

Lawrence Berkeley National Laboratory

Recent Work

Title

CHEMISTRY AND MORPHOLOGY OF COAL LIQUEFACTION Annual Report. Oct. 1, 1984 - Sept. 30, 1985.

Permalink

<https://escholarship.org/uc/item/5f14d2gg>

Authors

Heinemann, H.

Fish, R.H.

Publication Date

1985-09-01



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

RECEIVED
LAWRENCE
BERKELEY LABORATORY

NOV 20 1985

LIBRARY AND
DOCUMENTS SECTION

CHEMISTRY AND MORPHOLOGY OF COAL LIQUEFACTION
Annual Report. October 1, 1984 - September 30, 1985

H. Heinemann and R.H. Fish

September 1985

For Reference

Not to be taken from this room



LBL-20374
c.1

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.

October 1, 1984 - September 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.

Index

I.	Technical Program for FY 1985	2
II.	Highlights	3
III.	Progress of Studies	4
IV.	Future Directions	9
V.	Publications	10

Introduction

This report presents results obtained during the last quarter of fiscal year 1985 and briefly summarizes results previously reported in the three quarterly reports issued on January 1, April 1 and July 1985.

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 metalla-azacyclopropanes and dimetalla-azacyclobutenes. 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 such as nickel, rhodium and ruthenium supported on silica and alumina with 1,2,3,4-tetrahydroquinoline as the substrate and at temperatures of ≈ 300 °C and 1 atm H₂ gas to provide HDN chemistry under mild experimental conditions.

II. Highlights

1. Bond Cleavage Reaction of 1,2,3,4-Tetrahydroquinoline. We have found that a catalyst comprising ~~of~~ nickel (29 weight %) on silica can promote alkylcarbon-nitrogen bond cleavage reactions to produce aniline and methylaniline as well as promote hydrodenitrogenation (1 atm H₂) to give benzene and toluene, Ammonia, methane and small amounts of propane and ethane are the main side-products.
2. Morphology studies of the nickel on silica catalyst by transmission electron microscopy (TEM) and x-ray photoelectron spectroscopy (XPS) clearly shows face-center-cubic nickel and nickel crystallites of 100 to 2000 Å.
3. Synthesis and Reactions of Dimetalla-azacyclobutene Compounds of Ruthenium. The reactions of model coal, polynuclear heteroaromatic nitrogen compounds with triruthenium dodecacarbonyl (Ru₃(CO)₁₂) provided dimetalla-azacyclobutenes. The reaction with hydrogen gas of these complexes of quinoline (1); 1,2,3,4-tetrahydroquinoline, (2); 9,10-dihydrophenanthridine (3); and phenanthridine (4) gave the ligand and H₄Ru₄(CO)₁₂. The reaction of the quinoline and phenanthridine ruthenium complexes with lithium aluminium hydride gave no discernible products, while reaction of the phenanthridine-ruthenium complex with trifluoroacetic acid gave a new cluster with loss of CO and H₂ and addition of the trifluoroacetate group. We have not seen the reactions of carbon-nitrogen bond cleavage and will try to prepare the dimetalla-azacyclopropane compounds. Facile carbon-nitrogen bond cleavage with

metal clusters as models for heterogeneous catalysts could provide a major breakthrough in the basic understanding of HDN chemistry.

III. Progress of Studies

a) HDN Chemistry with Supported Nickel on Silica Catalysts

The 29% nickel catalyst gives the lowest amount of quinoline at 320°C (conditions: 0.14 ml/hr of 1,2,3,4-tetrahydroquinoline and 30 ml/min H₂ with 860 mg of 29 wt% Ni/SiO₂) and the formation of benzene, toluene, aniline, methylaniline, indole, methane and ammonia. (Table 1 compares the various products and conditions.)

Using 2-n-propylaniline as the substrate, and as a potential intermediate in formation of benzene, toluene, anilines, methane and propane, we found the same products including THQ (Table 2). Thus, ring opening, followed by sequential loss of methane and ammonia, is the apparent route to the observed products. Interestingly, cyclic products are also formed by a plausible free radical reaction.

Varying the amount of nickel on the catalyst, we found at 5 wt% nickel, excessive quinoline (dehydrogenation) and low conversions to benzene and toluene from 1,2,3,4-tetrahydroquinoline (Table 3). Other metals such as Cu, Zn, Cr, etc. were surveyed, along with a ZSM-5 zeolite catalyst, but no HDN chemistry was observed.

b) Transmission Electron Microscopy of the Active Nickel Catalyst

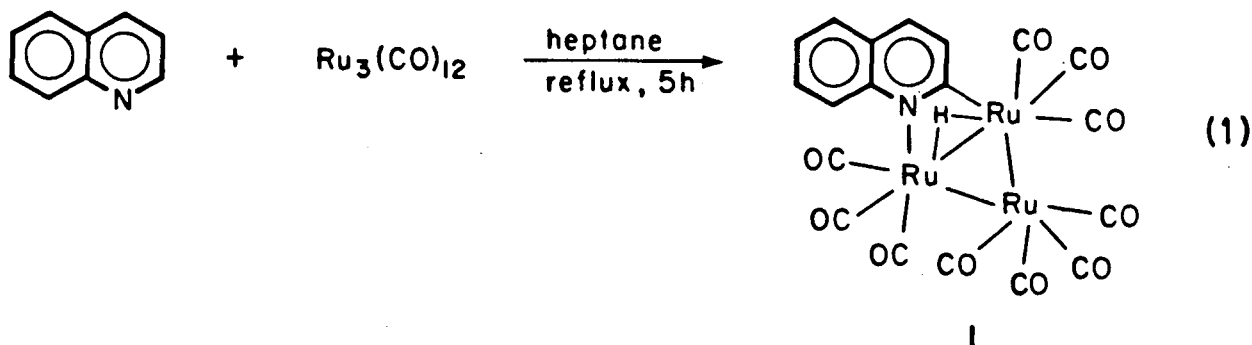
Transmission electron microscopy was performed on the 29% (by wt) nickel on silica catalyst. Figure (1) shows the crystallites of nickel with particle sizes of 100 to 2000 Å. Also observed was coking on the silica support. The diffraction pattern verified that the nickel single crystals were face-center-cubic. In addition, we also ran x-ray photoelectron spectra and found nickel (0) and small amounts of nickel (II) on the surface.

c) Synthesis and Reactions of Dimetalla-azacyclobutenes

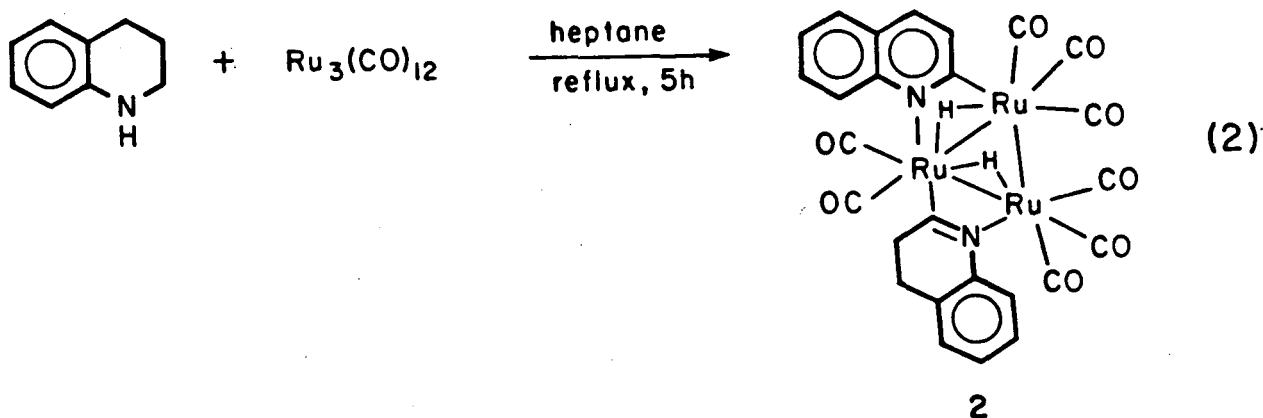
We wanted to determine possible methods for the cleavage of carbon-nitrogen bonds and studied the reactions of several model coal compounds containing a nitrogen atom with $\text{Ru}_3(\text{CO})_{12}$.

The reactions were run in a Parr pressure reactor at equimolar concentrations such that we could isolate and identify reaction products by various spectroscopic techniques.

The first reaction attempted, used quinoline as a model compound and provided a product, 1, that was identified by mass spectroscopy, nuclear magnetic resonance spectroscopy and elemental analysis (Eq. 1).

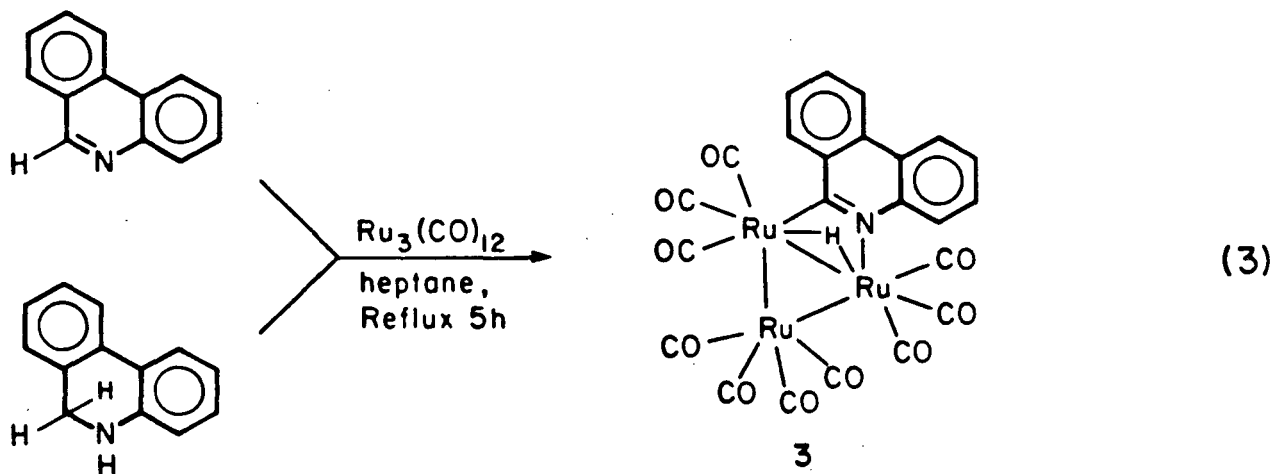


Thus the isolation of compound 1 and its structural identification clearly shows bonding of the metal cluster to both carbon and nitrogen. This is an exciting result, since it indicates that this type of bonding could be used to eventually cleave carbon-nitrogen bonds. The reaction of 1,2,3,4-tetrahydroquinoline with $\text{Ru}_3(\text{CO})_{12}$ also provided an interesting product, which we identified via spectroscopic analysis as compound 2 (Eq. 2).

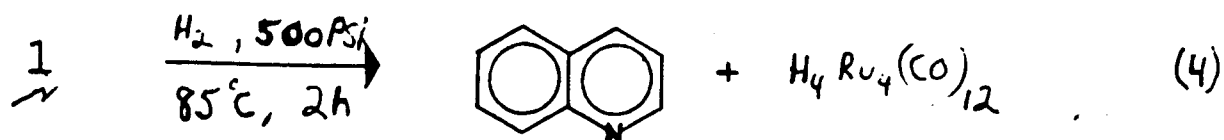


Compound 2 is a dimer; however, one nitrogen ring is unsaturated, while the other nitrogen ring is partially unsaturated.

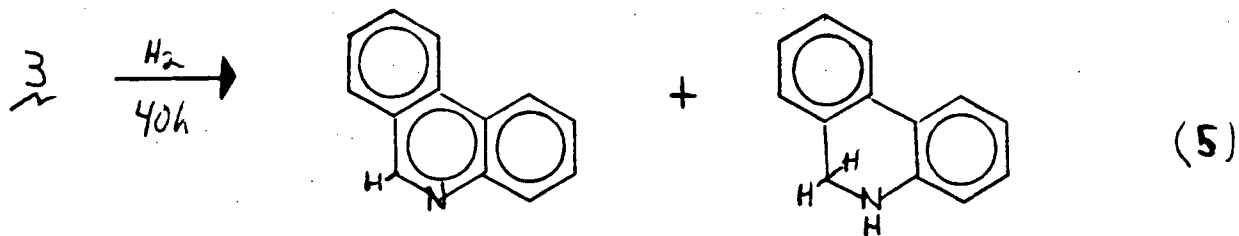
When we reacted phenanthridine or dihydrophenanthridine with $\text{Ru}_3(\text{CO})_{12}$, we obtained the same compound, 3, from either starting material (Eq. 3).



The reactions of compounds 1 with hydrogen gas gave quinoline and $H_4Ru_4(CO)_{12}$ (Eq. 4):

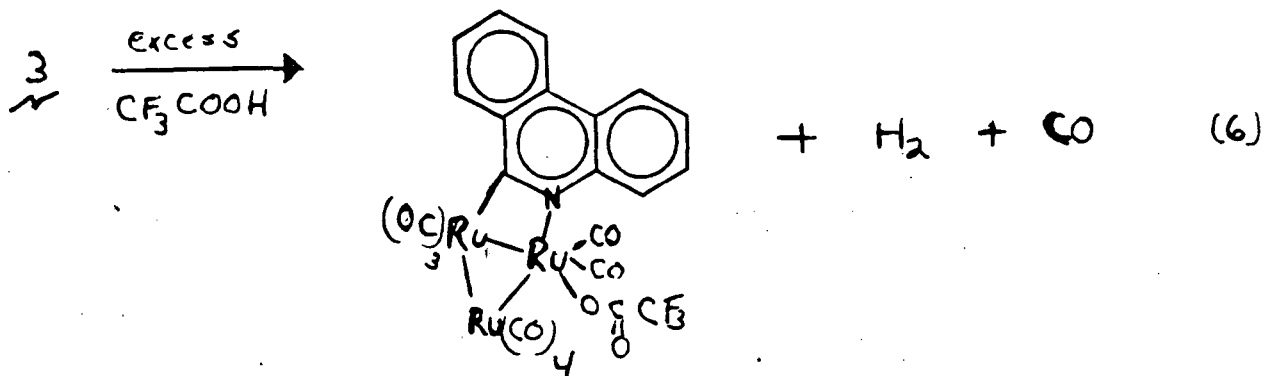


while the longer reaction time of the H_2 gas with 3 gave both phenanthridine and dihydrophenanthridine as well as $H_4Ru_4(CO)_{12}$ (Eq. 5).



The reaction of compounds 1 or 3 with lithium aluminium hydride provided no discernible product, a quite surprising result.

Reaction of 3 with excess trifluoroacetic acid gave a new product with loss of H_2 and CO and addition of the trifluoroacetate group : (Eq. 6)



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

The x-ray crystal structure of the phenanthridine derivative, 3, was recently completed. An ORTEP view (Figure 2) 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 $\text{Ru}(3)$ and $\text{Ru}(2)$. Distances to $\text{N}(1)$ and $\text{C}(11)$ to $\text{Ru}(3)$ and $\text{Ru}(2)$ 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 $\text{N}=\text{C}(11)$ bond length and the bonding distances of ruthenium atoms to these atoms are in the range of values expected for similar complexes.

The $\text{Ru}(2)$ - $\text{Ru}(3)$ bond, bridged by the hydride and heterocycle is somewhat longer than similar bonds in other triruthenium clusters. (2.866(1) Å) (Usu-

ally 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

Our results clearly show that high loadings of nickel on silica promote HDN chemistry at moderate temperatures ($\sim 300^{\circ}\text{C}$) and pressures of hydrogen (1 atm). Morphology studies on the catalyst will be continued. We will also define the possible sulfur compound effects on the HDN chemistry and will study other polynuclear heteroaromatic nitrogen compounds. We are also going to pursue the chemistry of the dimetalla-azacyclobutene compounds and prepare dimetalla-azacyclopropanes for models in carbon-nitrogen bond cleavage reactions.

V. Publications

R. H. Fish, A. D. Thormodsen and H. Heinemann, A Comparison of Polymer-Supported Chlorotris(triphenylphosphine)Rhodium(I) to its Homogeneous Analog in the Selective Reduction of Polynuclear Heteroaromatic Compounds, *J. Mol. Catal.*, 31 191 (1985).

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

R. H. Fish, T. J. Kim and J. W. Dupon, Synthesis and Reactions of Dimetallaazacyclobutene of Ruthenium, *Organometallics*, 1985 (in preparation).

Some Results with the 29% Ni on SiO₂ Catalyst

Products	320 °C	360 °C	380 °C	395 °C
Benzene	8.37%	12.17%	14.33%	16.14%
Toluene	1.44%	1.77%	1.80%	1.96%
Aniline	27.54%	18.91%	18.63%	17.34%
Methylaniline	7.18%	2.72%	2.42%	1.72%
Quinoline	33.97%	44.45%	41.05%	41.89%
Indole	6.45%	9.12%	9.88%	9.51%
1,2,3,4-THQ	5.34%	3.52%	3.94%	3.40%
Methylindole	2.13%	0.89%	0.86%	0.69%

^a Conditions: .14 ml/hr substrate, 30 ml/min H₂, 860 mg of 29% Ni/SiO₂ catalyst.

Table 2**HDN Chemistry with 2-n-propylaniline at 320 °C^a**

Benzene	19.28%
Toluene	2.90%
Propylbenzene	5.30%
Aniline	9.28%
Methylaniline	5.73%
Propylaniline	36.95%
1,2,3,4-THQ	5.77%
Methylindole	2.25%

^a Conditions: 0.14 ml/hr substrate, 30 ml/min H₂, 880 mg of 29% Ni/SiO₂ catalyst.

Table 3		
HDN Chemistry with 4.8% Ni/SiO₂		
	Run 1	Run 2
Benzene	0.84%	1.31%
Toluene	0.23%	0.30%
Aniline	2.92%	2.88%
Methylaniline	1.18%	1.19%
Quinoline	65.51%	57.86%
Indole	2.84%	1.82%
1,2,3,4-THQ	22.07%	29.25%
Methylindole	0.71%	0.53%

^a T = 320 °C, both runs under the same conditions as 29% Ni.

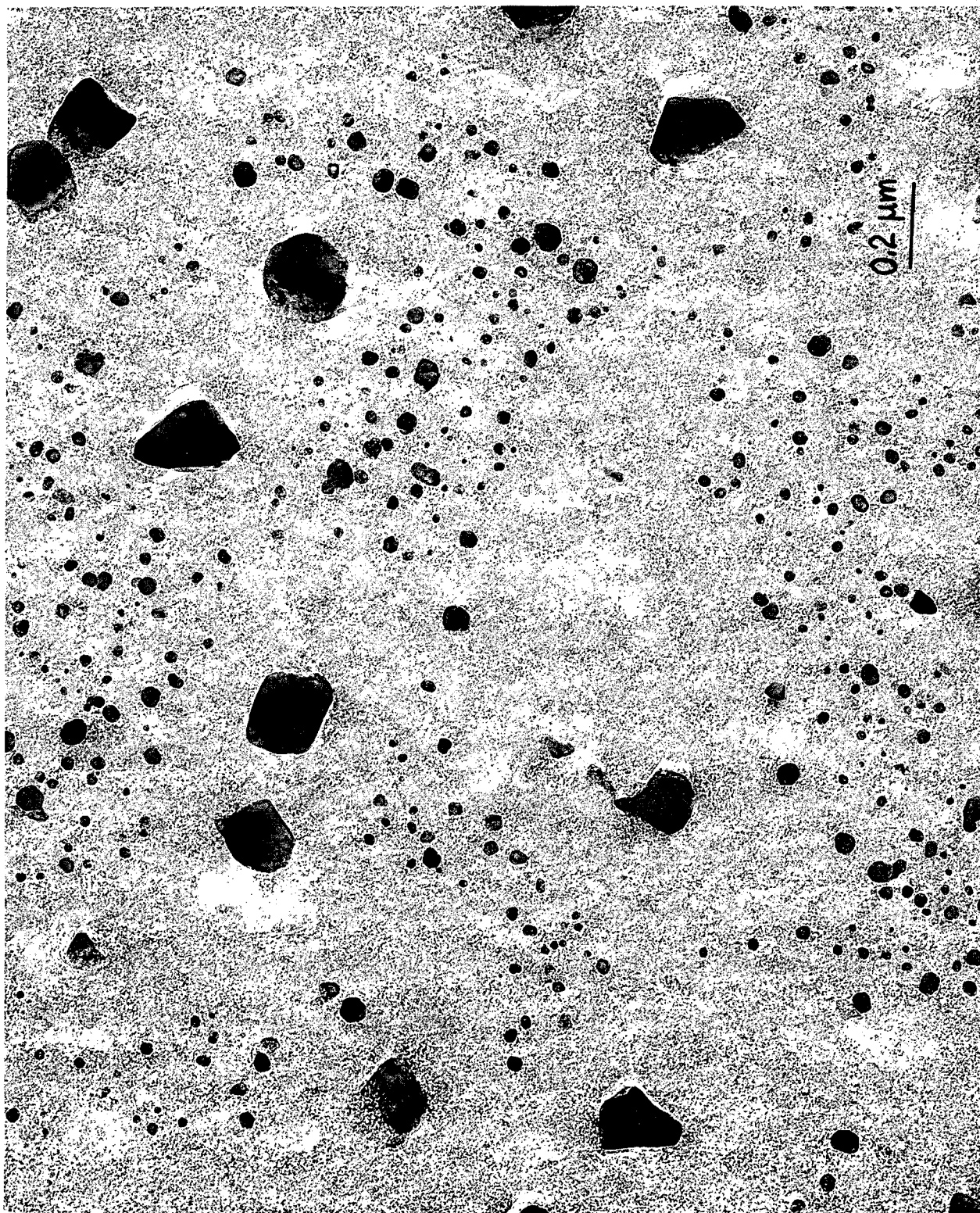
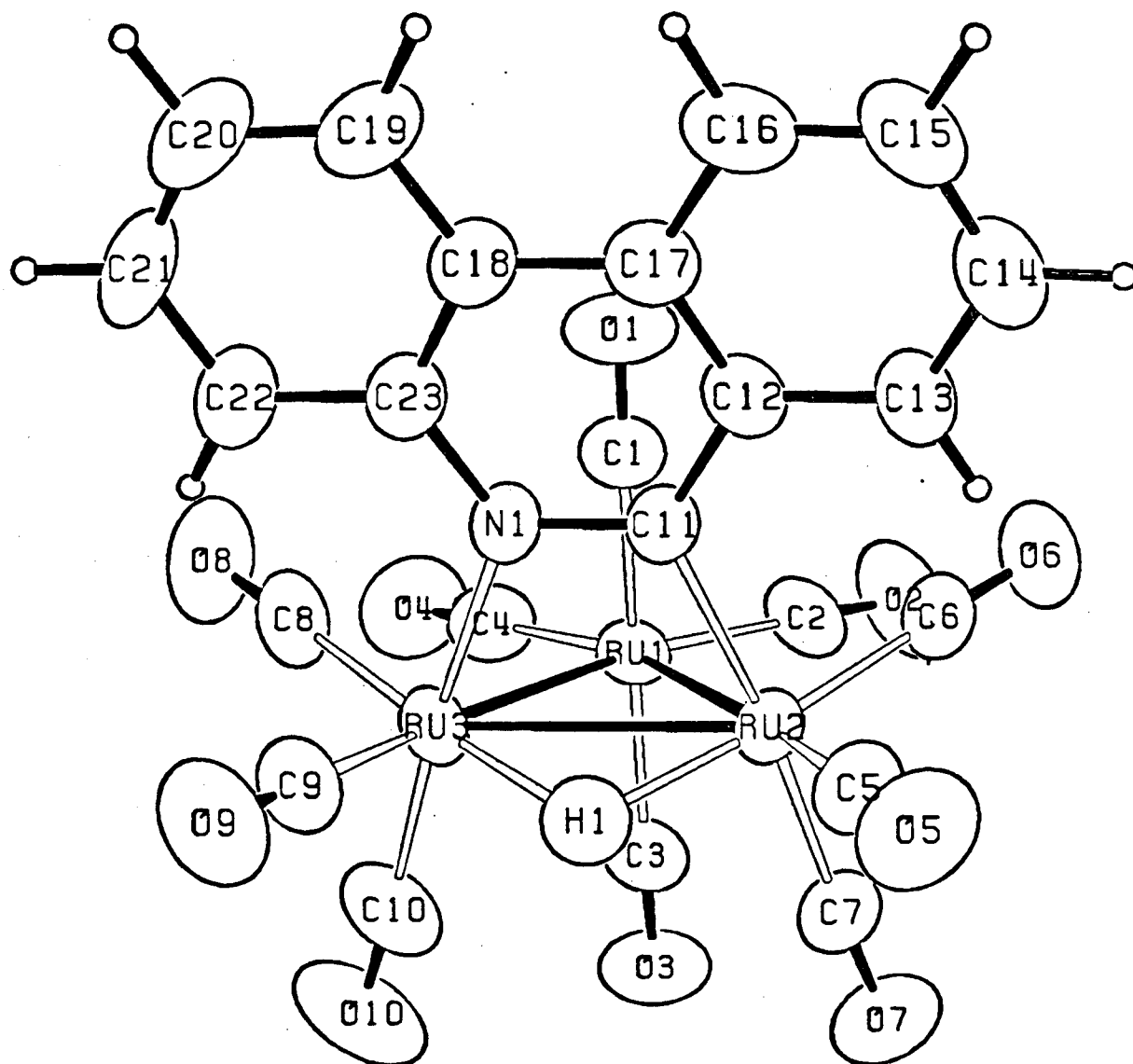


Figure 1 TEM of 29% Ni/SiO₂ Catalyst

Figure 2 ORTEP of 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)

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)

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*