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Preliminary communication

HYDRIDIC REDUCTIONS OF CARBON MONOXIDE TO HYDROCARBONS ON IRON COMPLEXES

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Summary

Treatment of $Cp_2Fe_2(CO)_4$ with $LiAlH_4$ produces CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_8 and C_4H_{10}. The exact ratio depends on the amount of $LiAlH_4$ used and on the length of reaction. All reactions were carried out with $LiAlD_4$, confirming that CO is reduced with $LiAlH_4$ as the only hydrogen source. By preparing potential intermediates ($CH_3FeCp(CO)_2$, $C_2H_5FeCp(CO)_2$ and $CH_3C(O)FeCp(CO)_2$) and treating them with $LiAlD_4$, we have found evidence for a CO insertion mechanism in chain propagation. Other hydridic reagents were used, the reactivity for the reduction of CO decreases $LiAlH_4 > NaBH_4 > LiEt_3BH$.

Reactions of complex hydrides with transition metal carbonyl complexes have been reported [1—12]. These hydrides have facilitated substitution reactions [1,2], and have been used to prepare transition metal hydrides [3], transition metal anions [4], and formyl-transition metal complexes from coordinated carbon monoxide [5—12].

The search for homogeneous analogues of Fischer—Tropsch chemistry has been vigorous in recent years [13—19]. Reduction of carbon monoxide to methane [16,17], methane and ethane [18,19], and mixtures of low molecular weight hydrocarbons have been observed [20]. Formylmetal complexes have been proposed as important intermediate in the reduction of CO [20—23]. A number of stable formyl complexes, both anionic and neutral, have been prepared by reaction of a metal carbonyl with a hydride transfer reagent such as HBR_3^- (R = ethyl and s-butyl) [8—12]. Formylmetal species were usually not observed when multihydridic reagents ($LiAlH_4$ or $NaBH_4$) were used [1,12,13]. It seemed most likely that formyl complexes were initially formed, but that the by-product MH_3 (M = Al, B) caused further reduction.

As a part of our investigation of the reactivity of CO with both carbon and oxygen coordinated, we have observed that $LiAlH_4$ can reduce a number of metal carbonyl complexes to hydrocarbons from C_1 to C_4.

In a typical reaction 0.5 mmol of $Cp_2Fe_2(CO)_4$ was mixed with a 10—30 fold excess of $LiAlH_4$ in a reaction vessel containing a syringe inlet. The vessel was evacuated and then solvent (10 ml) added via syringe. Gas samples were analyzed by gas chromatography (Varian 2440 and HP 5750) on Spherocarb (60°C) and Poropak Q (90°C) columns and by GC/mass spectrometry*.

The reaction of $Cp_2Fe_2(CO)_4$ with a 20-fold excess of $LiAlH_4$ in THF at room temperature was rapid with completion in about 1 h leading to the formation of CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_8 and C_4H_{10}**. Reaction of $LiAlH_4$ with THF also occurs on this time scale leading to CH_4, C_2H_4 and C_2H_6 in much smaller amounts. Although the solubility of $LiAlH_4$ in toluene is very small we found that the reaction of $Cp_2Fe_2(CO)_4$ with $LiAlH_4$ in toluene produced CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_8 and C_4H_{10} similar in amount and ratio to the reduction in THF. Use of $LiAlD_4$ in toluene at room temperature produced only totally deuterated hydrocarbons to the limits of detection confirming reduction of CO with $LiAlD_4$ as the only hydrogen source. The reductions in toluene were much slower with completion in about 10 days with the exact ratio of hydrocarbons varying with the amount of $LiAlH_4$ and with time**. The amounts of the three olefins (C_2H_4, C_3H_6, and C_4H_8) decrease very dramatically with time. Table 1 illustrates the products observed and the changes in time. The yield of hydrocarbons was 40% per mol of iron complex.

$LiCpFe(CO)_2$ and $Cp_2Fe_2(CO)_4$ both remained in solution (as shown by IR spectra) even when a 30-fold excess of $LiAlH_4$ was used [19]. It seems likely, however, that $HFe(Cp)(CO)_2$ formed initially, but then decomposed to $Cp_2Fe_2(CO)_4$ and H_2. Hydrogen is observed but the possibility of it arising from another reaction of $LiAlH_4$ cannot be ruled out. When the reduction is carried out with PBu_3 and a 10-fold excess of $LiAlH_4$, $LiCpFe(CO)_2$ and $HFe(Cp)(CO)PBu_3$ were the only products observed by IR and NMR in solution.

TABLE 1

GASEOUS PRODUCTS FROM THE REDUCTION OF CO ON $Cp_2Fe_2(CO)_4$ BY $LiAlH_4$ IN TOLUENE [a]

	30-fold $LiAlH_4$		Reduction by $LiAlH_4$ under an atmosphere of CO
	36 h	14 days	14 days
CH_4	0.028	0.178	0.038
C_2H_4	0.044	6×10^{-4}	0.691
C_2H_6	0.024	0.14	0.043
C_3H_6	5×10^{-3}	9×10^{-4}	0.009
C_3H_8	4×10^{-3}	0.023	0.006
C_4H_8	9×10^{-5}	3×10^{-4}	0.0005
C_4H_{10}	7×10^{-5}	5×10^{-4}	0.0005

[a] The yields reported are mmol of the hydrocarbon product per mmol of iron complex.

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*GC/MS work was done at the Mass Spectral Facility, Cornell University.

**Completion is when no more hydrocarbon production was observed. Only n-butane and 1-butene were observed.

We prepared several of the potential intermediates in the reaction of $Cp_2Fe_2(CO)_4$ with $LiAlH_4$, ($CH_3Fe(Cp)(CO)_2$, $C_2H_5Fe(Cp)(CO)_2$ and $CH_3C(O)Fe(Cp)(CO)_2$) and investigated their reactions with $LiAlD_4$ in toluene. The methyl complex produced primarily CH_3D and $C_2H_3D_3$ in a 1 to 2 ratio, respectively; the ethyl complex produced C_2H_5D and $C_3H_5D_3$ in a 1 to 2 ratio; and the acetyl complex produced primarily $C_2H_3D_3$, $C_3H_3D_3$ and $C_3H_3D_5$ in a 1/0.3/0.5 ratio. The acetyl reduction was very much more rapid (30 min) than either the methyl or ethyl reductions (2 days). In the methyl and ethyl reactions the C_{n+1} is the predominant product and this strongly suggests a CO insertion step for chain extension. The total yield of hydrocarbons was ~60% based on $RFe(Cp)(CO)_2$. The iron-containing products for the acetyl complex, $CH_3C(O)Fe(Cp)(CO)_2$, are $Cp_2Fe_2(CO)_4$ and $LiCpFe(CO)_2$, similar to the reduction of CO coordinated to $Cp_2Fe_2(CO)_4$ with $LiAlH_4$. For $CH_3Fe(Cp)(CO)_2$ and $C_2H_5Fe(Cp)(CO)$, no $Cp_2Fe_2(CO)_4$ was observed. Reduction of the acetyl complexes also produced propene in about the ratio (to propane) observed initially in the reduction of CO in $Cp_2Fe_2(CO)_4$. Thus an acetyl is implicated as an intermediate in the reduction of CO on $Cp_2Fe_2(CO)_4$. The rapidity of the reaction of $CH_3C(O)Fe(Cp)(CO)_2$ with $LiAlH_4$ forming hydrocarbon products is significant mechanistically. It has been previously reported that $CH_3C(O)Fe(Cp)(CO)_2$ was rapidly reduced to $C_2H_5Fe(Cp)(CO)_2$ [24] using $BH_3 \cdot THF$, however this reaction cannot be important in the formation of hydrocarbons from $LiAlH_4$ reduction because formation of products from the acetyl complex is much more rapid than from the ethyl complex. The formation of C_2H_6, C_3H_6 and C_3H_8 upon $LiAlH_4$ reduction of $CH_3C(O)Fe(Cp)(CO)_2$ must not occur through the ethyl complex.

The apparent significance of CO insertion in the reduction of CO on $Cp_2Fe_2(CO)_4$ led us to investigate the reduction under a CO atmosphere. The gaseous products were CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_8 and C_4H_{10} with the relative yields given in Table 1. The total yield was higher than reduction without a CO atmosphere, but the most obvious effect was the greatly enhanced production of ethylene. Further data must be collected before we can understand this enhanced production of ethylene under a CO atmosphere.

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