PREPARATION AND CHARACTERIZATION OF LIGAND TYPES INTERMEDIATE IN THE METAL CATALYZED CONVERSION OF COAL TO METHANE, METHANOL, AND HIGHER ALKANES AND ALCOHOLS. SECOND TECHNICAL PROGRESS REPORT, SEPTEMBER 1, 1979-FEBRUARY 28, 1981

CALIFORNIA UNIV., LOS ANGELES. DEPT. OF
CHEMISTRY

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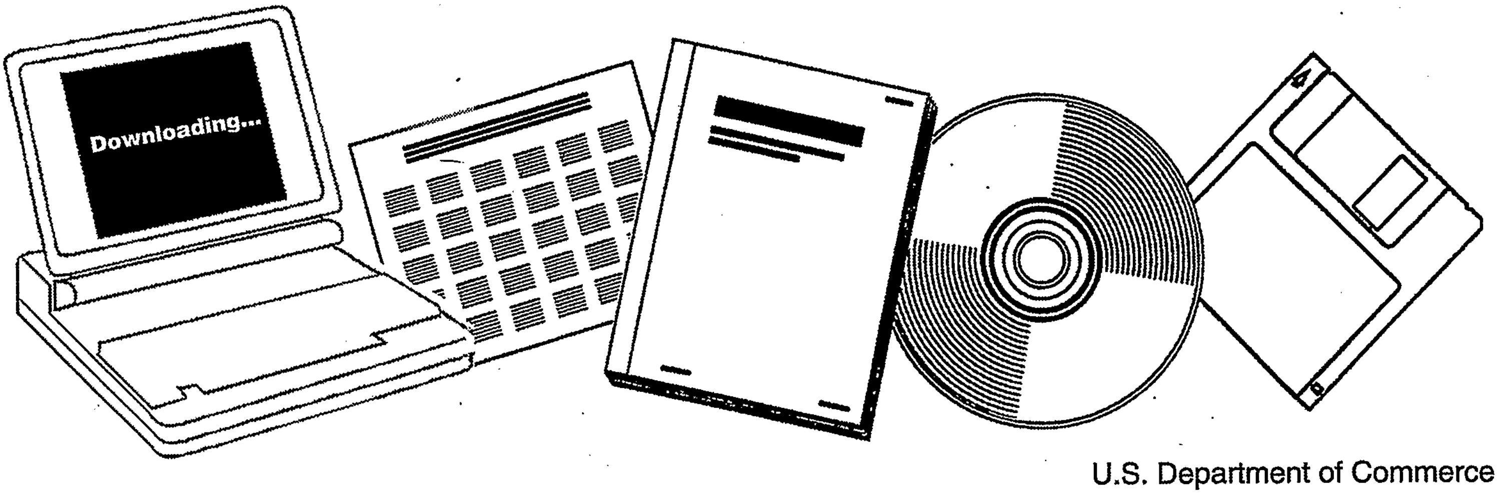

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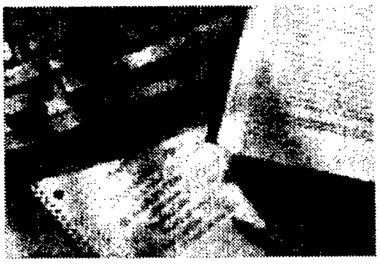

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Second Technical Progress Report

Department of Energy Project EY-76-S-03-0034

"The Preparation and Characterization of Ligand Types Intermediate in the Metal Catalyzed Conversion of Coal to Methane, Methanol, and Higher Alkanes and Alcohols"

PRINCIPAL INVESTIGATOR: Dr. John A. Gladysz, Assistant Professor

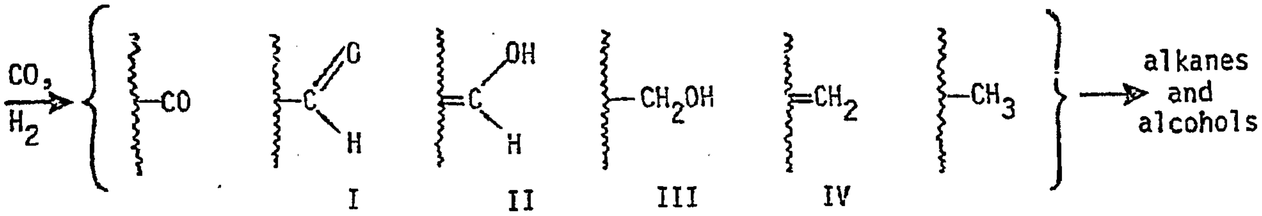
INSTITUTIONAL AFFILIATION: Department of Chemistry
University of California at Los Angeles
405 Hilgard Avenue
Los Angeles, CA 90024

REPORTING PERIOD: 1 September 1979 - 28 February 1981

DATE OF THIS REPORT: 10 November 1980

I. Introduction

In our original proposal, we outlined a program of preparation and characterization of reactive ligand types I-IV (believed to represent important catalyst bound intermediates in the Fischer-Tropsch process) on homogeneous metal centers.



I II III IV

Our objectives were:

(A) to develop mild and general methodology for the generation of ligand types I-IV, and insofar as stability permits, isolation of these species.

(B) to establish the general chemistry of each ligand type (thermal reactions, possible development of useful organic reactions),

(C) to explore the chemistry and interconvertability of these ligand types when reacted with H^- and H^+ sources,

(D) to define the reactivity of each ligand type toward H_2, in an attempt to model the CH_4 formation process, and

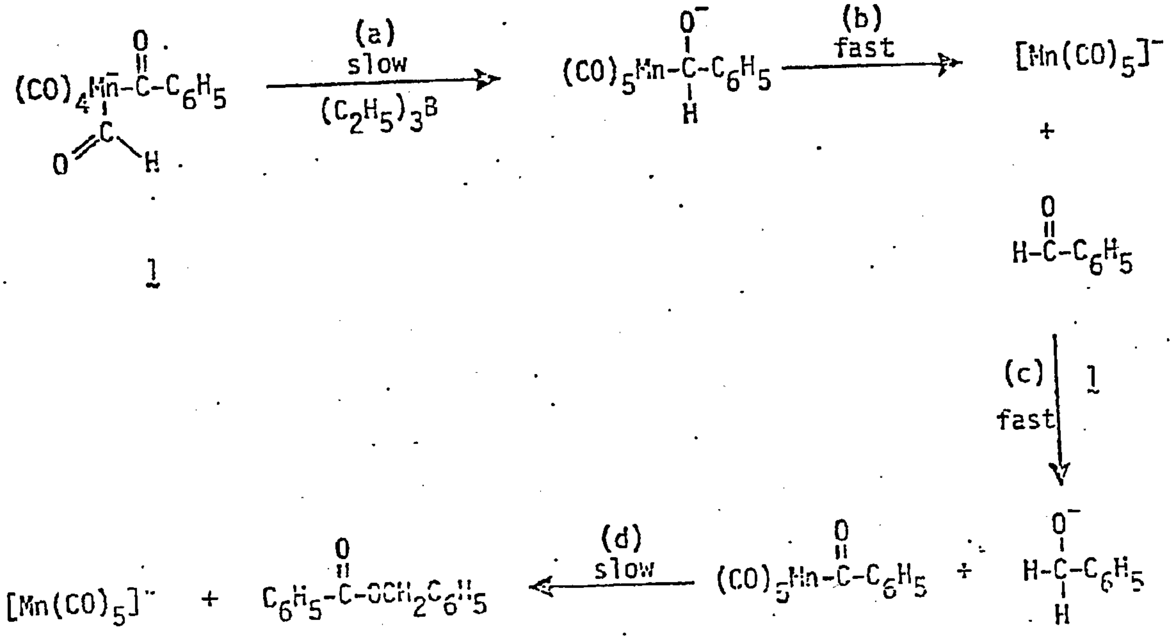
(E) to examine the reactions of CO with each ligand type, in the event unanticipated chain extension modes may be discovered.

Complexes containing each of the ligand types I-IV have been prepared and studied, as described in the following sections.

II. Anionic Metal-Formyl Complexes

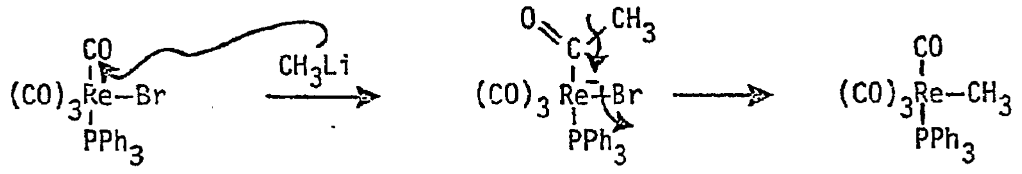
We are concluding our work with anionic formyl complexes with some mechanistic studies. We have examined the rate of decomposition of the formyl $(CO)_4Mn(COC_6H_5)(CHO)^-$ (**1**) as a function of counter-ion and trialkylborane present. We have also prepared the deutered formyl $(CO)_4Mn(COC_6H_5)(CDO)^-$ and monitored its decomposition by ^2H NMR. The data obtained indicate that the formyl decomposes by a disproportionative pathway as shown in Scheme I -- not by initial CO loss, as commonly noted for formyl complexes (publication B-2).

Scheme I. Proposed Decomposition Mechanism of $(CO)_4Mn(COC_6H_5)(CHO)^-$



We have shown α-elimination decomposition pathways previously demonstrated with formyl complexes are also available to anionic acyl complexes. We thought that many nucleophilic displacement reactions at metal carbonyl centers might take place by initial attack at CO, followed by an α-elimination. Accordingly, we confirmed the intermediacy of the previously unsuspected intermediate 2 in the substitution reaction shown in eq i by isolation, rate studies, and deuterium labeling (publication A-8).

(i)



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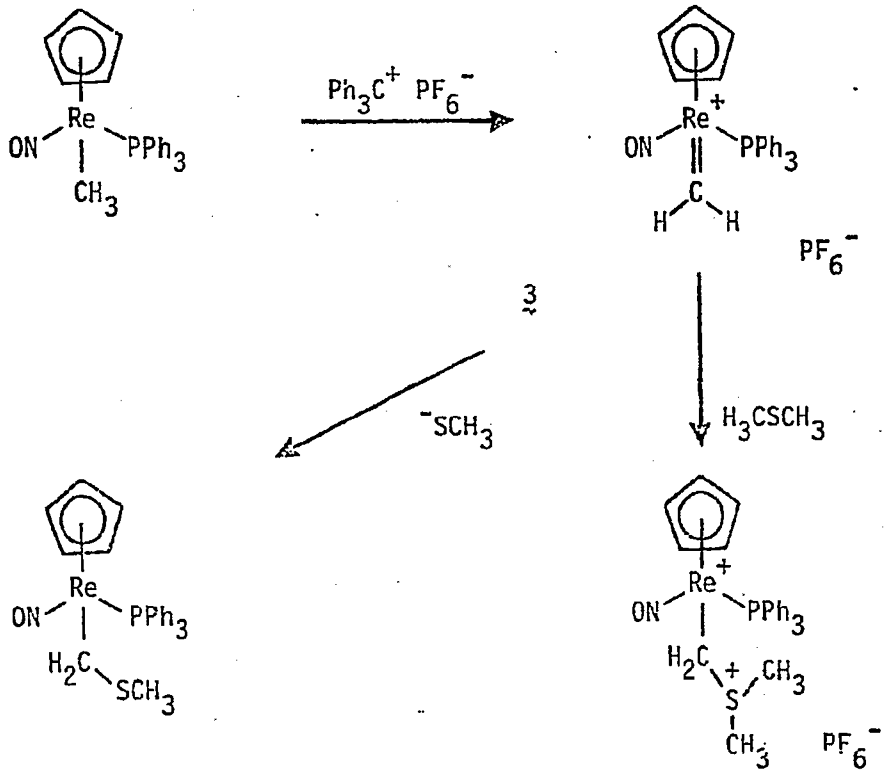
III. Neutral Formyl Complexes

We have continued our studies of the electrophile induced disproportionation of the neutral formyl $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHO)$ described in our previous report. The proposed mechanism (publications A-6 and B-3) has been further supported by the isolation of additional intermediates such as $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CHOSi(CH_3)_3)]^+ X^-$ and $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2)]^+ PF_6^-$ (3). The latter compound is under intensive study (below).

IV. Methylidene Complexes

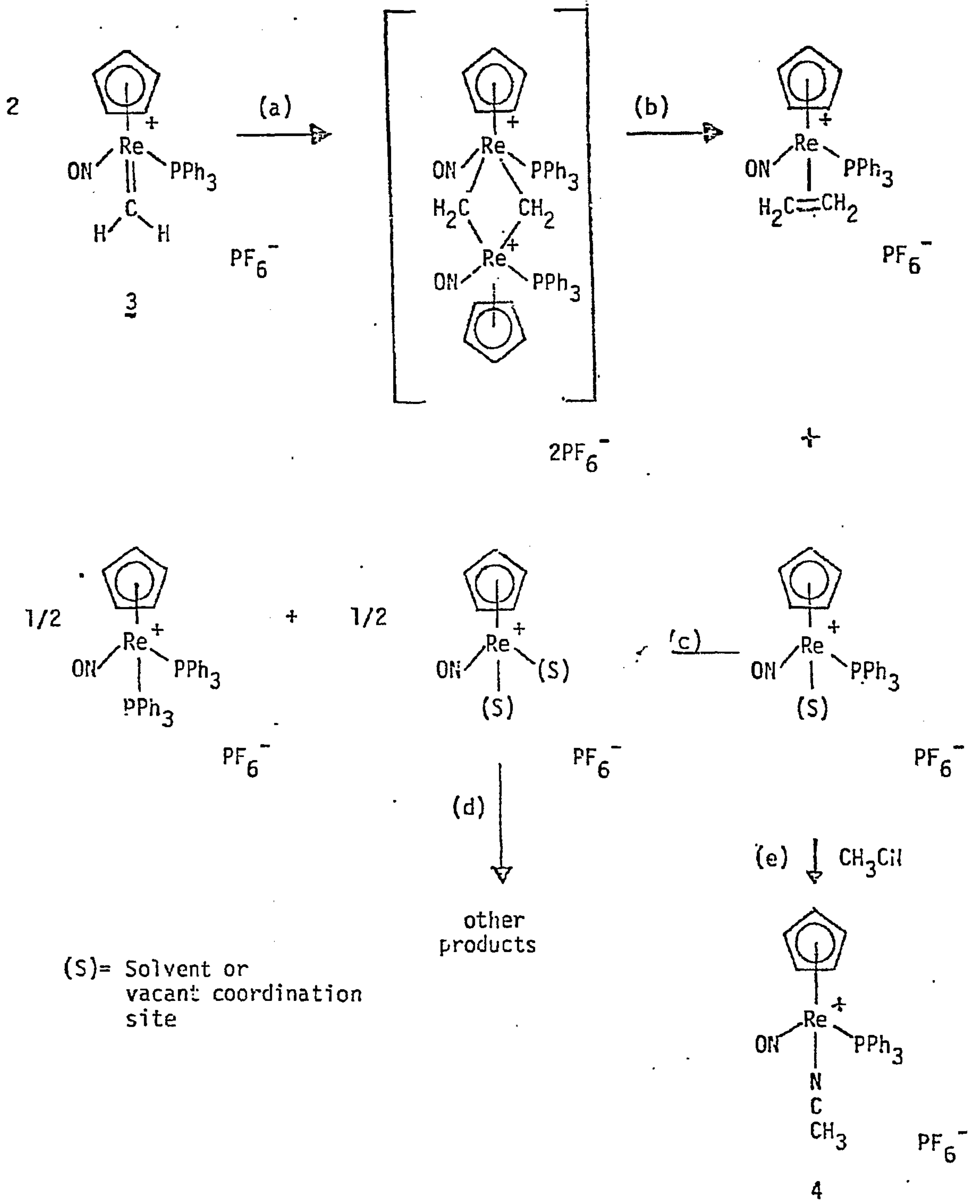
When the reaction shown in eq ii is worked up at -20 °C, methylidene 3 can be isolated in pure form. It is stable as a solid at room temperature. We are studying (among other types of derivatives) adducts of 3 with sulfur compounds, two of which are shown in eq ii.

(ii)



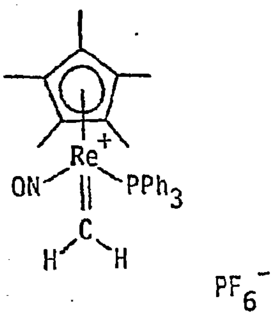
Methylidene **3** decomposes by a mechanism which is second order in **3**. This and other observations have prompted us to propose the decomposition mechanism shown in Scheme II.

Scheme II Proposed Pathway for the Decomposition of 3



(S)= Solvent or vacant coordination site

^1H NMR data requires restricted rotation about the rhenium-methylidene bond. To more precisely define the equilibrium geometry, we have prepared (by analogous synthetic methods) the much more stable pentamethylcyclopentadienyl methylidenes 4 and 5. The $C_5(CH_3)_5$ ligand provides enhanced stability whenever bimolecular decomposition mechanisms are important. Both 4 and 5 are crystalline, but upon X-ray deffraction analysis, 4 was found to be disordered. An X-ray crystal structure of 5 is in progress.



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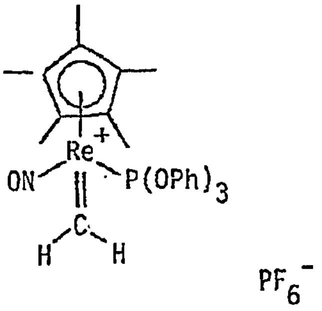

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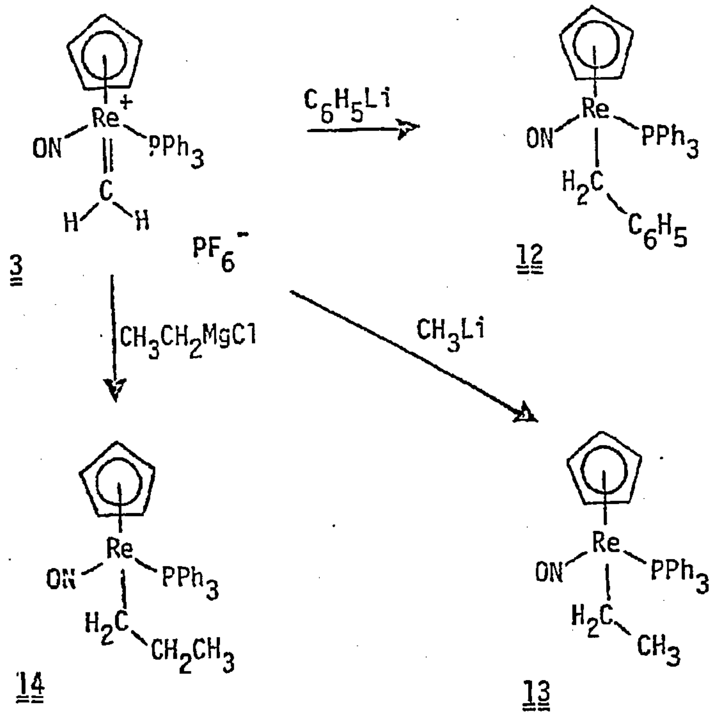
IV. Higher Alkylidene Complexes

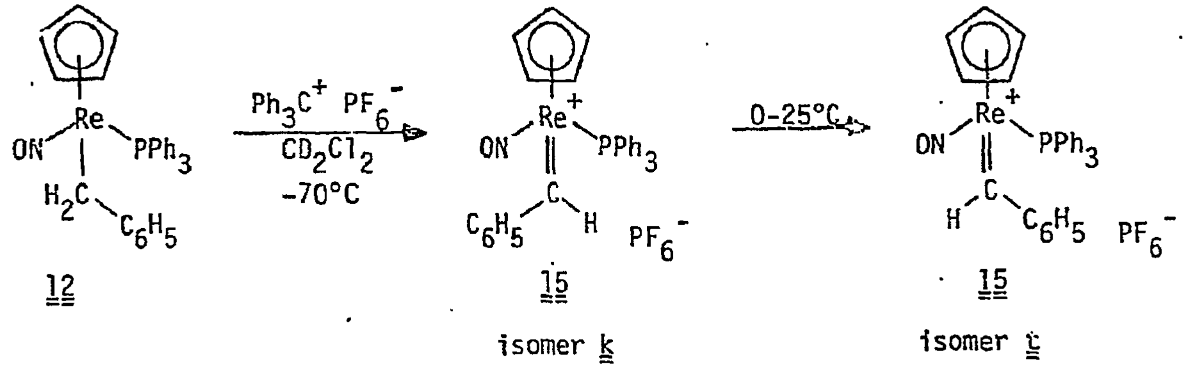
The methylidene complex 3 is an excellent precursor to a variety of rhenium alkyls (eq iv). Unoptimized isolated yields are 60-80%.

(iv)

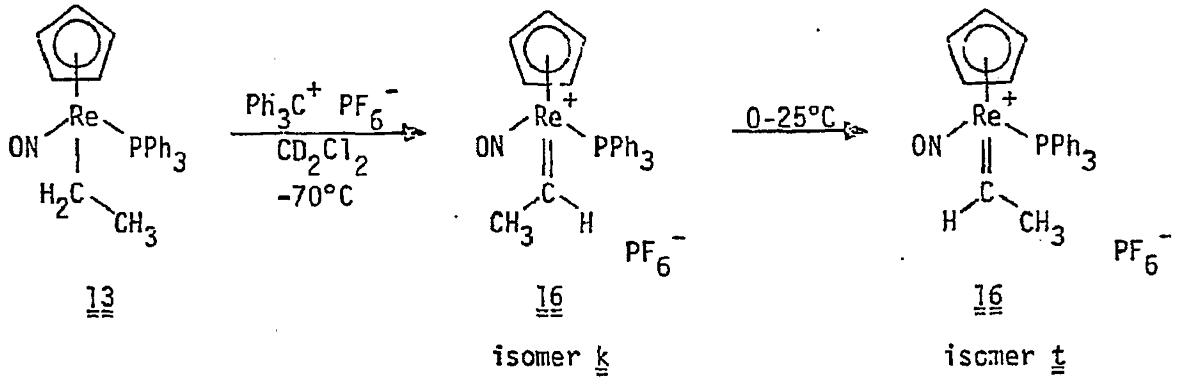


Alkyls 12-14 (eq iv) can be utilized to prepare additional alkylidene complexes (eq v-vii). Importantly, when these reactions are monitored by NMR, the alkylidene complex initially generated at -70 °C (kinetic or "k" isomers) converts to a new alkylidene (thermodynamic or "t" isomers) complex at 0-25 °C. Only in the case of 16k does a detectable amount (≤ 1%) remain at room temperature.

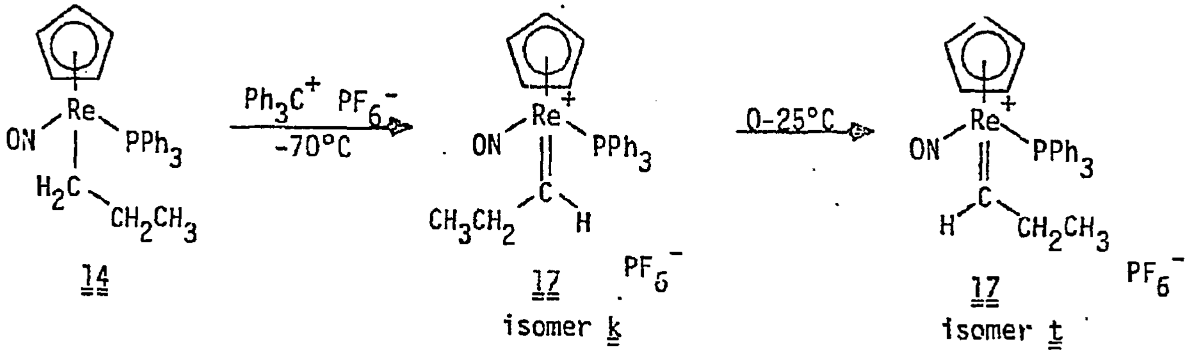
(v)



(vi)

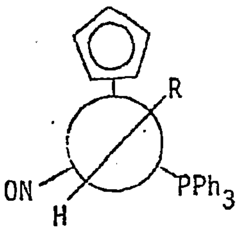


(vii)



In the above reactions, it is believed that restricted rotation about the rhenium alkylidene bond gives rise to simple geometric isomers. As would be expected, reaction of either 15k or 15t with the hydride nucleophile $Li(C_2H_5)_3BH$ affords 12.

Extrapolating from the probable structure of the methylidene 3, orientations I and II are the most likely candidates for these geometric isomers. Space filling models indicate I to be considerably more congested than II. Furthermore, extended Hückel MO calculations by Hoffman and co-workers indicate II to be of lower energy. Recently, we completed an X-ray crystal structure of 15t; the ORTEP plot in Figure 1 shows that the benzylidephenyl eclipses the NO ligand. Hence, the k and t isomers can be confidently assigned structures II and III, respectively.



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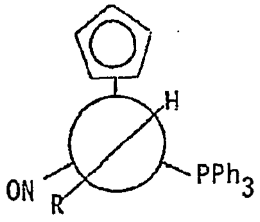
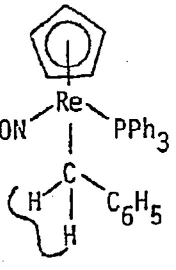


II

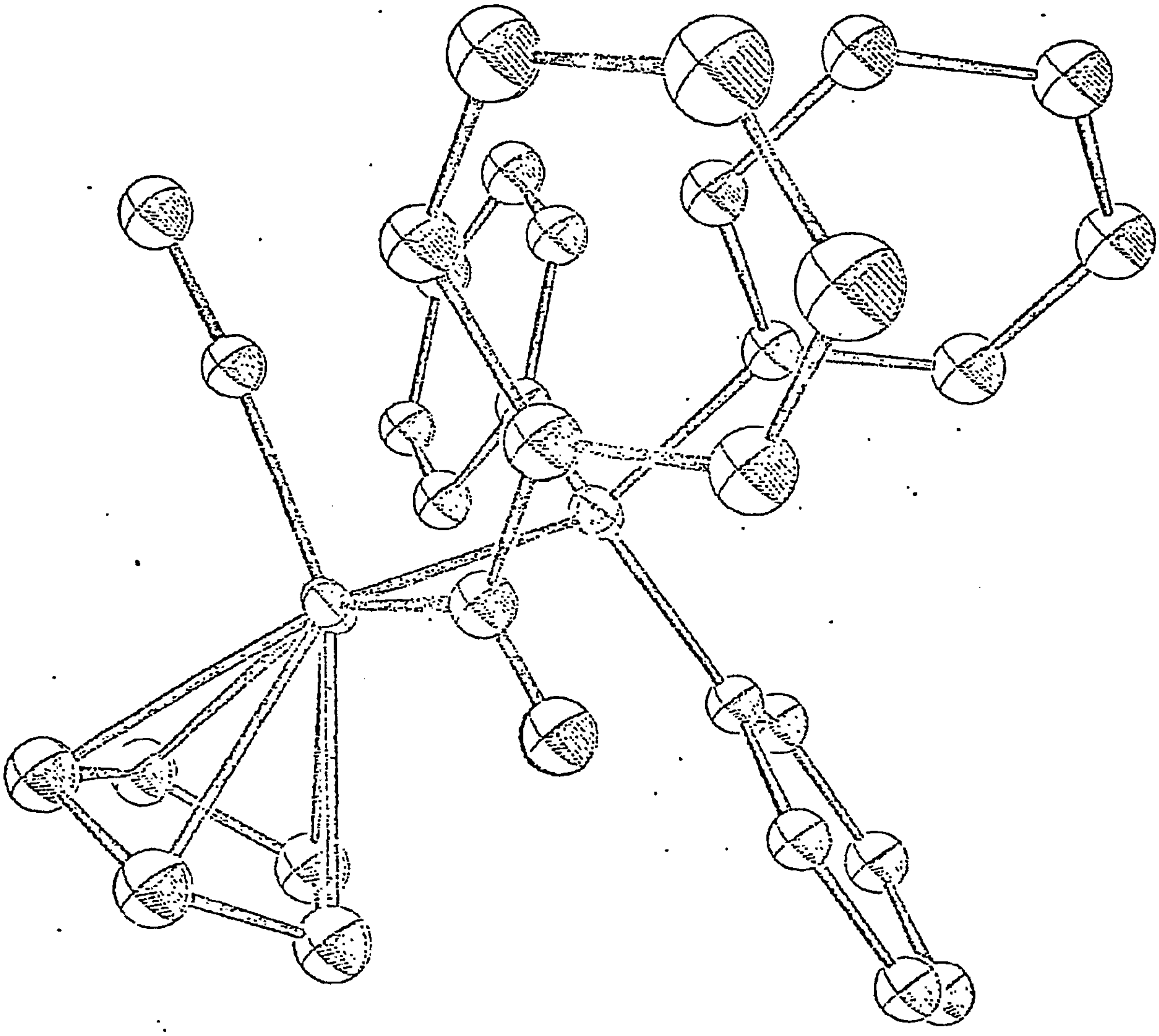
The uniform generation of only *one* alkylidene isomer from 12, 13, and 14 at -70 °C (eq v-vii) suggested to us that $Ph_3C^+ PF_6^-$ abstracts only one of the two available diasterotopic protons:

12



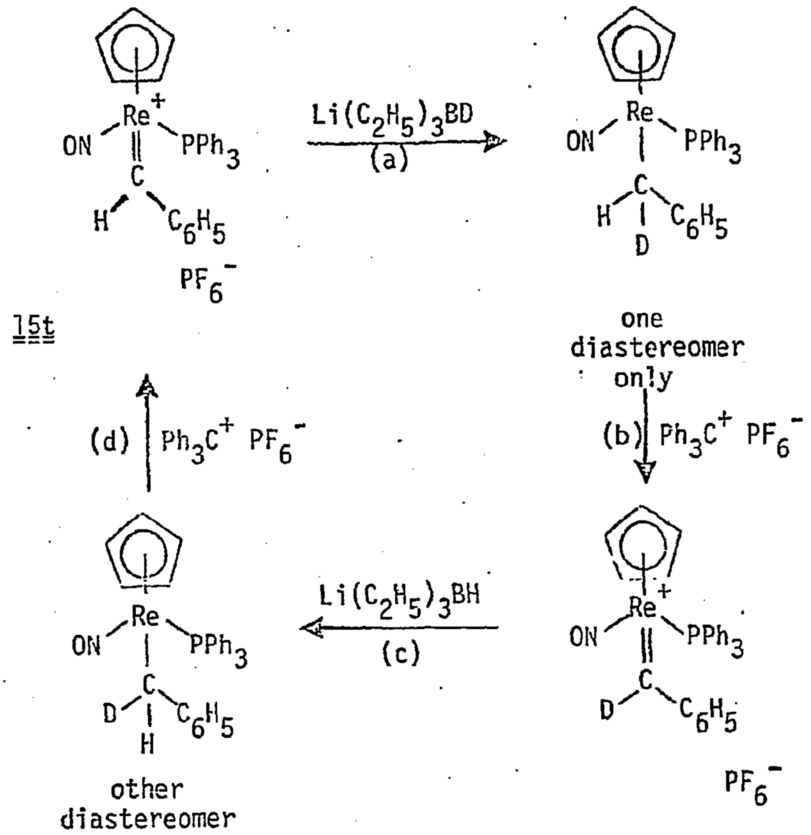
To test this hypothesis, an isotopically labeled alkyl was required. Thus, we reacted 15t with $Li(C_2H_5)_3BD$ to generate 12-α-d_1, a compound with two chiral centers (eq viii, step a). Much to our surprise, the ^1H NMR spectrum of this material indicated one of the two diastereotopic hydrogens normally present in 12 to be completely absent. This result shows that D^- attacks specifically *one face* of the benzylidene ligand (see II).

Figure 1. ORTEP plot of the Benzylidene Complex 15t



When the above 12-α-d_1 was reacted with $Ph_3C^+ PF_6^-$, 15k-d_1 and then 15t-d_1 were formed exclusively (eq viii, step b). Ph_3CH was isolated and contained Ph_3CD at natural abundance level. This result (subject to the control step d below) indicates that only one of the two diastereotopic α-hydrides of 12 is prone to abstraction by $Ph_3C^+ PF_6^-$.

(viii)

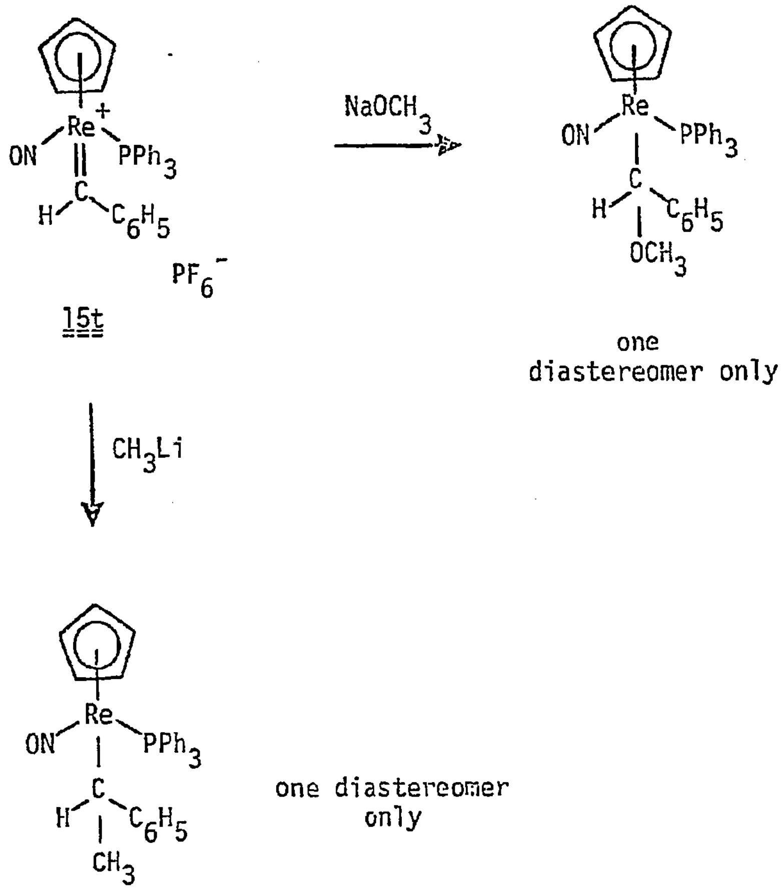


When 15t-d_1 was reacted with $Li(C_2H_5)_3BH$, 12-α-d_1 was again obtained, but with the absolute configuration opposite the isomer described above (eq viii, step c). When 15k (undeuterated kinetic isomer) was prepared *in situ* and treated with $Li(C_2H_5)_3BD$, this diastereomer was also the predominant one formed (92:8 ratio). Thus 15t and 15k undergo preferred nucleophilic attack on the same benzylidene face.

When the 12-α-d_1 prepared in step c (eq viii) was treated with $Ph_3C^+ PF_6^-$, a *ca.* 94:6 ratio of 15t-d_0 to 15t-d_1 was generated (eq viii, step d). The slight breakdown of stereospecificity in the final step is probably due to a kinetic isotope effect which partially counteracts the intrinsic stereospecificity.

These observations indicate an impressive degree of control by a chiral metal center upon the development of ligand based stereochemistry. We have observed related stereospecificity with other nucleophiles, as shown in eq ix. Thus important extensions of this work into asymmetric synthesis are anticipated (publications A-8, B-5).

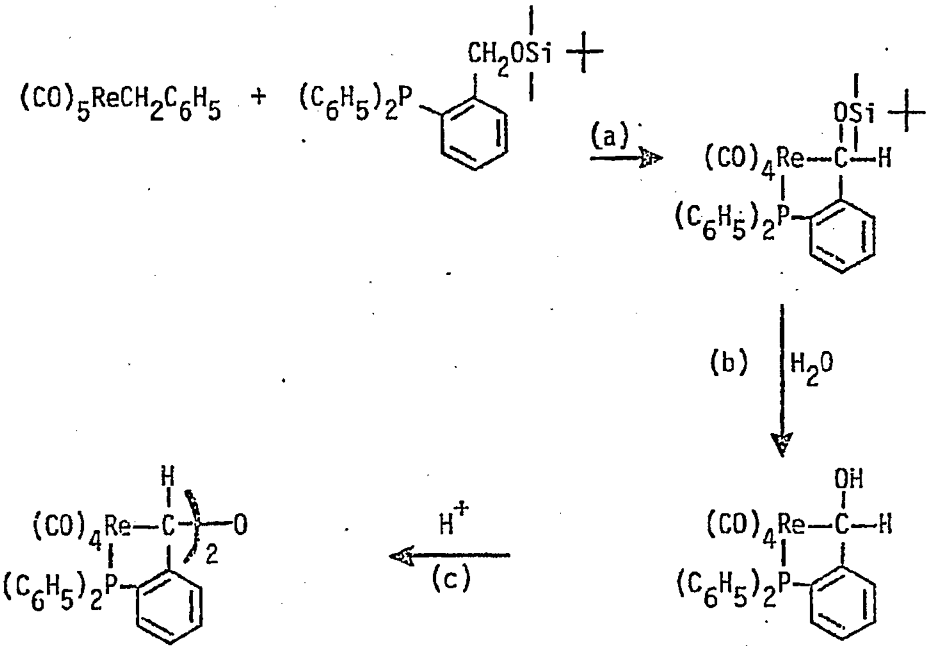
(ix)



V. Hydroxyalkyl Complexes

In very recent work, we have developed a novel and unprecedented "orthometalation" route to the rhenium α-hydroxyalkyl complex 18 (eq x). Step a (eq x) proceeds in 68% yield and constructs all key bonds. Subsequent aqueous protodesilylation affords α-hydroxyalkyl 18. We believe that 18 is stabilized by chelation, and are just starting to examine its properties. It undergoes facile dimerization to an ether, (step c).

(x)



18

Numerous attempts to prepare the hydroxyalkyl $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2OH)$ have been unsuccessful.

VII. Cumulative List of Publications Arising from this Project

(A) In Print:

(1) "α-Silyloxy and α-Hydroxy Manganese Alkyls; Generation Via a New Five-Membered Metallocycle," J.A. Gladysz, J.C. Selover, and C.E. Strouse, J. Am. Chem. Soc., 100, 6766 (1978).

(2) "Neutral Metal Formyl Complexes: Generation, Reactivity, and Models for Fischer-Tropsch Catalyst Intermediates," W. Tam, W.K. Wong, and J.A. Gladysz, J. Am. Chem. Soc., 101, 1589 (1979).

(3) "Trialkylborohydrides: Applications in Organometallic Synthese," J.A. Gladysz, Aldrichimica Acta, 12, 13 (1979).

(4) "Simplified in situ Syntheses of Anhydrous $HMn(CO)_5$", J.A. Gladysz, W. Tam, G.M. Williams, D.L. Johnson, D.W. Parker, Inorg. Chem., 18, 1163 (1979).

(5) "Molecular Structure and Chemical Transformations of the Neutral Metal Formyl $(\eta\text{-}C_5H_5)Re(PPh_3)(NO)(CHO)$," W.-K Wong, W. Tam, C.E. Strouse, and J.A. Gladysz, J. Chem. Soc., Chem. Commun., 530 (1979).

(6) "Electrophile Induced Disproportionation of the Neutral Formyl $(\eta\text{-}C_5H_5)\text{-}Re(PPh_3)(NO)(CHO)$; Generation of Cationic Rhenium Carbenes of the formula $[(\eta\text{-}C_5H_5)Re(PPh_3)(NO)(CHX)]^+$ ($X = H, OCH_3, OH$), W.K. Wong, W. Tam, and J.A. Gladysz, J. Am. Chem. Soc., 101, 5440 (1979).

(7) "Reactions of Benzaldehyde with Trialkylsilyl Metal Carbonyl Complexes," D.L. Johnson and J.A. Gladysz, J. Am. Chem. Soc., 101, 6433 (1979).

(8) "Substitution Mechanisms at Metal Carbonyl Centers; Conversion of $Ph_3P(CO)_4ReBr$ to $Ph_3P(CO)_4ReCH_3$ via an Anionic Acyl Intermediate," D.W. Parker, M.M. Marsi, and J.A. Gladysz, J. Organomet. Chem., 194, C1-C4 (1980).

(9) "Unprecedented Regiospecificity and Stereospecificity in Reactions of $Ph_3C^+PF_6^-$ with Rhenium Alkyls of the Formula $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2R)$," W.A. Kiel, G.-Y. Lin, and J.A. Gladysz, J. Amer. Chem. Soc., 102, 3299-3301 (1980).

(B) In Press:

(1) "Stereospecific and Chemospecific Interconversions of the Rhenium Alkylidene $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHC_6H_5)]^+ PF_6^-$ and the Rhenium Alkyl $(\eta\text{-}C_5H_5)\text{-}Re(NO)(PPh_3)(CH(OCH_3)C_6H_5)$," A.G. Constable and J.A. Gladysz, J. Organomet. Chem., in press.

(2) "Mononuclear Anionic Formyl Complexes; Synthesis and Properties," J.C. Selover, M. Marsi, D.W. Parker, and J.A. Gladysz, J. Organomet. Chem., in press.

(3) "Electrophile Induced Disproportionation of the Neutral Formyl (η-C_5H_5-Re(NO)(PPh_3)(CHO); Isolation and Properties of the Rhenium Methylidene [(η-C_5H_5)Re(NO)(PPh_3)(CH_2)]$^+$ PF_6^-," J.A. Gladysz, W.A. Kiel, G.-Y. Lin, W.-K Wong, and W. Tam, ACS Adv. Chem. Ser., in press.

(C) Submitted:

(1) "Isolation and Decomposition Chemistry of the Electrophilic Methylidene Complex [(η-C_5H_5)Re(NO)(PPh_3)(CH_2)]$^+$ PF_6^-," G.-Y. Lin, W.A. Kiel, and J.A. Gladysz, submitted to J. Organomet. Chem.

(2) "Reactions of $(CO)_5MnSi(CH_3)_3$ with Organic Carbonyl Compounds," D.L. Johnson and J.A. Gladysz, submitted to J. Amer. Chem. Soc.

VIII. Staffing

In addition to the principal investigator, the following co-workers were affiliated (in whole or in part) with this project during the past budget period.

(a) post-doctoral

1. Dr. Gong-Yu Lin
2. Dr. Anthony Constable

(b) pre-doctoral

1. Mr. Dennis Johnson
2. Mr. George Vaughn
3. Mr. William Kiel
4. Mr. Alan Patton
5. Ms. Marianne Marsi

IX. Other Accomplishments

(a) Student Dissertations

"Generation, Isolation, and Chemistry of Anionic and Neutral Transition Metal Formyl Complexes," by Wilson Tam, submitted September 1979 for the Ph.D. in Chemistry.

(b) Public Lectures Presented on this Research

1. University of California, Irvine, California, "Rhenium Formyl and Carbene Complexes: Some New and Unprecedented Organometallic Reactions, October 1, 1979.

2. Argonne National Laboratories, Argonne, Illinois, "Rhenium Formyl and Carbene Complexes: Some New and Unprecedented Organometallic Reactions," October 23, 1979.

3. University of Illinois, Urbana, Illinois, "Rhenium Formyl and Carbene Complexes: Some New and Unprecedented Organometallic Reactions," October 24, 1979.

4. Ohio State University, Columbus, Ohio, "Rhenium Formyl and Carbene Complexes: Some New and Unprecedented Organometallic Reactions," October 25, 1979.

5. Union Carbide Corporation, South Charleston, West Virginia, "Rhenium Formyl and Carbene Complexes: Some New and Unprecedented Organometallic Reactions", October 26, 1979.

6. University of California, Los Angeles, California, "Rhenium Formyl and Carbene Complexes: Some New and Unprecedented Organometallic Reactions," November 8, 1979.

7. Shell Development Company, Houston, Texas, "Rhenium Formyl and Carbene Complexes: Some New and Unprecedented Organometallic Reactions," January 29, 1980.

8. Rice University, Houston, Texas, "Rhenium Formyl and Carbene Complexes: Some New and Unprecedented Organometallic Reactions," January 30, 1980.

9. University of Southern California, Los Angeles, California, "Rhenium Formyl and Carbene Complexes: Some New and Unprecedented Organometallic Reactions," February 28, 1980.

10. Mobil Research and Development Laboratories, Edison, New Jersey, "Model Fischer-Tropsch Chemistry; some New and Unprecedented Transformations of Metal-Formyl and Metal-Alkylidene Complexes", March 3, 1980.

11. Massachusetts Institute of Technology, Cambridge, Massachusetts, "Rhenium Formyl and Carbene Complexes: Some New and Unprecedented Organometallic Reactions," March 5, 1980.

12. State University of New York, Buffalo, New York, "Rhenium Formyl and Carbene Complexes: Some New and Unprecedented Organometallic Reactions," March 6, 1980.

13. Allied Chemical Company, Buffalo, New York, "Rhenium Formyl and Carbene Complexes: Some New and Unprecedented Organometallic Reactions," March 7, 1980.

14. California Institute of Technology, Pasadena, California, "Rhenium Carbene and Formyl Complexes: Unprecedented New Reactions with Applications in Asymmetric Synthesis", May 8, 1980.

15. Raychem Corporation, Menlo Park, California, "Rhenium Formyl and Carbene Complexes: Some New and Unprecedented Organometallic Reactions," May 29, 1980.

16. University of California, Berkeley, California, "Rhenium Formyl and Carbene Complexes: Some New and Unprecedented Organometallic Reactions," May 30, 1980.

17. Occidental Research Corporation, Irvine, California, "Reactions of Rhenium Formyl and Carbene Complexes: Model Reactions for the Fischer Tropsch Process," June 19, 1980.

18. University of Pennsylvania, Philadelphia, Pennsylvania, "Rhenium Carbene and Formyl Complexes: Unprecedented New Reactions with Applications in Asymmetric Synthesis," September 8, 1980.

19. Rohm & Haas Corporation, Spring House, Pennsylvania, "Model Fischer-Tropsch Chemistry; some New and Unprecedented Transformations of Metal-Formyl and Metal-Alkylidene Complexes," September 9, 1980.

20. Union Carbide Corporation, Bound Brook, New Jersey, "Model Fischer-Tropsch Chemistry; some New and Unprecedented Transformations of Metal-Formyl and Metal-Alkylidene Complexes," September 10, 1980.

21. University of Rochester, Rochester, New York, "Rhenium Carbene and Formyl Complexes: Unprecedented New Reactions with Applications in Asymmetric Synthesis," September 12, 1980.

22. Cornell University, Ithaca, New York, "Rhenium Carbene and Formyl Complexes: Unprecedented New Reactions with Applications in Asymmetric Synthesis," September 15, 1980.

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