



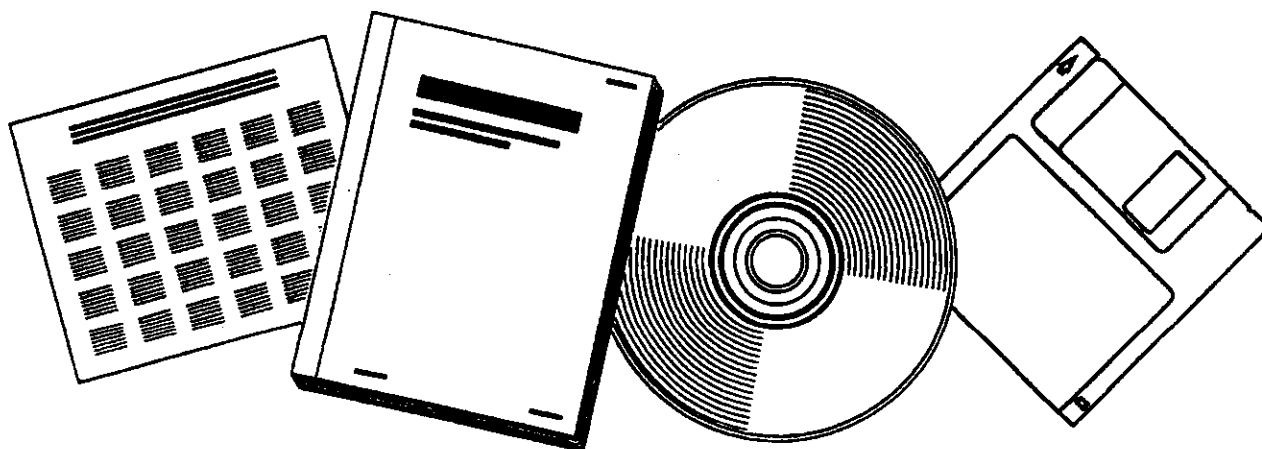
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FISCHER-TROPSCH CATALYSIS

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FISCHER-TROPSCH CATALYSIS

FINAL REPORT
(July - June 1983)

Gas Research Institute
8600 West Bryn Mawr Avenue
Chicago, Illinois 60631



FINAL REPORT

FISCHER-TROPSCH CATALYSIS

1 June 1982 - 31 May 1983

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For

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GRI Project Manager

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Title Fischer-Tropsch Catalysis

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 Final Report

Objective To study the reaction of transition metal alkyls with carbon monoxide in homogeneous solution.

Technical Perspective → Fischer-Tropsch catalysis, a heterogeneous catalytic reaction that converts carbon monoxide and hydrogen to organic alcohols and hydrocarbons, is an old though not well understood reaction. This lack of mechanistic understanding prevents the design of new and better catalytic systems. Our approach is to use homogeneous systems to model two fundamental reactions important in Fischer-Tropsch chemistry: insertion of carbon monoxide into a metal-carbon bond and carbon-carbon bond formation. ←

Results The initial thrust of the work has been the examination of hydrocarbon soluble metal alkyls of the type L_2MR_2 , where M is Ti, Zr, or Hf and R is a methyl, an ethyl or other groups and L is an anionic ligand, with carbon monoxide. To date we have shown that the R-group has a profound effect on the nature of the insertion reaction. When R is ethyl, we observe carbon-carbon bond formation. In contrast, when R is methyl, we observe cleavage of the carbon-oxygen bond of carbon monoxide.

A mechanism has been put forth to rationalize the diverse results which is based upon steric effects. The origin of the steric effects is fundamentally kinetic rather than thermodynamic.

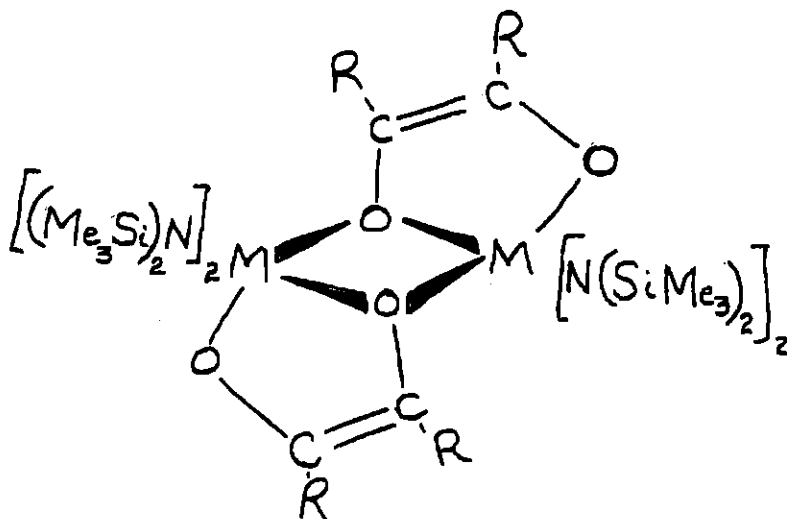
Technical Approach Our approach is to isolate and characterize (by nuclear magnetic resonance spectroscopy and X-ray crystallography) the products formed by insertion of carbon monoxide into metal-carbon bonds. These results will allow us to better understand, in an elementary way, the criteria for carbon-carbon bond formation and carbon-oxygen bond cleavage.

Summary

Reaction of the metal alkyls of the type $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{M}\text{Et}_2$, where M is Zr or Hf, with CO gives $[(\text{Me}_3\text{Si})_2\text{N}]_4\text{M}_2[\text{OC}(\text{Et})(\text{Et})\text{CO}]_2$, the result of CO insertion into the metal-carbon bond followed by carbon-carbon bond formation. The X-ray structure of the hafnium complex has been determined. Reaction of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{M}\text{Me}_2$ with CO takes a different course. When M is Zr, the oxoalkyl, $[(\text{Me}_3\text{Si})_2\text{N}]_4\text{Zr}_2\text{OMe}_2$ and $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Zr}[\text{OCC}(\text{Me})=\text{CMe}_2]$ are formed. Reaction of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Zr}(\text{Ph})_2$ with CO gives $[(\text{Me}_3\text{Si})_2\text{N}]\overline{\text{ZrCH}_2\text{Si}(\text{Me})_2\text{NSiMe}_3(\text{OCHPh}_2)}$. In addition, $[(\text{Me}_3\text{Si})_2\text{N}]\text{Zr}(\text{Cl})(\text{CH}_2\text{CMe}_3)$ with CO gives $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Zr}(\text{Cl})(\text{COCH}_2\text{CMe}_3)$. The enormous diversity of the reaction chemistry has been rationalized by a mechanism that is consistent with all of the experimental data.

This is a final report on Grant number 5080-363-0313. I will concentrate on what we have learned in the past three years about the insertion of carbon monoxide into metal to carbon bonds in molecules of the type $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{MR}_2$, where M is zirconium or hafnium and R is Me, Et, etc. This work will constitute the basis of a Ph.D. thesis of Roy P. Planalp, to be submitted in September. The report is divided into two parts, one is a summary of the experimental results and the other is a mechanistic postulate that rationalizes the experimental results. The experimental results are most reasonably divided into the types of alkyl groups that are bonded to the group IV A metals since the organic fragment plays the dominant role in the types of products that are formed. This is the most interesting aspect of the work and the most relevant with respect to Fischer-Tropsch chemistry.

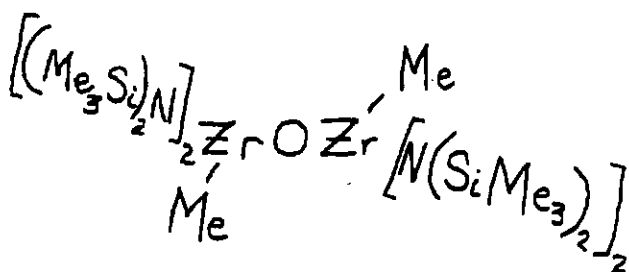
The compounds $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{M}\text{Et}_2$ and $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{MPr}^n$, where M is Zr or Hf and Pr^n is a propyl group, react with carbon monoxide to give I. The reactions occur at a partial pressure of CO of ca. 10 atm. in pentane. All of the compounds have been characterized by elemental analysis, mass spectroscopy, ^1H and ^{13}C NMR spectroscopy. In addition the crystal structure of I, M = Hf, R = Et, has been determined by X-ray crystallography. As can be seen, I, is the result of



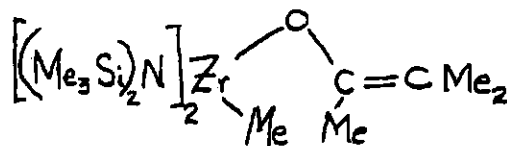
I

insertion of carbon monoxide into both metal to carbon bonds giving a molecule which is the result of the reductive dimerization of carbon monoxide and resulting in formation of a carbon-carbon double bond.

The most spectacular and surprising result is that $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{ZrMe}_2$ does not behave in an analogous fashion. Carbon monoxide reacts with the dimethyl zirconium derivative in pentane at 1 atm. pressure to give II and III.

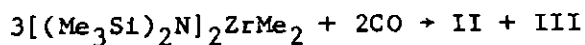


II



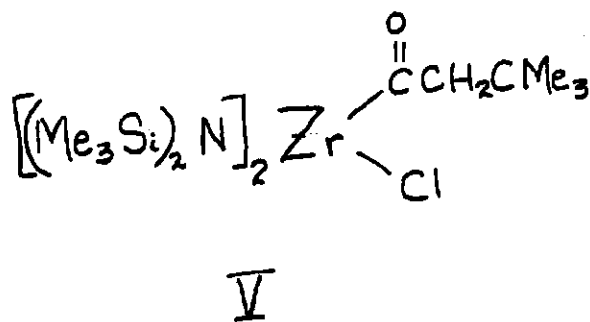
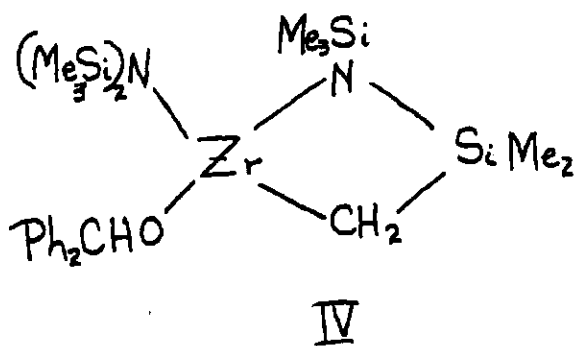
III

These two compounds have been characterized by elemental analysis, mass spectroscopy, and ^1H and ^{13}C NMR spectroscopy. In addition, the X-ray crystal structure of II was determined. If C^{18}O rather than C^{16}O was used, the oxygen atom of carbon monoxide was found in II, as determined by mass spectroscopy. Further if ^{13}CO was used, rather than ^{12}CO , the two carbon atoms were found, by ^{13}C NMR spectroscopy in the olefinic portion of III. Hence, there is no doubt that $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{ZrMe}_2$ reacts with carbon monoxide to cleave the triple bond of carbon monoxide, under



extraordinarily mild conditions. This result is highly significant since it is the only known homogeneous model for the initial event in heterogeneous Fischer-Tropsch catalyses, viz. the dissociative chemisorption of carbon monoxide. Somewhat surprisingly, $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{HfMe}_2$ does not react with carbon monoxide, even at pressures of 100 atm. We have no explanation for this most unusual result.

We have observed another type of reaction with $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Zr}(\text{Ph})_2$, where Ph is a phenyl group. This is interesting since an aryl group is an sp^2 -hybridized carbon atom, whereas the other molecules that we have studied are sp^3 -hybridized carbon to metal bonds. The aryl reacts with carbon monoxide at 10 atm. in pentane to give IV. Compound IV is the result of two phenyl groups migrating to

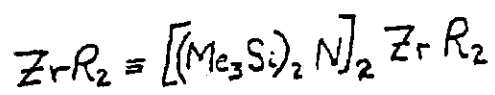
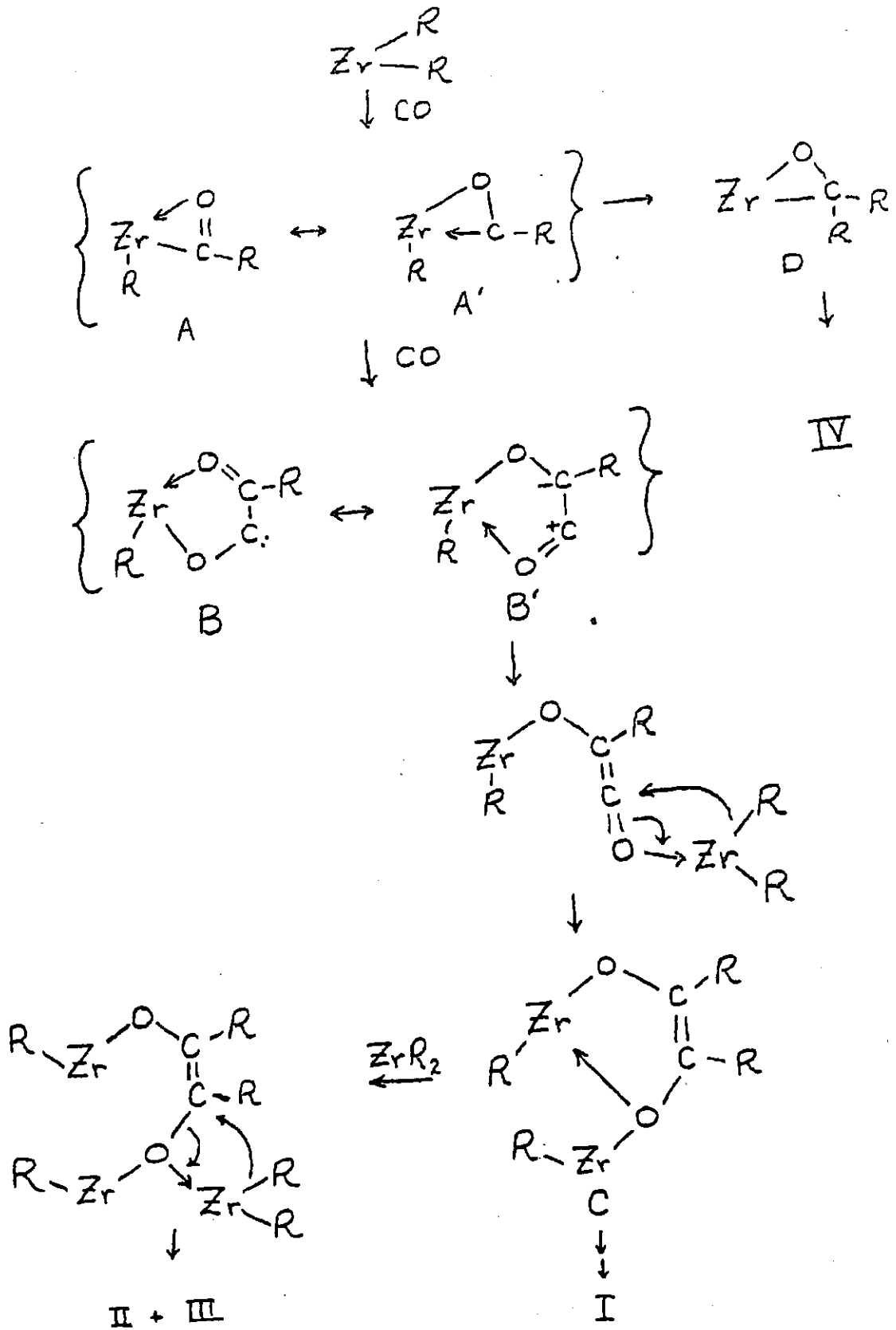


coordinated carbon monoxide followed by metallation of one of the γ -hydrogen atoms of a Me_3Si -group.

In order to get information about the initial event in the carbon monoxide insertion into metal-carbon bonds we have studied the simple molecule, $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Zr}(\text{CH}_2\text{CMe}_3)(\text{Cl})$, which contains only one metal-carbon bond. Carbon monoxide reacts at 2 atm. in pentane to give V. Compound V is the result of a straight forward insertion to give a metal-acyl.

Having acquired all of these results, it is essential that they be put into a mechanistic postulate that fits all of the available facts. Further, the postulate must be able to rationalize the diverse reaction chemistry that we have observed. This is particularly important since a trivial change of the alkyl group from a methyl to an ethyl group causes the reaction pathway to change dramatically.

One such postulate is shown in the Scheme. The first step is insertion of CO into a metal-carbon bond giving an aryl A or A', similar to the isolated molecule V. The aryl can react with an additional molecule of CO giving B or B' which can react with more $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{MR}_2$ to give C. C is the key intermediate since it can react with more CO to give I, when R is Et or Pr^n , or it can react with another molecule of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{MR}_2$, when R is Me, to give II and III. In addition, A or A' can rearrange to give D, a ketone complex of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Zr}$, by migration of R when R is Ph. This mechanism is not to be viewed as the last will and testament; it is only a scheme that is useful as a guide in our thinking about the Fischer-Tropsch reaction. The key intermediates are A and C. When an sp^2 -hybridized group is bound to the metal, migration occurs to give D. When an sp^3 -hybridized group is bound to the metal, further insertion occurs to give C. The difference between the products observed in the methyl and ethyl or propyl cases occurs at this point and the rationalization is steric hindrance. Since the steric size of an ethyl or a propyl group is larger than that of a methyl group, C is too sterically hindered in the case of R = Et or Pr^n , to allow attack by another molecule of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{MEt}_2$. When the steric hindrance is less, as in the case of R = Me, carbon monoxide bond cleavage results. Thus, the Scheme allows the experimental results to be rationalized on the basis of steric effects and the origin of the steric effects is in the relative rates (kinetics) rather than in thermodynamics.



Scheme

In summary, during the past three years we have been able to get significant results on the initial and propagation steps in Fischer-Tropsch by studying suitable model compounds in homogeneous solution. These results have allowed us to put forth a mechanism that accounts for the wide range of products observed in actual Fischer-Tropsch chemistry. This mechanism is based upon a steric argument whose origin is kinetic rather than thermodynamic.

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