

Lawrence Berkeley National Laboratory

Recent Work

Title

CHEMISTRY AND MORPHOLOGY OF COAL LIQUEFACTION. QUARTERLY REPORT, APRIL 1, 1985-JUNE 30, 1985.

Permalink

<https://escholarship.org/uc/item/5404p7kc>

Authors

Heinemam, H.
Fish, R.H.

Publication Date

1985-06-01



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

RECEIVED
JUN 2 1985
LIBRARY AND
DOCUMENTS SECTION

CHEMISTRY AND MORPHOLOGY OF COAL LIQUEFACTION
Quarterly Report, April 1, 1985-June 30, 1985

H. Heinemann and R.H. Fish

June 1985

TWO-WEEK LOAN COPY
*This is a Library Circulating Copy
which may be borrowed for two weeks.*



LBL-19855
e.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

QUARTERLY REPORT

April 1, 1985 - June 30, 1985

CHEMISTRY AND MORPHOLOGY OF COAL LIQUEFACTION

Project 4048

Principal Investigators: Heinz Heinemann and Richard H. Fish

Lawrence Berkeley Laboratory

University of California

Berkeley, CA 94720

This work was supported by the Assistant Secretary for Fossil Energy, Office of Coal Research, Liquefaction Division of the U.S. Department of Energy under Contract DE-AC03-76SF00098 through the Pittsburgh Energy Technology Center, Pittsburgh, PA.

TABLE OF CONTENTS

I. Technical Program for FY 1985 1

II. Highlights 2

III. Progress of Studies 3

IV. Future Directions 6

V. Publications 7

I. TECHNICAL PROGRAM FOR FY 1985

Hydrodenitrogenation - Novel Methods for Nitrogen Removal from Polynuclear Nitrogen Containing Heteroaromatic Coal Compounds

The removal of nitrogen from complex matrices such as coal liquids is an extremely important area to study. We recently discovered that polynuclear heteroaromatic nitrogen compounds can be selectively reduced only in the nitrogen containing ring. We now wish to focus on the aspects of carbon-nitrogen cleavage in the saturated nitrogen heterocyclic ring of model coal compounds in order to better understand how nitrogen can be removed without additional substantial use of hydrogen gas for that reaction to occur. A dual approach will be followed that will provide fundamental information on the cleavage of carbon-nitrogen bonds using metal complexes of rhenium, iridium and ruthenium. The important coordination of metal complexes to saturated nitrogen compounds followed by oxidative addition to a methylene group alpha to the nitrogen atom will allow formation of metall-azacyclopropanes and dimetalla-azacyclobutanes. These compounds will be reacted with nucleophiles to hopefully afford carbon-nitrogen bond cleavage. The compounds will also be reacted under hydrogenation conditions to provide a similar carbon-nitrogen bond cleavage reaction. The second approach carried out simultaneously will use various bulk metals and zeolite catalysts with incorporated metal ions such as rhodium and ruthenium in addition to hydrogen donors such as long-chain hydrocarbons for catalytic cracking.

II. Highlights

1. Bond Cleavage Reactions of 1,2,3,4-Tetrahydroquinoline. Catalysts comprising massive amounts of nickel (29 weight %) on silica and also catalysts comprising rhodium (5 weight %) on silica have been found to promote substantial ring cleavage in 1,2,3,4-tetrahydroquinoline (THQ). Major products are aniline and methylaniline as well as quinoline which of course is a dehydrogenation product of THQ. Quinoline could be recycled to the selective hydrogenation step. Some isomerization of THQ to indole derivatives was also observed with the nickel catalyst.
2. Reactions of Dimetalla-azacyclobutenes and X-Ray Crystal Structural Analysis of the Phenanthridine-Ru₃(CO)₁₂ Adduct. Several reactions of the triruthenium-phenanthridine complex were studied including hydrogenation and protonolysis. A crystal structure of the triruthenium-phenanthridine complex was also completed.

III. Progress of Studies

a) Novel Methods of Nitrogen Removal

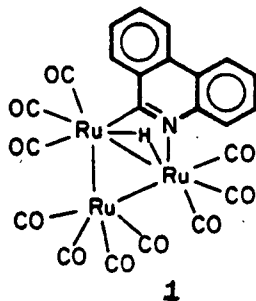
We have continued our perusal of metals and have found that rhodium (5%) on silica and nickel (29%) on silica (Tables 1 and 2) will produce substantial amounts of aniline when 1,2,3,4-tetrahydroquinoline (THQ) is passed over these catalysts at temperature ranges of 200-340°C. Other metals such as manganese and zirconium oxide produce very few products. We also evaluated a THQ/tetralin mixture (1.6% THQ in tetralin) with a ZSM-5 zeolite catalyst and found that THQ was being absorbed into the zeolite producing no THQ products. A copper/nickel catalyst (8%/18%) on silica gave quinoline when reacted with THQ at temperatures of 260-340°C.

The important aspect of these findings is that cleavage of the carbon-nitrogen alkyl bond of THQ seems to occur readily with the nickel and rhodium catalysts.

b) Synthesis and Reactions of Dimetalla-azacyclobutenes

We have improved on the yields of the reactions of quinoline, 1,2,3,4-tetrahydroquinoline and phenanthridine with $\text{Ru}_3(\text{CO})_{12}$ by using a closed Parr reactor. By using the Parr reactor, we have increased the yields to 60-80% from previous reactions that provided yields in the range of 20-30%.

We have studied the reaction of the phenanthridine $\text{Ru}_3(\text{CO})_{12}$ complex 1 with hydrogen gas and with a carboxylic acid.



The hydrogenation (85°C , 500 psi H_2) gave the ligands phenanthridine and dihydrophenanthridine and the $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ cluster. The complex 1 was also reacted with an excess of trifluoroacetic acid at 50°C forming a new cluster as indicated by a new set of IR absorption spectra and the disappearance of IR bands of the starting phenanthridine- $\text{Ru}_3(\text{CO})_{12}$ compound. We are presently in the process of finding out the structural aspects of this new compound by ^1H nmr spectroscopy.

C) X-Ray Crystal Structure of the Phenanthridine - $\text{Ru}_3(\text{CO})_{12}$ Complex

The x-ray crystal structure of the phenanthridine derivative, 1, was recently completed. An ORTEP view of the molecule is attached, with tables of pertinent bond lengths and angles. One interesting feature of the structure is the nearly planar, trans arrangement of the coordinated phenanthridine and bridging hydride ligands, with this assembly perpendicular to the Ru_3 plane. The hydride ligand is positioned equally (within experimental error) between Ru(3) and Ru(2). Distances to N(1) and C(11) to Ru(3) and Ru(2) are artificially constrained to be equal due to disorder in the structure arising from the pseudo mirror

plane dividing the 2 halves of the phenanthridine ligand. The N=C(11) bond length and the bonding distances of ruthenium atoms to these atoms are in the range of values expected for similar complexes.

The Ru(2)-Ru(3) bond, bridged by the hydride and heterocycle is somewhat longer than similar bonds in other triruthenium clusters. (2.866(1) Å) (Usually 2.79-2.85 Å) It has been suggested that while a bridging H atom normally causes a lengthening of a metal-metal bond, M-M bonds bridged by H and a second non-hydride ligand can be shorter due to a counter balancing effect of the latter ligand. This is apparently not the case in the present work. The phenanthridine ligand does not exert a strong bond shortening effect, perhaps because of its weak interaction with the cluster.

IV. Future Directions

Since we have shown, for the first time, a carbon-nitrogen alkyl bond cleavage reaction of THQ to aniline and its derivatives, we are going to verify that propylaniline is the precursor to the ring cleavage products as well as analyze for volatile products such as benzene, toluene, ethane, methane, propane, etc. The more important finding of no aromatic ring hydrogenation with these catalysts provides hope for processes that are economical with regard to hydrogen gas consumption.

We are also going to pursue the chemistry of the dimetalla-azacyclobutene compounds.

V. Publications

R. H. Fish, J. L. Tan and A. D. Thormodsen, Homogeneous Catalytic Hydrogenation 4. Regioselective Reduction of Polynuclear Heteroaromatic Compounds Catalyzed by Hydrido-chloro-tris(triphenylphosphine)ruthenium (I), Organometallics, 1985 (in press).

Table 1
Reaction of 1,2,3,4-Tetrahydroquinoline over 29% Nickel on Silica

Temperature (°C)	260	300-#1	300-#2	300-#3	340-#1	340-#2	340-#3	380
Conversion	65.3%	93.2%	82.8%	78.0%	96.8%	87.6%	92.6%	80.9%
Products: a,b								
Aniline	1.1%	9.3%	20.4%	15.4%	19.3%	19.7%	18.0%	21.8%
Methylaniline	1.8%	4.9%	10.9%	7.8%	5.2%	5.4%	4.7%	2.7%
Indole	6.5%	17.2%	13.0%	10.7%	20.4%	16.0%	18.3%	7.35
Methylindole	1.7%	2.4%	4.1%	3.2%	2.65	2.0%	2.1%	1.0%
Quinoline	78.6%	54.6%	40.9%	52.6%	39.9%	48.4%	47.4%	58.2%
Unidentified	10.3%	11.6%	10.7%	10.3%	12.6%	8.5%	9.5%	9.0%

a Identification by Capillary Column GC-MS

b Reactions done in the presence of hydrogen gas (14.7 psi)

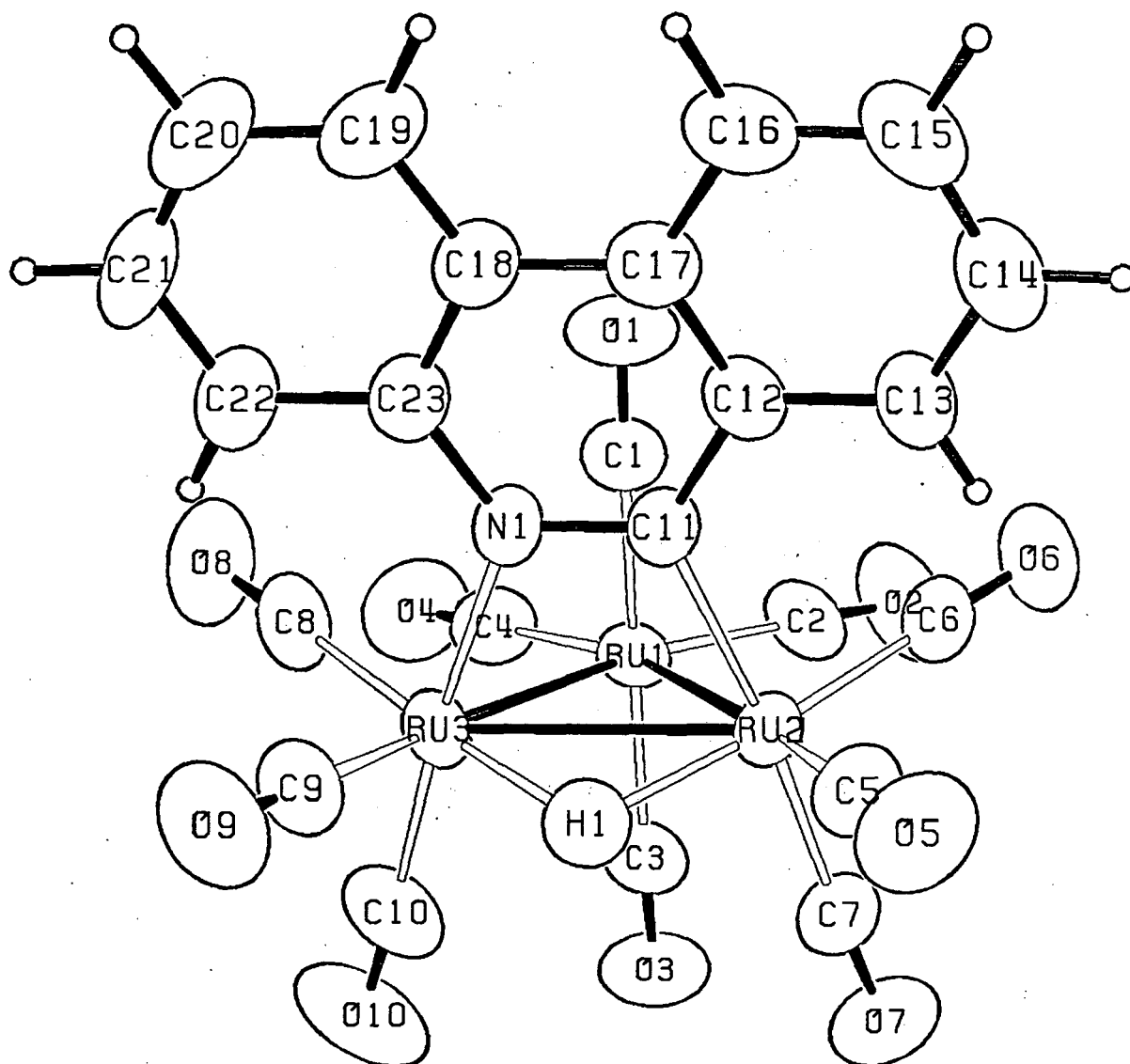
Table 2

Reaction of 1,2,3,4-Tetrahydroquinoline over 5% Rhodium on Silica

Temperature (°C)	300	260
Conversion	99	91
Products: a,b		
Aniline	6.2	1.7
Methylaniline	11.4	7.7
Indole	4.5	1.3
Methylindole	8.7	6.6
Quinoline	48.7	35.9
1,2,3,4-THQ	0.7	9.5
5,6,7,8-THQ	2.4	19.4
Unidentified	17.4	17.9

a Identification by Capillary Column GC-MS.

b Reactions done in the presence of hydrogen gas (14.7 psi).



Intramolecular Distances

ATOM 1	ATOM 2	DISTANCE
RU1	RU2	2.851(1)
RU2	RU3	2.866(1)
RU3	RU1	2.844(1)
RU1	C1	1.931(3)
RU1	C2	1.906(3)
RU1	C3	1.930(3)
RU1	C4	1.920(3)
RU2	C11	2.133(1)
RU2	C5	1.912(3)
RU2	C6	1.905(3)
RU2	C7	1.915(3)
RU2	H1	1.81(3)
RU3	N1	2.133(1)
RU3	C8	1.894(3)
RU3	C9	1.920(3)
RU3	C10	1.918(3)
RU3	H1	1.76(3)
N1	C11	1.312(0)
C11	C12	1.433(3)
C12	C13	1.399(4)
C12	C17	1.397(4)
C13	C14	1.356(4)
C14	C15	1.387(5)
C15	C16	1.358(5)
C16	C17	1.416(4)
C17	C18	1.450(4)
C18	C19	1.397(4)
C18	C23	1.401(4)
C19	C20	1.373(5)
C20	C21	1.363(5)
C21	C22	1.367(4)
C22	C23	1.419(4)
C23	N1	1.424(3)

Intramolecular Angles

ATOM 1	ATOM 2	ATOM 3	ANGLE
RU1	RU2	RU3	59.66(1)
RU2	RU3	RU1	59.92(1)
RU3	RU1	RU2	60.42(1)
RU2	H1	RU3	106.9(16)
H1	RU3	RU2	37.1(9)
H1	RU2	RU3	36.0(9)
C1	RU1	RU2	85.20(8)
C1	RU1	RU3	85.02(8)
C1	RU1	C2	93.42(12)
C1	RU1	C3	173.07(12)
C1	RU1	C4	94.55(12)
C7	RU2	RU1	88.21(9)
C7	RU2	RU3	106.17(9)
C7	RU2	C5	91.91(12)
C7	RU2	C6	91.14(12)
C7	RU2	C11	173.89(11)
C7	RU2	H1	91.6(8)
C10	RU3	RU1	87.80(9)
C10	RU3	RU2	106.00(11)
C10	RU3	N1	174.26(13)
C10	RU3	C8	90.99(14)
C10	RU3	C9	92.94(13)
C10	RU3	H1	91.1(8)

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

*LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720*