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PRINCIPAL INVESTIGATOR: John J. Eisch

AFFILIATION/ADDRESS: State University of New York at Binghamton

TELEPHONE NO.: (607) 777-4261

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 fifth quarter of this three-year grant the following aspects of our research program received attention: 1) a survey of the molecular basis for the nickel(0) catalysis in organic chemistry: J.J. Eisch and S.R. Sexsmith, "Intermediates and Reaction Mechanisms in the Interaction of Nickel(0) Complexes with Organic Substrates", accepted for publication in the March 1990 issue of Research on Chemical Intermediates, Elsevier, Amsterdam; 2) further studies on the reactions of nickel(0) complexes with aluminum hydrides, in the search for hydrogen transfer catalysts; 3) attempts to catalyze the simultaneous hydrogen transfer and heteroatom removal of aromatic compounds by organometallic Lewis acids; and 4) extensions of heteroatom removal by nickel(0) compounds from aromatic sulfides to aromatic nitrogen compounds.

ACHIEVEMENTS: We have been able to realize two significant transformations: 1) the hydrogen desulfurization of dibenzothiophene by the $MeAlCl_2$ catalyzed hydrogen transfer from 1,4-cyclohexadiene; and 2) the denitrogenation of benzonitrile by nickel(0) complexes.

DISCLAIMER

QUARTERLY TECHNICAL PROGRESS REPORT

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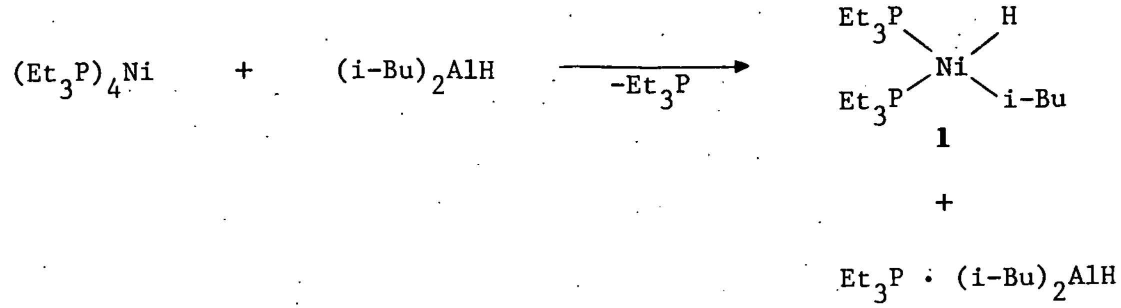
PERIOD OF PERFORMANCE: 9/01/89 - 11/30/89

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.

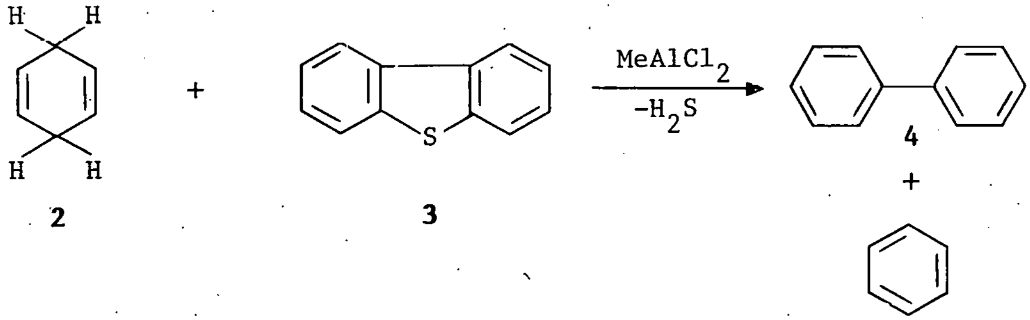
PRESENT WORK AND ACCOMPLISHMENTS: During the fifth quarter of this three-year grant an extensive review of our work on the catalytic action of nickel(0) complexes on the cleavage of carbon-carbon and carbon-hydrogen bonds, as well as the stoichiometric cleavage of C-S, C-O, C-X and C-N bonds, was prepared, upon invitation, by the principal investigator. The completed 65-page manuscript has been submitted to the journal, Reviews of Chemical Intermediates, upon request of it editor, J.K.S. Wan. This review has now been accepted for publication and is to appear in March, 1990.

In continuing our attempts to isolate organonickel intermediates in the nickel-catalyzed transfers of aluminum hydride, we have treated $(Et_3P)_4Ni$ with varying amounts of $(i\text{-}Bu)_2AlH$. During the admixing there is no significant gas evolution (hence no H_2 generation) and subsequent observation of the mixture's ^1H NMR spectrum reveals several high-field signals (<0 ppm, relative to Me_4Si), which are suggestive of the presence of Ni-H intermediates. Currently, we are attempting to isolate such intermediates, possibly having structure 1 (eq. 1), by allowing a 1 : 2 mixture of $(Et_3P)_4Ni$ and $(i\text{-}Bu)_3Al$ to interact in toluene at -78^{o}C:



(1)

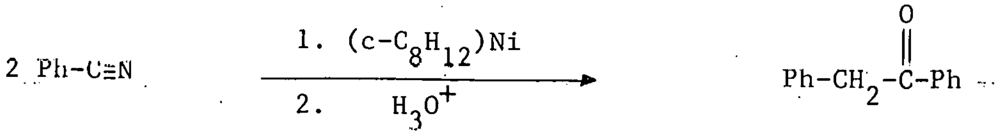
In continuation of our studies on catalyzed hydrogen transfer, we have begun to investigate whether such hydrogen transfer can be made to cause heteroatom-carbon bond cleavage. Specifically, we have been attempting to desulfurize aromatic heterocycles by such a transfer (eq. 2):



(2)

We are now pleased to report that a 1:1 mixture of 1,4-cyclohexadiene (2) and dibenzothiophene (3), upon being treated with 50 mole percent of $MeAlCl_2$ in toluene at 25°C, gives up to 20% of biphenyl (4). With this remarkable discovery in hand, we are encouraged to explore variations in experimental conditions, in order to optimize this novel desulfurization. Moreover, we are eager to learn whether other heteroatoms, such as nitrogen and oxygen, may be removed by this hydrogen-transfer process. Work now under way is examining the behavior of carbazoles and dibenzofurans.

Since previous work in this Laboratory has shown that nickel(0) complexes can desulfurize dibenzothiopene under mild conditions (J. Am. Chem. Soc. 108, 7763 (1986)), we wish to learn whether such complexes might also be able to denitrogenate certain aromatic nitrogen compounds. A noteworthy denitrogenation of benzonitrile has recently been observed: when benzonitrile and bis(1,5-cyclooctadiene)nickel were allowed to interact at 25°C in toluene and the mixture then treated with dilute, aqueous HCl, a 15% yield of benzyl phenyl ketone (5) was realized (eq. 3):



$$2\ \mathrm{Ph{-}C{\equiv}N} \xrightarrow[\text{2. } H_3O^+]{\text{1. } (c\text{-}C_8H_{12})Ni} \mathrm{Ph{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}Ph} \qquad (3)$$

Although the conversion is not yet large, the ease with which this heteroatom removal occurs is promising of future improvements in such denitrogenations.

PLANS FOR THE NEXT QUARTER: Lewis acid-catalyzed hydrogen transfers leading to carbon-heteroatom bond cleavages will be continued, as will attempts to detect crucial intermediates in nickel(0)-aluminum alkyl interactions.

PUBLICATION: The manuscript, "Intermediates and Reaction Mechanisms in the Interaction of Nickel(0) Complexes with Organic Substrates", by J.J. Eisch and S.R. Sexsmith will appear in the March 1990 issue of Research on Chemical Intermediates, Elsevier, Amsterdam.