**GEORGIA INSTITUTE OF TECHNOLOGY**
OFFICE OF CONTRACT ADMINISTRATION
**SPONSORED PROJECT INITIATION**

AAB

Date: January 10, 1977

Project Title: Synthesis & Synthetic Applications of Organometallic Compounds

Project No: G-33-620

Project Director: E. K. Barefield

Sponsor: National Science Foundation

Agreement Period: From 1/1/77 Until 6/30/78
*12 month budget period plus 6 months for submission of required reports, etc.

Type Agreement:
Grant No. Che 76-21758

Amount:
$27,200 NSF
6,883 GIT (G-33-389)
$34,083 Total

Reports Required:
Annual Letter Technical; Final Report

Sponsor Contact Person (s):

Technical Matters

Mr. James L. Bostick
Grants Officer
National Science Foundation
Washington, D. C. 20550
(202) 632-5965

Contractual Matters
(thru OCA)

Defense Priority Rating:

Assigned to: Chemistry (School/Laboratory)

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Other

CA-3 (3/76)

**GEORGIA INSTITUTE OF TECHNOLOGY**
OFFICE OF CONTRACT ADMINISTRATION

## SPONSORED PROJECT TERMINATION

Date: 1/11/79

Project Title: Synthesis & Synthetic Applications of Organometallic Compounds

Project No: G-33-620

Project Director: Dr. E. K. Barefield

Sponsor: National Science Foundation

Effective Termination Date: 6/30/78 (Grant Expiration)

Clearance of Accounting Charges: by 6/30/78

Grant/Contract Closeout Actions Remaining:

_ Final Invoice and Closing Documents
X Final Fiscal Report (FCTR only)
_ Final Report of Inventions
_ Govt. Property Inventory & Related Certificate
_ Classified Material Certificate
_ Other _____

NOTE: Follow-on project is G-33-644.

Assigned to: Chemistry (School/Laboratory)

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CA—4 (3/76)

G33-620

NATIONAL SCIENCE FOUNDATION
Washington, D.C. 20550

# FINAL PROJECT REPORT
NSF FORM 98A

*PLEASE READ INSTRUCTIONS ON REVERSE BEFORE COMPLETING*

## PART I–PROJECT IDENTIFICATION INFORMATION

| 1. Institution and Address | 2. NSF Program | 3. NSF Award Number |
|---|---|---|
| Georgia Institute of Technology<br>Atlanta, Georgia 30332 | Syn. Inorg., Organomet. | CHE-76-21758 |
| | 4. Award Period<br>From 1/1/77 To 6/30/78 | 5. Cumulative Award Amount<br>$27,200. |

6. Project Title

Synthesis and Synthetic Applications of Organometallic Compounds

## PART II–SUMMARY OF COMPLETED PROJECT *(FOR PUBLIC USE)*

This research is concerned with the synthesis of new metal compounds that are designed to test existing theories of bonding and/or chemical reactivity and with the development of new synthetically useful applications of metal reagents. Research has been concentrated in two areas: Organometallic Chemistry of Iminium Salts and Iron(II) Chemistry of Tetramethylcyclam. In the former area metal chemistry of important, readily available organic materials was investigated. Modes of binding of these species by metals in different oxidations states were studied and reductive coupling reactions of these salts using nickel(0) reagents were developed. This reaction provides a facile route to 1,2-diamines not easily available by any other method. Some of these materials may be valuable precursors for organic synthesis. Intermediates occurring in the course of this reaction have been isolated. Structural characterization of these intermediates is expected to provide information applicable to other organometallic coupling reactions. In the latter research area special stereochemical features of the macrocyclic tertiary amine, tetramethylcyclam, were utilized in the synthesis of iron(II) complexes for study of certain features of the electronic structure of iron(II) in biologically occurring molecules. New examples of iron-nitric oxide complexes were prepared and their structures determined. These results suggest that new extensions of existing bonding/structure relationships are required for describing these systems.

## PART III–TECHNICAL INFORMATION *(FOR PROGRAM MANAGEMENT USES)*

| 1. ITEM *(Check appropriate blocks)* | NONE | ATTACHED | PREVIOUSLY FURNISHED | TO BE FURNISHED SEPARATELY TO PROGRAM | |
|---|---|---|---|---|---|
| | | | | Check (√) | Approx. Date |
| a. Abstracts of Theses | | | | √ | 1/1/79 |
| b. Publication Citations | | √ | | | |
| c. Data on Scientific Collaborators | | √ | | | |
| d. Information on Inventions | √ | | | | |
| e. Technical Description of Project and Results | | √ | | | |
| f. Other *(specify)* | | | | | |

| 2. Principal Investigator/Project Director Name *(Typed)* | 3. Principal Investigator/Project Director Signature | 4. Date |
|---|---|---|
| E. Kent Barefield | | 9/26/78 |

NSF Form 98A (5-78) Supersedes All Previous Editions

Form Approved OMB No. 99R0015

## PART III - Technical Information

### 1a. Theses.

K. D. Hodges, Ph.D., 1978. "Iron Complexes of 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane and Nickel(II) Complexes of Penta- and Octamines Derived from the Fourteen Membered Macrocyclic Tetramine 1,4,8-Trimethyl-1,4,8,11-Tetraazacyclotetradecane." Abstract attached.

Dennis J. Sepelak, Ph.D., 1978 (anticipated). "Organometallic Chemistry of Iminium Salts." Abstract to be furnished separately.

### 1b. Publications.

"Electronic Structure of Three-Coordinate Nickel(I): EPR of Nickel-Doped Halobistriphenylphosphinecopper(I)," M. J. Nilges, E. K. Barefield, R. L. Belford and P. H. Davis, J. Am. Chem. Soc., 99, 755 (1977). Photocopies attached.

"Synthesis and Physical Properties of High-Spin Five-Coordinate Iron(II) Complexes of 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane," K. D. Hodges, R. G. Wollmann, E. K. Barefield and D. N. Hendrickson, Inorg. Chem., 16, 2746 (1977). Reprints attached.

"Mechanistic Studies on the Catalysis of Isomerization of Olefins by $(Ph_3P)_3NiX$," M. J. D'Aniello, Jr. and E. K. Barefield, J. Am. Chem. Soc., 100, 1474 (1978). Photocopies attached.

"Preparations and Properties of Nitrosyl Complexes of Iron-Tetramethylcyclam; X-Ray Structures of $[Fe(C_{14}H_{32}N_4)NO](BF_4)_2$, an S = 3/2 - 1/2 Spin-Equilibrium Complex, and $[Fe(C_{14}H_{32}N_4)(NO)(OH)](ClO_4)_2 \cdot CH_3CN$," K. D. Hodges, R. G. Wollmann, S. L. Kessel, D. N. Hendrickson, D. G. VanDerveer and E. K. Barefield, Accepted for publication in J. Am. Chem. Soc. Preprint attached; copies of printed version to be submitted.

"Organometallic Chemistry of Carbon-Nitrogen Multiple Bonds II. Reactions of Cyclopentadienylirondicarbonyl Anion with Iminium Salts; Chemistry of the Products," E. K. Barefield and D. J. Sepelak, to be submitted to J. Am. Chem. Soc. Preprint attached.

### 1b[1]. Papers Presented.

"Mechanism of the Isomerization of Olefins by Triphenylphosphine Nickel(I)," M. J. D'Aniello, Jr. and E. K. Barefield, 173rd ACS National Meeting, New Orleans, LA, Abstract INOR 149.

"Nitrosyl Chemistry of Iron(II)-Tetramethylcyclam," E. K. Barefield, K. D. Hodges, D. G. VanDerveer, R. Wollmann, S. L. Kessel and D. N. Hendrickson, 176th ACS National Meeting, Miami Beach, FL, Abstract INOR 8.

"Metal Assisted Coupling Reactions of Iminium Salts," E. K. Barefield, D. J. Sepelak, A. M. Carrier and D. G. VanDerveer, 176th ACS National Meeting, Miami Beach, FL, Abstract INOR 39.

"Cyclopentadienylbis(ligand)nickel(I); Synthesis and Characterization," E. K. Barefield, S. O'Rear and A. N. Williamson, 30th Southeastern Regional ACS Meeting, Savannah, GA.

PART III (cont'd)

1c. Scientific Collaborators.

David N. Hendrickson, Associate Professor, School of Chemistry, University of Illinois.

Don G. VanDerveer, Research Scientist, Georgia Tech.

Keith D. Hodges, graduate student, Georgia Tech.

Dennis J. Sepelak, graduate student, Georgia Tech.

Allen N. Carrier, graduate student, Georgia Tech.

S. L. Kessel, graduate student, University of Illinois

R. G. Wollmann, graduate student, University of Illinois

Shaun O'Rear, undergraduate research student, Georgia Tech.

1d. none

1e. Technical Description of Project and Results.

Work during this grant period was primarily in two areas, Organometallic Chemistry of Iminium Salts and Chemistry of Iron(II) Tetramethylcyclam with some work on Chemistry of Nickel(I). Brief summaries of goals and accomplishments in each area are given below.

I. Organometallic Chemistry of Iminium Salts

This work is directed to developing methods of synthesis of metal complexes containing these nitrogeneous unsaturates, a systematic understanding of the models of binding of the >C=N< moiety and reactivity patterns of the complexed forms and finally to developing metal assisted or catalyzed reactions of synthetic utility. A more complete discussion of the several phases of this work is given in the Introduction of my currently pending NSF renewal proposal.

a. Preparation, characterization and reactivity of aminoalkyl complexes derived from $CpFe(CO)_2^-$ and iminium salts.

This phase of work, which was to test the notion that nucleophilic reactions of metal complex anions with iminium salts would be a good way of

producing $\eta^1$-bonded iminium ion species (amino alkyls), is essentially complete. The results of this work are described in the attached preprint. Aside from the unusual intramolecular iron-nitrogen interactions detected in some of these complexes, they undergo a number of very interesting reactions that I expect to be general ones for other $\eta^1$-$CR_2NR_2$ species. These include N-alkylation and protonation to form new, extremely stable complexes that are formally derivable from the nitrogen ylides $\bar{C}R_2\overset{+}{N}R_3$ and $\bar{C}R_2\overset{+}{N}R_2H$. Since such ylides are not stable species these reaction are a convenient route to their complexes. Secondly we find that C-N bond cleavage can be effected in $CpFe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]$ and the ultimate product suggests that $CpFe(CO)_2CH_2^+$ is produced. Thus, such reactions may provide alternative routes to carbenes without heteroatom substituents. Work in both of these areas is continuing.

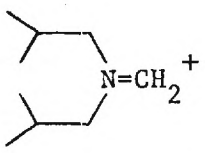
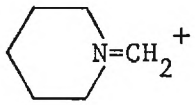
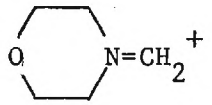
b. Reductive Coupling of Iminium Salts by Ni(o) Reagents.

Some of our most exciting and potentially useful chemistry has arisen from our initial attempts to oxidatively add iminium salts to nickel(0). Following our initial success in the preparation of $\eta^2$-bonded iminium ion species by reaction of $(Ph_3P)_3Ni$ with the iminium salts (published in J. Am. Chem. Soc., 98, 6178 (1976)), we turned to reactions of $Ni(COD)_2$ and $Ni(CO)_4$. These reactions took an entirely different course as outlined below. $Ni(COD)_2$ reacts with $[(CH_3)_2N{=}CH_2]Cl$ according to:

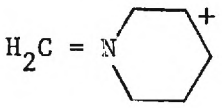
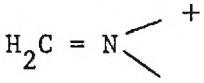
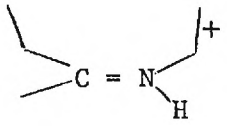
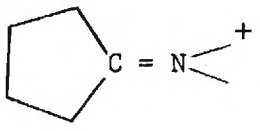
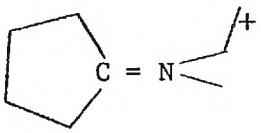
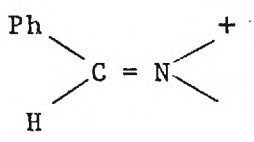
$$Ni(COD)_2 + 2[(CH_3)_2N{=}CH_2]Cl \rightarrow \underset{\text{red}}{\{Ni[(CH_3)_2N{=}CH_2]_2Cl_2\}} + 2COD$$

The infrared spectrum of the red product shows vinylic C-H stretching absorptions but no C=N stretching absorption. The red, diamagnetic product is converted thermally to a blue, paramagnetic material that yields $[(CH_3)_2NHCH_2CH_2NH(CH_3)_2](ClO_4)_2$ upon treatment with $HClO_4$ in ethanol. Our observations suggest that the coupling is concommitant with the red → blue

conversion. This is substantiated by the similarity in properties of the blue complex to those of the known, $[Ni(TMEDA)Cl_2]$. This reaction, which is analogous to the well-known allyl coupling reaction, has been successfully performed with other methylene iminium salts, e.g.

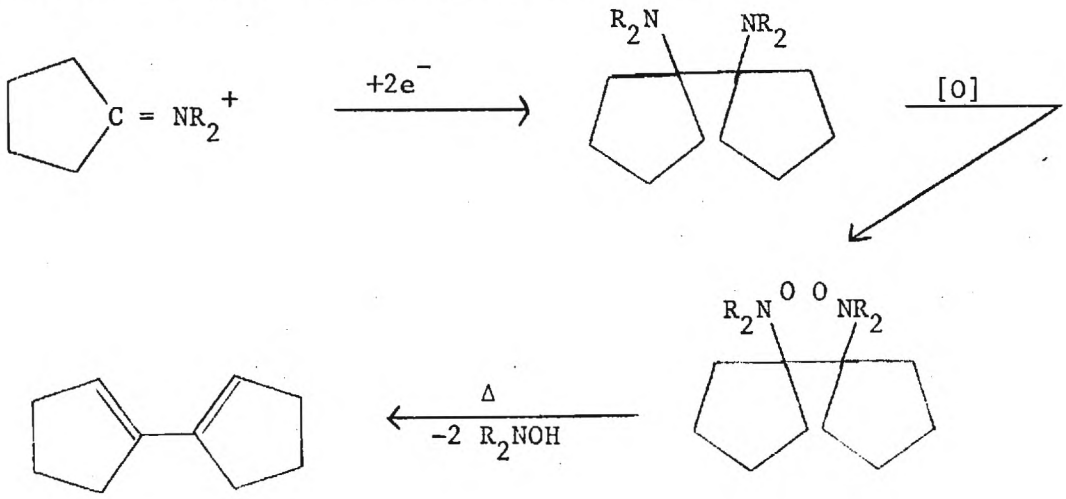




Yields of the diamines are moderate to high. Reductive coupling of iminium salts by chemical reagents have not been previously reported, although electrodimerization has been. The importance to organic synthesis of a carbon-carbon bond forming reaction using readily available starting materials is obvious; however, attempts to utilize $Ni(COD)_2$ for coupling of C-substituted iminium salts have given poor results. Very recent work using $Ni(CO)_4$ in $CH_3CN$ as the coupling reagent indicates that such reactions are possible for a wide range of carbon substituted ions. Substitution in the salts whose couplings have been attempted thus far is limited but includes the following:

PART III (cont'd)

In each case the isolated yields of the diamines were greater than 70%. These preliminary results are very exciting and if the reaction is indeed a general one, it has real synthetic utility. It undoubtly represents the best synthesis of substituted ethylenediamines presently available. More importantly it is a possible route to conjugated dienes via the amine oxide as illustrated by the following reaction sequence:



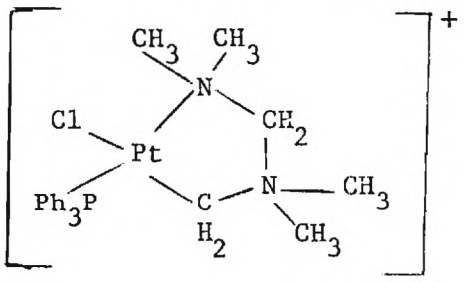

The diene product should be recognized as a valuable precursor for elaboration by Diels-Alder reaction into a fused carbotricyclic system. Although similar syntheses might be achieved via a pinacol coupling reaction of ketones, elimination of the diamine oxide should be stereospecific whereas dehydration of the corresponding pinacol (diol) would likely result in considerable rearrangment since carbonium ion intermediates are involved. Further work in this area is clearly in order.

The complexes $\{Ni[CH_2=N(CH_3)_2](CO)X\}$ (X=Cl, Br, I) have been isolated from reactions of the iminium salts with $Ni(CO)_4$ in THF. In acetonitrile these compounds react with additional $[(CH_3)_2N=CH_2]X$ to produce TMEDA and with other iminium salts to produce mixtures which include cross-coupled product. Of more synthetic interest is the fact that these compounds react with activated alkyl halides (e.g., benzylbromide) and with carboxylic

acid halides to produce amines that are not readily available by other routes. Thus these monocarbonyl may be useful organic reagents.

c. Reaction of $[(CH_3)_2N{=}CH_2]Cl$ with $(Ph_3P)_3Pt$.

In a follow-up of our earlier work on the reaction of $(Ph_3P)_3Ni$ with iminium salts, the title reaction was conducted. A complex of stoichiometry $\{(Ph_3P)Pt[CH_2N(CH_3)_2]_2Cl_2\}$ was obtained under the same reaction conditions. We have completed its X-ray structure determination and find that it contains a novel chelate ring, i.e.,




This surprising result can be rationalized by consideration of the difference in lability of Ni(II) and Pt(II) systems but more importantly it suggests new types of phosphorus ylide chemistry using reagents derived from functionalized phosphonium salts, e.g.,

$$(CH_3)_3PCH_2P(CH_3)_2 + \text{Base} \rightarrow \bar{C}H_2\overset{+}{P}(CH_3)_2CH_2P(CH_3)_2$$

II. Chemistry of Iron(II)-Tetramethylcyclam.

We have used our earlier work on the synthesis and stereochemical features of macrocyclic tertiary amine ligands (work done under NSF grant MPS 73-08709) as a basis for examining certain aspects of iron chemistry that required the unique stereochemical features of the tetramethylcyclam ligand. Of interest is the electronic structure of high-spin, five-coordinate iron(II), a form that occurs in certain naturally occurring heme derivatives, and the preparation of new penta coordinate $\{FeNO\}^{\eta}$ species to

further test current bonding-structure correlations. Results of these studies are detailed in the attached reprint and preprint.

III. Nickel(I)-Chemistry.

The importance of this oxidation state both as an intermediate and as an isolable species is increasing. Within the past two years at least a dozen new examples were isolated and characterized. Our own research activity has been minimal because of limited manpower. A review article detailing the known chemistry of the oxidation state is in preparation. Research activity is described below.

a. Mechanism of Olefin Isomerization by $(Ph_3P)_3NiX$.

The final experiments concerning this problem were completed and the manuscript prepared for publication. A photocopy of the paper is attached.

b. Cyclopentadienylbis(ligand)nickel(I).

Further work on characterization of this class of complexes, particularly with regard to their solution stability, has been done. We have established that certain of these systems are in equilibrium with $Cp_2Ni$ and $L_4Ni$ and that they are definitely intermediates in the formation of nickel(0) complexes from nickelecene plus excess ligand.