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PROJECT TITLE: Bimetallic Promotion of Cooperative Hydrogen Transfer and Heteroatom Removal in Coal Liquefaction

GRANT NO.: DE-FG22-88PC88930

## QUARTERLY SUMMARY

OBJECTIVES: The ultimate objective of this research is to uncover new catalytic processes for the liquefaction of coal and for upgrading coal-derived fuels by removing undesirable organosulfur, organonitrogen and organooxygen constituents. Basic to both the liquefaction of coal and the purification of coal liquids is the transfer of hydrogen from such sources as dihydrogen, metal hydrides or partially reduced aromatic hydrocarbons to the extensive aromatic rings in coal itself or to aromatic sulfides, amines or ethers. Accordingly, this study is exploring how such crucial hydrogen-transfer processes might be catalyzed by soluble, low-valent transition metal complexes and/or Lewis acids under moderate conditions of temperature and pressure. By learning the mechanism whereby  $H_2$ , metal hydrides or partially hydrogenated aromatics do transfer hydrogen to model aromatic compounds, with the aid of homogeneous, bimetallic catalysts, we hope to identify new methods for producing superior fuels from coal.

WORK: During the second quarter of this three-year grant a detailed study of the Lewis-acid catalyzed hydrogen transfer between aromatic and hydroaromatic hydrocarbons was brought to completion. Hydrogen transfer was observed between such acceptors as  $\alpha$ -methylstyrene, mesitylethylene, 1,4-cyclohexadiene and 1,1-diphenylethylene, and such donors as 9,10-dihydroanthracene, 9,10-dihydrophenanthrene and 4,5-dihydropyrene. A parallel study of hydrogen transfer catalyzed by nickel(0) complexes has now been launched and positive results have also emerged. With an eye to future studies on a possible synergistic action of 1:1 Lewis acid-nickel combinations, we have begun the search for coordinative binding between the two components.

ACHIEVEMENTS: The most important observations of this quarter are those supporting the intermediacy of a zwitterionic  $\sigma$ -complex in the hydrogen transfer occurring between 1,1-diphenylethylene and 9,10-dihydroanthracene. The Lewis acid,  $MeAlCl_2$  or  $AlCl_3$ , forms such a complex with 1,1-diphenylethylene and this complex initiates hydrogen transfer by hydride abstraction from 9,10-dihydroanthracene. Evidence for such a complex was adduced by capturing it with dihydrogen or a second mole of diphenylethylene.

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QUARTERLY TECHNICAL PROGRESS REPORT

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PERIOD OF PERFORMANCE: 12/01/88 - 2/28/89

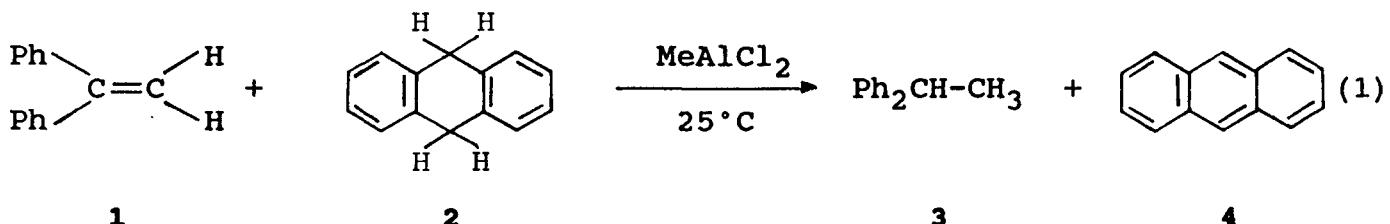
OBJECTIVES: The ultimate objective of this research is to uncover new catalytic processes for the liquefaction of coal and for upgrading coal-derived fuels by removing undesirable organosulfur, organonitrogen and organooxygen constituents. Basic to both the liquefaction of coal and the purification of coal liquids is the transfer of hydrogen from such sources as dihydrogen, metal hydrides or partially reduced aromatic hydrocarbons to the extensive aromatic rings in coal itself or to aromatic sulfides, amines or ethers. Accordingly, this study is exploring how such crucial hydrogen-transfer processes might be catalyzed by soluble, low-valent transition metal complexes and/or Lewis acids under moderate conditions of temperature and pressure. By learning the mechanism whereby  $H_2$ , metal hydrides or partially hydrogenated aromatics do transfer hydrogen to model aromatic compounds, with the aid of homogeneous, bimetallic catalysts, we hope to identify new methods for producing superior fuels from coal.

PRESENT WORK AND ACCOMPLISHMENTS: During the second quarter of this three-year grant we completed, to our satisfaction, sufficient mechanistic work on Lewis acid-catalyzed hydrogen transfer that we have decided to prepare a communication of our results for publication. In essence, we have established that a zwitterionic complex between the hydrogen acceptor and the aluminum halide initiates hydrogen transfer by hydride ion abstraction from the hydrogen donor. The same complex can also promote the addition of hydrogen gas, thus also functioning as a hydrogenation catalyst. The text of our manuscript submitted to Energy & Fuels is as follows:

Within the last decade, direct coal liquefaction in a two-staged, low-severity operation has achieved an improved dissolution of coal and efficient heteroatom removal, reducing the undesired cleavage of carbocyclic units and the overconsumption of hydrogen.<sup>3</sup> As usually conducted, in the first stage hydrogen is transferred thermally from

hydrogen donor solvents to the coal. In the second stage, hydrogen gas is catalytically added to the coal slurry, in order to rehydrogenate the solvent, remove heteroatoms and selectively cleave carbocyclic structures. However, if suitable catalysts could be employed in the first stage for hydrogen shuttling under low-severity conditions,<sup>4</sup> both liquefaction and upgrading of coal liquids might be done even more efficiently. Such mild conditions would minimize the overconsumption of hydrogen gas and the repolymerization of phenolic ring clusters that increases the amount of char.<sup>5</sup>

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-diphenylethene (1) and 9,10-dihydroanthracene (2) with 10 molar % of  $\text{AlCl}_3$  or  $\text{MeAlCl}_2$  in toluene solution at 25°C leads to almost a complete conversion to 1,1-diphenylethane (3) and anthracene within 15 min. (eq. 1):<sup>6</sup>



Similarly catalyzed hydrogen transfers have been observed between 1,1-diphenylethene and 9,10-dihydrophenanthrene, 1,1-diphenylethene and 4,5-dihydriodopyrene,  $\alpha$ -methylstyrene<sup>7</sup> and 9,10-dihydroanthracene, and mesitylethene and 9,10-dihydroanthracene. In addition,  $\text{MeAlCl}_2$  promoted the disproportioanative hydrogen transfer of 1,4-dihydrobenzene into cyclohexene and benzene and of 1,4-dihydronaphthalene into tetralin and naphthalene.<sup>8</sup>

That these hydrogen transfers are actually catalyzed by the Lewis acid and not by adventitious source of protons is clear from the following experimental tests: 1) the reactions were conducted under anhydrous conditions in an atmosphere of argon;<sup>9</sup> 2) intentional addition of traces of  $\text{H}_2\text{O}$  or  $\text{HCl}$  did not accelerate, but in fact retarded the hydrogen transfer somewhat; 3) with  $\text{MeAlCl}_2$  as catalyst, the C-Al bond would serve as a scavenger for any protons; and finally 4) heating 1 and 2 with anhydrous  $\text{HCl}$  or  $p$ -toluenesulfonic acid (without  $\text{MeAlCl}_2$ ) gave no hydrogen transfer, but only the well-known proton-catalyzed dimerization of 1.<sup>10</sup>

Further experimental observations can be adduced to support the proposal that the zwitterionic sigma-complex 5, formed from 1 and the aluminum halide, is the catalytic intermediate in these reactions. This complex would initiate hydrogen transfer by hydride abstraction from 2 to produce aluminate anion 5a and carbenium ion 2a. Proton transfer from 2a to 5a would complete the catalytic cycle (Scheme I). First, such a complex can readily explain the observed Lewis acid-

catalyzed dimerization of **1** to **6**.<sup>11</sup> Secondly, if **5** can abstract hydrogen from **2**, it might also react directly with dihydrogen.<sup>12</sup> Indeed, a 1:1 mixture of 1,1-diphenylethene and  $\text{MeAlCl}_2$  in toluene slowly absorbed  $\text{H}_2$  at  $0^\circ\text{C}$  to yield 1,1-diphenylethane.<sup>13</sup> Thirdly, if such a zwitterionic complex were to form with other terminal olefins having aryl substituents alpha to the C=C bond (**8**), skeletal rearrangements might be induced. In fact, when 3,3,3-triphenylpropene (**7**) was heated with  $\text{MeAlCl}_2$ , the olefin was completely converted into a mixture of 1,1,2-triphenylpropene (**10**) and 1,1,2-triphenylcyclopropane (**11**). The formation of both products can be nicely accounted for through the carbenium ion-induced 1,2-phenyl shift to produce **9**. Protodealumination to yield **10** or union of positively and negatively polarized carbons to generate **11** would be competing modes of consuming **8** (Scheme II).

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.<sup>3</sup>

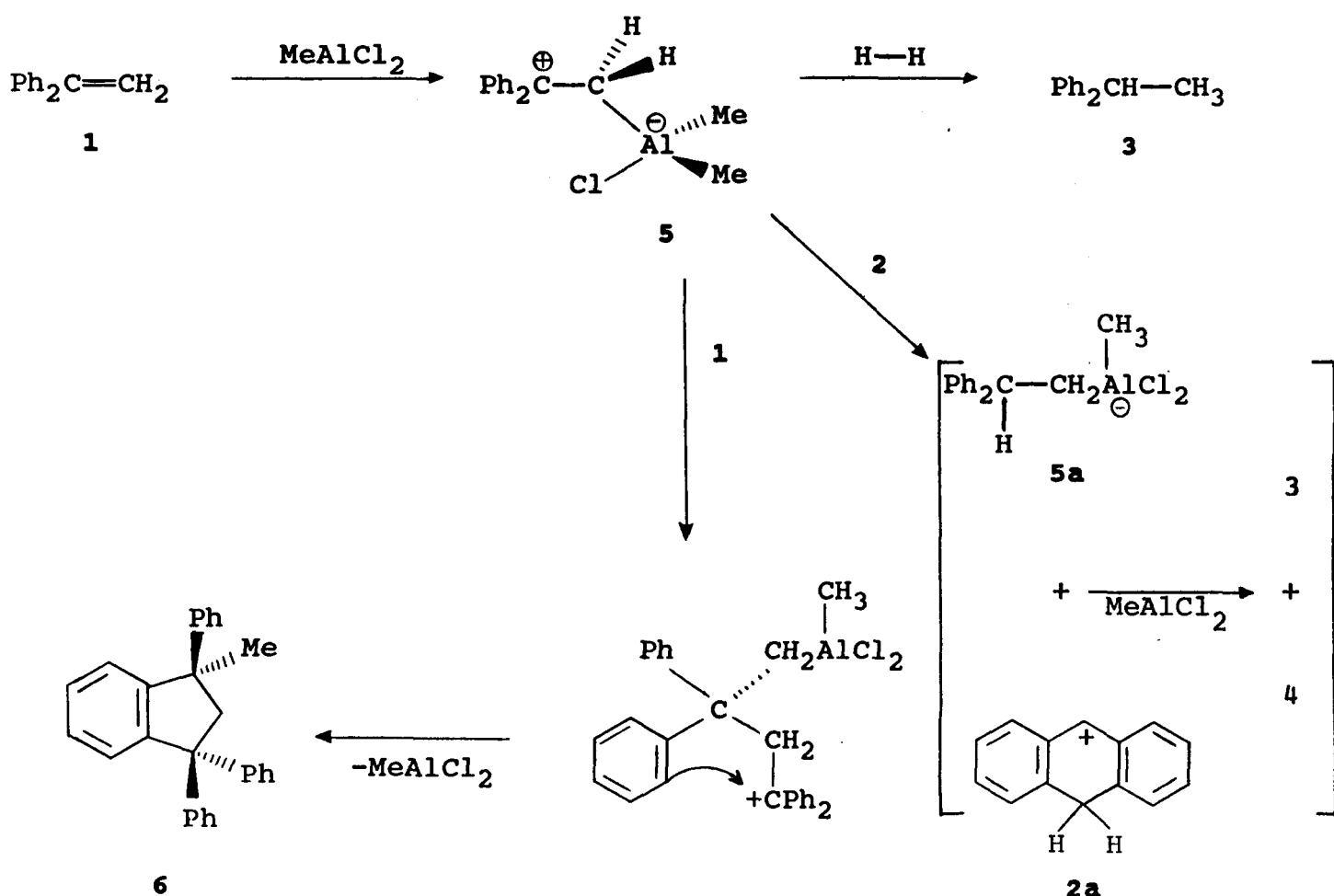
Acknowledgment. We are indebted to the Department of Energy for the support of this research under Grants DE-FG22-84PC70786 and DE-FG22-88PC88930.

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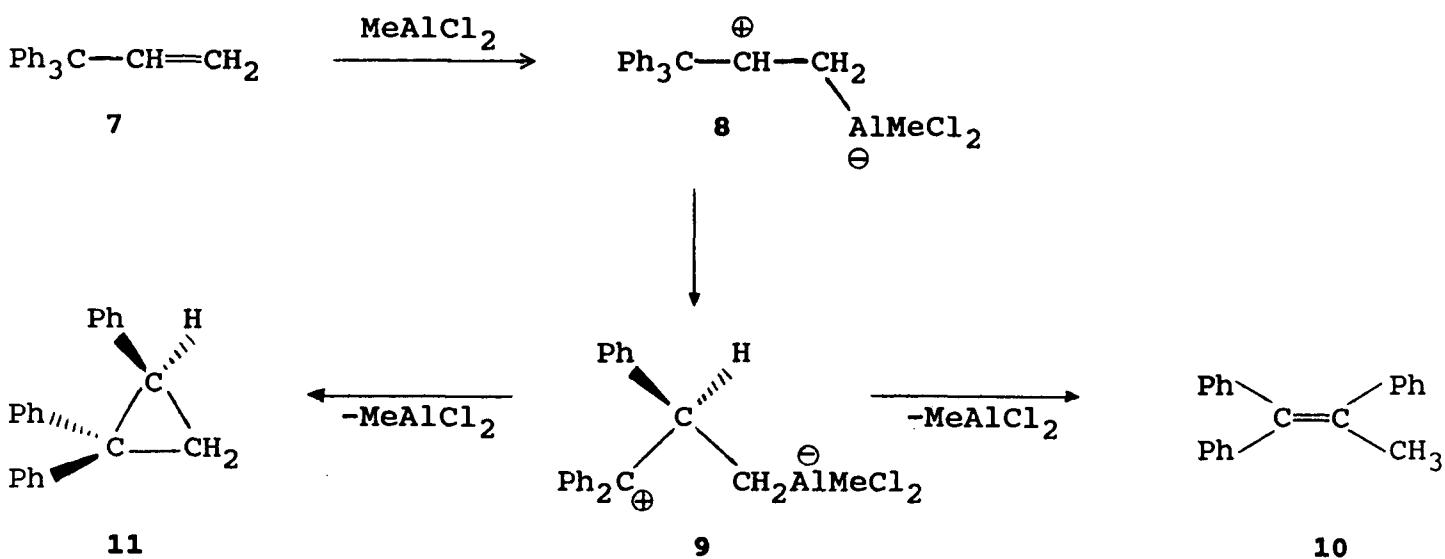
- (1) Part 2 of the series, Hydrogen Transfer Processes. A seminal article dealing with hydrogen shuttling in hydroazaaromatics can be considered as Part 1: J.J. Eisch and D.R. Comfort, J. Org. Chem. **1975**, 40, 2288.
- (2) Present address: Chemistry Department, Lebanon Valley College, Annville, PA 17003-0501.
- (3) Moroni, E.C. 193rd ACS Natl. Mtg., Division of Fuel Chemistry, April 5-10, 1987.
- (4) Derybshire, F., 196th ACS Natl. Mtg., Division of Fuel Chemistry, Sept. 25-30, 1988.
- (5) Siskin, M.; Aczel, T. Fuel, **1983**, 62, 1321.
- (6) Typical reaction conditions and analysis: Admixture of 2.80 mmol each of **1** and **2** in 15 ml. of toluene with 0.29 mmol of  $\text{MeAlCl}_2$  at  $25^\circ\text{C}$  led to an orange-colored solution. After 15 min. the reaction mixture was quenched with 5 ml of 1.5N aqueous HCl. Washing of the organic phase with aqueous  $\text{NaHCO}_3$ , drying over anhydrous  $\text{MgSO}_4$  and solvent evaporation gave a residue which was analyzed by gas chromatography. Samples were collected from the column and identified by  $^1\text{H}$  NMR, IR and MS techniques.
- (7) With  $\alpha$ -methylstyrene and mesitylethene there were significant amounts of Lewis acid-catalyzed dimerization and trimerization (Cf. **1**  $\rightarrow$  **6**, Scheme I).

- (8) Such disproportions were also promoted by nickel(0) complexes (J.J. Eisch and S.R. Sexsmith, Final Report, U.S. Department of Energy, Grant DE-FG22-84PC70786, October 1, 1987.)
- (9) All reactants, solvent and apparatus were scrupulously dried and deoxygenated prior to reaction.
- (10) Bergmann, E.; Taubadal, H.; Weiss, H. Chem. Ber. 1931, 64B, 1493.
- (11) Wolovsky, R.; Maoz, N. J. Org. Chem. 1973, 38, 4040.
- (12) A mixture of HCl and AlCl<sub>3</sub> has been reported to catalyze the hydrogenation of propene at -80°C under 100 atm pressure of dihydrogen (H. Koch; W. Gilfert, Brennst. Chem. 1949, 30, 413).
- (13) Interaction of 2.0 mmol of 1 with 0.20 mmol of MeAlCl<sub>2</sub> in 15 ml of toluene at -78°C under 6 atm of dihydrogen and then warming to 0°C over 2 hr. led, upon hydrolytic work-up, to 1,1-diphenylethane (3) and dimer 6.

Scheme I



Scheme II



PLANS FOR THE NEXT QUARTER: Having found that Lewis acids catalyze both hydrogen transfer and the hydrogenation of aromatic hydrocarbons, we intend to explore the generality of these reactions and their feasibility in coal liquefaction processes. In a parallel effort, we are beginning to study the scope of hydrogen transfers promoted by nickel(0) complexes. Ultimately, we wish to examine the synergistic action of 1:1 combinations of a Lewis acid and nickel(0) compounds on hydrogen transfer.

PUBLICATION: We have just submitted a manuscript entitled "Lewis-Acid Catalyzed Hydrogen Shuttling Between Aromatic and Hydroaromatic Hydrocarbons" for publication in Energy & Fuels.