AFRL-OSR-VA-TR-2015-0021

(NII) NOVEL CATALYTIC, SYNTHESIS METHODS FOR MAIN GROUP

ROBERT BERGMAN
REGENTS OF THE UNIVERSITY OF CALIFORNIA THE

12/23/2014
Final Report

DISTRIBUTION A: Distribution approved for public release.

Air Force Research Laboratory
AF Office Of Scientific Research (AFOSR)/RTE
Arlington, Virginia 22203
Air Force Materiel Command
16. AUTHOR(S)
Bergman, Robert G.
Arnold, John
Toste, F. Dean

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Regents of the University of California, Berkeley
2220 Piedmont Ave,
Berkeley, CA 94720

12. DISTRIBUTION/AVAILABILITY STATEMENT
Distribution A

14. ABSTRACT
In our efforts to develop reactive group 5 systems, we discovered that the combination of an imido group and the β-diketiminate (BDI) ligand provides a robust platform to support low-valent niobium complexes. We have since discovered that these well-defined niobium (III) complexes, in which low-valent Nb is stabilized by a labile arene ligand, are capable of activating fluoroaromatic substrates. The C-F activation shows unusual substrate selectivity in comparison with late transition metal compounds that activate C-F bonds. Under appropriate conditions, this hydrodefluorination reaction has been rendered catalytic for difluorobenzene, as well as for 1,2- and 1,3-difluorobenzene, releasing benzene and fluorobenzene respectively. We have also been able to use these low-valent niobium systems to access niobium bis(imido) systems that are reactive across their metal-nitrogen pi-bonds. Recently, we have observed that these niobium bis(imido) complexes react reversibly with H2 and irreversibly with silanes via 1,2- addition. We have also observed that these bis(imido) compounds react with aryl isocyanides to exchange nitrile fragments between a tert-butyl imido group and the isocyanide. DFT calculations suggest that this reaction proceeds through a [2+2]-like transition state.

15. SUBJECT TERMS
C-F Bond Activation with Low-Valent Niobium; Reactivity across M-N π-bonds in Niobium Bismido Complexes

16. SECURITY CLASSIFICATION OF:
<table>
<thead>
<tr>
<th>a. REPORT</th>
<th>b. ABSTRACT</th>
<th>c. THIS PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unclassified</td>
<td>Unclassified</td>
<td>Unclassified</td>
</tr>
</tbody>
</table>

17. LIMITATION OF ABSTRACT
UL

18. NUMBER OF PAGES
4

19a. NAME OF RESPONSIBLE PERSON
Robert G. Bergman

19b. TELEPHONE NUMBER (include area code)
510-642-2156
<table>
<thead>
<tr>
<th>INSTRUCTIONS FOR COMPLETING SF 298</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1. REPORT DATE.</strong> Full publication date, including day, month, if available. Must cite at least the year and be Year 2000 compliant, e.g. 30-06-1998; xx-06-1998; xx-xx-1998.</td>
</tr>
<tr>
<td><strong>2. REPORT TYPE.</strong> State the type of report, such as final, technical, interim, memorandum, master's thesis, progress, quarterly, research, special, group study, etc.</td>
</tr>
<tr>
<td><strong>3. DATES COVERED.</strong> Indicate the time during which the work was performed and the report was written, e.g., Jun 1997 - Jun 1998; 1-10 Jun 1996; May - Nov 1998; Nov 1998.</td>
</tr>
<tr>
<td><strong>4. TITLE.</strong> Enter title and subtitle with volume number and part number, if applicable. On classified documents, enter the title classification in parentheses.</td>
</tr>
<tr>
<td><strong>5a. CONTRACT NUMBER.</strong> Enter all contract numbers as they appear in the report, e.g. F33615-86-C-5169.</td>
</tr>
<tr>
<td><strong>5b. GRANT NUMBER.</strong> Enter all grant numbers as they appear in the report, e.g. AFORS-82-1234.</td>
</tr>
<tr>
<td><strong>5c. PROGRAM ELEMENT NUMBER.</strong> Enter all program element numbers as they appear in the report, e.g. 61101A.</td>
</tr>
<tr>
<td><strong>5d. PROJECT NUMBER.</strong> Enter all project numbers as they appear in the report, e.g. 1F665702D1257; ILIR.</td>
</tr>
<tr>
<td><strong>5e. TASK NUMBER.</strong> Enter all task numbers as they appear in the report, e.g. 05; RF0330201; T4112.</td>
</tr>
<tr>
<td><strong>5f. WORK UNIT NUMBER.</strong> Enter all work unit numbers as they appear in the report, e.g. 001; AFAPL30480105.</td>
</tr>
<tr>
<td><strong>6. AUTHOR(S).</strong> Enter name(s) of person(s) responsible for writing the report, performing the research, or credited with the content of the report. The form of entry is the last name, first name, middle initial, and additional qualifiers separated by commas, e.g. Smith, Richard, J, Jr.</td>
</tr>
<tr>
<td><strong>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES).</strong> Self-explanatory.</td>
</tr>
<tr>
<td><strong>8. PERFORMING ORGANIZATION REPORT NUMBER.</strong> Enter all unique alphanumeric report numbers assigned by the performing organization, e.g. BRL-1234; AFWL-TR-85-4017-Vol-21-PT-2.</td>
</tr>
<tr>
<td><strong>9. SPONSOR/MONITOR'S NAME(S) AND ADDRESS(ES).</strong> Enter the name and address of the organization(s) financially responsible for and monitoring the work.</td>
</tr>
<tr>
<td><strong>10. SPONSOR/MONITOR'S ACRONYM(S).</strong> Enter, if available, e.g. BRL, ARDEC, NADC.</td>
</tr>
<tr>
<td><strong>11. SPONSOR/MONITOR'S REPORT NUMBER(S).</strong> Enter report number as assigned by the sponsoring/monitoring agency, if available, e.g. BRL-TR-829; -215.</td>
</tr>
<tr>
<td><strong>12. DISTRIBUTION/AVAILABILITY STATEMENT.</strong> Use agency-mandated availability statements to indicate the public availability or distribution limitations of the report. If additional limitations/ restrictions or special markings are indicated, follow agency authorization procedures, e.g. RD/FRD, PROPIN, ITAR, etc. Include copyright information.</td>
</tr>
<tr>
<td><strong>13. SUPPLEMENTARY NOTES.</strong> Enter information not included elsewhere such as: prepared in cooperation with; translation of; report supersedes; old edition number, etc.</td>
</tr>
<tr>
<td><strong>14. ABSTRACT.</strong> A brief (approximately 200 words) factual summary of the most significant information.</td>
</tr>
<tr>
<td><strong>15. SUBJECT TERMS.</strong> Key words or phrases identifying major concepts in the report.</td>
</tr>
<tr>
<td><strong>16. SECURITY CLASSIFICATION.</strong> Enter security classification in accordance with security classification regulations, e.g. U, C, S, etc. If this form contains classified information, stamp classification level on the top and bottom of this page.</td>
</tr>
<tr>
<td><strong>17. LIMITATION OF ABSTRACT.</strong> This block must be completed to assign a distribution limitation to the abstract. Enter UU (Unclassified Unlimited) or SAR (Same as Report). An entry in this block is necessary if the abstract is to be limited.</td>
</tr>
</tbody>
</table>
The following is a brief summary of the research results obtained as a result of support from the AFOSR. For a more exhaustive report of these results, please see our recent publications.

**C-F Bond Activation with Low-Valent Niobium**

Low-valent complexes of tantalum and niobium undergo a variety of unusual reactions with both organic and inorganic substrates. In our efforts to develop reactive group 5 systems, we discovered that the combination of an imido group and the diketiminate (BDI) ligand provides a robust platform to support low-valent niobium complexes (Scheme 1). These complexes have been shown to undergo a variety of interesting stoichiometric and catalytic reactivity, including activation of strong aromatic and benzylic carbon-fluorine and carbon-chlorine bonds.

Within the past two decades, there has been a surge of interest in the activation of C-X bonds (X = F, Cl) by transition-metal complexes aimed at both waste removal and synthetic applications. In addition to waste remediation, activation of C-F and C-Cl bonds can be applied in selective functionalization of organic molecules. In recent chemistry relevant to this problem, we reported remarkable reactivity leading to dis-assembly of benzylic CF$_3$ groups via triple C-F bond activation (Scheme 2) that proceeds through a Nb(III) η$^6$-arene intermediate. We have since discovered that the well-defined niobium (III) complex 2, in which low-valent Nb is stabilized by a labile arene ligand, is capable of activating fluoroaromatic substrates (Scheme 3). Dissociation of the coordinated arene from 2 occurs readily at room temperature leading to the formation of a three-coordinate transient intermediate, 5. Fluorobenzene then coordinates to give 6, which undergoes C-F activation to form the aryl fluoride niobium (V) compound 7. In this system, 6 appears to be a key intermediate for the C-F activation step since non-aromatic fluorinated species do not undergo C-F activation.

The C-F activation observed leading to complex 7 shows unusual substrate selectivity in comparison with late transition metal compounds that activate C-F bonds. We found that the niobium metal center is
highly reactive with the C-F bonds of fluorobenzene, difluorobenzenes, and some trifluorobenzenes, but does not react with pentafluorobenzene or hexafluorobenzene to any appreciable extent. In stark contrast, electron-rich late metals (i.e. group 7-10) tend to react preferentially with highly fluorinated arenes (e.g. C₆F₆), which have more highly polarized C-F bonds. DFT calculations suggest that the mechanism of C-F oxidative addition to complex 6 goes through a bimetallic transition state leading to an intermediate analogous to compound 8 (Scheme 4). These binuclear species may help to explain the unusual selectivity observed in this system in relation to the few examples of other transition metal systems that oxidatively add C-F bonds.

We have found that treating complex 7 with n-butylsilane results in H/F exchange, followed by reductive elimination of the hydrodefluorinated arene (Scheme 5, top). Under appropriate conditions, this hydrodefluorination reaction has been rendered catalytic for fluorobenzene, as well as for 1,2- and 1,3-difluorobenzene, releasing benzene or fluorobenzene respectively. In the case of the difluorobenzenes, further catalytic hydrodefluorination to benzene occurs, but at a significantly slower rate, indicating that we may be able to use 7 to selectively functionalize only a single C-F bond in polyfluoroaromatics. We have also observed that treating complex 7 with tert-butyl isocyanide (Scheme 5, bottom) leads to the clean and rapid (t₁/₂ ~ 2 min) formation of the insertion product, complex 9. This reacts with silane (PhSiH₃ or tBuSiH₃) resulting in an H/F exchange and reductive elimination similar to that observed in the hydrodefluorination transformation, leading to the formation of an imine bound species 10.

**Reactivity across M-N π-bonds in Niobium Bisimido Complexes**

We are interested in designing systems containing very reactive metal-ligand π bonds in the hope of activating a range of C-H bonds, as well as heteroatom-hydrogen (E-H) bonds (i.e. B-H, Si-H, N-H, and P-H) under mild conditions with the eventual goals of functionalizing chemical feedstocks and carrying out dehydrocoupling reactions to prepare useful materials and materials precursors. In addition to activating C-H and E-H bonds, we also are interested in using [2+2] and [3+2] reactions across metal imido bonds in order to functionalize unsaturated hydrocarbon substrates.

Recently, we have observed that the niobium bis(imido) complex 11 supported by a bulky BDI ligand also reacts reversibly with H₂ via 1,2-addition (Scheme 6). In this case, the equilibrium favors the hydrogenated product under reasonable pressures of H₂, allowing its
isolation and full characterization. 11 also reacts irreversibly with boranes and silanes via 1,2-addition to give borylamido and silylamido hydride species 13. We are continuing to investigate the activation of other E-H bonds across the imido group, and are working toward utilizing these 1,2-additions to carry out processes such as dehydrocoupling.

Two routes we have used to prepare 11 are shown in Scheme 7. The more direct route involves transfer of a nitrene group from an azide to a low-valent Nb fragment (Scheme 7, top). In the second route, hydrogenolysis of 1 in diethyl ether first results in transfer of a nitrene fragment from the BDI ligand to the niobium center via intramolecular reductive C-N cleavage to give the monoazabutadiene (MAD) supported niobium bis(imido) complex 14 (Scheme 7, bottom). Interestingly, the BDI backbone can then be regenerated via reaction with tert-butylazide, thus demonstrating that like 2, the niobium 5 complex 14 can act as a source of low-coordinate BDINb(N′Bu). Our studies have shown that generation of 11 from 14 proceeds through a tetrazine-type intermediate formed from [3+2] cycloaddition of tert-butylazide.

Compound 14 has also been shown to undergo [2+2] cycloaddition reactions with alkynes and strained olefins, clearly demonstrating that it is reactive across its Nb-N π-bonds.

We have observed that treatment of 11 with either tert-butylisocyanate or carbon disulfide results in generation of a bis-μ-oxo or bis-μ-sulfido product, respectively, which presumably result from dimerization of an initially generated terminal oxo-imido or sulfido-imido complex generated from [2+2] processes (Scheme 8, top). The same compounds are accessed through reaction of 2 or in-situ generated Nb(III) with oxygen or sulfur oxidants (Scheme 8, bottom). We have also observed that compound 11 reacts with 2,6-dimethylphenyl isocyanide (XylNC) to give compound 18, which results from exchange of nitrene fragments between an imido group and the isocyanide (Scheme 9). DFT calculations suggest that this reaction proceeds through a [2+2]-like transition state to give an intermediate that resembles a reduced carbodiimide, then undergoes a
retro [2+2] reaction to give the product. Kinetic and mechanistic studies on this unusual reaction are ongoing.
1.

1. Report Type
   Final Report

Primary Contact E-mail
Contact email if there is a problem with the report.
   rbergman@berkeley.edu

Primary Contact Phone Number
Contact phone number if there is a problem with the report
   5106422156

Organization / Institution name
Regents of the University of California, Berkeley

Grant/Contract Title
The full title of the funded effort.
   (NII) Novel Catalytic, Synthesis Methods for Main Group Materials and Reagents for Organic Synthesis

Grant/Contract Number
AFOSR assigned control number. It must begin with "FA9550" or "F49620" or "FA2386".
   FA9550-11-1-0008

Principal Investigator Name
The full name of the principal investigator on the grant or contract.
   Robert G. Bergman

Program Manager
The AFOSR Program Manager currently assigned to the award
   Dr. Michael Berman

Reporting Period Start Date
   09/01/2013

Reporting Period End Date
   08/31/2014

Abstract
In our efforts to develop reactive group 5 systems, we discovered that the combination of an imido group and the β-diketiminate (BDI) ligand provides a robust platform to support low-valent niobium complexes. We have since discovered that these well-defined niobium (III) complexes, in which low-valent Nb is stabilized by a labile arene ligand, are capable of activating fluoroaromatic substrates. The C-F activation shows unusual substrate selectivity in comparison with late transition metal compounds that activate C-F bonds. Under appropriate conditions, this hydrodefluorination reaction has been rendered catalytic for fluorobenzene, as well as for 1,2- and 1,3-difluorobenzene, releasing benzene and fluorobenzene respectively.

We have also been able to use these low-valent niobium systems to access niobium bis(imido) systems that are reactive across their metal-nitrogen pi-bonds. Recently, we have observed that these niobium bis(imido) complexes react reversibly with H2 and irreversibly with silanes via 1,2-addition. We have also observed that these bis(imido) compounds react...
with aryl isocyanides to exchange nitrene fragments between a tert-butyl imido group and the isocyanide. DFT calculations suggest that this reaction proceeds through a [2+2]-like transition state. Kinetic and mechanistic studies on this unusual reaction are ongoing.

**Distribution Statement**

This is block 12 on the SF298 form.

**Explanation for Distribution Statement**

If this is not approved for public release, please provide a short explanation. E.g., contains proprietary information.

**SF298 Form**

Please attach your SF298 form. A blank SF298 can be found here. Please do not password protect or secure the PDF. The maximum file size for an SF298 is 50MB.

AFD - SF298 Form 12.22.14.pdf

Upload the Report Document. File must be a PDF. Please do not password protect or secure the PDF. The maximum file size for the Report Document is 50MB.


Upload a Report Document, if any. The maximum file size for the Report Document is 50MB.

**Archival Publications (published) during reporting period:**


9. Obenhuber, A.H.; Gianetti, T.L.; Berrebi, X.; Bergman, R.G.; Arnold, J. “Reaction of


Changes in research objectives (if any):
N/A

Change in AFOSR Program Manager, if any:
N/A

Extensions granted or milestones slipped, if any:
N/A

AFOSR LRIR Number

LRIR Title

Reporting Period

Laboratory Task Manager

Program Officer

Research Objectives

Technical Summary

Funding Summary by Cost Category (by FY, $K)

<table>
<thead>
<tr>
<th></th>
<th>Starting FY</th>
<th>FY+1</th>
<th>FY+2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salary</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equipment/Facilities</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Supplies</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Report Document

Report Document - Text Analysis

Appendix Documents
2. Thank You

E-mail user

Dec 22, 2014 20:08:20 Success: Email Sent to: rbergman@berkeley.edu