(1967).

(12) The ^1H NMR chemical shifts in $CHFCl_2$ in parts per million downfield from internal tetramethylsilane at − 10 °C are: 2.7 (broad, α-CH_2) and 1.5 (broad, NH, β- and γ-CH_2). At − 140 °C in $CHFCl_2$:CHF_2Cl (1:1), the shifts are: 2.93 (d, α-CH equatorial), 2.48 (t, α-CH axial), 1.71 (d, γ-CH equatorial), 1.55 (d, β-CH equatorial), 1.3–1.4 (m, β- and γ-CH axial), and 1.44 (s, NH). At − 174 °C the shifts are the same as at − 140 °C, except for the NH resonance which now shifts of about 1.2 and 1.6.

(13) J_{aa}(NH–CH) = 13 Hz in tetrahydro-1,3-oxazines and in 1-methyl-1,3-diazane, compounds that exhibit axial NH groups as a result of the anomeric effect.[5]

(14) Yousif and Roberts[7] present good evidence that acetone was not involved chemically with the amine. We have not found any reaction between I and acetone, as determined by ^{13}C NMR in the temperature range of +20 to −80 °C. The addition of acetone (2 equiv) to $CHFCl_2$ solutions of I had no observable effect on the nitrogen inversion process, as observed by ^{13}C NMR.

F. A. L. Anet,* Issa Yavari
Contribution Number 3752, Department of Chemistry
University of California
Los Angeles, California 90024

Received December 20, 1976

Metal Clusters in Catalysis.[1] 10. A New Fischer-Tropsch Synthesis

Sir:

We wish to report a new Fischer-Tropsch synthesis in which a catalytic hydrogenation of carbon monoxide yielded a set of aliphatic hydrocarbons with ethane the *primary* reaction product. Reactions rates at 180 °C and 1–2 atm were relatively high with average turnover times of about 10–15 min. The catalyst or catalyst precursor was tetrairidium dodecacarbonyl, $Ir_4(CO)_{12}$.

Earlier we demonstrated[2] a homogeneous methanation[3] reaction, eq 1,

$$3H_2 + CO \rightarrow CH_4 + H_2O \qquad (1)$$

for hydrogen and carbon monoxide at 130–160 °C and 1–3 atm using toluene solutions that contained certain transition metal clusters;[4] all mononuclear complexes investigated were found to be inactive. The most effective metal cluster in this reaction was $Ir_4(CO)_{12}$ and, with this cluster, the sole hydrocarbon product detected was methane.[5] Unfortunately, the rates in this reaction system proved so inordinately low that mechanistic studies have been precluded.

The guiding hypothesis[2,6] in our search for soluble catalysts for the hydrogenation of carbon monoxide has been that optimal activation of carbon monoxide for reduction would be achieved in a state where there is extensive interaction of both the carbon and oxygen atoms of carbon monoxide with metal atoms. Such a state[7] would be distinguished by a substantially lower carbon–oxygen bond order and a potentially facile mechanism for carbon–oxygen bond scission. An exemplary surface model is the dissociative chemisorption of carbon monoxide on some metals which include those that can catalyze either the methanation reaction or Fischer-Tropsch[8] syntheses. This hypothesis led to the initial selection of metal cluster catalysts and, now in our new modification, to the use of aluminum chloride for a possibly substantial oxygen–aluminum interaction (M–C–O–Al).[9]

Our new cluster-based synthesis comprised the following reagents and conditions. The synthesis gas was 3:1 H_2:CO,[10] the cluster catalyst reagent was $Ir_4(CO)_{12}$ in a 1:100 cluster:CO ratio and the solvent was molten $NaCl{\cdot}2AlCl_3$ in a 1000:1 Al:Ir ratio. All reactions were effected in sealed glass tubes at 180 °C and 1.5 atm, and, at reaction temperature, there was a yellow to amber solution and no solid phase evident on visual examination. Analyses of product gases were based on gas chromatography and high resolution mass spectrometry.[11] Conversion of carbon monoxide to hydrocarbon was essentially complete after 12–24 h, although detectable traces of carbon monoxide were present after reaction periods of up to 5 days and iridium carbonyl was detectable by IR analysis of the solidified reaction melt after such 5-day reaction periods. In the absence of the iridium carbonyl cluster, the reaction system produced no hydrocarbons in reaction times of 3 days. Iridium metal generated by reductive pyrolysis of the carbonyl cluster[12] and a very fine iridium dust were inactive as a catalyst substitute for the carbonyl cluster in our specific reaction system. An extensive, but not exhaustive, exploration of catalyst alternatives to $Ir_4(CO)_{12}$ was relatively nonproductive. Essentially inactive[13] were $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, $Re_2(CO)_{10}$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $Os_3(CO)_{12}$, $Co_2(CO)_8$, $Co_4(CO)_{12}$, and $NiCl_2$. Most notably, Na_3IrCl_6 was inactive; hence, the catalyst or catalyst precursor was not a chloroiridate complex. $Rh_6(CO)_{16}$ and $Rh_4(CO)_{12}$ were as active or slightly more active than $Ir_4(CO)_{12}$. However, because this rhodium-based system was heterogeneous at 180 °C, we do not know whether this catalytic reaction was wholly or even partially a solution phase process.[14b] $Ru_3(CO)_{12}$ was very active and appeared homogeneous in the early reaction stages. Slightly active were H_2PtCl_6 and $PdCl_2$, but both gave heterogeneous reaction systems.

The detectable hydrocarbon products of this relatively fast catalytic hydrogenation with $Ir_4(CO)_{12}$ were methane, ethane, propane, and isobutane. The latter two were invariably minor constituents. Interestingly, the relative amounts of methane and ethane varied rather significantly with reaction time. The ethane to methane ratio in the product gas fell from a 10:1 to 4:1 range after 3 h to ~1:2 after 0.5 to 3 days; the lowest observed ratio was about 1:2.5. This lowest ratio is far larger than that calculated from the equilibrium constant for reaction 2.

$$C_2H_6 + H_2 \rightleftharpoons 2CH_4 \qquad (2)$$

Since aluminum chloride is a quite effective catalyst for carbonium ion-based alkane isomerization and fragmentation,[15] this type of secondary catalytic reaction could explain the observed decrease in the C_2H_6:CH_4 ratio with reaction time increase. However, we found methane formation from ethane and hydrogen under our reaction conditions in the absence of the iridium cluster catalyst to be too slow to account for the product variation in the catalytic reaction, although, in the presence of the iridium cluster, there appeared to be a slightly more rapid fragmentation[16] (methane proved nonreactive under these conditions). In any case, our preliminary results raise the possibility of a high yield ethane synthesis.

We have evidence that the $Ir_4(CO)_{12}$ catalyst is not, at least wholly, converted to other complexes under the reaction conditions.[17] The reaction solution on cooling yielded solid phases including a minor one that had the characteristic yellow $Ir_4(CO)_{12}$ color. In the infrared spectrum of this phase, there were the characteristic CO stretching absorptions of $Ir_4(CO)_{12}$. Attempts to isolate the cluster in pure form from reaction mixtures have not been successful yet.

The $Ir_4(CO)_{12}$ catalyzed reactions were homogeneous[18] by the light scattering criterion. However, the possibility that very small *metal* aggregates were the actual catalyst cannot be excluded with the scattering criterion. Vannice's[19] kinetic expression for the iridium metal[20] catalyzed methanation reaction was used to calculate a rate for iridium metal catalysis at 180 °C. This calculated rate was slightly too low to account for our observed turnover rates with an assumption that all the $Ir_4(CO)_{12}$ was converted to metal aggregates in which *every* metal atom was catalytically active. In addition, a fine iridium metal dust[21] was examined as a catalyst for the CO hydrogenation reaction at 180 °C with a $NaCl{\cdot}2AlCl_3$ reaction medium and without the salt medium. The dust was slightly active; only small amounts of methane were detected in both types of reaction systems. We conclude that small metal particles probably were not responsible for the catalysis in this iridium system.[22,23]

A selective Fischer-Tropsch synthesis, of great technological significance, has never been demonstrated. Our new catalytic hydrogenation system based on $Ir_4(CO)_{12}$ clearly presents the possibility of such a selective synthesis. In addition, the preliminary results raise many intriguing scientific questions. For example, iridium *metal* is a relatively poor CO hydrogenation catalyst and iron and ruthenium *metal* are particularly active,[24] whereas in our reaction system $Ir_4(CO)_{12}$ is more active than $Ru_3(CO)_{12}$ and $Fe_3(CO)_{12}$ is inactive. What is the reaction mechanism here? Is there any formal mechanistic relationship between our reaction and the metal or metal oxide[8]-based syntheses? We offer no speculation on reaction mechanism,[25] but are investigating this complex issue through kinetic, spectroscopic, and isolation studies. Alternative catalyst precursors and alternative acidic or acceptor solvents are being examined. With respect to the latter, two observations are particularly noteworthy. The reaction medium appears to require "acidic" character since we find molten $NaAlCl_4$ to be relatively ineffective under our reaction conditions. Composition of the hydrocarbon product mixture is almost qualitatively altered in going from a chloride to a bromide-based melt in that propane became a major product with a $NaBr-2AlBr_3$ reaction medium. Hence, the character of the reaction medium may be varied to further control the distribution of hydrocarbon products.

Note Added in Proof. Further experiments have demonstrated the following effects upon rate and hydrocarbon product distribution. Higher reaction temperatures (200 °C) lowered both the apparent rate (conversion) and the C_2/C_1 product ratio; increased hydrogen chloride concentration had a similar effect. Short contact times shifted the product distribution to favor C_3H_8 and *i*-C_4H_{10}. Substitution of BBr_3 for the $NaCl \cdot 2AlCl_3$ reaction medium gave an active reaction system that produced CH_4, C_2H_6, C_3H_8, *i*-C_4H_{10}, and *n*-C_4H_{10} with the last two the major and minor constituents, respectively.

Acknowledgment. This research was supported by the National Science Foundation.

References and Notes

(1) K. G. Caulton, M. G. Thomas, B. A. Sosinsky, and E. L. Muetterties, *Proc. Natl. Acad. Sci. U.S.A.*, **73**, 4274 (1976).

(2) M. G. Thomas, B. F. Beier, and E. L. Muetterties, *J. Am. Chem. Soc.*, **98**, 1296 (1976).

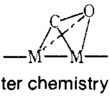
(3) Methanation is a reaction that is very effectively catalyzed by nickel surfaces.

(4) Active were $Ir_4(CO)_{12}$ and $Os_3(CO)_{12}$.

(5) Very small amounts of ethane were also detected when $Os_3(CO)_{12}$ was used.

(6) (a) E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **84**, 959 (1975); (b) *ibid.*, **85**, 451 (1976).

(7) An interaction of the form



is unknown in molecular cluster chemistry, but is common for acetylenes in clusters and is known for nitrogen in two very complex nickel clusters.[6b] Such a $\mu-\pi$ interaction for carbon monoxide rarely may be realized in an intermediate, but perhaps more commonly in transition states, for example, in the dissociative chemisorption of carbon monoxide on certain metal surfaces.

(8) (a) H. Storch, N. Golumbic, and R. Anderson, "The Fischer-Tropsch and Related Syntheses", Wiley, New York, N.Y., 1951; (b) Y. T. Eidus, *Russ. Chem. Rev.*, **36**, 338 (1967); (c) H. Pichler and H. Schultz, *Chem.-Ing.-Tech.*, **42**, 1162 (1970). M. A. Vannice, *Catal. Rev. Sci. Eng.*, **14**, 153 (1976).

(9) There is extensive evidence that aluminum(III) halides can interact with the oxygen atom of a carbonyl ligand in metal carbonyls; cf. J. F. Kristoff and D. F. Shriver, *Inorg. Chem.*, **13**, 499 (1974), and N. E. Kim, N. J. Nelson, and D. F. Shriver, *Inorg. Chim. Acta*, **7**, 393 (1973).

(10) Syntheses gas mixtures of D_2 and CO were also used to produce the perdeuterioalkanes for a further analytical confirmation of product identities through high resolution mass spectrometry.

(11) Chromatographic analyses employed a molecular sieve 5A (6 ft) column for CH_4–CO–air separations and a Poropak Q (12 ft) column for alkane separations.

(12) The iridium metal was thermally generated in vacuo from the cluster in the reaction vessel before the melt mixture was added. This metal was largely present as a shiny mirror on the glass walls.

(13) Trace quantities of methane were produced in these cases after a 3-day reaction period. All systems were visually homogeneous.

(14) (a) The hydrocarbon product was different than with the iridium catalyst. Typically, propane was the major product; a sample analysis was C_3H_8, C_2H_6, and CH_4 in 1.9:1.3:1 molar proportions, respectively. (b) With the more soluble $Rh_4(CO)_{12}$ cluster, the catalytic reaction was visually homogeneous, but only in the early stages of reaction.

(15) This was demonstrated for *n*-hexane at 160 °C with the formation of lower and higher alkanes.

(16) An accurate characterization requires a labeling study since $Ir_4(CO)_{12}$ reacts with hydrogen to produce hydrocarbons.[17] Other factors that undoubtedly influence the nature of the hydrocarbon products are the partial pressures[17] of hydrogen, carbon monoxide, and hydrogen chloride.

(17) Reaction of $Ir_4(CO)_{12}$ with a 3:1 H_2:argon mixture in a $NaCl \cdot 2AlCl_3$ reaction medium at 180 °C was homogeneous in the early reaction stages, but small shiny particles of iridium metal appeared later as hydrogenation became extensive. The hydrocarbon product was largely methane, ethane, and propane in about 3:4:1 molar proportions, respectively. The high propane content here is notable.

(18) Unless hydrogen was present in large excess, and the reaction time was extended beyond a 1- or 2-day period.[17]

(19) M. A. Vannice, *J. Catal.*, **37**, 462 (1975).

(20) The iridium metal was supported on alumina.[19]

(21) The metal was preheated in hydrogen at elevated temperatures. The sample of this metal was kindly supplied by Matthey Bishop, Inc.

(22) Also significant is our observation that $Ir_4(CO)_{12}$ is not especially active in a $NaAlCl_4$ melt at 180 °C. Rates were less than one-quarter those for $NaCl \cdot 2AlCl_3$ reactions.

(23) In progress are experiments to establish the "homogenety" and the active catalytic species for the rhodium and ruthenium carbonyl systems.

(24) For the metal catalyzed hydrogenation of CO (largely to CH_4) at atmospheric pressure, the rates decrease in the order Ru > Fe > Ni > Co > Rh > Pd > Pt > Ir.[19]

(25) Nor can we say at this stage whether the active catalyst is a mono- or polynuclear iridium species.

G. C. Demitras, E. L. Muetterties*
Department of Chemistry, Cornell University
Ithaca, New York 14853

Received November 29, 1976

An Extension of the Role of O(2) of Cytosine Residues in the Binding of Metal Ions. Synthesis and Structure of an Unusual Polymeric Silver(I) Complex of 1-Methylcytosine

Sir:

Extensive investigations into the interaction of metal ions with nucleic acids and nucleic acid constituents have identified the ring nitrogen atoms as the major binding sites on the heterocyclic purine and pyrimidine bases.[1,2] In comparison, fewer studies have definitively shown involvement in metal binding of the exocyclic groups of these heterocycles.[1,2] The interaction of Ag^+ ion with nucleic acids has been well studied and occurs primarily at guanosine-cytidine (G-C) regions of DNA.[1-4] Although this preferential binding has been exploited to separate nucleic acids of different G-C content,[4] there have been no structural studies on Ag(I) complexes of either G or C derivatives.

We report here on a study of the product formed between $AgNO_3$ and 1-methylcytosine. In the solid, the exocyclic oxygen at C(2) of the base unexpectedly exhibits strong binding to one Ag(I) and weaker, but still appreciable interaction, with a *second* Ag(I). Such bridging by an exocyclic group of a common nucleic acid base has not been previously observed.[1,2] The Ag(I) geometry has unusual features, and we are not aware of an analogous Ag(I) to carbonyl oxygen interaction. Furthermore, the columnar stacking of the 1-methylcytosine moieties affords a better comparison to the situation which might prevail in the biopolymer complex than is typically found in studies of monomer complexes.

The complex was prepared by the reaction of equal molar quantities of $AgNO_3$ and protonated 1-methylcytosine per-