convert $Fp–CH_3$[137,139] (and $Cp(CO)_3Mo–CH_3$, Scheme 13) to bimetallic acetyl complexes **84a** and **85a**. The additional CO required to



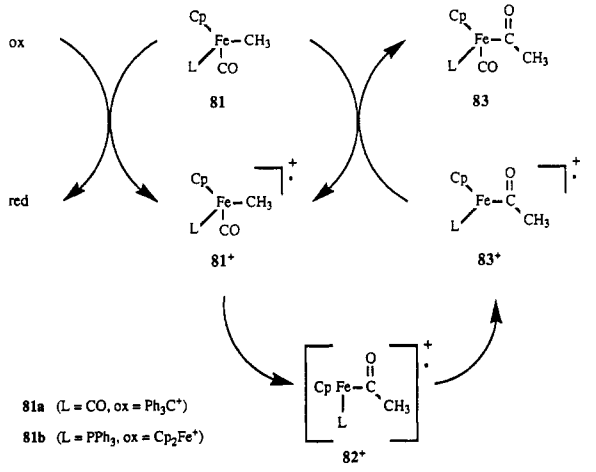
generate the bimetallic μ-(η^1-C,O)acetyl compounds originates within the starting complexes. Modest yields (40–50%) of **84a** and **85a** obtained by this route thus are attributed to overall disproportionation of **81a** to acetyl product plus insoluble iron residues. Substantially higher yields (70–85%) of the fully characterized μ-(η^1-C:η^1-O)acetyl complexes $Cp(L)(CO)Fe–C(CH_3)O–Fp^+$ (**84a**, L = CO; **84b**, L = PPh_3) and $Cp(L)(CO)Fe–C(CH_3)_3–Mo(CO)_3Cp^+BF_4^-$, PF_6^- (**85a**, L = CO; **85b** L = PPh_3) are obtained by reacting acetyl complexes $Cp(L)(CO)Fe–COCH_3$ (**83a,b**) with the appropriate Fp^+ and $Cp(CO)_3Mo^+$ precursors.[214]

Acidic hydrogens, present as proton-donor solvents, hydrogen-bonding solvents, or trace amounts of a strong acid, catalyze carbonylation reactions.[196] In the absence of acid, most organic solvents (including CH_2Cl_2, THF, methanol, and DMSO) do not support carbonylation at 6.5 atm of CO of $Cp(PPh_3)(CO)Fe–CH_3$ (**81b**) to its acetyl **83b** (Scheme 18). Nitromethane and 2,2,2-trifluoroethanol, however, are excellent solvents for carbonylating methyl complex **81b**. Thus, the acetyl complex **83b** quantitatively forms in nitromethane (after 6.5 atm of CO for 8 H) or in trifluoroethanol (1 atm of CO, <1 h). Even the less reactive $Fp–CH_3$ (**81a**) in CF_3CH_2OH and under 6.5 atm of CO slowly develops $Fp–COCH_3$ (**83a**), but only at 65 °C.

The relatively acidic solvents CH_3NO_2 and CF_3CH_2OH presumably form hydrogen bonds with or protonate the incipient acetyl ligand as it develops during the methyl–CO migration step (**82** in Scheme 18). Acetyl ligands on the products **83a,b**, for example, simultaneously form hydrogen-bond adducts with and undergo protonation by CF_3CH_2OH, giving hydroxycarbene ligands, as deduced from IR spectral studies.[196] Shriver[215] previously advanced this mechanism for acid-promoted carbonylation of $(CO)_5Mn–CH_3$ using haloacetic acids.

Both $Fp–CH_3$ (**81a**) and $Cp(PPh_3)(CO)Fe–CH_3$ (**81b**) carbonylate under extremely mild conditions in the presence of catalytic amounts of acids.[196] With $HBF_4·OEt_2$ (1% stoichiometric) in CH_2Cl_2, for example, both **81a** and **81b** rapidly add CO at 1 atm. Other useful catalysts include $Ph_2NH_2^+BF_4^-$ for **81a** and *p*-nitrophenol or pyridinium ($C_5H_5NH^+BF_4^-$) for **81b**.

SCHEME 19



The Lewis acids $Cp(L)(CO)Fe^+$, which result from protolytic cleavage of the iron–methyl bond,[69b,138] were ruled out as catalysts for these carbonylation reactions. Neither carefully purified $Fp(THF)^+$ nor $Fp–C(CH_3)–O–Fp^+BF_4^-$, for example, promotes carbonylation, though both iron salts reversibly afford the Fp^+ Lewis acid in solution.

One-electron oxidation of the iron methyl complexes **81a,b** greatly accelerates their carbonylation reactions. Catalytic amounts of oxidants (Ph_3C^+ for **81a** and Cp_2Fe^+ for **81b**) initiate radical chain reactions in which **81a,b** rapidly convert to their acetyl products **83a,b** under 1 atm of CO (Scheme 19).[7] Giering[216] further demonstrated that the chain reaction involving **81b** requires (1) that the iron methyl radical cation **81b**$^+$ (a 17e species) carbonylate very rapidly and (2) that the resulting acetyl cation radical **83b**$^+$ is a stronger oxidant than **81b**$^+$. The transient acetyl radical **83b**$^+$ thus immediately oxidizes starting methyl complex **81b** to **81b**$^+$ and releases product acetyl **83b**. Methyl cation radical **81b**$^+$ functions as the chain-carrying species.

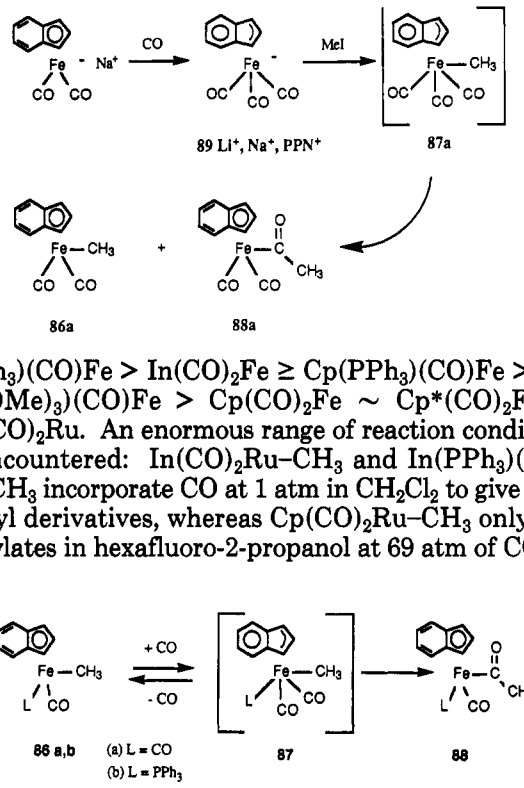
Recent studies by Giering[7a] and by Trogler[7b] have addressed the mechanism of the alkyl migration step in **81**$^+$ going to **82**$^+$. In the presence of polar solvents such as acetonitrile, methanol, or pyridine, the methyl cation radicals **81a**$^+$ and **81b**$^+$ apparently ligate solvent and give 19e adducts $Cp(L)(CO)(S)FeCH_3^+$ (S = solvent). The ensuing methyl migration involves a 19e to 17e structural transformation. In nonpolar solvents such as CH_2Cl_2, coordination of the acetyl O could be a driving force in converting **81**$^+$ to **82**$^+$.

These studies were done by using mainly electrochemical techniques below 0 °C, since the methanol adduct **82a**·CH_3OH^+ presumably is involved in the carbomethoxylation of **81a** (at 0–22 °C). Oxidative cleavage of both **81a** and **81b** in alcohol, the carboalkoxylation reaction (eq 7), gives acetic acid esters and unidentified iron residues.

2. The Indenyl Ligand in Promoting Carbonylation Reactions

The presence of an η^5-indenyl ligand (In) in place of η^5-Cp promotes the carbonylation of the iron[196] and ruthenium[217] methyl complexes $In(L)(CO)M–CH_3$ (M = Fe, Ru; L = CO, PPh_3). Relative carbonylation rates for a series of methyl complexes, without benefit of acid catalysis, are qualitatively ranked $In(CO)_2Ru \geq In(PPh_3)(CO)Fe > In(CO)_2Fe \geq Cp(PPh_3)(CO)Fe > Cp(P(OMe)_3)(CO)Fe > Cp(CO)_2Fe \sim Cp^*(CO)_2Fe \gg Cp(CO)_2Ru$. An enormous range of reaction conditions is encountered: $In(CO)_2Ru–CH_3$ and $In(PPh_3)(CO)Fe–CH_3$ incorporate CO at 1 atm in CH_2Cl_2 to give their acetyl derivatives, whereas $Cp(CO)_2Ru–CH_3$ only carbonylates in hexafluoro-2-propanol at 69 atm of CO/60 °C.

SCHEME 20



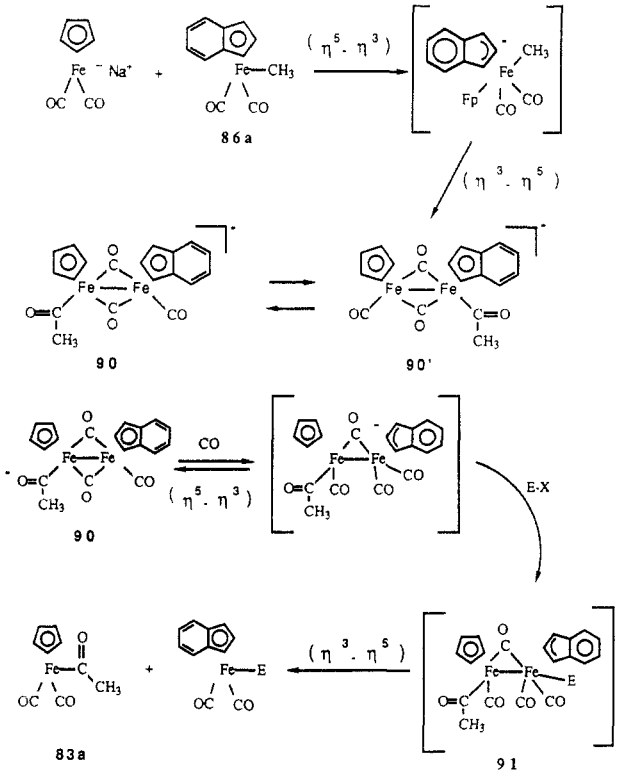
Synthetic procedures used in preparing the starting indenyl iron and ruthenium complexes represent minor modifications of standard preparations for Cp-containing analogues.[218]

Additional mechanistic studies are required in order to understand how the η^5-indenyl ligand promotes these carbonylation reactions. Indenyl ring slippage (η^5 to η^3)[219] and association of CO to give $(\eta^3\text{-In})(L)(CO)_2Fe–CH_3$ (**87a,b**) are a plausible working hypothesis. Intermediacy of **87a,b** presumably derives from benzenoid resonance stabilization of this ene–η^3-allyl intermediate. Methyl to carbonyl migration on **87** as the η^3-In returns to its thermodynamically favored η^5-In then affords **88a,b**. Conversion of **87** to **88** must be irreversible, since ^{13}C-labeled acetyl $In(CO)_2Fe–^{13}COCH_3$ does not move the label onto terminal carbonyl positions.[220]

Independent evidence linking CO association at iron, reversible η^5/η^3 In ligand shifts, and methyl–CO migration is available. Nucleophilic $In(CO)_2Fe^-Na^+$ rapidly and irreversibly associates CO (at 1 atm) to give $(\eta^3\text{-In})(CO)_3Fe^-Na^+$ (**89Na**$^+$), which was characterized as its stable salt **89PPN**$^+$ ($PPN^+ = Ph_2PNPPh_2^+$) (Scheme 20).[221] An X-ray structure determination of **89PPN**$^+$ established that the nonplanar indenyl ligand has a 21° fold angle between its η^3-allyl and benzenoid fragments. Methyl iodide reacts with **89PPN**$^+$ in THF solution under 1 atm of CO to give a 1:3 mixture of iron acetyl **88a** and methyl **86a** complexes. The η^3-In iron methyl intermediate **87a** again is presumed to couple its η^3–η^5 indenyl tautomerization with both methyl–CO migration (giving **88a**) and CO dissociation (giving **86a**). The analgous $(\eta^3\text{-In})(CO)_3Ru^-Na^+$ quantitatively affords its acetyl derivative $(\eta^5\text{-In})(CO)_2Ru–COCH_3$ under similar reaction conditions.[221]

Reversible η^5–η^3 indenyl ligand ring slippage[219b] evidently is the driving force in a newly developed two-step, metalate-promoted carbonylation procedure in-

SCHEME 21



volving (η^5-In)$(CO)_2$Fe–alkyl complexes (Scheme 21).[220] Treating $In(CO)_2Fe–CH_3$ (**86a**), for example, first with 1 mol equiv of metalate Fp^-Na^+ or $In(CO)_2Fe^-Na^+$ and then with an electrophile (E–X in Scheme 21) in the presence of 1 atm of CO gives an acetyl complex. With Fp^- as the metalate, the acetyl ligand ends up on the Fp moiety. Using $In(CO)_2Fe^-$ as the metalate provides $In(CO)_2Fe–COCH_3$, the apparent carbonylation product of the starting methyl complex **86a**. Alkylating agents E–X that are used include MeI, EtI, and Ph_3SnCl.

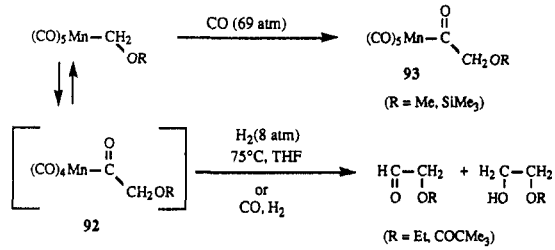
Bimetallic compounds $CpIn(CO)_3Fe_2(COCH_3)^-$ (**90**) and $In_2(CO)_3Fe_2(COCH_3)^-$, key intermediates in this carbonylation procedure, are isolated and fully characterized as their PPN^+ salts. An X-ray structure determination of the mixed CpIn dimer **90** established that it crystallizes with the terminal acetyl ligand on the CpFe end (**90′**), and that the overall structure has a cis array of the Cp and planar η^5-In groups. In solution, **90** exists as a 1:1 mixture of **90** and **90′**. The acetyl ligand shuttle between the iron centers that interconverts **90** and **90′** was studied by ^1H NMR magnetization transfer experiments.[220]

Interconverting **90** and **90′** requires intermediacy of a precedented μ-oxycarbene intermediate $Cp(CO)Fe(\mu\text{-}C(O^-)Me)(CO)Fe(CO)In$.[222d,e] Several examples of nucleophilic metal carbonylates promoting alkyl–CO insertion at another metal center are documented. The resulting bimetallic acyl complexes, however, typically alkylate at the acyl O and give bimetallic alkoxycarbene (terminal) compounds.[222]

In the second step of this carbonylation procedure, bimetallic acetyl compounds **90** and $In_2(CO)_3Fe_2CO\text{-}CH_3^-$ fragment to give their mononuclear acetyl products. Both a CO atmosphere and the presence of the alkylating agent E–X are simultaneously required for dimer fragmentation; neither CO nor E–X acting alone suffices. Scheme 21 presents a hypothesized reaction pathway that involves reversible η^5–η^3 indenyl ring shifts both in forming and in subsequently fragmenting the bimetallic intermediate **90**.

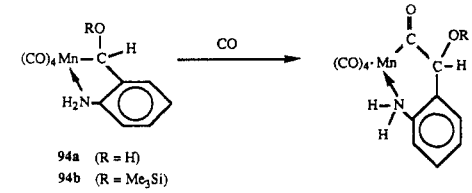
B. Alkoxymethyl to Carbonyl Migratory Insertion

The migratory insertion of alkoxymethyl ligand to carbonyl is important in generating C_2 oxygenated molecules using $CO–H_2$. Dombek[223] demonstrated that hydrogenation of $(CO)_5Mn$(alkoxymethyl) and $(CO)_5Mn$((acyloxy)methyl) complexes under mild conditions, for example, releases glycol aldehyde and ethylene glycol derivatives, consistent with the intermediacy of alkoxyacetyl and (acyloxy)acetyl intermediates. Observation of an induction period, autocatalysis once the reaction starts, and inhibition of aldehyde hydrogenation by CO suggest a binuclear reductive elimination[123b,224] step in this pathway. Unidentified manganese hydrides apparently intercept the coordinatively unsaturated or loosely solvated alkoxyacetyl intermediate **92**. Indeed, Dombek found that the hydride complex $(CO)_5Mn–H$ can replace H_2 in producing the same aldehyde and alcohol products.



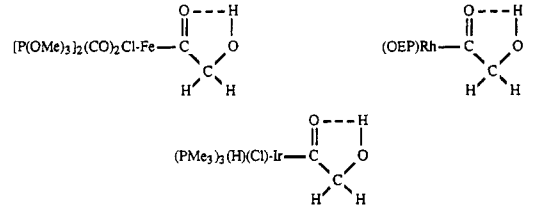
Carbonylation of manganese alkoxymethyl complexes produces stable alkoxyacetyl compounds $(CO)_5Mn–COCH_2OR$ (**93**).[225] The presence of an electron-withdrawing α-oxy substituent on starting $(CO)_5Mn–CH_2OR$ retards the rate of alkyl–CO migration compared to that of the methyl complex $(CO)_5Mn–CH_3$. Relative carbonylation rates decrease in the order $(CO)_5Mn–CH_3$ > $(CO)_5Mn–CH_2OSiMe_3$ > $(CO)_5Mn–CH_2OMe$ > $(CO)_5Mn–CH_2Ph$. The 3.5-fold rate increase in carbonylating $(CO)_5Mn–CH_2OSiMe_3$ over $(CO)_5Mn–CH_2OMe$ (24 °C, CD_3CN, 52–103 atm of CO) may in part be due to the silicon interacting with the acyl oxygen in the transition state, although no such interaction is apparent for the product $(CO)_5Mn–COCH_2OSiMe_3$.[225b]

α-Hydroxyalkyl complexes also carbonylate more readily than their α-alkoxyalkyl and α-((trimethylsilyl)oxy)alkyl analogues. Gladysz[89c] demonstrated that although both the hydroxyalkyl complex **94a** and its



((trimethylsilyl)oxy)alkyl derivative **94b** carbonylate when treated with 25 atm of CO in nitromethane, the carbonylation rate of **94a** is 16 times faster than that of **94b**. This rate enhancement is attributed to intramolecular hydrogen bonding to the acyl oxygen, which stabilizes the coordinatively unsaturated acyl interme-

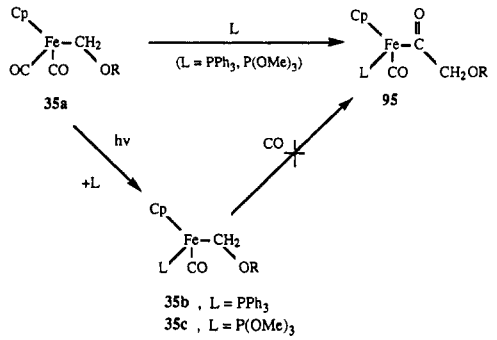
diate (analogous to **92**) as it forms. Several hydroxyacetyl compounds have been characterized recently. The iron[226] and rhodium[227] examples are products of carbonylating hydroxymethyl complexes, and the iridium[228] analogue results from oxidative addition of glycol aldehyde to an Ir(I) center.



Intramolecular hydrogen bonding is prevalent in these hydroxyacetyl complexes,[89c] as deduced by results of IR spectral studies and an X-ray structure determination for the iridium compound.

Labile cobalt hydroxyacetyl complexes $(CO)_nCo-COCH_2OH$ (n = 3, 4) are presumed intermediates during hydroformylation of formaldehyde with $HCo(CO)_4$ and CO (1 atm).[229] This reaction selectively gives glycol aldehyde, which can be accounted for by bimolecular reductive elimination[224c,230] between either the hydroxymethyl compound $(CO)_4Co-CH_2OH$ or its hydroxyacetyl $(CO)_4Co-COCH_2OH$ and $HCo(CO)_4$. Hydroformylation systems are often mechanistically complex, and more than one mechanism may be involved.[231]

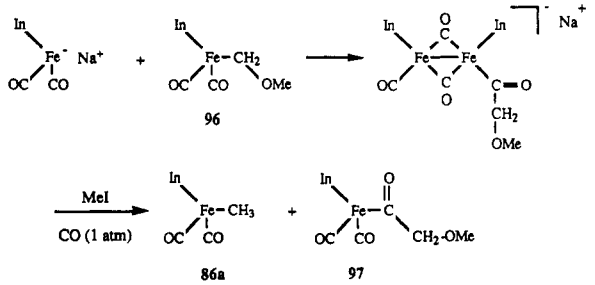
Resistance of the Fp(methoxymethyl) complex **35a** to undergo migratory insertion is evident by its diminished reactivity toward PPh_3 and $P(OMe)_3$. Alkoxyacetyl compounds **95b,c** are obtained in moderate yields only after refluxing acetonitrile solutions containing **35a** and excess PPh_3[232] or $P(OMe)_3$[85,232b] for 4 and 10 days, respectively. In contrast, phosphine- and phosphite-promoted methyl to CO migration under analogous reaction conditions provides the acetyl complexes $Cp(L)(CO)Fe-COCH_3$ (**83b,c**) after only 8 and 20 h, respectively. The parent methoxyacetyl complex $Fp-COCH_2OMe$ (**95a**) is readily available after metalating methoxyacetyl chloride, $ClCOCH_2OMe$, with Fp^-Na^+.[166]



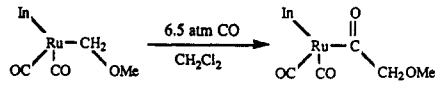
Attempts to carbonylate CpFe(methoxymethyl) complexes have been unsuccessful.[196] Both **35a** and **35b** are inert to CO under a variety of reaction conditions. Neither **35b** nor $In(PPh_3)(CO)Fe-CH_2OMe$ reacts with CO at 69 atm in CH_2Cl_2 with $Ph_2NH_2^+BF_4^-$ present. In nitromethane solution, CO (6.5 atm) replaces the phosphine on $In(PPh_3)(CO)Fe-CH_2OMe$ to give $In(CO)_2Fe-CH_2OMe$. The use of Lewis acids as carbonylation catalysts, particularly $Cp(CO)_2Fe^+$ and $Cp(CO)_3Mo^+$, is thwarted by the high reactivity of methoxymethyl complexes with these Lewis acids (section IIID2). The hydroxymethyl complexes $Cp(CO)_2M-CH_2OH$ (M = Fe, Ru)[87] and $Cp^*(CO)_2Ru-CH_2OH$[88a,c] likewise proved inert toward CO (273 atm).

Attempts to oxidatively promote the carbonylation of $Cp(PPh_3)(CO)Fe-CH_2OMe$ (**35b**) using $Cp_2Fe^+PF_6^-$ or $AgPF_6$ produced only the carbonyl salt $Cp(PPh_3)(CO)_2Fe^+$ and insoluble residues.[233] This failure is tentatively attributed to the instability of the methoxyacetyl cation radical $Cp(PPh_3)(CO)Fe-COCH_2OMe^+$ (**95b**$^+$). Chemical or electrochemical (cyclic voltammetric) oxidation of **95b** is irreversible, although similar oxidation of methoxymethyl **35b** is reversible.

Two recent developments for carbonylating methoxymethyl complexes depend on the unique properties of the indenyl ligand. The first approach involves the two-step bimetallic route (cf. Scheme 21). Treating the methoxymethyl iron complex $In(CO)_2Fe-CH_2OMe$ (**96**) first with $In(CO)_2Fe^-Na^+$ and then with MeI/CO (1 atm), performed as a "one-pot" operation, provides the desired methoxyacetyl complex **97** in 60% yield after column chromatography.[234]



The second approach entails direct carbonylation of η^5-indenyl ruthenium complexes. The presence of even relatively low CO pressure converts $In(CO)_2Ru-CH_2OMe$ to its methoxyacetyl compound without recourse to acid catalysis.[217] Forty-eight percent conversion is realized after 20 h (6.5 atm of CO, CH_2Cl_2, 22 °C).



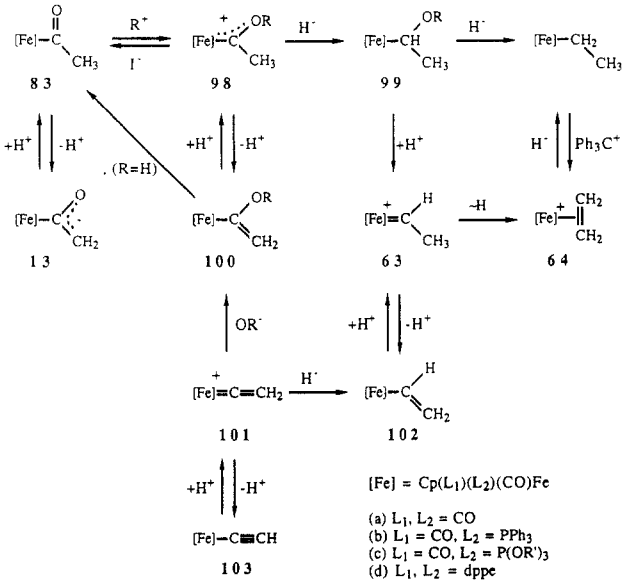
A limited number of other alkoxyacetyl complexes are available by alkyl–CO migration reactions. Phosphine-promoted migrations provide $(PPh_3)(CO)_3Co-COCH_2OMe$,[235] $(PPh_2Me)_2(CO)_2Co-COCH_2OMe$,[236] $(PPh_3)(CO)_4Mn-COCH_2OMe$,[157] and $Cp(PPh_3)(CO)_2Mo-COCH_2OMe$.[157] Examples of alkoxyacetyl complexes that have been obtained by carbonylating alkoxymethyl complexes include $[P(OMe)_3]_2(CO)_2IFe-COCH_2OMe$,[226] $(PPh_2Me)(CO)_3Co-COCH_2OMe$, $(PPh_2Me)_2(CO)_2Co-COCH_2OMe$,[236] and $(dppe)(CO)_2Co-COCH_2OR$ (R = Me, Et).[237]

C. Acetyl Ligand as a C_2 Template

1. C_2 Ligand Transformations

A network of coordinated ligand reactions involving $Cp(L_1)(L_2)Fe$ complexes (L_1, L_2 = CO, PPh_3, $P(OR')_3$, dppe) and their Ru and Cp* congeners that interconvert acetyl and other η^1-alkyl ligands is depicted in Scheme 22. Starting acetyl complexes add a variety of electrophiles at the acetyl O to generate carbenoid species.[101] Strong acids reversibly protonate acetyl com-

SCHEME 22



plexes,[196] and one example of a hydroxycarbene compound, $Cp(PPh_3)(CO)Fe{=}C(OH)CH_3^+BF_4^-$, has been isolated.[238,239a] Strong bases, on the other hand, deprotonate the acetyl complexes $Fp{-}COCH_3$[13a,46,240] and $Cp(PPh_3)(CO)Fe{-}COCH_3$.[3,241] The enolate in the latter system is chiral and undergoes diastereofacial selective C-alkylation to give homologated acyl complexes.[3]

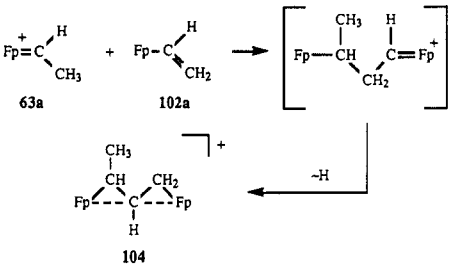
O-Alkylation of an iron acetyl complex **83** to give an alkoxycarbene compound **98** and subsequent reduction to its α-alkoxyethyl derivative **99** serve as a prototype for acyl ligand activation and reduction. Unless activated as an electrophilic alkoxycarbene, these acyl complexes preferentially react with nucleophilic hydride donors at an ancillary carbonyl ligand.[13c,130,242] Electrophilic alkylating reagents transform starting acetyl complexes **83** to examples of methoxy- or ethoxycarbene compounds: $Fp{=}C(OR)CH_3^+$ (**98a**),[165,169,243,244] $Cp(PPh_3)(CO)Fe{=}C(OR)CH_3^+$ (**98b**),[165,168,169,232a,244-247] (R = Me, Et), $Cp(P(OR')_3)(CO)Fe{=}C(OR)CH_3^+$ (**98c**) (R' = Me,[85] Ph[165,244]), and $Cp(PMe_3)(CO)Fe{=}C(OMe)CH_3^+$.[247] The readily available dialkoxycarbenium salts $(RO)_2CH^+BF_4^-$ or $(RO)_2CH^+PF_6^-$ (R = Me, Et) are especially convenient alkylating agents for synthesizing larger quantities of **98a–c**.[244]

Reduction of alkoxycarbene compounds **98a–c** gives either or both α-alkoxyethyl **99a–c** and ethyl complexes (Scheme 22). Green[238] and Davison[168] first reported the $NaBH_4$ reduction of $Cp(PPh_3)(CO)Fe{=}C(OR)CH_3^+BF_4^-$ (**98b**, R = Me, Et) to **99b**. Davison[168] also observed that $NaBH_4$ reacts with **98b** in ethanol to give equimolar amounts of the ethyl complex $Cp(PPh_3)(CO)Fe{-}CH_2CH_3$. Ethyl complexes are the only products of treating **98b**[232a] or **98c** (R' = Me)[85] with 1 molar equiv of $Ph_3PMe^+BH_4^-$ in methylene chloride. The presence of these ethyl complexes can be accounted for by residual borane (BH_3) reducing **99b** and **99c**. For example, BH_3 converts $Cp(PPh_3)(CO)Fe{-}CH_2OMe$ (**35b**) to $Cp(PPh_3)(CO)Fe{-}CH_3$ (**81b**).[160] Excess borane also reduces the starting acetyl complexes $Cp(L)(CO)Fe{-}COCH_3$ [**83a**, L = CO;[100,248a] **83b**, L = PPh_3, $P(OPh)_3$,[100] PMe_3[248b]] to their ethyl derivatives (Scheme 7).

Hydride donors that transform the alkoxycarbene compounds **98** selectively to their α-alkoxyethyl complexes are available. Brookhart[246] introduced the use of excess $NaBH_4$ in methanol containing NaOMe; Cutler[165,232a] employed 1 equiv of $LiHBR_3$ (R = Et, *sec*-Bu) in THF for selective monohydridic reduction of the iron alkoxycarbene complexes **98a–c**. The metal hydrides $Cp(PPh_3)(CO)Fe{-}H$[169] and $(PPh_3CuH)_6$[249] also have been used in converting **98a** and **98c** (R' = Me, Ph), respectively, to their α-methoxyethyl complexes. The latter reaction, moreover, exhibits high diastereofacial selectivity (100:1 mixtures of two diastereomers of **99c**, R' = Me or Ph), in accord with results of similar studies by Davies[172,250] on several $Cp(PPh_3)(CO)Fe$-(alkoxycarbene)$^+$ compounds.

Treatment of the α-alkoxyethyl complexes **99a–c** at −78 °C with acid (HBF_4, HPF_6, HOTf), Ph_3C^+,[165] or trimethylsilyl triflate[246] in methylene chloride generates the methylcarbene complexes **63**. The Ph_3P- and $P(OPh)_3$-substituted methylcarbene complexes **63b** and **63c** (PF_6^-) are isolated as yellow solids that slowly isomerize in CH_2Cl_2 at room temperature to give their η^2-ethylene complexes. This isomerization has been characterized by Brookhart as an intramolecular hydride migration.[246] NMR spectral data in CD_2Cl_2 for the α-CH group of **63b**, for example, are diagnostic for carbenoid hydrogen, δ 17.94 (q, J_{HH} = 7.8 Hz), and carbenoid carbon, δ 380.0 (d, J_{PC} = 25.1 Hz), sites.

Alkoxide abstraction from **99a** generates Fp-(methylcarbene)$^+$ (**63a**), but it has not been detected even at −78 °C.[165,246] Depending on the reaction conditions, either **63a** isomerizes to $Fp(CH_2{=}CH_2)^+$ (**64a**) or it forms the bimetallic-stabilized β-carbenium ion **104**. Bimetallic **104** is the product of electrophilic

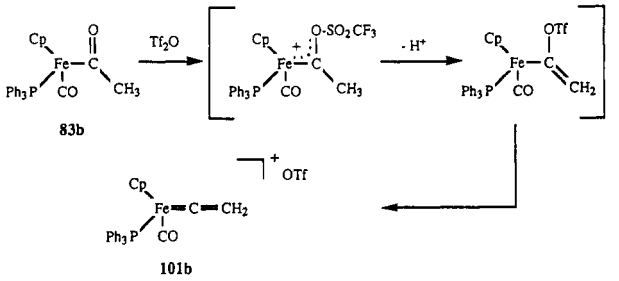


addition of **63a** to the β-position of the η^1-vinyl complex **102a**, analogous to the previously discussed reaction between $Fp{=}CH_2^+$ (**67a**) and **102a** (section IIID2). The resulting carbene intermediate isomerizes via β-hydride transfer to the observed **104**. The Fp(vinyl) (**102a**) necessary for this reaction arises during the deprotonation of the methylcarbene **63a**, which in turn originates by protonating **99a**.[165] Higher alkylcarbene complexes, in contrast, degrade exclusively by hydride migration: $Fp{=}CHCH_2CH_3^+$ rapidly gives $Fp(\eta^2{-}CH_2{=}CHCH_3)^+$[246] (at −78 °C), whereas $Fp{=}C(CH_3)_2^+BF_4^-$ slowly isomerizes ($t_{1/2}$ = 1 h, −10 °C) to the same propene salt.[243]

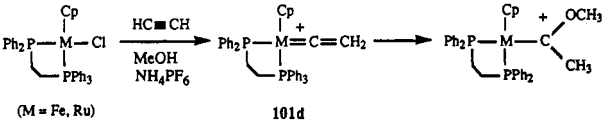
The iron η^2-ethylene compounds $Cp(L)(CO)Fe$-$(CH_2{=}CH_2)^+BF_4^-$ and $Cp(L)(CO)Fe(CH_2{=}CH_2)^+PF_6^-$ [**64a**, L = CO;[251a] **64b**, PPh_3;[252] **64c**, $P(OMe)_3$[85]] also interconvert with their ethyl complexes through thoroughly documented hydride addition and abstraction reactions. Trityl carbocations $Ph_3C^+BF_4^-$ and Ph_3C^+-PF_6^- regioselectively abstract hydride from the β-carbon of ethyl complexes to give the η^2-ethylene compounds.[7c,d,187a,251] An alternative pathway involving one-electron oxidation by Ph_3C^+ and then hydrogen atom removal from the α-carbon of the ethyl complex by $Ph_3C^{\bullet}$[253] and isomerization of **63** can be ruled out.

Carbene complexes **98** and **63** deprotonate to give their respective α-alkoxyvinyl **100** and vinyl **102** systems. The more stable phosphine- and phosphite-substituted methylcarbene complexes **63b,c** afford their vinyl complexes **102b,c** in 50–60% isolated yields upon treatment with ethyldiisopropylamine.[165] This reaction is reversible. Protonation of these vinyl compounds **102b,c** as well as Fp–CH=CH_2 (**102a**)[165,254] at −80 °C generates their methylcarbene complexes **63**. Alkoxyvinyl compounds **100a**,[243,171] **100b**,[168,171,247] and Cp(PMe$_3$)(CO)Fe–C(OMe)=CH_2[247] also form reversibly from the alkoxycarbene complexes. Davies[172,255] demonstrated that alkoxyvinyl complexes similar to **100b** engender high stereochemical control in both their formation and also their addition of organic electrophiles. Gladysz has observed similar efficient 1,3-asymmetric induction in alkylating α-methoxyvinyl Cp(PPh$_3$)(NO)Re–C(OMe)=CHR and vinyl Cp(PPh$_3$)(NO)Re–CH=CHR complexes.[257]

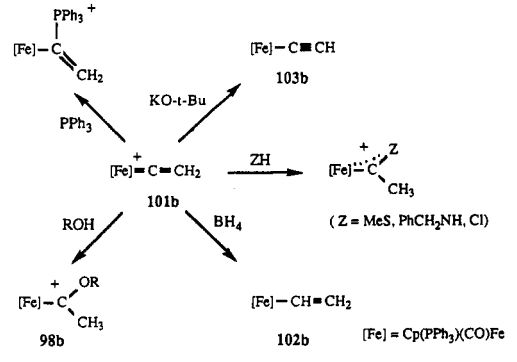
Vinylidene complexes Cp(L)(CO)Fe=C=CH_2^+ [**101a**, L = CO;[256] **101b**, L = PPh$_3$;[239a,b] **101c**, L = P(OMe)$_3$[258]] and Cp(dppe)Fe=C=CH_2^+ (**101d**)[259] are useful intermediates in interconverting acetyl and acetylide systems[260] (Scheme 22). Hughes[239] introduced the use of triflic anhydride as a convenient reagent for transforming the acetyl ligand to a vinylidene group.



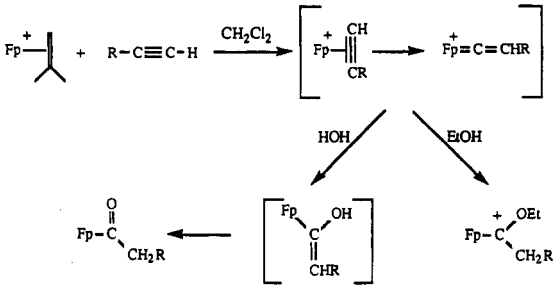
Other examples of iron and ruthenium vinylidene complexes[261] are available by replacing labile chloride with ethyne. The presumed η^2-ethyne intermediates tautomerize to isolable η^2-vinylidene complexes, **101d**[261a] and Cp(PMe$_3$)$_2$Ru=C=$CH_2^+PF_6^-$.[261b] Subsequent reaction of vinylidene complexes with alcohols, apparently a general reaction, provides alkoxycarbene compounds **98**.



Nucleophilic addition and deprotonation are prevalent reactions of vinylidene complexes, as exemplified by the results of Hughes' study of Cp(PPh$_3$)(CO)Fe=C=$CH_2^+BF_4^-$ (**101b**).[239]

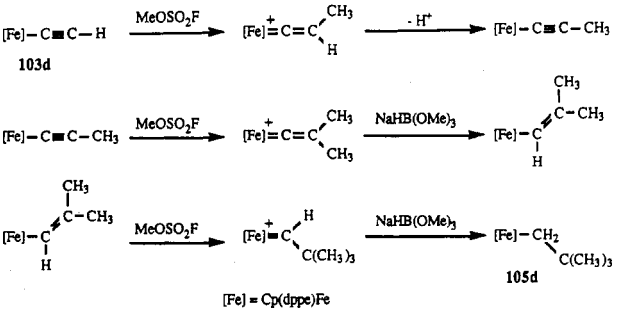


Substituted vinylidene complexes also are presumed intermediates during solvolysis of η^2-(monosubstituted alkyne) compounds to give alkoxycarbene products[258,259c,260,262] or acyl complexes.

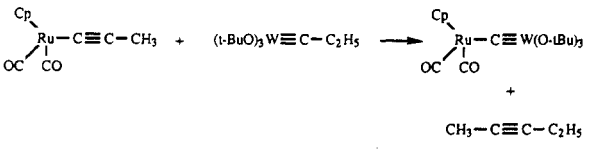


The prototropic rearrangement of an η^2-(monosubstituted alkyne) compound to its η^1-vinylidene tautomer prevails.[260] A number of stable η^2-(disubstituted alkyne) complexes Cp(L)(CO)Fe(RC≡CR′)$^+$ (L = CO, PPh$_3$, P(OPh)$_3$), on the other hand, have been characterized.[12]

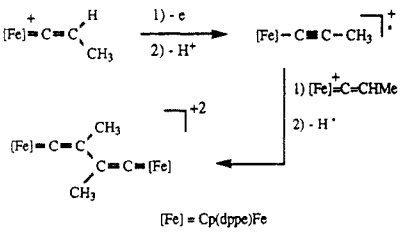
Davison[259] initially noted that η^1-(unsaturated hydrocarbyl) ligands regioselectively react with electrophiles and nucleophiles. Hydrocarbyl ligands thus containing unsaturation conjugated to the metal center[175c] (i.e., vinylidene, carbene, vinyl, and alkynide) of Cp(L$_1$)(L$_2$)Fe systems typically add electrophiles to C_β and nucleophiles to C_α. An excellent example of this regioselectivity is the stepwise conversion of the ethynyl complex Cp(dppe)Fe–C≡CH (**103d**) to the neopentyl compound Cp(dppe)Fe–CH_2CMe_3 (**105**).[259b] The electrophilic methylating agent reacts at C_β of alkynide and vinyl ligands, whereas hydride addition to vinylidene and carbene intermediates occurs at C_α.[239,260,262b,c]



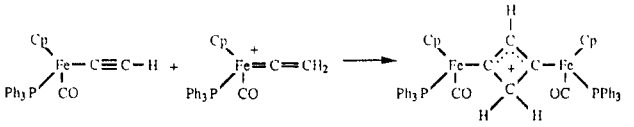
Two significant developments in vinylidene/alkynide ligand reactions have been reported recently by Selegue. First, a ruthenium propynide complex, reacting as a disubstituted alkyne, undergoes alkyne metathesis with a tungsten–alkylidyne system.



An X-ray structure determination of the organometallic product established it as a heterobinuclear μ-carbide compound.[263] Selegue also demonstrated that oxidation of an iron methylvinylidene compound affords a bimetallic system with a 2,3-dimethyl-1,3-butadiene-1,4-diylidene ligand bridging the two irons.[264] The mechanism advanced for this dimerization of the vinylidene ligand incorporates the reaction between the 17e propynide and 18e vinylidene complexes.

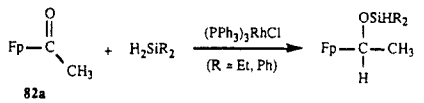


For comparison, metal-assisted cycloaddition of alkynide and vinylidene complexes (both 18e) gives four-membered rings.[259]



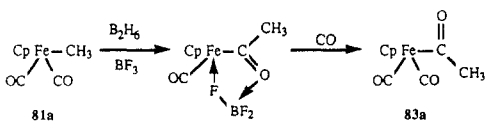
2. Reactions Centered on the Acetyl Ligand: Activation and Reduction

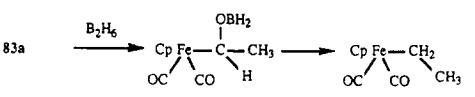
Catalytic hydrosilation of Fp–$COCH_3$ (**82a**) reduces the acetyl ligand to an α-(silyloxy)ethyl group.[265] This reaction is complete within 2 h (22 °C in CH_2Cl_2) using excess dialkylsilane and 0.5–10% $RhCl(PPh_3)_3$ as the catalyst. The products are stable once isolated (70–80%). The choice of the dialkylsilane is critical: trialkylsilanes are unreactive, and use of monoalkylsilanes engenders side reactions, including reduction of the acetyl system to give Fp–CH_2CH_3. In the absence of silane, Wilkinson's catalyst efficiently decarbonylates Fp–$COCH_3$ (**82a**) to Fp–CH_3 (**81a**).[266]



A reasonable model for hydrosilation of Fp acetyl is the catalytic hydrosilation of aldehydes and ketones.[267] Wilkinson's catalyst, $(PPh_3)_3RhCl$, also promotes this reaction, although little mechanistic work has been reported. Most workers assume a mechanism similar to that operating during homogeneous hydrogenation of alkenes, at least with the Rh(I) systems. Studies in progress address the scope of metal acyl hydrosilation, the mechanism, and the extension to catalytic asymmetric homogeneous hydrosilation of acyl complexes.

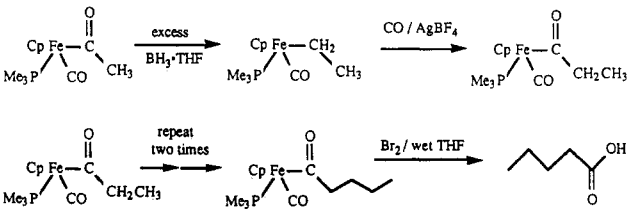
Sequentially coupling the reduction of an acyl ligand with carbonylation of the resulting alkyl group gives alkyl chain growth (homologation). Stimson and Shriver[268] established that treating the manganese methyl complex $(CO)_5Mn–CH_3$ with CO/B_2H_6 produces a mixture of C_1–C_4 alkenes and alkanes after quenching and working up the reaction with HCl–ethanol. Results of labeling studies confirm that diborane is the hydrogen source in the products and that the carbon atoms derive from CO. Adding BF_3 to the reaction mixture favors a product distribution of longer chains and more saturated hydrocarbons, although the overall hydrocarbon yields are still low (<17%). Analogous treatment of Fp–CH_3 (**81a**) requires the presence of BF_3 in order to get a 13% yield of C_2 and C_3 hydrocarbons.



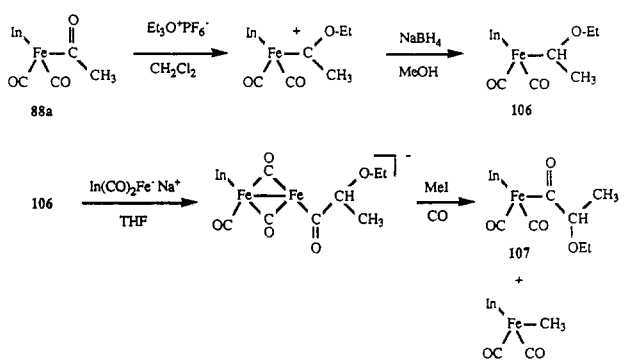


Three stages are envisioned in this reaction sequence: (1) BF_3 (or BH_3) promoted carbonylation[134] of the alkyl complex to the next homologous acyl ligand, (2) borane reduction of the acetyl or homologous acyl ligand (Scheme 7), and (3) hydrocarbon product formation. Alkanes result from protonolysis of the alkyl complexes with HCl or as a side reaction of the borane reduction, and alkenes could originate in protonation of the borane reduction intermediate Fp–$CH(OBH_2)CH_3$, for example. This protonation would generate $Fp{=}CHMe^+$ (**63a**), which affords $Fp(\eta^2\text{-}CH_2{=}CH_2)^+$ (**64a**) (Scheme 22) and free ethylene.

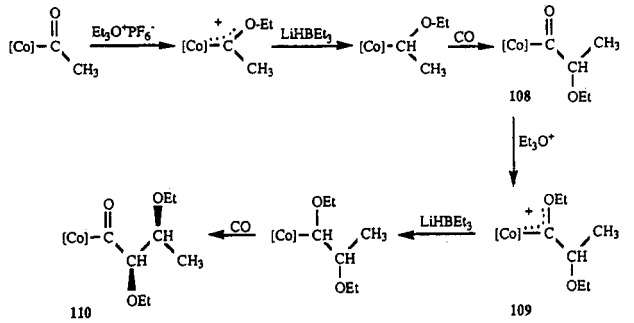
Davies[269] performed sequential borane reduction of the acyl ligand and carbonylation (oxidatively promoted) steps in preparing pentanoic acid from carbon monoxide. Reduction ($LiAlH_4$ in THF) of $Cp(PMe_3)(CO)_2Fe^+$ provided the starting methyl complex $Cp(PMe_3)(CO)Fe–CH_3$, which was carbonylated (1 atm of CO) in the presence of 2–5% $AgBF_4$. The resulting acetyl was homologated by repeating this acyl reduction and carbonylation sequence to give the pentanoyl complex $Cp(PMe_3)(CO)Fe–CO(CH_2)_3CH_3$. Bromination of this pentanoyl complex in wet THF released pentanoic acid.



Alkylation and monohydride reduction of the acyl ligand followed by carbonylation are intrinsically more demanding, since the intermediate α-alkoxyalkyl complexes are more difficult to carbonylate. Cutler and co-workers[270] used a two-step bimetallic carbonylation procedure (Scheme 21) to carbonylate the α-ethoxyethyl complex **106**, which was formed by activation and reduction (Brookhart's procedure[246]) of the starting acetyl compound (**88a**). Treatment of **106** with the metalate $(\eta^5\text{-indenyl})Fe(CO)_2^-$ affords the bimetallic α-ethoxypropionyl compound. This intermediate cleaves to the desired α-ethoxypropionyl complex **107** (63% yield after isolation by column chromatography) upon reacting with methyl iodide and CO (1 atm). Attempts to directly carbonylate **106** to **107** (55 atm of CO) instead returned starting material.

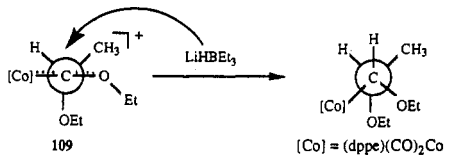


Cutler and Tso[237] used the more labile cobalt system $(dppe)(CO)_2Co$ in order to carbonylate α-alkoxyalkyl complexes. These are involved in converting its acetyl complex to the α,β-diethoxybutanoyl compound **110**.



Sequential activation ($Et_3O^+PF_6^-$), reduction ($LiHBEt_3$), and carbonylation (1 atm, 8 h) convert the starting acetyl compound into its α-ethoxypropionyl derivative **108** (81% yield). Repeating this three-step sequence of ligand reactions on **108** provides its α,β-diethoxybutanoyl homologue **110** (74%, from **108**) as the threo (syn) diastereomer.

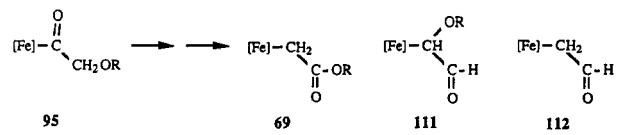
Results of an X-ray structure determination of **110** confirmed its threo configuration and established that the dppe phenyl rings do not shield the proximate face of the acyl carbonyl.[237] These phenyl rings do not hinder reagent access to one face of the acyl carbonyl on **110** and therefore are not responsible for the diastereofacial selectivity observed in reducing the alkoxycarbene compound **109**. (This deduction is predicted on the reasonable assumption that the starting configuration of alkoxycarbene **109** resembles that of the acyl **110**.) A Felkin–Anh transition-state argument,[271] in which 1,2-asymmetric induction originates in hydride delivery antiperiplanar to the β-ethoxy group, does account for the high diastereofacial selectivity.



D. Alkoxyacetyl and Carboalkoxymethyl Ligands as C_2 Templates

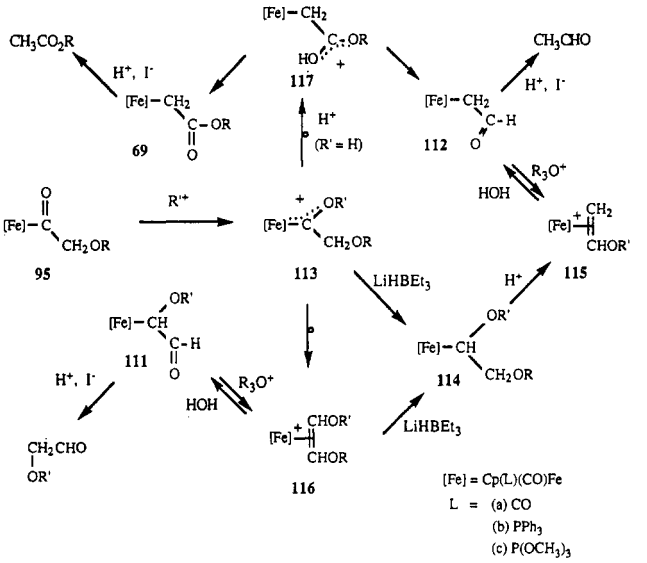
1. Alkoxyacetyl-Derived Ligands

The alkoxyacetyl ligand on organoiron complexes $Cp(L)(CO)Fe–COCH_2OR$ [**95a**, L = CO; **95b**, L = PPh_3, **95c**, L = $P(OMe)_3$] serves as a template for generating other C_2 oxygen-containing ligands.[232]



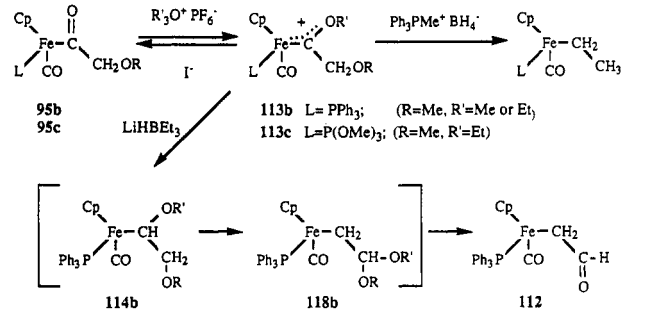
In particular, alkoxyacetyl complexes **95** can be isomerized selectively to carboalkoxymethyl **69** or to alkoxyformylmethyl **111** and can be reduced to formylmethyl **112** compounds. Compounds **69**, **111**, and **112** eliminate C_2 oxygen-bearing molecules upon protonolysis. In principle, both skeletal carbons originate from

SCHEME 23



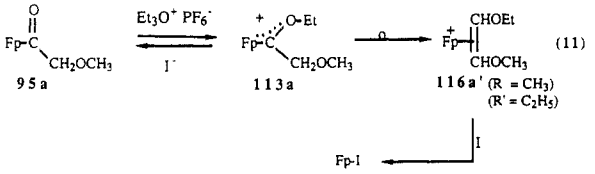
ligated CO. Scheme 23 outlines the ligand reactions that are used in transforming alkoxyacetyl **95** to acetic acid ester (via carboalkoxymethyl **69**), to glycol aldehyde ether (via alkoxyformylmethyl **111**), and to acetaldehyde (via formylmethyl **112**).

Alkylation of PPh_3- and $P(OMe)_3$-substituted alkoxyacetyl complexes **95b,c** with trimethyl- or triethyloxonium hexafluorophosphate salts provides the alkoxycarbene compounds **113b**[232a] and **113c**,[85] respectively, in moderate yields. Once purified, **113b,c** are stable in methylene chloride solution; adding iodide quantitatively regenerates starting **95b,c**



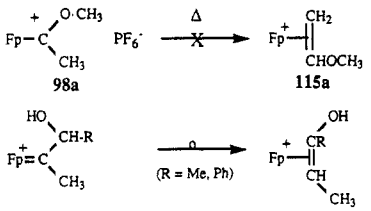
Borohydride reagents selectively reduce the alkoxycarbene complex **113b**.[232] For example, $PPh_3Me^+BH_4^-$ in methylene chloride converts **113b** to its ethyl complex (69% yield). The absence of detectable α- or β-alkoxyethyl derivatives is consistent with subsequent BH_3 reduction of these intermediates. Monohydridic reduction of **113b** with $LiHBEt_3$ or $LiHB(sec\text{-}Bu)_3$ provides exclusively the formylmethyl system **112b** in 63% isolated yield. This product can be accounted for by electrophile (e.g., BEt_3) induced ionization of an α,β-dialkoxyethyl intermediate **114b** first to η^2-vinyl ether intermediate **115b** and then to formylmethyl acetal **118b**, which is the precursor to the observed **112b**. These transformations involving the postulated intermediates **114b**, **115b**, and **118b** follow from the documented reaction chemistry of their $Cp(CO)_2Fe$ congeners.

Alkylation of the Fp methoxyacetyl **95a** (L = CO, R = CH_3) with triethyloxonium hexafluorophosphate (eq 11) is complicated by slow irreversible isomerization ($t_{1/2}$ 24 h) of the alkoxycarbene kinetic product **113a**



to the Fp(η^2-*cis*-1,2-dialkoxyethylene) compound **116a′** (R = Me, R′ = Et).[188] By careful control of the reaction conditions, either spectroscopically pure **116a′** or an 85:15 mixture of **113a** and **116a′** are obtained. The relative proportions of **113a** and **116a′** are deduced easily from direct NMR spectral monitoring of the reaction mixture before and after quenching with iodide. This iodide treatment regenerates **95a** from **113a** and immediately intercepts **116a′** to give FpI plus free olefin.

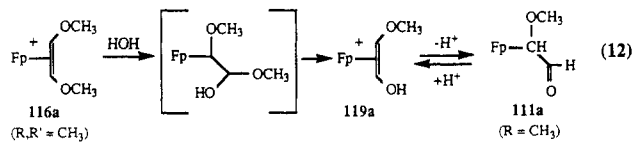
Isomerization of **113a** to the dialkoxyethylene compound **116a′** apparently involves shifting a hydride from the β-carbon to the α-carbon analogous to that observed with electrophilic alkylidene complexes (Scheme 22). This isomerization is unusual in that alkoxycarbene compounds have not been reported to undergo this carbene-to-alkene rearrangement.[167]



The methoxycarbene complex **98a** (R = CH_3) containing only the one alkoxy group, for example, does not isomerize in refluxing CH_2Cl_2 within 18 h to the stable η^2-methyl vinyl ether compound **115a** (R′ = Me).[188] Presence of the alkoxy group on the β-carbon bearing the migrating hydride apparently facilitates the hydride transfer. Indeed, Fp(carbene)$^+$ salts that have β-OH or β-OR substituents regioselectively isomerize to their η^2-vinyl alcohol or η^2-vinyl ether complexes.[272]

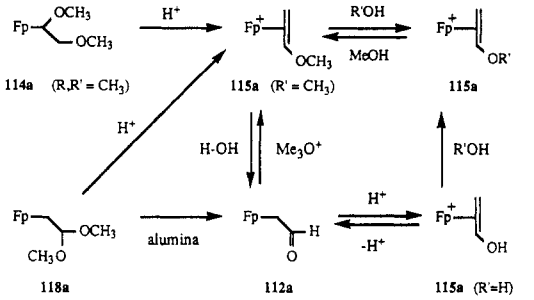
The PPh_3- and $P(OMe)_3$-containing alkoxycarbene compounds [Cp(L)(CO)Fe=C(OR′)CH_2OR]$^+$ (**113b,c**) do not isomerize to η^2-dialkoxyethylene derivatives **116b,c**. The role of the phosphine and phosphite in retarding the isomerization of electrophilic carbene complexes is demonstrated with Cp(L)(CO)Fe=$CHCH_3^+$ (**63b,c**). These methylcarbene complexes rearrange much less readily to their η^2-ethylene compounds than does their Fp congener (L = CO).[165,246]

The readily accessible Fp(η^2-*cis*-dimethoxyethylene)$^+BF_4^-$ (**116a** R, R′ = CH_3) is a convenient precursor to the methoxyformylmethyl complex **111a**. Starting **116a** is available by displacing the olefin in Fp(isobutylene)$^+BF_4^-$[188,273,274] with *cis*-1,2-dimethoxyethylene. Hydrolysis of **116a** then affords **111a** in moderate yield (eq 12).[188] The *cis*-η^2-vinyl alcohol



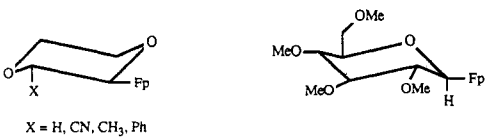
compound **119**, a postulated intermediate in this hydration sequence, is generated independently by protonating **111a**. Deprotonation of **119** regenerates **111a**, whereas treating **119** with iodide gives methoxyacetaldehyde plus FpI. Alkylation of **111a** using $Et_3O^+PF_6^-$ produces the η^2-*cis*-methoxyethoxyethylene compound **116a′**.

SCHEME 24



Reduction of the alkoxycarbene complex **113a** or of the dimethoxyethylene salt **116a** with $LiHBEt_3$ gives the Fp(α,β-dialkoxyethyl) compounds **114a′** (R′ = Et, R = Me) and **114a** (R′, R = Me).[188] Once isolated, these alkyl compounds **114a** and **114a′** are relatively stable in the absence of acidic contaminants. In methylene chloride solutions they neither isomerize to formylmethyl acetals—e.g., Fp–$CH_2CH(OMe)_2$ (**118a**)[166] from **114a** (R, R′ = CH_3)—nor degrade to the formylmethyl Fp–CH_2CHO (**112a**).[166,275] The former product would have resulted from ionization and readdition of alkoxide to the η^2-vinyl ether intermediate **115a**. Compound **112a** is the thermodynamically favored product of treating **118a** with a variety of electrophiles.[166] The α,β-dialkoxyethyl complexes **114a** thus are no less stable than other Fp(η^1-alkyl) complexes bearing only one alkoxy substituent at either the α-carbon (e.g., **99**) or the β-carbon (such as Fp–CH_2CH_2OMe[276] or Fp–$CH_2CH(OMe)_2$ (**118a**)[166]).

Transition-metal alkyl complexes containing alkoxy (or hydroxy) functionalities on *both* α- and β-carbons are rare, although complexes bearing one oxygen functionality at either α- or β-positions are well-known. An (α,β-dihydroxyethyl)rhodium porphyrin complex has been characterized by Wayland,[277] as has the carbonate derivative of this glycol ligand bound to a cobalt system.[278] Rosenblum[274b] recently reported a series of Fp(1,4-dioxan-2-yl) derivatives in which the ether functionalities (α and β to the Fp group) are incorporated into the dioxane ring. Finally, several examples of $(PPh_3)(CO)_3Co$-, $(CO)_5Mn$-, and Fp-substituted *C*-glycoside polyethers, available by metalating a glycosyl halide, offer further examples of α,β-dialkoxyalkyl transition-metal complexes.[279]



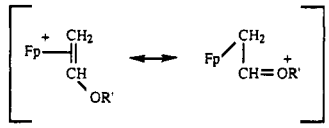
The Fp(α,β-dialkoxyethyl) complexes **114a** readily convert to Fp(η^2-vinyl ether)$^+BF_4^-$ or Fp(η^2-vinyl ether)$^+PF_6^-$ upon treatment with acid or with $Ph_3C^+PF_6^-$. Abstracting alkoxide from Fp-CH(OEt)CH_2(OMe) (**114a′**) is regioselective and gives the ethyl vinyl ether salt **115a** (R′ = Et). Subsequent hydrolysis of **115a** affords the formylmethyl **112a**, which releases acetaldehyde upon protonating in the presence of iodide.[188]

Coordinated ligand reactions involving Fp(η^2-vinyl ether)$^+$ compounds had been established previously (Scheme 24).[5a,6,166,280] For example, Fp(η^2-methyl vinyl

ether)$^+$ (**115a**, R = Me) is the product of reacting Fp-(formylmethyl dimethyl acetal) complex **118a** with acid or trityl carbocation. Compound **118a**, in turn, derives from metalating chloroacetaldehyde dimethyl acetal, $ClCH_2CH(OMe)_2$, with Fp^-Na^+.[166] Alternatively, **118a** upon contact with alumina converts to formylmethyl **112a**, and electrophilic methylating reagents (e.g., MeOTf, $Me_3O^+BF_4^-$) then convert **112a** to the methyl vinyl ether complex **115a** (R′ = Me). Protonation of **112a** yields the isolable Fp(η^2-vinyl alcohol)$^+$,[166] which iodide readily cleaves to acetaldehyde and FpI.[188] The fully characterized η^2-ethyl vinyl ether complex Cp(P(OMe)$_3$)(CO)Fe(CH_2=CHOEt)$^+PF_6^-$ (**115c**) likewise results from treating its formylmethyl complex Cp(P(OMe)$_3$)(CO)Fe–CH_2CHO (**112c**) with $Et_3O^+PF_6^-$.[85]

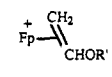
Both Fp(η^2-dialkoxyethylene)$^+$ (**116a**)[188,274] and the Fp(η^2-vinyl ether)$^+$ (**115a**)[6,280] systems readily add nucleophiles to the coordinated olefins. Transetherification of **115a** (Scheme 24) or of **116a** involves dissolving examples of either complex in the appropriate alcohol and then precipitating the new alkoxy olefin complex with ether. In these reactions, alcohols exchange the olefinic alkoxy groups by engaging in a series of solvolytic equilibria that involve adding the new alkoxide to give a formylmethyl acetal intermediate, which then eliminates the original alkoxy group as its alcohol. Similar equilibria operate during hydrolysis of the dimethoxyethylene complex **116a** to its α-methoxyformylmethyl **111a**,[188] a reaction involving the hemiacetal intermediate depicted (eq 12).

The regioselectivity observed in adding alcohols or a variety of other nucleophiles to η^2-vinyl ether complexes **115a** conforms with partial charge localization



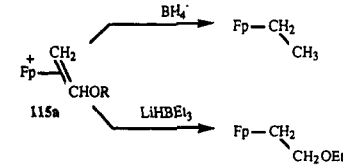
115a

at the substituted vinylic carbon. This charge localization indicates significant contribution of η^1-bonding of the vinyl ether ligand. Spectral correlations[6,166,185a] involving the IR absorption frequencies of the terminal carbonyls and the chemical shifts of the Cp ligands in the ^1H and ^{13}C NMR spectra also support charge localization at this alkoxy-bearing carbon. The results of an X-ray structure determination of the methyl vinyl ether complex **115a** (R′ = Me) support this view.[186] The vinyl ether coordinates as an unsymmetrically bound η^2-complex having the Fe–C_α bond distance 0.12 Å shorter than the Fe–C_β separation.

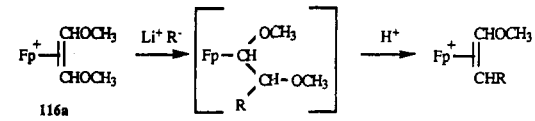


115a

Reduction of Fp(η^2-vinyl ether)$^+$ (**115a**) also is regioselective. For example, reduction with $LiHBEt_3$ gives β-alkoxyethyl complexes in 90% yields.[169] Treatment of Fp(η^2-CH_2=CHOR′) (**115a**) with 1 equiv of $Ph_3PMe^+BH_4^-$ in CH_2Cl_2 gives 50% conversion to the ethyl complex Fp–CH_2CH_3. This is the first demonstration that BH_3 also reduces β-alkoxyalkyl complexes, as previously documented with the α-alkoxyalkyl systems.



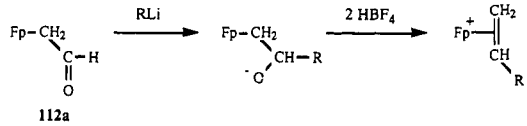
Rosenblum[5a] has used Fp(η^2-vinyl ether)$^+$ (**115a**) and Fp(η^2-dialkoxyethylene)$^+$ (**116a**) complexes as vinyl cation[6,280] and vinylene dication[274] synthetic equivalents, respectively. Carbanions readily add to these organoiron systems, and the resulting alkoxyalkyl complexes generate new η^2-alkene compounds after protonation.



116a

For example, the dimethoxyethylene complex **116a** when sequentially treated with an alkyllithium reagent and then acid affords new vinyl ether complexes corresponding to regioselective abstraction of β-substituted methoxide from the proposed intermediate. The remaining methoxy group likewise is replaced by repeating the sequence of alkylation (R′Li) and then protonation, with stereochemistry of the resulting η^2-alkene complex Fp(RCH=CHR′)$^+$ controlled by manipulating the reaction conditions.

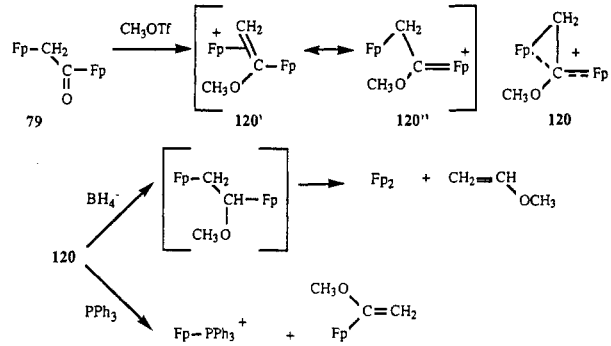
The formylmethyl complex **112a** also can be converted to η^2-alkene complexes. Marten and Akbari[281] recently reported that alkyllithium and Grignard reagents add to Fp–CH_2CHO (**112a**); the intermediate alkoxide complexes give the η^2-alkene products after protonation.



112a

The alkoxide intermediates correspond to those reported as the initial product of treating epoxides $RCHCH_2O$ with Fp^-.[187b]

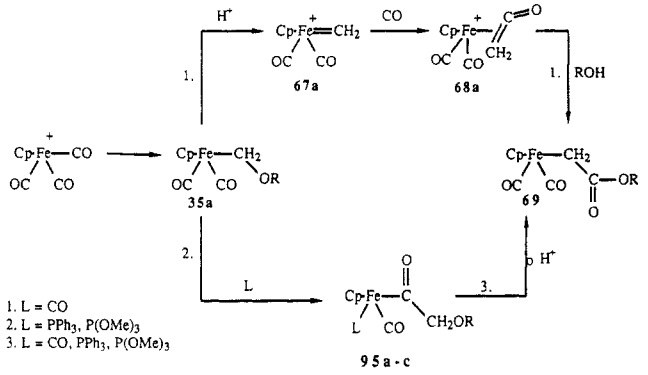
A bimetallic η^2-vinyl ether complex **120** is the result of alkylating the μ-ketene compound **79**.[46b] Spectral



79 **120′** **120″** **120**

data indicate a bimetallic system that is clearly intermediate between Fp(η^2-vinyl ether)$^+$ (resonance form **120′**) and Fp(η^1-alkoxycarbene)$^+$ (**120″**) structures, with charge delocalization over both iron centers (**120**). Borohydride reduction of **120** apparently generates Fp–$CH_2CH(OMe)$–Fp, which fragments into methyl vinyl ether plus Fp_2. Similar ethane-1,2-diyl systems Fp–CH_2CH_2–Fp are known to readily extrude ethylene and leave Fp_2.[10a] Triphenylphosphine reacts with **120** and releases the Fp(η^1-methoxyvinyl) complex.

SCHEME 25



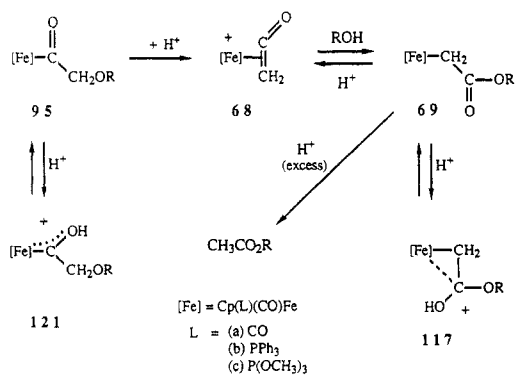
2. Carboalkoxymethyl-Derived Ligands

Two routes are available for synthesizing the C_2 carboalkoxymethyl ligand on Cp(L)(CO)Fe–CH_2CO_2R (**69a–c**) from two molecules of CO (Scheme 25).[232] The first route is the carbonylation of the transient methylene complex $Fp{=}CH_2^+$ (**67**) to its isolable ketene compound $Fp(CH_2CO)^+PF_6^-$ (**68a**) and alcoholysis (eq 10).[185] This reaction performed in situ gives Fp–CH_2CO_2Me (**69a**)[25a,16,282] in 55% yield, using protonolysis of Fp–CH_2OMe (**35a**) to generate **67**, or in 93% yield, using Fp–CH_2Cl (**60a**) and $AgPF_6$ to generate **67a**.[185b]

The second route is the acid-induced isomerization of alkoxyacetyl complexes **95a–c** to carboalkoxymethyl compounds **69a–c**.[85,232] The presence of between 0.2 and 1.0 equiv of triflic acid or $HBF_4{\cdot}OEt_2$ in methylene chloride quantitatively transformed **95**, and the resulting **69** are isolated (60–77% yields) after neutralization with triethylamine and column chromatography.

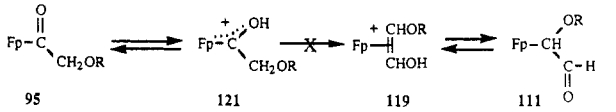
Direct spectral monitoring of these reactions starting with Fp–$COCH_2OMe$ (**95a**) or with $Cp(P(OMe)_3)$-(CO)Fe–$COCH_2OMe$ (**95c**) indicates the presence of four species for each system (**95**, **121** and **69**, **117**).[85,232] Their relative concentrations vary with reaction time and acid concentration. Complex **117a**, Fp–CH_2C-$(OH)(OMe)^+BF_4^-$, formally containing a ligated ketene hemiacetal, was characterized fully by Rosenblum.[166]

Under comparable reaction conditions, hydroxycarbene complexes $Cp(L)(CO)Fe{=}C(OH)CH_3^+$ (L = CO, PPh_3,[238,283] $P(OMe)_3$[85]), which are generated by protonating the parent acetyl compounds, are stable.[196]



Ketene complexes **68a–c** are plausible, if unobserved, intermediates in the isomerization of **95a–c** to **69a–c**. Both Fp(methoxyacetyl) (**95a**) and Fp(carbomethoxymethyl) (**69a**) convert to the ketene complex **68** in CH_2Cl_2 or CH_3NO_2 solution with at least 3 equiv of FSO_3H.[284] This product was identified by IR and ^1H and ^{13}C NMR spectroscopy. Under similar conditions, $HBF_4{\cdot}OEt_2$ converts both **95a** and **69a** to Fp–CH_2C-$(OMe)(OH)^+BF_4^-$ (**117a**). Aumann and Wormann[282b] proposed that dissolution of Fp–CH_2CO_2H in HSO_3F–SO_2ClF generates **68**, as indicated by the ^1H NMR spectrum.

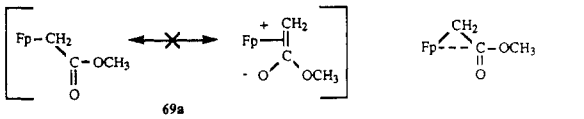
Carboalkoxymethyl complexes **69** are the only products of acid-promoted isomerization of alkoxyacetyl systems **95**. Interestingly, the alkoxyformylmethyl isomers **111** are not detected. Although hydroxycarbene complexes **121a–c** appear in the reaction mixtures, they evidently do not isomerize to vinyl alcohol compounds **119** under the reaction conditions.[85,232]



The phosphine- and phosphite-substituted alkoxyacetyl complexes **95b** and **95c**, when treated with excess triflic acid (24 h), release methyl or ethyl acetate in 70–90% yields.[85,232] Protonolysis of the carbalkoxymethyl complexes **69b** and **69c**, as observed for other Fp–alkyl complexes,[285] accounts for the observed alkyl acetate. Flood[285a] previously had noted the acid sensitivity of **69b**.

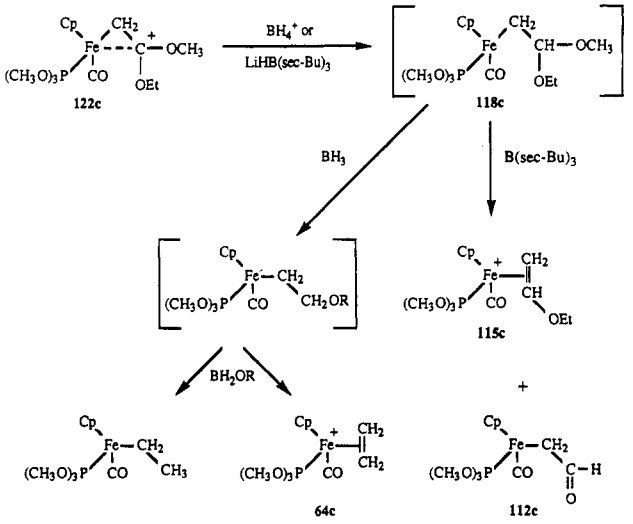
Protic isomerization of alkoxyacetyl complexes **95a–c** actually serves as the most convenient synthesis of carboalkoxymethyl complexes **69**. In previous preparations of **69**, metalation of methyl or ethyl chloroacetate with Fp^- gave very low yields of the desired product.[25a,166,282a] Of the large variety of transition-metal carboalkoxymethyl complexes—also referred to as 2-oxaallyl (η^1-(C)enolate) compounds—that have been characterized, most were procured using an alkyl haloacetate and a nucleophilic metal system.[286] The PPh_3-substituted carbomethoxymethyl complex Cp-$(PPh_3(CO)Fe$–CH_2CO_2Me (**69b**) has been prepared previously by photolytic replacement of CO by PPh_3 on **69a** (R = Me).[90a]

Analysis of spectral and structural data for carboalkoxymethyl complexes **69** indicates a metal interaction with the β-acyl group. IR spectra of **69** thus indicate a reduced acyl C–O bond order: the ester ν(CO) of Fp–CH_2CO_2Me is 1678 cm^{-1}, vs 1738 cm^{-1} for methyl acetate (in CH_2Cl_2).[85] The results of X-ray structure determinations of Fp–CH_2CO_2H,[282a] $Cp(PPh_3)(CO)Fe$–CH_2CO_2(menthyl),[90b] and other transition-metal carboalkoxymethyl complexes,[286] however, indicate the absence of significant contribution from a dipolar resonance form involving an η^2-ketene acetal structure.



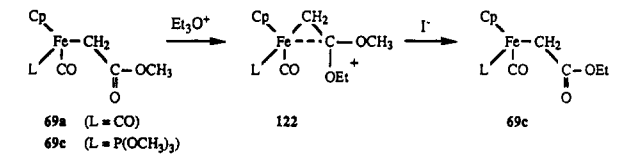
Rather, these structure determinations suggest that the ester π-system generally is oriented to allow interaction with the metal. A through-space interaction involving the β-acyl π-system and the appropriate metal orbitals (originally hypothesized as the "β-effect" by Green[287]) results in metal stabilization of a developing β-carbocation center as electrophiles add to the β-acyl functionality. This metal stabilization accounts for the high

SCHEME 26



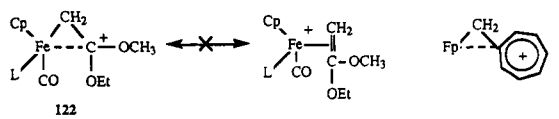
reactivity of carboalkoxymethyl complexes **69** (as well as formylmethyl systems) toward electrophiles.

The carbomethoxymethyl complexes **69a,c** readily react with triethyloxonium hexafluorophosphate to give fully characterized (dialkoxycarbenio)methyl complexes **122**.[85,166]



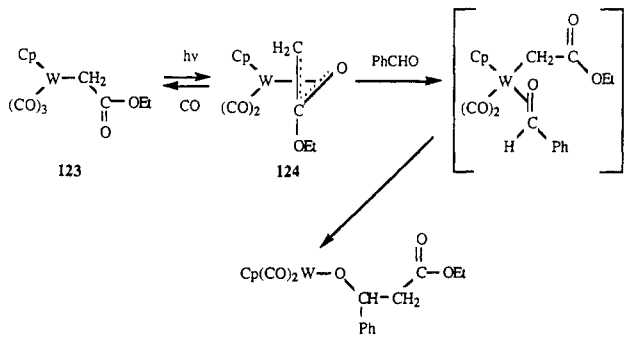
Iodide dealkylates **122a,c** and rapidly regenerates **69a,c**. An interesting application of this reaction is the transesterification of the carbo*methoxy*methyl **69c** to the carbo*ethoxy*methyl **69c**.[85] A similar selectivity in S_N2 displacement (using iodide) of methyl vs ethyl groups from alkoxycarbene complexes has been noted.[160] This iodide assay for **69** was used to establish that isomerization of the alkoxycarbene **113a** (eq 11 and Scheme 23) exclusively goes to the dialkoxyethylene system **116a**, with none of the isomeric **122a** being detected.[188]

Spectral data for **122a,c** are consistent with the Fe-stabilized β-dialkoxycarbenium ion structure depicted.[6,85,166,185] Alternative structures either lacking delocalization of charge onto the iron on **122** or involving an η^2-ketene acetal can be eliminated. The structures **122a,c**, furthermore, resemble that of the Fp–η^1-heptafulvene salt, which in agreement with spectral data and results of an X-ray structure determination favors delocalization of charge from the β-position to the iron.[288]

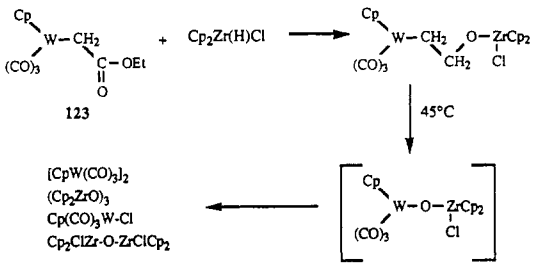


The (dialkoxycarbenio)methyl complex **122c** is an activated form of the otherwise unreactive carboalkoxymethyl system **69c**.[85] For example, **69c** is inert toward BH_4^-. Sodium borohydride (1 equiv) in ethanol, however, converts **122c** to a 1:1 mixture (total yield, 65%) of the η^2-ethylene and η^1-ethyl complexes, whereas $Ph_3PMe^+BH_4^-$ in CH_2Cl_2 quantitatively gives the ethyl complex. $LiBH(sec\text{-}Bu)_3$, in contrast, cleanly reduces **122c** in THF (–80 °C) to a 1:1.2 mixture of η^2-ethyl vinyl ether **115c** and formylmethyl **112c** complexes. Scheme 26 outlines hypothesized pathways leading to these products; the formylmethylacetal and β-alkoxyethyl intermediates were not detected.

Bergman and Heathcock[286] recently established that the tungsten carboethoxymethyl complex $Cp(CO)_3W$–CH_2CO_2Et (**123**) undergoes a photochemical aldol condensation with aldehydes to give isolable tungsten aldolate complexes. Photolysis of **123** affords a stable η^3-oxaallyl **124**. Photolysis of **123** and benzaldehyde in a closed system, however, generates an η^1-O aldolate complex (90% yield), which upon protonation releases the organic aldol.



The same tungsten carboethoxymethyl complex **123** in undergoing reduction with $[Cp_2Zr(H)Cl]_x$ gives a WZr μ-oxaalkyl complex.[289] Upon warming, this product extrudes ethylene and leaves a complex mixture of organometallic products.



The independently characterized heterodinuclear μ-oxo$Cp(CO)_3W$–O–$ZrClCp_2$ is a likely intermediate in this thermolysis.

V. Summary

The $Cp(L_1)(L_2)Fe$ moiety (L_1, L_2 = CO, phosphine, phosphite) is proving to be extremely useful in investigating coordinated ligand reactions that involve C_1 and C_2 oxygen-containing ligands. Their complexes often are sufficiently robust that multiple synthetic sequences interconverting these ligands are practiced, and intermediates during these ligand reactions are detected spectroscopically if not actually isolated. We have emphasized those reactions in which ligand skeletal carbon centers originated with CO_2 or CO. An understanding of these ligand reactions, including stereochemical details, is relevant to understanding (and developing) certain homogeneous catalytic systems and to adopting transition organometallic ligand reactions in organic synthesis. A combination of the stereoelectronic requirements involving the iron centers in these ligand reactions, the presence of iron-based chirality (when L_1 and L_2 differ), and the overall "stability" of these com-

plexes undoubtedly will ensure the continued popularity of these organoiron compounds.

The versatility of $Cp(L_1)(L_2)Fe$ complexes is further evident through "fine-tuning" the metal center. Rates of reactions and thermodynamic stabilites of these complexes vary enormously with changes in the ancillary ligands Cp and L, and even in the metal center, although the types of ligand reactions available for these congeners does not vary. Thus adopting a strategy of incorporating Cp* or phosphine and phosphite ligands or Ru and Os centers into these complexes greatly enhances their stabilities. These observations are particularly noteworthy concerning the "bench stabilities" of this group of complexes bearing C_1 ligands, and indeed the role of Cp* in enhancing the kinetic stability of its organometallic compounds is well established.[290]

A more recent development is to perturb $Cp(L_1)(L_2)Fe$ complexes in order to increase their lability. One application is to promote the carbonylation of iron alkyl complexes, toward which two approaches appear particularly promising. Oxidatively promoted carbonylation reactions are particularly facile for CpFe complexes bearing at least one phosphine center, and the presence of an η^5-indenyl ligand in these iron (and ruthenium) systems also facilitates alkyl to CO migration reactions.

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Registry No. CO, 630-08-0; CO_2, 124-38-9.

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