Anal. Calcd for $C_9H_{11}O_2Re$: C, 32.04; H, 3.29. Found: C, 32.32; H, 3.31.

**Preparation of $(\eta\text{-}C_5H_5)Re(CO)_2(C_4H_6O_2)$ (8).** The tetraethylammonium salt of the anion prepared above (0.15 g, 0.26 mmol) was stirred with acetyl chloride (50 mg, 0.64 mmol) in 10 mL of tetrahydrofuran for 10 h. Solvent was removed (vacuum), and the residue was extracted with heptane (30 mL); IR spectrum showed product plus some $(\eta\text{-}C_5H_5)Re(CO)_3$ and 2. This heptane extract was placed on a 50-g florisil column. Elution with 100 mL of a 1:1 mixture of dichloromethane and heptane removed the two carbonyl impurities, and then 75 mL of pure dichloromethane eluted the product. Evaporation of the solvent and sublimation of the residue under vacuum resulted in a pale yellow solid product (50 mg, 50%): mp 38–41 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 6.49 (dd, 1 H), 5.30 (s, 5 H, cyclopentadienyl), 2.28 (dd, 1 H), 2.13 (dd, 1 H), 2.03 (s, 3 H); mass spectrum, $M^+$, $(M - CO)^+$, $(M - 2CO)^+$, $(C_4H_6O_2)^+$.

Anal. Calcd for $C_{11}H_{11}O_4Re$: C, 33.59; H, 2.80. Found: C, 33.70; H, 2.95.

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**Registry No.** 2, 80952-45-0; 4, 79061-68-0; 5, 80925-98-0; 6, 80925-99-1; 7, 80952-46-1; 8, 80926-00-7; $[Et_4N]_2[(\eta\text{-}C_5H_5)Re(CO)_2]$, 80926-02-9; $Et_2SiH_2$, 542-91-6; $SnCl_4$, 7646-78-8; $Me_3SnCl$, 1066-45-1; acetyl chloride, 75-36-5.

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# Reductive Carbonylation of $Mn(CO)_5(CH_3)$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2(CH_3)$ To Produce Hydrocarbons and Oxygen-Containing Products

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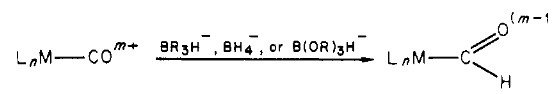
Under a CO atmosphere $Mn(CO)_5(CH_3)$ reacts with diborane to produce alkanes and olefins up to $C_4$. The yield drops greatly from $C_2$ through $C_4$ products, suggesting a chain growth mechanism. Addition of $BF_3$ to the reaction mixture alters the product distribution by increasing the yield of the longer chain and more saturated hydrocarbons. The reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(CH_3)$ with CO and diborane requires the presence of $BF_3$ to produce $C_2$ and higher products, and the function of $BF_3$ is to promote CO migratory insertion. Isotopic labeling experiments confirm diborane as a source of hydrogen in the products and also demonstrate that carbon atoms in the hydrocarbon products are derived from CO. These general observations are consistent with a repetitive series of migratory insertion and reduction steps, but the presence of unsaturated hydrocarbons and oxygen-containing organics as well as the isotopic composition of the hydrocarbons indicate a complex set of intermediate steps.

## Introduction

Since the initial report in 1939,[1] the reduction of organic carbonyl groups by boron and aluminum hydrides has received widespread application.[2] The varying strengths and selectivities of these reagents allow considerable control over the specific reaction. More recently these inorganic hydrides have found application as well in organometallic systems.[3–15] The course of the reactions differs slightly in the organic and organometallic systems. In a typical organic procedure the initial reduction is followed by a hydrolysis step to produce an alcohol, while in the organometallic systems hydrolysis is not always required to produce a boron-free product.

As seen in the following examples, the extent of reaction varies from transfer of a single hydride (eq 1) to more complex reactions involving several equivalents of hydride (eq 2). A borohydride reagent, $BH_4^-$, $BR_3H^-$, or $B(OR)_3H^-$, can attack and transfer a single hydride to the electrophilic



(1)

$m = 0, 1$

$$[(\eta^5\text{-}C_5H_5)(NO)(CO)_2Re]^+ \xrightarrow{BH_4^-} (\eta^5\text{-}C_5H_5)(NO)(CO)Re(CH_3) \quad (2)$$

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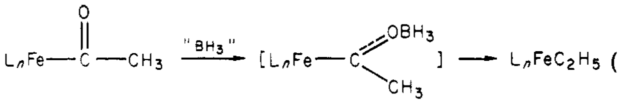
carbon in Fischer-type carbenes,[3-5] thioformyl complexes,[6] cationic ethylene complexes,[7] and cationic and neutral metal carbonyls.[8-10] Under more stringent conditions the reduction can proceed to the formation of metal alkyls (eq 2)[9,11] or in some cases the free alkane.[12]

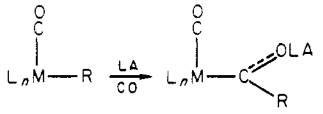
Diborane and alane are also effective reducing agents for metal carbonyl complexes. Diborane converts metal formyls[8,10,13] and acetyls[14] to the corresponding methyl and ethyl complexes, respectively. The more powerful $AlH_3$ produces hydrocarbons from $Ru_3(CO)_{12}$.[15] The major difference between the borohydride reagents and diborane appears to lie in the site of initial attack. The electron-rich borohydride reagents react at an electrophilic center by hydride transfer as shown in eq 1. In contrast, the Lewis acids borane and alane are thought to attack an electron-rich site such as a carbonyl oxygen, which is followed by hydride transfer. It is this mode of reaction leading to the Lewis acid adduct intermediate I which is proposed in the reduction of metal acetyls to metal alkyls (eq 3).[14]



(3)

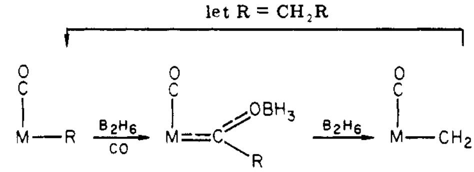
I

Lewis acid adducts of metal acetyls are known,[16] and recently it was shown that molecular Lewis acids dramatically increase the rate of migratory alkyl insertion of CO (eq 4).[17] The rate of reaction may be enhanced by a factor of at least $10^7$,[18] and the position of the equilibrium can be altered by the Lewis acid to favor the insertion product.



(4)

The present research was designed to explore the possible combination of Lewis acid promoted migratory CO insertion with borane reduction to effect the buildup of alkyl chains from CO by successive insertion and reduction steps (eq 5). In reaction 5 diborane might play the dual



(5)

role of assisting the CO insertion reactions as well as reducing the resulting metal acyl but the studies reported here include stronger Lewis acids in addition to the diborane in the reaction mixture.

## Experimental Section

**Materials.** The compounds $Mn(CH_3)(CO)_5$,[19a] $Mn(C(O)CH_3)(CO)_5$,[20] $(\eta^5\text{-}C_5H_5)Fe(CH_3)(CO)_2$,[19b] and $(\eta^5\text{-}C_5H_5)Fe(C(O)CH_3)(CO)_2$[21] were prepared by modifications of literature procedures, and products were judged pure by proton NMR and IR spectra. Diborane and $B_2D_6$ were prepared by the method of Norman and Jolly using $NaBH_4$ (Aldrich, 99+%) and $NaBD_4$ (Aldrich, 98 atom %).[22] The diborane and $BF_3$ (Linde) were purified by trap-to-trap distillation until their vapor pressures agreed with literature values.[23] A 1 M THF solution of $BH_3$·THF was used as received (Aldrich). Carbon monoxide (Matheson, CP grade) and $^{13}CO$ (Monsanto Research Corp., 99+ atom %) were used as received and stored over silica gel. Hydrogen chloride (Matheson, technical 99.0%) was used without further purification. The Amberlyst A21 ion-exchange resin was dried under vacuum before use. Under $N_2$, toluene, THF, dioxane, and diglyme were distilled from sodium benzophenone ketyl; $CH_2Cl_2$, $C_6H_5Cl$, and $o\text{-}C_6H_4Cl_2$ were distilled from $P_2O_5$; ethanol and methanol were distilled from magnesium turnings, and pyridine was distilled from barium oxide.

**General Procedures.** All sample manipulations were carried out by using standard inert-atmosphere techniques. The Lewis acids and more volatile solvents were measured and transferred on a preparative high vacuum line.

In a typical reaction a flask was charged with 0.3–0.5 mmol of metal complex. The solvent, $BF_3$, and $B_2H_6$ were measured and condensed at −196 °C into the reaction vessel on the vacuum line. Carbon monoxide was admitted to the frozen reaction flask and the amount determined by the pressure change in a known volume. After the mixture was stirred for several hours to several days, the reaction was frozen and the noncondensable gases analyzed. The remaining CO and any $CH_4$ formed were generally collected by adsorption on $SiO_2$ at −196 °C, and the total quantity of gas was determined by *PVT* measurement. Quantitative IR spectroscopy was employed to measure the $CH_4$. The condensable products were usually fractionated on the vacuum line. The most volatile fraction was passed through a bed of the amine resin to remove excess borane. Amounts of the remaining gaseous products were determined by *PVT* measurements. After initial removal of volatiles, 5–16 mmol of HCl and 5–9 mL of ethanol (or methanol) was distilled into the remaining solution. The reaction was stirred for several hours followed by a second product separation, including removal of excess HCl by the amine resin. The gaseous products were analyzed by GC, GC-MS, or high-resolution mass spectrometry. The higher boiling products which remained in solution were analyzed by GC or GC-MS. Organometallic products were sublimed or recrystallized and characterized by IR.

Gas-phase hydrocarbon samples were analyzed on a PE-820 gas chromatograph equipped with 6 ft × $^1/_8$ in. Spherocarb (80/100 mesh) columns. Solutions were analyzed on 6 ft × $^1/_8$ in. Porapak Q columns (80/100 mesh).

**Reactions with $Mn(CH_3)(CO)_5$ (A).** Diborane (0.98 mmol) was trapped into a 0.05 M toluene solution of $Mn(CH_3)(CO)_5$ (0.27 mmol). After addition of Co (4.10 mmol) the solution was stirred 40.5 h. Removal of unreacted CO and protolysis were followed by neutralization and gas analysis which showed a 7% yield of $CH_4$ and a 13% yield of hydrocarbons (based on Mn). An IR of the remaining solution indicated $Mn_2(CO)_{10}$ as one of the manganese-containing products.

Reactions B, C, D, and E were run under conditions similar to A, differing only in the presence or absence of $BF_3$ (see Table I).

**Reactions in the Absence of CO (F).** To a 0.062 M toluene solution of $Mn(CH_3)(CO)_5$ (0.355 mmol) were added $B_2H_6$ (1.07 mmol) and $BF_3$ (0.38 mmol). The reaction was stirred 41.5 h and then treated with acid. Product separation at −45 °C and neutralization on the amine resin resulted in a 3.8% hydrocarbon yield (based on Mn). The manganese dimer was detected by solution IR in toluene.

Reaction G (see Table I) was analogous to reaction F except for the presence of $BF_3$.

**Reaction in the Absence of Diborane (H).** Boron trifluoride (0.35 mmol) was added to 0.31 mmol of $Mn(CH_3)(CO)_5$ in 6.2 mL of toluene. The reaction was stirred at room temperature under CO (2.66 mmol) for 4.5 h. The initially formed golden solution

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Table I. Data for the Diborane Reduction Reactions with $Mn(CH_3)(CO)_5$ and $(\eta^5\text{-}C_5H_5)Fe(CH_3)(CO)_2$

| reaction | reaction time, h | $BF_3/M^a$ | $B_2H_6/M^a$ | $CO/M^a$ | $P$,$^b$ mm | M, mmol | $[M]$,$^c$ mol/L | % yield$^d$ | $C_2H_6/C_2H_4$ | $C_3H_6/C_3H_8$ | $C_2/C_3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| A | 40.5 | 0 | 3.7 | 15.2 | 1039 | 0.27 | 0.05 | 13 | 0.31 | large | 16 |
| B | 24.5 | 0 | 6.0 | 13.0 | 1303 | 0.343 | 0.05 | 27 | 0.15 | large | 7.9 |
| C | 24.0 | 1 | 3.0 | 9.4 | 1360 | 0.47 | 0.05 | 2.3 | 22 | 4.8 | 0.78 |
| D | 25.5 | 1 | 6.0 | 11.6 | 1458 | 0.38 | 0.05 | 17 | 26 | 6.3 | 1.7 |
| E | 25.0 | 0.14 | 6.1 | 12.8 | 1611 | 0.414 | 0.05 | 7.7 | 9.5 | 11.8 | 8.9 |
| F | 41.5 | 0 | 3.0 | 0 | 336 | 0.355 | 0.06 | 3.8 | 0.68 | trace | large |
| G | 41.5 | 1.1 | 3.0 | 0 | 511 | 0.305 | 0.06 | 2.4 | large | $C_3H_8$<br>1.0 | large |
| H | 4.5 | 1 | 0 | 8.6 | 525 | 0.31 | 0.05 | 2.3$^e$ | 0 |  | 0 |
| J | 61.0 | 1 | 2.9 |  | 3500 | 0.40 | 0.05 | 7.6 | 1.2 | >>1 | 1.3 |
| O | 65.0 | 1 | 3.0 | 9.2 | 965 | 0.365 | 0.05 | 13 | 0.72 | 6.8 | 3.4 |
| P | 59.5 | 0 | 3.0 | 8.8 | 0.37 | 0.365 | 0.05 | 0 |  |  |  |

[a] Ratio of moles of reactant to moles of metal complex, M. The metal complex was $Mn(CH_3)(CO)_5$ in reactions A through H and J through N. For reactions O and P the metal complex was $(\eta^5\text{-}C_5H_5)Fe(CH_3)(CO)_2$. [b] Total initial pressure of CO + $B_2H_6$ + $BF_3$ in the reaction vessel. [c] Molar concentration of metal complex in toluene. [d] Total yield of $C_2$ through $C_4$ hydrocarbons collected before and after protolysis. The yield of $CH_4$ was low for reactions employing $Mn(CH_3)(CO)_5$. [e] Ethylene was the sole hydrocarbon product. Ethyl acetate also was produced.

became paler, and a light-colored precipitate appeared. After removal of unreacted CO and photolysis, the reaction mixture was fractionated and neutralized to produce a 2.3% hydrocarbon yield. A GC of the solution showing the presence of ethyl acetate was confirmed by GC-MS. An IR of the remaining orange solid dissolved in toluene demonstrated the presence of $Mn_2(CO)_{10}$.

**Blank Reaction (I).** To 1.28 mmol of $B_2H_6$ and 0.46 mmol of $BF_3$ in 8.6 mL of toluene was added 3.88 mmol of CO. The solution which was stirred at room temperature for 20.5 h remained colorless. No hydrocarbon products were isolated after the protolysis, separation, and neutralization steps.

**Elevated Pressure Reaction (J).** To a 0.40-mmol sample of $Mn(CH_3)(CO)_5$ in a Fischer-Porter pressure vessel were added 8 mL of toluene, 0.43 mmol of $BF_3$, and 1.14 mmol of $B_2H_6$ on a vacuum line. The reaction mixture was warmed to room temperature and pressurized with CO (4.1 atm). Stirring for 61 h at room temperature was followed by removal of CO and fractionation and neutralization of products to produce a 2% yield of hydrocarbons. After protolysis of the remaining solution a second product separation and neutralization resulted in a 5.6% yield of hydrocarbons. Sublimation of the yellow solid left after solvent removal yielded $Mn_2(CO)_{10}$ which accounted for 40% of the original manganese.

**Labeling Experiments (K).** To 0.429 mmol of $Mn(CH_3)(CO)_5$ in 8.6 mL of toluene were added 0.44 mmol of $BF_3$, 1.27 mmol of $B_2D_6$, and 4.58 mmol of CO. Stirring the reaction for 37 h was followed by product separation and neutralization to produce a 2.5% yield of hydrocarbons. Protolysis of the remaining solution followed by neutralization and fractionation of products produced a 2.8% yield of hydrocarbons. A trace of ethyl acetate was identified by GC-MS analysis of the remaining solution.

**(L).** To a 0.1 M toluene solution of $Mn(CH_3)(CO)_5$ (0.433 mmol) were added 0.9 mmol of $B_2D_6$, 2.01 mmol of THF, and 1.45 mmol of CO. After the reaction was stirred 38.5 h the CO was removed and the reaction was neutralized with 1.8 mmol of pyridine. Upon product separation <10% yield of hydrocarbons was obtained. An IR of the remaining solid in toluene showed the presence of $Mn_2(CO)_{10}$.

**(M).** To a 0.1 M toluene solution of $Mn(CH_3)(CO)_5$ (0.73 mmol) were added 3.0 mmol of THF-$d_8$, 1.49 mmol of $B_2H_6$, and 1.09 mmol of CO. The reaction was stirred at room temperature for 3 days. Analysis of the noncondensible gases showed 1.3% $CH_4$ based on Mn charged. Neutralization of the excess diborane with 3.7 mmol of pyridine was followed by product separation at −78 °C.

**(N).** To a solution of 0.38 mmol of $Mn(CH_3)_8(CO)_5$ in 7.7 mL of toluene were added boron trifluoride (0.40 mmol), diborane (1.36 mmol), and $^{13}CO$ (4.17 mmol). After being stirred at room temperature for 24 h, the mixture was frozen and methanol (3.4 mmol) and HCl (12.8 mmol) were added, and stirring was continued for 40 h at room temperature. The yield of hydrocarbons which were volatile at −78 °C was less than 12%. GC-MS of the remaining liquid phase showed the presence of ethanol, ethyl chloride, and 1,1-dichloroethane.

**Reactions with $(\eta^5\text{-}C_5H_5)Fe(CH_3)(CO)_2$ (O).** To a 0.05 M toluene solution of $(\eta^5\text{-}C_5H_5)Fe(CH_3)(CO)_2$ (0.365 mmol) were added 0.38 mmol of $BF_3$, 1.1 mmol of $B_2H_6$, and 3.34 mmol of CO. The reaction was stirred 65 h. Analysis of the noncondensable gases before and after protolysis showed 3.6 and 4.8% $CH_4$, respectively. After product separation and neutralization, the hydrocarbon yield was found to be 13% (based on Fe). An IR of a toluene solution of the product remaining after removal of all volatiles indicated the presence of $(\eta^5\text{-}C_5H_5)Fe(Cl)(CO)_2$.

Reaction P was run as described for (O) but in the absence of $BF_3$ (see Table I). Analysis for $CH_4$ before and after addition of HCl showed yields of 18% and 31% (based on Fe), respectively. No other hydrocarbon products were isolated, and the organometallic product was determined by IR to be $(\eta^5\text{-}C_5H_5)Fe(Cl)(CO)_2$.

**CO-Uptake Experiment (Q).** Diborane (1.58 mmol), THF (3.58 mmol), and CO (1.68 mmol) were added to a 0.1 M toluene solution of $Mn(CH_3)(CO)_5$ (0.476 mmol) in the tensimeter, and the reaction mixture was equilibrated at 18.8 °C. After the reaction was stirred for 5.5 days, 0.944 mmol of $H_2$ (2 equiv based on Mn charged), 1.37 mmol of CO (2.9 equiv based on Mn), and a trace of $CH_4$ were collected.

**Alternate Solvent Systems.** In an attempt to find a system with solubility properties better than toluene, several chlorocarbon and ether solvents were explored. In general the solubility in the chlorocarbons, $CH_2Cl_2$, $C_6H_5Cl$, and $o\text{-}C_6H_4Cl_2$, was no better than in toluene. Although the solubility in THF, diglyme, and dioxane was good, solvent cleavage and production of interfering hydrocarbons precluded further study.

## Results

Hydrocarbons of varying chain length and degree of saturation were isolated as products of the reduction reaction (eq 6). The yields and product distribution depend

$$Mn(CH_3)(CO)_5 + B_2H_6 \xrightarrow[\text{toluene}]{CO} \xrightarrow[C_2H_5OH]{HCl} \text{hydrocarbons} \quad (6)$$

on the reaction conditions, Table I. In all cases where gaseous products were isolated before and after the reaction with HCl, the products before protolysis were found to be saturated and those isolated after protolysis were unsaturated. Typically the hydrocarbon yield decreased with increasing chain length, $C_2 > C_3 > C_4$, and the $C_4$ products were detected only by GC-MS.

**Reactions with $Mn(CH_3)(CO)_5$.** For reaction A, in which 3.7 equiv of diborane was employed, the products were found to be ethylene, ethane, and propylene in a total yield of 13% (Table I). Butylene and isobutane were detected by mass spectrometry. When the amount of diborane was increased to 6 equiv (reaction B), the product yield increased to 27% and the formation of $C_3$ products was enhanced. In both reaction A and reaction B the production of unsaturated vs. saturated products was favored, and in neither case was propane detected.

Because $BF_3$ is known to promote the CO insertion reaction for $Mn(CH_3)(CO)_5$,[17] several reactions were run in the presence of 1 equiv of this strong Lewis acid. Reaction C in Table I, with 3 equiv of diborane and 1 equiv of $BF_3$, produced a 2.3% yield of the hydrocarbons—ethylene, ethane, propylene, and propane. The reactions in which $BF_3$ was employed show a marked difference in product distribution. Compared with reactions A and B, these reactions favored formation of the saturated products ethane and propane, as well as longer chain hydrocarbons as evidenced by a lower $C_2/C_3$ ratio.

To test whether $BF_3$ was acting catalytically or stoichiometrically in these systems, reaction E was run with less than 1 equiv of $BF_3$/Mn. The distribution of saturated vs. unsaturated products was intermediate between the reactions with and without $BF_3$ (reactions B and D). The total yield was low and the high $C_2/C_3$ ratio resembled the reactions without $BF_3$, but the presence of propane and a large ethane/ethylene ratio showed that $BF_3$ played a role similar to that in reactions C and D.

To check the role of the CO atmosphere, two reactions were set up without added CO (reactions F and G). In both reactions (without and with $BF_3$) not only was the yield low (3.8 and 2.4%, respectively), but also the $C_2/C_3$ ratio was very large and only traces of $C_3$ products were detected by GC. The differences observed between the reactions with and without $BF_3$ again were apparent as the $BF_3$-containing reaction tended toward formation of saturated products.

Because a CO atmosphere enhanced product formation, reactions at elevated CO pressures were explored. Reaction J contained 1 equiv of $BF_3$ and was run at a CO pressure of 4.1 atm. The isolated gaseous products were ethylene, ethane, propylene, and propane. Compared with the analogous lower pressure reaction (C), the product yield was better, though the $C_2/C_3$ ratios were comparable. The major difference is seen in the much larger production of ethylene relative to ethane and propylene relative to propane.

An experiment performed according to eq 7 (reaction Q) indicated 2.9 mol of CO were consumed per mol of $Mn(CH_3)(CO)_5$ after 5.5 days. This is a minimum value for CO uptake because a small amount of noncondensable methane was also present in the remaining CO.

$$Mn(CH_3)(CO)_5 + 6.6BH_3{\cdot}THF \xrightarrow[\text{toluene}]{\text{CO}} \text{products} \qquad (7)$$

In order to check possible sources of hydrocarbons other than the proposed insertion–reduction reaction, two experiments were run—one without diborane and one without a metal complex. In the first (reaction H), $Mn(CH_3)(CO)_5$ reacted with $BF_3$ under a CO atmosphere to form initially the cyclic adduct, which added CO to precipitate a noticeable amount of the fully saturated adduct. Acid treatment of these adducts produced a 2.3% yield of ethylene as well as a considerable amount of ethyl acetate, the expected product of acid cleavage of a metal acetyl (eq 8).

$$\begin{aligned} &Mn(CH_3)(CO)_5 + BF_3 \xrightarrow[\text{toluene}]{\text{CO}} \\ &\quad Mn(C(OBF_3)CH_3)(CO)_5(\downarrow) + \\ &\quad \overline{Mn(C(OBF}F_2)CH_3)(CO)_4 \xrightarrow[C_2H_5OH]{HCl} \\ &\qquad C_2H_4 + CH_3CO_2C_2H_5 \end{aligned} \qquad (8)$$

A blank reaction was performed to check reagent purity (reaction I, eq 9), and workup procedures were run as in a typical reduction reaction. The only products detected by GC were the trace $CO_2$ and $C_2H_2$ impurities known to be present in the HCl.

$$BF_3 + 3B_2H_6 \xrightarrow[\text{toluene}]{\text{CO}} \xrightarrow[C_2H_5OH]{HCl} \text{no hydrocarbons} \qquad (9)$$

**Reactions with $(\eta^5\text{-}C_5H_5)Fe(CH_3)(CO)_2$.** The $(\eta^5\text{-}C_5H_5)Fe(CH_3)(CO)_2$ system provides an interesting comparison to $Mn(CH_3)(CO)_5$. The unassisted CO insertion reaction for this iron complex is not observable at subatmospheric pressures of CO and at room temperature; but with $BF_3$ as promoter, the insertion occurs immediately as in the manganese reaction.[17] The $(\eta^5\text{-}C_5H_5)Fe(CH_3)(CO)_2$ in the presence of $BF_3$ (reaction O) under insertion–reduction conditions produced a 13% yield of hydrocarbons—ethylene, ethane, propylene, and propane. Approximately equal amounts of methane were detected in the noncondensable gases before and after protolysis to give a total yield of 8.4% (based on Fe complex charge). The major difference between this reaction and that of $Mn(CH_3)(CO)_5$ (reaction C) was the high yield of ethylene relative to ethane and the slightly lower yield of the $C_3$ products in the iron reaction.

In a similar reaction of $(\eta^5\text{-}C_5H_5)Fe(CH_3)(CO)_2$ without added $BF_3$ (reaction P) no chain growth was observed. The only product isolated was methane in yields of 18 and 31% before and after addition of acid, respectively.

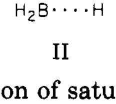
**Isotopic Labeling Experiments.** Diborane as the source of hydrogen in the products was confirmed by deuterium-labeling experiments with $BD_3{\cdot}THF$ and $B_2D_6$. The acid cleavage step was omitted in reaction to L (in which $BD_3{\cdot}THF$ was used), and the major hydrocarbon products were $CH_3CD_3$ and $CH_3CD_2CD_3$ as detected by GC-MS. The mass spectrum also showed the presence of lower molecular weight ethanes and propanes as well as traces of propane-$d_8$, -$d_7$, and -$d_6$, but relative amounts could not be determined from this low-resolution spectrum. The presence of traces of $C_2H_6$ and $C_3H_8$ resulting from THF cleavage also could not be ruled out. Interference due to the decomposition of THF was clearly seen in an analogous reaction with $BH_3{\cdot}THF\text{-}d_8$ (reaction M). The products in this reaction were $C_2H_6$, $C_3H_8$, $C_3D_8$, and traces of $C_2H_4$, $n\text{-}C_4H_{10}$, and $i\text{-}C_4H_{10}$. Ethane was the major product, and the propanes were present in approximately equal amounts. Gaseous products from a second experiment with the labeled reducing agent $B_2D_6$ (reaction K) were analyzed by high-resolution mass spectrometry. The data obtained for ethane and propylene showed the following isotopic distributions: $C_2HD_5$ (<1%), $C_2H_3D_3$ (42%), $C_2H_4D_2$ (43%), $C_2H_5D$ (12'), and $C_2H_6$ (2%); $C_3H_3D_3$ (trace), $C_3H_4D_2$ (trace), and $C_3H_5D$ (100%). There is a discrepancy, however, in the propylene data. In a second analysis of reaction K, a GC-MS of the reaction solution (after product separation) showed the presence of propylene-$d_3$, and qualitative analysis of the mass spectrum suggests the $d_2$ and $d_1$ species were also produced.

The same reaction performed in an atmosphere of $^{13}CO$ produced hydrocarbons containing varying amounts of $^{13}C$ (reaction N). The separation and analysis were done by GC-MS and the relative abundance of each isotopic species was determined from the low-resolution mass spectrum by simultaneous equations. The results showed no $^{13}C$ incorporation in the $C_2$ product ($C_2H_6$ = 100%); but a substantial amount of $^{13}C$ appeared in the $C_3$ products: $C_3H_6$ (68%), $^{13}CC_2H_6$ (32%), $C_3H_8$ (41%), $^{13}CC_2H_8$ (29%), $^{13}C_2CH_8$ (29%), and $^{13}C_3H_8$ (1.6%).

**Oxygenated Products.** The low hydrocarbon yields of these reactions suggest that a substantial amount of product is remaining in solution, perhaps in a partially reduced state. If a metal acyl or its Lewis acid adduct remains after the reduction step, the acid cleavage in ethanol would produce the corresponding ethyl ester, as described by Johnson and Pearson[24] for a metal acyl and as seen in reaction H for a Lewis acid adduct. GC analyses of the solutions remaining after separation of the gaseous products in reactions B and D show small amounts (<5%) of ethyl propionate. A GC-MS analysis of the solution from reaction K shows ethyl acetate and from reaction N shows ethanol, ethyl chloride, and 1,1-dichloroethane. The absence of esters in reaction N is likely due to the limited amount of methanol employed in the cleavage reaction. The alcohol in these reactions also is consumed by the boron products in the formation of $B(OR)_3$. In reaction R, $B(OCH_3)_3$ is confirmed by GC-MS. The $C_2$ products from reaction N, ethanol, ethyl chloride, and 1,1-dichloroethane, show no $^{13}C$ incorporation in agreement with the observed 100% yield of nonlabeled ethane in the gaseous fraction. The mass spectrum analysis of the ethanol from a reaction employing $B_2D_6$ as reducing agent shows no incorporation of deuterium, indicating that the product of the initial insertion is not reduced by diborane; instead, it reacts with the HCl to form ethanol. Another case of ethanol formation from the protolysis of C- and O-bonded acetyl was recently reported.[25]

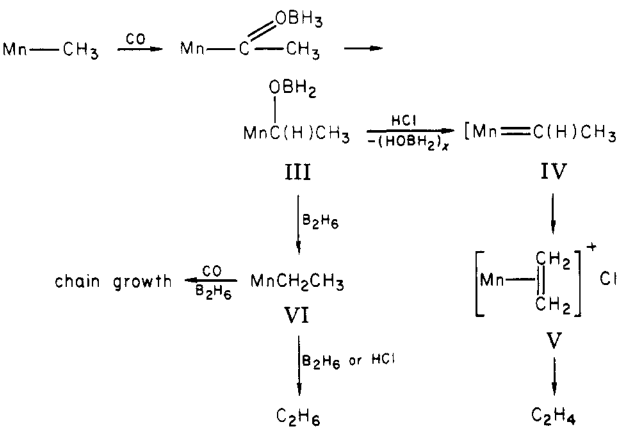
## Discussion

Both $Mn(CH_3)(CO)_5$ and $(\eta^5\text{-}C_5H_5)Fe(CH_3)(CO)_2$ react in the presence of CO, diborane, and $BF_3$ to form alkanes and olefins up to $C_4$, as well as some partially reduced oxygenated products. The isotopic labeling studies confirm that the hydrocarbons are products of the reduction of CO by diborane, and the $^{13}CO$- and CO-uptake experiments show that gaseous CO is incorporated into these products. The presence of $BF_3$ significantly alters the product distribution in the $Mn(CO)_5(CH_3)$ system, and in the $(\eta^5\text{-}C_5H_5)Fe(CO)_2(CH_3)$ reactions, $BF_3$ is necessary for any chain growth to occur. The reaction is clearly more complicated than originally proposed in eq 5. One apparent side reaction is the production of saturated hydrocarbons before acid cleavage of the reaction mixture. It is probable that borane promotes alkane formation from a metal alkyl complex either by direct reaction or through formation of an intermediate metal hydride. For example, borane attack on a metal cetner,[26] followed by alkane elimination from a four-membered ring intermediate (II), may account for the direct production of saturated hydrocarbons. A similar reaction may also explain methane formation before cleavage in the $(\eta^5\text{-}C_5H_5)Fe(CH_3)(CO)_2\text{–}B_2H_6\text{–}CO$ system with no added $BF_3$, where no evidence of chain growth is observed. Alternatively, a metal hydride or hydrido alkyl may react intra- or intermolecularly to produce alkane products.[27] Metal hydride formation was observed in the initial report of metal acetyl reduction by diborane.[14]



II

Scheme I



A second obvious complexity in the reaction is the production of a significant proportion of unsaturated hydrocarbons in the protolytic workup of the reaction mixture. Scheme I outlines one possible mechanism to explain the formation of unsaturates only after protolysis. Incomplete reduction of the metal acyl could produce an intermediate such as III. The action of HCl on this partially reduced species would eliminate "$HOBH_2$" and form a cationic carbene IV. Rearrangement of the carbene to a $\pi$-bound olefin complex (V) and subsequent olefin elimination may account for the unsaturated products. Trace amounts of alkanes also are observed after acid addition and may arise from acid cleavage of a metal alkyl (VI), or they may simply to be the result of an incomplete initial product separation.

The mechanism described by Scheme I allows for chain growth via CO insertion, formation of saturated hydrocarbons before and after HCl addition, and production of alkenes after protolysis. The route of alkene products involving cationic carbene and olefin intermediates does have precedence in the literature. Though the information on neutral carbenes is more abundant,[28,29] stable cationic carbenes also have been isolated[30,31] or proposed as intermediates in olefin metathesis.[32] Evidence for carbene rearrangement is found in the decomposition of $W(C(CH_3)C_6H_5)(CO)_5$ to styrene which is proposed to occur via an olefin complex.[29] Rearrangement of a cationic carbene to olefin is suggested by the reaction of $(\eta^5\text{-}C_5H_5)Fe(c\text{-}C_3H_6)(CO)_2$ with acid to produce $[(\eta^5\text{-}C_5H_5)Fe(CH_3CH{=}CH_2)(CO)_2]^+$.[33]

If the initial methyl migration is the slow step in the reaction, addition of 1 equiv of $BF_3$ as promoter should overcome this barrier by formation of the cyclic adduct $\overline{Mn(C(OB}F_2)CH_3)(CO)_4$. This strong Lewis acid significantly alters the product distribution; thus it appears to participate in the reaction beyond the first insertion step. With $BF_3$ in the system, the hydride source may no longer be diborane but some product of a $BF_3/B_2H_6$ redistribution reaction. The redistribution product, $BF_2H$, reportedly is obtained by heating $BF_3$ and $B_2H_6$ at 100 °C for 16 h.[34] This exchange reaction also occurs under less

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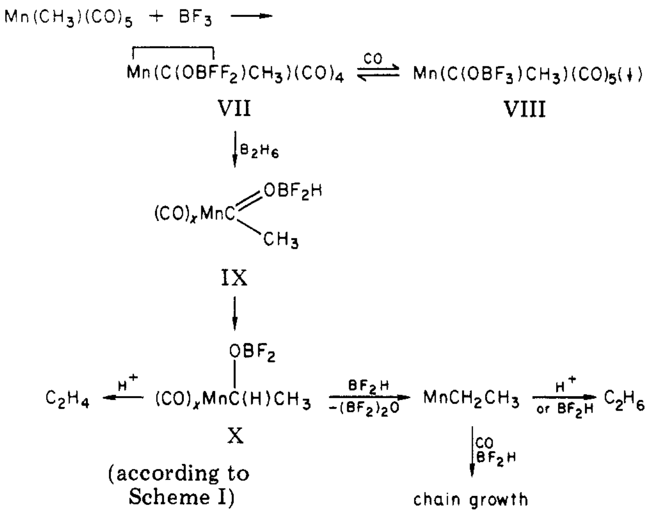
Scheme II



vigorous conditions when $BCl_3$, $BBr_3$, or oxygenated products such as ether or methanol are present as catalysts.[35] The acetyl group formed in the present system may catalyze this exchange; thus $BF_2H$, a strong Lewis acid as well as potential hydride donor, could be the active species.

The initial reaction in the $BF_3$-containing system as described in Scheme II may be the very fast Lewis acid assisted CO insertion to form VII. This cyclic adduct can either add CO to precipitate VIII or undergo H/F exchange with diborane to produce IX. Hydride addition across the CO double bond would yield X, which can further react with $BF_2H$ or acid to form saturated and unsaturated hydrocarbons as proposed in Scheme I.

An unproductive side reaction occurring in the $BF_3$-containing reactions is the formation of insoluble VIII (isolated and characterized by infrared). This solid adduct disappears during the course of the reaction, indicating a slight solubility in toluene or dissociation of CO or $BF_3$ to give toluene-soluble VII or $Mn(CH_3)(CO)_5$, respectively.

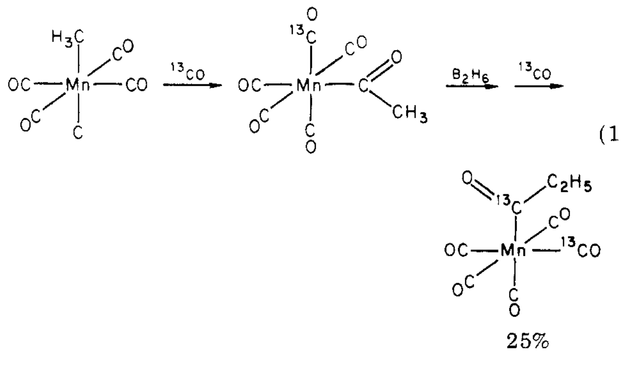
The change in product distribution observed when $BF_3$ is added to the system may be due to the change in Lewis acid strength of the active species. In both reactions (without and with $BF_3$) the proposed first steps are adduct formation and addition across the CO double bond, producing intermediates II and X, respectively. At this point the reactions diverge. In the absence of $BF_3$ the major $C_2$ product is ethylene, indicating that intermediate III remains in solution (without further reaction with $B_2H_6$) until HCl is added (Scheme I). In contrast, ethane is preferentially formed when $BF_3$ (or $BF_2H$) is present. In this proposed reaction, intermediate X does not remain in solutions, instead it reacts with a second molecule of $BF_2H$ producing ethane via an ethyl complex. The Lewis acidity of $BF_2H$ may be enough greater than that of $B_2H_6$ to enhance the second attack at intermediate X, thus accounting for the preferential formation of saturated over unsaturated products. The same argument with the analogous $C_3$ intermediates also would explain the formation of propane in the $BF_3$ reactions when none is detected in the absence of $BF_3$.

The possibility that the reaction might be run with catalytic quantities of $BF_3$ is discounted by reaction E where less than 1 equiv of $BF_3$ is used. The product distribution is intermediate between the reactions without and with 1 equiv of $BF_3$, indicating that both mechanisms (Scheme I and II) are operative.

The higher yields of alkenes relative to alkanes in the elevated pressure reaction J, compared with reaction C, also can be explained according to Scheme II. In the proposed mechanism intermediate X can react either with acid forming ethylene, or with $BF_2H$ forming the ethyl compound. Under CO pressure the equilibrium between alkyl and acyl complexes will favor the latter and thus lower the alkane yields result from cleavage of the metal alkyls.

**Hydrocarbon Source.** Several experiments have been performed to check whether the hydrocarbons are true products of the metal-based reduction of CO rather than impurities or the products of solvent degradation. Reactant purity has been checked in a blank reaction (reaction I, no metal) run under conditions similar to reaction C and no hydrocarbons are isolated. Reaction H is a potential hydrocarbon source via an alternate mechanism. In this reaction without diborane, both adducts $\overline{Mn(C(OBF}F_2)CH_3)(CO)_4$ and $Mn(C(OBF_3)CH_3)(CO)_5$ are present, and the acid cleavage step does produce a small amount (2.3%) of ethylene. There are two pieces of evidence, however, that suggest this reaction is not important under the present reduction conditions. First, ethylene is the major product in the reactions without $BF_3$; and, second, in the $BF_3$-containing reactions only trace amounts of ethylene are produced (≪2%).

The labeling experiments with $B_2D_6$ and $^{13}CO$ provide the most convincing evidence that the observed hydrocarbons do not arise from an extraneous source, although the isotopic distribution in the products is not entirely consistent with a simple mechanism of successive CO insertion and reduction. If the mechanisms outlined in Schemes I and II are operative, then a reaction with $B_2D_6$ should produce the alkanes $CH_3CD_3$, $CH_3CD_2CD_3$, etc. and alkenes (after addition of HCl) $CH_2CHD$, $CH_3CD{=}CD_2$, etc. (providing that no exchange reactions are occurring concurrently). Also according to the proposed mechanisms, if chain growth occurs solely through successive alkyl migrations, a reaction run under an atmosphere of $^{13}CO$ should show incorporation of $^{13}C$ only in the $C_3$ (and higher) products. The mechanism for alkyl migration calls for 25% $^{13}C$ in the $C_3$ products on the basis of a nonfluctional intermediate and migration of the alkyl group to one of four cis carbonyls (eq 10).[36]



(10)

In the initial deuterium labeling experiments with $BD_3 \cdot THF$ (and $BH_3 \cdot THF\text{-}d_8$), the products ethane and propane were analyzed by GC-MS. The mass spectrometry data indicate the predominant species in each case is $C_2H_3D_3$ and $C_3H_3D_5$, as expected if the mechanism of

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Scheme I is operative. The low-resolution mass spectrometry data, however, do not allow clear analysis of lower molecular weight products (containing less deuterium), although their presence is determined by qualitative interpretation of the spectra.

Although there is a disparity between the high-resolution and GC mass spectrometry data, both sets of results indicate some production of hydrocarbons containing less deuterium than predicted by Schemes I and II. For the saturated products isolated before HCl addition, the excess hydrogen must come from either the starting methyl complex or the solvent. The results for ethane show approximately equal amounts of $d_3$ and $d_2$ products, both of which may be formed according to Scheme II, differeing only in the cleavage step. While the $d_3$ species may arise from borane cleavage of the ethyl complex, the $d_2$ product may be the result of an interaction between the ethyl complex and a second metal alkyl or hydride. For example, $\beta$-H elimination from $Mn(CD_2CH_3)(CO)_5$ or the less likely $\alpha$-H elimination from $Mn(CH_2CH_3)(CO)_5$ would produce a metal hydride, thus supplying the final hydrogen in the alkane products.

The low-resolution mass spectrometry data on propylene indicate the $d_1$ species is important, even if not the only product as suggested by the high-resolution mass spectrum results. Formation of propylene-$d_1$, after HCl addition, may occur by a deviation of Scheme II in which the acid supplies the excess hydrogens. Insertion of CO into the metal carbene bond of an intermediate such as IV would produce a $C_3$ fragment containing only one borane hydrogen (deuterium).[37] Subsequent reaction with HCl would give propylene-$d_1$. Alternatively, any unsaturate has the potential to recoordinate and undergo H/D exchange at a Mn center, but this type of reaction is not likely to be specific to one product.

The results of the $^{13}CO$ experiment definitely show that the mechanisms proposed in Schemes I and II cannot account for all observed products. As predicted by an insertion–reduction mechanism the ethane contains no $^{13}C$. However, the $C_3$ products do not conform quite as well. The isotopic distribution in propylene (68% $^{13}CC_2H_6$, 32% $C_3H_6$) is close to that expected (75% $^{13}CC_2H_6$, 25% $C_3H_6$); but the propane products show a much greater incorporation of $^{13}CO$.

The reaction between $Mn(CH_3)(CO)_5$ and $BF_3$ forming cyclic adduct VII is very fast and can account for the $C_2$ products with no $^{13}C$, but this initial interaction cannot be the chain building step responsible for propanes containing more than one $^{13}C$. It is likely that several mechanisms are operative in the production of hydrocarbons. The intermediates VII and IX may offer possible routes to an enriched molecule either by labilizing the terminal carbonyls or by providing an open coordination site on the metal.

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**Registry No.** $Mn(CH_3)(CO)_5$, 13601-24-6; $(\eta^5\text{-}C_5H_5)Fe(CH_3)(CO)_2$, 12080-06-7; $B_2H_6$, 19287-45-7.

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# Alkyl and Hydride Derivatives of (Pentamethylcyclopentadienyl)zirconium(IV)†

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Cp*Li (Cp* = $\eta^5$-$C_5Me_5$) reacts with $ZrCl_4$ in toluene to form $(Cp^*ZrCl_3)_x$. The trialkyls $Cp^*ZrR_3$ (R = $CH_3$, $CH_2Ph$, Ph), the dialkyl $Cp^*ZrCl(CH_3)_2$, and the alkyls $(Cp^*ZrCl_2R)_x$ (R = $CH_3$, $CH_2Ph$) are prepared via the treatment of $(Cp^*ZrCl_3)_x$ with a stoichiometric amount of RMgX. $Cp^*Zr(BH_4)_3$, prepared from $(Cp^*ZrCl_3)_x$ and $LiBH_4$, is treated with $N(CH_3)_3$ to afford $[Cp^*Zr(H)(BH_4)(\mu\text{-}H)]_2$. "Mixed" ring complexes were also prepared: $Cp^*CpZrCl_2$, $Cp^*(MeInd)ZrCl_2$ (MeInd = 1-methylindenyl), $Cp^*Cp'ZrCl_2$ (Cp′ = 1,2,4-trimethylcyclopentadienyl), $Cp^*CpZr(CH_3)_2$, $Cp^*(MeInd)Zr(CH_3)_2$, $Cp^*Cp'Zr(CH_3)_2$, $(Cp^*CpZrH_2)_2$, and $Cp^*Cp'ZrH_2$.

## Introduction

The chemistry of dicyclopentadienyl[1,2] and bis(pentamethylcyclopentadienyl) zirconium hydrides[3,4] and alkyls has been explored extensively, yet the corresponding reactivity of the cyclopentadienylzirconium moiety (CpZr) has thus far received little attention. Several complexes containing the CpZr unit have been synthesized, but virtually all of these contain Zr–O, Zr–N, or Zr–X (X = F, Cl, Br, I) bonds.[1] Few monocyclopentadienylzirconium complexes containing Zr–C or Zr–H bonds have been characterized, although tetraalkylzirconium species[5] and $Zr(BH_4)_4$[6] are well-known. In general, the aforementioned dicyclopentadienylzirconium compounds are conveniently prepared from the readily available dichloride $Cp_2ZrCl_2$. $CpZrCl_3$, a logical starting material for the preparation of

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† Contribution No. 6576.

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