

INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

Bell & Howell Information and Learning
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
800-521-0600

UMI[®]



Université d'Ottawa • University of Ottawa



National Library
of Canada

Acquisitions and
Bibliographic Services

395 Wellington Street
Ottawa ON K1A 0N4
Canada

Bibliothèque nationale
du Canada

Acquisitions et
services bibliographiques

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence

Our file Notre référence

The author has granted a non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of this thesis in microform, paper or electronic formats.

The author retains ownership of the copyright in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

L'auteur a accordé une licence non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de cette thèse sous la forme de microfiche/film, de reproduction sur papier ou sur format électronique.

L'auteur conserve la propriété du droit d'auteur qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

0-612-57037-1

Canada

ABSTRACT

$\text{SmI}_2(\text{THF})_5$ acted as a reducing agent in the reaction with phenylenebis(3,5- $\text{Bu}^t_4\text{salicylidene}$)iminato sodium, $(3,5\text{-Bu}^t_4\text{salophen})\text{Na}_2(\text{THF})_2$, to yield a dimeric compound $[\text{Sm}_2(\text{SB-SB})(\text{THF})_3] \cdot 2\text{toluene}$ (**2.2**) [$\text{SB-SB} = \text{C-C}$ bonded (3,5- $\text{Bu}^t_4\text{salophen}$ dimer] arising from the reductive C-C coupling of two imine functional groups of two (3,5- $\text{Bu}^t_4\text{salophen}$)Sm units. Complex **2.2** reacts with MeLi resulting in a novel oxo-bridged dimer, $\{[(\text{Me}_2\text{-SB})\text{Sm}(\mu\text{-CH}_3)\text{Li}(\text{THF})][(\text{Me}_2\text{-SB})\text{Sm}(\mu\text{-CH}_3)\text{Li}(\text{THF})_2\text{Li}(\text{THF})_2]\}(\mu\text{-O})(\mu\text{-Li})_3$ (**2.3**) [$\text{Me}_2\text{SB} = \text{phenylenebis}(3,5\text{-Bu}^t_4\text{salicyl})\text{dimethyldiamidato}$], featuring alkylation of both Sm atoms and arising from cleavage of the C-C bond connecting the two units, as well as complete reduction of the imine groups of the two salophen ligands and THF deoxygenation. Similar cleavage of the connecting C-C bond of complex **2.2** was also observed during the reaction with dry O_2 to form a distorted cuboid cluster in which four Sm atoms are bridged by four hydroxyl groups $[(3,5\text{-Bu}^t_4\text{salophen})\text{Sm}(\text{OH})]_4 \cdot 4\text{toluene}$ (**2.4**).

Trivalent samarium methyl and vinyl derivatives supported by the calix-tetrapyrrole ligand system $(\text{Et}_8\text{-calix-pyrrole})(\text{R})\text{Sm}[\text{Li}(\text{THF})]_2[\text{Li}(\text{THF})_2](\mu^3\text{-Cl})$ [$\text{R} = \text{Me}$ (**3.2a**), $\text{CH}=\text{CH}_2$ (**3.2b**)] were prepared via reaction of $(\text{Et}_8\text{-calix-pyrrole})(\text{R})\text{Sm}(\mu^3\text{-Cl})[\text{Li}(\text{THF})]_2[\text{Li}(\text{THF})_2]$ (**3.1**) with the corresponding organolithium reagent. Complex **3.2a** reacts readily with H_2 at room temperature and atmospheric pressure to afford the corresponding mononuclear samarium hydride $(\text{Et}_8\text{-calix-pyrrole})(\text{THF})\text{Sm}[\text{Li}(\text{THF})]_2(\mu^3\text{-H})$ (**3.3**). Complexes **3.2a** and **3.3** are thermally robust. Conversely, the vinyl derivative **3.2b** rapidly and spontaneously decomposes at room

temperature to afford the Sm^{II} derivative $(\text{Et}_8\text{-calix-pyrrole})(\text{THF})\text{Sm}[\text{Li}(\text{THF})]_2[\text{Li}(\text{THF})_2](\mu^3\text{-Cl})$ (**3.4a**).

The nature of the substituents present on the calix-tetrapyrrole tetra-anion ligand $\{[\text{R}_2\text{C}(\text{C}_4\text{H}_2\text{N})]_4\}^{4-}$ [$\text{R} = 1/2\text{-(CH}_2)_5\text{-}$ (**a**), Et (**b**)] determines the type of reactivity of the corresponding $\text{Sm}(\text{II})$ compounds with acetylene. Where $\text{R} = 1/2\text{-(CH}_2)_5\text{-}$, dehydrogenation occurred to yield the nearly colorless dinuclear diacetylide complex $[\{[-(\text{CH}_2)_5\text{-}]_4\text{-calix-pyrrole}\}\text{Sm}]_2(\mu\text{-C}_2\text{Li}_4)\cdot\text{THF}$ (**5.1a**) as the only detectable reaction product. Conversely, where $\text{R} = \text{Et}$, acetylene coupling in addition to dehydrogenation resulted in the formation of a dimeric butatrienediyl enolate derivative $\{(\text{Et}_8\text{-calix-pyrrole})\text{SmLi}[\text{Li}(\text{THF})]_2(\mu^3\text{-OCH=CH}_2)\}_2(\mu, \eta^2, \eta'^2\text{-HC=C=C=CH})$ (**5.2b**). Reaction of the trivalent hydride $(\text{Et}_8\text{-calix-pyrrole})(\text{THF})\text{Sm}(\mu\text{-H})[\text{Li}(\text{THF})]_2$ or of the terminally bonded methyl derivative $\{(\text{Et}_8\text{-calix-pyrrole})(\text{CH}_3)\text{Sm}[\text{Li}(\text{THF})]_2[\text{Li}(\text{THF})_2](\mu^3\text{-Cl})\}$ with acetylene resulted in a mixture of the carbide $\{(\text{Et}_8\text{-calix-pyrrole})\text{Sm}\}_2(\mu\text{-C}_2\text{Li}_4)\text{Et}_2\text{O}$ (**5.1b**) and the dimerization product **5.2b** which were separated by fractional crystallization and characterized. The same reaction also yielded a third product, a trivalent complex $\{[(\text{Et}_8\text{-calix-pyrrole}^*)\text{Sm}]\{[\text{Li}(\text{THF})_2]\}_2\}$ (**5.3**), in which the macrocycle was isomerized by shifting the ring attachment of one of the four pyrrole rings.

Reaction of the mononuclear and trivalent $(\text{R}_n\text{-calix-pyrrole})\text{ClSm}[\text{Li}(\text{THF})]_2[\text{Li}(\text{THF})_2](\mu^3\text{-Cl})$ [$\text{R}_n = \text{Et}_8$ (**6.1a**), Cy_4 (**6.1b**)] with lithium under Ar in THF afforded the mononuclear divalent $(\text{R}_n\text{-calix-pyrrole})(\text{L})\text{Sm}[\text{Li}(\text{THF})]_2[\text{Li}(\text{THF})_2](\mu^3\text{-X})$ [$\text{X} = \text{Cl}$, $\text{L} = \text{THF}$, $\text{R}_n = \text{Cy}_4$ (**6.2b**); $\text{X} = \text{OCH=CH}_2$, $\text{L} = \text{ether}$, $\text{R}_n = \text{Et}_8$ (**6.3a**)] where the enolate was formed by a THF cleavage process. In the case of direct reaction of $\text{SmI}_2(\text{THF})_5$ with the tetralithiated form of the

R_n -calix-pyrrole ligand, the two isomorphous enolates (**6.3a** and **6.3b**) were the only isolated products. Complexes **6.3** react reversibly with ethylene to afford the corresponding light-green dinuclear ethylene adducts.

The nature of the alkyl substituents present on the macrocycle calix-terapyrrole ligand also determines the extent of dinitrogen reduction in the reaction of the Sm(II) derivatives with dinitrogen.

Recrystallization of $\{(\text{Cy}_4\text{-calix-tetrapyrrole})(\text{THF})\text{Sm}[\text{Li}(\text{THF})]_2[\text{Li}(\text{THF})_2](\mu^3\text{-Cl})\}$ from THF/hexane resulted in a mixture of two compounds, the labile dinitrogen complex $\{(\text{Cy}_4\text{-calix-tetrapyrrole})\text{Sm}[\text{Li}(\text{THF})]_2[\text{Li}(\text{THF})_2](\mu^3\text{-Cl})\}_2(\mu\text{-N}_2)$ (**7.2**) as well as the enolate $\{(\text{Cy}_4\text{-calix-tetrapyrrole})(\text{THF})\text{Sm}[\text{Li}(\text{THF})]_2[\text{Li}(\text{THF})_2](\mu^3\text{-OCH=CH}_2)\}$ (**7.3**).

Recrystallization of **7.2** from diethyl ether lead to the formation of a new Sm(II) complex $\{(\text{Cy}_4\text{-calix-tetrapyrrole})(\text{L})\text{Sm}[\text{Li}(\text{THF})]_2[\text{Li}(\text{THF})_2](\mu^3\text{-Cl})\}(\text{Et}_2\text{O})_{1.5}$ [$\text{L} = \text{Et}_2\text{O}$ (**7.4**)]

Reaction of $\text{SmI}_2(\text{THF})_2$ with the disodium or dipotassium salt of the diphenyl dipyrromethanyl dianion lead to the tetranuclear and trivalent samarium complex $\{[\mu\text{-Ph}_2\text{C}(\eta^1:\eta^5\text{-C}_4\text{H}_3\text{N})_2]\text{Sm}\}_4(\mu\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-N}_2)$ (**8.1**) containing a coordinated dinitrogen. The long N-N distance and the irreversibility of the coordination indicates that a four-electron reduction process arose from the cooperative interaction of four dipyrromethanyl Sm units on the same dinitrogen molecule. The dinitrogen molecule is placed in the center of the square plane defined by the four samarium atoms and appears to be side-on bonded to two metal centers and end-on bonded to the others. Similar reaction carried out under Ar atmosphere led to the formation of a divalent ionic cluster $[\{[\mu\text{-Ph}_2\text{C}(\eta^1:\eta^5\text{-C}_4\text{H}_3\text{N})_2]\text{Sm}\}_5(\mu\text{-I})]^{(-)}[\{[\mu\text{-Ph}_2\text{C}(\eta^1:\eta^5\text{-C}_4\text{H}_3\text{N})_2]_2[\text{Sm}(\text{THF})]_3(\mu\text{-I})\}^{(+)}$ (**8.2**) which does not react with dinitrogen. However, elimination of the formal SmI_2 unit *via* reaction with

KH afforded the dinitrogen complex in good yield. Reduction of (diphenylmethyldipyrrolide)Sm-Cl with K under N₂ afforded a new tetranuclear Sm^{II} compound $\{[\mu\text{-Ph}_2\text{C}(\eta^1\text{:}\eta^5\text{-C}_4\text{H}_3\text{N})_2]\text{Sm}\}_4(\mu\text{-Cl})[\text{K}(\text{THF})_2]$ (**8.3**) with the same square planar arrangement of the tetrametallic unit of **8.1** but with a chlorine atom located in the center instead of the dinitrogen molecule.

Reduction of an *in situ* generated “[R₂C(C₄H₃N)₂]Sm}Cl” [R = Ph] precursor with sodium under nitrogen and in THF afforded the paramagnetic $\{([\text{Ph}_2\text{C}(\text{C}_4\text{H}_3\text{N})_2]\text{Sm})_4\}\{\text{Na}(\text{THF})_6\}$ (**9.1**) which was isolated as a dark purple crystalline material. Spectroscopic characterization and chemical degradation indicated that this species is a Sm(II) hydride. A similar reduction carried out on the corresponding cyclohexyldipyrrolide derivative [R = 1/2 -(CH₂)₅-] afforded the dinitrogen complex $\{[(\text{CH}_2)_5\text{C}(\text{C}_4\text{H}_3\text{N})_2]\text{Sm}\}_4(\mu\text{-N}_2)[\text{Na}(\text{THF})]_2$ (**9.2**) formally a mixed-valence Sm(II)/Sm(III) compound.

The nature of the substituents present on a dipyrrolide dianion ligand determines the assembly of Sm(II) clusters which participate to various extents in dinitrogen fixation and THF cleavage. Reaction of SmI₂(THF)₂ with the methylphenyl dipyrromethanyl dianion resulted in the pentameric cluster $\{[\text{MePhC}(\text{C}_4\text{H}_4\text{N})_2]\text{Sm}\}(\mu\text{-I})[\text{K}(\text{THF})_6]$ (**10.1**) which exhibited no reactivity with dinitrogen. Conversely, reaction of SmI₂(THF)₂ with the cyclohexyl dipyrromethanyl dianion resulted in THF cleavage to yield the tetranuclear oxo-bridged complex $\{[\text{Cy}(\text{C}_4\text{H}_3\text{N})_2]\text{Sm}\}_4(\mu\text{-O})$ (**10.2**).

Acknowledgements

First and foremost, I wish to thank my supervisor, Dr. Sandro Gambarotta, a truly gifted scientist whose energy and creative approach to chemistry inspired me. His patience and encouragement guided me through this work and his unique sense of humour kept me smiling.

A special thanks also to Dr. Darrin Richeson, Dr. Christian Detellier and Dr. Susannah Scott for sharing their expertise through valuable feedback and helpful advice.

To lab mates I have had the absolute pleasure of knowing during the course of this work. I owe a debt of gratitude for your help, kindness and friendship. Through your diversity you have made the lab a unique and special place.

Thanks also to support staff Dr. Glenn Facey and Raj Capoor for ASAP nmr spectra, as well as Dr. Corrine Bensimon and Dr. Glenn Yap for crystallographic work. Without your skilled help this wouldn't have been possible.

To my mother, Bruna, the strongest person I have ever known. Your support and dedication to our family have made me the privileged person that I am. To my father, Jack, of whom I am immeasurably proud, whose confidence in me has taught me to believe in myself. To my brother, David, for setting an example of the kind of person I am striving to become.

To Chris, who kept me sane. There's a place in my heart that will always be yours.

for Mom and Dad

List of Publications

1. T. Dubé, S. Gambarotta, G.P.A. Yap. Preparation and Reactivity of a Compartmental Schiff-Base Samarium Dinuclear Complex *Organometallics* **1998**, *17*, 3967-3973.
2. T. Dubé, S. Gambarotta, G.P.A. Yap. Reversible Fixation of Ethylene on a Sm(II) Calix-pyrrole Complex *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 1432-1435.
3. T. Dubé, S. Conoci, S. Gambarotta, G.P.A. Yap, G. Vaşapollo. Tetrametallic Reduction of Dinitrogen: Formation of a Tetranuclear Samarium Dinitrogen Complex *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 3657-3659.
4. T. Dubé, S. Gambarotta, G.P.A. Yap. Preparation and Characterization of Two Mixed-Valence Samarium Octameric Clusters *Organometallics* **2000**, *19*, 115-117.
5. T. Dubé, S. Gambarotta, G.P.A. Yap. Samarium Hydride, Methyl and Vinyl Complexes Supported by Calix-tetrapyrrole Ring Macrocycle. Thermal Decomposition to Samarium (II) *Organometallics* **2000**, *19*, 121-126.
6. T. Dubé, D. Freckmann, S. Conoci, S. Gambarotta, G.P.A. Yap. Monomeric and Octameric Divalent Ytterbium Complexes of Diphenylmethyl Dipyrrolyl Dianion *Organometallics* **2000**, *19*, 209-211.
7. T. Dubé, S. Gambarotta, G.P.A. Yap. Dinuclear Complexes of Di-, Tri- and Mixed-Valence Samarium Supported by the Calix-tetrapyrrole Ligand *Organometallics* **2000**, *19*, 817-823.
8. T. Dubé, S. Conoci, S. Gambarotta, G.P.A. Yap. Divalent and Mixed-Valence Samarium Clusters Supported by the Dipyrrolide Ligand *Organometallics* **2000**, *19*, 1182-1185.
9. T. Dubé, S. Gambarotta, G.P.A. Yap. The Reactions of Sm(II) and Sm(III) Complexes of Calix-tetrapyrrole with Acetylene: Formation of an "N-confused" Calix-tetrapyrrole Ring. *Eur. J. Inorg. Chem.* In press.
10. T. Dubé, S. Conoci, S. Gambarotta, G.P.A. Yap. Tetrametallic Divalent Samarium Cluster Hydride and Mixed-Valence Sm(II)/Sm(III) Dinitrogen Complex. *Organometallics* In press.

11. J. Guan, T. Dubé, S. Gambarotta, G.P.A. Yap. Dinitrogen Labile Coordination v.s. Four-Electron Reduction in the Chemistry of (calix-tetrapyrrole)Sm(II) Complexes. *Chem. Commun.* Submitted.

Table of Contents

Abstract	II
Acknowledgements	VI
Dedication	VII
List of Publications	VIII
List of Abbreviations	XV
 Chapter I	
Introduction	1
1.1	
N ₂ fixation: General Considerations	1
1.2	
<i>In vitro</i> dinitrogen fixation	4
1.3	
Bonding modes	5
1.4	
Lanthanides: General Characteristics	8
1.5	
N ₂ fixation by f-elements	14
1.6	
Magnetism in Lanthanide Complexes	18
1.7	
Scope and Summary of Thesis	19
References	22
 Chapter II	
Synthesis and reactivity of a Schiff-base samarium dinuclear complex:	
Reversible C-C formation	
II.1	
Introduction	30
II.2	
Experimental Section	32

II.3	Results and Discussion	37
II.4	X-ray Crystallography	42
II.5	Conclusions	51
	References	52
Chapter III	Terminally-bonded samarium hydride, methyl and vinyl supported by calix-tetrapyrrole ring macrocycle. Thermal decomposition to Sm(II)	
III.1	Introduction	58
III.2	Experimental Section	59
III.3	Results and Discussion	64
III.4	X-ray Crystallography	68
	References	76
Chapter IV	Dinuclear Sm(II), Sm(III), alkyl and mixed-valence compounds of calix-tetrapyrrole	
IV.1	Introduction	80
IV.2	Experimental Section	82
IV.3	Results and Discussion	87
IV.4	X-ray Crystallography	92
IV.5	Conclusions	100
	References	101

Chapter V	The reactions of Sm(II) and Sm(III) complexes of calix-tetrapyrrole with acetylene: Formation of an “N-confused” calix-tetrapyrrole ring.	
V.1	Introduction	106
V.2	Experimental Section	108
V.3	Results and Discussion	112
V.4	X-ray Crystallography	120
V.5	Conclusions	126
	References	127
Chapter VI	Reversible fixation of ethylene promoted by a Sm(II) calix-tetrapyrrole enolate complex	
VI.1	Introduction	129
VI.2	Experimental Section	130
VI.3	Results and Discussion	133
VI.4	X-ray Crystallography	135
	References	140
Chapter VII	Reversible coordination of dinitrogen facilitated by Sm(II) calix-tetrapyrrole as a possible prelude to further dinitrogen reduction	
VII.1	Introduction	144
VII.2	Experimental Section	145
VII.3	Results and Discussion	147

VII.4	X-ray Crystallography	152
	References	153
Chapter VIII Formation of a tetranuclear samarium dinitrogen complex via cooperative, tetrametallic reduction of dinitrogen		
VIII.1	Introduction	155
VIII.2	Experimental Section	156
VIII.3	Results and Discussion	158
VIII.4	X-ray Crystallography	162
	References	167
Chapter IX Tetrametallic divalent samarium cluster hydride and mixed-valence Sm(II)/Sm(III) dinitrogen reduction		
IX.1	Introduction	169
IX.2	Experimental Section	170
IX.3	Results and Discussion	172
IX.4	X-ray Crystallography	175
	References	178
Chapter X THF deoxygenation versus cluster formation and N ₂ fixation in the chemistry of Sm(II) dipyrrolides		
X.1	Introduction	180

X.2	Experimental Section	181
X.4	Results and Discussion	184
X.5	X-ray Crystallography	188
	References	189
Chapter XI	Conclusions	192
Appendix		196

List of Abbreviations

Å	angstroms
δ	chemical shift
μ _{eff}	effective magnetic moment in Bohr magnetons
cm ⁻¹	wave number
Cp	cyclopentadienyl
Cy	cyclohexyl
g	grams
i-Pr	isopropyl
Me	methyl
MHz	frequency in megahertz
ml	milliliter
mmol	millimoles
NMR	nuclear magnetic resonance
Ph	phenyl
ppm	parts per million
Py	pyridine
R	alkyl group
t-Bu	tert-butyl
THF	tetrahydrofuran
TMS	trimethylsilane
X	halogen

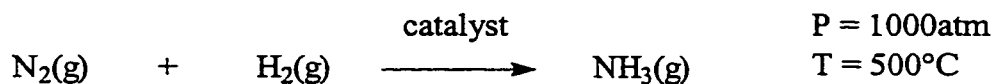
CHAPTER I

Introduction

I.1: N₂ fixation: General Considerations

One of the processes of dinitrogen fixation involves converting highly abundant atmospheric dinitrogen, N₂, into ammonia and nitrogenous compounds.¹ This process is of considerable interest for a number of reasons. Firstly, N₂ fixation is a very important step in the nitrogen cycle, providing available nitrogen for plant nutrition. It is a fascinating process since it occurs readily in various bacteria, blue-green algae, yeasts, and symbiotic bacteria-legume associations under mild conditions. However, dinitrogen stubbornly resists ordinary chemical attack, even under stringent conditions.

Molecular nitrogen, N₂, is so unresponsive to ordinary chemical reactions that it has been characterized as “almost as inert as a noble gas”.² The very large triple bond energy (945 kJmol⁻¹) tends to make the activation energy prohibitively large. Thus, in spite of the fact that the overall enthalpy of formation of ammonia is exothermic by approximately 50 kJmol⁻¹, the common Haber process of ammonia production in industry requires about 1000 atm pressure and 500°C temperatures to proceed, even in the presence of the best Haber catalyst. Nonetheless, this process is very efficient and well-entrenched, and it can produce large volumes of product in short time periods.



In addition to the purely pragmatic task of furnishing the huge supply of nitrogen compounds necessary for industrial and agricultural uses as cheaply as possible, chemists

are intrigued by the possibility of discovering processes that will work under less drastic conditions.

In nature, the active enzyme in nitrogen fixation is nitrogenase.³ It is not a unique enzyme but appears to differ somewhat from species to species. Nevertheless the various enzymes are very similar in the sense that two proteins are involved (Fig. 1.1). The smaller has a molecular weight of 57 000-73 000 and contains an Fe_4S_4 cluster. The larger protein is a tetramer with a molecular weight of 220 000-240 000 containing two molybdenum atoms, about 30 iron atoms, and approximately 30 labile sulfide ions.⁴ The iron-sulfur clusters are believed to act as redox centers. It is possible to isolate a soluble, protein-free cofactor containing molybdenum and iron. Recombination of the cofactor with inactive nitrogenase restores the activity.

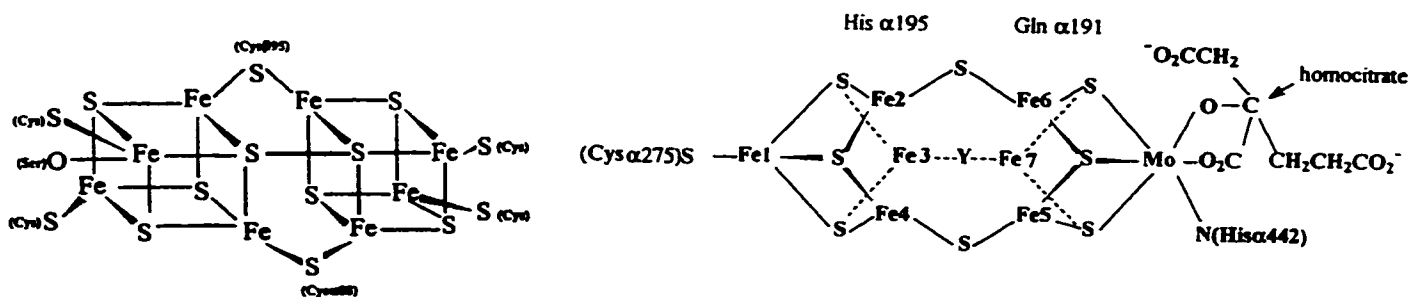
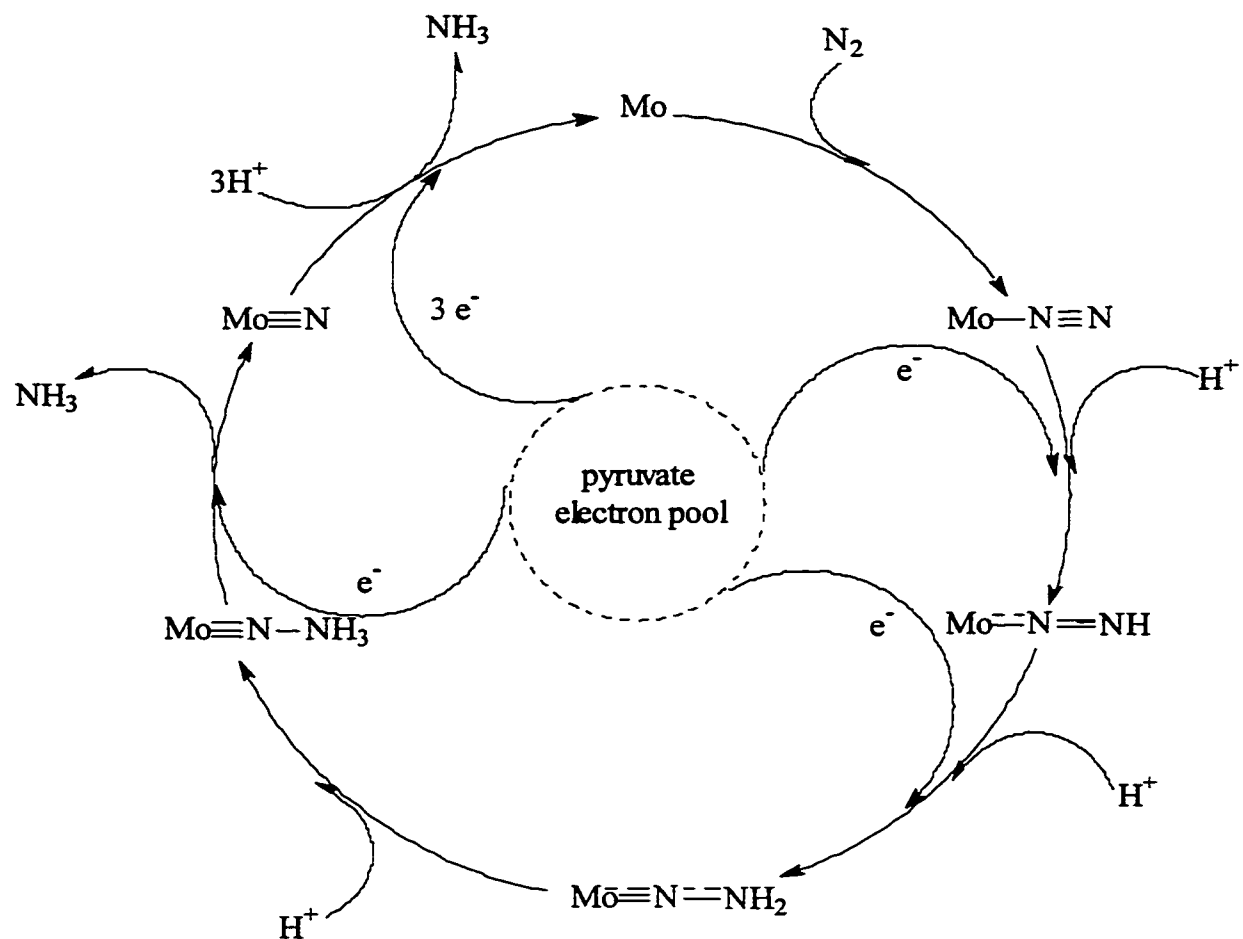


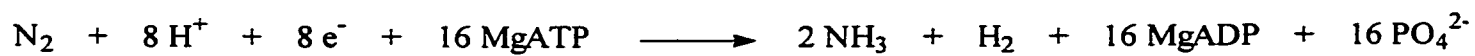
Fig. 1.1

It seems likely that the active site for dinitrogen binding involves the molybdenum atom.⁵ The ultimate source of the reductive capacity is pyruvate, and the electrons are transferred via ferredoxin to nitrogenase. There is some evidence that Mo(III) is involved. Two Mo(III) atoms cycling through Mo(VI) would provide the six electrons necessary for reduction of dinitrogen. Alternatively, since the enzyme is rich in ferredoxin-type clusters, there should be a ready flow of electrons, and the molybdenum may stay in one or two oxidation states that most readily bind dinitrogen and its

intermediate reductants. The overall catalytic cycle and overall equation for the process are shown:



Scheme 1.2



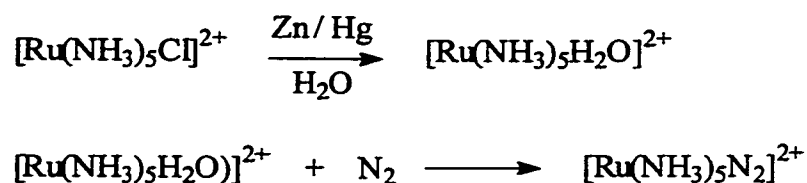
1.2 *In vitro* dinitrogen fixation

Molecular nitrogen, N₂, is isoelectronic with both carbon monoxide and the nitrosyl ion but, despite numerous complexes of CO and NO⁺, for many years it proved to be impossible to form complexes of dinitrogen. This difference in behaviour was usually ascribed to the lack of polarity of N₂ and a resultant inability to act as a π -acceptor. The discovery that dinitrogen was capable of forming stable complexes with transition metals led to an extensive investigation of the possibility of fixation via such complexes. An important development was the discovery that certain phosphine complexes of molybdenum and tungsten containing dinitrogen readily yield ammonia in acidic media:⁶



Both reactions take place at room temperature and atmospheric pressure and the reducing agent is a Grignard reagent. This reaction sequence is important because it models the *in vivo* nitrogenase systems that appear to employ molybdenum.

The first dinitrogen complex, characterized in 1965 by Allen and Senoff⁷, resulted from the reduction of commercial ruthenium trichloride by hydrazine hydrate. The pentammine(dinitrogen)ruthenium(II) cation that formed could be isolated in a variety of salts. Soon other methods were found to synthesize the complex, including direct reaction with nitrogen gas:

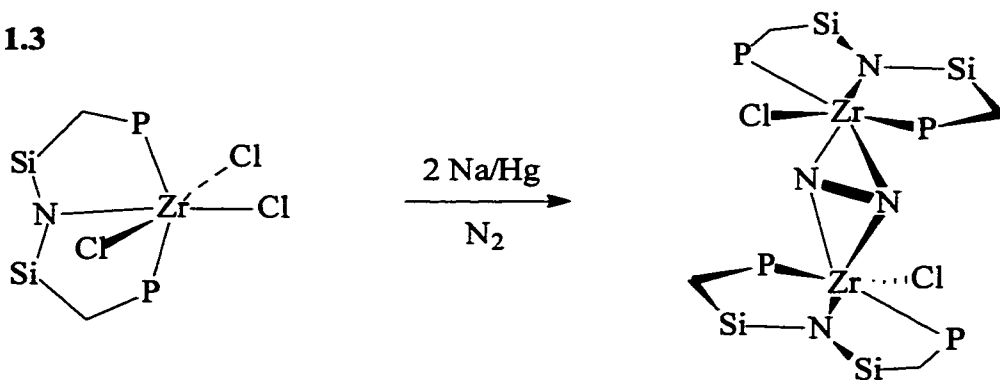


I.3: Bonding modes

The ability to synthesize complexes containing dinitrogen, especially those with considerable alteration of the electronic state of dinitrogen, opens up possibilities of direct fixation of dinitrogen from the atmosphere, a long-standing challenge to the chemist. It also provides insight into the closely-related process of biological fixation of nitrogen and the enzyme systems involved. Through coordination to one or more metal centers, the dinitrogen ligand, which is extremely inert in free form, acquires a different degree of activation⁸ (Table 1.1). In principle, systems suitable for protonation reactions are those with “moderate”⁹ to “strong”¹⁰ activation as well as compounds which cleave the N_2 ¹¹ molecule upon coordination. However, if the aim is to achieve relevance to the biological process, “mild” conditions are important. “Nonactivated” systems, although not protonable, may also provide information fundamental to understanding the metal- N_2 bond. Since the type of bonding adopted by dinitrogen is a crucial prerequisite for further activation, the attention of researchers has been focussed on the preparation of new complexes containing dinitrogen bound in a variety of modes. As a result, a library of compounds has been prepared containing end-on (both terminal and bridging) dinitrogen while the side-on bonding mode remains relatively uncommon. Following the initial proposal by Lappert that a Zr(III) complex might be able to coordinate dinitrogen in a side-on bonding fashion¹², this unusual bonding mode was regarded as particularly

promising for activation purposes. In fact, this type of coordination implies a significant donation of charge from the metal to the π^* orbitals of N_2 , which corresponds to significant reduction. This theory was recently substantiated by the findings of Fryzuk, whose side-on bonded dinitrogen possesses the longest ever observed N-N distance [N-N = 1.548 Å].^{10a}

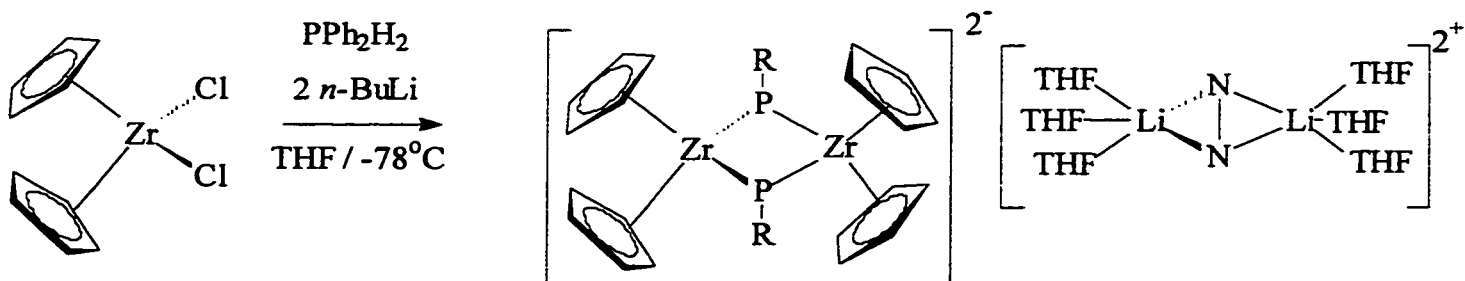
Scheme 1.3



As well, theoretical calculations carried out on related compounds¹³ support the idea that the presence of suitable d-orbitals, able to give δ overlap with the π^* orbital of dinitrogen, is a factor capable of determining the coordination mode.

To date, the chemistry of dinitrogen has been dominated by transition metals for which dinitrogen complexes are known of almost all the elements in most oxidation states. There is a general agreement that the coordination of dinitrogen to a metal center is a prerequisite for further transformations and that the availability of d electrons¹⁴, in addition to a highly reactive oxidation state¹⁵, are crucial for the interaction of the metal with an exceedingly stable molecule such as dinitrogen. In keeping with this notion, there is no reported example of coordination of dinitrogen performed by a d^0 transition metal. However, the recently reported reversible, side-on coordination of dinitrogen to a Li^+ cation¹⁶ (Scheme 1.4) contradicts these expectations and brings to light interesting

possibilities in the field of reactivity of dinitrogen. In recent years it has been demonstrated that even the lanthanide and actinide elements are capable of fixing dinitrogen.



Scheme 1.4

Table 1.1 Bonding Modes for Dinitrogen

bonding mode	metal	degree of activation
$\text{L}_n\text{M}-\text{N}\equiv\text{N}$	Fe(II)	nonactivated
$\text{M} \rightarrow \begin{array}{c} \text{N} \\ \\ \text{N} \end{array} \leftarrow \text{M}$	Sm(III), U(III)	
$\text{L}_n\text{M}-\text{N}\equiv\text{N}$	Mo^0, W^0	moderately activated
$\text{L}_n\text{M}-\text{N}-\text{N}-\text{ML}_n$	Ti(I)/Ti(II)	strongly activated
$\begin{array}{c} \text{N} \\ / \quad \backslash \\ \text{M} \quad \quad \text{M} \\ \backslash \quad / \\ \text{N} \end{array}$	Zr(II), Ti(I)/Ti(II)	
$\text{M}\equiv\text{N}$	$\text{M} = \text{Li}, \text{Mo}(\text{NRAr})_3$	cleavage

I.4: Lanthanides-General Characteristics

The lanthanides are the 14 elements following lanthanum in the periodic table. During the last two decades, the chemistry of the lanthanides has developed from a minor field into an important area in organometallic chemistry.¹⁷ This activity is a reflection of the growing realization that these elements have unique and interesting chemical properties. Until the early eighties, organolanthanide chemistry was mainly limited to cyclopentadienyl species such as Cp_3Ln and $[\text{Cp}_2\text{LnCl}]_2$ ¹⁸. As well, a number of homoleptic compounds such as $\text{Li}[\text{LnPh}]_4$ ¹⁹ and $\text{Ln}[(\text{CH}_2)_2\text{PMe}_2]_3$ ²⁰ in addition to a few less well-defined carbyls obtained by metal-vapour synthesis had been reported²¹. At the time, the bonding in organolanthanides was considered to be predominantly ionic.²² As a result, the chemistry was expected to resemble closely that of group 1 and 2 elements rather than the transition metals and was consequently thought to be less interesting. Activation of interesting, small molecules such as CO, hydrogen, olefins, and acetylenes had not been reported and was also not expected on the basis of the supposed ionic character of the compounds.

However, the status of organolanthanide chemistry has changed dramatically. Stable, well-defined and well-characterized organolanthanides with Ln-C and Ln-H σ -bonds have now been reported and most of them display unprecedented structures and very interesting reactivity.²² Several of these compounds are active catalysts for important commercial processes such as alkene oligomerization²³, polymerization²⁴, hydrogenation²⁵ and isomerization²⁶, alkyne polymerization²⁷ and hydrogenation²⁸, nitrile hydrogenation²⁹, and dimerization²⁹.

In the lanthanide series, the 4f-shell is sequentially filled with electrons. The most common oxidation state for the lanthanides and group 3 elements is +3. However, some of the elements also have a stable di- and or tetravalent oxidation state available. Ce^{+4} is stable in aqueous solution and is a well-known oxidizing agent in lanthanide chemistry. Europium, samarium, and ytterbium have a stable divalent oxidation state.^{22c,17f} Sm^{+2} is a strong reducing agent with a reduction potential of -1.5V^{30} in aqueous solution. The organometallic chemistry of Sm^{+2} has revealed very interesting features and resembles the redox chemistry of alkali metals. None of the metals has both the +4 and the +2 oxidation states available. *As a result, oxidative additions or reductive eliminations, two important fundamental steps in transition metal chemistry³¹, are not possible on a single lanthanide center.*

Compared to the transition metals, the lanthanides have large ionic radii.³² On going from lanthanum ($1.032\text{\AA}$) to lutetium ($0.861\text{\AA}$), the ionic radius of the lanthanide ions gradually decreases.^{32,33} This effect, well-known as the lanthanide contraction, is a consequence of the poor shielding of the f-electrons.³² As a consequence of the large ionic radius, the coordination sphere of the lanthanides is relatively large and allows for high coordination numbers. Lanthanide ion coordination numbers of 8 are very common and some as large as 12 have been observed.¹⁷ Trivalent lanthanide ions are rather electropositive and are considered to behave as hard Lewis acids.³⁴

The energy and spatial orientation of the f-orbitals fall rapidly as the atomic number increases.¹⁷ Calculations have shown that the 4-f orbitals do not extend beyond the $5s^2$ and $5p^6$ orbitals.³⁵ As a consequence, a trivalent lanthanide ion looks like a closed shell inert gas cloud with a +3 charge. Orbital interactions, therefore, are much less important

than in transition metal chemistry and the chemistry tends to be rather ionic. The absence of extensive interactions with 4-f orbitals also implies that the valuable covalent interactions such as π -back donation are not likely to occur in organolanthanide compounds. On the other hand, lack of ligand field stabilizing effects may give very flexible coordination geometries for which processes such as ligand rearrangements and geometry modifications are quite facile. The large size, the electropositive character, and the absence of f-orbital constraints mean that the lanthanide elements have the potential to display unprecedented and unique chemistry.

Almost all lanthanide complexes containing two cyclopentadienyl rings have one to three additional ligands in the coordination sphere of the metal. This is consistent with the large size of these metals and their tendency toward steric saturation in stable complexes. The first structurally characterized simple bis(cyclopentadienyl) system analogous to ferrocene was published in 1986³⁶. The surprising structure of Cp^*_2Sm is shown in Fig. 1.2.

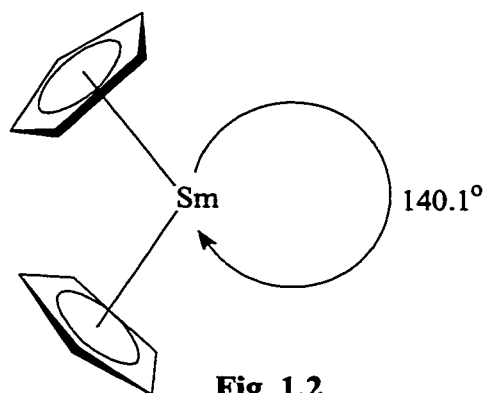
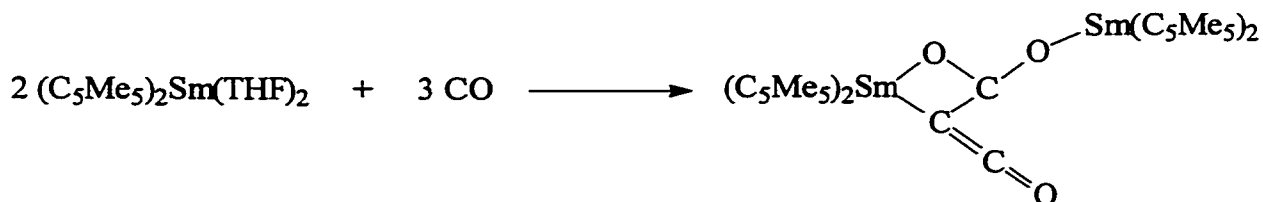


Fig. 1.2

The molecule crystallizes as a monomer with a (ring centroid)-metal-(ring centroid) angle of 140.1° rather than the 180° angle anticipated for a parallel ring structure analogous to that found for ferrocene or decamethyl ferrocene. The (ring centroid)-metal-(ring

centroid) angle in Cp^*_2Sm is only slightly larger than the 136.7° angle found for $\text{Cp}^*_2\text{Sm}(\text{THF})_2$ ³⁷, as though removal of the two THF ligands had no effect on this structural feature. The unusual bending phenomenon displayed by samarocene remains a theoretical challenge.

Most of the unusual chemical reactivity observed for divalent lanthanides is found with Sm(II) species. The greater reducing power of Sm(II) compared to Yb(II) and Eu(II)³⁸ opens up avenues for reactivity for Sm(II) which are unavailable to other divalent lanthanide systems. A remarkable chemistry based on Cp^*_2Sm and $\text{Cp}^*_2\text{Sm}(\text{THF})_2$ has been exploited by Evans.³⁹ Divalent samarium has proven to be a unique, one electron reductant due to its special combination of physical properties. The reduction of CO by $\text{Cp}^*_2\text{Sm}(\text{THF})_2$ provides an excellent example of the unique reactivity available through this divalent oxidation state. $\text{Cp}^*_2\text{Sm}(\text{THF})_2$ reacts under a variety of conditions with CO to give complex mixtures of products.⁴⁰ Under 90 psi of CO in THF, a crystalline product separates which was crystallographically characterized.

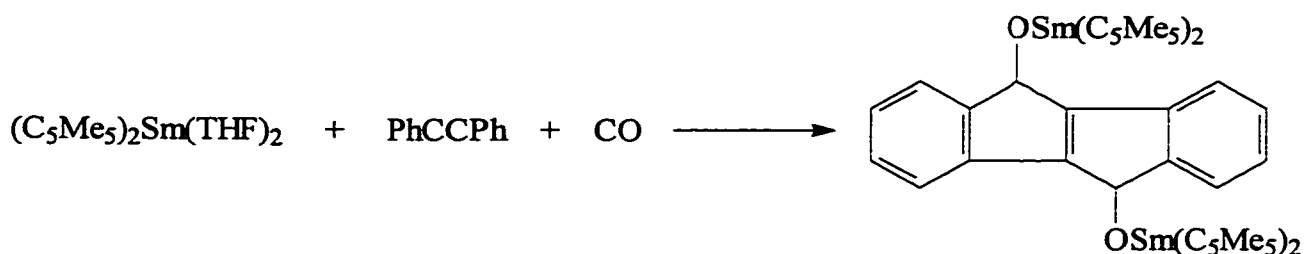


Scheme 1.5

The remarkable dimeric product contains four Sm(III) centers and the equivalent of 6 CO molecules. Hence, 6 units of CO have been reduced by four electrons and the reductive homologation has formed two ketene carboxylate units. The most interesting feature in the formation of the ketene carboxylate complex is that complete cleavage of one CO triple bond must have occurred to give the central oxygen-free carbon of the $\text{C}=\text{C}-\text{C}$

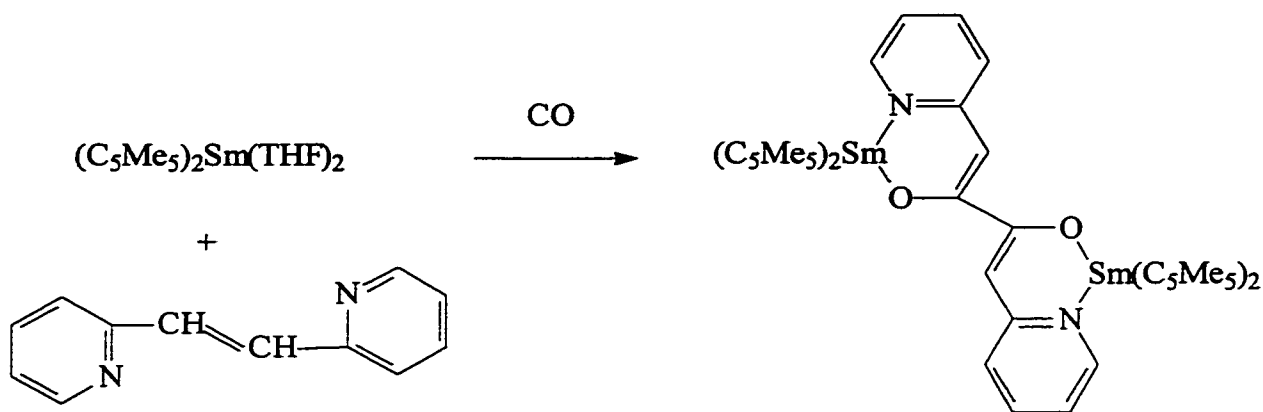
skeleton. Although CO cleavage is thought to occur in heterogeneous Fischer-Tropsch⁴¹ systems, this rarely occurs in homogeneous systems.

$\text{Cp}^*_2\text{Sm}(\text{THF})_2$ reacts with diphenyl acetylene to give $\text{Cp}^*_2\text{SmPhC}\equiv\text{CPh-SmCp}^*_2$. Further treatment with CO led to the stereospecific synthesis of the indenoindenediolate complex via CO insertion and subsequent insertion of the resulting carbene centers into ortho C-H bonds to generate the two five-membered rings.⁴²

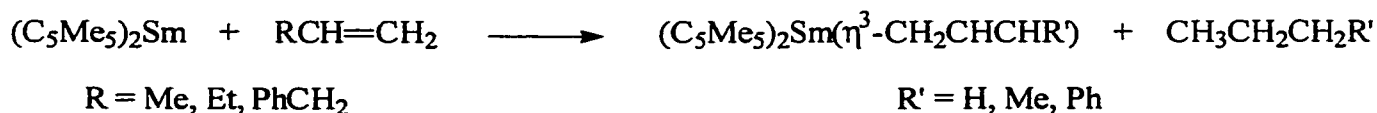


Scheme 1.6

Reaction of $\text{Cp}^*_2\text{Sm}(\text{THF})_2$ with azobenzene allowed the intermediate $\text{Cp}^*_2\text{Sm-NPh-NPhSmCp}^*_2$ to be isolated and crystallographically identified.⁴³ Reaction of $\text{Cp}_2\text{Sm}(\text{THF})_2$ with two equivalents of azobenzene, however, afforded $[\text{Cp}^*_2\text{Sm}_2]_2(\text{N}_2\text{Ph}_2)_2$.⁴³ In THF, ligand redistribution slowly occurs to the mono- Cp^* complex $[\text{Cp}^*(\text{THF})\text{Sm}]_2(\text{N}_2\text{Ph}_2)_2$ which possesses two $\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2\text{Ph}_2$ ligands, rather than $\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_2\text{Ph}_2$, as in $[\text{Cp}^*_2\text{Sm}]_2(\text{N}_2\text{Ph}_2)$. Reaction of $[\text{Cp}^*_2\text{Sm}]_2(\text{N}_2\text{Ph}_2)$ with CO was attempted to parallel the reaction of $\text{Cp}^*_2\text{Sm}(\text{THF})_2$ with diphenyl acetylene and CO. This afforded, however, a quite different product $[\text{Cp}^*_2\text{Sm}]_2[\mu\text{-}\eta^4\text{-(PhN)OCCO(NPh)}]$.⁴⁴



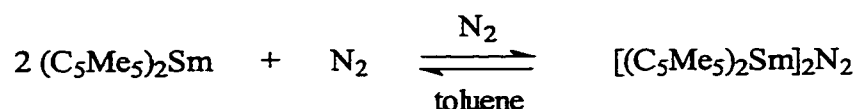
It has generally been observed that $\text{Cp}^*_2\text{Sm}(\text{THF})_2$ reacts with unsaturated molecules to give reductive coupling. For example, reaction of Cp^*_2Sm with $\text{PhHC}=\text{CHPh}$ or styrene, affords the μ -alkene $[\text{Cp}^*_2\text{Sm}]_2(\mu^2:\eta^4\text{-alkene})$.⁴⁵ Different reactivity is observed with non-phenyl-substituted alkenes that cannot interact with Sm via the phenyl group. $(\text{C}_5\text{Me}_5)_2\text{Sm}$ reacts with excess propene, 1-butene, and allylbenzene to give the corresponding allylic species:⁴⁶



Consistent with the strongly reducing tendency of Cp^*_2Sm , it is readily oxidized. Thus reaction with NO, N_2O , $\text{C}_5\text{H}_5\text{NO}$, or the epoxide 1,2-epoxybutane, affords $[\text{Cp}^*_2\text{Sm}]_2(\mu\text{-O})$.⁴⁷ Although treatment of oxophilic, highly reducing Cp^*_2Ln led to $\mu\text{-E}$ species, slow crystallization of Cp^*_2Sm from toluene under N_2 gave the first dinitrogen complex of an f-element $[\text{Cp}^*_2\text{Sm}]_2(\mu\text{-}\eta^2:\eta^2\text{-N}_2)$, which is discussed in the following section.

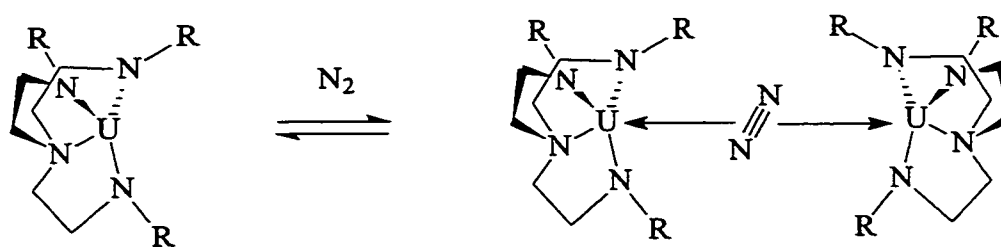
I.5: N₂ fixation by f-elements

The first dinitrogen complex reported for an f-element is on samarium. The samarocene dinitrogen complex [Cp*₂Sm]₂(μ-N₂) described by Evans in 1988⁴⁸ was also the first complex with planar, side-on bonded dinitrogen ligand between two metal atoms. Slow crystallization of dark green Cp*₂Sm from toluene over a four week period gave quantitative yield of dark, red-brown crystals of a new dinitrogen complex:



Scheme 1.8

The N-N bond distance in this complex [1.088Å] is strikingly short and is even shorter than in gaseous N₂. This suggests minimal N₂ reduction. The coordinated dinitrogen ligand in this complex is labile and is easily eliminated with reformation of samarocene, which is achieved via simple treatment of the complex with toluene. Last year, the first complex of an actinide was reported.⁴⁹ The crystal structure showed similar binding of the N₂ ligand as in the samarocene case in that the N₂ ligand was located side-on with respect to two uranium centers coordinated to a ligand of the triamidoamine variety.

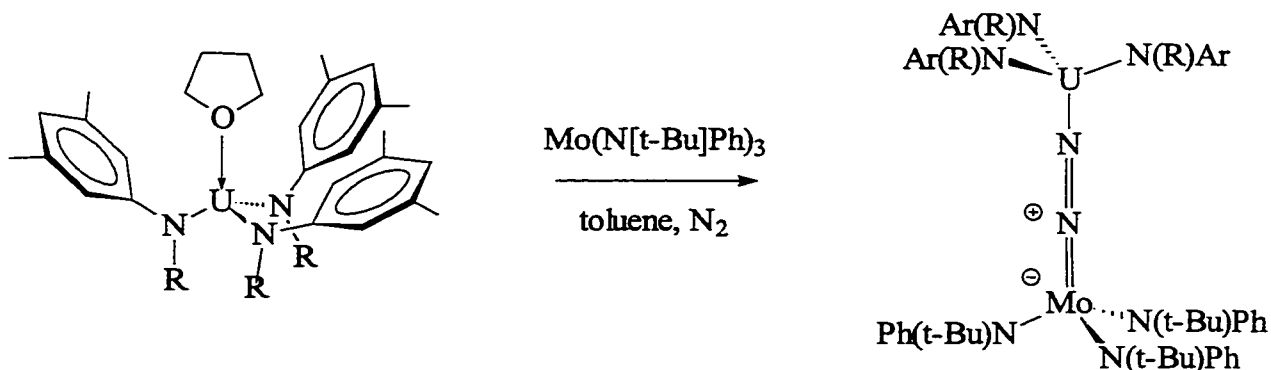


R = TMS

Scheme 1.9

As in the case of samarocene, the fixation was labile and the N-N distance was even shorter than in free N_2 despite oxidation of the two uranium centers as confirmed by magnetic susceptibility data.

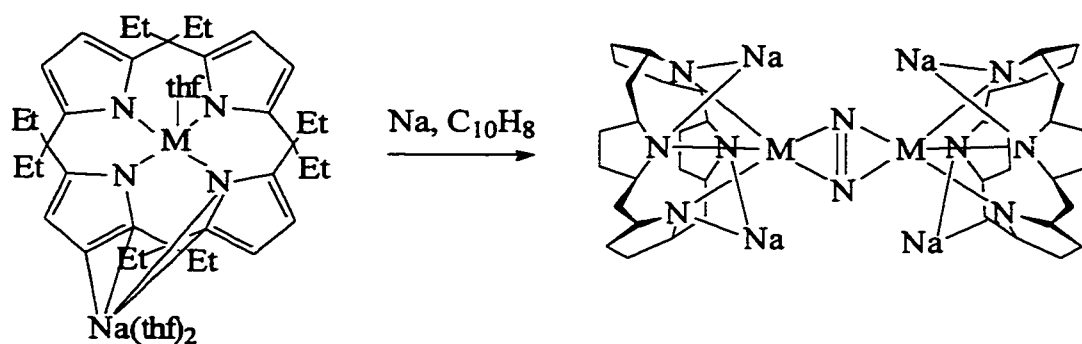
The same year, Cummins reported the first example of end-on coordination of the dinitrogen ligand by a uranium center via cooperative attack on the N_2 molecule with a Mo(III) amide to assemble heterodinuclear complexes.⁵⁰ The supporting ligands in this case were also of the N-donor variety. An X-ray crystal structure determination revealed an end-on bridging bonding mode for the N_2 ligand. Substantial reduction of the N_2 molecule was demonstrated by an N-N distance of 1.232(11)Å, longer by 0.13Å than in free N_2 . As in the previous example, some degree of multiple bonding between N_2 and uranium was indicated by the short U-N(N_2) distance compared with the three U-N(amide) distances.



Scheme 1.10

Earlier results in this area indicated that the calix-tetrapyrrole anion, a chelating tetraanionic amide, provides a versatile tool in the stabilization of lower oxidation states of early transition metals and lanthanides, a criterion believed to be a prerequisite for N_2 reduction. Recently, dinitrogen complexes of praeosodymium and neodymium of the same ligand system were isolated in which the N_2 ligand was bound side-on with respect

to two metal centers. Elongation of the N-N distance [1.254 Å (M = Pr)] was indicative of a two electron reduction of N₂.⁵¹

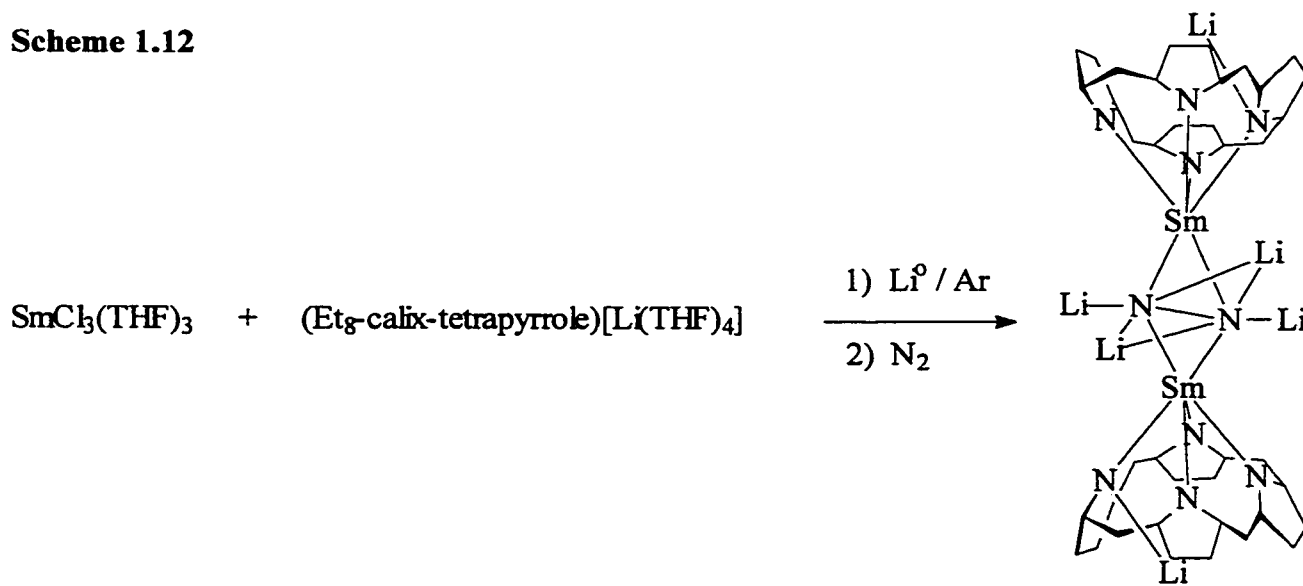


M = Pr, Nd

Scheme 1.11

Nonetheless, given that Nd and Pr do not possess a stable +2 oxidation state, limitations arise in terms of studying the process of N₂ activation promoted by these elements. By contrast, in the case of samarium, the reaction of [Et₈-calix-tetrapyrrole][Li(THF)₄] yielded a yellow crystalline complex which, upon reduction with metallic lithium under argon, produced a dinuclear side-on dinitrogen complex upon recrystallization under N₂.⁵²

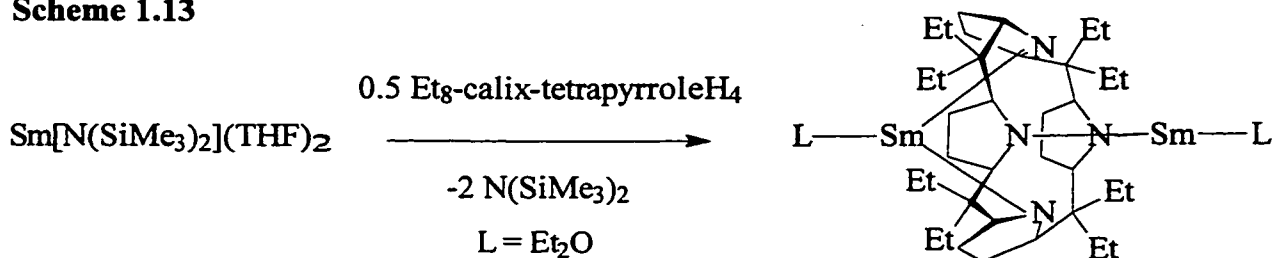
Scheme 1.12



This dimeric complex has two $(\text{THF})_2\text{Li}[\text{Et}_8\text{-calix-tetrapyrrole}]\text{Sm}$ units bridged by a planar N_2Li_4 moiety. The molecule of N_2 is encapsulated in the Sm_2Li_4 octahedron and is coaxial with one Li-Li diagonal. The N_2Li_4 core is formed by one N_2 unit with two side-on lithium atoms and the other two coplanar and coaxial with the N-N vector. The Sm atoms are symmetrically placed side-on with respect to the N_2 moiety above and below the N_2Li_4 plane. The very long N-N distance in this species [$1.525\text{\AA}$], is indicative of a significant extent of reduction of dinitrogen which, of course, given the side-on bonding mode, is in striking contrast to the cyclopentadienyl dinitrogen complex reported by Evans. The stoichiometry of this compound indicates that N_2 has undergone a 4-electron reduction. Given that Sm(II) can transfer only one electron, the structure of the complex suggested that the reaction probably followed a multi-step pathway likely proceeding through formation of a polynuclear intermediate. A possible rationale for the striking difference between these two sole samarium dinitrogen complexes might be derived from the presence of the alkali ion which could assist an efficient electron transfer from samarium to the dinitrogen molecule. These results prompted attempts to prepare a Sm(II) complex of the same ligand in the absence of alkali cation.

The reaction of $[\{\text{Me}_3\text{Si}\}_2\text{N}\}_2\text{Sm}(\text{TMEDA})]$ with $\text{Et}_8\text{-calix-tetrapyrroleH}_4$ formed a Sm(II) complex via a simple transamination reaction.⁵³

Scheme 1.13



The complex was found to possess a $\text{Sm}_2(\text{Et}_2\text{O})_2$ unit which is almost linear and which is surrounded by the macrocyclic ligand. The complex does not contain dinitrogen thus indicating that indeed lithium cations play a crucial role in this system in assisting and promoting the coordination of dinitrogen.

I.6 : Magnetism in Lanthanide Complexes

Analysis of the magnetic susceptibility of lanthanide compounds is complex.^{54,55} As originally explained by Van Vleck⁵⁴, the moments and populations of the contributing energy states of the metal must be considered in addition to the effect of the ligands on these states. Variable temperature studies including low temperature measurements are necessary in order to fully define the paramagnetic properties of a given complex. In this regard, few generalizations can be made.⁵⁶ Nonetheless, the magnetic moments of many lanthanide complexes at room temperature may often be approximated by the simple expression $\mu_J = g[J(J+1)]^{1/2}$ (where $g = [S(S+1) - L(L+1) + 3J(J+1)]/[2J(J+1)]$), a relationship originally reported by Hund.^{54,56} This expression arises directly from the Van Vleck equation for magnetic susceptibility⁵⁴ where certain conditions are met by the system. For many lanthanide complexes, these conditions are met at room temperature. For complexes of Eu^{3+} , Sm^{3+} , and Sm^{2+} , however, the separation in J states is comparable to kT at room temperature and this expression does not hold true. For example, magnetic susceptibility values for Sm(II) complexes typically fall within $3.5\text{--}3.8\mu_B$ ($\mu_{J\text{approx}} = 0\mu_B$) and Sm(III) $1.36\text{--}1.9\mu_B$ ($\mu_{J\text{approx}} = 0.84\mu_B$).⁵⁶

Despite the paramagnetism of Sm(III) species, the linewidths of the NMR resonances are relatively narrow and in most cases all proton and carbon resonances are observable.

In the case of Sm(II) complexes, however, the resonances are generally largely displaced from their diamagnetic field positions.

I.7: Scope and Summary of Thesis

The aim of this investigation was to explore the reactivity and properties of well-defined, low-valent compounds of samarium, and to rationalize our observations in terms of the highly-exploited samarocene system. For this purpose, ligands featuring nitrogen donor atoms were thought to be particularly promising for the stabilization of divalent samarium. Amides are well-known for their electronic flexibility in addition to their inherent ability to stabilize low-valent transition metals and lanthanides, to promote polynuclear aggregation, and to enhance chemical reactivity.

Samarium was chosen for this study because, in comparison with divalent europium and ytterbium, Sm^{+2} is the strongest reducing agent in aqueous solution. As a result, most of the unusual reactivity observed for divalent lanthanides is found with Sm(II) species. Possibly the most remarkable transformations promoted by Sm(II) are those involving highly inert dinitrogen. In particular, the two known dinitrogen complexes of samarium display different degrees of activation for the N_2 molecule from reversible coordination in the case of samarocene to four-electron reduction in the case where the calix-tetrapyrrole ligand system was employed. Given that Sm(II) is exclusively a one-electron reducing agent, we explored the possibility of cooperative dinitrogen reduction promoted by multiple Sm(II) centers in order to gain mechanistic insight into the generation of the tetralithium hydrazide derivative.

The relative unavailability of Sm(II) systems involving alternative ligand systems to cyclopentadienyl may be attributed to a strong reduction potential as well as to a tendency to support high coordination numbers. Stabilization of Sm(II) using the chelating salophen ligand thus resulted in the formation of a Sm(III) species through imine reduction and C-C bond formation in the assembly of a dinuclear structure with a short intermetallic distance. Formally a Sm(III) compound, this species was observed to behave as a source of divalent samarium. However, ligand interference precluded the possibility for employing this ligand system for the purpose of studying dinitrogen reduction.

A goal of this research was to determine the nature of the Sm(III) and Sm(II) precursors to the tetralithium hydrazide calix-tetrapyrrole derivative. At the level of trivalent lanthanides, a rich chemistry has been developed relevant to catalytic processes involving alkene and alkyne oligomerization, polymerization, and hydrogenation. In this regard, alkyl and hydride complexes are known to display a particularly enhanced reactivity. Given that only a handful of non-Cp lanthanide hydrides exist in the literature, the reactivity of the Sm(III) chloride calix-tetrapyrrole species was investigated. Consequently, a series of well-defined alkyls and hydrides were prepared in high yield from salt elimination reactions involving trivalent samarium chloride derivatives.

In contrast to the chemistry of samarocene, the reactivity of Sm(II) complexes of calix-tetrapyrrole is extremely sensitive to the nature of the ligand substituent, as well as to the nature of the alkali cation and halide ions present. As in the case of salophen, reactions were often complicated by solvent activation as well as alkali metal retention due to the tetraanionic nature of the ligand. In order to eliminate the problems of alkali-

metal retention and solvent molecule activation routinely observed in the calix-tetrapyrrole chemistry of divalent and trivalent samarium, the dipyrromethanyl ligand system was investigated as a possible alternative to the bridged cyclopentadienyl systems. This ligand system was expected to be particularly suitable for investigation of the reactivity of divalent samarium with dinitrogen on the basis of previous results demonstrating the ability of pyrrole-based ligands to act as π -donors. As well, the dianionic and chelating nature of dipyrromethane was anticipated to be ideal for studying the role of the alkali cation and halide anion in terms of reactivity with dinitrogen.

References

1. (a) Hidai, M.; Mizobe, Y. *Reactions of Coordinated Ligands* Brateman, P.S. Ed., Plenum Press, New York, NY, **1989**.
 (b) Coloquohun, H.M. *Acc. Chem. Res.* **1984**, *17*, 23.
 (c) Henderson, R.A. *Trans. Met. Chem.* **1990**, *15*, 330.
 (d) Leigh, G. *J. Mol. Cat.* **1988**, *47*, 363.
 (e) Leigh, G. *Acc. Chem. Res.* **1992**, *25*, 177.
 (f) Allen, A.D.; Harris, R.O.; Loescher, B.R.; Stevens, J.R.; Whiteley, R.N. *Chem. Rev.* **1973**, *73*, 11.
 (g) Chatt, J. *J. Organomet. Chem.* **1975**, *100*, 17.
 (h) Pelikan, P.; Boka, R. *Coord. Chem. Rev.* **1984**, *55*, 55.
2. Jolly, W.L. *The Chemistry of Non-metals*; Prentice-Hall: Englewood Cliffs, NJ, **1966**, 72.
3. (a) Howard, J.B.; Rees, D.C. *Chem. Rev.* **1996**, *96*, 2965.
 (b) Burgess, B.K.; Lowe, D.J. *Chem. Rev.* **1996**, *96*, 2983.
 (c) Eady, R.R. *Chem. Rev.* **1996**, *96*, 3013.
4. (a) Stiefel, E.I. *Prog. Inorg. Chem.* **1977**, *22*, 1.
 (b) Nelson, M.J.; Lindahl, P.A.; Orme-Johnson, W.H. *Adv. Inorg. Biochem.* **1982**, *4*, 1.
 (c) Georgiadis, M.M.; Komiya, H.; Chakrabarti, P; Woo, D.; Kornuc, J.J.; Rees, D.C. *Science*, **1992**, *257*, 1653.
 (d) Kim, J.; Rees, D.C. *Science* **1992**, *257*, 1677.

5. (a) Cramer, S.P.; Hodgson, K.O.; Gillum, W.O.; Mortenson, L.E. *J. Am. Chem. Soc.* **1978**, *100*, 3398.
(b) Conradson, S.D.; Burgess, B.K.; Newton, W.E.; Mortenson, L.E.; Hodgson, K.O. *J. Am. Chem. Soc.* **1987**, *109*, 7507.
6. Jolly, W.L. *The Chemistry of the Non-metals*; Prentice-Hall: Englewood Cliffs, NJ, **1966**, 72.
7. Allen, A.D.; Senoff, C.V. *J. Chem. Soc. Chem. Commun.* **1965**, 621.
8. Tuzek, F.; Lehnert, N. *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 2636.
9. (a) Hidai, M.; Mizobe, Y. *Chem. Rev.* **1995**, *95*, 1115.
(b) Leigh, G.J. *Acc. Chem. Res.* **1992**, *25*, 177.
(c) Henderson, R.A.; Leigh, G.J.; Pickett, C.J. *Adv. Inorg. Chem. Radiochem.* **1983**, *27*, 197.
(d) Nishibayashi, Y.; Iwai, S.; Hidai, M. *Science* **1998**, *279*, 540.
(e) Jia, G.; Morris, R.H.; Schweitzer, C.T. *Inorg. Chem.* **1991**, *30*, 594.
10. (a) Fryzuk, M.D.; Love, J.B.; Rettig, S.J.; Young, V.G. *Science* **1997**, *275*, 1445.
(b) Duchateau, R.; Gambarotta, S.; Beydoun, N.; Bensimon, C. *J. Am. Chem. Soc.* **1991**, *113*, 8986.
11. Laplaza, C.E.; Cummins, C.C. *Science* **1995**, *268*, 861.
12. Gynane, M.J.S.; Jeffery, J.; Lappert, M.F. *J. Chem. Soc. Chem. Commun.* **1978**, 37.
13. Cohen, J.D.; Mylvaganam, M.; Fryzuk, M.D.; Loehr, T.M. *J. Am. Chem. Soc.* **1994**, *116*, 9529.
14. (a) Luneva, N.P.; Moravsky, A.P.; Shilov, A.E. *Nouv. J. Chim.* **1982**, *6*, 245.

- (b) Luneva, N.P.; Nikonova, L.A.; Shilov, A.E. *Kinet. Katal.* **1977**, *18*, 212.
- (c) Denisov, N.T.; Efimov, O.N.; Shuvalova, N.I.; Shilova, A.K.; Shilov, A.E. *Zh. Fiz. Khim.* **1970**, *44*, 2694.
- (d) Shilov, A.E.; Denisov, N.T.; Efimov, O.N.; Shubalov, N.F.; Shuvalova, N.I.; Shilova, E. *Nature (London)* **1971**, *231*, 460.
- (e) Luneva, N.; Mironova, S.A.; Shilov, A.E.; Antipin, M.Y.; Struchkov, Y.T. *Angew. Chem. Int. Ed. Engl.* **1993**, *23*, 1178.
- (f) Sobota, P.; Janas, Z. *Inorg. Chim. Acta.* **1981**, *53*, L11.
- (g) Edema, J.J.H.; Duchateau, R.; Gambarotta, S.; Heines, R.; Gabe, E. *Inorg. Chem.* **1991**, *30*, 156.
15. (a) Edema, J.J.H.; Gambarotta, S.; Meetsma, A. *J. Am. Chem. Soc.* **1989**, *111*, 6878.
- (b) Ferguson, R.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 396.
- (c) Buijink, J.K.; Meetsma, A.; Teuben, J.H. *Organometallics* **1993**, *32*, 396.
- (d) Beydoun, N.; Duchateau, R.; Gambarotta, S. *J. Chem. Soc. Chem. Commun.* **1992**, 244.
- (e) Wilkinson, G.; Cotton, F.A.: *Advanced Inorganic Chemistry*: Wiley Ed. 5th Ed. New York.
16. Ho, J.; Drake, R.J.; Stephan, D.W. *J. Am. Chem. Soc.* **1993**, *115*, 3792.
17. (a) Schumann, H.; Meese-Marktscheffel, J.A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865.

- (b) Edelmann, F.T. in *Comprehensive Organometallic Chemistry II*; Abel, E.W., Stone, F.G.S., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 4, Chapter 2 and references therein.
- (c) Schaverien, C.J. *Adv. Organomet. Chem.* **1994**, *36*, 283 and references therein.
- (d) Evans, W.J. *Adv. Organomet. Chem.* **1985**, *24*, 131 and references therein.
- (e) Kagan, H.B.; Namy, J.L. in *Handbook on the Physics and Chemistry of Rare Earths*; Gschneider, K.A., Eyring, L., Eds.; Elsevier: Amsterdam, 1984; Chapter 50.
- (f) Marks, T.J.; Ernst, R.D. in *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F.G.S., Abel, E.W. Eds.; Pergamon Press: Oxford, U.K., 1982; Chapter 21 and references therein.
18. (a) Wilkinson, G.; Birmingham, J.M. *J. Am. Chem. Soc.* **1954**, *76*, 6210.
 (b) Maginn, R.E.; Manastyrskyj, S.; Dubeck, M. *J. Am. Chem. Soc.* **1963**, *85*, 672.
19. Hart, F.A.; Massey, A.G.; Saran, M.S. *J. Organomet. Chem.* **1970**, *21*, 147.
20. Schumann, H.; Hohmann, S. *Chem. Z.* **1976**, *100*, 336.
21. (a) Evans, W.J.; Engerer, S.C.; Neville, A.C. *J. Am. Chem. Soc.* **1978**, *100*, 331.
 (b) Evans, W.J.; Engerer, S.C.; Coleson, K.M. *J. Am. Chem. Soc.* **1981**, *103*, 6672.
22. (a) Marks, T.J.; Fragala, I.L.; Reidel, D. Eds. *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; Dordrecht, 1985.
 (b) Schumann, H. *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 474.

- (c) Evans, W.J. *Polyhedron* **1987**, *6*, 803.
- (d) Evans, W.J. *J. Organomet. Chem.* **1983**, *250*, 217.
23. (a) Thompson, M.E.; Bercaw, J.E. *Pure Applied Chemistry* **1984**, *56*, 1.
- (b) Burger, B.J.; Thompson, M.E.; Bercaw, J.E.; Cotton, W.D. *J. Am. Chem. Soc.* **1990**, *112*, 1566.
- (c) Parkin, G.; Bunel, E.; Burger, B.J.; Trimmer, M.S.; van Asselt, A.; Bercaw, J.E. *J. Mol. Cat.* **1987**, *41*, 21.
24. (a) Jeske, G.; Lauke, H.; Mauermann, P.N.; Swepston, P.N.; Schumann, H.; Marks, T.J. *J. Am. Chem. Soc.* **1985**, *107*, 8091.
- (b) Jeske, G.; Schock, L.E.; Swepston, P.N.; Schumann, H.; Marks, T.J. *J. Am. Chem. Soc.* **1985**, *107*, 8103.
- (c) Watson, P.L.; Parshall, G.W. *Acc. Chem. Res.* **1985**, *18*, 51.
25. Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T.J. *J. Am. Chem. Soc.* **1985**, *107*, 8111.
26. Bunel, E.; Burger, B.J.; Bercaw, J.E. *J. Am. Chem. Soc.* **1988**, *110*, 976.
27. Shen, Z. *Inorg. Chim. Acta* **1987**, *140*, 7.
28. (a) Evans, W.J.; Bloom, I.; Engerer, S.C. *J. Cat.* **1983**, *84*, 468.
- (b) Evans, W.J.; Bloom, I.; Hunter, W.E.; Atwood, J.L. *J. Am. Chem. Soc.* **1983**, *105*, 1401.
29. Bercaw, J.E.; Davies, D.L.; Wolczanski, P.T. *Organometallics* **1986**, *5*, 443.
30. (a) Morss, L.R. *Chem. Rev.* **1976**, *76*, 827.
- (b) Varlashkin, P.G.; Peterson, J.R. *J. Less Comon Met.* **1983**, *4*, 33.

31. Collman, J.P.; Hegedus, L.S.; Norton, J.L.; Finke, R.J. *Principles and Applications of Organotransition Metal Chemistry*. University Science Books: Mill Valley, C.A., 1980.
32. Huheey, J.E. *Inorganic Chemistry; Principles of Structure and Reactivity*. 2nd edition, Harper and Row: New York, 1978, 681.
33. Shannon, R.D. *Acta. Cryst.* **1976**, *A32*, 751.
34. Pearson, R.G. *Hard and Soft Acids and Bases*. Donden, Hutchinson and Ross: Stroudsburg, Pa, 1973.
35. Freeman, A.J. Watson, R.E. *Phys. Rev.* **1962**, *127*, 2058.
36. (a) Evans, W.J.; Hughes, L.A.; Hanusa, T.P. *Organometallics* **1986**, *5*, 1285.
(b) Tilley, T.D.; Andersen, R.A.; Spencer, B.; Ruben, H.; Zalkin, A.; Templeton, D. *Inorg. Chem.* **1980**, *19*, 2999.
37. (a) Evans, W.J.; Grate, J.W.; Choi, H.W.; Bloom, I.; Hunter, W.E.; Atwood, J.L. *J. Am. Chem. Soc.* **1985**, *107*, 941.
(b) Evans, W.J.; Bloom, I.; Hunter, W.E.; Atwood, J.L. *J. Am. Chem. Soc.* **1981**, *103*, 6507.
38. Bratsch, R.; Lagowski, J.J. *J. Phys. Chem.* **1985**, *89*, 3317.
39. See for example:
(a) Evans, W.J.; Bloom, I.; Grate, J.W.; Hughes, L.A.; Hunter, W.E.; Atwood, J.L. *Inorg. Chem.* **1985**, *24*, 4630.
(b) Evans, W.J.; Bloom, I.; Hunter, W.E.; Atwood, J.L. *Organometallics* **1985**, *4*, 112.

- (c) Evans, W.J.; Bloom, I.; Hunter, W.E.; Atwood, J.L. *J. Am. Chem. Soc.* **1983**, *105*, 1401.
 - (d) Evans, W.J.; Ansari, M.A.; Ziller, J.W. *Organometallics* **1995**, *14*, 3.
 - (e) Evans, W.J.; Keyer, R.A.; Rabe, G.W.; Drummond, D.K.; Ziller, J.W. *Organometallics* **1993**, *12*, 4664.
 - (f) Evans, W.J.; Ulibarri, T.A.; Ziller, J.W. *J. Am. Chem. Soc.* **1990**, *112*, 2314.
 - (g) Evans, W.J.; Leman, J.T.; Ziller, J.W. *Inorg. Chem.* **1996**, *35*, 4283.
40. (a) Evans, W.J.; Grate, J.W.; Hughes, L.A.; Zhang, H.; Atwood, J.L. *J. Am. Chem. Soc.* **1985**, *107*, 3728.
- (b) Evans, W.J.; Bloom, I.; Hunter, W.E.; Atwood, J.L. *J. Am. Chem. Soc.* **1981**, *103*, 6507.
41. (a) Storch, H.H.; Golumbic, N.; R.B. Anderson. *The Fischer-Tropsch Reaction and Related Syntheses*. Wiley, New York (1951).
- (b) Ponc, V. *Catal. Rev.-Sci. Eng.* **1978**, *18*, 1515.
- (c) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61.
- (d) Dombek, B.D. *Adv. Catal.* **1983**, *322*, 325.
- (e) Klier, K. *Adv. Catal.* **1982**, *31*, 243.
42. (a) Evans, W.J.; Bloom, I.; Hunter, W.E.; Atwood, J.L. *J. Am. Chem. Soc.* **1981**, *103*, 1401.
- (b) Evans, W.J.; Hughes, L.A.; Drummond, D.K.; Zhang, H., Atwood, J.L. *J. Am. Chem. Soc.* **1986**, *108*, 1722.
43. Evans, W.J.; Drummond, D.K.; Bott, S.G.; Atwood, J.L. *Organometallics* **1986**, *5*, 2389.

44. (a) Evans, W.J.; Drummond, D.K. *J. Am. Chem. Soc.* **1986**, *108*, 7440.
 (b) Evans, W.J.; Drummond, D.K.; Chamberlain, L.R.; Doedens, R.J.; Bott, S.G.; Zhang, H.; Atwood, J.L. *J. Am. Chem. Soc.* **1988**, *110*, 4983.
45. Evans, W.J.; Ulibarri, T.A.; Ziller, J.W. *J. Am. Chem. Soc.* **1990**, *112*, 219.
46. (a) Fagan, P.J.; Manriquez, J.M.; Marks, T.J.; Day, V.W.; Vollmer, S.H.; Day, C.S. *J. Am. Chem. Soc.* **1980**, *102*, 5393.
 (b) Evans, W.J.; Ulibarri, T.A.; Ziller, J.W. *J. Am. Chem. Soc.* **1990**, *112*, 2314.
47. Evans, W.J.; Grate, J.W.; Bloom, I.; Hunter, W.E.; Atwood, J.L. *J. Am. Chem. Soc.* **1985**, *107*, 405.
48. Evans, W.J.; Ulibarri, T.A.; Ziller, J.W. *J. Am. Chem. Soc.* **1988**, *110*, 6877.
49. Roussel, P.; Scott, P. *J. Am. Chem. Soc.* **1998**, *120*, 1070.
50. Odom, A.L.; Arnold, P.L.; Cummins, C.C., *J. Am. Chem. Soc.* **1998**, *120*, 5836.
51. Campazzi, E.; Solari, E.; Floriani, C.; Scopelliti, R. *J. Chem. Soc. Chem. Commun.* **1998**, 2603.
52. Jubb, J.; Gambarotta, S. *J. Am. Chem. Soc.* **1994**, *116*, 4477.
53. Song, J.; Gambarotta, S. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2141.
54. Van Vleck, J.H. *Theory of Electric and Magnetic Susceptibilities*. Oxford. Univ. Press, New York (1932).
55. Siddall III, T.H.; Casey, A.T.; Mitra, S. in Bodreaux, E.A. and Mulay, L.N. (Eds.). *Theory and Applications of Molecular Paramagnetism*. Wiley, New York (1976) Ch. 4,5.
56. Evans, W.J.; Hozbor, M.A. *J. Organomet. Chem.* **1987**, *326*, 299.

CHAPTER II

Synthesis and reactivity of a Schiff-base samarium dinuclear complex: Reversible C-C bond formation

II.1: Introduction:

Throughout the last two decades, the chemistry of lanthanides has developed from a minor field into an important area of organometallic chemistry.¹ This activity is a result of the growing awareness of the unique and interesting chemical properties specific to these elements. In view of the radial extension and ionic character of the lanthanides, cyclopentadienyl ligands have been particularly versatile for the stabilization of organolanthanide derivatives because they meet the electronic and steric requirements necessary to form thermally stable, isolable complexes. For Sm(II), the most powerful reductant of the three lanthanides which exist in the +2 oxidation state², the C₅Me₅ ligand has been especially efficient in providing soluble complexes. To date, permethylated cyclopentadienyl anions have allowed for the isolation of some of the most highly reactive organolanthanide derivatives providing new classes of complexes³ exhibiting remarkable structures⁴ and unique reactivities⁵. Given the caliber of the transformations and the number of structurally characterizable, metal-containing products afforded by the (C₅Me₅)₂Sm(THF)₂ system with a variety of substrates, the scope of Sm(II) chemistry has widened in order to accommodate other ligands. Nonetheless, examples of well-defined, non-Cp containing Sm(II) systems remain relatively few save for a handful of examples of divalent samarium complexes with phosphorous⁶, nitrogen⁷, and oxygen-based⁸ ligand systems.

Recently, a low-valent, macrocyclic Sm complex based on the tetraanionic calix-tetrapyrrole ligand was shown to either reduce dinitrogen⁹ or to form a divalent, dinuclear Sm complex with an intriguingly short Sm-Sm contact¹⁰ depending upon the reaction conditions.

In the view of expanding the chemistry of low-valent samarium with polydentate ligands, we have now used tetradentate Schiff bases (salen-type) for which lanthanide complexes prepared in nonaqueous media comprise relatively few.¹¹ Since these ligands are known to display a limited resistance to strongly reducing agents,¹² possible involvement of the ligand in the reactivity of the metal center was anticipated.

The following describes the results of our attempts to prepare a Sm(II) tetradentate Schiff base complex and the unusual reactivity displayed by this derivative.

II.2: Experimental Section:

All operations were performed under an inert atmosphere of a nitrogen-filled drybox or by using standard Schlenk-type glassware in combination with a nitrogen-vacuum line. $\text{SmCl}_3(\text{THF})_3$ ¹³, $\text{SmI}_2(\text{THF})_5$ ¹⁴, phenylenebis(3,5-Bu^t₄salicylideneimine [3,5-Bu^t₄salophen-H₂], and $(3,5\text{-Bu}^t_4\text{salophen})\text{Na}_2(\text{THF})_2$ ¹⁵ were prepared according to literature procedures. C₆D₆ and toluene-d⁸ were dried over Na/K alloy, vacuum-transferred into ampoules, and stored under nitrogen prior to use. NMR spectra were recorded on a Varian Gemini 200 and on a Bruker AMX-500 spectrometer using vacuum sealed NMR tubes prepared inside a drybox. Infrared spectra were recorded on a Mattson 3000 FTIR instrument from Nujol mulls or KBr pellets prepared inside the drybox. Samples for magnetic susceptibility measurements were carried out at room temperature using a Gouy balance (Johnson Matthey). Magnetic moments were calculated by following standard methods¹⁶ and corrections for underlying diamagnetism were applied to the data¹⁷. Elemental analyses were carried out using a Perkin-Elmer Series II CHN/O 2400-analyzer.

Preparation of $\text{Sm}(3,5\text{-Bu}^t_4\text{salophen})(\text{Cl})(\text{Et}_2\text{O})$ (2.1):

A stirred suspension of $\text{SmCl}_3(\text{THF})_3$ (2.6 g, 5.5 mmol) in 100ml THF was treated with $(3,5\text{-Bu}^t_4\text{salophen})\text{Na}_2(\text{THF})_2$ (4.0 g, 5.5 mmol). The resulting clear orange solution was allowed to stir at room temperature for 16 hours. The solvent was removed *in vacuo* and the residual solid was dissolved in diethyl ether (120 ml). Filtration of NaCl, followed by concentration to 75 ml and subsequent standing at room temperature for 2 days, yielded

light orange microcrystals of **2.1** (1.0 g, 1.2 mmol, 44%). El. Anal. Calcd (Found) for $C_{40}H_{56}N_2O_3SmCl$: C 60.15(61.52), H 7.07(7.37), N 3.51(3.43). IR (Nujol mull, cm^{-1}): 1605(vs, C=N stretch), 1578(vs, C=N stretch), 1531(vs, aromatic), 1319(m), 1254(s), 1198(m), 1167(s), 1026(w), 931(w), 873(w), 832(m), 750(vs). 1H -NMR (C_6D_6 , 500 MHz, 23°C) δ : 8.12 (d, 2H, phenyl), 8.02 (d, 2H, phenyl), 6.50 (m., 2H, phenylene), 6.30 (m., 2H, phenylene), 4.34 (s, 2H, C-H imine), 3.25 (q, 4H, diethyl ether), 1.75 (s, 18H, Bu^t), 1.15 (s, 18H, Bu^t), 1.01 (t, 6H, diethyl ether). ^{13}C -NMR (C_6D_6 , 125.72 MHz, 23°C) δ : 170.84, 170.00, 145.69, 137.99, 137.09 (quaternary aromatic), 131.27, 129.28, 127.81, 116.41 (C-H aromatic), 71.70 (C-H imine), 65.86, 15.48 (diethyl ether), 36.22, 34.89 (quaternary Bu^t), 31.99, 29.79 (Bu^t). $\mu_{eff} = 1.60 \mu_B$.

Preparation of $[Sm_2(SB-SB)(THF)_3] \cdot 2$ toluene (2.2**) [SB-SB = C-C bonded 3,5- Bu^t_4 salophen dimer]**

Method A: The addition of (3,5- Bu^t_4 salophen) $Na_2(THF)_2$ (2.5 g, 3.4 mmol) to a stirred solution of $SmI_2(THF)_5$ (1.9 g, 3.5 mmol) in THF (100 ml) rapidly formed a deep red solution. Stirring was continued for 1.5 hours followed by removal of the solvent *in vacuo*. The dark red solid residue was redissolved in toluene (100 ml) and NaI was removed by filtration. Red needles of **2.2** (2.1 g, 1.2 mmol, 70%) separated upon allowing the filtrate to stand at room temperature for 2 days. Crystals suitable for X-ray analysis were obtained by subsequent recrystallizations from toluene. El. Anal. Calcd (Found) for $C_{98}H_{132}N_4O_7Sm_2$: C 66.18(66.98), H 7.48(7.05), N 3.15(3.32). I.R. (Nujol mull, cm^{-1}): 1605(s, C=N stretch), 1588(s, C=N stretch), 1544(m, aromatic), 1441(s), 1335(s),

1315(m), 1292(s), 1264(s), 1167(s), 1148(m), 1106(m), 1033(w), 905(m), 750(vs). ^1H -NMR (C_6D_6 , 500 MHz, 23°C) δ : 11.42(s, 1H, C-H imine), 8.65(s, 1H, C-H phenylene ring), 8.30 (s, 1H, C-H phenylene ring), 8.11(s, 1H, Ph), 7.73 (pseudo-d, 1H, C-H amidate), 7.03 (two multiplets, 4H, toluene), 5.75 (s, 1H, Ph), 5.71(pseudo-t, 1H, Ph), 5.35 (pseudo-t, 1H, Ph), 4.69 (pseudo-d, 1H, C-H amidate), 3.25 (s, 6H, THF), 2.45 (s, 9H, Bu^t), 2.21 (s, 9H, Bu^t), 2.09 (s, 6H, THF), 2.03 (s, 3H, Me toluene), 0.47 (broad s, 9H, Bu^t), 0.27 (s, 9H, Bu^t). ^{13}C -NMR (C_6D_6 , 125.72 MHz, 23°C) δ : 174.1 (imine), 169.78, 163.23, 157.15, 138.18, 137.90, 137.04, 136.33, 133.80, 131.59, 131.31 (quaternary aromatic), 129.28, 128.30, 126.35 (C-H toluene), 128.51, 128.20, 128.11, 128.00, 127.92, 127.81, 125.64, 123.03 (C-H aromatic), 112.90, 112.36, 112.04 (C-H aromatic), 97.98 (quaternary reduced imine), 68.48 (C-H reduced imine), 33.36, 33.18, 32.55, 31.79 (Bu^t), 20.04 (toluene). $\mu_{\text{eff}} = 2.41 \mu_{\text{B}}$ per formula unit.

Method B: A stirred solution of **2.1** (1.0 g, 1.2 mmol) in THF (75 ml) was treated at room temperature with metallic lithium (50 mg, 7.2 mmol). Within 1 hour the color changed from light orange to dark red. Stirring was continued for about 16 hours during which no further color changes were noted. The solvent was evaporated to dryness *in vacuo* and the residual solid was re-dissolved in toluene. Removal of LiCl by filtration followed by standing at room temperature yielded microcrystals of **2** (0.22 g, 0.13 mmol, 11%) over a period of four days.

Preparation of $\{[(\text{Me}_2\text{-SB})\text{Sm}(\mu\text{-CH}_3)\text{Li}(\text{THF})][(\text{Me}_2\text{-SB})\text{Sm}(\mu\text{-CH}_3)\text{Li}(\text{THF})_2\text{Li}(\text{THF})_2]\}(\mu\text{-O})(\mu\text{-Li})_3$ (2.3) [$\text{Me}_2\text{-SB}$ = phenylenebis(3,5- $\text{Bu}^t_4\text{salicyl}$)dimethyldiamidato]

The dropwise addition of 1.4M MeLi in diethyl ether (2.9 ml, 4.1 mmol) at room temperature to a stirred solution of **2.2** (1.0 g, 0.58 mmol) in 100 ml THF resulted in a color change from dark red to light brown. Stirring was continued for 24 hours. The solvent was removed *in vacuo* and the residual deep yellow solid was dissolved in 75 ml hexane. Filtration followed by concentration to 30 ml and subsequent standing at room temperature for 7 days yielded yellow needles of **2.3** (0.30 g, 0.15 mmol, 26%). I.R. (Nujol mull, cm^{-1}): ν 1550(m, C=N stretch), 1533(m, aromatic), 1364(w), 1250(s), 1126(m), 1042(s), 879(m), 833(m), 790(w), 739(m). $^1\text{H-NMR}$ ($\text{d}^8\text{-THF}$, 500 MHz, 23°C) δ : 7.09 (s, 1H, phenyl), 6.92 (mult, 1H, phenylene), 6.90 (s, 1H, phenyl), 6.77 (s, 1H, phenylene), 5.43 (pseudo-q, 1H, C-H amidate), 4.42 (pseudo-q, 1H, C-H amidate), 3.62 (s, 4H, THF), 1.72 (s, 4H, THF), 1.49 (s, 18H, Bu^t), 1.40 (pseudo-dd, 3H, CH_3 amidate). $^{13}\text{C-NMR}$ (THF-d^8 , 125.72 MHz, 23°C) δ : 164.23, 141.13, 137.73, 133.71, 131.54 (quaternary aromatic), 123.76, 122.62, 122.19, 120.46 (C-H aromatic), 67.74, 31.16 (THF), 59.92 (amidate), 35.83, 34.45, 32.82, 32.46, 32.24, 31.16 (Bu^t), 20.68, 15.66 (CH_3 amidate). $\mu_{\text{eff}} = 2.30\mu_{\text{B}}$.

Preparation of [(3,5-Bu^tsalophen)Sm(OH)]₄·4toluene (2.4)

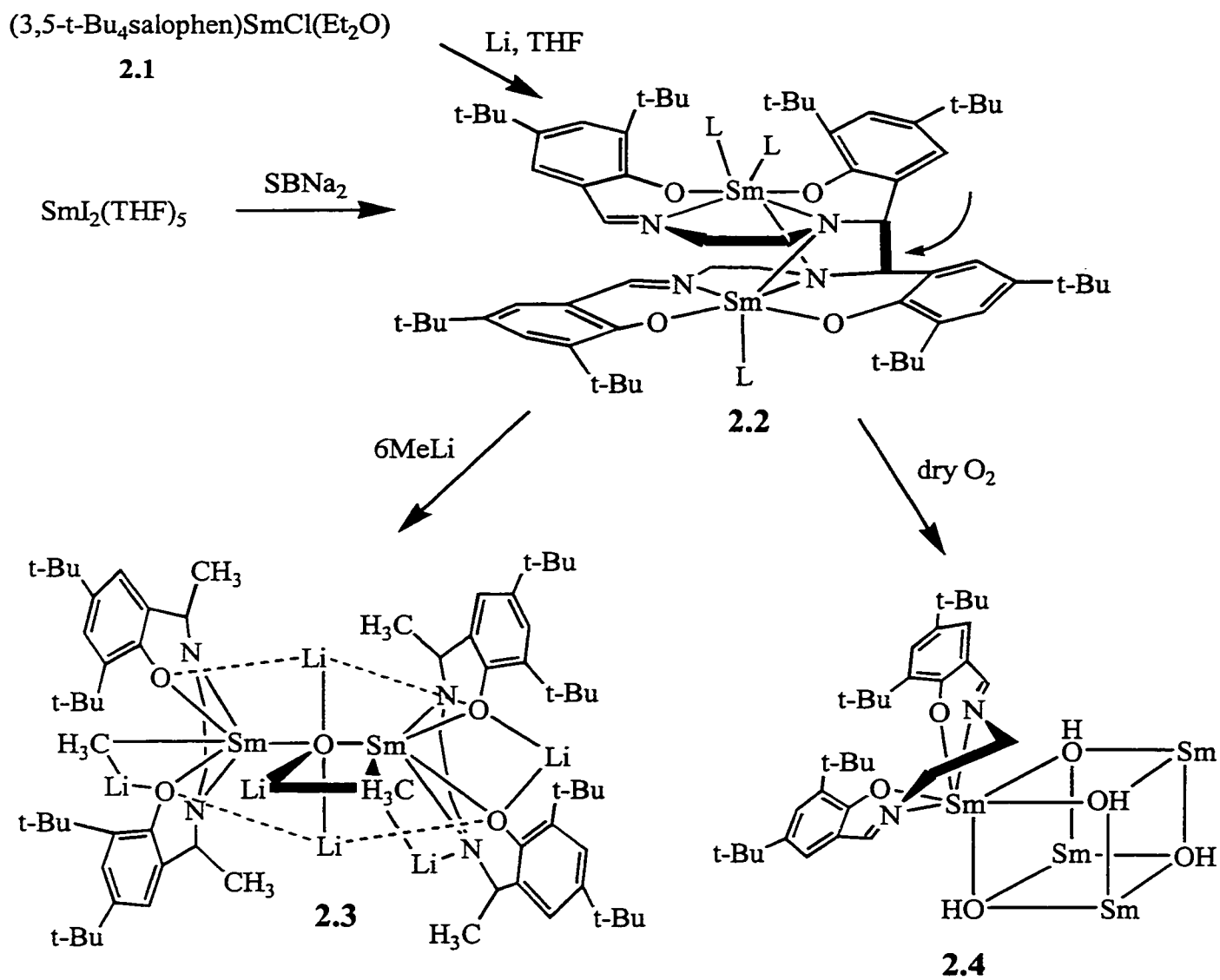
Exposure of a stirred toluene solution (50 ml) of **2.2** (1.0 g, 0.58 mmol) at room temperature to excess dry O₂ resulted in a brown solution after 24 hours. Yellow crystals of **2.4** (0.30 g, 0.095 mmol, 33%) separated upon standing at room temperature for 5 days. El. Anal. Calcd. (Found) for C₁₇₂H₂₂₀N₈O₁₂Sm₄: C 64.69(64.78), H 6.94(6.91), N 3.51(3.57). ¹H-NMR (C₆D₆, 500 MHz, 23°C) δ: 13.99 (s, 1H, OH), 8.13 (s, 2H, C-H aromatic), 7.62 (pseudo-d, 2H, aromatic), 7.31 (s, 2H, aromatic), 7.01 (m, 5H, toluene), 6.75 (m, 2H, aromatic), 2.10 (s, 3H, toluene), 1.85(s, 2H, C-H imine), 1.64 (s, 18H, Bu^t), 1.33 (s, 18H, Bu^t). ¹³C-NMR (C₆D₆, 125.72 MHz, 23°C) δ: 203.78, 159.34, 143.09, 140.40, 137.82, 137.66 (quaternary aromatic and toluene), 165.11, 130.35, 127.45, 127.34, 125.62, 120.08, 119.08 (C-H aromatic and toluene), 35.48 (toluene), 34.25 (C-H imine), 31.63, 29.96 (methyl Bu^t), 32.27, 32.01 (quaternary Bu^t). I.R. (KBr, Nujol mull, cm⁻¹) ν: 3583(s, stretch O-H), 2960(vs), 2905(s), 2866(m), 1609(vs, stretch C=N), 1579(vs, stretch C=N), 1529(vs, aromatic), 1408(s), 1258(s), 1166(vs), 876(m), 835(w), 760(s), 637(w), 503(m). μ_{eff} = 4.25μ_B per formula unit.

II.3: Results and Discussion:

The room temperature reaction of $\text{SmI}_2(\text{THF})_5$ with one equivalent of $(3,5\text{-Bu}^t_4\text{salophen})\text{Na}_2(\text{THF})_2$ in THF formed a deep red, air-sensitive solution from which bright red needles of dimeric $[\text{Sm}_2(\text{SB-SB})(\text{THF})_3] \cdot 2\text{toluene}$ (**2.2**) [SB-SB = C-C bonded salophen dimer] were isolated in good yield upon crystallization from toluene. The light color suggested that the Sm metal center was oxidized to the trivalent state while qualitative halogen and flame tests indicated the absence of both iodine and sodium. Combustion analysis data were in agreement with the formulation as elucidated by an X-ray crystal structure (Figure 2.1). Solution NMR spectra were well resolved and accordingly displayed four distinct resonances for the Bu^t groups. A new resonance attributed to the C-H engaged in the formation of the C-C bond connecting the two monomeric units was observed at 4.69 ppm. Complex **2.2** was also conveniently prepared via reduction of $(3,5\text{-Bu}^t_4\text{salophen})\text{SmCl} \cdot \text{ether}$ **2.1** with metallic lithium in THF (Scheme 2.1).

Complex **2.2** arises from the reduction of the ligand performed by the low-valent samarium center. In other words, the intermediate $\text{Sm(II)}(3,5\text{-Bu}^t_4\text{salophen})$ derivative, presumably originated in the first step of the reaction, reduces one of the ligand imino functions thus forming a Sm(III) and a mainly carbon-centered radical. Obviously, the extensive π -delocalization of this particular ligand provides a sufficiently long lifetime to allow for coupling with an identical unit to form the final dimeric structure. The compartmental ligand formed in this process wraps the dimetallic samarium unit with a network of bridging interactions (Figure 2.1).

Scheme 2.1



(bridging phenylene ring was omitted for clarity)

The metal-promoted reductive coupling of tetradentate Schiff bases has a few precedents in the literature of first row transition metals.²¹ However, these reactions are usually performed by strong reductants (alkali metals) with the role of the T.M simply being that of a mediator or of a templating agent. Conversely, in the reaction described above the reductive coupling is exclusively originated by the one-electron oxidation of Sm(II). In addition, the C-C bond which results from the dimerization reaction and which is typically rather long and easily cleaved by mild oxidizing agents, is in this case normal [$C(15)-C(51) = 1.569\text{\AA}$] and rather robust.

As expected for a formal Sm(III) derivative, complex **2.2** proved to be unreactive towards mild oxidizing agents such as MeI or PhCH₂Cl. On the other hand, it was surprising that no reaction was also observed with strong reductants such as Mg, Na, and Li upon stirring at room temperature or in refluxing THF. No visible evidence of reaction was observed over prolonged periods and unreacted starting material was always recovered. However, reaction of **2.2** with PhCH₂MgCl gave a sudden color change from red to light yellow. The I.R. spectrum of the resulting yellow microcrystalline solid, isolated in modest yield from hexane, indicated the absence of any C=N resonance. Similarly, the NMR spectrum did not show any signal which could possibly be attributed to the C-H amidate of the reduced imino function. Unfortunately, it was not possible to grow crystals of suitable size for X-ray analysis. Therefore, complex **2.2** was reacted with excess MeLi at room temperature. When MeLi was added to complex **2.2**, the reaction proceeded to completion in a matter of minutes, and no further color changes were noted even after prolonged periods. Yellow, extremely air-sensitive crystals of a new compound

2.3 were isolated in reasonable yield after filtration, solvent replacement with hexane and standing. Even in this case, the absence of C=N resonances in the I.R. spectrum indicated a complete reduction of the imine functions. The formulation of this new species as $\{[(\text{Me}_2\text{-SB})\text{Sm}(\mu\text{-CH}_3)\text{Li}(\text{THF})][(\text{Me}_2\text{-SB})\text{Sm}(\mu\text{-CH}_3)\text{Li}(\text{THF})_2\text{Li}(\text{THF})_2]\}(\mu\text{-O})(\mu\text{-Li})_3$ (**2.3**) [Me_2SB = phenylenebis(3,5- $\text{Bu}^t_4\text{salicyl}$)dimethyldiamidato] was elucidated by an X-ray crystal structure (Figure 2.2). Due to the high sensitivity and pyrophoricity, difficulties were encountered in obtaining meaningful combustion analysis data for complex **2.3**. The NMR spectra showed a pattern consistent with the solid state crystal structure. Two C-H amidate signals were observed as multiplets at 5.43 and 4.42 ppm corresponding to the inequivalent coordination environments about Sm(1) and Sm(2). As well, solution NMR spectra showed two signals each for THF (3.63, 1.72 ppm) and d^8 -THF (3.62, 1.78 ppm) indicating slow exchange of coordinated THF with that of the solvent. Unfortunately, it was not possible to conclusively locate the resonances of the CH_3 groups attached to Sm either due to overlap with ligand signals or to direct effect of the close vicinity of the paramagnetic center. However, a Toepler pump experiment involving bulk degradation of **2.3** with anhydrous HCl, yielded 77% of the expected amount of CH_4 .

Although the origin of the oxygen atom in complex **2.3** cannot be conclusively explained at this stage, it seems that its likely source is the THF solvent. It may be argued that small amounts of oxygen, adventitiously present in the reaction mixture, should lead to methoxy derivatives rather than alkyls. In addition, given the excess of MeLi employed in the reaction, the tremendous sensitivity to air and moisture of the resulting complex, and the yield in which **2.3** may be isolated on a reproducible basis, the possibility that the

formation of **2.3** may be the result of trace oxygen present in the reaction mixture may be confidently ruled out. In addition, the gas-chromatogram of the reaction mixture showed the presence of a substantial amount of ethylene thus confirming a process involving THF deoxygenation. Deoxygenation and fragmentation of THF by early transition metal and lanthanides to generate oxo derivatives or other exotic functions is well documented in the literature.²² The formation of an oxo-metal derivative and ethylene implies the reduction of THF by two electrons. This requires that upon the attack of MeLi on both the ligand and the metal center of complex **2.2** the two electrons, used for the formation of the C-C bond connecting the two samarium units, are transferred back to the two metal centers and are used in the THF deoxygenation process. The high oxophilicity of samarium and the consequent stability of the Sm-O-Sm bond may well provide the necessary energy for this reaction to take place. In addition, the overall reaction requires the addition of six equivalents of MeLi per dimeric unit, four methyl groups to be attached to the four imine carbon atoms and two to the two Sm atoms.

As mentioned above, solutions of complex **2.2** are sensitive to air and moisture. To further explore the reactivity of this species, its behavior in the presence of dry oxygen was investigated. When a toluene solution of **2.2** was exposed to an excess of dry O₂, the color turned to brown. After 5 days, yellow cubic crystals appeared in the reaction mixture which were isolated in reasonable yield. This compound, confirmed by a single and sharp I.R. stretch at 3585cm⁻¹ to be an hydroxide, was observed to be stable in the presence of air and moisture. The resonance of the OH group as a singlet at 13.99 ppm of the ¹H-NMR spectrum was clearly identified by HQMC and deuterium labeling experiments (see below).

Questions arise about the genesis in compound **2.4** of the hydroxyl group. Consistent with our observations, O'Halloran and coworkers²³ recently showed that reaction of the Mn(III)PHAB dimer with O₂ in the absence of external oxidants and under anhydrous conditions results in the catalytic de-hydroxylation of THF and formation of a Mn(V) hydroxyl derivative. We speculate that during the reduction of dioxygen operated by the *in situ* generated (salophen)Sm(II) a superoxide intermediate similar to that isolated and characterized by Takats²⁴ abstracts a hydrogen atom from the solvent, thus reforming in the process one-half equivalent of dioxygen. At this stage it is impossible to distinguish between these two or other reasonable pathways. At least to verify the hypothesis that the solvent (toluene) is the donor of the hydrogen atom, we have carried out the reaction in deuterated toluene. The product had spectral features identical to those of **2.4** except for the resonance at 13.99 ppm which was absent in the ¹H-NMR spectrum but was clearly visible in the ²H-NMR spectrum.

II.4: X-ray Crystallography

Suitable crystals were mounted with cooled viscous oil on thin glass fibers. Data were collected on a Bruker AG SMART 1k CCD diffractometer using a proprietary hemisphere scan routine. Cell constants were calculated from reflection data obtained from 60 data frames collected at different parts of the Ewald sphere. No absorption corrections were applied. The reflection data for **2.3** were consistent for $P2_1/m$ and $P2_1$, however, solution in the centric option yielded chemically reasonable and computationally stable results of refinement. The data for **2.2** and **2.4** were uniquely

consistent with the reported space groups. The structures were solved by direct methods, completed with subsequent Fourier synthesis and refined with full-matrix least-squares procedures based on F^2 . The compound molecule **2.3** was located on a mirror plane. A lithium atom and a molecule of coordinated THF were located disordered by the mirror plane symmetry. The compound molecule **2.4** is located at a 4-fold rotoinversion axis. Two half molecules of co-crystallized toluene solvent were each located disordered at inversion centers. Two molecules of toluene solvent were also located in the asymmetric unit of **2.2**. The carbon and nitrogen atoms of **2.2** were refined isotropically to conserve a reasonable data/parameter ratio. For **2.3** and **2.4** all non-hydrogen atoms, excluding the atoms of the interstitial molecules of solvent, were refined with anisotropic displacement coefficients. Phenyl groups of the cocrystallized solvent in **2.4** and all the phenyl groups in **2.2** were treated as idealized, flat, rigid hexagons. Hydrogen atoms were assigned with idealized geometry, and constrained with an isotropic, riding model. Crystallographic details are presented the Appendix, Table 1.

Complex **2.2** is dimeric and is formed by two similar (3,5-Bu^t₄salophen)Sm moieties. The linkage between the two units is realized via a C-C bond that connects the two reduced imine carbon atoms of the two ligands. The C-C bond joining the two salophen units [C(15)-C(51) = 1.549(16)Å] is only slightly longer than a regular C-C bond and compares well with those of the Bu^t groups. The C-N bond distances of the reduced imino functions [N(1)-C(15) = 1.485(14)Å] are as expected for a C-N single bond, while the C-N bonds of the intact imine functions are somewhat shorter and are consistent with the presence of some extent of C-N double bond character [N(2)-C(22) = 1.303(13)Å]. As a result of the sp³ hybridization of the carbon atoms, the ligands are no

longer planar as would be expected based on the structural parameters featured in transition metal-based complexes of the same type.¹⁸ The reduction of one of the two imino functions of each ligand also imparts a tetrahedral sp^3 geometry to the nitrogen atoms which bridge the two metal centers. The Sm-N bond distances are rather short in comparison to those of other complexes of nitrogen-donor based macrocyclic ligands¹⁹ [Sm(1)-N(1) = 2.418(8)Å, Sm(1)-N(3) = 2.465(8)Å, Sm(2)-N(1) = 2.453(8)Å, Sm(2)-N(3) = 2.368(8)Å]. In spite of the fairly similar organization of the two tetradentate moieties around the dimetallic unit, the two metal centers display two different coordination geometries. One of them is six-coordinated and is bound to two oxygen atoms [Sm(2)-O(3) = 2.180(7)Å, Sm(2)-O(4) = 2.219(8)Å], one imine nitrogen [Sm(2)-N(4) = 2.503(9)Å] and two reduced imine nitrogens as well as to one molecule of THF [Sm(2)-O(7) = 2.478(7)Å] (Figure 1). The second Sm atom is seven-coordinate with basically the same coordination geometry aside from one additional molecule of THF.

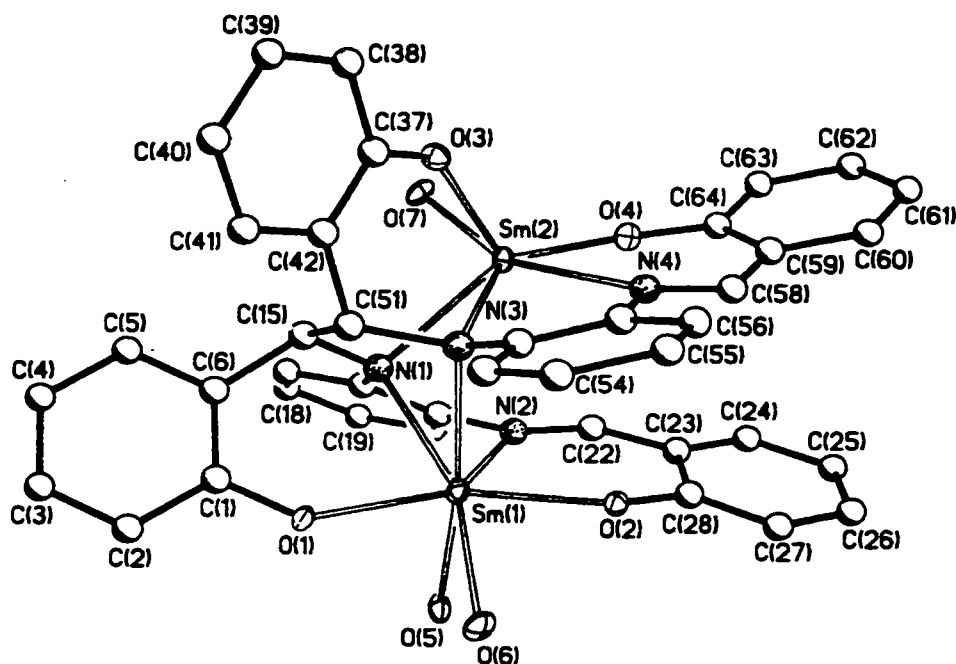


Fig. 2.1. X-ray Structure of 2.2, [Sm₂(SB-SB)(THF)₃]·2toluene

The four Bu^t groups have been deleted for clarity. Selected Bond Distances (Å) and Angles (°): Sm(1)-O(1) = 2.217, Sm(1)-O(2) = 2.240(7), Sm(1)-N(1) = 2.418(8), Sm(1)-N(2) = 2.546(8), Sm(1)-N(3) = 2.465(8), Sm(1)-O(5) = 2.453(7), Sm(1)-O(6) = 2.522(7), C(15)-C(51) = 1.549(16), Sm(2)-O(3) = 2.180(7), Sm(2)-O(4) = 2.219(8), Sm(2)-O(7) = 2.478(7), Sm(2)-N(3) = 2.368(8), Sm(2)-N(4) = 2.503(9), C(22)-N(2) = 1.303(13), C(15)-N(1) = 1.485(14), O(1)-Sm(1)-O(2) = 161.5(3), O(1)-Sm(1)-O(5) = 85.7(3), O(1)-Sm(1)-O(6) = 80.0(3), O(1)-Sm(1)-N(1) = 77.6(3), O(1)-Sm(1)-N(2) = 125.6(3), O(2)-Sm(1)-O(5) = 89.9(3), O(2)-Sm(1)-O(6) = 81.6(3), O(2)-Sm(1)-N(1) = 120.9(3), O(2)-Sm(1)-N(2) = 70.1(3), O(5)-Sm(1)-O(6) = 82.2(3), N(1)-Sm(1)-N(2) = 61.2(3).

Complex **2.3** is also dimeric with two non-equivalent Sm atoms bridged by a single oxygen atom [Sm(1)-O(1) = 2.293(6)Å, Sm(2)-O(1) = 2.314(6)Å]. The slightly bent Sm-O-Sm array [Sm(1)-O(1)-Sm(2) = 168.2(3)°] lies on a crystallographic mirror plane. Each samarium is surrounded by a tetradentate and tetra-anionic diaryloxo/diamido ligand (Me₂SB) arising from the methylation of each carbon atom [C(34)-C(35) = 1.539(10)Å, C(15)-C(16) = 1.542(10)Å] of both imino functions of the original 3,5-Bu^t₄salophen ligand [Sm(1)-O(2) = 2.318(5)Å, Sm(1)-N(1) = 2.435(6)Å, Sm(2)-O(3) = 2.385(5)Å, Sm(2)-N(2) = 2.405(6)Å]. As a result of the alkylation of the imino functions and consequent change in the hybridization of the C and N atoms [N(1)-C(15)-C(16) = 112.5(6)°, N(1)-C(15)-C(5) = 111.3(6)°], the carbon atoms display a regular tetrahedral geometry. The two amidato nitrogen atoms of each ligand are engaged in bridging interactions with three lithium atoms [N(1)-Li(3) = 2.111(15)Å, N(2)-Li(4) = 2.18(3)Å, N(2A)-Li(2) = 2.245(14)Å]. Both samarium atoms possess a distorted coordination geometry [N(1)-Sm(1)-N(1A) = 64.5(3)°, O(2)-Sm(1)-O(2A) = 118.1(2)°, N(1)-Sm(1)-O(1) = 146.00(15)°, C(39)-Sm(1)-N(1) = 84.5(2)°]. Each samarium atom also bears a methyl group [Sm(1)-C(39) = 2.606(10)Å, Sm(2)-C(40) = 2.570(11)Å]. The first has the methyl pointing away from the molecular core and is placed in *trans* position with respect to the bridging oxo atom [O(1)-Sm(2)-C(40) = 177.5(3)°]. This methyl is also bonded to a Li(THF) moiety [C(40)-Li(4) = 2.21(3)Å] which in turn is attached to one nitrogen atom of the tetradentate amidato ligand, thus forming a planar Sm-CH₃-Li-N unit [torsion angle Sm(2)-C(40)-Li(4)-N(2) = 0(1)°]. The second samarium atom has the methyl group

placed in *cis* position with respect to the bridging oxygen [O(1)-Sm(1)-C(39) = 85.1(3)°]. The lithium atom connected to the two nitrogen atoms of the second samarium amidate moiety bears two THF molecules rather than one [O(4)-Li(3)-O(5) = 102.2(9)°]. The molecular core is formed by the Sm-O-Sm array and three lithium atoms. The Li₃O plane [Li(1)-O(1)-Li(2) = 113.4(4)°, Li(1)-O(1)-Li(1A) = 133.1(8)°] is perpendicular to the Sm-O-Sm vector and is arranged in such a manner that the central lithium atom is also coplanar with the Sm-O-Sm array [Li(1)-O(1)-Sm(1) = 92.0(4)°, Li(1)-O(1)-Sm(2) = 92.7(4)°] thus lying on the crystallographic mirror plane. As a result, the central oxygen atom is pentacoordinated and adopts a distorted trigonal bipyramidal geometry defined by two axial samarium atoms and three equatorial lithiums [Li(2)-O(1)-Li(1) = 113.4(4)°]. Two of the equatorial lithium atoms are also bonded to two oxygens from the two tetradentate ligands of the two moieties [Li(1)-O(2) = 1.977(13)Å, Li(1)-O(3) = 1.901(12)Å, O(2)-Li(1)-O(3) = 160.3(8)°]. Conversely, the third one, which is coplanar with the bridging oxo and the two samarium atoms, is bonded to the two nitrogen atoms [Li(2)-N(2) = 2.245(15)Å] of one ligand attached to one samarium and the methyl group [Li(2)-C(39) = 2.129(19)Å] attached to the second samarium atom (in *cis* position with respect to the bridging oxo). A fifth lithium atom is connected to this methyl group [Li(5)-C(39) = 2.56(2)Å] and to four phenyl carbon atoms [Li(5)-C(18) = 2.702(17)Å, Li(5)-C(19) = 2.487(19)Å] of the salophen ligand of the second Sm unit. The large network of bridging interactions between the two samarium moieties results in rather unusual coordination geometries of the donor atoms. The salophen oxygen atoms possess a distorted T-shape geometry [Li(1)-O(2)-Sm(1) = 89.5(4)°, Li(1)-O(2)-C(6) = 141.1(6)°] while the nitrogen atoms are severely distorted pentacoordinated. The methyl group

engaged in the formation of the core has also a distorted T-shape geometry [$\text{Li}(2)\text{-C}(39)\text{-Li}(5) = 162.1(8)^\circ$, $\text{Li}(2)\text{-C}(39)\text{-Sm}(1) = 76.8(5)^\circ$, $\text{Li}(5)\text{-C}(39)\text{-Sm}(1) = 121.0(6)^\circ$]. As in the case of **2.2**, there is no planar arrangement of the $[\text{SmN}_2\text{O}_2]$ set of atoms due to complete reduction of both imine functions. Accordingly, the C-N bond distances are slightly longer than in the coordinated salophen ligand and are consistent with the presence of some C-N single bond character [$\text{C}(34)\text{-N}(2) = 1.463(10)\text{\AA}$, $\text{N}(1)\text{-C}(15) = 1.446(10)\text{\AA}$].

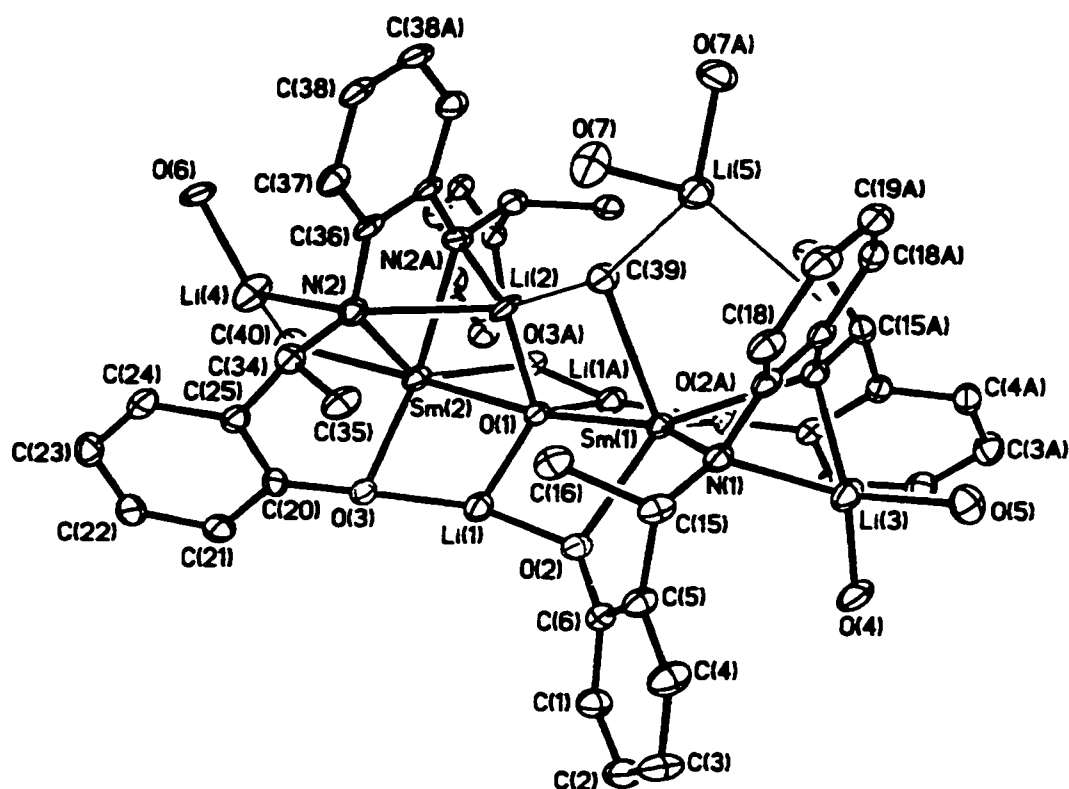


Fig. 2.2 X-ray Structure of **2.3**, $\{[(\text{Me}_2\text{-SB})\text{Sm}(\mu\text{-CH}_3)\text{Li}(\text{THF})][(\text{Me}_2\text{-SB})\text{Sm}(\mu\text{-CH}_3)\text{Li}(\text{THF})_2\text{Li}(\text{THF})_2]\}(\mu\text{-O})(\mu\text{-Li})_3$

The four Bu^t groups have been deleted for clarity. Selected Bond Distances ($\text{\AA}$) and Angles ($^\circ$): $\text{Sm}(1)\text{-O}(1) = 2.293(6)$, $\text{Sm}(1)\text{-O}(2) = 2.318(5)$, $\text{Sm}(1)\text{-N}(1) = 2.435(6)$,

Sm(1)-C(39) = 2.606(10), Sm(2)-C(40) = 2.570(11), Sm(2)-O(1) = 2.314(6), Sm(2)-O(3) = 2.385(5), Sm(2)-N(2) = 2.405(6), N(1)-C(15) = 1.446(10), C(15)-C(16) = 1.542(10), N(2)-C(34) = 1.463(10), C(34)-C(35) = 1.539(10), O(1)-Sm(1)-O(2) = 79.35(14), O(1)-Sm(1)-N(1) = 146.00(15), O(1)-Sm(1)-C(39) = 85.1(3), O(1)-Sm(2)-C(40) = 177.5(3), Sm(1)-O(1)-Sm(2) = 168.2(3), O(1)-Sm(2)-O(3) = 76.59(12), O(1)-Sm(2)-N(2) = 87.50(19), Li(1)-O(1)-Li(2) = 113.4(4), Li(1)-O(1)-Li(1A) = 133.1(8), Sm(1)-O(1)-Li(1) = 92.0(4), Sm(1)-O(1)-Li(2) = 89.1(5), Sm(1)-O(1)-Li(2) = 89.1(5), Sm(1)-O(1)-Li(1A) = 92.0(4).

The tetrameric structure of **2.4** consists of a distorted cuboid core formed by four samarium atoms and four μ^3 -OH bridging groups [Sm-O(3) = 2.573(5)Å, Sm-O(3C) = 2.470(5)Å, Sm-O(3B) = 2.433(5)Å] (Figure 2.3). The Sm-O distances compare well with those observed in the hydroxo-bridged [Cp₂Sm(OH)]₂.²⁰ The distortion arising from the compression alongside each Sm-Sm diagonal is introduced by the small bridging hydroxides [Sm-O(3)-Sm(A) = 102.43(18)°, Sm-O(3)-Sm(C) = 112.15(19)°, Sm(A)-O(3)-Sm(C) = 105.49(18)°] and originates short Sm..Sm contacts [Sm..Sm(A) = 3.9023(8)Å]. Each of the four identical Sm atoms occupying opposite corners of the distorted cube possesses a distorted seven-coordinate geometry [O(1)-Sm-O(2) = 89.7(2)°, N(1)-Sm-N(2) = 62.4(2)°, N(1)-Sm-O(1) = 70.8(2)°, O(1)-Sm-O(3) = 143.66(17)°]. Three of the seven coordination sites of samarium are engaged by the bridging hydroxyl groups [O(3)-Sm-O(3C) = 66.94(19)°, O(3)-Sm-O(3B) = 70.37(19)°, O(3B)-Sm-O(3C) = 93.11(18)°]. The coordination geometry is completed by two oxygens [Sm-O(1) = 2.260(5)Å, Sm-

O(2) = 2.205(5)Å] and two nitrogens [Sm-N(1) = 2.542(6)Å, Sm-N(2) = 2.566(6)Å] of one 3,5-Bu^tsalophen ligand. The ligand adopts a rather normal and slightly distorted geometry [O(2)-Sm-N(1) = 119.0(2)°, O(1)-Sm-N(2) = 108.48(19)°] surrounding the metal on the side opposite to that occupied by the three bridging hydroxyl groups. The C=N bond distances are as expected for a coordinated Schiff base and are comparable with those of 2.2 [N(1)-C(15) = 1.31(1)Å, N(2)-C(22) = 1.30(1)Å].

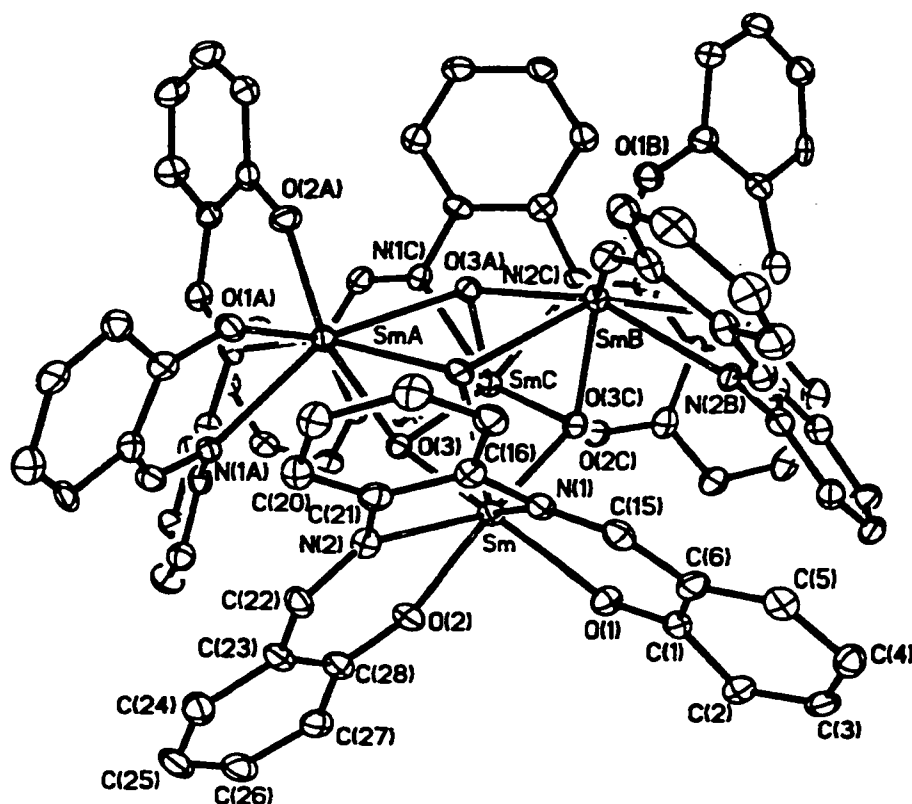


Fig. 2.3 X-ray Structure of 2.4, [(3,5-Bu^tsalophen)Sm(OH)]₄·4toluene

The four Bu^t groups have been deleted for clarity. Selected Bond Distances (Å) and Angles (°): Sm-O(1) = 2.260(5), Sm-O(2) = 2.205(5), Sm-O(3) = 2.573(5), Sm-O(3B) = 2.433(5), Sm-O(3C) = 2.470(5), Sm-N(1) = 2.542(6), Sm-N(2) = 2.566(6), N(1)-C(15) =

1.310(10), N(2)-C(22) = 1.303(10), Sm-O(3)-Sm(A) = 102.43(18), Sm-O(3)-Sm(C) = 112.15(19), Sm(A)-O(3)-Sm(C) = 105.49(18), O(3)-Sm-O(3C) = 66.94(19), O(3)-Sm-O(3B) = 70.37(19), O(1)-Sm-O(2) = 89.7(2), N(1)-Sm-N(2) = 62.4(2), O(1)-Sm-N(1) = 70.8(2), O(2)-Sm-N(2) = 71.5(2), O(1)-Sm-N(2) = 108.48(19).

II.5: Conclusions

In view of the reactivity of transition metal systems stabilized by tetradentate schiff bases, it is surprising that complex **2.2** did not show a more pronounced reactivity towards electron-accepting molecules. However, such behavior may be understood if **2.2** is regarded as a pseudo-samarium (II) species which is effectively stabilized by storing two electrons in the C-C bond linking the two 3,5-Bu^t₄salophen units. The C-C bond may be cleaved and the two electrons made available to the metal centers either by the attack of oxidizing agents directly on the metal centers or of nucleophiles on the two carbon atoms.

References

1. (a) Evans, W. J.; Hozbor, M. A. *J. Organomet. Chem.* **1987**, 326, 299 and ref. cited therein.
 (b) Schaverien, C. J.; *Adv. in Organomet. Chem.*, **1994**, 36, 283 and ref. cited therein.
 (c) Marks, T. J.; Ernst, R. D. in "Comprehensive Organometallic Chemistry" Chapt. 21. Pergamon, Oxford, **1982**.
 (d) Evans, W. *Adv. in Organomet. Chem.*, **1985**, 24, 131.
 (e) Wainwright, K. P. *Coord. Chem. Rev.* **1977**, 166, 35.
 (f) Cotton, S. A. *Coord. Chem. Rev* **1997**, 160, 93.
 (g) Pikramenou, Z *Coord. Chem. Rev* **1997**, 164, 189.
 (h) Gunko, Y. K.; Edelmann F. T *Comm. in Inorg. Chem.* **1997**, 19, 153.
 (i) Gunko, Y. K.; Edelmann F. T. *Coord. Chem. Rev* **1996**. 156, 1.
 (j) Parker D.; Williams J. A. *J. Chem. Soc. Dalton Trans.* **1996**, 3613.
 (k) Edelmann, F. T. *Angew. Chem. Int. Ed. Engl.* **1995**, 34, 2466.
2. Girard, P.; Namy, J. L.; Kagan, H. B.; *J. Am. Chem. Soc.*, **1980**, 102, 2693.
3. (a) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L., *J. Am. Chem. Soc.* **1983**, 105, 1401.
 (b) Evans, W. J.; Engerer, S. C.; Neville, A. C., *J. Am. Chem. Soc.* **1978**, 100, 331.
 (c) Evans, W. J.; Engerer, S. C.; Piliero, P. A.; Wayda, A. L. *J. Am. Chem. Soc. Chem. Comm.*, **1979**, 101, 1007.
 (d) Evans, W. J.; Engerer, S. C.; Piliero, P. A.; Wayda, A. L.; *Fundamentals of Homogeneous Catalysis*, Tsutsui, M. Ed., Plenum Press, New York, **1979**, vol. 3.

- (e) Evans, W. J.; Ansari, M. A.; Ziller, J. W. *Organometallics*, **1995**, *14*, 3.
4. (a) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W.; *J. Am. Chem. Soc.*, **1990**, *112*, 219.
- (b) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *Organometallics*, **1986**, *5*, 1285.
- (c) Evans, W. J.; Hughes, L. A.; Hanusa, T. P., *J. Am. Chem. Soc.*, **1984**, *106*, 4270.
- (d) Evans, W. J.; Drummond, D. K.; Bott, S. G.; Atwood, J. L., *Organometallics*, **1986**, *5*, 2389.
- (e) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W., *J. Am. Chem. Soc.*, **1988**, *110*, 6877.
- (f) Evans, W. J.; Keyer, R. K.; Zhang, H.; Atwood, J. L., *J. Chem. Soc. Chem. Comm.*, **1987**, 837.
- (g) Evans, W. J.; Drummond, D. K.; Grate, J. W.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.*, **1987**, *109*, 3928.
- (h) Evans, W. J.; Drummond, D. K.; *J. Am. Chem. Soc.*, **1989**, *111*, 3329.
5. (a) Evans, W. J.; Keyer, R. A.; Rabe, G. W.; Drummond, D. K.; Ziller, J. W. *Organometallics*, **1993**, *12*, 4664.
- (b) Evans, W. J.; Grate, J. W.; Doedens, R. J.; *J. Am. Chem. Soc.*, **1985**, *107*, 1671.
- (c) Evans, W. J.; Ulibarri, T. A.; *J. Am. Chem. Soc.*, **1987**, *109*, 4292.
- (d) Evans, W. J.; Grate, J. W.; Hughes, L. A.; Zhang, H.; Atwood, J. L., *J. Am. Chem. Soc.*, **1985**, *107*, 3728.
- (e) Evans, W. J.; Drummond, D. K., *J. Am. Chem. Soc.*, **1988**, *110*, 2772.
- (f) Evans, W. J.; Drummond, D. K., *Organometallics*, **1988**, *7*, 797.

- (g) Evans, W. J.; Drummond, D. K.; Chamberlain, L. R.; Doedens, R. J., Bott, S. G., Zhang, H.; Atwood, J. L., *J. Am. Chem. Soc.*, **1988**, *110*, 4983.
- (h) Evans, W. J.; Drummond, D. K., *J. Am. Chem. Soc.*, **1986**, *108*, 7440.
- (i) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W., *J. Am. Chem. Soc.*, **1990**, *112*, 2314.
- (j) Evans, W. J.; Leman, J. T.; Ziller, J. W. *Inorg. Chem.* **1996**, *35*, 4283.
6. see for example:
- (a) Nief, F; Ricard, L. *J. Organomet. Chem.*, **1994**, *464*, 149.
- (b) Rabe, G.; Riede, J.; Schier, A. *Inorg. Chem.* **1996**, *35*, 2680.
- (c) Gosink, H. J.; Nief, F.; Ricard, L.; Mathey, F. *Inorg. Chem.* **1995**, *34*, 1306.
- (d) Fryzuk, M. D.; Haddad, T. S.; Rettig, S. J. *Organometallics* **1992**, *11*, 2967.
7. see for example:
- (a) Chebolu, V.; Whittle, R. R.; Sen, A., *Inorg. Chem.*, **1985**, *24*, 3082.
- (b) Evans, W. J.; Drummond, D. K.; Zhang, H.; Atwood, J. L., *Inorg. Chem.*, **1988**, *27*, 575.
- (c) Evans, W. J.; Rabe, G. W.; Ziller, J. W.; *Inorg. Chem.*, **1994**, *33*, 3072.
- (d) White III, J. P.; Deng, H.; Boyd, E. P.; Gallucci, J.; Shore, S. G.; *Inorg. Chem.*, **1994**, *33*, 1685.
- (e) Evans, W. J.; Rabe, G. W.; Ziller, J. W., *Organometallics*, **1994**, *13*, 1641.
- (f) Minhas, R.; Song, J.; Ma, Y.; Gambarotta, S. *Inorganic Chemistry* **1996**, *35*, 1866.
- (g) Evans, J. W.; Ansari, M. A.; Ziller, J. W. *Inorg. Chem.* **1996**, *35*, 5435.
- (h) Schaverin, C. J.; Orpen, A. G. *Inorg. Chem.* **1991**, *30*, 4968
- (i) Edelmann, F. T. *Coord. Chem. Rev.* **1995**, *137*, 403.

- (k) Schumann, H.; Rosenthal, E. C. E.; Winterfield, J.; Kociok-Kohn, G.; *J. Organomet. Chem.* **1995**, *495*, C12.
8. (a) Sen, A.; Chebolu, V.; Rheingold, A. L.; *Inorg. Chem.*, **1987**, *26*, 1821.
 (b) Evans, W. J.; Anwender, R.; Ansari, M. A.; Ziller, J. W.; *Inorg. Chem.*, **1995**, *34*, 5.
 (c) Hitchcock, P. B.; Holmes, S. A.; Lappert, M. F.; Tian, S. *J. Chem. Soc. Chem. Commun.* **1994**, 2691.
 (d) Biagini, P.; Lugli, G.; Abis, L.; Millini, R. *J. Organomet. Chem.* **1994**, *474*, C16.
9. Jubb, J.; Gambarotta, S., *J. Am. Chem. Soc.*, **1994**, *116*, 4477.
10. Song, J.; Gambarotta, S., *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2141
11. (a) Runte, O.; Priermeier, T.; Anwender, R., *J. Chem. Soc. Chem. Commun.*, **1996**, 1385 and references cited therein.
 (b) Deacon, G. B.; Feng, T.; Junk, P. C.; *J. Chem. Soc. Chem. Commun.*, **1997**, 341.
12. Jacobsen, E. N., in *Comprehensive Organometallic Chemistry II*, ed. E.W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, New York, **1995**, *12*, ch. 11.1.
13. Anhydrous SmCl_3 was prepared following a standard procedure:
 (a) Freeman, J. H.; Smith, M. L., *J. Inorg. Nucl. Chem.*, **1958**, *7*, 224 and was transformed into the corresponding tetrahydrofuranate.
 (b) Manzer, L. E., *Inorg. Synth.*, **1982**, *21*, 135.
14. Evans, W. J.; Grate, J. W.; Choi, H. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L., *J. Am. Chem. Soc.*, **1985**, *107*, 941.

15. Lorrow, J. F.; Jacobsen, E. N.; Gao, Y.; Hong, Y.; Nie, X; Zepp, C. M., *J. Org. Chem.*, **1994**, *59*, 1939.
16. Mabbs, M. B.; Machin, D.; *Magnetism and Transition Metal Complexes*; Chapman and Hall; London, **1973**.
17. Foese, G.; Gorter, C. J.; Smits, L. J., *Constantes Selectionnees, Diamagnetisme, Paramagnetisme Relaxation Paramagnetique*; Masson, Paris, 1957.
18. Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc. Chem. Comm.*, **1982**, 756 and references therein.
19. see for comparison:

Abid, K. K.; Fenton, D.; Casellato, U.; Vigato, A.; Graziani, R. *J. Chem. Soc. Dalton Trans.* **1984**, 351
20. Hitchcock, P. B.; Lappert, M. F.; Prashar, F. *J. Organomet. Chem.* **1991**, *413*, 79.
21. (a) Gambarotta, S.; Urso, F.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.*, **1983**, *22*, 3966.

(b) Gambarotta, S.; Mazzanti, M.; Floriani, C.; Zehnder, M. *J. Chem. Soc. Chem. Commun.*, **1984**, 1116.
22. see for example:

(a) Jubb, J.; Gambarotta, S.; Duchateau, R.; Teuben, J. *J. Chem. Soc. Chem. Commun.*, **1994**, 2641.

(b) Aspinall, H. C., Tillotson, M. R., *Inorg. Chem.*, **1996**, *35*, 2163.

(c) Evans, W. J., Dominguez, R., Hanusa, T. P., *Organometallics*, **1986**, *5*, 1291.
23. MacDonnell, F. M.; Fackler, N. L., Stern, C.; O'Halloran, T. V. *J. Am. Chem. Soc.*, **1994**, *116*, 7431.

24. Takats, J.; Zhang, X.; Lopnow, G. R.; McDonald, R. *J. Am. Chem. Soc.*, **1995**, *117*, 7828.

CHAPTER III

Terminally-bonded samarium hydride, methyl and vinyl supported by calix-tetrapyrrole ring macrocycle. Thermal decomposition to Sm(II)

III.1 Introduction

The very high reactivity of hydride complexes of the lanthanides is responsible for a number of attractive transformations¹ and, as a result of the growing interest in the reactivity of these species, synthetic efforts have multiplied. Today, examples of dinuclear hydride-bridged complexes,² hydroaluminates³ and borohydrides⁴ are abundant in the literature. Only lanthanide complexes containing terminally bonded hydrides remain rare⁵ probably due to a particularly enhanced reactivity which can be expected for these species.

The employment of the calix-tetrapyrrole ligand system in lanthanide chemistry^{6,7} provides an interesting alternative to the traditional cyclopentadienyl derivatives. For example, this family of macrocyclic polyanions has allowed for both reversible fixation⁸ and reduction^{6,7} of dinitrogen and has provided a unique case in lanthanide chemistry of ethylene reversible fixation.⁹

Given the rarity of samarium hydrides^{2b,c,f,j,10} which to the best of our knowledge have been isolated exclusively with Cp-based ligands, we have now probed the possibility of exploiting the unique features of the calix-tetrapyrrole ligand system to stabilize novel Sm hydride and alkyl derivatives. In this chapter, we wish to describe the preparation and characterization of novel mononuclear calix-tetrapyrrole samarium

hydride, methyl and vinyl complexes, and the spontaneous decomposition of the vinyl derivative to a Sm(II) complex.

III.2 Experimental Section

All operations were performed under an inert atmosphere of a nitrogen-filled drybox or by using standard Schenk-type glassware in combination with a nitrogen-vacuum line. $\text{SmCl}_3(\text{THF})_3$,¹² $\text{Et}_8\text{-calix-tetrapyrrole}$ and $\text{Cy}_4\text{-calix-tetrapyrrole}$ were prepared according to literature procedures.⁶⁻⁹ C_6D_6 and THF-d^8 were dried over Na/K alloy, vacuum-transferred into ampoules, and stored under nitrogen prior to use. NMR spectra were recorded on a Varian Gemini 200 and on a Bruker AMX-500 spectrometer using vacuum sealed NMR tubes prepared inside a drybox. Infrared spectra were recorded on a Mattson 3000 FTIR instrument from Nujol mulls or KBr prepared inside the drybox. Samples for magnetic susceptibility measurements were carried out at room temperature using a Gouy balance (Johnson Matthey). Magnetic moments were calculated by following standard methods¹³ and corrections for underlying diamagnetism were applied to the data.¹⁴ Elemental analyses were carried out using a Perkin-Elmer Series II CHN/O 2400-analyzer.

Preparation of $(\text{Et}_8\text{-calix-pyrrole})(\text{Cl})\text{Sm}[\text{Li}_2(\text{THF})_3]$ (3.1):

$\text{SmCl}_3(\text{THF})_3$ (2.1 g, 4.4 mmol) and $(\text{Et}_8\text{-calix-tetrapyrrole})\text{Li}_4(\text{THF})_4$ (3.8 g, 4.4 mmol) were combined in 100 mL freshly distilled anhydrous THF to give a suspension which was heated gently for 10 minutes. The resulting golden yellow solution was stirred for 2 hours. The solvent was removed *in vacuo* and the pale yellow solid residue was

resuspended and decanted with 30 mL of diethyl ether. After repeating the operation two more times, the solid was dried at room temperature and *in vacuo* to yield **3.1** as a pale yellow powder (4.0 g, 3.7 mmol, 84%). I.R. (Nujol mull, cm^{-1}) ν : 3012(w), 3080(w), 2732(w), 2704(w), 1610(w), 1456(s), 1370(s), 1322(m), 1256(m), 1210(w), 1160(w), 1110(s), 1045(s), 967(w), 933(w), 880(s), 760(s), 732(s). El. Anal. Calcd (Found) for $\text{C}_{48}\text{H}_{78}\text{N}_4\text{O}_3\text{SmLi}_2\text{Cl}$: C 60.12 (61.24), H 8.20 (8.06), N 5.84 (6.00). $\mu_{\text{eff}} = 1.61 \mu_{\text{B}}$

Preparation of $(\text{Et}_8\text{-calix-pyrrole})(\text{Me})\text{Sm}(\mu^3\text{-Cl})[\text{Li}(\text{THF})]_2[\text{Li}(\text{THF})_2]$ (3.2a**):**

A solution of MeLi (1.4 mL, 1.9 mmol) was added dropwise to a stirred suspension of **3.1** (2.0 g, 1.9 mmol) in diethyl ether (100 mL). The solution immediately became bright orange and stirring was continued for 30 minutes. The solution was filtered to remove LiCl, concentrated to 50 mL and allowed to stand overnight at -30°C . Yellow-orange crystals of **3.2a** separated (1.5 g, 77%). El. Anal. Calcd (Found) for $\text{C}_{53}\text{H}_{83}\text{N}_4\text{O}_4\text{SmLi}_3\text{Cl}$: C 60.80(60.43), H 7.99(8.07), N 5.35(4.99). I.R. (Nujol mull, cm^{-1}) ν : 3071(w), 2752(w), 2724(w), 1622(m), 1584(m), 1376(s), 1323(m), 1260(m), 1188(s), 1135(w), 1046(s), 970(m), 924(m), 889(s), 835(w), 871(s), 751(s), 687(w). $^1\text{H-NMR}$ (d^6 -benzene, 500 MHz, 23°C) δ : 8.15 (m, 3H, Me ethyl), 6.33 (s, 2H, CH pyr), 6.28 (s, 2H, CH pyr), 5.86 (s, 2H, CH pyr), 5.83 (s, 2H, CH pyr), 4.20 (d, 1H, CH_2 ethyl), 3.96 (d, 1H, CH_2 ethyl), 3.65 (m, 16H THF), 3.26 (q, 4H, CH_2 , ether), 2.19 (q, 2H, CH_2 ethyl), 1.99 (m, 8H, CH_2 ethyl), 1.85 (m, 8H, CH_2 ethyl), 1.62 (s, 3H, CH_3 Me), 1.48 (m, 1H, CH_2 ethyl), 1.19 (m, 1H, CH_2 ethyl), 1.45 (m, 16H, THF), 1.11 (t, 3H, CH_3 ether), 0.99 (m, 2H, CH_2 ethyl), 0.92 (t, 3H, CH_3 ethyl), 0.53 (t, 3H, CH_3 ethyl), 0.51 (t, 12H, CH_3 ethyl), 0.41 (t, 3H, CH_3 ethyl). $^{13}\text{C-NMR}$ (d^6 -benzene, 125.72 MHz, 23°C) δ : 107.00, 103.47, 99.73,

99.86 (CH pyr), 87.19, 30.61, 30.48, 30.20, 25.51 (CH₂ ethyl), 105.99, 8.39, 8.31, 9.02, 8.73 (CH₃ ethyl), 65.84, 8.88 (ether), 68.17, 25.60 (THF), 9.81 (Me), 46.8 (quaternary C ring), 154.26, 153.78, 142.71, 141.63 (quaternary C pyrrole). $\mu_{\text{eff}} = 1.67 \mu_{\text{B}}$

Preparation of (Et₅-calix-pyrrole)(vinyl)Sm(μ^3 -Cl)[Li (THF)]₂[Li(THF)₂] (3.2b):

A suspension of **3.1** (1.6 g, 1.54 mmol) in diethyl ether (100 mL) was treated with a freshly-prepared solution of CH₂CHLi in diethyl ether (0.5 mL, 3.2 M, 1.55 mmol). The color immediately changed to bright yellow. After stirring for 10 minutes the solution was filtered to remove a small amount of LiCl and concentrated to 50 mL. Prolonged stirring at room temperature results in darkening of the solution to green with lower yields of **3.2b**. Upon standing at -30°C for 2 days, the solution separated light yellow crystals of **3.2b** (0.89 g, 0.840 mmol, 55%). El. Anal. (Calcd.) for C₅₄H₈₃Li₃N₄O₄SmCl: C 61.33 (61.25), H 7.87(7.90), N 5.05(5.29). I.R. (Nujol mull, cm⁻¹) ν : 3081(w), 2725(w), 1650(w), 1575(w), 1457(s), 1377(s), 1324(m), 1259(m), 1025(w), 1043(s), 970(w), 924(m), 890(s), 855(m), 792(s), 784(s), 670(w). H¹-NMR (d⁸-THF, 500 MHz, -20°C) δ : This thermally unstable complex is fluxional at low T and shows two distinct series of resonances for the vinyl groups: 8.10, 7.90 (two pseudo-t, 1H, CH_{vinyl}), 5.62, 5.52, 5.49, 5.47 (four broad-s, 8H, CH_{pyrr}), 3.56 (partly overlapping broad-s, 16H, THF), 3.32 (q, 4H, ether), 3.01, 2.15, 2.67, 1.99 (two doublets, 1H, CH_{2vinyl}), 2.61, 2.42, 1.81, 1.70 (four broad-s, 16H, CH_{2Et}), 1.73 (broad-s, 16H, THF), 1.06 (t, 6H, ether), 0.93, 0.22 (two broad-s, 24H, CH_{3Et}). C¹³-NMR (d⁸-THF, 125.72MHz, -20°C) δ : 155.92, 154.74, 141.74 (ring and pyrr. quaternary C), 123.71, 122.98 (CH_{2vinyl}), 101.20, 100.93, 99.05,

97.74 (CH_{pyrr}), 66.48, 15.81 (ether), 68.23, 26.37 (ether), 10.33, 10.15, 9.21, 9.14 ($\text{CH}_{3\text{ethyl}}$), 32.27, 32.03, 27.64, 27.60 ($\text{CH}_{2\text{ethyl}}$), $\mu_{\text{eff}} = 1.51 \mu_{\text{B}}$

Preparation of $(\text{Et}_8\text{-calix-pyrrole})(\text{THF})\text{Sm}(\mu\text{-H})[\text{Li}(\text{THF})]_2 \cdot 3\text{THF}$ (3.3).

Method A. An orange solution of **3.2** (1.7 g, 1.9 mmol) in THF (75 mL) was stirred at room temperature under 1 atm H_2 for 1 hour during which time the color lightened to pale yellow. The clear solution was concentrated to 30 mL. After standing at -30°C for 24 hours large, light yellow crystals of **3.3** separated (1.2 g, 1.0 mmol, 53%). El. Anal. Calcd (Found) for $\text{SmLi}_2\text{C}_{60}\text{H}_{97}\text{N}_4\text{O}_6$: C 63.51(63.10), H 8.62(8.82), N 4.94(4.82). I.R. (Nujol mull, cm^{-1}) ν : 3068(m), 2721(w), 1657(w), 1571(w), 1461(s), 1375(s), 1323(w), 1262(m), 1240(m), 1208(w), 1154(w), 1130(w), 1047(s), 973(m), 886(s), 841(m), 780(s), 735(s), 693(w), 665(m). ^1H -NMR ($\text{d}^8\text{-THF}$, 500 MHz, 23°C) δ : 6.12 (s, pyrrole, 4H), 5.72 (s, pyrrole, 4H), 4.08 (m, CH_2 ethyl, 4H), 3.61 (m, free THF, 12H), 3.58 (broad s, THF attached to Li, 8H), 2.12 (m, CH_2 ethyl, 4H), 2.11 (m, CH_2 ethyl, 4H), 1.84 (pseudo t, THF attached to Sm, 4H), 1.79 (m, free THF, 12H), 1.75 (broad s, THF attached to Li, 8H), 1.43 (t, CH_3 ethyl, 12H), 1.11 (m, CH_2 Et, 4H), 0.59 (pseudo t, THF attached to Sm, 4H), 0.29 (t, CH_3 ethyl, 12H). ^{13}C -NMR ($\text{d}^8\text{-THF}$, 125.72MHz, 23°C) δ : 162.79 (quaternary C pyrrole), 140.00 (quaternary C pyrrole), 97.87 (C-H pyrrole), 95.73 (C-H pyrrole), 68.13 (CH_2 coord. THF), 67.75 (CH_2 coord. THF), 50.94 (quaternary C ring), 31.32 (CH_2 ethyl), 26.37 (CH_2 ethyl), 25.19 (CH_2 coord. THF), 24.70 (CH_2 coord. THF), 9.88 (CH_3 ethyl), 8.07 (CH_3 ethyl). $\mu_{\text{eff}} = 1.32 \mu_{\text{B}}$.

Method B. A solution of **3.1** (1.5 g, 1.4 mmol) in 75 mL THF was treated with LiAlH_4 (0.05 g, 1.4 mmol). The color immediately changed from golden yellow to light greenish-

yellow. The mixture was stirred for 2 hours at room temperature. After filtration, the solution was concentrated to 30 mL and was kept at -30 °C for 24 hours to yield pale yellow crystals of **3.3** (yield 66%).

Method C: A solution of NaHB(C₂H₅)₃ (1.4 mL, 1.0 M) in toluene was added to a solution of **3.1** (1.5 g, 1.4 mmol) in 75 mL THF. The color immediately lightened. After stirring for 1 hour the pale, light yellow solution was concentrated to 25 mL. After standing for 24 hours at -30 °C crystals of **3.3** separated (yield 49%).

Preparation of [Et₈-calix-pyrrole](THF)Sm(μ³-Cl)[Li(THF)]₂[Li(THF)₂] (3.4a**):**

A light yellow solution of **3.2b** (1.5 g, 1.4 mmol) in diethyl ether (150 mL) was stirred at room temperature for 2 days. The solvent of the resulting dark green solution was removed *in vacuo* and the solid residue redissolved in hexane (50 mL). A small amount of insoluble material was eliminated by filtration and the filtrate concentrated to small volume (25 mL). Dark green microcrystalline **3.4a** (0.5 g, 0.5 mmol, 35%) separated upon allowing the resulting solution to stand at -20°C for two days. El. Anal. (Calcd.) for SmLi₃ClC₅₆H₈₈N₄O₅: C 60.92(60.73), H 8.03(8.02), N 5.07 (5.05). I.R. (Nujol mull, cm⁻¹) ν: 3076(w), 2729(w), 1606(m), 1456(vs), 1377(vs), 1325(w), 1308(w), 1259(s), 1211(w), 1091(m), 1043(s), 1024(s), 976(m), 926(m), 889(m), 796(m), 752(s). μ_{eff} = 3.55 μ_B

Preparation of {[-(CH₂)₅]-₄-calix-pyrrole}(THF)Sm (μ³-Cl)[Li(THF)]₂[Li(THF)₂] (3.4b**)**

A suspension of SmCl₃(THF)₃ (3.5 g, 7.4 mmol) in freshly distilled anhydrous THF (150 mL) under Ar was treated with colorless {[-(CH₂)₅]-₄-calix-pyrrole}Li₄ (4.3 g, 7.4 mmol).

The resulting golden yellow suspension was heated gently for 10 minutes until complete dissolution of the solid was reached and then was allowed to stir at room temperature for 2 hours. Metallic lithium (0.07 g, 10 mmol) was added to the reaction mixture. The color deepened from yellow to dark green over 30 minutes. After stirring for 18 hours the solvent was removed *in vacuo* and the resulting deep green solid residue was extracted with a few portions of diethyl ether (total 75 mL). Deep-green crystals of **3.4b** (7.7 g, 5.5 mmol, 75%) separated upon concentration and allowing the extracts to stand at room temperature for 24 hours. I.R. (Nujol mull, cm^{-1}) ν : 3090(w), 2730(w), 2662(w), 1550(w), 1355(m), 1315(w), 1286(s), 1270(s), 1256(s), 1191(s), 1140(m), 1074(s), 970(m), 845(m), 780(s). El. Anal. Calcd (Found) for $\text{SmLi}_3\text{ClC}_{60}\text{H}_{88}\text{N}_4\text{O}_5$: C 62.55 (62.93), H 7.70(7.22), N 4.86(4.75). $\mu_{\text{eff}} = 3.70 \mu_{\text{B}}$

III.3: Results and Discussion

The mononuclear and trivalent $(\text{Et}_8\text{-calix-pyrrole})(\text{Cl})\text{Sm}[\text{Li}_2(\text{THF})_3]$ (**3.1**) was the precursor for the preparations described in this work. Its preparation was obtained via simple metathetic reaction of $\text{SmCl}_3(\text{THF})_3$ with one equivalent of the tetralithium derivative of the calix-tetrapyrrole anion. The complex can either be easily isolated or more conveniently may be prepared and used *in situ*. This species displays fluxional behavior at room temperature and, different from the other compounds reported in this work, produced uninformative NMR spectra. Further reaction of **3.1** with equivalent amounts of RLi [$\text{R} = \text{Me}$, vinyl] (Scheme 3.1) afforded the corresponding terminally-bonded derivatives $(\text{Et}_8\text{-calix-pyrrole})(\text{R})\text{Sm}(\mu^3\text{-Cl})[\text{Li}(\text{THF})]_2[\text{Li}(\text{THF})_2]$ [$\text{R} = \text{Me}$ (**3.2a**), vinyl(**3.2b**)] which have been isolated in crystalline form.

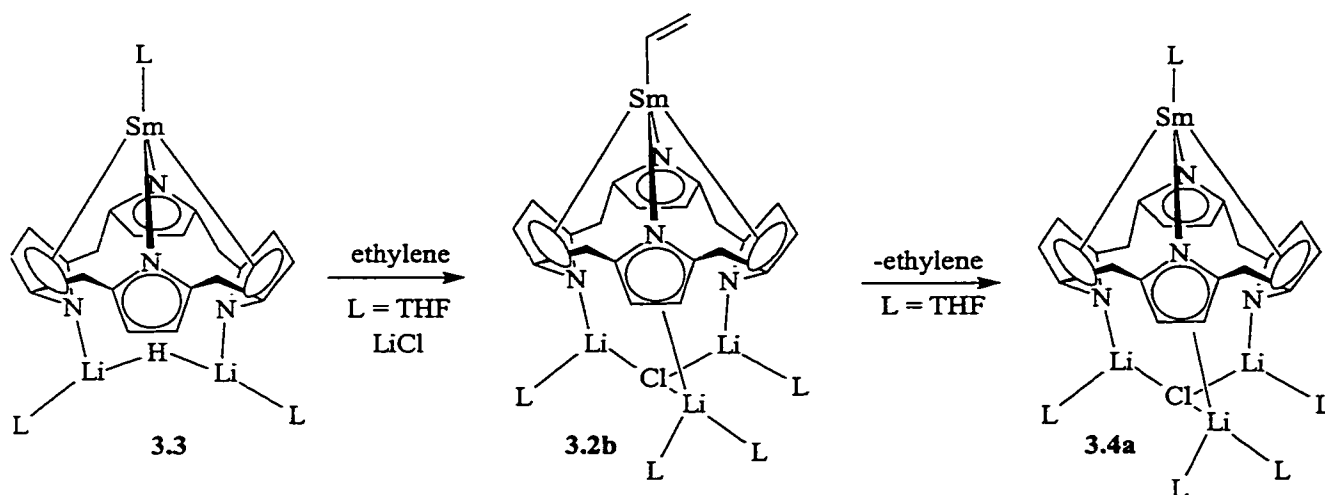
conveniently prepared via direct reaction of **3.1** with either LiAlH_4 or NaHBET_3 or via reaction of **3.2** with PhSiH_3 .

The ^1H -NMR spectra of **3.2a**, **3.2b** and **3.3** are characterized by the same strong magnetic anisotropy previously observed in other samarium complexes of the same ligand system.^{8,9} The ^{13}C -NMR resonances of the methyl and vinyl α -carbon atoms attached to Sm could not be located in the HQMC spectra, probably because of their vicinity to the paramagnetic center. In the ^1H -NMR spectra, the Me group of **3.2a** displays a broad resonance at 8.15 ppm, while the vinyl protons of **3.2b** show two sets of vinyl signals each featuring one pseudo-triplet and two doublets. The fluxional behavior of **3.2b**, whose spectrum was necessarily recorded at -30°C due to its high thermal instability, is likely to be responsible for the presence of the two independent vinyl groups. Similar to the case of $(\text{Cp}^*_2\text{SmH})_2$,¹¹ difficulties were also encountered in locating the resonance of the hydride in the ^1H -NMR spectrum. The only difference between the ^1H -NMR spectrum of **3.3** and that of the corresponding deuteride is the absence in the deuteride spectrum of a very broad resonance at 7.91 ppm. Since this resonance was uncoupled to either hydrogen or carbon resonances, we tentatively assign it to the hydride. Unfortunately, further efforts to substantiate this proposal have been hampered by the fact that complex **3.3** does not exchange with D_2 gas (room temperature, 1 atm.). Furthermore, the I.R. of **3.3** was identical to that of the corresponding deuteride, prepared via reaction of **3.1** with LiAlD_4 and, regrettably, no resonance could be assigned to the Sm-H stretching. However, degradation experiments of **3.3** carried out with a Toepler pump and four equivalents of anhydrous HCl afforded 76% of the expected amount of H_2 , thus confirming the presence of the hydride function. Finally, reaction of

3.3 with ethylene gas gave a clean conversion to **3.2b** which was accompanied by the evolution of H_2 (Scheme 3.2).

Compounds **3.2a** and **3.3** are thermally robust and we found no signs of degradation upon allowing their THF solutions to stand for a few weeks at room temperature or for a few hours at 60°C . Conversely, the vinyl-Sm derivative ($\text{Et}_8\text{-calix-pyrrole})(\text{CH}=\text{CH}_2)\text{Sm}(\mu^3\text{-Cl})[\text{Li}(\text{THF})]_2[\text{Li}(\text{THF})_2]$ (**3.2b**) (Scheme 3.2) decomposes rapidly at room temperature to yield a deep green divalent samarium compound [$\text{Et}_8\text{-calix-pyrrole})(\text{THF})\text{Sm}(\mu^3\text{-Cl})[\text{Li}(\text{THF})]_2[\text{Li}(\text{THF})_2]$ (**3.4a**) which was isolated as a dark green crystalline solid. The formation of **3.4a** is accompanied by the evolution of an equivalent amount of ethylene that could be identified in NMR tube experiments in spite of the broad features arising from the paramagnetism of **3.4a**.

Scheme 3.2



Crystals of suitable quality could be grown only for the cyclohexyl homologue $\{[-(\text{CH}_2)_5\text{-}]_4\text{-calix-pyrrole}\}(\text{THF})\text{Sm}(\mu^3\text{-Cl})[\text{Li}(\text{THF})]_2[\text{Li}(\text{THF})_2]$ (**3.4b**) which was more conveniently prepared via reduction of the corresponding trivalent chloride derivative with Li under Ar.

The transformation of **3.2b** to **3.4** with simultaneous formation of ethylene implies homolytic cleavage of the Sm-C_{vinyl} bond with one hydrogen atom from a solvent molecule likely undergoing abstraction by the vinyl radical. At first glance, the fact that complexes **3.4** did not give fixation of either ethylene or dinitrogen (both available to **3.4** during its formation) seems to be in contradiction with the reactivity of previously reported Sm(II) calix-tetrapyrrole complexes.^{6,8} However, it should be reiterated that the extent of fixation of these substrates by these complexes (dinitrogen reduction⁶ *versus* dinitrogen reversible fixation⁸) is determined by the nature of the anion attached to the three lithium atoms (enolate *versus* chloride).^{8,9} In addition, the substituents attached to the macrocyclic rings are also capable of determining the extent of ethylene and dinitrogen fixation.^{8,9} Finally, the solvent (ether *versus* THF) also plays a critical role with this respect. This enhanced sensitivity of the reactivity of the metal center to minor ligand modifications, and to the nature of groups not directly attached to the Sm center, is surprising. This behavior provides insight into rationalizing and fine tuning the reactivity of divalent samarium which is notoriously uncontrollable.

III.3: X-ray Crystallography

Suitable crystals were mounted with cooled viscous oil on thin glass fibers. Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° ω -scans at 0, 90, and 180° in ϕ . Unit-cell parameters were determined from 60 data frames collected at

different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections¹⁵ were applied. No symmetry higher than triclinic was observed for **3.2a** and **3.2b**. The reflection data for **3.3** were consistent for *Pnma* and *Pn2₁a* (*Pna2₁*). However, solutions in the centric space group options, for **3.2a**, **3.2b** and **3.3**, yielded chemically reasonable and computationally stable results of refinement. The data for **3.4b** were uniquely consistent with the reported space group. The structures were solved by direct methods, completed with subsequent Fourier synthesis and refined with full-matrix least-squares procedures based on F^2 .

Two symmetry-unique compound molecules were located in the asymmetric units of **3.2a** and **3.2b**. The compound molecule **3.3** was located on a mirror plane. A molecule of coordinated THF and three half-molecules of cocrystallized, noncoordinated THF molecules were also located, disordered by the mirror plane symmetry. The carbon atoms of **3.4b** and the atoms of the cocrystallized solvent molecules of **3.3** were refined isotropically to conserve a reasonable data/parameter ratio. All other non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were assigned with idealized geometry, and constrained with an isotropic, riding model. Crystallographic details are presented in the Appendix, Table 2.

The X-ray crystal structures of complexes **3.2a** and **3.2b** showed two nearly isostructural species. In both structures, the samarium atom is placed in the center of the macrocycle and is bonded to the four pyrrole rings by adopting both the π - and σ -bonding modes. The two centroids of the two nearly parallel π -bonded rings define, together with the two nitrogen atoms of the two σ -bonded rings and the terminally bonded methyl (or vinyl) group, an almost regular trigonal bipyramidal coordination geometry (Figures 3.1

and 3.2). On the side of the molecule opposite to that of the terminally bonded alkyl, three lithium atoms bridged by one chlorine are connected to the pyrrole rings of the macrocycle. Two are σ -bonded to the N atom while the third is π -bonded to one of the four pyrrole rings. A total of four molecules of coordinated THF complete the coordination geometry around the three lithium atoms.

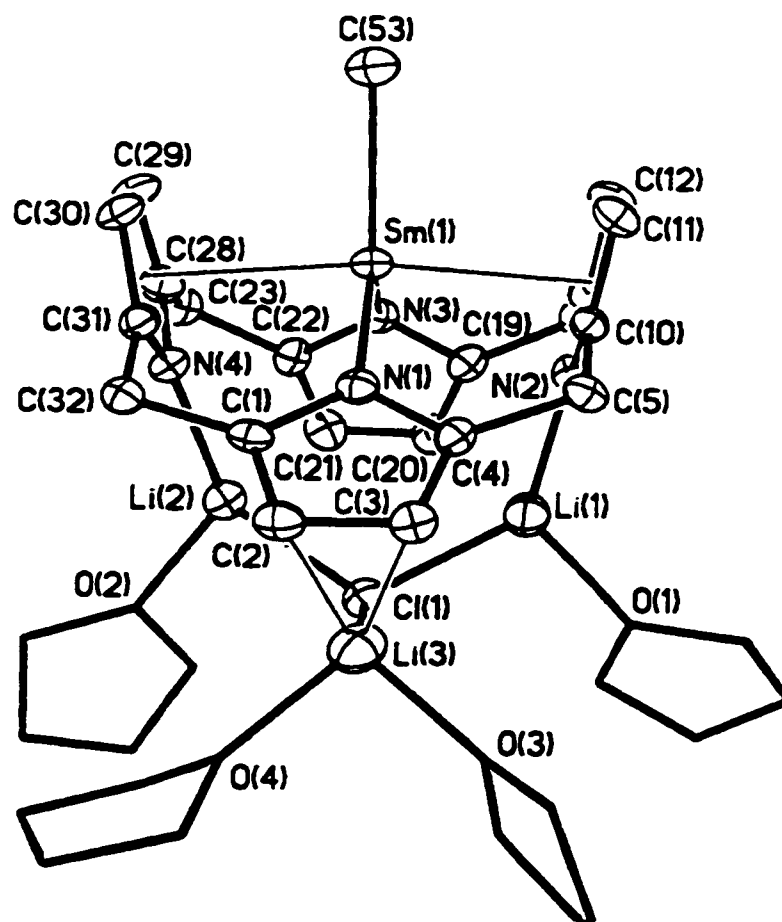


Fig. 3.1 X-ray Structure of 3.2a, (Et₈-calix-pyrrole)(Me)Sm(μ^3 -Cl)[Li(THF)]₂[Li(THF)₂]

Selected Bond Distances (Å) and Angles (°): Sm-C(53) = 2.496(6), Sm(1)-N(1) = 2.465(5), Sm(1)-N(2) = 2.716(5), Sm(1)-C(10) = 2.800(6), Sm(1)-C(11) = 2.970(7), Sm(1)-C(12) = 2.966(7), Sm(1)-C(13) = 2.821(6), Li(1)-N(2) = 1.977(12), Li(3)-N(1) = 3.136(14), Li(3)-C(1) = 2.870(14), Li(3)-C(2) = 2.394(13), Li(3)-C(3) = 2.379(14), Li(3)-C(4) = 2.851(14), Li(1)-O(1) = 1.989(12), Li(1)-Cl(1) = 2.228(12), Li(2)-Cl(1) = 2.270(10).

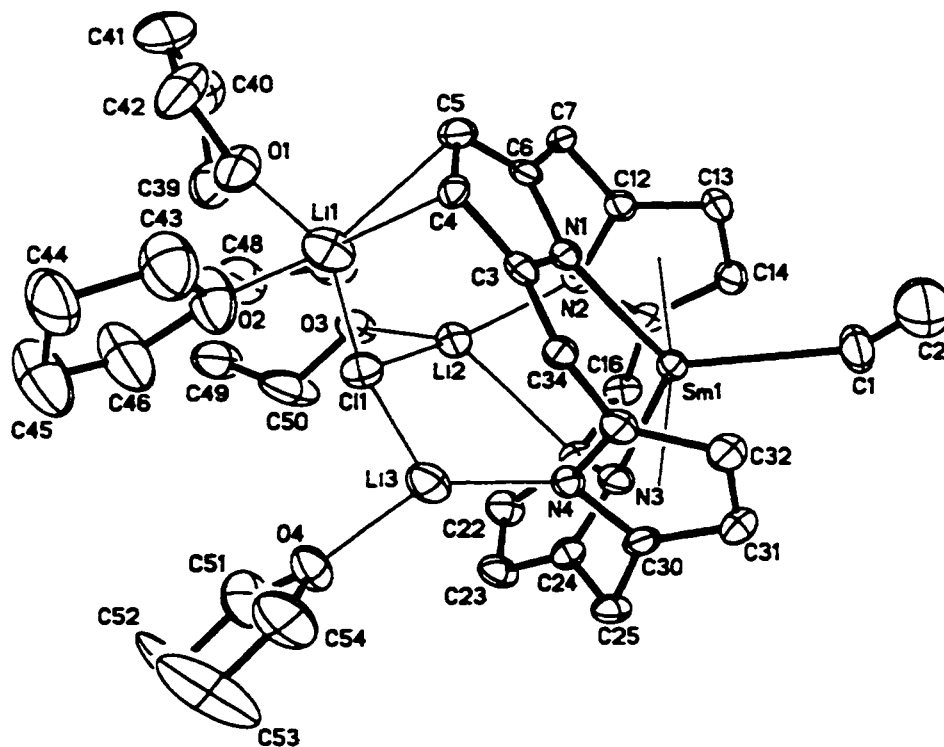


Fig 3.2 X-ray Structure of 3.2b, (Et₈-calix-pyrrole)(vinyl)Sm(μ^3 -Cl)[Li(THF)]₂[Li(THF)₂]

Selected Bond Distances (Å) and Angles (°): Sm(1)-C(1) = 2.468(10), C(1)-C(2) = 1.209(16), Sm(1)-N(1) = 2.491(7), Sm(1)-N(2) = 2.698(7), Sm(1)-C(12) = 2.803(8), Sm(1)-C(13) = 2.935(9), Sm(1)-C(15) = 2.801(9), Li(2)-N(2) = 2.020(16), Li(3)-N(4) = 1.999(18), Li(1)-C(4) = 2.381(14), Li(1)-C(5) = 2.375(18), Li(1)-N(1) = 3.105(18), Li(1)-Cl(1) = 2.287(17), Li(2)-Cl(1) = 2.270(16), Li(3)-Cl(1) = 2.166(17), Sm(1)-C(1)-C(2) = 137.6(16).

Complex 3.3 is formed by a samarium atom surrounded by the macrocycle (Figure 3.3). Similar to complexes 3.2, two of the four pyrrole rings are π -bonded to the metal while the other two are coplanar with samarium and with which they form σ -bonds through the two nitrogen atoms. Each of the pyrrole rings σ -bonded to samarium is also π -bonded to one lithium atom. Each of the two lithium atoms is in turn σ -bonded to the nitrogen atom of a second ring and to one molecule of THF. The two N-Li-O vectors are significantly bent and, as a result, the two lithium atoms are oriented towards each other. One molecule of THF is bonded to samarium and is placed on the axis perpendicular to the plane defined by the four nitrogen atoms of the macrocycle. One hydride, whose position was located and satisfactorily refined, was found in the middle of the SmLi₂ triangle and placed coaxial to the Sm-O_{THF} vector. The Sm-H distance [2.203 Å] is rather long in comparison with those of the few cyclopentadienyl samarium hydride derivatives reported in the literature.^{2b,e,f,j,10}

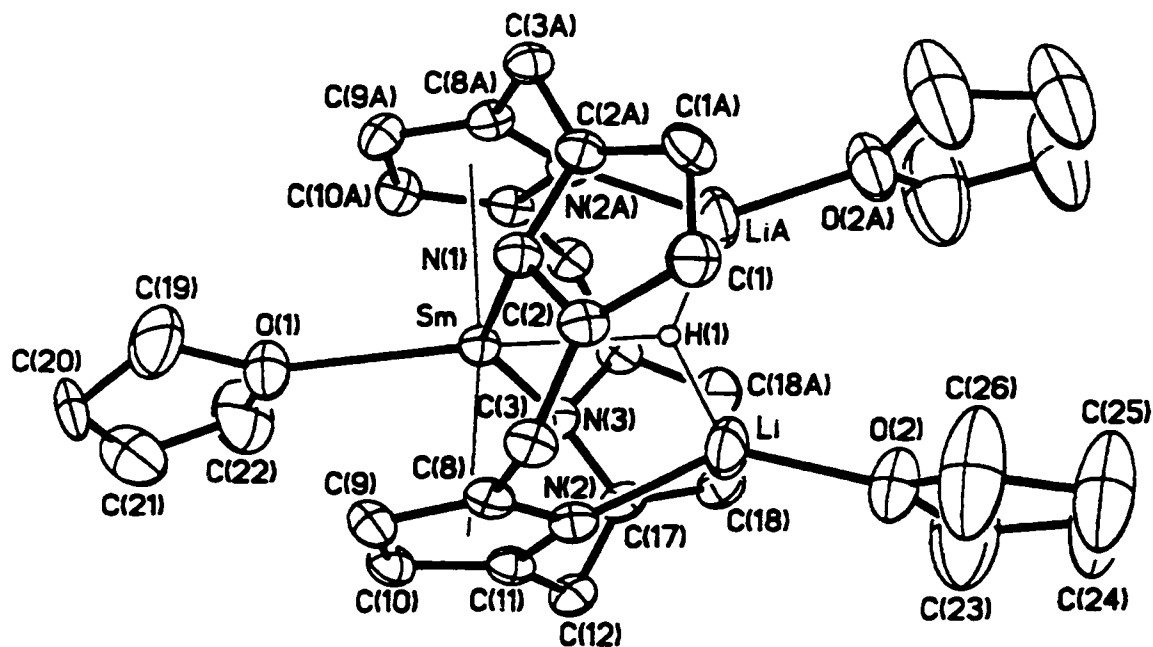


Fig. 3.3 X-ray Structure of 3.3, (Et₈-calix-pyrrole)(THF)Sm(μ-H)[Li(THF)]₂·3THF

Selected Bond Distances (Å) and Angles (°): Sm-N(1) = 2.436(5), Sm-N(2) = 2.682(4), Sm-C(8) = 2.785(5), Sm-C(9) = 2.934(5), Sm-C(10) = 2.926(5), Sm-C(11) = 2.799(5), Sm-O(1) = 2.559(6), Sm-H(1) = 2.203, Li-N(2) = 1.950(13), Li-H(1) = 1.686(3), N(2)-Li-O(2) = 135.1(7), Sm-H(1)-Li = 110.7(7), Li-H(1)-Li(a) = 138.6(7), O(1)-Sm-H(1) = 171.9(7).

The structure of **3.4b** is very similar to **3.2**, the only difference arising from the replacement of the vinyl group with one molecule of THF (Figure 3.4). Consistent with the lower oxidation state of samarium, the bond distances are, on average, slightly longer than those observed in complexes **3.2**.

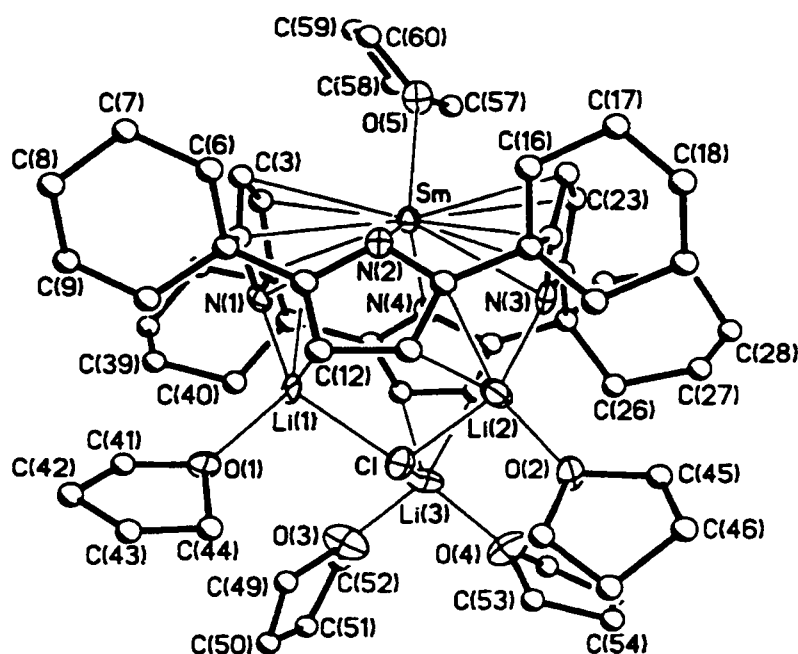


Fig. 3.4 X-ray Structure of **3.4b**, $\{[-(\text{CH}_2)_5\text{-}]_4\text{-calix-pyrrole}\}(\text{THF})\text{Sm}(\mu^3\text{-Cl})[\text{Li}(\text{THF})]_2[\text{Li}(\text{THF})_2]$

Selected Bond Distances (Å) and Angles (°): Sm-N(1) = 2.898(9), Sm-N(2) = 2.567(9), Sm-N(3) = 2.851(8), Sm-N(4) = 2.541(9), Sm(1)-C(1) = 2.886(11), Sm(1)-C(2) = 2.930(11), Sm(1)-C(3) = 2.936(10), Sm(1)-C(4) = 2.929(11), Sm-O(5) = 2.612(8), Cl-Li(1) = 2.306(19), Cl-Li(2) = 2.27(2), Cl-Li(3) = 2.33(2), N(2)-Sm-N(4) = 126.6(3), N(2)-Sm-O(5) = 126.2(3), N(4)-Sm-O(5) = 107.2(3).

References

- 1 for comprehensive reviews on lanthanide chemistry see for example:
 - a) Edelmann, F. T. *Comprehensive Organometallic Chemistry* Eds.: Abel, E.W., Stone, F. G. A., Wilkinson, G. ; Pergamon: Oxford **1995**;
 - b) Ephritikhine, M. *Chem. Rev.* **1997**, *97*, 2193;
 - c) Edelmann, F. T.; Gun'ko, Y. K. *Coord. Chem. Rev.* **1997**, *165*, 163;
 - d) Zakharov, L. N.; Struchkov, Y. T. *J. Organomet. Chem.* **1997**, *536*, 65;
 - e) Pikramenou, Z. *Coord. Chem. Rev.* **1998**, *172*, 99;
 - f) Schumann, H.; Meese-Marktscheffel, J. A.; Esser, L. *Chem. Rev.*, **1995**, *95*, 865;
 - g) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51.
2. see for example:
 - a) Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 2008;
 - b) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 1401;
 - c) Schumann, H.; Genthe, W.; Hahn, E.; Hossain, M. B.; Van der Helm, D. *J. Organomet. Chem.* **1986**, *299*, 67;
 - d) Fisher, R. D.; Qiao, K. *J. Organomet. Chem.* **1993**, *456*, 185;
 - e) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *Organometallics* **1991**, *10*, 134;
 - f) Gun'ko, Y. K.; Bulychiev, B. M.; Soloveichik, G. L.; Belsky, V. K. *J. Organomet. Chem.* **1992**, *424*, 289;
 - h) Stern, D.; Sabat, M.; Marks, T.J. *J. Am. Chem. Soc.* **1990**, *112*, 9558;

- i) Hultzs, K. C.; Spaniol, T. P.; Okuda, J. *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 227;
- j) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T.J. *J. Am. Chem. Soc.* **1985**, *107*, 8103;
- k) Coughlin, E. B.; Bercaw, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 7606;
- l) Yasuda, H.; Yamamoto, H.; Yokota, K.; Miyake, S.; Nakamura, A. *J. Am. Chem. Soc.*, **1992**, *114*, 4908;
- m) Heeres, H. J.; Meetsma, A.; Teuben, J. H.; Rogers, R. D. *Organometallics*, **1989**, *8*, 255;
- n) Schaverien, C. J. *Organometallics* **1994**, *13*, 69.
- 3 a) Knjazhanski, S. Y.; Bulychev, B. M.; Belskii, V. K.; Soloveichik, G.L. *J. Organomet. Chem.* **1987**, *327*, 173;
- b) Gun'ko, Y. K.; Bulychev, B. M.; Sizov, A. I.; Bel'sky, V. K., Soloveichik, G. L. *J. Organomet. Chem.* **1990**, *390*, 153;
- c) Belsky, V. K.; Gun'ko, Y. K.; Bulychev, B. M.; Soloveichik, G. L. *J. Organomet. Chem.* **1991**, *419*, 299.
- 4 a) Shinomoto, R.; Zalkin, A.; Edelstein, N. M. *Inorg. Chim. Acta.* **1987**, *139*, 97;
- b) White, J. P.; Deng, H.; Shole, S. G. *Inorg. Chem.* **1991**, *30*, 2337;
- c) Lobkovsky, E. B.; Gun'ko, Y. K.; Bulychev, B. M.; Belsky, V. K.; Soloveichik, G. L.; Antipin, M. Y. *J. Organomet. Chem.* **1991**, *406*, 343;
- d) Shaimuradov, I. B.; Badalov, A. B.; Marufi, V. K.; Mirsaidov, U. *Zh. Neorg. Khim.* **1991**, *36*, 1353;

- e) Daoli, D.; Zheng, X.; Qian, C.; Sun, J.; Zhang, L. *J. Organomet. Chem.* **1994**, *95*, 466;
- f) Schumann, H.; Keitsch, M. R.; Demtschuk, S.; Mühle, S. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1811;
- g) Cendrowski-Guillame, S. M.; Nierlich, M.; Lance, M.; Ephritikhine, M. *Organometallics* **1998**, *17*, 786.
- 5 a) Ilinski, A. L.; Porai-Koshits, M. A.; Aslanov, L. A.; Lazarev, P. I. *Zh. Strukt. Khim.* **1972**, *13*, 277;
- b) Prozorovskii, A. E.; Yaroslavtsev, A. B.; Prozorovskaya, Z. N. *Zh. Neorg. Khim.* **1989**, *34*, 2622;
- c) Butman, L. A.; Aslanov, L. A.; Porai-Koshits, M. A. *Zh. Strukt. Khim.* **1970**, *11*, 46.
- d) Booiij, M.; Kiers, N. H.; Heeres, H. J.; Teuben, J. H. *J. Organomet. Chem.* **1989**, *364*, 79.
- f) Albrecht, I.; Schumann, H. *J. Organomet. Chem.* **1986**, *310*, C29.
- g) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203.
- h) Thompson, M. E.; Bercaw, J. E. *Pure Appl. Chem.* **1984**, *56*, 1.
- i) Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett* **1990**, 74.
- j) den Haan, K. H.; Wielstra, Y.; Teuben, J. H. *Organometallics* **1987**, *6*, 2053.
- 6 Jubb, J.; Gambarotta, S. *J. Am. Chem. Soc.*, **1994**, *116*, 4477.
- 7 Campazzi, E.; Solari, E.; Floriani, C.; Scopelliti, R. *J. Chem. Soc. Chem. Commun.* **1998**, 2603.

- 8 Dube', T.; Gambarotta, S.; Yap, G. P. A. *J. Chem. Soc. Chem. Commun* submitted.
- 9 Dube', T.; Gambarotta, S.; Yap, G. P. A. *Angew. Chem. Int. Ed. Engl.* 1999, **38**, 1432.
10. Radus, N. S.; Gantzel, P. K.; Tilley, T.D. *J. Chem. Soc. Chem. Commun.* **1994**, 1175.
11. Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. *J. J. Am. Chem. Soc.* **1985**, *107*, 8091.
12. Anhydrous SmCl_3 was prepared following a standard procedure:
(a) Freeman, J. H.; Smith, M. L., *J. Inorg. Nucl. Chem.*, **1958**, *7*, 224 and was transformed into the corresponding tetrahydrofuranate.
(b) Manzer, L. E., *Inorg. Synth.*, **1982**, *21*, 135.
13. Mabbs, M. B.; Machin, D.; *Magnetism and Transition Metal Complexes*; Chapman and Hall; London, **1973**.
14. Foese, G.; Gorter, C. J.; Smits, L. J., *Constantes Selectionnes, Diamagnetisme, Paramagnetisme Relaxation Paramagnetique*; Masson, Paris, 1957.
15. Blessing, R., *Acta Cryst.*, **1995**, *A51*, 33-38

CHAPTER IV

Dinuclear Sm(II), Sm(III), alkyl and mixed-valence compounds of calix-tetrapyrrole

IV.1: Introduction

The steady growth of interest enjoyed by organolanthanides is continuously fueled by the remarkable catalytic performances discovered in both the past and the present for the Ln-C functionality. For example, it has been documented that organolanthanide complexes are attractive catalysts for olefin hydrogenation¹, dehydroamination², hydrosilation³, hydroboration⁴, oligomerization⁵ and reductive cyclization⁶. Complexes with the formula $(C_5Me_5)_2LnX$ ⁷ [X = alkyl, hydride] have been shown to be among the most versatile, catalytically-active species. Remarkably, even low-valent samarium organometallic compounds of cyclopentadienyl-based, constrained-geometry-type ligands have shown versatility as olefin polymerization catalysts⁸ and as powerful catalysts in metal-promoted organic synthesis.⁹ These types of compounds are also desirable as models for investigating the characteristic bending of samarocene which, to date, has remained unexplained and poses a theoretical challenge. The ability of low-valent samarium to act as a strong reducing agent is, in principle, limited to only one-electron reduction processes. Nevertheless, the cooperative interaction of more low-valent samarium centers on the same substrate, which appears to be a rather characteristic behavior of this metal, has allowed for multi-electron processes which include four-electron reduction of dinitrogen, complex organic transformations, CO oligomerization/deoxygenation, etc. Thus the possibility of assembling polynuclear structures containing two or more low-valent samarium atoms becomes particularly attractive in view of the above-mentioned transformations.

Although metallocene derivatives are still the most extensively studied compounds of the lanthanides, there is rapidly growing interest in organometallic compounds of these elements stabilized by other ligands. While low-valent samarium alkoxides,¹⁰ amides,¹¹ phosphides¹² and pyrazolylborates¹³ have been prepared and characterized and have been shown to display promising reactivity, these species are exclusively mononuclear which obviously might be a limitation for reactivity studies. Aside from the triple-decker $(C_5Me_5)(THF)_xSm(C_8H_8)Sm(THF)_x(C_5Me_5)$ ($x = 0,1$),¹⁴ examples of bimetallic lanthanide compounds remain limited to the only example of a dinuclear complex of the calix-tetrapyrrole ligand¹⁵. This compound is particularly interesting on account of its very short intermetallic distance and corresponding unusually low paramagnetism as well as its potential for use as an alkali-free starting material for further transformations.

In this chapter we report a dinuclear series of Sm(II), Sm(III), alkyl and mixed-valence compounds of the calix-tetrapyrrole ligand and the reaction of one of them to afford a rare example of a mononuclear Sm(III)-hydride species.

IV.2: Experimental Section

All operations were performed under an inert atmosphere of a nitrogen-filled drybox or by using standard Schlenk-type glassware in combination with a nitrogen-vacuum line. Solvents were dried by passing through a column of Al_2O_3 under an inert atmosphere prior to use, degassed *in vacuo* and transferred and stored under inert atmosphere. $\text{SmCl}_3(\text{THF})_3$ ¹⁶, $\text{SmI}_2(\text{THF})_2$ ¹⁷, and $(\text{Et}_8\text{-calix-tetrapyrrole})[\text{Li}(\text{THF})]_4$ ¹⁸ were prepared according to literature procedures. PhSiH_3 was dried over molecular sieves prior to use. THF-d^8 was dried over Na/K alloy, vacuum-transferred into ampoules, and stored under nitrogen prior to use. NMR spectra were recorded on Varian Gemini 200 and on a Bruker AMX-500 spectrometer using vacuum-sealed NMR tubes prepared inside a drybox. Infrared spectra were recorded on a Mattson 3000 FTIR instrument from Nujol mulls prepared inside the drybox. Samples for magnetic susceptibility measurements were carried out at room temperature using a Gouy balance (Johnson Matthey). Magnetic moments were calculated by following standard methods and corrections for underlying diamagnetism were applied to the data.¹⁹ Elemental analyses were carried out using a Perkin-Elmer Series II CHN/O 2400 analyzer.

Preparation of $(\text{Et}_8\text{-calix-tetrapyrrole})\text{Sm}_2\{(\mu\text{-Cl})_2[\text{Li}(\text{THF})_2]\}_2 \cdot 2\text{THF}$ (4.1)

A suspension of $\text{SmCl}_3(\text{THF})_3$ (2.4 g 5.2 mmol) in THF (100 mL) was treated with $(\text{Et}_8\text{-calix-tetrapyrrole})(\text{LiTHF})_4$ (2.2 g, 2.6 mmol). Within minutes the solid dissolved and the color changed to deep orange. After stirring at room temperature for 2 hours, the solution was concentrated to 30 mL and subsequently allowed to stand at -30°C for 2 days yielding air-sensitive orange crystals of **4.1** (2.5 g, 1.8 mmol, 72%). I.R. (Nujol

mull, cm^{-1}) ν : 3109(w), 3097(w), 2729(w), 1520(w), 1494(s), 1458(vs), 1379(s), 1327(w), 1277(m), 1261(m), 1240(m), 1161(m), 1134(w), 1074(m), 1039(vs), 1024(s), 980(m), 914(m), 893(s), 827(m), 791(s), 771(s), 721(w), 677(w). $^1\text{H-NMR}$ (d^8 -THF, 500 MHz, 23°C) δ : 7.18 (broad s, pyrrole, 8H), 6.26 (sext, CH_2 ethyl, 8H), 3.56 (m, free THF, 4H), 3.53 (broad s, coord. THF, 16H), 3.34 (sext, CH_2 ethyl, 8H), 1.79 (broad t, CH_3 ethyl, 24H), 1.72 (m, free THF, 4H), 1.68 (broad s, coord. THF, 16H). $^{13}\text{C-NMR}$ (d^8 -THF, 125.72 MHz, 23°C) δ : 149.02 (quaternary C pyrrole), 103.11 (C-H pyrrole), 68.22 (CH_2 free THF), 67.45 (CH_2 coord THF), 55.71 (quaternary C ring), 26.38 (coord. THF), 25.62 (CH_2 ethyl), 25.48 (free THF), 9.77 (CH_3 ethyl). El. Anal. Calcd. (Found) for $\text{C}_{60}\text{H}_{96}\text{N}_4\text{O}_6\text{Sm}_2\text{Li}_2\text{Cl}_4$: C 50.54(49.99), H 6.79(6.83), N 3.93(4.09). $\mu_{\text{eff}} = 2.84\mu_{\text{B}}$

Preparation of [(Et₈-calix-tetrapyrrole)Sm₂{(μ-CH₃)₂[Li(THF)₂]}]₂•2Et₂O (4.2)

A solution of **4.1** (2.0 g, 1.5 mmol) in diethyl ether (100 mL) was treated at room temperature with a solution of MeLi in ether (4.2 ml, 1.4 M, 5.9 mmol). The color of the solution lightened slightly during the following minutes of stirring. After 30 minutes, the solution was filtered to remove LiCl and the resulting solution was concentrated to 75 mL. Standing at -30°C for 2 days produced yellow prisms of **4.2** (1.5 g, 1.3 mmol, 85%). I.R. (Nujol mull, cm^{-1}) ν : 3093(w), 2773(w), 2727(w), 1620(w), 1464(vs), 1379(s), 1325(m), 1275(s), 1242(s), 1159(s), 1134(m), 1117(w), 1051(vs), 1022(s), 978(s), 918(s), 891(s), 827(s), 791(s), 764(vs), 712(w), 679(w), 586(s). $^1\text{H-NMR}$ (d^8 -THF, 500 MHz, 23°C) δ : 7.48 (s, 8H, pyrrole), 3.72 (m, 8H, CH_2 ethyl), 3.65, 3.58 (free and coord. THF), 2.11 (s, 12H, Me), 1.77, 1.72 (free and coord. THF), 1.27 (m, 8H, CH_2 ethyl), 0.20 (m, 24H, CH_3 ethyl). $^{13}\text{C-NMR}$ (d^8 -THF, 125.72 MHz, 23°C) δ : 103 (broad resonance CH

pyrrolyl), 144.72 (quaternary pyrrolyl ring), 90.63 (Me groups), 67.40 (THF), 50.58 (quaternary ring), 25.46 (THF), 24.41 (CH₂ ethyl), 8.08 (Me, ethyl). El. Anal. Calcd. (Found) for C₆₄H₁₁₂N₄Sm₂O₆Li₂: C 57.18(56.77), H 8.10(7.95), N 4.17(4.12). $\mu_{\text{eff}} = 2.90\mu_{\text{B}}$

Preparation of (Et₈-calix-tetrapyrrole)Sm₂(THF)₂(μ -Cl)₂[Li(THF)₂] (4.3)

Solid LiAlH₄ (0.032 g, 0.8 mmol) was added to an orange solution of **4.1** (2.0 g, 1.5 mmol) in THF (100 mL) resulting in a vigorous reaction with effervescence and an immediate color change to deep red. Stirring was allowed to continue for an additional 3 hours. The solution was concentrated to 75 mL and was allowed to stand overnight at room temperature during which time dark red crystals of **4.3** separated (1.5 g, 1.2 mmol, 84%). I.R. (Nujol mull, cm⁻¹) ν : 3089(w), 2723(w), 1506(w), 1487(s), 1458(vs), 1377(s), 1342(w), 1325(m), 1275(s), 1246(s), 1159(m), 1134(w), 1043(vs), 978(s), 920(s), 891(vs), 829(m), 793(w), 769(vs), 754(s), 735(w), 683(w), 667(w), 588(m). El. Anal. Calcd. (Found) for C₅₂H₈₀N₄O₄Sm₂LiCl₂: C 51.88(51.60), H 6.70(6.79), N 4.65(4.55). $\mu_{\text{eff}} = 3.46\mu_{\text{B}}$.

Preparation of (Et₈-calix-tetrapyrrole)Sm₂(THF)₄•3THF (4.4)

Method A: Treatment of a solution of SmI₂(THF)₂ (2.5 g, 4.6 mmol) in THF (80 mL) with solid (Et₈-calix-tetrapyrrole)[Li(THF)₄] (1.9g, 2.3 mmol) resulted in a brown solution which deposited orange microcrystalline solid within minutes. The reaction mixture was stirred for an additional 2 hours during which time more solid accumulated. The suspension was heated gently until everything went into solution. Subsequent

standing at -30°C for 2 days produced dark brown crystals of **4.4** (1.8g, 1.60 mmol, 70%). I.R. (Nujol mull, cm^{-1}) ν : 3091(w), 3076(w), 2721(w), 1591(w), 1458(s), 1375(s), 1358(m), 1323(w), 1269(m), 1248(m), 1211(w), 1157(w), 1103(m,br), 1039(vs), 1018(m), 974(w), 922(w), 889(s), 829(w), 800(w), 754(vs), 667(w). El. Anal. Calcd. (Found) for $\text{C}_{64}\text{H}_{104}\text{N}_4\text{O}_7\text{Sm}_2$: C 57.27(57.36), H 7.81(7.71), N 4.17(4.03). $\mu_{\text{eff}} = 3.98 \mu_{\text{B}}$

Method B: A solution of **4.1** (2.0 g, 1.5 mmol) in THF (100 mL) was treated with excess LiAlH_4 (0.12 g, 3.2 mmol). The resulting deep red suspension was refluxed for 2 hours until the solution turned brown. Concentration to 75 mL and standing at -30°C for 2 days yielded crystals of **4.4** (65%).

Method C: Excess metallic lithium (0.025 g, 3.6 mmol) was added to a solution of **4.1** (1.5 g, 1.1 mmol) in THF (100 mL) under Ar. Stirring at room temperature for 16 hours resulted in a dark brown solution which was filtered to remove unreacted lithium. Concentration to 50 mL and standing at -30°C yielded crystalline **4.4** (60%).

Reaction of **4.2** with PhSiH_3 (**4.5**)

Dropwise addition of PhSiH_3 (3.2 mmol) to stirred solution of **4.2** (2.0 g, 1.6 mmol) in THF (100 mL) resulted in color change to light yellow, then gradually to pale orange-yellow during the course of 1 hour. The solvent was removed under reduced pressure and the yellow residue was extracted with diethyl ether (50 mL). Concentration of the extracts to 15 mL and standing at -30°C overnight resulted in the accumulation of bright yellow blocks (0.8 g, 24%). The mass was composed by two different components. The minor one was identified as $(\text{Et}_8\text{-calix-pyrrole})(\text{THF})\text{Sm}(\mu\text{-H})[\mu\text{-OCH=CH}_2]_2\text{Li}_4(\text{THF})_2$ (**4.5**) while the second was identified as $(\text{Et}_8\text{-calix-pyrrole})(\text{THF})\text{Sm}(\mu\text{-H})[\text{Li}(\text{THF})_2]_2$ (**4.6**).

Recrystallization of the solid mass from ether/THF mixtures afforded analytically pure **4.6•3THF**. El. Anal. Calcd (Found) for $\text{SmLi}_2\text{C}_{60}\text{H}_{97}\text{N}_4\text{O}_6$: C 63.51(63.10), H 8.62(8.82), N 4.94(4.82). I.R. (Nujol mull, cm^{-1}) ν : 3068(m), 2721(w), 1657(w), 1571(w), 1461(s), 1375(s), 1323(w), 1262(m), 1240(m), 1208(w), 1154(w), 1130(w), 1047(s), 973(m), 886(s), 841(m), 780(s), 735(s), 693(w), 665(m). ^1H -NMR (d^8 -THF, 500 MHz, 23°C) δ : 6.12 (s, pyrrole, 4H), 5.72 (s, pyrrole, 4H), 4.08 (m, CH_2 ethyl, 4H), 3.61 (m, free THF, 12H), 3.58 (broad s, THF attached to Li, 8H), 2.12 (m, CH_2 ethyl, 4H), 2.11 (m, CH_2 ethyl, 4H), 1.84 (pseudo t, THF attached to Sm, 4H), 1.79 (m, free THF, 12H), 1.75 (broad s, THF attached to Li, 8H), 1.43 (t, CH_3 ethyl, 12H), 1.11 (m, CH_2 Et, 4H), 0.59 (pseudo t, THF attached to Sm, 4H), 0.29 (t, CH_3 ethyl, 12H). ^{13}C -NMR (d^8 -THF, 125.72MHz, 23°C) δ : 162.79 (quaternary C pyrrole), 140.00 (quaternary C pyrrole), 97.87 (C-H pyrrole), 95.73 (C-H pyrrole), 68.13 (CH_2 coord. THF), 67.75 (CH_2 coord. THF), 50.94 (quaternary C ring), 31.32 (CH_2 ethyl), 26.37 (CH_2 ethyl), 25.19 (CH_2 coord. THF), 24.70 (CH_2 coord. THF), 9.88 (CH_3 ethyl), 8.07 (CH_3 ethyl). $\mu_{\text{eff}} = 1.32 \mu_{\text{B}}$.

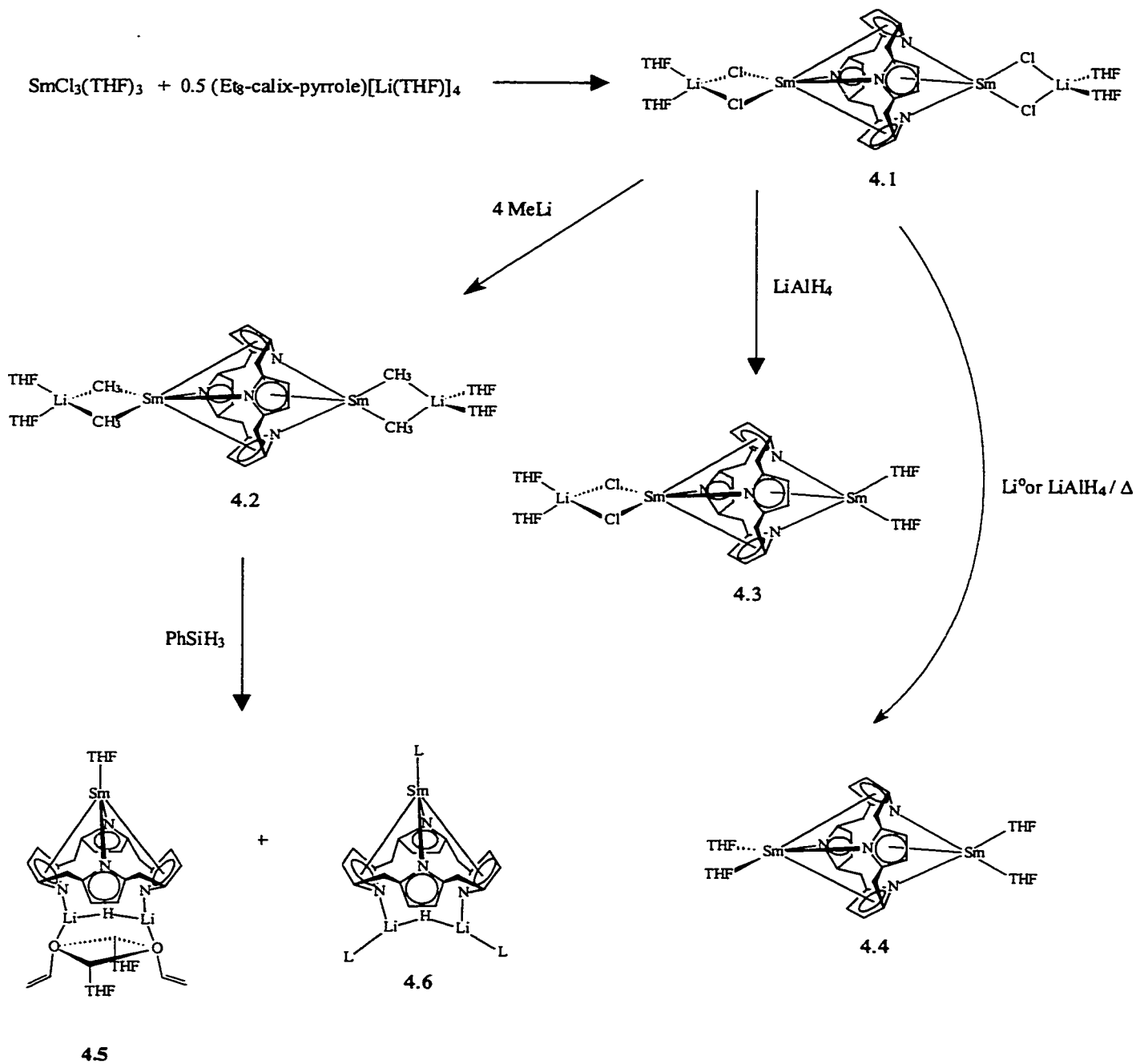
IV.3: Results and Discussion

The room temperature reaction of two equivalents of $\text{SmCl}_3(\text{THF})_3$ with $(\text{Et}_8\text{-calix-tetrapyrrole})[\text{Li}(\text{THF})]_4$ in THF formed an orange, air-sensitive solution from which orange blocks of the paramagnetic $(\text{Et}_8\text{-calix-tetrapyrrole})\text{Sm}_2\{(\mu\text{-Cl})_2[\text{Li}(\text{THF})_2]\}_2$ (**4.1**) were isolated in good yield upon crystallization from THF (Scheme 4.1). Combustion analysis data were in agreement with the formulation as elucidated by an X-ray crystal structure. Solution NMR spectra were well resolved and consistent with the high symmetry of the molecule. Only one resonance was present in both the ^1H and ^{13}C -NMR spectrum for the pyrrolyl CH groups, while the ethyl groups produced two well-separated resonances for the two geminal methylene hydrogens as two reasonably well-solved pseudo-sextuplets centered at 6.26 and 3.34 ppm and coupled to the same resonance at 25.62 of the ^{13}C -NMR spectrum. Conversely, the corresponding CH_3 groups gave only one poorly solved triplet centered at 1.79 ppm.

A simple metathetic reaction of **4.1** with MeLi in ether afforded yellow crystals of $(\text{Et}_8\text{-calix-tetrapyrrole})\text{Sm}_2\{(\mu\text{-CH}_3)_2[\text{Li}(\text{THF})_2]\}_2$ (**4.2**) in high yield. The complex is basically isostructural with the starting **4.1** with the crystal structure showing the same solid state features and arrangement of the ligand around the two metal centers. The ^1H -NMR spectrum also showed only one signal for the pyrrole ring C-H groups and two well separated resonances for the geminal hydrogens of the CH_2 groups. Only one resonance was observed for the methyl groups of the ethyl substituents. The strong magnetic anisotropy of the two geminal CH_2 hydrogens is surprising yet it is a rather common feature among trivalent samarium complexes of this particular ligand system. Solutions of

4.2 are indefinitely stable in ether while solutions in THF slowly turn brown at room temperature.

Scheme 4.1



Attempts to form dinuclear samarium hydroaluminate compounds of similar structure were carried out by reacting complex **4.1** with LiAlH_4 affording instead two different compounds depending on the reaction conditions with both arising from reduction of the metal center. Room temperature reaction resulted in the formation of a deep red solution accompanied by significant effervescence. Deep red crystals of the mixed valence $(\text{Et}_8\text{-calix-tetrapyrrole})\text{Sm}_2(\text{THF})_2(\mu\text{-Cl})_2[\text{Li}(\text{THF})_2]$ (**4.3**) were obtained in good yield. The molecular structure as elucidated by the X-ray crystal structure revealed the same dinuclear arrangement as observed in **4.1** and **4.2** but with two non-equivalent samarium atoms. The first samarium is formally in its divalent state since is simply attached to two molecules of THF while the second displays the same structural features of the starting **4.1**. Complex **4.3**, a rare example of a mixed-valent Sm compound, is paramagnetic with the expected magnetic moment for the mixed-valence state.

Conversely, reaction of excess LiAlH_4 with **4.1** in refluxing THF produced a brown solution from which the dinuclear and divalent $(\text{Et}_8\text{-calix-tetrapyrrole})\text{Sm}_2(\text{THF})_4 \cdot 3\text{THF}$ (**4.4**) was obtained in acceptable yield and crystalline form. The divalent oxidation state was clearly identified by the solid state crystal structure showing the same dinuclear structure of the complexes described above. In this case, however, each of the two samarium atoms is coordinated to two molecules of THF. The magnetic moment of **4.4** is surprisingly low and is even lower than in the mixed-valent **4.3**. This is probably a result of the remarkably short Sm-Sm distance $[3.4417(9)\text{\AA}]$ which perhaps is at the origin of some sort of intramolecular magnetic coupling. Solution NMR spectra display very broad signals and did not allow for reasonable spectral interpretation.

Complex **4.4** may also be conveniently prepared by direct reaction of $\text{SmI}_2(\text{THF})_2$ with $(\text{Et}_8\text{-calix-tetrapyrrole})[\text{Li}(\text{THF})]_4$, or by reduction of **4.1** with metallic lithium under Ar.

The failure of this ligand system to support aluminohydride structures was rather surprising to us in the view that, in the chemistry of trivalent Sm supported by cyclopentadienyl ligands, aluminohydrides are readily prepared from reaction of LiAlH_4 with the corresponding halides to form dimeric and polymetallic complexes.²⁰ Thus further attempts to prepare hydride complexes were carried out by attempting both reaction of **4.2** with PhSiH_3 and hydrogenolysis. The reaction of arylsilanes with transition metal alkyls is a well-established method for preparing hydride derivatives.²¹ The reaction of the dinuclear alkyl derivative **4.2** with PhSiH_3 was carried out at room temperature in THF and resulted in an immediate color change to pale yellow and then to pale orange-yellow over the course of 1 hour. Subsequent removal of the solvent *in vacuo* and extraction of the residue with diethyl ether and crystallization of the extracts at -30°C resulted in a crystalline mass composed of two different compounds. The very minor component (less than 10%) was of sufficient quality to undertake a crystal structure determination. This compound is formulated as the mononuclear hydride derivative $(\text{Et}_8\text{-calix-tetrapyrrole})(\text{THF})\text{Sm}(\mu\text{-H})[\mu\text{-OCH=CH}_2]_2\text{Li}_4(\text{THF})_2$ (**5.5**). The structure of **5.5** is unique. Besides the presence of a hydride encapsulated between the samarium and two lithium atoms, the molecule possesses two Lienolate functions which are retained at the periphery of the molecule. These two functions are clearly generated from THF cleavage and are likely to be the result of the attack on THF by two molecules of MeLi released by the samarium centers during the reaction. Accordingly, significant amounts of ethylene were found in the reaction mixtures. The enolate fragments are scavenged by the hydride

precursor derivative $(\text{Et}_8\text{-calix-tetrapyrrole})(\text{THF})\text{Sm}(\mu\text{-H})[\text{Li}_2(\text{THF})_2]$ to form the final compound. The reaction however, requires a major molecular reorganization since one samarium atom has been removed from the molecular frame and whose fate remains so far unclear. Attempts to further spectroscopically characterize **4.5** were prevented by the ease of dissociation of the enolate groups. Simple room temperature recrystallization from THF gave a complete transformation to the previously reported $(\text{Et}_8\text{-calix-tetrapyrrole})(\text{THF})\text{Sm}(\mu\text{-H})[\text{Li}_2(\text{THF})_2]$ (**4.6**). Accordingly, NMR spectra of **4.5** were identical to those of **4.6** in spite of the different structure and the presence of the two enolate groups. Reaction of **4.2** at room temperature and under 1 atm of H_2 also led to exclusively formation of the hydride derivative $\{(\text{Et}_8\text{-calix-pyrrole})(\text{THF})\text{Sm}(\mu\text{-H})[\text{Li}(\text{THF})]_2\}$ with no sign for the presence of **4.5** or of enolate moieties.

Obviously, the reaction of **4.2** with PhSiH_3 is rather complex and yields a mixture of products. The first step in the reaction may involve formation of a dinuclear silane with elimination of methane. Subsequent Si-H activation promoted by the Sm center results in a dinuclear Sm-hydride with concomitant formation of $[\text{PhSiH}_2]_n$ which remains in solution. The dinuclear structure may then collapse into the monomeric hydride. Although this is rather surprising, and interesting compounds could conceivably be formed in the process, it was not possible to identify other Sm-containing products in the reaction mixture.

IV.4: X-ray Crystallography

Suitable crystals were selected, mounted on thin glass fibres using viscous oil and cooled to the data collection temperature. Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° ω -scans at 0, 90, and 180° in ϕ . Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied

No symmetry higher than triclinic was evident from the diffraction data of **4.3**. Systematic absences in the diffraction data and unit-cell parameters were consistent for space groups *C2/c* (no. 15) and *Cc* (no. 9) for **37** and **4.5** and, uniquely, *Pbcn* (no. 60) for **4.2**. A close inspection of the diffraction data for **4.4** suggested merohedral twinning of Laue class *4/m* simulating Laue class *4/mmm*. The systematic absences in the data for **4.4**, in Laue class *4/m*, were uniquely consistent for space group *I4₁/a* (no. 88). In cases of ambiguous space group assignment, solution in the centric options yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed with difference Fourier syntheses and refined with full-matrix least-squares procedures based on F^2 . The compound molecules for **4.1** and **4.5** are located on two-fold axes. The compound molecule of **4.2** is located at an inversion center. The compound molecule of **4.4** is located at a four-fold rotoinversion axis. A coordinated thf molecule, a half-occupied cocrystallized thf molecule and a quarter-occupied cocrystallized thf molecule was each located disordered in two positions in a roughly 50/50 site distribution for **4.4**. Identification of the oxygen atom positions for the cocrystallized thf molecules in **4.4** was not possible because of the severe disorder, and the ring positions were refined with carbon atom identities each approximating a

[(1/5O)/(4/5CH₂)] fragment, but the correct empirical formula was used in intrinsic property calculations. A solvent molecule was each located cocrystallized in the asymmetric units of **4.1** (thf) and **4.2** (diethyl ether). All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions except the hydride ligand in **4.5** which was located from the difference map and refined with a riding model. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 5.10 program library (Sheldrick, G. M., Bruker AXS, Madison, WI, 1997).

The molecular structure of **4.1**, as determined by X-ray diffraction, consists of a Sm₂ unit surrounded by the calix-tetrapyrrole ligand. The ligand is centered on the Sm-Sm vector and adopts a nearly symmetric conformation in which each pair of pyrrole rings at opposite positions on the macrocycle are almost parallel to one another. Each pair of rings coordinates one of the two Sm atoms in an η^5 fashion, thus assembling a samarocene-type structure. The two N atoms of each pair of parallel pyrrole rings are also σ -bonded to the second samarium atom, which is therefore connected to the four pyrrole rings in an η^1, η^5 -bonding fashion. The second set of pyrrole rings displays an identical arrangement with the second samarium atom. Two chlorides bridge each samarium and a lithium atom which is, in turn, coordinated to two molecules of THF. The coordination geometry about each Sm may be viewed as severely distorted octahedral, the two σ -bonded nitrogens, and the bridging chlorides define, together with the lithium atom, the equatorial plane, while the two centroids of the two η^5 -bonded rings occupy the axial positions.

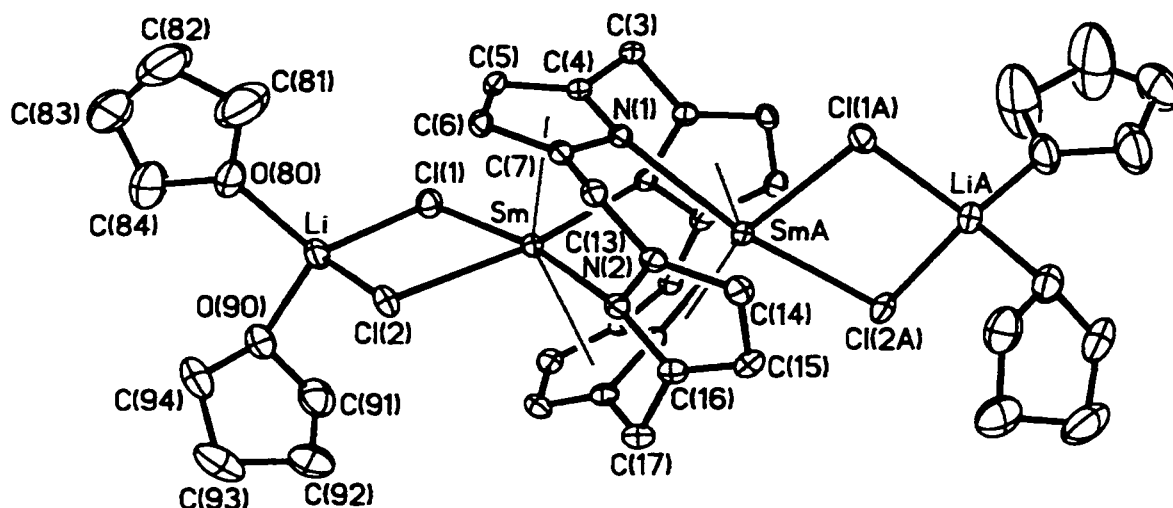


Figure 4.1 X-ray Structure of **4.1**, $(\text{Et}_8\text{-calix-tetrapyrrole})\text{Sm}_2\{(\mu\text{-Cl})_2[\text{Li}(\text{THF})_2]\}_2 \cdot 2\text{THF}$

Selected Bond Distances (Å) and Angles (°): Sm-Cl(1) = 2.7231(9), Sm-Cl(2) = 2.7237(8), Cl(2)-Li(1) = 2.354(7), Cl(1)-Li = 2.329(6), Li-O(80) = 1.924(7), Li-O(90) = 1.949(7), Sm-C(13) = 2.863(3), Sm-C(5) = 2.970(3), Sm-C(6) = 2.967(3), Sm-N(2) = 2.648(3), SmA-N(1) = 2.654(3), SmA-C(14) = 3.017(3), N(2)-Sm-N(1) = 66.69(8), N(2)-Sm-Cl(1) = 87.68(6), N(1)-Sm-Cl(1) = 120.24(5), O(80)-Li-O(90) = 104.2(3), O(80)-Li-Cl(1) = 108.6(3).

Complex **4.2** consists of a symmetry-generated dinuclear molecule with similar structural parameters to **4.1**. The calix-tetrapyrrole ligand bridges two samarium atoms which are further separated from one another [$\text{Sm-Sm} = 3.485(0)\text{Å}$] than in the starting chloride

[Sm-Sm = 3.390(1)Å]. The positions of the chloride atoms in complex **4.1** are occupied by methyl groups which coordinate each samarium atom as well as a lithium atom which is coordinated to two molecules of THF. Thus **4.2** may be regarded as the MeLi adduct of (Et₈-calix-pyrrole)[Sm(CH₃)]₂. The Sm-C bond distances are, within error limits, similar to those observed in terminally-bonded Sm complexes of the same ligand system.¹⁵

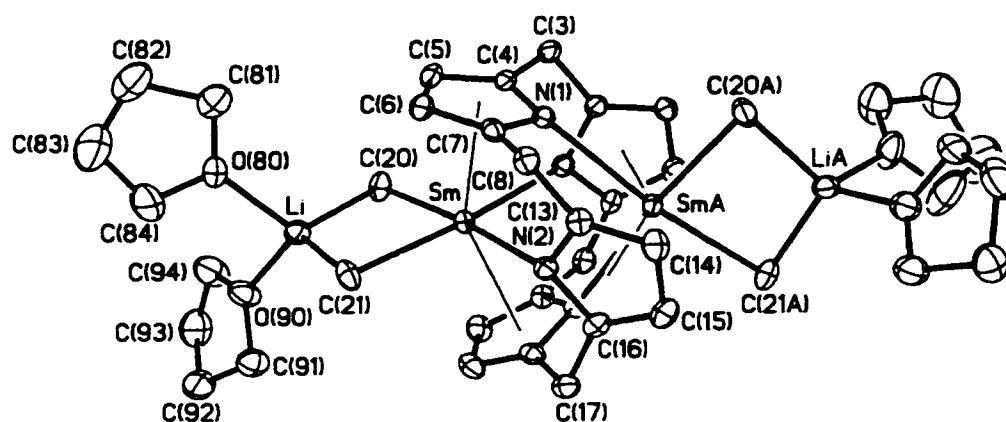


Figure 4.2 X-ray Structure of **4.2**, [(Et₈-calix-tetrapyrrole)Sm₂{(μ-CH₃)₂[Li(THF)₂]}₂•2Et₂O

Selected Bond Distances (Å) and Angles (°): Sm-C(20) = 2.582(4), Sm-C(21) = 2.579(3), Sm-C(4) = 2.885(3), Sm-N(2) = 2.721(3), Sm-C(7) = 2.896(3), SmA-N(1) = 2.706(3), SmA-C(14) = Sm-N(1) = 2.769(3), Li-C(21) = 2.171(8), Li-C(20) = 2.163(7), SmA-N(1) = 2.706(3), SmA-N(2) = 2.766(3).

The molecular structure of **4.3** is also dinuclear. Similar to **4.1** and **4.2**, each samarium shares the same calix-tetrapyrrole ligand with which it engages in both σ and

π -bonding interactions. Whereas each samarium atom in **4.1** and **4.2** is in a similar environment, however, complex **4.3** is asymmetric. Two chlorides bridge one samarium atom and a lithium atom which is solvated by two molecules of THF while the second samarium atom bears two molecules of THF. The Sm-Sm distance in **4.3** [3.430(2)Å] is comparable to those observed for **4.2** and **4.1**.

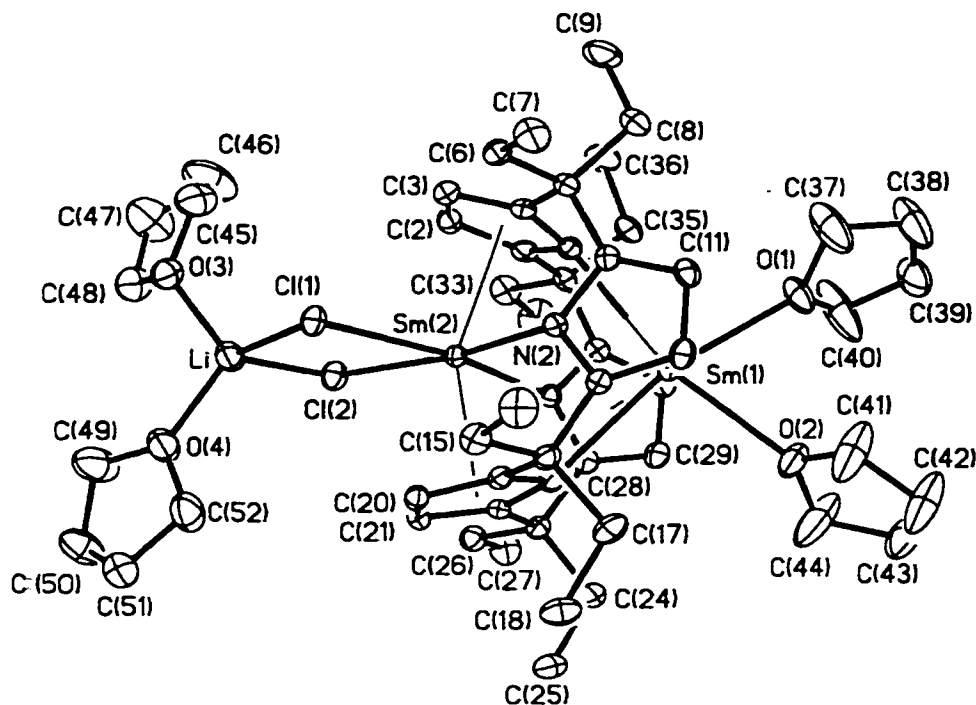


Figure 4.3 Xray Structure of **4.3**, (Et₈-calix-tetrapyrrole)Sm₂(THF)₂(μ-Cl)₂[Li(THF)₂]

Selected Bond Distances (Å) and Angles (°): Sm(1)-N(1) = 2.775(3), Sm(1)-O(1) = 2.589(4), Sm(1)-O(2) = 2.613(4), Sm(1)-N(3) = 2.790(4), Sm(1)-N(4) = 2.798(4), Sm(1)-N(2) = 2.828(3), Sm(1)··Sm(2) = 3.4300(4), Sm(2)-N(4) = 2.607(3), Sm(2)-N(2) = 2.623(4), Sm(2)-N(1) = 2.744(4), Sm(2)-N(3) = 2.751(3), Sm(2)-Cl(2) = 2.7638(12), Sm(2)-Cl(1) = 2.8006(11), Sm(2)-C(4) = 2.834(4), Cl(1)-Li = 2.370(10), Cl(2)-Li =

2.358(9), O(1)-Sm(1)-O(2) = 73.60(14), O(1)-Sm(1)-N(1) = 92.01(12), N(1)-Sm(1)-N(3) = 165.52(12), Cl(2)-Sm(2)-Cl(1) = 78.63(3).

Complex **4** is isostructural with the previously reported (Et₈-calix-pyrrole)[Sm(Et₂O)]₂, the only notable differences arising from the substitution of two molecules of THF per each Sm instead of one molecule of diethyl ether. As a consequence, the Sm-Sm distance [3.4417(9)Å] in **4** is slightly longer than that reported for (Et₈-calix-pyrrole)[Sm(Et₂O)]₂ [3.3159(5)Å].

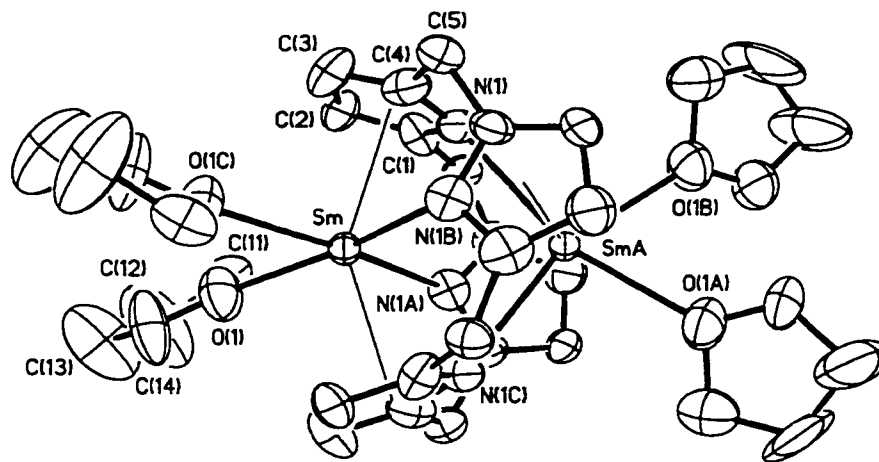


Figure 4.3 Xray Structure of **4.4**, (Et₈-calix-tetrapyrrole)Sm₂(THF)₄

Selected Bond Distances (Å) and Angles (°): Sm-O(1) = 2.634(4), Sm-N(1) = 2.748(4), Sm-N(1A) = 2.865(4), Sm-C(4A) = 2.931(5), Sm-C(1A) = 3.022(4), Sm...Sm(A) = 3.4417(9), O(1)-Sm-O(1A) = 74.2(2), O(1)-Sm-N(1A) = 162.67(16), O(1)-Sm-N(1) = 89.37(15), Sm-N(1)-Sm(A) = 75.62(10).

The monomeric **4.5** is formed by a samarium atom surrounded by the macrocycle. Two of the four pyrrole rings are π -bonded to the metal while the other two are coplanar with samarium and with which they form σ -bonds with the two nitrogen atoms. Each of the pyrrole rings σ -bonded to samarium is also π -bonded to one lithium atom. Each of the two lithium atoms is in turn σ -bonded to the nitrogen atom of a second ring. Each lithium atom is also bound to the oxygen atom of a Lienolate moiety. The enolate lithium atoms are each bound to one molecule of THF as well as to the lithium atom of the other enolate fragment, thus forming a Li-O-Li-O ring which caps the cavity of the macrocycle opposite to the samarium atom. The four lithium atoms define a rather regular tetrahedron. One molecule of THF is bonded to samarium and is placed on the axis perpendicular to the plane defined by the four nitrogen atoms of the macrocycle. The hydride was located in the center of the Sm_2Li_2 triangle and is obviously responsible for the substantial bending of the N-Li-O vector.

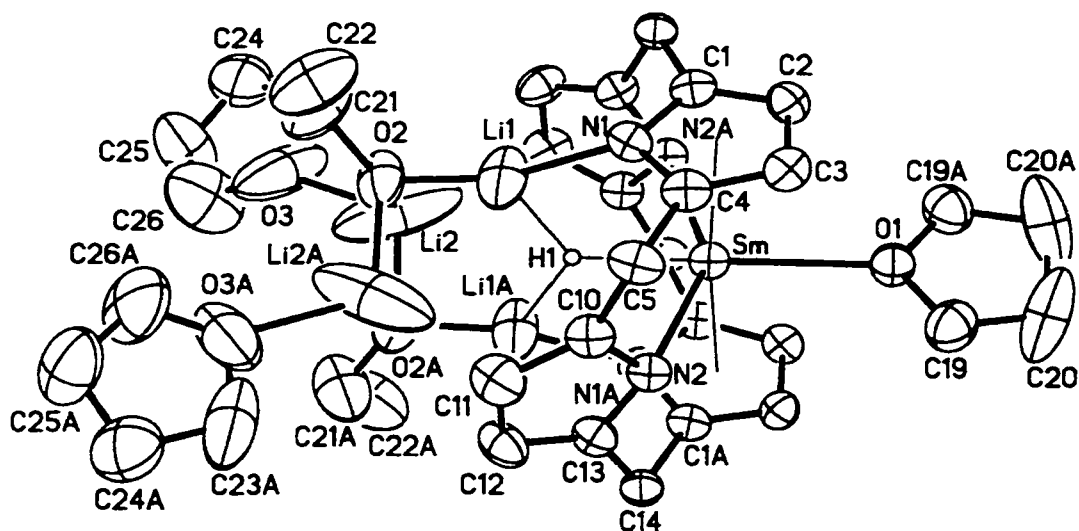


Figure 4.5, Xray Structure of (Et₃-calix-tetrapyrrole)(THF)Sm(μ-H)[μ-OCH=CH₂]₂Li₄(THF)₂ (5.5)

Selected Bond Distances (Å) and Angles (°): Sm-N(2) = 2.448(6), Sm-O(1) = 2.600(8), Sm-N(1) = 2.691(6), Sm-C(1) = 2.795(7), Sm-C(4) = 2.790(7), Sm-C(3) = 2.924(8), Sm-C(2A) = 2.921(8), O(1)-C(19) = 1.456(10), O(2)-C(21) = 1.453(15), O(2)-Li(1) = 1.757(19), O(2)-Li(2A) = 1.80(4), C(21)-C(22) = 1.374(19), N(2)-Sm-C(1) = 110.8(2), C(21)-O(2)-Li(1) = 122.9(9), C(22)-C(21)-O(2) = 110.2(13).

IV.5: Conclusions

The calix-pyrrole ligand is a versatile ligand system, effective in the stabilization of Sm(II), Sm-alkyl, Sm-chloride, and Sm(II)/Sm(III) dinuclear species. These dinuclear compounds may be synthesized cleanly and in good yield. Attempts to synthesize a Sm-calix-pyrrole aluminohydride complex were unsuccessful. Whereas the monomeric Sm-calix-pyrrole reacts with LiAlH_4 to yield the corresponding hydride, the dinuclear complex undergoes reduction in the presence of LiAlH_4 to produce either a Sm(II) complex or a mixed-valence Sm(II)/Sm(III) complex depending upon the reaction conditions. The ability of this dinuclear species to undergo either one or two- electron reduction may demonstrate the potential of these compounds in terms of catalytic applications. Reaction of the dinuclear methyl complex **4.2** with PhSiH_3 results in formation of a monomeric hydride, rather than a dinuclear species. Accompanying the rearrangement was generation of enolate fragments, presumably originating from THF-cleavage promoted by MeLi released by the samarium center during the reaction.

References

1. (a) Molander, G.A.; Hoberg, J.O. *J. Org. Chem.* **1992**, *57*, 3266.
 (b) Jeske, G.; Jauke, H.; Mauermann, H.; Schumann, H.; Marks, T.J. *J. Am. Chem. Soc.* **1985**, *107*, 8111.
 (c) Evans, W.J.; Bloom, I.; Hunter, W.E.; Atwood, J.L. *J. Am. Chem. Soc.* **1983**, *105*, 1401.
2. (a) Li, Y.; Marks, T.J. *J. Am. Chem. Soc.* **1996**, *118*, 9295.
 (b) Li, Y.; Marks, T.J. *Organometallics* **1996**, *15*, 3770.
 (c) Li, Y.; Marks, T.J. *J. Am. Chem. Soc.* **1996**, *118*, 707.
 (d) Gagné, M.R.; Nolan, S.P.; Marks, T.J. *Organometallics* **1990**, *9*, 1716.
3. (a) Takahashi, T.; Hasegawa, M.; Suzuki, N.; Saburi, M.; Rousset, C.J.; Fanwick, P.E.; Nagishi, E.J. *J. Am. Chem. Soc.* **1991**, *113*, 8564.
 (b) Fu, P.F.; Brard, L.; Li, Y.; Marks, T.J. *J. Am. Chem. Soc.* **1995**, *117*, 7157.
 (c) Molander, G.A.; Julius, M. *J. Org. Chem.* **1992**, *57*, 6347.
4. (a) Bijpost, E.A.; Duchateau, R.; Teuben, J.H. *J. Mol. Catal.* **1995**, *95*, 121.
 (b) Harrison, K.N.; Marks, T.J. *J. Am. Chem. Soc.* **1992**, *114*, 9220.
5. (a) Thompson, M.E.; Bercaw, J.E. *Pure Applied Chemistry* **1984**, *56*, 1.
 (b) Burger, B.J.; Thompson, M.E.; Bercaw, J.E.; Cotton, W.D. *J. Am. Chem. Soc.* **1990**, *112*, 1566.
 (c) Parkin, G.; Bunel, E.; Burger, B.J.; Trimmer, M.S.; van Asselt, A.; Bercaw, J.E. *J. Mol. Cat.* **1987**, *41*, 21.
5. (a) Molander, G.A.; Nichols, P.J. *J. Am. Chem. Soc.* **1995**, *117*, 4415.
 (b) Molander, G.A.; Hoberg, J.O. *J. Am. Chem. Soc.* **1992**, *114*, 3123.

7. (a) Marks, T.J.; Fragala, I.L.; Reidel, D. Eds. *Fundamental and Technological Aspects of Organo-f-Element Chemistry*: Dordrecht, 1985.
(b) Schumann, H. *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 474.
(c) Evans, W.J. *Polyhedron* **1987**, *6*, 803.
(d) Evans, W.J. *J. Organomet. Chem.* **1983**, *250*, 217.
8. (a) Jeske, G.; Lauke, H.; Mauermann, P.N.; Swepston, P.N.; Schumann, H.; Marks, T.J. *J. Am. Chem. Soc.* **1985**, *107*, 8091.
(b) Jeske, G.; Schock, L.E.; Swepston, P.N.; Schumann, H.; Marks, T.J. *J. Am. Chem. Soc.* **1985**, *107*, 8103.
(c) Watson, P.L.; Parshall, G.W. *Acc. Chem. Res.* **1985**, *18*, 51.
9. see for example:
(a) Schumann, H.; Meese-Marktscheffel, J.A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865.
(b) Edelmann, F.T. in *Comprehensive Organometallic Chemistry II*; Abel, E.W., Stone, F.G.S., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 4, Chapter 2 and references therein.
(c) Schaverien, C.J. *Adv. Organomet. Chem.* **1994**, *36*, 283 and references therein.
(d) Evans, W.J. *Adv. Organomet. Chem.* **1985**, *24*, 131 and references therein.
(e) Kagan, H.B.; Namy, J.L. in *Handbook on the Physics and Chemistry of Rare Earths*; Gschneider, K.A., Eyring, L., Eds.; Elsevier: Amsterdam, 1984; Chapter 50.

- (f) Marks, T.J.; Ernst, R.D. in *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F.G.S., Abel, E.W. Eds.; Pergamon Press: Oxford, U.K., 1982; Chapter 21 and references therein.
10. (a) Sen, A.; Chebolu, V.; Rheingold, A. L.; *Inorg. Chem.*, **1987**, 26, 1821.
- (b) Evans, W. J.; Anwender, R.; Ansari, M. A.; Ziller, J. W.; *Inorg. Chem.*, **1995**, 34, 5.
- (c) Hitchcock, P. B.; Holmes, S. A.; Lappert, M. F.; Tian, S. *J. Chem. Soc. Chem. Commun.* **1994**, 2691.
- (d) Biagini, P.; Lugli, G.; Abis, L.; Millini, R. *J. Organomet. Chem.* **1994**, 474, C16.
11. (a) Chebolu, V.; Whittle, R. R.; Sen, A., *Inorg. Chem.*, **1985**, 24, 3082.
- (b) Evans, W. J.; Drummond, D. K.; Zhang, H.; Atwood, J. L., *Inorg. Chem.*, **1988**, 27, 575.
- (c) Evans, W. J.; Rabe, G. W.; Ziller, J. W.; *Inorg. Chem.*, **1994**, 33, 3072.
- (d) White III, J. P.; Deng, H.; Boyd, E. P.; Gallucci, J.; Shore, S. G.; *Inorg. Chem.*, **1994**, 33, 1685.
- (e) Evans, W. J.; Rabe, G. W.; Ziller, J. W., *Organometallics*, **1994**, 13, 1641.
- (f) Minhas, R.; Song, J.; Ma, Y.; Gambarotta, S. *Inorganic Chemistry* **1996**, 35, 1866.
- (g) Evans, J. W.; Ansari, M. A.; Ziller, J. W. *Inorg. Chem.* **1996**, 35, 5435.
- (h) Schaverin, C. J.; Orpen, A. G. *Inorg. Chem.* **1991**, 30, 4968
- (h) Edelmann, F. T. *Coord. Chem. Rev.* **1995**, 137, 403.

- (k) Schumann, H.; Rosenthal, E. C. E.; Winterfield, J.; Kociok-Kohn, G.; *J. Organomet. Chem.* **1995**, *495*, C12.
12. (a) Nief, F.; Ricard, L. *J. Organomet. Chem.*, **1994**, *464*, 149.
 (b) Rabe, G.; Riede, J.; Schier, A. *Inorg. Chem.* **1996**, *35*, 2680.
 (c) Gosink, H. J.; Nief, F.; Ricard, L.; Mathey, F. *Inorg. Chem.* **1995**, *34*, 1306.
 (d) Fryzuk, M. D.; Haddad, T. S.; Rettig, S. J. *Organometallics* **1992**, *11*, 2967.
13. (a) Takats, J. *J. Alloys Compd.* **1997**, *249*, 52.
 (b) Hasinoff, L.; Takats, J.; Zhang, X.W.; Bond, A.H.; Rogers, R.D. *J. Am. Chem. Soc.* **1994**, *116*, 8833.
 (c) Ferrence, G.M.; McDonald, R.; Takats, J. *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 2233.
14. Evans, W.J.; Clark, R.D.; Ansari, M.A.; Ziller, J.W. *J. Am. Chem. Soc.* **1998**, *120*, 9555.
15. Song, J.; Gambarotta, S. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2141.
16. Anhydrous SmCl_3 was prepared following a standard procedure:
 (a) Freeman, J. H.; Smith, M. L., *J. Inorg. Nucl. Chem.*, **1958**, *7*, 224 and was transformed into the corresponding tetrahydrofuranate.
 (b) Manzer, L. E., *Inorg. Synth.*, **1982**, *21*, 135.
17. Evans, W. J.; Grate, J. W.; Choi, H. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L., *J. Am. Chem. Soc.*, **1985**, *107*, 941.
18. P.A. Gale, J.L. Sessler, V. Král, V. Lynch, *J. Am. Chem. Soc.* **1996**, *118*, 5140.
19. (a) Mabbs, M. B.; Machin, D.; *Magnetism and Transition Metal Complexes*; Chapman and Hall; London, **1973**.

- (b) Foese, G.; Gorter, C. J.; Smits, L. J., Constantes Selectionnes,
Diamagnetisme, Paramagnetisme Relaxation Paramagnetique; Masson, Paris,
1957.
19. a) Knjazhanski, S. Y.; Bulychiev, B. M.; Belskii, V. K.; Soloveichik, G.L. *J. Organomet. Chem.* **1987**, 327, 173.
- b) Gun'ko, Y. K.; Bulychiev, B. M.; Sizov, A. I.; Bel'sky, V. K., Soloveichik, G. L. *J. Organomet. Chem.* **1990**, 390, 153;
- c) Belsky, V. K.; Gun'ko, Y. K.; Bulychiev, B. M.; Soloveichik, G. L. *J. Organomet. Chem.* **1991**, 419, 299.
21. Ephritikhine, M. *Chem. Rev.* **1997**, 97, 2193.

CHAPTER V

The reactions of Sm(II) and Sm(III) complexes of calix-tetrapyrrole with acetylene: Formation of an "N-confused" calix-tetrapyrrole ring.

V.I : Introduction

The coordination chemistry of divalent samarium supported by Cp-based ligand systems is characterized by a series of remarkable transformations¹ that can be rationalized in terms of carbene-like reactivity. The two electrons necessary for this type of transformation are typically provided by the cooperative attack of two or more divalent samarium centers on the same substrate. It is thus surprising that, given the uniqueness of this chemistry and the potential provided by these systems, information about the reactivity of divalent complexes based on ligand systems other than Cp derivatives remains so scarce.

As part of our efforts to develop the chemistry of divalent samarium with alternative ligand systems, we have been investigating the behavior of divalent samarium complexes with polypyrrole anions. The results have so far been encouraging. Four novel dinitrogen complexes have been isolated and characterized by using di- and tetrapyrrole ligands.² The calix-tetrapyrrole ligand in particular has proven to be rather versatile since it has allowed for both the reversible fixation³ and the encapsulation of dinitrogen into a Sm₂Li₄ octahedral cage⁴. In addition, the sole example in lanthanide chemistry of reversible fixation of ethylene⁵ has also been documented with this ligand system.

A few years ago, Evans described the preparation and characterization of [(C₅Me₅)₂Sm(THF)]₂(μ-η¹:η¹-C₂) obtained upon reaction of samarocene with acetylene.

This species contains a C_2 unit bridging the two samarium centers in an end-on fashion.⁶ We were particularly attracted by this strange reaction since the C_2 moiety is isoelectronic with N_2 and thus it may provide an interesting and convenient model for studying the remarkable complexity of factors which promote the fixation and reduction of dinitrogen. Our primary objective was an assessment of the role of the alkali cations, invariably retained within the calix-tetrapyrrole frame, which, similar to the case of dinitrogen reduction, might also play an important role in acetylene activation.

Herein we describe the reactivity of both Sm(II) and Sm(III) calix-tetrapyrrole complexes with acetylene as well as a rare example of ring isomerization closely reminiscent of the so-called N-confused systems reported in a few cases in porphyrine chemistry.

V.2 : Experimental Section

All operations were performed under an inert atmosphere of a nitrogen-filled drybox or by using standard Schlenk-type glassware in combination with a nitrogen-vacuum line. Solvents were dried by passing through a column of Al_2O_3 under an inert atmosphere prior to use, degassed *in vacuo* and transferred and stored under inert atmosphere. $(\text{Et}_8\text{-calix-pyrrole})(\text{CH}_3)\text{Sm}[\text{Li}(\text{THF})]_2[\text{Li}(\text{THF})_2](\mu^3\text{-Cl})\}^7$ $(\text{Et}_8\text{-calix-pyrrole})(\text{THF}) \text{Sm}(\mu\text{-H})[\text{Li}(\text{THF})]_2 \cdot 3\text{THF}$,⁷ and $(\text{R}_8\text{-calix-pyrrole})(\text{L})\text{Sm}[\text{Li}(\text{THF})_2][\text{Li}(\text{THF})]_2(\mu_3\text{-OCH=CH}_2)$ [$\text{R} = 1/2 \text{-(CH}_2\text{)}_5\text{-}$, $\text{L} = \text{THF}$; $\text{R} = \text{Et}$, $\text{L} = \text{Et}_2\text{O}$]⁵ were prepared according to literature procedures. C_6D_6 and THF-d^8 were dried over Na/K alloy, vacuum-transferred into ampoules, and stored under nitrogen prior to use. NMR spectra were recorded on a Varian Gemini 200 and on a Bruker AMX-500 spectrometer using vacuum sealed NMR tubes prepared inside a drybox. Infrared spectra were recorded on a Mattson 3000 FTIR instrument from Nujol mulls prepared inside the drybox. Samples for magnetic susceptibility measurements were carried out at room temperature using a Gouy balance (Johnson Matthey). Magnetic moments were calculated by following standard methods⁸ and corrections for underlying diamagnetism were applied to the data⁹. Elemental analyses were carried out using a Perkin-Elmer Series II CHN/O 2400 analyzer.

Preparation of $(\{[-(\text{CH}_2)_5\text{-}]_4\text{-calix-pyrrole}\}\text{Sm})_2(\mu\text{-C}_2\text{Li}_4) \cdot \text{THF}$ (5.1a).

The exposure of a deep green solution of $\{[-(\text{CH}_2)_5\text{-}]_4\text{-calix-tetrapyrrole}\}(\text{THF}) \text{Sm}[\text{Li}(\text{THF})]_2[\text{Li}(\text{THF})_2](\mu_3\text{-OCH=CH}_2)$ (4.3 g, 3.9 mmol) in hexanes (100 mL) to 1 atm of acetylene turned the color immediately to purple then gradually to light yellow

over a 20 minute period. Pale yellow **5.1a** separated as a fine, microcrystalline solid upon standing for 3 hours at room temperature (1.5 g, 0.9 mmol, 46%). Crystals suitable for X-ray were grown at room temperature by layering a concentrated THF solution of **5.1a** with hexanes. I.R. (Nujol mull, cm^{-1}): 3088(w), 2731(w), 2664(w), 1658(w), 1564(w), 1344(s), 1309(m), 1290(s), 1267(s), 1235(s), 1136(m), 1070(s), 1050(s), 983(w), 932(w), 898(s), 876(s), 831(m), 777(s), 735(s), 688(m), 582(m). El. Anal. Calcd (Found) for $\text{C}_{86}\text{H}_{106}\text{N}_8\text{O Sm}_2\text{Li}_4$: C 64.70(64.02), H 6.69(6.36), N 7.029(6.91). $\mu_{\text{eff}} = 2.37\mu_{\text{B}}$.

Preparation of $\{(\text{Et}_8\text{-calix-pyrrole})\text{Sm}\}_2(\mu\text{-C}_2\text{Li}_4)\cdot\text{Et}_2\text{O}$ (**5.1b**)

A stirred solution of $(\text{Et}_8\text{-calix-tetrapyrrole})(\text{THF})\text{Sm}(\mu\text{-H})[\text{Li}(\text{THF})]_2$ (2.5 g, 2.2 mmol) in THF (50 mL) was saturated with acetylene (1 atm, room T). After 30 minutes, the resulting purple-red solution was evaporated to dryness and the residue was extracted with diethyl ether (100 mL). After standing for 24 hours at room temperature a mixture of red crystals of **5.2b** (32%) as well as colorless crystals of **5.1b** (1.0 g, 0.7 mmol, 25%) was obtained and the two components fractionally separated. El. Anal. Calcd (Found) for $\text{C}_{78}\text{H}_{106}\text{N}_8\text{OSm}_2\text{Li}_4$: C 62.44(62.42), H 7.12(7.37), N 7.47 (7.16). I.R. (Nujol mull, cm^{-1}) ν : 3083(w), 2736(w), 2610(w), 1660(w), 1578(w), 1360(s), 1323(m), 1281(s), 1270(s), 1155(m), 1075(s), 1030(s), 965(w), 933(w), 895(m), 855(s), 830(m), 760(m), 730(s), 680(m).). ^1H -NMR ($\text{d}^8\text{-THF}$, 500 MHz, 23°C) δ : 6.20, 5.96 (two pseudod., pyrrole rings 4H and 4H), 2.17, 4.56, 3.17 (broad s, m, and quadruplet for CH_3 and CH_2 groups of two ethyl group, 12H, 4H, 4H), 1.75, 3.58, 2.02 (broad s, m, broad quadruplet for CH_3 and CH_2 groups of four ethyl group, 24H, 8H, 8H), 0.65, 1.95 (sharp triplet, broad quadruplet

for CH₃ and CH₂ groups of two ethyl group, 12H, 8H), 1.10, 3.25 (t and quadruplet for CH₃ and CH₂ groups of ether, 6H and 4H). C¹³-NMR (d⁸-THF, 125.72MHz, 23°C) δ: 105.45, 92.05 (CH pyrrole), 10.63, 8.81, 27.73 (CH₃ of ethyl groups), 34.24, 28.63, 26.01 (CH₂ of ethyl groups), 28.13, 8.41 (CH₂ and CH₃, ether), 189.98, 135.08 (ring quaternary C atoms). $\mu_{\text{eff}} = 2.45 \mu_{\text{B}}$.

Preparation of {(Et₈-calix-pyrrole)SmLi[Li(thf)]₂(μ³-OCH=CH₂)}₂(μ,η²,η'²-HC=C=C=CH) (5.2b)

Method A: The exposure of a solution of (Et₈-calix-pyrrole)(Et₂O)Sm[Li(THF)]₂[Li(THF)₂](μ³-OCH=CH₂) (1.3 g, 1.2 mmol) in diethyl ether (100 mL) to acetylene (1 atm, room T) instantly turned the color to purple-red. After standing at room temperature for 2 days, cherry-red crystals of **5.2b** separated (0.8 g, 0.4 mmol, 66%). I.R. (Nujol mull, cm⁻¹) 3072(w), 2722(w), 1589(w), 1539(m), 1324(s), 1286(w), 1260(s), 1244(s), 1208(w), 1152(m), 1132(m), 1104(m), 1041(s), 971(m), 922(m), 889(s), 835(s), 781(s), 747(s), 672(w). El. Anal. Calcd (Found) for C₉₆H₁₃₆Li₆N₈O₆Sm₂: C 62.64(62.44), H 7.45(7.56), N 6.09(5.93).). H¹-NMR (d⁸-THF, 500 MHz, 23°C) δ: 6.31 (s, pyrrole rings, 8H), 3.35, 1.35 (two broad s, coordinated THF, 16H, 16H), 2.25, 2.30, 4.35 (three broad multiplets, CH₃ and CH₂ of four ethyl groups, 12H, 4H, 4H), 0.10, 1.01, 2.12 (three broad multiplets, CH₃ and CH₂ of four ethyl groups, 12H, 4H, 4H), 4.55 (broad s, CH butatrienyl, 1H), enolate resonances could not conclusively be located. C¹³-NMR (d⁸-THF, 125.72MHz, 23°C) δ: 96.19 (CH pyrrole), 25.31, 27.28 (CH₂ THF), 10.14, 30.19 (CH₃ and CH₂ of four ethyl groups), 7.81, 28.19 (CH₃ and CH₂ of four ethyl groups),

100.53 (CH butatrienediyl group), 169.23, 150.51, 98.79, 49.50 (quaternary C atoms).

$\mu_{\text{eff}} = 2.54 \mu_{\text{B}}$.

Method B: A solution of (Et₈-calix-pyrrole)(CH₃)Sm[Li(thf)]₂[Li(thf)](μ³-Cl) (2.5 g, 2.4 mmol) in THF (100 mL) was exposed to acetylene (1 atm, room T) causing a colour change to purple-red. After stirring the solution for 2 hours at room temperature, the solvent was evaporated to dryness and the residue extracted with diethyl ether (100 mL). After filtration to remove a small amount of insoluble solid, the solution was allowed to stand at room temperature. After 24 hours a mixture of **5.2b** (34%) as well as **5.1b** (30%) separated. The products were identified on the basis of their analytical, spectroscopic and crystallographic properties.

Preparation of {[Et₈-calix-pyrrole*]Sm}[Li(thf)₂]₂ (5.3b**)**

The mother liquor of the above preparation (method A) was allowed to stand at room temperature for 7 days resulting in the separation of large, bright yellow crystals of **5.3b** (0.15 g, 0.09 mmol, 15%). El. Anal. Calcd (Found) for C₈₈H₁₂₄N₈O₄Sm₂Li₂: C 63.19(63.42), H 7.47(7.97), N 6.70 (6.76). I.R. (Nujol mull, cm⁻¹) ν: 3080(w), 2730(w), 2600(w), 1640(w), 1568(w), 1340(s), 1300(m), 1295(s), 1260(s), 1125(m), 1075(s), 1030(s), 980(w), 930(w), 895(s), 875(s), 830(m), 770(s), 730(s), 688(m). H¹-NMR (d⁸-THF, 500 MHz, 23°C) δ: 6.95 (s, CH pyrrole, 1H), 6.37 (s, CH pyrrole, 2H), 5.95 (broad s, CH₃ ethyl, 6H), 5.81(s, CH pyrrole, 1H), 5.03 (s, CH pyrrole, 2H), 4.67 (s, CH pyrrole, 1H), 4.07 (s, CH pyrrole, 1H), 3.59 (broad s, CH₂ THF, 16H), 3.40 (q, CH₂ ethyl, 1H), 2.44 (broad q, CH₂ ethyl, 1H), 2.13 (q, CH₂ ethyl, 4H), 1.73 (bs, CH₂ THF, 16H), 1.50 (q, CH₂ ethyl, 1H), 1.41 (t, CH₃ ethyl, 6H) 1.06 (tt, CH₃ ethyl 3H), 0.78 (broad q, CH₂ ethyl,

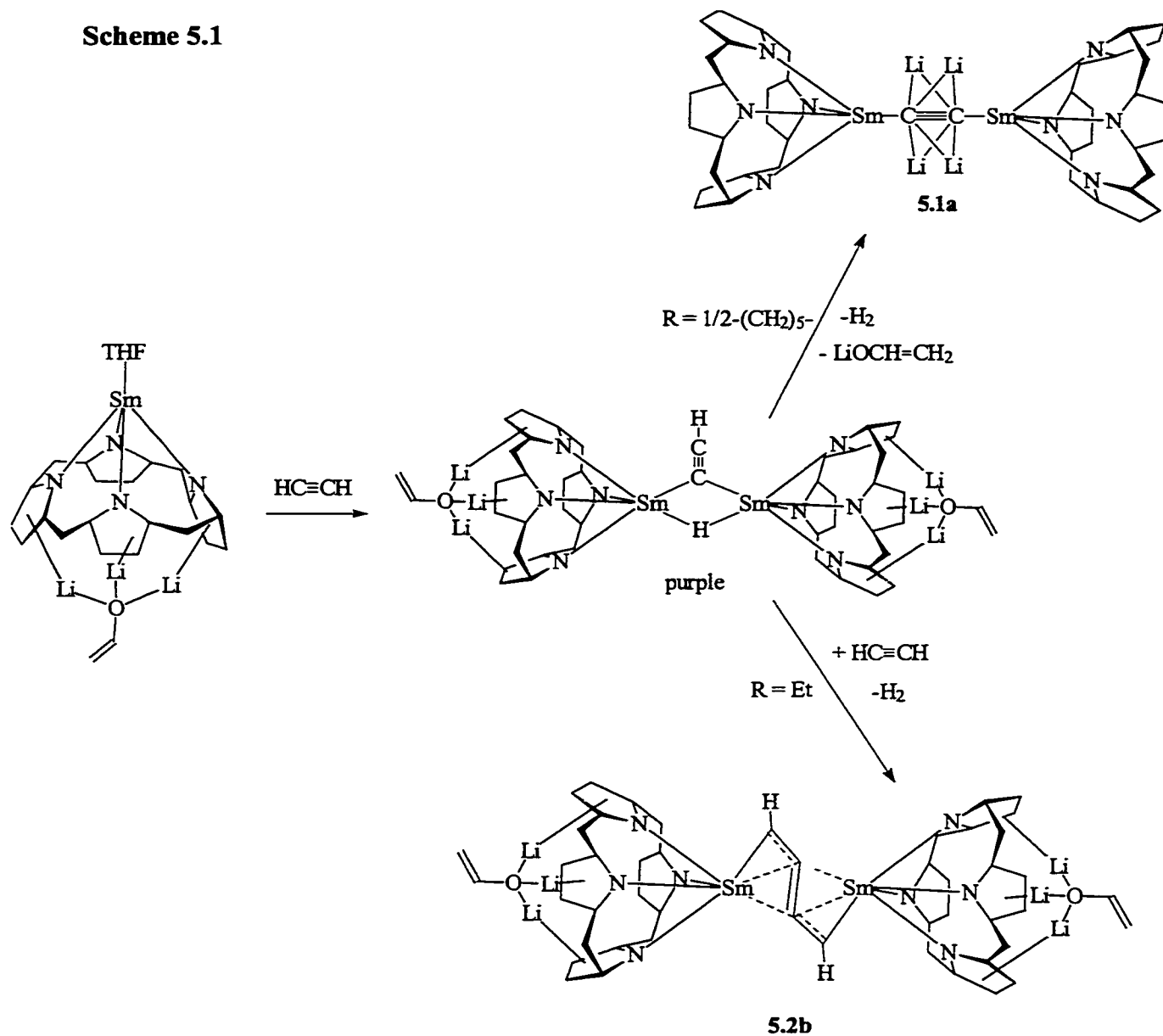
1H), 0.62 (q, CH₂ ethyl, 4H), 0.61 (q, CH₂ ethyl, 1H), 0.60 (q, CH₂ ethyl, 2H), 0.52 (broad q, CH₂ ethyl, 1H), 0.09 (t, CH₃ ethyl, 3H), -1.53 (broad s, CH₃ ethyl, 3H), -4.56 (broad s, CH₃ ethyl 3H). C¹³-NMR (d⁸-THF, 125.72MHz, 23°C) δ: 10.69, 9.75, 9.55, 9.21, 8.84, 8.30, 7.90, 7.04 (Me ethyl), 28.73, 30.99 (CH₂ ethyl), 105.44, 99.81 (CH pyrrole), 50.77 (quaternary C ring), 68.22, 26.38 (CH₂ THF). Quaternary carbon atoms of pyrrole could not be located. $\mu_{\text{eff}} = 2.57 \mu_{\text{B}}$.

V.3 : Results and Discussion

The exposure of a dark emerald green solution of [$\{(-\text{CH}_2)_5\}_4\text{-calix-pyrrole}\}(\text{THF})\text{Sm}\{\text{Li}(\text{thf})_2\{\text{Li}(\text{thf})_2\}(\mu_3\text{-OCH=CH}_2)\}^5$ in hexane to an excess of acetylene gas resulted in a sudden color change to dark purple. However, upon a period of minutes at room temperature the solution discolored to originate a pale yellow solution from which nearly colorless crystals of a new complex [$\{(-\text{CH}_2)_5\}_4\text{-calix-pyrrole}\}\text{Sm}[\text{Li}(\text{THF})_2]_2(\mu\text{-C}_2\text{Li}_4)$ (**5.1a**) separated (Scheme 5.1). The formation of the trivalent **5.1a** implies the one electron oxidation of two Sm(II) starting complexes. Thus, given that equivalent amounts of H₂ gas were released during the reaction, it is reasonable to envision the reaction as resulting from the cooperative oxidative addition of two divalent metal centers on the same acetylene molecule to form an intermediate hydride/acetylide species. The formation of an intense purple color during the first minutes of the reaction time strongly indicates the formation of an intermediate species. Subsequent elimination of H₂ (probably driven by the a relatively high acidity of the

acetylide residual hydrogen atom) and dissociation of Li(enolate) affords the final compound.

Scheme 5.1



The structure of **5.1a** as revealed by an X-ray diffraction analysis shows some interesting structural analogies with the encapsulated dinitrogen complex⁴ of the same ligand system. Even in this case, the C_2 unit is encapsulated within a rather regular

Sm_2Li_4 octahedron. Different from N_2 , however, the C_2 unit is placed end-on with respect to the two Sm centers and side-on with respect to the four lithium cations. Also in contrast to the encapsulated dinitrogen complex, the C-C distance is very short and is indicative of minimal extent of acetylene reduction. The light color of **5.1a**, as well as magnetic susceptibility data ($\mu_{\text{eff}} = 2.37\mu_{\text{B}}$ per dimer) also confirms the presence of two trivalent Sm centers and are consistent with the presence of an intact C-C triple bond.

Reaction carried out under identical conditions but with (Et_8 -calix-pyrrole) $(\text{Et}_2\text{O})\text{Sm}[\text{Li}(\text{THF})]_2[\text{Li}(\text{THF})_2](\mu^3\text{-OCH=CH}_2)^5$ and acetylene also resulted in an instant color change from green to dark purple-red. In this case, however, the intense color persisted and cherry-red crystals of a new compound formulated as $\{[(\text{Et}_8\text{-calix-pyrrole})\text{SmLi}][\text{Li}(\text{thf})]_2(\mu^3\text{-OCH=CH}_2)\}_2(\mu, \eta^2, \eta'^2\text{-HC=C=C=CH})$ (**5.2b**) were isolated in good yield and analytically pure form from diethyl ether (Scheme 5.1). The complex is obviously formed by the coupling of two acetylene molecules accompanied by the release of H_2 . The reaction may be rationalized in terms of formation of the same $\{[(\text{Et}_8\text{-calix-pyrrole})\text{SmLi}][\text{Li}(\text{thf})]_2(\mu^3\text{-OCH=CH}_2)\}_2(\mu\text{-CCH})(\mu\text{-H})$ intermediate which, in the case of the cyclohexyl derivative, led to the formation of **5.1a**. However, metathesis of a second molecule of acetylene, instead of H_2 elimination, presumably results in a dimeric $\{[(\text{Et}_8\text{-calix-pyrrole})\text{SmLi}][\text{Li}(\text{thf})]_2(\mu^3\text{-OCH=CH}_2)\}_2(\mu\text{-CCH})_2$ complex which isomerizes to generate **5.2b**.

Surprisingly, both reactions proceed selectively towards the formation of the two compounds regardless of variations in solvent system or temperature. In neither case was it possible to isolate the purple intermediate even by carrying out the reactions at -78°C , nor did we observe evidence for the presence of other compounds in the reaction

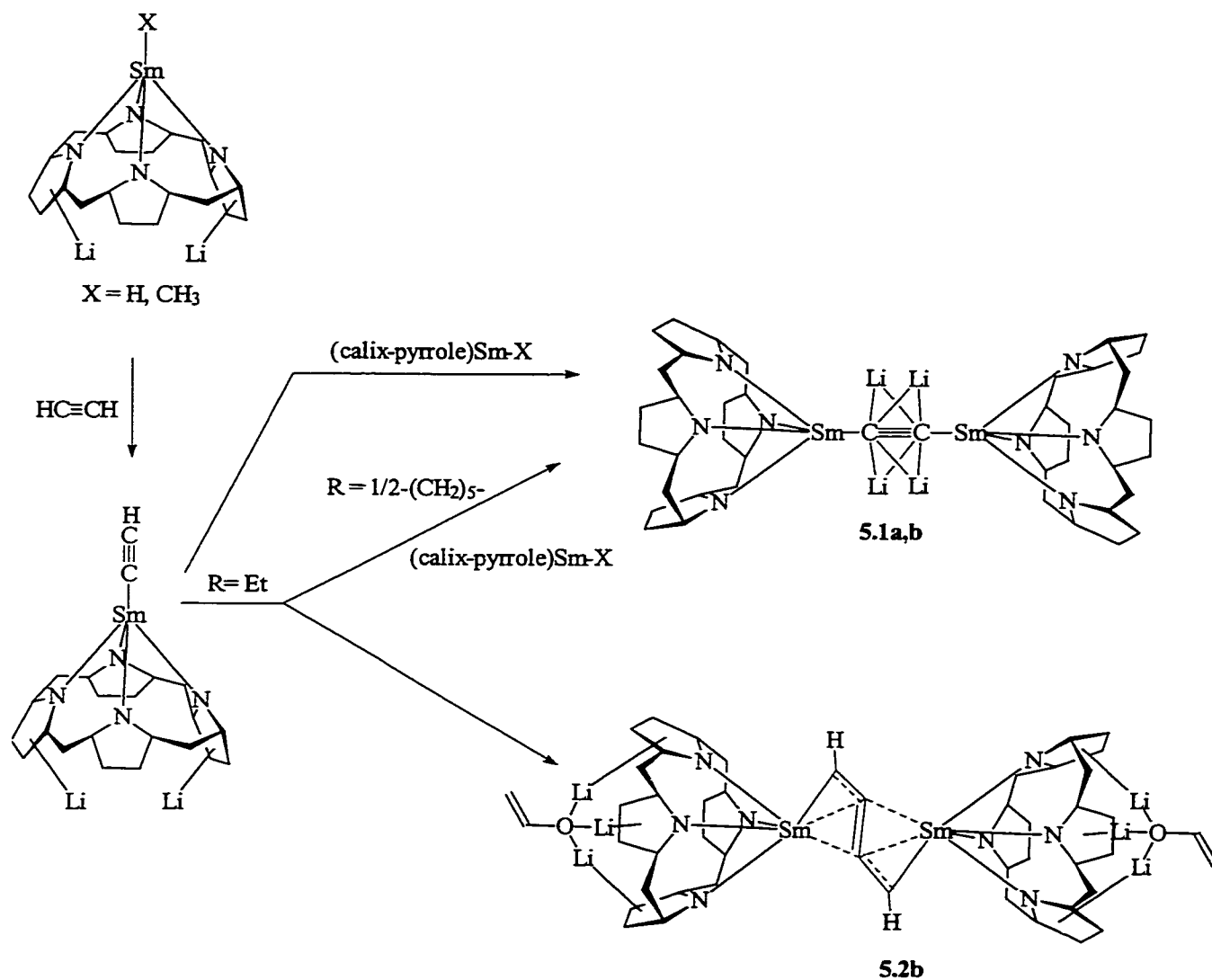
mixtures. Both **5.1a** and **5.2b** showed no signs of reactivity with H₂ while both compounds were found to be indefinitely stable at 70°C.

Considering the close steric and electronic similarity between the two calix-tetrapyrrole ligands, the only explanation for the diversity of the reaction pathways relies on kinetic factors. We propose that the formation of the two compounds results from two different reaction pathways of the same intermediate. Obviously, the nature of the substituents plays an important role in modifying the activation energies of the two competitive processes (dehydrogenation versus methathesis/coupling) thus determining, in the end, the nature of the final product. The situation is closely reminiscent of the behavior of the same compounds with dinitrogen to the extent that the degree of N₂ activation is extremely sensitive to the nature of the ligand substituents. Whereas labile fixation of N₂ occurs when R = 1/2 -(CH₂)₅-, irreversible N₂ reduction with considerable increase in the N-N distance occurs when R = Et. It should also be reiterated that both Sm(II) calix-tetrapyrrole systems [R = Et, 1/2 -(CH₂)₅-] form isostructural π -complexes with ethylene. Although in both cases the ethylene moiety is symmetrically π -bonded between the two Sm(calix-pyrrole) units, the extent of ethylene fixation is remarkably sensitive to the nature of the substituents.

As mentioned in Scheme 5.1, a key intermediate in the formation of both **5.1a** and **5.2b** may be a trivalent hydride species. In order to probe this possibility, we explored the reactivity of the recently prepared trivalent samarium hydride and alkyl tetrapyrrole derivatives⁷ with acetylene. Treatment of either (Et₈-calix-pyrrole)(THF)Sm(μ -H)[Li(THF)]₂ or {(Et₈-calix-pyrrole)CH₃Sm[Li(THF)]₂[Li(THF)](μ^3 -Cl)} with acetylene resulted in rapid reactions from which similar mixtures of the two complexes in similar

ratios, the colorless $[(\text{Et}_8\text{-calix-pyrrole})\text{Sm}]_2[\mu\text{-Li}_4\text{C}_2]$ (**5.1b**) and the bright-red $\{[(\text{Et}_8\text{-calix-pyrrole})\text{SmLi}][\text{Li}(\text{THF})]_2(\mu^3\text{-OCH=CH}_2)\}(\mu, \eta^2, \eta'^2\text{-HC=C=C=CH})$ (**5.2b**), were obtained in crystalline form and acceptable yield (Scheme 5.2).

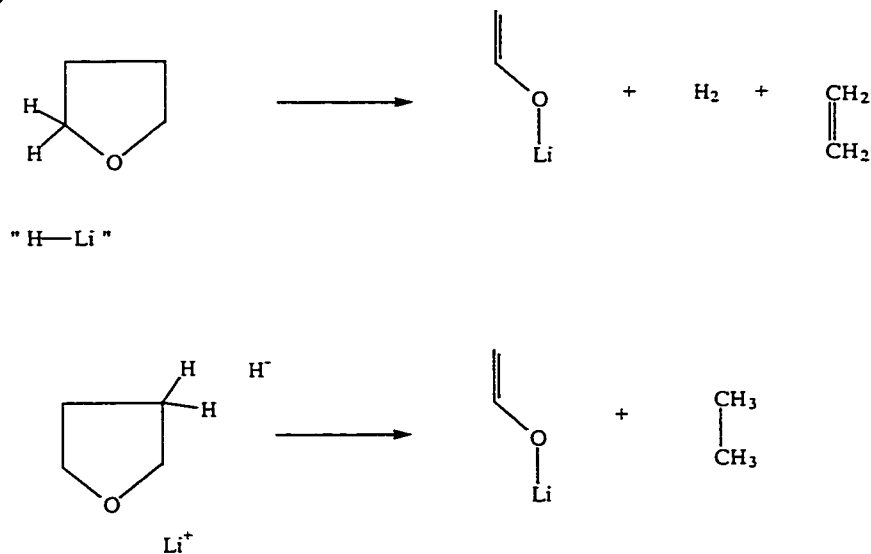
Scheme 5.2



Even in this case the reaction was very sensitive to the nature of the ligand substituents. As in the case of the reaction of $\text{Sm}(\text{II})$ complexes with acetylene, the

formation of **5.2b** resulting from partial dehydrogenation and dimerization of two acetylene molecules was observed only in the case where $R = Et$. Conversely, when $R = 1/2 -(CH_2)_5-$, complex **5.1a** was the only product isolated from clean reactions involving either Sm(II), Sm-alkyl, or Sm-hydride precursors. The fact that the same products obtained from the reaction of the divalent samarium compounds with acetylene were also obtained by using Sm(III) precursors supports the idea that indeed a Sm-hydride is involved in the reactivity of divalent samarium with acetylene. However, although the formation of the butatrienediyil moiety of **5.2b** from a Sm(III) hydride or alkyl can be easily explained in terms of carbenoid-type coupling of two Sm-acetylide moieties, its formation implies the presence of Li(enolate) which, in contrast to the Sm(II) reagents, *is absent in the samarium hydride and methyl compounds*. The Li(enolate) unit arises from THF cleavage which can be achieved through either radical or anionic attack involving either the THF α -hydrogen or β -carbon atoms (Scheme 5.3). Both processes afford, in addition to the enolate anion, a mixture of ethylene/ H_2 or ethane, respectively.

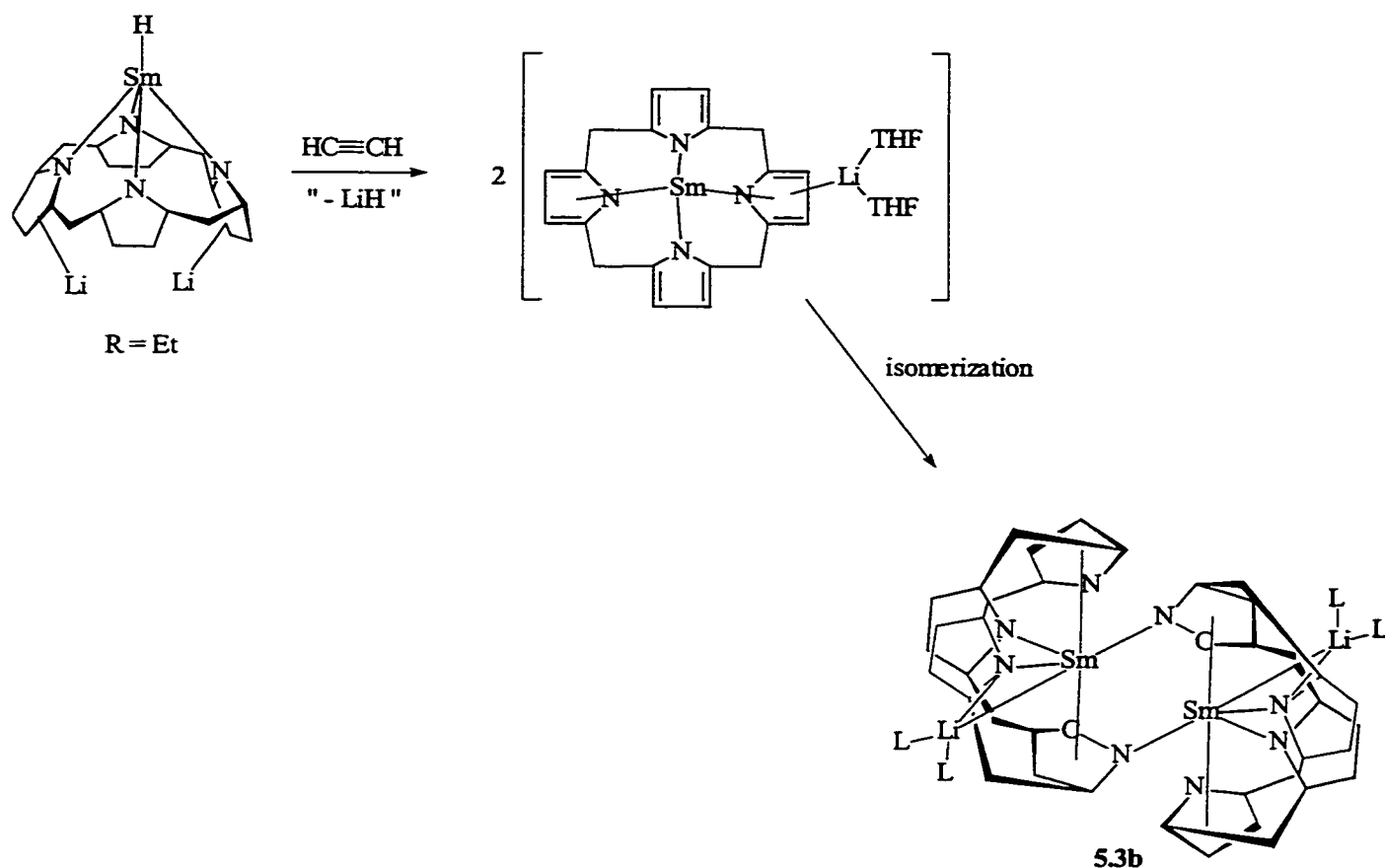
Scheme 3



It is not uncommon to find these products altogether in reaction mixtures where THF cleavage occurs as a result of lack of selectivity. The THF cleavage process also may be favored by the coordination of Lewis acids to the oxygen atom. Obviously the trivalent Sm-R [R = H, Me] compounds used in this work cannot be responsible *per se* for the formation of the two enolate anions present in **5.2b** since both are indefinitely stable in THF even at higher temperatures. The process leading to the formation of **5.1** also cannot be responsible, since the two lithium atoms present in the structure of the Sm-R reagents must be retained in the structure of **5.1a,b** and therefore cannot be made available for THF cleavage. Thus the presence of the enolate fragment in **5.2b** implies that another product must be formed during the reaction with acetylene. In other words, the reaction must necessarily also lead to the formation of another species in which both the hydride (or alkyl) group and the lithium cation participate in forming Li(enolate).

Accordingly, a third product (**5.3b**) was isolated in low yield (7%) from the mother liquor of the reaction of (Et₈-calix-pyrrole)(thf)Sm(μ -H)[Li(thf)]₂ with acetylene (Scheme 5.4). Its structure, as indicated by X-ray analysis, is unique in the sense that the ligand has undergone of a $\alpha \rightarrow \beta$ migration of the alkyl chain.

Scheme 5.4



The reorganized calix-tetrapyrrole macrocycle of **5.3b** is reminiscent of the "N-confused porphyrins"¹⁸ isolated by Furuta¹⁹ and Latos²⁰ and whose rational synthesis was more recently achieved by Dolphin.²¹ Given the low yield, the possibility that the presence of the N-confused calix-tetrapyrrole may be caused in this case by adventitious (yet reproducible) carrying on from the original ligand preparation cannot be conclusively excluded. However, it should be reiterated that **5.3b** was isolated after *four* subsequent reactions, and purification of *three* different precursors. Thus, assuming that the formation of **5.3b** is indeed triggered by the reaction with acetylene, questions arise about the factors that promoted the isomerization of the macrocycle with consequent

assembly of the dinuclear structure. At this stage we cannot offer a detailed explanation for the formation of **5.3b**. However, the possibility that the rearrangement could be triggered by attack on the pyrrole β -hydrogen by one strongly basic function (perhaps a vinyl formed via insertion of acetylene into the Sm-H bond) followed by chain shifting can be confidently ruled out. The recently characterized trivalent (calix-tetrapyrrole)Sm-vinyl, isostructural with the methyl derivative used in this work, rather produces a Sm(II) species upon thermolysis.⁷ Thus, we can only observe that the formation of **5.3b** from the hydride samarium complex during the reaction with acetylene implies the *formal* dissociation of a LiH unit followed by ring reorganization. A LiR [R = H, alkyl] unit is precisely what is necessary for the cleavage of a THF molecule and the formation of the Li(enolate) present in **5.2b**, as well as balancing the overall stoichiometry of the reaction.

V.4 : X-ray Crystallography

Suitable crystals were selected, mounted on thin, glass fibres using paraffin oil and cooled to the data collection temperature. Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° ω -scans at 0, 90, and 180° in ϕ . Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied.¹⁰

Systematic absences in the diffraction data and unit-cell parameters were uniquely consistent with the reported space group. The structures were solved by direct methods, completed with difference Fourier syntheses and refined with full-matrix least-squares

procedures based on F^2 . A molecule of cocrystallized diethyl ether solvent was located in **5.1a**. The compound molecule of **5.3b** and two symmetry-unique compound molecules of **5.2b** were located at inversion centres. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 5.03 program library (Sheldrick, 1997, WI.). Crystal data are summarized in the Appendix, Table 4.

Complex **5.1b** is dinuclear with two calix-tetrapyrrole Sm units bridged by a C_2Li_4 fragment. The calix-tetrapyrrole ligand surrounds the samarium atom by adopting the characteristic basket-like conformation. The coordination geometry of Sm is distorted pseudo trigonal bipyramidal. Two centroids of two π -bonded pyrrole rings occupy the equatorial positions together with a carbon atom from the bridging carbide, while the other two nitrogen atoms of two σ -bonded pyrroles are located on the axial plane [N(2)-Sm(1)-N(3) = 88.14(19)°, N(5)Sm(2)-N(7) = 163.5(2)°, N(1)-Sm(1)-C(81) = 74.1(2)°, N(5)-Sm(2)-C(82) = 81.2(2)°]. The dinuclear structure is held together by a nearly linear C_2 unit [Sm(1)-C(81)-C(82) = 179.3(7)°; C(81)-C(82)-Sm(2) = 178.7(7)°] which bridges the two samarium atoms in an end-on fashion. The C-C distance [C(81)-C(82) = 1.224(10)Å] compares well with that observed in other lanthanide carbide complexes¹¹ and is only slightly longer than that observed in free acetylene [1.205Å]¹². The Sm-C bond distances [Sm(1)-C(81) = 2.559(8)Å, Sm(2)-C(82) = 2.578(8)Å] are, within error limits, similar to those observed in terminally bonded and alkyl bridged Sm complexes of the same ligand system.^{7,13} The four lithium cations are located in the region between the two Sm(calix-tetrapyrrole) units forming a flattened tetrahedron bisected by the Sm-CC-

Sm vector. The lithium atoms are asymmetrically side-on connected to the two carbon atoms of the C_2 unit forming both short and long Li-C distances [Li(1)-C(82) = 2.353(15)Å, Li(1)-C(81) = 2.530(15)Å, Li(2)-C(81) = 2.292(15)Å, Li(2)-C(82) = 2.504(15)Å]. In addition, they are also connected to the pyrrole nitrogen atoms of two separate Sm(calix-tetrapyrrole) units [Li(3)-N(6) = 2.082(16)Å, Li(2)-N(3) = 2.080(14)Å, Li(1)-N(8) = 2.099(15)Å] using both σ - and π -interactions.

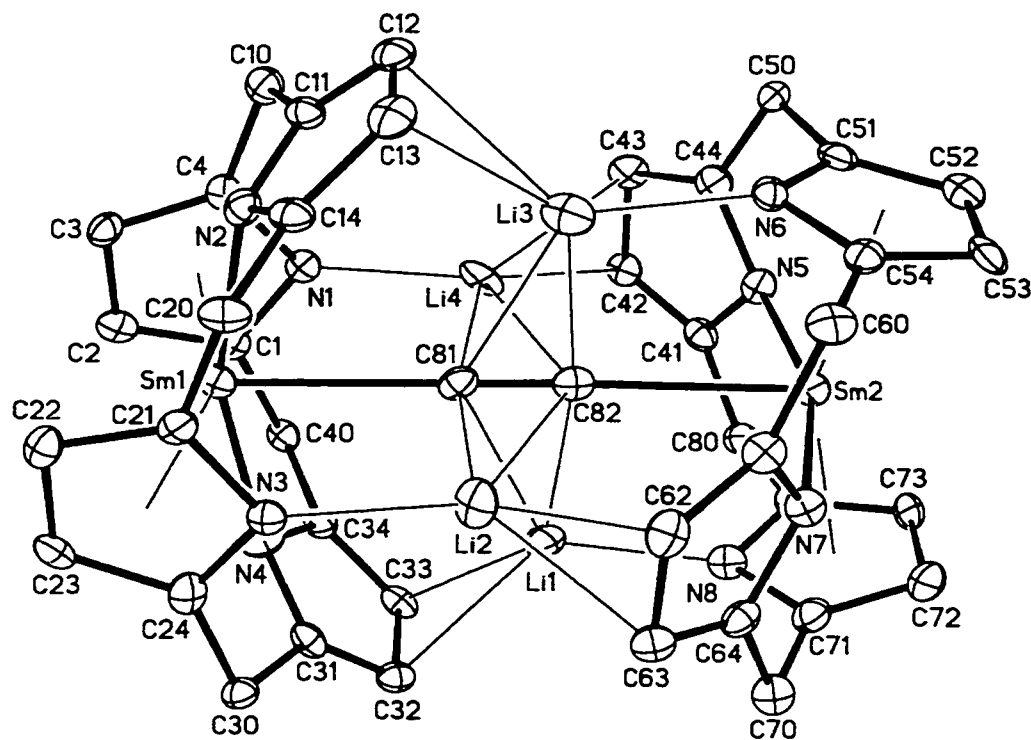


Fig. 5.1. X-ray Structure of 5.1b, $\{(\text{Et}_8\text{-calix-pyrrole})\text{Sm}\}_2(\mu\text{-C}_2\text{Li}_4)\cdot\text{Et}_2\text{O}$

Selected Bond Distances (Å) and Angles (°): C(81)-C(82) = 1.224(10), Sm(1)-C(81) = 2.559(8), Sm(2)-C(82) = 2.578(8), Li(1)-C(82) = 2.353(15), Li(1)-C(81) = 2.530(15), Li(2)-C(81) = 2.292(15), Li(2)-C(82) = 2.504(15), Li(3)-N(6) = 2.082(16), Li(2)-N(3) = 2.080(14), Li(1)-N(8) = 2.099(15), N(2)-Sm(1)-N(3) = 2.639(6), N(5)-Sm(2)-N(7) =

163.5(2), N(1)-Sm(1)-C(37) = 74.1(2), N(5)-Sm(2)-C(82) = 81.2(2), Sm(1)-C(81)-C(82) = 179.3(7), C(81)-C(82)-Sm(2) = 178.7(7).

Complex **5.2b** is a symmetry-generated dimer with each samarium atom surrounded by one calix-tetrapyrrole ligand. The macrocycle ligand adopts the usual conformation by arranging the four pyrrole rings in both σ - and π -bonding fashions around the samarium center. On the opposite side of the cavities defined by each of the calix-tetrapyrroles, three lithium atoms, all bridged by an enolate fragment, are either σ or π -bonded [Li(3)-C(22) = 2.137(18) Å, Li(2)-N(2) = 1.985(13) Å] to the pyrrole rings of the ligand. One C₄H₂ moiety is located between the two metal centers, holding together the dinuclear core. Similar to the molecular structures of (Cp*₂M)₂(μ -RC₄R) (M = La, R = Ph¹⁴, M = Sm, R = Ph¹⁵, M = La, R = Me¹⁶, M = Ce, R = tBu¹⁶), the four bridging carbon atoms are coplanar with the two Sm atoms and form a fully conjugated bridge [C(37)-C(38) = 1.295(9) Å, C(37)-C(37A) = 1.298(14) Å]. Samarium is primarily bound to the terminal carbon atom of the C₄ bridge [Sm(1)-C(38) = 2.426(7) Å, Sm(1)-C(37) = 2.734(7) Å]. The Sm-C bond distances are within the estimated standard deviations of the range of those found for analogous lanthanide species with substituted alkynes. The crystal structure was of sufficient quality to locate and refine the hydrogen atoms attached to the coordinated butatrienediyl group. The hydrogen atoms attached to each terminal carbon are located *trans* to one another in the SmC₄ plane and point in the opposite direction with respect to the neighbouring samarium atom resulting in a formal sp² hybridization of each terminal carbon. Similar to other compounds of this type, and in contrast to the dilithiated butatrienediyl¹⁷, the bridging C₄ fragment is bent [C(38)-C(37)-

$C(37A) = 155.0(10)^\circ$]. This may be attributed to secondary interactions between samarium and the internal carbon atoms of the bridge $[Sm(1)-C(37A) = 3.076(7)\text{\AA}]$, the sum of the ionic radii of which are within those expected for a Sm-C bond.

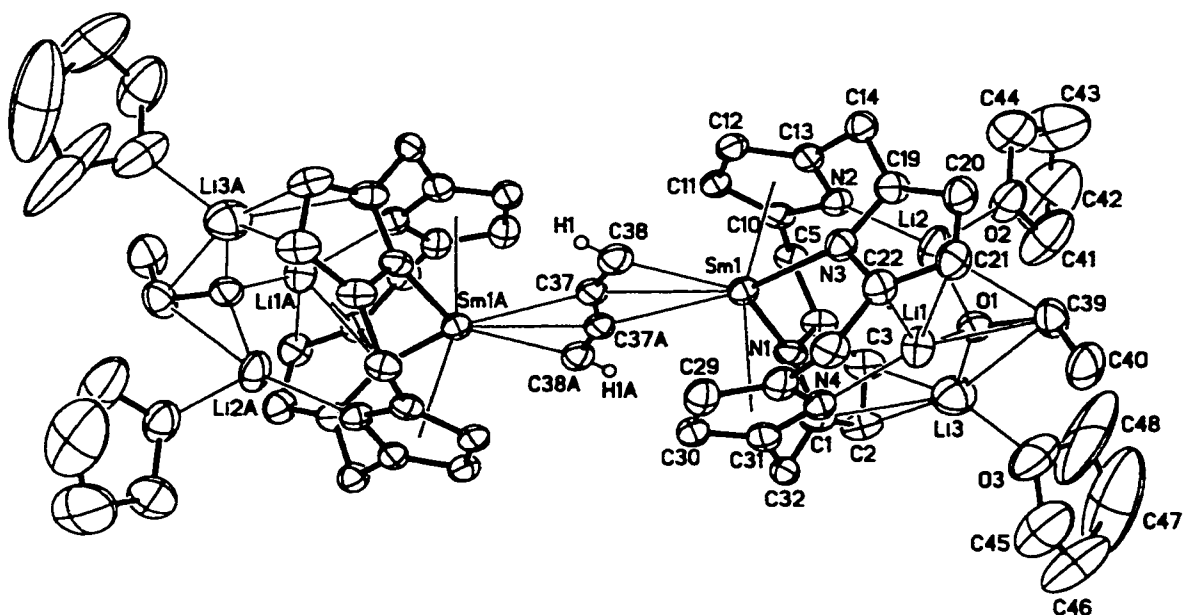


Fig. 5.2b, $\{(\text{Et}_8\text{-calix-pyrrole})\text{SmLi}[\text{Li}(\text{thf})]_2(\mu^3\text{-OCH=CH}_2)\}_2(\mu, \eta^2, \eta'^2\text{-}$

$\text{HC=C=C=CH})$

Selected Bond Distances in $\text{\AA}$ and Angles in deg ($^\circ$): $\text{Sm-N}(1) = 2.781(6)$, $\text{Sm-C}(1) = 2.777(7)$, $\text{Sm-C}(2) = 2.854(6)$, $\text{Sm-C}(3) = 2.825(7)$, $\text{Sm-C}(4) = 2.796(7)$, $\text{Sm-N}(2) = 2.458(6)$, $\text{Sm-N}(4) = 2.455(6)$, $\text{Sm-N}(3) = 2.659(6)$, $\text{Sm-N}(1A) = 2.479(5)$, $\text{Li-N}(3) = 1.985(14)$, $\text{N}(1A)\text{-Sm-N}(2) = 99.49(19)$.

Complex **5.3b** is also dinuclear and is formed by two identical $\{[(\text{Et}_8\text{-calix-pyrrole})\text{Sm}]\{[\text{Li}(\text{THF})_2]\}$ units in which one of the pyrrole rings has undergone a $\alpha \rightarrow \beta$ migration of the alkyl chain. This new macrocycle adopts the usual geometry with two of

the four pyrrole rings in a π -coordination bonding mode with respect to Sm while the other two are connected to samarium *via* Sm-N σ -bonds [Sm(1)-N(3) = 2.659(6)Å, Sm(1)-N(1) = 2.781(6)Å, Sm(1)-N(1A) = 2.479(5)Å]. The nitrogen atom of the “confused” pyrrole is bonded to the samarium atom of a second identical unit, thus assembling the dinuclear structure. Two lithium cations located trans to one another and at opposite ends of the molecule are σ -bonded to the nitrogen atom of one pyrrole ring macrocycle. Each lithium is σ bonded to one of the two N-confused pyrrole rings [Li-N(3) = 1.985(14)Å] and which, in turn, is π -bonded to samarium. Two molecules of THF complete the coordination environment of each trigonal planar lithium.

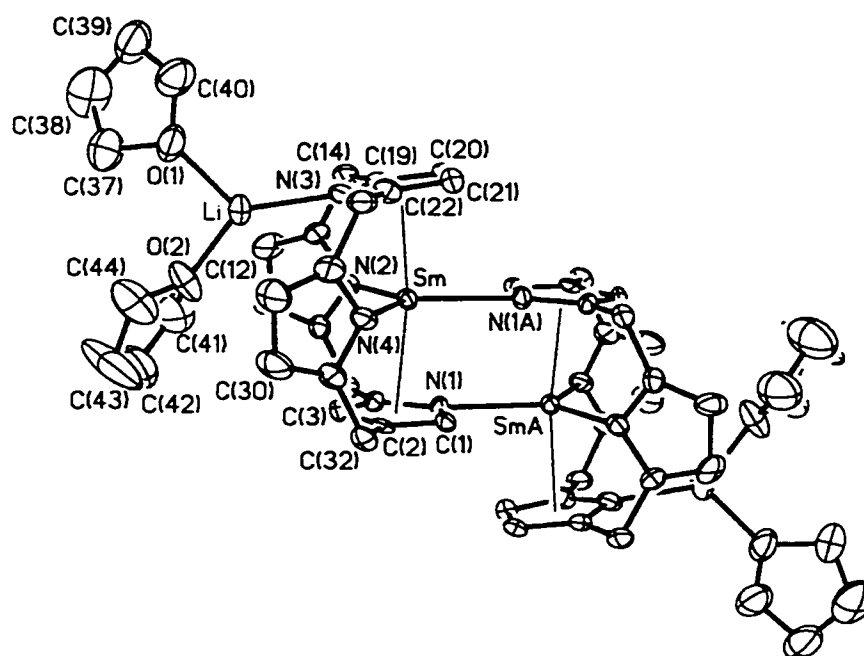


Fig. 5.3. X-ray Structure of 5.3b, $\{[(\text{Et}_5\text{-calix-pyrrole}^*)\text{Sm}][\text{Li}(\text{thf})_2]\}_2$

Selected Bond Distances in ang (Å) and Angles in deg (°): Sm-N(1) = 2.781(6), Sm-C(1) = 2.777(7), Sm-C(2) = 2.854(6), Sm-C(3) = 2.825(7), Sm-C(4) = 2.796(7), Sm-N(2) = 2.458(6), Sm-N(4) = 2.455(6), Sm-N(3) = 2.659(6), Sm-N(1a) = 2.479(5), Li-N(3) =

1.985(14), N(1a)-Sm-N(2) = 99.49(19), N(1a)-Sm-N(4) = 129.8(2), N(2)-Sm-N(4) = 130.66(19).

V.5: Conclusions

The type of reactivity observed with Sm(II) calix-pyrrole species and acetylene is strongly dependent upon the nature of the bridging substituent on the ligand. Acetylene double metallation to form a bridging C₂ unit or partial dehydrogenation and coupling to form a butatrienediyl derivative, are simply the result of the different nature of the substituents located on the macrocycle ring. The remarkable selectivity of these reactions is likely to be ascribed to kinetic factors since both reactions seem to proceed via the same dark purple Sm(III) hydride/acetylide intermediate. In addition, the close similarity with the reaction of Sm-alkyl and hydride with acetylene reinforces the observation that the +2 oxidation state is not necessary for either the coupling or the metallation processes to occur. Conversely, the cooperative interaction of two divalent samarium centers is probably necessary for performing oxidative addition on the acetylene C-H bond. Reaction of the trivalent hydride (Et₈-calix-pyrrole)(thf)Sm(μ-H)[Li(thf)]₂ with acetylene results in a mixture of products, the most unique of which arises from a complicated ligand reorganization possibly promoted by the *formal* dissociation of LiH.

References

1. (a) Evans, W.J.; Grate, J.W.; Hughes, L.A.; Zhang, H.; Atwood, J.L. *J. Am. Chem. Soc.* **1985**, *107*, 3728.
 (b) Evans, W.J.; Hughes, L.A.; Drummond, D.K.; Zhang, H.; Atwood, J.L. *J. Am. Chem. Soc.* **1986**, *108*, 1722.
 (c) Evans, W.J.; Drummond, D.K.; *J. Am. Chem. Soc.* **1988**, *110*, 2772.
 (d) Evans, W.J.; Drummond, D.K.; Bott, S.G.; Atwood, J.L. *Organometallics* **1986**, *5*, 2389.
 (e) Evans, W.J.; Grate, J.W.; Bloom, I.; Hunter, W.E.; Atwood, J.L. *J. Am. Chem. Soc.* **1985**, *107*, 405.
 (f) Evans, W.J.; Gonzales, S.L.; Ziller, J.W. *J. Am. Chem. Soc.* **1991**, *113*, 9880.
 (g) Evans, W.J.; Ulibarri, T.A.; Ziller, J.W. *J. Am. Chem. Soc.* **1988**, *110*, 6877.
 (h) Evans, W.J.; Leman, J.T.; Ziller, J.W. *Inorg. Chem.* **1996**, *35*, 4283.
2. (a) Dubé, T.; Conoci, S.; Gambarotta, S.; Yap, G.P.A.; Vasapollo, G. *Angew. Chem. Int. Ed. Engl.* in press.
 (b) Dubé, T.; Conoci, S.; Gambarotta, S.; Yap, G.P.A. *Angew. Chem. Int. Ed. Engl.* submitted.
3. Dubé, T.; Gambarotta, S.; Yap, G.P.A. *J. Chem. Soc. Chem. Commun.* submitted.
4. Jubb, J.; Gambarotta, S. *J. Am. Chem. Soc.*, **1994**, *116*, 4477.
5. Dubé, T.; Gambarotta, S.; Yap, G.P.A. *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 1432.
6. Evans, W.J.; Rabe, G.W.; Ziller, J.W. *J. Organomet. Chem.* **1994**, *483*, 21.
7. Dubé, T.; Gambarotta, S.; Yap, G.P.A. *Organometallics* submitted.

8. Mabbs, M.B.; Machin, D. *Magnetism and Transition Metal Complexes*; Chapman and Hall; London, 1973.
9. Foese, G.; Gorter, C.J.; Smits, L.J. *Constantes Selectionnes, Diamagnetisme, Paramagnetism, Relaxation Paramagnetique*; Masson, Paris, 1957.
10. Blessing, R. *Acta Cryst.* **1995**, *A51*, 33.
11. St. Clair, M.; Schaefer, W.P.; Bercaw, J.E. *Organometallics* **1991**, *10*, 525.
12. Overend, J.; Thompson, H.W. *Proc. R. Soc. A.* **1956**, *234*, 306.
13. Dubé, T.; Gambarotta, S.; Yap, G.P.A. manuscript in preparation.
14. Forsyth, C.M.; Nolan, S.P.; Stern, C.L.; Marks, T.J. *Organometallics* **1993**, *12*, 3618.
15. (a) Evans, W.J.; Keyer, R.A.; Ziller, J.W. *Organometallics* **1993**, *12*, 2618.
(b) Evans, W.J.; Keyer, R.A.; Ziller, J.W. *Organometallics* **1990**, *9*, 2628.
16. Heers, H.J.; Nijhoff, J.; Teuben, J.H. *Organometallics* **1993**, *12*, 2609.
17. Neugebauer, W.; Geiger, G.A.P.; Kos, A.J.; Stezowski, J.J.; Schleyer, P.R. *Chem. Ber.* **1985**, *118*, 1504.
18. Sessler, J.L. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1348
19. Furuta, H.; Asano, T.; Ogawa, T. *J. Am. Chem. Soc.* **1994**, *116*, 767
20. Chmielewski, P.J.; Latos-Grazynski, L.; Rachlewicz, K.; Glowiak, T. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 779
21. Liu, B.Y.; Bruckner, C.; Dolphin, D. *J. Chem. Soc. Chem. Commun.* **1996**, 2141

CHAPTER VI

Reversible fixation of ethylene promoted by a Sm^{II} calix-pyrrole enolate complex.

VI.1: Introduction

The chemistry of lanthanides became a very important field of inorganic chemistry and received a major development only in the eighties when a series of reports describing the unique richness and variety of reactivity of Sm^{II} rejuvenated the interest in this field.¹ These findings acted as a powerful stimulus to promote a wide range of chemical research in the chemistry of lanthanides.² Cyclopentadienyl and related ligands were used to develop the major part of the chemistry of Sm^{II} .³ Given the caliber of transformations afforded by Cp^*_2Sm , it is not surprising that several attempts have been made to prepare complexes of divalent samarium in different ligand environments.⁴ However, in spite of interesting progresses made in this direction,⁵ so far no other ligand system has been able to display the same variety of reactivity as discovered with decamethylsamarocene.

Attempts to isolate a Sm^{II} complex of a calix-pyrrole ligand⁶ led to the isolation of a unique case of encapsulation of dinitrogen into a Sm_2Li_4 cage.⁷ The rarity of this transformation and the considerable extent of reduction of N_2 indicated that this ligand system is perhaps a valid alternative to the Cp systems. In this chapter we wish to report the isolation and characterization of Sm^{II} complexes of two calix-pyrrole ligands and their reaction with ethylene which provides the first example of reversible ethylene fixation in lanthanide chemistry.⁸

VI.2: Experimental Section

All operations were performed under an inert atmosphere of a nitrogen-filled drybox or by using standard Schlenk-type glassware in combination with a nitrogen-vacuum line. Solvents were dried by passing through a column of Al_2O_3 under an inert atmosphere prior to use, degassed *in vacuo* and transferred and stored under inert atmosphere. $\text{SmCl}_3(\text{THF})_3$ ⁹, $\text{SmI}_2(\text{THF})_2$ ¹⁰ and $[(\text{R}_8\text{-calix-pyrrole})\{\text{Li}(\text{THF})\}_4]$ ($\text{R} = \text{Et}_8$, $\{-(\text{CH}_2)_5-\}_{0.5}$) were prepared according to literature procedures. C_6D_6 and THF-d^8 were dried over Na/K alloy, vacuum-transferred into ampoules, and stored under nitrogen prior to use. NMR spectra were recorded on a Varian Gemini 200 and on a Bruker AMX-500 spectrometer using vacuum sealed NMR tubes prepared inside a drybox. Infrared spectra were recorded on a Mattson 3000 FTIR instrument from Nujol mulls prepared inside the drybox. Samples for magnetic susceptibility measurements were carried out at room temperature using a Gouy balance (Johnson Matthey). Magnetic moments were calculated by following standard methods¹¹ and corrections for underlying diamagnetism were applied to the data¹². Elemental analyses were carried out using a Perkin-Elmer Series II CHN/O 2400 analyzer.

Preparation of $\{(\{-(\text{CH}_2)_5-\}_{0.5}\text{-calix-pyrrole})(\text{THF})\text{Sm}[\text{Li}(\text{THF})]_2[\text{Li}(\text{THF})_2](\mu^3\text{-Cl})\}(\text{Et}_2\text{O})_{1.5}$ (6.2b)

A suspension of $\text{SmCl}_3(\text{THF})_3$ (3.20 g, 6.80 mmol) in THF (150 mL) was treated with colorless $(\text{R}_8\text{-calix-pyrrole})(\text{LiTHF})_4$ [$\text{R} = \{-(\text{CH}_2)_5-\}_{0.5}$] (6.80 mmol). The resulting golden yellow suspension was heated gently for about 10 minutes and stirred at room temperature for 2 hours. Lithium foil (70 mg, 10 mmol) was added to the reaction

mixture under Ar. The color changed from yellow to deep green over 30 minutes. After stirring for 18 hours the solvent was removed *in vacuo* and the resulting deep green solid residue was extracted with diethyl ether (75 mL). After concentration to small volume (50 mL) and standing at -30°C overnight, large dark green crystals of **6.2b** separated (75%). Crystals suitable for X-ray analysis were grown at room temperature upon cooling a concentrated THF solution. I.R. (Nujol mull, cm^{-1}) $\nu = 3090(\text{w})$, $2730(\text{w})$, $2662(\text{w})$, $1550(\text{w})$, $1355(\text{m})$, $1315(\text{w})$, $1286(\text{s})$, $1270(\text{s})$, $1256(\text{s})$, $1191(\text{s})$, $1140(\text{m})$, $1074(\text{s})$, $970(\text{m})$, $845(\text{m})$, $780(\text{s})$. El. Anal. Calcd (Found) for $\text{SmLi}_3\text{ClC}_{56}\text{H}_{80}\text{N}_4 = \text{C}$ 62.28(63.22), H 7.47(8.31), N 5.19 (5.88). $\mu_{\text{eff}} = 3.70 \mu_{\text{B}}$.

Preparation of $\{(\text{Et}_8\text{-calix-pyrrole})(\text{Et}_2\text{O})\text{Sm}[\text{Li}(\text{THF})]_2[\text{Li}(\text{THF})_2](\mu^3\text{-LiOCHCH}_2)\}(\text{Et}_2\text{O})_{1.5}$ (6.3a**)**

A similar procedure to that described for **6.2b** was followed for this preparation. Yield 79%. I.R. (Nujol mull, cm^{-1}) $\nu = 3090(\text{w})$, $2723(\text{w})$, $1625(\text{m})$, $1585(\text{m})$, $1322(\text{s})$, $1260(\text{s})$, $1195(\text{s})$, $1156(\text{w})$, $1104(\text{w})$, $1046(\text{s})$, $975(\text{s})$, $925(\text{w})$, $888(\text{s})$, $799(\text{s})$, $756(\text{s})$. El. Anal. Calcd (Found) for $\text{Sm}_2\text{Li}_6\text{C}_{104}\text{H}_{166}\text{N}_8\text{O}_9 = \text{C}$ 62.06(61.94), H 8.21(7.91), N 5.56 (5.57). $\mu_{\text{eff}} = 3.62 \mu_{\text{B}}$ $^1\text{H-NMR}$ [500 MHz, C_6D_6 , 23°C] $\delta = 14.53$ (s, 4H, CH_{pyrr}), 14.22 (broad s, 4H, CH_2 ether), 8.73 (s, 4H, CH_{pyrr}), 5.35 (t, 6H, CH_3 ether), 3.85 (broad s, 8H, THF), 3.75 (s, 4H, CH_2 ethyl), 1.20 (s, 4H, CH_2 ethyl), 0.97 (s, 8H, THF), -2.98 (s, 12H, CH_3 ethyl), -4.67 (broad s, 1H, enolate), -5.01 (s, 12H, CH_3 ethyl), -6.95 (broad s, 1H, enolate), -7.03 (s, 8H, CH_2 ethyl), -15.62 (broad s, 1H, enolate).

Preparation of $[(R_8\text{-calix-pyrrole})[(CH_2=CHO)Li][Li(THF)]_2Sm]_2(\mu\text{-CH}_2CH_2)$

(6.4a,b)

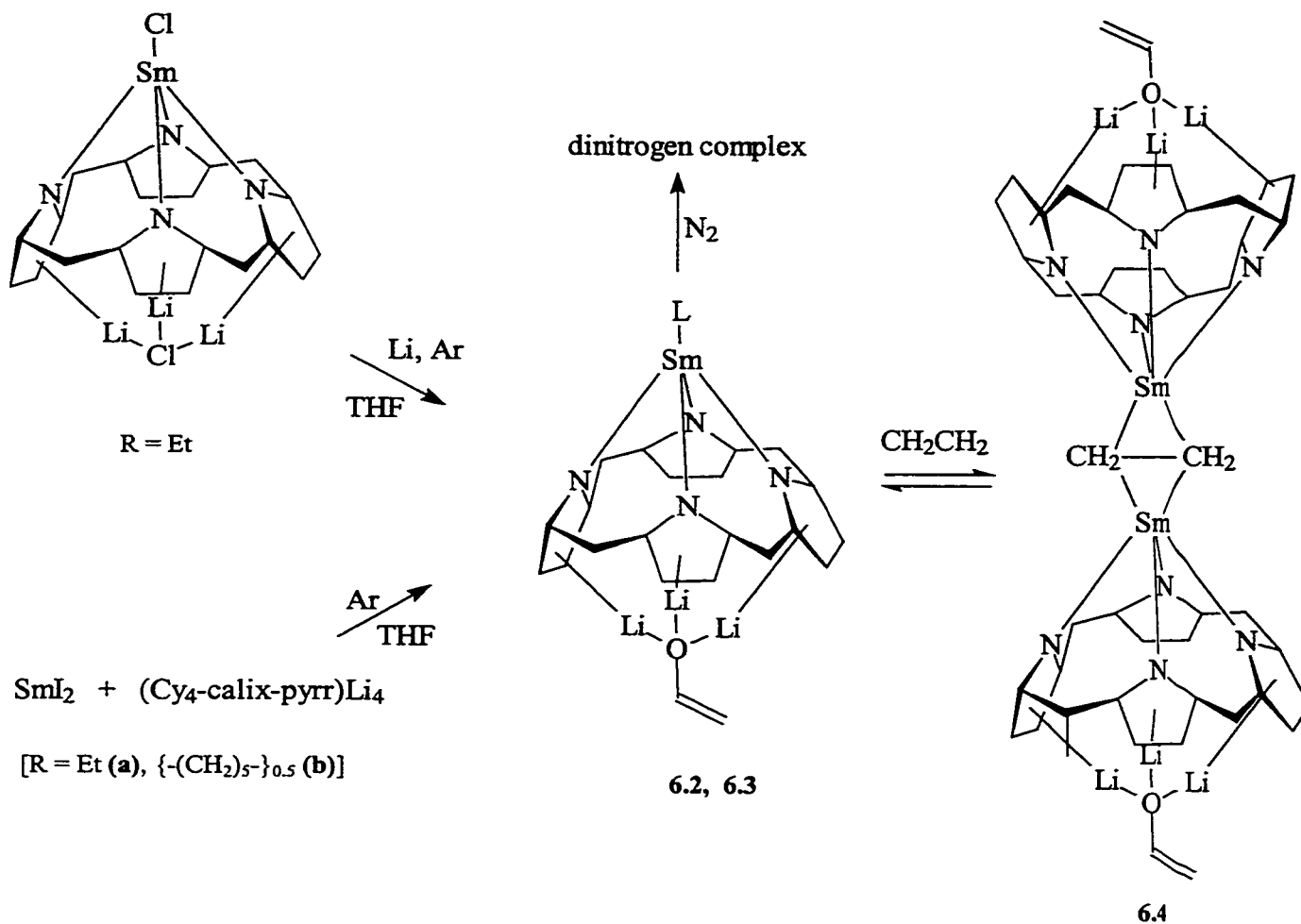
A stirred solution of $SmI_2(THF)_2$ (2.0 g, 3.65 mmol) in THF (75 mL) was treated with $(R_8\text{-calix-pyrrole})Li_4$ (2.23 g, 3.66 mmol). The resulting reddish-brown solution was refluxed for 2 hours then stirred at room temperature overnight. The solvent was removed *in vacuo* yielding a deep green solid residue which was extracted with hexane (100 mL). Upon exposure of the deep green hexane solution to 1 atm of ethylene the color changed to a lighter green. After standing at room temperature for 2 days, light green crystals of **6.4b** separated (1.5 g, 0.78 mmol, 43%). I.R. (Nujol mull, cm^{-1}) ν = 3088(w), 2731(w), 2664(w), 1564(w), 1350(m), 1309(s), 1267(s), 1240(s), 1185(s), 1140(m), 1070(s), 1040(s), 978(m), 898(s), 877(s), 830(m), 777(s), 740(s), 690(m). El. Anal. Calcd (Found) for $Sm_2Li_6C_{102}H_{138}O_6N_8$: C 62.08(61.30), H 7.65(7.00), N 6.16(5.45). $\mu_{eff} = 1.40 \mu_B$. A similar procedure was followed for the preparation of **6.4a**. Yield (39%). The extreme air-sensitivity and spontaneous loss of ethylene prevented obtaining satisfactory analytical data. 1H -NMR [500 MHz, C_6D_6 , 23°C] δ = 19.08 (br.s, 2H, ethylene), 18.97 (br. s, 2H, ethylene), 8.60 (br. s, 8H, THF), 7.17 (s, 16H, CH pyrrole), 4.01 (br.s, 8H, CH_2 ethyl), 3.47 (br.s, 8H, THF), 2.13 (br.s, 8H, CH_2 ethyl), 1.25 (br.s, 8H, CH_2 ethyl), 1.22 (br.s, 8H, CH_2 ethyl), -0.66 (br.s, 24H, CH_3 ethyl), -2.68 (br.s, 24H, CH_3 ethyl), -4.53(br.s, 2H, enolate), -6.75(br.s, 2H, enolate), -15.60 (br.s, 2H, enolate).

VI.3: Results and Discussion

Reduction of $(R_8\text{-calix-pyrrole})\text{ClSm}[\text{Li}(\text{THF})]_2[\text{Li}(\text{THF})_2](\mu^3\text{-Cl})$ [$R = \text{Et}$ (**6.1a**), $\{-(\text{CH}_2)_5-\}_{0.5}$ (**6.1b**)]⁷ with lithium under Ar formed dark green solutions. The result of the reduction reaction depended on the aliphatic chains attached to the macrocycle. Two compounds formulated as $\{(R_8\text{-calix-pyrrole})(\text{L})\text{Sm}[\text{Li}(\text{THF})]_2[\text{Li}(\text{THF})_2](\mu^3\text{-X})\}(\text{Et}_2\text{O})_{1.5}$ [$R = \{-(\text{CH}_2)_5-\}_{0.5}$, $X = \text{Cl}$, $L = \text{THF}$ (**6.2b**); $R = \text{Et}$, $X = \text{OCHCH}_2$, $L = \text{ether}$ (**6.3a**)] were isolated in good yield and characterized in both cases (Scheme 6.1). In the case of the octaethyl derivative the enolate group, probably arising from a THF cleavage process¹³ replaced the Cl anion. Reaction of the tetralithium salts of both ligands^{13g-14} with $\text{SmI}_2(\text{THF})_2$ afforded low yield of the two isomorphous enolate derivatives **6.3a** and **6.3b**. Both complexes are paramagnetic. Informative NMR spectra were obtained only in the case of **6.3a**.

Both enolate Sm^{II} derivatives **6.3a** and **6.3b** react reversibly with ethylene through a fast reaction, the extent of which depends on the nature of R . Upon exposure to ethylene, the initially dark green color persists in the case of **6.3a** but becomes light green in the case of **6.3b**. Light green paramagnetic crystals of $[(R_8\text{-calix-pyrrole})[(\text{CH}_2=\text{CHO})\text{Li}][\text{Li}(\text{THF})]_2\text{Sm}]_2(\mu\text{-CH}_2\text{CH}_2)$ (**6.4a,b**) may be isolated in good yield. The magnetic moment measured at room temperature for **6.4b** [$\mu_{\text{eff}} = 1.40 \mu_{\text{BM}}$ per metal center] supports the premise that complete oxidation to Sm^{III} occurred. In each case crystals suitable for X-ray analysis were obtained.

Scheme 6.1



In spite of the presence of a significant Sm-C_{ethylene} σ -bond character, the fixation of ethylene is a reversible process as indicated by the behavior of solutions of both **6.4a** and **6.4b**. Addition of pale green crystals of **6.4** to C₆D₆ originated dark green solutions where the peak of free ethylene was clearly visible at 5.23 ppm. In addition, the resonances characteristic of **6.2** were also clearly identified in the NMR spectrum although partly overlapping with the resonance of **6.4**. Conversely, subsequent saturation of the same NMR tube with ethylene conferred the characteristic pale green color to the solution in the case of **6.4a**, while the resonances of the enolate starting complex disappeared. In the case of **6.4b**, however, the solutions always remained dark green and

the peaks of the starting **6.3b** were invariably present in the NMR spectra. The peaks of coordinated ethylene in complex **6.4a** were clearly identified by using C_2D_4 and are present as two resonances of equal intensity at 19.08 and 18.97 ppm in the 2H -NMR spectrum.

In spite of the dominant σ - character of the Sm- $C_{ethylene}$ bond, this complex does not insert further ethylene under normal reaction conditions and does not perform polymerization which strikingly contrasts with the fact that decamethylsamarocene is an ethylene polymerization initiator.¹²

VI.4: X-ray Crystallography

Suitable crystals were selected, mounted on thin, glass fibres using paraffin oil and cooled to the data collection temperature. Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° ω -scans at 0, 90, and 180° in ϕ . Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied. Crystallographic details are presented in the Appendix, Table 5.

Systematic absences in the diffraction data and unit-cell parameters were uniquely consistent with the reported space group. The structures were solved by direct methods, completed with difference Fourier syntheses and refined with full-matrix least-squares procedures based on F^2 . All non-hydrogen atoms were located and refined anisotropically. Hydrogen atoms were introduced at their idealized positions and refined

with a riding mode. Absorption corrections (SADABS) were applied to the data. Two crystallographically independent but chemically equivalent molecules and one molecule of ether were found in the unit cell of **6.3a**. Hydrogen atoms in **6.4a** were located from different Fourier maps and refined with a riding mode.

The crystal structure of **6.3a** consists of a samarium atom surrounded by a calix-pyrrole ligand arranged in a basket-like conformation (Figure 6.1). The coordination geometry of the samarium atom is distorted pseudo-trigonal bipyramidal and is defined by two nitrogen atoms of two pyrroles (σ -bonded), two centroids of the other two pyrrole rings (π -bonded) and the oxygen atom of one molecule of coordinated solvent (ether or THF). On the opposite side of the macrocycle, three lithium atoms are bonded to the pyrrole rings adopting either σ - or π - bonding mode and are also connected to the oxygen atom of the enolate group (or a chlorine atom as in the case of **2b**).

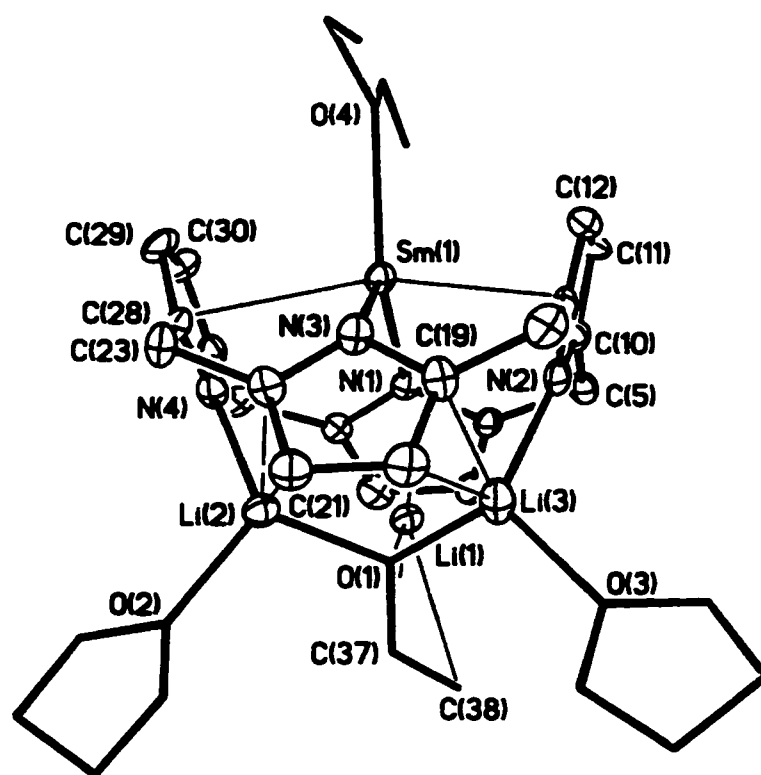


Fig. 6.1. X-ray Structure of 6.3a, $\{(\text{Et}_8\text{-calix-pyrrole})(\text{Et}_2\text{O})\text{Sm}[\text{Li}(\text{THF})]_2[\text{Li}(\text{THF})_2](\mu^3\text{-LiOCHCH}_2)\}(\text{Et}_2\text{O})_{1.5}$

Bond distance are in ang (Å) and angles in deg (°): Sm(1)-N(1) = 2.597(7), Sm(1)-N(3) = 2.602(7), Sm(1)-N(2) = 2.853(6), Sm1-C(10) = 2.913(8), Sm(1)-C(11) = 2.986(8), Sm(1)-C(12) = 2.976(9), Sm(1)-C(13) = 2.901(8), Li(2)-N(4) = 2.09(2), Li(1)-N(1) = 2.16(2), Li(1)-C(1) = 2.18(2), Li(1)-C(2) = 2.22(2), Li(1)-C(3) = 2.24(2), Li(1)-C(4) = 2.17(2), Li(1)-O(1) = 1.84(2), Li(2)-O(1) = 1.93(2), Li(3)-O(1) = 1.90(2), O(1)-C(37) = 1.330(11), C(37)-C(38) = 1.303(13), Li(1)-C(37) = 2.37(2), Li(1)-C(38) = 2.67(2), N(1)-Sm(1)-N(3) = 123.2(2), N(1)-Sm(1)-O(4) = 114.6(3), N(3)-Sm(1)-O(4) = 122.2(3), centr-Sm(1)-centr = 161.6(3), O(1)-C(37)-C(38) = 125.1(10), Li(1)-O(1)-Li(2) = 104.5(7), Li(1)-O(1)-Li(3) = 102.1(7), Li(2)-O(1)-Li(3) = 110.0(8).

The structure of **6.4a** consists of a dimer lying on an inversion center where each samarium atom is surrounded by the calix-pyrrole ligand (Figure 6.2). One C₂ unit is placed between the two metal centers in a distorted side-on fashion [Sm-C(37) = 2.427(5)Å, Sm-C(37a) = 2.711(5)Å] but still forming a planar SmCCSm core. On the opposite side of the cavity defined by each calix-pyrrole, three lithium atoms are bonded to the pyrrolyl rings. The rather long coordinated ethylene C-C bond distance [C(37)-C(37a) = 1.487(10)Å] is indicative of the presence of a C-C single bond, thus suggesting, in combination with the light color, that complete reduction of ethylene and oxidation of the two metal centers occurred. The crystal structure was of sufficient quality to locate and refine the hydrogen atoms attached to the coordinated ethylene. According to their position, the ethylene molecule is perpendicular to the Sm₂ vector. The hydrogen atoms attached to each carbon deviate from the ethylene plane and point in the opposite direction with respect to the neighboring samarium thus conferring to the carbon a distorted tetrahedral geometry [Sm-C(37)-H(37a) = 112.9°; Sm-C(37)-H(37b) = 115.4°; H(37a)-C(37)-H(37b) = 107.2°]. This indicates that ethylene predominantly adopted a σ - rather than π -bonding mode which is also consistent with the remarkable elongation of the C-C bond and the zigzag conformation of the Sm₂C₂ core.

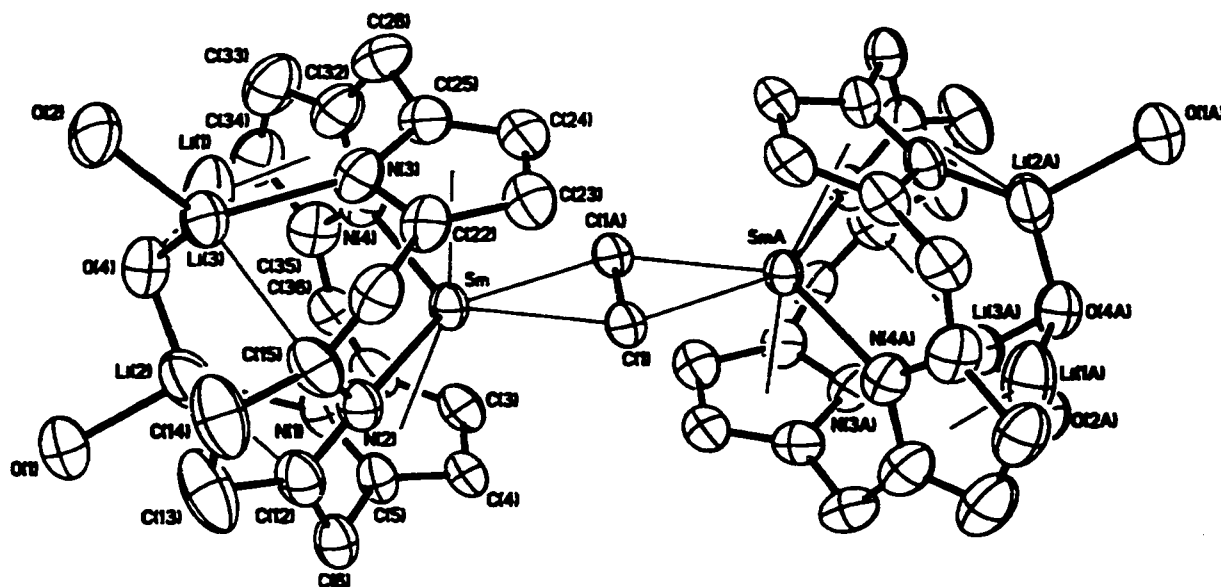


Fig. 6.2. X-ray Structure of 6.4a [(Et₈-calix-pyrrole)[CH₂=CHO)Li][Li(THF)]₂Sm]₂(μ-CH₂CH₂)

Bond distance are in angstroms (Å) and angles in deg (°). C(37)-C(37a) = 1.493(15), Sm-C(37) = 2.427(5), Sm-C(37a) = 2.711(5), Sm-N(2) = 2.738(4), Sm-N(4) = 2.720(3), Sm-N(1) = 2.549(4), Sm-C(10) = 2.855(4), Sm-C(11) = 2.899(9), Sm-C(12) = 2.892(9), Sm-C(13) = 2.853(4), N(2)-Li(1) = 2.014(9), N(4)-Li(2) = 2.024(9), Li(3)-N(1) = 2.512(10), Li(3)-C(1) = 2.434(10), Li(3)-C(2) = 2.318(10), Li(3)-C(3) = 2.312(10), Li(3)-C(4) = 2.433(10), O(1)-Li(1) = 1.860(9), O(1)-Li(2) = 1.886(9), O(1)-Li(3) = 1.859(9), O(1)-C(38) = 1.399(6), C(38)-C(39) = 1.427(8), C(37)-Sm-C(37a) = 33.0(2), centr-Sm-centr = 165.1(3), N(2)-Sm-N(4) = 122.4(2), O(1)-C(38)-C(39) = 114.6(5).

References

1. (a) Evans, W.J.; Hughes, L.A.; Hanusa, T.P. *Organometallics* **1986**, *5*, 1285.
- (b) Evans, W.J.; Hughes, L.A.; Hanusa, T.P. *J. Am. Chem. Soc.* **1984**, *106*, 4270.
- (c) Evans, W.J.; Drummond, D.K.; Bott, S.G.; Atwood, J.L. *Organometallics* **1986**, *5*, 2389.
- (d) Evans, W.J.; Ulibarri, T.A. Ziller, J.W. *J. Am. Chem. Soc.* **1988**, *110*, 6877.
- (e) Evans, W.J.; Keyer, R.A.; Zhang, H.; Atwood, J.L. *J. Chem. Soc. Chem. Comm.* **1987**, 837.
- (f) Evans, W.J.; Drummond, D.K.; Grate, J.W.; Zhang, H.; Atwood, J.L. *J. Am. Chem. Soc.* **1987**, *109*, 3928.
- (g) Evans, W.J.; Drummond, D.K. *J. Am. Chem. Soc.* **1989**, *111*, 3329.
- (h) Evans, W.J.; Keyer, R.A.; Rabe, G.W.; Drummond, D.K.; Ziller, J.W. *Organometallics* **1993**, *12*, 4664.
- (i) Evans, W.J.; Grate, J.W.; Doedens, R.J. *J. Am. Chem. Soc.* **1985**, *107*, 1671.
- (j) Evans, W.J.; Ulibarri, T.A. *J. Am. Chem. Soc.* **1987**, *109*, 4292.
- (k) Evans, W.J.; Grate, J.W.; Hughes, L.A.; Zhang, H.; Atwood, J.L. *J. Am. Chem. Soc.* **1985**, *107*, 3728.
- (l) Evans, W.J.; Drummond, D.K. *J. Am. Chem. Soc.* **1988**, *110*, 2772.
- (m) Evans, W.J.; Drummond, D.K. *Organometallics* **1988**, *7*, 797.
- (n) Evans, W.J.; Drummond, D.K.; Chamberlain, L.R.; Doedens, R.J.; Bott, S.G.; Zhang, H.; Atwood, J.L. *J. Am. Chem. Soc.* **1988**, *110*, 4983.
- (o) Evans, W.J.; Drummond, D.K. *J. Am. Chem. Soc.* **1986**, *108*, 7440.

- (p) Evans, W.J.; Leman, J.T.; Ziller, J.W. *Inorg. Chem.* **1996**, *35*, 4283.
2. (a) Evans, W.J.; Hozbor, M.A. *J. Organomet. Chem.* **1987**, *326*, 299 and references cited therein;
- (b) Schaverien, C.J. *Adv. in Organomet. Chem.*, **1994**, Vol. 36, 283 and references cited therein.
- (c) Marks, T.J.; Ernst, R.D. in “*Comprehensive Organometallic Chemistry*” Chapt. 21. Pergamon, Oxford, **1982**.
- (d) Evans, W. *Adv. in Organomet. Chem.*, **1985**, *24*, 131.
- (e) Ephritikhine, M. *Chem. Rev.* **1997**, 2193.
- (f) Hubert-Pfalzgraf, L.G. *New J. Chem.* **1995**, *19*, 727.
3. (a) Ernst, R.D.; Marks, T.J. *J. Organomet. Chem.* **1987**, *318*, 29.
- (b) Ernst, R.D. *J. Organomet. Chem.* **1990**, *392*, 51.
- (c) Meese-marktscheffel, J.A.; Esser, L.; Schumann, H. *Chem. Rev.* **1995**, *95*, 865.
4. see for example:
- (a) Nief, F.; Ricard, L. *J. Organomet. Chem.* **1997**, *529*, 357.
- (b) Hou, Z.; Fujita, A.; Yoshimura, T.; Jesorka, A.; Zhang, Y.; Yamazaki, Y.; Wakatsuki, Y. *Inorg. Chem.* **1996**, *35*, 7190.
- (c) Rabe, G.W.; Riede, J.; Schier, A. *Organometallics* **1996**, *15*, 439.
- (d) Minhas, R.; Ma, Y.; Gambarotta, S. *Inorg. Chem.* **1996**, *35*, 1866.
- (e) Song, J.; Gambarotta, S. *Angew. Chem. Intl. Ed. Engl.* **1995**, *34*, 2141.
- (f) Mashima, K.; Nakayama, Y.; Shibahara, T.; Fukumoto, H.; Nakamura, A. *Inorg. Chem.* **1996**, *35*, 93.

- (g) Sen, A.; Chebolu, V.; Rheingold, A.L. *Inorg. Chem.* **1987**, *26*, 1821.
- (h) Rabe, G.; Schier, A. *Inorg. Chem.* **1996**, *35*, 2680.
5. (a) Takats, J.; Zhang, X.W. *Organometallics* **1993**, *12*, 4286.
- (b) Xie, Z.; Chiu, K.; Wu, B.; Mak, T.C.W. *Inorg. Chem.* **1996**, *35*, 5957.
- (c) Takats, J.; Zhang, X.; Lopnow, G.R.; McDonald, R. *J. Am. Chem. Soc.* **1995**, *117*, 7828.
- (d) Evans, W.J.; Drummond, D.K.; Zhang, H.; Atwood, J.L. *Inorg. Chem.*, **1988**, *27*, 575.
- (e) Reger, D.L.; Knox, S.J.; Lindeman, J.A.; Leboida, L. *Inorg. Chem.* **1990**, *29*, 416.
- (f) Recknagel, A.; Steiner, A.; Noltemeyer, M.; Brooker, S.; Stalke, D.; Edelmann, F.T. *J. Organomet. Chem.* **1991**, *414*, 327.
- (g) Schumann, H.; Keitsch, M.R.; Winterfeld, J.; Demtschuk, J. *J. Organomet. Chem.* **1996**, *525*, 279.
- (h) Swamy, S.J.; Leobel, J.; Schumann, H. *J. Organomet. Chem.* **1989**, *379*, 51.
6. P.A. Gale, J.L. Sessler, V. Král, V. Lynch, *J. Am. Chem. Soc.* **1996**, *118*, 5140.
7. Jubb, J.; Gambarotta, S., *J. Am. Chem. Soc.*, **1994**, 116, 4477.
8. (a) Evans, W.J.; Coleson, K.M.; Engerer, S.C. *Inorg. Chem.* **1981**, *20*, 4320.
- (b) Evans, W.J.; Engerer, S.C.; Neville, A.C. *J. Am. Chem. Soc.* **1978**, *100*, 331.
- (c) Kasai, P.H.; McLeod Jr., D.; Watanabe, T. *J. Am. Chem. Soc.* **1977**, *99*, 3521.
- (d) Burns, C.J.; Andersen, R.A. *J. Am. Chem. Soc.* **1987**, *109*, 915.
- (e) Evans, W.J.; Ulibarri, T.A.; Ziller, J.W. *J. Am. Chem. Soc.* **1990**, *112*, 219.
- (f) Evans, W.J.; Ulibarri, T.A.; Ziller, J.W. *J. Am. Chem. Soc.* **1990**, *112*, 2314.

9. (a) Freeman, J.H.; Smith, M.L. *J. Inorg.Nucl. Chem.* **1958**, *7*, 224.
(b) Manzer, L.E. *Inorg. Synth.* **1982**, *21*, 135.
10. Evans, W.J.; Grate, J.W.; Choi, H.W.; Bloom, I.; Hunter, W.E.; Atwood, J.L. *J. Am. Chem. Soc.* **1985**, *107*, 941.
11. Mabbs, M.B.; Machin, D. *Magnetism and Transition Metal Complexes*; Chapman and Hall, London, 1973.
12. Foese, G.; Gorter, C.J.; Smits, L.J. *Constantes Selectionnes, Diamagnetism, Paramagnetism Relaxation Paramagnetique*; Masson, Paris, 1957.
13. (a) Jubb, J.; Gambarotta, S.; Duchateau, R.; Teuben, J. *J. Chem. Soc. Chem. Commun.* **1994**, 2641.
(b) Aspinall, H.C.; Tillotson, M.R. *Inorg. Chem.* **1996**, *35*, 2163.
(c) Evans, W.J.; Dominguez, R.; Hanusa, T.P. *Organometallics* **1986**, *5*, 1291.
(d) Jubb, J.; Gambarotta, S. *Inorg. Chem.* **1994**, *33*, 2503.
(e) Jubb, J.; Gambarotta, S. *J. Am. Chem. Soc.* **1993**, *115*, 10410.
(f) Dubé, T.; Gambarotta, S.; Yap, G.P.A. *Organometallics* **1998**, *17*, 3967.
(g) De Angelis, S.; Solari, E.; Floriani, C.; Chiesi-Villa, A. *J. Chem. Soc. Dalton Trans.* **1994**, 2467.
14. (a) Floriani, C.; Solari, E.; Chiesi-Villa, A.; Rizzoli, C. *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 2245 and refs cited therein.
(b) Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1997**, *16*, 508.
15. Evans, W.J.; DeCoster, D.M.; Greaves, J. *Macromolecules.* **1995**, *28*, 7929 and references cited therein.

CHAPTER VII

Reversible coordination of dinitrogen facilitated by Sm(II) calix-tetrapyrrole as a possible prelude to further dinitrogen reduction.

VII.1: Introduction

In the few existing dinitrogen lanthanide complexes, the spectator ligand and the nature of the metal play a particularly enhanced role in determining the extent of dinitrogen reduction (from labile coordination¹ to two-² and four-electron reduction³). The starting point of this work was the observation that the four-electron reduction of dinitrogen occurring during the formation of the encapsulated [(Et₈calix-tetrapyrrole)Sm Li]₂Li₄N₂ complex^{3a} has no explanation given that the complex contains only two samarium atoms. In addition, we have recently observed that the same Sm(II) Et₈-calix-tetrapyrrole complex which gave *irreversible* dinitrogen encapsulation^{3a} is also capable of *reversibly* coordinating a molecule of ethylene in a side-on fashion.⁴ The reversibility of the ethylene fixation was rather surprising considering that dinitrogen notoriously is a substrate more difficult than ethylene to be reduced. We also observed that the ability of the calix-tetrapyrrole samarium complexes to interact with ethylene was greatly sensitive to relatively minor variations in the macrocycle substituents [less labile coordination with Et₈-calix-tetrapyrrole and more labile with Cy₄-calix-tetrapyrrole], and to the nature of additional groups (LiO-CH=CH₂ *versus* LiCl) coordinated to the complex. These observations prompted us to revisit the dinitrogen activation process in divalent samarium calix-tetrapyrrole complexes with the help of the recently prepared Cy₄-calix-tetrapyrrole tetra-anion ligand.⁴

VII.2: Experimental Section

All operations were performed under an inert atmosphere of a nitrogen-filled drybox or by using standard Schlenk-type glassware in combination with a nitrogen-vacuum line. Solvents were dried by passing through a column of Al_2O_3 under an inert atmosphere prior to use, degassed *in vacuo* and transferred and stored under inert atmosphere. $\{(\text{Cy}_4\text{-calix-tetrapyrrole})\text{Sm}(\text{THF})[\text{Li}(\text{THF})]_2[\text{Li}(\text{THF})_2](\mu^3\text{-Cl})\}$ was prepared according to literature procedures⁵. C_6D_6 and THF-d^8 were dried over Na/K alloy, vacuum-transferred into ampoules, and stored under nitrogen prior to use. NMR spectra were recorded on a Varian Gemini 200 and on a Bruker AMX-500 spectrometer using vacuum sealed NMR tubes prepared inside a drybox. Infrared spectra were recorded on a Mattson 3000 FTIR instrument from Nujol mulls prepared inside the drybox. Samples for magnetic susceptibility measurements were carried out at room temperature using a Gouy balance (Johnson Matthey). Magnetic moments were calculated by following standard methods⁶ and corrections for underlying diamagnetism were applied to the data⁷. Elemental analyses were carried out using a Perkin-Elmer Series II CHN/O 2400 analyzer.

Preparation of $\{(\text{Cy}_4\text{-calix-tetrapyrrole})\text{Sm}[\text{Li}(\text{THF})]_2[\text{Li}(\text{THF})_2](\mu^3\text{-Cl})\}_2(\mu\text{-N}_2)$

(7.2) and $\{(\text{Cy}_4\text{-calix-tetrapyrrole})(\text{THF})\text{Sm}[\text{Li}(\text{THF})]_2[\text{Li}(\text{THF})_2](\mu^3\text{-OCH=CH}_2)\}$

(7.3)

A deep green solution of 7.1 (4.5 g, 3.2 mmol) in freshly distilled THF (50 mL) under an atmosphere of Ar was concentrated to small volume (5mL). Hexane (200 mL) was added and the resulting suspension was heated to 60°C until most of the dark green solid was dissolved. The hot solution was filtered to remove a small amount of insoluble solid.

After cooling to room temperature, the solution was exposed to N₂ and was allowed to stand at room temperature. After 2 days, a red crystalline mass containing a mixture of **7.2** and **7.3** separated (2.1g). Analytically pure samples for combustion analysis and spectroscopic characterization were obtained by separating the crystals of different shape using a stereomicroscope. **7.2**: I.R. (Nujol mull, cm⁻¹) ν : 3095(w), 3076(w), 2729(w), 2684(w), 1645(w), 1458(s), 1377(s), 1342(m), 1273(m), 1261(s), 1232(w), 1151(w), 1105(m,br), 1047(s), 980(m), 897(m), 876(m), 804(s), 771(w), 733(m), 704(w). El. Anal. Calcd. (Found) for C₁₁₂H₁₆₀N₁₀O₈Sm₂Cl₂Li₆: C 61.48(61.33), H 7.37(7.28), N 6.40(6.31). $\mu_{\text{eff}} = 2.82 \mu_{\text{B}}$ (per formula unit). **7.3**: I.R. (Nujol mull, cm⁻¹) ν : 3094(w), 3074(w), 2709(w), 2671(w), 1637(w), 1458(s), 1379(s), 1342(m), 1294(m), 1259(s), 1182(w), 1132(w), 1106(s), 1047(vs), 982(w), 877(s), 833(m), 769(s), 737(s), 719(w). El. Anal. Calcd. (Found) for C₅₀H₆₇N₄Li₃O₃Sm : C 63.66(62.98), H 7.16(7.05), N 5.94(5.87). $\mu_{\text{eff}} = 3.70 \mu_{\text{B}}$.

Preparation of {(Cy₄-calix-tetrapyrrole)(L)Sm[Li(THF)]₂[Li(THF)₂](μ^3 -Cl)}(Et₂O)_{1.5} [L = Et₂O (7.4**)]**

Under an atmosphere of N₂, a red crystalline **7.2** physically separated from **7.3** (0.8 g, 0.36 mmol) was dissolved in diethyl ether (100 mL) to form a deep green solution which was filtered to separate a small amount of insoluble solid. Concentration to 30 mL and standing at -30°C for 5 days yielded dark green crystals of **7.4** (0.5 g, 0.43 mmol, 59%). I.R. (Nujol mull, cm⁻¹) ν : 3079(w), 3067(w), 2739(w), 2678(w), 1465(vs), 1387(s), 1286(w), 1251(m), 1138(w), 1048(s), 899(w), 885(m), 800(w), 748(m), 636(m). El.

Anal. Calcd. (Found) for $C_{60}H_{94}Li_3N_4O_5SmCl$: C 62.23(62.19), H 8.18(8.07), N 4.84(4.75). $\mu_{eff} = 3.20 \mu_{BM}$

VII.3: Results and Discussion

Upon recrystallizing $\{(Cy_4\text{-calix-tetrapyrrole})(THF)Sm[Li(THF)]_2[Li(THF)_2](\mu^3\text{-Cl})\}$ (7.1) from boiling hexane/THF mixture and allowing the dark-green solution to stand under nitrogen gas for two days, a bright-red crystalline mass separated in good yield from the dark-green solution. A visual inspection showed that the crystalline red mass was composed of two different compounds, one minor (7.2) and one major (7.3), of similar color but with distinctively different shapes (rectangular versus hexagonal prisms). The two components of the orange crystalline mixture were physically separated according to their different crystal shape and characterized. Both types of crystals were extremely air-sensitive and independently generated dark green solutions upon dissolving in ether or THF. In the case of 7.2, the dissolution process was accompanied by vigorous N_2 evolution thus suggesting the presence of labile coordination of dinitrogen in this species.

A single crystal structural determination confirmed that complex 7.2 indeed contains a coordinated dinitrogen molecule (Scheme 7.1). The complex formulated as $\{(Cy_4\text{-calix-tetrapyrrole})Sm[Li(THF)]_2[Li(THF)_2](\mu^3\text{-Cl})\}_2(\mu\text{-}N_2)$ is dinuclear and is formed by two samarium calix-tetrapyrrole moieties side-on coordinated to the opposite sides of one dinitrogen molecule.⁴ Three lithium atoms bridged by one chlorine are located on the exterior of the molecule pointing away from the molecular core and are connected to the ligand pyrrole rings using both π - and σ -bonding interactions

Scheme 7.1

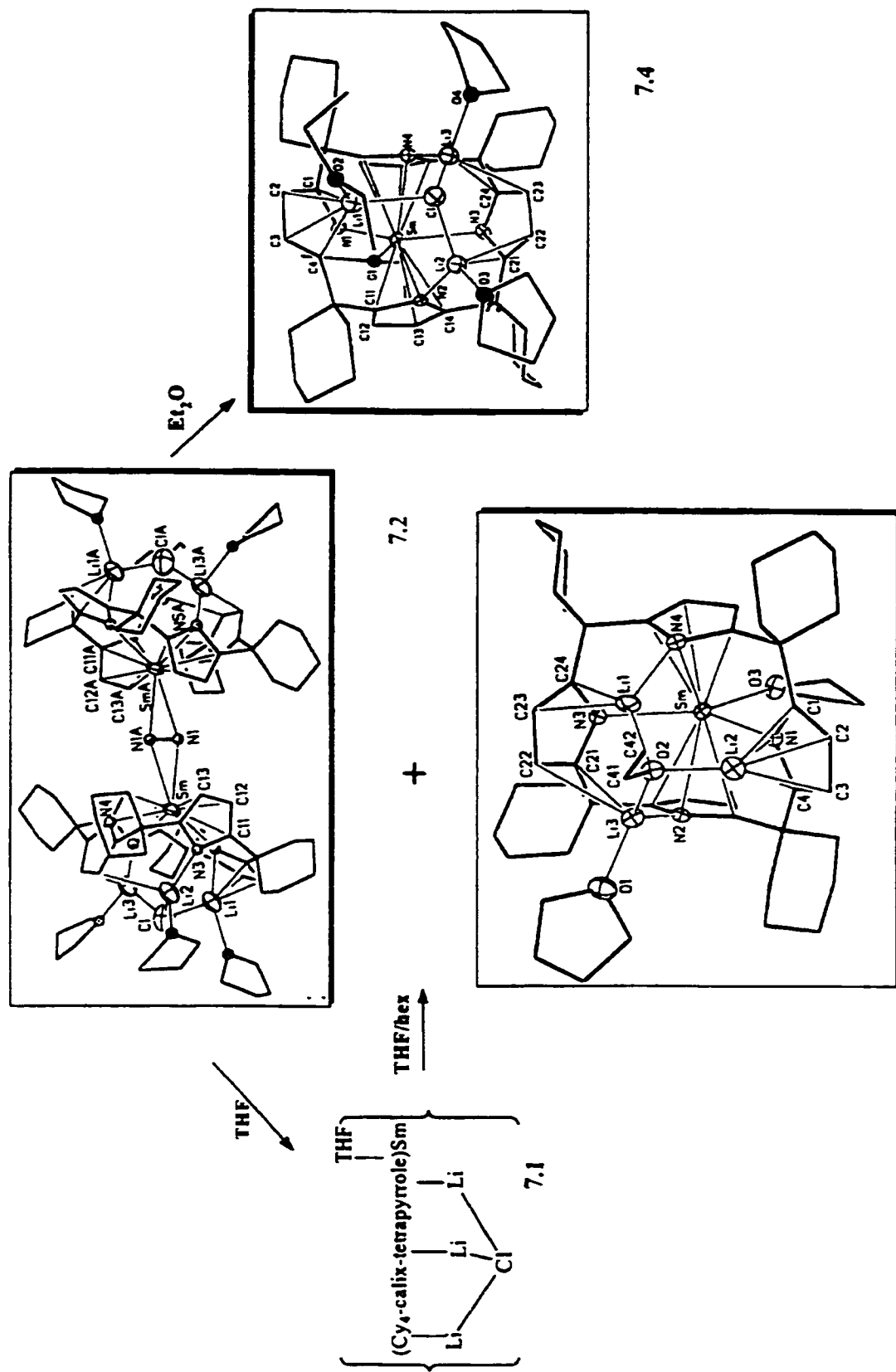


Table 7.1 Selected Bond Distances (Å) and Angles (deg).

7.2	7.3	7.4
N(1)-N(1a) = 1.08(3)	Sm-O(3) = 2.630(6)	Sm-O(1) = 2.618(8)
Sm-N(1) = 2.880(18)	Sm-N(2) = 2.855(6)	Sm-N(1) = 2.569(9)
Sm-N(1a) = 2.974(18)	Sm-C(11) = 2.901(8)	Sm-N(2) = 2.868(8)
Sm-N(3) = 2.84(2)	Sm-C(12) = 2.956(8)	Sm-N(3) = 2.602(9)
Sm-C(11) = 2.90(2)	Sm-C(14) = 2.892(8)	Sm-C(11) = 2.910(11)
Sm-C(13) = 2.93(3)	Sm-N(1) = 2.601(6)	Sm-C(12) = 2.934(12)
Sm-C(14) = 2.85(3)	Li(2)-N(1) = 2.152(16)	Sm-C(13) = 2.918(11)
Sm-N(2) = 2.573(19)	Li(2)-C(1) = 2.167(17)	Sm-C(14) = 2.882(10)
Sm-N(4) = 2.68(2)	Li(2)-C(2) = 2.242(17)	Li(1)-Cl = 2.25(2)
Li(1)-Cl = 2.18(6)	Li(2)-C(3) = 2.248(18)	Li(2)-Cl = 2.29(2)
Li(2)-Cl = 2.09(5)	Li(2)-C(4) = 2.177(17)	Li(3)-Cl = 2.28(2)
Li(3)-Cl = 2.14(6)	Li(1)-C(23) = 2.410(19)	Li(2)-N(2) = 1.99(2)
	Li(1)-C(24) = 2.275(18)	Li(2)-C(21) = 2.74(3)
	Li(1)-O(2) = 1.871(16)	Li(2)-C(22) = 2.74(3)
	Li(2)-O(2) = 1.826(16)	
	Li(3)-O(2) = 1.933(14)	
	O(2)-C(41) = 1.425(8)	
	C(41)-C(42) = 1.326(14)	
	O(2)-C(41)-C(42) = 122.1(9)	

The N-N distance [N(1)-N(1a) = 1.08(3)Å] is very short and, within experimental error, is in the same range of that determined by Evans in the labile decamethylsamarocene dinitrogen complex.¹

The second crystalline compound **7.3** present in the crude reaction mass is a Sm(II) enolate derivative $\{(\text{Cy}_4\text{-calix-tetrapyrrole})(\text{THF})\text{Sm}[\text{Li}(\text{THF})]_2[\text{Li}(\text{THF})_2](\mu^3\text{-OCH=CH}_2)\}$. The complex is monomeric and possesses a structure closely related to that of the divalent **7.1**⁵ and **7.4** (see below), the major differences being the presence of an enolate group (from THF cleavage)⁸ bridging the three lithium atoms instead of the bridging chlorine. The red color of the single crystals is most unusual for the oxidation state +2 of samarium and also contrasts with the more conventional dark green color of the divalent **7.1**.⁵ This, together with the severe bending of the $\text{O}_{\text{enolate}}\text{-Sm-O}_{\text{THF}}$ vector [O(2)-Sm-O(3) = 150.4(2)°] at first glance suggested that complex **7.3** might perhaps be a trivalent hydride. However, a comparable distortion is also present in the crystal structure of the dark-green **7.2** and similar to the case of the dinitrogen complex **7.2**, single red crystals of **7.3** also formed THF or ether solutions with the characteristic dark-green color. The magnetic moment was also in agreement with the divalent samarium formulation.

When crystals of **7.2** were redissolved in either THF or ether, nitrogen gas was released and dark green solutions were formed from which dark green crystals of either the starting **7.1** or the corresponding etherate $\{(\text{Cy}_4\text{-calix-tetrapyrrole})(\text{L})\text{Sm}[\text{Li}(\text{THF})]_2[\text{Li}(\text{THF})_2](\mu^3\text{-Cl})\}(\text{Et}_2\text{O})_{1.5}$ [L = Et₂O (**7.4**)] were isolated, respectively. As a common feature to other divalent Sm compounds of this particular ligand system,^{4,5} the NMR spectra of **7.4** were uninformative due to the large magnetic anisotropism. The magnetic moment was comparable to that of the starting

complex **7.1** and satisfactory analytical data in agreement with the proposed formulation were obtained. The only structural difference of **7.1** with respect to **7.4** consists of the presence of a chlorine instead of the enolate group and an almost linear arrangement of the Cl-Sm-O_{ether} vector.

In sharp contrast to the case of **7.1**, treatment of crystalline **7.4** with boiling hexane under nitrogen, followed by overnight standing at room temperature under N₂, afforded unreacted **7.4** as the only isolable compound. This indicates that the formation of the dinitrogen complex **7.2** can be reversed, but *only* in THF.

The labile fixation of dinitrogen as displayed by **7.2** as well as the short N-N distance sharply contrasts with the 4-electron reduction observed with the octaethyl derivative of the same ligand system.^{3a} However, the isolation of this new complex provides a straightforward, possible explanation for the encapsulation of dinitrogen as performed by the Et₈- derivative. If we assume that a complex similar to **7.2** is also formed in the case of the Et₈-calix-tetrapyrrole complex, simple attack of two molecules of unreacted divalent (Et₈calix-tetrapyrrole)Sm(THF)Li₃Cl might deliver the two additional electrons necessary for the four-electron reduction of N₂, and remove two chloride anions



CP = R₈-calix-tetrapyrrole tetra-anion

in return. Thus the formation of the encapsulated [(Et₈-calix-tetrapyrrole)SmLi]₂(N₂Li₄) complex should be accompanied by the formation of two equivalents of the trivalent

(Et₈calix-tetrapyrrole)Sm(Cl)[Li(THF)]₂[Li(THF)₂](μ³-Cl) whose preparation from Sm(III) precursors was previously described.^{3a,5}

VII.4: X-ray Crystallography

Suitable crystals were selected, mounted on thin, glass fibres using paraffin oil and cooled to the data collection temperature. Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° ω-scans at 0, 90, and 180° in φ. Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied.

All non-hydrogen non-solvent atoms were located and refined anisotropically. Atoms of interstitial molecules of THF and diethyl ether were refined isotropically. Hydrogen atoms were introduced at their idealized positions and refined with a riding mode. In the case of **7.2**, the Sm, Cl, O and Li atoms were refined anisotropically. All the other non-hydrogen atoms were refined isotropically to conserve a reasonable data/parameter ratio. Absorption corrections (SADABS) were applied to the data. Selected bond distances and angles are given in Table 7.1. Crystallographic details are presented in the Appendix, Table 6.

References

1. Evans, W.J.; Ulibarri, T.A.; Ziller, J.W. *J. Am. Chem. Soc.* **1988**, *110*, 6877.
2. Campazzi, E.; Solari, E.; Floriani, C.; Scopelliti, R. *J. Chem. Soc. Chem. Commun.* **1998**, 2603.
3. a) Jubb, J.; Gambarotta, S. *J. Am. Chem. Soc.* **1994**, *116*, 4477.
b) Dubé, T.; Conoci, S.; Gambarotta, S.; Yap, G.P.A. and Vasapollo, G. *Angew. Chem. Int. Ed. Engl.* In press.
c) Dubé, T.; Conoci, S.; Gambarotta, S. and Yap, G.P.A. *Angew. Chem. Int. Ed. Engl.* submitted.
4. a) Dubé, T.; Gambarotta, S.; Yap, G.P.A. *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 1432.
b) Brown, W.H.; Hutchinson, B.J.; McKinnon, M.H. *Can. J. Chem.* **1971**, *49*, 4017.
5. Dubé, T.; Gambarotta, S.; Yap, G.P.A. *Organometallics* submitted.
6. Mabbs, M.B.; Machin, D. *Magnetism and Transition Metal Complexes*; Chapman and Hall; London, 1973.
7. Foese, G.; Gorter, C.J.; Smits, L.J. *Constantes Selectionnes, Diamagnetisme, Paramagnetism Relaxation Paramagnetique*; Masson, Paris, 1957.
8. a) Jubb, J.; Gambarotta, S.; Duchateau, R.; Teuben, J. *J. Chem. Soc. Chem. Commun.* **1994**, 2641.
b) Aspinall, H.C.; Tillotson, M.R. *Inorg. Chem.* **1996**, *35*, 2163.
c) Evans, W.J.; Dominguez, R.; Hanusa, T.P. *Organometallics* **1986**, *5*, 1291.
d) Jubb, J.; Gambarotta, S. *Inorg. Chem.* **1994**, *33*, 2503.

- e) Jubb, J.; Gambarotta, S. *J. Am. Chem. Soc.* **1993**, *115*, 10410.
- f) Dubé, T.; Gambarotta, S.; Yap, G.P.A. *Organometallics* **1998**, *17*, 3967.
- g) De Angelis, S.; Solari, E.; Floriani, C.; Chiesi-Villa, A. *J. Chem. Soc. Dalton Trans.* **1994**, 2467.
- h) Rupp, K.B.; Gambarotta, S.; Bensimon, C.; Yap, G.P.A. *Inorg. Chim. Acta* **1998**, *280*, 143.

CHAPTER VIII

Formation of a tetranuclear samarium dinitrogen complex via cooperative, tetrametallic reduction of dinitrogen

VIII.1: Introduction:

Examples of dinitrogen complexes are rare in lanthanide chemistry and have been documented for only four cases.^{1,2} In the case of samarium in particular, the two existing complexes display a completely different extent of dinitrogen reduction.¹ Thus, in an attempt to evaluate the role played by the nature of the ligand in promoting dinitrogen reduction, we have now pursued the preparation of a novel diphenylmethyldipyrrolide dianion and investigated its ability to stabilize Sm^{II} complexes.³ Herein we describe the first example where a four-electron dinitrogen reduction is achieved through the cooperative one-electron oxidation of four metal centers. To the best of our knowledge, this type of process has been observed only in the enzyme nitrogenase.⁴

VIII.2: Experimental Section

All operations were performed under an inert atmosphere of a nitrogen-filled drybox or by using standard Schlenk-type glassware in combination with a nitrogen-vacuum line. Diphenyl dipyrromethane was prepared according to a modification of the existing procedure.³ $\text{SmCl}_3(\text{THF})_3$ ⁵ and $\text{SmI}_2(\text{THF})_2$ ⁶ were prepared according to literature procedures.⁶⁻⁹ Infrared spectra were recorded on a Mattson 3000 FTIR instrument from Nujol mulls or KBr pellets prepared inside the drybox. Samples for magnetic susceptibility measurements were carried out at room temperature using a Gouy balance (Johnson Matthey). Magnetic moments were calculated by following standard methods⁷ and corrections for underlying diamagnetism were applied to the data.⁸ Elemental analyses were carried out using a Perkin-Elmer Series II CHN/O 2400-analyzer.

Preparation of $\{[\mu\text{-Ph}_2\text{C}(\eta^1\text{:}\eta^5\text{-C}_4\text{H}_3\text{N})_2]\text{Sm}\}_4(\mu\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-N}_2)\}$ (8.1):

Method A: A solution of potassium diphenylmethyldipyrrolide (1.3 g, 3.4 mmol) in THF (100 mL) was treated under N_2 with $\text{SmI}_2(\text{THF})_2$ (1.8 g, 3.4 mmol). The color immediately changed to dark purple-brown. Stirring was continued for 12 hours after which the solution was filtered to eliminate a small amount of insoluble material. The filtrate was concentrated to small volume (50 mL). Addition of toluene (50 mL) and standing at room temperature for 24 hours yielded large, red-brown crystals of **8.1** (1.3 g, 0.66 mmol, 78%). El. Anal. Calcd. (Found) for $\text{Sm}_4\text{C}_{92}\text{H}_{80}\text{O}_2\text{N}_{10}$: C 56.40(56.35), H 4.12(4.08), N 7.15(7.09). I.R. (Nujol mull, cm^{-1}) ν : 3048(w), 1597(w), 1491(m), 1464(s), 1417(w), 1377(s), 1261(w), 1182(w), 1147(m), 1078(w), 1043(s), 985(w), 874 (w), 798(m), 785(m), 756(s), 740(s), 696(s), 658(w), 640(m). $\mu_{\text{eff}} = 6.55 \mu_B$ per formula unit.

Method B: A solution of **8.2** (0.7 g, 0.25 mmol) in THF (50 mL) under N₂ was treated with KH (0.050 g, 1.2 mmol). A vigorous reaction with effervescence and a color change to purple-brown was immediately observed. The solution was allowed to stir for 30 minutes followed by filtration to remove a small amount of insoluble material. Layering with toluene and standing at room temperature for 3 days produced crystals of **8.1** (Yield 76%).

Preparation of $[\{\mu\text{-Ph}_2\text{C}(\eta^1:\eta^5\text{-C}_4\text{H}_3\text{N})_2\}\text{Sm}\}_5(\mu\text{-I})]^{(-)}[\{\mu\text{-Ph}_2\text{C}(\eta^1:\eta^5\text{-C}_4\text{H}_3\text{N})_2\}[\text{Sm}(\text{THF})]_3(\mu\text{-I})]^{(+)}$ (8.2**):**

A solution of diphenylmethyldipyrrolide (1.0 g, 3.4 mmol) in THF (100 mL) was stirred with KH (0.3 g, 6.7 mmol) at room temperature under Ar and for 30 minutes. Subsequent addition of SmI₂(THF)₂ (1.8 g, 3.4 mmol) resulted in an immediate color change to dark brown. After stirring overnight the solution was filtered to eliminate a small amount of dark insoluble material, concentrated to small volume (50 mL), and layered with toluene (25 mL). The mixture was allowed to stand for 24 hours at room temperature resulting in the precipitation of large, dark red crystals of **8.2** (1.0 g, 0.22 mmol, 53% calculated relatively to Sm). El. Anal. Calcd. (Found) for Sm₈N₁₄O₇C_{206.5}H_{205.5}: C 59.07(58.88), H 4.93(4.81), N 4.67(4.59). I.R. (Nujol mull, cm⁻¹) ν : 3049(w), 1595(w), 1489(m), 1464(s), 1419(w), 1377(s), 1263(w), 1234(w), 1184(w), 1151(m), 1076(m), 1038(s), 980(w), 964(w), 926(w), 891(m), 848(m), 789(m), 748(s), 704(s), 658(w), 634(m). $\mu_{\text{eff}} = 9.14 \mu_B$ per formula unit.

Preparation of $[\{\mu\text{-Ph}_2\text{C}(\eta^1:\eta^5\text{-C}_4\text{H}_3\text{N})_2\}\text{Sm}\}_4(\mu\text{-Cl})[\text{K}(\text{THF})_2]$ (8.3):

A THF solution (100 mL) of diphenylmethyldipyrrolide (1.1 g, 3.7 mmol) was treated with KH (0.3 g, 7.5 mmol). Stirring was continued at room temperature for 30 minutes until all of the KH had been consumed. Subsequent addition of $\text{SmCl}_3(\text{THF})_3$ (1.7 g, 3.7 mmol) resulted in the formation of a yellow suspension which was stirred for 1 hour. Metallic potassium (0.15 g, 3.8 mmol) was then added to the reaction mixture together with catalytic amount of naphthalene (0.01 g, 78 μmol). Within minutes the color began to deepen to reddish-brown. After 4 hours all the potassium was consumed. The solution was filtered to remove a small amount of insoluble material. The dark brown filtrate was concentrated (50 mL) and layered with toluene (30 mL). After standing at room temperature for 2 days large, dark brown crystals of **8.3** separated (1.2 g, 0.5 mmol, 58%). El. Anal. Calcd.(Found) for $\text{C}_{104}\text{H}_{104}\text{N}_8\text{O}_5\text{KClSm}_4$: C 56.21(56.11), H 4.72(4.66), N 5.04(4.97). I.R. (Nujol mull, cm^{-1}) ν : 3050(w), 1597(w), 1493(m), 1464(s), 1415(w), 1377(s), 1261(m), 1236(w), 1182(w), 1151(m), 1091(m), 1078(m), 1039(s), 980(w), 924(w), 879(w), 849(m), 795(m), 760(s), 700(s), 660(m), 636(m). $\mu_{\text{eff}} = 7.02 \mu_B$ per tetramer.

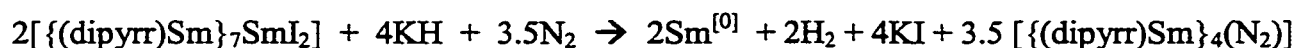
VIII.3: Results and Discussion:

The reaction of $\text{SmI}_2(\text{THF})_2$ with one equivalent of diphenylmethyldipyrrolide dianion (either disodium or dipotassium salt) at room temperature and under N_2 yielded a dark purple-brown solution from which dark brown crystals of $[\{\mu\text{-Ph}_2\text{C}(\eta^1:\eta^5\text{-C}_4\text{H}_3\text{N})_2\}\text{Sm}\}_4(\mu\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-N}_2)]$ (**8.1**) (Scheme 8.1) were isolated in good yield and

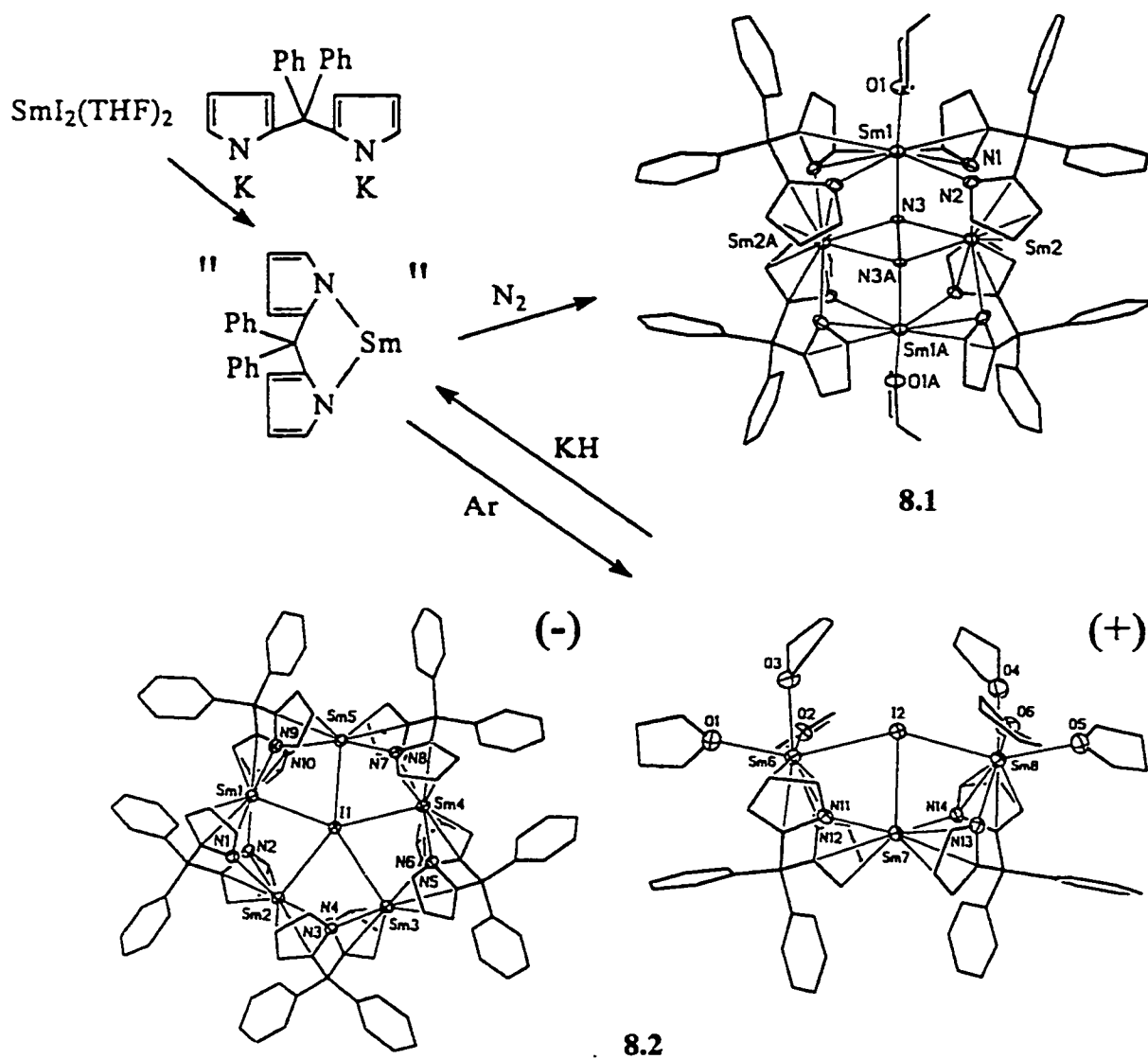
analytically pure form on a reproducible basis. Unlike $[\{N(CH_2CH_2NSiBu^tMe_2)_3U\}_2(\mu-\eta^2:\eta^2-N_2)]^9$ or $[\{(\eta^5-C_5Me_5)_2Sm\}_2(\mu-\eta^2:\eta^2-N_2)]^{1a}$ and similar to the case of the calix-tetrapyrrole derivative,^{1b} complex **8.1** showed no sign of reversible coordination of dinitrogen and remained unchanged upon prolonged exposure to heat or vacuum.

The N-N distance and the fact that degradation with anhydrous HCl did not release N₂, indicates that the Sm atoms are definitely present in the formal trivalent state.¹⁰ The same reaction carried out under Ar atmosphere afforded dark red crystals of a new ionic compound formulated as $[[\{\mu-Ph_2C(\eta^1:\eta^5-C_4H_3N)_2\}Sm\}_5(\mu-I)]^{(-)}[[\mu-Ph_2C(\eta^1:\eta^5-C_4H_3N)_2][Sm(THF)]_3(\mu-I)]^{(+)}$ (**8.2**).

Complex **8.2** does not show any appreciable sign of reaction with nitrogen gas even after long periods and upon heating. Thus questions arise about the striking diversity of behavior resulting in the formations of **8.1** and **8.2**. Complex **8.2** exclusively contains divalent samarium atoms. The formula unit formally consists of seven $[\{Ph_2C(C_4H_3N)_2\}Sm]$ units and one SmI₂ organized in stable cluster structures around the two halogen atoms. The presence of the two iodine atoms is likely to be the factor responsible for the lack of reactivity with dinitrogen. Attempts to avoid their presence, for example by carrying out the preparation of **8.2** with excess ligand, did not modify the result. The elimination of the formal SmI₂ unit was obtained *via* reaction of **8.2** with KH which resulted in an immediate color change and concomitant release of H₂ according to the equation 8.1:



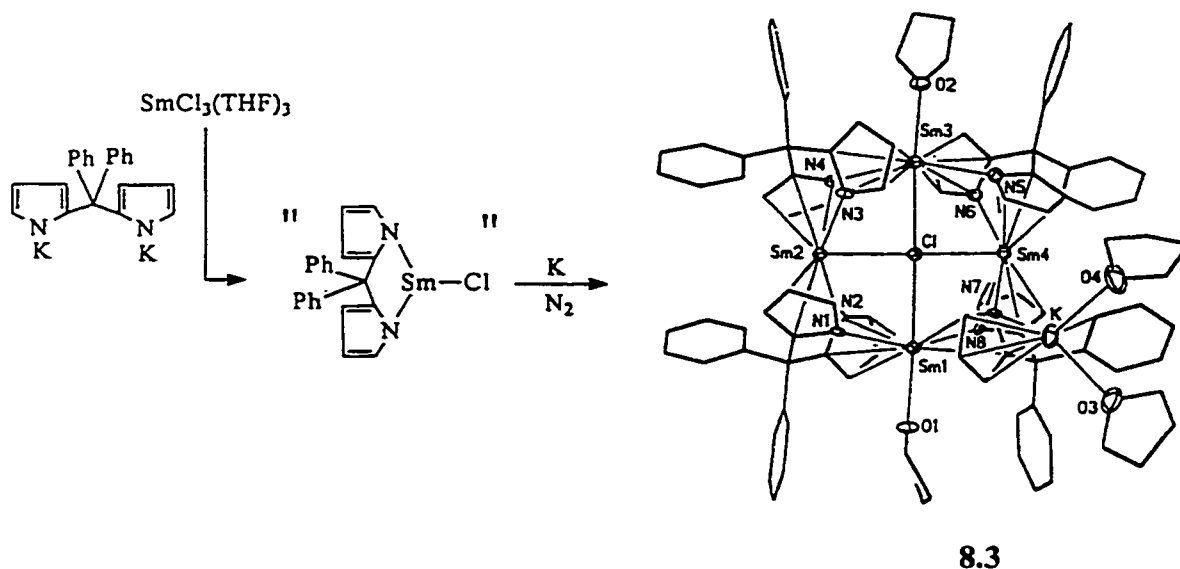
Scheme 8.1



The fact that this reaction afforded **8.1** in good yield suggests that halogen elimination from **8.2** dissociates the cluster structures releasing "[{ $Ph_2C(C_4H_3N)_2$ Sm}]" fragments free to react with dinitrogen.

In an effort to further clarify the role of the halogen atom, attempts were made to generate the "[Ph₂C(C₄H₃N)₂]Sm]" unit via reduction of a "[{[Ph₂C(C₄H₃N)₂]Sm}Cl]" precursor with potassium under nitrogen and in THF (Scheme 8.2).

Scheme 8.2



The reaction yielded a new Sm^{II} compound formulated as $[\{\mu\text{-Ph}_2\text{C}(\eta^1:\eta^5\text{-C}_4\text{H}_3\text{N})_2\}\text{Sm}\}_4(\mu\text{-Cl})[\text{K}(\text{THF})_2]]$ (**8.3**). Similar to the case of **8.2**, **8.3** showed no signs of reactivity towards dinitrogen despite the striking structural similarity of its tetrametallic core with that of **8.1**. This result confirms that the halogen has indeed an inhibitory effect on the ability of the samarium diphenylmethyldipyrrolyl system to interact with dinitrogen. It should be observed that in spite of the oxophilicity of samarium, the presence of THF does not prevent dinitrogen fixation.

VIII.4: X-ray Crystallography

Suitable crystals were mounted with cooled viscous oil on thin glass fibers. Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° ω -scans at 0, 90, and 180° in ϕ . Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied.

The presence of a molecule of coordinated dinitrogen in the molecular structure of **8.1** was demonstrated by an X-ray crystal structure (Fig. 8.1). The complex is formed by four $[\{\text{Ph}_2\text{C}(\text{C}_4\text{H}_3\text{N})_2\}\text{Sm}]$ units with the four metal atoms arranged to form a slightly distorted lozenge. A dinitrogen molecule is placed in the center and is coordinated side-on to two metal atoms and end-on to the others. Crystallographic details are presented in the Appendix, Table 7.

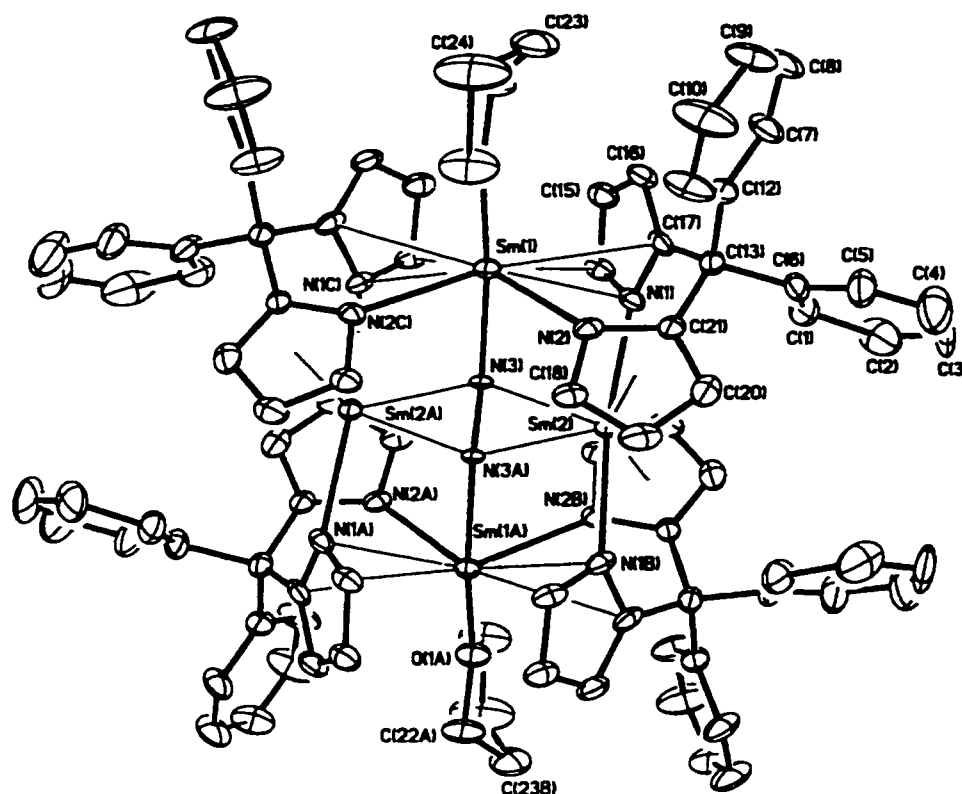


Fig. 8.1 X-ray Structure of 8.1, $[[\{\mu\text{-Ph}_2\text{C}(\eta^1:\eta^5\text{-C}_4\text{H}_3\text{N})_2\}\text{Sm}\}_4(\mu\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-N}_2)]$

Bond distances are in Å and angles in deg (°): N(3)-N(3a) = 1.412(17), Sm(1)-N(3) = 2.177(8), Sm(2)-N(3) = 2.327(3), Sm(2)-N(3a) = 2.327(3), Sm(1)...Sm(2) = 3.602(9), Sm(2)..Sm(2a) = 4.434(9), Sm(1)..Sm(1a) = 5.678(9), Sm(1)-N(1) = 2.701(8), Sm(1)-N(2) = 2.736(8), Sm(2)-N(1) = 2.574(8), Sm(2)-N(2) = 2.697(7), Sm(1)-N(3)-N(3a) = 156.6(11), O(1)-Sm(1)-N(3) = 150.5(4);

The ionic structure of Complex 8.2 is formed by a trinuclear cation and a pentanuclear anion. The cation consists of three samarium atoms bridged by one nearly coplanar iodine atom adopting a distorted "T-shape" geometry. Two diphenylmethyldipyrroliide dianions also bridge the three samarium atoms adopting the same bonding mode observed in

Complex 8.1. The counter-anion is a pentanuclear samarium complex with five samarium atoms pentagonally arranged around a central and coplanar iodine atom. The five diphenylmethyldipyrrolide dianions adopt the usual π - and σ -bonding modes with each ligand bridging two samarium centers.

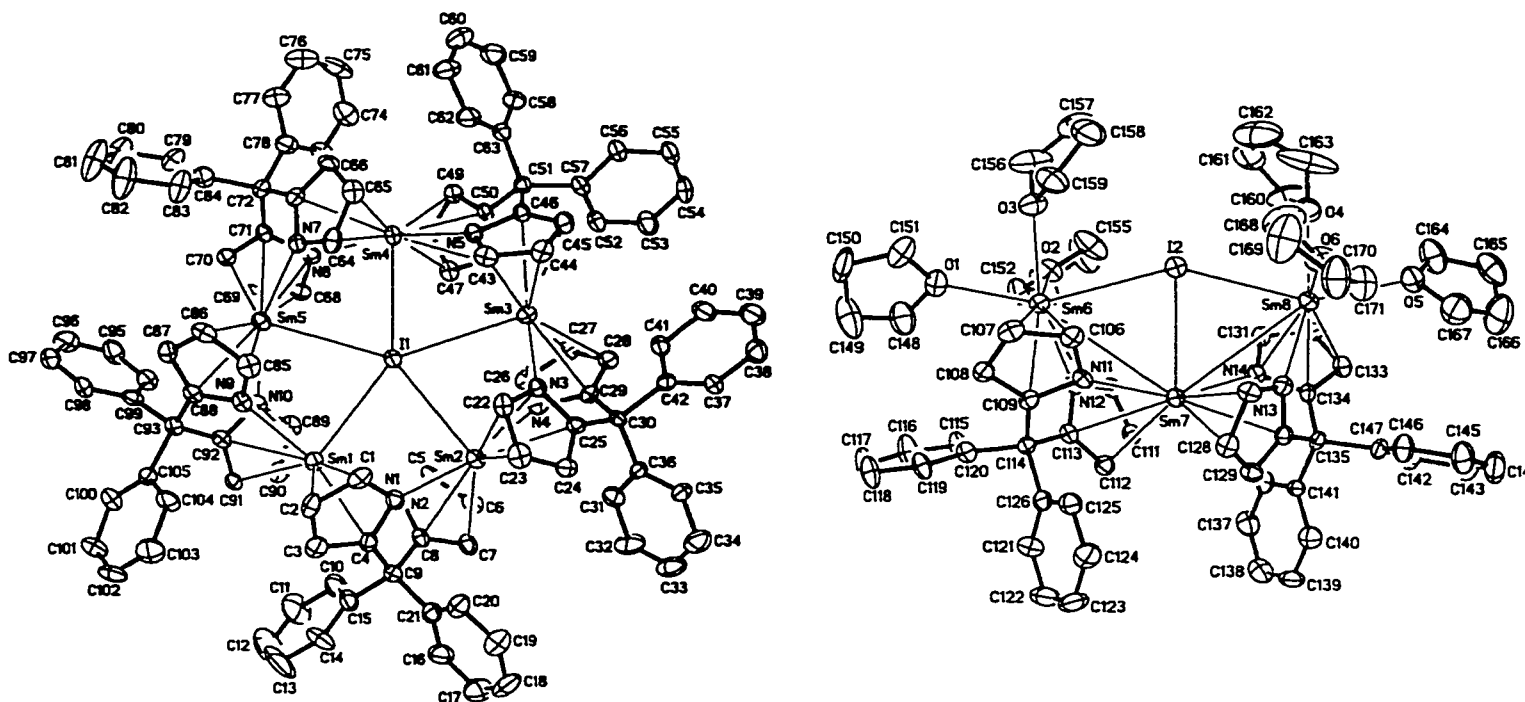


Fig. 8.2. X-ray Structure of 8.2, $[[\{\mu\text{-Ph}_2\text{C}(\eta^1:\eta^5\text{-C}_4\text{H}_3\text{N})_2\}\text{Sm}\}_5(\mu\text{-I})]^{(-)}\{[\{\mu\text{-Ph}_2\text{C}(\eta^1:\eta^5\text{-C}_4\text{H}_3\text{N})_2\}_2[\text{Sm}(\text{THF})]_3\}(\mu\text{-I})]^{(+)}$

Bond distances are in Å and angles in deg ($^\circ$): Sm(1)-I(1) = 3.434 (1), Sm(2)-I(1) = 3.480(1), Sm(3)-I(1) = 3.634(1), Sm(4)-I(1) = 3.455(1), Sm(5)-I(1) = 3.520(1), Sm(1) - N(1) = 2.810(7), Sm(1)-N(2) = 2.670(7), Sm(1)-N(9)) = 2.664(7), Sm(1)-N(10) = 2.768(7), Sm(6)-I(2) = 3.3168(8), Sm(7)-I(2) = 3.369(1) , Sm(8)-I(2) = 3.3047(9), Sm(1)..Sm(2) = 4.123(1), Sm(1)..Sm(5) = 4.101(1), Sm(7)..Sm(6) = 4.028(1), Sm(7)..Sm(8) = 4.038(1), Sm(1)-I(1)-Sm(2) = 73.211(18), Sm(1)-I(1)-Sm(5) =

72.260(16), Sm(7)-I(2)-Sm(6) = 74.090(18), Sm(7)-I(2)-Sm(8) = 74.468(18), Sm(6)-I(2)-Sm(8) = 148.35(2).

An X-ray crystal structure determination of Complex 8.3 (Fig. 8.3) revealed a molecular structure very similar to that observed for 8.1 except that a chlorine atom is present instead of N₂ in the center of the square plane defined by the four samarium atoms. A single potassium atom is π -bonded to one of the pyrrole rings already engaged in σ - and π -bridging interactions with the two samarium centers.

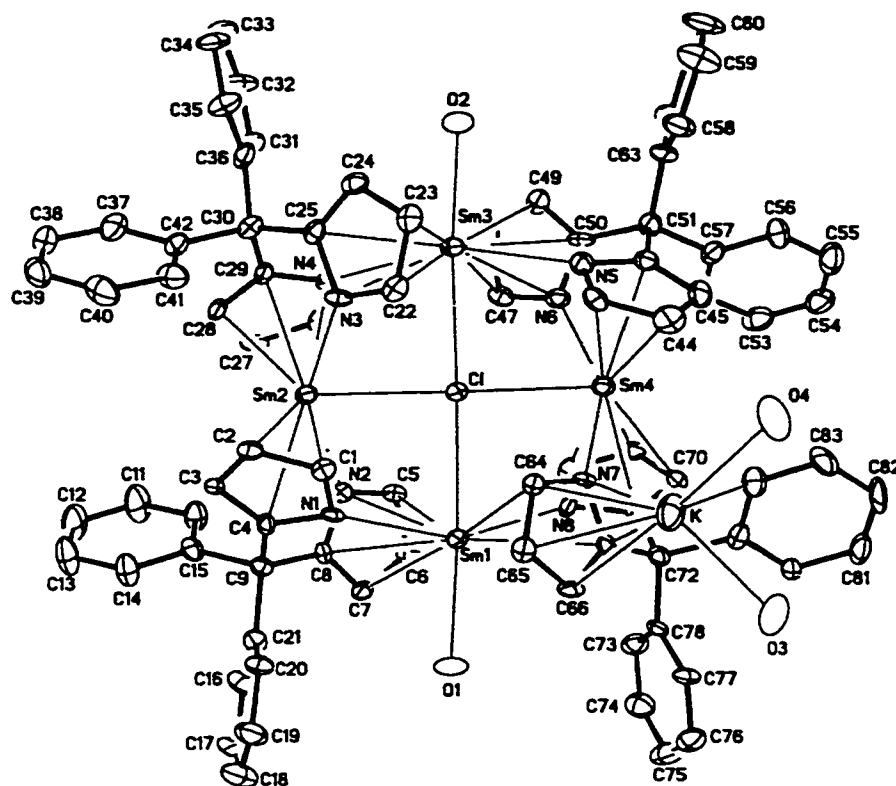


Fig. 8.3. X-ray Structure of 8.3, $[[\mu\text{-Ph}_2\text{C}(\eta^1\text{:}\eta^5\text{-C}_4\text{H}_3\text{N})_2]\text{Sm}]_4(\mu\text{-Cl})[\text{K}(\text{THF})_2]$

Bond distances are in Å and angles in deg (°): Sm(1)-Cl = 3.045(2), Sm(2)-Cl = 2.847(2), Sm(3)-Cl = 3.042(2), Sm(4)-Cl = 2.845(2), Sm(1)-N(1) = 2.726(6), Sm(1)-N(2)

= 2.849(6), Sm(1)-N(7) = 3.040(8) , Sm(1)-N(8) = 2.712(7), Sm(1)..Sm(2) = 4.136(2),
Sm(1)..Sm(4) = 4.240(2), Sm(1)..Sm(3) = 6.087(2), Sm(2)..Sm(4) = 5.689(2), Sm(1)-Cl-
Sm(2) = 89.10(6), Sm(1)-Cl-Sm(3) = 178.30(8), Sm(1)-Cl-Sm(4) = 92.03(6), Sm(2)-Cl-
Sm(4) = 176.69(9), O(1)-Sm(1)-Cl = 168.53(13).

References

1. (a) Evans, W.J.; Ulibarri, T.A.; Ziller, J.W. *J. Am. Chem. Soc.* **1988**, *110*, 6877.
(b) Jubb, J.; Gambarotta, S. *J. Am. Chem. Soc.*, **1994**, *116*, 4477.
2. Campazzi, E.; Solari, E.; Floriani, C.; Scopelliti, R. *J. Chem. Soc. Chem. Commun.* **1998**, 2603.
3. (a) Dolphin, D.; Liu, B.Y.; Brückner, C. *Chem. Commun.* **1996**, 2141 and references therein;
(b) Lee, C.H.; Lindsey, S. *Tetrahedron* **1994**, *50*, 11427.
4. (a) Howard, J.B.; Rees, D.C. *Chem. Rev.* **1996**, *96*, 2965.
(b) Burgess, B.K.; Lowe, D.J. *Chem. Rev.* **1996**, *96*, 2983.
(c) Eady, R.R. *Chem. Rev.* **1996**, *96*, 3013.
5. (a) Freeman, J.H.; Smith, M.L. *J. Inorg.Nucl. Chem.* **1958**, *7*, 224.
(b) Manzer, L.E. *Inorg. Synth.* **1982**, *21*, 135.
6. Evans, W.J.; Grate, J.W.; Choi, H.W.; Bloom, I.; Hunter, W.E.; Atwood, J.L. *J. Am. Chem. Soc.* **1985**, *107*, 941.
7. Mabbs, M.B.; Machin, D. *Magnetism and Transition Metal Complexes*; Chapman and Hall, London, 1973.
8. Foese, G.; Gorter, C.J.; Smits, L.J. *Constantes Selectionnes, Diamagnetism, Paramagnetism Relaxation Paramagnetique*; Masson, Paris, 1957.
9. Roussel, P.; Scott, P. *J. Am. Chem. Soc.* **1998**, *120*, 1070.
10. Accordingly, the Sm-N(pyrr) and Sm-C(pyrr) distances compare reasonably with those of the trivalent (COT)Sm(pyrrrole)(THF) complex: H. Schumann, E.C.E.

Rosenthal, J. Winterfeld, R. Weimann, J. Demtschuk *J. Organomet. Chem.* **1996**, *507*, 287.

CHAPTER IX

Tetrametallic Divalent Samarium Cluster Hydride and Mixed-Valence

Sm(II)/Sm(III) Dinitrogen Complex.

IX.1: Introduction

Among the few lanthanides that can be made available as low-valent complexes,¹ samarium certainly occupies an important place because of the unique richness and variety² of the chemical transformations displayed by the few existing divalent samarium complexes.³ As usual, the nature of the ancillary ligand plays a prominent role in determining the reactivity of these species and, with this respect, pyrrole-based ligand systems seem to be particularly versatile. For example, calix-tetrapyrrole anions are able to stabilize very reactive divalent samarium complexes,⁴ to promote ethylene reversible coordination⁴ and either dinitrogen labile coordination^{5a} or 4-electron reduction.^{5b} The recently described diphenylmethyldipyrrolide dianion has enabled the preparation and characterization of a series of divalent and mixed-valence cluster compounds and of a unique trivalent and tetranuclear dinitrogen complex.⁶

This work describes the isolation and characterization of an unprecedented tetranuclear divalent samarium hydride cluster supported by the diphenylmethyl dipyrrolide ligand system,⁷ as well as the first example of a mixed-valence Sm(II)/Sm(III) dinitrogen complex.

IX.2: Experimental Section:

All operations were performed under an inert atmosphere of a nitrogen-filled drybox or by using standard Schenk-type glassware in combination with a nitrogen-vacuum line. $\text{SmCl}_3(\text{THF})_3$,⁸ $\text{SmI}_2(\text{THF})_2$,⁹ and cyclohexyl dipyrromethane were prepared according to literature procedures.¹⁰ Diphenyl dipyrromethane was prepared according to a modification of the literature procedure.⁷ THF-d⁸ was dried over Na/K alloy, vacuum-transferred into ampoules, and stored under nitrogen prior to use. NMR spectra were recorded on a Varian Gemini 200 and on a Bruker AMX-500 spectrometer using vacuum sealed NMR tubes prepared inside a drybox. Infrared spectra were recorded on a Mattson 3000 FTIR instrument from Nujol mulls or KBr pellets prepared inside the drybox. Samples for magnetic susceptibility measurements were carried out at room temperature using a Gouy balance (Johnson Matthey). Magnetic moments were calculated by following standard methods¹¹ and corrections for underlying diamagnetism were applied to the data.¹² Elemental analyses were carried out using a Perkin-Elmer Series II CHN/O 2400-analyzer.

Preparation of $\{([\text{Ph}_2\text{C}(\text{C}_4\text{H}_3\text{N})_2]\text{Sm})_4(\text{H})\}\text{Na}(\text{THF})_6\}$ (9.1):

A solution of diphenylmethyldipyrrole (3.2 g, 10.7 mmol) in THF (200 mL) was treated at room temperature with NaH (0.5 g, 22.5 mmol). The resulting suspension was stirred for 2 hours at room temperature until no further effervescence was observed. Subsequent addition of $\text{SmCl}_3(\text{THF})_3$ (4.9 g, 10.4 mmol) resulted in an instantaneous color change to light yellow. After stirring at 60°C for 30 minutes, sodium metal (0.3 g, 13.0 mmol) was introduced in the presence of a catalytic amount of C_{10}H_8 (10 mg, 78 μmol). Vigorous

stirring at room temperature for 18 hours produced a deep purple-brown solution which was filtered to remove an appreciable amount of insoluble solid. Addition of toluene (75 mL), concentration to small volume and standing overnight at room temperature resulted in the separation of dark purple, microcrystalline **9.1** (2.5 g, 1.05 mmol, 39%). El. Anal. Calcd.(Found) for $C_{116}H_{128}N_8NaO_8Sm_4$: C 58.37(58.31), H 5.41(5.35), N 4.69(4.64). I.R. (Nujol mull, cm^{-1}) ν : 3190(w), 3051(w), 2729(w), 2671(w), 1595(w), 1577(w), 1489(m), 1456(vs), 1377(vs), 1261(w), 1147(m), 1092(br,m), 1043(s), 984(w) 891(w), 848(m), 798(m), 740(s), 700(s), 656(w), 634(w). 1H -NMR (d^8 -THF, 500 MHz, 23°C) δ : 31.01 (s, pyrrole, 8H), 25.25 (s, pyrrole, 8H), 8.59 (s, phenyl, 4H), 8.45 (q, phenyl, 8H), 7.15 (s, phenyl, 16H), 7.01 (q, phenyl, 8H), 5.92 (dd, phenyl, 4H), 4.17 (br. s, pyrrole, 8H), 3.75 (m, THF, 32H), 1.86 (m, THF, 32H), -3.91 (br.s, hydride, 1H). C^{13} -NMR (d^8 -THF, 125.72MHz, 23°C) δ : 145.29, 38.23, -23.31 (C-H, pyrrole), 153.32, 133.43, 131.47, 129.97, 126.13, 124.75 (C-H, phenyl), 86.13 (quaternary. The other quaternary carbons could not be located), 68.24, 67.78, 67.60, 67.43, 67.25, 67.08, 26.36, 25.61, 25.46, 25.30, 25.14, 24.98 (CH_2 , THF), $\mu_{eff} = 7.07\mu_B$

Preparation of $\{[(CH_2)_5C(C_4H_3N)_2]Sm\}_4(\mu-N_2)[Na(THF)]_2$ (9.2**)**

Solid NaH (0.7 g, 30.1 mmol) was added to a THF solution (150 mL) of 1,1-cyclohexyldipyrrole (3.4 g, 15.0 mmol). The mixture was stirred for 30 minutes at room temperature until no further effervescence was observed. Addition of $SmCl_3(THF)_3$ (6.9 g, 14.6 mmol) resulted in a bright yellow suspension which was heated to 60°C for 30 min. Excess metallic sodium (0.5 g, 21.7 mmol) and a catalytic amount of naphthalene (10 mg, 78 μ mol) were introduced and the mixture was stirred at room temperature for 16

hours. The resulting dark greenish-brown solution was filtered, concentrated to 50 mL, and layered with hexanes (50 mL). Standing at room temperature for 2 days yielded crystals of **9.2** (3.0 g, 1.5 mmol, 42 %). El. Anal. Calcd.(Found) for $C_{80}H_{112}N_{10}Na_2O_6Sm_4$: C 49.09(48.77), H 5.77(5.66), N 7.16(7.00). I.R. (Nujol mull, cm^{-1}) ν : 3107(w), 3091(w), 1597(w), 1462(s), 1377(vs), 1278(m), 1261(m), 1149(m), 1151(m), 1124(m), 1078(m, br), 1038(m), 1024(s), 956(m), 902(m), 874(w), 829(w), 760(vs), 729(w), 632(m), 571(s). $\mu_{eff} = 4.05 \mu_B$ per formula unit. Very poor solubility in the most common inert solvents including THF and pyridine has prevented NMR characterization.

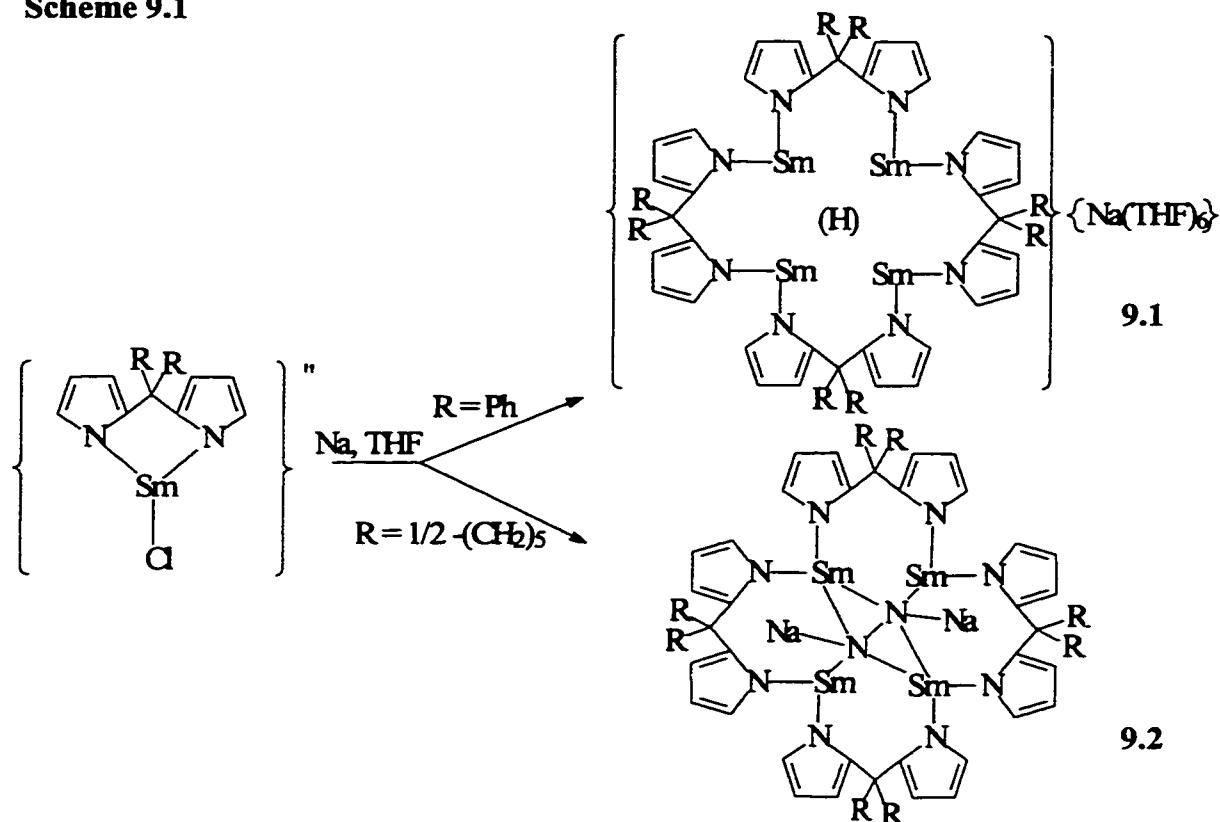
IX.3: Results and Discussion

Reduction of a “ $\{[R_2C(C_4H_3N)_2]Sm\}Cl$ ” [$R = Ph$] precursor with sodium under nitrogen and in THF afforded the paramagnetic $\{([Ph_2C(C_4H_3N)_2]Sm)_4\} \{Na(THF)_6\}$ (**9.1**) which was isolated as a dark purple crystalline material (Scheme 9.1).

The connectivity of complex **9.1** as indicated by the crystal structure might suggest either a mixed-valence $\{([Ph_2C(C_4H_3N)_2]Sm)_4\} \{Na(THF)_6\}$ or a divalent $\{([Ph_2C(C_4H_3N)_2]Sm)_4(H)\}Na(THF)_6$ hydride formulation. Consistent with both possibilities, chemical degradation carried out by reacting **9.1** with eight equivalents of gaseous hydrochloric acid produced the expected 5/2 equivalents of H_2 (93%) per formula unit. Similar to the case of the other Sm(II) clusters of the same ligand system,⁶ the magnetic moment was hardly informative. However, the 1H -NMR spectrum of **9.1** showed a broad peak at -3.91 ppm which did not correlate with any carbon atom. Exposure of a solution of **9.1** in d^8 -THF to D_2 gas at 1 atmosphere led to the disappearance of this resonance while the rest of the spectrum remained unmodified. A corresponding resonance appeared in the H^2 -NMR spectrum. The I.R. spectrum of the compound after having been exposed to deuterium gas showed no modification except for a band at 1261 cm^{-1} which shifted to 966 cm^{-1} . On the basis of these observations, it seems reasonable to conclude that complex **9.1** is indeed a Sm(II) hydride compound rather than an unlikely mixed-valence Sm(II)/Sm(I) species. It may be regarded as the formal addition product of one molecule of NaH to $\{[R_2C(C_4H_3N)_2]Sm\}_4$.

We have no explanation for the origin of the hydride in complex **9.1**. We simply observe that its formation is strikingly similar to the case of the reduction of $Cp_2Lu(THF)Cl$ with Na in THF which afforded a good yield of the corresponding hydride $Na(THF)_6[(Cp_2LuH)_3H]$.¹³

Scheme 9.1



In close analogy to the chemistry of Sm(II) supported by the calix-tetrapyrrole ligand system,^{4,5} the reduction of the trivalent “[$\text{R}_2\text{C}(\text{C}_4\text{H}_3\text{N})_2\text{Sm}\}\text{Cl}$ ” precursor displayed a remarkable sensitivity to the nature of the substituents (Scheme 9.1). In the case of the 1,1-cyclohexyldipyrrolide derivative [$R = 1/2 -(\text{CH}_2)_5-$] the same reaction carried out under identical conditions afforded the dinitrogen complex $\{[(\text{CH}_2)_5\text{C}(\text{C}_4\text{H}_3\text{N})_2]\text{Sm}\}_4(\mu\text{-N}_2)[\text{Na}(\text{THF})]_2$ (9.2) which was isolated in crystalline form.

Although the geometrical parameters of the Sm_4N_2 core are comparable to those of 9.1 we found no evidence that 9.1 may react with dinitrogen. The presence in 9.2 of two sodium cations coordinated to nitrogen and the N-N distance [$\text{N-N} = 1.371(16)\text{\AA}$], indicative of a 2-electron reduction of N_2 , attribute a formal oxidation state of +2.5 to the

four samarium atoms. We found rather surprising that in spite of the availability of more electrons on the samarium metals no further dinitrogen reduction occurred.

IX.4: X-ray Crystallography

Suitable crystals were mounted with cooled viscous oil on thin glass fibers. Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° ω -scans at 0, 90, and 180° in ϕ . Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Unfortunately, the crystals of **9.1** diffracted poorly in spite of their good quality and repeated attempts. However, the data quality was sufficient for the elucidation of the molecular connectivity and the formula.

Semi-empirical absorption corrections based on equivalent reflections were applied. Crystallographic details are presented in the Appendix, Table 8.

The connectivity of **9.1** was determined according to an X-ray crystal structure determination. The molecule is formed by four $\{[\text{Ph}_2\text{C}(\text{C}_4\text{H}_3\text{N})_2]\text{Sm}\}$ units with the four samarium atoms arranged to form a rhomb (Figure 9.1). Each dipyrromethanyl dianion bridges two metal atoms with the pyrrole rings being in turn π -bonded to one samarium and σ -bonded to another. Each of the two samarium atoms placed on the two acute vertices of the tetrametallic core bears one molecule of THF. One sodium atom, solvated by six molecules of THF and unconnected to the cluster, completes the structure.

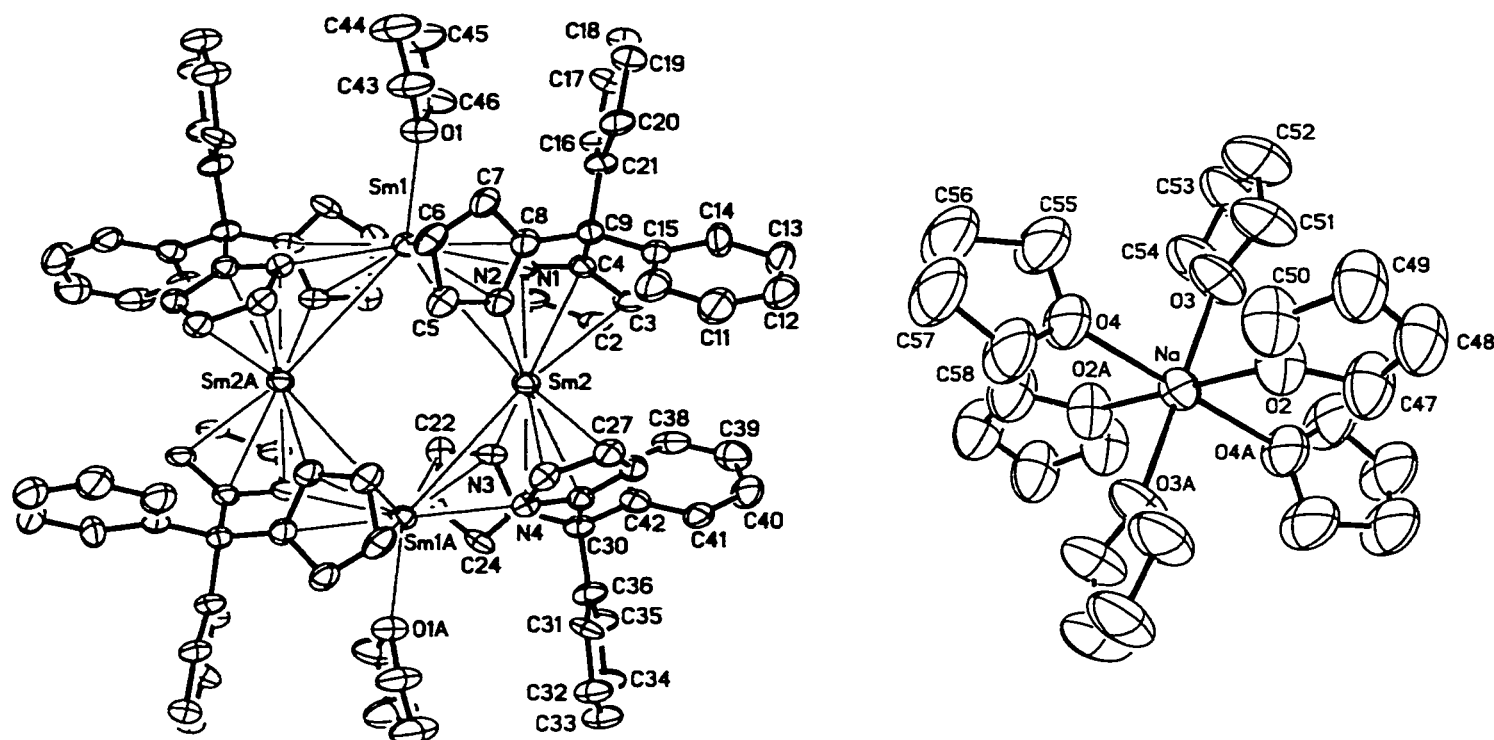


Fig. 9.1. X-ray Structure of 9.1, $\{([Ph_2C(C_4H_3N)_2]Sm)_4(H)\}Na(THF)_6\}$

Selected Bond Distances (Å) and Angles (°): Sm(1)-N(1) = 2.668(17), Sm(1)-N(2) = 2.842(18), Sm(1)-C(5) = 2.93(2), Sm(1)-C(6) = 3.01(2), Sm(1)-C(7) = 3.01(2), Sm(1)-C(8) = 2.91(2), Sm(1)-O(1) = 2.597(14), Sm(2)-N(1) = 2.801(17), Sm(2)-N(2) = 2.622(17), Sm(2)-N(3) = 2.601(17), Sm(2)-N(4) = 2.795(17), Sm(2)-C(1) = 2.86(2), Sm(2)-C(2) = 2.93(2), Sm(2)-C(3) = 2.95(2), Sm(2)-C(4) = 2.85(2), Sm(1)...Sm(2) = 3.9132(16), Sm(1)-Sm(2)-Sm(1a) = 102.0(5), Sm(2)-Sm(1)-Sm(2a) = 78.0(5).

The structure of Complex 9.2, as revealed by X-ray diffraction analysis (Figure 9.2), consists of four Sm atoms and four dipyrromethanyl dianions defining a rhomb-type structure similar to that of complex 9.1. Even in this case four ligands bridge the four

metal centers adopting both the σ and π bonding modes. A dinitrogen molecule, placed in the center of the tetranuclear core, adopts the side-on bonding mode with two Sm atoms and the end-on bonding mode with the other two and with the two sodium atoms.

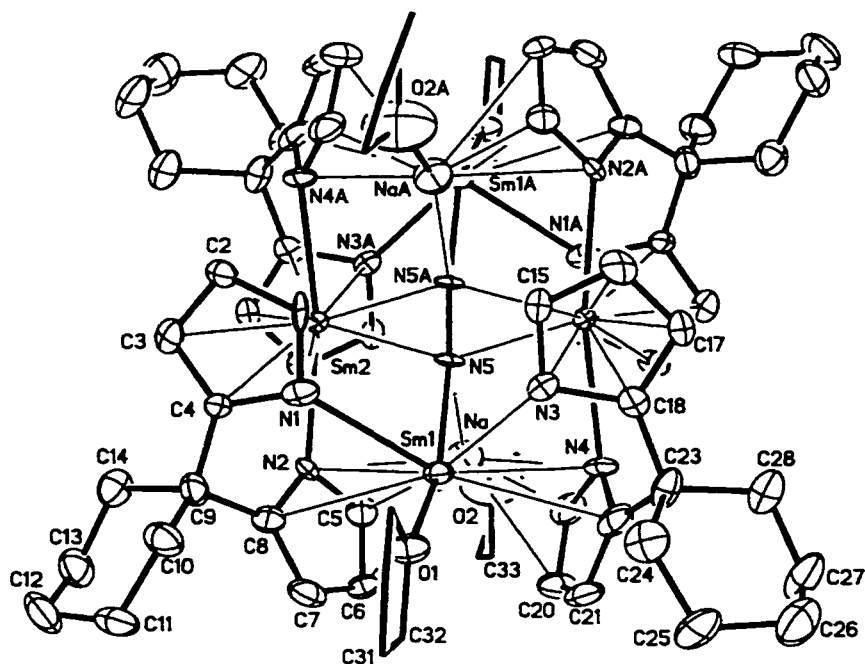


Fig. 9.2. X-ray structure of 9.2, $\{[(\text{CH}_2)_5\text{C}(\text{C}_4\text{H}_3\text{N})_2]\text{Sm}\}_4(\mu\text{-N}_2)[\text{Na}(\text{THF})]_2$

Bond distances are in $\text{\AA}$ and angles in $^\circ$. Sm(1)-N(1) = 2.714(12), Sm(1)-N(2) = 2.723(10), Sm(1)-N(3) = 2.727(11), Sm(1)-N(4) = 2.731(12), Sm(1)-N(5) = 2.178(10), Sm(1)-O(1) = 2.512(9), Sm(1)-C(19) = 2.875(15), Sm(1)-C(20) = 3.116(15), Sm(1)-C(21) = 3.104(15), Sm(1)-C(22) = 2.915(16), Sm(2)-N(1) = 2.719(11), Sm(2)-N(3a) = 2.696(11), Sm(2)-C(1) = 2.766(13), Sm(2)-C(2) = 2.902(13), Sm(2)-C(3) = 2.937(14), Sm(2)-C(4) = 2.815(14), Sm(2)-N(5) = 2.332(11), Sm(2)-N(5a) = 2.324(11), N(5)-N(5a) = 1.371(19), N(5)-Na = 2.259(12), Na-O(2) = 2.684(16), Sm(1).. $\text{Sm}(2)$ = 3.5848(12), Sm(1)-N(5)-N(5a) = 155.4(11), Sm(1)-Sm(2)-Sm(1a) = 103.4(3), Sm(2)-Sm(1)-Sm(2a) = 76.6(3), Sm(1)-N(5)-Na = 67.2(3).

References

1. Edelmann, F.T. in *Comprehensive Organometallic Chemistry* E.W. Abel, F.G.A. Stone, G. Wilkinson Eds. Pergamon: Oxford 1995.
2. (a) Evans, W.J.; Clark, R.D.; Ansari, M.A.; Ziller, J.W. *J. Am. Chem. Soc.* **1998**, *120*, 9555.
 (b) Zhang, X.; Loppnow, G.R.; McDonald, R.; Takats, J. *J. Am. Chem. Soc.* **1995**, *117*, 7828.
 (c) Sen, A.; Chebolu, V.; Rheingold, A.L. *Inorg. Chem.* **1987**, *26*, 1821.
 (d) Evans, W.J.; Anwender, R.; Ansari, M.A.; Ziller, J.W. *Inorg. Chem.* **1995**, *34*, 5.
 (e) Berardini, M.; Enige, T.J.; Breuman, J.C. *Inorg. Chem.* **1995**, *34*, 5327.
 (f) White III, J.P.; Deng, H.; Boyd, E.P.; Gallucci, J.; Shore, S.G. *Inorg. Chem.* **1994**, *33*, 1685.
 (g) Rabe, G.W.; Yap, G.P.A.; Rheingold, A.L. *Inorg. Chem.* **1995**, *34*, 4521.
 (h) Song, J.; Gambarotta, S. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2141.
 (i) Ihara, E.; Nodono, M.; Katsura, K.; Adachi, Y.; Yasuda, H.; Yamagashira, M.; Hashimoto, H.; Kanehisa, N.; Kai, Y. *Organometallics* **1998**, *17*, 3945.
3. (a) Evans, W.J.; Grate, J.W.; Choi, H.W.; Bloom, I.; Hunter, W.E.; Atwood, J.L. *J. Am. Chem. Soc.* **1985**, *107*, 991.
 (b) Chebolu, V.; Whittle, R.R.; Sen, A. *Inorg. Chem.* **1985**, *24*, 3082.
 (c) Evans, W.J.; Drummond, D.K.; Zhang, H.; Atwood, J.L. *Inorg. Chem.* **1988**, *27*, 575.
 (d) Evans, W.J.; Rabe, G.W.; Ziller, J.W. *Inorg. Chem.* **1994**, *33*, 3072.

- (e) Evans, W.J.; Rabe, G.W.; Ziller, J.W. *Organometallics* **1994**, *13*, 1641.
- (f) Minhas, R.; Ma, Y.; Song, J.; Gambarotta, S. *Inorg. Chem.* **1996**, *35*, 1866.
4. Dubé, T.; Gambarotta, S.; Yap, G.P.A. *Angew. Chem. Int. Ed. Engl* **1999**, *38*, 1432.
- 5 (a) Dubé, T.; Gambarotta, S.; Yap, G.P.A. submitted.
- (b) Jubb, J.; Gambarotta, S. *J. Am. Chem. Soc.*, **1994**, *116*, 4477.
6. Dubé, T.; Conoci, S.; Gambarotta, S.; Yap, G.P.A.; Vasapollo, G. *Angew. Chem. Int. Ed. Engl.* submitted.
7. (a) Dolphin, D.; Liu, B.Y.; Brückner, C. *Chem. Commun.* **1996**, 2141 and refs cited therein.
- (b) Lee, C.H.; Lindsey, S. *Tetrahedron* **1994**, *50*, 11427.
8. (a) Freeman, J.H.; Smith, M.L. *J. Inorg. Nucl Chem.* **1958**, *7*, 224.
- (b) Manzer, L.E. *Inorg. Synth.* **1982**, *21*, 135.
9. Evans, W.J.; Grate, J.W.; Choi, H.; Bloom, I.; Hunter, W.E.; Atwood, J.L. *J. Am. Chem. Soc.* **1985**, *107*, 941.
10. Brown, W.H.; Hutchinson, B.J.; McKinnon, M.H. *Can. J. Chem.* **1971**, *49*, 4017.
11. Mabbs, M.B.; Machin, D. *Magnetism and Transition Metal Complexes*; Chapman and Hall; London, 1973.
12. Foese, G.; Gorter, C.J.; Smith, L.J. *Constantes Selectionnees, Diamagnetisme, Paramagnetisme Relaxation Paramagnetique*; Masson, Paris, 1957.
13. Shumann, H.; Genthe, W.; Hahn, E.; Hossain, M.B.; van der Helm, D. *J. Organomet. Chem.* **1986**, *299*, 67.

CHAPTER X

THF deoxygenation versus cluster formation and N₂ fixation in the chemistry of Sm(II) dipyrrolides.

X.1: Introduction

Pyrrole-based polyanionic ligands have shown particular versatility in divalent samarium chemistry as possible alternatives to the traditionally used cyclopentadienyl-based systems.¹ This family of ligands is apparently capable of enhancing the strong one-electron reductant behavior of Sm(II),² thus making possible the occurrence of a variety of promising transformations. Calix-tetrapyrrole anions, for example, are able to stabilize divalent samarium complexes,³ to promote reversible coordination of ethylene⁴ and dinitrogen,⁵ and to enable dinitrogen reduction.⁶ This versatility may be attributed not only to an intrinsic robustness of the ligand towards strongly reducing agents but also to its polydentate nature as well as to the ability of the pyrrole moiety to adopt either the σ or the π coordination modes. Nonetheless, limitations arise due to the inevitable retention of alkali metal ions in these complexes. For this reason, we are currently focussing on di- and tripyrroles, namely substituted di- and tripyrromethanes. The diphenyl $[\text{Ph}_2\text{C}(\text{C}_4\text{H}_4\text{N})_2]^{-2}$ dianion has already enabled a variety of transformations in Sm(II) chemistry including the tetrametallic reduction of dinitrogen.⁷ By modifying the substituents on the dipyrrolide ligand system, we have now isolated and characterized a pentanuclear Sm(II) complex as well as a tetranuclear, mixed-valent Sm(II)/Sm(III) oxo-complex arising from a THF-cleavage process. Herein we describe our findings.

X.2: Experimental Section

All operations were performed under an inert atmosphere of a nitrogen-filled drybox or by using standard Schlenk-type glassware in combination with a nitrogen-vacuum line. $\text{SmCl}_3(\text{THF})_3$,⁸ $\text{SmI}_2(\text{THF})_2$ ⁹ and cyclohexyl dipyrromethane were prepared according to literature procedures.¹⁰ Diphenylmethyl dipyrromethane was prepared according to a modification of the literature procedure.¹¹ Infrared spectra were recorded on a Mattson 3000 FTIR instrument from Nujol mulls or KBr pellets prepared inside the drybox. Samples for magnetic susceptibility measurements were carried out at room temperature using a Gouy balance (Johnson Matthey). Magnetic moments were calculated by following standard methods¹² and corrections for underlying diamagnetism were applied to the data.¹³ Elemental analyses were carried out using a Perkin-Elmer Series II CHN/O 2400-analyzer.

Preparation of $[\{\text{[MePhC(C}_4\text{H}_4\text{N)}_2\text{]Sm}\}(\mu\text{-I)}][\text{K(THF)}_6]$ (10.1)

Solid KH (0.2 g, 5.0 mmol) was added to a solution of methylphenyl dipyrromethane (0.6 g, 2.5 mmol) in 75 mL THF resulting in immediate effervescence. The suspension was stirred at room temperature for 20 minutes until an appreciable amount of microcrystalline solid had accumulated and the gas evolution stopped. The addition of $\text{SmI}_2(\text{THF})_2$ (1.3 g, 2.4 mmol) resulted in an immediate color change to dark purple-brown. After stirring at room temperature under N_2 for 24 hours and removal of KI by filtration, the solution was concentrated to about 25 mL. Addition of toluene (25 mL) and standing at room temperature for 2 weeks resulted in precipitation of dark brown crystals of **10.1** (0.5 g, 0.2 mmol, 42%). El. Anal. Calcd.(Found) for $\text{C}_{104}\text{H}_{118}\text{N}_{10}\text{O}_6\text{I KSm}_5$: C 49.53(49.60), H 4.72(4.32), N 5.55(5.49). I.R. (Nujol mull, cm^{-1}) ν : 3084(w),

3088(w), 1691(w), 1595(w), 1487(m), 1462(vs), 1420(w), 1377(s), 1284(w), 1259(m), 1170(m), 1151(w), 1101(m), 1052(m), 1034(s), 1024(s), 939(m), 895(w), 802(w), 746(vs), 702(s), 877(w), 834(m), 580(s). $\mu_{\text{eff}} = 8.57 \mu_{\text{B}}$ per formula unit.

Preparation of {[Cy(C₄H₃N)₂]Sm}₄(μ -O) (10.2)

Method A: A solution of cyclohexyl dipyrromethane (3.9 g, 18.2 mmol) in THF (100 mL) was treated with KH (1.5 g, 37.0 mmol). Stirring proceeded for 30 minutes at room temperature until the effervescence stopped and an appreciable amount of colorless crystalline material accumulated. Subsequent addition of SmI₂(THF)₂ (9.4 g, 17.2 mmol) resulted in a rapid reaction with a color change to deep purple-red. After stirring for 16 hours at room temperature followed by filtration to remove a significant amount of light-colored solid, the solution was concentrated to 50 mL. Layering with hexanes (25 mL) and standing at room temperature for 2 days yielded purple-red crystals of 10.2 (1.5 g, 0.8 mmol, 20%). I.R. ν : 3087(w), 2729(w), 2671(w), 1626(w), 1462(s), 1427(s), 1402(w), 1377(s), 1350(w), 1298(m), 1281(m), 1261(s), 1232(w), 1213(w), 1192(m), 1153(vs), 1122(vs), 1095(vs), 1068(vs), 1038(vs), 960(m), 895(s), 870(m), 829(m), 802(m), 769(vs), 740(vs), 688(w), 631(m). El Anal. Calcd.(Found) for C₇₂H₉₆N₈O₅Sm₄ C 49.27(48.37), H 5.51(5.32), N 6.38(6.59). $\mu_{\text{eff}} = 5.15 \mu_{\text{B}}$ per formula unit.

Method B: Addition of NaH (0.8 g, 33.3 mmol) to a solution of cyclohexyl dipyrromethane (3.7 g, 17.3 mmol) in THF (150 mL) and stirring for 1 hour at room temperature resulted in the formation of a significant amount of microcrystalline solid. Subsequent treatment with SmCl₃(THF)₃ (7.6 g, 16.1 mmol) yielded a yellow suspension

which was stirred for 1 hour at room temperature. The suspension was thoroughly degassed and metallic sodium (0.37 g, 16.2 mmol) was introduced under an Ar atmosphere with a catalytic amount of naphthalene (0.06 g, 0.5 mmol). Stirring for an additional 16 hours at room temperature produced a deep purple-red solution which was filtered to remove insoluble solid. Concentration to small volume (50 mL) followed by layering with hexanes (50 mL) and standing at room temperature for 4 days resulted in the separation of crystals of **10.2** (1.8 g, 1.0 mmol, 26%).

X.3: Results and Discussion

Treatment of $\text{SmI}_2(\text{THF})_2$ with the potassium salt of the methylphenyl dipyrromethanyl dianion under a nitrogen atmosphere and in THF resulted in a rapid reaction with formation of $[\{\text{[MePhC(C}_4\text{H}_4\text{N)}_2\text{]Sm}\}(\mu\text{-I)}][\text{K(THF)}_6]$ (**10.1**) which was isolated as a dark brown crystalline material (Scheme 10.1). This paramagnetic complex is formed by a pentanuclear anion consisting of five $\{\text{[PhCH}_3\text{C(C}_4\text{H}_3\text{N)}_2\text{]Sm}\}$ units with the five samarium atoms pentagonally arranged around a central iodine atom. Each ligand bridges two samarium atoms with the pyrrole rings being in turn π -bonded to one samarium and σ - to a second. As a result, each samarium atom exhibits a structure reminiscent of samarocene with two π -bonded rings from one ligand and two σ -bonded from another. The five ligands are arranged such that the phenyl substituents are all oriented in the same direction thus capping the empty coordination site about each samarium. The negative charge of the cluster is balanced by a potassium cation which is solvated by six molecules of THF and which is unconnected to the pentameric anion.

The similarity of the methylphenyl dipyrrolide ligand to the diphenylmethyl dipyrrolide system, which formed a tetrametallic Sm(III) dinitrogen complex under similar reaction conditions,^{7a} is significant. It is therefore surprising that, in view of the tremendous sensitivity to air and moisture of **10.1**, we observed no sign of reaction towards dinitrogen. Thus, given the rarity of divalent lanthanide clusters¹⁴ and the apparent role of the ligand substituents in favoring or disfavoring interaction with dinitrogen, we explored the possibility of preparing other similar, related species bearing different substituents on the dipyrrolide ligand. Reaction of $\text{SmI}_2(\text{THF})_2$ with the potassium salt of the cyclohexyl dipyrrolyl dianion afforded a dark purple-red solution

which produced crystals of $\{[\text{Cy}(\text{C}_4\text{H}_3\text{N})_2]\text{Sm}\}_4(\mu\text{-O})$ (**10.2**) upon work-up (Scheme 10.1).

Scheme 10.1

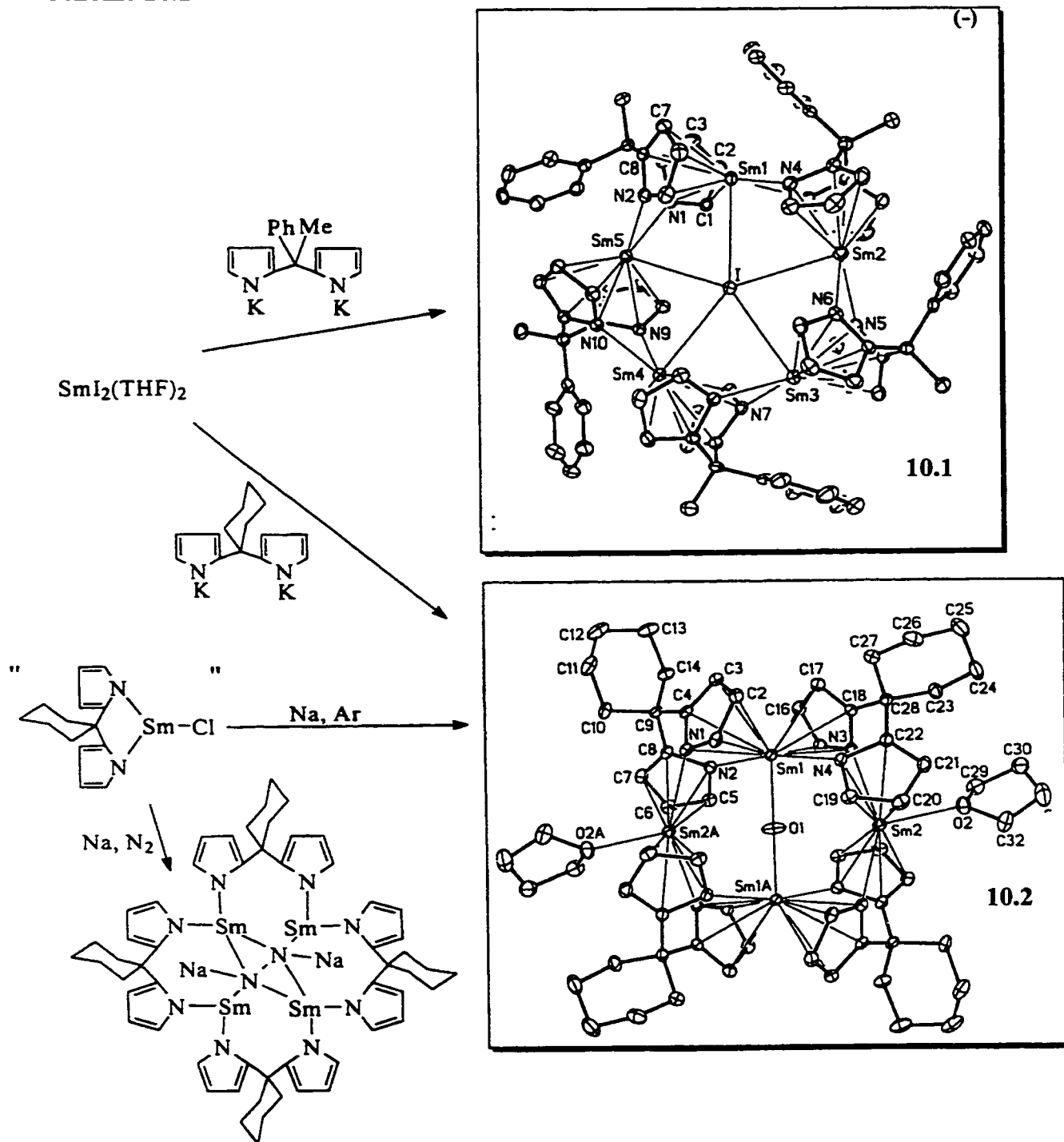


Table 10.1 Selected Bond Distances (Å) and Angles (deg). For **10.1** and **10.2**

10.1	10.2
Sm(1)-I = 3.5321(6)	Sm(1)-O(1) = 2.1844(4)
Sm(2)-I = 3.526(1)	Sm(1)-N(1) = 2.672(3)
Sm(3)-I = 3.535(1)	Sm(1)-N(2) = 2.507(4)
Sm(4)-I = 3.517(1)	Sm(1)-N(3) = 2.658(3)
Sm(5)-I = 3.5566(6)	Sm(1)-N(4) = 2.546(4)
Sm(1)-N(1) = 2.799(3)	Sm(1)..Sm(2) = 3.730(4)
Sm(1)-N(2) = 2.820(3)	Sm(1)-C(2) = 2.850(4)
Sm(1)-C(1) = 2.928(4)	Sm(2)-O(1) = 3.028(1)
Sm(1)-N(4) = 2.627(3)	Sm(2)-O(2) = 2.609(3)
Sm(1)..Sm(2) = 4.195(1)	Sm(1)-O-Sm(1A) = 179.1(2)
Sm(1)-Sm(5) = 4.169(1)	N(1)-Sm(1)-N(3) = 172.74(10)
Sm(1)-I-Sm(2) = 144.467(10)	Sm(1)-N(3)-Sm(2) = 88.59(10)
Sm(1)-I-Sm(5) = 72.048(8)	
Sm(1)-N(1)-Sm(5) = 101.34(10)	

The connectivity of complex **10.2** as indicated by an X-ray crystal structure determination revealed a tetramer formed by four $\{[\text{Cy}(\text{C}_4\text{H}_3\text{N})_2]\text{Sm}\}$ units arranged to form a tetrametallic, planar core. Also in this case, four ligands bridge the four metal centers adopting both the σ and π - bonding modes. In contrast to **10.1**, however, the metallocenic-type structure of each samarium is realized with two π -bonded pyrrolyl rings from two different ligands rather than from the same ligand. A single oxygen atom, located in the center of the plane, bridges two of the samarium atoms in a linear fashion thus forming a mixed-valent Sm(II)/Sm(III) cluster.

Refinement of the central atom as nitrogen yielded only slightly worse agreement factors. Thus, given the presence of four heavy atoms in **10.2**, the possibility that the central atom might be a nitride could not be conclusively ruled out according to X-ray and analytical data alone. Moreover, we have previously reported that reduction of an *in situ* generated trivalent “ $\{[\text{Cy}(\text{C}_4\text{H}_3\text{N})_2]\text{Sm}\}\text{Cl}$ ” precursor in the presence of metallic sodium and under nitrogen affords the first example of a mixed-valent Sm(II)/Sm(III) dinitrogen complex,^{7b} the core of which shares strikingly similar structural parameters to **10.2** and to the diphenyl derivative $[\text{Ph}_2\text{C}(\text{C}_4\text{H}_3\text{N})\text{Sm}]_4(\text{N}_2)$. Nonetheless, identical reduction carried out *under an argon atmosphere* also yielded **10.2** thus supporting the identification of the central atom as oxygen.

The presence of the oxygen atom in **10.2** is believed to have arisen from cleavage of THF, a process which is well-documented in lanthanide chemistry.¹⁵ Accordingly, significant amounts of propylene and ethylene were clearly identified in the GC-MS of the reaction mixture. The formation of propylene during a THF deoxygenation process is

rather unusual and possibly indicates the presence of other products in the reaction mixture.

The variety of the transformations summarized in Scheme 10.1 (cluster formation, THF deoxygenation versus dinitrogen fixation) is purely depending upon the nature of the organic groups attached to the carbon atoms bridging the two pyrrolyl rings. This behavior may be related to steric factors or, more likely, to the modification of the metal redox potential via modification of its interaction with the pyrrole rings. This striking sensitivity is reminiscent of that observed with calix-tetrapyrrole samarium derivatives⁴⁻⁶ except that in the dipyrrole systems the effect is considerably more enhanced.

X.5: X-ray Crystallography

Suitable crystals were mounted with cooled viscous oil on thin glass fibers. Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° ω -scans at 0, 90, and 180° in ϕ . Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Hydrogen atoms were introduced at their idealized positions and refined with a riding mode. Absorption corrections (SADABS) were applied to the data.

Semi-empirical absorption corrections based on equivalent reflections were applied. Crystallographic details are presented in the Appendix, Table 9. One molecule of THF was located in the unit cell of **10.2**.

References

1. see for example:

- (a) Evans, W.J.; Seibel, C.A.; Ziller, J.W. *J. Am. Chem. Soc.*, **1998**, *120*, 6745.
- (b) Evans, W.J.; Forrestal, K.J.; Ansari, M.A.; Ziller, J.W. *J. Am. Chem. Soc.*, **1998**, *120*, 2180.
- (c) Evans, W.J.; Seibel, C.A.; Ziller, J.W. *Inorg. Chem.* **1998**, *37*, 770.
- (d) Evans, W.J.; Seibel, C.A.; Ziller, J.W.; Doedens, R.J. *Organometallics*, **1998**, *17*, 2103.
- (e) Evans, W.J.; Clark, R.D.; Ansari, M.A.; Ziller, J.W. *J. Am. Chem. Soc.* **1998**, *120*, 9555.
- (f) Ihara, E.; Koyama, K.; Yasuda, H.; Kanchisa, N.; Kai, Y. *J. Organomet. Chem.* **1999**, *574*, 40.
- (g) Xie, Z.W.; Wang, J.W.; Zhou, Z.Y.; Mak, T.C.W. *Organometallics* **1998**, *17*, 1907.
- (h) Ihara, E.; Nodono, M.; Katsura, K.; Adachi, Y.; Yasuda, H.; Yamagashira, M.; Hashimoto, H.; Kanehisa, N.; Kai, Y. *Organometallics* **1998**, *17*, 3945;

2. For reviews on Ln(II) chemistry see:

- (a) Evans, W.J. *Polyhedron*, **1987**, *6*, 803.
- (b) Schaverien, C.J. *Adv. Organomet. Chem.* **1994**, *36*, 283.
- (c) Edelmann, F.T. *Coord. Chem. Rev.* **1997**, *165*, 163.

3. Dubé, T.; Gambarotta, S.; Yap, G.P.A. *Organometallics* submitted

4. Dubé, T.; Gambarotta, S.; Yap, G.P.A. *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 1432.

5. Dubé, T.; Gambarotta, S.; Yap, G.P.A. *J. Chem. Soc. Chem. Commun.* submitted.

6. Jubb, J.; Gambarotta, S. *J. Am. Chem. Soc.* **1994**, *116*, 4477.
7. (a) Dubé, T.; Conoci, S.; Gambarotta, S.; Yap, G.P.A.; Vasapollo, G. *Angew. Chem. Int. Ed. Engl.* in press
(b) Dubé, T.; Conoci, S.; Gambarotta, S.; Yap, G.P.A. *Angew. Chem. Int. Ed. Engl.* submitted.
8. (a) Freeman, J.H.; Smith, M.L. *J. Inorg. Nucl. Chem.* **1958**, *7*, 224.
(b) Manzer, L.E. *Inorg. Synth.* **1982**, *21*, 135.
9. Evans, W.J.; Grate, J.W.; Choi, H.W.; Bloom, I.; Hunter, W.E.; Atwood, J.L. *J. Am. Chem. Soc.* **1985**, *107*, 941.
10. Brown, W.H.; Hutchinson, B.J.; McKinnon, M.H. *Can. J. Chem.* **1971**, *49*, 4017.
11. (a) Dolphin, D.; Liu, B.Y.; Brückner, C. *J. Chem. Soc. Chem. Commun.* **1996**, 2141.
(b) Lee, C.H.; Lindsey, S. *Tetrahedron* **1994**, *50*, 11427.
12. Mabbs, M.B.; Machin, D. *Magnetism and Transition Metal Complexes*. Chapman and Hall: London, 1973.
13. Foese, G.; Gorter, C.J.; Smits, L.J. *Constantes Selectionnes, Diamagnetisme, Paramagnetisme, Relaxation Paramagnetique*; Masson, Paris, 1957.
14. See for example:
 - a) Bottomley, D.E.; Paez, P.S.; White, J. *J. Organomet. Chem.* **1985**, *291*, 35.
 - b) Constantine, S.P.; DeLima, G.M.; Hitchcock, P.B.; Keates, J.M.; Lawless, G.A. *J. Chem. Soc. Chem. Commun.* **1996**, 2421.
15. (a) Dubé, T.; Gambarotta, S.; Yap, G.P.A. *Organometallics* **1998**, *17*, 3967.
(b) Jubb, J.; Gambarotta, S.; Duchateau, R.; Teuben, J. *J. Chem. Soc. Chem. Commun.* **1994**, 2641.

- (c) Aspinall, H.C.; Tillotson, M.R. *Inorg. Chem.*, 1996, **35**, 2163;
- (d) Evans, W.J.; Dominguez, R.; Hanusa, T.P. *Organometallics* **1986**, *5*, 1291.

CHAPTER 11

Conclusions

A new series of well-defined, low-valent compounds of samarium have been prepared and characterized. Whereas the calix-tetrapyrrole ligand system was found to be suitable for the stabilization of Sm(II), the chelating salophen ligand resulted in the formation of a Sm(III) species through imine reduction and C-C bond formation in the assembly of a dinuclear structure with a short intermetallic distance. Formally a Sm(III) compound, this species was observed to behave as a source of divalent samarium in the presence of strong reducing agents and nucleophiles. The reactivity of the *in situ* generated Sm(II) was observed to be uncontrollable, however, to the extent that activation of solvent molecules was repeatedly observed.

The chemistry of divalent samarium supported by the calix-tetrapyrrole ligand was observed to parallel the chemistry of samarocene in several cases. Nevertheless, important differences were also developed. For example, whereas decamethylsamarocene is an established ethylene polymerization catalyst, the calix-tetrapyrrole system reversibly binds ethylene. As well, the degree of reversibility of ethylene coordination is surprisingly sensitive to the nature of the ligand substituent. The effect in terms of kinetics is even more pronounced in the case of reactivity with acetylene in which interesting patterns dictated by the nature of the substituent present on the macrocycle were revealed. When R = Cy, metallation occurred according to a clean reaction which yielded a carbide complex analogous to that observed upon reaction of decamethylsamarocene with the same substrate. In contrast to the dinitrogen complex of

the same macrocycle, however, the C_2Li_4 fragment in the carbide was coordinated end-on. When $R = Et$, either reductive coupling and dehydrogenation occurred when the reaction involved $Sm(II)$, or a mixture of coupled product and carbide were obtained in the case of a metathesis route. We attribute this difference in reactivity to kinetic factors and propose that both pathways involve a similar intermediate, namely a hydride species. However, when the monomeric Sm -hydride ($R = Et$) was exposed to acetylene, a complicated reaction ensued from which a third product resulting from calix-tetrapyrrole ring isomerization was isolated. The mechanism of this reaction remains unclear.

Similarly, reactivity with dinitrogen revealed very different results depending upon the nature of the substituent on the macrocycle. Rather than the expected irreversible reduction, reversible coordination analogous to that observed in the case of decamethyl samarocene was found when the macrocycle was substituted with a cyclohexyl group. This observation may be rationalized by considering a mechanism involving either cooperative interaction of two Sm centers ($R = Cy$) or of four Sm centers on the same dinitrogen molecule ($R = Et$), a phenomenon which was clearly demonstrated during the course of this work.

In order to eliminate the problems of alkali-metal retention and solvent molecule activation routinely observed in the calix-tetrapyrrole chemistry of divalent and trivalent samarium, the dipyrromethanyl ligand system was investigated as a possible alternative to the bridged cyclopentadienyl systems. As a result, a rich and interesting cluster chemistry was developed based on derivatives of dipyrromethane which functioned as both a σ - and a π - donors in all of the complexes which were isolated. This is a consequence of the tendency of lanthanides to extend their coordination numbers, when coordinatively

unsaturated, through the formation of ligand bridges. As in the case of calix-tetrapyrrole, the reactivity observed was dependent upon the nature of the bridging substituent. For example, cooperative action of four Sm centers on one N_2 molecule resulted in the assembly of an tetranuclear dinitrogen complex preceded only in the chemistry of the naturally-occurring nitrogenase. When one of the phenyl substituents on the ligand bridge was replaced with a methyl group, however, only a pentanuclear Sm(II) complex was isolated. As well, no reactivity with dinitrogen was observed when a cyclohexyl substituent was present and instead a tetranuclear oxo complex resulted according to a THF cleavage process. Also mirrored in the chemistry of calix-tetrapyrrole Sm(II) was a sensitivity in terms of reactivity to the nature of the alkali cation present. Whereas reduction of a trivalent precursor with metallic potassium yielded a stable divalent complex, reduction with metallic sodium resulted in a tetranuclear Sm(II) hydride species. The origin of the hydride in this complex, however, remains unclear. In substituting the diphenyl substituents for a cyclohexyl group, dinitrogen activation again results. Also in this case a tetranuclear complex is assembled. However, the presence of two sodium cations coupled with a N-N distance consistent with a four electron reduction suggests, at first glance, an improbable precursor featuring two Sm(I) centers. As an alternative, and consistent with the reactivity of the diphenyl Sm(III) complex with metallic sodium, we tentatively propose a transient hydride precursor.

Thus the conclusions of this work may be summarized as follows:

(i) Reactivity of divalent samarium species with dinitrogen is dependent upon the enforcement of steric unsaturation about the metal center which may be effected through the employment of rigid, pyrrole-based systems. However, competitive activation of

solvent molecules often hampers dinitrogen activation. In order to eliminate this difficulty, a THF-free environment may be favourable.

(ii) A pronounced substituent effect influences the reactivity of calix-tetrapyrrolyl and dipyrromethanyl Sm(II) with unsaturated substrates such as ethylene, acetylene, and dinitrogen. Subtle changes in steric and electronic features of the ligand result in vastly different reaction outcomes as kinetics often dictate different reaction pathways.

(iii) The dipyrromethanyl ligand system has been used to effectively illustrate the cooperative effect of alkali cation and halide anion in promoting or disfavours dinitrogen reduction. Although cooperative, 4-electron reduction of dinitrogen has been demonstrated in the chemistry of Sm(II), we are unable at this stage to absolutely rationalize this reactivity and only observe that the system is extremely sensitive to minor variations. In this regard, solvent effects must also be investigated. As well, the exact nature of the precursor to the tetranuclear dinitrogen system has yet to be determined. This precursor may potentially serve as an ideal host to a variety of small molecules.

APPENDIX

Table 1 Crystal Data and Structure Analysis Results for **2.2**, **2.3** and **2.4**

	2.2	2.3	2.4
Formula	$C_{98}H_{132}N_4O_7Sm_2$	$C_{98}H_{148}N_4O_{10}Li_6Sm_2$	$C_{172}H_{220}N_8O_{12}Sm_4$
formula weight	1778.78	1884.54	3192.96
space group	P2(1)/n	P2(1)/m	I4(1)/a
a (Å)	18.0333(2)	18.0906(6)	31.4914(5)
b (Å)	17.2026(2)	17.1075(6)	31.4914(5)
c (Å)	29.3537(2)	19.5591(6)	16.203(3)
β (deg)	100.529(1)	114.073(1)	
V (Å ³)	8952.77(6)	5526.8(3)	16068(3)
Z	4	2	4
Radiation (K α Å)	0.71073	0.71073	0.71073
T (°C)	-100	-100	-100
D _{calcd} (g cm ⁻³)	1.320	1.132	1.320
μ_{calcd} (cm ⁻¹)	1.354	1.101	1.500
R, wR ² , GoF	0.0654,0.156,1.013	0.0555,0.162,1.074	0.0501,0.104,1.016
$R = \sum F_0 - F_c / \sum F_0 \quad R_w = [(\sum (F_0 - F_c)^2 / \sum w F_0^2)]^{1/2}$			

Table 2 Crystal Data and Structure Analysis Results for **3.2a**, **3.2b**, **3.3** and **3.4b**

	3.2a	3.2b	3.3	3.4b
Formula	C ₅₃ H ₈₃ Li ₃ N ₄ O ₄ SmCl	C ₅₄ H ₈₃ Li ₃ N ₄ O ₄ SmCl	C ₆₀ H ₉₇ Li ₂ N ₄ O ₆ Sm	SmLi ₃ ClC ₆₀ H ₈₈ N ₄ O ₅
Form. weight	1046.95	1058.86	1134.65	1151.96
Space group	<i>P</i> -1	<i>P</i> -1	<i>Pnma</i>	<i>P</i> 2(1)/ <i>n</i>
a (Å)	12.771(8)	12.6505(12)	22.7546(9)	11.617(2)
b (Å)	21.395(9)	21.515(2)	13.8541(7)	26.453(3)
c (Å)	22.818(9)	22.788(2)	18.9224(9)	18.812(2)
α (deg)	112.85(4)	112.769(2)	90	90
β (deg)	100.51(5)	99.908(2)	90	95.390(3)
γ (deg)	91.85(5)	91.522(2)	90	90
V (Å ³)	5612(5)	5604.0(9)	5965.2(5)	5756(1)
Z	4	4	4	4
Radiation (Kα Å)	0.71073	0.71073	0.71073	0.71073
T (°C)	-70	-70	-70	-70
D _{calcd} (g cm ⁻³)	1.253	1.255	1.263	1.329
μ _{calcd} (cm ⁻¹)	1.140	1.141	1.035	1.117
R, wR ² , GoF	0.0503, 0.0981, 1.076	0.0510, 0.1471, 1.008	0.0533, 0.1408, 1.091	0.0641, 0.1340, 1.060
$R = \sum \ F_0 - F_c \ / \sum F_0 $		$R_w = [(\sum (F_0 - F_c)^2 / \sum w F_0^2)]^{1/2}$		

Table 3 Crystal Data and Structure Analysis Results for **4.1**, **4.2**, **4.3**, **4.4** and **4.5**

	4.1	4.2	4.3	4.4	4.5
Formula	C ₆₀ H ₉₆ N ₄ O ₆ Sm ₂ Li ₂ Cl ₄	C ₃₂ H ₁₁₂ Li ₂ N ₄ O ₆ Sm ₂	C ₅₂ H ₇₉ Li ₄ N ₄ O ₅ Sm	C ₅₂ H ₈₀ N ₄ O ₄ LiSm	C ₆₄ H ₁₀₄ N ₄ O ₇ Sm ₂
Formula weight	1425.94	1344.27	1020.32	1203.74	1342.21
Space group	C2/c	Pbcn	C2/c	P-1	I4(1)/a
a (Å)	22.2398(5)	14.2174(7)	14.686(3)	11.661(1)	14.564(2)
b (Å)	14.9113(3)	21.748(2)	19.930(3)	11.770(1)	14.564(2)
c (Å)	20.5018(4)	22.209(2)	18.362(3)	22.869(3)	31.130(7)
α (deg)	90	90	90	76.997(2)	90
β (deg)	101.968(1)	90	97.805(3)	88.379(2)	90
γ (deg)	90	90	90	61.691(2)	90
V (Å ³)	6651.1(2)	6866.7(9)	5325(2)	2681.2(5)	6603(2)
Z	4	8	4	2	4
Radiation (Kα Å)	0.71073	0.71073	0.71073	0.71073	0.71073
T (°C)	-100	-70	-70	-70	-70
D _{calcd} (g cm ⁻³)	1.420	1.304	1.273	1.491	1.350
μ _{calcd} (cm ⁻¹)	1.957	1.741	1.149	2.313	1.812
R, wR ² , GoF	0.0234, 0.0591, 1.020	0.0423, 0.0977, 1.073	0.0575, 0.1367, 1.041	0.0378, 0.0852, 1.002	0.0320, 0.0807, 1.137
$R = \sum \ F_o - F_c \ / \sum F_o $		$R_w = [(\sum (F_o - F_c)^2 / \sum w F_o^2)]^{1/2}$			

Table 4 Crystal Data and Structure Analysis Results for **5.1a**, **5.2b** and **5.3a**

	5.1a	5.2b	5.3a
formula	C ₈₆ H ₁₀₆ Li ₄ N ₈ OSm ₂	C ₉₆ H ₁₃₆ Li ₆ N ₈ O ₆ Sm ₂	C ₈₈ H ₁₂₄ Li ₂ N ₈ O ₄ Sm ₂
formula weight	1596.25	1840.47	1672.53
space group	P2(1)/c	P2(1)/c	P2(1)/n
a (Å)	12.645(3)	20.351(3)	14.070(4)
b (Å)	30.089(7)	22.207(3)	14.752(4)
c (Å)	20.604(5)	20.972(3)	21.220(6)
β (deg)	106.372(4)	97.927(3)	106.298(5)
V (Å ³)	7522(3)	9387(2)	4228(2)
Z	4	4	2
Radiation (Kα Å)	0.71073	0.71073	0.71073
T (°K)	203	203	203
D _{calcd} (g cm ⁻³)	1.410	1.302	1.314
μ _{calcd} (cm ⁻¹)	1.598	1.293	1.428
F ₀₀₀	3288	3832	1740
R, R _w ² , G.o.F	0.0451,0.1148,1.004	0.0413,0.0981,1.048	0.0544,0.887,1.007

$$R = \sum^{\circ} F_0^3 - \sum^{\circ} F_c^{\circ} / \sum^{\circ} F_0^3$$

$$R_w = [(\sum^{\circ} F_0^3 - \sum^{\circ} F_c^{\circ})^2 / \sum w F_0^2]^{1/2}$$

Table 5 Crystal Data and Structure Analysis Results for **6.3a** and **6.4a**

	6.3a	6.4a
Formula	$C_{104}H_{166}Li_6N_8O_9Sm_2$	$C_{94}H_{138}Li_6N_8O_6Li_6Sm_2$
Formula weight	2014.79	1818.46
Space group	P-1	Pbca
A (Å)	13.6634(2)	20.926(2)
B (Å)	15.7346(2)	20.614(2)
C (Å)	27.7960(5)	21.577(2)
α (deg)	100.779(1)	90
β (deg)	91.537(1)	90
γ (deg)	91.893(1)	90
V (Å ³)	5863.9(2)	9308(1)
Z	2	4
Radiation (K α Å)	0.71073	0.71073
T (°C)	-100	-100
D _{calcd} (g cm ⁻³)	1.141	1.298
μ_{calcd} (cm ⁻¹)	1.354	1.101
R, wR ² , GoF	0.0715,0.1560,1.011	0.0318,0.0869,1.024
$R = \sum \ F_0 - F_c\ / \sum F_0 \quad R_w = [(\sum (F_0 - F_c)^2 / \sum w F_0^2)]^{1/2}$		

Table 6 Crystal Data and Structure Analysis Results for 7.2, 7.3 and 7.4

	7.2	7.3	7.4
Formula	C ₁₁₂ H ₁₆₀ Li ₆ N ₁₀ O ₈ Sm ₂	C ₅₀ H ₆₇ Li ₃ N ₄ O ₃ Sm	C ₆₀ H ₉₄ Li ₃ N ₄ O ₅ Sm
Formula weight	2187.74	943.25	1158.01
space group	P2(1)/n	P2(1)/c	P-1
a (Å)	15.594(4)	20.780(3)	12.957(2)
b (Å)	16.407(4)	18.755(3)	13.273(2)
c (Å)	21.718(5)	12.126(2)	18.715(3)
α (deg)	90	90	85.417(3)
β (deg)	96.970(6)	99.509(2)	78.577(3)
γ (deg)	90	90	72.577(3)
V (Å ³)	5516(2)	4661(1)	3009.2(8)
Z	2	4	2
Radiation (Kα Å)	0.71073	0.71073	0.71073
T (°K)	203	203	203
D _{calcd} (g cm ⁻³)	1.317	1.344	1.278
μ _{calcd} (cm ⁻¹)	1.598	1.293	1.068
F ₀₀₀	2284		1220
R, R _w ² , G.o.F	0.0923,0.2264,1.035		0.0703,0.1643,1.006

$$R = \sum |F_o^3 - F_c^3| / \sum F_o^3$$

$$R_w = [(\sum (F_o^3 - F_c^3)^2 / \sum w F_o^2)]^{1/2}$$

Table 7 Crystal Data and Structure Analysis Results for 8.1, 8.2 and 8.3

	8.1	8.2	8.3
Formula	C ₉₂ H ₈₀ N ₁₀ O ₂ Sm ₄	C _{206.5} H _{205.5} I ₂ N ₁₄ O ₇ Sm ₈	C ₁₀₄ H ₁₀₄ N ₈ O ₅ KClSm ₄
Formula weight	1059.32	4451.95	2221.90
space group	C2/m	P2(1)/c	P-1
a (Å)	21.542(6)	18.186(2)	13.462(1)
b (Å)	19.232(6)	23.349(2)	17.534(2)
c (Å)	12.437(3)	43.492(4)	20.970(2)
α (deg)	90	90	110.006(1)
β (deg)	116.96(3)	90.169(2)	100.343(2)
γ (deg)	90	90	90.421(1)
V (Å ³)	4593(2)	18467(3)	4562.8(7)
Z	2	4	2
Radiation (Kα Å)	0.71073	0.71073	0.71073
T (°K)	203	203	203
D _{calcd} (g cm ⁻³)	1.405	1.601	1.617
μ _{calcd} (cm ⁻¹)	2.567	2.895	2.670
F ₀₀₀	1900	8802	2216
R, R _w ² , G.o.F	0.0546,0.1696,1.007	0.0553,0.1086,1.018	0.0385,0.1010,1.047

$$R = \Sigma^{\circ} F_0^3 - {}^3 F_c^{\circ} / \Sigma {}^3 F_0^3$$

$$R_w = [(\Sigma ({}^3 F_0^3 - {}^3 F_c^3)^2 / \Sigma w F_0^2)]^{1/2}$$

Table 8 Crystal Data and Structure Analysis Results for 9.1 and 9.2

	9.1	9.2
Formula	$C_{116}H_{128}N_8NaO_8Sm_4$	$C_{80}H_{112}N_{10}Na_2O_6Sm_4$
Formula weight	2386.65	1957.18
Space group	C2/c	P2(1)/c
A (Å)	21.464(4)	13.495(4)
B (Å)	26.796(5)	25.092(7)
C (Å)	24.835(5)	12.698(4)
α (deg)	90	90
β (deg)	102.345(3)	117.602(5)
γ (deg)	90	90
V (Å ³)	13954(5)	3810(2)
Z	4	2
Radiation (K α Å)	0.71073	0.71073
T (°C)	-100	-100
D _{calcd} (g cm ⁻³)	1.136	1.706
μ_{calcd} (cm ⁻¹)	1.707	3.108
R, wR ² , GoF	0.1068,0.2819,1.024	0.0581,0.1460,1.010
$R = \Sigma \ F_0 - F_c \ / \Sigma F_0 \quad R_w = [(\Sigma (F_0 - F_c)^2 / \Sigma w F_0^2)]^{1/2}$		

Table 9 Crystal Data and Structure Analysis Results for 10.1 and 10.2

	10.1	10.2
Formula	$C_{104}H_{118}N_{10}IKNaO_6Sm_5$	$C_{72}H_{96}N_8O_5Sm_4$
Formula weight	2521.83	1754.97
Space group	P2(1)/n	C2/c
A (Å)	13.949(2)	23.116(4)
B (Å)	22.679(4)	11.836(2)
C (Å)	31.193(3)	24.932(4)
α (deg)	90	90
β (deg)	94.22(1)	96.820(2)
γ (deg)	90	90
V (Å ³)	9841(2)	6773(2)
Z	4	4
Radiation (K α Å)	0.71073	0.71073
T (°C)	-100	-100
D _{calcd} (g cm ⁻³)	1.702	1.721
μ_{calcd} (cm ⁻¹)	3.351	3.473
R, wR ² , GoF	0.0315,0.0519,1.004	0.0364,0.0899,1.005
$R = \Sigma \ F_0 - F_c \ / \Sigma F_0 \quad R_w = [(\Sigma (F_0 - F_c)^2 / \Sigma w F_0^2)]^{1/2}$		