The trinuclear → tetranuclear core conversion demonstrated is the first example of this process for synthetic Fe-S clusters. In terms of the initial trinuclear structure this process apparently is not the same as the $Fe_3S_x \rightarrow Fe_4S_4$ reactions noted at the outset for aconitase[10] and *D. gigas* ferredoxin II.[11,12] In the oxidized (3Fe(III)) state these proteins are characterized by an EPR signal at $g \cong 2.01$.[11,12,46] This signal is found for all known oxidized Fe_3S_x sites even though there are apparent structural differences.[8,9] The recent EXAFS analysis of *D. gigas* ferredoxin II leads to the possibility of a site configuration with two Fe–Fe separations of ~2.7 Å,[9] in marked contrast to the cyclic structure of *A. vinelandii* ferredoxin I, with Fe–Fe distances of ~4.1 Å.[8] The EPR spectrum of $[Fe_3S_4(SEt)_4]^{3-}$ ($g = 4.2$) is inconsistent with the electronic structures of the protein sites, indicating a different type of trinuclear arrangement. The reverse reaction, $Fe_4S_4 \rightarrow Fe_3S_x$, has been demonstrated with several proteins under reducing[12] and oxidizing[47-49] conditions. We have not observed a corresponding reaction with synthetic clusters. Conversion reactions involving Fe_4S_4 clusters are currently limited to reactions 5, 13, and 14, $[Fe_2S_2(SR)_4]^{3-} \rightarrow [Fe_4S_4(SR)_4]^{2-}$[42] and $[Fe_4S_4Cl_4]^{2-} \rightarrow [Fe_2S_2Cl_4]^{2-}$, the last being carried out under oxidizing conditions.[45]

Summary. This research has demonstrated the occurrence of all reactions in Scheme II, leading to the synthesis of Fe_2S_2, Fe_3S_4, Fe_4S_4, and Fe_6S_9 clusters from the readily accessible (but extremely oxidatively sensitive) mononuclear complex $[Fe(SEt)_4]^{2-}$. Also provided are the detailed structures of examples of the two newest types of Fe–S–SR clusters, $[Fe_3S_4(SR)_4]^{3-}$ and $[Fe_6S_9(SR)_2]^{4-}$. Judging from the time dependence of signal intensities in Figure 4, the initial sequence of events in cluster formation is $[Fe(SEt)_4]^{2-} \rightarrow [Fe_2S_2(SEt)_4]^{2-} \rightarrow [Fe_3S_4(SEt)_4]^{3-}$. Roughly coincident with the formation of trinuclear cluster is the appearance of a paramagnetic species with a signal at −8.3 ppm. Inasmuch as the intensity of this signal decays as $[Fe_4S_4(SEt)_4]^{2-}$ and $[Fe_6S_9(SEt)_2]^{4-}$ are produced at 80 °C, this species lies on the reaction pathway to one or both clusters. Given the independent occurrence of reaction 13, our present hypothesis is that the −8.3 ppm species is a product of $[Fe_3S_4(SEt)_4]^{3-}$ and is a precursor to $[Fe_6S_9(SEt)_2]^{4-}$. Attempts to isolate and characterize this species are in progress. Finally, because the actual reaction sequences leading to cluster formation in the overall reactions 8, 10, and 11 are unknown, we have refrained from expressing these reactions in any stoichiometric form. Limiting stoichiometries for the other reactions of Scheme II are obvious, and these and related expressions have been presented elsewhere in connection with the derivation of Scheme I.[4]

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Registry No. $(Et_4N)_2[Fe(SEt)_4]$, 82661-04-9; $(Me_3NCH_2Ph)_2[Fe(SEt)_4]$, 85585-64-4; $(Et_4N)_2[Fe(SPh)_4]$, 77403-03-3; $(Me_3NCH_2Ph)_2[Fe_2S_2(SEt)_4]$, 85647-21-8; $(Et_4N)_3[Fe_3S_4(SEt)_4]$, 85647-20-7; $(Et_4N)_3[Fe_3S_4(SPh)_4]$, 82661-12-9; $(Et_4N)_4[Fe_6S_9(SEt)_2]$, 85585-66-6; $(Et_4N)_4[Fe_6S_9(SEt)_2]\cdot 4MeCN$, 85585-67-7; $(n\text{-}Bu_4N)_2[Fe_4S_4(SEt)_4]$, 53433-48-0; $(Et_4N)_2[FeCl_4]$, 15050-84-7.

Supplementary Material Available: Thermal and cation positional parameters, calculated hydrogen atom positions, and values of $10|F_o|$ and $10|F_c|$ for $(Et_4N)_3[Fe_3S_4(SPh)_4]$; thermal parameters, cation and solvate molecule positional parameters, calculated hydrogen atom positions, and values of $10|F_o|$ and $10|F_c|$ for $(Et_4N)_4[Fe_6S_9(SEt)_2]\cdot 4MeCN$ (80 pages). Ordering information is given on any current masthead page.

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Mechanistic Aspects of a Homogeneous Carbon Monoxide Hydrogenation Catalyst—$Ir_4(CO)_{12}$ in Molten $AlCl_3$-NaCl

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Abstract: The "homogeneous Fischer–Tropsch catalysis" first described by Muetterties et al. was kinetically examined in both a single-pass flow reactor and a continuous recycle apparatus. In our hands the $Ir_4(CO)_{12}$ precatalyst in molten aluminum chloride–sodium chloride (2:1) at 175 °C and 1 atm of hydrogen and carbon monoxide (3:1) produces methane, ethane, and chloromethane as the major carbon-containing products. In addition, a stoichiometric amount of methane is formed when the $Ir_4(CO)_{12}$ is introduced into the molten $AlCl_3$–NaCl at the onset of catalysis. Flow rate studies and the effect of added chloromethane on the active catalytic system implicate chloromethane (or methanol) as a primary reaction intemediate. Heterogeneous iridium-on-alumina catalysts show different behavior under these reaction conditions, whereas a mononuclear precatalyst, $IrCl(CO)_3$, shows similar chemistry. From the experimental evidence presented here, we conclude that this reaction involves the homogeneous reduction of CO to chloromethane, followed by homologation and/or hydrogenation reactions leading to the hydrocarbon products. Because these results differ significantly from those reported earlier, we conclude that this system must involve a different active catalyst.

Intense interest in new technology to supplement a dwindling petroleum supply has fostered renewed activity in Fischer–Tropsch chemistry. Along with advances in traditional heterogeneous catalysis[2,3] (especially with regard to reaction mechanism),[4,5] homogeneous carbon monoxide reduction has been a subject of active study during the past decade.[6,7] With the potential to offer increased selectivity to desired products, more control at the catalytic site, and greater tolerance to poisoning from sulfur-

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containing feedstocks, homogeneous catalysts may have some practical advantages over the heterogeneous systems. In addition, it is hoped that soluble catalysts will be easier to study and to interpret than their heterogeneous counterparts.

There have been many reports of homogeneous reduction of carbon monoxide with hydrogen,[8-21] the most studied of these involving catalysis by carbonyl complexes of cobalt, rhodium, and ruthenium.[8-18] At high pressures (up to 3000 atm), these systems produce a mixture of oxygenated products, primarily methanol, methyl formate, and ethylene glycol. Recent studies have led to the conclusion that these reactions proceed through formaldehyde as an intermediate.[10,12,16] Thus, although heterogeneous catalysts can produce hydrocarbon products (through hydrogenolysis of surface carbon species produced by dissociative adsorption of carbon monoxide), homogeneous catalysts afford oxygenated products. Some researchers have suggested that hydrocarbon production (especially methane) may be indicative of a heterogeneous catalyst,[11,23] even when the chemistry is initiated with a soluble precatalyst.

In 1977, Muetterties and co-workers discovered that tetrairidium dodecacarbonyl, $Ir_4(CO)_{12}$, in molten aluminum chloride–sodium chloride catalyzed the conversion of carbon monoxide and hydrogen to light hydrocarbons, primarily ethane, at 1 atm and 180 °C[20] (eq 1). This novel reaction is significant for several

$$CO + 3H_2 \xrightarrow[\substack{AlCl_3\text{-}NaCl\ (2:1) \\ 180\ ^\circ C\ (1\text{-}2\ atm)}]{Ir_4(CO)_{12}} C_2H_6\ (\text{major}) + CH_4 + C_3H_8(\text{tr}) + i\text{-}C_4H_{10}(\text{tr}) \quad (1)$$

reasons: (1) it appears that the strong Lewis acid solvent allowed the reduction of CO to occur at very low pressures; (2) the products derived from this reaction are saturated hydrocarbons without evidence for oxygenates; and (3) it offers some of the first chemical evidence for the similarity of metal clusters to metal surfaces[24] in an actual catalytic system. Since the initial account, a further study of the same system under flow conditions reported a faster production of heavier hydrocarbons (C_3–C_6) with a minimum of methane and ethane, again without formation of oxygenated or chlorinated products.[21]

Along with the importance of this interesting reaction with its unusual product distribution, our previous interest in Lewis acid promoted chemistry of organometallics[25] and our interest in the distinction between homogeneous and heterogeneous catalysis[26] led us to examine this system in more detail. It was our hope that a wide-ranging kinetic study would enable us to determine which of three plausible reaction mechanisms was operating: (1) a direct homogeneous reduction of CO to saturated hydrocarbons; (2) a homogeneous reduction of CO to intermediate oxygenated products which were then converted to the observed products under reaction conditions; or (3) a decomposition of the $Ir_4(CO)_{12}$ catalyst precursor to a finely dispersed and highly active metal particle catalyst which carried on the reaction heterogeneously. (If the reaction proved to be homogeneous, we were also interested in whether the active catalyst was mononuclear or an intact cluster.) Although our results do not conclusively establish oxygenates as primary products, we find the evidence compellingly in favor of the homogeneous reduction of CO to alcohol-like products which undergo secondary reactions to yield hydrocarbons. (However, it is not clear that we have obtained the same catalytic system as that described by Muetterties, vide infra.) The experimental support for this contention is described below.

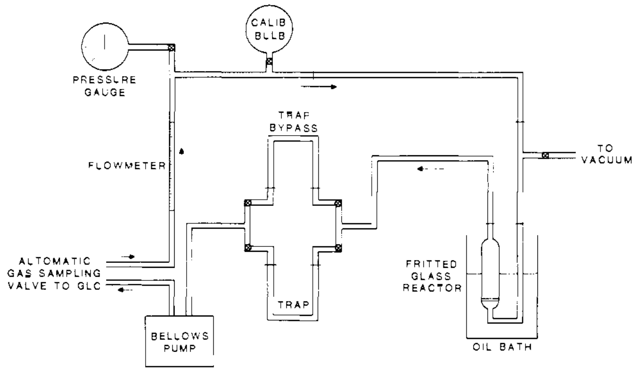

Figure 1. Schematic of recycle kinetics apparatus.

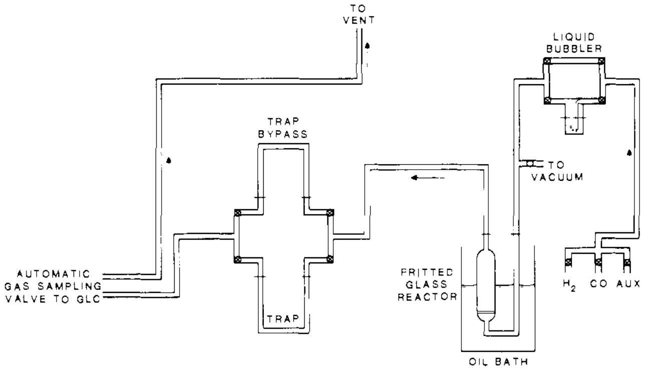

Figure 2. Schematic of single-pass flow kinetics apparatus.

Experimental Section

All reactant gases used in these experiments (carbon monoxide, hydrogen, deuterium, carbon dioxide, helium, chloromethane, chloroethane, ethylene, propylene, ethane, isobutane, *n*-butane, 1-butene, and hydrogen chloride) were purchased from Liquid Carbonic. $Ir_4(CO)_{12}$ was purchased from Strem Chemicals and Pressure Chemical Co. as well as prepared and purified by literature methods.[27] (These samples all exhibited the same catalytic behavior, irrespective of source or purification.) $IrCl(CO)_3$ was also purchased from Strem Chemicals and used without further purification. $IrCl_3\cdot(H_2O)$ was obtained from Engelhard. Aluminum chloride (Baker sublimed reagent) was purified by sublimation through aluminum powder (Baker) at ≃160 °C and 40 torr, and sodium chloride (Baker) was dried overnight at 140 °C. Methanol, acetyl chloride, acetaldehyde, ethanol, *s*-trioxane, and paraformaldehyde were reagent grade chemicals from Aldrich, and deuterium oxide, methanol-d_4, and acetyl-d_3 chloride were obtained from Merck.

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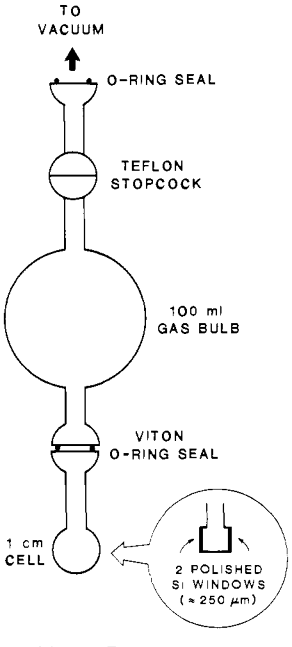

Figure 3. Schematic of inert IR cell.

The 5% Ir/Al_2O_3 catalyst was prepared with the minimum amount of aqueous $IrCl_3$ solution needed to wet the Woelm TLC grade alumina (SA = 110 m^2/g), while the 1% Ir/Al_2O_3 sample was made by precipitating $Ir_4(CO)_{12}$ from a saturated cyclohexane solution. Both catalysts were then dried overnight at 110 °C and reduced in flowing H_2 for 2 h at 350 °C. Formaldehyde was used immediately following its generation from paraformaldehyde at 150 °C. The chloromethane-d_3 was prepared by copyrolysis of the tosylate from methanol-d_4 with lithium chloride at 175 °C and trapped in a cold finger.[28]

Apparatus. Schematic representations of the flow and recycle reaction apparatus are shown in Figures 1 and 2. The recycle system incorporated a stainless-steel bellows pump (Met-Bel) fitted with a variable electric motor, and gases were transferred from a high vacuum (10^{-6} torr) manifold. The flow system employed three flowmeters (Matheson, fitted with Model 610 tubes) capable of mixing any three gases. In addition, the inlet line of the flow was fitted with a bubbler to introduce liquid samples at their vapor pressures. The reactor was heated by a proportional temperature controller (Omega), and the flow rates were measured by a rotameter in the recycle system and a manual bubble meter at the flow exit. Gases were sampled by an automatic 6-port sampling valve (Valco) on line with an HP-5880A gas chromatograph. Separations were achieved by using a 10 ft × $^1/_8$ in. Poropak Q column, and the analysis was carried out by splitting the effluent to both a thermal conductivity and a flame ionization detector. FID and TCD response factors were determined through use of a standard gas mixture from Matheson Gas Products (0.25% each of methane, ethylene, ethane, and chloromethane in helium), and the FID was externally calibrated with each run. Samples for GC/MS analysis were collected by flushing out septum-sealed vials, and samples for H_2–HD–D_2 exchange determination by MS were obtained by in-line sample tubes.

The IR cell design is shown in Figure 3. It was assembled by the anodic bonding (at 450 °C and 1.4 kV)[29] of two 250-μm silicon wafers to a highly polished Pyrex body with a 1 cm path length. Affixed to this cell by an O-ring seal is a 100-mL gas bulb with a stopcock to a vacuum line connector. Heating of the cell was accomplished with a small Pyrex tube (fitted with a thermocouple), which was wrapped with heating tape, and the entire ensemble was placed in the IR beam.

Procedure. In a nitrogen-filled glovebag, the reactor was loaded with 18 g of freshly sublimed $AlCl_3$ and 3.9 g NaCl, after which 50 mg of $Ir_4(CO)_{12}$ was suspended in a bored hole in a Teflon stir bar by an external magnet at the top of the vessel. In the recycle system, the apparatus was evacuated and back-filled several times with CO before the introduction of H_2 and CO at the desired pressures. Then these gases were circulated to effect mixing prior to heating the reactor. For the flow system, the N_2-filled reactor was purged with an H_2 and CO stream for 2 h prior to the application of a preheated oil bath. After the solids had melted to a clear, colorless melt (10–15 min) and the background gases were checked for activity, the magnet was removed, and the analysis was begun (with 250-μL gas samples taken every 20–30 min). Additional reagents were added into the gas stream of the flow system, either via the auxiliary flowmeter (for gases) or through the vapor pressure introduction of liquids by the bubbler apparatus. For the recycle system, additional gases were isolated in the trap prior to the reaction, where they could be circulated into the gas loop when necessary. Each catalytic run was repeated at least once, and the results were highly reproducible (errors of approximately 5% for the homogeneous systems and to ≃10% for the heterogeneous catalysts). After the termination of each run, the reactor was cleaned with an oxidizing solution of bleach and HCl and no residual activity was ever observed.

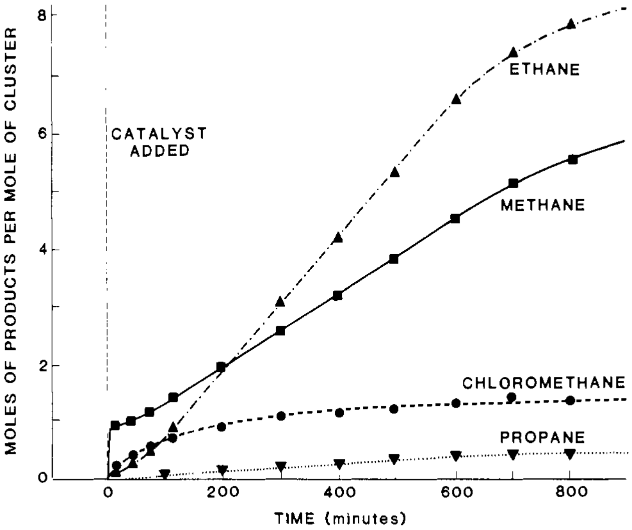

Figure 4. Recycle kinetics—$Ir_4(CO)_{12}$ added to 2:1 $AlCl_3$–NaCl at 175 °C under 3:1 H_2–CO at 1 atm.

Results and Discussion

The kinetic behavior of this $Ir_4(CO)_{12}/AlCl_3$–NaCl system was examined in both a closed, continuous recycle apparatus and a single-pass flow assembly. In both cases, the addition of $Ir_4(CO)_{12}$ to a preheated solution of 2:1 $AlCl_3$–NaCl at 180 °C under a 3:1 mixture of hydrogen and carbon monoxide at 1 atm shows the production of low molecular weight hydrocarbons and methyl chloride in the gas phase. There is, however, a major difference in the ratio of products formed in the single-pass assembly compared to the recycle apparatus.

In the recycle apparatus, in which a closed system of the reactant gases is circulated continuously through the reaction zone, the production of hydrocarbon products can be represented by the profile in Figure 4. By being suspended in a bored Teflon stir bar above the heated reactor via an external magnet, the $Ir_4(CO)_{12}$ precatalyst can be kept cool (<50 °C) while the solid NaCl and $AlCl_3$ mixture is melted. This also allows the reactor to be checked for background activity prior to the introduction of the catalyst. When the magnet is removed, the $Ir_4(CO)_{12}$ is introduced into the melt and is immediately dispersed, forming a clear yellow solution. The kinetic behavior shown in Figure 4 represents the accumulation of products in the gas phase over time and is characterized by three major regions with respect to hydrocarbon production. Initially, there is a period of slightly increasing rate over the first 2 h. This is followed by a period of relatively stable activity (2–12 h), with the methane/ethane ratio approximately 1:2, and then a slow deactivation. In addition, there is a very rapid (before the first gas chromatograph sample at 10 min) production of almost 1 equiv of methane/cluster when the precatalyst is delivered to the reaction mixture. Markedly different behavior is observed for the production of chloromethane in this system. It shows an initial period of high activity which decreases over the first 4–5 h, after which its concentration in the gas phase remains relatively constant. Since chloromethane was not reported in the original communication[20] and in our recycle system it is a minor product which shows virtually no *net* production during most of the reaction, it is a possible intermediate on the way to methane and ethane.

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Table I. Catalytic CO and H_2 Conversion in Molten 2:1 $AlCl_3$-NaCl at 175 °C and 1 atm

expt	catalyst	r or f[p]	gas ratios H_2-CO-He	rate[a]	product distribution,[b] % CH_4	C_2H_4	C_2H_6	CH_3Cl	C_3H_8	i-C_4H_{10}
1	none	f (6)	3:1:0	0.0						
2	none	r	3:1:0	0.0						
3	$Ir_4(CO)_{12}$[c]	r	3:1:0	1.55[d]	28	tr	59	6	5	tr
4	$Ir_4(CO)_{12}$	f (6)	3:1:0	1.85	16	tr	55	25	3	tr
5	$Ir_4(CO)_{12}$[e]	f (6)	3:1:0	1.82	17	tr	55	23	4	tr
6	$Ir_4(CO)_{12}$[f]	f (6)	3:1:0	1.90	14	tr	49	32	3	tr
7	$Ir_4(CO)_{12}$[g]	f (6)	3:1:0	1.80	18	tr	53	24	4	tr
8	$Ir_4(CO)_{12}$	f (2)	3:1:0	1.60	22	tr	57	16	5	tr
9	$Ir_4(CO)_{12}$	f (12)	3:1:0	2.17	15	tr	47	35	3	tr
10	$Ir_4(CO)_{12}$	f (24)	3:1:0	2.45	14	1	34	49	2	tr
11	$Ir_4(CO)_{12}$	f (24)	1:1:2	1.08	22	tr	46	30	2	tr
12	$Ir_4(CO)_{12}$	f (24)	1:3:0	0.85	13	tr	38	45	3	tr
13	$Ir_4(CO)_{12}$	f (24)	3:3:2	1.31	14	tr	37	46	2	tr
14	$Ir_4(CO)_{12}$	r	1:3:0	0.40	22	2	62	6	6	tr
15	$Ir_4(CO)_{12}$	r	1:1:2	0.53	33	tr	55	7	4	tr
16	$Ir_4(CO)_{12}$	r	1:1:0	0.82	35	tr	52	6	5	tr
17[h]	$Ir_4(CO)_{12}$	f (12)	3:1:0	0.23	16	2	48	30	3	tr
18[i]	$Ir_4(CO)_{12}$	f (12)	3:1:0	10.4	54	tr	30	10	5	tr
19	$IrCl(CO)_3$	f (6)	3:1:0	1.50[j]	22	tr	46	26	3	tr
20	5% Ir/Al_2O_3[k]	f (12)	3:1:0	4.4[l]	50	tr	12		18	16
21	1% Ir/Al_2O_3[m]	f (12)	3:1:0	4.8[l]	51	tr	18		15	15
22	1% Ir/Al_2O_3[n]	f (12)	3:1:0	0.15[l]	90	5	5			
23	1% Ir/Al_2O_3[o]	f (12)	3:1:0	2.50[l]	92	3	5			

[a] Rate after 240 min (g equiv of C in hydrocarbons/mol of $Ir_4(CO)_{12}$ per h). [b] Product distribution after 240 min (% of volatile hydrocarbons). [c] Standard catalyst charge of 50 mg of $Ir_4(CO)_{12}$ in 20 g of melt. [d] Rate as measured by CO consumption at 240 min = 2.5 (mol of CO/mol of Ir_4 per h). [e] 100 mg of $Ir_4(CO)_{12}$ in 20 g of melt. [f] 10 mg of $Ir_4(CO)_{12}$ in 20 g of melt. [g] 50 mg of $Ir_4(CO)_{12}$ in 5 g of melt. [h] Reaction temperature 150 °C. [i] Reaction temperature 200 °C–deactivates quickly and rate and product distribution reported after 90 min. [j] For comparison, rate reported as g equiv of C in HC/4 mol of $Ir(Cl)(CO)_3$ per h. [k] 5% Ir/Al_2O_3 prepared from aqueous $IrCl_3 \cdot (H_2O)_x$ and added with the $AlCl_3$ and NaCl solids prior to melting. [l] For comparison rate reported as g equiv of C in HC/4 surface Ir atoms per h after 1 h. [m] 1% Ir/Al_2O_3 prepared from $Ir_4(CO)_{12}$ in cyclohexane and added with the $AlCl_3$ and NaCl solids prior to melting. [n] Solid gas reaction (without 2:1 $AlCl_3$–NaCl melt) at 175 °C. [o] Solid gas reaction (without 2:1 $AlCl_3$–NaCl melt) at 280 °C. [p] r, recycle; f, flow (cm^3 min^{-1}).

In order to test this hypothesis and to obtain more accurate kinetic data, the identical system was examined in a single-pass flow apparatus. In this arrangement, carbon monoxide and hydrogen are mixed with standard gas flowmeters and are allowed to bubble through the reaction mixture on a single pass. The effluent is then analyzed before being vented through an oil bubbler to the hood. In contrast to the recycle system, where the gas samples show the accumulation of products in the gas phase, the flow data reflect the instantaneous rate of production since a cross section of the gas flow is analyzed as it leaves the reactor. A representative plot of the reaction kinetics of this flow system is shown in Figure 5. This analysis is much more sensitive to small changes in rate, and the three previously mentioned regions of the methane and ethane production curves can be seen more clearly.

The initial feature is a brief but large production of methane and ethane, which corresponds to the approximately 1 equiv of methane seen in the recycle system. The sensitivity of the analysis also allows for the detection of ethane in this immediate burst of products (approximately 9:1 methane/ethane is formed). This is followed by a period of increasing rate over the next 3 h, which reaches a level of fairly constant rate for all products. It should be noted that although methane levels off quickly after the initially active period, chloromethane and ethane production parallel each other and are slower to reach the sustained levels. (This does not appear to be a consequence of solubility differences in the melt.[30]) These results point toward chloromethane as a reaction intermediate and, since methanol is the likely precursor to chloromethane, imply the involvement of oxygenates in this reaction system.

Many experiments have been carried out by using both of these kinetic systems in an attempt to unravel the basic reaction pathways which operate in this unusual solvent. From data obtained by varying the ratios and pressures of reactant gases, flow rates, and temperature and by introducing possible intermediates into the system, a picture consistent with a plausible mechanism began to emerge. Some of the relevant data are collected in Table I.

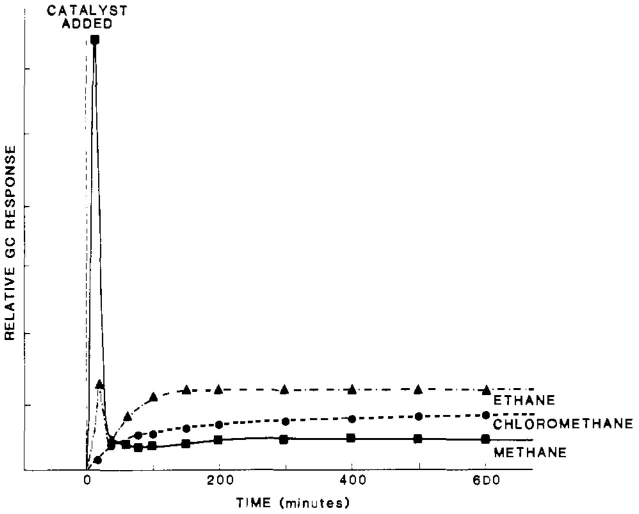

Figure 5. Flow kinetics—$Ir_4(CO)_{12}$ added to 2:1 $AlCl_3$–NaCl at 175 °C with 3:1 H_2–CO at 12 cm^3 min^{-1} and 1 atm.

Standard experimental conditions involved the addition of 50 mg of $Ir_4(CO)_{12}$ to approximately 20 g of (2:1) aluminum chloride–sodium chloride melt at 175 °C under 1 atm of hydrogen–carbon monoxide (3:1). Without the precatalyst, the molten $AlCl_3$–NaCl produces no volatile carbon-containing products under reaction conditions. Also, because $Ir_4(CO)_{12}$ is dropped into the preheated reactor, it is possible to demonstrate, prior to each experiment, that the reactor retained no residual activity from previous runs. By comparing runs, 4, 5, 6, and 7, it can be seen that the turnover frequency based on hydrocarbons produced per hour is directly dependent on the amount of precatalyst added

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(30) Presaturation of the melt with methane, ethane, and chloromethane has virtually no effect on the catalysis.

and is independent of its apparent concentration. Doubling the amount of $Ir_4(CO)_{12}$ added, reducing the amount by a factor of 5, or reducing the melt volume by a factor of 4 results in virtually the same rate of hydrocarbon production per mole of $Ir_4(CO)_{12}$. These changes also have only minor effects on the product distribution.

Since both the recycle and flow apparatus are limited to total pressures of 1 atm, experiments to detect the effect of hydrogen and carbon monoxide partial pressures could only span a very limited range. This range is even further restricted since carbon monoxide partial pressures of less than 0.1 atm result in the irreversible decomposition of the catalyst to a metal precipitate. This decomposition is characterized by a rapid methane evolution, followed by a rapid deactivation as gray iridium metal deposits on the stir bar and reactor sides. Nevertheless, comparison of runs 10 and 11 or runs 3 and 15, where the partial pressure of CO is held constant as the hydrogen partial pressure is reduced from 0.75 to 0.25 atm, indicates a direct positive rate dependence on hydrogen pressure. Runs 11 and 12 or 14 and 15 show the slightly inhibiting effect on the rate of increasing carbon monoxide pressure at constant hydrogen partial pressure. Thus, over this very limited range the rate shows a positive (almost first order) dependence on hydrogen pressure, while displaying a slightly negative dependence on carbon monoxide.

In the recycle reactor, it is possible to monitor the consumption of carbon monoxide as well as the production of hydrocarbon products by gas chromatography. In run 3, where the hydrocarbon production rate is 1.55 mol of C/Ir_4 per h, the rate of CO consumption is 2.5 mol of CO/Ir_4 per h. Thus, the volatile carbon-containing products in the gas phase represent only 60% of the carbon monoxide consumed. The logical conclusion is that the aluminum chloride is responsible for the fate of the other organic products. Treatment of the $AlCl_3$-NaCl melt with C_1–C_3 saturated hydrocarbons shows no apparent interaction (butanes are isomerized but are only slowly cracked on the reaction timescale). On the contrary, other organics (chloromethane, olefins, alcohols, ethers, aldehydes, etc.), when added to the reaction system, react, at least partially, with the $AlCl_3$ to give a nonvolatile polyolefinic orange oil which can be isolated from the quenched melt. This conversion has precedence in the older Friedel–Crafts literature.[31] These products are attributable to Lewis acid catalyzed carbonium ion reactions and probably account for the mass balance discrepancy noted above, as a similar oil can be isolated from the catalytic system after long reaction times.

The effect of reactant gas flow rate (contact time) on the hydrocarbon production rate and distribution gives further evidence for the secondary reactions postulated above. At a low flow rate of 2 cm^3 min^{-1} (see run 8), ethane is the major product, with chloromethane making up $\simeq$16% of the gaseous products. As the flow rate is increased (decrease in contact time), the distribution steadily changes, as can be seen in the progression of runs 8, 4, 9, and 10, with chloromethane becoming the dominant product at flow rates above 20 cm^3 min^{-1}. It should also be noted that the methane and ethane production remains nearly the same and the major effect appears to be a rate enhancement due to an increase in chloromethane reaching the gas phase. In this way, the gross mass balance discrepancy in the recycle system can be understood as a continuation of the above trend to long contact times in which the aluminum chloride can effect side reactions leading to nonvolatile products.

Temperature also has a marked effect on this reaction. At reaction temperatures above 200 °C, decomposition of the catalytic system is apparent as the normally clear yellow solution darkens. This is accompanied by a shift in the product distribution to favor methane and a rapid deactivation. (Similar behavior is observed at 175 °C with CO partial pressures of <0.1 atm and appears to be the result of hydrogenation of the precatalyst to metal.) In the functionally limited temperature range of 150–200 °C (the 2:1 $AlCl_3$-NaCl mixture does not readily melt below 140 °C), the reaction shows a positive dependence on increasing temperature, with the rate an order of magnitude slower at 150 °C than at 175 °C (as shown in runs 9, 17, and 18). It should be noted that the initial burst of 1 equiv of hydrocarbon products (CH_4/C_2H_6, 9:1) is unaffected by this temperature change. Only the ensuing catalysis shows a temperature dependence.

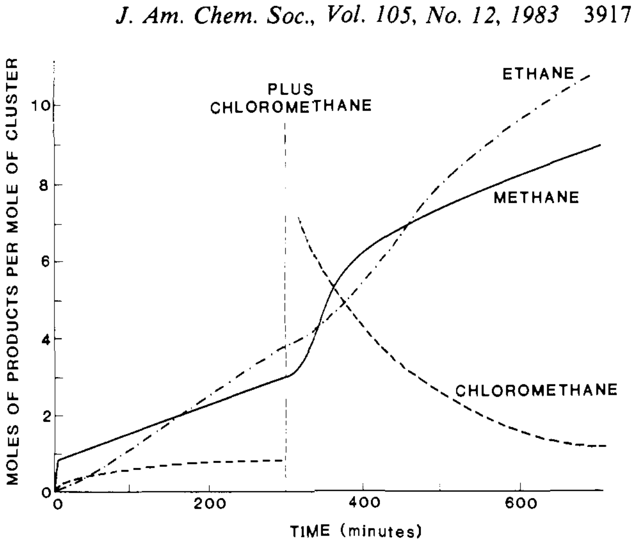
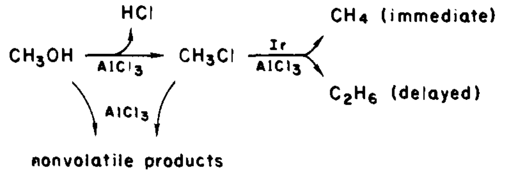


Figure 6. Chloromethane added to normal recycle kinetics—$Ir_4(CO)_{12}$ in 2:1 $AlCl_3$-NaCl at 175 °C under 3:1 H_2-CO at 1 atm.

Additives. In order to test the efficacy of chloromethane as an intermediate and the possible involvement of oxygenates in this system, these reactants were introduced into the syngas feed. These reactions were performed on the pristine melt and also in the presence of the $Ir_4(CO)_{12}$ precatalyst. As reported here and elsewhere,[21] when chloromethane is added to a hydrogen and carbon monoxide stream and fed into a reactor containing only $AlCl_3$ and NaCl at 175 °C, no volatile hydrocarbons are observed (except unreacted chloromethane) and a nonvolatile orange oil can be isolated from the melt.[32] However, when chloromethane is added to the active catalytic system, an increase in all hydrocarbon products is observed, as displayed in Figure 6. As the graph indicates, this enhanced activity shows a marked time dependence, with an immediate increase in methane production followed by a delayed but more sustained ethane increase. (Propane and isobutane also show delayed enhancements, but to a lesser extent.) This behavior is observed in both the flow and recycle systems, with a large mass balance deficit again showing up in the recycle apparatus. The conversion of chloromethane under reaction conditions to light hydrocarbons is thus a reasonable explanation for its absence in the gas phase of a static reactor system. In addition, this reactivity, coupled with the secondary aluminum chloride reactions, can easily account for the "steady-state" behavior of chloromethane in the recycle apparatus, where its consumption rate is equal to its production rate. Methanol, the logical precursor to chloromethane and a major product of many homogeneous CO reductions, was found to be its equivalent in the 2:1 $AlCl_3$-NaCl melt. Methanol reacts to form HCl and chloromethane and gives rise to identical product enhancements in the active system (eq 2).



(2)

Several two-carbon molecules were similarly introduced into the reactant gas stream. Ethanol, ethyl chloride, and ethylene

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[31] Olah, G. "Friedel-Crafts and Related Reactions"; Wiley: New York, 1963; pp 86–91.

[32] Without carbon monoxide present, additional hydrocarbons are formed which are all saturated and predominantly in the C_3–C_5 range.

Table II. Olefin Reactions in 2:1 $AlCl_3$-NaCl Melts at 175 °C and 3:1 H_2-CO at 6 cm^{-1} and 1 atm (with and without $Ir_4(CO)_{12}$ Precatalyst)

% of volatile HC's	ethylene 50% convn[a]	 99% convn[b,c]	propylene 100% convn[a]	 100% convn[b]	1-butene 100% convn[a]	 100% convn[b]	Muetterties[21]
methane	2		1	1	0.5	0.5	1.5
ethane	4	94→78	0.5	0.5	0.3	0.1	1.5
propane	30	5→20	5	17	22	16	17
isobutane	43	1→2	45	56	50	59}	54[d]
n-butane	12	...	10	11	12	11}	
pentanes	10	...	23	12	12	12	17
hexanes	...	...	10	2	3	2	6
highers	...	...	5	...	...	...	...

[a] Without Ir_4. [b] With Ir_4. [c] Initial value → value after 1 h. [d] Combined iso- and *n*-butane.

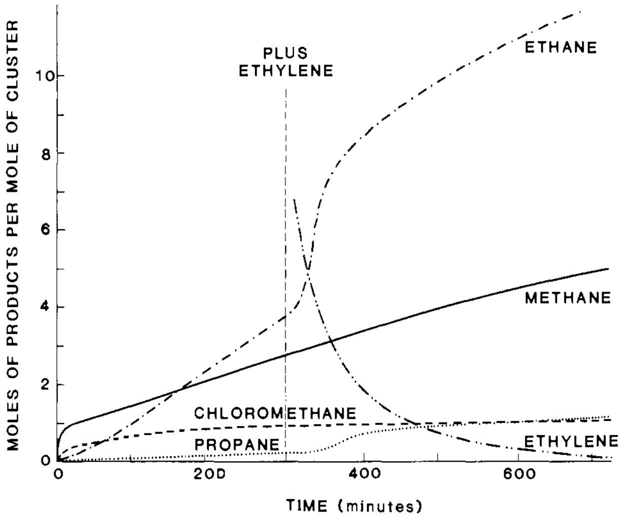
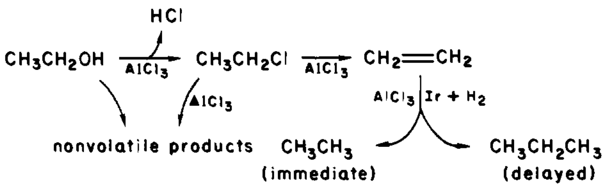


Figure 7. Ethylene added to normal recycle kinetics—$Ir_4(CO)_{12}$ in 2:1 $AlCl_3$-NaCl at 175 °C under 3:1 H_2-CO at 1 atm.

exhibited equivalent behavior under these reaction conditions. Ethanol is converted to ethyl chloride and ethylene (major product) with concurrent production of HCl, without the iridium catalyst. Likewise, ethyl chloride eliminates HCl to generate ethylene. An orange oil can also be isolated from these three reactions and C_2–C_6 hydrocarbons are also produced, reflecting the carbonium ion chemistry mentioned above. When these same reactants are added to an operating catalytic system ($Ir_4(CO)_{12}$ present), the results are simpler, as all three reagents are converted to ethane and propane. Figure 7 shows that the behavior is again time dependent, initially producing 95% ethane and 5% propane but becoming 70% ethane and 30% propane after 1 h. Methane and chloromethane are virtually unaffected by the addition of ethylene. This system is a good hydrogenation catalyst and is capable of hydrogenating ethylene over 50 times faster than it can reduce carbon monoxide. We propose that it is this fact which severely limits hydrocarbon homologues above ethane (eq 3).



(3)

Whereas the hydrogenation of ethylene by the iridium catalyst is effectively competitive with the aluminum chloride side reactions, such is not the case with higher olefins, as shown in Table II. The major volatile products from the treatment of the melt with these olefins (with or without the iridium catalyst) were saturated hydrocarbons in the C_3 to C_5 range, with isobutane representing approximately half the total. As noted before, these products arise from aluminum chloride reactions of an isolable polyolefinic oil fraction. These observed product ratios are also very similar to those observed by Muetterties in his flow system and as such may not reflect the primary reaction products in that system.

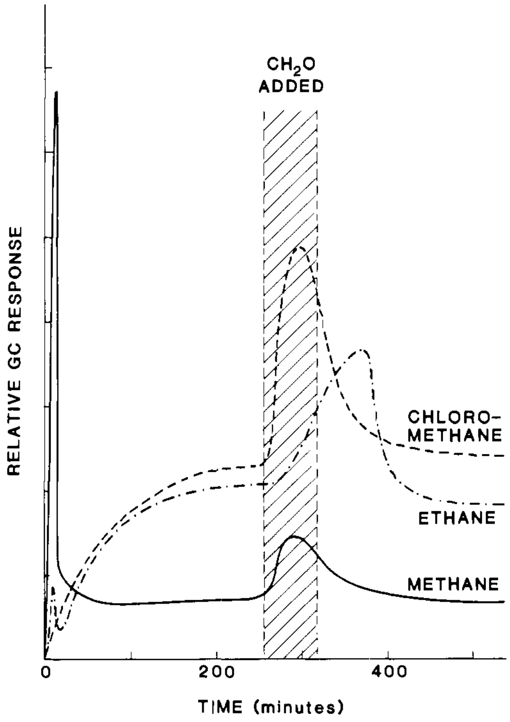


Figure 8. Formaldehyde added to normal flow kinetics—$Ir_4(CO)_{12}$ in 2:1 $AlCl_3$-NaCl at 175 °C with 3:1 H_2-CO at 12 cm^3 min^{-1} and 1 atm.

Since aldehydes are generally considered to be the primary products (even when undetected) in most homogeneous CO reduction systems, freshly prepared formaldehyde monomer was added to the gas stream.[33] Although most of the formaldehyde reacts to give other products (HCl, CO_2, and a nonvolatile oil fraction), there is a proportional enhancement of methane, ethane, and chloromethane, as shown in Figure 8.[34] In this case, methane and chloromethane respond immediately to the addition, while the ethane (and propane) increase is delayed. The fact that all of the "normal products" can be produced in the expected ratios as the only voltaile carbon-containing products besides CO_2 supports the viability of formaldehyde as a primary reaction intermediate. Similarly, upon injection into the catalytic system, acetaldehyde and acetyl chloride are also largely converted to HCl, CO_2, and nonvolatile products, but in these cases the active system also shows an increased production of ethane and propane.

Since carbon dioxide is a byproduct of some of the previous reactions and is only a very minor product under normal conditions, we checked for water gas shift (WGS) activity. (Catalysis of the

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(33) Paraformaldehyde and *s*-trioxane were less effective than the monomer in the production of volatile hydrocarbons.

(34) Similar conversion of formaldehyde in related systems has been reported. Roth, J. A.; Orchin, M. *J. Organomet. Chem.* **1979**, *172*, C27–C28; Spencer, A. *Ibid.* **1980**, *194*, 113–123.

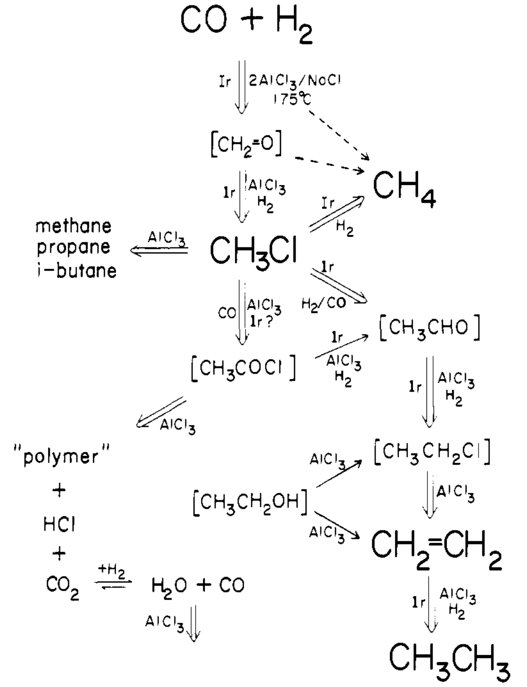

Figure 9. Summary of proposed reaction pathways in molten 2:1 $AlCl_3$-NaCl at 175 °C.

water gas shift reaction must always be considered in any syngas conversion.) Addition of carbon dioxide to the gas stream of an

$$H_2 + CO_2 \rightleftharpoons CO + H_2O \rightarrow AlCl_3 \qquad (4)$$

active system causes a reversible reduction in the rate of hydrocarbon production. Also, the carbon dioxide is converted to carbon monoxide with additional HCl production. In fact, the overall catalytic reaction can occur, although at a reduced rate, by using carbon dioxide as the sole carbon source along with hydrogen. It appears that the aluminum chloride is capable of driving the WGS reaction to convert CO_2 to CO by removing the water (eq 4). When hydrogen chloride is added to the feed, the rate is again reversibly diminished (without CO_2 generation). The rate reduction observed for HCl and CO_2 is probably due to competition for catalytic sites and has a more pronounced effect on methane than on ethane production. The inhibition by HCl is also a likely reason for the reduced activity of the recycle system compared to the flow system, as the closed recycle loop accumulates HCl during the reaction.

Proposed Reaction Pathways. From our studies, it is apparent that almost all organic compounds (except methane, ethane, and propane) are at least partially transformed by the molten aluminum chloride mixture. With the iridium catalyst present, some of these reactions can be effectively diverted to other products. One of the puzzling aspects of this work, as well as the original Muetterties communication,[20] was the virtual termination of hydrocarbon products at the two-carbon length. Previous workers[35,36] have explained selective ethane production from the hydrogenation of metal carbonyls via a dimerization of metallocarbene complexes. Although we cannot rule out a carbene as the source of our products, our results are consistent with chloromethane production giving rise to the observed products by hydrogenation and homologation reactions. A summary of the reaction pathways that have been described appears in Figure 9. It presents our proposal that the $Ir_4(CO)_{12}/AlCl_3$ system catalyzes the conversion of CO and H_2 to a complexed formaldehyde species. Further reduction in aluminum chloride converts this intermediate to chloromethane in competition with side reactions leading to nonvolatile products. Then the iridium/aluminum chloride catalyst carries out the hydrogenolysis of chloromethane to methane as well as its homologation to an ethanol equivalent, presumably ethyl chloride. This unobserved product eliminates HCl in the melt, generating ethylene, which is rapidly hydrogenated to ethane.

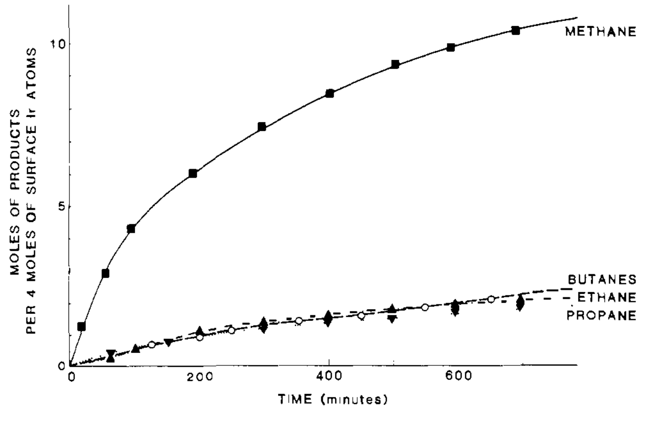

Figure 10. recycle kinetics—1% Ir on Al_2O_3 in 2:1 AlCl-NaCl at 175 °C under 3:1 H_2-CO at 1 atm.

Heterogeneous vs. Homogeneous. One of the initial incentives for this study was the hope that a detailed kinetic investigation would distinguish between a soluble catalyst and a highly dispersed metal particulate catalyst resulting from the decomposition of the cluster. It seemed reasonable that such a decomposition might manifest itself in an induction period followed by catalytic activity similar to that of known heterogeneous catalysts under these reaction conditions, both in terms of rate and product distribution. To this end, two heterogeneous iridium on alumina catalysts were prepared. A 5% iridium on alumina sample was made by standard incipient wetness techniques[37] from aqueous iridium trichloride and the 1% sample was made by precipation of $Ir_4(CO)_{12}$ from cyclohexane solution.[38] Both catalysts were reduced in flowing hydrogen at 350 °C. The resulting catalysts proved to be fairly well dispersed by CO adsorption measurements (5% Ir/Al_2O_3, 65% surface atoms; 1% Ir/Al_2O_3, 89% surface atoms) and the heterogeneous syngas reactions compared well with literature values[39] (see run 23).

Although these heterogeneous catalysts are not very active at 175 °C in the solid–gas reaction (see run 22) and produce almost exclusively methane under those conditions, they show markedly different behavior in the aluminum chloride melt. (Because of the relatively low loadings and subsequently larger catalyst amounts, the heterogeneous catalysts were premixed with the $AlCl_3$ and NaCl solids.) The major product of both catalysts in the Lewis acid mixture is also methane, but the rate is faster and the mixture favored higher hydrocarbons (see runs 20 and 21). The product ratio is approximately methane/ethane/propane/butane, 4:1:1:1, after 1 h. As Figure 10 clearly shows, the total rate of hydrocarbon production declines steadily and the product distribution favors higher alkanes with time because the methane production decreases more rapidly than the higher homologs.

The behavior of these heterogeneous iridium catalysts differs most noticeably from the $Ir_4(CO)_{12}$ system in the preponderance of methane and the absence of chloromethane in the gas phase. Moreover, the heterogeneous system is *almost totally unreactive* toward added chloromethane, in stark contrast to the soluble cluster precatalyst. Although the initial rate, based on available iridium surface sites, is more than twice as fast as the standard system, the gray suspension deactivates more rapidly and is only one-fifth as active after 10 h. This deactivation is also accompanied by a significant loss of surface area, as shown by CO adsorption measurements on the alumina isolated from the quenched reaction.[40]

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(35) Masters, C.; van de Woude, C.; van Doorn, J. *J. Am. Chem. Soc.* **1979**, *101*, 1633–1634.

(36) Labinger, J. A.; Wong, K. S. In "Catalytic Activation of Carbon Monoxide"; Ford, P. C. Ed.; American Chemical Society: Washington, DC, 1981; *ACS Symp. Ser. No. 152*, pp 253–264.

(37) Anderson, R.; Dawson, P. "Experimental Methods in Catalytic Research"; Academic Press: New York, 1976; Vol II, pp 55–70.

(38) Ichikawa, M. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2268–2272.

(39) Vannice, M. *J. Catal.* **1975**, *37*, 449–461.

Although these results do not preclude a highly active metal particle catalyst (as particle size can have drastic effects on reaction rates and selectivities[41,42] and the decomposition product of the cluster could be much smaller than either Ir/Al_2O_3 sample), they offer no apparent support for surface catalysis in the cluster precatalyst system. Since the heterogeneous system is only slightly more active, displays a different product distribution, does not react with added chloromethane, and deactivates in the aluminum chloride melt, we conclude that the cluster-based catalytic system is probably homogeneous.

The nature of the catalytic species was further probed by the substitution of other iridium-containing compounds for the $Ir_4(CO)_{12}$ precatalyst. Although all the compounds tested showed at least some activity,[43] addition of $Ir(Cl)(CO)_3$ to the aluminum chloride melt was the most interesting (see run 19). When this brown-black solid is dropped into the reaction mixture, the still clear melt takes on the yellow color characteristic of the cluster system. Moreover, the resulting volatile products are the same as the original reaction (methane/ethane/chloromethane, 1:3:1, at 6 cm^{-1}). The rate of this reaction is only 20% slower per iridium atom than the cluster system, and methane and ethane production can be enhanced by adding chloromethane. The major difference between the $IrCl(CO)_3$ and the $Ir_4(CO)_{12}$ is the absence of an initial hydrocarbon burst with the mononuclear precatalyst. Thus, these two complexes appear to give rise to nearly identical catalytic systems, the cluster with production of a stoichiometric amount of hydrocarbons, and the results cast some doubt upon the necessity of an intact cluster for catalysis.

These catalytic systems were also investigated by using infrared spectroscopy under reaction conditions. These studies were carried out in a 1-cm Pyrex cell with silicon wafer windows which could be heated in the IR sample chamber by a small tube furnace. Although no definitive structural information could be obtained from these experiments, they showed strong similarities between the two soluble precatalysts as compared with the heterogeneous system. Both the $Ir_4(CO)_{12}$ and the $Ir(Cl)(CO)_3$ give rise to a multiband pattern in the 2000–2200-cm^{-1} range under CO and H_2, whereas the Ir/Al_2O_3 catalyst shows a broad absorption, as expected for a heterogeneous metal surface, centered at $\simeq 2100$ cm^{-1}. The shift of the CO stretching frequencies for the cluster carbonyls from the 2000–2080 cm^{-1} region to higher frequencies in the melt may reflect oxidation of the metal center.[21] Thus, an iridium chloride carbonyl complex may be the active catalyst.

Deuterium Labeling and Kinetic Isotope Effects. In an attempt to learn more about the reaction mechanism, several experiments were performed substituting deuterium for hydrogen. As expected, when the hydrogen gas is replaced by deuterium, the products are all perdeuterated. Unexpectedly, the reaction with deuterium appears to be faster than the standard system. The observed inverse isotope effect of $k_{H_2}/k_{D_2} = 0.75$[44] is very similar to that measured for a high-pressure homogeneous cobalt system at 180 °C.[45] This has been interpreted in the literature as an indication of a transition state involving the addition of H_2 to a metal formyl.[45] In this case, although it may indeed involve a metal formyl, we conclude only that the inverse isotope effect is indicative of a preequilibrium step in the reaction mechanism.

Although the aluminum chloride–sodium chloride melt does not appreciably isotopically scramble H_2–D_2 or DCl–H_2 under flow reaction conditions, labeling experiments were complicated by metal-catalyzed exchange reactions. Nonetheless, GC/MS analysis of the volatile products from several experiments help to confirm earlier results. As expected, ethylene is cleanly converted to ethane-d_2 under reaction conditions employing CO and D_2. In addition, the methane produced from chloromethane under the same conditions, CO and D_2, proved to be singly labeled. Both cases appear to be the result of direct hydrogenation pathways. To the contrary, attempts to obtain evidence relating to the ethane production pathway were complicated by an additional exchange mechanism. When chloromethane-d_3 is used with CO and H_2, the ethane produced shows significant loss of the deuterium label, with only 50% retaining even one deuteron. Experiments using acetyl-d_3 chloride, however, resulted in less exchange, and analysis indicated a large fraction of ethane-d_2 less ethane-d_1, and virtually no ethane-d_3. This unusual distribution is evidence supporting an elimination–hydrogenation pathway to ethane, as shown in eq 5. These results are supplemented by experiments with DCl added to the H_2–CO gas stream, which show that more deuterium is incorporated into the ethane product than into methane. These results are consistent with an exchangeable ethane precursor, and our speculation is that the α-protons of a metal acyl intermediate are responsible for this behavior.

$$CD_3CH_2OH \xrightarrow[AlCl_3]{} CD_2{=}CH_2 \xrightarrow{H_2} CD_2HCH_3 \qquad (5)$$

Mechanism. Whereas the number of reported homogeneous conversions of synthesis gas to oxygenated products continues to grow, the reports of homogeneous catalysis to hydrocarbons have been viewed with increasing skepticism.[46] This has led some workers to conclude that alkane products, methane in particular, are indicative of a heterogeneous catalyst.[11,23] Although this $Ir_4(CO)_{12}/AlCl_3$ system is unique due to its strong Lewis acid solvent (reactant) and low-pressure conditions, we feel the results are most consistent with homogeneous conversion of carbon monoxide to chloromethane as a primary product.

When the $Ir_4(CO)_{12}$ precatalyst is dropped into the 2:1 $AlCl_3$–NaCl melt, approximately 1 equiv of hydrocarbon products, primarily methane, is produced very rapidly. This is followed by a new regime in which chloromethane and ethane are produced as major products. (Neither the initial burst of products nor catalytic activity is observed when $Ir_4(CO)_{12}$ is dropped into molten hexamethylbenzene at 180 °C under CO and H_2.) We attribute this behavior to a stoichiometric reaction of the precatalyst with the highly Lewis acidic melt which generates the active catalyst with concurrent reduction of one carbonyl ligand to hydrocarbons. The details of this conversion are unknown, but the observation of similar catalysis from the $IrCl(CO)_3$ precatalyst without this initial methane production and the shift of the CO stretching frequencies to higher energy suggest a possible oxidative fragmentation reaction. A similar reaction has been observed by Shriver et al.[47] upon treatment of an iron cluster with strong acids (eq 6).

$$Fe_4(CO)_{13}^{2-} \xrightarrow[3\text{ days, }25\ °C]{HSO_3CF_3} CH_4 + Fe^{2+} + CO + H_2 + \text{iron carbonyls} \qquad (6)$$

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[40] The dispersion of the 1% Ir/Al_2O_3 sample was found to be 30% surface sites, one-third the original value.

[41] Nijs, H.; Jacobs, P.; Uytterhoeven, J. *J. Chem. Soc., Chem. Commun.* **1979**, 1095–1096.

[42] Fuentes, S.; Figueras, F. *J. Catal.* **1980**, *61*, 443–453.

[43] Both anhydrous $IrCl_3$ and hydrated $IrCl_3$ showed some activity, but dissolution was slow. Vaska's complex, $IrCl(CO)(PPh_3)_2$, also showed some activity, but with additional decomposition products.

[44] The deuterium rate calculation assumes a 5% flame ionization detector response enhancement for all deuterated products, as this is the value measured for CD_4 vs. CH_4. The response factors for ethane-d_6 and chloromethane-d_3 would have to be eight times larger than that observed for methane to negate entirely the increased GC response with deuterium.

[45] Rathke, J. W.; Feder, H. M.; Chen, M. J.; Curtiss, L. A. In "Catalytic Activation of Carbon Monoxide"; Ford, P. C., Ed.; *Americal Chemical Society*: Washington, DC, 1981; *ACS Symp. No. 152*, pp 19–34. See also: Howarth, O. W.; McAteer, C. H.; Moore, P.; Morris, G. E. *J. Chem. Soc., Chem. Commun.* **1982**, 745–747.

[46] Two of the early reports of homogeneous conversion of CO to hydrocarbons have been shown to be in error, see: Doyle, M. J.; Kouwenhoven, A. P.; Schaap, C. A.; Van Oort, B. V. *J. Organomet. Chem.* **1979**, *174*, C55–C58 (re. Masters, C.; van Doorn, J. A. Offenlegungsschrift 2 644 185, 1977; U. K. Patent Appl. 75/40 322, 1975. Brenner, L. S.; Lai, Y.-H; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1981**, *103*, 3609–3611 (re. Henrici-Olivé, G.; Olivé, S. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 77–78). In addition, polymer-bound catalysts similar to the Fischer–Tropsch active system recently reported by Vollhardt et al. (Perkins, P.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1979**, *101*, 3985–3987) were reported to be inactive (Stille, J. K.; Verdet, L. *Organometallics* **1982**, *1*, 380–381. Stille, J. K.; Sekiya, A. *J. Am. Chem. Soc.* **1981**, *103*, 5096–5100).

[47] Whitmire, K.; Shriver, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 1456–1457.

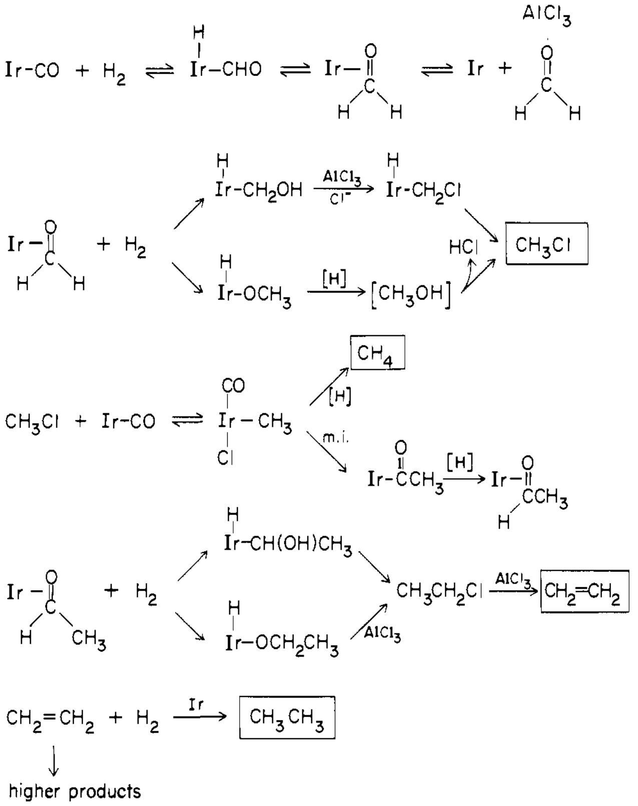

Figure 11. Proposed mechanistic scheme for CO hydrogenation with $Ir_4(CO)_{12}$ precatalyst in 2:1 $AlCl_3$–NaCl at 175 °C under CO and H_2 at 1 atm.

The proposed reaction mechanism for the reduction of carbon monoxide (shown in Figure 11) correlates the evidence presented here with a growing body of knowledge in homogeneous syngas chemistry.[48] The initiation step is suggested to be the migration of a metal hydride to a coordinated carbonyl. This step has only recently been observed for the first time and for unrelated systems,[49,50] but it has gained wide acceptance in the homogeneous CO reduction literature. Since the Lewis acid enhancement of alkyl migrations to coordinated CO has been well established,[51] the aluminum chloride is almost certainly the reason this reaction occurs under such mild conditions of temperature and pressure. This unfavorable equilibrium could account for the slow conversion of CO at these low pressures. An alternate initiation route,[52] involving the equilibrium formation of formyl chloride without metal catalysis (eq 7) can be ruled out because of HCl inhibition, normal temperature dependence, and labeling experiments.

$$HCl + CO \rightleftharpoons HC(=O)Cl \qquad (7)$$

Although the conversion of synthesis gas to methanol is slightly unfavorable thermodynamically at 180 °C, significant conversions can be obtained at pressures above 250 bar. The formation of free formaldehyde as a major product, however, is precluded on the same thermodynamic grounds. Representative numbers are shown below in Table III. In high-pressure reactions, several authors have persuasively argued for a kinetically viable formaldehyde intermediate,[10,12,16] but in our ambient-pressure reaction the thermodynamics require that formaldehyde be complexed to be considered a plausible intermediate. (This could involve stabilization by the metal or by the aluminum chloride.) Nonetheless, we consider it the most likely pathway. The reduction of a formaldehyde complex would yield methanol which is converted under reaction conditions to chloromethane.

Table III. Thermodynamic Parameters on the Formation of Methanol and Formaldehyde[12] from Synthesis Gas

	T, °C	p, atm	$\Delta G°$, kcal	K
CH_3OH	0	1	−7.15	5.3×10^5 atm^{-2}
	200	1	+3.82	1.7×10^{-2} atm^{-2}
CH_2O	25	1	8.27	8.7×10^{-7} atm^{-1}
	200	1	13.8	9.0×10^{-7} atm^{-1}
	200	1367		9×10^{-5} M^{-1}

Although there are many possible routes to the hydrocarbon products, it has been shown that chloromethane can give rise to both methane and ethane as well as other nonvolatile products. Because the flow system demonstrates that chloromethane can be a major product and other experiments show that all other products can be derived from chloromethane, there is no reason to invoke any other pathway. Alternative routes, such as those involving metal–carbene intermediates, are not ruled out but appear unnecessary. (The generation of carbenes by Lewis or Brønsted acid treatment of hydroxymethyl species is known,[53-55] and chloride attack on this intermediate could yield the proposed chloromethyl moiety.) The proposed mechanism for hydrocarbon formation from chloromethane is similar to that of the Monsanto acetic acid process,[56] with the addition of subsequent hydrogenation steps. The chloromethane should oxidatively add to the metal center. The resulting complex, then, can either reductively eliminate methane or form the acyl by migration of the methyl group to CO. The migration pathway may predominate due to the Lewis acid enhancement mentioned previously. Further reduction eventually gives rise to ethane. This series of steps, probably involving the formation of an ethanol equivalent which forms ethylene in the melt and is subsequently hydrogenated, accounts for the delayed production of ethane and the virtual termination of products at the two-carbon level.

We have not proposed the migration of a hydroxymethyl group to CO in the ethane production pathway, although the possibility is not prohibited. (In recent mechanistic schemes, this has been the branching point for ethylene glycol and related products.[10,12,16,34]) The products resulting from this pathway usually show a strong dependence on pressure, only becoming significant at high pressures.[12,13] In addition, the present system involves a good hydrogenation catalyst, and all products can be accounted for by methanol homologation reactions.

Conclusion

We have presented evidence to support our contention that the $Ir_4(CO)_{12}$-based catalyst system in molten aluminum chloride–sodium chloride is a homogeneous reaction which proceeds through chloromethane as an intermediate. An analogous system using $Os_3(CO)_{12}$ in boron tribromide has been reported which displays similar behavior.[22] This reaction produces methane, ethane, methyl bromide, and ethyl bromide as major products, and $Os_2(CO)_6Br_2$ is considered to be the enduring catalyst. The activity of approximately two turnovers/h, after an initially more active period, and the presence of alkyl halides in the reaction products are similar to our studies.

The results here do not differ greatly from the original Muetterties communication of this system. Under static conditions, chloromethane could have gone undetected since it is effectively converted to the observed products in the melt. Rates and product distributions can also be accommodated. However,

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Muetterties' more recent flow system is in marked contrast to the experimental data presented here. Whereas our flow reactor yields results complementary to our recycle system, showing an increase in chloromethane production and more complete conversion of CO to volatile products, the Muetterties flow system shows quite different chemistry. The latter reaction is approximately four times faster than both our catalytic systems and the initially reported static reaction and produces higher hydrocarbon products, predominantly propane (17%), isobutane (54%), and pentanes (17%), *without alkyl halides*. Muetterties rationalizes the discrepancy in chain length as arising from cracking reactions of the heavier alkanes in the static reactor. This runs contrary to literature reports[31,57] and our observations, which show isomerization as the major reaction of C_4–C_6 hydrocarbons, accompanied by minor cracking but very little methane or ethane production. In addition, there is a dramatic difference in the initial stages of the two reactions, one showing a very active period representing tens of turnovers to three- and four-carbon products, while ours produces only a stoichiometric amount of alkanes, primarily methane.

Attempts to duplicate these recently reported experimental results in our laboratory have been unsuccessful. (Changes in catalyst preparation, catalyst pretreatment, catalyst concentration, reactant purification procedures, flow rates, and temperature all lead to results similar to those described herein.) The two systems are so dramatically different that we must conclude that they represent two different active catalysts, albeit from the same precatalyst under similar conditions. Thus, the Muetterties flow reaction remains a novel and intriguing syngas transformation. Since we have been unable to reproduce this catalytic system, we have confined speculation to our own results, which appear to be both self-consistent and consistent with the homogeneous literature.

Finally it should be evident that a catalytic CO–H_2 process which consumes $AlCl_3$ has no technological significance. In spite of this, the present study may have some heuristic merit.

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Registry No. NaCl, 7647-14-5; CO, 630-08-0; tetrairidium dodecacarbonyl, 18827-81-1; methane, 74-82-8; ethane, 74-84-0; methyl chloride, 74-87-3; methanol, 67-56-1; aluminum chloride, 7446-70-0.

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Kinetics and Mechanism of the Formation of Nitrosoalkane Complexes by Migratory Insertion of Coordinated Nitric Oxide into Cobalt–Carbon Bonds

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Abstract: Treatment of $[CpCoNO]_2$ with Na/Hg in Et_2O results in the formation of the salt $Na^+[CpCoNO]^-$ (**4**). Reaction of **4** with CH_3I in THF at −40 °C gives the methyl nitrosyl complex **5a**, which decomposes at higher temperatures in the absence of phosphines. When solutions of **5a** are warmed above −40 °C in the presence of at least 1 equiv of PPh_3, clean conversion to a product formed by NO migratory insertion, $CpCo(RNO)PPh_3$ (R = CH_3, **6a**), is observed. In a similar manner, treatment of **4** in the presence of PPh_3 with the appropriate alkylating agents afforded the series of nitrosoalkane complexes **6**, where R = Et, *i*-Pr, and *p*-methylbenzyl. All of these complexes were isolated and fully characterized. One method of removing the organic ligand from the nitrosoalkane complexes was demonstrated by treating **6d** with $LiAlH_4$, which gave a high yield of *p*-methylbenzylamine. The bonding in these complexes, in particular the η^1-nitrosoalkane ligand, was established by an X-ray diffraction analysis of **6b** (R = Et). Labeling studies showed that the insertion is an intramolecular process and that β elimination, when possible, does not compete with the NO insertion. Kinetic studies indicated that the rate of reaction ($k = 1.6 \times 10^{-3}\ s^{-1}$ at 18 °C) of **5a** to **6a** does not vary as a function of $[PPh_3]$. This result requires the rate-determining formation of an intermediate, which in the phosphine concentration range studied (0.05–0.20 M), is always trapped by a ligand faster than it can return to starting material. One possible formulation of this intermediate is the coordinatively unsaturated complex $CpCo(CH_3NO)$ (**7**). When **5a** is generated in the presence of PEt_3, a new complex is formed, which was identified on the basis of spectroscopic data as $CpCo(NO)(CH_3)(PEt_3)$ (**8a**), where the coordinated NO group has adopted a bent geometry. Complex **8a** undergoes insertion to give the nitrosomethane complex **6e**. Kinetic studies showed that the reaction of **8a** to **6e** is not a simple unimolecular process but that **8a** must undergo dissociation of the PEt_3 ligand to regenerate **5a** before the migratory insertion can occur. This result is analyzed in terms of the relative binding energies of PEt_3 to the nitrosyl methyl complex **5a** and to the transition state leading to NO insertion, $\mathbf{5}^{\ddagger}$. A mechanism consistent with the kinetic and labeling data is proposed and discussed.

Migratory insertion of CO into transition-metal–carbon bonds (eq 1) is one of the most ubiquitous and well-studied reactions in organotransition-metal chemistry.[1] In addition to its fundamental importance, CO migratory insertion is a critical step in many important carbon–carbon bond forming processes involving homogeneous transition-metal catalysts.[2] In contrast, migratory insertion of NO into metal–carbon bonds (eq 2) is much less common and in most cases has only been inferred as one step in a more complicated overall transformation.

$$R{-}M(CO) + L \rightarrow R{-}C({=}O){-}M(L) \qquad (1)$$

$$R{-}M(NO) + L \rightarrow R{-}N({=}O){-}M(L) \qquad (2)$$

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