oximation procedure. After extraction with ether to remove acrolein, propanal, acetone, and quinone, another portion of the aqueous phase was again analyzed to give β-hydroxypropanal plus acetol. The other carbonyls extracted by ether were then calculated by difference. The Fehling's solution analysis on another portion of the ether extracted aqueous phase gave total acetol. Since some Cu_2O is lost during filtration, the actual yield of acetol is believed to be slightly higher than that given by this analysis. By difference, the β-hydroxypropanal yield is then determined.

Next, the (2,4-dinitriphenyl)hydrazone derivatives of the reaction mixture were prepared and chromatographed as previously described to separate the acrolein, propanal, and acetone derivatives.[1] The composition of these lower molecular weight products was determined by ^1H NMR. No acetone was detected. The ratios of the other two products were found by comparing the integrations of the $CH_2{=}CH$— and CH_3CH_2— protons or the $CH_2{=}CHCH{=}$ and $CH_3CH_2CH{=}$ protons. Chemical shifts are given in ref 1. To ensure that propanal was not formed by reduction of acrolein during removal of Pd(II) with Zn dust, the hydrazones were prepared from a portion of one reaction mixture that had not been treated with Zn dust. The propanal yield was unaffected.

The reaction was also run in a closed system attached to gas burets. No gaseous products, such as propene, were formed.

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Registry No. **5**, 107-18-6; **10** ($R = CH_2OH$), 115141-69-0; **11a**, 115160-79-7; $PdCl_4^{2-}$, 14349-67-8; quinone, 106-51-4.

$NaBH_4$ Reduction of CO in the Cationic Iron Carbonyl Complexes $[C_5Me_5Fe(CO)_2L]^+PF_6^-$ (L = CO or Phosphine)

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The complex $[Fp^*CO]^+PF_6^-$ (**1**; $Fp^* = Cp^*Fe(CO)_2$, $Cp^* = (\eta^5\text{-}C_5(CH_3)_5)$) reacts with $NaBH_4$ at −80 °C in THF to give specifically Fp^*CHO (**2**); warming the reaction mixture to −60 °C yields Fp^*CH_2OH (**3**); further warming to 0 °C gives Fp^*CH_3 (**4**; 91% yield). In the presence of H_2O, the same reaction gives only Fp^*H (**5**). Compound **3** is best synthesized by using CH_2Cl_2 as the reaction solvent (72% yield). It slowly decomposes to Fp^*_2 (**6**) in C_6D_6 at 40 °C and rapidly gives **4** in CD_3NO_2 or CD_3OD. Protonation of **3** using aqueous HBr yields 30% MeOH and Fp^*Br (**13**) whereas CH_4 and C_2H_6 are obtained by using $H^+BF_4^-$ in Et_2O. Methane and **14** are obtained by protonation of **4**. The long-known hydride reduction of $[FpPPh_3]^+PF_6^-$ ($Fp = (\eta^5\text{-}C_5H_5)Fe(CO)_2$) to $(\eta^4\text{-}C_5H_6)Fe(CO)_2PPh_3$ at −80 °C proceeds via the formyl intermediate $CpFe(CO)(PPh_3)CHO$. The complexes $[Fp^*PR_3]^+PF_6^-$ (R = *n*-Bu (**9a**), CH_3 (**9b**), or Ph (**9c**)) react with $NaBH_4$ only at −30 °C in THF giving mixtures of $Cp^*Fe(CO)(PR_3)CHO$ (**10**) and $Cp^*Fe(CO)(PR_3)(CHO{\cdot}BH_3)$ (**11**) detected by ^1H NMR. Warming the reaction mixtures to −20 °C leads to the direct observation of $Cp^*Fe(CO)(PR_3)CH_3$ (**12**) that can be extracted in 46–82% yields. However, direct reaction of **9** and $NaBH_4$ at 20 °C only gives **5**. The reaction between **2** and BH_3 (1 equiv) yields a mixture of **1** and **4** while that between **10** and BH_3 gives **9** and **12**. In contrast, reactions of $\mathbf{2}{\cdot}BH_3$ with H_2O or $\mathbf{10}{\cdot}BH_3$ (**11**) with PPh_3 only lead to **5**. Three equivalents of $NaBH_4$ are necessary to reduce **1** and **9**, and the use of $NaBH_4/NaBD_4$ mixture confirms that the reduction is intermolecular. Complex **1** is also reduced by the transition-metal hydrides **5** and $H_4Mo(dppe)_2$. Free carbon monoxide is reduced to 240% yield (vs $[Fp^*THF]^+PF_6^-$ (**7**)) by using excess **5**.

Introduction

"The recognition that petroleum reserves are finite has resulted in renewed interest in coal as an alternative source for petrochemical feedstock and fuels. Many of the promising processes for coal conversion such as Fischer–Tropsch reactions involve hydrogenation of carbon monoxide in the presence of transition-metal catalysts".[1] This motive is found at the start of a great many papers on hydride reduction of transition metal carbonyls since the late 1970s.[1-8] Whether it will remain valid in the future is speculative, but is has promoted immense research efforts in the area of reductive CO polymerization by homogeneous[9-15] and heterogeneous[16-20] catalysts and its mimicking in organometallic chemistry of model complexes.

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Almost 20 years ago, Treichel and Shubkin[21] reported the reduction of transition-metal coordinated CO to metal methyl complexes and postulated the reaction sequence shown in eq 1. Although the first formyl complexes,

$$M^+\text{-}CO \rightarrow M\text{-}CHO \rightarrow M\text{-}CH_2OH \rightarrow M\text{-}CH_3 \quad (1)$$

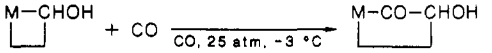
$[Fe(CO)_4CHO]^-$ reported in 1973 by Collman and Winter[22] and $Os(CO)_2(PPh_3)_2(Cl)(CHO)$ reported by Roper[23] in 1976, were made by indirect routes, Gladysz established that hydride reduction of neutral or cationic transition-metal carbonyl complexes is a general route to formyl complexes.[24-26] This finding is relevant to the numerous catalytic studies that involve transition-metal carbonyl catalysts that give Fischer–Tropsch products by reduction of CO with H_2. Anionic formyl complexes are somewhat stabilized by the transition-metal carbene limiting resonance form bearing the negative charge on the oxygen atom (eq 2).[25-29]

$$L_nM{-}CO + H^- \rightarrow [L_nM{-}CHO]^- \rightarrow L_nM{=}CH{-}O^- \quad (2)$$

The less stable neutral transition-metal formyl complexes[29,31-33] are better models of the intermediates of catalyzed CO reduction by hydrides generated from the transition-metal catalyst and H_2. The endergonic CO migratory insertion into a metal–hydride bond partly explains why it is unlikely to occur in Fisher–Tropsch catalysis (only a few model cases are known[34-38]). Intermolecular reaction of a metal carbonyl with a metal hydride is indeed a reasonable assumption for the first step of CO reduction. The subsequent behavior of metal formyl complexes has also been investigated extensively by Casey[39,42] and Gladysz,[25,40,41] and these studies have stressed the strong hydride donor ability of formyl complexes and their electrophile-induced disproportionation. The most interesting model studies were performed on piano-stool CpRe carbonyl complexes by Graham,[1,33,43] Gladysz,[25,40,41] and Casey.[30,31,39] These authors were able to observe all the steps of the borohydride reduction of the rhenium-coordinated CO and to isolate the formyl, hydroxymethyl, and methyl complexes. Whereas the first step, carbonyl reduction by "H^-", involves nucleophilic attack, the second one first involves interaction of an electrophile with the formyl oxygen. The reduction of formyl parallels that of acyl (eq 3).

$$M\text{-}C(R)O{\cdot}BH_3 \rightarrow M\text{-}CH_2R$$
$$R = H, CH_3 \quad (3)$$

Many hydroxymethyl complexes have now been synthesized and studied.[29,30,31,33-39,42-53] Berke and Huttner[51] first showed that CO migratory insertion into the metal–hydroxymethyl bond occurs in the unstable complex $Fe(CO)_2[P(OMe)_3]_2(Cl)(CH_2OH)$. An isolated metallacyclic rhenium hydroxyalkyl complex was later shown by Gladysz[53] to react with CO (eq 4). These C–C bond formations are relevant to the Fischer–Tropsch and related processes such as the hydroformylation of formaldehyde to glycolaldehyde, a precursor of ethylene glycol. The "Fischer–Tropsch" sequence that consists of the reduction of CO to methyl followed by C–C bond formation and reduction to alkanes is long-known in the Fp series from the work of Atwood.[54] Cutler's studies consisted of the transformation of $CpFe^+(CO)_3$ into a variety of C_2 organic molecules such as $CpFeCH_2OCH_3$ (eq 5).[55,56]



(4)

$$CpFe^+(CO)_3 \xrightarrow[\text{MeOH}]{\text{NaBH}_3\text{CN}} CpFe(CO)_2CH_2OCH_3 \quad (5)$$

In 1983, we reported[44] $[Fp^*CO]^+PF_6^-$ (1) was reduced by $NaBH_4$ to Fp^*CH_2OH (3), Fp^*CH_3 (4),[57] or Fp^*H (5)

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depending on the solvent. We report here full details of the reduction of $[Fp^*L]^+PF_6^-$ (L = CO (**1**), P-*n*-Bu_3 (**9a**), PMe_5 (**9b**), or PPh_3 (**9c**)) by $NaBH_4$ and that of **1** by the transition-metal hydrides **5** and $H_4Mo(dppe)_2$ (**8**).[65] The reactivities of the hydride reduction products especially those of the formyl and hydroxymethyl complexes are discussed. Several aspects of this work have been published as preliminary communications.[44,62,65,66]

Results

1. Reduction of $[Fp^*CO]^+PF_6^-$ by $NaBH_4$, Fp*H, and $H_4Mo(dppe)$. The reduction of **1** by $NaBH_4$ in THF at −80 °C followed by warming to 20 °C produces a 91% yield of a single reaction product, the known yellow methyl complex Fp^*CH_3 (**4**)[57,60] (eq 6). If this reaction is carried out at 20 °C, 20% of Fp*H (**5**) is also formed. The reduction at −80 °C can be monitored by ^1H NMR in THF-d_8. Filtration of the reaction mixture after 30 min of stirring followed by recording the ^1H NMR (manipulations performed at −80 °C) shows the presence of Fp*CHO (**2**) as the single organoiron product (δ_{CHO} 13.72; eq 7). The signals of the hydroxymethyl complex Fp^*CH_2OH (**3**) appear only when this reaction mixture is warmed to −60 °C, progressively replacing those of **2**. Two equivalents $NaBH_4$ is the minimum amount needed to convert all of **1** to **3**. Complex **3** is characterized "inter alia" by the doublet resonance ascribed to the methylene protons at δ 4.02 (^3J = 3 Hz; eq 8). The last step of the reduction, formation of **4** from **3** (eq 9), is observed at 0 °C, the methyl singlet of **4** at δ 0.23 progressively replacing the methylene doublet of **3**. Also **4** is the product of the reaction between **3** and 1 equiv $NaBH_4$ in THF at 20 °C (eq 9). Thus, the complete series of $NaBH_4$ reduction products have been observed in a homogeneous reaction medium by monitoring the reaction by ^1H NMR at various temperatures between −80 °C and 20 °C in THF-d_8 (eq 10).

$$\underset{\mathbf{1}}{[\mathrm{Fp^*CO}]^+} + \mathrm{NaBH_4} \xrightarrow[20\ ^\circ\mathrm{C}]{\mathrm{THF}} \underset{\mathbf{4}}{\mathrm{Fp^*CH_3}} \tag{6}$$

$$\underset{\mathbf{1}}{[\mathrm{Fp^*CO}]^+} + \mathrm{NaBH_4} \xrightarrow[-80\ ^\circ\mathrm{C}]{\mathrm{THF}} \underset{\mathbf{2}}{\mathrm{Fp^*CHO}} + \mathrm{BH_3} \tag{7}$$

$$\underset{\mathbf{2}}{\mathrm{Fp^*CHO}} + \mathrm{BH_3} \xrightarrow[\mathrm{THF}\text{-}d_8,\ -60\ ^\circ\mathrm{C}]{\mathrm{NaBH_4}} \underset{\mathbf{3}}{\mathrm{Fp^*CH_2OH}} \tag{8}$$

$$\underset{\mathbf{3}}{\mathrm{Fp^*CH_2OH}} + \mathrm{NaBH_4} \xrightarrow[20\ ^\circ\mathrm{C}]{\mathrm{THF}} \underset{\mathbf{4}}{\mathrm{Fp^*CH_3}} \tag{9}$$

$$\mathbf{1} \xrightarrow{-80\ ^\circ\mathrm{C}} \mathbf{2} \xrightarrow[\text{in situ}]{-60\ ^\circ\mathrm{C}} \mathbf{3} \xrightarrow[\text{in situ}]{0\ ^\circ\mathrm{C}} \mathbf{4} \tag{10}$$

What happens after the formation of **2** if no excess $NaBH_4$ or BH_3 is present in the THF solution?. As shown above 3 equiv of $NaBH_4$ are necessary to convert **1** to **4** (eq 7–9). If less than 3 equiv of $NaBH_4$ are added to **1** in THF at −80 °C, (conditions where **1** is consumed to give **2**), **1** is recovered together with **4** after the reaction mixture is warmed from −80 °C to 20 °C. If 1, 2, 3, or 4 equiv of $NaBH_4$ are added to 1 equiv of **1** under these conditions, the ratios of the two compounds (**1**:**4**) obtained are respectively (from ^1H NMR) 70:30, 40:60, 10:90, or 2:98. These results confirm that the stoichiometry of reduction is 3 equiv of $NaBH_4$/equiv of **1**. Compound **2** reacts with 1 equiv of BH_3 to give **1** and **4** (eq 11). Indeed if water is added to the formyl complex **2**, the hydride complex **5** is isolated in pure form.

$$\underset{\mathbf{2}}{\mathrm{Fp^*CHO}} + \mathrm{NaPF_6} \xrightarrow[\mathrm{THF}]{\mathrm{BH_3}} \underset{\mathbf{4}}{\mathrm{Fp^*CH_3}} + \underset{\mathbf{1}}{[\mathrm{Fp^*CO}]^+} \tag{11}$$

When **1** is reduced by $NaBH_4$ in a mixture of THF and water (90:10) at 20 °C, or even in water at 0 °C (1.5 h), a 69% yield of the off-white complex **5**, analytically pure, is isolated (eq 12). In these experiments, water hydrolyses BH_3, which prevents the reaction shown in eq 11. Under these conditions, we observe the decomposition of unstable **2** (eq 13).

$$\underset{\mathbf{1}}{[\mathrm{Fp^*CO}]^+} + \mathrm{NaBH_4} \xrightarrow{\mathrm{THF/H_2O}} \underset{\mathbf{5}}{\mathrm{Fp^*H}} \tag{12}$$

$$\underset{\mathbf{2}}{\mathrm{Fp^*CHO}} \xrightarrow[-\mathrm{CO}]{} \underset{\mathbf{5}}{\mathrm{Fp^*H}} \tag{13}$$

In contrast to the Cp series, $NaBH_3CN$ reduces **1** in methanol to give an 85% yield of **5**. The hydroxymethyl complex **3**, an intermediate in the $NaBH_4$ reduction of **1** in THF, can be specifically synthesized by using dichloromethane instead of THF. The $NaBH_4$ reduction of **3** to **4** (eq 9) does not proceed in dichloromethane. Complex **3** is isolated as a pure orange solid in 72% yield (eq 14). It is air-sensitive and nearly thermally stable at 20 °C in the solid state.

$$\underset{\mathbf{1}}{[\mathrm{Fp^*CO}]^+} + \mathrm{NaBH_4} \xrightarrow[20\ ^\circ\mathrm{C},\ 16\ \mathrm{h}]{\mathrm{CH_2Cl_2}} \underset{\mathbf{3}}{\mathrm{Fp^*CH_2OH}} \tag{14}$$

In a sealed ^1H NMR tube under N_2, a C_6D_6 solution of **3**, at 40 °C, slowly gives Fp^*_2 (**6**) (40% in 5 h, 90% in 16 h; eq 15). On the other hand, in polar solvents (CD_3OD or CD_3NO_2), **4** (d_0) is obtained immediately (20 °C) in 50% yield after sublimation (eq 16). Protonation of **3** may occur at the metal or at the oxygen atom. The results depend on the reaction medium and on the strength of the acid and its counteranion. Reaction of **3** with excess 48% aqueous HBr in CH_2Cl_2 at 20 °C gives 30% of MeOH, 20% of **4**, and 80% of Fp*Br (**13**) (eq 17). Reaction of **3** with H^+BF_4 in ether, diluted in dichloromethane at −80 °C, gives a 80:20 mixture of CH_4/C_2H_4 (eq 18). The same

$$\underset{\mathbf{3}}{\mathrm{Fp^*CH_2OH}} \xrightarrow{\mathrm{C_6D_6},\ 40\ ^\circ\mathrm{C}} \underset{\mathbf{6}}{[\mathrm{Fp^*}]_2} \tag{15}$$

$$\underset{\mathbf{3}}{\mathrm{Fp^*CH_2OH}} \xrightarrow{\mathrm{CD_3OD\ or\ CD_3NO_2}} \underset{\mathbf{4}}{\mathrm{Fp^*CH_3}} \tag{16}$$

$$\underset{\mathbf{3}}{\mathrm{Fp^*CH_2OH}} \xrightarrow[\mathrm{CH_2Cl_2},\ 20\ ^\circ\mathrm{C}]{\mathrm{HBr\ (aq)}} \mathrm{CH_3OH} + \underset{\mathbf{13}}{\mathrm{Fp^*Br}} + \mathbf{4} \tag{17}$$

$$\underset{\mathbf{3}}{\mathrm{Fp^*CH_2OH}} \xrightarrow[\mathrm{CH_2Cl_2},\ 20\ ^\circ\mathrm{C}]{\mathrm{HBF_4{\cdot}Et_2O}} \mathrm{CH_4} + \mathrm{C_2H_4} \tag{18}$$

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reaction at −80 °C in the presence of cyclohexene gives a 10% yield of norcarane, a lower yield than reactions involving $CpFeCH_2OCH_3$[81,86c] or $Fp^*CH_2OCH_3$.[86e,f]

When **1** is reduced by **5** instead of $NaBH_4$ in THF, a 20% yield of a mixture of **3** and **4** (50:50) is obtained (stoichiometry of **5**:**1** = 1, 20 °C, overnight; eq 19). On

$$\underset{\mathbf{1}}{[Fp^*CO]^+} \xrightarrow{Fp^*H} \underset{\mathbf{3}\ (10\%)}{Fp^*CH_2OH} + \underset{\mathbf{4}\ (10\%)}{Fp^*CH_3} \qquad (19)$$

the other hand, if a 5-fold excess of **5** is reacted with $[Fp^*THF]^+PF_6^-$ (**7**) under 1.2 atom of CO at 40 °C over a period of 16 h, **4** is obtained in 40% yield. Using a 100-fold excess of **5** at 20 °C for 10 days under 1.2 atm of CO gives a 240% yield of **4** (vs **7**). Thus, in eq 13, the amount of **5** is not sufficient to convert all of **3** to **4** (because of side reactions). When excess **5** is present, **3** is no longer formed and **4** is the only reduction product obtained. In eq 20, the ligand is rapidly replaced by CO under the reaction conditions.[65]

$$\underset{\mathbf{7}}{[Fp^*THF]^+} \xrightarrow[\text{THF, Fp*H}]{\text{CO (1.2 atm)}} \underset{\mathbf{4}}{Fp^*CH_3} \qquad (20)$$

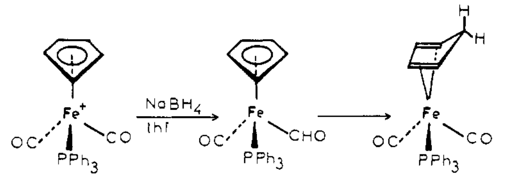
16 h, 40 °C, 5Fp*H; 40%
10 days, 20 °C, 100Fp*H; 240%

With $H_4Mo(dppe)_2$ (**8**) as the hydride source, **1** is reduced in THF at 20 °C over a period of 12 h to give a 7.5% yield of the hydroxymethyl complex **3** and 7.5% yield of the dimer **6** (eq 21). The molybdenum hydride is clearly

$$\underset{\mathbf{1}}{[Fp^*CO]^+} \xrightarrow[\text{THF, 20 °C}]{H_4Mo(dppe)_2} \underset{\mathbf{3}}{Fp^*CH_2OH} + \underset{\mathbf{6}}{[Fp^*]_2} \qquad (21)$$

not as efficient a reducing agent as the iron hydride, since none of the methyl complex **4** is obtained with **8**.

We have also reexamined the $NaBH_4$ reduction of $[\eta^5\text{-}CpFe(CO)_2(PPh_3)]^+PF_6^-$ (**15**) which is known to give $(\eta^4\text{-}C_5H_6)Fe(CO)_2(PPh_3)$[37,64] (**16**). The reduction of **15** by $NaBH_4$ in THF-d_8 at 80 °C was followed by ^1H NMR. A mixture of **16** and $(\eta^5\text{-}Cp)Fe(CO)(PPh_3)(CHO)$ (**17**) is subsequently converted into the diene complex **16** (eq 22).

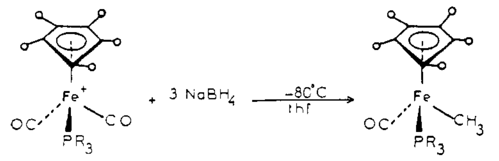


15 17 • 16 16 (22)

2. Reduction of $[Fp^*PR_3]^+PF_6^-$ by $NaBH_4$. The complexes $[Fp^*PR_3]^+PF_6^-$ (**9**) can be prepared as shown in eq 23.[60] Reduction of $[Fp^*PBu_3]^+PF_6^-$ (**10a**),

$$\underset{\mathbf{6}}{[Fp^*]_2} \xrightarrow[\text{THF}]{[Cp_2Fe]^+} \underset{\mathbf{7}}{[Fp^*THF]^+} \xrightarrow[CH_2Cl_2]{PR_3} \underset{\mathbf{9}}{[Fp^*PR_3]^+} \qquad (23)$$

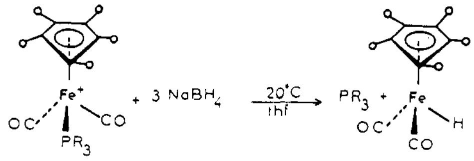
$[Fp^*PMe_3]^+PF_6^-$ (**10b**),[59] and $[Fp^*PPh_3]^+PF_6^-$ (**10c**)[58,60] by $NaBH_4$ in THF at −80 °C gives good yields of the methyl complexes $Cp^*Fe(CO)(PR_3)(CH_3)$ as the only organoiron products (**12a**, R = *n*-Bu; **12b**, R = Me; **12c**, R = Ph; eq 24). Complexes **12** are slightly air-sensitive, orange solids



(24)

that show resonances at high field for methyl hydrogens ($\delta < 0$) coupled with phosphorus (doublets in the ^1H and $\{^1H\}^{13}C$ NMR spectra).

On the other hand, when these $NaBH_4$ reductions are directly effected at 20 °C, only the hydride complex **5**[44,63] is isolated whatever the phosphine (66–82% yield, eq 25). The reactions are specific in each case at 20 °C as well as at −80 °C.



(25)

When the low-temperature reactions are monitored by ^1H NMR in THF-d_8, only the starting materials **9** are observed at −80 °C, in contrast to the case of the reduction of **1**. Indeed, the reduction is not observed until −40 °C for **9c** and at −30 °C for the more "electron-rich" cations **9a**[67] and **9b**. At these temperatures, the first reduction step, hydride transfer to **9** giving the formyl complexes, is observed (eq 26). However, in contrast to the case of **2**, two formyl complexes show ^1H NMR signals for each $NaBH_4$ reduction. These signals are attributed to the free formyl complex **10** and to the BH_3 adduct **11** (not observed in the case of **2**). The ratio of these two complexes depends on the basicity of the phosphine and, consequently, of the formyl oxygen; formyl complexes bearing trialkylphosphines bind BH_3 more strongly than their triphenylphosphine analogues (the ratios **10b**:**11b** and **10a**:**11a** = 1 and **10c**:**11c** = 2.5). The resonance for the formyl proton appears as a doublet near 14.3 ppm ($^3J_{PH}$ = 5.4 Hz) whereas in the BH_3 adduct the formyl proton resonance appears as a broad multiplet near 12.8 ppm. If the reaction mixture is allowed to warm to −15 °C, the BH_3 adduct of **11** transfers BH_3 to the solvent THF to give **10** (eq 26); this almost irreversible transformation can be monitored by ^1H NMR after the transformation of **11a** into **10a** (the ratio **11a**:**10a** is then less than 0.02). Complex **10a** also can be characterized by its ^{13}C NMR spectrum (δ_{CHO} 306.5 (d, $^2J_{PC}$ = 26 Hz, $^1J_{CH}$ = 127 Hz)). If the hydride reduction is effected in the presence of PPh_3 in order to trap BH_3, **10a** is formed exclusively (eq 27) and then disproportionates to **9a** and **12a**. These complexes (**9a** and **12a**) can be isolated in 69 and 23% yields, respectively (eq 28).

$$\underset{\mathbf{9}}{[Fe]^+CO} \xrightarrow[(26)]{NaBH_4,\ -80\ °C} \underset{\mathbf{11}}{[Fe]CHO\cdot BH_3} \xrightarrow[(27)]{PPh_3,\ -80\ °C} \underset{\mathbf{10}}{[Fe]CHO}$$

$$\underset{\mathbf{10a}}{[Fe]CHO} \xrightarrow{THF\cdot BH_3} \underset{\mathbf{9a}\ (69\%)}{[Fe]^+CO} + \underset{\mathbf{12a}\ (23\%)}{[Fe]CH_3} \qquad (28)$$

$$[Fe] = Cp^*Fe(CO)(PR_3)$$

The low-temperature reduction of **9** in THF initially provides a mixture of **10** and **11**; **11**, then decomposes to **10**. The methyl complexes **12** are formed between −20 °C

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(67) (a) The good solubility of the reaction mixture **9** + $NaBH_4$ in THF at −80 °C, even before reaction, contrasts with the insolubility of each of these two reaction components alone in THF. This is taken into account by the formation of new ion pairs (and their aggregates): $[Fp^*L^+,PF_6^-] + [Na^+,BH_4^-] \rightarrow [Fp^*L^+,BH_4^-] + [Na^+PF_6^-]$. (b) We initially observed $NaBH_4$ reduction of **9** at lower temperatures, which was attributed to the sequence: formyl, (hydroxymethylene)iron intermediates.[62] However, we found later that this hydride reduction was that of the impurity $[Fp^*THF]^+PF_6^-$ (present in some of the samples of **9**) actually leading to the formyl complex $Cp^*Fe(CO)(THF)(CHO)$ and its BH_3 adduct at −80 °C.

and 10 °C, but no intermediate hydroxymethyl analogues of **3** are observed. Formation of the methyl complexes is accompanied by that of the starting material **9** when the amount of $NaBH_4$ is lower than 3 equiv, as is the case for the reduction of **1** (eq 22). However, in the presence of excess BH_3, only 1 equiv of $NaBH_4$ is necessary; indeed, a solution of **10a** and **11a** gives **12a** if excess THF·BH_3 is added to it (eq 28). The amount of **10a** is not changed by addition of excess THF·BH_3, consistent with the irreversible conversion of **11a** into **10a** (eq 29).

$$\underset{\mathbf{10a}}{[Fe]CHO} + \underset{\mathbf{11a}}{[Fe]CHO{\cdot}BH_3} \xrightarrow{THF{\cdot}BH_3} \underset{\mathbf{12a}}{[Fe]CH_3} \quad (29)$$

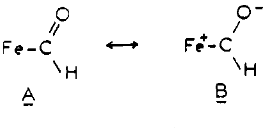
$$[Fe] = Cp^*Fe(CO)(PR_3)$$

The intermolecularity of the overall reduction is also shown by the reduction of **9a** with a mixture of $NaBH_4$ and $NaBD_4$ giving **12a** as a mixture of d_0 (34%), d_1 (42%), d_2 (21%), and d_3 (3%); the isotope effect is large, as expected.

In eq 28, the presence of the THF·BH_3 adduct is crucial to the disproportionation of **10a**. Indeed, if PPh_3 is added as in eq 21, **10a** does not give **9a** and **12a**, but only **5** (compare eq 13 and 29). This confirms the thermal instability of the formyl iron complexes of this series.

Discussion

1. First Hydride Transfer: Generation of Formyl Complexes. Not surprisingly,[25] formyl complexes are always formed from the starting carbonyl complexes,[37,67] but the rates of formation depend drastically on the nature of the ancillary ligand. In a gross sense, replacing one CO ligand by a phosphine has an effect similar to that obtained by permethylation of the Cp ligand. Hydride reduction of CO to formyl occurs at −80 °C for both **1** and **15**, but combining both structural modifications inhibits the carbonyl reduction below −30 °C; $\{Cp^*Fe(CO)dppe]^+PF_6^-$ cannot be reduced by $NaBH_4$ at any temperature.[79] Contrary to the rhenium formyl complexes,[1] **2** is not formed as a BH_3 adduct because iron is much less electron rich than rhenium. Some compensation can be brought about with the donor phosphine ligands, especially trialkylphosphines[68] in **11a** and **11b**. The chemical shift value observed by ^{13}C NMR (306.46 ppm) for **9a** is the largest ever observed for a metal formyl complex, indicative of the importance of mesomeric form B. This is corroborated by the low infrared frequency (1590 cm^{-1}) of the formyl group. This polarization favors the formation of the BH_3 adduct, even in THF solution.



The latter complexes lose BH_3 thermally or upon reaction with H_2O or PPh_3: i.e., in the iron series the influence of these parameters on the BH_3–formyl bond is finely balanced. The solvent here serves as a reference; the THF oxygen atom always appears more basic than the one in the formyl complexes (**2**, **10**). Evidently there is a kinetic barrier in removing BH_3 from **11a**.

The reduction of **9b** by $LiAlH_4$ was reported to give **12b** via a "formyl complex" observed by ^1H NMR (14.19 ppm).[63] With $NaBH_4$, it is probable that this formyl complex is the free formyl **10b** (14.38 ppm (d, $^4J_{PH}$ = 4.7 Hz), THF-d_8 at −30 °C); the formation of **10b** is accompanied by that of **11b** (12.83 ppm (d, $^4J_{PH}$ = 1.2 Hz)). The BH_3 adduct is also expected to have a large contribution of the zwitterionic carbenoid limiting resonance form. However, free rotation about the Fe–C bond should proceed as in the homologous methoxycarbene complex.[73] The formyl·BH_3 adduct **11** adopts a geometry closer to the "alkylidene-like" structure[40] than **10**, as expected if the zwitterionic form is a more important resonance contributor in the adduct than in the free formyl complex. For such an orientation of the ligands, the angle between the Fe–P and C–H bonds is supposed to be close to 90°. Thus, from the Karplus equation, one expects[69-71] (as is observed) a much larger coupling constant, $^3J_{PH}$, in the free formyl.

2. Reactivity of the Formyl Complexes. How the formyl complexes **2** and **10** decompose (in the absence of BH_3 or $NaBH_4$) to **5** is not known. Many formyl complexes have been shown to be unstable,[71a,76] whereas others are thermally stable[72b] and several modes of decomposition have been proposed.[25,72-78] It is also noteworthy that **5** is the only product of the $NaBH_4$ reduction of **9** at 20 °C, an observation also made by others in the case of **9b**.[37,72] Complex **5** may be formed from **10** (eq 30), from **9** by direct attack at the metal (eq 31), or, less likely, by electron-transfer from $NaBH_4$ to **9** (eq 32). This latter mechanism operates with $[(C_5Me_5)Fe(CO)(dppe)]^+$.[79]

$$\mathbf{9} + NaBH_4 \rightarrow \mathbf{10} \rightarrow \mathbf{5} \quad (30)$$

$$\mathbf{9} + NaBH_4 \rightarrow \mathbf{5} \quad (31)$$

$$\mathbf{9} + NaBH_4 \rightarrow 19e \rightarrow 17e \xrightarrow[\text{or } BH_3]{NaBH_4} \mathbf{5} \quad (32)$$

In the presence of BH_3, the disproportionation observed for the formyl complexes compares with the electrophile-induced disproportionation of rhenium complexes; the production of rhenium methyl complexes by disproportionation is known.[72c] One equivalent of BH_3 is insufficient to reduce the formyl complex, and no reduction interme-

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[68] The difference in basicity of the metal upon replacing CO by a phosphine ligand is reflected "inter alia" by the differences in Mössbauer isomer shift and infrared ν_{CO}.[59]

[69] Drago, R. S. *Physical Methods in Chemistry*; W. B. Saunders: London, 1977; pp 217–223.

[70] (a) Karplus, M. *J. Am. Chem. Soc.* **1963**, *85*, 2870. (b) Gorenstein, G. *Prog. Nucl. Magn. Reson. Spectrosc.* **1983**, *16*, 1.

[71] For a recent controversy concerning the conformational effects on coupling constants in Fp complexes, see: (a) Cameron, A. D.; Baird, M. C. *J. Chem. Soc., Dalton Trans.* **1985**, 2691 and references cited therein. (b) Hunter, B. K.; Baird, M. C. *Organometallics* **1985**, *4*, 1481. (c) Davies, S. G. *J. Organomet. Chem.* **1987**, *320*, C19.

[72] (a) For examples of unstable formyl complexes, see ref 25 and Selover, J. C.; Marsi, M.; Parker, D. W.; Gladysz, J. A. *J. Organomet. Chem.* **1981**, *206*, 317. For studies of the decomposition of formyl to hydride complexes, see ref 25, 74, and 75. For chain mechanism of the catalytic loss of CO, see ref 76. (b) For examples of stable rhenium formyl complexes, see ref 1, 25, 40, 42, and: Sontag, C.; Grama, O.; Berke, H., submitted for publication. For stable neutral manganese[74] and tungsten[75] formyl complexes, see the interesting recent reports by Berke.[74,75]

[73] Davies, S. G. *Appl. Catal.* **1986**, *e5*, 87.

[74] Berke, H.; Huttner, G.; Scheidsteger, O.; Weiler, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 735.

[75] Berke, H.; Kundel, P. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1986**, *41B*, 527.

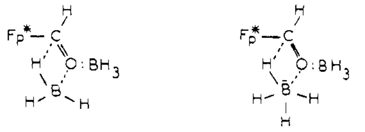
[76] Chain mechanism for the decomposition of formyl to hydride complexes has been shown to operate for binuclear rhenium formyl compounds.[77] (Note that if the complex bears a phosphine ligand, the 19e intermediate generally loses the phosphine rather than CO. For instance the decomposition 10 to 5 could go by this pathway.) Hydrogen atom donors such as n-Bu_3SnH stabilize formyl complexes susceptible to decompose in such a way.[78]

[77] Narayanan, B. A.; Amatore, C.; Casey, C. P.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 6351.

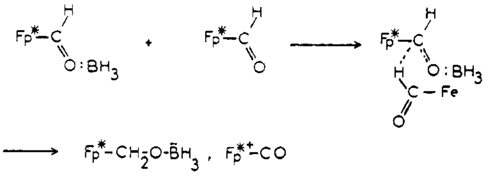
[78] (a) Narayanan, B. A.; Amatore, C.; Kochi, J. K. *Organometallics* **1984**, *3*, 802. (b) Kochi, J. K. *J. Organomet. Chem.* **1986**, *300*, 139.

[79] For electron-transfer processes from $NaBH_4$ or $LiAlH_4$ to 18-electron organoiron complexes giving H_2 and 19-electron intermediates, see ref 61, 66, and 80. Final reaction products arise from the H atom transfer from the neutral or from the anionic hydride to the 19-electron intermediate (onto a ligand[80] or onto the metal[60]). These reaction products may or may not be the same as those arising from hydride transfer. For discussion of this latter point, see ref 61 and 63.

diate is observed. Evidently each BH_3 or BH_4^- cannot transfer more than one hydrogen. This is consistent with the proposal that boron hydrides react with the formyl complexes in a dichotomic type of activation, viz., as a Lewis acid (BH_3 necessarily) and as a nucleophile.



Re-formation of the starting carbonyl complex is best explained by the fact that the formyl hydrogen is hydridic (as shown by the studies of the Canizarro-type reaction of the Re complexes reported by Casey and Gladysz). Thus **10** can behave as a reducing agent when a boron hydride is lacking (eq 33).

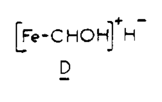


(33)

The hydridic properties of **2** and **10** are enhanced by the absence of BH_3 in **2** and the loss of BH_3 in **10**. When the formyl oxygen is coordinated to BH_3, the Lewis acid withdraws much of the electron density of the formyl through its oxygen and develops a fractional positive charge on the formyl carbon. Finally these iron formyl complexes show great thermodynamic and kinetic instability[25,76] unlike Re, Os, and even Mn formyl complexes (see, for instance, the X-ray crystal structures of the latter by Berke and Huttner[72b–75]).

Mechanistic details as well as analogy with the hydride reduction of organic carbonyls have been discussed by Graham.[1] Perhaps the most intriguing question generated by the present study is why the formation of **3** does not necessarily require hydrolysis, unlike that of organic alcohols.

3. Reactivity of the Hydroxymethyl Complexes. The nature of CO reduction intermediates in the versatile iron chemistry depends "inter alia" on the nature of the ancillary ligands. This is also true for hydroxymethyl complexes since **3** is easily observed in THF and synthesized in dichloromethane, whereas such an intermediate cannot be observed in the course of the reduction of **9**. Most interesting is the finding by Cutler[56] that even without the protecting permethylation of the Cp ligand, an analogous system ("vide supra") must yield $Cp(CO)_2FeCH_2OMe$, notably via $CpFe(CO)_2CH_2OH$. We know that the isostructural complexes $[CpM(CO)_3]^+$ (M = Fe, Ru)[52] also give even more stable hydroxymethyl analogues of **3** by hydride reduction, a chemistry which parallels that of the Re complexes. Thus, a member of hydroxymethyl and hydroxyalkyl transition-metal complexes are known, but their synthesis has been difficult. Indeed, hydroxyalkyl complexes are elusive. The only (hydroxymethyl)iron complex ever observed is **3**. Discussion of **3** must take into account the ionic forms B and variations C and D of A.



An important property of hydroxymethyl complexes is that they are reduced easily to methyl complexes. This property contrasts sharply with organic alcohols that cannot be reduced to alkanes under comparable conditions.[82] It has already been recognized[1] that this property results from the stabilization of a positive charge on the carbon atom that renders it susceptible to hydride attack (ionic form B) and explains why **3** is quickly reduced by $NaBH_4$ to **4**.

Another type of polarization taking into account the "etherification" in MeOH found by Cutler[56,81] and later for **3** is the ionic form C. Lin et al.[52] reported that very weak Brønsted bases such as PMe_3 or $P(OMe)_3$ catalyze the decomposition of $CpM(CO)_2CH_2OH$ to $[CpM(CO)_2]_2$ (M = Fe, Ru) and formaldehyde and concluded that these complexes are strong acids. Such a decomposition was precedented[47,48] by the base-promoted decomposition of $[Ir(H)(CH_2OH)(PMe_3)_4]^+$, and formaldehyde is also produced by β-elimination of the CH_2OH ligand at the Os center in the course of the thermal decomposition of the Os analogue of **3**.[43] Stable iron formaldehyde complexes are also known.[95–97] In the light of these reports, the slow decomposition of **3** to **6** in an inert solvent could be explained by a process similar to that cited above for the Os analogue.

The rapid formation of **4** from **3** at 20 °C in CD_3NO_2 or CD_3OD is noteworthy, first because it is an unknown reaction relevant to the Fischer–Tropsch process but second because it is unexpected given the classical "etherification" already reported by Lin et al.[52a] under these reaction conditions (CH_3OH) and suggested by Cutler.[56] However, we know that the reaction of $H^+PF_6^-$ in ether (or etherate) with $Fp^*CH_2OCH_3$ gives $[Fp^*CH_2]^+$ which decomposes to **4**, CH_4 (via **4**), and C_2H_4.[81,86a] We now find that the same reaction with **3**, under identical conditions, also gives the same products CH_4 and C_2H_4. Interestingly, protonation of **3** using aqueous HBr also gives 20% of **4**, besides Fp^*Br[83b] and CH_3OH resulting from protonation at Fe. Thus the decomposition of **3** in polar solvents, its protonation at the oxygen atom, and the same protonation of Fp^*CH_2OMe all lead to CH_4. These observations taken together suggest that $[Fp^*CH_2]^+$ is the intermediate in the decomposition of **3** in polar solvents, consistent with the stabilization of the polar form C favored in CD_3NO_2 or CD_3OD. Decomposition of **3** into **4** is analogous to the $NaBH_4$ reduction of **3** to **4** accounted for by the polarity of **3** discussed above. What is then the hydride source in polar solvents in the absence of $NaBH_4$?

Another canonical form may be written for the (hydroxymethyl)- and (alkoxymethyl)iron complexes involving the stabilized Fischer-type iron carbene complex ionic form

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(80) Michaud, P.; Astruc, D.; Ammeter, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 3755.

(81) Jolly, P. W.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 5044.

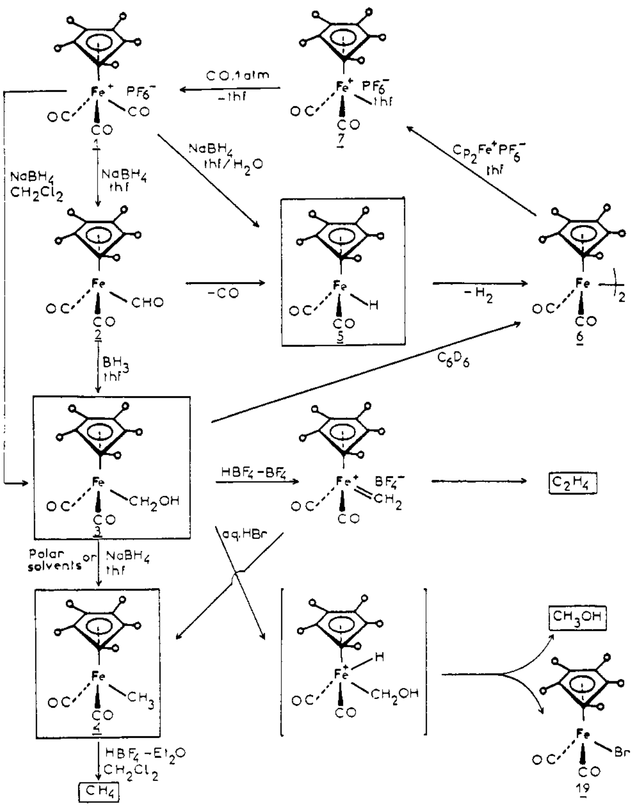
(82) For a valuable discussion on the mechanism of the $NaBH_4$ stepwise reduction of CO in cationic carbonyl complexes and the comparison with the reduction of organic carbonyls, see the paper by Graham[1] and references quoted therein.

(83) For discussions on the protonation of piano-stool iron alkyl complexes, see: (a) Johnson, M. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 4, p 331. See also ref 84 and 85. (b) Anderson, S. N.; Cooksey, C. J.; Holton, S. G.; Johnson, M. D. *J. Am. Chem. Soc.* **1980**, *102*, 2312. (c) Attig, T. G.; Teller, R. G.; Wu, S.-M.; Bau, R.; Wojacki, A. J. *Ibid.* **1979**, *101*, 619. (d) Rogers, W. N.; Baird, M. C. *J. Organomet. Chem.* **1979**, *182*, C65. Isolation of an Os^{IV} complex by protonation of Os^{II} has been recently achieved by Baird's group.[83e] (e) Sanderson, L. J.; Baird, M. C. *J. Organomet. Chem.* **1986**, *307*, C1.

(84) Guerchais, V.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1985**, 837.

(85) Hamon, J.-R.; Astruc, D.; Michaud, P. *J. Am. Chem. Soc.* **1981**, *103*, 758.

Scheme I



D. One can recognize in the ionic form D that **3**, as well as $Fp^*CH_2OCH_3$,[86c–f] must be excellent hydride donors (hydride abstraction from (methoxymethyl)iron complexes is known to give the Fischer-type iron carbene complexes[86–88]). Given the stability of **4**, iron methylene cations

$$\underset{\mathbf{3}}{2\mathrm{Fp^*CH_2OH}} \rightarrow \underset{\mathbf{4}}{\mathrm{Fp^*CH_3}} + [\mathrm{Fp^*{=}CHOH}]^+,\mathrm{OH^-} \tag{34}$$

$$[\mathrm{Fp^*{=}CHOH}]^+,\mathrm{OH^-} \xrightarrow{-\mathrm{H_2O}} \underset{\mathbf{2}}{\mathrm{Fp^*CHO}} \xrightarrow{-60\ ^\circ\mathrm{C}} \underset{\mathbf{5}}{\mathrm{Fp^*H}} \xrightarrow{-\mathrm{H_2}} \underset{\mathbf{6}}{\mathrm{Fp^*_2}} \tag{35}$$

must be excellent hydride acceptors and the decomposition of **3** to **4** can be understood as a combination of the B and D limiting resonance forms (see also Scheme I).

In the protonation of **3** with aqueous HBr the site of protonation (Fe vs O) very much depends on the reaction conditions: protonation at iron is known in piano-stool iron alkyl complexes, and the intermediacy of Fe^{IV} has been proposed. (Os^{IV} has been recently isolated by Baird from the protonation of Os^{II} alkyl complexes.[83e]) Both paths for the protonation of **3** are shown in Scheme I. That no hydroxymethyl intermediate is observed when monitoring the hydride reduction of **9** is explained in light of the above discussion. Several striking precedents have been reported. First, Pettit[89] showed that a $M-CO_2H$ complex is stable under its neutral form in $CpFe(CO)(PPh_3)(COOH)$, whereas $[CpFe(dppe)(CO)]^+$ yields the ion pair $[CpFe(dppe)(CO)^+,OH^-]$. The higher positive charge on the α-carbon atom in $Cp^*Fe(CO)(PR_3)CH_2OH$ than in **3** and $[CpFe(dppe)(CO)]^+$ make them much more reactive toward a hydride source than **3**. Alternatively, the ion pair $[Cp^*Fe(CO)(PPh_3)(CH_2)^+,OH^-]$ may be the reactive intermediate rather than the hydroxymethyl complex. (This cationic methylene complex has been shown to be stable up to −10 °C.[86])

4. Attempts To Achieve a Catalytic Cycle for the Reduction of CO by Fp*H. The studies effected using neutral transition-metal hydrides indicate that they are, as expected, less efficient than $NaBH_4$, especially in the reduction of hydroxymethyl to methyl. Of course, neutral transition-metal hydrides are better models than $NaBH_4$ or even BH_3, and it is not surprising to observe similarities (formation of hydroxymethyl compounds).

If one uses **5**[90] to reduce coordinated CO in **1**, the metal that activates CO and transfers the hydride is the same and the coordination spheres are similar. One can draw an analogy to Fischer–Tropsch chemistry by starting from CO instead of **1**[58,60] and using **7**, a source of the activated 16-electron species $[Fp^*]^+$. Note that in such a system **5** gives **7** after hydride transfer, and more CO can be activated again. In principle, such a system should be catalytic: i.e. several equivalents of CO/equiv of **7** should be reduced to **3** or **4** by using excess **5**. Indeed **5** can reduce **1** to **4** in more than 100% yield if only 10 equiv of **5** are used. The weakest point in this process probably is the reversibility of the first hydride transfer to **1** by **5**. We know that even BH_3 does not bind **2**, and Fp* appears to be a rather weak Lewis acid for the activation of the formyl oxygen of **2**. Altogether, 2–3 equiv of CO are reduced in 10 days, seven hydride transfers being successful out of a possible maximum of 100. This cyclic system is represented in Scheme II.[100]

Experimental Section

Reagent grade tetrahydrofuran, diethyl ether, and pentane were dried by distillation from sodium benzophenone ketyl under nitrogen just before use. Sodium borohydride was dried in vacuo over a 2-day period at 120 °C and then stored under argon. All other chemicals were used as received. All manipulations were done by Schlenk techniques or in glovebags. Infrared spectra were recorded with a Pye-Unicam SP 1100 infrared spectrophotometer

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[86] (a) Stevens, A. E.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 2854. (b) Davies, S. G.; Maberly, J. R. *J. Organomet. Chem.* **1985**, *986*, C37. (c) Cutler, A. R. *J. Am. Chem. Soc.* **1979**, *101*, 604. (d) Guerchais, V.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1986**, 663. (e) Guerchais, V.; Lapinte, C. *Ibid.* **1986**, 894. (f) Guerchais, V.; Lapinte, C.; Thépot, J.-Y. *Organometallics* **1988**, *7*, 604.

[87] Reactions of this kind have been shown by Gladysz to occur in rhenium chemistry.[40]

[88] It has been shown that hydride abstraction, with Ph_3C^+ as hydride acceptor, from (hydroxymethyl)- and (methoxymethyl)iron compounds does not proceed through the same pathway.[86d,e]

[89] Grice, N.; Kav, S. C.; Pettit, R. *J. Am. Chem. Soc.* **1979**, *101*, 1628.

[90] The molybdenum complex $H_4Mo(dppe)_2$[91] is less efficient.[65,66]

[91] Crabtree, R. H.; Hlatky, G. G. *Inorg. Chem.* **1982**, *21*, 1273.

[92] The side-on coordination of carbon monoxide by transition metals is well-known, both the carbon and the oxygen atom being synergistically activated by the same metal.[93] Interestingly, the side-on coordination of CO in an acyl ligand and of formaldehyde has also been established by Berke and Huttner in iron complexes.[94–97]

[93] (a) Os–η_2-CH_2O: Brown, K. L.; Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 503. (b) Mo–η^2-benzaldehyde: Brunner, H.; Wachter, J.; Bernal, I.; Creswick, M. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 861. (c) Zr–η^2-acyl: Farchinetti, G.; Floriani, C.; Marchetti, F.; Merlino, S. *J. Chem. Soc., Chem. Commun.* **1976**, 522. (d) Ru–η^2-acyl: Fachinetti, G.; Floriani, C.; Stoeckli-Evans, H. *J. Chem. Soc., Dalton Trans.* **1977**, 2297. (e) Th–η^2-acyl: Fagan, P. J.; Maata, F. A.; Marks, T. J. ref 55, p 53 and references cited therein. (f) Ta–η^2-acetone: Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5421.

[94] Birk, R.; Berke, H.; Huttner, G.; Zsolnai, L. *J. Organomet. Chem.*, in press.

[95] Berke, H.; Huttner, G.; Weiler, G.; Zsolnai, L. *J. Organomet. Chem.* **1981**, *219*, 353.

[96] Berke, H.; Birk, R.; Huttner, G.; Zolnai, L. *Z. Naturforsch., B: Anorg. Chem. Org. Chem.* **1984**, *39B*, 1380.

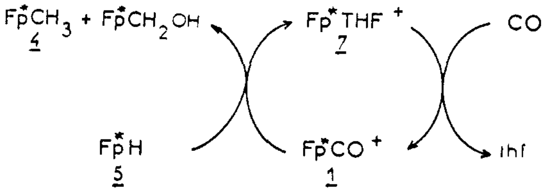
[97] Berke, H.; Bandhart, W.; Huttner, G.; v. Seyerl, J.; Zsolnai, L. *Chem. Ber.* **1981**, *114*, 2754.

[98] King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967**, *287*, 8.

[99] (a) Duggan, D. M.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 955.

[100] This work overlaps with the "These d'Etat" of D.C., Rennes, Feb 1985 (preceding part: ref 60).

Scheme II



calibrated with polystyrene. Samples were prepared between KBr disks in Nujol. ^{1}H NMR spectra were recorded with Varian EM 360 (60 MHz) and Brücker WP 80, AM 360, and AM 500 spectrometers. ^{13}C NMR spectra were obtained at 20.115 or 75.45 MHz. All chemical shifts were reported in parts per million (δ, ppm) with reference to tetramethylsilane (Me_4Si). Mass spectra were recorded with a Varian MAT 3112 spectrometer. Elemental analyses were performed by the Center of Microanalyses of the CNRS at Lyon-Villeurbanne, France.

I. Reduction of the [Fp*(CO)]PF_6 (1) with $NaBH_4$. 1. Reduction of 1 Using $NaBH_4$. A. To 0.840 g (2 mmol) of 1 suspended in 30 mL of THF was added 0.760 g (20 mmol) of $NaBH_4$, at −80 °C. The resulting suspension was stirred 60 min, warming to 20 °C, and the solvent was removed in vacuo. The orange residue was extracted with pentane. Removing the solvent yields 0.478 g (1.82 mmol, 91%) of 4.

B. To 0.840 g (2 mmol) of 1 dissolved in 30 mL of CH_2Cl_2 was added 0.380 g (10 mmol) of $NaBH_4$. The mixture was stirred for 16 h at 20 °C and extracted with pentane after CH_2Cl_2 was removed in vacuo. Pentane was removed slowly until orange microcrystals precipitate. The mixture was then cooled to −80 °C, and 3 was collected by filtration. After being dried under vacuum, 0.400 g (1.44 mmol, 72%) of pure 3 was recovered. Hydrolysis was effected by addition of 1 mL of H_2O in CH_2Cl_2 before the solvent was removed and pentane extracted. After the pentane solution was dried by using $MgSO_4$, 0.420 g (1.51 mmol, 75%) of 3 was isolated.

Fp*CH_2OH (3): air-sensitive, gradual decomposition over a week at 20 °C; IR (cm^{-1}, pentane) ν(CO) 1940, 2000; ^{1}H NMR (δ, CD_2Cl_2) 1.78 (s, 15 H, $C_5(CH_3)_5$), 4.02 (d, 2 H, ^3J = 3 Hz, CH_2OH); ^{13}C NMR (δ, CD_2Cl_2) 11.1 ($C_5(CH_3)_5$), 67.2 (CH_2OH, triplet off-resonance), 97.2 ($C_5(CH_3)_5$), 220.7 (CO). Anal. Calcd for $C_{13}H_{18}FeO_3$: C, 56.14; H, 6.52. Found: C, 55.96; H, 6.29.

C. To 0.840 g (2 mmol) of 1 dissolved in 30 mL of a mixture of THF/water (90:10 v/v) was added 0.380 g (10 mmol) of $NaBH_4$ at 20 °C in THF. The resulting solution was stirred 60 min, and the solvent was removed; the yellow residue was extracted with pentane. Pentane was slowly removed until the precipitation of a yellow powder which was recovered by filtration at −80 °C. After being dried in vacuo, 0.342 g (1.38 mmol, 69%) of the analytically pure complex 5 was obtained.

D. Under identical conditions, in 20 mL of pure water, the reaction was achieved in 30 min; then, 50 mL of pentane was added and the mixture stirred with the aqueous solution for 2 min and then cooled to −80 °C; the solid aqueous layer was removed by filtration. The workup was continued as in C which gave a 90% yield of yellow crystals of 5.

$(C_5Me_5)Fe(CO)_2H$ (5): IR (cm^{-1}, Nujol) ν(CO) 1950, 2010; ^{1}H NMR (δ, C_6D_6) −11.74 (s, 1 H, FeH), 1.65 (s, 15 H, $C_5(CH_3)_5$); ^{13}C NMR (δ, C_6D_6) 8.7 ($C_5(CH_3)_5$), 94.7 ($C_5(CH_3)_5$), 219.0 (CO). Anal. Calcd for $C_{12}H_{16}FeO_2$: C, 58.09; H, 6.50; Fe, 22.51. Found: C, 58.25; H, 6.35; Fe, 21.95.

2. Stoichiometry of the $NaBH_4$ Reduction of 1. $NaBH_4$ was added to a suspension of 0.420 g (1 mmol) of 1 in 30 mL of THF: (1) 0.038 g (1 mmol); (2) 0.076 g (2 mmol); (3) 0.114 g (3 mmol); (4) 0.152 g (4 mmol); (5) 0.190 g (5 mmol). After the mixtures were stirred for 16 h, the solvent was removed and the residue was analyzed by ^{1}H NMR spectroscopy. Only 1 and 4 were present in the following ratios (1:4): (1) 70:30; (2) 40:60; (3) 10:90; (4) 2:98; (5) 0:100.

3. Monitoring the Reduction of 1 by NMR. 1 (0.020 g, 0.048 mmol) was stirred in 0.6 mL of THF-d_8. Then the solution was cooled to −80 °C, and 0.010 mg of $NaBH_4$ (0.27 mmol) was added. The solution was stirred for 30 min and then filtered in a ^{1}H NMR tube at −80 °C. The ^{1}H NMR spectra recorded from −80 °C to −60 °C indicate the quantitative formation of the formyl complex 2 (δ, THF-d_8): 13.72 (s, 1 H, CHO), 1.95 (s, 15 H, $C_5(CH_3)_5$). Up to −60 °C signals attributed to 2 decrease and the formation of the hydroxymethyl complex 3 was observed simultaneously: δ 4.02 (d, 2 H, $-CH_2OH$), 1.80 (s, 15 H, $C_5(CH_3)_5$). Up to 0 °C the signal of complex 2 decreases and the formation of 4 was observed: δ 0.23 (s, 3 H, CH_3), 1.43 (s, 15 H, $C_5(CH_3)_5$).

4. Decomposition of Fp*CH_2OH (3). A. In a nonpolar solvent, 3 (0.015 g, mmol) was dissolved in 0.4 mL of C_6D_6 in a sealed NMR tube stored at 40 °C. ^{1}H NMR spectra were recorded at the following intervals: 1 h, minute amounts of 6; 5 h, 10% of Fp*$_2$ (6); 16 h, 90% of 6; 48 h, no traces of 3 and 100% of 6.

B. In a polar solvent, 0.280 g (1 mmol) of 3 was dissolved in methanol or nitromethane. The orange complex immediately turned yellow. Removing the solvent in vacuo and sublimation allowed the isolation of 4 in 50% yield. The same reaction was performed in methanol-d_1 and in nitromethane-d_3 and MS analyses only showed the presence of 4-d_0.

5. Protonation of 3. A. To 0.560 g (2.01 mmol) of 3 in CH_2Cl_2 was added an excess of 48% aqueous HBr (0.5 mL) at −80 °C; the mixture was then stirred 10 min before the solution was allowed to warm to room temperature. GC analysis using *tert*-butyl alcohol as internal standard showed the formation of 30% of methanol. After evaporation of the solvent, ^{1}H NMR spectra in C_6D_6 indicated the presence of the known complexes Fp*Br (13) and Fp*CH_3 (4) in a ratio of 80:20. Thin-layer chromatography and IR spectroscopy confirmed this analysis.

B. To 0.560 g (2.01 mmol) of 3 in CH_2Cl_2 (5 mL) at −80 °C was added a stoichiometric amount of $HBF_4 \cdot Et_2O$, diluted in 0.5 mL of CH_2Cl_2. The orange solution immediately became dark red. Mass spectroscopy of the gas phase indicated the presence of CH_4 and C_2H_4 in a ratio of 80:20.

C. To 0.560 g (2.01 mmol) of 3 in CH_2Cl_2 (5 mL) at −80 °C was added 10 g (10 mmol) of cyclohexene. The mixture was cooled to −80 °C, and a stoichiometric amount of $HBF_4 \cdot Et_2O$, diluted in 0.5 mL of CH_2Cl_2, was added. The solution was then allowed to warm to room temperature. GC analysis, using *o*-xylene as internal standard, indicates the formation of norcarane in 10% yield.

6. Reduction of 3. To 0.418 g of 3 (1.5 mmol) dissolved in 10 mL of THF was added 0.056 g (1.5 mmol) of $NaBH_4$ at 20 °C. The resulting suspension was stirred 15 min, and the solvent was then evaporated in vacuo. The orange residue was extracted by using pentane. After removal of the solvent, 0.327 g (1.25 mmol, 82%) of pure 4 was obtained.

7. Reduction of 1 Using Fp*H (5). A. To 0.840 g (2 mmol) of 1 suspended in 10 mL of THF was added 0.496 g (2 mmol) of 5 at 20 °C in 10 mL of THF. After the mixture was stirred 12 h and the solvent removed, the extraction using pentane allowed a mixture (0.108 g, 20%) of 3 and 4 to be isolated in an ^{1}H NMR ratio of 1:1.

B. To 0.930 g (2 mmol) of $[Fp^*THF]^+PF_6^-$ (7) suspended in 10 mL of THF was added 1.240 g (10 mmol) of 5. The reaction was carried out under 1.2 atm of CO overnight at 40 °C. Workup as in A gave 0.209 g (40% with respect to 7) of 4.

C. Following the procedure described in B, after 10 days at 20 °C, 1.258 g of 4 (240% with respect to 7) was recovered.

8. Reduction of 1 Using $H_4Mo(dppe)_2$ (8). To 0.420 g (1 mmol) of 1 suspended in 10 mL of THF was added 1.500 g (3 mmol) of 8. After the mixture was stirred 12 h at 20 °C the solvent was evaporated and 0.060 g (15% yield) of a mixture of 3 and 6 was extracted by using pentane in an ^{1}H NMR ratio of 1:1.

II. Reduction of the Complexes $[Fp^*PR_3]^+PF_6^-$ (9). 1. Synthesis of $[Fp^*P\text{-}n\text{-}Bu_3]PF_6^-$ (9a). To 0.988 g (2.0 mmol) of Fp*$_2$ (6) suspended in a mixture 80:20 CH_2Cl_2/THF (10 mL) was added 1.224 g of $[Cp_2Fe]PF_6$ (4.0 mmol). After the solution was stirred overnight, the solvent was evaporated and 0.808 g of P-*n*-Bu_3 (4.0 mmol) was added in 10 mL of CH_2Cl_2. After 1 h, the solvent was removed in vacuo. The solid residue was washed in ether and chromatographed over silica gel in acetone. The "eluate" was concentrated after addition of hexane until it started to precipitate. Cooling to −20 °C for 12 h provided 1.85 g of yellow crystals (3.12 mmol, 78% yield) of 9a: IR (cm^{-1}, Nujol) ν_{CO} 2040, 1965; ^{1}H NMR (δ, CD_3CN) 1.95 (s, 15 H, $C_5(CH_3)_5$), 1.53 (m, 18 H, CH_2), 1.00 (t, 9 H, CH_3); ^{13}C NMR (δ, CD_3CN) 214.2 (d, CO, $^2J_{PC}$ = 23.2 Hz), 100.7 (s, $C_5(CH_3)_5$), 27.7, 26.3, 26.2, 24.9, 24.2 (s, CH_2), 13.94 (s, CH_3), 10.13 (s, $C_5(CH_3)_5$). Anal. Calcd for

$C_{24}H_{42}FeO_2P_2F_6$: C, 48.50; H, 7.12; Fe, 9.40; P, 10.42. Found: C, 48.52; H, 7.09; Fe, 9.54; P, 10.34.

2. Reduction of 9 Using $NaBH_4$. A. To 1.188 g (2 mmol) of **9a** dissolved in 30 mL of THF was added 0.380 g (10 mmol) of $NaBH_4$ at 20 °C. The resulting mixture was stirred 20 min, and the solvent was removed in vacuo. The yellow residue was extracted in pentane. A yellow powder was isolated by removing pentane slowly and filtering at −80 °C. After the mixture was dried in vacuo, 0.409 g (1.65 mmol, 82%) of the pure hydride complex **5** was obtained. (Complex **5** was also obtained by reducing 0.936 g (2 mmol) of **9b** (1.58 mmol, 79%) and 1.708 g (2 mmol) of **9c** (1.32 mmol, 66%).)

B. To 1.188 g (2 mmol) of **9a** dissolved in 30 mL of THF cooled to −80 °C, was added 0.380 g (10 mmol) of $NaBH_4$. The solution was stirred and allowed to warm slowly to room temperature in 3 h. After THF was removed in vacuo, the yellow residue was extracted with pentane and isolated as a yellow powder by filtration at −80 °C. After recrystallization from pentane, 0.322 g (1.04 mmol, 52%) of pure **12a** was recovered.

[FeCp*(P-*n*-Bu$_3$)(CO)CH$_3$] (**12a**): slightly air-sensitive in the solid state; IR (cm^{-1}, pentane) ν_{CO} 1910 cm^{-1}; ^{1}H NMR (δ, THF-d_8) −0.63 (d, 3 H, $^3J_{PH}$ = 4.7 Hz, CH$_3$), 1.05 (m, 3 H, $-(CH_2)_3CH_3$), 1.52 (m, 6 H, $-(CH_2)_3CH_3$), 1.85 (s, 15 H, C$_5$(CH$_3$)$_5$); {^{1}H}^{13}C NMR (δ, THF-d_8) −10.0 (d, $^2J_{PC}$ = 20.0 Hz, CH$_3$), 9.73 (s, C$_5$(*CH*$_3$)$_5$), 14.60 (s, $-(CH_2)_3CH_3$), 26.00 (m, $-(CH_2)_3CH_3$), 90.65 (s, C$_5$(CH$_3$)$_5$), 224.6 (d, $^2J_{PC}$ = 32.0 Hz CO).

Complexes **9b** and **9c** were reduced following the same procedure. Complex **12b** was isolated as a light orange powder: 0.694 g (1.28 mmol, 64%). The dark yellow compound **12c** was obtained by evaporation of pentane, and 0.406 g was recovered (0.93 mmol, 46%).

[FeCp*(PMe$_3$)(CO)CH$_3$] (**12b**): slightly air-sensitive in the solid state; IR (cm^{-1}, pentane) ν_{CO} 1910; ^{1}H NMR (δ, C$_6$D$_6$) 1.75 (s, 15 H, C$_5$(CH$_3$)$_5$), 1.17 (d, 9 H, J_{PH} = 13.6 Hz, P(*CH*$_3$)$_3$); −0.60 (d, 3, J_{PH} = 7.6 Hz, CH$_3$); {^{1}H}^{31}P NMR (δ, THF, external H$_3$PO$_4$, 85% D$_2$O) 39.02 (s).

[FeCp*(PPh$_3$)(CO)CH$_3$] (**12c**): slightly air-sensitive in the solid state; IR (cm^{-1}, Nujol) ν_{CO} 1890; ^{1}H NMR (δ, CD$_3$COCD$_3$) 0.55 (d, 3 H, $^3J_{PH}$ = 6.5 Hz, CH$_3$), 1.43 (s, 15 H, C$_5$(CH$_3$)$_5$), 7.30 (m, 15 H, P(C$_6$H$_5$)$_3$); {^{1}H}^{13}C NMR (δ, C$_6$D$_6$) 11.34 (d, $^2J_{CP}$ = 20.7 Hz, CH$_3$), 9.40 (s, C$_5$(*CH*$_3$)$_5$), 91.68 (s, C$_5$(CH$_3$)$_5$), 127.9, 133.8, 134.4 (s, C$_6$H$_5$, m, p, o), 137.4 (d, J_{PC} = 26.2 Hz, C$_6$H$_5$, ipso), 225 (d, J_{PC} = 29.4 Hz, CO). Anal. Calcd for $C_{30}H_{33}FeOP$: C, 72.58; H, 6.65; Fe, 11.29; P, 6.25. Found: C, 72.85; H, 6.75; Fe, 10.69; P, 6.20.

3. Monitoring the Reduction of 9a with $NaBH_4$ by NMR. A. 9a (0.03 g, 0.05 mmol) was stirred in 0.6 mL of THF-d_8. The solution was then cooled to −80 °C, and 0.010 g of $NaBH_4$ (0.27 mmol) was added. The solution was stirred 30 min and filtered into a ^{1}H NMR tube at −50 °C. ^{1}H NMR spectra recorded below −30 °C indicated that the reduction was not yet accomplished. At −30 °C, the reduction of **9a** gives rise to the formation of the formyl complex **10a** and to its borane adducts **11a** (δ, THF-d_8): 14.39 (d, 0.5 H, $^3J_{PH}$ = 5.4 Hz, CHO, **10a**); 12.80 (br d, 0.5 H, J_{PH} = 1.3 Hz, *C*HOBH$_3$, **11a**), 1.80 (s, 7.5 H, C$_5$Me$_5$, **10c**), 1.77 (s, 7.5 H, C$_5$Me$_5$, **10c**), 1.41 (m, 18 H, $-(CH_2)_3CH_3$, **10a**, **11a**). When the temperature increased slowly (10 °C/15 min), the transformation of **11a** was not detected. The formation of the alkyl complex **12a** begins at −20 °C, and the reaction was over at 10 °C.

B. 9a (0.03 g, 0.05 mmol) was stirred in 0.5 mL of THF-d_8. After the suspension was cooled to −80 °C and 0.002 g of $NaBH_4$ (0.05 mmol) was added, the solution was filtered and the ^{1}H NMR spectra were recorded between −30 °C and 20 °C. At −20 °C the reduction of **9a** to the formyl complex **10a** and its borane adduct **11a** was complete. Between −20 °C and −10 °C, the slow transformation of **11a** into **10a** was observed. Above −10 °C, the formation of the alkyl complex **12a** was observed together with the formation of the starting material **9a** in the ratio **9a**:**12a** = 7:3.

4. Monitoring the Reduction of 9b with $NaBH_4$ by NMR. Following the procedure described for **9a**, the observation of the reduction started at −30 °C and the ^{1}H NMR data indicated the formation of **10b** and **11b** in the same ratio (δ, THF-d_8): 14.38 (d, 0.5 H, J_{PH} = 4.7 Hz, CHO, **10b**), 12.83 (d, 0.5 H, J_{PH} = 1.2 Hz, 0.5 H, *C*HOBH$_3$, **11b**), 1.91 (s, 7.5 H, C$_5$Me$_5$, **11b**), 1.88 (s, 7.5 H, C$_5$Me$_5$ **10b**), 1.20 (d, 9 H, J_{PH} = 30 Hz, PCH$_3$). Formation of small amounts of **12b** was also observed. The increase of the temperature did not allow the observation of the transformation of **11b** to **10b** before the formation of the alkyl complex **12b**. At 0 °C, the disappearance of the low-field signals and the formation of the iron alkyl compound **12b** were observed.

5. Monitoring Reduction of 9c with $NaBH_4$ by NMR. Following the procedure described for **9a**, the beginning of the reduction was observed at −40 °C and the ^{1}H NMR data indicated the formation of **10c** and **11c** in the ratio **10c**:**11c** = 2.5 (δ, THF-d_8): 14.26 (d, 0.7 H, J_{PH} = 1.5 Hz, CHO, **10c**), 12.48 (br d, 0.3 H, J_{PH} = 1.5 Hz, *C*HOBH$_3$, **11c**). The evolution of the ratio **10c**:**11c** was not observed when the temperature was increased. The formation of the alkyl complex **12c** occurs at −20 °C.

6. Reduction of 9a by $NaBH_4$ in the Presence of PPh_3 or H_2O. 9a (0.010 g, 0.02 mmol) was stirred in 0.5 mL of THF-d_8. The suspension was cooled down to −80 °C, and 0.010 g of $NaBH_4$ (0.27 mmol) was added. The solution was allowed to warm to −40 °C and filtered. The ^{1}H NMR confirmed the presence of **10a** and **11a** in a 1:1 ratio; 0.005 g of PPh$_3$ (0.02 mmol) was then added into the NMR tube at −60 °C. ^{1}H NMR: +60 °C, **10a** (see section II.3); −20 °C, **5** (see section I.1.C).

7. Reaction of 10a and 11a with THF·BH$_3$. In a THF-d_8 solution of **10a** and **11a** prepared from **9a** and $NaBH_4$ as described above (see section II.3.B), 10 μL of 1 M solution of the THF·BH$_3$ complex was added at −80 °C and the reaction was monitored by ^{1}H NMR. The BH$_3$·THF complex does not influence the reaction, and, in particular, the transformation of **11a** to **10a** was not inhibited. Conversion of the formyl complex **10a** into the alkyl complexes **9a** occurs without formation of the starting material **9a**.

8. Attempted Isolation and Characterization of 10a. A. The cation **9a** (0.297 g, 0.5 mmol) was dissolved in 4 mL of THF-d_8. The solution was cooled to −78 °C, and 0.038 g of $NaBH_4$ (1 mmol) was added and the mixture was allowed to warm slowly to −15 °C. The solution was then filtered in a ^{13}C NMR tube after being cooled to −50 °C. NMR spectra indicate the quantitative formation of **10a**: ^{13}C NMR (δ, THF-d_8, −50 °C) 306.46 (d, $^2J_{PC}$ = 26 Hz, $^1J_{CH}$ = 127 Hz, CHO), 220.02 (d, J_{PC} = 27.5 Hz, CO), 100.79 (s, *C*$_5$(CH$_3$)$_5$), 27.5 (m, P(*CH*$_2$)$_3$CH$_3$), 14.44 (s, P(CH$_2$)$_3$*C*H$_3$), 10.06 (s, C$_5$(*C*H$_3$)$_5$); IR (THF, cm^{-1}) ν_{CO} 1890, 1590.

B. To 1.190 g (2 mmol) of **9a** and 1.210 g (5 mmol) of PPh$_3$ dissolved in 20 mL of THF was added 0.076 g (2 mmol) of $NaBH_4$ after the solution was cooled to −78 °C. The reaction was monitored by IR under these conditions (ν_{CO} = 1590 cm^{-1}); while the temperature was increased from −78 °C to 20 °C over 4 h, the transformation of **9a** to **10a** was complete. The solvent was then removed in vacuo, and the IR spectrum of the solid residue revealed the disproportionation of the formyl complex **10a** into **9a** and **12a**. After workup, **9a** and **12a** were recovered with 69% and 23% yields, respectively.

9. Reduction of 9a by $NaBH_4$/$NaBD_4$ (1/1). To 1.190 g (2 mmol) of **9a**, dissolved in 30 mL of THF cooled to −78 °C, was added 0.076 g (2 mmol) of $NaBH_4$ and 0.084 g of $NaBD_4$. The solution was stirred and allowed to warm to room temperature over 3 h. After workup, the yellow alkyl compound **12a** was isolated (0.65 mmol, 22%). Mass spectroscopic analysis of **12a** indicates the following isotopic distribution: d_0, 34.3%; d_1, 41.7%; d_2, 20.5; and d_3, 3%.

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