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**BIMETALLIC PROMOTION OF COOPERATIVE HYDROGEN TRANSFER AND
HETEROATOM REMOVAL IN COAL LIQUEFACTION**

**Final Technical Report on the Project for the Period September 1, 1988–
December 31, 1991**

**By
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FINAL TECHNICAL REPORT ON THE PROJECT

***"Bimetallic Promotion of Cooperative Hydrogen Transfer and
Heteroatom Removal in Coal Liquefaction"***

**U.S. Department of Energy Grant DE-FG22-88PC88930
for the period
September 1, 1988 through December 31, 1991**

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I. ABSTRACT of the Research Performed on the Topic, *"Bimetallic Promotion of Cooperative Hydrogen Transfer and Heteroatom Removal in Coal Liquefaction"*

The ultimate objective of this research has been to uncover novel reagents and experimental conditions for heteroatom removal and hydrogen transfer processes, which would be applicable to the liquefaction of coal under low-severity conditions. To this end, one phase of this research has investigated the cleavage of carbon-heteroatom bonds involving sulfur, oxygen, nitrogen and halogen by subvalent transition-metal complexes. A second phase of the study has assessed the capability of the same transition-metal complexes or of organoaluminum Lewis acids to catalyze the cleavage of carbon-hydrogen bonds in aromatics and hence to promote hydrogen shuttling. Finally, a third phase of our work has uncovered a remarkable synergistic effect of combinations of transition metals with organoaluminum Lewis acids on hydrogen shuttling between aromatics and hydroaromatics. From such studies the following accomplishments can be cited: 1) the stoichiometric or catalytic cleavage of C-H, C-Al, C-O, C-X, C=O, C=S and C≡N bonds by nickel(0) complexes; 2) the catalyzed transfer of hydrogen between aromatics and hydroaromatics either by nickel(0) complexes or by aluminum Lewis acids; 3) the observation of a novel synergistic catalysis of hydrogen transfer between aromatics and hydroaromatics, as brought about by combinations of nickel(0) complexes and organoaluminum Lewis acids; and 4) the observation of a novel desulfurization effected through a Lewis-acid catalyzed hydrogen transfer. In future work, these findings will be brought to bear on designing new catalysts for coal liquefaction.

II. INTRODUCTION TO THE RESEARCH PROBLEM

A. Problems Encountered in Coal Liquefaction.

1. Hydrogen Transfer. In the process of liquefying coal, the aromatic and partially hydrogenated aromatic rings of benzene and naphthalene types must be cleaved apart and nitrogen-, oxygen- and sulfur-containing heterocycles must be hydrogenated.¹ These processes require either that hydrogen already in coal be shuttled from one bonding site to another, or that hydrogen be added from an external source. External hydrogen can be introduced as hydrogen gas or as partially hydrogenated aromatic solvents that act as hydrogen donors.² Both such hydrogen-shuttling and hydrogen-donation processes require elevated temperatures. If the temperature and contact time required are too high, then charring and coke-formation will be favored, thus working against the liquefaction processes.³

Therefore, new or improved methods of coal liquefaction would result if the following modifications could be uncovered:⁴

- a. Ways to increase the efficiency of hydrogen utilization without generating excessive gaseous products;
- b. Avoidance of overhydrogenation of hydrogen-donor solvents used in liquefaction;
- c. Superior catalysts, effective at lower temperatures, for hydrogen shuttling or hydrogen donation to molecular units present in coal; and
- d. Avoidance of high temperatures and long reaction times for the processes required for the hydrogenolysis of carbon-carbon bonds.

From a standpoint of the underlying organic chemistry, therefore, finding improved liquefaction processes demands that we find new catalysts for making and breaking C-C and C-H bonds under milder conditions.

2. Heteroatom Removal. Not only must C-C and C-H bonds be broken in coal liquefaction processes, but organically bonded sulfur, nitrogen and, if practical, oxygen should be removed during the liquefaction process. The presence of the former two elements in the final liquid fuel will cause the generation of oxides of sulfur and of nitrogen during combustion and hence the pollution of the environment.⁵ Although the presence of organooxygen components in the liquid fuel poses no environmental problem, in the form of phenols or phenolic ethers such components can foster aromatic-ring condensation reactions in the early stages of liquefaction and thus produce coke solids that are difficult to liquefy. The overall result is then inefficient liquefaction.⁶

3. Challenge. Therefore, a major practical problem in coal research is discovering new, efficient ways of cleaving C-H, C-C, C-S, C-N and C-O bonds in both coal and its conversion products, so as to maximize the conversion to coal liquids and to minimize the atmospheric or process pollution caused by sulfur or nitrogen oxides, sulfides, mercaptans and amines in coal-derived fuels and chemicals. The intelligent approach to this practical problem raises, in its turn, theoretical questions: What types of C-C bonds are present in coal and how are organic nitrogen, sulfur and oxygen bonded in native coal? Information on how these atoms are actually bonded to the basic carbon skeletons is extremely valuable,⁷ both for developing geochemical theories on the origin of fossil fuels and for guiding the organic chemist in choosing suitable processes for the degradation of coal and the purification of the products.

Since the existing procedures for heteroatom removal generally require elevated temperatures, high pressures of hydrogen and the use of heterogeneous catalysts, such methods are unsuitable for the mild, controlled, stepwise degradation of coal required for coal structural studies. At the same time, such severe processes are not the most efficient or economical for the practical purification of coal-derived fuels and chemicals.

By replacing certain heterogeneous transition-metal catalysts by homogeneous or polymer-bonded catalysts, many important reactions, such as hydrogenation, unsaturated-hydrocarbon oligomerization and hydroformylation, shows significant gains in rate or selectivity.⁸ Therefore, it is appealing to consider whether the catalytic scission of carbon-carbon-, carbon-sulfur, carbon-nitrogen and carbon-oxygen bonds might be achievable at much lower temperatures and pressures by the use of soluble transition metal catalysts. Such mild conditions might mean a saving of time, energy and equipment expenses for industrial processes used in purifying coal-derived fuels and chemicals. In addition, homogeneous agents capable of cleaving covalent bonds at low temperatures could be valuable in selectively degrading the macrostructure of various coals themselves into fragments suitable for structural studies.

B. Objectives and Selected Approach of the Present Study

1. Origin of this Investigation. Previous DOE-supported research in the principal investigator's Laboratory had established that the cleavage of C-C, C-H, C-S, C-O and C-N bonds can be effected in the temperature range of 25-50°C, either in a stoichiometric or a catalytic manner, as the following reactions (eqs. 1 - 5) illustrate:

In most recent DOE-sponsored studies we have now found that strong Lewis acids, such as MeAlCl₂, can similarly promote both hydrogen transfer (eq. 6) and the cleavage of some carbon-heteroatom bonds (eq. 7):

In addition, we have discovered that combinations of the transition metal catalyst

(e.g., $(\text{Cod})_2\text{Ni}$) and the Lewis acid exert a pronounced synergistic or cocatalytic effect on the rate of such hydrogen transfer reactions¹⁶ (eqs. 8 - 9):

This exciting discovery of the cocatalytic action of Lewis acids and low-valent transition metal complexes on hydrogen transfer has important implications for coal liquefaction. If one can understand, on a molecular basis, the mechanisms both for the individual catalytic action of a transition metal complex or a Lewis acid, as well as the mechanism for the cocatalytic action of the two components, one would be in an excellent position to undertake the rational design of novel coal liquefaction catalysts. For this reason, we have been encouraged to pursue the following objectives:

2. Specific Objectives. a. Previous DOE-supported research in this author's Laboratory has uncovered novel nickel(0) and cobalt(I) reagents that desulfurize dibenzothiophene, a common constituent of coal tar, in a homogeneous medium at temperatures below 100°C . Although the molecular basis for such desulfurizations is now reasonably well-understood,^{11, 17} the scope and mechanisms for analogous C-O and C-N cleavages remain unclear. Accordingly, the first objective of this proposed research was to uncover more powerful transition metal reductants for cleaving oxygen- and nitrogen-carbon bonds. From our recent results, we judge that the following are the most promising: 1) $(\text{Cod})_2\text{Ni} + i\text{-Bu}_3\text{Al}$; 2) $(\text{Cod})(\text{C}_8\text{H}_{13})\text{Co} + \text{LiAlH}_4$; and 3) $\text{Ti}(\text{BH}_4)_2$. Accompanying this study of their stoichiometric utility in cleaving C-O and

C-N bonds will be a scrutiny of their reaction mechanisms.

b. The second objective was a continued study of the scope and mechanisms whereby Lewis acids, unaided by transition metals, promote the transfer of hydrogen (eq. 6) or the cleavage of carbon-sulfur bonds (eq. 7). The mechanisms of these reactions (which are also promoted by strong Brønsted acids) remain obscure and their scope of application to cleaving C-O and C-N bonds is yet to be ascertained. Such a fundamental mechanistic understanding of this acid catalysis must be achieved before novel catalysts for coal liquefaction can be designed intelligently.

c. With the firm understanding of how transition metal catalysts and Lewis acid catalysts function individually in such hydrogen-transfer processes, we hoped then to be in a superior position to attack our third objective, the scope of application and the mechanism of action of combined transition metal and Lewis acid catalysts on the rate of hydrogen transfer. A thorough understanding of this synergistic effect we judge to be the key to devising novel hydrogen-transfer catalysts suitable for upgrading coal liquids and for liquefying coal under low-severity conditions.

C. Relevance to the Nation's Energy Needs

Since the proposed research seeks to develop new transition metal and Lewis acid catalysts that will cleave C-C, C-H, C-S, C-N and C-O bonds in homogeneous media under mild conditions, the findings of this work would have a clear and broad relevance to the utilization of fossil fuels. Any liquid fuels derived from coal could be made environmentally more acceptable by processes based upon such studies.

D. Possibility of Applications or Technology Transfer

The proposed research has the very high possibility of influencing future modes of

upgrading coal-derived fuels and chemicals. We base such confidence on the undeniably effective technology transfer that occurred in the area of homogeneous hydrogenation catalysis. The basic work of Nobel laureate, Geoffrey Wilkinson, on soluble rhodium catalysts was put into superb industrial practice by William Knowles of Monsanto for the synthesis of naturally occurring amino acids, such as L-dopa.¹⁸

E. Relevance to the Mission of the Department of Energy

The development of novel processes for both heteroatom removal and hydrogen transfer would seem to lie squarely within the mission of the Department of Energy. Indeed, in a review of government energy research, a committee headed by Sol Buchsbaum of Bell Laboratories stressed the need for basic research on fossil fuels and observed that "an industry of ancient origins" was devoting almost no effort to refining the final product.¹⁹ Clearly, an expanded role for coal in the fuel and raw material industries demands greater development of efficient purification procedures for coal liquids.

To our knowledge, no other research group in either industrial or academic research centers is working on the kinds of soluble hydrogen-transfer or heteroatom-removal agents we have developed. We are aware of the efforts of several groups, in the United States (Exxon), the Soviet Union (S.P. Gubin) and Canada (H. Alper), that are evaluating metal carbonyls for desulfurization.²⁰ Professor Alper has been studying the action of metal carbonyls supported on silica (a heterogeneous system).²¹

F. Past and Ongoing Efforts in the Field of Liquefaction

1. Heterogeneous Desulfurization and Denitrogenation. Various heterogeneous catalysts based on iron, cobalt, tin, molybdenum, tungsten or nickel have been used for the primary hydrogenation of coal or of middle oil.²² As the first stage in such reactions, most of the sulfur-containing components undergo dehydrosulfurization.²³ Apparently the

corresponding metals and metal sulfides are the active components for the rupture of carbon-sulfur linkages. A huge number of other catalytic mixtures has been suggested for heteroatom removal; the following patents are only illustrative: Ni, Fe, Co or Mo on Al_2O_3 at 400° for the desulfurization of thiophene;¹⁴ Mo-Ni or Co-Ni mixtures for treating light crude oils;²⁵ NiS + Mn, Cr, Cu or Zn for crude oils;²⁶ and W-Mo or Co-Ni for residual oils.²⁷ All these are high-temperature heterogeneous processes.

In addition, alkali metals, such as sodium,^{28,29} potassium,^{30,31} and lithium,^{32,33} are known to cleave carbon-sulfur linkages in heterocycles and coal-like products. Raney nickel, either activated (previously treated with base and having adsorbed hydrogen) or unactivated, is known to effect the desulfurization of various organic compounds, but its mode of action is not clearly understood.³⁴ But in all the foregoing cases, the desulfurizing reagent is present as a heterogeneous phase.

2. Homogeneous Desulfurization and Denitrogenation. Twenty years ago, this investigator demonstrated the superiority of solubilized lithium reagents over heterogeneous lithium metal in cleaving carbon-sulfur and carbon-nitrogen bonds in dibenzothiophene and in triphenylamine, respectively.³⁵ Thus, the yield of the dilithio salt II was 50% when the reaction was conducted with a lithium metal dispersion in warm tetrahydrofuran:³² (eq. 10)

On the other hand, when the blue-green, THF-soluble 2:1 lithium adduct of biphenyl (III) was employed, the cleavage proceeded rapidly at 0° to yield at least an 84% yield of derivative II.³⁵ In recent work,¹¹ we have found a similar effect with nickel-promoted

carbon-sulfur bond cleavages of dibenzothiophene. Thus, although dibenzothiophene is inert towards various soluble nickel(0) complexes, such as bis(1,5-cyclooctadiene) nickel(0) (IV) and tetrakis(triphenylphosphine)nickel(0), warming this heterocycle in tetrahydrofuran solution with a 1:1 mixture of IV and 2,2'-bipyridyl leads to extensive desulfurization. The active desulfurizing agent has been shown to be V,^{11,17} (eq. 11):

Interaction of V with dibenzothiophene (I) and hydrolytic workup leads to biphenyl (VI) and hydrogen sulfide (eq. 12):

This nickel(0)-promoted desulfurization is remarkable in that it occurs under mild conditions in a homogeneous phase (at least initially, before nickel sulfide is deposited) and in the absence of molecular hydrogen.

3. Catalyzed Hydrogen Transfer. In addition to continuing our studies of heteroatom removal from heterocycles by transition metal complexes, our most DOE grant has been concerned with hydrogen-transfer catalysis. Two of our pivotal findings are the nickel(0)-catalyzed transfer of hydrogen between two molecules of 1,4-cyclohexadiene to produce benzene and cyclohexene (*cf. supra*, eqs. 8 - 9), and the MeAlCl_2 -catalyzed hydrogen transfer occurring between 9,10-dihydroanthracene and 1,1-diphenylethylene (eq. 6). In the nickel(0)-catalyzed process it has been shown the hydrogen donation by the dihydroaromatic decreases in the series, 1,4-dihydrobenzene > 1,4-dihydronaphthalene >

9,10-dihydroanthracene = 4,5-dihdropyrene. The most significant finding to have emerged from our current DOE grant is the discovery of the synergistic or cocatalytic effect of nickel(0) complexes combined with organoaluminum Lewis acids on hydrogen transfer in homogeneous media.

These synergistic hydrogen transfers bear a significant relationship to the hydrocarbon isomerizations by combinations of transition metal and superacid catalysts, currently under study by Wender and co-workers.³⁶

III. METHODOLOGY OF THE INVESTIGATION

A. Rationale for the Selected Approach

Previous DOE-sponsored research has demonstrated that well-defined transition metal complexes of nickel, cobalt, titanium, molybdenum and zirconium can reductively cleave C-C, C-H, C-S, C-N and C-O bonds in organic compounds similar in structure to components found in coal and coal liquids.³⁷ In fact, these same complexes have been shown capable of reducing the sulfur and nitrogen content of SRC coal liquids.³⁸ The cleavage of C-H bonds by these transition-metal complexes is particularly noteworthy, for this reaction is central to hydrogen-donation or hydrogen-shuttling occurring between partially hydrogenated aromatic and fully aromatic subunits in coal and recycle solvents used in liquefaction. If such hydrogen transfer could be catalyzed, then both coal liquefaction and heteroatom removal could be effected under milder reaction conditions. Such milder conditions would minimize coke formation and thus avoid inefficient liquefaction and would lead to far more economical processes.

A second significant finding of our previous research is that organoaluminum Lewis acids and hydrides greatly enhance the hydrogen transfer and heteroatom-removal activity of these transition metal catalysts.¹⁴ Hence, we wished to investigate the synergistic action of such cocatalysts on bond cleavage reactions in model compounds, in comminuted coals

and in SRC coal liquids.

B. Design of Experiments

1. Mechanism of Catalytic Action. Although we now have a solid understanding on the molecular level of how 2,2'-bipyridyl(1,5-cyclooctadiene)nickel and its combination with LiAlH_4 desulfurize dibenzothiophene and other aryl sulfides, we must understand the mechanisms of the following processes: a) the denitrogenation of carbazoles (eq. 5) by combinations of nickel or titanium complexes with lithium or LiAlH_4 ,¹³ b) the deoxygenation of phenols by combinations of titanium complexed with LiBH_4 ,³⁹ c) the cleavage of C-C bonds by nickel complexes and LiAlH_4 ,⁹ and d) the cleavage of C-H bonds and hydrogen transfer catalyzed by nickel complexes and RAlCl_2 .¹⁰ By conducting such studies in a careful manner, we should learn how to optimize the synergistic action of these cocatalytic reagents for use in coal liquefaction and coal liquid upgrading.

These mechanistic studies aimed at the promoted cleavage of C-C, C-H, C-O and C-N bonds were conducted with the following model compounds, whose test C-E bond is similar to the types of linkages holding together the principal subunits in coal itself (VI - XI):

2. Attaching Heteroatom-Removal and Hydrogen-Transfer Agents to Solid

Supports. After their mode of reaction in homogeneous media is understood, combinations of such subvalent transition metal complexes and aluminum reagents were to be deposited on solid supports of the metal oxide (Al_2O_3 , SiO_2) or organic polymer type (P). The technique involves a slurry of the solid support in a toluene solution of the transition metal salt and desired ligands (L). The aluminum alkyl or hydride is then added to generate the low-valent transition metal as a deposit on the support (eq. 13):

The resulting supported agent would then be slurried with SRC liquids (or vacuum gas oil) or SRC liquids would be percolated through a heated bed of this solid reagent, to test the heteroatom-removal activity of such reagents.

After such supported heteroatom removal agents are developed, regeneration of the spent sulfided or nitrified columns while purging them with dry HCl or a similar procedure should remove the sulfur as H_2S and the nitride as NH_4^+ . Although "aged" NiS does not react readily with acids, we have found that the NiS formed in these processes does react promptly with HCl.

3. Partially Hydrogenated Aromatics as Hydrogen Sources for Heteroatom-Removal and for Catalyzed Coal Liquefaction. After we have perfected new, potent heteroatom-removal and hydrogen-transfer agents, which are effective under 100°C and in a stoichiometric manner, we would strive to make the reactions catalytic. Such a transition-metal catalytic process will require a hydrogen source, in order to reduce the metal sulfide, nitride or oxide formed during the reaction. This hydrogen source could be hydrogen gas, a metal hydride or a hydrogen donor, such as a hydroaromatic compound.

Because hydrogen gas requires pressure equipment and metal hydrides are expensive, hydroaromatics would have the greatest appeal. Now in our studies of nickel(0)

desulfurization we have observed that carbon-sulfur bonds are cleaved with much of the resulting carbon-hydrogen bonds being formed from the solvent S(R'H) (eq. 14):

Under suitable conditions, such hydrogen-donation could lead to a catalytic process. We therefore planned to examine whether hydroaromatics can furnish the requisite hydrogen for the desulfurization of thiophenes, if bimetallic catalysts of the $\text{Ni}^0\text{-AlCl}_3$ or $\text{Co}^I\text{-AlCl}_3$ type are employed.

4. Hydrogen Shuttling and Heteroatom Removal with Comminuted Coals. Based upon our success with model compounds and SRC liquids, we then intended to study the activity of such bimetallic catalysts on slurries of comminuted coal types in hydrogen-donor solvents (SCTL), such as tetralin, 9,10-dihydroanthracene, 9,10-dihydrophenanthrene or similar media. We have obtained samples of six different coals from the PETC and we shall conduct such trials under nitrogen with high-speed stirring at the reflux temperature of the donor solvent. Solubilized coal will be analyzed for S, N and O and the efficacy of the solubilization noted as a function of temperature, catalyst and solvent.

C. Sequence of Experimental Studies

1. We have completed our studies of the scope, intermediates, activation by amines and experimental variations for the desulfurization of aromatic sulfur compound by the well-defined bipyridyl-(1,5-cyclooctadiene)nickel(0) reagent. We have made much progress with the powerful desulfurizing reagent obtained by combining V with lithium aluminum hydride. Therefore, we now wished to extend such studies with nickel(0)-desulfurizations to denitrogenation and deoxygenation reactions as well.

2. Understanding gleaned from nickel(0)-hydride reagents would be applied to analogous reagents produced from cobalt, iron, molybdenum and titanium complexes in combination with lithium aluminum hydride or aluminum alkyls. Such parallel studies

might lead to the discovery of even more potent stoichiometric heteroatom-removal agents, or to agents that remove heteroatoms smoothly and catalytically in transition metal.

3. In a parallel effort, a systematic exploration of ways of attaching subvalent nickel, cobalt or titanium to solid supports was to be explored. We believe that the key to a practical heteroatom-removal procedure is to devise a column through which the coal liquids can simply be percolated. Regeneration of such supported reagents was also examined.

4. The insights gained from points 1 and 2 guided our modifications of heteroatom-removal agents to be attached to solid supports, so as to develop superior, economical and convenient processes for purifying coal liquids.

5. In tandem with the foregoing, studies of hydrogen-shuttling, as catalyzed by transition metals, were undertaken, both to find a catalytic process for heteroatom removal (S or N) and to learn if coal liquefaction(SCTL) can be catalyzed by transition metals. From our present DOE research, we already know that nickel(0) and certain Lewis acids cocatalyze such shuttling (eqs. 6 and 7) and we are eager to pursue this exciting observation.

D. Anticipated Findings and Logical Extensions

In our previous DOE-sponsored research we have uncovered two types of nickel(0) desulfurizing agents. After we had defined their structure, it was most appropriate to determine the scope and limitations of their desulfurizing activity as stoichiometric reagents toward coal liquids. Analogous extrapolations with nickel or other transition metals to other heteroatom-removal or hydrogen-transfer then became appropriate. After we then maximized their activity by varying their ligands and solvents, it was then logical to try to regenerate nickel(0) or other low-valent transition-metal complexes in situ by using hydrogen sources to make the process catalytic. Finally, it is appealing to learn whether hydrogen-transfer and heteroatom-removal processes can be made cooperative.

E. Anticipated Problems and Measures for Their Resolution.

The significant hurdles foreseen in this research are: a) attaching low-valent metals to a solid support without greatly reducing their heteroatom-removal activity; b) regenerating "spent" columns in practical ways; c) finding conditions for a catalytic process; and d) finding suitable experimental conditions for hydrogen shuttling compound under mild conditions.

F. Anticipated Implications for Future Coal Liquefaction

If this research were successful, the implications for coal liquefaction and upgrading coal liquids are manifest. Would SRC or similar coal liquids show a marked decrease in sulfur and/or nitrogen simply by percolation through a solid-phase reagent below 100°C, this would be most valuable. Use of such purified liquids for fuel would be very desirable from an environmental standpoint. Moreover, such a purification process would be economically attractive, since no pressure equipment or higher temperature would be required. Finally, acceleration of hydrogen shuttling from hydroaromatics to coal would enhance the efficiency, and lessen the severity of coal liquefaction processes.

IV. RESULTS

A. Introduction

Our investigation aimed at developing bimetallic catalysts for coal liquefaction falls naturally into two parts: 1) finding novel transition agents for cleaving carbon-heteroatom bonds, such as C-H, C-S, C-N and C-O linkages; and 2) identifying hydrogen-transfer catalysts that will promote the hydrogen-shuttling necessary to cleave both C-C, C-H and C-E bonds (E = heteroatom) in coal depolymerization. Once individual metallic agents for each of these functions had been developed, the search then turned to identifying a rate-enhancing synergism on such covalent bond cleavages by combining the reagents into

a bimetallic combination. For example, the hydrogen transfer whereby 1,4-cyclohexadiene disproportionates into benzene and cyclohexene (eq. 2) is catalyzed by bis(1,5-cyclooctadiene)-nickel and the simultaneous presence of methylaluminum dichloride markedly accelerates the reaction (eq. 15):

B. Transition Metal-Promoted Covalent Bond Scission

Preliminary model studies on the cleavage of the C-S bond in dibenzothiophene by transition metal compounds ($L_nM_t^x$, where M_t = transition metal, L = ligand and x = oxidation state) demonstrated that a variety of low-valent metals, such as Ti, Mo, Fe, Co and Ni, could effect desulfurization (eq. 16), with or without a supplemental hydrogen source:¹¹

However, the most efficacious metal complexes for this purpose were those of nickel(0) and cobalt(I); these therefore received our prime attention in continuing cleavage studies.

Having probed the cleavage of C-S,¹⁷ C-O¹² and C-N¹³ bonds in previous work, we now concentrated on cleaving C=S, C=O and C≡N bonds. We entertained hopes of generating some unusual transition metal intermediates through such efforts. These mechanistic insights were expected to give us a better control of heteroatom removal in coal liquefaction.

1. Scission of the thiocarbonyl group. As our test substrate we chose thiobenzophenone (XII) and as the metal complex, bis (1,5-cyclooctadiene)-nickel (IV). from their interaction in THF the principal product isolated was tetraphenylethylene (XIII) and the minor product (~5%) was episulfide XIV (eq. 17):

Analogous to the behavior of thioketone XII, dichlorodiphenylmethane (XV) reacts readily with $(\text{Cod})_2\text{Ni}$ in THF to form tetraphenylethylene (XIII) (eq. 18):

In both of these coupling reactions, which involve $\text{C} \cdots \text{E}$ bond cleavages, we hypothesized that a nickel-carbene intermediate XVI is generated (eq. 19):

The coupling would then ensue thus (eq. 20):

Two approaches have been undertaken to obtain evidence supporting the formation of nickel-carbenes like XVI. First, thioketone XII has been treated with 2 equivalents of (Cod)₂Ni at lower temperatures in the presence of 2,2-bipyridyl, with the hope that a stabilized complex of XVI, namely XVIII, could be isolated (eq. 21):

Thus far, we have separated nickel sulfide from an unknown purple solid, whose structure we hope to prove as being XVII.

Second, we sought to trap nickel-carbene XVI through a cycloaddition reaction similar to that proposed in eq. 20 as leading to XVII. In this case, however, we employed benzaldehyde by adding it to a 1 : 2 mixture of XII and IV in which the nickel-carbene was thought to have been generated (cf. eq 21). Hydrolytic work-up of the reaction mixture led to the isolation of a good yield of 1,2,3,3-tetraphenyl-1-propanone XIX. As depicted in Scheme I, this product can be considered as the result of trapping the nickel-carbene XVI with two equivalents of benzaldehyde.

SCHEME I

From these results, therefore, it is most probable that nickel-carbenes are intermediates in these desulfurizations. If we are able to verify that the purple solid generated in eq. 21 has the suggested structure XVIII, the matter will be beyond doubt.

2. Scission of the carbonyl group. Our studies on the cleavage of the C=O bond in aldehydes and ketones are only in their preliminary stages. Although it is already apparent from Scheme I that aldehydes react readily with nickel-carbene intermediates, their reaction with nickel(0) complexes is not yet clear. The reaction of benzophenone (XX) with (Cod)₂Ni in THF leads to the development of red color but subsequent hydrolysis yields only starting ketone. On the other hand, such colored solution give a strong ESR signal, consistent with a reversible single-electron transfer (SET) (eq. 22):

Further studies will attempt to drive such reactions to the right with the complete scission of the C-O bond.

3. Scission of the nitrile group. Although the denitrogenation of nitriles by the reductive scission of the C≡N might seem unlikely, such was found to be the case. The interaction of benzonitrile (XXI) and (Cod)₂Ni in THF, followed by hydrolysis, led to a 20% yield of benzyl phenyl ketone (XXII, eq. 23):

This remarkable outcome piqued our curiosity about what unusual nickel intermediates might be involved in this transformation. Conducting the reaction of benzonitrile with (Cod)₂Ni or (Et₃P)₄Ni for different lengths of time led to other products, in addition to XXII, namely benzaldehyde (XXIII), benzamide (XXIV) and 2,4,6-triphenyltriazine (XXV):

A further observation is worthy of noting: The initial admixture of the yellow solution of 1 : 1 benzonitrile- $(\text{Cod})_2\text{Ni}$ leads to the formation of a bright-red precipitate XXVI, whose hydrolysis produces benzaldehyde. This observation can mean that the red adduct is a 1 : 1 interaction of XXI and nickel, namely 3-phenylnickelaazirine (XXVI, eq. 24):

In light of these experimental data, we began to discern a similarity between nitriles and acetylenes as to their manner of interacting with nickel(0) complexes. Accordingly, the following scheme was proposed (Scheme II) : 1) a 1 : 1 adduct of nitrile and Ni(0) is formed (cf. eq. 24); 2) adduct XXVI could add a second nitrile in either of two ways, forming a 1,2-diazacyclobutadiene-nickel(0) complex (XXVII) or 1,3-diazacyclobutadiene-nickel(0) complex (XXVIII); 3) complex XXVIII could isomerize to the 2,4-diazanickelole XXIX and complex XXVII could isomerize to the 2,3-diazanickelole XXX; 4) 2,4-diazanickelole XXIX could undergo a Diels-Alder reaction with a third nitrile to produce the triazine XXV after extrusion of nickel(0); and 5) the 2,3-diazanickelole XXX could be too stable to react with a third nitrile and would persist till hydrolysis to ketone XXII.

SCHEME II

Finally, the origin in this scheme of the benzamide obtained upon hydrolysis would be the persistence of some of the 1,3-diazacyclobutadiene-nickel complex (XXVIII). Hydrolysis of this ligand would produce benzamide (eq. 25):

More work remains to be done to understand such C≡N scissions fully but it is evident that the mechanisms involved are of unusual interest.

4. Scission of carbon-hydrogen bonds. Our studies on the transition metal-mediated C-H bond cleavages were conducted through the model reaction of the disproportionation of dihydroaromatics into aromatics and tetrahydroaromatics (eq. 26):

The pertinence of this reaction to the catalysis of the hydrogen shuttling involved in coal liquefaction should be immediately apparent. Although our results in this area have already been published elsewhere,¹⁰ a summary of our findings is included here for the sake of completeness.

a. *Dihydroaromatic compounds with nickel(0) complexes.* The following dihydroaromatic compounds were treated with nickel(0) complexes, either in stoichiometric or in catalytic amounts: 1,4-dihydrobenzene; 1,2-dihydrobenzene; 1,4-dihydronaphthalene; 1,2p-dihydronaphthalene; and 9,10-dihydroanthracene. 1,4-Dihydrobenzene and an equimolar amount of bis(1,5-cyclooctadiene)nickel in THF at 50°C gave a quantitative conversion after 24 h to a 63/37 mixture of benzene and cyclohexene. In addition, 26% of the hydrogen from 1,4-dihydrobenzene had been transferred to 1,5-cyclooctadiene to produce cyclooctene (eq. 27):

Although such a disproportionation in THF is 35% complete in 3 h at 50°C, a similar reaction performed in toluene is 100% complete after 3 h at 25°C. Use of other nickel(O) complexes, such as 2,2'-bipyridyl(1,5-cyclooctadiene)nickel-(XXXII) and tetrakis(triethylphosphine)nickel-(XXVIII), proved to be markedly less effective in promoting disproportionation of XXXI: at 25°C little or no disproportionation occurred over several hours; at 50°C both XXXII and XXXIII caused about 35% of disproportionation over 3 h. Catalytic amounts of IV, XXXII and XXXIII (5 molar-%), however, caused almost complete disproportionation of XXXI (eq. 27) after 24 h at 50°C.

In an analogous manner, heating 1,2-dihydrobenzene (XXXIV) with an equimolar amount of (Cod)₂Ni (IV) for 24 h in THF or in toluene gave a quantitative conversion to benzene and cyclohexene, together with some cyclooctene from the 1,5-cyclooctadiene (eq. 28):

By contrast with the behavior of XXXI, however, the interaction of XXXIV with (Cod)₂Ni in toluene after 3 h at 25°C gave no benzene; only a 36% conversion of XXXIV to cyclohexene was observed. Hence, the 1,2-dihydrobenzene was distinctly less reactive than the 1,4-isomer. This result suggests that XXXIV simply formed a π -complex XXXV, which underwent protodenickelation and thus 1,4-reduction (eq. 29):

Again, Bpy(Cod)Ni was less reactive: heating 1/1 mixtures of XXXIV and XXXII at 50°C for 24 h yielded only 20% of benzene.

With the isomeric dihydronaphthalenes, both showed a comparable tendency to undergo disproportionation when heated at 50° C in toluene with an equimolar amount of (Cod)₂Ni. After 24 h the 1,4-isomer had formed 45% of tetralin (XXXVII) and 55% of naphthalene (XXXVI); the 1,2-isomer gave 47% of XXXVI and 53% of XXXVII. The conversion of these dihydronaphthalenes was approximately 75%. Thus, the dihydronaphthalenes were much less reactive than dihydrobenzenes (eq. 30).

All attempts to induce disproportionation with 9,10-dihydroanthracene (XXXVIII) with even the most effective nickel reagent, (Cod)₂Ni met with uniform failure. However, modest amounts of hydrogen transfer from XXXVIII to *trans*-stilbene (10%) were observed (eq. 31).

Finally, the cocatalytic action of certain aluminum compounds on the catalytic activity of (Cod)₂Ni in the disproportionation of 1,4-dihydrobenzene (XXXI) (eq. 27) was noted: 5 molar-% of IV caused the conversion of 7% of XXXI at 25° C after 75 min. When 5 molar-% of Me₃Al was also added, the conversion rose to 11%. But if instead 5 molar-% of MeAlCl₂ was introduced, the conversion climbed sharply to 54%.

In this disproportionation reaction the order of catalytic activity of the nickel(0) catalysts employed was the following: (Cod)₂Ni > (Bpy)(Cod)Ni >> (Et₃P)₄Ni.

A second aspect of carbon-hydrogen bond scission studied during this project was

the nickel-catalyzed transfer of aluminum hydride from aluminum alkyls to olefins and acetylenes, a process related to and important for hydrogen shuttling in coal liquefaction. Again, these results have been published elsewhere already¹⁰ and are merely summarized here.

b. *Uncatalyzed and nickel-catalyzed hydroalumination and aluminum-hydride transfer to alkynes.* Extensive rate studies of hydroalumination have already been carried out.⁴⁰ The purpose in this study was simply to obtain an estimate of the magnitude of nickel-catalyzed hydroaluminations. For this purpose, the rate of uncatalyzed hydroalumination of 1-phenylpropyne (XXXIX) by (i-Bu₂)AlH was determined in the temperature range of 25 to 40° C. The plot of the logarithm of the rate constant versus 1/T yielded a straight line with a correlation coefficient of 0.9957. The measured rates at 25°C and at 40°C were 8.50 x 10⁻⁵ and 4.87 x 10⁻⁴ min⁻¹. (Table 1)

TABLE 1.

Initial rates for the uncatalyzed and the nickel-catalyzed additions of diisobutylaluminum hydride to 1-phenylpropyne

	Temperature (°C)	Initial rate (min ⁻¹)
Uncatalyzed addition	24.9	8.50 x 10 ⁻⁵
	30.4	15.0 x 10 ⁻⁵
	34.8	30.5 x 10 ⁻⁵
	40.0	48.7 x 10 ⁻⁵
Nickel-catalyzed addition	0.25	131.0 x 10 ⁻⁵
	40.0 ^a	51000 10 ⁻⁵

^a Estimated by multiplying the rate at 0° C by 2.5⁴.

In the nickel-catalyzed reaction the starting concentrations of the 1-phenylpropyne and the (i-Bu₂AlH) were the same as in the uncatalyzed reaction. The only difference was the inclusion of 1.5 molar-% of nickel(II) acetylacetonate. However, the catalysis was so pronounced that rate measurements had to be made at 0.25°C. The initial rate was still very high, $131.0 \times 10^{-5} \text{ min}^{-1}$, but the rate did not show stable behavior. It decreased quickly and appeared to approach an asymptotic limiting value of $28 \times 10^{-4} \text{ min}^{-1}$ after 150 min. The final rate was still higher than that of the uncatalyzed reaction (Table 1).

The product of the uncatalyzed reaction was exclusively *cis*-β-methylstyrene (XL). The regioselectivity of the (i-Bu₂AlH) addition, XLI and XLII, was determined by a deuteriolytic work-up with D₂O and an examination of the extent of vinyl-deuteration of XL by ¹H NMR spectroscopy.. Such an analysis revealed an 82/18 proportion of XLI/XLII.

In the nickel-catalyzed reaction, *cis*-β-methylstyrene was also the major product (66%), but now it was accompanied by 22% of n-propylbenzene (XLIII) and 6% of (E,E-2,3-dimethyl-1,4-diphenyl-1,3-butadiene (XLIV). An analogous work-up with D₂O and ¹H NMR analysis of XL showed that in the reaction a 56/44 proportion of XLI/XLII was formed (Scheme III).

Relative rates of uncatalyzed and nickel-catalyzed aluminum-hydride transfers between 1/1 mixtures of diphenylacetylene (XLV) and triisobutylaluminum were similarly measured. At 70° C after 3 h only about 50% of the XLV had been hydroaluminated to *cis*-stilbene (XLVI) in the absence of any nickel catalyst. In the presence of 0.2 molar-% of Ni(acac)₂, 50% of XLV had reacted in 10 min and all of XLV was consumed in 60 min. In the catalyzed reaction, small amounts of *trans*-stilbene (XLVII) and (E,E)-1,2,3,4-tetraphenyl-1,3-butadiene (XLVIII) (3-6%) were also formed (Scheme IV).

SCHEME III

SCHEME IV

C. Lewis Acid-Catalyzed Hydrogen Transfer.

Again, in our search for the Lewis acid catalysis of hydrogen transfer, we have relied on model systems and have studied in detail the interaction of 1,1-diphenylethylene (XLIX) with 9,10-dihydroanthracene (L) as catalyzed by methylaluminum dichloride. A summary of our findings, which have been published elsewhere,¹⁴ is given below.

In our search for hydrogen-shuttling catalysts with model aromatic compounds, we have observed a remarkably facile transfer of hydrogen between aromatic and hydroaromatic hydrocarbons that is catalyzed by Lewis acids. For example, admixing equimolar amounts of 1,1-diphenylethylene (XLIX) and 9,10-dihydroanthracene (L) with 10 mol % of AlCl_3 or MeAlCl_2 in toluene solution at 25°C leads to almost a complete conversion to 1,1-diphenylethane (LI) and anthracene (LII) within 15 min (eq. 32).

Similarly catalyzed hydrogen transfers have been observed between 1,1-diphenylethene and 9,10-dihydrophenanthrene 1,1-diphenylethene, and 4,5-dihdropyrene, α -methylstyrene and 9,10-dihydroanthracene, and mesitylene and 9,10-dihydroanthracene. In addition, MeAlCl_2 promoted the disproportionative hydrogen transfer of 1,4-dihydrobenzene into cyclohexene and benzene and of 1,4-dihydronaphthalene into tetralin and naphthalene.

That these hydrogen transfers are actually catalyzed by the Lewis acid and not by adventitious source of protons, such as HCl possibly generated from moisture and the aluminum chloride, is clear from the following experimental tests: 1) the reactions were conducted under rigorously anhydrous conditions in an atmosphere of argon; 2) intentional addition of traces of H_2O or HCl did not accelerate but, in fact, retarded the hydrogen transfer somewhat; 3) with MeAlCl_2 as catalyst, the $\text{C}-\text{Al}$ bond would serve as a

scavenger for any protons; finally, 4) heating XLIX and L with anhydrous HCl or p-toluenesulfonic acid (without MeAlCl_2) gave no hydrogen transfer, but only the well-known proton-catalyzed dimerization of XLIX (Scheme V).

SCHEME V

SCHEME VI

Further experimental observations can be adduced to support the proposal that the zwitterionic σ complex LIII, formed from 1 and the aluminum halide, is the catalytic intermediate in these reactions. This complex would initiate hydrogen transfer by hydride abstraction from L to produce aluminate anion and carbenium ion LIV. Proton transfer from LIV to LV would complete the catalytic cycle (Scheme V). First, such a complex can readily explain the observed Lewis acid catalyzed dimerization of XLIX to LVI. Second, if LIII can abstract hydrogen from L, it might also react directly with dihydrogen. Indeed, a 1 : 1 mixture of 1,1-diphenylethene and MeAlCl_2 in toluene slowly absorbed H_2 at 0°C to yield 1,1-diphenylethane. Third, if such a zwitterionic complex were to form with other terminal olefins having aryl substituents α to the $\text{C}=\text{C}$ bond, skeletal rearrangements might be induced. In fact, when 3,3,3-triphenylpropene (LVII) was heated with MeAlCl_2 , the olefin was completely converted into a mixture of 1,1,2-triphenylpropene (LVIII) and 1,1,2-triphenylcyclopropane (LIX). The formation of both products can be nicely accounted for through the well-precedented carbenium ion induced 1,2-phenyl shift to produce LX.

Protodealumination to yield LVIII or union of positively and negatively polarized carbons to generate LIX would be competing modes of consuming LX (Scheme VI).

Alternative mechanistic pathways for these hydrogen transfers, such as radical-cation formation or hydride abstraction by the aluminum chloride, appear less probable on the basis of the following observations. First, the course of the reaction between XLIX and L can be monitored by ^1H NMR spectroscopy without the occurrence of signal broadening, which would be expected if paramagnetic intermediates were involved. Secondly, treatment of L with MeAlCl_2 and hydrolytic workup leads to unchanged L. Were hydride ion abstracted, L should have yielded anthracene.

Ongoing work is attempting to convert such homogeneous Lewis acid catalysts to anchored catalysts of predetermined structure, so that hydrogen transfer can be effected by heterogeneous catalysis in a catalytic-bed reactor.

D. Synergistic Hydrogen Transfer-Cocatalysis by Nickel(0) and an Organoaluminum Lewis Acid.

Earlier in this report we mention that we had observed how a combination of bis(1,5-cyclooctadiene)nickel and methylaluminum dichloride accelerated the disproportionation of 1,4-dihydrobenzene into benzene and cyclohexene over the rate caused by $(\text{Cod})_2\text{Ni}$ alone (section B, eqs. 8 - 9). An even more striking example of such synergism by combinations of a nickel complex and an organoaluminum Lewis acid has been observed in the following hydrogen transfer (eq. 33):

Treating 1 : 1 mixtures of L and XLV with one equivalent of $(\text{Cod})_2\text{Ni}$ or one equivalent of $i\text{-Bu}_3\text{Al}$ alone gives little or no hydrogen transfer (maximum of 5%). But admixing one

equivalent each of L, XLV (Cod)₂Ni and i-Bu₃Al in toluene and exposing the solution to light ($\lambda > 300$ nm) gives quantitative hydrogen transfer thus (eq. 34):

These and other mechanistic observations, which are currently under further study, can be interpreted to indicate that nickel(0) undergoes an oxidative addition into at carbon-aluminum sigma-bond and that homolysis of the resulting nickel-carbon bond produces radicals that react in the following manner (Scheme VII):

SCHEME VII

This unique hydrogen-transfer process is worthy of further investigation to determine its scope and applicability to coal liquefaction.

E. Lewis-Acid Catalyzed Hydrogen Transfer with Concomitant Carbon-Sulfur Bond Cleavage.

Since it was established during this project that Lewis acids catalyze hydrogen transfer (section C), we hoped to use such catalysis to cleave carbon-sulfur bonds at the same time. The model system we chose for study was the interaction of dibenzothiophene (I) with 1,4-dihydrobenzene (XXXI) as catalyzed by MeAlCl_2 (eq. 35):

Indeed, such a reaction has led to a 25% yield of biphenyl, with the formation of other, unknown products. Clearly, such a reaction would be of great importance to desulfurization during coal liquefaction since it occurs under mild conditions. This reaction therefore merits additional study, in order to optimize conversion to sulfur-free products.

V. DISCUSSION

A. Overview and Mechanistic Implications of Covalent Bond Cleavages of Nickel(0) Complexes.

As part of this investigation a literature survey of the mechanisms of sigma A-B bond cleavages and pi $\text{A} \equiv \text{B}$ bond cleavages by nickel(0) complexes was conducted and

published as a review.⁴¹ In the present study such cleavages were extended to encompass C-H, C-Al, C-Cl, C=S, C=O and C≡N linkages. As is detailed in the Results section, most of these reactions appear to involve intermediates formed by oxidative addition of Ni⁰ to A-B or A≡B, such as A-Ni-B and $\begin{array}{c} \text{Ni} \\ \diagup \quad \diagdown \\ \text{A} \quad \text{B} \end{array}$. Clearly, the experimental conditions fostering such cleavages are important as guides to achieving heteroatom removal in coal liquefaction.

In contrast to such oxidative additions, which are really a two-electron transfer or nucleophilic attack by Ni⁰ on A-B (eq. 36),

such cleavage reactions may also occur via a single-electron transfer (SET, eq. 37):

The charge separation and the development of positive charge on nickel, in both electron-transfer processes, make the accelerating role of donor solvents, like THF, phosphines and TMEDA, readily understandable. Also, in either process substrate A-B or A≡B must be able to accept electron density from Ni⁰. Such will be especially the case when A or B is an electronegative group, such as C, N, O, S or X.

Two-electron transfers seem to obtain for the interactions of C=C, C=S, C≡N and C≡C bonds with nickel(0); SET reactions, producing free radicals, seem most likely for

cleavages of C=O, C-S, C-X and $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \text{---} \text{C} \end{array}$ bonds.

B. Lewis Acid-Catalyzed Hydrogen Transfer.

In such hydrogen transfers observed in this study the role of the Lewis acid, such as MeAlCl₂, was to form a zwitterionic complex with the hydrogen-accepting molecule, such

as $\text{Ph}_2\text{C}=\text{CH}_2$, and have the resulting complex abstract first a hydride, then a proton, from the hydrogen-donating molecule, such as 9,10-dihydroanthracene (eqs. 38 - 40):

It is evident from our results that such Lewis acid-catalyzed hydrogen shuttling is especially common when partially reduced aromatics, such as dihydro derivatives, are involved. Thus in applications for coal liquefaction this type of catalyst should be used in a hydrogen gas atmosphere, under which such dihydroaromatics could be generated and used as a hydrogen source for catalyzed delivery to other aromatic units in the coal structure. Also, for such coal liquefaction the Lewis acid should be made insoluble, possibly by immobilizing the MeAlCl_2 through attachment to the surface of solid Al_2O_3 .

C. Synergistic Hydrogen Transfer

Our investigations have shown that in homogeneous media hydrogen transfer from a

dihydroaromatic donor to some unsaturated hydrocarbon substrate can individually be catalyzed by either nickel(0) complexes or aluminum Lewis acids. Furthermore, we observed several situations where the combined action of a nickel(0) complex and an organoaluminum compound yield a synergistic acceleration of hydrogen transfer (eqs. 8 - 9 and Scheme VII).

In attempting to apply these insights to coal liquefaction, we foresee the value of preparing modified alumina catalysts, whose surface is impregnated with both a nickel(0) complex and an organoaluminum Lewis acid. In future DOE-sponsored work we intend to prepare and to evaluate of such heterogeneous catalysts for improved hydrogen transfer and more efficient coal liquefaction under milder conditions.

D. Catalyzed Hydrogen Transfer with Concomitant Heteroatom Removal.

In this and previous studies we have shown that the individual action of stoichiometric amounts of either nickel(0) complexes or an aluminum Lewis acid with a hydrogen donor can desulfurize dibenzothiophene (eq. 41):

These observations suggest to us the value of examining the combined action of nickel(0) complexes and aluminum Lewis acids on such desulfurizations. Two possible synergistic effects might be observed: 1) the stoichiometric desulfurization might become catalytic, especially under a hydrogen gas atmosphere; and 2) the rate of desulfurization might be synergistically accelerated. Again, as with our intended further studies on simple hydrogen transfer, we would attempt to prepare heterogeneous catalysts having both components attached to the surface. After successful studies with model systems, such catalysts would then be evaluated for their efficiency in coal liquefaction.

VI. SUMMARY OF ACCOMPLISHMENTS UNDER THIS GRANT

A. Cleavage of Carbon-heteroatom Bonds.

In model studies we have demonstrated that nickel(0) complexes can cleave, stoichiometrically or catalytically, C-H, C-Al, C-O, C-X, C=O, C=S and C≡N bonds.

B. Hydrogen Transfer by Nickel(0) Complexes.

Nickel(0) complexes have been shown to catalyze hydrogen transfer in dihydroaromatics to yield aromatics and tetrahydroaromatics.

C. Hydrogen Transfer by Aluminum Lewis Acids.

Methylaluminum dichloride has been shown to catalyze hydrogen transfer between partially hydrogenated aromatics.

D. Synergistic Catalysis of hydrogen Transfer.

The combined action of nickel(0) complexes and organoaluminum Lewis acids has been shown to accelerate the rate of hydrogen transfer between partially hydrogenated aromatics over that of the individual rates.

E. Desulfurization by Lewis Acids.

Although not yet an efficient or completely understood process, methylaluminum dichloride and a hydrogen donor can convert dibenzothiophene into biphenyl.

VII. SCIENTIFIC PRESENTATIONS

A. Lectures

1. "Stoichiometric and Catalytic Reactions of Nickel(0) Complexes in Organic Synthesis", German Democratic Republic-Poland Colloquy on Organometallic Chemistry, Holzgau, GDR, April 24-29, 1989.
2. "Organometallic Chemistry: Recent Developments in the Reactions of Small Molecules with Nickel(0) Complexes", XIX ACS Northeast Regional Meeting, Albany, N.Y., June 18-21, 1989.
3. "Bimetallic Promotion of Cooperative Hydrogen Transfer and Heteroatom Removal in Coal Liquefaction", DOE University Coal Research Symposium, Pittsburgh, PA, July 10-13, 1989.
4. "Cyclic Organonickel Intermediates in the Controlled Oligomerization of Unsaturated Monomers," XIII International Congress of Heterocyclic Chemistry, Corvallis, OR, August 11-16, 1991.
5. "Bimetallic Promotion of Cooperative Hydrogen Transfer and Heteroatom Removal in Coal Liquefaction", DOE University Coal Research Symposium, Pittsburgh, PA, July 25-27, 1991.

B. Seminars

Research lectures on our DOE research were delivered at the following institutions:

1. Case Western Research University
2. University of Illinois at Chicago
3. Iowa State University
4. Max Planck Institute for Coal Research, Mülheim, Federal Republic of Germany.
5. University of Bayreuth, FRG

6. University of Akron
7. Institute of Metal Compounds, Moscow, USSR.
8. Akzo Research Laboratories, Dobbs Ferry, N.Y.

C. Publications

1. "Molecular Hydrogen and Aluminum Hydride Transfers Mediated by Nickel(0) Complexes: The Intermediacy of Nickel Hydrides in the Ziegler-Nickel Effect", J.J. Eisch, S.R. Sexsmith and K.C. Fichter, J. Organomet. Chem., **382**, 273-293 (1990).
2. "Hydroalumination of C= and C≡C Linkages", J.J. Eisch in Comprehensive Organic Synthesis, B.M. Trost and I. Fleming, Editors, Pergamon Press, Oxford, United Kingdom, Vol. 8, p. 733-762, 1991.
3. "Lewis Acid-Catalyzed Hydrogen Shuttling Between Aromatic and Hydroaromatic Hydrocarbons", J.J. Eisch, S.R. Sexsmith and M. Singh, Energy & Fuels, **3**, 761-762 (1989).
4. "Intermediates and Reaction Mechanisms in the Interaction of Nickel(0) Complexes with Organic Substrates," J.J. Eisch and S.R. Sexsmith, Res. Chem. Intermed., **13**, 149-192 (1990).

VIII RESEARCH PERSONNEL

The following persons were engaged in research on this grant:

<u>Name</u>	<u>Position</u>	<u>Period</u>
A. John J. Eisch	Principal Investigator	9/01/88-12/31/91
B. Mona Singh	Research Assistant	9/01/88-12/31/91
C. Xin Ma	Research Assistant	9/01/89-12/31/91
D. Karen Caldwell	Research Associate	9/01/88-11/30/91

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X. APPENDIX

Reprints of Scientific Publications resulting from this investigation (those currently available): Copies of available reprints forwarded to Dr. Karl T. Schroeder.

- A. "Molecular Hydrogen and Aluminum Hydride Transfers Mediated by Nickel(0) Complexes: The Intermediacy of Nickel Hydrides in the Ziegler-Nickel Effect", J.J. Eisch, S.R. Sexsmith and K.C. Fichter, J. Organomet. Chem., **382**, 273-293 (1990).
- B. "Hydroalumination of C= and C $\equiv$ C Linkages", J.J. Eisch in Comprehensive Organic Synthesis, B.M. Trost and I. Fleming, Editors, Pergamon Press, Oxford, United Kingdom, Vol. 8, p. 733-762, 1991.
- C. "Lewis Acid-Catalyzed Hydrogen Shuttling Between Aromatic and Hydroaromatic Hydrocarbons", J.J. Eisch, S.R. Sexsmith and M. Singh, Energy & Fuels, **3**, 761-762 (1989).
- D. "Intermediates and Reaction Mechanisms in the Interaction of Nickel(0) Complexes with Organic Substrates," J.J. Eisch and S.R. Sexsmith, Res. Chem. Intermed., **13**, 149-192 (1990).

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