

11:25:45


OCA PAD AMENDMENT - PROJECT HEADER INFORMATION

02/27/95

Active

Project #: G-33-E59
Center #: 10/24-6-R8067-0A0Cost share #:
Center shr #:Rev #: 3
OCA file #:
Work type : RES
Document : CONT
Contract entity: GTRCContract#: 139020
Prime #: F49620-93-C-0069

Mod #: DELIVERABLE SCH

Subprojects ? : N
Main project #:CFDA:
PE #: N/AProject unit:
Project director(s):
REES W SCHEMISTRY
CHEMISTRYUnit code: 02.010.136
(404)894-4002Sponsor/division names: SPIRE CORPORATION OF MA
Sponsor/division codes: 218/ BEDFORD, MA
/ 105Award period: 940121 to 950831 (performance) 950831 (reports) 

Sponsor amount	New this change	Total to date
Contract value	0.00	86,983.00
Funded	0.00	86,983.00
Cost sharing amount		0.00

Does subcontracting plan apply ? : N

Title: ER-DOPED SEMICONDUCTORS

PROJECT ADMINISTRATION DATA

OCA contact: E. Faith Gleason

894-4820

Sponsor technical contact

Sponsor issuing office

DR. ANTON GREENWALD
(617)275-6000STEPHEN BOORSCHTEIN
(617)275-6000SPIRE CORPORATION
ONE PATRIOTS PARK
BEDFORD, MA 01730-2396PROCUREMENT MANAGER____(PH. EXT. 275)
SPIRE CORPORATION
ONE PATRIOTS PARK
BEDFORD, MA 01730-2396
FAX: (617) 275-7470

Security class (U,C,S,TS) : U

ONR resident rep. is ACO (Y/N): N

Defense priority rating :

GOVT supplemental sheet

Equipment title vests with: Sponsor X

GIT

FAR CLASUE 52.244.5, ALT I

Administrative comments -

REVISION ISSUED TO ADD FINAL REPORT, IAW SPIRE LETTER DATED 9/14/94. DUE DATE
FOR FINAL REPORT IS CORRECTED TO END DATE OF SUBCONTRACT.

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT

Closeout Notice Date 10/09/95

Project No. G-33-E59

Center No. 10/24-6-R8067-0A0

Project Director REES W S

School/Lab CHEMISTRY

Sponsor SPIRE CORPORATION OF MA/BEDFORD, MA

Contract/Grant No. 139020

Contract Entity GTRC

Prime Contract No. F49620-93-C-0069

Title ER-DOPED SEMICONDUCTORS

Effective Completion Date 950831 (Performance) 950831 (Reports)

Closeout Actions Required:	Y/N	Date Submitted
Final Invoice or Copy of Final Invoice	Y	
Final Report of Inventions and/or Subcontracts	Y	
Government Property Inventory & Related Certificate	Y	
Classified Material Certificate	N	
Release and Assignment	Y	
Other	N	

Comments

Subproject Under Main Project No.

Continues Project No.

Distribution Required:

Project Director	Y
Administrative Network Representative	Y
GTRI Accounting/Grants and Contracts	Y
Procurement/Supply Services	Y
Research Property Management	Y
Research Security Services	N
Reports Coordinator (OCA)	Y
GTRC	Y
Project File	Y
Other	N
	N

NOTE: Final Patent Questionnaire sent to PDPI.

#3 G-33-E59

20 April 1994

Monthly Letter Report

Georgia Institute of Technology

Project G-33-E59

Professor W. S. Rees, Jr., Project Director

Spire Corporation of MA, Sponsor

1. All remaining necessary initial chemicals were ordered and received.
2. All necessary glassware has been requisitioned, and some orders have been filled.
3. Negotiations are continuing with Florida State University for the release of necessary equipment, impounded upon the move of the P. I. in December 1993.
4. Laboratory safety renovation plans have been submitted to the campus office of design.

5

Georgia Tech

School of Chemistry and Biochemistry

Georgia Institute of Technology

Atlanta, Georgia 30332-0400

USA

+01-894-4002

+01-894-7452 Fax

G-33-E59

#4

13 May 1994

Dr. Anton Greenwald
Spire Corporation
One Patriots Park
Bedford, Massachusetts 01730-2396

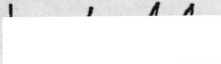
Dear Anton:

Thank you for your phone call of the other day. I sincerely enjoyed hearing about the results of the high levels of erbium doping and, also found the incorporation of small amounts of silicon to be of potential technological interest. Likewise, the erbium migration issue would appear to be worthy of technical note and, perhaps, even a manuscript at this stage if you feel sufficient data are available.

After discussing it with my postdoctoral associate, we think that we can meet the time frame of approximately the end of this month for the delivery of the second erbium compound for testing. We anticipate the receipt of your bubbler, we will clean the bubbler thoroughly, and only return it to you if the compound is pure. I will keep you updated on the status of purification over the next three weeks.

Regarding a technical report for the AFOSR, please see the attached page.

Sincerely yours,


William S. Rees, Jr.
Associate Professor
School of Chemistry and Biochemistry and
School of Materials and Engineering

WSR/fc

Enclosure

TECHNICAL REPORT ON SUBCONTRACT SBIR PHASE II FROM
SPIRE CORPORATION TO THE GEORGIA INSTITUTE OF TECHNOLOGY

AFOSR AWARD FOR ERBIUM DOPING OF SEMICONDUCTING MATERIALS

13 May 1994
William S. Rees, Jr

Item 1. All necessary chemicals have been ordered, and received at Georgia Tech, as well as designs for new precursors being completed.

Item 2. Almost all miscellaneous supplies (glassware, solvents, consumables) have been ordered and most are on hand now.

Item 3. Personnel have become familiar with the synthetic strategies to be employed for the preparation of erbium amides.

Item 4. Synthesis of the first new erbium amide to be delivered to Spire has been initiated, and completion is anticipated within the next reporting period.

Item 5. Equipment, retained by Florida State University, still is to be replaced. We anticipate receipt of some of the new equipment, purchased on new funds, within the next few months. This continues to be a *minor* impediment to the overall objectives of the project.

8

G-33-E59

7

Monthly letter report to Spire

15 July 1994

One bubbler was filled with a new Er source compound and sent to Spire this month.

William S. Rees, Jr.

([REDACTED])

G-33-E59
8

Monthly letter report to Spire

16 August 1994

Purification of a different Er compound is in progress.

William S. Rees, Jr.

10
[Redacted]

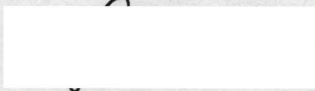
G-33-E59
70

Monthly letter report to Spire

18 September 1994

A new compound has been made, and efforts directed at scaling up the preparation are in progress.

William S. Rees, Jr.



RECEIVED
OCT 30 1994
ADMINISTRATION
OFFICE OF COMPLIANCE

19 May 1995

Contract Deliverable # 13

G-33-E59

AFOSR Contract to Spire Corp.

Spire Corp. Subcontract to GIT

Prof. W. S. Rees, Jr.

Received one empty bubbler from Spire. Work in progress to clean and refill bubbler, prior to return shipment to Spire.

1 [REDACTED]

William S. Rees, Jr.

G-33-E-59

#14

19 May 1995

Contract Deliverable

G-33-E59

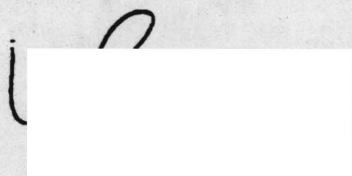
AFOSR Contract to Spire Corp.

Spire Corp. Subcontract to GIT

Prof. W. S. Rees, Jr.

Received one empty bubbler from Spire. Work in progress to clean and refill bubbler, prior to return shipment to Spire.

William S. Rees, Jr.



ERBIUM *TRIS*(AMIDE) COMPOUNDS AS SOURCE MOLECULES FOR RARE-EARTH DOPING OF SEMICONDUCTING MATERIALS, Oliver Just and William S. Rees Jr., Georgia Institute of Technology, School of Chemistry and Biochemistry and School of Materials Science and Engineering and Molecular Design Institute, Atlanta, GA 30032-0400; Anton C. Greenwald, Spire Corporation, One Patriot Park, Bedford, MA 01730-2396; Herbert Schumann, Technische Universität Berlin, Berlin, Germany.

Due to its unique electronic properties (characteristic intra-4f shell emission at 1.54 nm) erbium emerged among the lanthanides as a suitable dopant for preparation of epitaxially grown semiconducting films. Since the originally employed erbium *tris*(cyclopentadienyl) and -(tetramethylheptanedionate) CVD compounds deposit carbon and/or fluorine during the decomposition process, erbium *tris*(amides) have been selected as a new class of compounds possessing no direct metal-carbon or metal-oxygen interactions. Evaluations of {*tris*[*bis*(trimethylsilyl)]amido}erbium demonstrated its suitability for doping of GaAs and AlGaAs laser diodes. Further investigations have confirmed the high incorporation efficiency and apparent edge, when compared with alternative erbium sources. In continuation of the studies on erbium *tris*(amide) compounds, numerous higher volatile examples featuring one -SiR₃-fragment replaced by a -CR₃-moiety have been obtained, and currently are being studied by MOCVD for their potential toward silicon and carbon incorporation, as well as enhancing effect on erbium content of the deposited materials.

13 July 1995

Contract Deliverable #16


G-33-E59

AFOSR Contract to Spire Corp.

Spire Corp. Subcontract to GIT

Prof. W. S. Rees, Jr.

Abstract of work completed to this point entitled "Incorporation of Erbium into Semiconducting Materials Employing MOCVD of Various Erbium Amides," is attached.


William S. Rees, Jr.

Attachment

INCORPORATION OF ERBIUM INTO SEMICONDUCTING MATERIALS EMPLOYING MOCVD OF VARIOUS ERBIUM AMIDES, Oliver Just and William S. Rees Jr., Georgia Institute of Technology, School of Chemistry and Biochemistry and School of Materials Science and Engineering and Molecular Design Institute, Atlanta, GA 30032-0400; Anton C. Greenwald, Spire Corporation, One Patriot Park, Bedford, MA 01730-2396; Herbert Schumann and Roman Weimann, Technische Universität Berlin, Berlin, Germany.

Due to its unique electronic properties (characteristic intra-4f shell emission at 1.54 nm) erbium emerged among the lanthanides as a suitable dopant for preparation of epitaxially grown semiconducting films. Since the originally employed erbium *tris*(cyclopentadienyl) and -(tetramethylheptanedionate) CVD compounds deposit carbon and/or fluorine during the decomposition process, erbium-*bis*(amides) have been selected as a new class of compounds possessing no direct metal-carbon or metal-oxygen interactions. Evaluations of {*tris*[*bis*(trimethylsilyl)]amido}erbium demonstrated its suitability for doping of GaAs and AlGaAs laser diodes. Further investigations have confirmed the high incorporation efficiency and apparent edge, when compared with alternative erbium sources. In continuation of the studies on erbium *tris*(amide) compounds, numerous higher volatile examples featuring one -SiR₃-fragment replaced by a -CR₃-moiety have been obtained, and currently are being studied by MOCVD for their potential toward silicon and carbon incorporation, as well as enhancing effect on erbium content of the deposited materials.

4 October 1995

Contract Deliverable #17


G-33-E59

AFOSR Contract to Spire Corp.

Spire Corp. Subcontract to GIT

Prof. W. S. Rees, Jr.

Abstract of work completed to be presented at the Fall Materials Research Society meeting in Boston, MA. entitled "Erbium Tris (Amide) Compounds as Source Molecules for Rare-Earth Doping of Semiconducting Materials" is attached.


William S. Rees, Jr.

Attachment

ERBIUM *TRIS*(AMIDE) COMPOUNDS AS SOURCE MOLECULES FOR RARE-EARTH DOPING OF SEMICONDUCTING MATERIALS, Oliver Just and William S. Rees Jr., Georgia Institute of Technology, School of Chemistry and Biochemistry and School of Materials Science and Engineering and Molecular Design Institute, Atlanta, GA 30032-0400; Anton C. Greenwald, Spire Corporation, One Patriot Park, Bedford, MA 01730-2396; Herbert Schumann and Roman Weimann, Technische Universität Berlin, Berlin, Germany.

Due to its unique electronic properties (characteristic intra-4f shell emission at 1.54 nm) erbium emerged among the lanthanides as a suitable dopant for preparation of epitaxially grown semiconducting films. Since the originally employed erbium *tris*(cyclopentadienyl) and -(tetramethylheptanedionate) CVD compounds deposit carbon, oxygen and/or fluorine during the decomposition process, erbium *tris*(amides) have been selected as a new class of compounds possessing no direct metal-carbon or metal-oxygen interactions.

Evaluations of {*tris*[*bis*(trimethylsilyl)]amido}erbium demonstrated its suitability for doping of GaAs and AlGaAs laser diodes. Further investigations have confirmed the high incorporation efficiency and apparent edge, when compared with alternative erbium sources. In continuation of the studies on erbium *tris*(amide) compounds, numerous higher volatile examples featuring one -SiR₃-fragment replaced by a -CR₃-moiety have been obtained, and currently are being studied by MOCVD for their potential toward silicon and carbon incorporation, as well as enhancing effect on erbium content of the deposited materials.

Deliverable #18

4 October 1995


Deliverable #18 on G-33-E59

Presented at: the Gordon Research Conference on Solid State Chemistry, Irsee, Germany

On: September 26, 1995

By: Dr. William S. Rees, Jr.

Entitled: "Rare Earth Doped Semiconducting Materials: Getting Light out of an Indirect Bandgap"

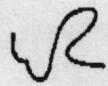

William S. Rees, Jr.

AFOSR contract to: Spire, Corp.


Subcontract to: Georgia Institute of Technology

on OMVPE Doping of AlGaAs with Er

✓ Spire P.I.: Dr. Anton Greenwald

Georgia Tech P.I.: Dr. William S. Rees, Jr. 

Interim Progress Report
14 March 1994

1. Personnel have been hired and are now on-board.
 2. Chemicals have been ordered and are beginning to arrive.
 3. Necessary custom glassware has been ordered, and should begin to arrive within the next four weeks.
- 

22 June 1994

404-894-4049 direct voice

404-894-1144 direct FAX

Dr. Anton Greenwald
Spire Corporation
One Patriots Park
Bedford, Massachusetts 01730-2396

Dear Anton:

Attached please find the most recent technical report on our sub-contract.

Best regards,

William S. Rees, Jr.
Associate Professor
School of Chemistry and Biochemistry and
School of Materials Science and Engineering

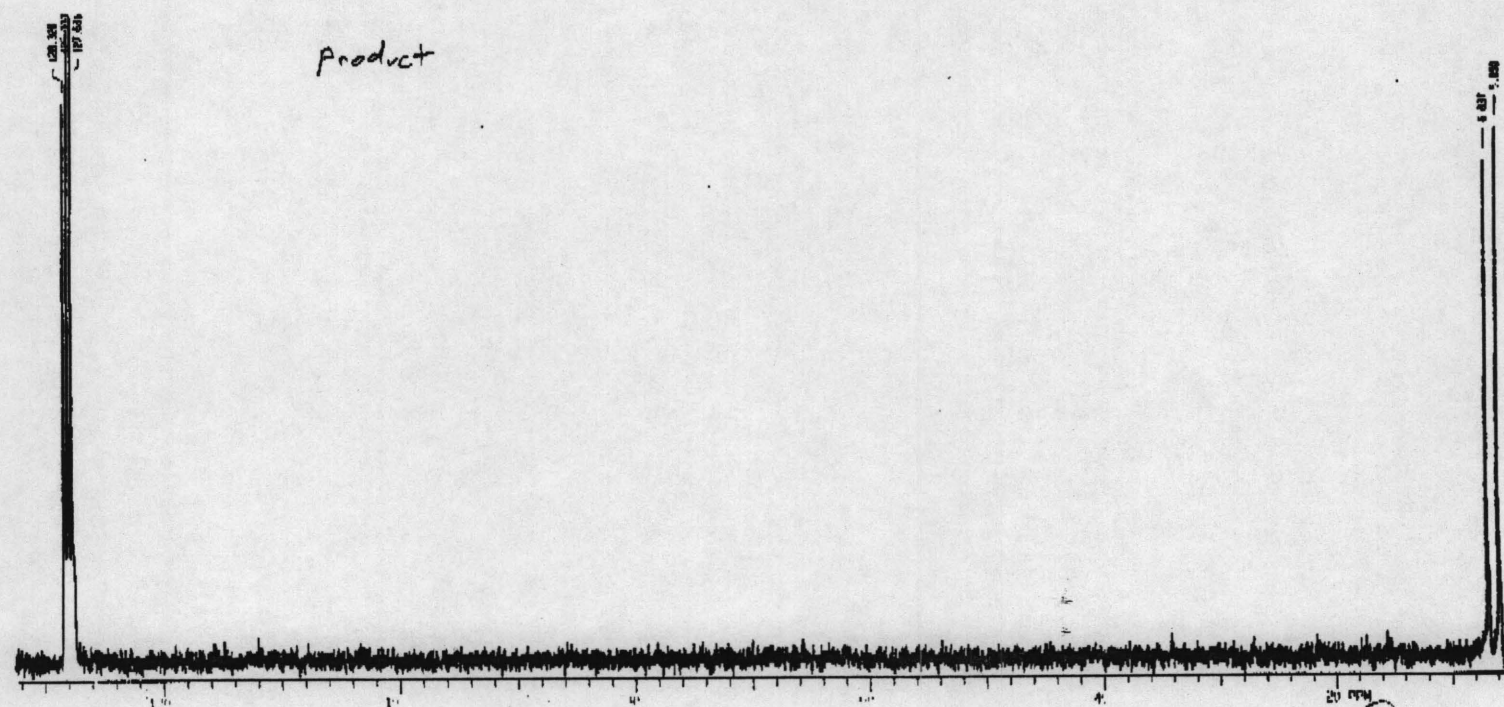
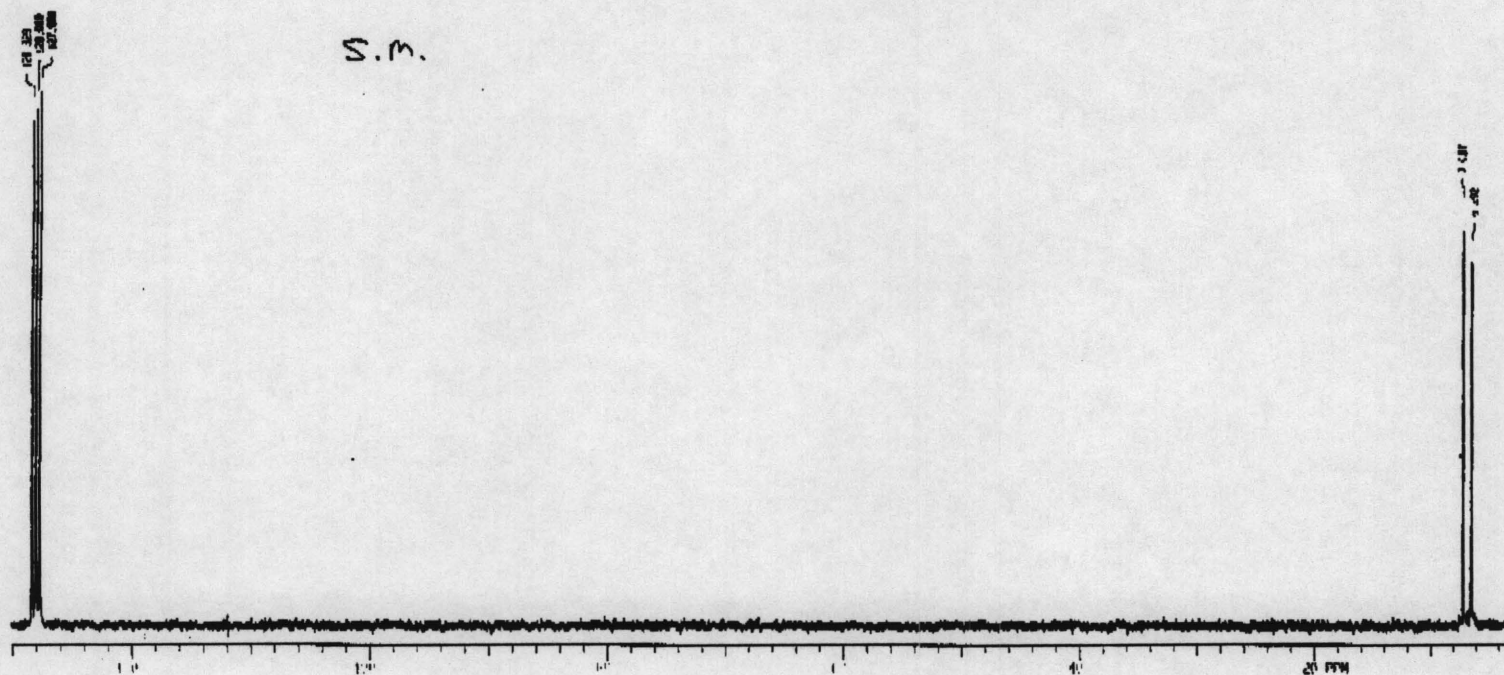
Enclosure

Interim Technical Report on Georgia Institute of Technology
Subcontract from Spire Corporation on Prime Contract
from Ballistic Missile Defense Organization as Monitored
by the Air Force Office of Scientific Research
on "Erbium Doping of AlGaAs Lasers"

From: Professor William S. Rees, Jr., Georgia Institute of Technology
To: Dr. Anton C. Greenwald, Spire Corporation

21 June 1994

1. Purification of $\text{Er}\{\text{N}[(\text{Si}(\text{CH}_3)_3)(\text{C}(\text{CH}_3)_3)]\}_3$ continues. The present known impurity is lithium.
2. Preparation of $\text{Er}\{\text{N}[\text{Si}(\text{CH}_2\text{CH}_3)_3]_2\}_3$ has been initiated. $^{13}\{\text{^1H}\}$ NMR spectral data are attached.



G-33-E59
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Interim Quarterly Technical Report on Georgia Institute of Technology
Subcontract from Spire Corporation on Prime Contract
from Ballistic Missile Defense Organization as Monitored
by the Air Force Office of Scientific Research
on "Erbium Doping of AlGaAs Lasers"

From: Professor William S. Rees, Jr., Georgia Institute of Technology
To: Dr. Anton C. Greenwald, Spire Corporation

22 September 1994

The quarterly report is attached (5 pages).

OCT 1994
OCT 1994
OCT 1994

Georgia Institute of Technology

Atlanta, Georgia 30332-0400

USA

404•894•4002

404•894•7452 Fax

22 June 1994

404-894-4049 direct voice

404-894-1144 direct FAX

Dr. Anton Greenwald
Spire Corporation
One Patriots Park
Bedford, Massachusetts 01730-2396

Dear Anton:

Attached please find the most recent technical report on our sub-contract.

Best regards,



William S. Rees, Jr.
Associate Professor
School of Chemistry and Biochemistry and
School of Materials Science and Engineering

Enclosure

10

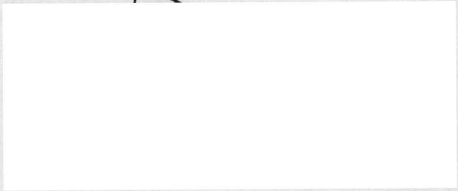
QR
G-33-E59
114 12
Deliverable #11

18 April 1995

Deliverable #11, 20 Feb 1995, on G-33-E59

Presented at: the Florida Advanced Materials Chemistry Conference, Palm Coast, Florida
On: March 21, 1995
By: Drs. Oliver Just and William S. Rees, Jr.
Entitled: "Incorporation of Erbium in Semiconducting Materials Employing OMVPE
of Various Erbium-Amide Sources"

William S. Rees, Jr.



Deliverable #12

18 April 1995

Deliverable #12, 15 Mar 1995, on G-33-E59

Presented at: American Chemical Society National Meeting, Anaheim, California

On: April 5, 1995

By: Dr. William S. Rees, Jr.

Entitled: "Chemical Issues in Semiconductor Doping" (see attached abstract)

William S. Rees, Jr.

Attachment



Chemical Issues in Semiconductor Doping

William S. Rees, Jr.
School of Chemistry and Biochemistry and
School of Materials Science and Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

Frequently electronic materials have a need to be controllably and reproducibly doped with heteroatoms in a site-specific manner. Such three-dimensional structure control is required for achievement of optimum optical and electronic properties. The challenge for the materials chemist is the design of suitable precursor compounds to achieve this objective in a CVD process. Two specific materials systems will be the focus of discussion (p-type ZnSe and Er doped GaAs).

From a chemical perspective, the precursors must obey traditional coordination chemistry guidelines regarding coordination number and electroneutrality. From a materials perspective, the final thin film must be grown at temperatures compatible with other device components and possess not only the proper doped structure, but also must avoid the incorporation of undesired heteroatoms. One fundamental objective of our research in this area is the reconciliation of these two competing issues.

Several problems are intrinsic to semiconductor doping by OMVPE. Among the most important are dopant identity and concentration. It is only by the controllable location of atoms in a site-specific manner that the entire dopant concentration is permitted to be electronically active. In the absence of exercising such control, the percentage of inactive dopant atoms is increased greatly. This discussion will focus on issues which are related to the achievement of such site-determining objectives.

There are several wide bandgap materials of potential interest as optoelectronic targets in the blue region of the spectrum. Among the present candidates, diamond, SiC, GaN and ZnSe, each has emerged as a promising candidate for device fabrication. In the example of ZnSe, fabrication of a diode demands a ready preparative method for both p- and n-type material. Although achievement of n-type ZnSe has been demonstrated by OMVPE, the success with p-type material has been substantially less dramatic.

MBE growth of nitrogen-doped ZnSe has been demonstrated to produce usable blue light devices. To date, CVD routes have not been successful in meeting the requirements/demands of this materials system. In order to grow epitaxial surface areas of sufficient size to introduce economic and technological viability into this materials system, MBE has met its present limitations. Thus, investigators have focused on proven techniques for the production of semiconductors on large surface areas. Among the candidate methods, OMVPE perhaps has the highest combination of many of the most attractive features.

One intrinsic property of all semiconductors is a temperature-dependent bandgap. One potential route to address this issue capitalizes on the f-f transition manifold of lanthanide or actinide elements. In order to wavelength-match emitters and receivers with present large volume optical fiber networks, operating at 1.54 μ , erbium has been selected as a target dopant. GaAs/AlGaAs laser technology is a relatively mature technology, which is readily available for wavelength-insensitive applications. It has been selected, therefore, as one host of choice for erbium doping.

APR 13 1996

Georgia Institute of Technology
Office of Contract Administration
Atlanta, Georgia 30332-0420 USA

Rees

OFFICE OF THE DIRECTOR
J. W. DEES, Associate Vice President
for Research and Director
404•894•4810

Fax: 404•894•3120
E-mail: julian.dees@oca.gatech.edu

April 6, 1995

MEMORANDUM

TO: Deans, Directors, Associate Directors

FROM: G. Duane Hutchison, Associate Director *GDH*

SUBJECT: Overdue Deliverables for the Period Ending March 31, 1995

Attached is the draft list of overdue deliverables on sponsored projects for your units for the period ending March 31, 1995, according to our records. As in the past, I am distributing this advance copy for your review and comments, if appropriate, before submitting the final report. **ALL COMMENTS MUST BE RECEIVED BY 5:00 P.M. May 4, 1995.** In the past couple of quarters, some comments have come in a week or more after the requested deadline. It is important that we have all comments in prior to the deadline in order to review and consider them prior to preparation of the final report.

A copy of this draft report has been forwarded to the Program Administration Division of OCA. Requests for changes to the deliverable schedule requiring sponsor approval should be directed to your contracting officer.

As always, we appreciate your timely response and the special attention given to this matter.

GDH/lkm

Attachment

cc: J. W. Dees
R. D. Simpkins

14 June 1995

Contract Deliverable #15


G-33-E59

AFOSR Contract to Spire Corp.

Spire Corp. Subcontract to GIT

Prof. W. S. Rees, Jr.

A copy of the work completed to this point entitled "Initial Structural Characterization of a Lanthanoid *tris* Agostic Interaction" is attached.


William S. Rees, Jr.

Attachment

Initial Structural Characterization of a
Lanthanoid tris Agostic Interaction**

William S. Rees, Jr.,* Oliver Just, Herbert Schumann,*
Roman Weimann

[*] Prof. Dr. William S. Rees, Jr., Dr. Oliver Just

Georgia Institute of Technology

School of Chemistry and Biochemistry and School of Materials Science and
Engineering

Atlanta, Georgia 30332-0400 (USA)

Telefax: Int. code + (404)894-1144

Prof. Dr. Herbert Schumann, Dr. Roman Weimann

Institut für Anorganische und Analytische Chemie

Technische Universität Berlin

Straße des 17. Juni 135, D-10623 Berlin (Germany)

Telefax: Int. code + (30)314-22168

[**] This work was supported by the Deutsche Forschungsgemeinschaft and the U.S. Air Force Office of Scientific Research (Small Business Innovation Research contract from the Ballistic Missile Defense Organization to Spire Cooperation subcontract to Georgia Institute of Technology).

As demands for speed and area efficiency in silicon-based electronic circuitry reach near-theoretical limits, attention has been turned increasingly in recent years toward the potential for optical communication, computation and connection. One approach to overcome the intrinsic direct band gap of silicon is to capitalize on the rich electronic manifold inherent in rare earth elements. Such an example was demonstrated by Pomrenke^[1] for ion-implanted samples. In an effort to move this highly promising research out of the laboratory and into the realm of commercial production, techniques which do not demand ultra high vacuum conditions have been sought. The tool of CVD (Chemical Vapor Deposition) is respected widely in the electronic components community as a large volume throughput, economically attractive and rapidly implemented method for fabrication of thin films of exceptional quality materials on non-uniform substrates. The initial work in this area^[2] was followed by a variety of results of CVD grown rare earth doped lattices.^[3] As one component of research in the area of designed dopant sources for CVD use, previous success had been garnered employing metal amide compositions for nitrogen doping of ZnSe.^[4,5] Thus, it was of interest to explore the potential for $RE(NR_2)_3$ (RE=rare earth) compounds as dopants in epitaxial semiconducting layers. Following preliminary success in this area,^[6] a demand for higher vapor pressure sources emerged.^[7] During this exploration, a novel interaction of Si-H and

erbium was observed for one of these precursors. The present report contains details related to what is, to the best of our knowledge, the initial finding of what is attributed to be a tris(agostic) interaction for a lanthanoid element.

The initial reports of tris lanthanide amide compounds^[8] made reliance upon the well-known bis(trimethylsilyl) moiety popularized by decades of success in Lappert's group.^[9] It was unsurprising that these compounds were observed to be three coordinate, due to the rather large effective cone angle of $\text{N}[\text{Si}(\text{CH}_3)_3]_2^-$ as a ligand, coupled with its electron donating properties to the electropositive Ln^{+3} cation. Subsequent structurally characterized examples include the very recent dysprosium and erbium tris[bis(trimethylsilyl)amide] entries.^[10] As a consequence of this rarity of coordination number three for lanthanides, it was of interest to probe the boundaries of utilizing less spacially demanding, and concomitantly less electron donating, substituents on the nitrogen atom. The first step in such a progression was the preparation of $\text{Er}\{\text{N}[\underline{\text{t}}\text{Bu}][\text{Si}(\text{CH}_3)_3]\}_3$, pseudoisosteric with $\text{Er}\{\text{N}[\text{Si}(\text{CH}_3)_3]_2\}_3$, yet electronically perturbing to the Er^{+3} ion. Following comparison of the vapor pressure of these two compounds $\{\text{Er}\{\text{N}[\underline{\text{t}}\text{Bu}][\text{Si}(\text{CH}_3)_3]\}_3$: v.p.= 10^{-3} Torr/ 120°C and $\text{Er}\{\text{N}[\text{Si}(\text{CH}_3)_3]_2\}_3$: v.p.= 10^{-4} Torr/ 140°C }, attention next was turned toward the selective replacement of substituents at the silyl subunit. During the present investigation,

independent publications of structural characterization of five-coordinate yttrium and neodymium^[10] compounds $[ML_3S_2]$, as well as a four coordinate neodymium^[11] derivative occurred. The vapor pressure of $Er\{N[[tBu][Si(CH_3)_2(H)]]\}_3$ was observed to be surprisingly high, in comparison with other known examples of compounds of this class (scheme 1). Additionally, the melting point was seen to deviate substantially from the range of derivatives evaluated previously.^[12] Thus, a search for the origin of these properties compelled an appeal to crystallographic characterization of the compound.

Scheme 1.

The molecular configuration^[13] of compound 3 is depicted in figure 1. Emerging quickly is the noteworthy regiochemistry displayed by the presence of all *t*Bu groups on the same face of the N_3 plane. An additional feature of the structure is the uniform rotation of each $Si[(CH_3)_2(H)]$ subunit to place all six methyl groups toward the periphery of the opposing hemisphere of the molecule. This rotation presumably is dictated by the attraction exhibited between the three silyl hydrides and the erbium center. In 1983 Brookhart and Green^[14] coined the term agostic to describe interactions of this type. Since then, several examples have

been reported^[15] for transition metals and C-H, as well as N-H, units. Very recently, $\eta^2(\text{H}_2)$ interactions^[16] have been extended to $\eta^2(\text{Si-H})$ investigations^[17] for transition elements. A rigorous comparison of agostic and η^2 interactions presently is unwarranted, based on available data. To our knowledge, no earlier publications describe potential interactions between lanthanide elements and Si-H units, either originating from inter- or intramolecular coordination.

Figure 1.

As can be gleaned from an examination of the interatomic distance and angle data (Table 1), the present compound has substantially closer M-N contacts (220 pm vs all other reported data). Additionally, the N-M-N interatomic angles reside in a tightly clustered group around $116^\circ \pm 2^\circ$. A comparison may be made with the four coordinate entity $\text{Nd}\{\text{N}[\text{C}_6\text{H}_5][\text{Si}(\text{CH}_3)_3]\}_3(\text{THF})$, which exhibits a dispersed average of $111^\circ \pm 3^\circ$. The present case is considerably closer to the predicted value of 120° for a VSEPR-optimized three-coordinate structure. This value is approximated for other sterically demanding homoleptic tris(ligand) lanthanide derivatives^[18].

Table 1.

In support of the notion of the possible presence of the above-described Si-H-Er interactions, comparative data for $\text{HN}[\underline{t}\text{Bu}][\text{Si}(\text{CH}_3)_2(\text{H})]$ and $\text{Er}\{\text{N}[\underline{t}\text{Bu}][\text{Si}(\text{CH}_3)_2(\text{H})]\}_3$ are summarized in table 2. Most notable is the 253 cm^{-1} shift in the IR vibration attributed to Si-H^[19]. The well documented difficulty in obtaining precise NMR data on lanthanide compounds has hampered an examination of T_1 for the protons present in compound 3. Such a probe of the classical agostic character is restricted in the present case.^[20]

Table 2.

In conclusion, a possible source of the origin of the observed high vapor pressure and low melting point for $\text{Er}\{\text{N}[\underline{t}\text{Bu}][\text{Si}(\text{CH}_3)_2(\text{H})]\}_3$ has been uncovered by an examination of the solid state structure.

Experimental Procedure

An aliquot of ErCl_3 (0.91 g, 3.35 mmole) was suspended in Et_2O (40 mL) and stirred at 0°C for 1 h. Freshly synthesized $\text{LiN}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]$ (1.38 g, 10.07 mmole) in Et_2O (60 mL) was added dropwise with rapid stirring. After attaining ambient temperature, the resultant pink solution was stirred overnight. Subsequently, the clear ether phase was decanted and evaporated. The residue from the ether solution was extracted with hexanes (50 mL). The resultant solution was filtered and its volume reduced in vacuum to 20 mL. Pink crystals of compound 3, obtained from this solution after three days at -80°C , were washed three times with cold (-78°C) hexane and dried at 20°C and 10^{-2} Torr. Ensuing sublimation at 100°C and 10^{-2} Torr yielded an air sensitive, pink powder. M.p.= 48°C . Yield=0.78 g (42%). MS(EI, 70 eV, m/z(%), 156°C): 559 (6.6) [$M^+ + 1$], 558 (17.5) [M^+], 543 (20.7) [$M^+ - \text{Me}$], 528 (1.0) [$M^+ - 2\text{Me}$], 501 (2.0) [$M^+ - \text{tBu}$], 499 (2.7) [$M^+ - \text{Si}(\text{CH}_3)_2(\text{H})$], 485 (2.4) [$M^+ - \text{N}[\text{Si}(\text{CH}_3)_2(\text{H})]$], 428 (3.5) [$M^+ - \text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]$], 427 (4.7) [$M^+ - \text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})] - (\text{H})$], 412 (21.7) [$M^+ - \text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})] - (\text{CH}_3)(\text{H})$], 397 (9.8) [$M^+ - \text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})] - (\text{CH}_3)_2(\text{H})$], 369 (12.8) [$M^+ - \text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})] - [\text{Si}(\text{CH}_3)_2(\text{H})]$], 355 (8.0) [$M^+ - \text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})] - \text{N}[\text{Si}(\text{CH}_3)_2(\text{H})]$], 298 (2.4) [$M^+ - \text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})] - \text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]$], 130 (6.5) [$\text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]^+$], 116 (100) [$[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]^+$], 73 (20.3) [$\text{N}[\text{Si}(\text{CH}_3)_2(\text{H})]^+$], 59 (38.1) [$\text{Si}(\text{CH}_3)_2(\text{H})]^+$.

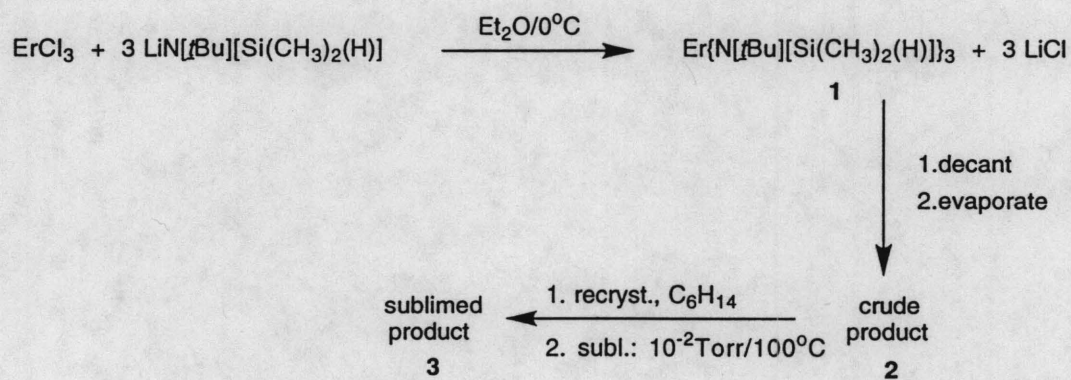
Keywords: homoleptic erbium amide, agostic interactions.

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Scheme 1: Synthetic route to $\text{Er}\{\text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]\}_3$.



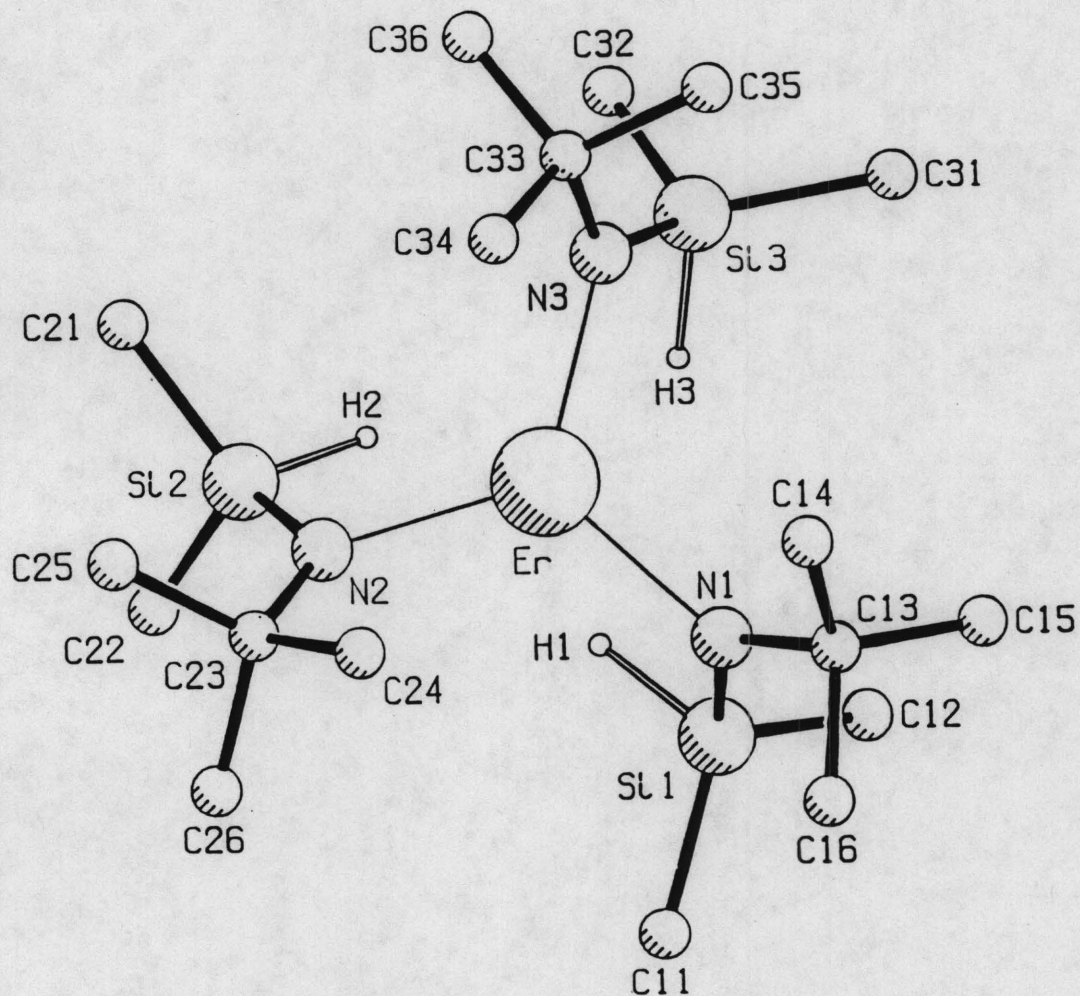


Figure 1: Representation of the molecular structure of $\text{Er}\{\text{N}[\text{CH}(\text{CH}_3)_2]\text{Si}(\text{CH}_3)_2(\text{H})\}_3$. Selected interatomic angles [°] and distances [pm]: Er-N1 220.6(2), Er-N2 220.6(2), Er-N3 220.6(2), Er-H1 231.7, Er-H2 240.7, Er-H3 236.7, N1-Si1 168.9(3), N1-C13 147.6(4), N2-Si2 169.1(3), N2-C23 146.3(4), N3-Si3 168.6(3), N3-C33 147.5(4); N1-Er-N2 118.97(9), N1-Er-N3 114.60(9), N2-Er-N3 116.85(9), Er-N1-Si1 99.34(11), Si1-N1-C13 126.23(2), Er-N1-C13 133.63(2), Er-N2-Si2 99.85(11), Si2-N2-C23 126.90(2), Er-N2-C23 133.06(2), Er-N3-Si3 99.73(11), Si3-N3-C33 127.09(2), Er-N3-C33 133.10(9).

Table 1: Interatomic angles [°] and distances [pm] involving M-N interactions for homoleptic *tris*(amide) lanthanide compounds.

	M-N distances	MN ₂ angles
Er{N[<i>t</i> Bu][Si(CH ₃) ₂ (H)]} ₃ [*]	Er-N1 220.6(2)	N1-Er-N2 118.9(9)
	Er-N2 220.6(2)	N1-Er-N3 114.6(9)
	Er-N3 220.6(2)	N2-Er-N3 116.8(9)
Nd{N[C ₆ H ₅][Si(CH ₃) ₃] ₃ (THF) ^[11]	Nd-N1 230.8(3)	N1-Nd-N2 107.8(1)
	Nd-N2 229.8(2)	N1-Nd-N3 109.4(1)
	Nd-N3 232.0(3)	N2-Nd-N3 114.0(1)
Nd{N[Si(CH ₃) ₂ (H)] ₂] ₃ (THF) ₂ ^[10]	Nd-N1 235.3(4)	N1-Nd-N2 113.7(2)
	Nd-N2 232.6(5)	N1-Nd-N3 129.9(2)
	Nd-N3 235.1(5)	N2-Nd-N3 129.2(2)
Y{N[Si(CH ₃) ₂ (H)] ₂] ₃ (THF) ₂ ^[10]	Y-N1 227.5(4)	N1-Y-N2 111.1(1)
	Y-N2 222.9(4)	N1-Y-N3 134.8(1)
	Y-N3 227.6(4)	N2-Y-N3 116.9(2)

[*] This work.

Table 2: Spectroscopic data for $\text{HN}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]$ and $\text{Er}\{\text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]\}_3$.

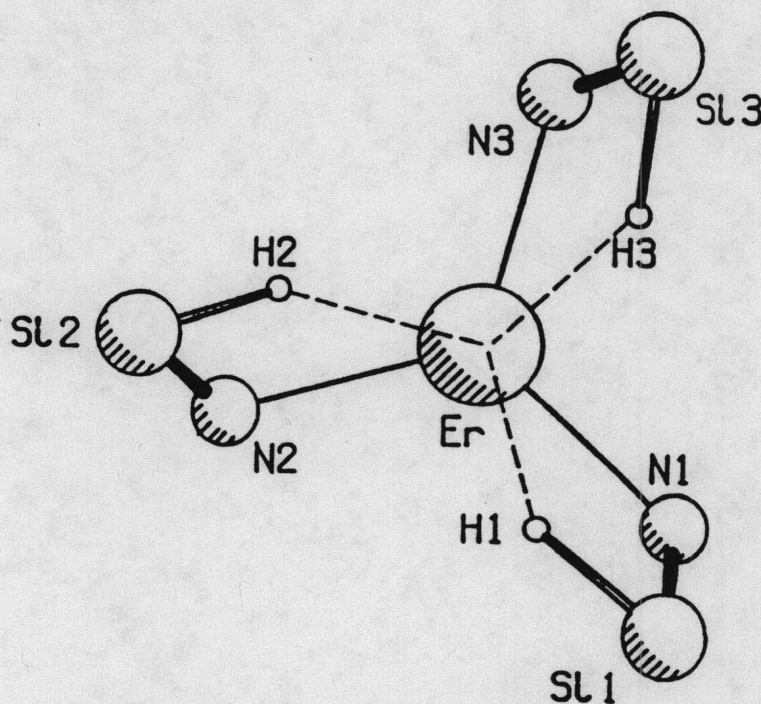
	$\text{HN}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]$	$\text{Er}\{\text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]\}_3$
IR (C_6D_6 , $\tilde{\nu}$ [cm^{-1}])	2111 (Si-H)	1858 (Si-H)*
^{13}C NMR (100.5690 MHz, C_6D_6 , 22°C, δ [ppm])	49.49 (s, $\text{C}(\text{CH}_3)_3$)	-227.12 (s, $\text{C}(\text{CH}_3)_3$)
	33.70 (s, $\text{C}(\text{CH}_3)_3$)	-127.75 (s, $\text{C}(\text{CH}_3)_3$)
	0.87 (s, $\text{Si}(\text{CH}_3)_2$)	-8.99 (s, $\text{Si}(\text{CH}_3)_2$)
^{29}Si NMR (79.4521 MHz, C_6D_6 , 22°C, δ [ppm], external standard: $\text{Si}(\text{Me}_4)$)	-18.70 (d, $^1J(\text{Si},\text{H})=193.86$ Hz)	-429 (s, $\text{Si}(\text{CH}_3)_2(\text{H})$)

[*] unperturbed Si-H = 2081-1972 cm^{-1}

Mo $\eta^2(\text{Si-H})$ = 1730-1750 cm^{-1} [21]

Table of contents

Structural characterization of $\text{Er}\{\text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]\}_3$ has revealed that all the tBu groups reside on the same face of the N_3 plane, whereas all Si-CH_3 groups are rotated toward the periphery of the molecule. This results in erbium-hydrogen interatomic distances of 231.7-236.7 pm for the silyl hydride moieties folding into the metal center.



4 October 1995

Contract Deliverable #19 Final Report


G-33-E59

AFOSR Contract to Spire Corp.

Spire Corp. Subcontract to GIT

Prof. W. S. Rees, Jr.

The following revised manuscript entitled "Initial Structural Characterization of a Lanthanoid *Tris* Agostic Interaction," is submitted as the final report for Project G-33-E59.


William S. Rees, Jr.

Attachment

**INITIAL STRUCTURAL CHARACTERIZATION
OF A LANTHANOID TRIS AGOSTIC INTERACTION**

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Submitted for Publication in

Angewandte Chemie

as a Communication

Revised Version

Manuscript Number: Z8100

Date Received: 16 June 1995

Initial Structural Characterization of a
Lanthanoid tris Agostic Interaction**

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[**] This work was supported by the Deutsche Forschungsgemeinschaft and the U. S. Air Force Office of Scientific Research (Small Business Innovation Research contract from the Ballistic Missile Defense Organization to Spire Cooperation subcontract to Georgia Institute of Technology).

As demands for speed and area efficiency in silicon-based electronic circuitry reach near-theoretical limits, attention has been turned increasingly in recent years toward the potential for optical communication, computation and connection. One approach to overcome the intrinsic direct band gap of silicon is to capitalize on the rich electronic manifold inherent in rare earth elements. Such an example was demonstrated by Pomrenke^[1] for ion-implanted samples. In an effort to move this highly promising research out of the laboratory and into the realm of commercial production, techniques which do not demand ultra high vacuum conditions have been sought. The tool of CVD (Chemical Vapor Deposition) is respected widely in the electronic components community as a large volume throughput, economically attractive and rapidly implemented method for fabrication of thin films of exceptional quality materials on non-uniform substrates. The initial work in this area^[2] was followed by a variety of results of CVD grown rare earth doped lattices.^[3] As one component of research in the area of designed dopant sources for CVD use, previous success had been garnered employing metal amide compositions for nitrogen doping of ZnSe.^[4,5] Thus, it was of interest to explore the potential for $\text{RE}(\text{NR}_2)_3$ (RE = rare earth) compounds as dopants in epitaxial semiconducting layers. Following preliminary success in this area,^[6] a demand for higher vapor pressure sources emerged.^[7] During this exploration, a novel interaction of Si-H and

erbium was observed for one of these precursors. The present report contains details related to what is, to the best of our knowledge, the initial finding of what is attributed to be a tris(agostic) interaction for a lanthanoid element.

The initial reports of lanthanide tris(amide) compounds^[8] made reliance upon the well-known bis(trimethylsilyl) moiety popularized by decades of success in Bradley's group.^[9] It was unsurprising that these compounds were observed to be three coordinate, due to the rather large effective cone angle of $\text{N}[\text{Si}(\text{CH}_3)_3]_2^-$ as a ligand, coupled with its electron donating properties to the electropositive Ln^{3+} cation. Subsequent structurally characterized examples include the very recent dysprosium and erbium tris[bis(trimethylsilyl)amide] entries.^[10] As a consequence of this rarity of coordination number three for lanthanides, it was of interest to probe the boundaries of utilizing less spacially demanding, and concomitantly less electron donating, substituents on the nitrogen atom. The first step in such a progression was the preparation of $\text{Er}\{\text{N}[\underline{\text{t}}\text{Bu}][\text{Si}(\text{CH}_3)_3]\}_3$, pseudoisosteric with $\text{Er}\{\text{N}[\text{Si}(\text{CH}_3)_3]_2\}_3$, yet electronically perturbing to the Er^{3+} ion. Following comparison of the vapor pressure data for these two compounds $\{\text{Er}\{\text{N}[\underline{\text{t}}\text{Bu}][\text{Si}(\text{CH}_3)_3]\}_3$: v.p. = 10^{-3} Torr/ 120°C and $\text{Er}\{\text{N}[\text{Si}(\text{CH}_3)_3]_2\}_3$: v.p. = 10^{-4} Torr/ 140°C }, attention next was turned toward the selective replacement of substituents at the silyl subunit. During the present investigation,

independent publications of structural characterization of five-coordinate yttrium and neodymium^[10] compounds $[ML_3S_2]$, as well as a four coordinate neodymium^[11] derivative occurred (L = anionic amide ligand; S = neutral coordinated THF). The vapor pressure of $Er\{N[\underline{t}Bu][Si(CH_3)_2(H)]\}_3$ was observed to be surprisingly high, in comparison with other known examples of compounds of this class (Scheme 1). Additionally, the melting point was seen to deviate substantially from the range of derivatives evaluated previously.^[12] Thus, a search for the origin of these properties compelled an appeal to crystallographic characterization of the compound.

Scheme 1.

The molecular configuration^[13] of compound 3 is depicted in Figure 1. Emerging quickly is the noteworthy regiochemistry displayed by the presence of all $\underline{t}Bu$ groups on the same face of the N_3 plane. An additional feature of the structure is the uniform rotation of each $Si[(CH_3)_2(H)]$ subunit to place all six methyl groups toward the periphery of the opposing hemisphere of the molecule. This rotation presumably is dictated by the attraction exhibited between the three silyl hydrides and the erbium center, as no indication of structure-influencing intramolecular forces was found in the unit cell. In 1983 Brookhart and Green^[16] coined

the term agostic to describe interactions of this type. Since then, several examples have been reported^[17] for transition metals and C-H, as well as N-H, units. Very recently, $\eta^2(\text{H}_2)$ interactions^[18] have been extended to $\eta^2(\text{Si-H})$ investigations^[19] for transition elements. A rigorous comparison of agostic and η^2 interactions presently is unwarranted, based on available data. To our knowledge, no earlier publications describe potential interactions between lanthanide elements and Si-H units, either originating from inter- or intramolecular coordination.

Figure 1.

As can be gleaned from an examination of the interatomic distance and angle data (Table 1), the present compound has substantially closer M-N contacts (220 pm vs all other reported data). Furthermore, the N-M-N interatomic angles reside in a tightly clustered group around $116^\circ \pm 2^\circ$. A comparison may be made with the four coordinate entity $\text{Nd}\{\text{N}[\text{C}_6\text{H}_5][\text{Si}(\text{CH}_3)_3]\}_3(\text{THF})$, which exhibits a dispersed average of $111^\circ \pm 3^\circ$. The present case considerably is closer to the predicted value of 120° for a VSEPR-optimized three-coordinate structure. This value is approximated for other sterically demanding homoleptic tris(ligand) lanthanide derivatives.^[20] Additionally, the dihedral angles are grouped closely around

0° [H(n)-Si(n)-N(n)-Er; n = 1: 2.5(13)°; n = 2: -4.6(11)°; n = 3: -0.1(11)°], as the consequence of the above-mentioned rotation of the dimethylsilyl groups. This further reinforces the concept that the structural motif of compound 3 is dominated by the controlling influence of the *tris* agostic Er-H-Si interactions.

Table 1.

In support of the notion of the possible presence of the above-described Er-H-Si interactions, comparative data for $\text{HN}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]$ and $\text{Er}\{\text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]\}_3$ are summarized in Table 2. Most notable is the 253 cm^{-1} shift in the IR vibration attributed to Si-H.^[21] The well documented difficulty in obtaining precise NMR data on lanthanide compounds has hampered an examination of $^2\text{J}(\text{Si},\text{H})$ for the silyl-bound hydrogen atoms present in compound 3. Such a probe of the "unstretched" Si-H character is restricted in the present case.^[22] The Si-H interatomic distances (141 - 148 pm) are, however, within the range of rather rare unstretched complexes, as compared to the typical stretched complexes.^[22a] Presumably such an observation is predominately attributable to the influence of a d^0 metal center. In such instances, the possibility of back donation is eliminated, and all indications favor the highly unusual unstretched case. It is noted, furthermore, that compound 3,

unlike the $\text{CH}(\text{TMS})_2^-$ unit, does not fall under the $\gamma\text{-C-H-Ln}$ vs $\beta\text{-Si-Me-Ln}$ interaction discussion.^[23] Examples of Ln-N-Si-Me also have been reported,^[24] as well as other γ -agostic or β -methyl interactions.^[25] For each of these, the tris agostic M-H-Si described here is unique in its interactions.

Table 2.

In conclusion, a possible source of the origin of the observed high vapor pressure and low melting point for $\text{Er}\{\text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]\}_3$ has been uncovered by an examination of the solid state structure.

Experimental Procedure

An aliquot of ErCl_3 (0.91 g, 3.35 mmole) was suspended in Et_2O (40 mL) and stirred at 0°C for 1 h. Freshly synthesized $\text{LiN}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]$ (1.38 g, 10.07 mmole) in Et_2O (60 mL) was added dropwise with rapid stirring. After attaining ambient temperature, the resultant pink solution was stirred overnight. Subsequently, the clear ether phase was decanted and evaporated. The residue from the ether solution was extracted with hexanes (50 mL). The resultant solution was filtered and its volume reduced in vacuum to 20 mL. Pink crystals of compound 3, obtained from this solution after three days at -80°C , were washed three times with cold (-78°C) hexane and dried at 20°C and 10^{-2} Torr. Ensuing sublimation at 100°C and 10^{-2} Torr yielded an air sensitive, pink powder. M.p. = 48°C . Yield = 0.78 g (42%); ^{13}C NMR (100.569 MHz, C_6D_6 , 22°C , $\text{Si}(\text{CH}_3)_4$ relative to residual $\text{C}_6\text{D}_5\text{H}$): δ = -227.12 (s, $\text{C}(\text{CH}_3)_3$), -127.75 (s, $\text{C}(\text{CH}_3)_3$), -8.99 (s, $\text{Si}(\text{CH}_3)_2$); ^{29}Si NMR (79.4521 MHz, C_6D_6 , 22°C , external standard: $\text{Si}(\text{CH}_3)_4$): δ = 429 (s, $\text{Si}(\text{CH}_3)_2(\text{H})$); MS(EI, 70 eV, 156°C): m/z(%): 559 (6.6) [$\text{M}^+ + 1$], 558 (17.5) [M^+], 543 (20.7) [$\text{M}^+ - \text{Me}$], 528 (1.0) [$\text{M}^+ - 2 \text{ Me}$], 501 (2.0) [$\text{M}^+ - \text{tBu}$], 499 (2.7) [$\text{M}^+ - \text{Si}(\text{CH}_3)_2(\text{H})$], 485 (2.4) [$\text{M}^+ - \text{N}[\text{Si}(\text{CH}_3)_2(\text{H})]$], 428 (3.5) [$\text{M}^+ - \text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]$], 427 (4.7) [$\text{M}^+ - \text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})] - (\text{H})$], 412 (21.7) [$\text{M}^+ - \text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})] - (\text{CH}_3)(\text{H})$], 397 (9.8) [$\text{M}^+ - \text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})] - (\text{CH}_3)_2(\text{H})$], 369 (12.8) [$\text{M}^+ - \text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})] - [\text{Si}(\text{CH}_3)_2(\text{H})]$], 355 (8.0) [$\text{M}^+ - \text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})] - \text{N}[\text{Si}(\text{CH}_3)_2(\text{H})]$], 298 (2.4) [$\text{M}^+ - \text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})] - \text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]$], 130 (6.5) [$\text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]^+$], 116 (100) [$[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]^+$], 73 (20.3) [$\text{N}[\text{Si}(\text{CH}_3)_2(\text{H})]^+$], 59 (38.1) [$\text{Si}(\text{CH}_3)_2(\text{H})^+$].

Keywords: homoleptic erbium amide, agostic interactions.

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- [12] A slight increase in vapor pressure for the purified product **3** vs the crude product **2** was noticed. One potential source for the observation of a depression in the vapor pressure in the crude product is the presence of 'ate' complexes. Recently such species have been isolated in this laboratory by reacting ErCl_3 with three equivalents of $\text{LiN}([\text{iBu}][\text{Si}(\text{CH}_3)_3])$ and ensuing crystallization of the reaction product from Et_2O . Details of crystallographic characterization of the obtained $\{[\text{Li}(\text{Et}_2\text{O})_3][\text{Er}\{\text{N}[\text{iBu}][\text{Si}(\text{CH}_3)_3]\}_3\text{Cl}]\}$ will be reported separately. It is noted that the formation of such 'ate' species appears to be irreversible, i.e. once formed, they resist successful removal of

LiCl and subsequent conversion to a neutral, homoleptic lanthanide tris[(silyl)(alkyl)amide] species.

- [13] X-ray crystal structure analysis data: $C_{16}H_{48}N_3Si_3Er$, $M_r = 534.10$ g mol⁻¹, monoclinic, space group $P2_1/n$, $a = 11.128(2)$, $b = 14.430(3)$, $c = 17.943(3)$ Å, $\beta = 90.73(2)^\circ$, $V = 28.810(9)$ Å³, $Z = 4$, $\rho_{calcd} = 1.231$ g cm⁻³, crystal size 0.33 x 0.53 x 0.4 mm³, number of reflections for lattice parameters = 25 ($19.5^\circ \leq 2\theta \leq 26.6^\circ$), $T = 185$ K, $\mu = 3.041$ mm⁻¹, $F(000) = 1100$. Data collection and correction: Enraf-Nonius CAD-4 diffractometer, $MoK\alpha$ radiation ($\lambda = 0.71073$ Å), graphite monochromator, aperture 2.5 mm, scan time variable, max. 45 s, scan angle $(0.93 + 0.35 \tan\theta)^\circ$, scan technique $\omega-2\theta$, range $2^\circ < 2\theta < 48^\circ$, hkl boundaries: $-12 \leq h \leq 12$, $0 \leq k \leq 16$, $0 \leq l \leq 20$, total number of measured reflections: 4971, unique reflections: 4346 ($R = 0.0227$), observed reflections with $[|F_o| \geq 4\sigma|F_o|]$: 4340, corrections: Lorentz, polarization, absorption (DIFABS: correction factors: min.: 0.917, max.: 1.164). Solution and refinement: structure solution by Patterson method, full-matrix least-squares refinement, 236 parameters refined. The methyl groups in the *t*Bu moiety attached to nitrogen N1 were found to be disordered over two sites (C14-C16/C141-C161), each occupying a population parameter of 0.5. The disordered carbon atoms and the agostic hydrogen atoms H1, H2, H3 each were refined with isotropic, whereas all other non-hydrogen atoms were refined with anisotropic, thermal parameters. All hydrogen atoms were calculated in idealized positions (C-H 96 pm, $U_{iso} = 0.08$ Å², final residue value $R_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o| = 0.0190$, $R_2 = [\Sigma_w(|F_o| -$

$|F_c|)^2 / \sum_w (|F_o|^2)^{1/2} = 0.0417$ ($w = 1/\sigma^2(F_o)$), $\text{Goof} = [\sum_w (|F_o| - |F_c|)^2 / (n-p)]^{1/2} = 1.051$, $\Delta\rho(\text{max./min.}) = \text{max. } 0.404 \text{ e\AA}^{-3}$ and $\text{min. } -0.300 \text{ e\AA}^{-3}$. All refinements were performed using the SHELXL-93 program system.^[14] Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Loepoldshafen (Germany) on quoting the dispository number CSD-XXXXX.

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Scheme 1: Synthetic route to $\text{Er}\{\text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]\}_3$.

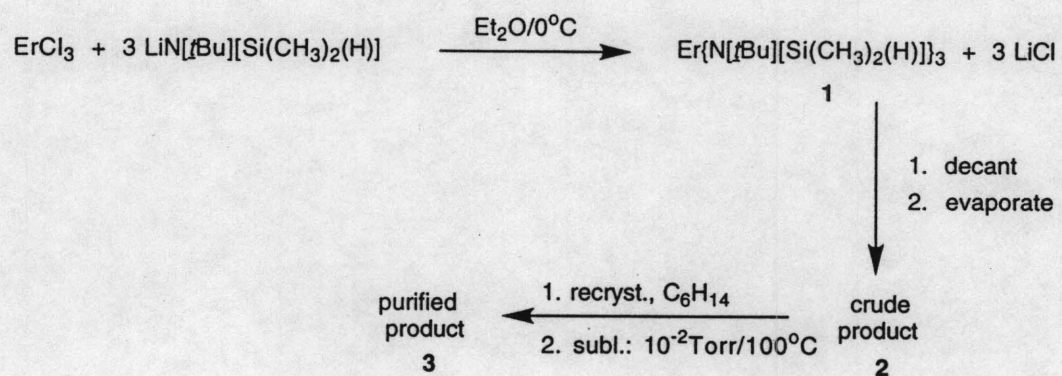


Fig. 1: ZORTEP plot^[15] of $\text{Er}\{\text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]\}_3$ (thermal ellipsoids are scaled to the 30% probability level). Selected interatomic angles [°] and distances [pm] (standard deviations are given in parentheses):

Er-N1 220.6(2), Er-N2 220.6(2), Er-N3 220.6(2), Er-H1 232(3), Er-H2 241(3), Er-H3 237(3), N1-Si1 168.9(3), N1-C13 147.6(4), N2-Si2 169.1(3), N2-C23 146.3(4), N3-Si3 168.6(3), N3-C33 147.5(4); Si1-H1 141.1(3), Si2-H2 146.1(3), Si3-H3 148.1(3), N1-Er-N2 118.97(9), N1-Er-N3 114.60(9), N2-Er-N3 116.85(9), Er-N1-Si1 99.34(11), Si1-N1-C13 126.2(2), Er-N1-C13 133.6(2), Er-N2-Si2 99.85(11), Si2-N2-C23 126.9(2), Er-N2-C23 133.1(2), Er-N3-Si3 99.73(11), Si3-N3-C33 127.1(2), Er-N3-C33 133.1(2).

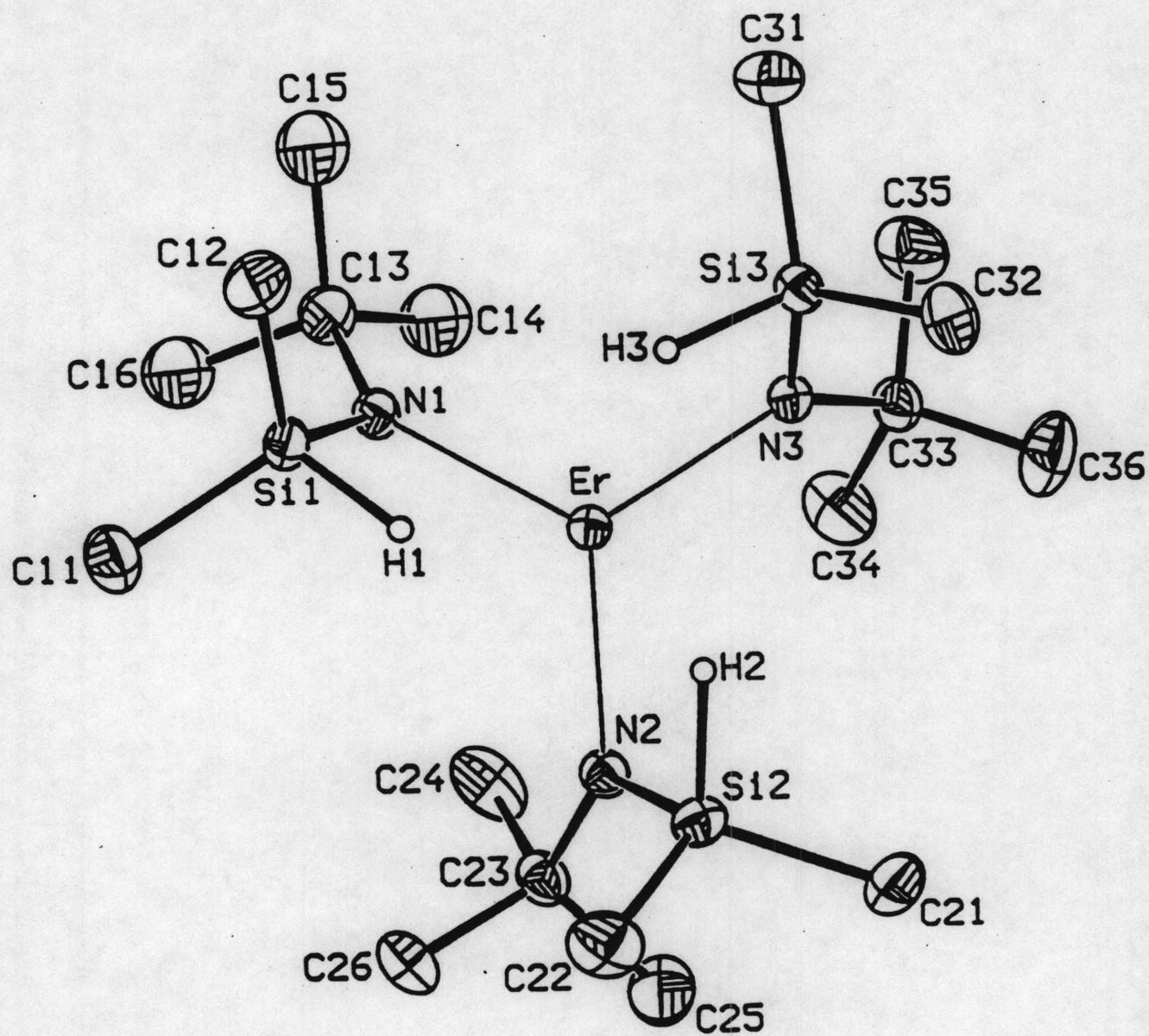


Table 1: Interatomic angles [°] and distances [pm] involving M-N interactions for homoleptic lanthanide *tris*(amide) compounds.

	M-N distances	MN ₂ angles
$\text{Er}\{\text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]\}_3^{[\text{a}]}$	Er-N1 220.6(2)	N1-Er-N2 118.97(9)
	Er-N2 220.6(2)	N1-Er-N3 114.60(9)
	Er-N3 220.6(2)	N2-Er-N3 116.85(9)
$\text{Nd}\{\text{N}[\text{C}_6\text{H}_5][\text{Si}(\text{CH}_3)_3]\}_3(\text{THF})^{[\text{11}]}$	Nd-N1 230.8(3)	N1-Nd-N2 107.8(1)
	Nd-N2 229.8(2)	N1-Nd-N3 109.4(1)
	Nd-N3 232.0(3)	N2-Nd-N3 114.0(1)
$\text{Nd}\{\text{N}[\text{Si}(\text{CH}_3)_2(\text{H})]_2\}_3(\text{THF})_2^{[\text{10}]}$	Nd-N1 235.3(4)	N1-Nd-N2 113.7(2)
	Nd-N2 232.6(5)	N1-Nd-N3 129.9(2)
	Nd-N3 235.1(5)	N2-Nd-N3 129.2(2)
$\text{Y}\{\text{N}[\text{Si}(\text{CH}_3)_2(\text{H})]_2\}_3(\text{THF})_2^{[\text{10}]}$	Y-N1 227.5(4)	N1-Y-N2 111.1(1)
	Y-N2 222.9(4)	N1-Y-N3 134.8(1)
	Y-N3 227.6(4)	N2-Y-N3 116.9(2)

[a] This work.

Table 2: Infrared spectroscopic data for compounds possessing metal-(Si-H) interactions and representative values for non-interacting systems.

Compound	Si-H (cm ⁻¹)	Reference
HN[<i>i</i> Bu][Si(CH ₃) ₂ (H)]	2111	This work ^[a]
Er{N[<i>i</i> Bu][Si(CH ₃) ₂ (H)]} ₃	1858	This work ^[a]
unperturbed Si-H	2081-1972	[26]
Mo η^2 (Si-H)	1750-1730	[26]

[a] In C₆D₆ solution

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Structural characterization of $\text{Er}\{\text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]\}_3$ has revealed that all the tBu groups reside on the same face of the N_3 plane, whereas all Si-CH_3 groups are rotated toward the periphery of the molecule. This results in erbium-hydrogen interatomic distances of 231.7-236.7 pm for the silyl hydride moieties folding into the metal center.