Project #: G-33-E59  
Cost share #:  
Rev #: 3  
OCA file #:  
Work type : RES  
Contract entity: GTRC

Center #: 10/24-6-R8067-0A0  
Center shr #:  
Mod #: DELIVERABLE SCH  
Document : CONT

Contract#: 139020  
Prime #: F49620-93-C-0069

Subprojects ?: N  
Main project #:  

Project unit: CHEMISTRY  
Unit code: 02.010.136

Project director(s): REES W S  
CHEMISTRY

Sponsor/division names: SPIRE CORPORATION OF MA  
/ BEDFORD, MA  
Sponsor/division codes: 218  
/ 105

Award period: 940121 to 950831 (performance)  
950831 (reports)  

Sponsor amount  
Contract value 0.00  
Funded 0.00  
Total to date 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  
Sponsor technical contact  
DR. ANTON GREENWALD  
(617)275-6000  
SPIRE CORPORATION  
ONE PATRIOTS PARK  
BEDFORD, MA 01730-2396

Sponsor issuing office  
STEPHEN BOORSCHTEIN  
(617)275-6000  
PROCUREMENT MANAGER (PH. EXT. 275)  
SPIRE CORPORATION  
ONE PATRIOTS PARK  
BEDFORD, MA 01730-2396  
FAX: (617) 275-7470

Security class (U,C,S,TS) : U  
Defense priority rating :  
Equipment title vests with: Sponsor X  
FAR CLAUSE 52.244.5, ALT I  
Sponsor X  
GIT

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

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.
NOTICE OF PROJECT CLOSEOUT

Closeout Notice Date 10/09/95

Project No. G-33-E59
Project Director REES W S
Sponsor SPIRE CORPORATION OF MA/BEDFORD, MA
Contract/Grant No. 139020
Prime Contract No. F49620-93-C-0069
Title ER-DOPED SEMICONDUCTORS
Effective Completion Date 950831 (Performance) 950831 (Reports)

Closeout Actions Required:

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Comments: _____________________________

Subproject Under Main Project No. __________
Continues Project No. ________________

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NOTE: Final Patent Questionnaire sent to PDPI.
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.
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
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.
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.
Monthly letter report to Spire

16 August 1994

Purification of a different Er compound is in progress.

William S. Rees, Jr.
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.
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.

William S. Rees, Jr.
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
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 -(tetramethylheptanediionate) 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.
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

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
1. Purification of \( \text{Er}\{\text{N}\[(\text{Si(CH}_3)_3)(\text{C(CH}_3)_3)]\}\}_3 \) continues. The present known impurity is lithium.

2. Preparation of \( \text{Er}\{\text{N}\[(\text{Si(CH}_2\text{CH}_3)_3)\}_2\}\}_3 \) has been initiated. \(^{13}\{^{1}H\}\) NMR spectral data are attached.
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).
22 June 1994

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
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.
MEMORANDUM

TO: Deans, Directors, Associate Directors
FROM: G. Duane Hutchison, Associate Director
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
A copy of the work completed to this point entitled "Initial Structural Characterization of a Lanthanoid \textit{tris} Agostic Interaction" is attached.

William S. Rees, Jr.

Attachment
Initial Structural Characterization of a Lanthanoid \textit{tris} Agostic Interaction**

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

[**] 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\textsuperscript{[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\textsuperscript{[2]} was followed by a variety of results of CVD grown rare earth doped lattices.\textsuperscript{[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.\textsuperscript{[4,5]} Thus, it was of interest to explore the potential for RE(NR\textsubscript{2})\textsubscript{3} \textsuperscript{(RE=rare earth)} compounds as dopants in epitaxial semiconducting layers. Following preliminary success in this area,\textsuperscript{[6]} a demand for higher vapor pressure sources emerged.\textsuperscript{[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 N[Si(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 concommitantly less electron donating, substituents on the nitrogen atom. The first step in such a progression was the preparation of Er{N[tBu][Si(CH$_3$)$_3$]}$_3$, pseudoisosteric with Er{N[Si(CH$_3$)$_3$]$_2$}, yet electronically perturbing to the Er$^{+3}$ ion. Following comparison of the vapor pressure of these two compounds {Er{N[tBu][Si(CH$_3$)$_3$]}$_3$: v.p. = 10$^{-3}$ Torr/120°C and Er{N[Si(CH$_3$)$_3$]$_2$}: 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\textsuperscript{10} compounds [ML\textsubscript{3}S\textsubscript{2}], as well as a four coordinate neodymium\textsuperscript{11} derivative occurred. The vapor pressure of Er(N[\{tBu\}[Si(CH\textsubscript{3})\textsubscript{2}(H)]\textsubscript{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.\textsuperscript{12} Thus, a search for the origin of these properties compelled an appeal to crystallographic characterization of the compound.

Scheme 1.

The molecular configuration\textsuperscript{13} of compound 3 is depicted in figure 1. Emerging quickly is the noteworthy regiochemistry displayed by the presence of all tBu groups on the same face of the N\textsubscript{3} plane. An additional feature of the structure is the uniform rotation of each Si[(CH\textsubscript{3})\textsubscript{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\textsuperscript{14} coined the term agostic to describe interactions of this type. Since then, several examples have
been reported\cite{15} for transition metals and C-H, as well as N-H, units. Very recently, $\eta^2(H_2)$ interactions\cite{16} have been extended to $\eta^2(Si-H)$ investigations\cite{17} for transition elements. A rigorous comparison of agostic and $\eta^2$ 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.

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Figure 1.

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As can be gleened 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°±2°. A comparison may be made with the four coordinate entity Nd\{N[C_6H_5][Si(CH_3)]_3\}_3(THF), which exhibits a dispersed average of 111°±3°. 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 $\text{tris}(\text{ligand})$ lanthanide derivatives\cite{18}.
In support of the notion of the possible presence of the above-described Si-H-Er interactions, comparative data for HN[\text{tBu}][\text{Si(CH}_3)_2(\text{H})] and Er{N[\text{tBu}][\text{Si(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.$^{20}$

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

An aliquot of ErCl₃ (0.91 g, 3.35 mmole) was suspended in Et₂O (40 mL) and stirred at 0°C for 1 h. Freshly synthesized Li[N(₄Bu)[Si(CH₃)₂(H)]] (1.38 g, 10.07 mmole) in Et₂O (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⁺-Me], 528 (1.0) [M⁺-2Me], 501 (2.0) [M⁺-₄Bu], 499 (2.7) [M⁺-Si(CH₃)₂(H)], 485 (2.4) [M⁺-N[Si(CH₃)₂(H)]], 428 (3.5) [M⁺-N[₄Bu][Si(CH₃)₂(H)]], 427 (4.7) [M⁺-N[₄Bu][Si(CH₃)₂(H)]-(H)], 412 (21.7) [M⁺-N[₄Bu][Si(CH₃)₂(H)]-(CH₃)(H)], 397 (9.8) [M⁺-N[₄Bu][Si(CH₃)₂(H)]-(CH₃)₂(H)], 369 (12.8) [M⁺-N[₄Bu][Si(CH₃)₂(H)]-(Si(CH₃)₂(H))], 355 (8.0) [M⁺-N[₄Bu][Si(CH₃)₂(H)]-N[₄Bu][Si(CH₃)₂(H)]], 298 (2.4) [M⁺-N[₄Bu][Si(CH₃)₂(H)]-N[₄Bu][Si(CH₃)₂(H)]], 130 (6.5) [N[₄Bu][Si(CH₃)₂(H)]⁺, 116 (100) [[₄Bu][Si(CH₃)₂(H)]⁺, 73 (20.3) [N[Si(CH₃)₂(H)]⁺, 59 (38.1) [Si(CH₃)₂(H)]⁺.

Keywords: homoleptic erbium amide, agostic interactions.


[12] A slight increase of vapor pressure for the purified product 3 vs 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 ErCl₃ with three equivalents of LiN([iBu][Si(CH₃)₃]) and ensuing crystallization of the reaction product from Et₂O. Details of crystallographic characterization of the obtained {[Li(Et₂O)₃][ErN[iBu][Si(CH₃)₃]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: ?


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

$$\text{ErCl}_3 + 3 \text{LiN}[\text{Bu}][\text{Si(CH}_3]_2(\text{H})] \xrightarrow{\text{Et}_2\text{O/0°C}} \text{Er}[\text{tBu}[\text{Si(CH}_3]_2(\text{H})]]_3 + 3 \text{LiCl}$$

1. recryst., $\text{C}_6\text{H}_{14}$
2. subl.: $10^{-2}$ Torr/100°C

1. decant
2. evaporate

Sublimed product
Crude product
Figure 1: Representation of the molecular structure of Er(\text{N}[\text{tBu}][\text{Si(CH}_3]_2(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 \textit{trig}(amide) lanthanide compounds.

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

[*] This work.
Table 2: Spectroscopic data for HN[t-Bu][Si(CH$_3$)$_2$(H)] and Er[N[t-Bu][Si(CH$_3$)$_2$(H)]]$_3$.

<table>
<thead>
<tr>
<th></th>
<th>HN[t-Bu][Si(CH$_3$)$_2$(H)]</th>
<th>Er[N[t-Bu][Si(CH$_3$)$_2$(H)]]$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR (C$_6$D$_6$, $\bar{v}$ [cm$^{-1}$])</td>
<td>2111 (Si-H)</td>
<td>1858 (Si-H)$^*$</td>
</tr>
<tr>
<td>$^{13}$C NMR (100.5690 MHz, C$_6$D$_6$, 22°C, $\delta$[ppm])</td>
<td>49.49 (s, C(CH$_3$)$_3$)</td>
<td>-227.12 (s, C(CH$_3$)$_3$)</td>
</tr>
<tr>
<td></td>
<td>33.70 (s, C(CH$_3$)$_3$)</td>
<td>-127.75 (s, C(CH$_3$)$_3$)</td>
</tr>
<tr>
<td></td>
<td>0.87 (s, Si(CH$_3$)$_2$)</td>
<td>-8.99 (s, Si(CH$_3$)$_2$)</td>
</tr>
<tr>
<td>$^{29}$Si NMR (79.4521 MHz, C$_6$D$_6$, 22°C, $\delta$[ppm], external standard: Si(Me$_4$))</td>
<td>-18.70 (d, $^1J$(Si,H)=193.86 Hz)</td>
<td>-429 (s, Si(CH$_3$)$_2$(H))</td>
</tr>
</tbody>
</table>

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

Mo $\eta^2$(Si-H) = 1730-1750 cm$^{-1}$[21]
Structural characterization of $\text{Er[N[Bu][Si(CH_3)_2(H)]]}_3$ has revealed that all the $\text{Bu}$ groups reside on the same face of the $N_3$ plane, whereas all $\text{Si-CH}_3$ 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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Revised Version

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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\textsuperscript{[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\textsuperscript{[2]} was followed by a variety of results of CVD grown rare earth doped lattices.\textsuperscript{[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.\textsuperscript{[4,5]} Thus, it was of interest to explore the potential for RE(NR\textsubscript{2})\textsubscript{3} (RE = rare earth) compounds as dopants in epitaxial semiconducting layers. Following preliminary success in this area,\textsuperscript{[6]} a demand for higher vapor pressure sources emerged.\textsuperscript{[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 \textit{trig} (agostic) interaction for a lanthanoid element.

The initial reports of lanthanide \textit{tris} (amide) compounds\cite{8} made reliance upon the well-known \textit{bis} (trimethylsilyl) moiety popularized by decades of success in Bradley's group.\cite{9} It was unsurprising that these compounds were observed to be three coordinate, due to the rather large effective cone angle of N\{Si(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 \textit{tris} [\textit{bis} (trimethylsilyl) amide] entries.\cite{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 Er\{N[\text{t-Bu}]\{Si(CH$_3$)$_3$\}\}$_3$, pseudoisosteric with Er\{N[Si(CH$_3$)$_3$]$_2$\}$_3$, yet electronically perturbing to the Er$^{3+}$ ion. Following comparison of the vapor pressure data for these two compounds \{Er\{N[\text{t-Bu}]\{Si(CH$_3$)$_3$\}\}$_3$: v.p. = 10$^{-3}$ Torr/120°C and Er\{N[Si(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\textsuperscript{[10]} compounds [ML\textsubscript{3}S\textsubscript{2}], as well as a four coordinate neodymium\textsuperscript{[11]} derivative occurred (L = anionic amide ligand; S = neutral coordinated THF). The vapor pressure of Er[N[Bu][Si(CH\textsubscript{3})\textsubscript{2}(H)]]\textsubscript{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.\textsuperscript{[12]} Thus, a search for the origin of these properties compelled an appeal to crystallographic characterization of the compound.

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Scheme 1.

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The molecular configuration\textsuperscript{[13]} of compound 3 is depicted in Figure 1. Emerging quickly is the noteworthy regiochemistry displayed by the presence of all tBu groups on the same face of the N\textsubscript{3} plane. An additional feature of the structure is the uniform rotation of each Si[(CH\textsubscript{3})\textsubscript{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\textsuperscript{[16]} coined
the term agostic to describe interactions of this type. Since then, several examples have been reported\textsuperscript{[17]} for transition metals and C-H, as well as N-H, units. Very recently, $\eta^2(H_2)$ interactions\textsuperscript{[18]} have been extended to $\eta^2(Si-H)$ investigations\textsuperscript{[19]} for transition elements. A rigorous comparison of agostic and $\eta^2$ 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.

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 \textit{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 Nd(N[C$_6$H$_5$][Si(CH$_3$)$_3$])$_3$(THF), which exhibits a dispersed average of $111^\circ\pm 3^\circ$. The present case considerably is closer to the predicted value of $120^\circ$ for a VSEPR-optimized three-coordinate structure. This value is approximated for other sterically demanding homoleptic \textit{tris}(ligand) lanthanide derivatives.\textsuperscript{[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 HN[MeBu][Si(CH₃)₂(H)] and Er[NMeBu][Si(CH₃)₂(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 ²J(Si,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 d⁰ 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 CH(TMS)$_2$-unit, does not fall under the $\gamma$-C-H-Ln vs $\beta$-Si-Me-Ln interaction discussion.$^{[23]}$ Examples of Ln-N-Si-Me also have been reported,$^{[24]}$ as well as other $\gamma$-agostic or $\beta$-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 Er(N[\&Bu][Si(CH$_3$)$_2$(H)])$_3$ has been uncovered by an examination of the solid state structure.
Experimental Procedure

An aliquot of ErCl₃ (0.91 g, 3.35 mmole) was suspended in Et₂O (40 mL) and stirred at 0°C for 1 h. Freshly synthesized Li[N[Bu][Si(CH₃)₂(H)]] (1.38 g, 10.07 mmole) in Et₂O (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%); ¹³C NMR (100.569 MHz, C₆D₆, 22°C, Si(CH₃)₄ relative to residual C₆D₅H): δ = -227.12 (s, C(CH₃)₃), -127.75 (s, C(CH₃)₃), -8.99 (s, Si(CH₃)₂); ²⁹Si NMR (79.4521 MHz, C₆D₆, 22°C, external standard: Si(CH₃)₄): δ = 429 (s, Si(CH₃)₂(H)); MS(EI, 70 eV, 156°C): m/z (%): 559 (6.6) [M⁺+1], 558 (17.5) [M⁺], 543 (20.7) [M⁺-Me], 528 (1.0) [M⁺-2 Me], 501 (2.0) [M⁺-tBu], 499 (2.7) [M⁺-Si(CH₃)₂(H)], 485 (2.4) [M⁺-N[Si(CH₃)₂(H)]], 428 (3.5) [M⁺-N[tBu][Si(CH₃)₂(H)]], 427 (4.7) [M⁺-N[tBu][Si(CH₃)₂(H)]-(H)], 412 (21.7) [M⁺-N[tBu][Si(CH₃)₂(H)]-(CH₃)⁺-(H)], 397 (9.8) [M⁺-N[tBu][Si(CH₃)₂(H)]-(CH₃)₂(H)], 369 (12.8) [M⁺-N[tBu][Si(CH₃)₂(H)]-N[Si(CH₃)₂(H)]], 355 (8.0) [M⁺-N[tBu][Si(CH₃)₂(H)]-N[Si(CH₃)₂(H)]], 298 (2.4) [M⁺-N[tBu][Si(CH₃)₂(H)]-N[tBu][Si(CH₃)₂(H)]], 130 (6.5) [N[tBu][Si(CH₃)₂(H)]⁺, 116 (100) [[tBu][Si(CH₃)₂(H)]⁺, 73 (20.3) [N[Si(CH₃)₂(H)]⁺, 59 (38.1) [Si(CH₃)₂(H)]⁺.

Keywords: homoleptic erbium amide, agostic interactions.


[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 ErCl₃ with three equivalents of LiN([iBu][Si(CH₃)₃]) and ensuing crystallization of the reaction product from Et₂O. Details of crystallographic characterization of the obtained {[Li(Et₂O)₃][Er(N[iBu][Si(CH₃)₃])₃Cl]} 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
\textit{tris[(silyl)(alkyl)amide]} species.

[13] X-ray crystal structure analysis data: \( \text{C}_{16}\text{H}_{48}\text{N}_{3}\text{Si}_{3}\text{Er}, M_{r} = 534.10 \text{ g mol}^{-1} \), monoclinic, space group \( P2_{1}/n \), \( a = 11.128(2), b = 14.430(3), c = 17.943(3) \text{ Å}, \beta = 90.73(2)^{\circ}, V = 28.810(9) \text{ Å}^{3}, Z = 4, \rho_{\text{calc}} = 1.231 \text{ g cm}^{-3} \), crystal size \( 0.33 \times 0.53 \times 0.4 \text{ mm}^{3} \), number of reflections for lattice parameters = 25 \((19.5^{\circ} \leq 2\Theta \leq 26.6^{\circ})\), \( T = 185 \text{ K}, \mu = 3.041 \text{ mm}^{-1}, F(000) = 1100. \) Data collection and correction: Enraf-Nonius CAD-4 diffractometer, \( \text{MoK}_{\alpha} \) radiation \((\lambda = 0.71073 \text{ Å})\), 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 \text{tBu} moiety attached to nitrogen N1 were found to be disordered over two sites \((\text{C14-C16/C141-C161})\), 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 \((\text{C-H} 96 \text{ pm}, U_{iso} = 0.08 \text{ Å}^{2}\), final residue value \( R_{1} = \Sigma(||F_{o}||-||F_{c}||)/\Sigma||F_{o}|| = 0.0190, R_{2} = \Sigma w(||F_{o}||-||F_{c}||)/\Sigma w||F_{o}|| = 0.0195\).
\[ \frac{|F_c|^2}{\sum |F_o|^2}^{1/2} = 0.0417 \quad (w = 1/\sigma^2(F_o)), \quad \text{Goof} = \left[ \sum_w (|F_o| - |F_c|)^2 / (n-p) \right]^{1/2} = 1.051, \quad \Delta \rho(\text{max.}/\text{min.}) = \text{max.} 0.404 \text{ eA}^{-3} \text{ and min. } -0.300 \text{ eA}^{-3}. \] All refinements were performed using the SHELXL-93 program system. 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-xxxxxx.


Scheme 1: Synthetic route to $\text{Er}\{\text{N[\delta Bu][Si(CH}_3\text{)2(H)]}\}_3$. 
\[
\text{ErCl}_3 + 3 \text{Li[N[\text{Bu}][\text{Si(CH}_3)_2(\text{H})]]} \xrightarrow{\text{Et}_2\text{O/0°C}} \text{Er[N[\text{Bu}][\text{Si(CH}_3)_2(\text{H})]]}_3 + 3 \text{LiCl}
\]

1. recryst., \(\text{C}_6\text{H}_{14}\)
2. subl.: \(10^{-2}\text{Torr/100°C}\)
Fig. 1: ZORTEP plot[15] of $\text{Er}(\text{N}[\text{Bu}]\text{[Si(CH$_3$)$_2$(H)]})_3$ (thermal ellipsoids are scaled to the 30% probability level). Selected interatomic angles [°] and distances [pm] (standard deviations are given in parentheses):

- $\text{Er}-\text{N}1$ 220.6(2), $\text{Er}-\text{N}2$ 220.6(2), $\text{Er}-\text{N}3$ 220.6(2), $\text{Er}-\text{H}1$ 232(3), $\text{Er}-\text{H}2$ 241(3), $\text{Er}-\text{H}3$ 237(3), $\text{N}1-\text{Si}1$ 168.9(3), $\text{N}1-\text{C}13$ 147.6(4), $\text{N}2-\text{Si}2$ 169.1(3), $\text{N}2-\text{C}23$ 146.3(4), $\text{N}3-\text{Si}3$ 168.6(3), $\text{N}3-\text{C}33$ 147.5(4);
- $\text{Si}1-\text{H}1$ 141.1(3), $\text{Si}2-\text{H}2$ 146.1(3), $\text{Si}3-\text{H}3$ 148.1(3), $\text{N}1-\text{Er}-\text{N}2$ 118.97(9), $\text{N}1-\text{Er}-\text{N}3$ 114.60(9), $\text{N}2-\text{Er}-\text{N}3$ 116.85(9), $\text{Er}-\text{N}1-\text{Si}1$ 90.34(11), $\text{Si}1-\text{N}1-\text{C}13$ 126.2(2), $\text{Er}-\text{N}1-\text{C}13$ 133.6(2), $\text{Er}-\text{N}2-\text{Si}2$ 90.85(11), $\text{Si}2-\text{N}2-\text{C}23$ 126.9(2), $\text{Er}-\text{N}2-\text{C}23$ 133.1(2), $\text{Er}-\text{N}3-\text{Si}3$ 99.73(11), $\text{Si}3-\text{N}3-\text{C}33$ 127.1(2), $\text{Er}-\text{N}3-\text{C}33$ 133.1(2).
Table 1: Interatomic angles [*] and distances [pm] involving M-N interactions for homoleptic lanthanide **tris** (amide) compounds.

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<th>MN₂ angles</th>
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<td>Er-N₁ 220.6(2)</td>
<td>N₁-Er-N₂ 118.97(9)</td>
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<td>N₁-Er-N₃ 114.60(9)</td>
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<td>Er-N₃ 220.6(2)</td>
<td>N₂-Er-N₃ 116.85(9)</td>
</tr>
<tr>
<td>Nd[N₁C₅H₅][Si(CH₃)₃]₃(THF)₁[₁]</td>
<td>Nd-N₁ 230.8(3)</td>
<td>N₁-Nd-N₂ 107.8(1)</td>
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<td>Nd-N₂ 229.8(2)</td>
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<td>Nd-N₃ 232.0(3)</td>
<td>N₂-Nd-N₃ 114.0(1)</td>
</tr>
<tr>
<td>Nd[N₁Si(CH₃)₂(H)]₂₃(THF)₁[₁]</td>
<td>Nd-N₁ 235.3(4)</td>
<td>N₁-Nd-N₂ 113.7(2)</td>
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<tr>
<td></td>
<td>Nd-N₂ 232.6(5)</td>
<td>N₁-Nd-N₃ 129.9(2)</td>
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<td></td>
<td>Nd-N₃ 235.1(5)</td>
<td>N₂-Nd-N₃ 129.2(2)</td>
</tr>
<tr>
<td>Y[N₁Si(CH₃)₂(H)]₂₃(THF)₁[₁]</td>
<td>Y-N₁ 227.5(4)</td>
<td>N₁-Y-N₂ 111.1(1)</td>
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<tr>
<td></td>
<td>Y-N₂ 222.9(4)</td>
<td>N₁-Y-N₃ 134.8(1)</td>
</tr>
<tr>
<td></td>
<td>Y-N₃ 227.6(4)</td>
<td>N₂-Y-N₃ 116.9(2)</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Si-H (cm⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HN[渤][Si(CH₃)₂(H)]</td>
<td>2111</td>
<td>This work[a]</td>
</tr>
<tr>
<td>Er[N[渤][Si(CH₃)₂(H)]₃]</td>
<td>1858</td>
<td>This work[a]</td>
</tr>
<tr>
<td>unperturbed Si-H</td>
<td>2081-1972</td>
<td>[26]</td>
</tr>
<tr>
<td>Mo η²(Si-H)</td>
<td>1750-1730</td>
<td>[26]</td>
</tr>
</tbody>
</table>

[a] In C₆D₆ solution
Structural characterization of Er(N[Bu][Si(CH₃)₂(H)])₃ has revealed that all the tBu groups reside on the same face of the N₃ plane, whereas all Si-CH₃ 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.