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INVESTIGATION OF THE MECHANISM OF HYDRIDIC REDUCTIONS OF CARBON MONOXIDE TO HYDROCARBONS ON IRON COMPLEXES BY ISOTOPIC LABELING

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Summary

The reduction of coordinated CO on $Cp_2Fe_2(CO)_4$ by $LiAlH_4$ has been investigated with isotopic labeling in an attempt to delineate the chain formation step. Reduction with $LiAlD_4$ resulted in formation of perdeutero-hydrocarbons. Reduction under an atmosphere of ^{13}CO resulted in substantial incorporation of ^{13}C into the hydrocarbon products. Reaction of the complexes $RFeCp(CO)_2$, R = CH_3, C_2H_5 and $CH_3C(O)$, with LAD and with LAH under ^{13}CO are reported. Reaction of $CH_3{}^{13}C(O)FeCp(CO)_2$ with LAH is also reported. The results of these reactions suggest that chain extension occurs by a CO insertion reaction, probably by CO insertion into an alkylidene—metal bond.

We recently communicated the reduction of carbon monoxide to hydrocarbons with chain lengths up to C_4 by treatment of $Cp_2Fe_2(CO)_4$ (Cp = η^5-C_5H_5) with $LiAlH_4$ (LAH) [1]. We report herein the results of labeling studies which place constraints on possible mechanisms for chain formation.

The search for homogeneous CO reduction systems has been vigorous in recent years. Recent reviews cover much of the pertinent literature [2,3]. Unlike the typical Fischer-Tropsch reactions, most homogeneous reductions (which are stoichiometric) yield methane or methanol as primary products; in only a few systems were higher hydrocarbon chains observed [2,3]. Demitras and Muetterties observed formation of methane, ethane, propane and isobutane in the ratio 1 : 4 : trace : trace upon treatment of $Ir_4(CO)_{12}$ with synthesis gas in molten NaCl · 2 $AlCl_3$ at 180°C [4]. Schwartz and co-workers observed chain formation in a zirconium-based system (Cp_2ZrCl_2, $(i\text{-}Bu)_2AlH$ and CO at a few atmospheres of pressure) which produced alcohols (methanol, ethanol, 1-propanol and 1-butanol in a molar ratio of 1.0 : 0.12 : 0.15 : 0.03) upon hydrolysis

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at room temperature [5—7]. Masters and co-workers observed the formation of methane, ethane, propane and butane upon treatment of $Ru_3(CO)_{12}$ with AlH_3 [8]. Ethane or ethylene (C_2 hydrocarbons) have been observed in a few cases [8—10].

Experimental

All solvents were dried over sodium/benzophenone before use. $Cp_2Fe_2(CO)_4$ was purchased from Strem Chemical Company and used without further purification. The compounds, $CH_3FeCp(CO)_2$ [11], $C_2H_5FeCp(CO)_2$ [11], $CH_3C(O)FeCp(CO)_2$ [12] and $CH_3{}^{13}C(O)FeCp(CO)_2$ [13] were prepared as previously described. The infrared spectra were in good agreement with those previously reported [11—13]. The ^{13}C-labeled compounds, ^{13}CO and $CH_3{}^{13}C(O)Cl$, were purchased in 90 atom % purity from Merck, Sharp and Dohme and used without purification. LAD in 98 atom % purity was purchased from Aldrich.

In a typical reaction, 0.5 mmol $Cp_2Fe_2(CO)_4$, $LiAlH_4$ (10—30 fold molar excess) and a Teflon stir bar were transferred into a glass vessel (120 cm × 2.2 cm) equipped with a Kontes Teflon high vacuum stopcock connected to a ball joint and with a small septum-covered stopcock for sample removal. The apparatus was evacuated and ~5 ml of solvent, previously dried by extended refluxing over sodium metal and benzophenone, was vacuum distilled into a glass vessel at —196° C. When required, carbon monoxide could subsequently be transferred into the glass vessel. The reaction mixture was allowed to warm and react at room temperature. Gas samples were withdrawn through the septum-covered stopcock directly with a gas-tight syringe (Hamilton Co.) and analyzed by a Varian 2440 gas chromarograph with flame ionization detectors or by GC-mass spectrometry *. Chromatographic separations were obtained with a 6 ft × 1/8 in stainless-steel column of Spherocarb (Analab, 80/100 mesh), for separations of H_2, N_2, CO, and light hydrocarbons C_1 to C_3. A 6 ft × 1/8 in stainless-steel column of Porapak Q (Analab, 80/100 mesh) was used for separation of C_1 to C_5 hydrocarbons. The helium flow rate was ~20 ml/min and column temperature ranged from ambient to 150° C. Peaks were identified by comparing retention times with known samples and peak areas were converted into mole quantities by comparison with standard samples.

Soluble products in the reaction mixture were analyzed by infrared and NMR spectroscopy. ^1H NMR spectra were obtained on a Varian T-60 spectrometer with TMS (0.00 ppm) or benzene (8.23 ppm) as standards. IR spectra were obtained on a Perkin-Elmer 521 infrared spectrophotometer. The reaction mixture was first suction filtered through a fine porosity glass frit inside a glove box (Vacuum Atmosphere HE-43-2) under an argon atmosphere, and was placed in NaCl cells (International Crystals, Inc.) of path length 0.1 or 0.5 cm with Teflon stoppers.

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

TABLE 1

GASEOUS PRODUCTS FROM THE REDUCTION OF CO ON $Cp_2Fe_2(CO)_4$ BY 30-FOLD EXCESS $LiAlH_4$ IN TOLUENE [a]

	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_8	C_4H_{10}
36 hours	0.028	0.044	0.024	5×10^{-3}	4×10^{-3}	9×10^{-5}	7×10^{-5}
14 days	0.178	6×10^{-4}	0.14	9×10^{-4}	0.023	5×10^{-5}	5×10^{-4}
PBu_3 [b]	0.108	0.376	0.224	0.022	0.016	7×10^{-4}	9×10^{-4}
CO [c]	0.144	0.511	0.045	0.011	6×10^{-3}	3×10^{-4}	2×10^{-4}

[a] The yields reported are mmol of the hydrocarbon product per mmol of iron complex. [b] Reduction was accomplished in the presence of an equivalent of PBu_3. [c] Reduction was done under an atmosphere of CO.

Results and discussion

Reaction of $Cp_2Fe_2(CO)_4$ with LAH

The results obtained upon treatment of $Cp_2Fe_2(CO)_4$ with LAH have been previously communicated [1]. The hydrocarbon products from this reaction are summarized in Table 1. The total yield of hydrocarbon for the reaction between $Cp_2Fe_2(CO)_4$ and LAH was ~40% (0.4 mmol of hydrocarbon product per mmol of iron starting material). $LiCpFe(CO)_2$ and $Cp_2Fe_2(CO)_4$ * were both in solution after the reaction as shown by infrared spectra even when a 30-fold excess of LAH was used. We believe that $HCpFe(CO)_2$ was formed initially, but because of its thermal instability, decomposed to H_2 and $Cp_2Fe_2(CO)_4$. Support for this came from the observations that (1) hydrogen was observed and (2) when the reaction was carried out with ~0.01 mmol of PBu_3 and a 10-fold excess of LAH, $LiCpFe(CO)_2$ and the thermally stable $HCpFe(CO)PBu_3$ were the only products in solution as determined by IR and NMR spectra **. The presence of PBu_3 in the reaction mixture also changed the ratio of hydrocarbon products with a significant enhancement in the production of ethylene as shown by the distribution of products in Table 1.

The formation of higher hydrocarbons (C_2 to C_4) requires forming C—C bonds. Several possibilities have been suggested for C—C bond formation in Fischer-Tropsch systems [3,14]. Methyl migration (CO insertion) has been suggested as one possibility [15]. To assess the importance of CO insertion in this system we have investigated the reaction of $Cp_2Fe_2(CO)_4$ with LAH under a CO atmosphere. The results are reported in Table 2. A net increase in CO reduction product is observed under CO, but the most dramatic difference is the greatly enhanced production of ethylene. This is similar though greater in magnitude than the production of C_2H_4 in the presence of PBu_3 as shown in Table 2. Reaction of LAH with $Cp_2Fe_2(CO)_4$ was also investigated under a ^{13}CO atmosphere with substantial incorporation of ^{13}C into the hydrocarbon product as shown in Table 3. The wide distribution of label in the hydrocarbon product indicates a

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* $Cp_2Fe_2(CO)_4$ was identified by infrared absorptions at 1993vs, 1952s, 1787vs. $LiCpFe(CO)_2$ was identified by infrared absorption at 1884s, 1867s, 1812s, 1710s [10].

** $HFeCp(CO)(PBu_3)$ had an infrared absorption at 1916(br) and NMR resonance (τ) at 5.83 singlet (Cp), 8.67—9.15 multiplet (Bu) and 24.0 doublet (H: J(P—H) = 76 Hz).

TABLE 2

INCORPORATION OF ^{13}CO INTO THE HYDROCARBON PRODUCT IN THE REACTION OF $Cp_2Fe_2(CO)_4$ WITH $LiAlH_4$ UNDER ^{13}CO

Product	Extent of incorporation [a]			
	No ^{13}C	One ^{13}C	Two ^{13}C	Three ^{13}C
methane	0.70	0.30		
ethylene	0.20	0.40	0.40	
ethane	0.20	0.40	0.50	
propene	0.23	0.23	0.37	0.17
propane	0.15	0.35	0.35	0.15

[a] The numbers give the relative amounts of the enriched products.

TABLE 3

PRODUCTS FROM THE REACTION OF $RFeCp(CO)_2$ WITH $LiAlD_4$

R	Primary hydrocarbons formed	Ratio
CH_3	CH_3D, $C_2H_3D_3$	1 : 2
C_2H_5	C_2H_5D, $C_3H_5D_3$	1 : 2
$CH_3C(O)$	$C_2H_3D_3$, $C_3H_3D_3$, $C_3H_3D_5$	3 : 0.8 : 1

complicated reaction scheme with considerable mixing of the labeled CO. The amount of label in methane is larger than expected and indicates that CO exchange may have occurred during reduction *. For each hydrocarbon, the species with only one ^{12}C is among the predominent products, which suggests that a CO insertion mechanism is operative.

Reaction of $Cp_2Fe_2(CO)_4$ with $NaBH_4$ led to similar reduction products though the yield was less than 5% of that seen with LAH. Reaction of $LiBEt_3H$ effected reduction less than 0.3% of that observed with LAH.

Reaction of $MeFeCp(CO)_2$, $EtFeCp(CO)_2$ and $CH_3(CO)FeCp(CO)_2$ with LAD

To further investigate the importance of CO insertion in the build-up of hydrocarbon chains upon reduction of CO on $Cp_2Fe_2(CO)_4$ with LAH we have prepared the possible intermediates $CH_3FeCp(CO)_2$, $C_2H_5FeCp(CO)_2$ and $CH_3C(O)FeCp(CO)_2$ and investigated their reactivity towards LAD. The results are presented in Table 4. These reactions were carried out in toluene with a 10-fold excess of LAD with total yields of hydrocarbons at 50—60% (0.5—0.6 mmol hydrocarbon per mmol $RFeCp(CO)_2$). These reactions were stopped after fairly short times (30 minutes) so that the reduction would occur primarily at the R group with only a small contribution from CO reduction. In addition to the primary products listed in Table 4, other hydrocarbons were also observed ranging from C_1—C_4 in considerably smaller amounts than the primary products.

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* Some $^{13}CH_4$ is present in the ^{13}CO, so a precise determination of the amount of $^{13}CH_4$ is impossible.

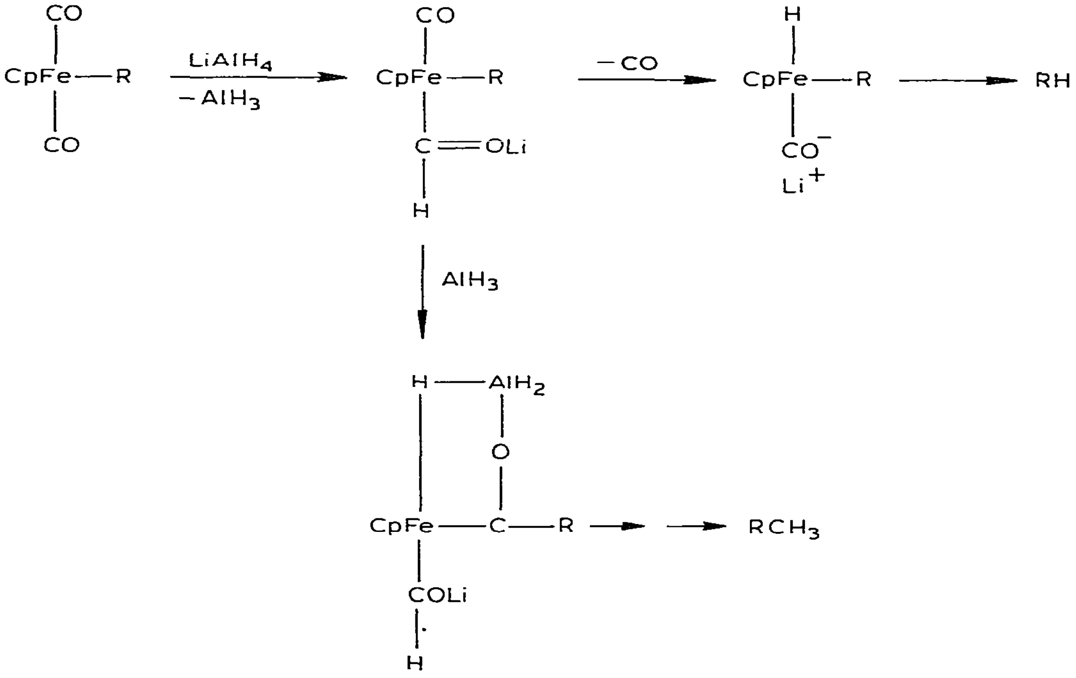
Many of these had quite high deuterium enrichments and we believe that these products are the result of competing CO reduction.

Reduction of the species $RFeCp(CO)_2$ with LAH in the presence of ^{13}CO led to no ^{13}C-incorporation into the primary products. This is consistent with the expectations from a CO insertion/alkyl migration step for chain propagation. To further delineate the steps involved in these reactions we prepared CH_3-$^{13}C(O)FeCp(CO)_2$ and reduced it with LAH. The primary products (ethane, propene and propane) contained one ^{13}C as expected for reaction upon the acetyl group. Some products with no ^{13}C were observed; these probably arise by migration of the methyl to an unsubstituted CO before reduction, but could be the result of reduction at a terminal CO.

Reduction of the acetyl proceeded much more rapidly than reduction of the ethyl complex. Thus the intermediacy of the ethyl complex, $C_2H_5FeCp(CO)_2$, is ruled out in formation of products from the acetyl complex *. The normal alkyl migration must not be involved in forming propene and propane. Alkylidene dimerization would more readily form butene and butane and is unlikely to be involved in formation of propene and propane. We suggest, as discussed later, that CO insertion into an alkylidene is the chain extension step for reduction of $CH_3C(O)FeCp(CO)_2$.

SCHEME 1

A POSSIBLE SCHEME FOR THE REDUCTION OF $RFeCp(CO)_2$ WITH LAH (R = Me, Et)



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* These experiments do not rule out the formation of a different ethyl complex or possible insertions into a different ethyl complex.

For the reductions of the methyl and ethyl complexes with LAH the C_{n+1} alkane was the major product with the C_n product present to a significant extent. These two products could arise by the following sequence.
The presence of AlH_3 would assist the alkyl migration and the intermediate suggested is analogous to those Shriver has isolated [16—18]. The reaction of $CH_3C(O)FeCp(CO)_2$ and $CH_3FeCp(CO)_2$ with LAH under ^{13}CO resulted in no incorporation of ^{13}C into the C_n and C_{n+1} products. No incorporation would be expected for Scheme 1.

Reduction of $CH_3C(O)FeCp(CO)_2$ with LAH produces some ethylene. The ethylene appears to be formed by different reactions than the reactions which led to primary products. Reaction of $CH_3C(O)FeCp(CO)_2$ with LAD produced C_2HD_3, C_2D_4, and $C_2H_2D_2$ in a 2 : 1 : 1 ratio. Reaction of $CH_3{}^{13}C(O)FeCp(CO)_2$ with LAH produced C_2H_4 and $^{13}CCH_4$ in a 2 : 1 ratio, respectively. In both of these examples extensive mixing of labels has occurred in the ethylene product, contrary to the results for the primary products. For the deuterium incorporation an equilibrium must be established that exchanges H for D on the acetyl methyl group. The most obvious route would be β-elimination of the hydrogen from an ethyl group forming an ethylene-iron complex. An equilibrium of this type would equilibrate deuteride on the iron with hydrogen on the methyl(ethyl) group. However, the ethane formed has the expected formulation ($C_2H_3D_3$) for no equilibration between hydrogen and deuterium. The mixing of the label must occur from a different species. We suggest a reversible oxidative-addition of the C—H bond at an intermediate stage of the reduction. The ^{13}C enrichment upon reduction of $CH_3{}^{13}C(O)FeCp(CO)_2$ suggests an equilibration of the three carbonyl ligands during the reduction process. This equilibration must occur without dissociation of CO since no ^{13}C incorporation into ethylene is seen when $CH_3C(O)FeCp(CO)_2$ is allowed to react with LAH under a ^{13}CO atmosphere.

Mechanistic observations on formation of hydrocarbons upon reaction of $Cp_2Fe_2(CO)_4$ with LAH

There is little doubt that the initial step in the reduction of $Cp_2Fe_2(CO_4)$ with LAH involves formation of a formyl complex by addition of a hydride to coordinated CO [1]. The formyl complex will not be "free" but will almost certainly have aluminum coordinated to the oxygen. Further reduction to a methyl could occur as was observed in $NaBH_4$ reduction of $CpRe(CO)_2NO$ [19]. We have demonstrated in a separate experiment that methane is formed when $CH_3FeCp(CO)_2$ is allowed to react with LAH.

$$CH_3FeCp(CO)_2 + LAD \rightarrow CH_3D + LiCpFe(CO)_2 + AlD_3$$

More interesting is the formation of higher hydrocarbons which involves forming carbon—carbon bonds. We believe from the data discussed in an earlier section that the higher hydrocarbons are formed as a result of a CO insertion process. While our system has the characteristics of a CO insertion, we do not think that the insertion occurs by alkyl migration as has usually been postulated. Comparison of the results of the LAH reduction of $CH_3FeCp(CO)_2$, $C_2H_5FeCp(CO)_2$ and $CH_3C(O)FeCp(CO)_2$ with LAH reduction of $Cp_2Fe_2(CO)_4$ show that propagation by alkyl migration is unlikely. We believe that the CO insertion occurs at a partially hydrogenated stage, probably via an alkylidene migration (CO insertion into an alkylidene) reaction. The CO insertion to an iron-ketene complex has been previously observed by Stevens and Beauchamp [20]. This type of insertion has also been observed by Herrmann and Planck with conversion of diphenylcarbene and CO into a diphenylketene manganese complex [21].

We have presented a new system for formation of hydrocarbons from coordinated carbon monoxide. By preparing and reducing possible intermediates we have shown that an insertion step is important in the chain formation and suggest a scheme involving CO insertion into a carbene. Isotopic labeling has suggested several equilibria are occurring which must be accounted for in any mechanism.

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