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Great Wonders of f-Chemistry: Synthetic, Structural and Reactivity Investigation of Low Valent f-Block Metal Complexes.

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Abstract

The inspiration behind the synthesis and reactivity studies of the *f*-block metal complexes generally originated from several well defined basic purposes. The main goals in the field of lanthanide and actinide centered chemistry could be separated onto: (i) exploration of the fundamental chemistry of *f*-block elements with their reactivity and coordination behavior; (ii) understanding the nature of the bonding interactions between the metal centers and the ligands as well as between different metal centers within the same heterometallic complex; and finally, (iii) exploration of the possibility to use new complexes in catalytic or sensor related applications. This thesis is manly focused on the investigation of the preparation and the reactivity investigation of the several low valent compounds of Sm, Tm, U and Th with non-cyclopentadienyl ligands. Despite exceptionally high reactivity and rather unpredicted transformations demonstrated by some of the species in this class, an overall picture of the chemical activity remained rather scattered and considerably poorly investigated. In attempt to contribute to the understanding of the reactivity patterns in the field of *f*-block metal chemistry Chapter 2 of this thesis explored the chemical behavior of Sm complexes supported by the bulky aryloxides ligands. Application of the aluminum alkyls led to the appearance of a new coordination mode of aryloxide ligands to lanthanide, affording an unusually stable Sm(II) compounds. Attempted insertion reactions afforded several new complexes and provided more information about the stabilization influence of Lewis acids in zwitterionic compounds. The application of similar strategy to Sm(III) species resulted in the isolation of rare non-cyclopentadienyl single component ethylene polymerization catalyst.

In Chapter 3 the reaction of Tm complexes supported by the combination of dimethyl-pyrrole with aluminum alkyl produced a very unusual product of C-H bond activation by the Tm metal center. Utilization of the Lewis acidic aluminum alkyls enforced the ligand to thulium π-bonding and a

formation of Zwitterionic structure. Upon treatment with hydrogen or $PhSiH_3$ as hydrogenating agent the initial species exhibited a series of very unusual transformations, leading to the isolation of rare case of SiH_3 coordination to the *f*-block metal center.

Chapter 4 discovered unexpected reactivity of uranium complex with bulky amido- ligand in halogen replacement alkylation processes or during the reduction of the metal center. The alkylation reactions yielded extensive γ-deprotonation and formation of cluster compounds. Two first structurally characterized uranium carbines were discovered and documented in the course of this exploratory work. Reduction of the mixed Uranium amido-halogenates proceeded with the formation of transient low valent species and immediate re-oxidation at the expense of the ligand, affording new amido-imino- or amido-alkyl- complexes of U(V).

Multiple attempts of lowering the oxidation state of uranium metal center supported by new bis-amido-benzene ligand, presented in Chapter 5, resulted in the isolation of several new solvent fragmentation products. The reactivity displayed by the related ligand systems together with the additional support, provided by the isolation of complexes of this type, suggested the presence of highly reactive low valent synthons. Reduction reactions afforded the new uranium complex with the lowest reported oxidation state of the metal centers. However, the DFT calculations revealed that all the excessive electron density was situated on the ligand delocalized π-systems, forcing the ligand to act as electron storage.

Chapter 6 discussed the possibility of sterically enforcing π-bonding ligands to stabilize the low valent oxidation state of Th metal center. Utilization of the bis-pyrrolide base ligand allowed the isolation of the thorium complex with significant π-interaction of the metal center with the aromatic system of the ligand. Reduction of this system afforded the isolation of the rare example of Th(III) complex. Similarly to the complexes of U reported in the previous chapter, DFT calculation displayed significant presence of the electronic density on the π-system of the ligand fragment. Nevertheless, it was demonstrated by the reactivity examples that stored electronic density could be delivered back to the metal center, initiating the transformations expected for low valent f-block element compounds.

f-Chemistry – Yours to Discover

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List of Publications

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List of Common Abbreviations

An	actinide metal
Ar	aromatic group
Bz	benzyl
COT	1,3,5,7-cyclooctatetraene
Cp	cyclopentadienyl, (C_5H_5)
Cp*	pentamethylcyclopentadienyl, ($C_5(CH_3)_5$)
DME	1,2-dimethoxyethane
Et	ethyl
Et_2O	diethyl ether
Et_4PG	octaethyl-calix-tetra-pyrrolato tetra-anion
i-Pr	iso-propyl
L	ligand
Ln	lanthanide metal
M	metal atom
Me	methyl
Mw	molecular weight
nacnac	β-diketiminate
NMR	nuclear magnetic resonance
PE	polyethylene
Ph	phenyl
R	alkyl group
t-Bu	tert-butyl
THF	tetrahydrofurane
TMS	trimethilsilane

UHMWPE	ultra-high molecular weight polyethylene

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Chapter One

Introduction.

The official birth of organometallic transition metal chemistry can be dated back to 1760 with the isolation of the first organometallic compounds containing a genuine metal-carbon σ-bond.[1] Since then, the normally high reactivity of the metal-carbon bonds has always challenged chemists to surpass the boundaries of stable oxidation states. In turn, this has provided even greater challenges for studying very unstable oxidation states and confronting an increased chemical reactivity. When the reactivity is increased beyond the threshold of the reduction of water, reduced complexes become sensitive to gases present in the atmosphere including dinitrogen. Therefore, handling these materials has required the development of special techniques. The knowledge we today posses, along with the advance of spectroscopic techniques for monitoring chemical reactions and their outcomes, has allowed to bring these developments to an extreme and discover a remarkable wealth of chemical transformation spanning a very diversified range.

The field of molecular activation is one of the many areas where the potential of low-valent metal compounds displays its full magnitude. The modern literature is replete of examples showing that the presence of excessive electron density on the metal center enables charge transfer to a variety of substrates,[2,3] initiating bond cleavage and eventually leading to functionalization.[2,3] The metal center in this case not only provides the reducing power for the process but also plays a significant role in directing the reactivity through the coordination of the substrate. The coordination of the substrate and the reducing power of the low-valent species, together, may facilitate the transformation of substrates otherwise unreactive. One of the most illustrative examples is the industrial preparation of NH_3 from nitrogen gas. The process requires very substantial temperatures and pressures as well as the presence of a catalyst to overcome unfavorable thermodynamics. On the other hand, the formation of ammonia as catalyzed by natural enzymes is efficiently carried out at room temperature and atmospheric pressure. Seminal work of Schrock in this direction has demonstrated that the utilization of low-valent reactive metal complexes[4] may result in the catalytic transformation on N_2 into NH_3 under similarly mild reaction conditions.

Among highly reactive low-valent complexes, lanthanides and actinides compounds occupy a very special place having provided the greatest variety of astonishing chemical transformations. Now it is widely acknowledged that in some processes complexes of *f*-block elements not only surpass the transition metal complexes in activity and productivity but also support transformations never observed for the transition metal compounds. What is unique in the chemistry of highly reducing *f*-block compounds is that the majority of their metal-promoted transformations results from the cooperative interaction of more than one reduced metal on the same substrate. This may be explained with the ability of these elements to stabilize intermediates where the metal has transferred one electron to the substrate. By providing the radical-type intermediate with sufficiently long life-time, it is possible to promote radical-type of couplings.

Before reviewing the chemistry of *f*-block metal complexes, it should be emphasized that, due to the space restriction, this chapter does not provide a comprehensive review of the chemistry supported by low valent lanthanides and actinides. This part is much rather designed as a snap shot of the modern *f*-block element chemistry. It was intended to reveal the main tendencies in this field as well as to present several "key-notes" aiming at identifying the ligand features required for the stabilization of the low valent compounds.

It is the last 20 years that the chemistry of lanthanides and actinides has experienced the most spectacular developments with the amount of new isolated and characterized complexes steadily increasing every year. The employment of exotic ligand has resulted in the isolation of low valent compounds for element previously considered to be impossible to be reduced.[5] New examples of molecular activation have been reported with elements never thought to be involved in molecular activation processes.[6, 7, 68, 76, 120, 124a, 125, 127] Low-valent Sm, and to a lesser extent low valent Tm, Nd and Pr are certainly the protagonist of this chemistry. More recently, a flurry of reports has started to highlight the potential of uranium for unusual transformations.

In this Introduction I will be reviewing some aspects of the chemistry of Sm, Tm, U and Th with particular focus on the factor which allow the formation of low oxidation state species. I will also emphasize the features of compounds which are responsible for the initiation of the reduction of different substrates. The contribution of various π-systems in the ligand framework for stabilization of lower oxidation states will be discussed and requirements leading to reactivity will be highlighted. This literature is relevant to the results presented in the following chapters.

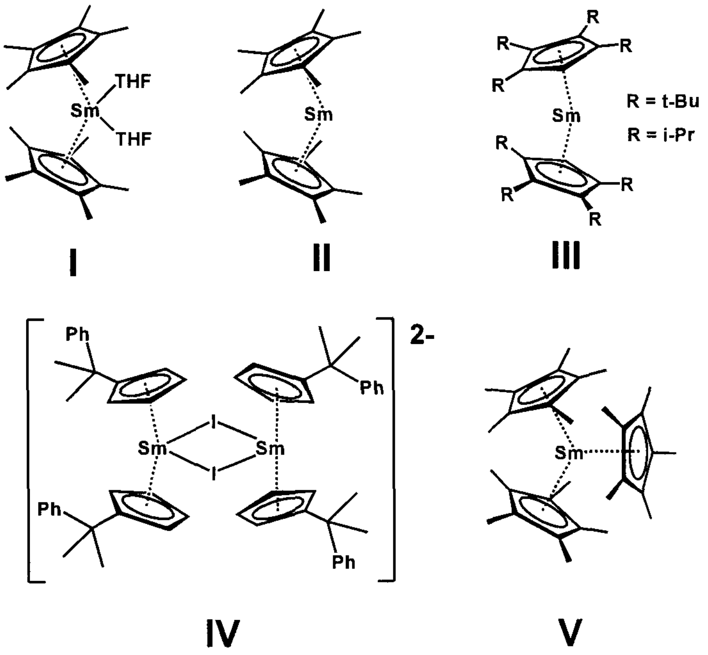
1. Complexes of low valent samarium.

The extensive work on samarocene derivatives initiated by Evans since the 80s, has triggered the revival of interest for a chemistry which before was simply confined to higher oxidation states of a series of the periodic table previously considered as nothing more than an unexciting chemical curiosity.

1.1 Sm cyclopentadienyl based systems.

The first successful attempt to isolate a cyclopentadienyl complex of low valent samarium dated back to 1981.[8] Evans *et al.* reported that joint condensation of samarium metal vapor with penta-methylcyclopentandiene afforded the un-solvated bis-cyclopentadienyl samarium complex, which could be later recrystallized from THF. Reasonable solubility of this compound permitted full characterization of the complex including an X-ray structure determination. Another significant discovery made in the same year was the quantitative preparation of $SmI_2(THF)_2$ complex from metallic Sm and 1,2-diiodoethane, reported by the group of Kagan.[9] This starting material remains up to these days the key to enter the chemistry of divalent organo-samarium complexes such as $Sm(Cp^*)_2(THF)_2$ and $[Sm(Cp^*)(\mu\text{-}I)_2]_2$.[10] There are two general methods for preparing divalent Sm compounds. The first consists of the reaction of an anionic form of the ligand with $SmI_2(THF)_2$. The second includes the preparation of suitable Sm(III) precursor followed by reduction.

A few typical examples of low valent Sm mono- and bis-cyclopentadienyls are presented in the Scheme 1.1. As expected compounds of this type have been prepared with a large variety of substituents on the Cp rings[8, 11b-d] including several "-ate" species.[11a]



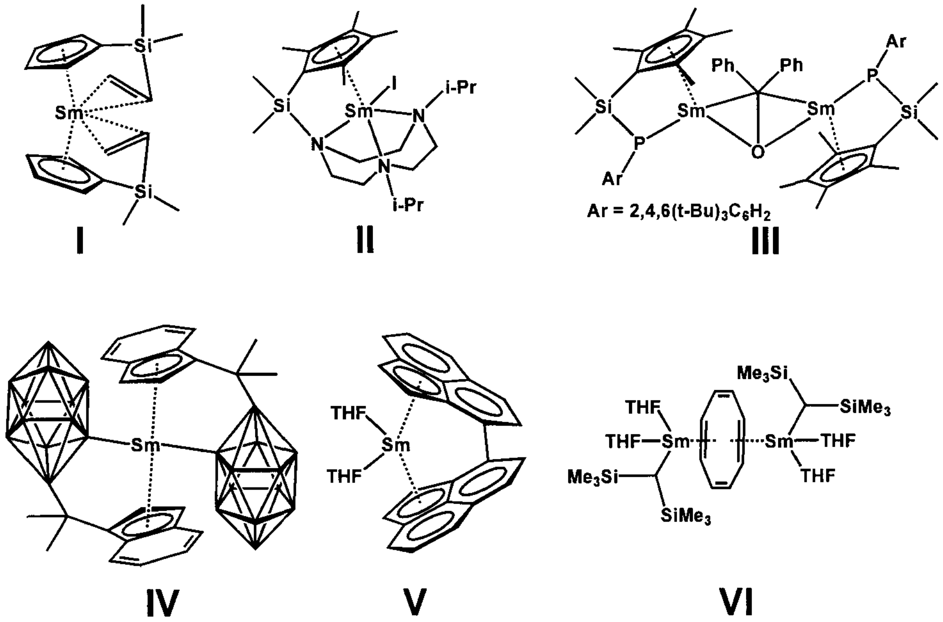
Scheme 1.1.

The only example of trivalent samarium compound (Scheme 1.1, Complex III) was included on this scheme due its ability to act as a "reducing agent". This complex is a sterically overcrowded tris-(penta-methyl-cyclopentadienyl) species and it was first reported by Evans et al.[12] almost ten years after the isolation of the bis-(penta-methyl-cyclopentadienyl) analog.

For a long time this compound was considered impossible to prepare. However, after its successful synthesis was achieved in 1991, reactivity studies have shown that this species has an unusual chemical behavior in the sense that it could act as a reducing agent despite of the trivalent state. The chemistry of both $Sm(Cp^*)_2$ and $Sm(Cp^*)_3$ is characterized by a great variety of unusual transformations that warrant a separate discussion (*vide infra*).

1.1.1. Stabilization of the Sm(II) metal center through π-coordination.

One of the most interesting variation in this versatile family of compounds was the introduction of the so called constrained-geometry cyclopentadienyls with two rings interconnected by one carbon or silicon atom link.



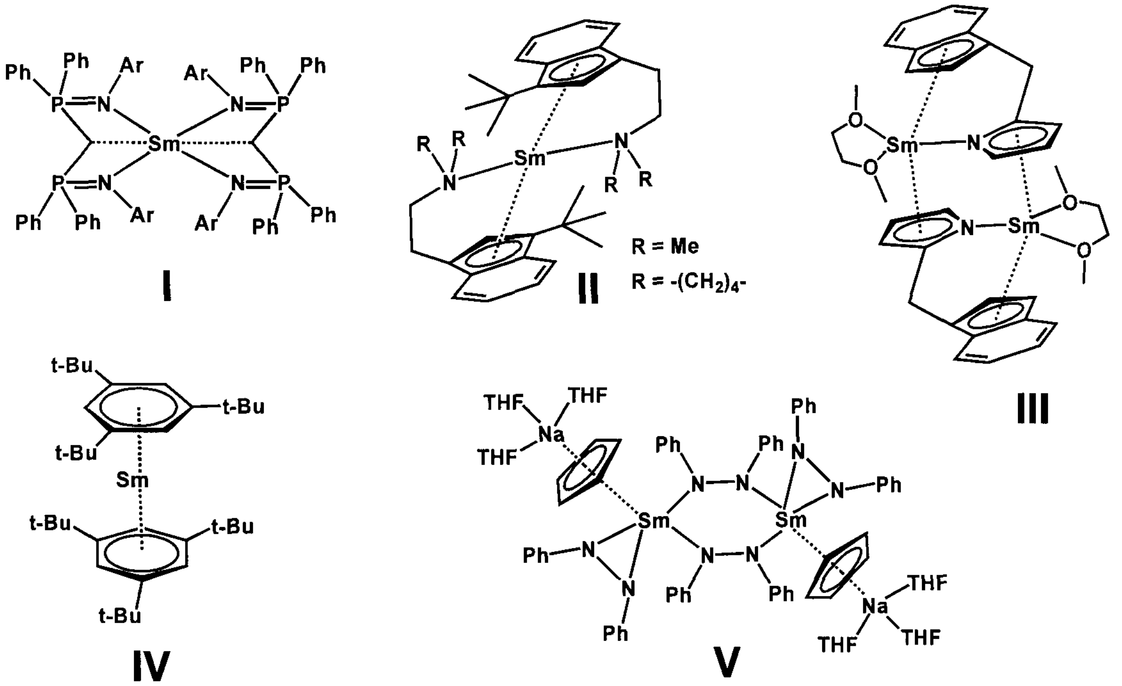
Scheme 1.2.

Another interesting modification consists of the addition of a donor atoms positioned on the side "arm" of the cyclopentadiene ring. Such arrangement allows the utilization of additional coordinating fragments, varying from simple moieties[13a] to rather complex multidentate parts.[13b] Several examples of such complexes are displayed in the Scheme above.

The distinctive properties of the modified cyclopentadienyl systems are exemplified by the work of Hou[14] with cyclopentadienyl ligand connected to silylene pendant with phosphorus donor atom. Simple salt metathesis afforded a solvated 1:1 complex of Sm(II). This species reacted further with di-phenyl ketone, resulting in the formation of a reduced ketyl moiety trapped between two SmCp" fragments (Scheme 1.2, Complex III). This reaction is just one of the many examples of small molecules cooperative activation as frequently performed by low valent Sm metal centers. Another example of activation accompanied by increase of the oxidation state was described by Xie and coworkers in 2000.[15] Reaction of $SmI_2(THF)_2$ with Cp-based monoanionic ligand leads to the deprotonation of the one carbon atom of *nido*-borane units and formation of "-ate"salt (Scheme 1.2, Complex IV). Another example was reported by Bochakrev group in 2001 with the formation of C-C bond in the direct reaction of activated metallic Sm with acenaphthylene yielding a solvated *ansa*-metallocene type of Sm(II) complex (Scheme 1.2, Complex V).[16] This reaction is closely reminiscent of the initial approach used for the isolation of $Sm(Cp^*)_2$.[8] In the former case, however, the electron transfer to the extended π-system of the ligand results in reductive coupling of two aromatic molecules. "One pot" reaction of $SmI_2(THF)_2$ with potassium salt of cyclooctatetraene and potassium salt of bulky amido- yielded an "inverted" sandwich compound of Sm(II),[17] where two Sm metal centers are coordinated to the same extended π-system from two opposite sides (Scheme 1.2, Complex VI). This is one of the few examples in the chemistry of low valent *f*-block elements where a large π-system is shared between two metal atoms.

Among the complexes presented in Scheme 1.3, the only one which does not posses a π-system coordinated to Sm(II) metal center (Scheme 1.3, Complex I) was reported by Michael Hill and Peter Hitchcock in 2003.[18] Despite the formal simplicity of this compound, detailed studies revealed that unsaturated P=N double bonds are involved in significant π-interaction with the metal center, which allowed to interpret this result as an unconventional π-complex of Sm(II). This compound was also presented as the first bis-imino-phosphine stabilized alkyl of Sm(II), based on short CH–Sm contacts.

Going back to the conventional coordinated π-systems, it should be noted, that variation of the aliphatic substituents on the Cp ring is not the only possibility to modify steric and electronic properties of the ligand environment around the metal center. It was already demonstrated that Sm could accommodate additional π-systems with different degrees of hapticity.



Scheme 1.3.

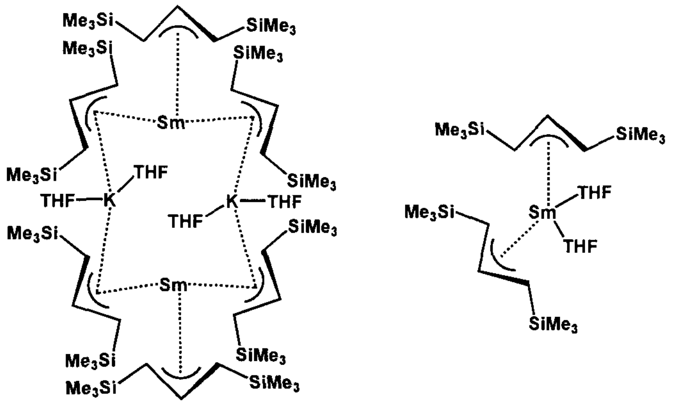
Accordingly, a variety of ligands based on the indenyl framework were successfully used in the chemistry of low valent samarium. Two examples of indenyl based complexes are given in Scheme 1.3.

When neutral donor atoms are present on the pendant side arm the ligands tend to form 1:2 adducts with Sm metal (Scheme 1.3, Complex II). Sheng et al. reported in 2004[19] that coordination to two ligand systems with to the sterically demanding σ-donor containing substituents on the side arm afforded the first racemic mixture of amino-indenyl complex of Sm(II). Another variation of Sm-indenyl motive was reported by Pi et al. in 2006.[20] In this case, the pendant arm contained a pyrrolide ring representing a di-anionic ligand system. Such ligand system was reacted with $SmI_2(THF)_2$ and produced the compound with ligand to metal ratio of 1:1 (Scheme 1.3, Complex III). This structure indicates that in certain conditions a negatively charged pyrrolide fragment can adopt both σ- and π- coordination mode assisting the formation of a poly-metallic unit. This tendency of pyrrolide based ligands will be extensively discussed later.

A remarkable result underlining the strong reducing power of Sm(II) and its versatility in performing cooperative attack is provided by the "one pot" reaction reported by Yuan et al.[21] who reacted Sm metal powder, diazobenzene and sodium cyclopentadienyl. The transformation was catalyzed by small amount of iodine and yielded the first Sm complex with two different type of hydrazido-ligands (Scheme 1.3, Complex V). Diazobenzene is known to be readily oxidized and to act as a two electron acceptor. Because of this property, diazobenzene is frequently used as a trapping agent for catching low-valent intermediates. In the present case four diazobenzene molecules have been oxidized by two atoms of Sm metal with two out of four molecules acquiring hydrogen atoms and yielding two monoanionic fragments.

As mentioned above, π-system coordination seems to be a crucial factor for the stabilization of low oxidation state and which in the case of Sm may even go towards lower states beyond the divalent. One of the rare examples of crystallographically characterized complex of Sm(0) (Scheme 1.3, Complex IV), was reported by the group of Cloke in 1989.[22] Theoretical calculation revealed that the stabilization of the zero-valent center is due to both electronic and steric factors. The electronic contribution consists of the possibility of promoting one electron from f^ns^2 to $f^{(n-1)}d^1s^1$ orbitals and subsequent transfer of spin density to the aromatic ring. The increased steric bulk of the alkyl substituents on the benzyl ring also contributed to the stabilization by sterically preventing disproportionation reactions. Once again, it was obvious from these findings that the large coordinated π-system allowed delocalization of an excess of electron density from the metal center into the ligand, therefore partially quenching the extreme reactivity.

Another system, clearly indicating the possibility of providing stabilization via a combination of π-bonding induced stabilization and steric protection was based on the utilization of bulky allyl ligands around the Sm(II) metal center. A rare examples of Sm(II) allyl species (Scheme 1.4, Complex I and II) was discovered by group of Bochmann in 2003.[23]



I II

Scheme 1.4.

Depending on the metal to ligand ratio it was also possible to isolate a neutral and anionic compound as well as evaluating the ability of catalyzing various polymerization processes.

In spite of the great diversity of reported complexes of Sm(II) as highlighted above, only a few compounds have been targeted with systematic and comprehensive studies to rationalize their behavior. Most of the complexes reported above were produced with catalytic applications in mind, therefore general reactivity pathways, *vis-a-vis* small molecules activation, as well as other red-ox transformations were rarely explored. Three are the low-valent Sm systems, based on somewhat related π-ligands, which have received considerable attention and provided unique transformations.

1.1.2. Reactivity of $Sm(Cp^*)_2$ and related species.

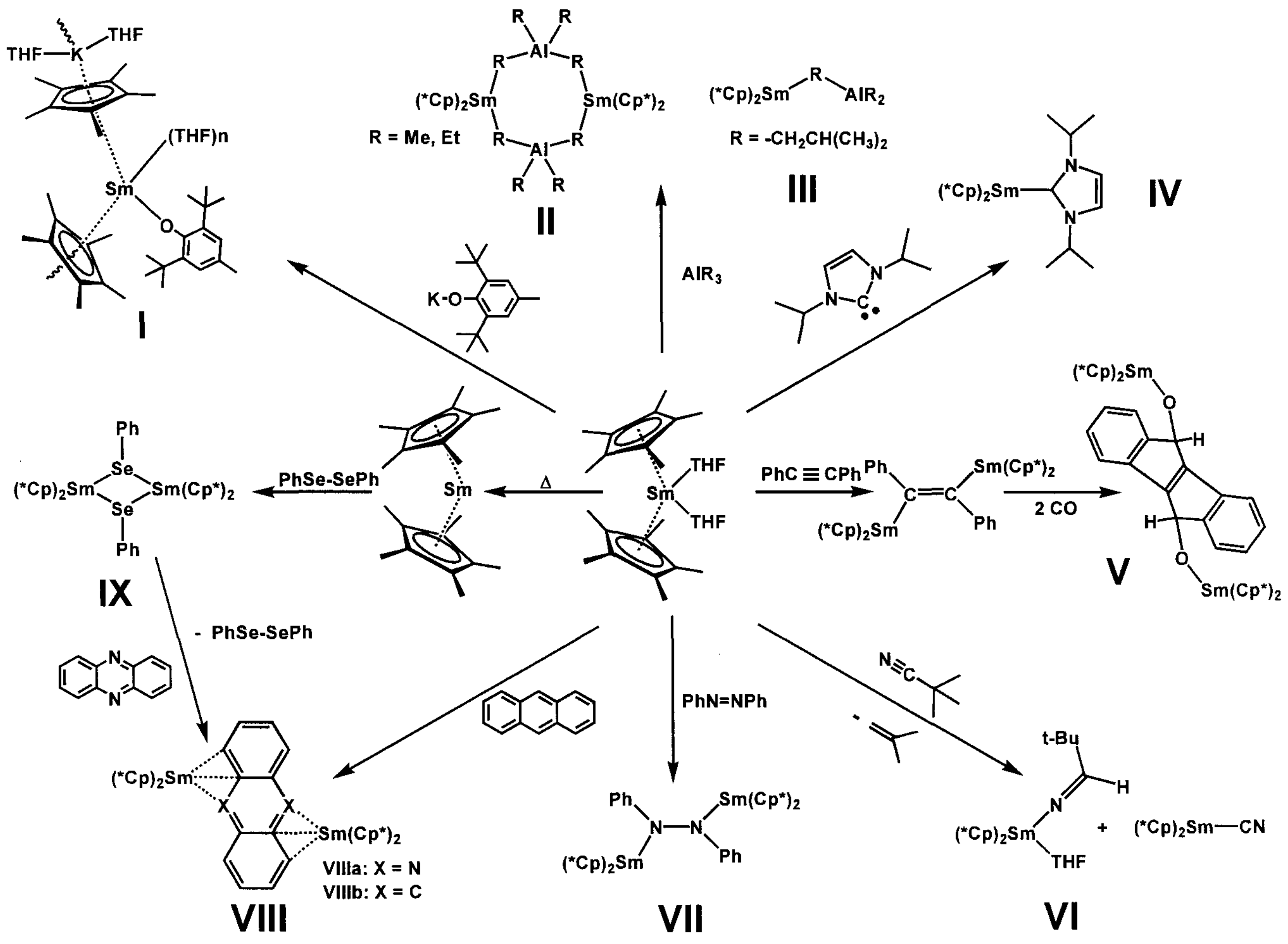
The complex of Sm(II) with pentamethyl-cyclopentadienyl ligand was isolated and fully characterized for the first time by Evans and colleagues in 1981,[8] followed by the preparation and characterization of unsolvated analogue in 1984.[11d] The reactivity displayed by these species could be separated into two distinctively different transformation pathways. One type of reactions consists of the replacement of the coordinating solvent molecules by the additional neutral or anionic ligands while the oxidation state of Sm remains unaltered. The other pathway represents the red-ox transformation with the oxidation of the metal center to tri-valent state is accompanied by electron transfer to the target substrate.

1.1.2.1 Solvent / Ligand exchange in the coordination sphere of $Sm(Cp^*)_2$ complex.

The coordination of heterocyclic carbene, reported by Schumann et al.,[24] is a classical example of introduction of neutral ligand in the coordination sphere of Sm(II) preserving at the same time the monomeric structure of the final compound (Scheme 1.5.1, Complex IV).

Anionic ligand coordination usually yields polymeric "-ate" structures through coordination of one or several ligands in bridging mode. Depending on the relative basicity of the ligand it is possible to formally interpret the addition of the ligand salt to a Sm complex(II) as a cation exchange reaction with the retention of "neutral" KCp* unit in the close proximity to Sm metal center (Scheme 1.5.1, Complex I).

As described by Hou and colleagues in 2000,[25] such change in the coordination environment can greatly affect the catalytic ability of the complexes. Another example of neutral ligand addition to a $Sm(Cp^*)_2$ unit consists of the interaction with different Lewis acids. Similar results have been obtained by exploring the reactivity with alanes, revealing a rather common tendency to produce hetero-bi-metallic structures[26, 27] with bridging alkyl groups linking together Sm and Al metal centers (Scheme 1.5.1, Complexes II and III). It was also demonstated by Evans[27] that the increase of steric bulk of aluminum alkyl substituents will lead to the collapse of polymetallic associates, preserving only one bridging alkyl within bi-metallic Sm/Al monomeric unit (Scheme 1.5.1, Complex III).



Scheme 1.5.1.

All these transformations were explored with the goal of changing the coordination sphere of Sm(II) metal center.The aim of such study was to determine the influence of those changes on the catalytic activity of samarium complexes in different processes, mainly focusing on polymerization and copolymerization of different unsaturated hydrocarbon monomers.

1.1.2.2 Red-Ox reactivity and molecular activation supported by Sm(Cp*)$_2$ complex. Multi-metal cooperative transformations.

The strong reduction potential of the Sm(III)/Sm(II) redox couple directly reflects into the ability of the metal center to transfer one electron from the divalent center into the anti-bonding orbital of the coordinated π-system. Such transfer necessarily results in bond weakening and could potentially lead to partial or complete bond cleavage. The number of electrons received by the π-system depends on the number of the metal centers involved in the interaction with one molecule of substrate. Because of the availability of only one electron from each Sm(II) metal center, the simultaneous attack of several Sm units toward one molecule of substrate becomes a common motif of Sm(II) red-ox chemistry. The reaction of Sm(Cp*)$_2$(THF)$_2$ with diazobenzene could be the regarded as one of the most illustrative and simple examples of multiple bond reduction. It has already mentioned above that diazobenzene is commonly used as a trapping agent for low valent metal centers. This molecule accepts two electrons and transforms N=N double bond into N-N single bond. The resulting hydrazydo fragment is usually retained in the coordination sphere of the oxidized metal center, therefore providing some insides about the reaction mechanism. The reaction of diazobenzene with Sm(Cp*)$_2$(THF)$_2$, reported by Evans in 1986,[28] followed the multi-metallic oxidation concept illustrated above. The transformation of the double bond into a single bond required two electrons and resulted in the formation of a hydrazido fragment entrapped between two oxidized metal centers (Scheme 1.5.1, Complex VII). Similar reaction with diphenylacetylene as a substrate led to the formation of ethylenido-fragment.[29] Interestingly enough, the presence of bulky phenyl groups prevented the coordination of additional Sm(II) metals to the partially reduced fragment therefore preventing further reduction of the double bond. An unprecedented transformation was discovered when this etylenido-di-samarocene complex was reacted with CO under mild conditions. The reaction proceeded through the expected CO insertion into Sm-C bond. The oxygen atom of the inserted molecule was oriented toward the Sm metal center and the insertion was followed by an intra-molecular attack of the carbon atom on the neighboring phenyl ring generating a new C-C bond and transferring one H atom. Overall, this transformation represents a stereospecific formation of a new tetra-cyclic carbon alkoxide, entrapped between two Sm(III) metal centers: indeed a very unusual transformation (Scheme 1.5.1, Complex V).

A reduction reaction resulting in the homolytic bond cleavage with the assistance of a Sm(II) center was reported by the same group in 2005.[30] This time, it was necessary to perform de-solvation of Sm metal center. Unsolvated $Sm(Cp^*)_2$ reacted with diphenylselenide cleaving Se-Se bond and producing Sm(III) dimeric unit bridged by two $(\text{-Se-Ph})^-$ fragments (Scheme 1.5.1, Complex IX). Interestingly enough, this compound appeared as a Sm(III) species, yet it was able to engage in red-ox transformations with the large aromatic π-system of the phenazine molecule. The reaction proceeded through the reforming of Se-Se bond, removal of di-selenide unit and consequent reaction of Sm(II) with phenazine moiety. Each Sm metal center did coordinate to phenazine and transferred one electron to large delocalized π-system, forming an "Sm(III)-allyl" type arrangement with three planar atoms of the aromatic molecule (Scheme 1.5.1, Complex VIII). This electron transfer and subsequent delocalization was regarded as the driving force behind this transformation therefore reiterating the potential of the availability of π-systems in the reactivity of the divalent state.

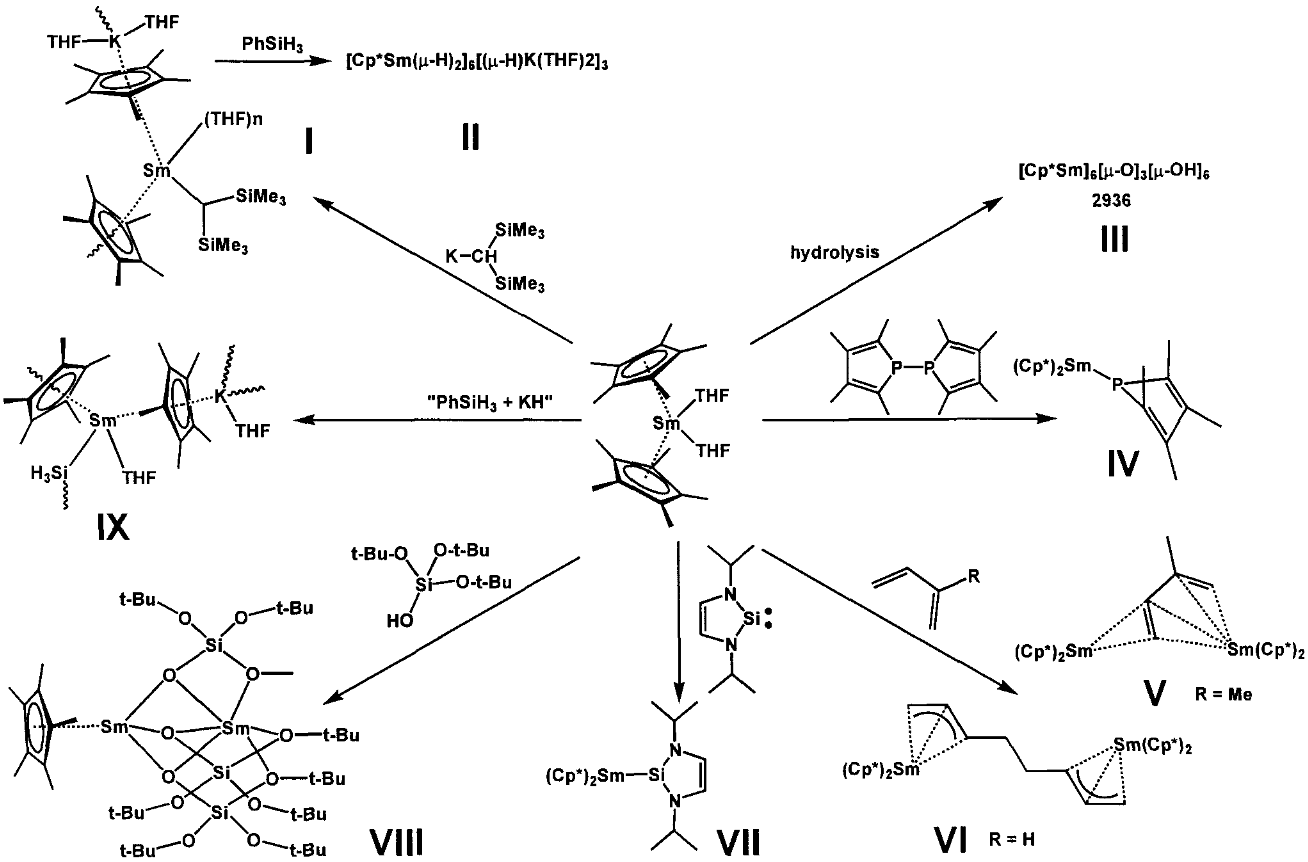
A similar delocalization was observed in a previous case when the solvated bis-samarocene was reacted with antracene.[31] The reaction yielded a dimeric unit with two Sm(III) metal centers connected to the dianionic aromatic residue in two allyl-type bonding nodes (Scheme 1.5.1, Complex VIII).

An example of more complex red-ox transformation was reported in 2000 by the same group of Evans,[32] with Sm(II) metal center engaging in the reactivity with an unsaturated bond of *tert*-butylnitrile. In contrast with previous reactivity examples, such interaction did not result in the formation of a dimeric unit. It rather went through the formation of the radical followed by hydrogen abstraction from the other molecule of the substrate. The final products of this reaction included two different Sm(III) species. The first complex was the result of radical quenching through hydrogen abstraction (Scheme 1.5.1, Complex VI). The second species was generated by the expulsion of 2-

methylpropene and formation of a Sm(III)-cyano complex (Scheme 1.5.1, Complex VI). This is another example of unusual radical-type reduction pathway. This reaction is rationalized with the generation of a radical followed by quenching of the unpaired electron through coupling, hydrogen abstraction or eviction of an organic radical.

1.1.2.3 Red-Ox reactivity and molecular activation supported by of Sm(Cp*)$_2$ complex. Reactivity of single metal center.

An unusual example of radical abstraction may be observed in the transformation of SmCp*$_2$(THF)$_2$ into polymetallic poly-hydride cluster as described by the group of Hou in 2001.[33]



Scheme 1.5.2.

The first step of the reaction of Sm(Cp*)$_2$ with bis-(trimethylsilyl)-methyl potassium afforded the alkyl group transfer to samarium metal center leading to the appearance of formally "neutral" KCp* unit.

A molecule of potassium cyclopentadienyl was retained in the structure of Sm(II) complex. X-ray data revealed that the presence of the KCp* unit was primarily responsible for the formation of the polymeric structure (Scheme 1.5.2, Complex I). It was speculated by the authors, that the presence of an alkali metal cyclopentadienyl might acts as an additional stabilizing ligand in the formation of hydride species. In the second stage of the transformation, treatment of the isolated Sm(II) material with PhSiH$_3$ yielded a complex structure formally composed of six SmCp*H$_2$ units and three KH(THF)$_2$ fragments (Scheme 1.5.2, Complex II). Before attempting to rationalize the following transformation it should be noted that PhSiH$_3$ is often used as a reagent for the conversion of alkyl to hydride. Such conversions are widely represented in both transition metals and lanthanide metals chemistry. However, the reactivity of this species could also be switched from Si-H bond to Si-C bond metathesis. Such transformations, involving Si-C bond reactivity remained significantly less common up to these days. A rare example of this unusual chemistry was reported by Hou and coworkers in 2003.[34] Treatment of Sm(Cp*)$_2$(THF)$_2$ with the specially prepared "KSiH$_2$Ph" reagent yielded trapping of a very unusual SiH$_3$ unit between Sm and K metal centers (Scheme 1.5.2, Complex IX). The "KSiH$_2$Ph" reagent was produced as a colorless insoluble powder from the reaction of KH with PhSiH$_3$ in THF and used as obtained without detailed characterization. It was also discovered that addition of pure PhSiH$_3$ to the reaction mixture increase significantly the yield of the polymeric Sm(II)-SiH$_3$ containing material.

In all the cases of mono-metallic red-ox reactivity it was speculated, that the first step of the molecular activation of the substrate consisted of the preliminary formation of a donor – acceptor adduct where the divalent state of Sm was preserved. Such THF replacement at Sm(Cp*)$_2$(THF)$_2$ may be achieved with a large variety of Lewis bases. Some of these transformations are straightforward, other instead can be highly significant. For example, reaction with heterocyclic silylene results in the substitution of coordinated THF solvent molecules and formation of the first crystallographically characterized silylene (Scheme 1.5.2, Complex VII) of low valent lanthanide.[35] Extended π-system may be used for the same purpose. The group of Evans described in 2001[36] the reaction of unsolvated Sm bis-cyclopentadienyl starting material with 2-methyl-1,3-butadiene (isoprene) affording coordination of one molecule of isoprene, in a bridging mode with two Sm atoms (Scheme 1.5.2, Complex V). The coordination mode of the butadiene fragment is curiously asymmetric with one Sm metal center interacting with four carbon atoms of the π-system whereas second Sm metal is interacted only with 2 carbon atoms of the butadiene-type π-system. Structural parameters of the isolated complex are consistent with the presence of Sm(III) rather then Sm(II) metal center. The same information has been confirmed by the NMR data recorded for the complex under investigation. However, it was also reported that at higher temperature this species regenerates $Sm(Cp^*)_2(THF)_2$ as a solvated form of starting material, indicating that the electron density transfer process may be reverted in this case. Instead, when there were no substituents on the butadiene molecule, the reaction irreversibly proceeded to the radical dimerization of the substrate (Scheme 1.5.2, Complex VI) with the formation of bis-allyl moiety.[37]

Nief and Ricard reported in 2001 a transformation proceeding through reductive radical E-E bond cleavage.[38] It was discovered by these researchers that reaction of samarocenes with bis-phospholyl afforded either dimeric or monomeric structures with Sm-P σ-bond (Scheme 1.5.2, Complex IV). The outcome of the transformation was depending on the steric bulk of the starting *bis*-phospholyl molecule.

To conclude this brief survey of the reactivity of $Sm(Cp^*)_2(THF)_2$ and its unsolvated analog, two more transformations are worth of mentioning. Both reactions represent attempts of controlled hydrolysis. The first alcoholysis reaction was reported by Hou et al. in 2004,[39] describing the treatment of $Sm(Cp^*)_2(THF)_2$ with sterically demanding silanole. The complex obtained from this reaction revealed a very unusual dimeric asymmetric structure, where one Sm metal center completely lost all the Cp* ligands and was positioned in an octahedral environment, created by three bridging siloxo and three coordinated siloxo-ether groups (Scheme 1.5.2, Complex VIII). The second Sm metal center retained one cyclopentadienyl ligand and it was connected to the dimer through coordination of three bridging siloxo- moieties. Surprisingly, no radical oxidation of Sm(II) occurred in this case. Both metal centers involved in the transformation, preserved the oxidation state at the level of Sm(II). Therefore this reaction may also be considered as an acid-base proton exchange, where three cyclopentadienyl anions act as a base, deprotonating three acidic silanole fragments.

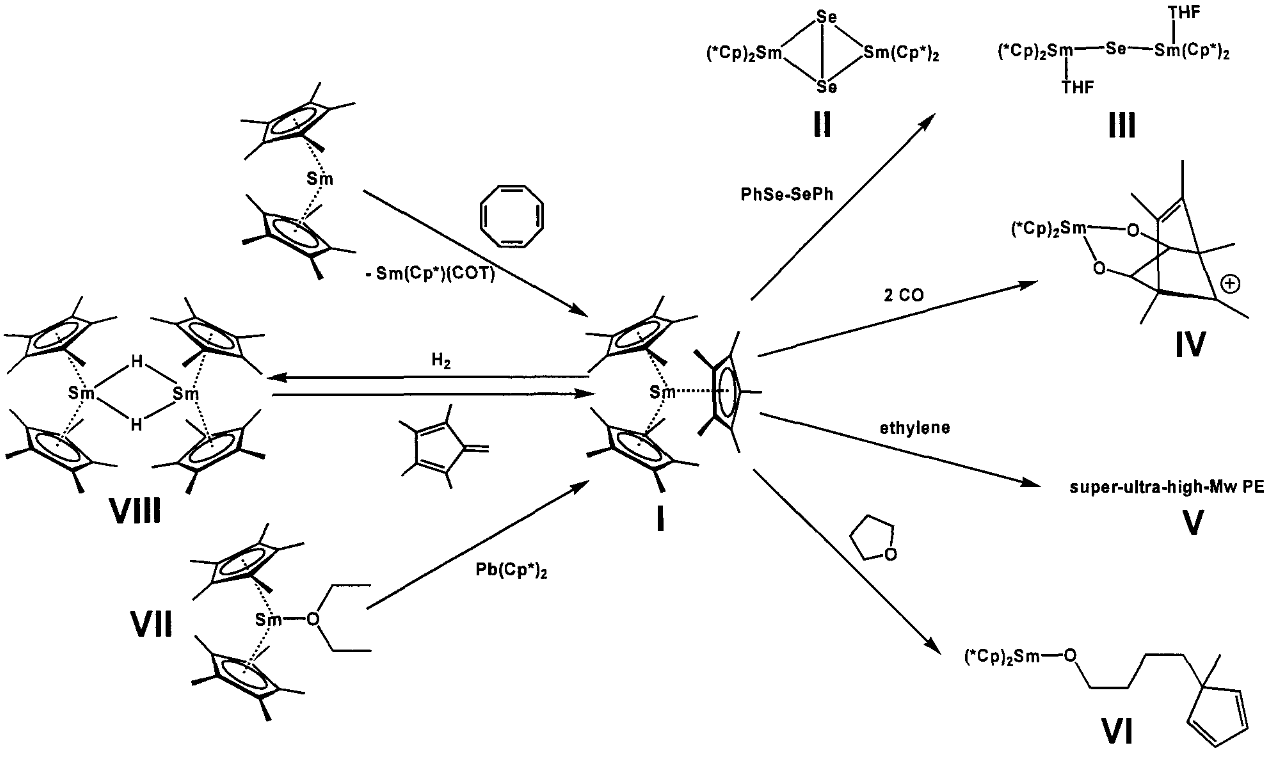
Hydrolysis of $Sm(Cp^*)_2(THF)_2$ was attempted by the group of Evans in 2001.[40] The product of the reaction was discovered to be a complex cluster consisting of six mono-cyclopentadienyl samarium units linked together through six μ-OH and three μ-O bridges (Scheme 1.5.2, Complex III). On the basis of charge balance considerations, it was concluded that in this case each Sm metal center not only lost one Cp anion to the acid-base reactivity with water, but was also oxidized to the trivalent state.

All the examples above clearly indicates that the reactivity of the single Sm(II) metal center is somewhat lower in comparison to the multi-metal transformations. When the cooperative attack of the several low valent metal units to the same substrate is impossible, the reaction proceeds through the radical pathway. However, if the radical formation is not favorable, then Sm(II) metal center could retain the oxidation state while being preferably involved in acid-base or ligand exchange transformations.

1.1.3. Reactivity of $Sm(Cp^*)_3$ and related species.

Among the enormous variety of Sm(III) complexes only $Sm(Cp^*)_3$ will be now surveyed because of its relevance to this thesis. The most important reason is the close relationship of the reactivity of this species with the Sm(II) analogue, in the sense that this complex may readily embark in red-ox transformations in spite of its trivalent state. The steric strain in $Sm(Cp^*)_3$ is so great that for long time it was believed that this complex could not be prepared. This was brilliantly disproved by the group of Evans in 1991.[41] When carrying out the reaction of unsolvated $Sm(Cp^*)_2$ with COT two products were isolated. The first complex is a Sm(III) metal center coordinated to one Cp* ligand and one COT dianionic unit. Given the reduction potential of $Sm(Cp^*)_2$, it was anticipated that the reaction of Sm(II) with COT ligand would lead to electron transfer to the π-system of COT. Result of this transfer would be the formation of Sm(III) species which in fact was observed. Surprisingly, the second complex contained three Cp* ligands symmetrically bonded to the Sm(III) metal center (Scheme 1.6, Complex I).

To overcome the synthetic limitation deriving for the formation of a mixture of products, two other preparative routes were later developed for preparing the target compounds in good to excellent yields.[42] One consists of the reaction of the dimeric $[Sm(Cp^*)_2(\mu\text{-}H)]$ with tetra-methyl-fulvene producing the target compound in quantitative yield (Scheme 1.6, Complex VIII). A viable alternative consisted of the oxidation of the diethyl ether solvate of $Sm(Cp^*)_2$ with $Pb(Cp^*)_2$ in ether (Scheme 1.6, Complex VII).



Scheme 1.6.

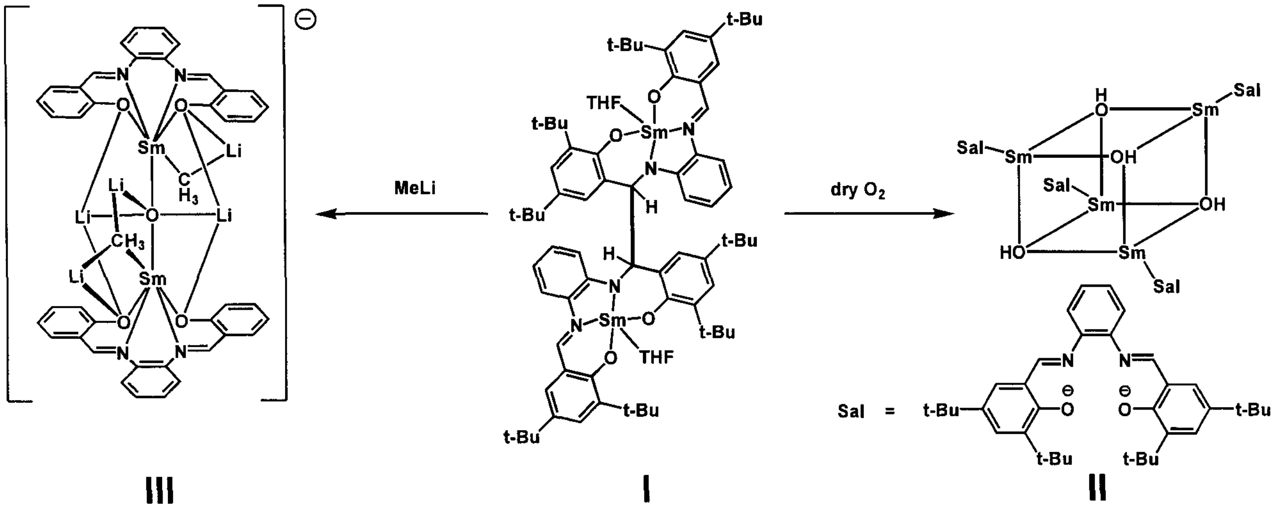
It was discovered that $Sm(Cp^*)_3$ exists as two different isomeric forms in equilibrium. Because of the great steric strain, one of the rings may undergo slippage with changing of the coordination mode from η^5-type to σ-bonding. Even though this equilibrium is greatly shifted toward the π-coordinated isomer, the presence of the second species is responsible for transformations, expected for a terminally bonded alkyl group. Ethylene polymerization,[43] CO insertion,[44] and hydrogenolysis[43] reactions are only a few examples of the transformations displayed by this system. Polymerization reaction, catalyzed by $Sm(Cp^*)_3$ produces polyethylene with molecular weight so high (Scheme 1.6, Complex V), that it could not be determined by NMR or field desorption mass spectroscopy.[43] Other typical examples of alkyl reactivity are the reaction with THF which proceeded immediately upon mixing the two compounds. This reaction afforded the opening of the THF cycle and insertion of the resulting fragment into Sm-C bond (Scheme 1.6, Complex VI).[43] One additional example of insertion reaction with formation of an unusual product was the reaction of $Sm(Cp^*)_3$ with two equivalents of CO.[44] In this reaction two CO molecules were inserted between Sm and two opposite carbon atoms of the cyclopentadienyl ring. The insertion product remained coordinated to the samarium metal center (Scheme 1.6, Complex IV). Moreover, the detailed NMR study, supported by crystallographic data, suggested that the atom in the center of the distorted triangular fragment bears a positive charge, therefore producing a rare example of metal coordinated cation. Finally, another confirmation of the presence of "Sm-alkyl" isomer was discovered in the hydrogenation reaction[43] which resulted in the formation of hydrogen bridged dimer (Scheme 1.6, Complex VIII). All these reactions could be explained by assuming ring slippage. However, several transformations were discovered that could not be explained by the ligand "slippage" concept. All these "unexplainable" transformations were characterized by red-ox behavior, which was predictable for Sm(III) compound. Reaction of $Sm(Cp^*)_3$ with diphenylselenide results in the formation of complex composed by two $Sm(Cp^*)_2$ units bridged by $(Se_2)^{2-}$ (Scheme 1.6, Complex II) or Se^{2-} (Scheme 1.6, Complex III) moieties, depending on the initial stoichiometry.[45] An explanation to the red-ox activity of Sm(III) came from careful analysis of the byproduct of this transformation. It was discovered that *bis*-cyclopentadiene was the main byproduct of the reduction reactions. The presence of this byproduct suggested that the reduction reactions were carried out not at the expense of the metal center but rather at the expense of the ancillary $(C_5Me_5)^-$ ligand. The possible oxidation half-reaction could be envisioned as $(C_5Me_5)^- \rightarrow \frac{1}{2}(C_5Me_5) + e^-$.

In concluding this section about the reactivity of the samarocenes, it should be reiterated that, despite high reducing potential of the Sm(II) metal center, it is still possible to control, partially quench or even reverse the reactivity by using supporting π-interactions of different ligand systems coordinated to Sm. Moreover, the π-system coordinated to the metal center could possess either aromatic nature or even represent simple multiple bond. It should be also noticed that steric factors are manly responsible for directing the red-ox behavior. In the cases where coordination of several metal centers to the same substrate was not possible, the radical character reaction resulted in dimerization, hydrogen abstraction from the reaction environment or fragment redistribution processes. When it was possible to obtain cooperative attack of two or more metal centers to the same substrate, then such interaction led to the reduction of the multiple or single bonds. The reduced fragments were often retained as bridging units between several Sm(III) metal centers. In some case, it was possible to perform the red-ox transformation at the expense of a Cp ligand moiety.

1.2 Sm non-cyclopentadienyl based systems.

As stated above, Sm(II) chemistry is dominated by the use of cyclopentadienyl ligands. Nevertheless, there are a few well charcaterized non-cyclopentadienyl systems which provide examples of promising Sm(II)-assisted reactions. Not surprisingly, the caliber of transformation displayed by the samarocenes has encouraged active research to create alternatives to the Cp ligand system. As a result, entire classes of Sm(II) compounds including amides, alkoxides, phosphides, etc. have been developed. Specialty ligands such as scorpionands and macrocycles also have been used. However, these efforts have in general produced attractive structures but not even a fraction of the caliber of reactivity displayed by the samarocenes. There are only a few exceptions were the certain ligand systems have raised reducing power of Sm(II) even higher then it was observed in case of cyclopentadienyl based compounds.

Complexes of bis-imino-aryloxo-Shiff base ligands are among the most widely investigated and established non-cyclopentadienyl systems. The presence of the large delocalized π-system, coupled with the semi-rigid chelating geometry, provides all the prerequisites to support a low valent metal center. Moreover, the variety of the substituents available on the backbone of the ligand and at the aryl rings allows a fine tuning of the reactivity of the metal center. Our lab was the first to study this ligand system for the purpose of stabilizing Sm(II).[46] The ligand with an aromatic backbone was attached to the Sm(II) metal center through metal-salt metathesis approach. Surprisingly, the final compound was always a trivalent species possibly obtained through either disproportionation or ligand reduction. In the case of the macrocyclic shiff base (Salen-type), two ligands underwent reductive coupling at the imine function with formation of a dimer (Scheme 1.7, Complex I). It appeared that coordination of the low valent metal center to the ligand was followed immediately by the transfer of the electron onto large delocalized π-system. Such transfer, in turn, ended in the formation of Sm(III) metal center, coordinated to the radical anion eventually leading to formation of a new C-C bond and transformation of the ligand into tris-anionic imino-amide-bis-aryloxide moiety.

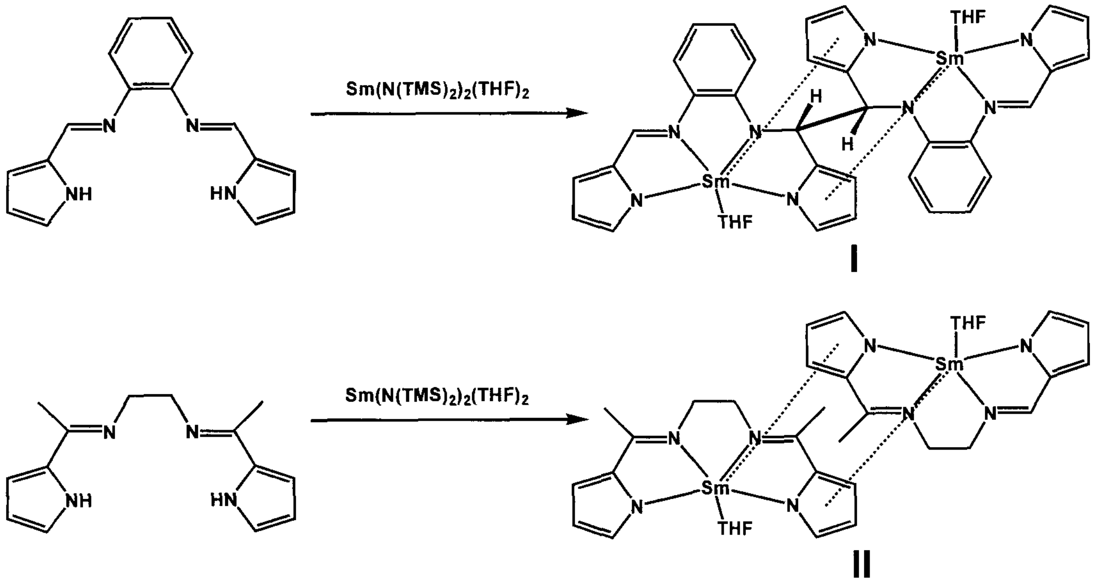


Scheme 1.7.

The oxidation of the metal center usually results in a complete quenching of the red-ox activity of the final complex. In this case instead, the ligand reductive coupling had a reversible character. It was discovered that interaction of the Sm(III) coupled unit with dry oxygen led to the cleavage of the C-C bond through intermediate restoration of the +2 oxidation state of the metal center (Scheme 1.7, Complex II). Upon treatment with MeLi, the C-C bond was also cleaved with re-appearance of the original Sm(II) compound. Moreover the reducing ability of this compound was so enhanced that the low valent metal center performed reductive cleavage of the THF solvent molecule, extracting the oxygen atom and forming ethylene as a byproduct (Scheme 1.7, Complex III). The process of THF ring opening required two electrons, which could be acquired from two Sm(II) centers.

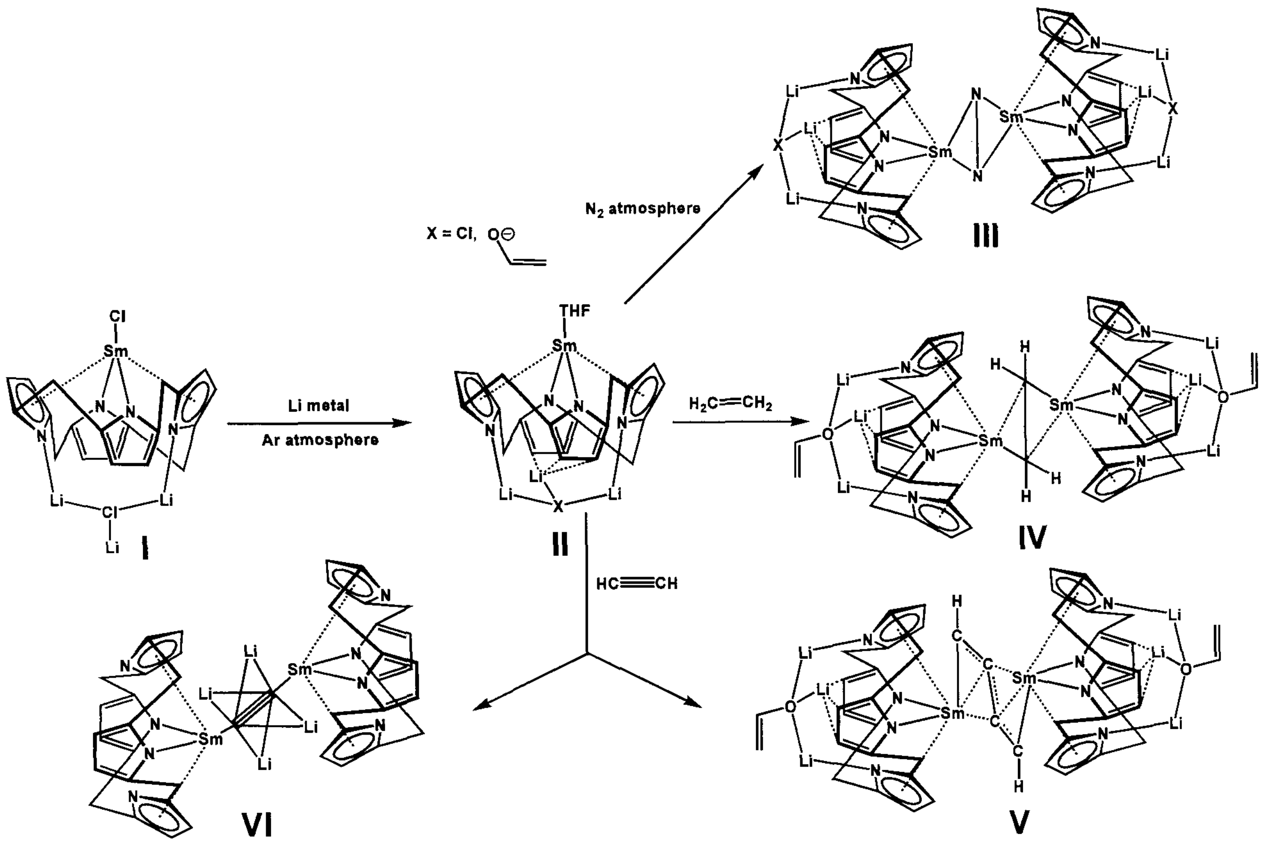
The merit of these transformations was to show that delocalization of the electrons onto the π-system may help to stabilize the low valent character of the metal center. "Conventional" localized C-C bond could be also used as the electrons storage.

A modification of the conventional *salen*-motif was reported by our group five years later.[47]



Scheme 1.8.

This Schiff base system possesses two imino-pyrrolide moieties instead of the conventional imino-aryloxide fragments. The pyrrolide anion was known to greatly enhance the stability of the divalent center due to the possibility of switching bonding modes. The second advantage of the pyrrolide moiety over the aryloxide was the proved ability to increase the reduction potential of Sm(II). The preparation of the complex of this ligand resulted again in the reductive coupling of two imine- functions with oxidation of the metal center and consequent dimerization (Scheme 1.8, Complex I). In this case, the formation of the C-C bond formation could not be reversed and further exploration of the red-ox chemistry was therefore impossible. In order to prevent the ligand radical coupling a modified version of the same system has been developed. The second generation of this ligand did not have an extended delocalized π-system because of the utilization of aliphatic backbone.



Scheme 1.9.

Methyl groups were introduced at the carbon atoms neighboring the imino-functions in an attempt to prevent dimerization. In this case, a new Sm(II) complex was obtained (Scheme 1.8, Complex II).

A rather interesting alternative to the cyclopentadienyl systems is provided by the pyrrolide anion. The two ligands share a very similar geometry and a rather similar electronic configuration. Characteristic of the pyrrolide anion is an enhanced tendency towards ring slippage which directly results from the presence of the negatively charged nitrogen atom.

The versatility of pyrrolide based ligand system became readily apparent in the case of porphyrinogen, a tetrapyrrolide macrocycle related to porphyrine but without extensive electronic conjugation. This system has provided the first case of cooperative reduction of dinitrogen in lanthanide chemistry (*vide infra*) thus significantly surpassing the reactivity of cyclopentadienyl based ligands which only supported reversible coordination.[48]

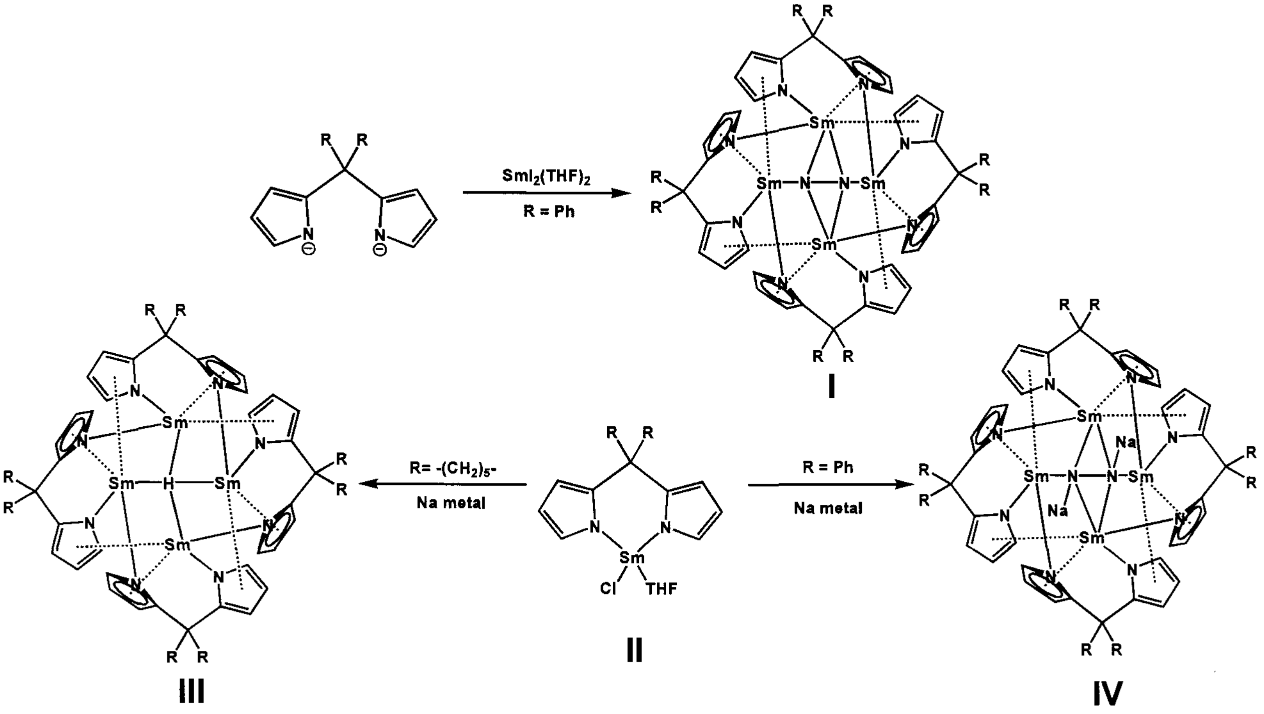
The tetra-anionic nature of the ligands created the predisposition to form "-ate" type of complexes with by retaining of two (or more) alkali counter-cations (Scheme 1.9, Complex II).[49] Coordination of the alkali metals affected the donor ability of the ring in turn, affecting the red-ox potential of the lanthanide. In fact the simple replacement of Li with Na greatly influenced the reactivity of the metal center.[50] Subsequent mechanistic studies have allowed a complete elucidation of the mechanism of dinitrogen reduction. The trapping of several intermediates has revealed the path through which dinitrogen underwent through from labile coordination to four electron reduction and remained encapsulated in a Sm_2N_2 fragment (Scheme 1.9, Complex III).[49, 50]

The reactivity of this system was not restricted to dinitrogen. When acetylene was used as a substrate two different complexes were isolated depending on the reaction conditions.[51] In one case the interaction of the low valent Sm compound with acetylene led to deprotonation of the acetylene unit accompanied with the oxidation of Sm metal center to the trivalent state and to the formation of hydrogen gas. The resulting $C\equiv C$ fragment remained entrapped between two Sm units (Scheme 1.9, Complex VI) involved in end-on bonding interactions. Such coordination mode was opposite to the previously discovered side-on coordination of the reduced dinitrogen fragment. The second product derived from acetylene dimerization is a butadiene-di-yl moiety remaining retained by bridging two Sm metal centers (Scheme 1.9, Complex V). In the later case, the oxidation state of Sm metal was also increased to +3 in the process. Conversely, the reaction with ethylene was found to be reversible, affording a divalent complex (Scheme 1.9, Complex III).[49] X-ray data revealed that metal center was coordinated to ethylene unit in side-on bridging interaction, displaying a distorted η^2-μ-bridging configuration.

In all this chemistry, the tetra-anionic nature of the ligand necessarily required at least two counter-cations being retained by the ligand. An attempt to modify the polypyrrolide ligand systems aimed at the low valent lanthanide stabilization was made by the research group of Gardiner in 2004.[52] The alkylation of two opposite nitrogen atoms of the tetrapyrrolide ligand allowed to eliminate two negative charges from the ligand and permitting the formation of neutral Sm(II) complexes. Although the complexes were successfully obtained and characterized they revealed no ability to interact with dinitrogen nor gave any signs of unusual reactivity. In turn, this suggested that the ancillary alkali counter-cations were indeed important at least at the preliminary step of dinitrogen fixation.

A valid alternative to the Gardiner system for avoiding the formation of "-ate" complexes was the design of the dipyrrolide ligand system.[53] The geometry adopted by these ligands was closely reminiscent that observed with the tetra-pyrrolide anions. At the same time, the two negative charges were balanced by the charges of Sm(II) cation, therefore avoiding the retention of the alkali metal. That simplified the reaction and allowed more control over the reactivity of Sm.

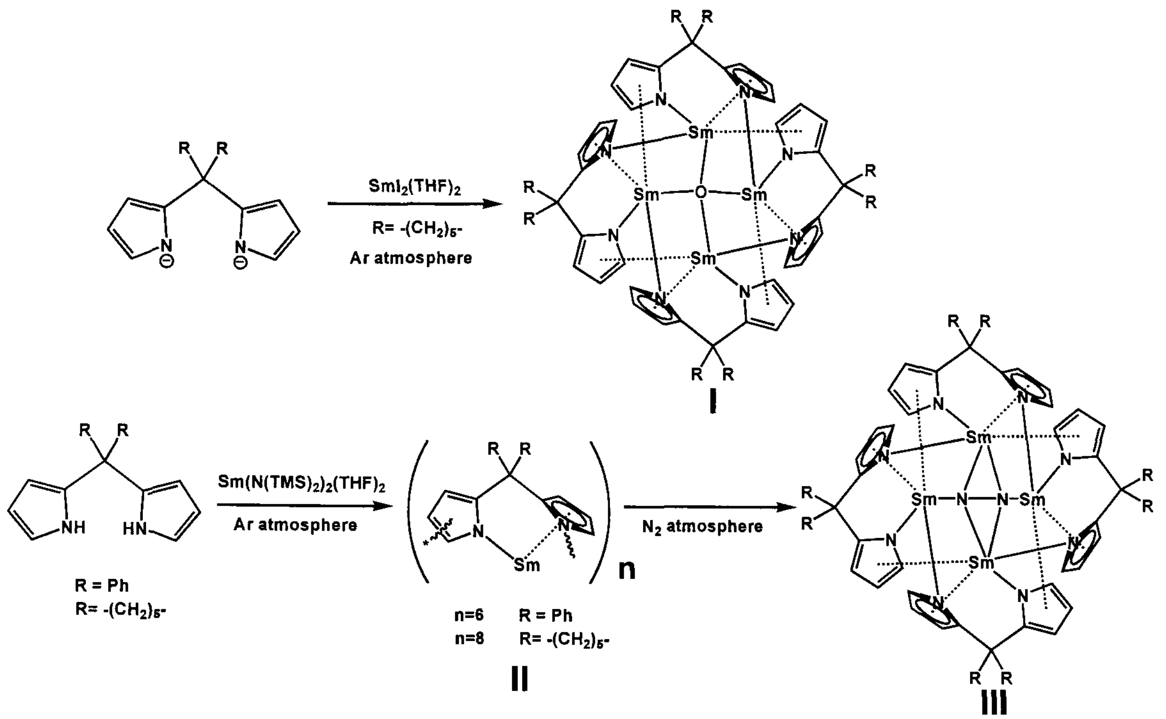
Following the same synthetic protocols $SmI_2(THF)_2$ was reacted with doubly-deprotonated salt of the dipyrrole.[54] The reaction afforded a tetra-nuclear dinitrogen complex with one dinitrogen unit encapsulated between four Sm dipyrrole units with a complex bridging end-on / side-on bonding mode (Scheme 1.10, Complex I). Identical results were obtained upon reducing a suitable trivalent precursor (Scheme 1.10, Complex II). The elongation of the coordinated dinitrogen unit suggested that the dinitrogen molecule underwent a four-electron reduction as the result of a cooperative multi-metal attack. Attempts to further reduce the coordinated dinitrogen unit and to obtain N-N cleavage were performed by using strong reducing agents.[55]



Scheme 1.10.

Surprisingly, the reaction simply resolved in the addition of two alkali cations around the tetra-nuclear structure and in a surprising *shortening* of the N-N distance (Scheme 1.10, Complex IV). This result clearly indicates that the cleavage of the N-N single bond is the most arduous step in dinitrogen activation and that Sm(II) pyrrolide which has the strength to reduce dinitrogen to tetrahydrazido anion, does not possess the sufficient reducing power required by the very final cleavage of the N-N single bond.

When the same reaction was carried out with a different ancillary substituent,[55] the reaction took a remarkably different pathway. A similar tetrameric structure was obtained, however, the central cavity was occupied by one hydrogen atom (Scheme 1.10, Complex III).



Scheme 1.11.

The origin of the hydride was ascribed to a THF fragmentation process possibly initiated by low valent Sm.

Finally, when reduction reaction was carried out in the absence of N_2 under Ar atmosphere, this reaction afforded another tetrameric cluster with the central location occupied by an oxygen atom (Scheme 1.11, Complex I). It was suggested that the oxygen atom located in the center of the tetramer results from a THF fragmentation reaction.[56]

In order to avoid the presence of THF in the reaction mixture a different reactivity protocol was employed based on proton exchange between the bulky amido-samarium compound and a free (protonated) ligand. The solubility of all the reagents in toluene allowed the elimination of THF from the reaction medium. Naturally, this approach prevented the formation of oxygen bridge, producing instead large circular cluster structures of Sm(II).[57] X-ray data revealed that the number of the monomeric unit involved in the formation of the clusters was highly depending on the nature of the ancillary substituents on the ligand backbone (Scheme 1.11, Complex II). It was also discovered that exposure of these clusters to dinitrogen resulted in immediate and quantitative transformations into the known tetrameric dinitrogen complexes discussed earlier[54] (Scheme1.11, complex III). In conclusion, the involvement of THF in the reactivity of these systems no only provides hydride[55] (*vide supra*) but also μ-oxo species[56] and more exotic enolate fragments.[49, 50, 58]

The next natural step of this chemistry was to explore the behavior of regular monodentate pyrrolide anions. The use of 2,5-dimethyl-pyrrole had only limited success. Attempt to prepare divalent species did not resolve in any dinitrogen activation process nor in solvent cleavage. The merit of this work was simply to confirm the previously observed dependence of the ligand bonding mode on the coordination of the ancillary alkali cation (with Li metal provoking π-bonding and potassium inducing σ-interaction of the pyrrolide with Sm metal center).[59]

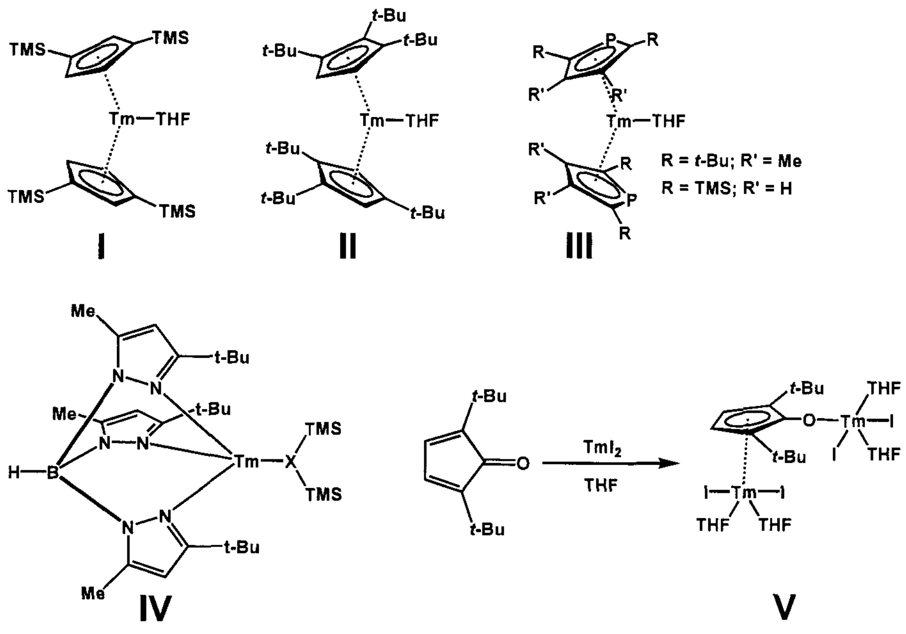
Another class of ligands capable of enhancing the reactivity of the Sm center was provided by the poly-phenols in spite of the fact that low valent samarium aryloxides did not receive significant attention. Early exploratory works were directed[60] more towards the polymerization activity of these derivatives rather than to small molecule activation. Nevertheless, one case of dinitrogen fixation was reported in 2007 by Guillemot *et al.*[61] Reduction of the trivalent precursor afforded a cluster compound where three Sm-ligand units and one sodium atom were connected together by a reduced dinitrogen unit. The N-N bond was found significantly elongated in comparison to free dinitrogen. Since dinitrogen activation is symptomatic for the presence of highly reactive Sm(II) precursors, this result opens interesting perspectives for the use of these poly-aryloxide ligands for Sm-supported molecular activation purposes.

The few selected discoveries highlighted in this section are just a few among the most spectacular examples of the great reducing potential displayed by low-valent samarium, since reduction-resilient molecules such as dinitrogen, ethylene or even different solvent molecules have been targeted by the extreme reactivity of Sm(II) species. However, the task of gaining control over such an extreme reactivity remains rather challenging even today. This problem continues to attract significant attention by the research community.

2. Complexes of low valent thulium.

If samarium strikes the right balance between high reactivity of the divalent state and sufficient stability of the complexes to allow preparation, characterization and reactivity studies, the same can not be said for thulium. The divalent state of this element is characterized by a substantially higher reduction potential and which make the results in chemistry of low-valent thulium somehow scattered and fragmentary. Low-valent Tm compound are represented by only a few complexes, mostly with cyclopentadienyl ligands or their derivatives. Reduction of Tm(III) precursors usually leads to uncontrolled decomposition and intractable materials. Therefore the preparation of a simple salt as $TmI_2(DME)_2$ reported in 1997 by the group of Bochkarev[62] and subsequently optimized by Evans[63] has marked a milestone in this area of chemistry. Given the near to extreme reactivity of Tm(II), even the utilization of $TmI_2(DME)_2$ for preparing derivative via mild condition metathesis very often results in massive decomposition, attack to solvent molecules, ligand fragmentation, etc. The situation is significantly complicated by the fact that both Tm(II) and Tm(III) metal centers are not NMR friendly normally producing substantial line broadening.

The first genuine organothulium (II) compound was obtained by Evans[64] with cyclopentadienyl based ligands (Scheme 1.12, Complexes I and II) by using the traditional approach of salt metathesis between potassium salt of sterically demanding cyclopentadienyl and $TmI_2(DME)_2$. Despite the reaction was carried out under nitrogen atmosphere, no dinitrogen fixation/reduction was observed.



Scheme 1.12.

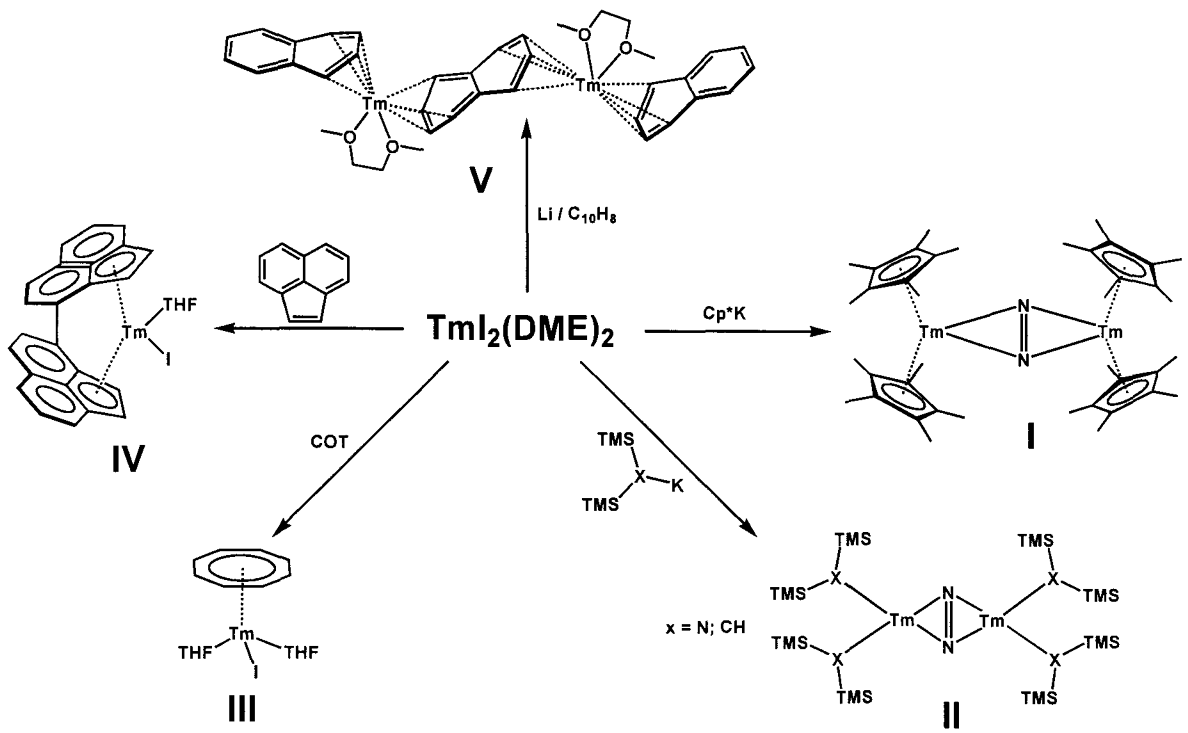
It was discovered by the groups of Nief[65] that employment of phosphorus based five member heterocyclic ligands also allows the preparation of divalent compounds. Reaction of these ligands bearing a variety of substituents with $TmI_2(DME)_2$ afforded a series of low-valent sandwich complexes (Scheme 1.12, Complex III). The first variation to the cyclopentadienyl motif was introduced by Takats et al.[66] with *tris*-pirazolyl-borate allowing the characterization of the first Tm(II) scorpionato complex. It was also discovered that the remaining iodine atom may be replaced by bulky amido- or alkyl ligands without provoking the oxidation of the Tm(II) metal center or causing the collapse of the structure (Scheme 1.12, Complex IV).

In spite of these encouraging results, the stability of these low-valent Tm compounds must be regarded as an exception. In several other instances the reduced ligands or units generated by solvent fragmentation remained connected to the metal center. Unfortunately, more often the oxidized Tm metal is simply coordinated to unchanged ligand systems and does not provided any hints about possible oxidation pathways or reaction byproducts of such re-oxidation. One of the simplest oxidative transformations was reported by Bochkarev in 2003.[67] Reaction of $TmI_2(DME)_2$ with substituted pentanone resulted in the reduction of ketone to cyclopentadienyl alcohol through cooperative attack of two metal centers on the same substrate. In this case the reduced molecule was retained by two metal centers with the oxygen donor atom forming σ-bond with one Tm and the ring interacting with the second metal center through a cyclopentadienyl-type of η^5-bonding interaction (Scheme 1.12, Complex V). Similarly to the chemistry of samarium, a cooperative attack of two thulium metal centers seems to be a common trend among reduced lanthanides.

The recurrence of dinitrogen fixation/activation certainly is a good probe for diagnosing the presence of outstanding reducing power. In his pioneering work with the thulocene complexes, Evans has observed that the reaction of less crowded cyclopentadienyl ligands with $TmI_2(DME)_2$ afforded dinitrogen complexes (Scheme 1.13, Complex I).[68]

The dinitrogen fragment in the isolated complex was clearly reduced by two electrons and remained coordinated between two bis-cyclopentadienyl Tm moieties. This was a major departure from the chemistry of samarocenes whose dinitrogen complexes demonstrated only labile coordination with no significant elongation of the N-N bond of the coordinated dinitrogen unit. The much stronger reducing power was also evident from the reaction of $TmI_2(DME)_2$ with bulky amido-ligand, which reaction again resulted in the isolation of a dinitrogen complex (Scheme 1.13, Complex II).[69] The geometry of Tm-N=N-Tm fragment in both isolated compounds appeared as very similar, with flat arrangement of the atoms and very similar bond distances for both N=N fragment. Considering all the information above it was possible to conclude, that both compounds represented a doubtless example of cooperative attack with two electron reduction of dinitrogen triple bond. It is worth reminding that in the case of samarium, the complexes of the same amide ligand are monomeric with no indication of ability to interact with dinitrogen.[70]

Another illustration of the great reducing power of Tm is offered by the reaction of $TmI_2(DME)_2$ with lithium naphthalenide, discovered by Bochkarev.[71] Lithium naphthalenide is commonly used as strong one-electron reducing agent. In the case of the reaction with $TmI_2(DME)_2$, it was the naphthalenide anion that undewent reduction rather than the Tm metal center. The resulting triple-decker compound has two Tm metal centers bridged by a significantly distorted naphthalenide moiety (Scheme 1.13, Complex V).



Scheme 1.13.

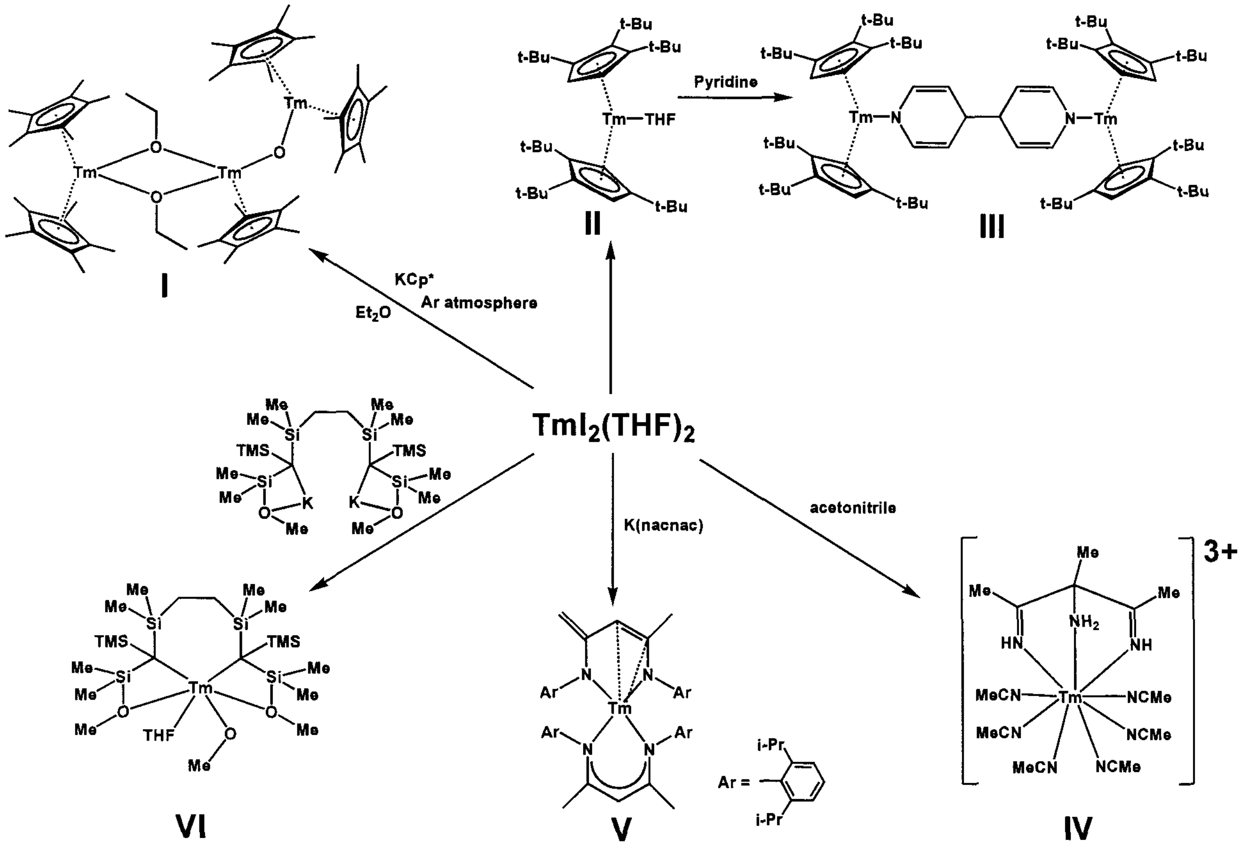
Two other naphthalenide fragments were coordinated to each thulium metal center. These fragments also displayed significant deviation of the coordinated rings from the planarity. Taking all these structural features into consideration, this structure was rationalized as with two oxidized(!) Tm(III) metal centers bonded to three dianionic naphthalenide fragments.

Two additional examples of "wild" reactivity were observed also by Bochkarev while studying the interaction of low valent metal centers with large aromatic π-systems.[72] Similar to the reaction of metallic Sm mentioned above,[16] the reaction of Tm bis-iodide with acenaphthylene resulted in the formation of a C-C bond between two aromatic ligands (Scheme 1.13, Complex IV). The resulting compound exhibited the *ansa*-metallocene type of coordination with Tm(III) metal center carrying one residual iodine atom and one molecule of coordinated THF solvent. The reaction of the same starting material with COT produced the COT complex of Tm(III).[72] In this compound the metal center is coordinated to the aromatic, double-anionic tetra-ene ring along with two THF and one residual iodine atom (Scheme 1.13, Complex III). All these examples of reactivity clearly emphasized the strong reducing nature of divalent thulium.

Surprisingly for a low valent metal center of such great reactivity, a thulium metal surrounded by the bulky ligands could easily tolerate THF as a solvent without inducing the reductive solvent cleavage and formation of the bridging μ-oxo compounds, which were so frequently encountered in the chemistry of samarium. Nonetheless, when less bulky cyclopentadienyl ligands were used as ligand system and dinitrogen gas was excluded from the reaction medium, diethyl ether reductive cleavage to a trimeric ethoxide (Scheme 1.14, Complex I) was observed by Evans.[68] One of these two metals retained only one cyclopentadienyl ligand. The same metal center was connected to the third $Tm(Cp^*)_2$ unit through a *μ*-oxo bridge. Pyridine *tail-to-tail* coupling was observed by Nief and coworkers while carrying on a simple treatment of a Tm(II) derivative of very bulky cyclopentadienyl (Scheme 1.14, Complex II).[73] Examples have been documented in the literature where a two-electron attack to pyridine results in ring opening.[3m] In this particular case, the steric bulk around the metal center prevents the cooperative attack of two Tm(II). As a result of the one electron attack, the pyridine ring localizes spin density in the ring *para-* position affording then a tail-to-tail dimerization (Scheme 1.14, Complex III).

Another example of Tm re-oxidation at the expense of the ligand system was reported by Izod.[74] Interaction of the di-potassium salt of dicarbanionic, sterically hindered, O-functionalized 1,2-bis(dimethylsilyl)ethane based ligand with $TmI_2(DME)_2$ produced a trivalent complex containing one methoxide moiety in the coordination sphere of the metal (Scheme 1.14, Complex VI).

It was suggested in the presented work[74] that the origin of such moiety could lay in the reductive cleavage of another ligand unit. Increase in the oxidation state of Tm metal center to +3 was regarded as a strong argument in favor of the ligand decomposition pathway. Nevertheless, it could not be excluded that the methoxy-fragment might in fact be generated by solvent decomposition, similarly to the examples found in the chemistry of low valent Sm.



Scheme 1.14.

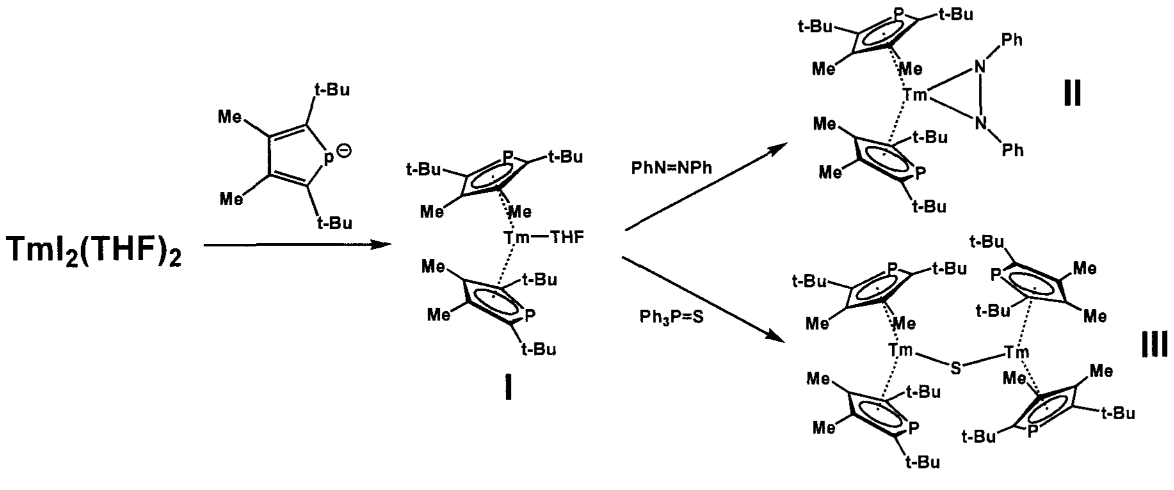
A clear case for ligand reduction was discovered by Lappert[75] during attempted preparation of a sterically demanding diketiminato salt. The crystal structure of the complex revealed that one of the two ligands connected to the metal center underwent reduction resulting in the loss of two hydrogen atoms and formation of two double bonds (Scheme 1.14, Complex V). The ligand in this process was transformed in a dianionic bis-amine. The two protons, removed from the ligand molecule, were transferred to another ligand molecule.

In contrast to the destructive reductive cleavage, a "constructive" reduction of the solvent was reported by Bochkarev and colleagues in 2003.[76] Simple solubilization of $TmI_2(DME)_2$ in acetonitrile resulted in the assembly of a new ligand composed by three coupled molecules of the solvent (Scheme

1.14, Complex IV). In this process not only two new carbon-carbon bonds were formed but also four protons in total were extracted from the reaction media. The authors speculated that such complex transformation was achieved through disproportionation of the "TmI_2" to "TmI_3" and an extremely reactive "TmI" transient moiety. Subsequent reaction of this fragment with the acetonitrile solvent produced the new bis-imino-amine ligand. The origin of the protons was not discussed in the report but it would be reasonable to assume that the source was the molecules of DME solvent.

In order to continue the survey of the reactivity of divalent thulium it is necessary to return to the *bis*-phosphinido system discovered by Nief discussed earlier. The preparation of the Tm(II) complex (Scheme 1.15, Complex I) was followed by reaction with azobenzene and triphenylphosphane sulfide in a two separate oxidation attempts.[77] Both reactions proceeded with the oxidation of the metal center to the trivalent state. In the case of diazobenzene the oxidation of the metal center was accompanied by formation of a reduced hydrazido moiety. The resulting hydrazido anion-radical was retained within the structure of the complex (Scheme 1.15, Complex II).

The second oxidation produced a dimeric Tm species with two monomeric Tm(phospholide)$_2$ fragment connected to the same sulfur atom (Scheme 1.15, Complex III).



Scheme 1.15.

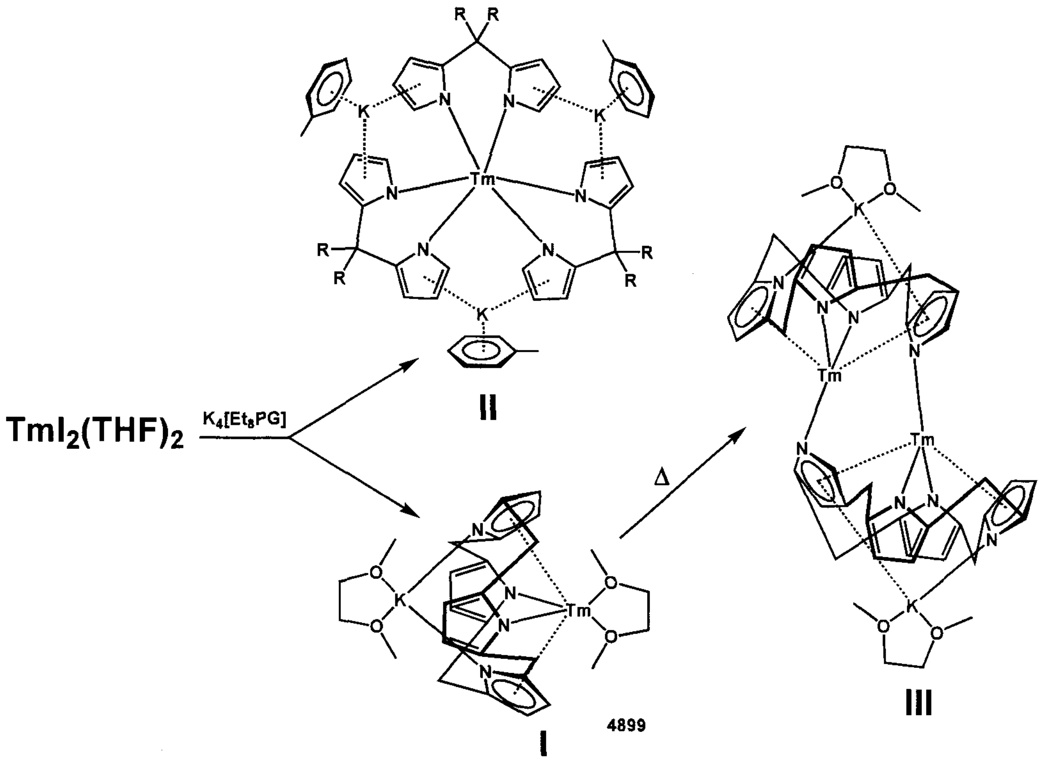
The oxidation state of the metal is clearly trivalent in the second compound as well. The authors noticed that the initial complex of Tm(II) did not react with dinitrogen, even at elevated temperatures.

It did not perform the reduction of anthracene, which was observed with Sm(II) cyclopentadienyl derivatives. Finally, the complex did not perform reductive solvent cleavage. Accordingly, it was concluded in the presented work[77] that the presence of the phosphorus heteroatom coupled with π-system coordination afforded an over-stabilization of the low valent metal center.

The reactivity of low valent Tm metal center was also explored in combination with the tetra-pyrrolide ligand system. The same ligand system that proved itself very rewarding in the chemistry of low valent Sm, was used to attempt the formation of the low valent Tm compounds. The reaction of divalent Tm starting material with the potassium salt of the tetrapyrrolide anion resulted in the formation of two different complexes from the same reaction mixture. The first compound was a simple complex of Tm(III) with tetra-pyrrole (Scheme 1.16, Complex I). The structural parameters of this compound were very similar to the other compounds of *f*-block elements isolated by the same group of authors.[79]

One potassium counter-cation was connected to the ligand system in order to warrant the electro-neutrality of the final Tm(III) species. Upon thermolysis a α-β proton shift in the core of the tetrapyrrolato ligand was observed. The resulting iso-tetrapyrrolyde had one ring connection to the core of the ligand shifted from position 2 to position 3 of the heterocycle. As a result the nitrogen donor atom of the "isomerized" ring becomes more exposed to the "front" (Tm metal side) of the ligand core. That allowed the dimerization of the two identical units through σ-coordination of the exposed nitrogen atom of "isomerized" ring on one unit to the Tm atom of the second unit (Scheme 1.16, Complex III).

The second compound, isolated from the original reaction mixture, revealed more interesting features. It appeared that the initial tetrapyrrole system was cleaved during the complex transformation affording two dypyrrolide units from one tetrapyrrole (Scheme 1.16, Complex II). Another di-pyrrole unit was gained in the process bringing the overall number of bidentate ligands to three. Three potassium atoms were retained around the complex structure by the series of π-interaction with the pyrrolide ring to warrant electro-neutrality of the final compound. Unfortunately, all attempts to clarify the nature of the other Tm species necessarily present in the reaction mixture as well as to understand the fate of the missing linking backbone fragments were unsuccessful.



Scheme 1.16.

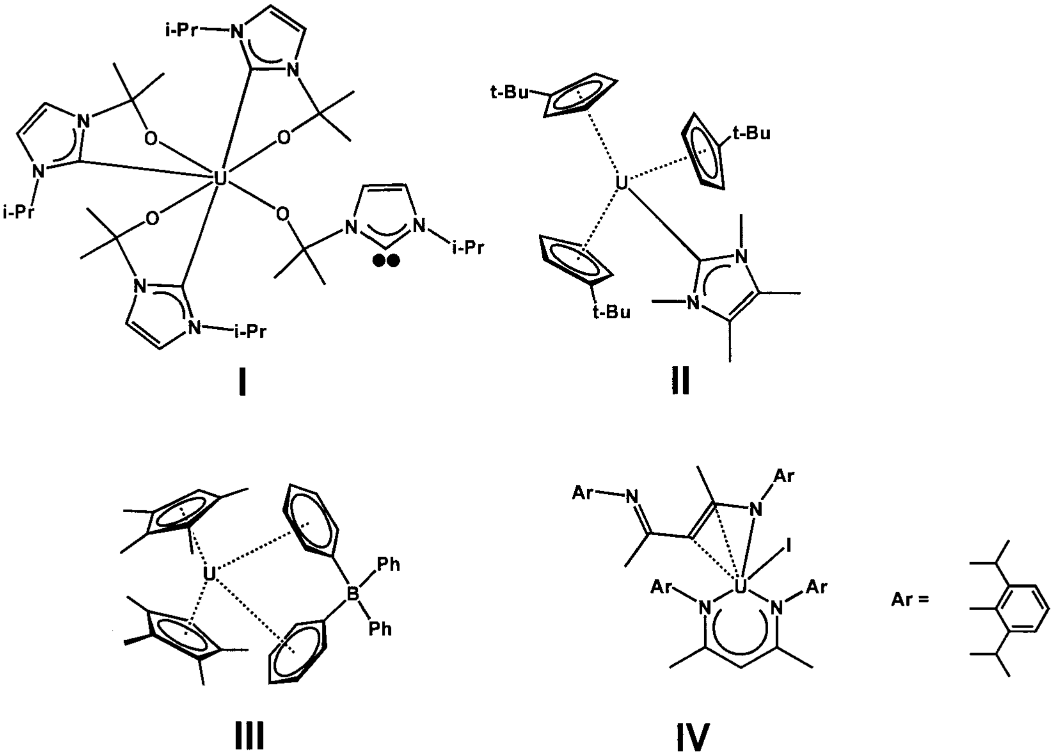
All these presented results lead to believe that, despite an extremely high and often unpredictable reactivity, it is possible to control and probably even direct the reducing power of low valent Tm. All the discoveries reported in the literature seem to indicate that the formation of low valent Tm species is not limited to cyclopentadienyl ligands. On the other hand, it is understandable that the π-coordination to the delocalized π-system together with the significant steric protection are two key prerequisites for the isolation of coordination compounds of low valent Tm.

3. Complexes of low valent uranium.

Among *f*-block elements uranium certainly occupies a very special place since it is the only element capable of existing in a wide range of oxidation states [from highly oxidizing and Lewis-acidic U(VI) to strongly reducing U(II)]. With the oxidation state +4 normally regarded as the most stable one, complexes of lower oxidation states will be reviewed in this part since they are relevant to this thesis work. One of the characteristics of uranium is its overwhelming oxophilicity which is often responsible for diverting the reactivity from the substrate to ethers, often used as solvent. Another feature is that the lower valent states are considerably underdeveloped possibly due to an extreme reactivity. An additional complication in working with low valent uranium complexes arises from the fact these species are rather NMR un-friendly, producing reasonably sharp signals only for U(IV). Due to this fact, the chemistry of the lower oxidation states heavily relies on X-ray structural characterization.

While the chemistry of divalent uranium is basically non-existing due to an intrinsic instability (see discussion below), the trivalent state displays a behavior which somewhat parallels that of divalent samarium in terms of rich and diversified reactivity which has been discovered. As per Sm and Tm, the discovery of a soluble starting material $UI_3(THF)_4$, made in 1994 by Sattelberger and Clark[79] provides the key to enter this chemistry by allowing mild-condition salt metathesis for the preparation of trivalent complex. As always, reduction of higher valent species remains a viable option. In any event, the intrinsic instability of the trivalent states often causes the same re-oxidation at the expense of the ligand and/or of the solvent, as frequently observed in the case of Tm. Disproportionation to metallic element is another very common pathway responsible for re-oxidation, and trivalent uranium compounds are not immune from that.

In fact, despite the availability of $UI_3(THF)_4$ starting material, even the utilization of this compound does not guarantee the isolation of tri-valent uranium complex. For example the simple coordination attempted by Arnold[80] to isolate the first U(III)-carbene containing compound afforded instead the corresponding U(IV) derivative. (Scheme 1.17, Complex I). This structural outcome does not provide any information about the nature of the lower-valent species or of the partner of the disproportionation.



Scheme 1.17.

Nevertheless the transformation gave a clear sign of a disproportionation oxidative pathway. A successful isolation of carbene coordinated U(III) species was reported by the group of Ephritikhine in 2005 in the same year.[81] This time, the coordination of heterocyclic carbene was achieved through the replacement of coordinated solvent with preformed cyclopentadienyl complex of U(III). The reaction afforded a rare example of low valent actinide carbene species (Scheme 1.17, Complex II). However, the work of this research group was mainly focused on the evaluation of the involvement of *f*-orbitals in donor-acceptor interaction, therefore no reactivity or catalytic data for this compound was provided.

With many other examples of spontaneous re-oxidation it would be reasonable to suggests that once isolated, trivalent compounds would display extremely high reactivity. The primary goal in this case would lie in controlling and directing the reactivity by "fine-tuning" the stability of the metal and the steric protection provided by the ligand systems. Similarly to the previously discussed lanthanide compounds, the stabilizing effect of a coordinated π-system could provide a very effective tool to achieve the target.

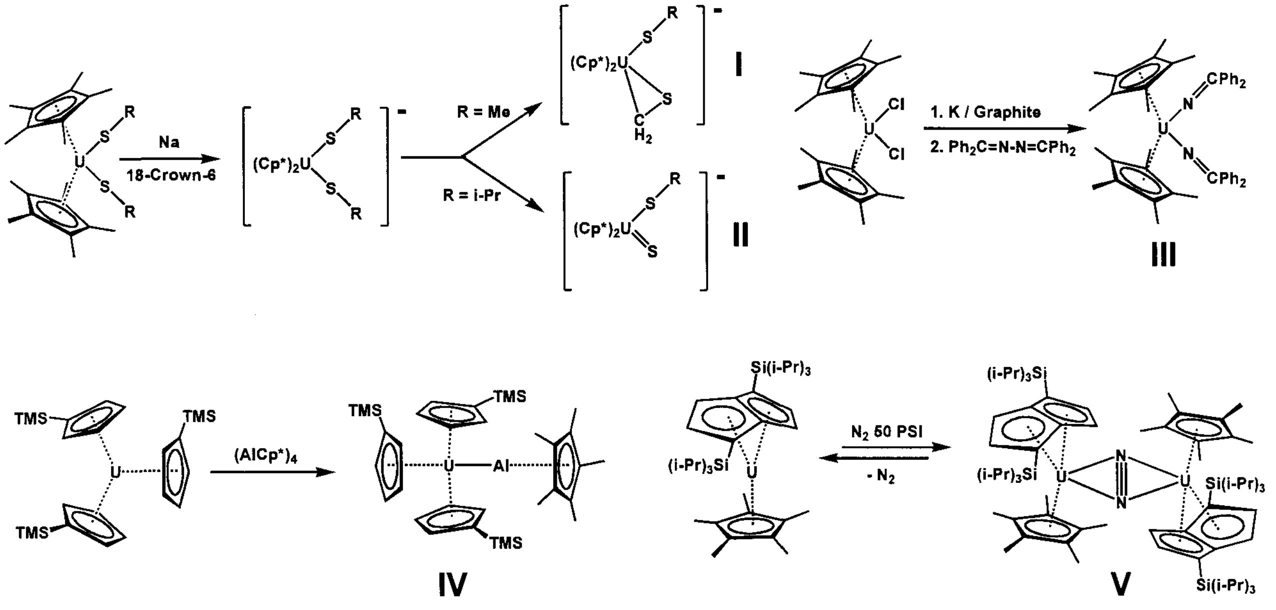
One of the first successful attempts to stabilize U(III) metal center without completely quenching the reactivity of the complex came from the group of Evans in 2005.[82] The enhanced tendency of trivalent uranium for π-ligation is apparent in this case from the bonding to the BPh_4 counter-anion (Scheme 1.17, Complex III). An ever stronger indication of the importance of coordinating π-system was provided by Kiplinger in 2004.[83] A trivalent complex was obtained from the reaction of uranium tris-iodide with the potassium salt of the bulky β-diketiminato ligand affording a bonding mode unprecedented for the β-diketiminato system (Scheme 1.17, Complex IV). However, taking into consideration the extremely high tendency of low valent U to π-coordination, it was possible to rationalize the formation of such unusual species.

3.1 U cyclopentadienyl based systems.

As it can be expected, the cyclopentadienyl systems play a major role in the coordination chemistry of trivalent uranium. The first uranium cyclopentadienyl compound was reported as early as 1964 by Ter Haar and Dubeck.[84] Since then, many other complexes were synthesized and a wide variety of different catalytic and stoichiometric processes involving these complexes was discovered. In reviewing this literature, we will focus on the most significant findings in the chemistry of low valent uranium cyclopentadienyl systems. The material selected for this introduction does not present a comprehensive picture of the all known transformations but rather gives a flavor of the outstanding reactivity that can be expected for the trivalent state.

Scheme 1.18 above summarizes such findings. Once the trivalent species is generated, re-oxidation may occur through internal or external activation processes by reducing coordinated ligands and/or non–

coordinated substrates. Ephritikhine et al. reported in 2001[85] that a tetravalent *bis*-cyclopentadienyl *bis*-sulfoxy-phenyl may be reduced with sodium amalgam, affording the corresponding U(III) derivative. When less sterically demanding sulfoxy-alkyl derivatives have been used, two intramolecular activation processes were discovered generating dianionic sulfo-alkyl groups (Scheme 1.18, Complex I) or sulfide- (Scheme 1.18, Complex II) species. In both complexes the metal center has been re-oxidized to the tetravalent state during the course of the transformation.



Scheme 1.18.

The approach of using low valent species as transient intermediates has been successfully designed by Kiplinger and Burns in 2002[86b] and later developed in similar work by Andersen.[86a] Both groups used the differently substituted bis-cyclopentadienyl-di-chloride complexes of U(IV) as starting materials. Both groups reduced tetravalent complexes *in situ* and treated the resulting reaction mixtures with oxidizing substrates (Scheme 1.18, Complex III). Expectedly, in both cases the cyclopentadienyl rings acted as spectator ligands showing no involvement in the reactivity.

A very unusual result was obtained by Arnolds,[87] providing deeper insight in the electronic structure of low valent uranium and the nature of donor-acceptor interaction of this metal center. Treatment of the

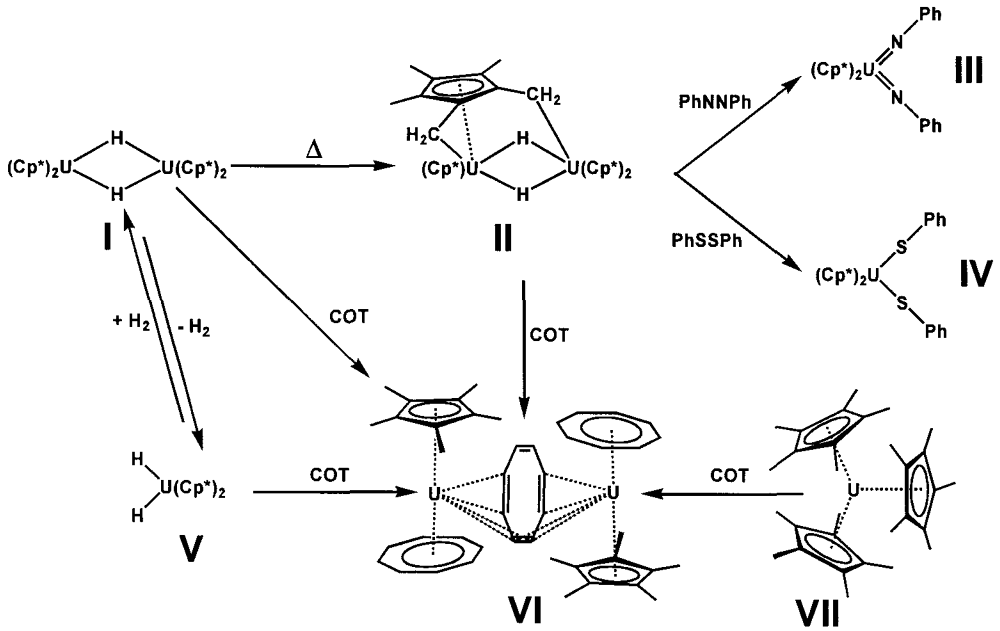
U(III) tris-cyclopentadienyl compound with aluminate-mono-cyclopentadienyl led to the formation of the first complex with actinide-aluminum unsupported metal-metal bond (Scheme 1.18, Complex IV). DFT calculations clearly showed the partially covalent bonding interaction with σ-character between two metals as resulting from charge transfer from Al to the U metal center.

The most spectacular example conclusively proving the outstanding reactivity that one could expected from π-ligated U(III) systems was obtained with the reaction of a trivalent salt with pentalene, a ligand closely related to the Cp anions.[88] The reaction afforded a rare case of dinitrogen complex although it required pressurization to allow formation of the complex (Scheme 1.18, Complex V) through a reaction which was spontaneously reverted under ambient conditions. The minimal elongation of the N-N distance indicated minor extent of activation on the line of what was displayed by samarocenes.

One of the largest contributions in the exploration of the low valent uranium chemistry was made by Evans. His research on the reactivity of sterically demanding pentamethylcyclopentadienyl uranium systems (Scheme 1.19, Complex VII) produced a large array of remarkable transformations (*vide infra*). The reaction of a sterically saturated uranium tris-cyclopentadienyl with neutral cyclooctatetraene molecule[89] resulted in oxidation of the uranium metal center and formation of the first inverted sandwich uranium complex. This arrangement was found to be so thermodynamically favorable that many other transformations with the participation of COT ligand led to the formation of the same complex.

While exploring the chemistry of the cyclopentadienyl hydrides of uranium it was discovered that both bis-cyclopentadienyl U(III) hydride and U(IV) bis-hydride were transformed to the same inverted COT compound by reaction with pure COT. The reactions proceed with liberation of H_2 gas and oxidation of the U metal center at the expense of COT.

The reversible inter-conversion between U(IV) and U(III) hydrides (Scheme 1.19, Complexes I and V) with evolution/uptake of hydrogen was confirmed in a separate experiment.[90] Thermally initiated metathetic attack of the hydride to the Cp* methyl groups has also been observed[91] affording the formation of unprecedented uranium alkyl-cyclopentadienyl species (Scheme 1.19, Complex II).

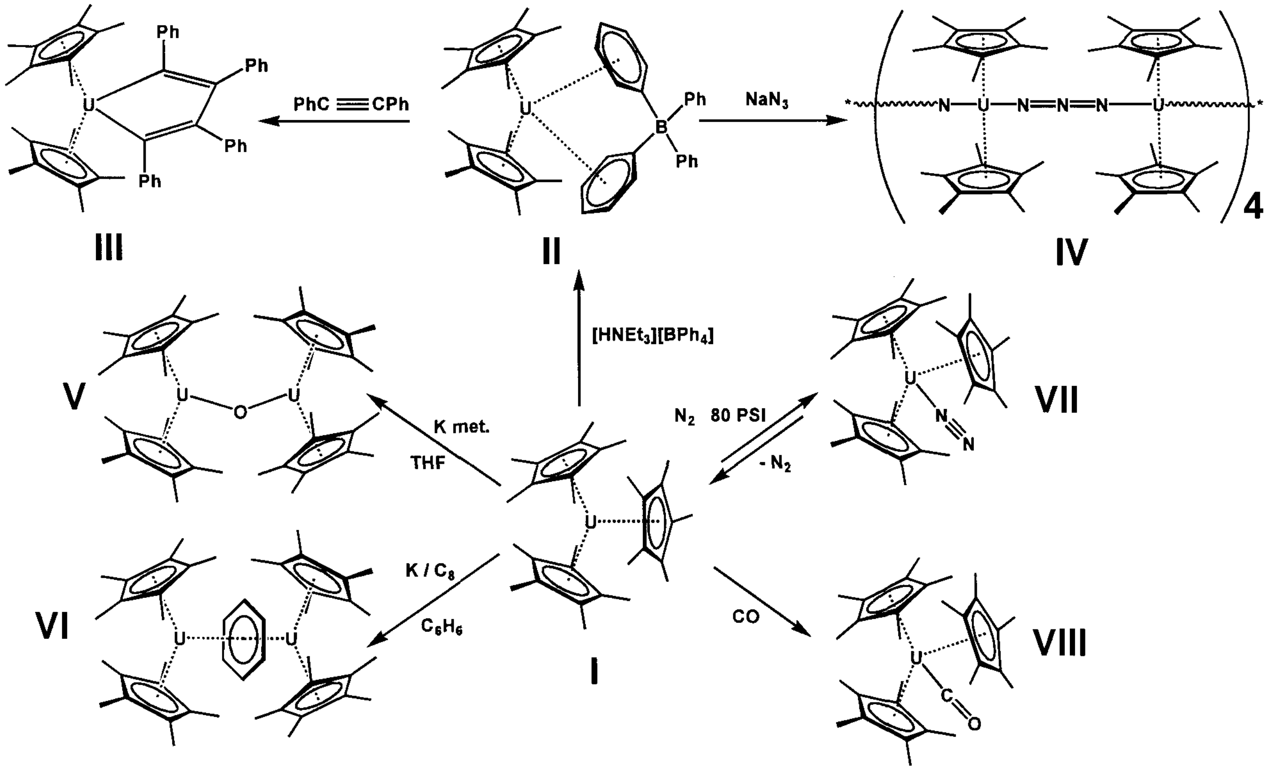


Scheme 1.19.

Treatment with protic ligands reformed the pentamethyl-cyclopentadienyl ligands and liberates hydrogen gas from the remaining hydrides. Deprotonated ligands were retained in the coordination sphere of the yielded U(IV) compound. Despite the relatively stable oxidation state, this uranium hydride performed reduction of diazobezene[92] affording complete cleavage of the substrate in a four-electron process (Scheme 1.19, Complex III). From the formal point of view, the oxidation state of the metal center increased only from +4 to +6. On the other hand, the hydrides disappeared while the Cp* methyl groups have been restored. On the same line, the reaction with diphenyldisulfide[93] proceeded with cleavage of the S-S bond and formation of the U(IV) bis-phenyl-sulfido compound (Scheme 1.19, Complex IV). Both red-ox processes could be rationalized with the transient formation of a formally divalent "U(Cp*)$_2$" capable of multi-electron reduction. However, formation of formal U(II) compounds without the additional support of large π-systems is regarded as unrealistic according to literature data. Therefore the authors suggested that the reduction-reoxidation transformations proceeded with a complex multi-step process involving several U(III) intermediates. It is this particular behavior which led to the use of the term of “divalent synthetic equivalent” or divalent synthon for species which are not divalent, due to an intrinsic instability of this oxidation state. However, such species could yet afford transformations expected for a genuine divalent compound. In the case presented above the electrons eventually used for the reductions are stored in the alkyl and hydride groups coordinated to the same metal center.

3.1.1 Red-Ox reactivity and molecular activation supported by U(Cp*)$_3$.

A complex which deserves a special attention is the sterically saturated Cp*$_3$U analogue of the samarium derivative discussed earlier. The main difference between the two species consists of a significantly larger size of the uranium ion and which results in significantly less strain in the coordination sphere.



Scheme 1.20.

Furthermore, a trivalent samarium complex is redox-inert since it is unable to perform reductions which would imply oxidation to an impossible tetravalent state. Instead, Cp^*_3U initiates the reductive transformations highlighted in the Scheme 1.20. While the coordination of CO (Scheme 1.20, complex VIII)[94] and N_2 (Scheme 1.20, Complex VII)[95] speaks for a particularly enhanced reactivity of this trivalent derivative, it should be noticed that the formation of the dinitrogen complex (Scheme 1.20, Complex VII) may be achieved exclusively under pressure.[95] This complex was the first example of a η^1-end-on coordination to an *f*-block element and the short N-N distance suggest little or no activation. Moreover, storing the complex at atmospheric pressure resulted in slow decomposition of reforming the initial $U(Cp^*)_3$.

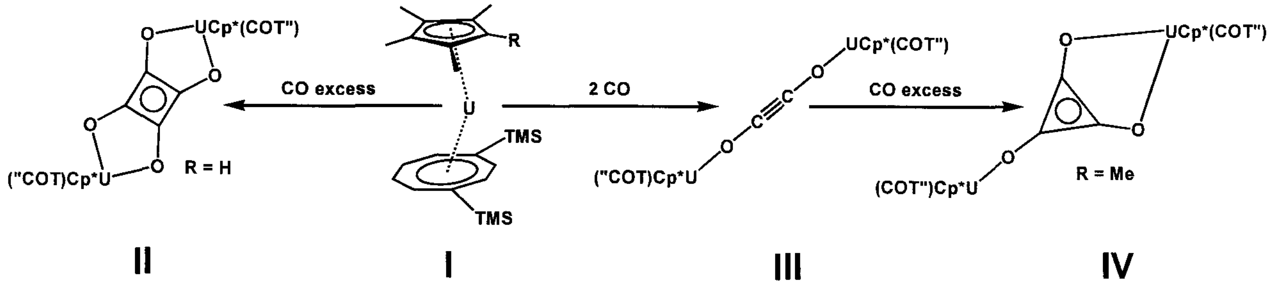
In the attempt to push the oxidation state of the metal center even below U(III), several reduction attempts were carried out by the research group of Evans. Reduction with metallic potassium[96] afforded THF deoxygenation accompanied by the formation of the corresponding μ-oxo derivative (Scheme 1.20, Complex V). Instead reduction with KC_8 in benzene yielded an interesting inverted sandwich compound (Scheme 1.20, Complex VI) with two $U(Cp^*)_2$ units symmetrically π-bonded on the two opposite sides of one benzene molecule.[97] According to the connectivity as yielded by the X-ray structure, one would conclude that the uranium centers were present in their divalent state. However, DFT calculation revealed that the metals were in fact tetravalent each containing only two unpaired electrons mainly 5*f* in character anti-ferromagnetically coupled to the two electrons residing on the second metal. Four additional electrons were located in the molecular orbitals localized mainly on the coordinated phenyl ring, with only minor contributions from both metal centers. This was the first example of a divalent uranium synthon. In this compound a divalent appearance of the metal center is, in fact, deceiving, since in reality the species is composed by higher valent metals and with the coordinated aromatic ring playing the role of electron storage.

Treatment of an inverted sandwich complex with tetraphenylborate reagent led to the reoxidation of the metal to +3 oxidation state and formation of zwitter-ionic species.[97] The same complex (Scheme

1.20, complex II) was also found to be the main product of the reaction between $U(Cp^*)_3$ and tetraphenyl-borate reagent. In the latter case the reaction did not proceed through red-ox mechanism but rather presented a simple ligand exchange transformation.[98] Upon further investigation of the reactivity, zwitterionic U(III) borate also revealed several unique transformations. It was discovered that treatment of this complex with two equivalent of acetylene resulted in the oxidation of the metal center to U(IV) and reductive coupling of acetylene (Scheme 1.20, Complex III).[99] Such coupling appeared somewhat similar to the acetylene coupling discovered previously in the chemistry of transition metals. The other byproducts of the reaction were discovered to be BPh_3 and Ph_2. The presence of the latest product is the result of a two-electron process during the one-electron U(III) to U(IV) transformation. It was assumed that reductive elimination of phenyl fragment was followed by radical coupling of two phenylene radicals. It was also implied the formation of a transient U(II) intermediate. The most unexpected transformation was discovered during the reaction of $U(Cp^*)_2$-phenylborate with sodium azide.[100] The reaction proceeded with formation of unique tetrameric cluster and liberation of nitrogen gas (Scheme 1.20, Complex IV). Each monomeric unit of the tetramer contained two $U(Cp^*)_2$ fragments interlinked with alternating $[N_3]$ and [N] units. The overall transformation was envisioned as the initial replacement of the phenyl-borated unit by azide ligands. The second stage required the simultaneous attack of the two U(III) metal centers to the same azide fragment, leading to the transfer of two electrons, oxidation of two metal centers to U(IV) and formation of one bridging nitride N^{3-} fragment, accompanied by liberation of nitrogen gas. Each of these stages has precedents in both transition metal and *f*-block elements literature. Nevertheless the unique combination of the reductive properties of U(III) coupled with steric requirements of the ligand system resulted in the isolation of the unprecedented cluster reported above. In summary, there is an analogy of behavior which can be observed in the high reactivity divalent samarium and trivalent uranium. The main difference between these two potent reductants resides on the fact that, different from samarium, uranium is capable of multi-electron reduction and is also susceptible of further reduction to form low-valent synthons.

3.1.2 Constructive molecular activation supported by U COT species.

This behavior is nicely illustrated by the carbonylation of a trivalent Cp*U(COT") derivative containing two bulky substituents. Depending on the steric of the cyclopentadienyl and on the amount of CO, the reactions afforded di-, tri- and tetramerization of carbon monoxide (Scheme 1.21, Complexes II - IV) generating rare or unprecedented units.



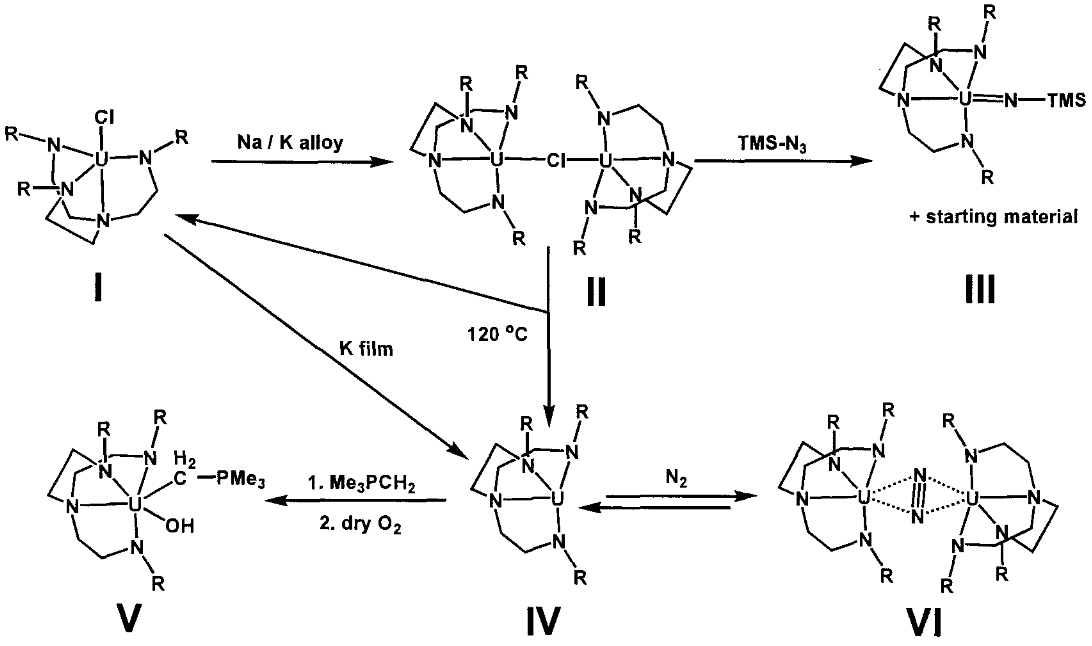
Scheme 1.21.

The formation of these three species implies that different numbers of electrons have been provided by the two uranium centers during the cooperative attack. The dimerization[101] has required two electrons and formation of two tetravalent uranium units (Scheme 1.21, Complex III). The trimerization[102] compound (Scheme 1.21, Complex IV) is a mixed valence U(IV)/U(V) species, while the tetramerization[103] product (Scheme 1.21, Complex II) contains two pentavalent uranium atoms. DFT calculations performed on these compounds unequivocally proved that the role of uranium metal center consisted not only of promoting the formation of the C-C bond but also of permitting the coordination of the additional CO molecules. It was suggested that coordination of this type was determined by the high Lewis acidity of the metal center. It was also established that the steric arrangement around the metal center were mainly responsible for preferred di- versus tri- and tetramerization transformation pathway.

3.2 U non-cyclopentadienyl based systems.

3.2.1 Complexes of low valent U supported by bulky σ-coordinating ligands.

Different from the chemistry of divalent samarium which is largely dominated by the employment of the cyclopentadienyl rings, the chemistry of trivalent uranium displays a considerable amount of interesting and promising reactivity with non-cyclopentadienyl systems.

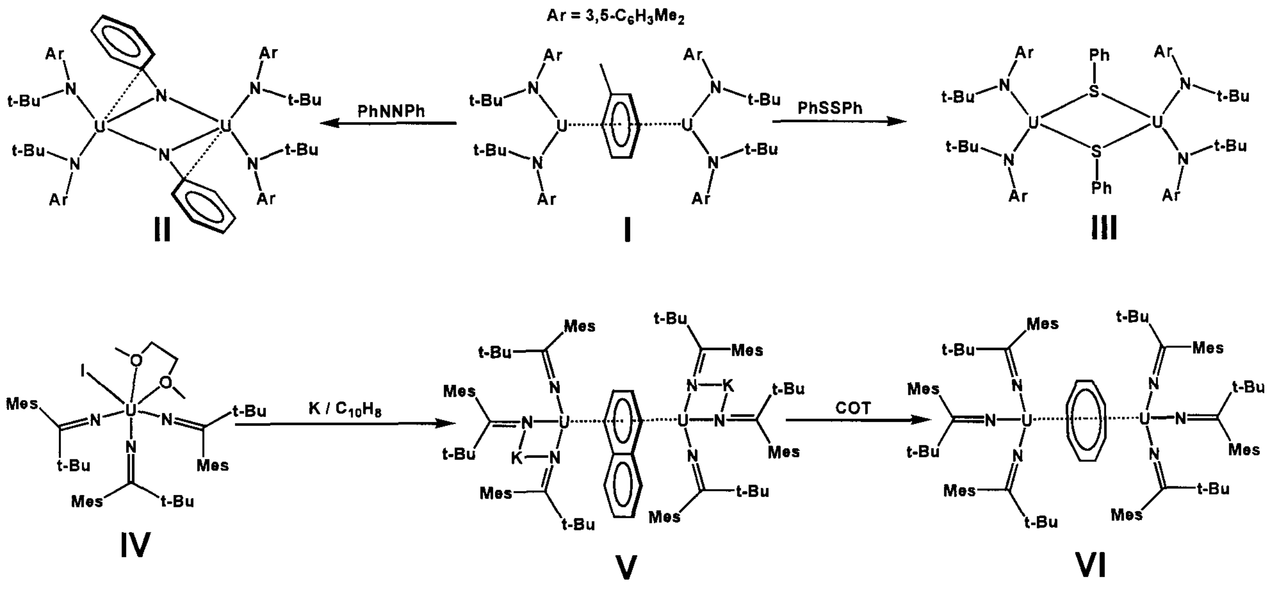


Scheme 1.22.

Of particular interest is the polydentate amide ligand which does not bear a π-system. The work of Scott reported in 1996[104, 105] described the reduction of a U(IV) tetradentated and trianionic amide (Scheme 1.22, Complex I) to a trivalent complex (Scheme 1.22, Complex IV) capable of reversibly coordinating dinitrogen.[105] The side-on coordination of N_2 was very similar to that observed in the samarocenes displaying a minimal extent of dinitrogen reduction. This complex was the first crystallographically characterized dinitrogen complex in the chemistry of actinides. Besides its relevance for dinitrogen chemistry, the merit of these findings is to emphasize that trivalent uranium has indeed an outstanding reducing power and does not necessarily require the presence of coordinated π-

systems. In turn this has encouraged a rather systematic exploration for using non-cyclopentadienyl ligands.

The major success in this direction has been achieved by Cummins in 2000. By using a very bulky monodentate amide ligand, the preparation of a trivalent precursor was attepted. However the reaction afforded instead a U(IV) compound with three amido-ligands and one remaining iodine atom coordinated to U metal center.[106] The reduction of U(IV) starting material with potassium graphite in toluene did not result in any reactivity with dinitrogen. However, the reaction afforded an inverted sandwich compound[107] with two uranium bis-amide groups symmetrically coordinated on the two different sides of the same toluene molecule (Scheme 1.23, Complex I). In common with the Evans inverted sandwich complex appeared in the literature five years later, the connectivity of this compound suggested the presence of divalent metal centers.



Scheme 1.23.

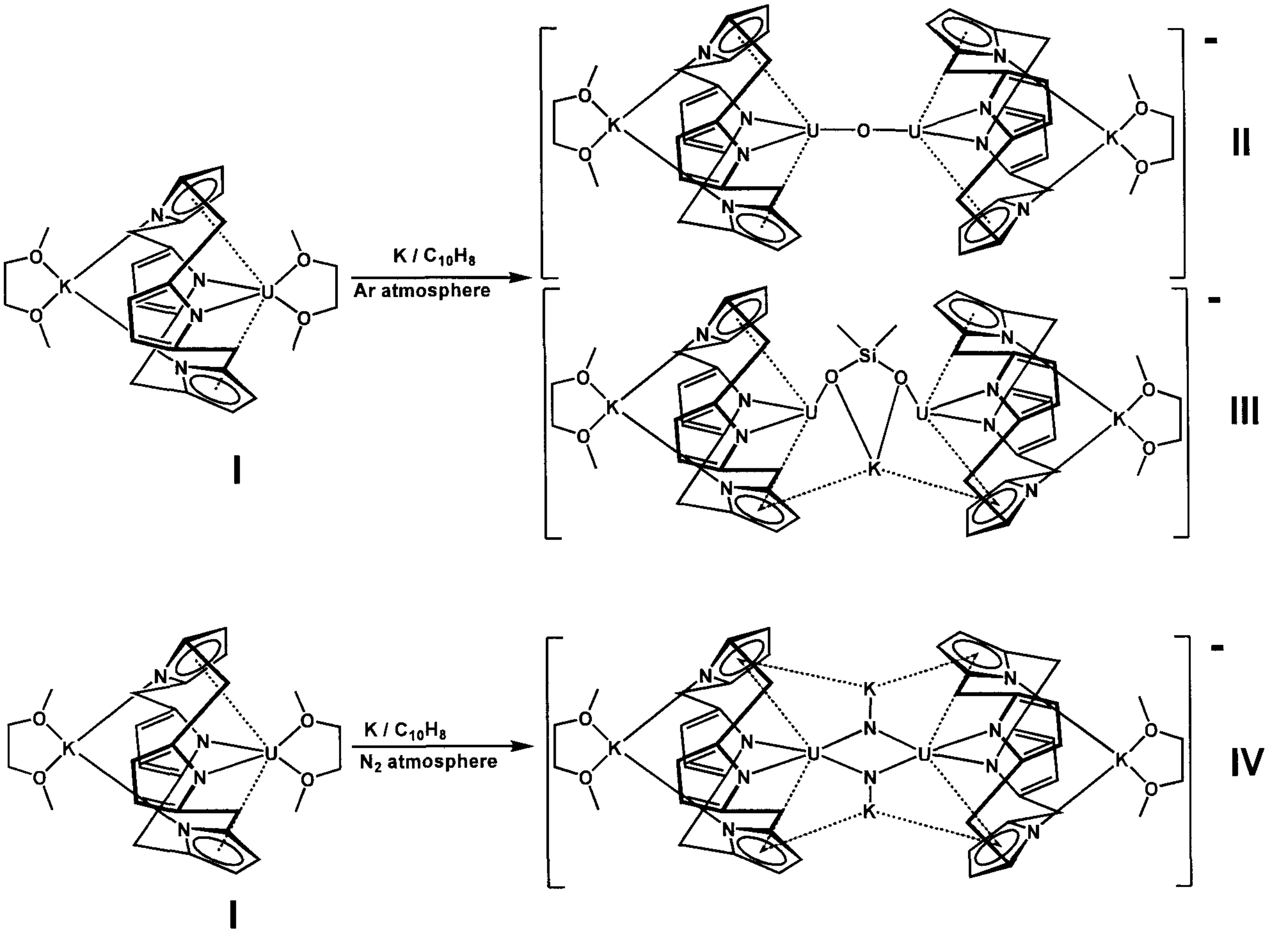
Again DFT calculation revealed the presence of significant spin density on the bridging benzyl ring as well as of three electrons located mainly on each uranium centers. Therefore, this complex was formed by trivalent metal centers and a significantly reduced aromatic ring. Nevertheless, this complex was able to provide the reactivity expected from divalent synthon. For example, reaction with diphenyldisulfide cleaved the S-S bond with formation of a dinuclear U(III) complex (Scheme 1.23, Complex III), resulting from the cooperative two-electron attack on a substrate. Instead reaction with diazobenzene cleaved the N=N double bond forming a U(IV) compound (Scheme 1.23, Complex II) resulting from the four-electron attack to the substrate.

The possibility of using aromatic rings as electron storage has been further generalized. By using less bulky ligand, the same author has discovered[108] that another divalent synthon may be prepared with different larger aromatic system of naphthalene (Scheme 1.23, Complex V). The lesser steric hindrance of the ligand allowed the retention of a third ligand which was counterbalanced by a potassium cation. Nevertheless, DFT calculation again attributed the much expected tetravalent state to the two metal centers with the bridging aromatic ring storing four electrons in its π–system. Interestingly, the bridging ring might be replaced with COT affording another inverted sandwich species where the formal oxidation state appears to be higher (Scheme 1.23, Complex VI).

3.2.2 Complexes of low valent U supported by calyx-[4]-tetrapyrrolide anions.

The poly-pyrrole based ligand systems have been proved extremely versatile in the chemistry of low valent samarium, displaying a considerable increase of reducing power with respect to the cyclopentadienyl based ligands. The same ligands have been also used in uranium chemistry. A much diversified range of transformations was discovered, spanning from the formation of dimers with the shortest U-U distance ever reported,[109] solvent fragmentation,[110] and ligand isomerization.[110] Perhaps the most remarkable reaction was observed during attempts to generate lower valent synthons.[111] The reaction of $UI_3(THF)_4$ with the tetra-potassium salt of the ligand gave the expected product with the ligand tetra-anion surrounding one trivalent uranium and one potassium counter-cation (Scheme 1.24, Complex I). The tetrapyrrolide system traditionally adopted dual σ-/π-bonding coordination mode. Further reduction with $K/C_{10}H_8$ gave the first example of dinitrogen cleavage in *f*-block chemistry

(Scheme 1.24, Complex IV). The product was the result of dinitrogen initial coordination, subsequent reduction and final cleavage. Since the final product appeared as formally a U(IV)/U(V) mixed valence species, together with the fact that the cleavage of dinitrogen required six electrons, it was apparent that during the reduction transient low-valent synthons have been generated and electron were continually funneled into the system from the K naphthalenide reducing agent.

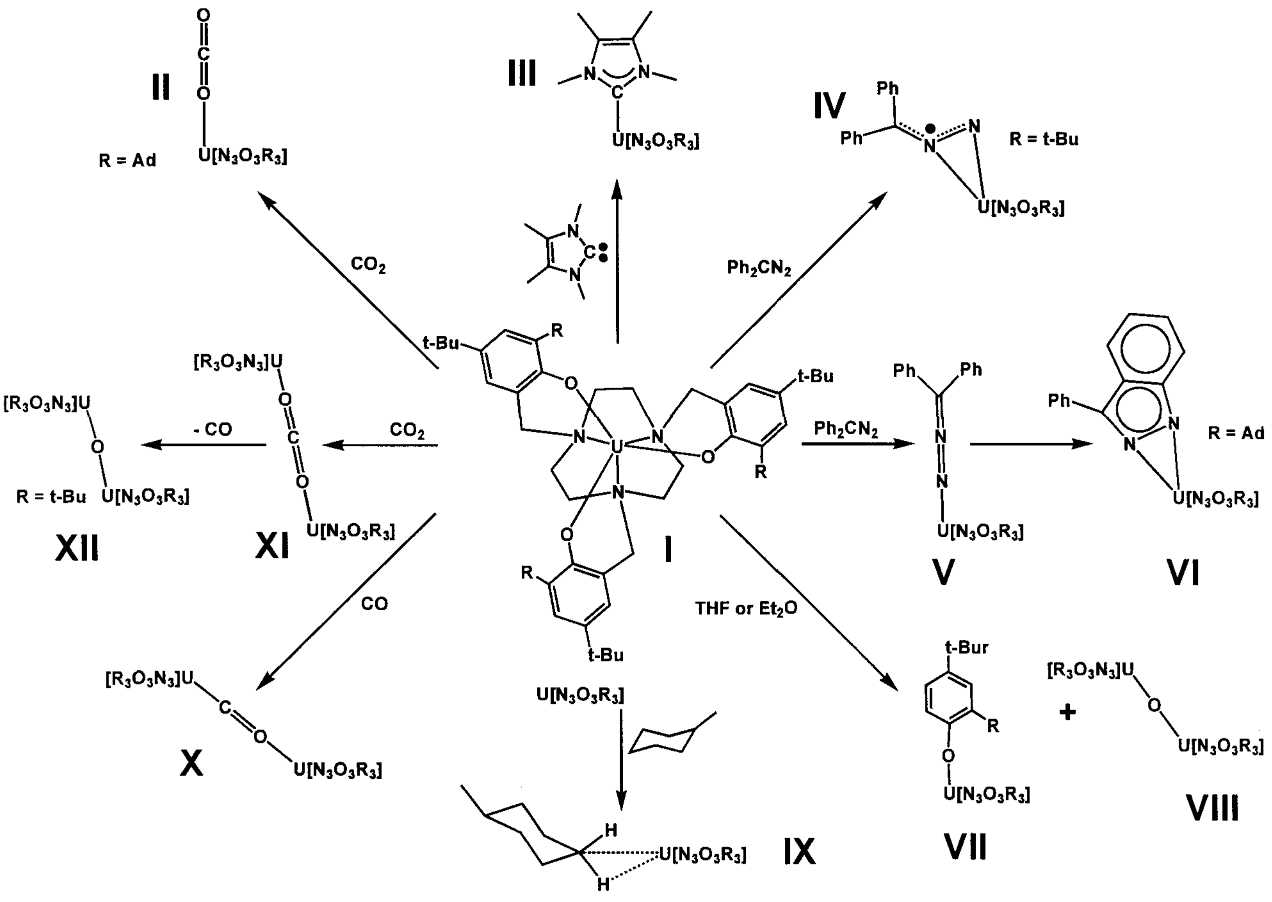


Scheme 1.24.

Reactions carried out under exclusion of nitrogen afforded solvent deoxygenation (Scheme 1.24, Complex II) and even a curious case of silicone grease depolymerization (Scheme 1.24, Complex III).

3.2.3 Complexes of low valent U supported by sterically demanding tri-azo-tris-aryloxide ligands.

A rather consistent and comprehensive picture of the chemistry of trivalent uranium has been developed by Mayer with the employment of a bulky, hexadentate, aryloxide-based ligand tri-azo-tris-phenoxide system.



Scheme 1.25.

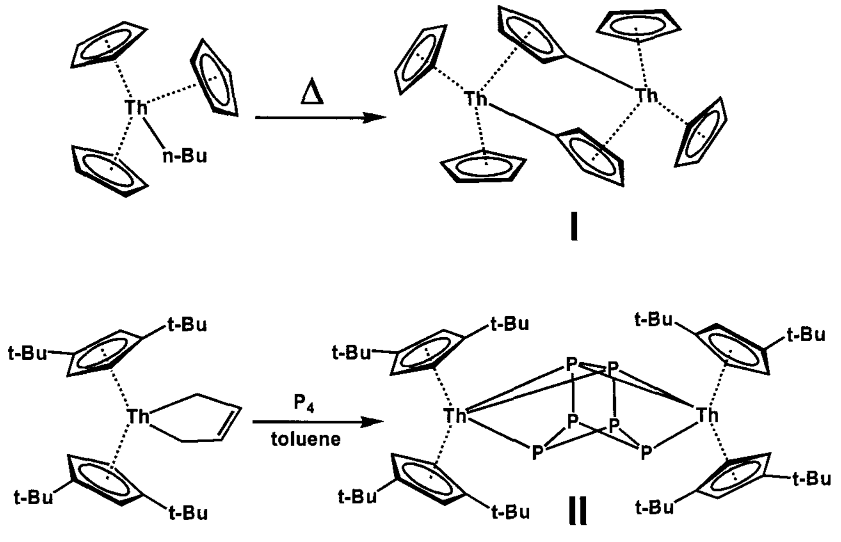
The presence of six σ-donor atoms in addition to the steric hindrance of the substituents allowed an almost complete encapsulation of the metal center leaving just one empty pocket available for the coordination of substrates. In turn, this provided a remarkable system to study the early stages of substrate coordination at the trivalent center prior to molecular activation process. Another distinguishing characteristic of this ligand system was that the large steric bulk prevents the cooperative attack of two metal centers on the same substrate, resulting in series of unprecedented transformations.

Scheme 1.25 above summarized these findings. The starting trivalent complex (Scheme 1.25, Complex I) was readily prepared via salt metathesis with $UI_3(THF)_3$. It was then found that the attempts to recrystallize this compound from the coordinating solvents as THF or diethyl ether, led to solvent deoxygenation with formation of the μ-oxo bridged dimer (Scheme 1.25, Complex VIII). The reaction also initiated ligand fragmentation, with the ligand fragment remaining retained by uranium metal center (Scheme 1.25, Complex VIII).[112] Among the most remarkable features of this system there was the ability to coordinate cyclohexane via simple agostic interaction (Scheme 1.25, Complex IX), providing a unique example of coordination of neutral hydrocarbon in the whole literature.[113] Also unique was the end-on bonding mode adopted by CO_2 in forming the corresponding complex (Scheme 1.25, Complexes II and XI).[114, 115] The formation of this species preluded a much expected deoxygenation of the carbon dioxide (Scheme 1.25, Complex XII). Moreover the deoxygenation process was initiated only in the case of favorable steric arrangements around the uranium metal center.[115] Coordination of heterocyclic carbene (Scheme 1.25, Complex III),[116] unprecedented coordination mode during fixation of CO (Scheme 1.25, Complex X)[117] and of another variety of substituents has also been observed. Particular attention perhaps may be given to the coordination of the diphenyldiazomethane and which afforded a diazido-radical coordinated to the oxidized U(IV) metal center[118] through σ-bonding to both nitrogen atoms of the fragment (Scheme 1.25, Complex IV). This interaction may be tuned by acting on the ligand steric hindrance.[118] It was discovered that steric arrangements of the ligand system were capable of switching the bonding mode of the diazo from side-on to end-on (Scheme 1.25, Complex V). The end-on coordination eventually evolved into a curious case of cyclization (Scheme 1.25, Complex VI) involving the phenyl ring *ortho-* hydrogen atom and releasing hydrogen gas in the process.[118]

The selection of reactivity compiled above proves that trivalent uranium has an outstanding reactivity in line with that of the most reducing of low-valent lanthanides. This reactivity appears to be particularly sensitive to the ligand environment and steric hindrance. Low-valent synthons may be prepared and characterized with the help of π-systems capable of acting as electron storage and supplier of electrons "on demand" during a red-ox transformation.

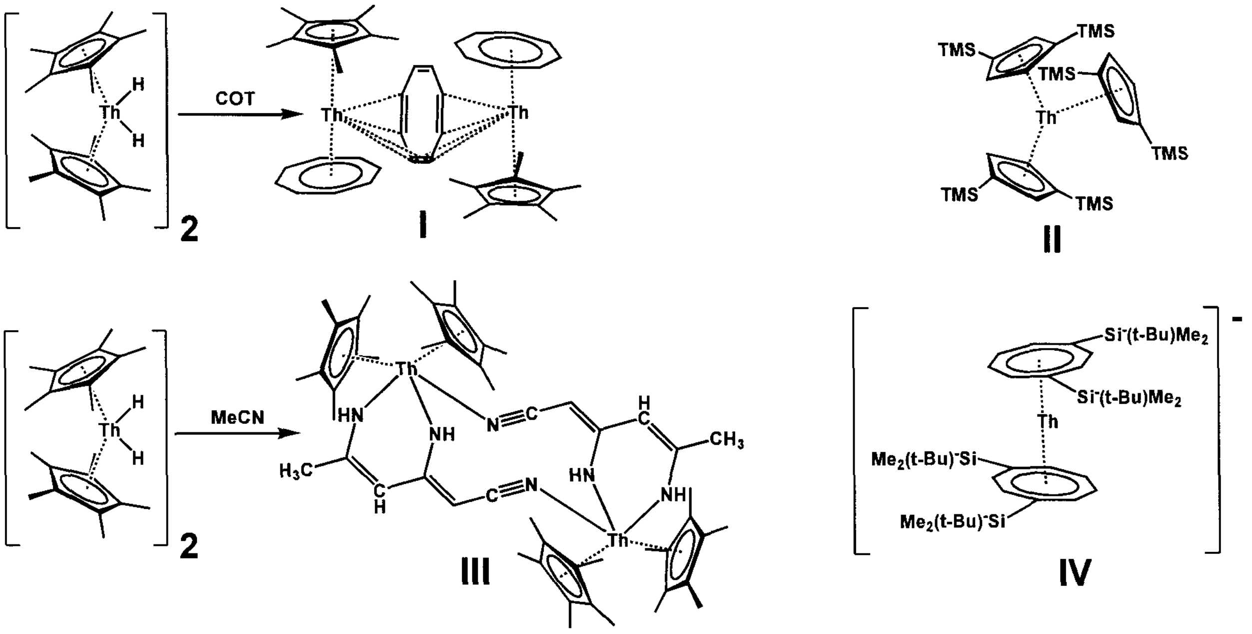
1.4 Complexes of low valent thorium.

The enthusiasm for studies aiming at discovering the chemistry of thorium are usually quenched by the toxicity of this element, its low-level of radioactivity and also the fact that the chemistry is exclusively limited to the tetravalent state. Even transformations which might suggest the involvement of low valent intermediates, similarly to those claimed in U(IV)/U(III) red-ox chemistry, were explained by assuming non-redox reactivity pathways.[119, 120] And yet, this chemistry may still provide some exciting surprises.



Scheme 1.26.

For example, the reaction of Th-cyclopentadienyl based compound with elemental phosphorus was discovered by the group of Scherer.[120] The transformation was initiated by the decomposition of a Th alkyl and resulted in the formation of a dimeric complex containing an evidently reduced $(P_4)^{4-}$ moiety entrapped between two Th metal centers (Scheme 1.26, Complex II). It was suggested that the transformation proceeded through convoluted multi-step pathway where the tetravalent state of the metal center has been always preserved. A simpler assumption that a transient Th(II) intermediate might be generated by reductive elimination was regarded as unacceptable since it would contradict the commonly accepted paradigm of thorium as an "irreducible" element. Nonetheless several serious attempts have been carried out to prepare low-valent species or synthons. The reaction of the Cp_2ThCl_2 with five fold excess of Na-K alloy in toluene was examined by Lappert.[121] The reaction yielded a dark colored paramagnetic material (Scheme 1.27, Complex II). The crystal structure showed an homoleptic Th tris-cyclopentadienyl complex but no further characterization (magnetic moment, EPR, or DFT) were provided until 2001, when the same group of researchers provided an additional evidence about the nature and the electronic structure of this compound.[121a] In the end it was accepted that this species was indeed the first structurally characterized authentic Th(III) complex.



Scheme 1.27.

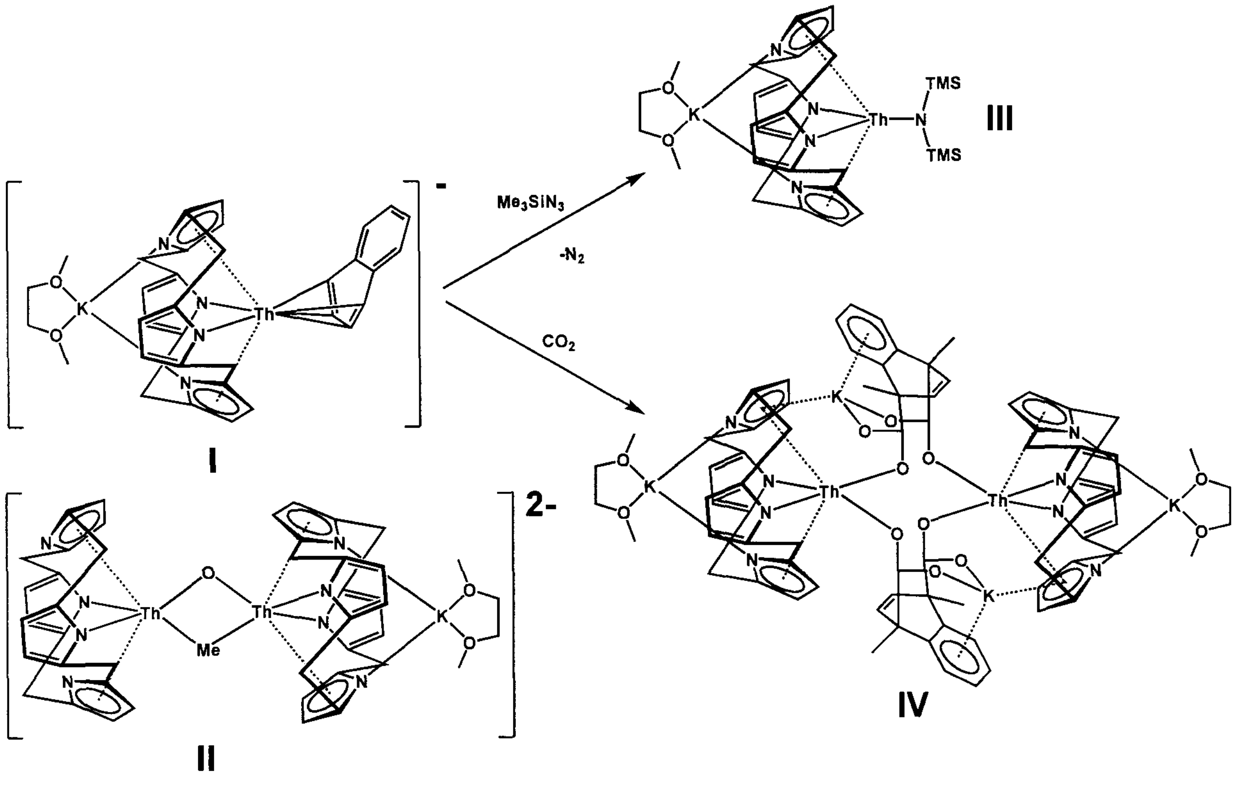
The reactivity and red-ox properties of actinide-bis-(cyclooctateraene) compounds was first reported by Zalkin et al. in 1972.[122] Cloke attempted the reduction of $Th(COT)_2$ obtaining an isostructural species which however contained an additional $K(DME)_2$ unit, thus suggesting the existence of a trivalent compound (Scheme 1.27, Complex IV). Accordingly, the EPR spectrum consisted of a single wave as expected for the presence of one unpaired electron.[123] On the basis of several indirect evidences extracted from the EPR, magnetic measurements and calculated energy levels of the orbitals in the parent Th(IV) complex, it was suggested by the authors that the unpaired electron resided on a 6d orbital of the metal center with $6d_z^2$ character.

In both the cases described above, a major steric protection by the ligands contributed, without doubt, to the stabilization of this extremely unusual oxidation state. The merit of these findings is to demonstrate that reduced Th at least as an intermediate may exist and help to rationalize complex reactivity patterns. For example, the tetravalent $ThH_2(Cp^*)_2$, reported recently by Evans, may be used as a source of trivalent species in the sense that some of its chemical transformations imply a red-ox behavior.[124] For example its reaction with COT afforded an inverted-sandwich compound (Scheme 1.27, Complex I) bridged by one COT ligand which may be regarded as the result of the addition of two trivalent Th(COT)Cp* unit to the same COT molecule.[124b] On the same line stood the reaction of trimerization of acetonitrile (Scheme 1.27, Complex III).[124a]

In the section reviewing the chemistry of low-valent uranium, the possibility has been discussed for low-valent synthons to be generated by using ligands or molecules which may act as electron storage. In the recent past, the same strategy has been actively pursued for thorium in our laboratory. This thesis is also in part a contribution to this work.

Reduction of Th(IV) tetrapyrrolato precursor by potassium naphthalenide gave a mixture of two compounds.[125] The structure of the minor product exhibited two thorium tetrapyrrolide units bridged by one methyl and one oxo- groups (Scheme 1.28, Complex II). Three potassium counter-cations (one directly bonded to the dimer and the other two solvated in the lattice) completed the structure of what appears to be the clear result of unusual DME solvent fragmentation. The formation of this complex clearly was suggesting the transient formation of a strongly reducing species. The second product confirmed this hypothesis. The complex was formed by the tetranionic ligand and two potassium atoms (one retained in the structure and the other in the lattice) with the actinide π-bonded to one of the two ring of naphthalene (Scheme 1.28, Complex I).

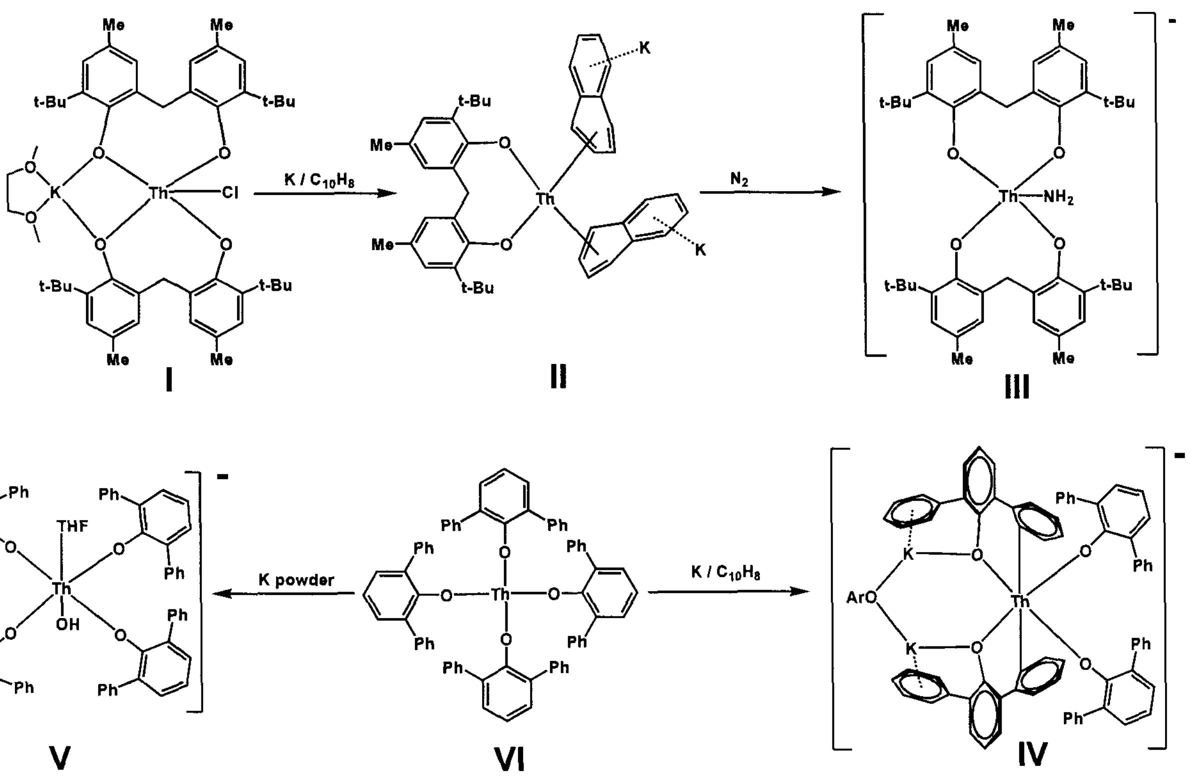
In this case, the tetravalent state was immediately apparent from the large distortion around the coordinated ring indicating that naphthalene has been transformed into the corresponding dianion.[125] Nonetheless, in spite of the tetravalent state, this species acted as a true divalent synthon as clearly illustrated by its reaction with TMS-azide.



Scheme 1.28.

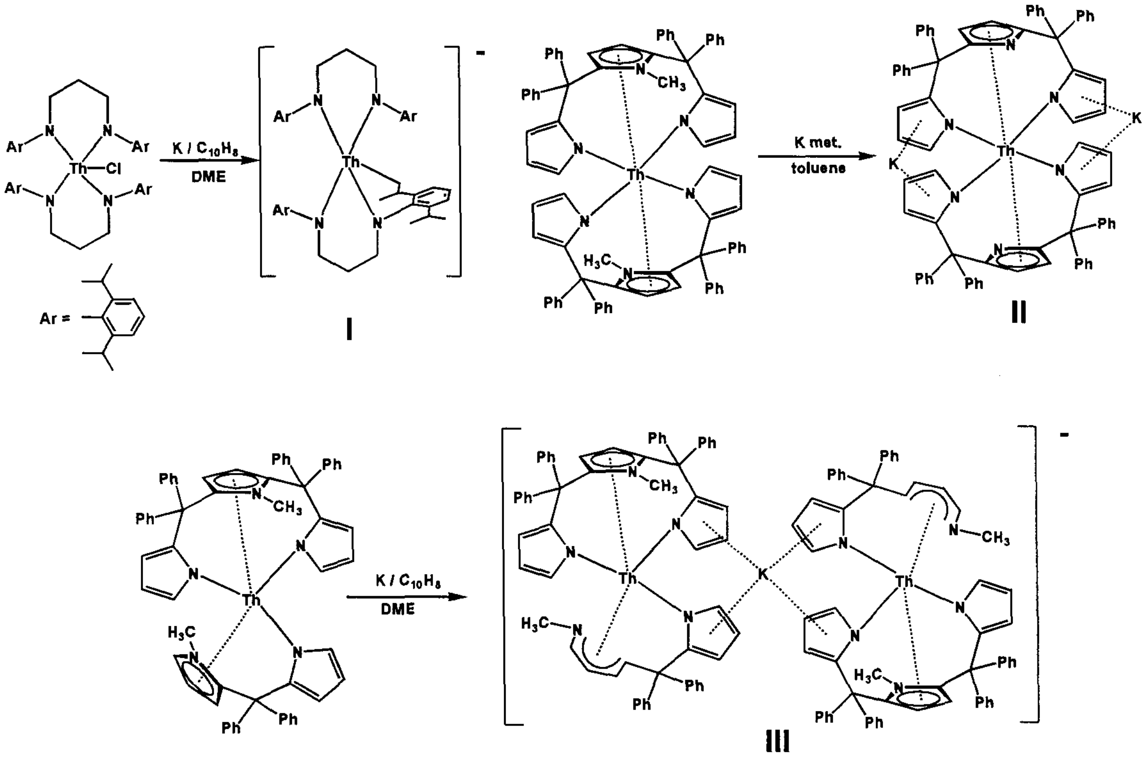
The reaction was accompanied by dissociation of intact naphthalene, formation of nitrogen, potassium azide and hexamethyl-disalazanate Scheme 1.28, Complex III). This complex transformation is in fact a two-electron red-ox process, which can only be explained with the involvement of the transient Th(II) species. In sharp contrast with this behavior, the reaction of the divalent naphthalenide synthon with CO_2 gave direct insertion into the Th-carbon bonds as one would expect for a genuine tetravalent complex (Scheme 1.28, Complex IV).[126]

Clear indication for the formation of low-valent synthons with an even larger extent of reduction has been obtained while exploring the reduction of Th complex with polydentate ligand system based on hard oxygen σ-donors (Scheme 1.29, Complex I). The reduction gave a compound containing a surprising -NH_2 fragment coordinated to the Th metal center (Scheme 1.29, Complex III).[127] By carrying out the same reduction under $^{15}N_2$ it was proved that the nitrogen atom of the amino- moiety was generated from dinitrogen gas. Such transformation necessarily required the transfer of six-electron in order to completely cleave nitrogen-nitrogen triple bond. In addition, the presence of the hydrogen atom indicated that the hydrogen atoms have been abstracted from the ethereal solvent.



Scheme 1.29.

In search for a low-valent intermediate capable of such a unique behavior, the amount of reducing agent was increased to a fourfold excess. The product containing one bis-phenolato with two potassium atom and the thorium metal coordinated to two naphthalenide rings (Scheme 1.29, Complex II). By using the same reasoning applied to the tetrapyrrolato based Th naphthalenide above, this species might be expected to act as a zerovalent synthon.[125] Of course, rationalization of the structure of such species unavoidably used the synthon paradigm. It was clearly indicated by the very visible distortion of the coordinated rings that Th metal center once again was resting in its tetravalent state. In addition, this species acted as electron transfer agent since two additional electrons were required for the transformation of dinitrogen into amido-ligand. Conversely, bulky mono-dentate aryloxides did not allow the isolation of low-valent synthons.



Scheme 1.30.

Upon reduction, these species gave the typical transformation (ligand scrambling, solvent cleavage and ring *ortho*-metallation, (Scheme 1.29, Complexes VI - VI) as arising from attack to the ligand system by a transient low-valent species of high instability.[128]

An unusual case of C-H bond activation and formation of Th-C bond was reported by our group while attempting to reduce a Th(IV) compound supported by bis-amido ligand.[129] The transformation led to the abstraction of the proton from the alkyl substituent, rather than from the aromatic ring (Scheme 1.30, Complex I). The oxidation state of Th metal center in both the reagent and the product of this reaction were clearly tetravalent. However, the presence of short lived low-valent synthon was suggested in this case. Given the versatility of the tetra-pyrrolide anion, a tri-pyrrole dianionic ligand has been designed for the characterization of low-valent synthons. The particular geometry of the ligand with the central pyrrolide ring being alkylated was designed with the purpose of providing π-ligation on demand.

Surprisingly, this ligand system afforded C-N bond cleavage. Upon reduction, the methyl group connected to the central pyrrole has been eliminated via radical cleavage (Scheme 1.30, Complex II). Replacement of one of the two tri-pyrrole with one similarly alkylated di-pyrrole ligand followed by reduction afforded instead a rare case of pyrrole ring opening and formation of a large dien-yl system (Scheme 1.30, Complex III).[130]

1.5 Aim of the Thesis.

The preceding pages of the introduction have highlighted the unique and diverse properties of f-block elements complexes. Despite all wealth of the information gathered for both lanthanide and actinide compounds, the preparation of low valent complexes and their reactivity remain rather scattered and poorly systematized. Very often the transformations initiated by the *f*-block elements afforded unprecedented results. However the rationalization of such transformations necessarily requires profound knowledge of the nature of the active intermediates. Unfortunately, the high activity of low valent lanthanides and actinides complexes responsible for diversified transformation pattern prevents, from the other side, the isolation and characterization of the active species. From the other side, the knowledge of such species properties is absolutely necessary to draw the fine line between spontaneous and uncontrolled decomposition from one side and completely quenched reactivity from the other side. It would also allow to control and direct the transformations. Therefore, the main goal of this work was to explore the application of several new and previously known ligand systems to stabilize low oxidation state of several *f*-block element complexes. The proposed research was aimed at exploring both lanthanides and actinides with the focus on the elements that were shown capable of forming reactive low valent compounds, which could be nevertheless, stabilized by the coordination environment of the metal centers. The first two chapters present the work in the fast expanding field of lanthanide hetero-bi-metallic compounds and the role of additional Lewis acid fragments in enforcing the desired coordination characteristics on different ligand systems as well as providing the stabilization to low valent oxidation states metal centers. The following three chapters are a contribution to the field of actinide chemistry.

1.5.1 Chapter 2.

Chapter two describes the research in the field of multi-dentate aryloxide supported complexes of both Sm(II) and Sm(III). It outlines the different strategies for preparation of several new hetero-bimetallic complexes of Al/Sm. The stabilization effect of Lewis acid coordination is discussed in this part. Quick exploration of the reactivity for such species in stoichiometric and catalytic processes is also presented.

1.5.2 Chapter 3.

Chapter three explores the effects of the zwitter-ionic pyrrolide coordination as induced by the coordination of aluminum alkyls. The partial cationization of the thulium metal center afforded a series of unprecedented C-H and C-Si bond activation processes caused by the presence of different hydrogenating reagents.

1.5.3 Chapter 4.

Chapter four discusses the alkylation reaction of the uranium complexes supported by the bulky amido– ligand. Replacement of the halogen by alkyl groups in the coordination sphere of uranium metal center initiates an extensive γ-deprotonation process yielding several new cluster compounds with the formal carbide unit, entrapped in bridging interaction between several U metals. The attempts of reduction of the same starting material in different reaction conditions give as a result the re-oxidation products with the oxidation state of the metal center even higher than in the starting material. Ligand scrambling and intermediate cluster formation appear to be two common motives in the reduction processes.

1.5.4 Chapter 5.

In chapter five the effect of large delocalized π-system on stability of the low valent U metal centers is discussed. The transformation reveals the ability of σ-bonded delocalized π-system to act as electron storage and electron funnel in order to support the stabilization of ultra low oxidation states as well as multi-electron transformations. Several multi-electron solvent activation processes are supported by the isolation of the unprecedented ultra low oxidation state uranium complexes. However the discussion of the electronic nature of such compounds reveals the presence of radical-anion fragments coordinated to the metal center.

1.5.5 Chapter 6.

Chapter six describes the attempt to use a new ligand system with sterically constrained π-coordination to the metal center in order to stabilize low oxidation state of Th metal center. Several reduction attempts gave some the insights on the reactivity, stability and decomposition pathways of an unprecedented low valent Th synthon. DFT calculation explains the nature of the reduced species through the ability of the ligand to act as electron storage. The relative stability allows the isolation and x-ray characterization whereas the red-ox behavior is demonstrated by the chemical behavior.

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Chapter Two

Aluminate Sm(II) and Sm(III) Aryloxides. Isolation of a Single-component Ethylene Polymerization Catalyst.

Introduction

Low-valent samarium displays one of the most remarkable and unpredictable chemical reactivity, which is characterized by a large variety of transformations with the most diversified substrates.[1-3] In fact, the appearance of the first of these remarkable findings in the literature almost 25 years ago[3], has marked the beginning of modern *f*-block organometallic chemistry. Perhaps the key to understand such a remarkable and unique chemical behavior is not only the strong reducing power of divalent samarium in performing one electron attacks, but also the ability to stabilize (at least for a sufficiently long time) the corresponding radical type of intermediates. In subsequent steps, a variety of radical-like couplings generate the final products.[1u, 2p, s, 4, 7] Indeed, the cooperative attack of more than one divalent center on the substrate is a trend in this chemistry.[1, 2, 4-6]

Given the versatility to promote C-C bond forming reactions, including a rare and desirable case of CO_2 reductive coupling,[7] the possibility of using divalent Sm for polymerizing olefins has not escaped the attention of researchers in the field.[2n, 6f, 8] Samarocene has provided one of the very first single-component ethylene polymerization catalysts[8h, 8l, 9] producing a polymer with molecular weight so high that could not be measured.[9] Even in this case, the polymerization initiation step may be envisioned as following the usual trend of cooperative attack of two metal centers at the two ends of the ethylene molecule. The thermal robustness[1u, 2a, n, 6f, 8a, e-h, j, 10] of Sm-C bond is most likely responsible at this stage for the endless chain growth and the uniqueness of the polymer generated.

As usual, the particular nature of the ligand system is central to the performances of divalent samarium. Using a large variety of ligands, other than Cp-like derivatives, has so far produced only remarkable structures but none were able to generate even a fraction of the complex transformations performed by the samarocenes.[1p, 1r, 2k-l, o-p, r-t, y, 4b, 7, 8l, 11] Only in the case of π-bonded polypyrrolide anions, somewhat related to the Cp rings, the reducing power has apparently surpassed the samarocenes. This was at least in the case of dinitrogen activation.[1q, 2b-c, j, 5f, 12] The reactivity with ethylene seems instead to have taken a step back with these particular complexes in the sense that no single-component catalytic activity has been observed but only *side-on* ethylene coordination.[13] On the other hand, we have observed that by using π-bonded ligand systems containing hetero-atoms, Lewis acidic alkali cations are very often retained,[2b-e, j, 5e-g, 12b, 13, 14] thereby significantly affecting the red-ox potential of the divalent Sm center. Thus, it seems possible that even ethylene activation (e.g. from labile coordination, to reduction and polymerization) could be fine tuned through the appropriate selection of the ancillary Lewis acids retained as part of the anionic metallate structures of divalent samarium.

In an attempt to clarify this behavior, we have carried out the present study in the chemistry of low-valent samarium by using aryloxides as ancillary ligands and alkyl aluminum as Lewis acids. The selection of bulky aryloxides was advised by the strong affinity for Al of the oxygen donor atom thereby enhancing the possibility for aggregation. We wished to verify the possibility that the strong coordination to an acidic AlR_3 residue could favor the π-bonding mode of the aryloxide aromatic ring, possibly enhancing the metal reducing power. We were also interested in assessing the ability of divalent samarium to perform pure insertion reactions rather than reductions. In other words we wish to understand whether a Sm(II)-R function could grow polyethylene chains via repetitive insertion into the Sm(II)-C bond.

While this work was in progress Anwander has reported a series of heterometallic Ln/alane complexes[15] determining two prevalent features in these complexes such as adduct formation and ligand rearrangement.[15b] Herein we report our independent observations.

Experimental Part

All manipulations were performed under nitrogen atmosphere with rigorous exclusion of oxygen and water using standard Schlenk and glove-box techniques. Hexane, toluene and THF solvents were purified by passing through Al_2O_3 filled columns and deoxygenated prior to use by several vacuum/nitrogen purges. DME was dried for 12 hours over $LiAlH_4$ and distilled under N_2 prior to utilization. Benzene-d^6, toluene-d^8 and THF-d^8 were obtained from "C/D/N isotopes", dried over freshly activated molecular sieves (4Å) for 10 days and distilled under N_2 atmosphere. Trimethylaluminum solution in hexane was purchased from Aldrich and used as received. 2,6-diphenylphenol and 2,2'-methylene-bis-(6-*tert*-butyl-4-methylphenol) were purchased from Aldrich dried under vacuum at room temperature for 48 hours and then used without further purification. Complexes $[Sm(AlMe_4)_2]_n$[16] and $Sm(N(TMS)_2)_3$[17] were synthesized according to literature procedures. NMR spectra were recorded at 293K on Varian Inova 500 MHz spectrometer. Chemical shifts were referenced to internal solvent resonances and reported in parts per million relative to Me_4Si. Elemental analyses were performed on Perkin Elmer 2400 CHN analyzer. Data for X-ray single crystal structure determination were collected with a Bruker diffractometer equipped with 1K SMART CCD area detector.

Catalytic performance of the complexes was tested in a 200 mL high-pressure Buchi reactor containing a heating/cooling jacket. A pre-weighed amount of catalyst was dissolved in 10 mL of toluene under N_2 and injected into the preheated reactor already charged with toluene and co-catalyst, if necessary (total volume 100 mL). Solutions were heated with a thermostatic bath and pressurized with ethylene, maintaining the desired pressure throughout the run. Polymerizations were quenched by addition of EtOH and HCl. The resulting polymer was isolated by filtration, sonicated with an acidified ethanol solution, rinsed, and thoroughly dried prior to mass determination. Molecular weight and molecular-weight distributions of the polymers were determined by means of gel permeation chromatography on a PL-GPC210 equipped with refractive-index and viscosity detectors and a 3 H PLgel 10 mm MIXED-B column set at 135 C with 1,2,4-trichlorobenzene as solvent. The molecular weight of PE was referenced to polystyrene (Mw=65500, PDI=1.02) standard sample.

Preparation of Sm[(μ-2,6-bis-phenyl-phenol)]$_2$[(μ-Me)(AlMe$_2$)]$_2$ (2.1)

Method A. A solution of 2,6-diphenylphenol (0.407 g, 1.65 mmol) in toluene (5 mL) was slowly added to a suspension of Sm(AlMe$_4$)$_2$ (0.268 g, 0.83 mmol) in toluene (5 mL). The reaction was accompanied by fast color change and vigorous gas evolution. After 4 hours of stirring at room temperature, the volume of the reaction mixture was reduced to 4 mL in vacuo and the mother liquor was allowed to stand at room temperature for crystallization. After 48 hours dark-red prisms of **2.1** separated and which were washed with cold (-35°C) toluene (3mL) and dried *in vacuo* (0.565 g, 0.72 mmol 87%). Elem. Anal. for $SmAl_2C_{42}H_{44}O_2$ found (calculated): C 64.11 (64.25), H 5.53 (5.65).

Method B. A solution of Sm(N(TMS)$_2$)$_3$ (0.200 g, 0.32 mmol) in toluene (5 mL) was treated with solution of AlMe$_3$ in toluene (0.97 mL, 1.94 mmol, 2.0 M). A slight color change occurred. The reaction mixture was stirred at room temperature for additional 30 min. After that period a solution of 2,6-diphenylphenol (0.108 g, 0.32 mmol) in toluene (5 mL) was added dropwise to the reaction mixture. The immediate color darkening was accompanied by a vigorous gas evolution. The solution was brought to the boiling point and evaporated to a volume of about 3 mL. The reaction mixture was slowly cooled to room temperature. After 12 hours, dark-red prisms of **2.1** separated (0.203 g, 0.26 mmol, 81%). Analytical data and crystallographic cell parameters were nearly identical to those of the material isolated by method A.

Preparation of Sm{[(μ-2,6-bis-phenyl-phenoxy)$_2$AlMe$_2$]-[μ-(acetato)-(2,6-bis-phenyl-phenoxy)AlMe$_2$][1,2-dimethoxyethane]}{C_6H_{14}}$_{0.25}$ (2.2)

A solution of **2.1** (0.450 g, 0.57 mmol) in toluene (7 mL) was exposed to CO_2 (1 atm). No color change was observed at room temperature and the reaction mixture was brought to the boiling point and refluxed under CO_2 atmosphere for 15 min. The reaction mixture was cooled to room temperature and toluene solvent was removed *in vacuo*. The resulting dark-red oil was redissolved in the minimum amount of DME (4 mL) under N_2 atmosphere. The DME solution was layered with hexanes (13 mL). After 48 hours, dark-red prisms of **2.2** were formed from the solution (0.283 g, 0.24 mmol, 42%). Upon drying *in vacuo* crystals rapidly deteriorate with formation of a red powdery material. Elem. Anal. for $SmAl_2C_{64}H_{64}O_7$ found(calculated): C 66.74 (66.87), H 5.57 (5.61). ^{1}H-NMR (500 MHz, benzene-d^6, 20°C) *δ*: 7.75(3H, *ortho-*, *para-*Ar'**H**), 7.74(3H, *ortho-*, *para-*Ar'**H**), 7.50(10H, Ar''**H**), 7.45(2H, *para-*Ar**H**), 7.36(1H, *para-*Ar**H**), 7.15(2H, *metha-*Ar**H**), 7.04(2H, *metha-*Ar'**H**), 6.96(4H, *metha-*Ar**H**), 6.90(2H, *metha-*Ar'**H**), 6.42(6H, *otho-,para-*Ar'**H**), 6.18(4H, *metha-*Ar'**H**), 3.48 (broad, 3H, **CH$_3$**-COO), 2.08(3H, Al-**CH$_3$**), 2.05(3H, Al-**CH$_3$**), -0.22(6H, Al-**CH$_3$**).

Preparation of catena-(Sm{μ-η6'-[6,6'-methylene-bis-(2-*tert*-butyl-4-methyl-phenoxy)][AlMe$_2$]}{μ-Me}$_2${AlMe})(μ-Me) (2.3)

A solution of bis-phenol (0.161 g, 0.47 mmol) in toluene (5 mL) was added to a suspension of $Sm(AlMe_4)_2$ (0.153 g, 0.47 mmol) in the same solvent (5 mL). Vigorous gas evolution and significant color change was observed upon mixing. The reaction mixture was brought to the boiling point and the volume was reduced by about 2 mL. The reaction mixture was allowed to cool to room temperature and after 24 hours dark-red plates of **2.3** were formed (0.272 g, 0.43mmol, 91%). Elem. Anal. for $SmAl_2C_{29}H_{48}O_2$ found (calculated): C 54.92 (55.02), H 7.55 (7.64).

Preparation of Sm{μ-[6,6'-methylene-bis-(2-*tert*-butyl-4-methyl-phenol)]-μ-[N-*tert*-butyl-acetamidate]AlMe}$_2${C_7H_8}$_{1.5}$ (2.4)

A solution of *tert*-butyl-isocyanate (0.045 g, 0.46 mmol) in toluene (5 mL) was added dropwise and with vigorous stirring to a solution of **2.3** (0.275 g, 0.43 mmol) in the same solvent (10 mL). No significant immediate color change was observed and stirring was continued for additional 5 hours. After that period of time, the volume was reduced *in vacuo* to about 4 mL. The solution was allowed to stand at room temperature for 3 days, after which, large green-brown prisms of **2.4** separated. The crystalline mass was isolated, washed with cold toluene (-35°C), and dried under N_2 atmosphere (0.235 g, 0.18 mmol, 43%.). Elem. Anal. for $SmAl_2C_{70.5}H_{102}N_2O_6$ found(calculated): C 66.21 (66.26), H 7.98 (8.05), N 2.15 (2.19).

Preparation of Sm{μ-[6,6'-methylene-bis-(2-*tert*-butyl-4-methyl-phenol)]$_2$-μ-AlMe$_2$}{THF}$_2${C_6H_{14}}$_{0.5}$ (2.5).

A solution of diazobenzene (0.059 g, 0.32 mmol) in toluene (4 mL) was added dropwise to a solution of **2.3** (0.410 g, 0.65 mmol) in toluene (10 mL). An immediate discoloration was observed upon mixing and stirring was continued for 3 hours at room temperature. After that time a significant amount of colorless solid separated from the mother liquor. The mother liquor was discarded and the colorless solid was redissolved in THF (5 mL). A very small amount of insoluble material was eliminated by centrifugation. The resulting clear solution was layered with hexane (10 mL) and left undisturbed at room temperature for three days. The colorless crystalline **2.5** thus separated was washed with cold hexane (-35°C) and dried under N_2 atmosphere (0.290 g, 0.27 mmol 42%). Upon drying *in vacuo* crystals rapidly deteriorated with the formation of white powdery material. Elem. Anal. for $SmAlC_{56}H_{82}O_6$ found(calculated): C 65.31 (65.39), H 7.97 (8.04). ^{1}H-NMR (500 MHz, THF-d^8, 20°C) δ: 6.94(4H, ArH), 6.79(4H, ArH), 4.02(2H, -CH$_2$-), 3.53(8H, THF), 3.25(2H, -CH$_2$-), 2.16(6H, Ar-

CH_3), 2.03(6 H, Ar-CH_3), 1.73(8H, THF), 1.36 (36H, -C(CH_3)$_3$), -0.31(3H, Al-CH_3), -0.68(3H, Al-CH_3).

Preparation μ-{Sm-μ-[6,6'-methylene-bis-(2-*tert*-butyl-4-methylphenol)]-μ-[Me]$_2$-AlMe$_2$}$_2$ (2.6)

A solution of Sm(N(TMS)$_2$)$_3$ (0.200 g, 0.32 mmol) in toluene (10 mL) was treated with a solution of $AlMe_3$ in toluene (0.97 mL, 2.0 M, 1.94 mmol) and stirred for 2 hours at room temperature. A solution of bis-phenol (0.108 g, 0.32 mmol) in toluene (7 mL) was then added dropwise to the reaction mixture. A vigorous gas evolution and significant color change were observed upon mixing and the reaction mixture was stirred for additional 3 hours. The solution was concentrated to 4 mL and allowed to cool down. Upon cooling, a large amount of bright-orange highly crystalline **2.6** separated and which was washed with cold toluene (-35°C) and dried *in vacuo* (0.156 g, 0.27 mmol, 84%). Elem. Anal. for $Sm_2Al_2C_{54}H_{84}O_4$ found(calculated): C 56.22 (56.30), H 7.07 (7.35). ^{1}H-NMR (500 MHz, toluene-d^8, 40°C) *δ*: 7.27(2H, ArH), 7.15(2H, ArH), 4.22(1H, -CH_2-), 3.61(1H, -CH_2-), 2.71(3H, Ar-CH_3), 2.28(3H, Ar-CH_3), 1.06(9H, -C(CH_3)$_3$), 0.44(9H, -C(CH_3)$_3$), -1.88(6H, Al-CH_3), -3.96(6H, Al-CH_3).

Preparation of Sm-{μ-[6,6'-methylene-bis-(2-tret-butyl-4-methylphenoxy)]}$_2$-μ-AlMe$_2$ (2.7)

A solution of bis-phenol (0.111 g, 0.33 mmol) in toluene (5 mL) was added to a solution of **2.6** (0.188 g, 0.33 mmol) in toluene (5 mL). Intense gas evolution was observed upon mixing and stirring was continued for additional 3 hours. The volume of the mixture was reduced to about 4 mL by evaporation, and the resulting solution was brought to the boiling point and allowed to cool undisturbed to room temperature. After six hours, yellow prisms of **2.7** were formed which were separated from the mother liquor and dried under N_2 atmosphere (0.248 g, 0.28 mmol, 85%). Elem. Anal. for $SmAlC_{48}H_{66}O_4$ found(calculated): C 65.03 (65.19), H 7.41 (7.52). ^{1}H-NMR (500 MHz, benzene-d^6, 20°C) *δ*: 10.58 (2H, ArH), 9.86 (2H, ArH), 8.13 (2H, ArH), 8.12 (2H, ArH), 4.92 (1H, -CH_2-), 4.09 (1H, -CH_2-), 3.83 (1H, -

CH_2-), 3.58 (3H, Ar-CH_3), 3.41 (1H, -CH_2-), 2.87 (3H, Ar-CH_3), 2.68 (3H, Ar-CH_3), 2.38 (3H, Ar-CH_3), 1.61 (18H, -$C(CH_3)_3$), 1.57 (18H, -$C(CH_3)_3$), -4.02 (3H, Al-CH_3), -4.15 (3H, Al-CH_3).

X-ray crystallography

For all the compounds, the results presented are the best of three data collection trials. The crystals were mounted on thin glass fibers using paraffin oil and cooled to the data collection temperature. Data were collected on a Bruker-AXS SMART 1k CCD diffractometer. Data for the compounds **2.1, 2.2, 2.3** and **2.7** were collected with a sequence of 0.3° ω scans at 0, 120, and 240° in φ. To obtain acceptable redundancy data for compound **2.4, 2.5** and **2.6** the sequence of 0.3° ω scans at 0, 90, 180, and 270° in φ was used. Initial unit cell parameters were determined from 60 data frames collected at the different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.[18] Systematic absences in the diffraction data-set and unit-cell parameters were consistent with monoclinic $\mathbf{P}2_1/n$ for **2.1** and **2.2,** monoclinic $\mathbf{P}2_1/c$ for **2.3** and **2.7**, triclinic $\mathbf{P}\bar{1}$ for **2.4, 2.5** and **2.6**. Solutions in centrosymmetric space groups for all of the compounds yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed with difference Fourier synthesis, and refined with full-matrix least-squares procedures based on F^2. In all structures compound molecules were located in general positions. Structure of complex **2.3** represent a polymeric chain with monomers connected through -CH_3 group coordination to the Sm metal center of the next monomeric unit. In this structure each monomeric unit is symmetry related to the next one through a 2_1 axes symmetry operator. Complex **2.6** demonstrates a dimeric arrangement where two monomeric units are related by inversion center symmetry operator. Carbon atoms of co-crystallized hexane solvent molecule in **2.2** as well as carbon atoms of co-crystallized toluene solvent molecules in **2.4** were refined isotropicaly due to partial occupancy coupled with significant thermal motion disorder and in order to maintain an optimal data to parameters ratio. In all the structures, all non-hydrogen atoms, with the exceptions mentioned above, were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions. All scattering factors are contained in several versions of the SHELXTL program library version 6.12.[19] Crystallographic data for all structures are reported in Tables 2.1 and 2.2.

Crystal Structure Descriptions

1. The crystal structure of **2.1** comprises a divalent Sm center in a distorted pseudo-octahedral environment (Figure 2.1). One axial and one equatorial position of the octahedron are occupied by two oxygen atoms of the two aryloxide ligands [Sm(1)-O(1) = 2.496(2) Å, Sm(1)-O(2) = 2.534(2) Å, O(1)-Sm(1)-O(2) = 115.04(7)°]. Two other equatorial positions are occupied by two methyl groups [Sm(1)-C(21) = 2.811(3) Å, Sm(1)-C(42) = 2.827(3) Å, C(21)-Sm(1)-C(42) = 100.19(10)°] in *cisoid*-type of arrangement [O(1)-Sm(1)-C(21) = 67.96(8)°, O(2)-Sm(1)-C(42) = 67.73(8)°]. Two η^6-coordinated ortho-phenyl groups [Sm(1)-centroid(1) = 2.956(3) Å, Sm(1)-centroid(2) = 2.954(3) Å, centroid(1)-Sm(1)-centroid(1) = 110.02(8)°] are situated on the second axial and equatorial positions, defining a "bent sandwich" type of structure.

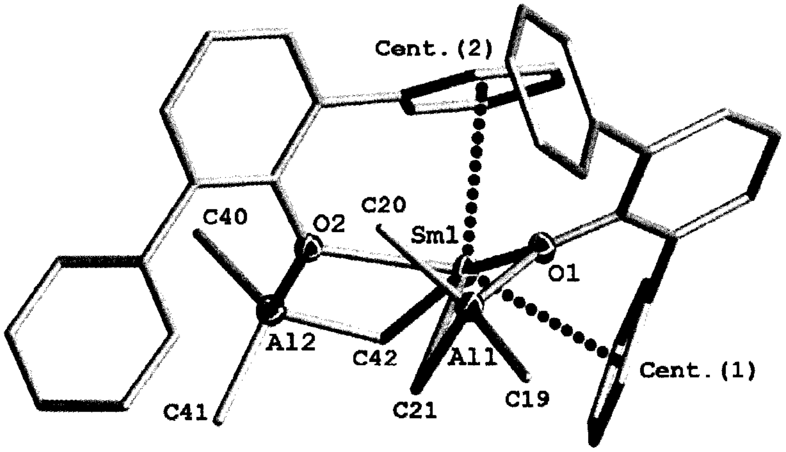


Figure 2.1. Partial thermal ellipsoid diagrams of **2.1** with thermal ellipsoid drawn at 50% probability level. Hydrogen atoms and thermal ellipsoids of carbon atoms have been omitted for clarity.

Each of the two aluminum atoms is tetrahedrally coordinated having two terminally bonded methyl groups [Al(1)-C(19) = 1.964(8) Å, Al(1)-C(20) = 1.968(8) Å, Al(2)-C(40) = 1.968(8) Å, Al(2)-C(41) = 1.964(8) Å, C(19)-Al(1)-C(20) = 113.76(16)°, C(40)-Al(2)-C(41) = 117.02(14)°]. A third methyl group is bridging to the Sm center [Al(1)-C(21) = 2.021(3) Å, Al(2)-C(42) = 2.035(3) Å, C(20)-Al(1)-C(21) = 104.67(15)°, C(41)-Al(2)-C(42) = 109.28(14)°] as the oxygen atom of one aryloxide ligand [Al(1)-O(1) = 1.844(2)Å, Al(2)-O(2) = 1.833(2) Å, O(1)-Al(1)-C(21) = 100.68(12)°, O(2)-Al(2)-C(42) = 101.43(11)°]. These oxygen atoms are also bridging to the lanthanide metal center.

2. In the structure of **2.2** the Sm(II) atom is placed in the center of a distorted pentagonal bipyramidal environment with the equatorial plane defined by two oxygen atoms of a coordinated DME molecule [Sm(1)-O(6) = 2.667(6) Å, Sm(1)-O(7) = 2.623(6) Å] and two oxygen atoms from two different aryloxide ligands [Sm(1)-O(1) = 2.558(6) Å, Sm(1)-O(2) = 2.603(6) Å, O(1)-Sm(1)-O(2) = 60.02(17) , O(2)-Sm(1)-O(6) = 85.4(2)]. Two aryloxide ligands are in turn bridging the same $AlMe_2$ unit [Al(1)-O(1) = 1.832(7) Å, Al(1)-O(2) = 1.831(6) Å, O(1)-Al(1)-O(2) = 89.6(3)] (Figure 2.2). The Al center adopts the usual tetrahedral coordination geometry [Al(1)-C(37) = 1.962(11) Å, Al(1)-C(38) = 1.968(10) Å, C(37)-Al(1)-C(38) = 112.3(5)].

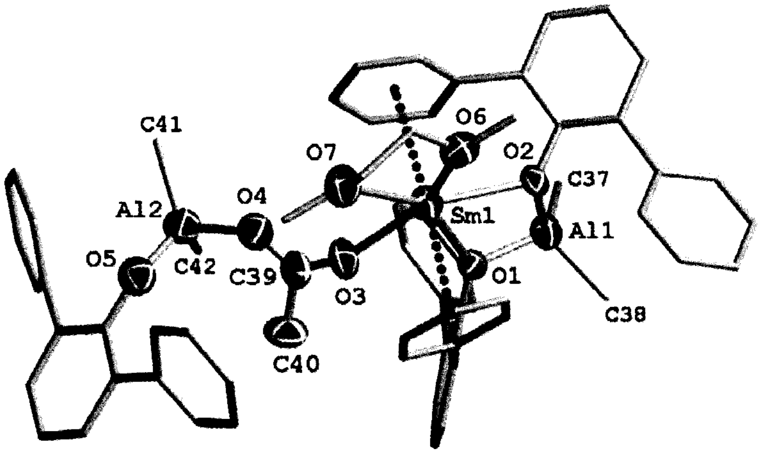


Figure 2.2. Partial thermal ellipsoid diagrams of **2.2** with thermal ellipsoid drawn at the 50% probability level. Hydrogen atoms and thermal ellipsoids of selected carbon atoms are omitted for clarity.

The fifth equatorial position around Sm is occupied by the oxygen atom of one acetate anions [Sm(1)-O(3) = 2.405(7) Å, O(3)-Sm(1)-O(7) = 78.5(2) , O(3)-Sm(1)-O(1) = 75.0(2)] and which in turn bridges an ArOAlMe$_2$ unit [Al(2)-O(4) = 1.827(8) Å] with Al tetrahedrally coordinated [Al(2)-C(41) = 1.960(11) Å, Al(2)-C(42) = 1.948(11) Å, Al(2)-O(5) = 1.761(8) Å, C(41)-Al(2)-C(42) = 117.7(5) , C(41)-Al(2)-O(5) = 110.7(4)]. The two axial positions of the pentagonal by-pyramid centered on samarium are occupied by the centroids of two coordinated phenyl substituents [Sm(1)-centroid(1) = 2.919(9) Å, Sm(1)-centroid(2) = 3.277(9) Å, centroid(1)-Sm(1)-centroid(2) = 175.2(5)] from two different aryloxides. Different from **1**, the two rings are almost parallel to each other, therefore forming a slightly-bent sandwich structure.

3. The structure of complex **2.3** consists of a divalent Sm center coordinated to one bis-aryloxide ligand and located in the center of a slightly distorted trigonal bipyramid (Figure 2.3).

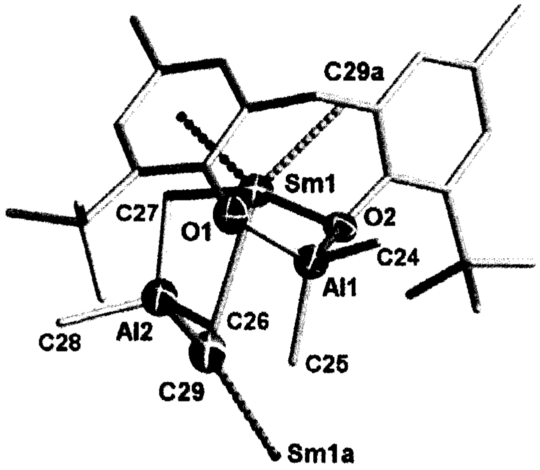


Figure 2.3. Partial thermal ellipsoid diagram of **2.3** with thermal ellipsoid drawn at the 50% probability level. Hydrogen atoms and thermal ellipsoids of selected carbon atoms are omitted for clarity.

One axial position is occupied by one of the two oxygen atoms of the phenoxide ligand [Sm(1)-O(2) = 2.520(3) Å]. The second oxygen atom of the phenoxide is instead bonded to one aluminum atom. Both phenoxide donor atoms chelate one Me$_2$Al residue. The second axial position around samarium contains a methyl group [Sm(1)-C(27) = 2.898(5) Å, C(27)-Sm(1)-O(2) = 160.84(14)] which in turn is bridging an $AlMe_3$ moiety [Al(2)-C(27) = 2.028(5) Å]. The unit is also using a second methyl group to bridge the Sm metal center [Al(2)-C(26) = 2.044(5) Å] by occupying one equatorial position [Sm(1)-C(26) = 2.776(5) Å, O(2)-Sm(2)-C(26) = 89.15(14)]. One of the two methyl groups of Al bridges the samarium center of the next unit [Al(2)-C(29) = 2.018(5) Å, C(29)-Sm(1A) = 2.930(5) Å], thus building a polymeric chain. In turn, a methyl group of another unit is placed in the second equatorial position of the Sm metal center [Sm(1)-C(29)A= 2.930(5) Å, O(2)-Sm(2)-C(29a) = 104.20(14) , C(26)-Sm(2)-C(29a) = 128.77(14)]. The last position of the equatorial plane is occupied by the centroid of the π-bonded phenyl ring of the ligand [Sm(1)-centroid(1) = 2.673(5) Å, centroid(1)-Sm(1)-O(2) = 91.20(14), centroid(1)-Sm(1)-O(2) = 114.06(14)]. Both aluminum metal centers are found in the usual tetrahedral environment has such environment defined by two oxygen atoms of the same bis-aryloxide ligand [Al(1)–O(1) = 1.806(3) Å, Al(1)–O(2) = 1.840(3) Å O(1)–Al(1)-O(2) = 98.21(14)] as well as two terminal methyl groups [Al(1)–C(24) = 1.964(5) Å, Al(1)–C(25) = 1.972(5) Å C(24)–Al(1)–C(25) = 113.8(2) , O(1)-Al(1)-C(24) = 113.8(2)]. The second is surrounded by four methyl groups.

4. The structure of **2.4** shows a monomeric complex consisting of a Sm center surrounded by two diphenoxide ligands and two acetamidates (Figure 2.4). Two AlMe residues are also part of the structure. The Sm center is located in the center of a very distorted octahedron defined by two oxygens, one from each of the two aryloxides, and the four donor atoms of the two acetamidate ligands [Sm(1)–N(1) = 2.702(4) Å, Sm(1)–O(2) = 2.562(3) Å, Sm(1)–O(3) = 2.538(3) Å, O(2)–Sm(1)–O(3) = 60.39(10) , O(3)–Sm(1)–N(1) = 49.40(12)]. One of the fourth equatorial positions is occupied by the oxygen atom of one aryloxide [Sm(1)–O(6) = 2.559(3) Å, O(2)–Sm(1)–O(6) = 127.50(11) , N(1)–Sm(1)–O(6) = 116.49(12)]. Two axial positions contain one oxygen of a second aryloxide [Sm(1)–O(4) = 2.581(3) Å, O(4)–Sm(1)–O(2) = 124.73(10) , O(4)–Sm(1)–N(1) = 111.49(12)] and one nitrogen [Sm(1)–N(2) = 2.651(4) Å, N(2)–Sm(1)–N(1) = 92.17(13) , N(2)–Sm(1)–O(2) = 105.26(12)]. Each of the two tetrahedral Al-Me units is chelated by the two oxygen atoms of one bis-aryloxide ligand. [Al(1)–O(1) = 1.707(3) Å, Al(1)–O(2) = 1.799(3) Å, O(1)–Al(1)–O(2) = 113.41(16)].

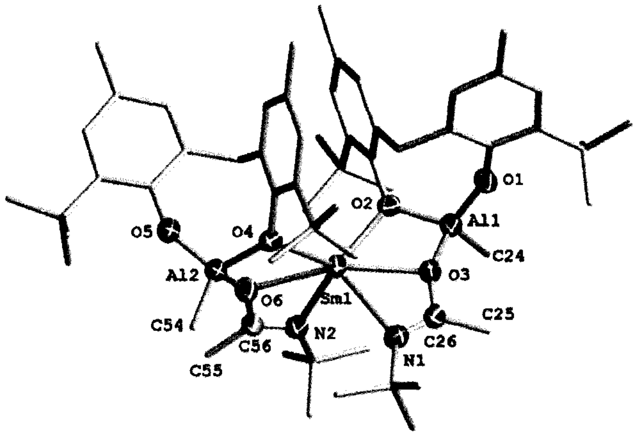


Figure 2.4. Partial thermal ellipsoid diagram of **2.4** with thermal ellipsoid drawn at the 50% probability level. Hydrogen atoms and thermal ellipsoids of selected carbon atoms are omitted for clarity.

The third position contains one oxygen atom of the acetamide ligand [Al(1)–O(3) = 1.787(4) Å, O(1)–Al(1)–O(3) = 111.10(19), O(2)–Al(1)–O(3) = 91.35(16)] and which in turn bridges the Sm metal center [f.ex.: Al(1)–O(3)–Sm(1) = 104.71(15)]. A terminally bonded methyl group [Al(1)–C(24) = 1.947(4) Å, C(24)–Al(1)–O(1) = 111.0(2), C(24)–Al(1)–O(3) = 111.9(2)] completes the coordination sphere of each Al metal center.

5. The structure of **2.5** features a samarium center in a distorted octahedral environment (Figure 2.5). The equatorial plane is defined by the four oxygen atoms of two bis-aryloxide ligands [Sm(1)–O(1) = 2.155(2) Å, Sm(1)–O(2) = 2.450(2) Å, Sm(1)–O(3) = 2.154(2) Å, Sm(1)–O(4) = 2.457(2) Å, O(1)–Sm(1)–O(2) = 104.99(9), O(3)–Sm(1)–O(4) = 104.91(9), O(1)–Sm(1)–O(3) = 111.39(9)]. Two of the four oxygen donor atom, one per each ligand, are bridged to a dimethylaluminum cation [Sm(1)–O(2)–Al(1) = 105.20(11), Sm(1)–O(4)–Al(1) = 104.84(11) Al(1)–O(2) = 1.836(3) Å, Al(1)–O(4) = 1.839(3) Å, O(2)–Al(1)–O(4) = 87.51(12)]. The two axial positions around samarium are occupied by two molecules of THF [Sm(1)–O(5) = 2.480(3) Å, Sm(1)–O(6) = 2.488(3) Å, O(5)–Sm(1)–O(6) = 148.50(9), O(3)–Sm(1)–O(5) = 81.11(9), O(2)–Sm(1)–O(6) = 79.10(9)].

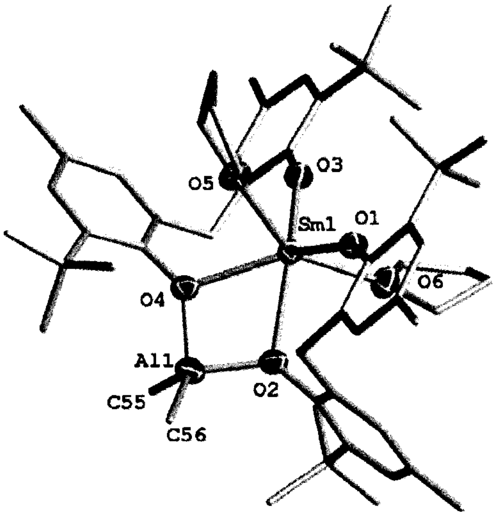


Figure 2.5. Partial thermal ellipsoid diagram of **2.5** with thermal ellipsoid drawn at the 50% probability level. Hydrogen atoms and thermal ellipsoids of selected carbon atoms are omitted for clarity.

The tetrahedral environment of the Al atom is completed by two terminal methyl groups [Al(1)–C(55) = 1.963(5) Å, Al(1)–C(56) = 1.957(5) Å, C(55)–Al(1)–C(56) = 118.7(2), C(55)–Al(1)–O(2) = 119.48(19)].

6. Complex **2.6** is as symmetry generated dimer (Figure 2.6) formed by two identical (bis-aryloxide)-Sm(AlMe$_4$) units and with a trigonal by-pyramidal coordination geometry around each Sm center.

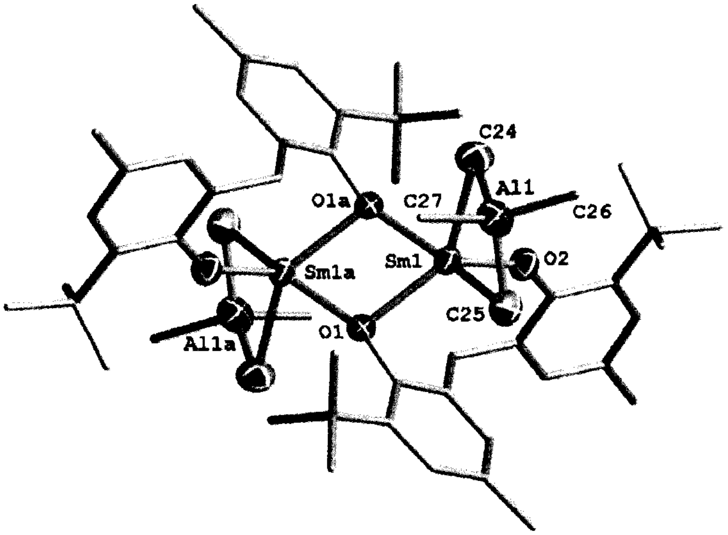


Figure 2.6. Partial thermal ellipsoid diagram of **2.6** with thermal ellipsoid drawn at the 50% probability level. Hydrogen atoms and thermal ellipsoids of selected carbon atoms are omitted for clarity.

The equatorial plane of the bi-pyramid is defined by two oxygen donor atoms of the same bis-aryloxide ligand system [Sm(1)–O(1) = 2.372(2) Å, Sm(1)–O(2) = 2.095(2) Å, O(1)–Sm(1)–O(2) = 117.12(9)]. The third position is occupied by one of the bridging methyl groups [Sm(1)–C(24) = 2.613(3) Å, C(24)–Sm(1)–O(1) = 140.66(10)] of the $AlMe_4$ moiety. One of the two axial positions is occupied by the second bridging methyl group [Sm(1)–C(25) = 2.632(3) Å, C(25)–Sm(1)–O(1) = 106.80(10), C(24)–Sm(1)–C(25) = 79.91(10)] of the same $AlMe_4$ unit. The second axial position around samarium is occupied by the oxygen donor atom of the bis-aryloxide ligand of the second identical monomeric unit [Sm(1)–O(1a) = 2.291(2) Å, O(1a)–Sm(1)–C(25) = 153.95(9), O(1a)–Sm(1)–C(24) = 87.02(10), O(1a)–Sm(1)–O(1) = 70.14(8)]. The two symmetry related oxygen atoms are responsible for the assembly of the dimer [Sm(1)–O(1)–Sm(1a) = 109.86(8)] by forming a planar $(Sm–O)_2$ core.

7. Complex **2.7** consists of a Sm center surrounded by two bis-aryloxide ligand one of each in turn bridging a Me_2Al residue (Figure 2.7).

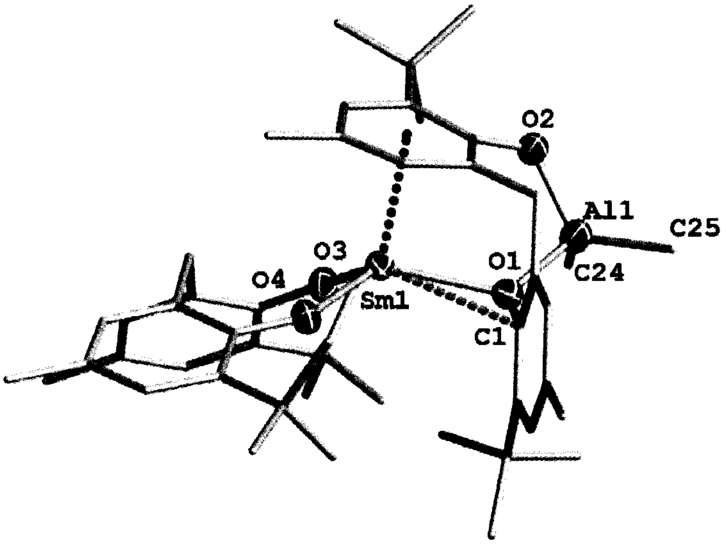


Figure 2.7. Partial thermal ellipsoid diagram of **2.7** with thermal ellipsoid drawn at the 50% probability level. Hydrogen atoms and thermal ellipsoids of selected carbon atoms are omitted for clarity.

The coordination geometry around samarium is an interesting piano-stool type of geometry with the apical position defined by the centroid of one aromatic ring of one of the two aryloxides [Sm(1)–

centroid = 2.607(5) Å, O(1)–Sm(1)–centroid = 90.30(15)]. The basal plane is defined by three oxygen donor atom, two from the same ligand [Sm(1)–O(3) = 2.124(4) Å, Sm(1)–O(4) = 2.092(4) Å, O(3)–Sm(1)–O(4) = 99.03(14) , O(1)–Sm(1)–O(3) = 117.28(12) , O(1)–Sm(1)–O(4) = 134.25(15)] and one only from the second ligand [Sm(1)–O(1) = 2.379(3) Å]. In turn the second oxygen atom of this second ligand bonds the tetrahedral Al residue [Al(1)–O(1)–Sm(1) = 101.66(15)]. Two terminally bonded methyl groups complete the aluminum coordination sphere [Al(1)–C(24) = 1.955(6) Å, Al(1)–C(24) = 1.956(7) Å, C(24)–Al(1)–C(25) = 115.1(3), Al(1)–O(1) = 1.859(4) Å, Al(1)–O(2) = 1.808(4) Å, O(1)–Al(1)–O(2) = 97.05(17) , O(1)–Al(1)–C(24) = 109.8(2) , O(1)–Al(1)–C(25) = 106.4(3)]. It should be also noticed that samarium displays a short contact with one of the carbon atoms of a second phenyl ring [Sm(1)–C(1) = 3.064(5) Å].

Table 2.1. Crystal Data and Data Collection Parameters of Complexes **2.1**, **2.2** and **2.3**

	2.1	**2.2**	**2.3**
Formula	$SmAl_2C_{42}H_{44}O_2$	$SmAl_2C_{65.50}H_{67.50}O_7$	$SmAl_2C_{29}H_{48}O_2$
FW	785.08	1170.00	632.98
Crystal system,	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a, Å	17.068(4)	16.472(4)	14.869(3)
b, Å	13.733(3)	17.573(4)	9.708(2)
c, Å	17.243(4)	22.170(5)	24.985(6)
α, deg	90	90	90
β, deg	113.802(4)	108.900(4)	117.424(3)
γ, deg	90	90	90
Volume, Å^3	3698.0(15)	6071(2)	3201.2(12)
Z	4	4	4
ρ_{calc} g/cm3	1.410	1.280	1.313
μ□ mm^{-1}	1.669	1.046	1.910
F(000)	1600	2414	1304
T range (deg)	1.42 - 28.34	1.75 - 21.96	1.77 - 24.74
Limiting indices (*h*, *k*, *l*)	±22, ±18, ±22	±17, ±18, ±23	±17, ±11, ±29
Reflections collected / unique	44573 / 9158	35076 / 7373	23230 / 5406
R_{int}	0.0437	0.1476	0.0324
GOF	1.039	1.029	1.045
R1 (obs / all)	0.0405 / 0.0472	0.0584 / 0.1288	0.0326 / 0.0483
wR2 (obs / all)	0.0721 / 0.0745	0.1227 / 0.1495	0.0804 / 0.0899

Table 2.1 (cont). Crystal Data and Data Collection Parameters of Complexes **2.4**, **2.5**, **2.6** and **2.7**

	2.4	**2.5**	**2.6**	**2.7**
Formula	$SmAl_2C_{70.50}H_{102}N_2O_6$	$SmAlC_{59}H_{89}O_6$	$Sm_2Al_2C_{54}H_{84}O_4$	$SmAlC_{48}H_{66}O_4$
FW	1277.85	1071.63	1151.87	884.34
Crystal system,	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a, Å	15.920(2)	9.9455(8)	10.716(3)	9.830(2)
b, Å	16.388(3)	13.4452(11)	10.928(3)	23.821(5)
c, Å	16.959(3)	22.0336(17)	13.541(3)	19.168(4)
α, deg	104.202(2)	80.7950(10)	83.106(3)	90
β, deg	107.624(2)	84.0630(10)	74.914(3)	95.280(3)
γ, deg	110.737(2)	83.5720(10)	66.868(3)	90
Volume, Å^3	3622.0(10)	2879.1(4)	1407.8(6)	4469.3(16)
Z	2	2	1	4
ρ_{calc} g/cm3	1.172	1.236	1.359	1.314
μ mm^{-1}	0.882	1.081	2.135	1.374
F(000)	1350	1132	590	1844
T range (deg)	1.45 - 24.81	1.54 - 24.79	2.03 - 24.77	1.37 - 24.78
Limiting indices (*h*, *k*, *l*)	±18, ±19, ±19	±11, ±15, ±25	±12, ±12, ±15	±11, ±28, ±22
Reflections collected / unique	36511 / 12334	29005 / 9810	14107 / 4744	32860 / 7624
R_{int}	0.0377	0.0370	0.0204	0.0377
GOF	1.053	1.048	1.031	1.045
R1 (obs / all)	0.0502 / 0.0654	0.0349 / 0.0458	0.0248 / 0.0278	0.0413 / 0.0581
wR2 (obs / all)	0.1351 / 0.1455	0.0860 / 0.0914	0.0671 / 0.0692	0.1036 / 0.1141

Table 2.2. Selected bonds (Å) and angles (deg) for complexes **2.1**-**2.3**

2.1	**2.2**	**2.3**
Sm(1)-O(1) = 2.496(2) Sm(1)-O(2) = 2.534(2) Sm(1)-C(21) = 2.811(3) Sm(1)-C(42) = 2.827(3) Sm(1)-C(28) = 2.910(3) Sm(1)-C(7) = 2.940(3) Sm(1)-C(8) = 3.030(3) Sm(1)-C(29) = 3.051(3) O(1)-Sm(1)-O(2) = 115.04(7) O(1)-Sm(1)-C(21) = 67.96(8) O(2)-Sm(1)-C(21) = 165.62(8) O(1)-Sm(1)-C(42) = 78.62(8) O(2)-Sm(1)-C(42) = 67.73(8) C(21)-Sm(1)-C(42) = 100.19(10) C(1)-O(1)-Sm(1) = 121.92(16) Al(1)-O(1)-Sm(1) = 102.25(9) C(22)-O(2)-Al(2) = 142.34(18) C(22)-O(2)-Sm(1) = 117.86(16) Al(2)-O(2)-Sm(1) = 98.35(9)	Sm(1)-O(3) = 2.405(7) Sm(1)-O(1) = 2.558(6) Sm(1)-O(2) = 2.603(6) Sm(1)-O(7) = 2.623(6) Sm(1)-O(6) = 2.667(6) Sm(1)-C(32) = 3.035(10) Sm(1)-C(31) = 3.061(9) Sm(1)-Al(1) = 3.532(3) O(3)-Sm(1)-O(1) = 75.0(2) O(3)-Sm(1)-O(2) = 133.5(2) O(1)-Sm(1)-O(2) = 60.02(17) O(3)-Sm(1)-O(7) = 78.5(2) O(1)-Sm(1)-O(7) = 151.0(2) O(2)-Sm(1)-O(7) = 147.90(19) O(3)-Sm(1)-O(6) = 140.7(2) O(1)-Sm(1)-O(6) = 139.4(2) O(2)-Sm(1)-O(6) = 85.4(2) O(7)-Sm(1)-O(6) = 63.1(2) O(3)-Sm(1)-Al(1) = 103.93(17) O(1)-Sm(1)-Al(1) = 29.91(14) O(2)-Sm(1)-Al(1) = 30.17(12) O(7)-Sm(1)-Al(1) = 175.15(16) O(6)-Sm(1)-Al(1) = 113.79(17)	Sm(1)-O(2) = 2.520(3) Sm(1)-C(6) = 2.855(4) Sm(1)-C(5) = 2.926(4) Sm(1)-C(29a) 2.930(5) Sm(1)-C(1) = 2.932(4) Sm(1)-C(13) = 3.003(4) Sm(1)-C(4) = 3.055(5) Sm(1)-Al(2) = 3.3673(15) Sm(1b) -C(29) = 2.930(5) O(2)-Sm(1)-C(29A) 104.20(12) C(6)-Sm(1)-C(29A) = 104.46(14) C(5)-Sm(1)-C(29A) 87.38(14) O(2)-Sm(1)-Al(2) = 125.92(7) C(6)-Sm(1)-Al(2) = 140.91(9) C(5)-Sm(1)-Al(2) = 132.23(10) C(29A)-Sm(1)-Al(2) = 106.53(11) Al(1)-O(2)-Sm(1) = 122.30(15) Al(2)-C(29)-Sm(1)B 167.4(3)

Table 2.2 (cont). Selected bonds (Å) and angles (deg) for complexes **2.4** and **2.5**

2.4	**2.5**
Sm(1)-O(3) = 2.538(3) Sm(1)-O(6) = 2.559(3) Sm(1)-O(2) = 2.562(3) Sm(1)-O(4) = 2.581(3) Sm(1)-N(2) = 2.651(4) Sm(1)-N(1) = 2.702(4) Sm(1)-C(56) = 3.058(5) Sm(1)-Al(1) = 3.4555(15) Sm(1)-Al(2) = 3.4645(15) O(3)-Sm(1)-O(6) = 161.24(11) O(3)-Sm(1)-O(2) = 60.39(10) O(3)-Sm(1)-O(4) = 132.65(11) O(2)-Sm(1)-O(4) = 124.73(10) O(6)-Sm(1)-N(2) = 49.88(12) O(3)-Sm(1)-N(1) = 49.40(12) O(6)-Sm(1)-N(1) = 116.49(12) N(2)-Sm(1)-N(1) = 92.17(13)	Sm(1)-O(1) = 2.155(2) Sm(1)-O(3) = 2.154(2) Sm(1)-O(2) = 2.450(2) Sm(1)-O(4) = 2.457(2) Sm(1)-O(5) = 2.480(3) Sm(1)-O(6) = 2.488(3) O(1)-Sm(1)-O(3) = 111.39(9) O(1)-Sm(1)-O(2) = 104.99(9) O(3)-Sm(1)-O(2) = 135.03(9) O(1)-Sm(1)-O(4) = 134.84(9) O(3)-Sm(1)-O(4) = 104.91(9) O(2)-Sm(1)-O(4) = 62.38(8) O(1)-Sm(1)-O(5) = 81.04(9) O(3)-Sm(1)-O(5) = 81.11(9) O(2)-Sm(1)-O(5) = 131.04(9) O(4)-Sm(1)-O(5) = 78.92(9) O(1)-Sm(1)-O(6) = 81.90(9) O(3)-Sm(1)-O(6) = 80.76(9) O(2)-Sm(1)-O(6) = 79.10(9)

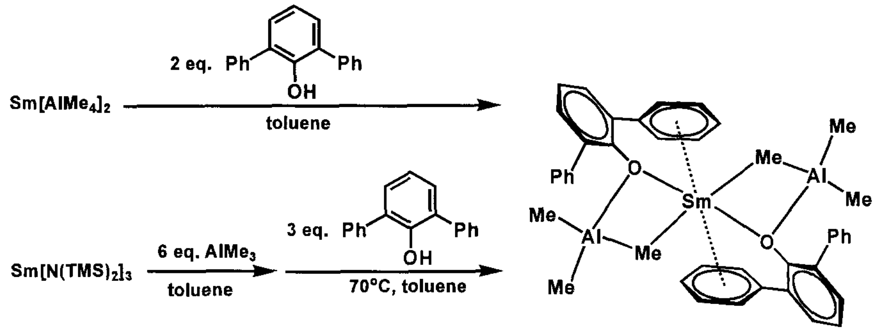
	O(4)-Sm(1)-O(6) = 130.80(9)
	O(5)-Sm(1)-O(6) = 148.50(9)

Table 2.2 (cont). Selected bonds (Å) and angles (deg) for complexes **2.6** and **2.7**

2.6	**2.7**
Sm(1)-O(2A) = 2.095(2) Sm(1)-O(1) = 2.291(2) Sm(1)-O(1A) = 2.372(2) Sm(1)-C(1A) = 2.802(3) Sm(1)-C(6A) = 3.047(3) Sm(1)-Sm(1A) = 3.8172(8)	Sm(1)-O(4) = 2.092(4) Sm(1)-O(3) = 2.124(4) Sm(1)-O(1) = 2.379(3) Sm(1)-C(18) = 2.873(5) Sm(1)-C(13) = 2.901(5) Sm(1)-C(14) = 2.945(5) Sm(1)-C(15) = 2.998(5) Sm(1)-C(16) = 3.012(5) Sm(1)-C(17) = 3.018(5) Sm(1)-C(1) = 3.064(5)
O(2A)-Sm(1)-O(1) = 107.74(9) O(2A)-Sm(1)-O(1A) = 117.12(9) O(1)-Sm(1)-O(1A) = 70.14(9) O(2A)-Sm(1)-C(1A) = 101.24(9) O(1)-Sm(1)-C(1A) = 98.61(8) O(1A)-Sm(1)-C(1A) = 29.63(8) O(2A)-Sm(1)-C(6A) = 73.76(9) O(1)-Sm(1)-C(6A) = 106.69(8) O(1A)-Sm(1)-C(6A) = 50.39(8) C(1A)-Sm(1)-C(6A) = 27.48(9) O(2A)-Sm(1)-Sm(1A) = 117.79(7) O(1)-Sm(1)-Sm(1A) = 35.77(5)	O(4)-Sm(1)-O(3) = 99.03(14) O(4)-Sm(1)-O(1) = 120.94(13) O(3)-Sm(1)-O(1) = 117.28(12) O(4)-Sm(1)-C(1) = 96.16(14) O(3)-Sm(1)-C(1) = 135.28(13) O(1)-Sm(1)-C(1) = 25.97(12) C(1)-O(1)-Sm(1) = 105.6(3) Al(1)-O(1)-Sm(1) = 121.40(17)

Results and Discussion

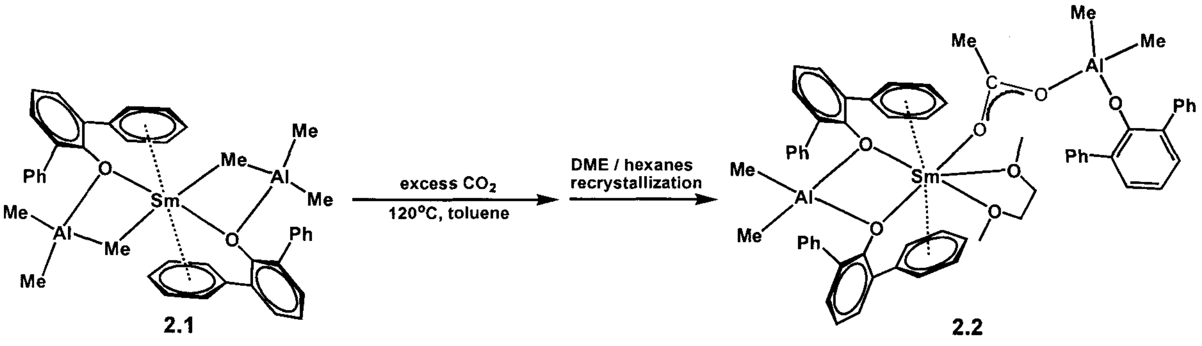
Following the strategy ingeniously designed by Evans$^{21b, 22}$ and Anwander,$^{16, 23}$ we have used the divalent Sm[AlMe$_4$]$_2$ and the *in situ* generated trivalent Sm[AlMe$_4$]$_3$ (obtained by reacting Sm[N(TMS)$_2$]$_3$ with 6 equivalents of Me$_3$Al in toluene)^{21a} as starting materials to be reacted with 2,6-Ph$_2$(C$_6$H$_4$)OH. The reaction in toluene was accompanied by vigorous gas evolution and significant color change. After suitable work-up, the divalent Sm[(μ-2,6-bis-phenyl-phenol)]$_2$[(μ-Me)(AlMe$_2$)]$_2$ (**1**) was obtained in high yield and crystalline form from either reaction, in disregard of the different metal oxidation state of the starting material (Scheme 2.1).



2.1

Scheme 2.1.

Anwander has previously proposed that complex **2.1** may be prepared via abstraction of THF by strong Lewis acid on the appropriate Sm complex.^{15b} The utilization of Sm-aluminate as a starting material reported here resulted in a transformation facilitating crystallization. Complex **2.1** is thermally robust and, in spite of the presence of Sm-C bonds and the expected labile sandwich structure, does not display single-component catalytic activity with ethylene even under harsh reaction conditions. The use of a variety of alkyl aluminum reagents as possible activators did not modify the outcome. This inertness was not anticipated and to further probe the reactivity of the Sm-C bond in this divalent organo-samarium complex, we have carried out the reaction of **2.1** with CO$_2$ aiming at: 1) assessing the ability of the Sm-C bond to insert CO$_2$ and 2) to probe the reducing power of the divalent center towards possible CO$_2$ reductive coupling.^{7} Upon exposure of a toluene solution of **2.1** to carbon dioxide only a slight color change was observed. Room temperature reactions required several hours for completion. Unfortunately, all crystallization attempts from non-coordinating solvents failed to yield crystalline material suitable for single crystal x-ray structure determination. Only upon layering a DME solution with hexanes it was possible to obtain complex **2.2** in crystalline form (Scheme 2.2, Figure 2.2).



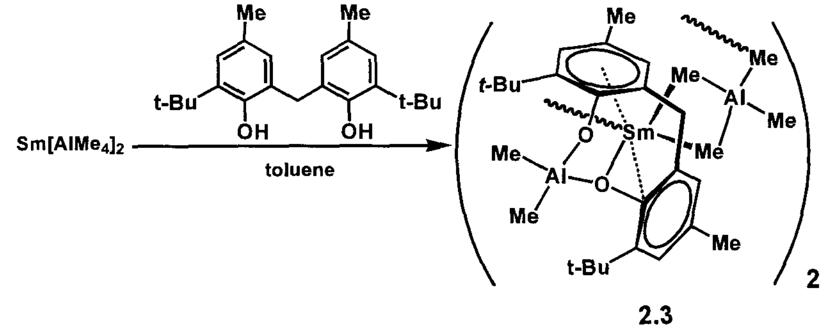
Scheme 2.2.

The structure of **2.2** has three significant features. Firstly, the divalent state of the Sm metal center has been preserved. The complex appears as generated by the simple insertion of CO_2 into the Sm-CH_3-Al unit. We found this behavior remarkable, given that to the best of our knowledge, substrate reduction and metal oxidation is the *leitmotif* of the reactivity of divalent samarium. In addition, CO_2 is well established to be an easy target for both one- and two-electron reduction reactions.[1e, 7, 20] Thus the failure of **2.1** to engage in a red-ox transformation with CO_2 is surprising and speaks for a very substantial decrease of the reduction potential of the Sm center with this ligand environment. Secondly, the presence of a third aryloxide on the acetate-bridged alane residue indicates that also ligand scrambling occurred during the insertion reaction. Unfortunately, we have not been able to isolate any other species from the reaction mixture, despite numerous attempts of fractional crystallization. Finally, the π-bonding mode of the two phenyl rings has been preserved in spite of the treatment with coordinating ethereal solvent.

Despite the presence of the paramagnetic Sm(II) metal center, the ^1H-NMR spectrum of **2.2** displays recognizable spectral features. A complex series of peaks is present in the aromatic region and which may be tentatively explained with the presence of two non-equivalent bis-phenyl phenol ligands in the ratio 1:2. Three peaks with relative intensities of 10:1:2 protons were attributed to the remote aluminum-phenoxide moiety. The resonance at 7.50 integrates for 10 protons and could be assigned to the two phenyl substituents attached to the central phenoxide ring. The other two peaks are generated by the *meta-* and *para*-protons of the central ring. This assumption is also confirmed by the multiplicity of these resonances with the doublet at 7.15 and the triplet at 7.36 integrating for two and one protons respectively. The two other phenoxide ligands are coordinated directly to the Sm(II) metal center and, as a result, reveal a more complicated pattern. Similar to the first aryloxide moiety though, the *meta-* and *para-* protons of the central phenoxide ring shows one triplet at 7.45 ppm coupled to a doublet at 6.96 and integrating for two and four protons respectively. The ortho-phenyl groups are magnetically non-equivalent as a possible result of the strong π-interaction of two phenyl rings with the Sm metal center. The coordinated phenyl substituents exhibit two slightly broadened signals at 7.74 and 7.75 ppm with intensity of three protons, each tentatively assigned to *ortho-* and *para*-protons. The two *meta*-protons on each of the two rings provide resonances at 7.04 and 6.94 ppm with the integration of two protons each. The other two resonances at 6.42 ppm and 6.18 ppm integrated for six and four protons and are assigned to two non-interacting rings of the ligands. Three protons of the bridging acetate unit are responsible for the appearance of broad signal at 3.48 ppm with the expected intensity. All the remaining resonances could be assigned to the methyl groups bonded to two different Al atoms. A strong singlet at -0.22 ppm integrated for 6 protons and represents two methyl groups of the $AlMe_2$ moiety separated from samarium by the acetate. The two remaining methyl groups appear to be magnetically different providing two resonances at 2.05 and 2.08 ppm with relative intensities of three protons each and are assigned to the second Me_2Al unit chelated by the two bridging aryloxides.

The spectral features suggest that the partial π-interaction of the Sm metal center with the phenyl rings is retained in solution. Altogether, these characteristics speak for the stability of this complex. It is conceivable that this seemingly strong interaction prevents the low-valent metal center from reducing a substrate such as CO_2. It may also explain the lack of reactivity with ethylene.

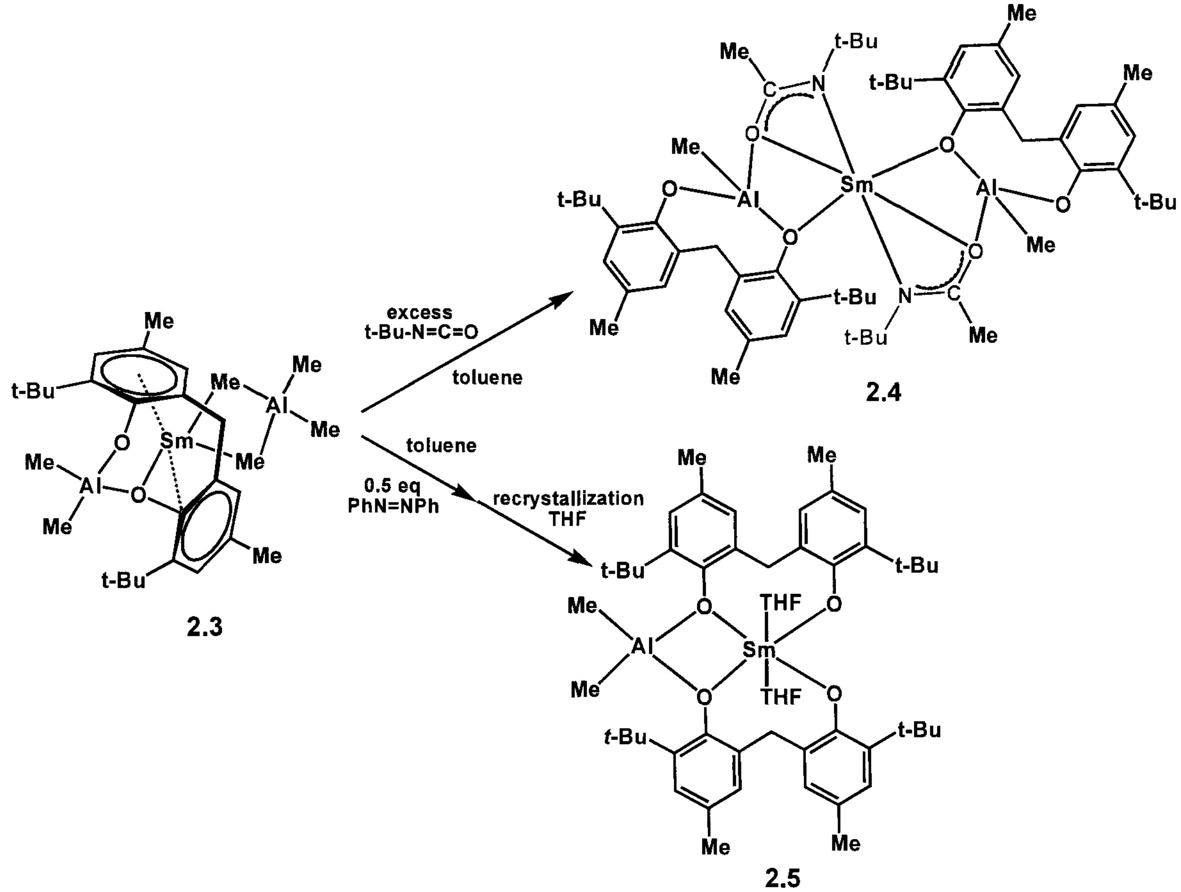
With the deliberate purpose of preventing or minimizing ligand scrambling, reactions the bidentate 6,6'-methylene-bis-(2-*tert*-butyl-4-methylphenol) was used for similar reactions. The presence of the bulky *t*-Bu groups in the proximity of the donor oxygen atom was expected to inhibit π-bonding to some extent, thus introducing some lability in the complexes. The same reactions leading to **2.1** and under identical reaction conditions afforded in this case also vigorous gas evolution and color change upon mixing. Dark-red crystalline solid was obtained directly from the mother liquor and the formulation of the new species as catena-(Sm{μ-η6'-[6,6'-methylene-bis-(2-*tert*-butyl-4-methyl-phenoxy)][$AlMe_2$]}{μ-Me}$_2${AlMe})(μ-Me) (**2.3**) was revealed by an X-ray crystal structure (Scheme 2.3).



2.3

Scheme 2.3.

In line with the behavior of **2.1**, complex **2.3** also appears to be unreactive towards ethylene with or without the presence of additional activators. We find this behavior even more puzzling since it is conceivable that the simple dissolution process would result in cleavage of the polymeric structure with consequent liberation of coordination sites around the Sm metal center. Unfortunately, the NMR spectra were uninformative in this case consisting of a series of sharp resonances overlapping with several broad signals which prevented an unequivocal interpretation. In order to evaluate the possibility of insertion versus oxidation of the samarium center, compound **2.3** was reacted with several cumulenes. All reaction mixtures were characterized by the formation of very dark colors indicating that the original oxidation state of Sm(II) was again being preserved. Crystallization attempts did not produce suitable crystals in any case with the only exception of the reaction with *tert*-butyl-isocyanate (Scheme 2.4) and with which it was possible to obtain a highly crystalline product in good yield.



Scheme 2.4.

The formation of **2.4** indicated that complex **2.3** behaved in a manner similar to the reaction of **2.1** with CO_2. Firstly the divalent oxidation state was preserved and neither reductive coupling, nor deoxygenation was observed. Secondly, the formulation of **2.4** clearly implies ligand redistribution given that one additional bis-aryloxide has been acquired by Sm during the transformation. Two ancillary Al atoms remained as part of the structure forming a bridge between bis-aryloxide moiety and newly-formed amido-residue. Overall, this process could be regarded as a simple insertion of a cumulene into a Sm-C-Al array. Such process could proceed through two different pathways. The first possibility requires a cleavage of Al-C bond with formation of terminal Sm-Me residue, followed by insertion of iso-cyanate and re-coordination of the transformed fragment to Al metal center. A second viable option would be assuming the formation of terminal Al-Me moiety accompanied by cleavage of the Me-Sm contact. In this event, the insertion would proceed at the Al center with formation of a much expected Al-amidate fragment. Subsequent re-coordination to the Sm metal center would not further affect the oxidation state of Sm(II).

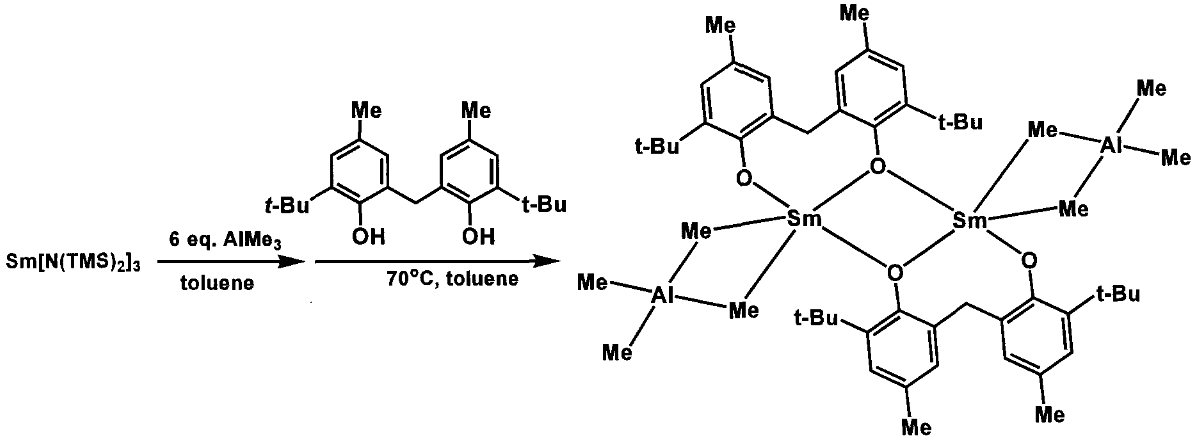
In order to evaluate the stability of Sm(II) toward re-oxidation, the slightly stronger oxidizing agent (azobenzene) was employed. Addition of this reagent to the solution of **2.3** resulted in instant discoloration with formation of a new trivalent species, formulated as Sm{μ-[6,6'-methylene-bis-(2-*tert*-butyl-4-methyl-phenol)]$_2$-μ-AlMe$_2$}{THF}$_2${C$_6$ H$_{14}$}$_{0.5}$ (**2.5**) (Scheme 2.4). In this complex the trivalent metal center is surrounded by two bis-aryloxide ligands. One dimethyl-aluminum unit remains coordinated to Sm-ligands core through coordination to the oxygen atoms of two ligand moeties. Unfortunately, the crystallization required the use of THF and therefore the crystal structure not necessarily reflects the product of the reaction. In addition, the products of azobenzene reduction, as well as fate of several Al-(Me)$_x$ units remain unaccounted for. It is also obvious, from the final product formulation, that ligand migration took place during the transformation, the fate of the second Sm atom which has lost the ligand system also remaining unclear.

The 1H-NMR solution data for **2.5** were consistent with the solid state structure. The largest resonance at 1.36 ppm integrated for 36 protons and could be unmistakably assigned to the *t*-butyl substituents on the phenyl rings of the ligands. Due to the retention of the AlMe$_2$ unit, both ligands have two rings in a magnetically non-equivalent environment as indicated by the slight difference of the aromatic signal locations. Two slightly broadened resonances at 6.94 and 6.79 ppm (4H each) are assigned to the Ar-H protons. The same non-equivalency also causes the splitting of the Ar-CH$_3$ resonances resulting in the appearance of two separate singlets at 2.16 ppm and 2.03 ppm (6H each). The most unusual feature consists of the substantial anisotropy of the two protons of the bridging -CH$_2$-

unit. These two hydrogen atoms display considerably different chemical shifts (3.25 and 4.02 ppm). Finally, the two methyl groups of the $AlMe_2$ unit produce two slightly separated sharp signals at -0.31 ppm and -0.68 ppm with the expected intensity.

As expected, complex **2.5** did not display catalytic activity as a single-component catalyst. Only negligible activity was observed under usual Ziegler-Natta catalytic condition, when several alkyl aluminum reagents were employed as activators. On the other hand, the presence of molecules of THF in the metal coordination sphere quite possibly is responsible for the quenching of the reactivity.

With all this information in hands, the preparation of a heterometallic, trivalent, samarium/aluminate bis-aryloxide complex has been attempted in a non-coordinating environment. The choice of the trivalent state was advised by the seemingly systematic failure of these divalent derivatives to react with ethylene. This failure is in sharp contrast with the behavior of the cyclopentadienyl samarium derivatives which act as a polymerization catalyst both as divalent[2n, 6f, 8] and trivalent species,[1u, 2a, n, 6f, 8a, e-h, j, 10] and speaks for a substantial decrease of the reducing power of the divalent center in the presence of oxygen-donor based ligands together with the strong Lewis acidic fragments.



2.6

Scheme 2.6.

In addition, the aryloxides also are versatile ligands to support ethylene polymerization catalysts with a number of early metals.[2a, 24] For this reason, we have reacted $Sm[N(TMS)_2]_3$ with 2,2'-methylene-bis-

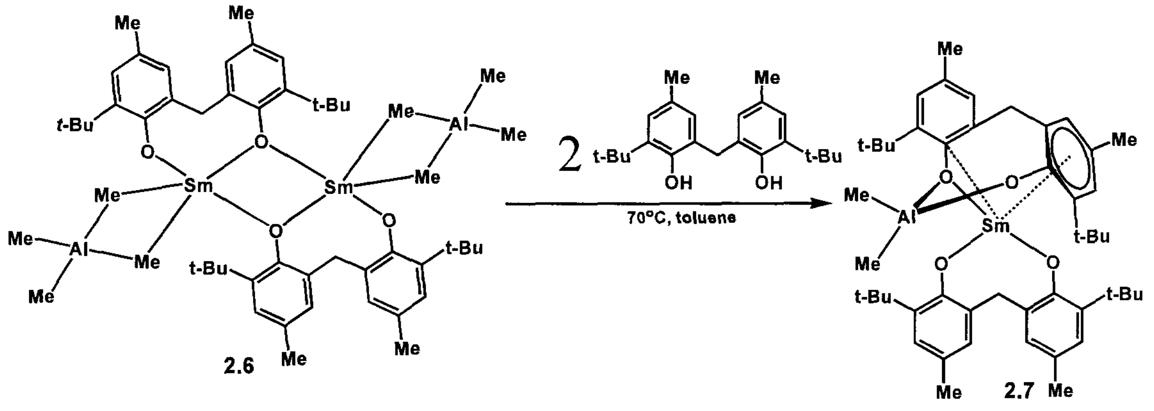
(6-*tert*-butyl-4-methylphenol) in the presence of $AlMe_3$ following the same procedure used for **2.1**. The new trivalent peralkylated complex **2.6** was thus conveniently prepared in a one pot-synthesis. Recrystallization from hot toluene, afforded **2.6** in reasonable yield of well-formed, extremely air-sensitive crystals (Scheme 2.6).

Complex **2.6** has considerably low solubility in non coordinating solvents at room temperature and only limited thermal stability, with some darkening of the color appearing at 110 C. Although no tractable material was obtained from extended thermolysis in this case, it is not unreasonable to expect that the thermolysis leads to Sm(II) species. The ^1H-NMR spectrum of **2.6** was recorded at moderate temperature (40^{0}C) to maximize solubility. The two strongest resonances at 1.06 ppm and 0.44 ppm and accounting for 9 protons each are attributed to two magnetically non-equivalent *t*-butyl groups. The two methyl substituents on the phenyl rings also exhibit different chemical shifts as two singlets at 2.71 ppm and 2.28 ppm with the expected intensity. Similarly to complex **5**, two protons of the methylene bridge between two phenyl rings appear as two separate doublets (J=3.67 Hz) at 3.61 ppm (1 proton) and 4.22 ppm (1 proton). The aromatic region contains only two peaks with intensities of 2 protons each at 7.15 ppm and 7.27 ppm. Finally, the methyl groups of the aluminate unit appear as two broadened singlets at -3.96 ppm and -1.88 ppm.

Compound **2.6** polymerizes ethylene at room temperature and atmospheric pressure as a *single-component catalyst.* The catalytic activity sharply increased (450 $kg*mol^{-1}*h^{-1}$) at 70°C and under ethylene pressure (600 psi). In all the runs, the GPC of the samples of PE produced by this single-component catalyst revealed the polymer to be broadly dispersed UHMWPE (M_w = 3,342,906, PD = 21.8).

The single-component catalytic activity of **2.6** observed under mild polymerization conditions suggests the importance of a pre-built Sm-C-Al function in combination with steric accessibility to the Sm(III) metal center for the appearance of catalytic performances.

We were in fact questioning whether a more secluded samarium center with the same functions and ligand system may or not display catalytic activity. For this purpose we have treated original samarium dimeric compound **2.6** with a two additional equivalents of bis-phenol ligand. The reaction proceeded with intense gas evolution and a new complex **2.7** was isolated with excellent yield.



Scheme 2.7.

The structure of **2.7** (Figure 2.7) basically shows a mononuclear complex where the samarium center was surrounded by two ligands in turn retaining one $AlMe_2$ unit by bridging two oxygen donor atoms of one of the two ligands. The structure of **2.7** also shows the re-appearance of the η^6- bonding of one of the phenyl rings, similar to those occurring in **2.3** and **2.1**. This feature indicates to us that unlikely this species may be a single-component catalyst considering that lability necessary to provide a vacant coordination sites may be significantly decreased in this system. Accordingly, complex **2.7** was not a single-component catalyst for ethylene polymerization even under considerable forcing of the reaction conditions.

Conclusions

Peralkylated heterometallic Al/Sm complexes when isolated or generated *in situ* can be used as a starting materials for proton-transfer ligand-exchange reactions. In this work we have investigated in detail these transformations with two mono- and bidentate aryloxides. The isolated complexes display a common tendency towards π-bonding to Sm metal center as well as a surprising inertness of the divalent state. Reactions with cumulene led to the formation of insertion products with no evidence for the occurrence of reductive couplings. A Sm(III) compound was obtained only with the chelating bis-aryloxide ligand. This species displayed substantial catalytic activity for ethylene polymerization without need for additional activation. This compound appears to be the first non-cyclopentadienyl single-component ethylene polymerization catalyst. The reappearance in the ligand scaffold of a *π*-interaction with samarium, as when a second ligand system was introduced, obliterated the catalytic activity.

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Chapter Three

Unusual Reactivity of a Tm-pyrrolide/aluminate Complex with a Metallocene-type of Motif.

Formation of Alumo-methylene and Trapping of a SiH_3 Unit.

Introduction

A characteristic of the chemistry of lanthanides is the ubiquitous use of the cyclopentadienyl ligands and derivatives.[1] While in combination with this established family of ligands, these elements have provided remarkable catalytic processes[1, 2,3h] as well as some of the most diversified and unpredictable chemical reactivity ever observed.[3] Naturally, this outstanding behavior has justified continuing attempts to probe alternative ligand systems.[1w, 4] However, despite of continuous efforts the alternative ligands seem incapable of matching the wealth of reactivity observed with the Cp counterparts. On this line, in the past we have used pyrrole-based poly-anions to support low-valent samarium. It was apparent that these ligands may enhance even further the already high reactivity of low-valent lanthanides and actinides. This at least has been the case with tetra-[5] and dipyrrolide poly-anions.[6] Interesting feature of these ligands is the simultaneous adoption of the σ- and π-bonding modes readily assembling polymetallic structures.[6b,6c,7,8]

With the aim at expanding the use of these pyrrolide-anions towards possible formation of lanthanide-based catalytic systems, we have recently embarked on a research project to develop the chemistry of tri-valent *f*-block elements with ligand systems resulting from the combination of pyrrolide anions and Lewis acids. The idea was based on the recent observation that a divalent vanadocene type of complex of the pyrrolide ligand was obtained when a strong Lewis acid such as an aluminate residue was coordinated to the pyrrolide N-atom sp^2 orbital.[9] The coordination of the aluminate causes σ/π oscillation of the ligand systems and alkyl shuttling between Al and the metal center. In this process, the donor ability of the π-system was weakened eventually leading to ligand dissociation and formation of empty coordination sites and of organometallic functions. The work of Evans has indicated that *f*-block elements with the $M(Cp^*)_3$ [M = Ln,[1z, 3e, 10] An[11]] type of structure also posses σ/π oscillation. [11b] In turn this is at the basis of the unusual reactivity of these systems. We have now pursued attempts to prepare complexes of *f*-block elements having the same structural motif but using instead aluminate pyrrolide anions. We were interested to probe whether the established hemilability of these ligands[9] in combination with the presence of reducing alkyl functions could provide even more reactive organometallic systems.

In this paper, we describe an attempt to prepare an (aluminate-pyrrolide)$_3$Tm species and which resulted in the formation of a terminally bonded CH_3-Tm complex with the *ansa*-metallocene structural motif and a bridging methylene group between Tm and two aluminate moieties. The behavior of this species with H_2 and $PhSiH_3$ was also examined.

Experimental Part

All operations were performed under inert atmosphere using standard Schlenk type techniques or with the use of nitrogen filled drybox. H_2 gas (5.0 UH grade) was purchased from BOC Gases and used as received. $PhSiH_3$ (95% purity) was purchased from Alfa Aesar, dried by over molecular sieves (4A) and then used without any additional purification. 2,3,4,5-tetramethylpyrrole was prepared according to a slight modification[12] of published procedure.[13] Tm(1,1,1,3,3,3-hexamethyl disilazanato)$_3$[14] was prepared according to the published procedure and recrystallized from cold hexane. NMR spectra were recorded at 293K on Varian Inova 500 MHz spectrometer. Chemical shifts were referenced to internal solvent resonances and reported in parts per million relative to Me_4Si. All solvents were dried by passing through Al_2O_3 filled columns and degassed prior to use. Elemental analyses were performed on Perkin-Elmer 2400 CHN analyzer. Data for X-ray single crystal structure determination were collected with a Brucker diffractometer equipped with 1K SMART CCD area detector.

Preparation of Tm(Me){μ-CH_2-[$AlMe_2(Me_4C_4N)]_2$} (3.1)

$Tm(NSi_2C_6H_{18})_3$ (0.214 g, 0.33 mmol) was solubilized in 10 mL of toluene. A solution of $Al(CH_3)_3$ (2.0 M) in toluene (1 mL, 2 mmol) was added dropwise and the resulting mixture stirred at room temperature for 30 min. A solution of 2,3,4,5-tetramethylpyrrole $C_8H_{12}NH$ (0.123g, 1.00 mmol) in 5 mL of toluene was added under vigorous stirring. After the initial gas evolution was completed, the reaction mixture has been stirred for an additional 4 hours. Then volume was reduced to about 3 mL. Light-yellow powder started to precipitate in 30 min. The suspension was heated to the boiling point. Small amount of toluene was added dropwise to the boiling solution to insure the complete solubilization of the powdery material. The clear solution was allowed to cool down to room temperature. Upon cooling large lemon-yellow prisms of (**3.1**) separated, which were washed with cold hexane and dried *in vacuo* (0.135 g, 0.24 mmol, 73%). El. Anal. Calcd. (Found) for $TmAl_2C_{22}H_{40}N_2$: C 47.48(47.43), H 7.43(7.29), N 5.03(5.49). ^{1}H-NMR (500 MHz, C_7D_8, 25°C) δ = -471.5 (s, 2H, CH_2), -165.3 (s, 3H, $AlCH_3$), -66.6 (s, 3H, $AlCH_3$), -25.7 (s, 3H, $PyrCH_3$), 0.4 (s, 1H, $TmCH_3$), 1.0 (s, 1H, $TmCH_3$), 1.3 (s, 1H, $TmCH_3$), 5.3 (3H $PyrCH_3$), 68.0 (3H, $PyrCH_3$), 176.3 (3H, $PyrCH_3$).

Preparation of Tm(μ-$AlMe_2$-$(Me_4C_4N)_2$)(μ'-Me-$AlMe_2$)(μ_3-CH_2)$AlMe_3$ (3.2)

A solution of **3.1** (0.253 g, 0.46 mmol) in toluene (60 mL) was placed in a high-pressure Parr reactor and pressurized with H_2 gas (650 psi) at room temperature. After 48 hours, the reactor was depressurized and the volume of the resulting solution reduced to about 10 mL *in vacuo*. *n*-Heptane (10mL) was added to the reaction mixture and the resulting dark-yellow solution was allowed to stand at -37°C for two days upon which, pale yellow prisms of **3.2** (0.115 g, 0.18 mmol, 39.1%) separated. The crystals were washed with cold hexane (-37°C) and dried under nitrogen atmosphere. El. Anal. Calcd. (Found) for $TmAl_3C_{25}H_{52}N_2$: C 47.62(47.58), H 8.31(8.23), N 4.44(4.49). ^{1}H NMR (500 MHz, C_7D_8, 25°C) δ = 4.83 (s, 3H, Pyr-**CH$_3$**), 4.63 (s, 6H, Pyr$_2$-Al-**CH$_3$**), 4.27 (s, 3H, Pyr-**CH$_3$**), 3.97 (s, 6H, Al-**CH$_3$**), 3.90 (s, 3H, Al-**CH$_3$**-Tm), 3.67 (s, 3H, Pyr-**CH$_3$**), 3.33 (s, 3H, Pyr-**CH$_3$**), 3.01 (s, 3H, Pyr-**CH$_3$**), 2.74 (s, 9H, Al-**CH$_3$**), 2.29 (s, 3H, Pyr-**CH$_3$**), 2.05 (s, 3H, Pyr-**CH$_3$**), 1.64 (s, 3H, Pyr-**CH$_3$**), 1.99 (br. s, 1H, **CH$_2$**), -0.87 (br. s, 1H, **CH$_2$**).

Preparation of $Tm[\mu\text{-}AlMe_2\text{-}(Me_4C_4N)_2](AlMe_3)(\mu_3\text{-}CH_2)(\mu_3\text{-}SiH_3)(AlMe_2)[AlMe_2\text{-}(Me_4C_4N)]$ (3.3)

Complex **3.1** (0.125 g, 0.23 mmol) was solubilized in 10 mL of toluene and neat $H_3SiC_6H_5$ (0.050 g, 0.45 mmol) was added dropwise under stirring. The solution was stirred at room temperature for 6 hours. The volume of the reaction mixture was then reduced to 3. 5 mL and heated to the boiling point. Small amount of toluene was added drop wise to ensure complete solubilization of the solid precipitated during the previous evaporation. After 12 more hours pale yellow prisms of **3.3** (0.076 g, 0.092 mmol, 40%) separated which were washed with cold hexane and dried *in vacuo*. El. Anal. Calcd. (Found) for $TmAl_4C_{34}H_{68}N_3Si$: C 49.57(49. 73), H 8.32(8. 03), N 5.10(5. 08). ^{1}H NMR (500 MHz, C_7D_8, 25°C) δ = 7.43 (s, 3H, Al-**CH$_3$**), 7.29 (s, 3H, Al-**CH$_3$**), 7.20 (s, 12H, Pyrrole-**CH$_3$**), 7.08 (s, 3H, Al-**CH$_3$**), 6.96 (s, 3H, Al-**CH$_3$**), 4.64 (s, 6H, Al-**CH$_3$**), 3.29 (br. s, 1H, -**SiH$_3$**), 2.87 (br. s, 1H, -**SiH$_3$**), 2.33 (br. s, 1H, -**SiH$_3$**), 2.17 (s, 12H, Pyrrole-**CH$_3$**), 2.03 (s, 12H, Pyrrole-**CH$_3$**), 1.43 (br.s, 1H, -**CH$_2$**), 0.50 (br.s, 1H, -**CH$_2$**), 0.17 (s, 3H, Al-**CH$_3$**), 0.14 (s, 3H, Al-**CH$_3$**), 0.07 (s, 3H, Al-**CH$_3$**).

X-ray crystallography

For all of compounds **3.1** to **3.3** results presented are the best of several data collection trials. The crystals were mounted on thin glass fibers using paraffin oil and cooled to the data collection temperature. Data were collected on a Bruker AXS SMART 1k CCD diffractometer. Data for the compounds **3.2, 3.3** were collected with a sequence of 0.3° ω scans at 0, 120, and 240° in φ. To obtain acceptable redundancy data for compound **3.1** the sequence of 0.3° ω scans at 0, 90, 180, and 270° in φ was used. Initial unit cell parameters were determined from 60 data frames collected at the different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied.[15] Systematic absences in the diffraction data-set and unit-cell parameters were consistent with triclinic $P\bar{1}$ for **3.1** and monoclinic $P2_1/m$ for both **3.2** and **3.3**. Solutions in centrosymmetric space groups for all of the compounds yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed with difference Fourier synthesis, and refined with full-matrix least-squares procedures based on F^2. The compound molecules were located in special positions (mirror plane) in the structures of **3.2** and **3.3**.In the structure of **3.1** complex molecule is located in general positions. All hydrogen atoms were treated as idealized contributions. All scattering factors are contained in several versions of the SHELXTL program library, with the latest version used being v.6.12[33]. Crystallographic data and relevant bond distances and angles are reported in Tables 3.1 and 3.2.

Crystal Structure Description.

1. The structure of **3.1** shows the Tm metal center in a pseudo-tetrahedral environment (Figure 3.1). One position is occupied by a terminally bonded methyl group [Tm(1)–C(21) = 2.389(9)Å]. The second position is occupied by the μ-CH_2 group interacting with Tm metal center through a seemingly agostic interaction [Tm(1)–C(22) = 2.429(9)Å, Tm(1)–H(22A) = 1.637(9)Å, C(21)–Tm(1)–C(22) = 101.6(8)°]. The positions of the corresponding hydrogen atoms were yielded by difference Fourier maps. The last two positions are occupied by the centroids of two η^5-coordinated Me$_4$pyrrolyl rings [Tm(1)–centroid(1) = 2.412(7)Å, Tm(1)–centroid(2) = 2.407(7)Å, centroid(1)–Tm(1)–centroid(2) = 137.1(3)°, centroid(1)–Tm(1)–C(21) = 102.4(8)°, centroid(2)–Tm(1)–C(22) = 104.5(8)°].

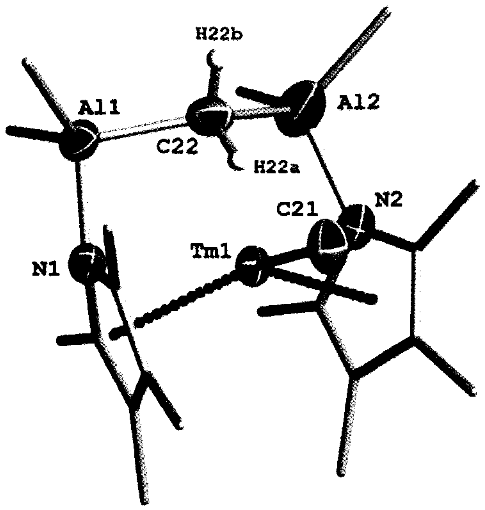


Figure 3.1. Partial thermal ellipsoid diagram of **3.1** with thermal ellipsoid drawn at the 50% probability level. Thermal ellipsoids for selected carbon atoms are omitted for clarity. Non-essential H atoms are omitted for clarity.

The two rings are σ-bonded through the nitrogen atoms to one Al atom each [Al(1)–N(1) = 1.982(7)Å, Al(2)–N(2) = 1.979(8)Å]. In turn, the two Al metal centers are linked by the same μ-CH_2 group [Al(1)–C(22) = 2.041(10) Å, Al(2)–C(22) = 2.046(10) Å, Al(1)–C(22)–Al(2) = 139.3(5)°, N(1)–Al(1)–C(22) = 99.0(3)°, N(2)–Al(2)–C(22) = 99.5(4)°] that interacts with the Tm atom. The tetrahedral environments of each Al is completed by two terminally bonded methyl groups [Al(1)–C(9) = 1.968(10)Å, Al(1)–C(10) = 1.980(10)Å, Al(2)–C(19) = 2.001(15)Å, Al(2)–C(20) = 1.974(13)Å, C(9)–Al(1)–C(10) = 109.2(5)°, N(1)–Al(1)–C(9) = 111.9(5)°, C(19)–Al(2)–C(20) = 109.7(5)° , N(2)–Al(2)–C(19) = 112.1(5)°].

2. The structure of **2** displays a motif closely reminiscent of the *ansa*-metallocene complexes (Figure 3.2) with two η^5-bonded Me_4pyrrolyl rings linked, via σ-coordination to the N atoms, by the same Me_2Al residue [Al(1)–N(1) = 1.975(5)Å, N1–Al(1)–N(1A) = 94.3(3)°]. The two centroids occupy two positions in the coordination sphere of Tm metal center [Tm(1)–centroid(1) = 2.457(7)Å] in a "bent metallocene" type of arrangement [centroid(1)–Tm(1)–centroid(1A) = 120.9(2)°]. The last two positions of the pseudo-octahedral geometry of the Tm center are occupied respectively by one methylene group, in turn bridging two Me_3Al groups [Tm(1)–C(11) = 2.188(6)Å, C(11)–Al(2) = 1.739(6)Å, C(11)–Al(3) = 1.700(6)Å, Al(2)–C(11)–Al(3) = 129.4(4)°, Al(2)–C(11)–Tm(1) = 95.1(3)°, Tm(1))–Al(2)-C(11))–Al(3) =180.0(2)°]], and one of the Me groups of one of the two Me_3Al [Tm(1)–C(12) = 2.329(7)Å, Tm(1)–C(12)–Al(2) = 87.4(4)°, C(11)–Tm(1)–C(12) = 76.1(2)°].

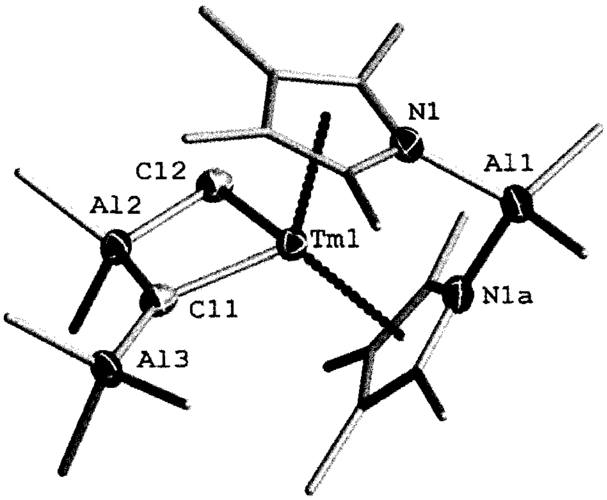


Figure 3.2. Partial thermal ellipsoid diagram of **3.2** with thermal ellipsoid drawn at the 50% probability level. Thermal ellipsoids for selected carbon atoms are omitted for clarity. Non-essential H atoms are omitted for clarity.

3. The positions of the corresponding hydrogen atoms were yielded by difference Fourier maps, again suggesting the presence of agostic interactions.The molecular structure of **3.3** maintained the same *ansa*-metallocene type of motif of **3.2** (Figure 3.3) with two Me_4pyrrolide units similarly linked by the dimethyl-aluminum residue [Al(1)–N(1) = 1.976(6)Å, N(1)–Al(1)–N(1A) = 93.7(3)°], and connected to Tm metal center in η^5-fashion [centroid(1)–Tm(1) = 2.447(6)Å, centroid(1)–Tm(1)–centroid(1A) = 120.7(2)°]. The third position in the coordination sphere of Tm is occupied by a carbon atom bridging one Me_3Al unit to a Me_2Al residue [Al(2)–C(19) = 1.719(8)Å, Al(3)–C(19) = 1.738(8)Å, Al(2)–C(19)–Al(3) = 127.3(5)° , Tm(1)–C(19)–Al(2) = 134.1(4)°, Al(2)-C(19)-Al(3)-Tm(1) = 180.0°]. In this case, the difference Fourier maps did not yield the positions of the corresponding hydrogen atoms but, on the basis of the structural similarity with the geometrical parameters of **3.2**, it is tempting to conclude that the arrangement with the Tm atom [Tm(1)–C(19) = 2.133(7)Å, Al(2)–C(19)–Tm(1) = 133.9(2)°, Al(3)–C(19)–Tm(1) = 98.5(2)°] is the same.

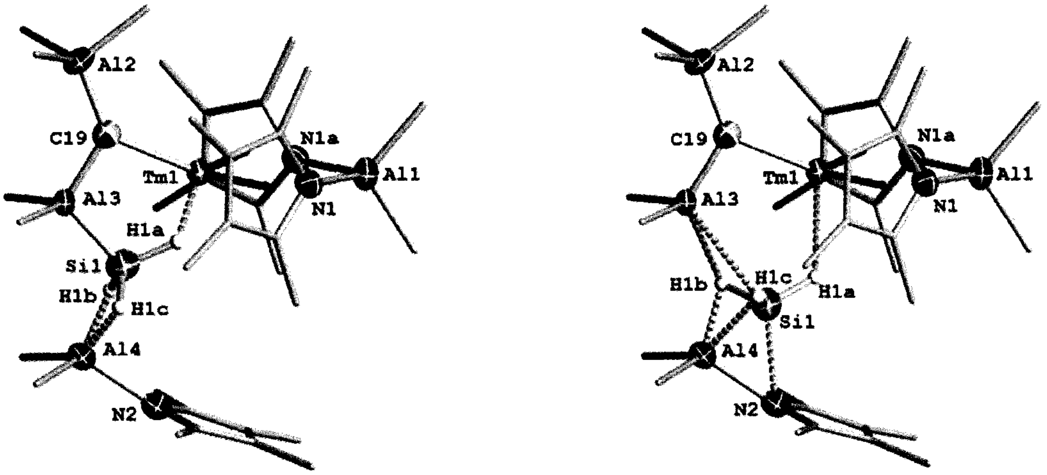


Figure 3.3. Partial thermal ellipsoid diagrams of **3.3** with thermal ellipsoid drawn at the 50% probability level. The two pictures illustrate the two disordered positions of the SiH_3 unit. Thermal ellipsoids for selected carbon atoms are omitted for clarity. Non-essential H atoms are omitted for clarity.

A silicon atom disordered over two positions with the occupancy 64% : 36% resides in the last position of the distorted pseudo-tetrahedral environment around the Tm metal [Tm(1)–Si(1) = 3.087(6)Å, Tm(1)–Si(1)` = 2.573(6)°, Si(1)–Tm(1)–C(19) = 92.5(2)°, Si(1)–Tm(1)–C(19) = 74.3(2)°]. In each of the two disordered positions, the Si atom appears to be anchored to Tm metal center through bridging H-atoms. In one position it lays within a bonding distance with the aluminum atom bonded to the bridging methylene [Si(1)`–Al(3) = 1.86(1) Å] and to another $Me_4$pyrrolyl-alane unit [Si(1)`–Al(4) = 2.15(1)Å, Al(3)–Si(1)`–Al(4) = 113.6(3)°]. In the second disordered position, it exhibits close contact to the N atom of the Me_4-pyrrolide-alane [Si(1)–N(2) = 2.19(2)Å]. In each of the two scenarios, the hydrogen atom positions were calculated and would exhibit an agostic type of interaction.

Table 3.1. Crystal Data and Data Collection Parameters of Complexes **3.1**, **3.2** and **3.3**.

	3.1	**3.2**	**3.3**
Formula	$TmAl_2C_{21}H_{40}N_3$	$TmAl_3C_{25}H_{50}N_2$	$TmAl_4C_{33}H_{66}N_4Si$
FW	557.45	630.56	823.84
Crystal system,	Triclinic	Monoclinic	Monoclinic
Space group	P-*1*	P2*1*/*m*	P2*1*/*m*
a, Å	9.093(2)	8.9511(8)	11.732(2)
b, Å	10.055(2)	14.246(1)	14.273(2)
c, Å	15.735(4)	11.702(1)	12.422(2)
α, deg	80.375(3)	90	90
β, deg	86.912(3)	106.223(1)	108.691(2)
γ, deg	63.563(2)	90	90
Volume, $Å^3$	1269.8(5)	1432.9(2)	1970.5(6)
Z	2	2	2
ρ_{calc} g/cm3	1.458	1.461	1.389
μ, mm^{-1}	3.573	3.203	2.398
F(000)	564	648	854
T range (deg)	2.29 - 24.78	2.31 - 24.76	1.73 - 24.79
Limiting indices (*h*, *k*, *l*)	±10, ±11, ±18	±10, ±16, ±13	±13, ±16, ±14
Reflections collected / unique	12535 / 4284	10763 / 2532	14704 / 3478
R_{int}	0.0330	0.0435	0.0294
GOF	1.052	1.055	1.043
R1 (obs / all)	0.0449 / 0.0488	0.0340 / 0.0434	0.0429 / 0.0462
wR2 (obs / all)	0.1125 / 0.1143	0.0833 / 0.0880	0.1104 / 0.1130

Table 3.2 Selected bonds (Å) and angles (deg) for complexes **3.1-3.3.**

3.1

Tm(1)-C(21) = 2.389(9)
Tm(1)-C(22) = 2.429(9)
C(22)-Al(1) = 2.041(10)
C(22)-Al(2) = 2.046(10)
Al(1)-N(1) = 1.983(7)
Al(2)-N(2) = 1.980(8)
Tm(1)-centroid(1) = 2.412(10)
Tm(1)-centroid(2) = 2.407(10)

C(22)-Tm(1)-C(21) = 101.6(4)
centroid(1)-Tm(1)-centroid(2) = 137.1(4)
C(22)-Tm(1)-centroid(1) = 103.8(4)
C(22)-Tm(1)-centroid(2) = 104.5(4)
Al(2)-C(22)-Al(1) = 139.3(5)
Tm(1)-C(22)-Al(1) = 93.2(4)
Tm(1)-C(22)-Al(2) = 92.7(4)
N(1)-Al(1)-C(22) = 99.0(3)
N(2)-Al(2)-C(22) = 99.5(4)

3.2

Tm(1)-C(11) = 2.188(6)
Tm(1)-C(12) = 2.329(7)
Tm(1)-N(1) = 2.640(4)
Tm(1)-centroid(1) = 2.457(5)
Al(1)-C(9) = 1.963(9)
Al(1)-N(1) = 1.975(5)
Al(2)-C(11) = 1.739(6)
Al(2)-C(12) = 1.857(8)
Al(2)-C(13) = 1.879(6)
Al(3)-C(11) = 1.700(6)
Al(3)-C(15) = 1.861(9)
Al(3)-C(14) = 1.876(7)

C(11)-Tm(1)-C(12) = 76.1(2)
C(11)-Tm(1)-N(1) = 140.72(12)
C(12)-Tm(1)-N(1) = 119.55(17)
centroid(1)-Tm(1)-centroid(1)A = 120.86(19)
C(11)-Tm(1)-C(1) = 132.16(13)
C(12)-Tm(1)-C(1) = 90.07(17)
C(11)-Tm(1)-C(3) = 92.13(12)
C(12)-Tm(1)-C(3) = 107.36(11)
C(11)-Tm(1)-C(2) = 103.30(12)
C(12)-Tm(1)-C(2) = 83.45(12)

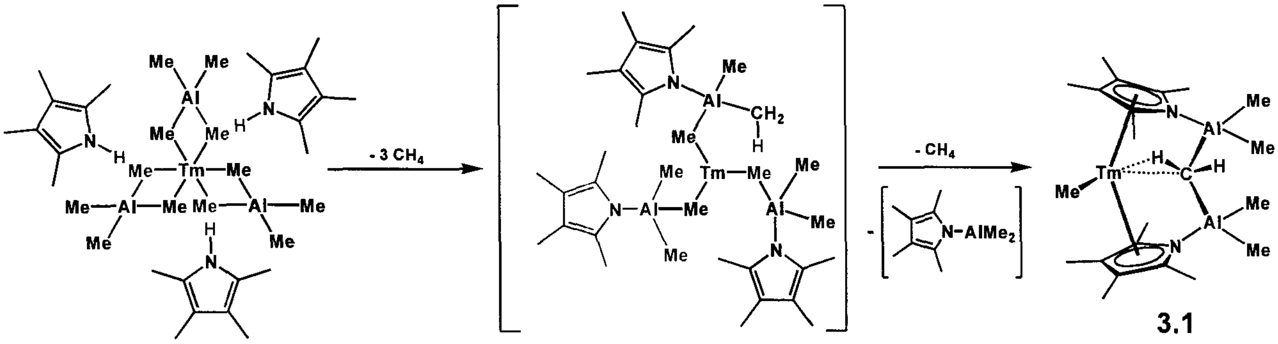
3.3

Tm(1)-C(19) = 2.133(7)
Tm(1)-Si(1) = 2.573(7)
Tm(1)-Si(1)' = 3.087(7)
Tm(1)-centroid = 2.447(7)
C(19)-Al(2) = 1.719(7)
C(19)-Al(3) = 1.738(8)
Al(3)-Si(1) = 2.875(6)
Al(4)-Si(1) = 1.757(6)
N(2)...Si(1) = 2.189(6)
Al(1)-N(1) = 1.975(6)

centroid(1)-Tm(1)-centroid(1)A = 120.74(18)
centroid-Tm(1)-C(19) = 116.(2)
N(1)-Al(1)-N(1a) = 93.7(3)
Al(2)-C(19)-Al(3) = 127.3(5)
N(2)-Si(1)-Al(3) = 147.01(8)
Al(3)-Si(1)-Al(4) = 89.50(7)

Results and Discussion

By following the procedure described by Evans[16] for the preparation of other $(Me_4Al)_3Ln$ [Ln = Y, La, Nd, Sm, Yb] we did not succeed in obtaining the Tm analogue. We have thus modified the procedure according to Anwander[17] and reacted $Tm(silazanate)_3$ with Me_3Al in toluene. The resulting mixture was treated *in situ* with 2,3,4,5-tetramethylpyrrole. The addition of three equivalents of pyrrole caused a visible color change from very pale yellow to intense yellow-orange. After suitable work-up, lemon-yellow crystals of a new species formulated as $TmCH_3\{(\mu\text{-}CH_2)[Al(CH_3)_2(Me_4C_4N)]_2\}$ (**3.1**) were isolated in good yield (72%) (Scheme 3.1). The connectivity of this unexpected complex was revealed by an X-ray crystal structure (Figure 3.1) showing one Tm atom bonded to a terminal CH_3 group. By adopting fairly symmetrical π-bonding modes, the two pyrrolide rings confer a bent-metallocene structural motif to the lanthanide.



Scheme 3.1.

Each N atom of the two pyrrolide rings is connected to one $AlMe_2$ residue which in turn is bridged to an identical unit and to the lanthanide by one CH_2 group thus forming a $Ln\text{-}(\mu_3\text{-}CH_2)\text{-}Al_2$ functionality. The presence of the bridging methylene and the identity of the terminally bonded atom were confirmed by the connectivity as yielded by the successful refinement of the crystallographic thermal parameter. Additionally, the IR spectrum revealed very weak and broadened signal at 3583 cm^{-1}. Such an unusual position and shape of the C-H stretch could be attributed to the simultaneous interaction with three metal centers. ^{1}H-NMR spectrum also indirectly confirmed this conclusion by showing an extreme shifting of the -CH_2- peak to -475.1 ppm of the ^{1}H-NMR spectrum.

Abstraction of hydrogen from an alkyl group is *not* a rarity in lanthanides chemistry. A number of compounds resulting from this type of transformation has been discovered over the years not only through NMR evidences of reactions carried out *in situ,* but also by isolating species and proving their molecular structure.[18-24] The formation of **3.1** seems to follow the same metal-assisted C-H bond activation of the Al-CH_3 methyl group as already observed by Anwander[20] and Evans.[24] Complex **3.1** adds a further example to the scanty list of characterized lanthanide complexes containing a terminally bonded -CH_3 group.[3, 15, 21]

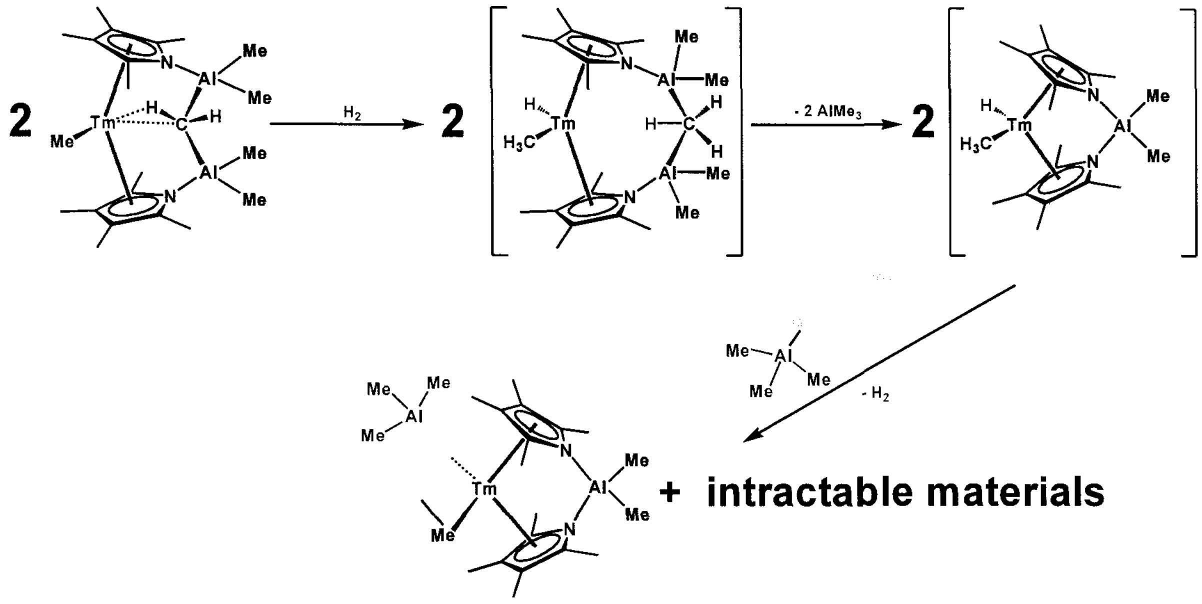
A possible rationalization for the formation of the complex is depicted in Scheme 1. It implies the attack of the three molecules of pyrrole to the *in situ* generated Tm-aluminate species. Consequent release of three equivalents of methane may afford an intermediate where the lanthanide is bonded to *three* pyrrolide-$AlMe_3$ anions. A further C-H σ-bond metathesis between two of these anions may give the final dipyrrolide aluminate dianion with the bridging methylene. Dissociation of a neutral pyrrolide$AlMe_2$ moiety from the third unit generates instead the terminally bonded Me group. This last transformation has been already witnessed in the chemistry of both divalent vanadium and chromium with the same pyrrolide/aluminate ligand systems. Dissociation of a pyrrolide$AlMe_2$ unit from a "metallocene" type of structure afforded M-R functions, in turn providing single-component polymerization activity of ethylene.[9]

Organo-lanthanide compounds in general provide a convenient entry into chemistry of lanthanide hydrides. Since the first discovery of a lanthanide hydrides more than 25 years ago,[25] these species remain in the focus of active research due to their unusual and high reactivity. Most of the achievements in the chemistry of lanthanide hydrides lay in the area of metallocene based compounds,[1g, 2b, 3c, 26] non-metallocene lanthanide hydride compounds remaining rare.[7e, 21i, 27] The two most common synthetic approaches to hydride complexes are based on metal carbon σ-bond metathesis with either hydrogen gas[28] or phenylsilane.[22b]

Reaction of **3.1** with H_2 was carried out with hydrogen at high pressure (600 PSI) for 48 hours at room temperature. After venting the reactor and work up, a new compound formulated as $Tm[(Me_4C_4N)_2AlMe_2][(\mu,\eta^3\text{-}CH_2)(AlMe_3)(AlMe_2)](\mu\text{-}CH_3)$ (**3.2**) was obtained in crystalline form. The most striking structural features of **3.2** in comparison to **3.1** are: a) the change of the Tm to Al ratio from 1:2 to 1:3; b) the disappearance of the terminally bonded Me group; c) the assembly of an *ansa*-type of arrangement via one additional $AlMe_2$ bridging the two pyrrolide rings, and d) the retention of the two methylene bridged alkylaluminum groups. Attempts to balance the reaction stoichiometry cannot be made unless assuming the presence of at least one Tm-containing byproduct. Unfortunately, the structure of this partner compound remained elusive despite numerous attempts of crystallization or obtaining meaningful information from NMR data of the reaction mixture. The reasonable sharpness of the NMR lines and the light color indicate that Tm has maintained the trivalent state. Considering that the overall charge of the *ansa*-like $(pyrrolide)_2AlMe_2$ moiety appears to be (-1) it becomes apparent that the organo-dialuminum fragment should posses a (-2) overall charge. Hence the presence of a *formal* $(\text{-}CH_2\text{-})^{-2}$ fragment must necessarily be assumed. Formation of such a fragment has been recently observed independently by Evans[24] and Anwander[20] groups.

The ^1H-NMR spectrum of **3.2** exhibits 8 broad singlets of equal intensity scattered between 1.64 and 4.83 ppm and which all could be attributed to 8 different methyl substituent groups of the two pyrrolide anions. An intense resonance at 2.75 integrating for nine protons is attributed to the three methyl groups on one of the "terminal" methyl-aluminum unit. The two methyl groups of the bridging methyl-alane coordinated to the methylene moiety appear at 3.97 ppm as a broadened strong signal with the appropriate intensity. Another broad signal at 4.63 ppm integrating for six protons could be attributed to the pyrrolide bridging the methyl-aluminum fragment. A broad resonance integrating for three protons is assigned to the methyl group bridging Al to Tm. The most interesting feature of the spectrum is a significant non-equivalency of two methylene protons appearing as two broad lines coupled to each other at -0.87 and 1.99 ppm. Each of these broad resonances is integrating with the correct intensity.

A possible and straightforward rationalization of this transformation is depicted in Scheme 3.2. It must be reiterated that the conversion of **3.1** into **3.2** *occurs exclusively in the presence of* H_2 and that no detectable methane evolution accompanies the transformation.



3.2

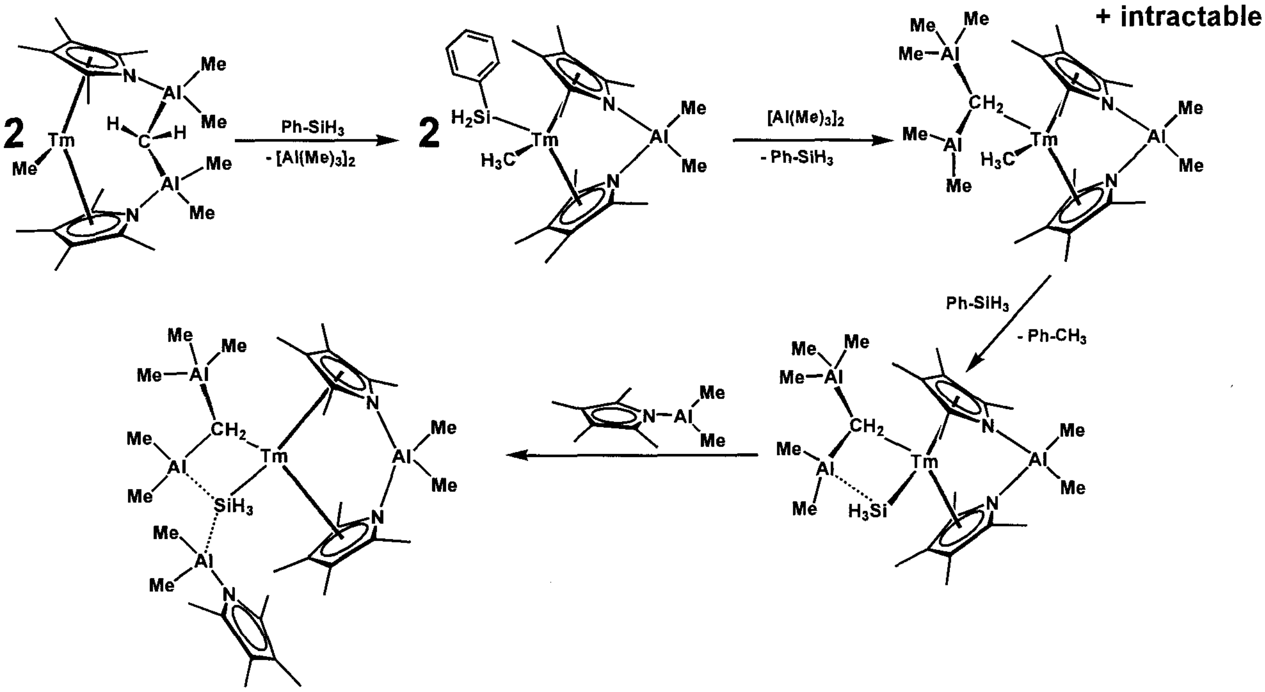
Scheme 3.2.

As mentioned above, the second attempt to hydrogenolize the Tm-CH_3 function was carried out with $PhSiH_3$ according to a well established procedure.[3o, 22, 23]

Treatment of **3.1** with $PhSiH_3$ in toluene at room temperature afforded a new complex **3.3** formulated as $[(Me_4C_4N)_2AlMe_2]Tm[(\mu,\eta^3\text{-}C)(AlMe_3)(AlMe_2)](\mu\text{-}SiH_3)[(Me_4C_4N)AlMe_2]$ on the basis of the X-ray crystal structure. The structure (Figure 3.3) displays the same *ansa*-metallocene type of structure observed in **3.2**. Different from the previous case, the $Me_3AlCH_2AlMe_3$ unit of **3.2** had a SiH_3 unit replacing one of the Me groups in turn bridging one PyrrolylAlMe$_2$ formally neutral unit. The Si atom is disordered over two positions with 64% : 36% occupancy. In each of the two positions a short contact is formed with either the pyrrolide N atom or an Al atom.

The pale color of **3.3** suggests that the Tm center is present in its trivalent state. This is also supported by ^{1}H-NMR data indicating minimal paramagnetic shifting. In turns, the trivalent state state of the metal center implies that the bridging methylene has remained unchanged. The close similarity of the structural data of this unit with those of **3.2** also supports the formulation. The ^{1}H-NMR spectrum exhibits a series of rather broad resonances. Three intense resonances (1:1:1) are assigned to the methyl group substituent of the pyrrolide units. The pyrrole methyl groups of monoanionic bis-pyrrolide alane unit are present as two resonances at 2.17 and 2.03 ppm with the appropriate intensity. Third pyrrolide moiety, located further from Tm metal center and in close vicinity of SiH_3 fragment, demonstrates significant shift of the methyl substituents resonance to 7.20 ppm. All three signals reveal similar signal intensity which is assigned to 12 protons each. A resonance at 4.64 accounting for 6 protons is tentatively assigned to two methyl groups of the bis-pyrrolide alane unit. All other methyl groups are present as seven broad resonances each integrating for three protons in the range 7.43 - 0.07 ppm. The two resonances expected for the two methyl groups of the [SiH_3-$Al(CH_3)_2$-Pyrrolide] unit are present at 7.08 ppm and 6.96 ppm. The proton of the SiH_3 unit display significant anisotropy and appear as three rather broad peaks, located at 3.29 ppm, 2.87 ppm and 2.33 ppm with the expected intensity. These three signals are not coupled to any carbon signal in the 2D-HMQC spectrum. Finally two other broad signals with the intensity of 1 proton each located at 1.43 ppm and 0.50 ppm, coupled to the same carbon atom, are assigned to two magnetically un-equivalent protons of bridging methylene unit.

The transformation of **3.1** to **3.3** clearly is the result of a complex series of events since two additional Al units have been acquired as well as one additional pyrrolide ring. The entrapped SiH_3 unit is obviously deriving from $PhSiH_3$ while the Ph moiety generated toluene (clearly visible in the GS-MS of the reaction mixtures carried out in benzene) by acquiring a Me from either the Tm-CH_3 function or the scrambling of the Me_3Al units. The appearance of the third ring once again reiterated that a second Tm-containing product must be generated during the reaction. A possible rationalization for the formation of **3.3** is provided in Scheme 3.3. It assumes that the reaction may follow in the beginning a path very similar to that forming **3.2.** The only difference is that the intermediate, rather than having the Me group transferred from Tm to Al as during the formation of **3.2**, metathesize the $PhSiH_3$ by releasing toluene and incorporating the SiH_3 unit. The third pyrrolide$AlMe_2$ unit may easily be provided during the decomposition of the second equivalent of **3.1** leading to intractable materials. Although unusual, this type of reactivity of $PhSiH_3$ has precedents in the chemistry of both transition metals[29] and *f*-block elements.[28, 31, 30]



3.3

Scheme 3.3.

Unfortunately, all the attempts to determine the nature of the Tm-containing byproduct were unsuccessful despite numerous crystallization attempts and extensive NMR analysis of the reaction mixture.

Conclusions

In summary, we have now tested the possibility of generating a complex of the aluminate-pyrrolide anion with the Cp_3Ln structural motif as a possible precursor to new highly reactive organo-Tm species. The target *tris*-Cp-like compound appeared as too unstable to be isolated and engaged in a C-H σ-bond metathesis eliminating methane and forming a metallocene-type of complex with a terminally bonded alkyl. Treatment of this complex with H_2 under mild condition resulted in loss of terminal alkyl group as well as ligand scrambling. The only isolated product of this reaction is bridging methylene complex supported by two Al and one Tm metal center. In turn, reaction of complex **1** with $PhSiH_3$ triggered ligand shuffling between two units and trapping of a SiH_3 moiety accompanied by preservation of $(-CH_2-)^{2-}$ fragment. Such behavior speaks for the mobility of aluminate/pyrrolide ligand system which, in turn, opens the door to a new series of possible chemical transformations. The unusual reaction with $PhSiH_3$ well illustrates the potential for this reactivity. At this stage it is interesting to observe that C-H bond reactivity of the alane methyl group appears only in case of Tm complexes. In fact, with Sm and other *f*-elements with less reducing divalent states, the same reactions have instead provided divalent complexes with regular "metallocene" type of structures.[32] In conclusion, the use of aluminate pyrrolide anions is indeed a promising strategy for expanding the reactivity of *f*-element complexes and for entering a new domain of unprecedented chemical transformations.

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Chapter Four

Involvement of the Ligand in the Reactivity of Uranium Amide Complexes

Introduction

It is today commonly accepted that low valent uranium has the potential for providing a rich and diversified chemical reactivity on the line of that observed for some divalent lanthanides. Among the most exciting and promising transformations reported in the literature there are dinitrogen activation / reduction[1] and cleavage,[2] depolymerization of poly-silanoles with cleavage of the Si-O bond,[2] CO oligomerization,[3] unusual coordination of small molecules,[4] including a unique case of *sp*^{3}-C-H bond coordination,[4d] and oxidative elimination of H_2.[5]

As usual, ligand features are central to the performances of the metal and to the stabilization of the low-oxidation state. For example, oxidation states lower than +3 are unknown for uranium. In the presence of a π-system however, a few reduced species or low-valent synthons have been prepared and characterized.[6-8] These species do not possess low-valent elements and yet may produce the sort of reactivity which has to be expected for genuine low-valent complexes.[6] The particular nature of the ligand donor atom also seems to be of primary importance. The reactivity of uranium becomes particularly enhanced in the presence of nitrogen donor atoms as indicated by the few cases of dinitrogen reversible fixation[1a,7] and cleavage.[8] The first documented reduction reaction, resulting in the formation of a so-called "inverted sandwich" synthon of U(II), was based on a complex containing U metal center in combination with bulky amido- ligands.[6a] Incidentally, the presence of coordinating solvent is normally undesirable in the chemistry of low-valent *f*-block elements. Thus, bulky amido-ligands may be effectively used also for the purpose of obtaining solvent-free compounds.[9]

Aiming at species of high reactivity containing the metal in low oxidation states we have revisited the chemistry of uranium supported by the *bis*-silazanate anion. This ligand has been successfully used by Andersen in his pioneering work in the chemistry of the uranium tetravalent state.[10] In the field of *f*-block elements chemistry, it is known to afford low coordinate complexes with excellent yields for many metals.[11] Low coordination numbers, absence of coordinated solvent molecules, high solubility in hydrocarbons and aromatic solvents, and high ligand basicity, altogether, make these derivatives excellent precursors for reactivity studies.[1d,7b,11,12] A characteristic feature discovered so far for this ligand system is its direct involvement in the organometallics chemistry of the metal center (γ-metallation). In the chemistry of uranium, products resulting from γ-metallation were utilized for a variety of organometallic transformations including nucleophilic reactivity in organic synthesis,[13] insertion reactions[14] and even for discovering examples of unusual behavior.[14a,14c] Furthermore, the lability of the Si-N bond, in combination with the availability of electrons provided by the reduced state, allows formation of bridging or terminally bonded imido groups[6b,13a,14b,15] via elimination of one of the two Me_3Si residues.[16] As far as the trivalent state is concern, $U[N(TMS)_2]_3$ is known but does not display unusual reactivity. This behavior is not typical for a U(III) metal center which when combined to N-donor atoms usually displays a well-documented list of examples of extreme reactivity.[1b-c, 3, 4, 17] On the other hand, the large bulk generated by the three equatorial ligands coupled with the agostic U-H-CH_2 interactions in both axial positions, makes the metal inaccessible to reagents other than protons. In this work, we have revisited the chemical reactivity of tetravalent uranium silazanate derivatives aiming at exploring the possibility of preparing lower-valent complexes for reactivity purpose. As correctly observed by Andersen, we find that this chemistry is indeed dominated by γ-metallation. Herein, we report how different extent of γ-deprotonation may lead to cluster formation. It was also discovered that attempts to lower the oxidation state with strong reductants resulted in re-oxidation of the metal center at the expense of the ligand.

Experimental Part

All operations were performed under nitrogen atmosphere with rigorous exclusion of oxygen and water using standard Schlenk and glove-box techniques. Hexane and toluene solvents were purified by passing through Al_2O_3 filled columns and deoxygenated prior to use by several vacuum/nitrogen purges. DME was dried over $LiAlH_4$ and distilled under N_2 prior to utilization. Benzene-d^6 was obtained from "C/D/N isotopes", dried over Na/K alloy, distilled and stored over molecular sieves (4Å). *n*-Butyl-lithium solution 2.5 M in hexane and methyl-litium solution 1.6 M in diethyl ether were purchased from Aldrich and used as received. $LiCH_2(SiC_3H_9)$ was prepared according to modified literature procedure[18] using boiling cyclohexane as a solvent. K/C_8 was prepared according to literature procedure.[19] Complexes $\{UCl_2[N(Si_2C_3H_9)_2]_2\}_2$ and $UCl_2[N(Si_2C_3H_9)_2]_2[C_4H_{10}O_2]$ were synthesized according to literature procedures.[20] 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.[21] NMR spectra were recorded at 293K on Varian Inova 500 MHz spectrometer. Chemical shifts were referenced to internal solvent resonances and reported in parts per million relatively to Me_4Si. Elemental analyses were performed on Perkin-Elmer 2400 CHN analyzer. Data for X-ray single crystal structure determination were collected with a Bruker diffractometer equipped with 1K SMART CCD area detector.

Preparation of $\{U[(\mu\text{-}CH_2\text{-}SiMe_2)N(TMS)]_2[\mu\text{-}Li(DME)]\}_2$ (4.1)

A solution of methyl-lithium (9 mL of 1.6 M, 14.4 mmol) in diethyl ether was slowly added to a cooled solution (-37°C) of $UCl_2[N(TMS)_2]_2(DME)$ (3.40 g, 4.72 mmol) in DME (20 mL). The reaction mixture was allowed to warm up to room temperature under vigorous stirring under which the color changed from the initial pale-green to intense brown-red while a colorless insoluble material separated. After 2 additional hours of stirring at room temperature, the solvent was removed *in vacuo* and the resulting orange solid suspended in hexane (35 mL). The Insoluble materials were eliminated by centrifugation and the volume reduced to 11 mL by evaporation *in vacuo*. The solution was allowed to stand at -37°C for 48 hours, after which dark red-orange prisms were formed. After washing with cold hexane (-37°C, 3mL) and drying for 30 min under N_2 crystalline **4.1** was obtained (2.87 g, 4.12 mmol, 87%). Upon further drying dark red-orange crystals of **4.1** deteriorated with the formation of yellow-orange powdery material. Elem. Anal. for $UC_{16}H_{44}LiN_2O_2Si_4$ found (calculated): C 29.31 (29.39), H 6.63 (6.78), N 4.23 (4.28). ^{1}H-NMR (500 MHz, benzene-d^6, 20°C) δ: 3.30(6H, *DME*, CH_3-O), 3.12(4H, *DME*, -CH_2-O), -13.10(12H, Si-$(CH_3)_2$), -28.57(18H, Si-$(CH_3)_3$), -47.02(4H, Si-CH_2-U).

Preparation of {U[(μ-CH$_2$-SiMe$_2$)N(TMS)][N(TMS)$_2$]}$_2${U[(μ^3-C-SiMe$_2$)N(TMS)][N(TMS)$_2$]}{μ-OMe} (4.2)

A solution of $UCl_2[N(TMS)_2]_2$(DME) (0.764 g, 1.0 mmol) in hexane (10 mL) was mixed with solution of $LiCH_2TMS$ (0.20 g, 2.2 mmol) in the same solvent (5 mL). An instant color change from pale green to dark orange, accompanied by the formation of pale insoluble material, was observed upon mixing. Stirring was continued at room temperature for additional 2 hours and the insoluble material was eliminated by centrifugation. The resulting solution was concentrated to about 5 mL and allowed to stand at -37°C. After three days, dark orange crystals of **4.2** were formed. Crystals were separated, washed with 3 mL of cold hexane (-37°C) and dried under N_2 atmosphere (0.44g, 0.26 mmol, 74%). Elem. Anal. for $U_3C_{37}H_{106}N_6OSi_{12}$ found(calculated): C 25.97 (26.10), H 6.14 (6.28), N 4.90 (4.94). ^{1}H-NMR (500 MHz, benzene-d^6, 20°C) δ: 29.36(27H, N-Si$(CH_3)_3$), 9.85(3H, O-CH_3), 7.19(54H, N[Si-$(CH_3)_3]_2$), -0.13(broad, 18H, Si-$(CH_3)_2$), -46.90(4H, Si-CH_2-U).

Preparation of {U[μ-(CH_2-$SiMe_2$)N(TMS)][N$(TMS)_2$]}$_2${U[(μ_3-C-$SiMe_2$)N(TMS)][(μ-CH_2-$SiMe_2$)N(TMS)]} (4.3)

A suspension of $UCl_2[N(TMS)_2]_2$ (0.45 g, 0.7 mmol) in hexane (20 mL) was mixed with solution of $LiCH_2TMS$ (0.14 g, 1.5 mmol) in the same solvent (5 mL). An instant color change from pale green to dark brown was observed upon addition of the Li reagent. After 6 hours of stirring at room temperature, the solvent was removed *in vacuo*. The resulting dark-brown powdery material was extracted with hexane (30 mL). The volume of the extract was reduced to 7 mL and the solution allowed to stand at -37°C for 4 days. Dark brown prisms of **4.3** were formed which were separated, washed with of cold hexane (5 mL, -37°C) and dried under N_2 atmosphere (0.26 g, 0.16 mmol, 67%). Elem. Anal. for $U_3C_{36}H_{102}N_6Si_{12}$ found(calculated): C 25.57 (25.89), H 6.07 (6.16), N 4.99 (5.03). ^{1}H-NMR (500 MHz, benzene-d^6, 20°C) δ: 24.11(36H, N-Si$(CH_3)_3$), 7.22(36H, N[Si-$(CH_3)_3]_2$), -13.48 (18H, Si-$(CH_3)_2$), -16.85(6H, Si-$(CH_3)_2$), -43.10(6H, Si-CH_2-U).

Preparation of {U-μ-Cl[N$(TMS)_2$][DME]}$_2${U-μ-Cl[N$(TMS)_2]_2$}{μ_3-Cl}$_2$ (4.4)

A solution of $UCl_2[N(TMS)_2]_2$[DME] (1.60 g, 2.2 mmol) in DME (25 mL) was treated with freshly prepared KC_8 (0.61 g, 4.5 mmol). The mixture was stirred at room temperature for 3 days, during which, the color slowly changed to dark red-purple. When no further color change could be detected, the solvent was removed *in vacuo* and the residual dark-red solid was extracted with boiling toluene (15 mL). The volume of the dark-red solution was reduced to 5 mL and allowed to stand at room temperature for 48 hours. Two different crystalline materials (dark-red blocks and purple needles) separated in mixture. After washing with hexanes (40 mL) at room temperature the needle-shaped crystals completely disappeared. Recrystallization of the remaining solid material from hot toluene led to the isolation of dark-red block of **4.4** (0.69 g, 0.4 mmol, 52%). Elem. Anal. for $U_3C_{39}H_{100}C_{15}N_4O_4Si_8$ found(calculated): C 25.87 (25.95), H 5.47 (5.58), N 3.09 (3.10). μ_{eff} = 1.47 μ_B. The hexane extracted were concentrated (10 mL) and allowed to stand at -37°C affording crystals of the second compound. A database search of the crystallographic cell parameters identified this second product as $U[N(TMS)_2]_3$.[22]

Preparation of $\{U\text{-}\mu\text{-}Cl[N(TMS)_2]_2[=N(TMS)]\}_2$ (4.5)

A suspension of $UCl_2[N(TMS)_2]_2$ (0.26 g, 0.4 mmol) in 20 mL of toluene was treated with freshly prepared KC_8 (0.17 g, 1.2 mmol). The reaction mixture was stirred at room temperature for 7 days, during which, the color steadily changed from pale green to deep brown-red. The solvent was then removed *in vacuo* and the residual dark brown-red solid extracted with hexanes (35 mL). The volume of hexane extracts was reduced *in vacuo* to 10 mL and allowed to stand at -37°C. After 3 days a mixture of crystals with two different shapes was obtained. Fractional crystallization from toluene/hexane mixtures afforded dark brown-red prisms of **4.5** (0.12 g, 0.1 mmol, 42%). Storage of the mother liquor at -37°C for 3 additional days afforded complex **4.6** in crystalline form (0.05g, 0.04 mmol, 18%). Elem. Anal. for $U_2C_{30}H_{90}Cl_2N_6Si_{10}$ found(calculated): C 26.40 (26.44), H6.47 (6.66), N6.15 (6.17); $\mu_{eff} = 4.40$ mμ_B

Preparation of $U[(\mu\text{-}CH_2\text{-}SiMe_2)N(TMS)]_2[N(TMS)_2]$ (4.6)

A suspension of $UCl_2[N(TMS)_2]_2$ (0.500 g, 0.79 mmol) in cold hexane (-37°C, 15 mL) was treated with a cooled solution of *n*-BuLi in the same solvent (0.65 mL, 2.5 M, 1.63 mmol). The reaction mixture was allowed to warm to room temperature while vigorously stirred. The color of the solution changed to dark purple-red and a visible amount of insoluble material appeared. After stirring for 4 hours at room temperature, the solvent was removed *in vacuo* and the resulting solid residue extracted with 30 mL of boiling hexane. The volume of the extract was reduced to 10 mL and the solution allowed to stand at -37°C. Dark-red prisms of **4.6** were formed in 3 days and which were washed with cold hexanes 3 mL and dried under N_2 atmosphere (0.183 g, 0.26 mmol, 33%). Elem. Anal. for $UC_{18}H_{52}N_3Si_6$ found(calculated): C 30.07 (30.15), H 7.17 (7.31), N 5.79 (5.86). $\mu_{eff} = 2.48$ μ_β.

X-ray crystallography

For all the compounds, the results presented are the best of several trials. The crystals were mounted on thin glass fibers using paraffin oil and cooled to the data collection temperature. Data were collected on a Bruker-AXS SMART 1k CCD diffractometer. Data for all the compounds were collected with a sequence of 0.3° ω scans at 0, 120, and 240° in φ. Initial unit cell parameters were determined from 60 data frames collected at the different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.[23] Systematic absences in the diffraction data-set and unit-cell parameters were consistent with monoclinic **P**$2_1/n$ for **4.1** and **4.5,** triclinic **P**$\bar{1}$ for **4.2**, **4.3** and **4.4**, and orthorhombic **P***nma* for **4.6**. Solutions in centrosymmetric space groups for all of the compounds yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed with difference Fourier synthesis, and refined with full-matrix least-squares procedures based on F^2. In all the structures, the compound molecules were located in general positions. Structure of complexes **4.1** and **4.5** represent dimeric formations with two monomeric units related by an inversion center symmetry operator. Structure of complex **4.6** displays a 50:50 disorder of the U moiety with two disordered units related by a mirror plane symmetry operator. Carbon atoms of co-crystallized hexane solvent molecule in **4.1** were refined isotropicaly due to partial occupancy coupled with significant thermal motion disorder and in order to maintain an optimal data to parameters ratio. In all the structures, all non-hydrogen atoms, with the exceptions mentioned above, were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions. All scattering factors are contained in several versions of the SHELXTL program library version 6.12.[24] Crystallographic data for all structures are reported in Tables 1. Selected bond distances and angles are given in Table 2.

Crystal Structure Descriptions

1. The crystal structure of **4.1** comprises a symmetry generated dimer formed by two uranium and two lithium centers surrounded by four deprotonated silazanate ligands. The sharing by uranium of one of its μ–CH_2–group with the second uranium centre of an identical unit and with one lithium cation assembles the polymetallic structure. Each uranium atom resides in the center of a distorted trigonal bipyramidal environment. One axial position of the bipyramid is occupied by the nitrogen atom of a methylene-pentamethydisilazane fragment [U(1)–N(2) = 2.296(10) Å, N(2)–U(1)–C(1) = 161.1(4)°] and whose methylene group located in equatorial position [U(1)–C(7) = 2.518(13) Å, C(7)–U(1)–C(1) = 90.9(4)] bridges one lithium center. The other axial position is occupied by the methylene of the second deprotonated silazanate ligand which bridges the second uranium and the lithium atom. The corresponding nitrogen occupies the second equatorial position [U(1)–C(1) = 2.362(12) Å, U(1)–N(1) = 2.302(10) Å, C(7)–U(1)–N(1) = 111.7(4) , C(1)–U(1)–N(1) = 79.0(3)] (Figure 4.1). The last equatorial position is occupied by the bridging methylene of the symmetry generated unit [U(1)–C(1A) = 2.372(10)Å, C(1A)–U(1)–C(7) = 131.9(4) , C(1A)–U(1)–C(1) = 80.4(4)].

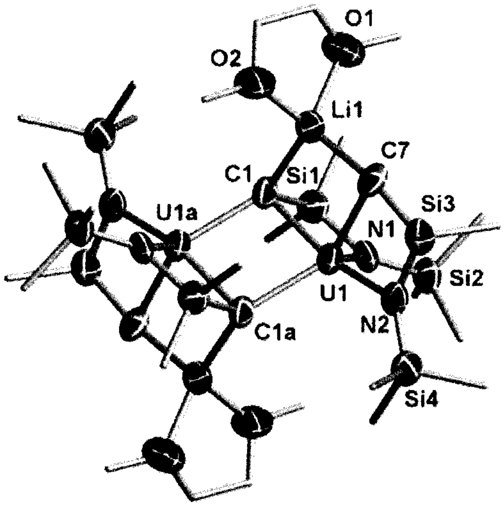


Figure 4.1. Thermal ellipsoid diagrams of **4.1** with thermal ellipsoid drawn at 50% probability level. Hydrogen atoms, methyl carbon atoms of SiMe$_3$ fragments and thermal ellipsoids of some carbon atoms have been omitted for clarity.

The lithium cation resides in the typical tetrahedral environment where two positions are defined by two methylene units of two different γ-metallated amido ligands [Li(1)–C(7) = 2.22(3) Å, Li(1)–C(1) = 2.24(3) Å, C(7)–Li(1)–C(1) = 102.5(11)] of the same monomeric unit. The two other positions are occupied by two oxygen donor atoms of the one DME solvent molecule [Li(1)–O(1) = 1.99(3) Å, Li(1)–O(2) = 1.98(3) Å, O(1)–Li(1)–C(1) = 132.6(13) , O(2)–Li(1)–C(7) = 133.9(12)]

2. The crystal structure of **4.2** reveals a trinuclear cluster consisting of three uranium metal centers each bearing one intact and one deprotonated silazanate ligand. One methoxide group bridging two of the three uranium centers completes the structure. The other three silazanate groups are deprotonated to different extent. Two are singly deprotonated each bridging with the methylene group one pair of uranium atoms, while the third appears to be triply deprotonated with the carbine group bridging the three uranium atoms. Each one of the uranium atoms is located in the center of a trigonal bipyramid. One of the axial positions of each bi-pyramid is occupied by the shared μ^3-carbine carbon atom [U(1)–C(31) = 2.362(19) Å, U(2)–C(31) = 2.284(19) Å, U(3)–C(31) = 2.415(6) Å] (Figure 4.2).

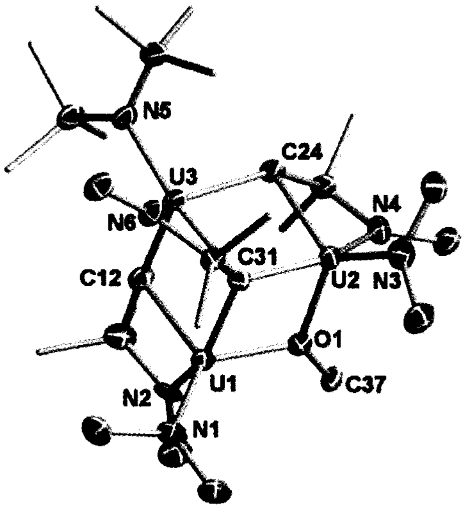


Figure 4.2. Thermal ellipsoid diagrams of **4.2** with thermal ellipsoid drawn at 50% probability level. Hydrogen atoms, methyl carbon atoms of some $SiMe_3$ fragments and thermal ellipsoids of some carbon atoms have been omitted for clarity.

One of the three uranium metals has the nitrogen donor atom of the unaltered hexamethyldisilazane in the second axial position [U(3)–N(5) = 2.313(16) Å, N(5)–U(3)–C(31) = 171.8(6)]. Instead both U(1) and U(2) bear in the second axial position a nitrogen donor atoms of the amido-methylene ligands [U(1)–N(2) = 2.240(15) Å, U(2)–N(4) = 2.231(15) Å, C(31)–U(1)–N(2) = 147.6(5) , C(31)–U(2)–N(4) = 145.2(5)]. Both atoms have also one of their equatorial positions occupied by the nitrogen of one intact hexamethyldisilazane units [U(1)–N(1) = 2.289(15) Å, N(1)–U(1)–N(2) = 100.8(5) , U(2)–N(3) = 2.323(15) Å, N(3)–U(2)–N(4) = 103.6(6)]. Their second equatorial positions are occupied by the oxygen atom of the bridging methoxy group [U(1)–O(1) = 2.288(12) Å, U(2)–O(1) = 2.313(13)Å, O(1)–U(1)–N(1) = 126.4(5) , O(1)–U(1)–N(2) = 97.7(5) , O(1)–U(2)–N(3) = 124.9(5) , O(1)–U(2)–N(4) = 90.3(5) , U(1)–O(1)–U(2) = 107.0(5)] while the third sites are occupied by the bridging methylene groups of the two methylene-pentamethyldisilazanate ligands [U(1)–C(12) = 2.62(2) Å, C(12)–U(1)–N(1) = 128.9(6) , C(12)–U(1)–N(2) = 69.0(6) , U(2)–C(24) = 2.62(2) Å, C(24)–U(2)–N(3) = 129.4(6) , C(24)–U(2)–N(4) = 70.9(6)]. In turn, the U(3) center has the two above methylene groups occupying the two equatorial positions [U(3)–C(12) = 2.57(2) Å, U(3)–C(24) = 2.66(2) Å, [U(1)–C(12)–U(3) = 90.9(6) , U(2)–C(24)–U(3) = 90.1(6)].C(12)–U(3)–C(24) = 94.8(7) , C(12)–U(3)–N(5) = 101.5(6) , C(24)–U(3)–N(5) = 92.5(6)], the last being occupied by the nitrogen atom of the carbine-amido ligand [U(3)–N(6) = 2.261(15) Å, N(6)–U(3)–N(5) = 107.1(6) , N(6)–U(3)–C(12) = 119.8(6)].

3. Complex **4.3** also is a tri-metallic cluster of structure reminiscent of **4.2,** being composed by three silazanate units and three additional silazanates deprotonated at different extent. The main difference with **4.2** consists of the replacement of the μ-OMe group with a μ-methylene moiety. As in **4.2**, each U metal center lies in the center of a trigonal bi-pyramid with one common axial position occupied by the tetrahedral carbine carbon atom C(31) μ^3-bonded to the three uranium metal centers [U(1)–C(31) = 2.361(4) Å, U(2)–C(31) = 2.352(5) Å, U(3)–C(31) = 2.339(4) Å] (Figure 4.3).

Each U metal center has the nitrogen donor atom from each of three γ-metallated-amido units in its second axial position [U(1)–N(2) = 2.286(4) Å, U(2)–N(4) = 2.276(4) Å, U(3)–N(5) = 2.275(4) Å, N(2)–U(1)–C(31) = 144.23(16) , N(4)–U(2)–C(31) = 141.06(15) , N(5)–U(3)–C(31) = 153.21(15)]. The three methylene atoms bridges a pair of uranium centers each [U(1)–C(10) = 2.658(6) Å, C(10)–U(2) = 2.557(6) Å, U(2)–C(22) = 2.677(5) Å, C(22)–U(3) = 2.602(5) Å, U(3)–C(28) = 2.634(5) Å, C(28)–U(1) = 2.553(5) Å] occupying equatorial positions of two neighboring U metal centers [C(10)–U(1)–C(31) = 78.71(18) , C(10)–U(1)–C(28) = 105.29(17) , C(22)–U(2)–C(31) = 81.08(15) , C(10)–U(2)–C(22) = 112.60(17) , C(28)–U(3)–C(31) = 84.05(15) , C(22)–U(3)–C(28) = 124.81(16)] and assembling the trimeric unit [U(1)–C(10)–U(2) = 93.06(18) , U(2)–C(22)–U(3) = 89.15(19) , U(3)–C(28)–U(1) = 89.03(18)].

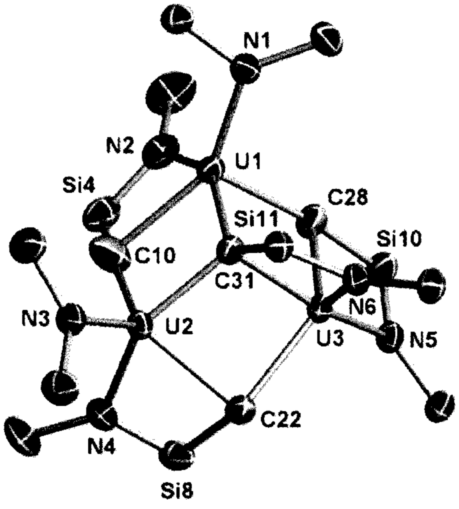


Figure 4.3. Partial thermal ellipsoid diagrams of **4.3** with thermal ellipsoid drawn at 50% probability level. Hydrogen atoms, methyl carbon atoms of several $SiMe_3$ fragments and thermal ellipsoids of some carbon atoms have been omitted for clarity.

The last equatorial positions in the coordination polyhedra of two uranium metal centers are occupied by two nitrogen donor atoms of two unaltered hexamethyldisilazane ligands [U(1)–N(1) = 2.303(4) Å, N(1)–U(1)–C(31) = 106.97(15) , N(1)–U(1)–C(10) = 147.6(2) , U(2)–N(3) = 2.315(4) Å, N(3)–U(2)–C(31) = 113.12(15) , N(3)–U(2)–C(22) = 129.25(15)]. The last equatorial position of the third uranium is occupied by the nitrogen atom of the same carbine-pentamethyldisilazane unit [U(3)–N(6) = 2.223(4) Å, N(6)–U(3)–C(31) = 75.97(15) , N(6)–U(3)–C(28) = 121.32(16)].

4. The structure of **4.4** is also trimeric but with the three uranium metal centers bridged by five chlorine atoms. Three are each bridging one pair of metals forming a rather planar U_3Cl_3 core [U(1)–Cl(1) = 2.841(5) Å, U(1)–Cl(2) = 2.809(5) Å, U(2)–Cl(1) = 2.843(4) Å, U(2)–Cl(3) = 2.812(4) Å, U(3)-Cl(3) = 2.875(5) Å, U(3)-Cl(2) = 2.891(5) Å, Cl(1)–U(1)–Cl(4) = 72.45(12) , Cl(2)–U(1)–Cl(4) = 73.57(13) , Cl(1)–U(1)–Cl(5) = 75.52(13) , Cl(2)–U(1)–Cl(5) = 76.39(13)], while the other two are placed in apical positions on the two opposite sides of the U_3Cl_3 plane, each being μ^3-bonded to the three metals [U(1)–Cl(4) = 3.103(5) Å, U(1)–Cl(5) = 2.885(4) Å, Cl(4)–U(1)–Cl(5) = 68.51(12) , U(2)–Cl(4) = 2.879(4) Å, U(2)–Cl(5) = 3.068(5) Å, Cl(4)–U(2)–Cl(5) = 69.09(12) , U(3)–Cl(4) = 3.074(5) Å, U(3)–Cl(5) = 3.065(4) Å, Cl(4)–U(3)–Cl(5) = 66.71(12)]. The three metals reside in different coordination environments.

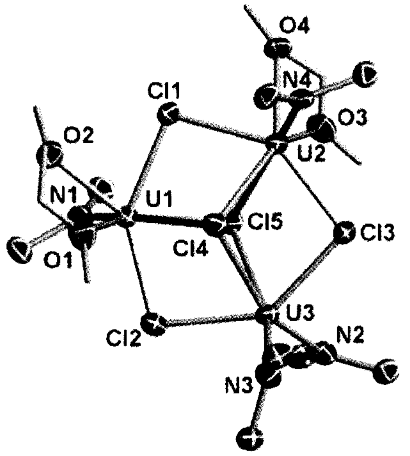


Figure 4.4. Partial thermal ellipsoid diagrams of **4.4** with thermal ellipsoid drawn at 50% probability level. Hydrogen atoms, methyl carbon atoms of several $SiMe_3$ fragments and thermal ellipsoids for all carbon atoms have been omitted for clarity.

Two have the same heavily distorted pentagonal bipyramidal geometry with four coordination sites occupied by the four bridging chlorine atoms, two by the oxygen of one coordinated DME [U(1)–O(1) = 2.593(13) Å, U(1)–O(2) = 2.592(12) Å, O(1)–U(1)–Cl(4) = 71.5(3), O(2)–U(1)–Cl(4) = 112.5(3) , O(1)–U(1)–Cl(2) = 84.3(3) , O(2)–U(1)–Cl(1) = 72.0(3)], and the last by the nitrogen atom of one intact silazanate group [U(1)–N(1) = 2.298(14) Å, N(1)–U(1)–Cl(4) = 163.9(3), U(2)–N(4) = 2.304(14) Å, N(4)–U(2)–Cl(4) = 96.7(3)]. The third U atom is located instead in the center of a distorted octahedron with four coordination sites occupied by the bridging chlorine atoms and two nitrogen atoms of two intact silazanate located in the two remaining *cis* positions [N(2)–U(3)–N(2) = 104.10(12)]. (Figure 4.4).

5. Complex **4.5** is dimeric and consists of two identical uranium-containing units bridged by two chlorine atoms. The coordination geometry of uranium is distorted trigonal bipyramidal with the axial positions occupied by one bridging chlorine [U(1)–Cl(1) = 2.829(2) Å, Cl(1)–U(1)–Cl(1A) = 72.79(6), U(1)–Cl(1)–U(1A) = 107.21(6)] and the second by the imido nitrogen atom [U(1)–N(3) = 2.081(5) Å, N(3)–U(1)–Cl(1A) = 154.87(13)] (Figure 4.5).

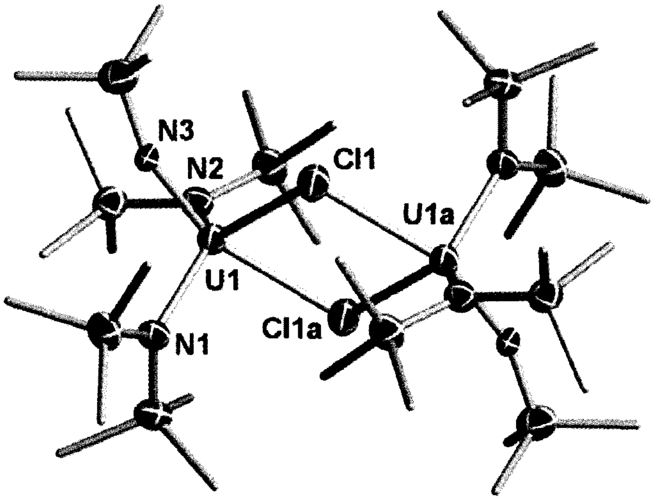


Figure 4.5. Partial thermal ellipsoid diagrams of **4.5** with thermal ellipsoid drawn at 50% probability level. Hydrogen atoms and thermal ellipsoids for all carbon atoms have been omitted for clarity.

The two equatorial positions are occupied by the nitrogen atoms of two hexamethyldisalazanate ligands [U(1)–N(1) = 2.237(5) Å, U(1)–N(2) = 2.249(5) , N(1)–U(1)–Cl(1) = 111.87(14) , N(2)–U(1)–Cl(1) = 126.54(13)] and by the second bridging chlorine atom [U(1)–Cl(1A) = 2.847(2) Å]. The terminally bonded imido group is almost linear [U(1)–N(3)–Si(5) = 160.8(2)] and forms the expected short U-N distance [U(1)–N(3) = 2.081(5) Å].

6. Complex **4.6** is monomeric and consists of a single uranium atom located in the center of a distorted trigonal bipyramid as determined by the carbon and nitrogen atoms of two methylene-pentamethyldisilazane ligands and the nitrogen of one intact silazanate [C(13)–U(1)–N(3) = 65.7(3), C(7)–U(1)–N(3) = 149.2(4), N(3)–U(1)–N(2) = 114.3(2) , C(13)–U(1)–N(2) = 91.3(4) , N(3)-U(1)-C(7) =]. The first methylene-pentamethyldisilazane ligand occupies one axial position with the nitrogen atom [U(1)–N(3) = 2.258(6) Å] and one equatorial with the methylene group [U(1)–C(13) = 2.985(19) Å]. The second has the same arrangement except that the nitrogen and methylene are respectively located on the equatorial [U(1)–N(2) = 2.241(7) Å] and axial positions [U(1)–C(7) = 2.830(18) Å] (Figure 4.6). The last equatorial position around the U metal center is occupied by the nitrogen donor atom of an un-altered hexamethyldisalazanate ligand [U(1)–N(1) = 2.240(7) Å, N(1)–U(1)–N(3) = 113.2(2) , N(1)–U(1)–C(13) = 143.2(4)].

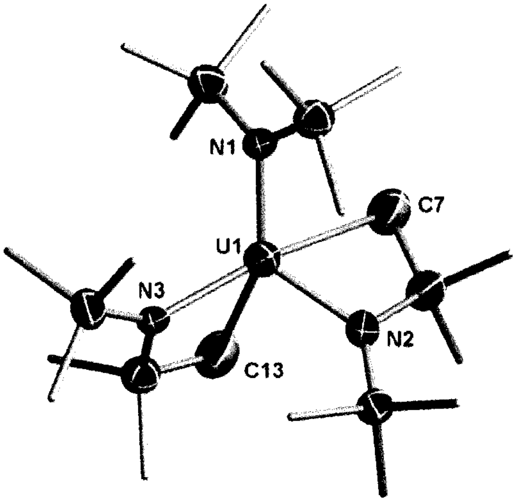


Figure 4.6. Partial thermal ellipsoid diagrams of **4.6** with thermal ellipsoid drawn at 50% probability level. Hydrogen atoms, methyl carbon atoms of the $SiMe_3$ fragments have been omitted for clarity.

Table 4.1. Crystal Data and Data Collection Parameters of Complexes **4.1**, **4.2** and **4.3**

	4.1	**4.2**	**4.3**
Formula	$U_2C_{38}H_{102}Li_2N_4O_4Si_8$	$U_3C_{37}H_{106}N_6OSi_{12}$	$U_3C_{36}H_{102}N_6Si_{12}$
FW	1393.90	1702.45	1670.41
Crystal system,	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	P-*1*	P-*1*
a, Å	14.862(3)	11.923(3)	14.826(3)
b, Å	11.980(2)	13.947(4)	15.141(3)
c, Å	18.250(3)	22.855(6)	15.561(3)
α, deg	90	79.887(6)	75.030(3)
β, deg	97.579(4)	75.655(5)	89.431(4)
γ, deg	90	67.832(5)	86.129(4)
Volume, $Å^3$	3220.8(10)	3395.7(15)	3366.8(12)
Z	2	2	2
ρ_{calc} g/cm3	1.437	1.665	1.648
μ□ mm^{-1}	5.203	7.378	7.438
F(000)	1384	1644	1608
T range (deg)	1.66 - 20.81	1.58 - 21.96	1.35 - 28.50
Limiting indices (*h, k, l*)	±14, 0 to +11, 0 to +18	±12, ±14, 0 to +23	±19, ±19, 0 to +20
Reflections collected / unique	3309 / 3309	8068 / 8068	23433 / 14059
R_{int}	0.0000	0.0000	0.0218
GOF	0.647	0.934	1.013
R1 (obs / all)	0.0476 / 0.0868	0.0668 / 0.1664	0.0285 / 0.0399
wR2 (obs / all)	0.0897 / 0.0961	0.0797 / 0.0985	0.0659 / 0.0706

Table 4.1 (contd.). Crystal Data and Data Collection Parameters of Complexes **4.4**, **4.5** and **4.6**

	4.4	**4.5**	**4.6**
Formula	$U_3C_{39}H_{100}Cl_5N_4O_4Si_8$	$U_2C_{30}H_{90}Cl_2N_6Si_{10}$	$UC_{18}H_{52}N_3Si_6$
FW	1805.29	1362.94	717.20
Crystal system,	Triclinic	Monoclinic	Orthorhombic
Space group	P-*1*	P*2₁/n*	P*nma*
a, Å	15.1810(17)	11.910(3)	18.607(3)
b, Å	15.6704(18)	14.303(3)	8.440(1)
c, Å	15.9987(18)	17.715(4)	21.682(3)
α, deg	78.675(2)	90	90
β, deg	87.335(2)	99.568(3)	90
γ, deg	66.676(2)	90	90
Volume, Å^3	3424.8(7)	2975.8(11)	3405.2(8)
Z	2	2	4
ρ_{calc} g/cm3	1.751	1.521	1.399
μ□ mm^{-1}	7.445	5.751	4.988
F(000)	1734	1340	1428
T range (deg)	1.75 - 21.96	1.84 - 28.90	2.17 - 21.96
Limiting indices (*h, k, l*)	±16, ±17, 0 to +17	±13, ±18, ±22	±19, ±8, ±22
Reflections collected / unique	30603 / 9777	16720 / 6814	23771 / 2383
R_{int}	0.2162	0.0597	0.0939
GOF	1.034	1.053	1.031
R1 (obs / all)	0.0631 / 0.1145	0.0475 / 0.0959	0.0448 / 0.0844
wR2 (obs / all)	0.1354 / 0.1467	0.0797 / 0.0907	0.0752 / 0.0848

Table 4.2. Selected bond distances (Å) and angles (deg) for Complexes **4.1**, **4.2** and **4.3**

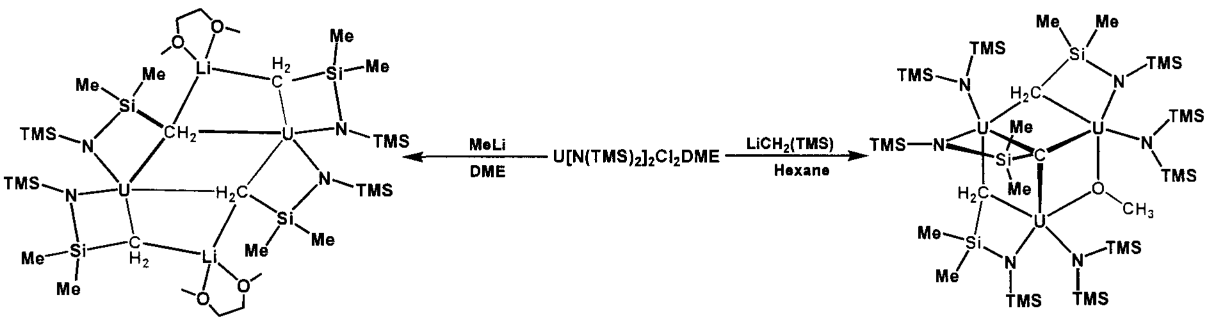
4.1	**4.2**	**4.3**
U(1)-N(1) = 2.302(10)	U(1)-N(2) = 2.240(15)	U(1)-N(2) = 2.286(4)
U(1)-N(2) = 2.296(10)	U(1)-O(1) = 2.288(12)	U(1)-N(1) = 2.303(4)
U(1)-C(1) = 2.362(12)	U(1)-N(1) = 2.289(15)	U(1)-C(31) = 2.361(4)
U(1)-C(1)A = 2.372(10)	U(1)-C(31) = 2.362(19)	U(1)-C(10) = 2.658(6)
U(1)-C(7) = 2.518(13)	U(1)-C(12) = 2.62(2)	U(1)-C(28) = 2.553(5)
U(1)-Li(1) = 3.11(2)	U(2)-N(4) = 2.231(15)	U(1)-U(3) = 3.6372(5)
U(1)-U(1)A = 3.6161(12)	U(2)-C(31) = 2.284(19)	U(1)-U(2) = 3.7854(7)
	U(2)-O(1) = 2.313(13)	U(2)-N(4) = 2.276(4)
N(1)-U(1)-N(2) = 112.1(4)	U(2)-N(3) = 2.323(15)	U(2)-N(3) = 2.315(4)
N(1)-U(1)-C(1) = 79.0(3)	U(2)-C(24) = 2.62(2)	U(2)-C(31) = 2.352(5)
N(2)-U(1)-C(1) = 161.1(4)	U(3)-N(6) = 2.261(15)	U(2)-C(22) = 2.677(5)
N(1)-U(1)-C(1)A = 112.8(4)	U(3)-N(5) = 2.313(16)	U(2)-C(10) = 2.557(6)
N(2)-U(1)-C(1)A = 107.4(4)	U(3)-C(31) = 2.415(6)	U(2)-U(3) = 3.7054(6)
C(1)-U(1)-C(1)A = 80.4(4)	U(3)-C(12) = 2.57(2)	U(3)-N(6) = 2.223(4)
N(1)-U(1)-C(7) = 111.7(4)	U(3)-C(24) = 2.66(2)	U(3)-N(5) = 2.275(4)
N(2)-U(1)-C(7) = 71.0(4)		U(3)-C(31) = 2.339(4)
C(1)-U(1)-C(7) = 90.9(4)	N(2)-U(1)-N(1) = 100.8(5)	U(3)-C(28) = 2.634(5)
C(1)A-U(1)-C(7) = 131.9(4)	O(1)-U(1)-N(1) = 126.4(5)	U(3)-C(22) = 2.602(5)
N(1)-U(1)-U(1)A = 97.5(3)	N(2)-U(1)-C(31) = 147.6(5)	
N(2)-U(1)-U(1)A = 144.5(3)	O(1)-U(1)-C(31) = 72.9(5)	N(2)-U(1)-N(1) = 108.25(15)
C(1)-U(1)-U(1)A = 40.3(2)	N(1)-U(1)-C(31) = 109.7(5)	N(2)-U(1)-C(31) = 144.23(16)
C(1)A-U(1)-U(1)A = 40.1(3)	N(2)-U(1)-C(12) = 69.0(6)	N(1)-U(1)-C(31) = 106.97(15)
C(7)-U(1)-U(1)A = 116.6(3)	O(1)-U(1)-C(12) = 104.6(6)	N(2)-U(1)-C(10) = 68.29(19)
Si(1)-U(1)-U(1)A = 68.25(9)	N(1)-U(1)-C(12) = 128.9(6)	N(1)-U(1)-C(10) = 147.6(2)
Si(3)-U(1)-U(1)A = 144.04(9)	N(4)-U(2)-C(31) = 145.2(5)	C(31)-U(1)-C(10) = 78.71(18)
Li(1)-U(1)-U(1)A = 78.1(4)	C(31)-U(2)-O(1) = 73.9(5)	N(4)-U(2)-N(3) = 105.22(15)
	C(31)-U(2)-N(3) = 111.0(6)	N(4)-U(2)-C(31) = 141.06(15)
	O(1)-U(2)-N(3) = 124.9(5)	N(3)-U(2)-C(31) = 113.12(15)
	N(4)-U(2)-C(24) = 70.9(6)	N(4)-U(2)-C(22) = 69.32(16)
	C(31)-U(2)-C(24) = 83.5(5)	N(3)-U(2)-C(22) = 129.25(15)
	O(1)-U(2)-C(24) = 105.6(6)	C(31)-U(2)-C(22) = 81.08(15)
	N(3)-U(2)-C(24) = 129.4(6)	N(6)-U(3)-C(31) = 75.97(15)
	N(6)-U(3)-N(5) = 107.1(6)	N(5)-U(3)-C(31) = 153.21(15)
	N(6)-U(3)-C(31) = 75.9(6)	N(6)-U(3)-C(28) = 121.32(16)
	N(5)-U(3)-C(31) = 171.8(6)	N(5)-U(3)-C(28) = 70.13(14)
	N(6)-U(3)-C(12) = 119.8(6)	C(31)-U(3)-C(28) = 84.05(15)
	N(5)-U(3)-C(12) = 101.5(6)	
	C(31)-U(3)-C(12) = 83.1(6)	
	N(6)-U(3)-C(24) = 134.4(6)	
	N(5)-U(3)-C(24) = 92.5(6)	
	C(31)-U(3)-C(24) = 80.3(6)	
	C(12)-U(3)-C(24) = 94.8(7)	

Table 4.2 (contd.). Selected bond distances (Å) and angles (deg) for Complexes **4.4**, **4.5** and **4.6**

4.4	**4.5**	**4.6**
U(1)-N(1) = 2.298(14)	N(1)-U(1)A = 2.240(7)	U(1)-N(3) = 2.081(5)
U(1)-O(2) = 2.592(12)	N(1)-U(1) = 2.240(7)	U(1)-N(1) = 2.237(5)
U(1)-O(1) = 2.593(13)	N(2)-U(1) = 2.241(7)	U(1)-N(2) = 2.249(5)
U(1)-Cl(2) = 2.809(5)	N(2)-U(1)A = 2.241(7)	U(1)-Cl = 2.8298(18)
U(1)-Cl(1) = 2.841(5)	N(3)-U(1) = 2.258(6)	U(1)-ClA = 2.8470(19)
U(1)-Cl(5) = 2.885(4)	N(3)-U(1)A = 2.258(6)	
U(1)-Cl(4) = 3.103(5)	U(1)-C(7) = 2.830(18)	N(3)-U(1)-N(1) = 99.45(19)
U(2)-N(4) = 2.304(14)	U(1)-C(13) = 2.985(19)	N(3)-U(1)-N(2) = 93.22(19)
U(2)-O(3) = 2.569(12)		N(1)-U(1)-N(2) = 121.37(18)
U(2)-O(4) = 2.584(11)	N(1)-U(1)-N(2) = 119.0(2)	N(3)-U(1)-Cl = 82.32(13)
U(2)-Cl(3) = 2.812(4)	N(1)-U(1)-N(3) = 113.2(2)	N(1)-U(1)-Cl = 111.87(14)
U(2)-Cl(1) = 2.843(4)	N(2)-U(1)-N(3) = 114.3(2)	N(2)-U(1)-Cl = 126.54(13)
U(2)-Cl(4) = 2.879(4)	N(1)-U(1)-C(7) = 86.8(4)	N(3)-U(1)-ClA = 154.87(13)
U(2)-Cl(5) = 3.068(5)	N(2)-U(1)-C(7) = 70.6(3)	N(1)-U(1)-ClA = 93.13(14)
U(3)-N(3) = 2.349(13)	N(3)-U(1)-C(7) = 149.2(4)	N(2)-U(1)-ClA = 98.69(14)
U(3)-N(2) = 2.357(14)	N(1)-U(1)-C(13) = 143.2(4)	Cl-U(1)-ClA = 72.79(6)
U(3)-Cl(3) = 2.875(5)	N(2)-U(1)-C(13) = 91.3(4)	
U(3)-Cl(2) = 2.891(5)	N(3)-U(1)-C(13) = 65.7(3)	
U(3)-Cl(5) = 3.065(4)	C(7)-U(1)-C(13) = 84.2(5)	
U(3)-Cl(4) = 3.074(4)		
N(1)-U(1)-O(2) = 82.3(5)		
N(1)-U(1)-O(1) = 123.3(4)		
O(2)-U(1)-O(1) = 61.5(4)		
N(1)-U(1)-Cl(2) = 100.0(4)		
N(1)-U(1)-Cl(1) = 107.9(4)		
N(1)-U(1)-Cl(5) = 95.8(3)		
N(1)-U(1)-Cl(4) = 163.9(3)		
O(2)-U(1)-Cl(4) = 112.5(3)		
Cl(5)-U(1)-Cl(4) = 68.51(12)		
N(4)-U(2)-O(3) = 122.9(4)		
O(3)-U(2)-O(4) = 63.0(4)		
N(4)-U(2)-Cl(3) = 102.4(3)		
N(4)-U(2)-Cl(1) = 105.1(3)		
Cl(3)-U(2)-Cl(1) = 142.37(14)		
N(4)-U(2)-Cl(4) = 96.7(3)		
Cl(1)-U(2)-Cl(4) = 75.90(13)		
N(4)-U(2)-Cl(5) = 165.8(3)		
Cl(4)-U(2)-Cl(5) = 69.09(12)		
N(3)-U(3)-N(2) = 104.1(5)		
N(2)-U(3)-Cl(3) = 88.6(4)		
N(3)-U(3)-Cl(2) = 92.7(4)		
N(3)-U(3)-Cl(5) = 158.8(4)		
Cl(2)-U(3)-Cl(5) = 72.41(12)		
N(3)-U(3)-Cl(4) = 94.9(4)		
Cl(5)-U(3)-Cl(4) = 66.71(12)		

Results and Discussion

As observed by Andersen,[10] attempts to alkylate the tetravalent uranium *tris*-amido-chloride complex $UCl[N(TMS)_2]_3$ inevitably afforded γ-deprotonation of the hexamethyldisilazane ligand. By using the poly-chlorinated uranium precursor $UCl_2[N(TMS)_2]_2(DME)$ we have now obtained multiple deprotonation and even reduction to the trivalent state depending on the nature of the organo-lithium reagent used. For example, low temperature reaction with two equivalents of methyl lithium gave rapid color change with formation of considerable amount of insoluble material. After separation and suitable work-up, the *trivalent* **4.1** was obtained in near to quantitative yield (Scheme 4.1). Complex **4.1** does not contain U-Me groups but had both silazanate groups deprotonated at one methyl group of each silazanate forming methylene groups. The presence of the lithium counteraction coordinated to the two methylene assigns the trivalent state to the metal center. The reaction is accompanied by the expected formation of methane (observed in the reaction mixtures of experiments performed in sealed NMR tubes). The ^{1}H-NMR spectrum of **4.1** supports the formulation yielded by the crystal structure showing the expected three broad singlets at -13.1, -28.6 and -47.0 ppm with relative intensity 6:9:2 and respectively assigned to the Si-(Me)$_2$, N-TMS, and -CH$_2$- groups. The DME resonances are located at 3.12 ppm and 3.30 ppm.



4.1 **4.2**

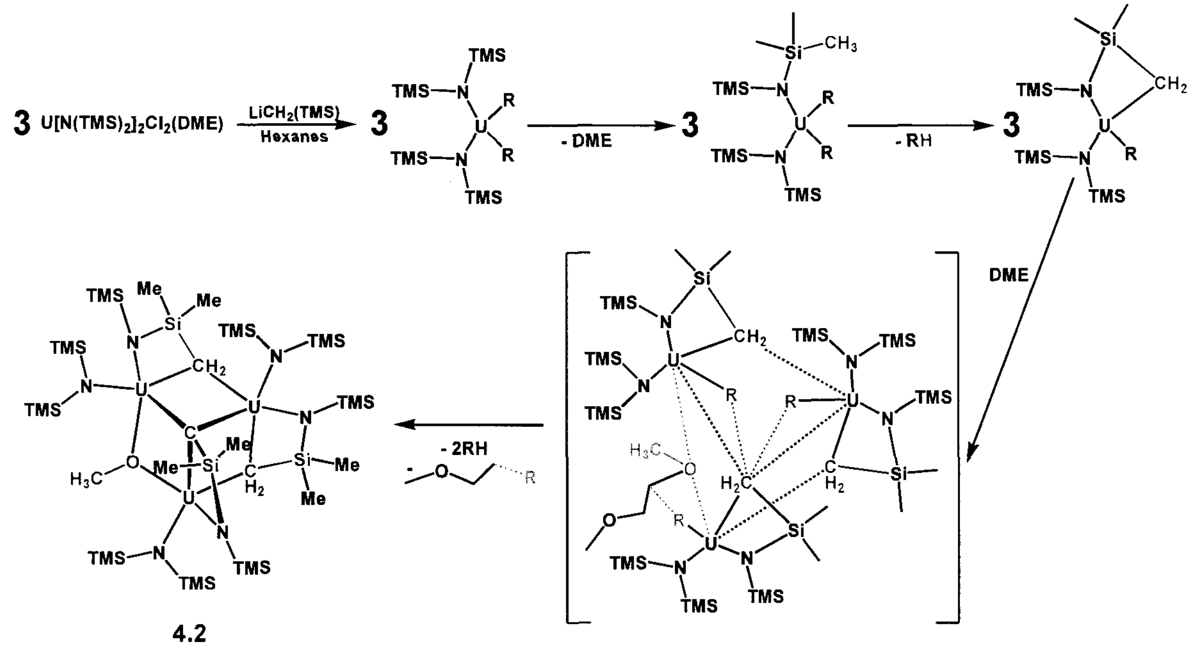
Scheme 4.1.

The formation of **4.1** implies two C-H σ-bond methatetic reactions of two silazanate Me groups by two incoming Me groups but also the intervention of a third equivalent of alkyl-lithium, exclusively acting as a reducing agent. In the attempt to prevent reduction of the metal center several experiments were carried out with smaller amount of MeLi. All these experiments always yielded the same compound **4.1** with lower yield.

A very similar reaction under comparable conditions and in hexane was carried out with [(trimethylsilyl)methyl]lithium. This reaction also proceeded with rapid color change and, after suitable work-up, the trimeric *tetravalent* uranium cluster **4.2** was isolated in crystalline form (Scheme 1). The trinuclear structure is composed by three "$U[N(TMS)_2]$" units each bearing another silazanate which has been deprotonated to a different extent. Two units displayed the same single deprotonation with formation of methylene. The third instead has undergone triple deprotonation with formation of a carbine which is capping the *triangulo* structure. One unanticipated bridging methoxy group, likely arising from DME cleavage, also is part of the structure. The ^{1}H-NMR spectrum was in complete agreement with the formulation showing five broadened singlets in the expected ratio 27:3:54:18:4. The large peak at 29.36 ppm integrating for 27H is assigned to the Me groups of the γ-deprotonated amido-ligands. The second peak with relative intensity of 3H situated at 9.85 ppm is assigned to the bridging methoxy group. The most intense peak of the spectrum positioned at 7.19 ppm (54H) is unequivocally assigned to the eighteen Me groups of three unaltered $N(TMS)_2$ ligands. The next resonance consists of two partly overlapping broad signals centered at -0.13 ppm assigned to the six $Si(Me)_2$ unit, carrying eighteen protons. Finally one remaining signal at -46.90 ppm with intensity of 4 is assigned to four protons of the bridging methylene groups.

At first glance, the formation of **4.2** seems the result of a complex transformation. Instead it can be easily visualized with the intermediate formation of three identical $[N(TMS)_2][\mu\text{-}CH_2\text{-}Si(Me)_2\text{-}N(TMS)]UR$ units. Two alkyls from two units methatesized the same $-CH_2-$ group of the third unit giving rise to the carbine. In turn, the third U-R group attacks DME solvent molecule, forming the -OMe group as a result (Scheme 4.2).

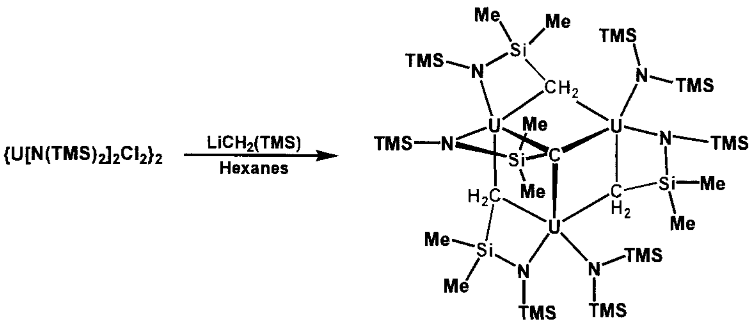
No reduction of the metal centers occurred in this case as a probable result of the lesser reducing power of the particular lithium-alkyl employed in this case.



4.2

Scheme 4.2

To prevent the interference of DME in the reactivity, an identical reaction was carried out by using the dimeric and solvent-free {U[μ-Cl]Cl[N(TMS)$_2$]$_2$}$_2$ as a starting material. Similar to the transformations described above and despite the very low solubility in hexane of the starting uranium complex, this reaction also occurred very rapidly upon mixing, affording complete solubilization and color change. Black crystals of **4.3** were obtained after suitable work-up (Scheme 4.3).



4.3

Scheme 4.3.

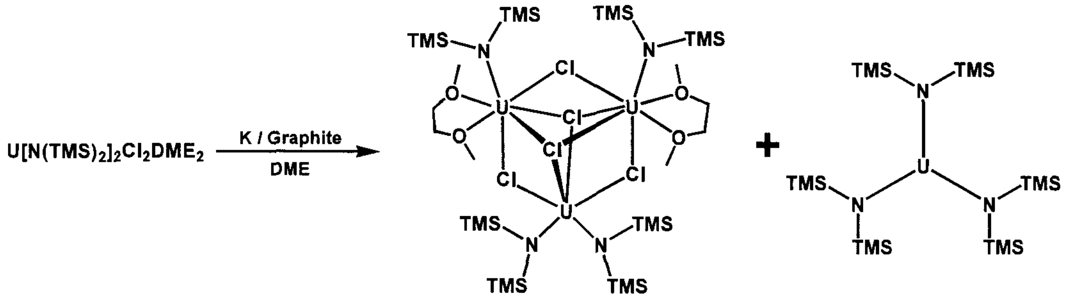
Complex **4.3** is also trimeric with an arrangement of the ligands closely reminiscent of **4.2**. The main difference consists in the absence of the MeO unit. Similarly deprotonated tri-capping group of **4.3** also became was identified as carbine. This formulation is not only indicated by the geometrical parameters provided by the crystal structure but also by the ^{1}H-NMR spectrum. The higher molecular symmetry reflects in a simpler spectrum consisting of five resonances in the ratio 6:6:3:1:1. The first resonance is observed at 24.11 ppm and is assigned to the protons of four N-TMS fragments of γ-deprotonated ligands. The second signal of same intensity at 7.22 ppm is assigned to four TMS groups, which belongs to unaltered hexamethyldisilazanate groups. Magnetically different environment for $Si(Me)_2$ protons of bridging versus tri-capped fragments results in the appearance of two peaks at -13.48 ppm and -16.85 ppm with the relative intensity of 3:1. Finally, the last resonance positioned at -43.10 ppm could be assigned to the 6 protons of 3 bridging $-CH_2-$ fragments.

The formation of **4.3** may be rationalized with the same arguments visualized in Scheme 2, the only difference being the attack of the third U-R alkyl function of the third unit on the other $Si\text{-}CH_3$ moiety, thus leading to the appearance of a third μ-CH_2- unit.

The spontaneous reduction observed during the formation of **4.1** encouraged us to attempt a more systematic exploration of the reduction chemistry of uranium to probe the ability of the silazanate ligand system to stabilize reduced species and hopefully low-valent synthons. It should be reiterated that a low-valent uranium supported by nitrogen donor ligand systems may possess a very high reactivity including dinitrogen fixation and cleavage.[1-2] The presence of two chlorine atoms in $\{U[\mu\text{-}Cl]Cl[N(TMS)_2]_2\}_2$ and $UCl_2[N(TMS)_2]_2[DME]$ make these species suitable candidates for these attempts.

Reduction of $UCl_2[N(TMS)_2]_2[DME]$ with K/C_8 in DME proceeds rather slowly, with the reaction being completed only after 3 days of stirring at room temperature. The reaction progress was indicated by both the color change of the reaction mixture as well as by the disappearance of the characteristic coloration of potassium graphite. After work-up and crystallization the dark red-purple **4.4** was isolated as a crystalline solid (Scheme 4.4). The crystal structure revealed a triangular cluster where three uranium atoms are bridged by five chlorines. Two metal centers bear only one silazanate while the third has retained two. The oxidation state is clearly trivalent and the ^{1}H NMR spectrum did not provide any additional information due to significant line broadening.

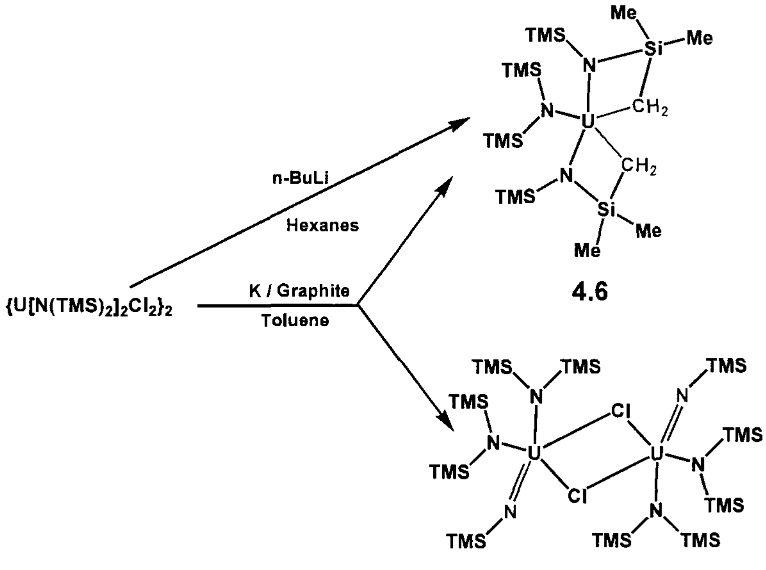
The only noticeable feature of this reaction is the ligand dissociation as partly occurred during the reduction. Variable amount of the tris-silazanate uranium complex accompanied this reaction thus reiterating that ligand scrambling is an important aspect of this transformation.



4.4

Scheme 4.4.

The presence of DME coordinated to two of the three uranium centers of the *triangulo* cluster might have a quenching power in the reactivity of the trivalent uranium centers. Seeking for signs of high reactivity, we have attempted an identical reduction of the DME-free tetravalent precursor $\{U[\mu\text{-}Cl]Cl[N(TMS)_2]_2\}_2$ with K/graphite in toluene. The reaction took almost seven days to come to completion possibly due to the very low solubility of both reagents in toluene. The progress of the reaction was indicated by the disappearance of the characteristic tint of K/C_8 as well as the increasing coloration of the mother liquor. Work-up of the reaction mixture followed by fractional crystallization afforded two separated compounds **4.5** and **4.6** both containing the metal center in its pentavalent state (Scheme 4.5). The formation of **4.5** implies acquisition of one additional silazanate and cleavage of one of them to form a terminally bonded imido-group. The residual chlorine is used for assembling the dinuclear U_2Cl_2 core. Complex **4.6** instead appears to be the result of the γ-metallation of two methyl groups of an hypothetical $U[N(TMS)_2]_3$ intermediate. In fact, the composition of both species clearly indicated that ligand scrambling occurred during their formation possibly as the result of the absence of DME.



4.6

4.5

Scheme 4.5.

The formation of both compounds containing relatively high valent uranium from a reduction carried out with a strong reducing reagent such as KC_8 is surprising. It can be explained only by assuming appearance of a transient reduced species followed by reoxidation at the expenses of the silazanate ligand system. Such internal re-oxidation resulted in the expulsion of one TMS group and formation of imido fragment in the case of complex **4.5**. The formation of **4.6** implies instead a *formal* elimination of H_2 from $U[N(TMS)_2]_3$ although the reaction must be more complicated given the fact that $U[N(TMS)_2]_3$ is a stable compound. In any event, this reaction certainly implies formation of other species as byproducts of the reaction, which structure unfortunately remains unknown.

While a rationalization for the formation of **4.5** may be easily envisioned, the formation of **4.6** is more puzzling. The employment of *n*-BuLi as both alkylating agent and reductant is well established in transition metal chemistry. Keeping in mind the formation of **4.1**, we reasoned that alkylation of $\{U[\mu\text{-}Cl]Cl[N(TMS)_2]_2\}_2$ with two equivalent of *n*-BuLi may provide the double γ-metallation of the two silazanate ligand. The acquisition of the third silazanate and the increase of the metal oxidation state may instead be achieved via a simple disproportionation assisted by the ligand migration. Accordingly, treatment of the suspension of uranium starting material with hexane solution of *n*-BuLi yields gave immediate solubilization and darkening of the reaction mixture. After suitable workup complex **4.6** was isolated in moderate yield and crystalline form (Scheme 4.5).

Conclusions.

Alkylation of DME-solvated and unsolvated forms of $U[N(TMS)_2]_2Cl_2$ in different reduction conditions resulted in the formation of the several γ-deprotonated products with multiple deprotonation having occurred at the same carbon atom. We have observed that either reduction of the metal center or solvent cleavage may accompany the transformation depending on the reaction conditions. Alkylation with *n*-butyllithium yielded a surprising pentavalent compound. The formation of compound with the metal center in oxidation state higher than in the starting material was accompanied by ligand migration. The re-oxidation of a transient highly-reactive low-valent intermediate at the expenses of the ligand is proposed as a mechanism for the formation of the complex. Deliberate reduction of the starting material with different reducing agents yielded U(III) or re-oxidized U(V) complexes, depending on the reductant.

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Chapter Five

Reduced Uranium Complexes with Bis-amino-benzene Ligand. Synthetic and DFT Study on the Role of π-ligation in the Stabilization of Uranium Species in a Formal Ultra-low-valent State.

Introduction

An extraordinary and unpredictable reactivity is the primary characteristic of low-valent complexes of *f*-block elements. [1-4] There are tangible signs in the literature that outstanding chemical reactivity, on the line of that discovered for divalent lanthanides may also be provided by reduced actinide complexes. [1a,3,4] For example, trivalent uranium complexes are widely established with a variety of σ- and π-donor ligand systems[5-7] providing remarkable examples of dinitrogen activation/ reduction[5b,e,6] and cleavage,[7] C-H bond activation,[8] solvent fragmentation,[7,8a,9] bonding of small molecules in unusual bonding modes[10] including a unique case of sp^3-C-H bond coordination,[8c] and oxidative elimination of H_2.[4i] Therefore, it is conceivable that an even higher reactivity may be expected if actinide species will be further reduced. The problem with reduced actinides is that these species embark on a very substantial electron-transfer interaction with the ligand system due to an intrinsic instability of the low-oxidation state. As an extreme case, even simple salts as UI_2 and ThI_2 have been regarded as consisting of higher valent species with *f*-spin density transferred into a sort of conduction band.[11] Given this tendency, π-bonded ligands may be particularly effective for stabilizing reduced species due to the possibility provided for elctron-transfer interaction and consequent delocalization. This idea is further supported by the observation that the sole cases of paramagnetic Th(III) derivatives[12] have been obtained exclusively with π-donor ligand systems (Cp and COT) and which again unlikely contain a genuine low-valent thorium metal center.[12c] Furthermore, seminal work by Cummins has shown that it is possible to prepare inverted sandwich π-arene actinide complexes with the formal appearance of divalent derivatives. [13] Even though theoretical calculations have clearly indicated that the actual oxidation state of uranium is in fact substantially higher, the chemical reactivity remarkably remained that of a genuine two-electron reductant. Thus the terms of low-valent synthons, or low-valent synthetic equivalents have been forged for such reduced species.

The behavior of thorium arenes[4a,14] obtained through reduction of tetravalent compounds is on the same line. In these complexes however, the distortion of the π-bonded aromatic rings as resulting from the presence of substantial back-bonding, is very visible and clearly attributes the tetravalent state to the Th atom. These species act as reactive low-valent synthons. Simple dissociation of the coordinated arene in its intact form triggers a variety of processes which include dinitrogen reduction and cleavage, solvent fragmentation, and deoxygenation.[4a,15]

Ligand systems which contains a *non*-coordinating large π-system can also achieve the purpose of stabilizing a reduced species. For example, the bis-imine pyridine ligand has shown versatility in the trapping of a highly reactive unit such as NdI_2.[16] This is possible only because this particular ligand efficiently embarks on metal-to-ligand electron transfer.[17] As a result, the actual oxidation state of the metal in these derivatives is higher. Remarkably however, the high reactivity expected for a genuine low-valent metal center is preserved.[18-21]

This background prompted us to attempt the reduction of uranium complexes of a di-anionic ligand system based on N donor atoms combined with a π-system and whose π-ligation could be only enforced by steric vicinity. Hence the selection for this particular study of the 1,3-bis-methylaryliminatobenzene 1,3-[2,5-(i-Pr)$_2$PhN=C(CH$_3$)]$_2$C$_6$H$_4$ ligand system.[22] We were expecting this ligand to preserve the established electron-storage capacity of the bis-iminato-pyridine ligand. At the same time, the replacement of the central pyridine with a regular aromatic ring was expected to either enforce a π-ligation or allowing ring metallation via C-H bond activation. In this event, more robust complexes resilient to further reducing conditions were anticipated. In any event, trivalent uranium was chosen as the target oxidation state since it provides highly reactive complexes[4c,5,] and it might be used as a starting material for further reduction.

In this study, we report some unusual observations obtained during the attempts of preparing low-valent uranium complexes of the 1,3-[2,5-(*i*-Pr)$_2$PhNC(=CH$_2$)]$_2$C$_6$H$_4$ ligand system and further reduction attempts of these compounds.

Experimental Part

All operations were performed under inert atmosphere using standard Schlenk type techniques or with the use of nitrogen filled drybox. Li, NaH, K, Naphthalene, and UO$_3$ were purchased from Aldrich and used as received. UCl$_4$(THF)$_4$ was prepared by recrystallization of freshly prepared UCl$_4$[23a] from THF. Solution of "UCl$_3$" was prepared according to the literature procedure[23b] and used immediately. Bis-iminobenzene ligand {1,3-[2,5-(*i*-Pr)$_2$PhN=C(CH$_3$)]$_2$C$_6$H$_4$} was prepared according to the literature procedure[22] and then converted to bis-amido-lithium salt similarly to procedure published for bis-imino-pyridine molecule. [16] All solvents were dried by passing through Al$_2$O$_3$ filled columns and degassed prior to use. Elemental analyses were performed on Perkin-Elmer 2400 CHN analyzer. Data for X-ray single crystal structure determination were collected with a Brucker diffractometer equipped with 1K SMART CCD area detector. Deuterated solvents were purchased from C/D/N Isotopes Inc., dried over freshly activated molecular sieves (4A) for 7 days and used as is after that. NMR spectra were recorded at 20°C on Varian INOVA 500 NMR spectrometer. ^{1}H- and ^{13}C- shifts were referenced to internal solvent resonances and reported in parts per million relative to Me$_4$Si.

Preparation of $\{1,3\text{-}[2,5\text{-}(i\text{-Pr})_2\text{PhNC}(=\text{CH}_2)]_2\text{C}_6\text{H}_4\}\text{UCl}_3]$□$\text{Li(THF)}_4$ (5.1).

Dilithium ligand salt $\{1,3\text{-}[2,5\text{-}(i\text{-Pr})_2\text{PhNC}(=\text{CH}_2)]_2\text{C}_6\text{H}_4\}\}\text{Li}_2(\text{THF})_4$ (1.104 g, 1.41 mmol) was solubilized in THF (5 mL). An emerald green solution of $\text{UCl}_4(\text{THF})_4$ (0.945 g, 1.42 mmol) in THF (7 mL) was rapidly added to the dark-orange reaction mixture. The color of the solution immediately changed to dark brown-red and some insoluble solid appeared. After additional 2 hours of stirring at room temperature the insoluble material was separated via centrifugation. The mother liquor was concentrated to 5 mL and then layered with hexane (15 mL). After 2 days of standing at room temperature, dark brown-red crystals of **5.1** were obtained (1.41 g, 1.26 mmol, 89%). El. Anal. Calcd. (Found) for $\text{C}_{50}\text{H}_{74}\text{N}_2\text{O}_4\text{ULiCl}_3$: C 53.69(53.37), H 6.67(6.52), N 2.50(2.47). ^{1}H-NMR (500 MHz, benzene-d^6, 20°C) δ: 49.72(1H ArH), 16.36(6H, $\text{-CH(C}\mathbf{H}_3)_2$), 15.39 (2H, $=\text{C}\mathbf{H}_2$), 13.79 (2H, -$\text{C}\mathbf{H}(\text{CH}_3)_2$), 10.80 (6H, $\text{-CH(C}\mathbf{H}_3)_2$), 9.94 (3H, Ar'**H**), 9.04 (3H, Ar'**H**), 2.26 (6H, $\text{-CH(C}\mathbf{H}_3)_2$), 0.51 (16H, ($\text{-CH}_2\text{-}$)THF), 0.35(16H, ($\text{-CH}_2\text{-}$)THF), -0.83(2H, Ar**H**) -1.70 (1H, Ar**H**), -3.68(2H, $\text{-C}\mathbf{H}(\text{CH}_3)_2$), -4.05(6H, $\text{-CH(C}\mathbf{H}_3)_2$), -14.30 (2H, $=\text{C}\mathbf{H}_2$).

Preparation of $\{1,3\text{-}[2,5\text{-}(i\text{-Pr})_2\text{PhNC}(=\text{CH}_2)]_2\text{C}_6\text{H}_4\}\text{U(THF)}(\mu\text{-Cl})_3(\text{Li(THF)}_2)_2$ (5.2).

A solution of $\text{UCl}_4(\text{THF})_4$ (0.410 g, 0.61 mmol) in THF (10 mL) was mixed at room temperature with a THF solution of K naphthalenide prepared from metallic K (0.024 g, 0.62 mmol) and naphthalene (0.079g, 0.61 mmol) in THF (10 mL). The color of the solution instantly changed to dark red upon mixing and considerable amount of dark red precipitate appeared. The reaction mixture was vigorously stirred for 20 min. A solution of dilithium ligand salt $\{1,3\text{-}[2,5\text{-}(i\text{-Pr})_2\text{PhNC}(=\text{CH}_2)]_2\ \text{C}_6\text{H}_4\}\text{Li}_2(\text{THF})_4$ (0.476 g, 0.61 mmol) in THF (10 mL) was added directly to the reaction mixture with vigorous stirring continuing for additional 2 hours. After that period, insoluble material was separated by centrifugation, the volume of the resulting solution was reduced to 5 mL under vacuum. The solution was layered with 10 mL of hexane and allowed to stand at room temperature. After 3 days dark red crystals of **5.2** separated (0.593 g, 0.53 mmol, 86%). El. Anal. Calcd. (Found) for $C_{50}H_{74}N_2O_4ULi_2Cl_3$: C 53.36(53.32), H 6.63(6.54), N 2.49(2.49).

Preparation of {1,3-[2,5-(*i*-Pr)$_2$PhNC(=CH$_2$)]$_2$C$_6$H$_4$}U(THF)(μ-Cl)$_2$Li(THF)$_2$ (5.3).

A dark red solution of **5.1** (0.300 g, 0.27 mmol) in THF (7 mL) was cooled to 0°C and then treated with a solution at 0°C of Li naphthalenide in THF (7 mL) prepared from Li metal (0.002 g, 0.29 mmol) and naphthalene (0.039 g, 0.30 mmol). The reaction mixture was stirred for 8 hours at low temperature and then warmed to ambient temperature. THF solvent was removed under vacuum at room temperature and replaced with diethyl ether (15 mL). Some insoluble material was separated by centrifugation. The volume of the residual solution was reduced to 7 mL. After standing in the freezer at -37°C for 3 days, red crystals of **5.3** (0.184 g, 0.18 mmol, 67%) separated. El. Anal. Calcd. (Found) for $C_{46}H_{70}N_2O_3ULiCl_2$: C 54.44(54.36), H 6.95(6.72), N 2.76(2.77).

Preparation of {1,3-[2,5-(*i*-Pr)$_2$PhNC(=CH$_2$)]$_2$C$_6$H$_3$}U(THF)-(μ-Cl)$_2$-Li(THF)$_2$ (5.4).

Method A. A dark-red solution of **5.1** (0.350 g, 0.31 mmol) in THF (4 mL) was treated with a THF solution (5 mL) of K/Naphthalene prepared from K (0.013 g, 0.33 mmol) and naphthalene (0.042 g, 0.33 mmol). Upon mixing the two solutions, no significant color change was observed. Nevertheless, after 4 hours of stirring at room temperature small amount of light-colored insoluble material appeared in the reaction vessel as well as some brightening of the reaction mixture. The insoluble material was removed by centrifugation and the mother liquor was concentrated to 5 mL and layered with hexanes (15 mL). Dark brown-orange crystals of **5.4** separated after 3 days (0.178 g, 0.18 mmol, 56%). El. Anal. Calcd. (Found) for $C_{46}H_{65}N_2O_3ULiCl_2$: C 54.71(54.67), H 6.49(6.35), N 2.77(2.73). ^{1}H-NMR (500 MHz, THF-d^8, 20°C) δ: 8.56(2H, Ar**H**), 7.87(1H. Ar**H**), 7.45 (4H, Ar'**H**), 7.39 (2H, Ar'**H**), 7.33 (2H, -C**H**(CH$_3$)$_2$), 7.16 (1H, =C**H**$_2$), 7.14 (1H, =C**H**$_2$), 3.82 (THF, –C**H**$_2$–), 3.09(2H, -C**H**(CH$_3$)$_2$), 2.18 (1H, =C**H**$_2$), 2.16 (1H, =C**H**$_2$), 1.94 (THF, –C**H**$_2$–), 1.47(12H, -CH(C**H**$_3$)$_2$), 1.44(12H, -CH(C**H**$_3$)$_2$).

Method B. A dark red solution of **2** (0.350 g., 0.31 mmol) in THF (15 mL) was placed in a glass high-pressure reactor and heated to 80 C in an oil bath. A color change occurred over the period of 6 hours. A visible amount of pale colored insoluble material gradually appeared. After the reaction mixture was cooled to room temperature, all the insoluble material was separated by centrifugation. The residual solution was concentrated to 4 mL and layered with hexanes (15 mL). After 3 days dark brown orange crystals (0.241 g, 0.24 mmol, 77%) of **5.4** separated. The identity of the isolated material was confirmed by both X-ray and ^{1}H NMR data.

Method C. A dark red solution of **5.3** (0.350 g, 0.35 mmol) in THF (15 mL) was placed in a glass high-pressure reactor and heated to 80 C in an oil bath. Similarly to Method B, the color of the solution became visibly lighter after 6 hours of stirring. The reactor was cooled to room temperature. Very small amount of dark colored insoluble material was separated by centrifugation. The residual solution was concentrated to 4 mL and layered with hexanes (15 mL). Dark brown-orange crystals of **5.4** separated after 4 days (0.272 g, 0.27 mmol, 77%). The identity of the complex was confirmed by both X-ray and ^{1}H NMR data.

Preparation of {({1,3-[2,5-(*i*-Pr)$_2$PhNC(=CH$_2$)]$_2$C$_6$H$_3$}U-(μ-Cl)-(μ-[O(CH$_2$)$_3$CH$_2$])[Li(DME)]} {Li(DME)$_3$} (5.5).

A dark-red solution of **5.1** (0.493 g, 0.44 mmol) in THF (4 mL) was treated with a freshly made THF solution (5 mL) of Li/Naphthalene prepared from Li (0.009 g, 1.31 mmol) and naphthalene (0.170 g, 1.33 mmol). The color of the reaction mixture did not change significantly upon mixing but some insoluble material appeared after 2 hours of stirring at room temperature. Solvent was removed from the reaction mixture and the resulting solid residue was re-suspended in DME (4 mL). After separation of the insoluble material by centrifugation, the resulting dark-red DME solution was layered with *n*-heptane (15 mL). Dark crystals of **5.5** separated after 3 days (0.181 g, 0.15 mmol, 34%). El. Anal. Calcd. (Found) for $C_{54}H_{89}N_2O_9ULi_2Cl$: C 54.15(53.87), H 7.49(7.35), N 2.34(2.32). ^{1}H-NMR (500

MHz, THF-d^8, 20°C) *δ*: 8.30(1H, ArH), 8.24(2H. ArH), 7.13 (4H, Ar'H), 7.03 (2H, Ar'H), 7.19 (1H, =CH_2), 6.87 (1H, =CH_2), 3.57 (THF, –CH_2–), 3.39 (DME, –CH_2–), 3.21 (DME, –CH_3), 2.77 (4H, -$CH(CH_3)_2$), 2.31 (1H, =CH_2), 2.17 (2H, cycle, –CH_2–), 1.97 (1H, =CH_2), 1.73 (THF, –CH_2–),1.15 (24H, -$CH(CH_3)_2$), 0.98 (2H, cycle, –CH_2–), -4.36 (2H, cycle, –CH_2–), -6.62 (2H, cycle, –CH_2–),

Preparation of co-crystallite [{1,3-[2,5-(*i*-Pr)$_2$PhNC(=CH_2)]$_2$$C_6H_3$}UCl($OCH_3$)][Li(DME)$_3$] (5.6a) and [{1,3-[2,5-(*i*-Pr)$_2$PhNC(=CH_2)]$_2$$C_6H_3$}U$Cl_2$][Li(DME)$_3$] (5.6b).

A solution of **5.1** (0.300 g, 0.27 mmol) in DME (5 mL) was quickly mixed with a solution of K/Naphthalene prepared from K (0.021 g, 0.54 mmol) and naphthalene (0.068 g, 0.53 mmol) in DME (5mL). The color of the reaction mixture did not change significantly but some light colored precipitate appeared after 1 hour of stirring at room temperature. The insoluble material was eliminated by centrifugation and the resulting dark brown-yellow solution was layered with n-heptane (20 mL). After 3 days, dark yellow crystals of the cocrystallite **5.6a/5.6b** separated (0.197 g, 0.17 mmol, 63%). El. Anal. Calcd. (Found) for $C_{50.47}H_{82.41}N_2O_{8.47}ULiCl_{1.57}$: C 52.56(52.18), H 7.20(7.04), N 2.43(2.39).

Preparation of {1,3-[2,5-(*i*-Pr)$_2$PhNC(=CH_2)]$_2$$C_6H_3$}U(μ-$OCH_3$)$_3$(μ,$\eta^6$-Na)[$\eta^3$-Na (DME)] (5.7).

Method A. A solution of **5.1** (0.350 g, 0.31 mmol) in DME (10 ml) was placed over NaH (0.100 g, 4.17 mmol). The reaction mixture was stirred at room temperature for 7 days. The insoluble material was separated by centrifugation. The resulting solution was concentrated to 5 mL and layered with heptane (15 mL). After 4 days, dark orange-brown crystals of **5.7** (0.247 g, 0.26 mmol, 84%) separated which were washed with hexane and dried. El. Anal. Calcd. (Found) for $C_{41}H_{60}N_2O_5UNa_2$: C 52.11(51.93), H 6.40(6.32), N 2.96(2.89). ^{1}H-NMR (500 MHz, THF-d^8) *δ*: 8.68 (1H. ArH), 8.21 (2H, ArH), 7.93 (1H, =CH_2), 7.84 (1H, =CH_2), 7.08 (4H, Ar'H), 6.93 (2H, Ar'H), 3.38 (DME, –CH_2-), 3.22 (DME, –CH_3), 2.90(1H, =CH_2), 2.73 (4H, -$CH(CH_3)_2$), 2.34 (1H, =CH_2), 2.26 (DME, –CH_2-), 2.12 (DME, –CH_3), 1.14 (12H, -$CH(CH_3)_2$), 1.13 (12H, -$CH(CH_3)_2$), 3.10(6H, -OCH_3), -4.60(3H, -OCH_3).

Method B. A solution of **5.6** (0.250 g, 0.22 mmol) in DME (10 mL) was placed over NaH (0.075 g, 3.13 mmol) and stirred for 7 days. The insoluble material was then removed by centrifugation. The solution was evaporated to about 4 mL and layered with hexane (10 mL). After 4 days dark brown-orange crystals of **5.7** (0.102 g, 0.11 mmol, 49%) were formed which were washed with hexanes and dried. The identity of this species was confirmed by comparison of X-ray and ^{1}H NMR data.

Preparation of $\{[\{1,3\text{-}[2,5\text{-}(i\text{-Pr})_2\text{PhNC}(=\text{CH}_2)]_2\text{C}_6\text{H}_3\}\text{U}\{1,3\text{-}[2,5\text{-}(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]_2\text{C}_6\text{H}_4\}][\text{Li}(\text{DME})(\text{THF})]\}$ (5.8).

A solution of **5.1** (0.500 g. 0.45 mmol) in DME (5 mL) was cooled to -37°C and treated with a cold solution (-37°C) of Li/naphthalene (Li: 0.006 g, 0.87 mmol; naphthalene 0.116 g, 0.91 mmol). The reaction mixture was stirred at -37°C for 2 days, during which, the color of the solution gradually changed from dark-red to dark-brown. Subsequently, DME was removed *in vacuo* while maintaining the temperature of the reaction mixture at -3°C. The solid residue was re-solubilized in cold THF (5 mL, -37°C). The insoluble material was eliminated by cold filtration, and the resulting solution was allowed to stand for 3 days at -37°C after been layered with n-heptane (10 mL). A dark colored oily substance separated which was redissolved in cold diethyl ether (10 mL) and layered with cold n-heptane (10 mL). After 3 additional days at -37°C dark brown-red crystals of **5.8** separated (0.283 g, 0.20 mmol, 44%). El. Anal. Calcd. (Found) for $\text{C}_{80}\text{H}_{113}\text{N}_4\text{O}_4\text{ULi}$: C 66.74(66.69), H 7.91(7.90), N 3.89(3.87).

Preparation of $\{[\{1,3\text{-}[2,5\text{-}(i\text{-Pr})_2\text{PhNC}(=\text{CH}_2)]_2\text{C}_6\text{H}_3\}\text{U}\{1,3\text{-}[2,5\text{-}(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]_2\text{C}_6\text{H}_4\}\{\text{Na}(\text{DME})_2\}][\text{Na}(\text{DME})_3]\}□(\text{C}_7\text{H}_8)_{0.5}$ (5.9).

A solution of **1** (0.500 g, 0.45 mmol) in toluene (10 mL) was stirred at room temperature in the presence of NaH (0.104 g, 4.52 mmol). During the 4 days of stirring at room temperature, the red color of the mixture gradually darkened. Toluene was removed *in vacuo* and the residual solid was redissolved in DME (10 mL). A small amount of insoluble material was eliminated via centrifugation.

The resulting solution was layered with hexanes(15 mL). After the diffusion was completed and no solid appeared in the crystallization vessel, the solution was cooled to -37°C. After 24 hours of standing at low temperature, dark-red crystals of **5.9** separated (0.304 g, 0.18 mmol, 40%). El. Anal. Calcd. (Found) for $C_{91.50}H_{139}N_4O_{10}UNa_2$: C 63.19(63.03), H 8.06(7.92), N 3.22(3.19).

Computational Details

All DFT calculations were performed using the Gaussian 03 package[24] using the PBE[25] exchange-correlation functional and the SDD and SDDall[26] effective-core potential (ECP) basis sets. Calculations with these two basis sets gave nearly identical results. Tight SCF convergence criteria were used for all calculations. The converged wave functions were tested to confirm that they correspond to the ground-state surface. All calculations for the analysis of the electronic structure, including Mulliken population analysis[27] and the calculation of Mayer 2- and 3-center bond order indices[28a,b], atomic valences[28a] and populations of fragment orbitals[28c] were performed using the AOMix software package. [29]

X-ray crystallography

For all the compounds, the results presented are the best of several data collection trials. The crystals were mounted on thin glass fibers using paraffin oil and cooled to the data collection temperature. Data were collected on a Bruker-AXS SMART 1k CCD diffractometer. Data for the compounds **5.1, 5.2, 5.5, 5.7** and **5.8** were collected with a sequence of 0.3° ω scans at 0, 120, and 240° in φ. To obtain acceptable redundancy data for compound **5.3, 5.4, 5.6** and **5.9** the sequence of 0.3° ω scans at 0, 90, 180, and 270° in φ was used. Initial unit cell parameters were determined from 60 data frames collected at the different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied. [30] Systematic absences in the diffraction data-set and unit-cell parameters were consistent with monoclinic $P2_1/m$ for **5.1,** orthorombic P*nma* for **5.2**, triclinic $P\bar{1}$ for **5.3, 5.4, 5.6, 5.9** and monoclinic *P2₁/n* for **5.5**, **5.7**, **5.8**. Solutions in centrosymmetric space groups for all of the compounds yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed with difference Fourier synthesis, and refined with full-matrix least-squares procedures based on F^2. The compound molecules were located in special positions (mirror plane) in the structures of **5.1** and **5.2**. In all the other complexes compound molecules were located in general positions. Structure of complex **5.8** represents a dimer where two monomeric units are related by inversion center. Carbon atoms of coordinated THF solvent molecules in **5.1** and **5.2**, carbon atoms of coordinated diethyl ether solvent molecules in **5.3** as well as carbon atoms of cocrystallized toluene solvent molecule in **5.9** were refined isotropicaly due to significant thermal motion disorder and in order to maintain an optimal data to parameters ratio. In all the structures, all non-hydrogen atoms, with the exceptions mentioned above, were refined with anisotropic displacement coefficients. The structures of all the complexes, except **5.7**, contain severely disordered solvent molecules, either in the lattice or coordinated to the alkaly cations. This significant disorder, sometimes coupled with the low quality of the collected datasets as resulting from small crystals size, led to the appearance of several A-alerts in the check-CIF files generated by *International Union of Crystallography* on-line check-CIF routine. Nevertheless, these disordered solvent molecules are spatially separated from the uranium-containing moieties and do not affect the refinement stability nor the errors in bonds and distances in key fragments of the structure. All hydrogen atoms were treated as idealized contributions. All scattering factors are contained in several versions of the SHELXTL program library, with the latest version used being v. 6.12.[31] Crystallographic data and relevant bond distances and angles are reported in Tables 5.1, 5.2.

Crystal Structures Description

1. The structure of complex **5.1** consists of an anionic metallate with an unconnected, THF-solvated lithium counter-cation. The anionic part contains the uranium metal center in a slightly distorted octahedral environment [Cl(1)-U(1)-Cl(2) = 173.3(1)°, Cl(1)-U(1)-Cl(3) = 87.2(2)°, Cl(3)-U(1)-Cl(2) = 86.6(2)°, Cl(1)-U(1)-N(1) = 96.0(4)°, Cl(1)-U(1)-N(2) = 92.1(5)°, Cl(2)-U(1)-N(1) = 88.8(4)°, Cl(2)-U(1)-N(2) = 88.7(4)°]. Five coordination sites are defined by three Cl atoms [U(1)-Cl(1) = 2.622(3) Å, U(1)-Cl(2) = 2.599(3) Å, U(1)-Cl(3) = 2.652(5) Å] and two N atoms of the ligand [U(1)-N(1) = 2.363(14) Å, U(1)-N(2) = 2.276(15) Å] (Figure 5.1). The sixth position is occupied by the C-H moiety of the central phenyl ring which is side-on coordinated to the metal center reaching a bonding contact with one of the phenyl ring carbon atoms [U(1)-C(8) = 2.678(12) Å, U(1)-H(8)A = 3.224(12) Å] in what is spatially reminiscent of an agostic interaction. The di-anionic character of the ligand system is apparent from the short C-C bond distances [C(1)-C(2) = 1.328(16) Å, C(9)-C(10) = 1.333(16) Å] formed by the two C atoms attached to the imino carbon as well as the fairly long C-N distances [C(2)-N(2) = 1.442(13) Å, C(9)-N(1) = 1.411(13) Å].

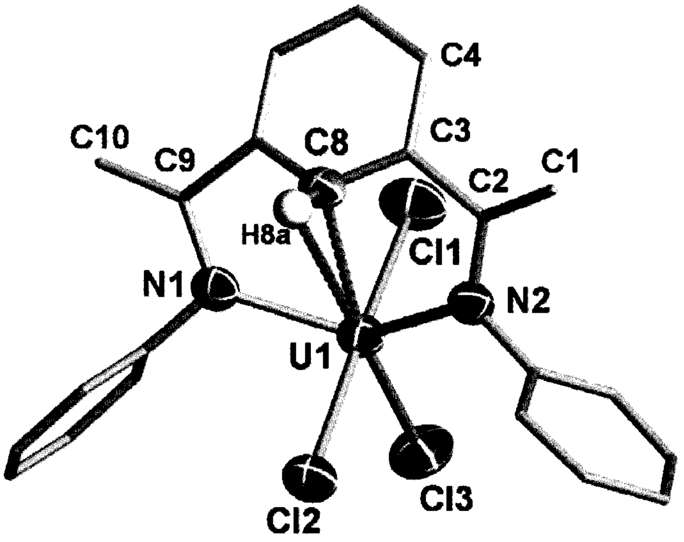


Figure 5.1. Partial thermal ellipsoid diagrams of **5.1** with thermal ellipsoid drawn at the 50% probability level. Iso-propyl substituents on phenyl rings were omitted for clarity.

The central ring of the ligand is not coplanar with the rest of ligand main core [C(1)-C(2)-C(3)-C(4) = 41.8(18)°] but it is not π-bonded to the uranium center either. A lithium cation tetrahedrally solvated by four molecules of THF [Li(1)-O(1) = 2.00(4) Å, Li(1)-O(2) =2.01(4) Å, Li(1)-O(3) = 1.90(4) Å, Li(1)-O(4) = 1.85(4) Å] and unconnected with the anionic moiety completes the structure.

2. The structure of complex **5.2** shows the uranium metal center in a symmetry-generated distorted octahedral coordination environment. Similarly to **5.1,** three of the four equatorial positions are occupied by three chlorine atoms [U(1)-Cl(1) = 2.757(3) Å, U(1)-Cl(2) = 2.880(3) Å, U(1)-Cl(3) = 2.751(3) Å, Cl(1)-U(1)-Cl(2) = 78.02(9)°, Cl(1)-U(1)-Cl(3) = 154.57(10)°]. Two nitrogen atoms of the bis-imino ligand reside in axial positions of the distorted octahedron [U(1)-N(1) = 2.402(7) Å, N(1)-U(1)-N(1)A = 118.8(3)°]. The last equatorial position is occupied by one C atom of the central phenyl ring [U(1)-C(6) = 2.769(9) Å, U(1)-H(6)A = 2.529(9) Å, N(1)-U(1)-C(6) = 61.95(17)°] with a short contact in the U-C σ-bonding range.

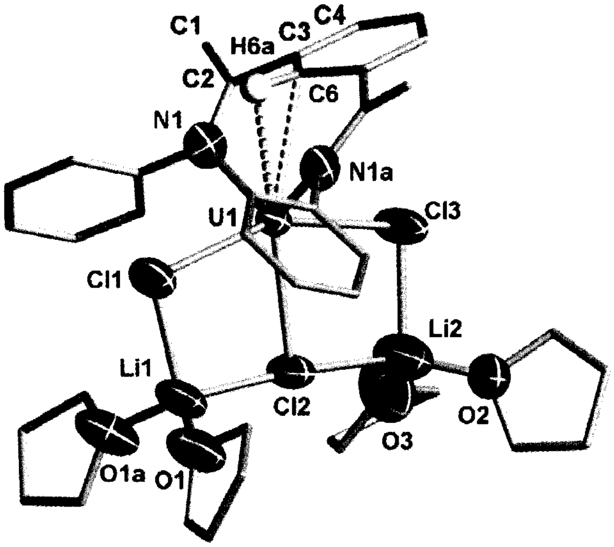


Figure 5.2. Partial thermal ellipsoid diagrams of **5.2** with thermal ellipsoid drawn at the 50% probability level. Iso-propyl substituents on phenyl rings were omitted for clarity.

The molecule is bisected by a mirror plane containing the metal center and the chlorine atoms. The bis-anionic nature of the ligand is apparent from the values of the C-C distances formed by the terminal carbon atoms and the C-N distances of the former imine functions [C(1)-C(2) = 1.342(13) Å, C(2)-N(1) = 1.381(11) Å]. As in complex **5.1**, the interaction of the metal center with the phenyl ring C-H bond causes a significant deviation of the ligand π-system from the planarity [C(1)-C(2)-C(3)-C(4) = 40.3(2)°]. The three chlorine atoms bridge in pairs two Li cations [Cl(1)-Li(1) = 2.38(2) Å, Cl(2)-Li(1) = 2.39(2) Å, Cl(2)-Li(2) = 2.41(3) Å, Cl(3)-Li(2) = 2.44(3) Å]. Each Li atom resides in a tetrahedral arrangement with two positions occupied by chlorines [Cl(1)-Li(1)-Cl(2) = 96.2(7)°, Cl(2)-Li(2)-Cl(3) = 91.9(11)°] and the other two by two molecules of coordinated THF [O(1)-Li(1) = 1.888(13) Å, O(2)-Li(2) = 1.67(3) Å, O(3)-Li(2) = 2.06(3) Å, Cl(1)-Li(1)-O(1) = 107.4(9)°, O(1)-Li(1)-O(1)A = 117.2(11)°, Cl(2)-Li(2)-O(2) = 134.1(12)°, O(2)-Li(2)-O(3) = 105.4(19)°]. Two of the THF molecules around the same Li atom are disordered over two positions with approximate equal occupancy.

3. Complex **5.3** consists of a uranium metal center in a distorted octahedral arrangement very similar to those of **5.1** and **5.2**. The coordination of the metal center is defined by two nitrogen placed in the two axial positions [U(1)-N(1) = 2.393(10) Å, U(1)-N(2) = 2.390(10) Å, N(1)-U(1)-N(2) = 123.4(3)°].

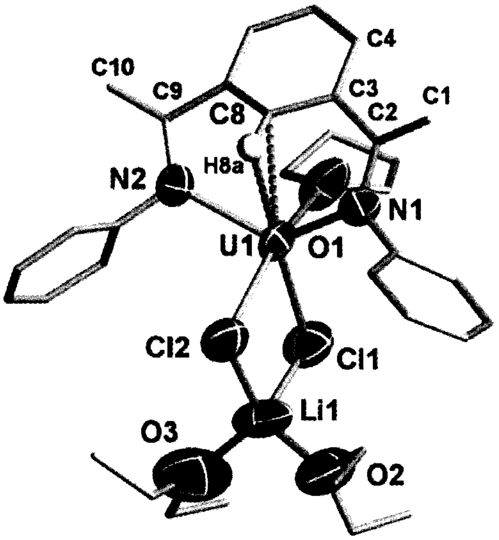


Figure 5.3. Partial thermal ellipsoid diagrams of **5.3** with thermal ellipsoid drawn at the 50% probability level. Iso-propyl substituents on phenyl rings are omitted for clarity.

Three of the four equatorial positions are defined by two chlorine atoms [U(1)-Cl(1) = 2.759(4) Å, U(1)-Cl(2) = 2.720(4) Å, Cl(1)-U(1)-Cl(2) = 80.28(13)°, N(1)-U(1)-Cl(1) = 117.0(3)°] and one oxygen atom of a coordinated THF molecule [U(1)-O(1) = 2.529(9) Å, Cl(1)-U(1)-O(1) = 78.03(3)°, N(1)-U(1)-

O(1) = 96.9(4)°]. The same short contact between the metal center and the C-H bond of the phenyl ring as observed in **5.1** and **5.2** is also present in **5.3** and which occupies the last equatorial position [U(1)-C(8) = 2.756(13) Å, U(1)-H(8)A = 2.456(14) Å, C(8)-U(1)-Cl(1) = 158.7(3)°, C(8)-U(1)-N(1) = 63.6(4)°]. In perfect analogy with the two complexes above, the di-anionic nature of the ligand is confirmed by the values of the C-C and C-N bonds distances [C(1)-C(2) = 1.335(19) Å, C(9)-C(10) = 1.350(18) Å, C(2)-N(1) = 1.407(17) Å, C(9)-N(2) = 1.373(16) Å]. Also very comparable is the deviation of the ligand from the planarity [C(1)-C(2)-C(3) – C(4) = 36.3(5)°]. Both chlorine atoms bridge the uranium center to lithium [Li(1)-Cl(1) = 2.36(3) Å, Li(1)-Cl(2) = 2.34(3) Å, Cl(1)-Li(1)-Cl(2) = 97.2(9)°]. The tetrahedral coordination environment of the Li cation is completed by two oxygen atoms of two coordinated molecules of diethyl ether [Li(1)-O(2) = 1.92(4) Å, Li(1)-O(3) = 1.96(4) Å, O(2)-Li(1)-O(3) = 108.7(14)°, Cl(1)-Li(1)-O(2) = 115.5(17)°].

4. The structure of compound **5.4** shows the ligand coordinated to the uranium center in a tridentate fashion and meridionally arranged. Two of the three positions are defined by the two amido- nitrogen donor atoms [[U(1)-N(1) = 2.241(10) Å, U(1)-N(2) = 2.273(10) Å, N(1)-U(1)-N(2) = 132.4(4)°]. The third position is occupied by the metallated carbon atom of the central phenyl ring [U(1)-C(8) = 2.388(13) Å, N(1)-U(1)-C(8) = 66.4(4)°]. The poly-anionic character of the ligand is confirmed by the C-C and C-N bond distances [C(1)-C(2) = 1.38(2) Å, C(9)-C(10) = 1.34(2) Å, C(2)-N(1) = 1.41(2) Å, C(9)-N(2) = 1.38(2) Å]. The ring metallation is responsible for the restoration of the ligand planarity [C(1)-C(2)-C(3)-C(4) = 9.0(2)°]. The last equatorial position is occupied by one of the two chlorine atoms [U(1)-Cl(1) = 2.792(3) Å, Cl(1)-U(1)-N(1) = 115.3(3)°, Cl(1)-U(1)-C(8) = 160.6(3)°]. The second chlorine atom fills the first axial position of the distorted octahedron [U(1)-Cl(2) = 2.665(4) Å, Cl(1)-U(1)-Cl(2) = 80.05(12)°, Cl(2)-U(1)-C(8) = 119.3(3)°]. The second axial position is occupied by the O atom of one coordinated THF solvent molecule [U(1)-O(1) = 2.477(9) Å, O(1)-U(1)-Cl(2) = 158.5(2)°, O(1)-U(1)-C(8) = 81.9(4)°].

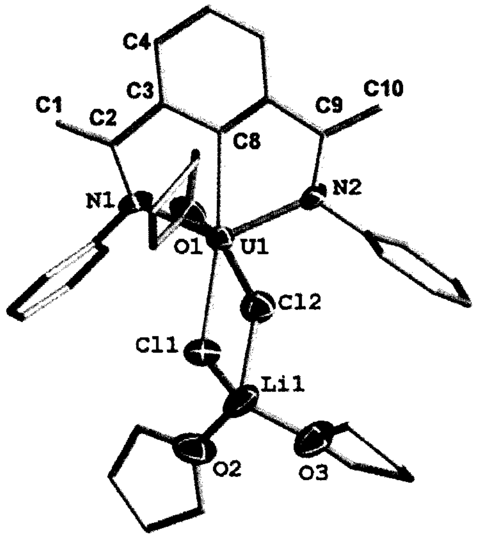


Figure 5.4. Partial thermal ellipsoid diagrams of **5.4** with thermal ellipsoid drawn at the 50% probability level. Iso-propyl substituents on phenyl rings are omitted for clarity.

Both chlorine atoms bridge uranium and lithium defining two positions of tetrahedral environment of the Li cation [Li(1)-Cl(1) = 2.35(3) Å, Li(1)-Cl(2) = 2.44(3) Å, Cl(1)-Li(1)-Cl(2) = 94.3(9)°]. Two THF solvent molecules complete the coordination geometry of the alkali cation [Li(1)-O(2) = 1.84(3) Å, Li(1)-O(3) = 1.90(3) Å, O(2)-Li(1)-O(3) = 109.8(13)°, Cl(1)-Li(1)-O(2) = 111.4(14)°].

5. Complex **5.5** is ionic with the anionic moiety containing uranium and a solvated lithium counteraction. The uranium center adopts the usual distorted octahedral arrangement. Similar to complex **5.4**, the ligand is tridentate and meridionally arranged with the metallation of the central aromatic ring. One equatorial coordination site is occupied by a σ-bonded C atom [U(1)-C(8) = 2.419(12) Å] of the central phenyl ring while the two nitrogen atoms of the bis-amido ligand [U(1)-N(1) = 2.391(11) Å, U(1)-N(2) = 2.372(11) Å, N(1)-U(1)-N(2) = 129.78(7)°] occupy two other equatorial sites. One of the axial sites is occupied by one chlorine atom [U(1)-Cl(1) = 2.846(4) Å, C(35)-U(1)-Cl(1) = 153.48(6)°]. The last two coordination equatorial and axial positions are occupied by the oxygen [U(1)-O(1) = 2.244(9)Å, O(1)-U(1)-C(8) = 157.86(6)°] and carbon atoms [U(1)-C(35) = 2.476(13) Å, C(35)-U(1)-O(1) = 78.91(6)°, C(35)-U(1)-C(8) = 79.756(6)°] of what appears to be the result of THF ring opening (Figure 5). The ene-bis-amido ligand adopts a nearly flat conformation with both amido-residues co-planar with the metallated phenyl ring. The bond distances formed by the ene-carbon atom [(C(1)-C(2) = 1.34(2)Å, C(9)-C(10) = 1.358(18)Å, C(2)-N(1) = 1.415(17) Å, C(9)-N(2) = 1.372(17) Å] confirmed the presence of the C-C double bonds and are in agreement with those of all the other complexes above. The oxygen atom of the cleaved THF molecule and the chlorine atom are bridging the Li cation [Li(1)-O(1) = 1.89(3) Å, Li(1)-Cl(1) = 2.30(3) Å]. The remaining two coordination sites of coordination tetrahedron of the Li atom are filled by two oxygen atoms of one molecule of DME [Li(1)-O(2) = 1.97(3) Å, Li(1)-O(3) = 1.94(3) Å]. The unconnected counteraction consists of a second Li cation octahedrally coordinated by six oxygen atoms of three DME molecules [Li(2)-O(4) = 2.30(3) Å, Li(2)-O(5) = 1.97(4) Å, Li(2)-O(6) = 2.08(3) Å, Li(2)-O(7) = 2.12(3) Å, Li(2)-O(8) = 2.11(4) Å, Li(2)-O(9) = 2.18(3) Å].

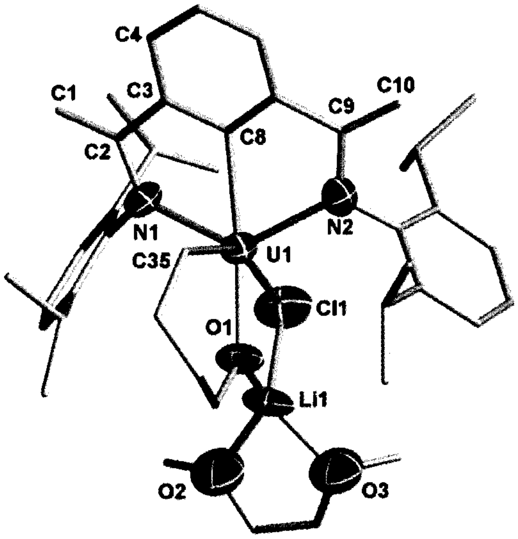
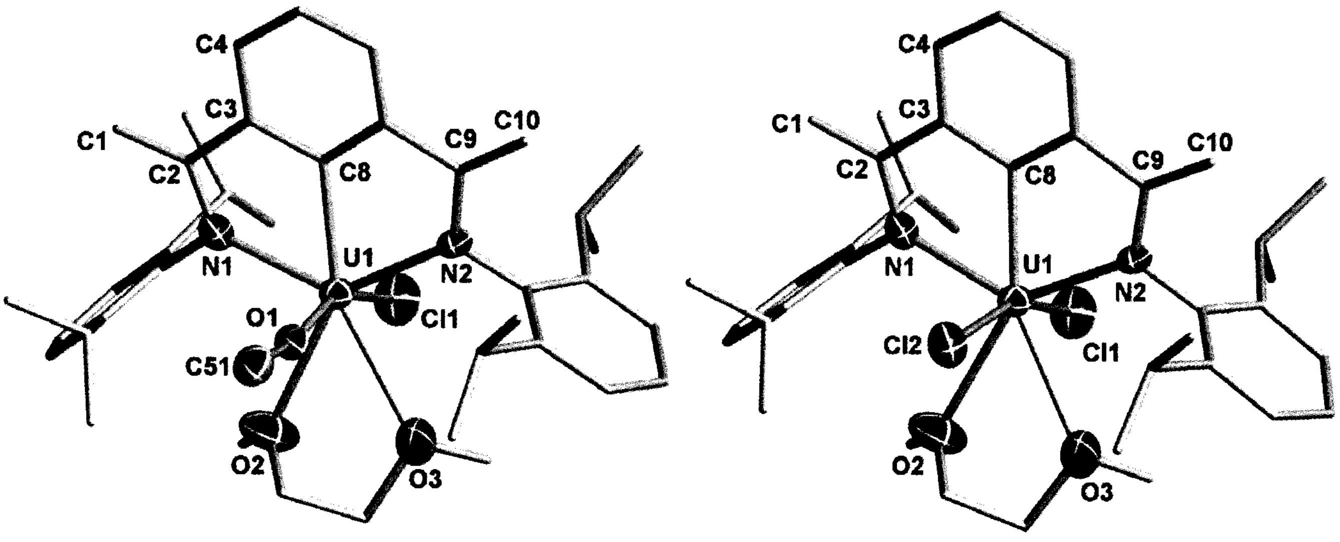


Figure 5.5. Partial thermal ellipsoid diagrams of **5.5** with thermal ellipsoid drawn at the 50% probability level. Isopropyl substituents on phenyl rings are omitted for clarity.

6. Structure of the cocrystallite **5.6a** and **5.6b** consists of two chemically different but crystallographically very similar compounds co-crystallized within the same unit cell. The difference between the two species consists of the replacement of one of the two chlorine atoms of **5.6a** with a partly occupied O-CH_3 group of **5.6b** (Figures 5.6). In both cases, the structures contain anionic fragment with heptacoordinated (pentagonal bi-pyramidal) U metal center and unconnected Li counter-cation solvated by DME. The coordination sphere of the U atom is defined by the planar ligand which occupies three equatorial coordination sites using two nitrogen atoms and one carbon atom of the deprotonated phenyl ring [U(1)-N(1) = 2.395(6) Å, U(1)-N(2) = 2.381(6) Å, U(1)-C(8) = 2.412(7) Å, N(1)-U(1)-N(2) = 132.3(2)°]. The two last equatorial positions are occupied by two oxygen atoms of a DME molecule [U(1)-O(2) = 2.810(6) Å, U(1)-O(3) = 2.844(7) Å, O(2)-U(1)-O(3) = 57.5(2)°, O(2)-U(1)-N(1) = 84.6(3)°, O(3)-U(1)-C(8) = 150.3(3)°]. One chlorine atom resides in the axial position of the coordination polyhedron [U(1)-Cl(1) = 2.668(2) Å, C(8)-U(1)-Cl(1) = 111.5(3)°]. The last axial coordination site is partly occupied by methoxy- group[U(1)-O(1) = 1.976(16)Å, O(1)-U(1)-C(8) = 95.3(3)°] in the case of **5.6a,** or by second chlorine atom [U(1)-Cl(2) = 2.628(7) Å, Cl(2)-U(1)-C(8) = 90.0(3)°] in **5.6b**.



5.6a **5.6b**

Figure 5.6. Partial thermal ellipsoid diagrams of **5.6a / 5.6b** with thermal ellipsoid drawn at the 50% probability level.

The overall ratio **6a:6b** was determined to be 43:57 based on the best crystallographic refinement of thermal parameters. The cationic fragment consists of a Li atom in octahedral coordination arrangement as defined by the oxygen atoms of three DME molecules [Li(2)-O(4) = 2.085(18) Å, Li(2)-O(5) = 2.229(17) Å, Li(2)-O(6) = 2.114(16) Å, Li(2)-O(7) = 2.210(18) Å, Li(2)-O(8) = 2.070(17) Å, Li(2)-O(9) = 2.169(16) Å].

7. The structure of **5.7** consists of a symmetry generated dimer. Each monomeric unit contains a uranium metal center in a distorted octahedral environment. The ligand exhibits the usual tridentate bonding mode by bonding the metal center through the N atoms and the C atom of the metallated central phenyl ring [C(1)-C(2)-C(3)-C(4) = 20.1(17)°] [U(1)-N(1) = 2.440(8) Å, U(1)-N(2) = 2.418(8) Å, U(1)-C(8) = 2.468(10) Å, N(1)-U(1)-N(2) = 130.3(3)°, N(1)-U(1)-C(8) = 65.2(3)°]. The tri-anionic character of the ligand is indicated by the corresponding C-C and C-N bond distances as well as by the bonding contact between the uranium metal center and the carbon atom of the ligand central phenyl ring [C(1)-C(2) = 1.316(13) Å, C(9)-C(10) = 1.355(15) Å, N(1)-C(2) = 1.401(12) Å, C(9)-N(2) = 1.405(13) Å, U(1)-C(8) = 2.468(10) Å].

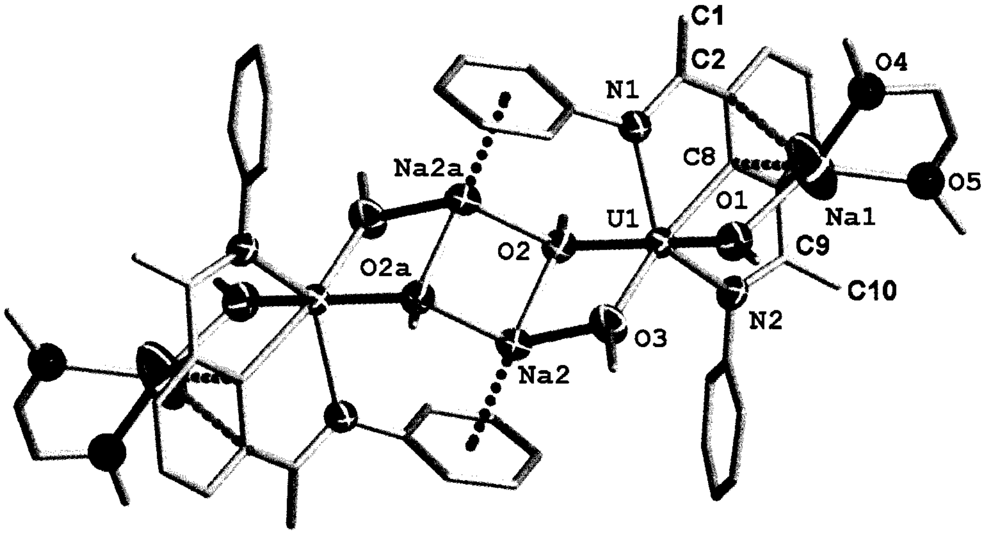


Figure 5.7. Partial thermal ellipsoid diagrams of **5.7** with thermal ellipsoid drawn at the 50% probability level. Iso-propyl substituents on phenyl rings are omitted for clarity.

The remaining equatorial and axial positions of the octahedron are filled by three CH_3O- groups [U(1)-O(1) = 2.178(7) Å, U(1)-O(2) = 2.296(6) Å, U(1)-O(3) = 2.207(6) Å, O(1)-U(1)-O(2) = 159.8(3)°, O(1)-U(1)-O(3) = 89.8(3)°, O(3)-U(1)-C(8) = 171.3(3)°]. Each of the three methoxy groups is bridging U to one of the two Na metal centers. The first Na atom is bonded to one methoxy group, to a portion of the central aromatic ring of the ligand and to the two oxygen of one DME molecule. The second instead is bonded to the other two methoxy groups. Additional bonding interaction is realized through methoxy group of a second identical unit as well as through one of the peripheral phenyl ring of the second unit, therefore assembling the dinuclear structure. [Na(1)-O(1) = 2.296(9) Å], [Na(1)-C(3) = 2.844(13) Å, Na(1)-C(7) = 3.060(12) Å, Na(1)-C(8) = 2.583(11) Å, O(1)-Na(1)-C(8) = 80.8(3)°]. [Na(1)-O(4) = 2.259(16) Å, Na(1)-O(5) = 2.315(16) Å, O(4)-Na(1)-O(5) = 68.3(6)°, O(4)-Na(1)-C(8) = 136.0(6)°, Na(2)-O(2) = 2.316(7) Å, Na(2)-O(3) = 2.328(8) Å, O(2)-Na(2)-O(3) = 73.8(2)°, Na(2)-O(2a) = 2.402(8) Å, O(2)-Na(2)-O(2a) = 97.5(2)°, Na(2)–centroid(1a) = 2.578(9) Å, O(2)-Na(2)-centroid(1a) = 129.8(3)°].

8. Complex **5.8** contains a uranium metal center surrounded by two ligands in an overall severely distorted heptacoordination. Three sites are occupied by two nitrogen and one carbon atoms of one ring-metallated ligand system [U(1)-N(1) = 2.372(4) Å, U(1)-N(2) = 2.371(4) Å, U(1)-C(8) = 2.420(5) Å, N(1)-U(1)-N(2) = 130.60(14)°, N(1)-U(1)-C(8) = 66.32(17)°]. This ligand appears to be tri-anionic according to the C-C and C-N bond distances [U(1)-C(8) = 2.420(5) Å, C(1)-C(2) = 1.342(8) Å, C(9)-C(10) = 1.348(7) Å, C(2)-N(1) = 1.413(6) Å, C(9)-N(2) = 1.402(6) Å,] as well as the planar configuration [N(1)-U(1)-C(8)-C(7) = 174.0(4)°, N(2)-U(1)-C(8)-C(3) = 178.6(4)°]. A second ligand is also bonded to uranium affording a diene-type η^4-interaction with the part of the extended π-system encompassing one imino- function and part of the central aromatic ring. In fact the two imino functions have been restored and the terminal carbon atom protonated in this second ligand system [U(1)-N(3) = 2.260(4) Å, U(1)-C(40) = 2.682(5) Å, U(1)-C(41) = 2.808(5) Å, U(1)-C(43) = 2.678(5) Å, η^4-centroid - U(1)-C(8) = 165.26(17)°, η^4-centroid - U(1)-N(1) = 115.80(16)°] C(35)-C(36) = 1.502(7) Å, C(43)-

C(44) = 1.508(7) Å] and short C-N [C(36)-N(4) = 1.292(6) Å, C(43)-N(3) = 1.425(6) Å]. The structure is completed by one Li cation in square pyramidal arrangement coordinated to second part of the same extended π-system of the second, formally neutral, ligand unit [Li(1)-N(4) = 2.120(11) Å, Li(1)-C(38) =2.713(12) Å].

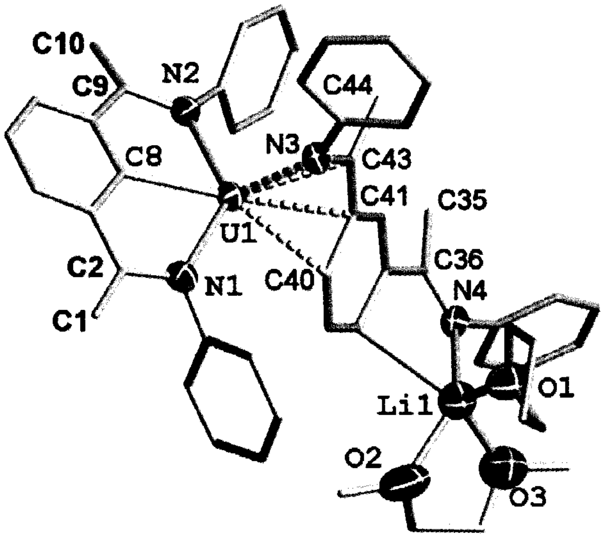


Figure 5.8. Partial thermal ellipsoid diagrams of **5.8** with thermal ellipsoid drawn at the 50% probability level. Iso-propyl substituents on phenyl rings are omitted for clarity.

One disordered molecule of THF and one of DME complete the coordination geometry of the alkali metal [Li(1)-O(2) = 2.083(12) Å, Li(1)-O(3) = 2.119(12) Å, O(2)-Li(1)-N(4) = 109.3(5)°, O(2)-Li(1)-C(38) = 153.4(5)°, O(3)-Li(1)-C(38) = 90.7(4)°][Li(1)-O(1) = 2.120(11) Å, O(1)-Li(1)-N(4) = 109.3(5)°, O(1)-Li(1)-O(2) = 107.8(5)°]. One non-coordinated molecule of the diethyl ether solvent per one molecule of uranium complex completes the structure.

9. The structure of **5.9** reveals two ligands attached to the same U metal center in an arrangement strikingly similar to that observed for **5.8**. An analysis of the bond distances around C(2) and C(9) in the first ligand system in comparison to the corresponding bond distances around C(36) and C(42) in the second ligand system suggests that the first molecule has retained the tris-anionic bis-amido configuration of the starting material [C(2)-C(1) = 1.382(16) Å, C(2)-N(1) = 1.409(14) Å, C(8)-C(9) = 1.321(15) Å, C(8)-N(2) = 1.378(14) Å].

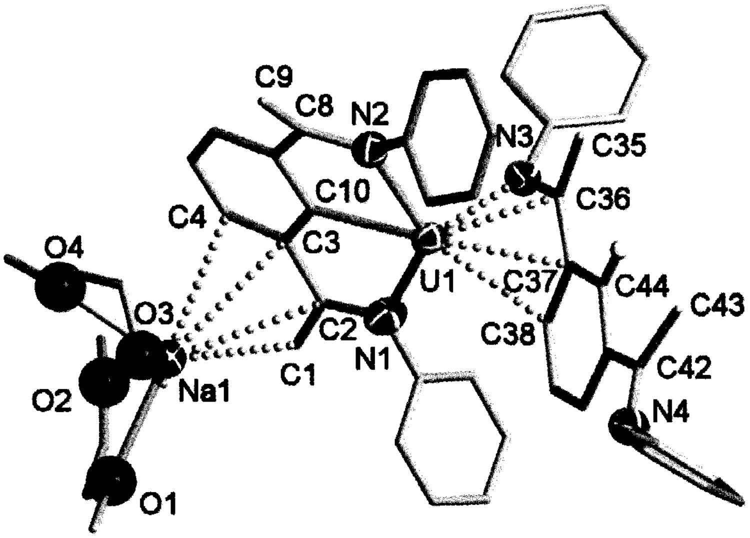


Figure 5.9. Partial thermal ellipsoid diagrams of **5.9** with thermal ellipsoid drawn at the 50% probability level. Iso-propyl substituents on phenyl rings are omitted for clarity.

The second ligand instead has gained three hydrogen atoms becoming a neutral bis-imine [C(36)-C(35) = 1.505(14) Å, C(36)-N(3) = 1.414(12) Å, C(42)-C(43) = 1.521(16) Å, C(42)-N(4) = 1.286(13) Å]. The uranium metal center is sited in a distorted trigonal bi-pyramidal coordination polyhedron. The two axial positions are occupied by two nitrogen atoms of the first (bis-amido) ligand system [U(1)-N(1) = 2.519(8) Å, U(1)-N(2) = 2.359(8) Å, N(1)-U(1)-N(2) = 129.5(3)°], while the carbon atom of the central phenyl ring occupies one equatorial position[U(1)-C(10) = 2.479(11) Å, N(1)-U(1)-C(10) = 64.7(3)°]. Two other equatorial positions are engaged in an interaction with the second ligand molecule. This molecule is connected to the metal center through the η^4-diene-type of π-bonding of one of the imino-groups [U(1)-N(3) = 2.325(8) Å, U(1)-C(36) = 2.654(10) Å, N(3)-U(1)-N(1) = 106.6(3)°] as well as one aromatic bond of the central phenyl ring [U(1)-C(37) = 2.846(10) Å U(1)-C(38) = 2.790(10) Å, C(38)-U(1)-C(10) = 148.2(3)°]. A sodium counter-cation solvated by two molecules of DME is also part of the structure by being bonded in η^4-diene-fashion through the π-system encompassing one double bond [C(1)-C(2) = 1.382(16) Å] and an aromatic bond of the central phenyl ring [C(3)-C(4) = 1.396(15) Å, (Na(1)-C(1) = 3.015(15)Å, Na(1)-C(2) = 3.280(15) Å, Na(1)-C(3) = 3.276(16) Å, Na(1)-C(4) = 3.157(16) Å] of the triply deprotonated ligand [Na(1)-O(1) = 2.597(12) Å, Na(1)-O(2) = 2.616(12) Å, Na(1)-O(3) = 2.487(18) Å, Na(1)-O(4) = 2.549(14) Å]. The presence of one additional Na counter-cation ensures the electroneutrality of the structure. This Na atom resides in octahedral environment, composed from 6 oxygen atoms of three DME solvent molecules [Na(2)-O(5) = 2.445(19) Å, Na(2)-O(6) = 2.405(17) Å, Na(2)-O(7) = 2.372(13) Å, Na(2)-O(8) = 2.388(14) Å, Na(2)-O(9) = 2.355(13) Å, Na(2)-O(10) = 2.389(12) Å]. One toluene solvent molecule in the lattice with partial occupancy of 50%, completes the structure.

Table 5.1. Crystal Data and Data Collection Parameters of Complexes **5.1**, **5.2** and **5.3**

	5.1	**5.2**	**5.3**
Formula	$ULiCl_3C_{50}H_{74}N_2O_4$	$ULi_2Cl_3C_{50}H_{74}N_2O_4$	$ULiCl_2C_{46}H_{70}N_2O_3$
FW	1118.43	1125.37	1014.91
Crystal system,	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1/m$	P*nma*	P-*1*
a, Å	11.638(3)	20.987(6)	12.078(3)
b, Å	19.638(4)	22.191(6)	12.843(4)
c, Å	12.081(3)	11.620(3)	18.629(5)
α, deg	90	90	74.947(4)
β, deg	105.992(3)	90	89.875(5)
γ, deg	90	90	62.150(4)
Volume, Å^3	2654.3(10)	5412(3)	2443.2(12)
Z	2	4	2
ρ_{calc} g/cm3	1.399	1.381	1.380
μ, mm^{-1}	3.250	3.188	3.468
F(000)	1132	2276	1026
T range (deg)	2.04 - 26.42	2.00 - 26.45	2.10 - 21.97
Limiting indices (*h, k, l*)	±14, ±24, ±15	±26, ±27, ±12	±12, ±13, ±19
Reflections collected / unique	28223 / 5554	29306 / 5623	14148 / 5919
R_{int}	0.0409	0.0560	0.0606
GOF	1.086	1.047	1.026
R1 (obs / all)	0.0422 / 0.0538	0.0515 / 0.0839	0.0636 / 0.0962
wR2 (obs / all)	0.1139 / 0.1221	0.1283 / 0.1506	0.1520 / 0.1693

Table 5.1 (contd.). Crystal Data and Data Collection Parameters of Complexes **5.4**, **5.5** and **5.6**

	5.4	**5.5**	**5.6**
Formula	$ULiCl_2C_{46}H_{65}N_2O_3$	$ULi_2ClC_{54}H_{89}N_2O_9$	$ULiCl_{1.58}C_{50.42}H_{82.28}N_2O_{8.43}$
FW	1009.87	1197.63	1152.16
Crystal system,	Triclinic	Monoclinic	Triclinic
Space group	P-*1*	$P2_1/n$	P-*1*
a, Å	10.944(4)	13.2626(15)	11.302(3)
b, Å	12.922(5)	26.292(3)	12.323(3)
c, Å	18.617(9)	17.4106(19)	20.387(5)
α, deg	70.233(6)	90	96.782(4)
β, deg	80.328(8)	95.039(2)	92.600(5)
γ, deg	67.287(6)	90	94.776(5)
Volume, $Å^3$	2283.4(16)	6047.6(12)	2805.4(12)
Z	2	4	2
ρ_{calc} g/cm3	1.469	1.315	1.364
μ, mm^{-1}	3.711	2.777	3.017
F(000)	1016	2456	1176
T range (deg)	2.37 - 23.46	1.55 - 21.97	1.84 - 28.45
Limiting indices (*h, k, l*)	±12, ±14, ±20	±13, ±27, ±18	±14, ±16, ±27
Reflections collected / unique	13823 / 6578	33077 / 7338	30188 / 13149
R_{int}	0.0787	0.1223	0.0576
GOF	1.084	1.013	1.094
R1 (obs / all)	0.0717 / 0.1151	0.0704 / 0.1209	0.0644 / 0.0973
wR2 (obs / all)	0.1497 / 0.1682	0.1517 / 0.1730	0.1441 / 0.1551

Table 5.1 (contd.). Crystal Data and Data Collection Parameters of Complexes **5.7**, **5.8** and **5.9**

	5.7	**5.8**	**5.9**
Formula	$UNa_2C_{41}H_{60}N_2O_5$	$ULiC_{80}H_{113}N_4O_4$	$UNa_2C_{91.50}H_{139}N_4O_{10}$
FW	944.92	1439.71	1739.08
Crystal system,	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	P-*1*
a, Å	13.850(3)	13.448(5)	12.4419(17)
b, Å	22.875(5)	40.927(15)	13.0471(17)
c, Å	14.573(3)	14.033(5)	30.090(4)
α, deg	90	90	81.013(2)
β, deg	111.063(3)	104.170(6)	84.265(2)
γ, deg	90	90	86.249(2)
Volume, Å^3	4308.5(16)	7489(5)	4794.2(11)
Z	4	4	2
ρ_{calc} g/cm3	1.457	1.277	1.205
μ, mm^{-1}	3.829	2.217	1.755
F(000)	1896	2992	1820
T range (deg)	1.74 - 21.96	1.58 - 26.37	1.38 - 21.97
Limiting indices (*h, k, l*)	±14, ±24, ±15	±16, ±50, ±17	±13, ±13, ±31
Reflections collected / unique	24042 / 5148	61066 / 15277	26868 / 11727
R_{int}	0.0820	0.0714	0.0777
GOF	1.039	1.080	1.060
R1 (obs / all)	0.0440 / 0.0783	0.0570 / 0.0917	0.0691 / 0.1033
wR2 (obs / all)	0.1003 / 0.1174	0.0965 / 0.1056	0.1633 / 0.1772

Table 5.2. Selected bonds (Å) and angles (deg) for complexes **5.1**-**5.3**

5.1	5.2	5.3
U(1)-N(1) = 2.221(9)	U(1)-N(1)a 2.402(7)	U(1)-N(2) = 2.393(10)
U(1)-N(2) = 2.378(8)	U(1)-N(1) = 2.402(7)	U(1)-N(1) = 2.390(10)
U(1)-Cl(2) = 2.596(2)	U(1)-Cl(3) = 2.751(3)	U(1)-O(1) = 2.529(9)
U(1)-Cl(1) = 2.615(2)	U(1)-Cl(1) = 2.757(3)	U(1)-Cl(2) = 2.720(4)
U(1)-Cl(3) = 2.649(3)	U(1)-C(6) = 2.769(9)	U(1)-C(8) = 2.756(13)
U(1)-C(8) = 2.751(10)	U(1)-Cl(2) = 2.880(3)	U(1)-Cl(1) = 2.759(4)
N(1)-C(23) = 1.440(14)		
N(1)-C(9) = 1.442(13)	N(1)a-U(1)-N(1) = 118.8(3)	N(2)-U(1)-N(1) = 123.4(3)
N(2)-C(2) = 1.411(13)	N(1)a-U(1)-Cl(3) = 98.68(16)	N(2)-U(1)-O(1) = 90.2(3)
7N(2)-C(11) = 1.434(13)	N(1)-U(1)-Cl(3) = 98.68(16)	N(1)-U(1)-O(1) = 96.9(4)
C(1)-C(2) = 1.328(16)	N(1)a-U(1)-Cl(1) = 94.16(16)	N(2)-U(1)-Cl(2) = 95.2(3)
C(9)-C(10) = 1.333(16)	N(1)-U(1)-Cl(1) = 94.16(16)	N(1)-U(1)-Cl(2) = 98.3(2)
	Cl(3)-U(1)-Cl(1) = 154.57(10)	O(1)-U(1)-Cl(2) = 157.5(3)
N(1)-U(1)-N(2) = 127.1(3)	N(1)a-U(1)-C(6) = 61.95(17)	N(2)-U(1)-C(8) = 62.3(4)
N(1)-U(1)-Cl(2) = 90.0(2)	N(1)-U(1)-C(6) = 61.95(17)	N(1)-U(1)-C(8) = 63.6(4)
N(2)-U(1)-Cl(2) = 88.7(2)	Cl(3)-U(1)-C(6) = 84.64(19)	O(1)-U(1)-C(8) = 80.8(4)
N(1)-U(1)-Cl(1) = 91.31(19)	Cl(1)-U(1)-C(6) = 120.79(19)	Cl(2)-U(1)-C(8) = 121.0(3)
N(2)-U(1)-Cl(1) = 95.6(2)	N(1)a-U(1)-Cl(2) = 120.55(17)	N(2)-U(1)-Cl(1) = 119.4(3)
Cl(2)-U(1)-Cl(1) = 173.42(7)	N(1)-U(1)-Cl(2) = 120.55(17)	N(1)-U(1)-Cl(1) = 117.0(3)
N(1)-U(1)-Cl(3) = 119.1(2)	Cl(3)-U(1)-Cl(2) = 76.55(10)	O(1)-U(1)-Cl(1) = 78.0(3)
N(2)-U(1)-Cl(3) = 113.6(2)	Cl(1)-U(1)-Cl(2) = 78.02(9)	Cl(2)-U(1)-Cl(1) = 80.28(13)
Cl(2)-U(1)-Cl(3) = 86.73(10)	C(6)-U(1)-Cl(2) = 161.19(19)	C(8)-U(1)-Cl(1) = 158.7(3)
Cl(1)-U(1)-Cl(3) = 87.00(10)		
N(1)-U(1)-C(8) = 65.5(3)		
N(2)-U(1)-C(8) = 64.1(3)		
Cl(2)-U(1)-C(8) = 105.6(2)		
Cl(1)-U(1)-C(8) = 80.7(3)		
Cl(3)-U(1)-C(8) = 167.1(3)		

Table 5.2 (contd.). Selected bonds (Å) and angles (deg) for complexes **5.4-5.6**

5.4	**5.5**	**5.6**
U(1)-N(2) = 2.241(10) U(1)-N(1) = 2.273(10) U(1)-C(8) = 2.388(13) U(1)-O(1) = 2.477(9) U(1)-Cl(2) = 2.665(4) U(1)-Cl(1) = 2.792(3) N(2)-U(1)-N(1) = 132.4(4) N(2)-U(1)-C(8) = 67.4(4) N(1)-U(1)-C(8) = 66.4(4) N(2)-U(1)-O(1) = 93.8(3) N(1)-U(1)-O(1) = 90.7(3) C(8)-U(1)-O(1) = 81.9(4) N(2)-U(1)-Cl(2) = 98.1(3) N(1)-U(1)-Cl(2) = 94.4(2) C(8)-U(1)-Cl(2) = 119.3(3) O(1)-U(1)-Cl(2) = 158.5(2) N(2)-U(1)-Cl(1) = 112.1(3) N(1)-U(1)-Cl(1) = 115.3(3) C(8)-U(1)-Cl(1) = 160.6(3) O(1)-U(1)-Cl(1) = 78.8(2) Cl(2)-U(1)-Cl(1) = 80.05(12)	U(1)-O(1) = 2.244(9) U(1)-N(2) = 2.372(11) U(1)-N(1) = 2.391(11) U(1)-C(8) = 2.419(12) U(1)-C(35) = 2.476(13) U(1)-Cl(1) = 2.846(4) O(1)-U(1)-N(2) = 119.4(4) O(1)-U(1)-N(1) = 110.8(4) N(2)-U(1)-N(1) = 129.8(4) O(1)-U(1)-C(8) = 157.9(4) N(2)-U(1)-C(8) = 66.8(4) N(1)-U(1)-C(8) = 65.8(4) O(1)-U(1)-C(35) = 78.9(4) N(2)-U(1)-C(35) = 92.6(4) N(1)-U(1)-C(35) = 94.4(5) C(8)-U(1)-C(35) = 79.6(5) O(1)-U(1)-Cl(1) = 75.6(3) N(2)-U(1)-Cl(1) = 93.4(3) N(1)-U(1)-Cl(1) = 101.4(3) C(8)-U(1)-Cl(1) = 126.3(3) C(35)-U(1)-Cl(1) = 153.5(4)	U(1)-O(1) = 1.976(16) U(1)-N(2) = 2.381(6) U(1)-N(1) = 2.395(6) U(1)-C(8) = 2.412(7) U(1)-Cl(2) = 2.628(7) U(1)-Cl(1) = 2.668(2) U(1)-O(2) = 2.810(6) U(1)-O(3) = 2.844(7) O(1)-U(1)-N(2) = 96.6(5) O(1)-U(1)-N(1) = 96.5(5) N(2)-U(1)-N(1) = 132.3(2) O(1)-U(1)-C(8) = 95.3(5) N(2)-U(1)-C(8) = 66.4(2) N(1)-U(1)-C(8) = 66.8(2) O(1)-U(1)-Cl(2) = 5.5(5) N(2)-U(1)-Cl(2) = 95.74(18) N(1)-U(1)-Cl(2) = 93.15(18) C(8)-U(1)-Cl(2) = 90.0(2) O(1)-U(1)-Cl(1) = 153.2(4) N(2)-U(1)-Cl(1) = 95.18(15) N(1)-U(1)-Cl(1) = 93.20(15) C(8)-U(1)-Cl(1) = 111.47(17) Cl(2)-U(1)-Cl(1) = 158.42(13) O(1)-U(1)-O(2) = 79.4(5) N(2)-U(1)-O(2) = 143.0(2) N(1)-U(1)-O(2) = 84.6(2) C(8)-U(1)-O(2) = 150.3(2) Cl(2)-U(1)-O(2) = 83.34(19) Cl(1)-U(1)-O(2) = 76.75(17) O(1)-U(1)-O(3) = 77.7(5) N(2)-U(1)-O(3) = 85.5(2) N(1)-U(1)-O(3) = 142.2(2) C(8)-U(1)-O(3) = 150.3(2) Cl(2)-U(1)-O(3) = 83.1(2) Cl(1)-U(1)-O(3) = 79.31(17) O(2)-U(1)-O(3) = 57.5(2)

Table 5.2 (contd.). Selected bonds (Å) and angles (deg) for complexes **5.7-5.9**

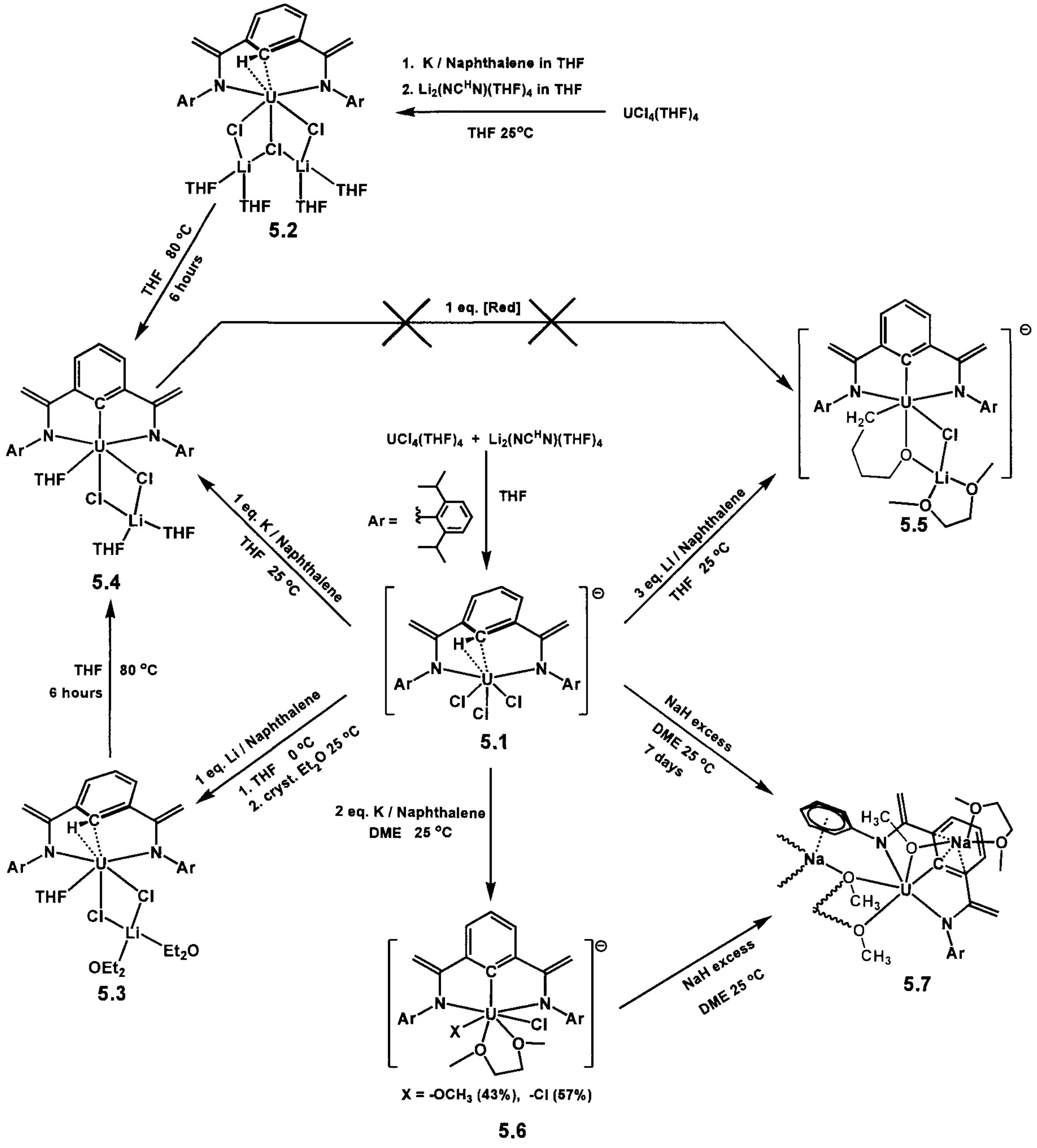
5.7	5.8	5.9
U(1)-O(1) = 2.178(7)	U(1)-N(3) = 2.260(4)	U(1)-N(3) = 2.325(8)
U(1)-O(3) = 2.207(6)	U(1)-N(2) = 2.371(4)	U(1)-N(2) = 2.359(8)
U(1)-O(2) = 2.296(6)	U(1)-N(1) = 2.372(4)	U(1)-C(10) = 2.479(11)
U(1)-N(2) = 2.418(8)	U(1)-C(8) = 2.420(5)	U(1)-N(1) = 2.519(8)
U(1)-N(1) = 2.440(8)	U(1)-C(40) = 2.682(5)	U(1)-C(32) = 2.623(12)
U(1)-C(8) = 2.468(10)	U(1)-C(43) = 2.678(5)	U(1)-C(36) = 2.654(10)
	U(1)-C(41) = 2.808(5)	U(1)-C(38) = 2.790(10)
O(1)-U(1)-O(3) = 89.8(3)		U(1)-C(37) = 2.846(10)
O(1)-U(1)-O(2) = 159.8(3)	N(3)-U(1)-N(2) = 106.13(15)	U(1)-C(34) = 3.008(13)
O(3)-U(1)-O(2) = 76.4(2)	N(3)-U(1)-N(1) = 111.53(15)	
O(1)-U(1)-N(2) = 95.5(3)	N(2)-U(1)-N(1) = 130.60(14)	N(3)-U(1)-N(2) = 100.6(3)
O(3)-U(1)-N(2) = 106.9(3)	N(3)-U(1)-C(8) = 124.88(16)	N(3)-U(1)-C(10) = 116.6(3)
O(2)-U(1)-N(2) = 102.5(3)	N(2)-U(1)-C(8) = 66.22(16)	N(2)-U(1)-C(10) = 65.2(3)
O(1)-U(1)-N(1) = 90.3(3)	N(1)-U(1)-C(8) = 66.32(17)	N(3)-U(1)-N(1) = 106.6(3)
O(3)-U(1)-N(1) = 122.4(3)	N(3)-U(1)-C(40) = 71.44(15)	N(2)-U(1)-N(1) = 129.5(3)
O(2)-U(1)-N(1) = 84.8(3)	N(2)-U(1)-C(40) = 133.82(14)	C(10)-U(1)-N(1) = 64.7(3)
N(2)-U(1)-N(1) = 130.3(3)	N(1)-U(1)-C(40) = 88.84(15)	N(3)-U(1)-C(32) = 127.6(3)
O(1)-U(1)-C(8) = 85.8(3)	C(8)-U(1)-C(40) = 153.54(17)	N(2)-U(1)-C(32) = 68.8(3)
O(3)-U(1)-C(8) = 171.3(3)	N(3)-U(1)-C(43) = 32.16(14)	C(10)-U(1)-C(32) = 105.1(4)
O(2)-U(1)-C(8) = 109.6(3)	N(2)-U(1)-C(43) = 96.87(15)	N(1)-U(1)-C(32) = 119.5(3)
N(2)-U(1)-C(8) = 66.1(3)	N(1)-U(1)-C(43) = 131.68(15)	N(3)-U(1)-C(36) = 32.1(3)
N(1)-U(1)-C(8) = 65.2(3)	C(8)-U(1)-C(43) = 149.08(16)	N(2)-U(1)-C(36) = 99.2(3)
	C(40)-U(1)-C(43) = 55.83(15)	C(10)-U(1)-C(36) = 145.0(3)
	N(3)-U(1)-C(41) = 56.31(14)	N(1)-U(1)-C(36) = 126.0(3)
	N(2)-U(1)-C(41) = 108.54(14)	C(32)-U(1)-C(36) = 96.8(3)
	N(1)-U(1)-C(41) = 118.57(14)	N(3)-U(1)-C(38) = 68.8(3)
	C(8)-U(1)-C(41) = 174.71(17)	N(2)-U(1)-C(38) = 146.6(3)
	C(40)-U(1)-C(41) = 30.51(15)	C(10)-U(1)-C(38) = 148.2(3)
	C(43)-U(1)-C(41) = 29.39(14)	N(1)-U(1)-C(38) = 83.6(3)
		C(32)-U(1)-C(38) = 92.2(3)
		C(36)-U(1)-C(38) = 54.6(3)
		N(3)-U(1)-C(37) = 55.6(3)
		N(2)-U(1)-C(37) = 118.2(3)
		C(10)-U(1)-C(37) = 171.2(3)
		N(1)-U(1)-C(37) = 112.2(3)
		C(32)-U(1)-C(37) = 83.7(3)
		C(36)-U(1)-C(37) = 29.5(3)
		C(38)-U(1)-C(37) = 29.4(3)
		N(3)-U(1)-C(34) = 154.9(3)
		N(2)-U(1)-C(34) = 63.0(3)
		C(10)-U(1)-C(34) = 75.5(4)
		N(1)-U(1)-C(34) = 98.4(3)
		C(32)-U(1)-C(34) = 30.9(3)
		C(36)-U(1)-C(34) = 127.2(3)
		C(38)-U(1)-C(34) = 113.5(3)
		C(37)-U(1)-C(34) = 113.3(3)

Results and Discussion

The reaction of the dianion $[1,3\text{-}[2,5\text{-}(i\text{-}Pr)_2PhN\text{-}C(=CH_2)]_2C_6H_4]^{2-}$ with $UCl_4(THF)_4$ afforded the corresponding tetravalent $\{1,3\text{-}[2,5\text{-}(i\text{-}Pr)_2PhNC\ (=CH_2)]_2C_6H_4\}UCl_3\cdot Li(THF)_4$ (**5.1**) (Scheme 5.1). The ligand system did not adopt the anticipated π-bonding mode (Figure 1). The main interaction between uranium and the aromatic ring appears to be realized only through one central C atom of the phenyl ring without any significant contributions from the corresponding C-H bond. The presence of this unconventional interaction is fully supported by DFT theoretical calculations (see below) and possibly indicates a partial charge transfer from the tetravalent uranium center to a portion of the aromatic ring. Furthermore, the interaction of the U metal center with the C atom of the ring promotes noticeable weakening of the corresponding C-H bond (see electronic structures discussion), which makes the aromatic ring incline towards direct metallation. In spite that the geometrical parameters of the U-C-H arrangement are similar to those observed for the coordination of cyclohexane to a U(III) metal center,[8c] it appears that no significant agostic interaction is present in this case.

The ^1H-NMR spectrum of **5.1** is characterized by a large spreading of 16 fairly sharp lines over the range +50/-14 ppm. Besides the two resonances of the THF coordinated to Li, which reside approximately in the expected regions, the other resonances could not be assigned conclusively. The only clearly recognizable feature was the C-H hydrogen of the central C atom of the central phenyl ring. Due to close proximity of paramagnetic U metal center, the signal of this hydrogen was located at +49.72 ppm and coupled to a broad carbon resonance at -0.25 ppm. Also clearly recognizable were the $=CH_2$ hydrogens which gave two resonances at +13.79 and -14.30 coupled to the same carbon at 134.61 ppm.

The behavior of this ligand system *vis a vis* the trivalent state of uranium was examined by reacting the same ligand di-anion with *in situ* prepared "UCl_3" (Scheme 5.1). The reaction afforded indeed a trivalent species formulated as $\{1,3\text{-}[2,5\text{-}(i\text{-}Pr)_2PhNC(=CH_2)]_2C_6H_4\}UCl_3][Li(THF)_2]_2$ (**5.2**). The configuration of the ligand system in this complex is similar to **5.1** with the same type of arrangement of



Scheme 5.1.

the central phenyl ring (Figure 5.2). The slight increase in the bond distances formed by the uranium metal center as well as the little stronger ring tilt could be attributed to an increase of the metal center size due to the lower oxidation state. The only significant difference in the structure of **5.2** is the presence of two Li cations connected to the U-ligand moiety through chlorine bridges, as required by the trivalent state of the metal center. NMR spectra were uninformative in this case only showing very broad resonances. No signals could be observed in the ^{13}C-NMR.

Further attempt to lower the oxidation state was attempted by reacting the tetravalent **1** with a series of reagents (Scheme 5.1). The outcome depended greatly on both the reducing agent and reaction conditions. Reaction of **5.1** with 1 equivalent of Li naphthalenide at 0°C although did not afford **5.2** yielded a closely related U(III) complex formulated as $\{1,3\text{-}[2,5\text{-}(i\text{-}Pr)_2PhNC(=CH_2)]_2C_6H_4\}UCl_2(THF)][Li(Et_2O)_2]$ (**5.3**). Complexes **5.2** and **5.3** only differ for the different extent of retention of LiCl. The ligand system showed the same arrangement in both complexes forming with the metal center the same unusual interaction with the central aromatic ring. As in the case of **5.2**, the NMR spectra were uninformative.

Both the trivalent **5.2** and **5.3** react thermally in boiling THF affording oxidation of the metal center to a new tetravalent compound $\{1,3\text{-}[2,5\text{-}(i\text{-}Pr)_2PhNC(=CH_2)]_2C_6H_3\}UCl_2(THF)][Li(THF)_2]$ (**5.4**) where the oxidation of the trivalent center occurred at the expense of the central phenyl ring C-H bond (Scheme 5.1). The fate of the hydrogen atom though is unclear since no hydrogen gas has been recovered from the reaction when the thermolysis was carried out in a close vessel connected to a Toepler pump. Also no significant distortions can be observed in the complex and which might indicate the presence of hydride. As a result of the metallation, the ring becomes almost co-planar with the uranium center, the small deviation of the metal from the plane being probably a result of the steric repulsion between the *i*-Pr substituents and the coordinated THF molecule (Figure 5.3). Despite the line broadening, the ^{1}H-NMR spectrum of complex **5.4** allows recognition of all the functional groups of the ligand system. The most striking spectral feature is the significant spread of the lines of the two non-equivalent $=CH_2$ protons of the two ene-amino moieties and which are also magnetically non-equivalent. These resonances are present as a pair of doublets at 7.17 and 7.13 ppm coupled to other doublets at 2.18 and 2.16 ppm respectively. The four *i*-Pr substituents give two distinctive doublets centered at 1.47 and 1.44 ppm with the correct integration. These resonances are coupled to two broad multiplets of the corresponding *ipso*-hydrogens located with proper integration at 3.09 ppm and 7.33 ppm respectively. The large difference of chemical shifts is not particularly surprising, given the very different structural environment experienced by these hydrogen atoms. In fact, two are oriented against the coordinated THF molecules while the other two point against a void space. The resonances of the three aromatic rings are located in the conventional range between 9.0 and 7.4 ppm.

The ready ring metallation accompanied by the one-electron oxidation of the metal center, as occurring under thermal conditions, clearly frustrated the possibility of using the π-coordination of the phenyl ring for possible stabilization of the lower oxidation states of the metal center. Therefore, further attempts to prepare complexes with uranium in low oxidation states were focused on the use of **5.1** as the most convenient starting material. In carrying out reduction reactions, we compensated for the consumption of the reductant by the seemingly unavoidable ring metallation by using larger stoichiometric ratios.

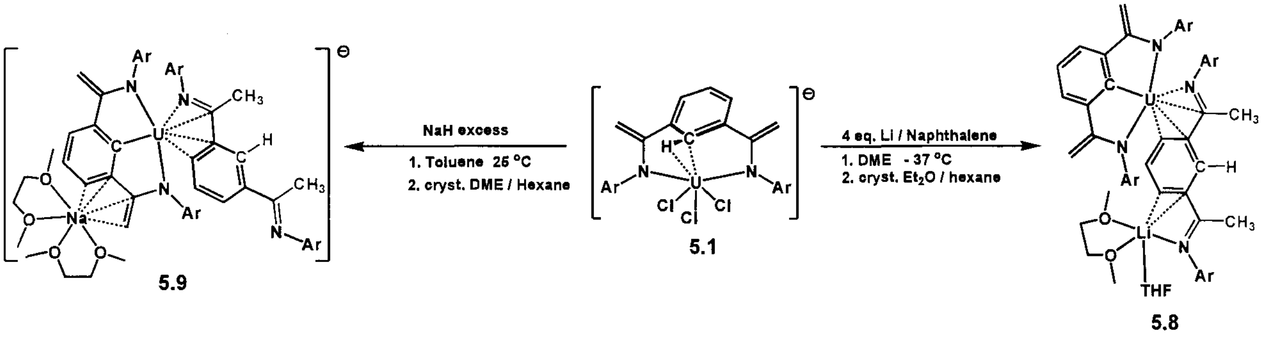
Reaction of **5.1** with three equivalent of Li naphthalenide at room temperature afforded $\{(\{1,3\text{-}[2,5\text{-}(i\text{-}Pr)_2PhNC(=CH_2)]_2C_6H_3\}U\text{-}(\mu\text{-}Cl)\text{-}(\mu\text{-}[O(CH_2)_3CH_2])[Li(DME)]\}\{Li(DME)_3\}$ **(5.5)** (Scheme 5.1). This species has the tetravalent metal center forming a six- member metallacycle ring with a moiety as arising from THF ring opening. Similar ring opening has been previously observed by Burns as the result of a non-redox insertion reaction of THF into the U-I bonds. [9a] In the present case instead, the ring opening is clearly the result of a two-electron reductive cleavage of the THF O-C bond. Given that the complex **5.5** contains tetravalent uranium, it is tempting to state that a transient divalent synthon or reduced species was responsible for the attack. The two ene-amido moieties remained unmodified during the reduction, while the ring metallation instead occurred as expected. The ^{1}H-NMR spectrum showed all aromatic resonaces located between 9.14 and 7.05 ppm. The four iso-propyl groups display only one doublet at 1.15 ppm coupled to a broad multiplet at 2.77 ppm with the expected integration.

Similarly to compound **5.4,** the ene-amino moiety protons are magnetically non-equivalent resulting in large splitting of one pair of broad signals at 7.19 and 6.87 respectively coupled to equally broad resonances at 2.31 and 1.97 ppm. The metallacycle –CH_2– groups appear as four distinct broad resonances. Two, which are tentatively assigned to U–CH_2– and U–O–CH_2– groups experience the most significant chemical shift to -6.62 and -4.36 ppm respectively. The other two –CH_2– groups were instead located in more normal range at 2.17 ppm and 0.98 ppm.

Overall, the THF ring opening and the phenyl ring metallation, as occurring during the formation of **5.5,** required a total of three electrons, assuming that the aromatic ring H atom was released as either hydrogen gas or transferred to some other acceptor. To better clarify this point, the same reaction was carried out in a sealed vessel connected to a Toepler pump showing that even no traces of hydrogen gas had been produced during the reaction. In addition, the fact that the reaction actually consumed *three* equivalents of reductant and that both starting material and final product contain the uranium metal in the tetravalent state, clearly suggested that a byproduct may have been formed. To remove the interference of THF cleavage, an identical reduction was performed in the more robust DME. Reduction of **5.1** in DME with 2 equivalents of K naphthalenide at room temperature afforded a mixture of two compounds of very similar structure. The two different species [{1,3-[2,5-(*i*-Pr)$_2$PhNC(=CH_2)]$_2$ C_6H_3}UCl(OCH_3)][Li(DME)$_3$] (**5.6a**) and [{1,3-[2,5-(*i*-Pr)$_2$PhNC(=CH_2)]$_2$$C_6H_3$}U$Cl_2$][Li(DME)$_3$] (**5.6b**) co-crystallized in the ratio very close to 1:1 in the same unit cell providing single crystals of mixed composition. The salient characteristic of the structure of the two compounds is again the ring metallation as observed in the previously reported compounds. While complex **5.6a** has one chlorine atom and one methoxy group, complex **5.6b** bears two chlorine atoms. The methoxy group is supposedly generated by DME cleavage and in both species the uranium oxidation state is tetravalent. In line with the previous case, no gaseous hydrogen gas was produced during the reaction.

Recent findings have shown that NaH may be a convenient reductant for the preparation of formally low-valent complexes[17b,18,19d,21] including examples of dinitrogen fixation. [18,19d,21] We have thus attempted the reduction of **5.1** with excess of NaH in DME. After a slow reaction, a new species formulated as $\{[\{1,3\text{-}[2,5\text{-}(i\text{-Pr})_2\text{PhNC}(=\text{CH}_2)]_2\text{C}_6\text{H}_3\}\text{U-}(\mu\text{-OCH}_3)[\text{Na(DME)}]\text{-}\mu\text{-}[\text{Na(OCH}_3)_2]\}_2$ **(5.7)** was isolated in significant yield. Once again the crystal structure revealed the presence of several methoxy groups coordinated to the U center in addition to the metallation of the ligand phenyl ring. Its formation unfolds some interesting aspects of the reduction process. The formation of a methoxy moiety from DME as the result of the attack by one or two low-valent metal centers has been observed also in the case of **5.6a/5.6b**. The presence in **5.7** of three methoxide units rises two different possibilities. The first consists of the formation of an "ultra-reduced" species followed by a three simultaneous or consecutive "two-electron oxidation" steps. Such a large storage of electrons in the complex clearly is an improbable event. More realistic is perhaps a one-electron reduction immediately followed by DME attack repeated three times, in what is reminiscent of the beginning of a catalytic process. ^{1}H-NMR data for **5.7** showed the usual features. All aromatic signals are very well resolved and are located between 8.68 and 6.93 ppm. The ene-amino protons show the enhanced magnetic non-equivalency with two doublets centered at 7.93 and 7.84 ppm coupled to two other doublets at 2.90 and 2.34 ppm respectively. The four iso-propyl groups display two doublets centered at 1.11 and 1.09 ppm coupled to the same multiplet at 2.74 ppm. The positions of the methoxy residues resonances are rather unusual. Two of the three methoxy groups have a broad resonance at -3.10 ppm, while the third is observed as a more sharp line at 4.60 ppm.

From the seemingly ubiquitous solvent cleavage and ring metallation it became apparent that milder reaction conditions are the only possibility to isolate intermediate reduced species of such a high reactivity. Thus, reduction of **5.1** was carried out at low temperature (-35°C) and with a larger amount of Li(naphthalenide) (4 equivalents). After suitable work-up, the new species $\{[\{1,3\text{-}[2,5\text{-}(i\text{-Pr})_2\text{PhNC}(=\text{CH}_2)]_2\text{C}_6\text{H}_3\}\text{U}\{1,3\text{-}[2,5\text{-}(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]_2\text{C}_6\text{H}_4\}][\text{Li(DME)(THF)}]\}\cdot\text{Et}_2\text{O}$ **(5.8)** was isolated in significant yield (Scheme 5.2). Even in this case, the uranium atom is surrounded by the much expected tri-anionic, ring-metallated ligand (Figure 5.7). However, a second ligand unit is this time surrounding the metal center bonded through a part of the π-system. The inspection of the structural parameters clearly indicated that this second ligand unit *has acquired two hydrogen atoms* and that the imine functions have been restored forming a neutral bis-iminobenzene unit. The formation of complex **5.8** from reduction of the tetravalent **5.1** is the result a complex series of transformations. In fact the presence of one intact *neutral* ligand implies that during the reaction, one doubly deprotonated ligand has regained the two hydrogen atoms, it has been demetallated and π-coordinated to a second "*formally reduced*" metal center.



Scheme 5.2.

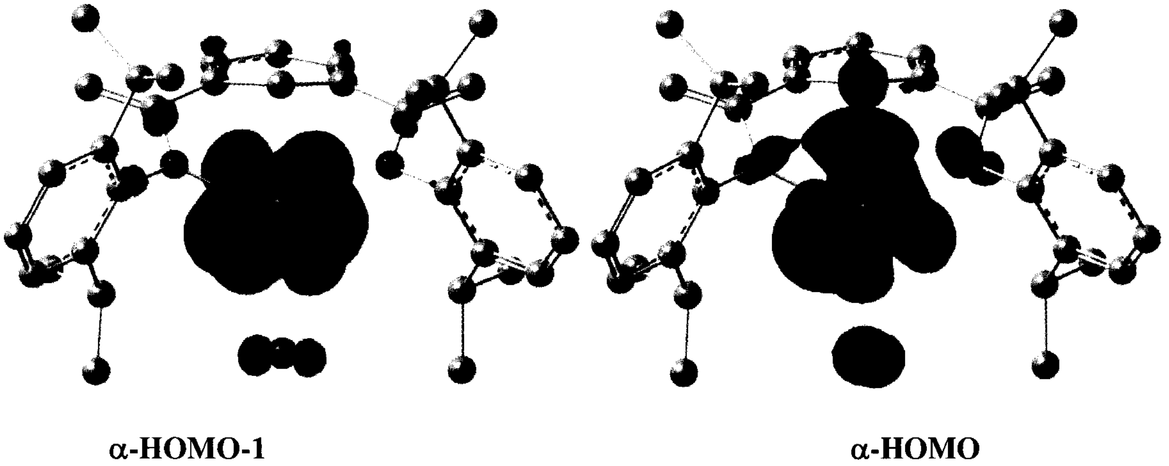
While the fate of the demetallated metal center remains unclear, the origin of the two hydrogen atoms can be tentatively ascribed to the phenyl rings of two other units which have been phenyl-metallated. Thus, it is possible that ring metallation is not the result of a direct red-ox transformation but of a C-H σ-bond metathetic process instead. In turn, this may explain the absence of hydrogen gas from the reaction mixtures. While this implies that even more uranium containing species may be partner products of this series of transformations, we observe that from the *formal* point of view this reaction can be interpreted as a two-electron reduction affording a "formally" U(II) bis-amino-benzene complex. Of course, given the π-coordination of the additional neutral ligand, the oxidation state is likely to be higher (see below). ^{13}C-NMR data did not provide any useful information due to very large peak broadening and overlapping. The only recognizable features of ^{1}H-NMR spectrum spread between +26 and -90 ppm are the methyl signals of the isopropyl group located in their normal positions at 1.29 and 1.85 ppm.

Even though complex **5.8** gives no evidence of having directly been involved in solvent cleavage, a reduction was also carried out at ambient temperature but in non-coordinating solvent. Reaction of **5.1** with excess of NaH in toluene proceeded slowly at room temperature affording significant yield of $\{[\{1,3\text{-}[2,5\text{-}(i\text{-Pr})_2\text{PhNC}(=\text{CH}_2)]_2\text{C}_6\text{H}_3\}\text{U}\{1,3\text{-}[2,5\text{-}(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]_2\text{C}_6\text{H}_4\}\{\text{Na}(\text{DME})_2\}][\text{Na}(\text{DME})_3]\}□(\text{C}_7\text{H}_8)_{0.5}$ (**5.9**) after crystallization from DME. Similar to **5.8**, the complex still contains one ring-metallated trianionic ligand and one intact ligand which has regained the H atoms and restored the two imine functions. The metric parameters of the anionic moiety compare well with those of **5.8**. The main difference consists of the presence of *two* solvated Na atoms instead of *one* Li cation. This assigns a *formal* monovalent state to uranium. Such a low-oxidation state is of course unrealistic for uranium which most likely embarks in a substantial back-bonding interaction with the π-system of the neutral ligand. In any event, this complex appears to be a species reduced to the largest extent ever observed so far. NMR data for this compound were completely un-informative due to wide line broadening and signals overlapping. Although **5.8** and **5.9** are formally highly reduced species, the reactivity of the metal center seems to have been substantially quenched by the acquisition of the second ligand system. These species are not active enough to perform cleavage of ethers. They also do not engage in reactivity with a range of mild oxidating agents at room temperature. All the attempts to initiate the reactivity by increasing the temperature resulted in extensive decomposition, producing only intracatble materials.

Electronic Structure.

The X-ray structures of complexes **5.1-5.3** revealed a presence of a close contact between the U metal center and the C-H bond of the central phenyl ring of the ligand. At first glance, the relative positions of all three atoms may suggest the presence of a three-center 2-electron agostic U-H-C interaction. DFT calculations, performed by using the crystallographic atomic coordinates, revealed however a rather different scenario. Full molecule geometry optimization was performed prior to electronic structure evaluation providing a satisfactory match with the X-ray structural data for all bonds and angles values.

The calculations established that the 3-centered bond order index for the U-C-H interaction in complex **5.1** is equal to 0, which rules out the presence of agostic interactions. Furthermore, calculations predicted only a minor elongation of the C-H bond from 1.094 Å to 1.103Å and which is smaller than the typical +0.07Å C-H bond expansion normally expected for a metal-H-C agostic interaction. [32] Accordingly, the U-H bond order is of only 0.07.Conversely, the U-C interaction was calculated to be



α-HOMO-1 **α-HOMO**

Figure 5.10. α-HOMO and α-HOMO-1 orbitals for the optimized structure of complex **5.1**.

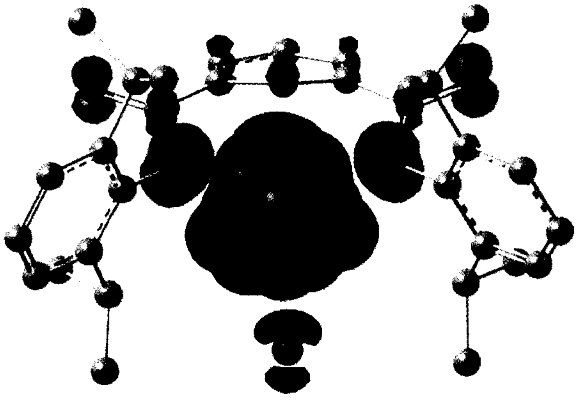
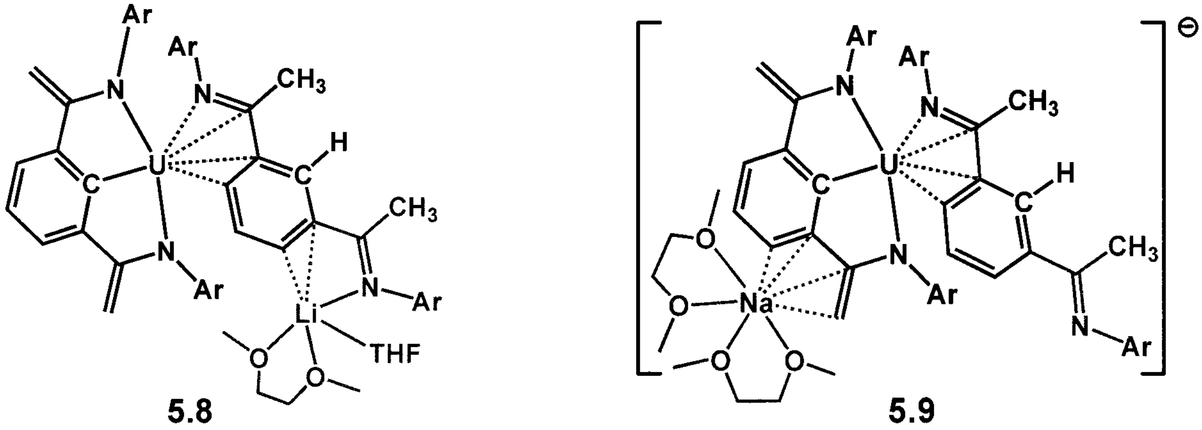


Figure 5.11. Spin density distribution for the optimized structure of complex **5.1**. Isosurface contour value of 0.0008 e□Å$^{-3.}$

much stronger, displaying a Mayer bond order of 0.23.Such interaction may be described in terms of a weak π-bonding with and electron density transfer of 0.06 from the portion of the π-orbital located over C(8) to the U(IV) atom. The spin density on the U atom was calculated as 2.22 and which reveals the presence of two unpaired $5f$ electrons (Figure 5.10). The uranium valence index of 6.9 supports this assumption indicating the existence of two free valences in addition to 5 conventional σ-bonds.

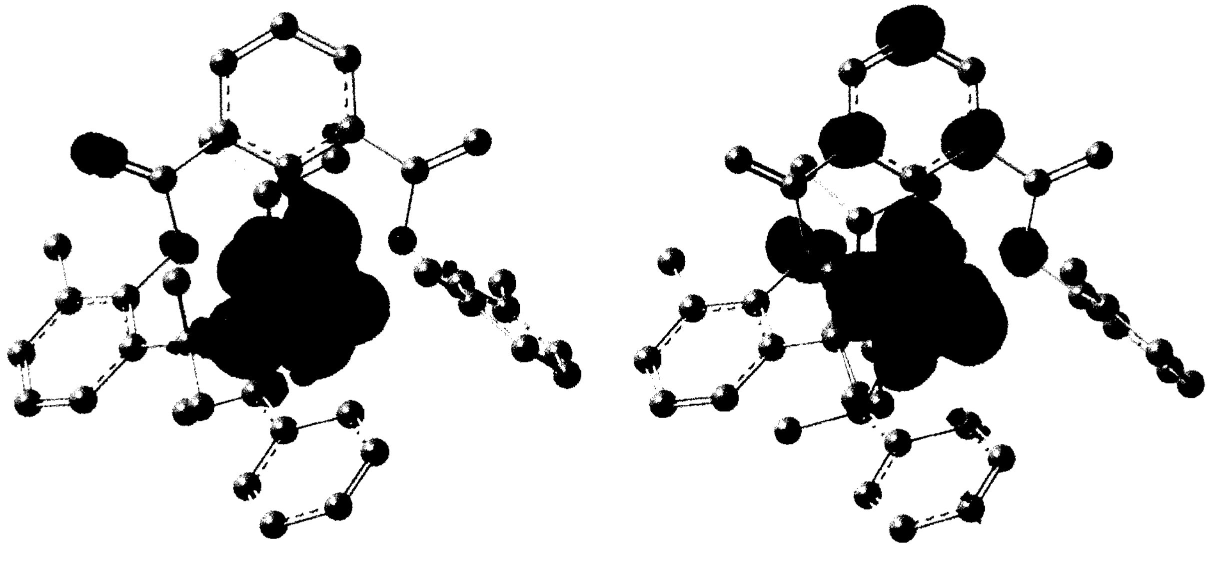
DFT calculations were also performed on both **5.8** and **5.9** to evaluate the most realistic oxidation state of the metal center. From the formal point of view, the two compounds contain the U metal center in the unrealistic low U(II) and U(I) oxidation states respectively. Both compound **5.8** and **5.9** possess two ligand systems each. In each compound, the two ligands bonded to the same metal are conceptually different in their electronic structures. One possesses three negatively charged donor atoms coordinated to the U metal center through 3 σ-bonds. The second displays the structural parameters typical for the neutral molecule and connected to the U metal center through a series of π-interactions. In complex **5.8** the same π-coordinated ligand system hosts an alkali cation (Scheme 5.3). This alkali cation is retained through several π-interactions and is situated on the remote part of the ligand system without significant interactions with U metal center. Therefore, in order to optimize calculation time for compound **5.8** and **5.9**, calculations were performed on truncated models obtained by replacement of distant half of the bis-imino-benzene molecules by hydrogen atoms. Such simplification is justified in light of the remote position of this moiety, resulting in total absence of any interaction with U metal center. The geometry of the ligands in both cases prevents the extensive conjugation as well as delocalization of the electrons through π-systems interactions. It should be also taken into consideration that the proposed simplification leads to the removal of alkali cation associated with the truncated part of the molecule for the case of compound **5.8**. Such cation removal causes the appearance of one additional negative charge on the model structure which otherwise would be compensated by the presence of positively charged metal center.



5.8 **5.9**

Scheme 5.3. Simplification of the structures for complexes **8** and **9**. Truncated parts are depicted in grey. Fragment shown in black is used for the electronic structure analysis.

Another model simplification consists of the replacement of three out of the four *i*-Pr groups in complex **5.8** with H. The last *i*-Pr group was not simplified because of its close proximity to the U metal center and possible influence on stabilization of the oxidation state through agostic interactions.



α-HOMO-1 **α-HOMO**

Figure 5.12. α-HOMO and α-HOMO-1 orbitals for the optimized structure of complex **5.8**.

All *i*-Pr substituents in the model of **5.9** were preserved for similar reasons. All alkali cations were removed from both structures together with their coordinated solvent molecules. All the other coordinates of heavy atoms were imported directly from X-ray data and used without further geometry optimization. All C-H bond distances were set to the 1.08Å length.

Calculations were performed for different multiplicities corresponding to a hypothetical U(II) f^4 and U(IV) f^2 for complex **5.8** and U(I) f^5 and U(III) f^3 complex **5.9** respectively. For complex **5.8** the possibilities of singlet S=0, triplet S=1 and pentet S=2 states were evaluated. The results clearly indicated that the triplet state S=1 is the ground state for **5.8** in further agreement with the substantial paramagnetism, as also suggested by the NMR data. For complex **5.9** three possibilities were analyzed namely the doublet <S=1/2>, quadruplet <S=3/2> and sextet <S=5/2> ground states. Calculation indicated that the doublet ground state has the lower total electronic energy with respect to the quadruplet and sextet states (□E_{tot} are 152.4 and 23.8 kcal/mol, respectively). The net electron spin density of the uranium metal center was determined as 2.24 for complex **5.8** and 1.27 for complex **5.9** accordingly.

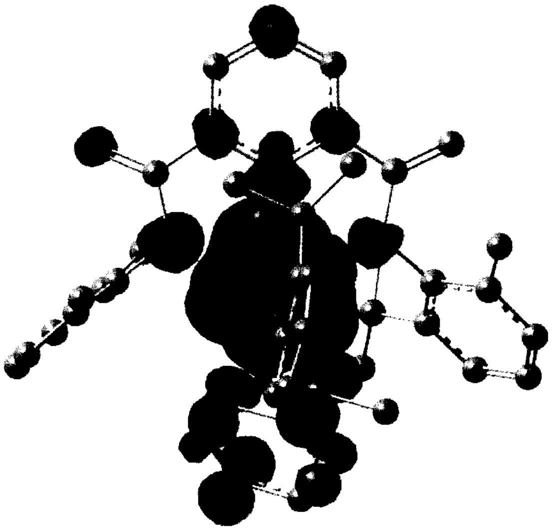
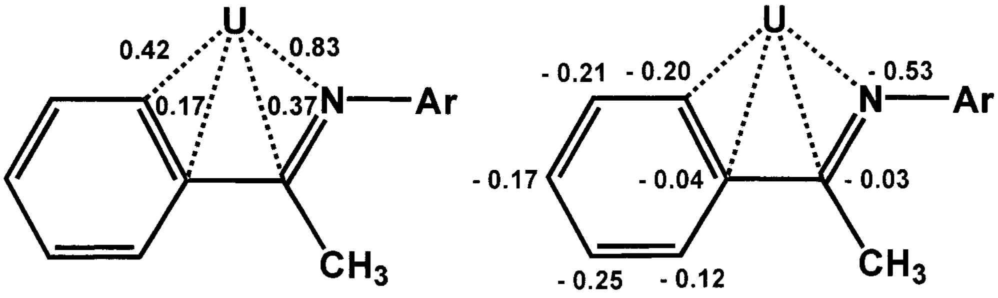


Figure 5.13. Spin density distribution for the simplified model structure of complex **5.8**. Isosurface contour value of 0.0008 e□Å^{-3}.

Mulliken population analysis (MPA) for compound **5.8** revealed two unpaired electrons nearly purely 5*f* in character (91% and 94% for the α-spin HOMO and HOMO-1, respectively, Figure 5.12), accounting for the spin density distribution shown in Figure 5.13.

In summary, the most realistic oxidation state of the uranium center in this species can be assigned as +4 with the ligand molecule playing the role of storage of electron density. The electrons hosted in the π-bonded ligand fragment are used for a diene-type of bonding with the U metal center (Scheme 5.4).



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Scheme 5.4. Mayer bond orders (in red) and MPA-derived atomic charges (a. u., in blue) of the π-bonded bis-imino-benzene fragment for **5.8**.

α-HOMO-1 **α-HOMO**

Figure 5.14. α-HOMO and α-HOMO-1 orbitals for the optimized structure of complex **5.9**.

Similarly to complex **5.8**, the MPA of **5.9** indicated that the complex has three electrons in three nearly degenerate U 5*f* non-bonding orbitals (89% U for the α-HOMO, 92% U for the α-HOMO-1, and 100% U for the β-HOMO, Figure 5.14) resulting in the spin density distribution shown in Figure 5.15.

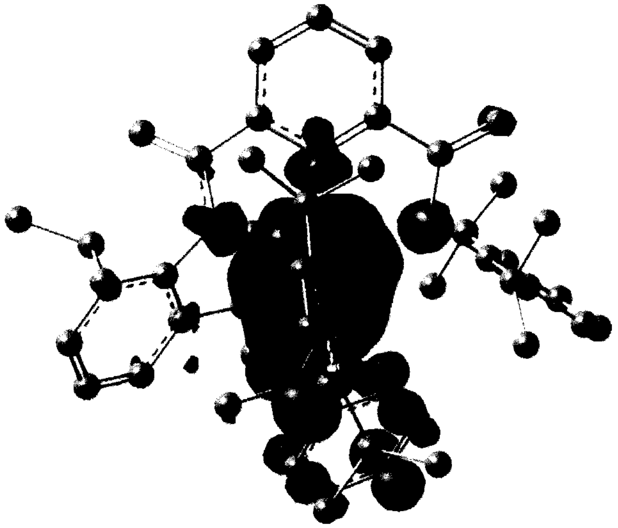
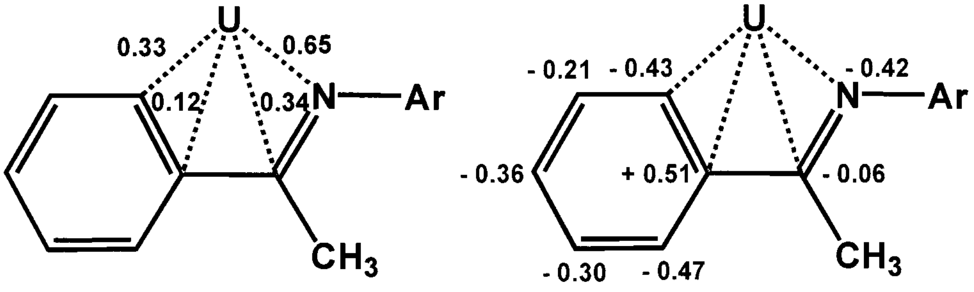


Figure 5.15. Spin density distribution for the simplified model structure of complex **5.9**. Isosurface contour value of 0.0008 e□Å$^{-3.}$

In this case, the most realistic oxidation state of the metal center could be regarded as +3 with the ligand hosting two "additional" electrons on delocalized π-system as presented on Scheme 5.5.



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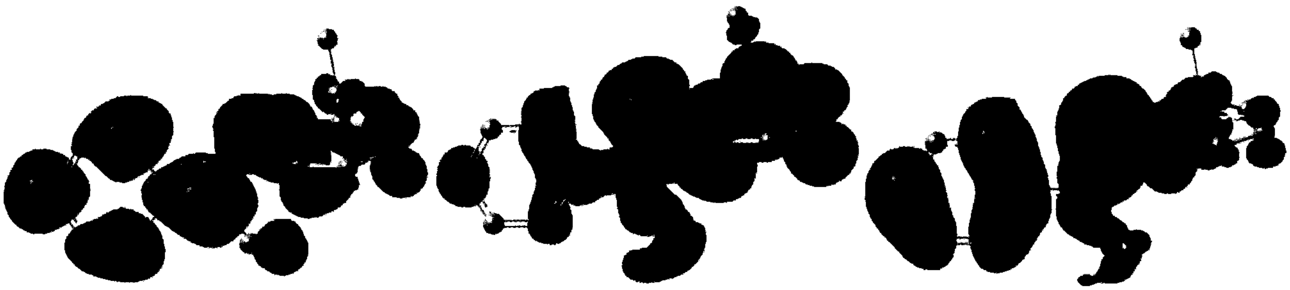
Scheme 5.5. Mayer bond orders (in red) and MPA-derived atomic charges (a. u., in blue) of the π-bonded bis-imino-benzene fragment for **5.9**.

Calculation on the π-bonded moiety holding a -2 overall charge indicates that for complex **5.8** as well as complex **5.9** two additional electrons are hosted mainly on three highest occupied fragment orbitals of *π-coordinated ligand* (Figure 5.16).



HOFO **HOFO- 1** **HOFO-2**

Figure 5.16. Highest occupied fragment orbitals (HOFOs) of the dianionic ligand that are interacting with the U^{IV} ion in complex **5.8**.

Overall the donor-acceptor interactions between the uranium ion and the dianionic π-bonded moiety in complex **5.8** are limited to charge transfer to metal from the three highest occupied fragment orbitals (HOFOs, Figure 5.16). This charge transfer is evident from the changes of the orbital occupancies upon complex formation:[28c] α-HOFO = 40.4%, β-HOFO = 27.2%, α-HOFO-1 = 13.3%, β-HOFO-1 = 11.3%, α-HOFO-2 = 13.1%, β-HOFO-2 = 11.4%. As it can be seen from the changes in occupancies, the HOFO of the ligand plays the most important role in charge transfer to the U(IV) ion. Since the nature of these orbitals in complexes **5.8** and **5.9** is nearly identical, the same orbitals contribute to covalent bonding between the metal and the ligand in complex **5.9**: α-HOFO = 43.0%, β-HOFO = 26.6%, α-HOFO-1 = 14.1%, β-HOFO- 1 = 11.4%, α-HOFO-2 = 12.1%, β-HOFO-2 = 10.2%. These large changes in donor orbital occupancies highlight the importance of metal-ligand covalent interactions in the stabilization of **5.8** and **5.9**.

The most significant difference observed between **5.8** and **5.9** is provided by the interaction of the metal center with the aliphatic carbons of iso-propyl groups. In the case of **5.8** such interaction is completely negligeable. Conversely, in the case of **5.9** several of the C□H bonds with of the isopropyl groups are oriented to interact with the U atom with one ipso C□H interaction being noticeably stronger. The significance of these interactions can be confirmed by the Mayer bond orders for the corresponding U-C and U-H contacts, the largest values for all U-C and U-H [U(1)□C(32) and U(1)□H(32)A] being 0.35 and 0.21, respectively. Although contributing to the stabilization of the complex, these interactions do not cause significant changes in C-H bonds lengths.

Conclusions

By using the bis-iminobenzene ligand it was possible to isolate several new U complexes. Reduction reactions mainly led to different solvent fragmentation products. In every case, the solvent fragmentation suggested transient formation of low-valent or reduced species. the ligand system instead appears to be sufficiently resilient, the only involvement into the reactivity of the metal center being the direct metallation of the aromatic ring. By lowering the temperature of the reduction or using non-coordinating solvent, it was possible to isolate complexes where the U metal center coordinates to two anionic-radical ligands. In this species, the metal center deceivingly appears as unusually low valent. In fact, DFT calculations unequivocally confirmed that the actual oxidation state of the U metal centers in the two latter complexes could be assigned as U(IV) and U(III) respectively, coupled to dianionic forms of the ligand and with the electron storage performed by the coordinated π-systems.

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Chapter Six

Reduction of Thorium Complex Stabilized by π-coordination: Isolation of a Paramagnetic Thorium Compound

Introduction

One of the primary characteristic of low-valent metals in unusual oxidation states is an outstanding reactivity encompassing many different aspects of molecular activation.[1-7,9k,11a] Important breakthroughs in the chemistry of *f*-block elements during the last three decades clearly indicate that efforts to generate unstable oxidation states are often rewarded with the most unpredictable and diversified reactivity.[3-7,11a] A survey of the chemistry of strongly reducing low-valent samarium,[4] neodymium,[5] thulium[5c,k-m,6] or uranium[7] gives the immediate sense of an exceptional red-ox reactivity. Dinitrogen activation,[4n,5a,i,k,6a,l,7n,p,8] a clear indication of the presence of an enhanced reducing power, is frequently encountered. In the cases where the low-oxidation state cannot be obtained due to intrinsic instability, formation of reduced species or low-valent synthons is a viable alternative. For the preparation of these species to be successful, the presence of a molecular unit capable to act as electron storage is a key requirement. Systems containing delocalized π-electrons seem to be versatile from this point of view since a few divalent uranium and lanthanides synthons have been prepared via coordination to arenes. The presence of a π-system as a part of the ligand framework either σ- or π-bonded to the metal center has been also useful for this purpose. It has allowed the characterization of species where, according to the connectivity, the metal appears to be as low-valent.[7i,m,9,11c] However, this appearance is in fact deceiving since substantial electron density is residing in low-lying ligand-centered MOs, with the metal being higher valent and the ligand present in the form of radical anion. What is truly remarkable in these species is that the chemical behavior remains as expected for a genuinely low-valent species,[7m,9c,n-o,r] the ligand system clearly acting as electron storage in this case. Because of this behavior, the name of "reduced species" or "low-valent synthons" has been forged.

The behavior of thorium from this point of view is in line with that of these species with some rather unique features. Firstly it should be noticed that low oxidation states are unknown for this element. Even the simple ThI_2 is regarded not as a divalent thorium but as containing a higher-valent element with electrons stored in conduction bands generated by the iodide anions.[10] There are only two cases reported to date of paramagnetic complexes appearing as trivalent thorium compounds.[11] However, DFT calculations clearly have indicated that, again, the oxidation state is higher, the unpaired electron residing in the ligand π-system.[11c-d] More recent attempts to generate low-valent thorium species have afforded naphthalenide complexes where the very visible distortion of the coordinated naphthalene ring doubtlessly indicated complete reduction of the aromatic ring.[9n-o] As expected, the thorium atom is present in the more standard tetravalent state. Nonetheless, these species work as low-valent synthons producing transformations which can be rationalized as generated by genuine low-valent species obtained during the dissociation of coordinated naphthalene in its neutral form.[9n-o] The formation of such highly reactive transient species has also permitted dinitrogen cleavage and partial hydrogenation.[9n] This rare transformation is possibly due to an enhancement of radical activity of the reduced dinitrogen moiety capable of abstracting hydrogen atom from the solvent.

Following these findings we have decided to explore a dianionic ligand system where two pyrrolide anions are linked in a *non*-conjugated fashion to one central phenyl ring.[1g,12] Since pyrrolide anions have been shown versatile in the chemistry of divalent samarium and making their derivatives capable of surpassing the reducing power of samarocenes,[4n,8g-j] we thought that their coordination, either in σ- or π-fashion might be incremental to reactivity. The central ring was expected to be constrained at bonding distance with the metal center and therefore providing a π-interaction on demand. Such interaction was expected to assist the reduction and the isolation of synthons. In this work we describe the preparation of the corresponding thorium complexes, and a study on the reduction chemistry of this system affording the third case of tri-valent synthon and indirectly landing support to its ability to embark in hydrogen abstraction reactions.

Experimental Part

All manipulations were performed under nitrogen atmosphere with rigorous exclusion of oxygen and water using standard Schlenk and glove-box techniques. Hexane, toluene and THF solvents were purified by passing through Al_2O_3 filled columns and deoxygenated prior to use by several vacuum/nitrogen purges. DME was dried for 12 hours over $LiAlH_4$ and distilled under N_2 prior to utilization. Benzene-d^6 and THF-d^8 were obtained from "C/D/N isotopes", dried over freshly activated molecular sieves (4A) for 10 days and distilled under N_2 atmosphere. Triethylaluminum solution in hexane was purchased from Aldrich and used as received. The ligand {1,3-bis-[1□- (pyrrol-2-yl)-1,1□-dimethyl]methyl}benzene was prepared according to the literature procedure.[12] Complex $ThCl_4(DME)_2$ was prepared according to literature procedure.[3m] NMR spectra were recorded at 293K on Varian Inova 500 MHz spectrometer. Chemical shifts were referenced to internal solvent resonances and reported in parts per million relative to TMS. Elemental analyses were performed on PerkinElmer 2400 CHN analyzer. Data for X-ray single crystal structure determination were collected with a Brucker diffractometer equipped with 1K SMART CCD area detector.

Preparation of $\{1,3\text{-}[(2\text{-}C_4H_3N)(CH_3)_2C]_2C_6H_4\}Li_2\cdot(Et_2O)_{0.5}$ (6.0)

A solution of $1,3\text{-}[(2\text{-}C_4H_3N)(CH_3)_2C]C_6H_4$ (5.00 g, 17.1 mmol) in Et_2O (50 mL) was treated dropwise over 20 minutes with a solution of MeLi in Et_2O (1.6 M, 23 mL, 36.8 mmol). The vigorous gas evolution terminated within 5 min from the end of the addition. Stirring was continued at room temperature for additional 3 hours. After that time the volume of the reaction mixture was reduced *in* *vacuo* to about 10 mL and the resulting solution was layered with hexanes (30 mL). The colorless product was obtained as microcrystalline material which was separated by filtration, washed with hexanes (5 mL) and dried *in vacuo* for 6 hours (5.19 g, 15.2 mmol, 89%) of. Elem. Anal. for $Li_2C_{22}H_{27}N_2O_{0.5}$ found (calculated): C 77.34 (77.41), H 7.87 (7.97), N 8.19 (8.21). ^{1}H-NMR (500 MHz, THF-d^8, 20°C) δ: 7.92 (1H, Ar**H**), 7.42 (3H, Ar**H**), 7.37 (2H, Pyrrole-**H**), 6.79 (2H, Pyrrole-**H**), 6.36 (2H, Pyrrole-**H**), 3.45 (2H, $(CH_3CH_2)_2O$), 1.88 (12H, $-CH_3$), 1.23 (3H, $(CH_3CH_2)_2O$).

Preparation of $[\eta^6\text{-}\{1,3\text{-}[(2\text{-}C_4H_3N)(CH_3)_2C]_2C_6H_4\}ThCl_3][Li(DME)_3]$ (6.1)

A solution of the ligand di-lithium salt (0.45 g, 1.3 mmol) in DME (20 mL) was added to a suspension of $ThCl_4(DME)_2$ (0.37 g, 0.7 mmol) in DME (20 mL). The reaction mixture was stirred for 6 hours at room temperature and centrifuged to eliminate some insoluble material. The supernatant was concentrated to about 7 mL *in vacuo* and layered with hexanes (20 mL) and allowed to stand at room temperature for two days. Large pale-yellow prisms of **6.1** separated from the solution which were collected and dried under N_2 atmosphere (0.52 g, 0.6 mmol, 87%). Elem. Anal. for $ThLiC_{32}H_{52}Cl_3N_2O_6$ found (calculated): C 42.34 (42.42), H 5.67 (5.78), N 3.05 (3.09). ^{1}H-NMR (500 MHz, THF-d^8, 20°C) δ: 8.05 (2H, Ar**H**), 7.87 (1H, Ar**H**), 7.77 (1H, Ar**H**), 7.17 (2H, Pyrrole-**H**), 5.72 (2H, Pyrrole-**H**), 5.57 (2H, Pyrrole-**H**), 3.39 (18H, DME, $-O-CH_3$), 3.22 (12H, DME, $-CH_2-O$), 1.65 (12H, $-CH_3$).

Preparation of $\{[\{1,3\text{-}[(\eta^5\text{-}2\text{-}C_4H_3N)(CH_3)_2C]_2C_6H_4\}Th(\mu\text{-}Cl\text{-}AlEt_2)_2](\mu\text{-}Cl)_2[\{1,3\text{-}[(\eta^5\text{-}2\text{-}C_4H_3N)(CH_3)_2C]C_6H_4\}Th](\mu\text{-}AlEt_2)Cl]\}\cdot(C_7H_8)_{0.5}$ (6.2a) and $\{[\{1,3\text{-}[(\eta^5\text{-}2\text{-}C_4H_3N)(CH_3)_2C]_2C_6H_4\}ThCl(\mu\text{-}Cl)_2[Li(DME)]_2$ (6.2b)

A solution of $AlEt_3$ (1.1 mL, 1.0 M, 1.1 mmol) in toluene was added dropwise to a suspension of complex **6.1** (0.20 g, 0.2 mmol) in the same solvent (10 mL). Stirring was continued at room temperature for additional 6 hours and the insoluble material was separated by centrifugation. The volume of the surnatant was reduced to about 5 mL and allowed to stand at -37°C for 3 days. Lemon yellow prisms of **6.2a** separated which were filtered, washed with cold (-37°C) hexane (5 mL) and dried under N_2 atmosphere (0.094 g, 0.06 mmol, 62%). Elem. Anal. for $Th_2Al_3C_{55.50}H_{78}Cl_5N_4$ (**6.2a**) found (calculated): C 43.69 (43.75), H 5.01 (5.16), N 3.65 (3.68). ^{1}H-NMR (500 MHz, THF-d^8, 20°C) δ: 7.31 (1H, Ar-**H**), 6.51 (2H, Ar-**H**), 6.30 (2H, Pyrrole-**H**), 5.46 (2H, Pyrrole-**H**), 5.26 (2H, Pyrrole-**H**), 1.35 (12H, -CH_3), 1.01 (4H, Al-CH_2-CH_3), 0.14 (6H, Al-CH_2-CH_3).

The solid material obtained with the previous centrifugation was dissolved in DME (10 mL), filtered and the resulting solution layered with hexane (20 mL). After 3 days small colorless prisms of **6.2b** separated from the mother liquor, which were filtered, washed with hexane (5 mL) and dried under N_2 atmosphere (0.031 g, 0.04 mmol, 17%). Elem. Anal. for $ThLi_2C_{28}H_{42}Cl_3N_2O_4$ (**6.2b**) found (calculated): C 40.79 (40.87), H 5.07 (5.14), N 3.35 (3.40).

Preparation of $[\{\eta^5\text{-}1,3\text{-}[(\eta^5\text{-}2\text{-}C_4H_3N)(CH_3)_2C]_2C_6H_4\}ThK(\mu\text{-}Cl)_3][Li(DME)_3]$ (6.3)

A solution of **6.1** (0.35 g, 0.3 mmol) in THF (15 mL) was stirred with metallic potassium (0.03 g, 0.7 mmol) at room temperature for 5 days. When potassium was completely consumed, the resulting dark purple-red solution was centrifuged to eliminate a small amount of insoluble materials. The volume of the liquid was reduced to about 5 mL and layered with hexane (15 mL). Dark purple prisms of **6.3** formed which were washed with hexane (5 mL) and dried under N_2 atmosphere (0.20 g, 0.2 mmol, 67%). Elem. Anal. for $ThKLiC_{32}H_{52}Cl_3N_2O_6$ found (calculated): C 40.59 (40.66), H 5.42 (5.55), N 2.83 (2.92).

Preparation of $\{\eta^6\text{-}1,3\text{-}[(2\text{-}C_4H_3N)(CH_3)_2C]_2C_6H_4\}Th\{\mu\text{-}\eta^5\text{-}1,3\text{-}[(\eta^5\text{-}2\text{-}C_4H_3N)(CH_3)_2C]_2C_6H_5\}K(DME)_2$ (6.4)

A suspension of **6.1** (0.62 g, 0.7 mmol) in DME (15 mL) was treated with a freshly prepared solution of K / Naphthalenide (0.06 g, 1.5 mmol of K with 0.19 g, 1.5 mmol of naphthalene) in the same solvent (10 mL). An immediate color change to dark red-brown was observed upon mixing and stirring was continued for additional four hours at room temperature. Some insoluble material was separated by centrifugation and the volume of the solution was reduced to about 5 mL by evaporation *in vacuo*. A slow discoloration of the solution was observed upon standing for three days at room temperature, and which was accompanied by the appearance of pale-pink prisms of **6.4**. The crystalline mass was filtered, washed with hexane (5 mL) and dried under N_2 (0.31 g, 0.30 mmol, 42%). Elem. Anal. for $ThKC_{48}H_{65}N_4O_4$ found (calculated): C 55.72 (55.80), H 6.24 (6.34), N 5.43 (5.42). ^{1}H-NMR (500 MHz, THF-d^8, 20°C) δ: 7.45 (1H, Ar'**H**), 7.33 (2H, Ar'**H**), 7.31 (1H, -**CH**-$^{(-)}$), 7.23 (1H, Ar'**H**), 7.20 (2H, =**CH**-), 6.79 (2H, Pyrrole'-**H**), 6.73 (2H, K-Pyrrole-**H**), 6.48 (2H, Pyrrole'-**H**), 6.40 (2H, Pyrrole'-**H**), 6.23 (2H, K-Pyrrole-**H**), 5.72 (2H, K-Pyrrole-**H**), 3.77 (1H, -CH_2-), 3.34 (12H, DME, O-CH_3), 3.54 (8H, DME, -CH_2-O), 2.60 (1H, -CH_2-), 1.80 (12H, -CH_3), 0.43 (12H, -CH_3).

Preparation of $[\{\eta^6\text{-}1,3\text{-}[(\eta^5\text{-}2\text{-}C_4H_3N)(CH_3)_2C]_2C_6H_4\}Th(\mu\text{-}\eta^2\text{-}PhNNPh)(\mu\text{-}Cl)(Cl)Li(DME)][Li(DME)_3]$ (6.5)

A suspension of **6.1** (0.38 g, 0.4 mmol) in DME (10 mL) was treated with a freshly prepared solution of Li/Naphthalene (0.006 g, 0.86 mmol Li and 0.108 g, 0.84 mmol naphthalene) in the same solvent (10 mL). An immediate color change from pale green to dark blue-red was observed upon mixing and stirring was continued at room temperature for additional three hours. A solution of diazobenzene (0.08 g, 0.4 mmol) in DME (5 mL) was added dropwise to the reaction mixture causing a further color change to intense orange. Stirring was continued for one additional hour after which the insoluble materials were separated by centrifugation. The volume was reduced to about 6 mL *in vacuo* and the solution layered with hexanes (15 mL). After 3 days brown-orange prisms of **6.5** were formed. The crystalline mass was filtered, washed with hexane (5 mL) of and dried under N_2 (0.29 g, 0.25 mmol, 60%). Elem. Anal. for $ThLi_2C_{48}H_{72}N_4O_8Cl_2$ found (calculated): C 50.13 (50.14), H 6.24 (6.31), N 4.81 (4.87). ^{1}H-NMR (500 MHz, THF-d^8, 20°C) δ: 7.50 (1H, Ar'**H**), 7.36 (1H, Ar**H**), 7.29 (2H, Ar**H**), 7.24 (2H, Ar'**H**), 7.16 (2H, Ar'**H**), 7.10 (2H, Ar'**H**), 6.99 (2H, Ar'**H**), 6.84 (1H, Ar'**H**), 6.48 (1H, Ar**H**), 6.76 (2H, Pyrrole-**H**), 6.27 (2H, Pyrrole-**H**), 6.22 (2H, Pyrrole-**H**), 3.48 (24H, DME, O-$\mathbf{CH_3}$), 3.30 (16H, DME, -$\mathbf{CH_2}$-O), 1.74 (12H, -$\mathbf{CH_3}$).

Computational Details

All DFT calculations were performed using the Gaussian 03 package[13] using the PBE[14] exchange-correlation functional and the SDD[15] effective-core potential (ECP) basis sets. Tight SCF convergence criteria were used for all calculations. The converged wave functions were tested to confirm that they correspond to the ground-state surface. All calculations for the analysis of the electronic structure, including Mulliken population analysis[16] and the calculation of Mayer 2- and 3-center bond order indices[17a,b] atomic valences[17a] and populations of fragment orbitals[17c] were performed using the AOMix software package.[18]

X-ray crystallography

For all the compounds, the results presented are the best of three data collection trials. The crystals were mounted on thin glass fibers using paraffin oil and cooled to the data collection temperature. Data were collected on a Bruker-AXS SMART 1k CCD diffractometer. Data for the compounds **6.1, 6.2a, 6.2b**, **6.3** and **6.5** were collected with a sequence of 0.3° ω scans at 0, 120, and 240° in φ. To obtain acceptable redundancy data for compound **6.4** the sequence of 0.3° ω scans at 0, 90, 180, and 270° in φ was implied. Initial unit cell parameters were determined from 60 data frames collected at the different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.[19] Systematic absences in the diffraction data-set and unit-cell parameters were consistent with monoclinic **P**$2_1/n$ for **6.1,** monoclinic **P**$2_1/c$ for **6.5,** orthorhombic **P***bca* for **6.2a**, orthorhombic **P***bcn* for **6.2b**, orthorhombic **P***nma* for **6.3**, triclinic **P**$\bar{1}$ for **6.4**. Solutions in centrosymmetric space groups for all of the compounds yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed with difference Fourier synthesis, and refined with full-matrix least-squares procedures based on F^2. In structures of compounds **6.2b** Th metal center is located on *2* rotation axes element of symmetry. In the structure of **6.3** molecule of the complexe resides on a mirror planes symmetry element. In structures of all the other compounds molecules of Th complexes are located in general positions. Structure of complex **6.3** represent a polymeric chain with monomers connected through bridging -Cl group coordination to the K metal center of the next monomeric unit. In this structure each monomeric unit is symmetry related to the next one through a *n* sliding plane symmetry operator. Carbon atoms of co-crystallized toluene solvent molecule in **6.2** as well as carbon atoms of DME solvent molecules coordinated to Li cations in the structure of **6.5** were refined isotropicaly due to partial occupancy coupled with significant thermal motion disorder and in order to maintain an optimal data to parameters ratio. In all the structures, all non-hydrogen atoms, with the exceptions mentioned above, were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions. All scattering factors are contained in several versions of the SHELXTL program library version 6.12.[20] Crystallographic data and selected bond distances and angles for all the structures are reported in Tables 6.1 and 6.2 respectively.

Crystal Structure Descriptions

1. The crystal structure of **6.1** consists of an anionic Th-containing unit and an unconnected Li counter-cation solvated by three molecules of DME. The anionic fragment contains a Th metal center in a rather regular octahedral environment. One axial position of coordination polyhedron is occupied by the centroid of the ligand phenyl ring engaged in a η^6-bonding interaction with the Th atom [Th(1)–centroid(1) = 2.701(8) Å]. The second axial position contains one chlorine atom [Th(1)–Cl(1) = 2.661(2) Å, centroid(1)–Th(1)–Cl(1) = 176.54(17)] (Figure 6.1). Two other chlorine atoms are located in two equatorial positions of the octahedron [Th(1)–Cl(2) = 2.698(2) Å, Th(1)–Cl(3) = 2.711(2) Å, Cl(2)–Th(1)–Cl(1) = 86.21(7) , Cl(3)–Th(1)–Cl(1) = 86.85(7) , Cl(2)–Th(1)–Cl(3) = 91.53(8)]. Finally, the two remaining equatorial positions hold two nitrogen donor atoms of the two pyrrolyde moieties of the ligand system [Th(1)–N(1) = 2.436(7) Å, Th(1)–N(2) = 2.420(6) Å, N(1)–Th(1)–Cl(1) = 90.81(16) , N(2)–Th(1)–Cl(1) = 90.80(15) , N(1)–Th(1)–N(2) = 88.8(2) , N(1)–Th(1)–Cl(2) = 90.39(16)].

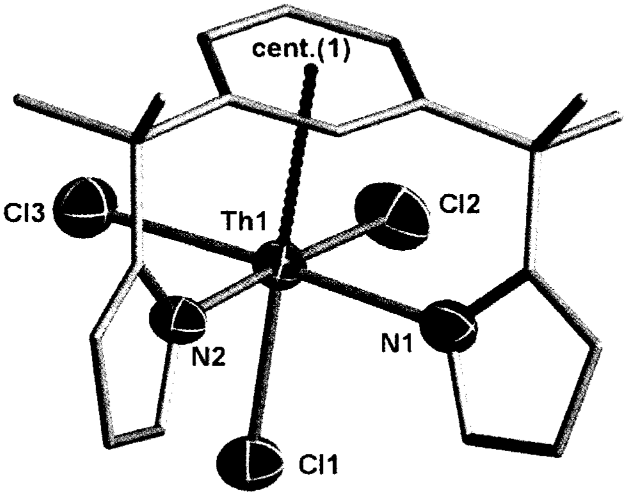


Figure 6.1. Partial thermal ellipsoid diagrams of **6.1** with thermal ellipsoid drawn at 50% probability level. Li(DME)$_3$ cation, hydrogen atoms and thermal ellipsoids of carbon atoms have been omitted for clarity.

The Li cation is in an octahedral environment, defined by the six oxygen atoms of three chelating DME molecules [Li(1)–O(1) = 2.162(16) Å, Li(1)–O(2) = 2.079(17) Å, Li(1)–O(3) = 2.120(17) Å, Li(1)–O(4) = 2.227(16) Å, Li(1)–O(5) = 2.116(17) Å, Li(1)–O(6) = 2.134(17) Å, O(1)–Li(1)–O(4) = 166.4(8) , O(2)–Li(1)–O(4) = 91.7(7) , O(1)–Li(1)–O(3) = 94.8(7) , O(1)–Li(1)–O(5) = 87.9(6) , O(1)–Li(1)–O(6) = 104.4(7) , O(2)–Li(1)–O(6) = 92.7(7) , O(3)–Li(1)–O(5) = 95.0(7)].

2. The structure of **6.2a** consists of two Th-containing units bridged by two chlorine atoms. The first contains the Th metal center in an octahedral environment. One axial position is occupied by a deprotonated carbon atom of the central phenyl ring of the ligand system [Th(1)–C(13) = 2.588(17) Å]. The second axial position is held by one terminal chlorine atom [Th(1)–Cl(3) = 2.751(4) Å, C(13)–Th(1)–Cl(3) = 176.9(4)]. Two additional chlorine atoms are situated in the two equatorial positions [Th(1)–Cl(1) = 2.836(4) Å, Th(1)–Cl(2) = 2.834(4) Å, Cl(1)–Th(1)–Cl(3) = 87.11(13), Cl(2)–Th(1)–

Cl(3) = 85.21(12), Cl(1)–Th(1)–Cl(2) = 68.96(11)] providing the bridging interaction with the second Th containing fragment [Th(1)–Cl(1)–Th(2) = 112.23(12) , Th(1)–Cl(2)–Th(2) = 112.95(12)] (Figure 2). The two remaining equatorial positions around the first Th atom hold the centroids of the two pyrrolide rings of the ligand system with each ring being η^5-coordinated to Th [Th(1)–centroid(1) = 2.636(14) Å, Th(1)–centroid(2) = 2.605(14) Å, centroid(1)–Th(1)–centroid(2) = 110.7(5) , centroid(1)–Th(1)–Cl(3) = 99.0(5) , centroid(2)–Th(1)–Cl(3) = 96.7(5) , centroid(1)–Th(1)–Cl(1) = 156.5(4)]. The nitrogen atoms of these two pyrrolide rings are each σ-bonded to the Al atom of one Et_2Al fragment [Al(1)–N(1) = 2.005(17) Å, Al(1)–N(2) = 2.003(14) Å, N(1)–Al(1)–N(2) =], [Al(1)–C(41) = Å, Al(1)–C(43) = Å, C(41)–Al(1)–N(1) = , C(43)–Al(1)–N(2) = 95.7(5)].

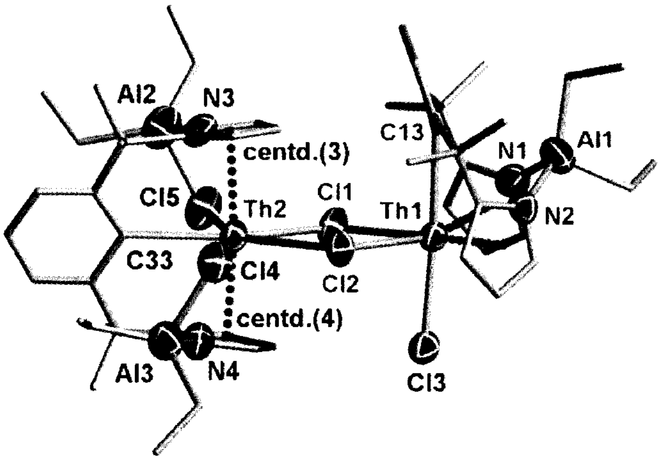


Figure 6.2. Partial thermal ellipsoid diagrams of **6.2a** with thermal ellipsoid drawn at 50% probability level. Toluene solvent molecule as well as hydrogen atoms and thermal ellipsoids of carbon atoms have been omitted for clarity.

The second Th atom of the second unit resides in the center of a pentagonal bi-pyramid, sharing two of the equatorial chlorine atoms with the first thorium containing unit (Figure 6.2) [Th(2)–Cl(1) = 2.964(4) Å, Th(2)–Cl(2) = 2.943(4) Å]. Two other equatorial positions contain other two chlorines [Th(2)–Cl(4) = 2.965(4) Å, Th(2)–Cl(5) = 2.954(5) Å, Cl(4)–Th(2)–Cl(5) = 156.9(5) , Cl(1)–Th(2)–Cl(5) = 134.5(4) , Cl(2)–Th(2)–Cl(4) = 134.3(5)], which are, in turn, involved into bridging interaction with a second and third Al metal centers [Th(2)–Cl(4)–Al(2) = 92.6(8) , Th(2)–Cl(5)–Al(3) = 94.5(7)]. The fifth equatorial position contains a σ-bonded carbon atom of the deprotonated central phenyl ring of the second ligand system [Th(2)–C(33) = 2.654(14) Å, C(33)–Th(2)–Cl(4) = 78.89(5) , C(33)–Th(2)–Cl(5) = 78.0(5)]. Both axial positions of the bipyramid are occupied by two centroids of the two pyrrolide rings of the ligand system [Th(2)–centroid(3) = 2.607(15) Å, Th(2)–centroid(4) = 2.595(14) Å, centroid(3)–Th(2)–centroid(4) = 174.1(5) , centroid(3)–Th(2)–C(33) = 87.2(5) , centroid(4)–Th(2)–C(33) = 87.0(5) , centroid(3)–Th(2)–Cl(1) = 92.2(5)], which are coordinated to the Th metal center through a η^5-interaction. Each nitrogen atom of the pyrrolide ring is σ-bonded to a Et_2Al metal center [N(3)–Al(3) = 1.985(15) Å, N(4)–Al(2) = 1.969(15) Å] in turn bridging one equatorial chlorine [Al(2)–Cl(4) = 2.290(18) Å, Al(3)–Cl(5) = 2.290(18) Å, N(3)–Al(3)–Cl(5) = 89.3(8) , N(4)–Al(2)–Cl(4) = 90.1(8)].

In complex **6.2b**, the Th center resides in the center of an octahedral coordination polyhedron. Overall the molecule of complex **6.2b** posses a C_2 symmetry with the 180 rotation axis along the Cl(1)–Th(1)–C(10) vector. The two axial positions are occupied by a chlorine atom [Th(1)–Cl(1) = 2.779(2) Å] and the σ-bonded carbon atom [Th(1)–C(10) = 2.612(8) Å, Cl(1)–Th(1)–C(10) = 180.0] of the central phenyl ring of the ligand system. The equatorial plane is determined by another chlorine atom [Th(1)–Cl(2) = 2.847(2) Å, Cl(2)–Th(1)–Cl(1) = 92.53(4)] as well as by its symmetry generated equivalent. These particular chlorine atoms are also involved in bridging interaction with the two lithium counteraction forming [Th(1)–Cl(2)–Li(1) = 88.7(3)]. The last two equatorial positions contain the centroids of the two η^5-bonded pyrrolide rings [Th(1)–centroid(1) = 2.576(6) Å, centroid(1)–Th(1)–Cl(2) = 89.67(15) , centroid(1)–Th(1)–Cl(1) = 92.03(15)] (Figure 6.3). Each pyrrolide ring is also σ-bonded to one Li atom by using the deprotonate nitrogen [N(1)–Li(1) = 1.994(13) Å]. The bridging chlorine [Li(1)–Cl(2) = 2.388(12) Å, Cl(2)–Li(1)–N(1) = 89.2(5)] and two oxygen donor atoms of

DME solvent molecule [Li(1)–O(1) = 1.986(13) Å, Li(1)–O(2) = 1.982(14) Å, O(1)–Li(1)–Cl(2) = 117.3(6) , O(1)–Li(1)–N(1) = 109.1(6)] complete the coordination environment of each lithium atom.

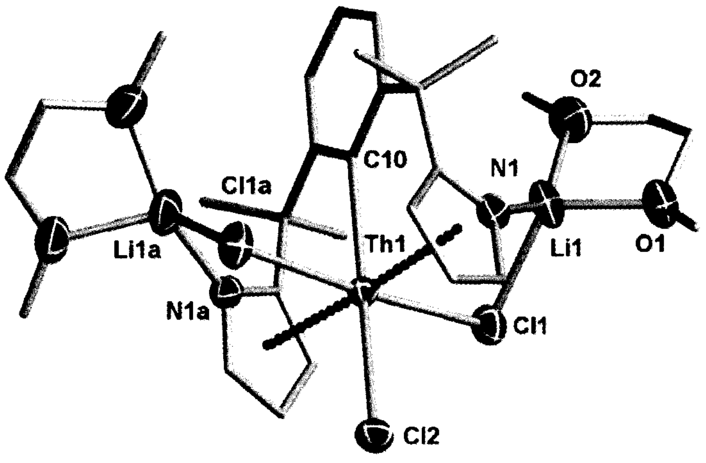


Figure 6.3. Partial thermal ellipsoid diagrams of **6.2b** with thermal ellipsoid drawn at 50% probability level. Hydrogen atoms and thermal ellipsoids of carbon atoms have been omitted for clarity.

3. The structure of **6.3** displays an infinite polymeric chain composed by anionic chlorine- and potassium-bridged Th containing monomers. The negative charge of each anionic Th/K unit is counterbalanced by one unconnected Li cation solvated by three molecules of DME. Each monomeric unit contains the Th metal in the center of an octahedral coordination polyhedron generated by an internal mirror plane of symmetry. One axial position of the coordination polyhedron is occupied by a centroid of five atoms of the former phenyl ring and which appears to be now become a [(C(8)=C(10)–C(11)–C(10A)=C(8A)] cyclohexadienide unit [Th(1)–centroid(1) = 2.463(7) Å]. As a result, the ring is severely distorted with one of the six carbon atom pointing away from the plane defined by the other five carbons. The ring C-C bond distances also indicate that the extruded carbon atom forms rather long bonds with the neighboring C atoms indicative of single bond character [C(8)–C(9) = 1.526(10) Å]. The second axial position contains one chlorine atom [Th(1)–Cl(1) = 2.764(2) Å, centroid(1)–Th(1)–Cl(1) = 85.41(14)]. Two other symmetry related chlorine atoms determine two- of the four equatorial positions of the coordination octahedron [Th(1)–Cl(2) = 2.735(2) Å, Cl(2)–Th(1)–Cl(2A) = 86.39(9)]. The potassium cation caps the triangular face of the octahedron as defined by the three facially oriented chlorine atoms [Th(1)–Cl(1)–K(1`) = 88.78(15), Th(1)–Cl(2)–K(1`) = 87.91(10)] (Figure 6.4).

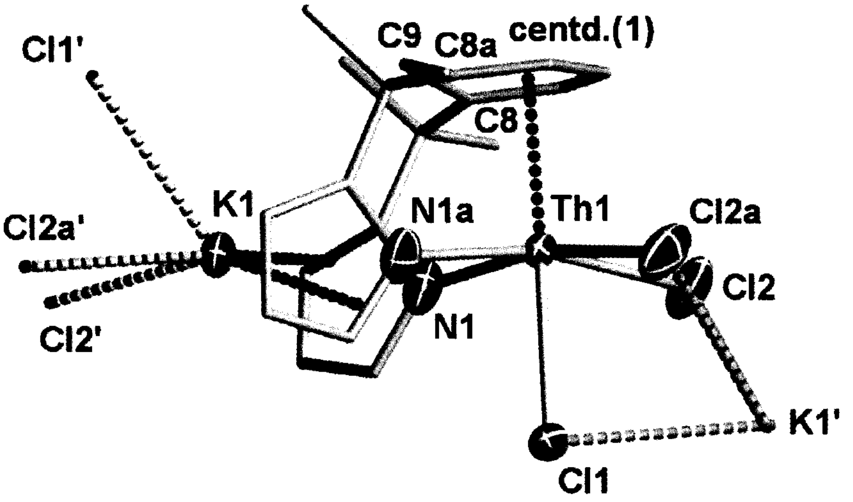


Figure 6.4. Partial thermal ellipsoid diagrams of **6.3** with thermal ellipsoid drawn at 50% probability level. Li(DME)$_3$ counter-cation, hydrogen atoms and thermal ellipsoids of carbon atoms have been omitted for clarity.

The two remaining equatorial positions are occupied by the σ-bonded nitrogen atoms of two symmetry related pyrrolide moieties [Th(1)–N(1) = 2.474(5) Å, N(1)–Th(1)–N(1A) = 83.0(2) , N(1)–Th(1)–Cl(1) = 85.41(14), N(1)–Th(1)–Cl(2) = 93.85(13)]. The pyrrolide rings are in turn η^5-binded to [K(1)–centroid(1) = 2.911(8) Å, centroid(1)–K(1)–centroid(1A) = 103.4(3)] and whose bridging interaction with chlorine of a second until build the polymeric array [K(1)–Cl(1`) = 3.120(3) Å, K(1)–Cl(2`) = 3.187(2) Å, Cl(1')–K(1)–Cl(2') = 69.5(4) , Cl(2')–K(1)–Cl(2A') = 71.9(3). The unconnected lithium counter-cation is octahedrally coordinated by six oxygen donor atoms of three DME solvent molecules [Li(1)–O(1) = 2.26(3) Å, Li(1)–O(2) = 2.22(3) Å, Li(1)–O(3) = 2.24(4) Å, Li(1)–O(4) = 2.05(3) Å, Li(1)–O(5) = 2.15(3) Å, Li(1)–O(6) = 2.27(3) Å].

4. Complex **6.4** shows the Th metal center in an octahedral coordination environment defined by two di-pyrrolide ligands. One ligand adopted a rather regular bonding mode, with the two nitrogen atoms of the two pyrrolide rings being σ-coordinated to the Th center in one equatorial and one axial position

[Th(1)–N(3) = 2.435(5) Å, Th(1)–N(4) = 2.442(5) Å, N(3)–Th(1)–N(4) = 82.84(16)]. A second equatorial position is occupied by the centroid of the central phenyl ring of the same ligand, which is π-bonded to the metal center in a regular η^6-fashion [Th(1)–centroid(2) = 3.481(7) Å, centroid(2)–Th(1)–N(4) = 74.97(18) , centroid(2)–Th(1)–N(3) = 77.16(17)]. The second ligand unit displays somewhat similar coordination mode. Two nitrogen atoms of the two pyrrolide rings occupy one equatorial and one axial positions respectively [Th(1)–N(1) = 2.464(5) Å, Th(1)–N(2) = 2.458(5) Å, N(1)–Th(1)–centroid(2) = 92.11(17) , N(2)–Th(1)–N(4) = 104.81(16) , N(1)–Th(1)–N(3) = 83.56(17) , N(2)–Th(1)–N(3) = 95.89(16)]. The central ring of this second ligand adopted the η^5-bonding mode, with the centroid resting in the second axial position of octahedron [Th(1)–centroid(1) = 2.497(7) Å, centroid(1)–Th(1)–N(3) = 170.88(17) , centroid(1)–Th(1)–N(2) = 92.81(17) , centroid(1)–Th(1)–N(4) = 97.61(17)] (Figure 5). The uncoordinated C atom is extruded from the plane defined by the other five atoms and forms bonds with the neighboring carbon atom in the normal range for single bonds [C(13)–C(8) = 1.511(9) Å, C(13)–C(12) = 1.500(9) Å].

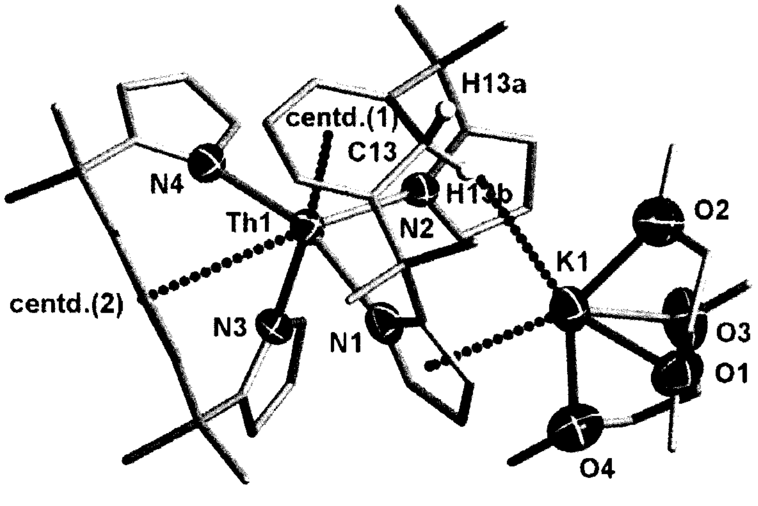


Figure 6.5. Partial thermal ellipsoid diagrams of **6.4** with thermal ellipsoid drawn at 50% probability level. All hydrogen atoms, except H13a and H13b, and thermal ellipsoids of carbon atoms have been omitted for clarity.

The centroids of the two pyrrolide rings of this particular ligand occupy two equatorial positions of an octahedrally coordinated potassium [K(1)–centroid(3) = 3.053(6) Å, K(1)–centroid(4) = 3.284(6) Å, centroid(3)–K(1)–centroid(4) = 93.66(18)]. The other two equatorial and two axial positions of potassium coordination environment are defined by four coordinated oxygen donor atoms of two DME solvent molecules [K(1)–O(1) = 2.803(5) Å, K(1)–O(2) = 2.783(6) Å, K(1)–O(3) = 2.785(6) Å, K(1)–O(4) = 2.934(5) Å, O(2)–K(1)–O(4) = 142.49(18) , O(1)–K(1)–O(3) = 80.52(18)].

5. The structure of **6.5** is formed by one anionic fragment containing both Th and Li metals, and one unconnected Li counter cation solvated by three solvent DME molecules. The Th metal center is located in the center of a pentagonal bipyramid. One axial position is occupied by a chloride [Th(1)–Cl(1) = 2.724(2) Å], which is also bridging the Li cation [Th(1)–Cl(1)–Li(1) = 81.0(4)]. A second chlorine atom is terminally bonded and resides in one of the equatorial positions [Th(1)–Cl(2) = 2.790(2) Å, Cl(1)–Th(1)–Cl(2) = 86.28(7)].

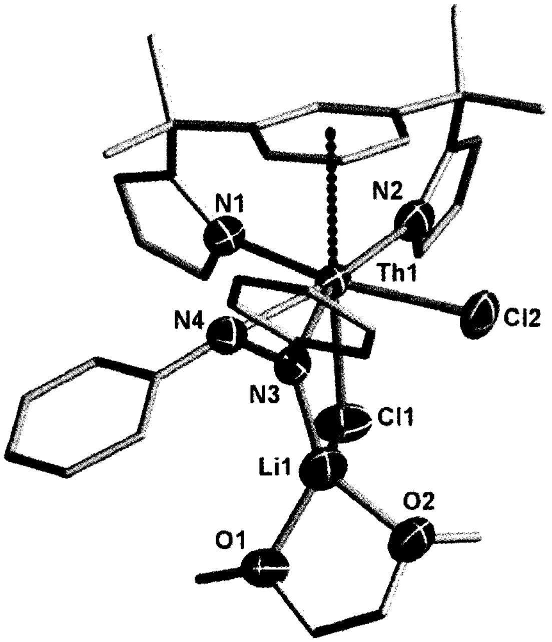


Figure 6.6. Partial thermal ellipsoid diagrams of **6.5** with thermal ellipsoid drawn at 50% probability level. The Li(DME)$_3$ counter-cation, hydrogen atoms and thermal ellipsoids of carbon atoms have been omitted for clarity.

Two other equatorial positions are occupied by two σ-bonded nitrogen atoms of two pyrrolide rings of the ligand [Th(1)–N(1) = 2.499(6) Å, Th(1)–N(2) = 2.533(7) Å, N(1)–Th(1)–N(2) = 81.16(19) , N(1)–Th(1)–Cl(1) = 93.06(14) , N(2)–Th(1)–Cl(2) = 82.58(14)] and whose central phenyl ring is η^6-bonded with the centroid occupying the second axial position [Th(1)–centroid(1) = 2.732(7) Å, centroid(1)–Th(1)–Cl(1) = 174.52(15) , centroid(1)–Th(1)–Cl(2) = 93.54(15)]. The last two equatorial positions contain two nitrogen atoms of a π-bonded diazobenzene unit [Th(1)–N(3) = 2.465(6) Å, Th(1)–N(4) = 2.310(6) Å, N(3)–Th(1)–Cl(1) = 81.44(14) , N(4)–Th(1)–Cl(1) = 84.82(16) , N(3)–Th(1)–N(1) = 115.25(19) , N(4)–Th(1)–Cl(2) = 116.28(15)] and whose N-N distance [N(3)–N(4) = 1.464(8) Å] is as expected for a N-N single bond (Figure 6.6). Of the two azobenzene nitrogen atoms, one bridges the Li cation [Th(1)–N(3)–Li(1) = 97.6(5) , Li(1)–N(3) = 2.012(16) Å] while the second forms with thorium and the aromatic ring an strange linear array [Th(1)–N(4)–C(27) = 153.9(5)] with the coordination geometry of the N atom being almost T-shape [(C27)–N(4)–N(3) = 117.2(5) ,Th(1)–N(4)–N(3) = 78.1(3)]. Two oxygen atom of one coordinated DME molecule occupy the last two tetrahedral sites of the lithium atom [Li(1)–O(1) = 1.976(16) Å, Li(1)–O(2) = 1.988(15) Å, O(1)–Li(1)–N(3) = 132.2(8) , O(2)–Li(1)–Cl(1) = 108.7(7)]. The unconnected Li counter-cation is instead octahedrally coordinated by three disordered molecules of DME [Li(2)–O(3) = 2.208(13) Å, Li(2)–O(4) = 2.113(18) Å, Li(2)–O(5) = 2.50(3) Å, Li(2)–O(6) = 2.066(16) Å, Li(2)–O(7) = 2.02(3) Å, Li(2)–O(8) = 2.162(14) Å].

Table 6.1. Crystal data and data collection parameters of complexes **6.1**, **6.2a** and **6.2b**

	6.1	**6.2a**	**6.2b**
Formula	$ThLiC_{32}H_{52}Cl_3N_2O_6$	$Th_2Al_3C_{55.50}H_{78}Cl_5N_4$	$ThLi_2C_{28}H_{42}Cl_3N_2O_4$
FW	906.09	1523.49	822.91
Crystal system,	Monoclinic	Orthorhombic	Orthorhombic
Space group	**P***$2_1/n$*	**P***bca*	**P***bcn*
a, Å	20.172(3)	17.726(10)	17.3301(15)
b, Å	8.5670(12)	25.649(14)	15.0454(13)
c, Å	23.886(3)	28.124(15)	12.5834(11)
α, deg	90	90	90
β, deg	112.636(2)	90	90
γ, deg	90	90	90
Volume, $Å^3$	3809.8(9)	12786(12)	3281.0(5)
Z	4	8	4
ρ_{calc} g/cm3	1.580	1.583	1.666
μ□ mm^{-1}	4.165	4.933	4.822
F (000)	1800	5944	1612
T range (deg)	1.85 - 24.74	1.57 - 24.62	2.35 - 26.41
Limiting indices (*h, k, l*)	±23, ±10, ±28	±20, ±28, ±27	±21, ±18, ±15
Reflections collected / unique	27375 / 6443	58792 / 10651	26350 / 3333
R_{int}	0.0425	0.0877	0.0437
GOF	1.061	1.043	1.052
R1 (obs / all)	0.0390 / 0.0549	0.0643/ 0.1156	0.0305 / 0.0561
wR2 (obs / all)	0.1029 / 0.1117	0.1611 / 0.1990	0.0770 / 0.0907

Table 6.1 (contd.). Crystal data and data collection parameters of complexes **6.3**, **6.4** and **6.5**

	6.3	**6.4**	**6.5**
Formula	$ThKLiC_{32}H_{52}Cl_3N_2O_6$	$ThKC_{48}H_{65}N_4O_4$	$ThLi_2C_{48}H_{72}Cl_2N_4O_8$
FW	945.19	1033.18	1139.84
Crystal system,	Orthorhombic	Triclinic	Monoclinic
Space group	P*nma*	$P\bar{1}$	P*2₁/c*
a, Å	16.2998(8)	11.2955(10)	18.323(4)
b, Å	14.5464(8)	12.9840(11)	13.882(3)
c, Å	16.3612(9)	18.0443(15)	22.994(5)
α, deg	90	79.8520(10)	90
β, deg	90	84.5960(10)	112.910(3)
γ, deg	90	65.3730(10)	90
Volume, Å^3	3879.3(4)	2367.4(4)	5387.4(19)
Z	4	2	4
ρ_{calc} g/cm3	1.618	1.449	1.418
μ□ mm^{-1}	4.199	3.282	2.918
F (000)	1876	1044	2328
T range (deg)	1.87 - 30.55	1.15 - 24.75	1.75 - 24.69
Limiting indices (*h, k, l*)	±23, ±20, ±23	±13, ±15, ±21	±21, ±16, ±26
Reflections collected / unique	111954 / 6106	23720 / 8037	39355 / 9095
R_{int}	0.0737	0.0414	0.0550
GOF	1.033	1.050	1.049
R1 (obs / all)	0.0505 / 0.0801	0.0368 / 0.0528	0.0439 / 0.0694
wR2 (obs / all)	0.1098 / 0.1255	0.0873 / 0.0956	0.1072 / 0.1205

Table 6.2. Selected bonds distances (Å) and angles (deg) for complexes **6.1**, **6.2a** and **6.2b**

6.1	**6.2a**	**6.2b**
Th(1)-N(2) = 2.420(6) Th(1)-N(1) = 2.436(7) Th(1)-Cl(1) = 2.661(2) Th(1)-Cl(2) = 2.698(2) Th(1)-Cl(3) = 2.711(2) N(2)-Th(1)-N(1) = 88.8(2) N(2)-Th(1)-Cl(1) = 90.80(15) N(1)-Th(1)-Cl(1) = 90.81(16) N(2)-Th(1)-Cl(2) = 176.90(15) N(1)-Th(1)-Cl(2) = 90.39(16) Cl(1)-Th(1)-Cl(2) = 86.21(7) N(2)-Th(1)-Cl(3) = 89.10(16) N(1)-Th(1)-Cl(3) = 176.86(15) Cl(1)-Th(1)-Cl(3) = 86.85(7) Cl(2)-Th(1)-Cl(3) = 91.53(8)	Th(1)-C(13) = 2.588(17) Th(1)-N(1) = 2.740(13) Th(1)-N(2) = 2.737(12) Th(1)-Cl(3) = 2.751(4) Th(1)-Cl(2) = 2.834(4) Th(1)-Cl(1) = 2.836(4) Th(2)-C(33) = 2.645(14) Th(2)-N(4) = 2.731(14) Th(2)-N(3) = 2.762(12) Th(2)-Cl(2) = 2.943(4) C(13)-Th(1)-N(1) = 66.0(5) C(13)-Th(1)-N(2) = 67.2(5) C(13)-Th(1)-Cl(3) = 176.9(4) N(1)-Th(1)-Cl(3) = 116.7(3) N(2)-Th(1)-Cl(3) = 115.0(3) C(13)-Th(1)-Cl(2) = 92.6(4) N(1)-Th(1)-Cl(2) = 107.6(3) N(2)-Th(1)-Cl(2) = 159.7(3) C(13)-Th(1)-Cl(1) = 90.1(4) N(1)-Th(1)-Cl(1) = 156.0(3) N(2)-Th(1)-Cl(1) = 108.8(3) C(33)-Th(2)-N(4) = 71.8(4) C(33)-Th(2)-N(3) = 72.4(4) N(4)-Th(2)-N(3) = 144.1(4) C(33)-Th(2)-Cl(2) = 146.7(3) N(4)-Th(2)-Cl(2) = 116.4(3) N(3)-Th(2)-Cl(2) = 94.3(3) Th(1)-Cl(1)-Th(2) = 112.23(12) Th(1)-Cl(2)-Th(2) = 112.95(12)	Th(1)-C(10) = 2.612(8) Th(1)-N(1) = 2.702(5) Th(1)-Cl(1) = 2.7787(19) Th(1)-Cl(2) = 2.8470(16) C(10)-Th(1)-N(1) = 73.41(10) N(1A)-Th(1)-N(1) = 146.8(2) C(10)-Th(1)-Cl(1) = 180.000(1) N(1)-Th(1)-Cl(1) = 106.59(10) C(10)-Th(1)-Cl(2) = 87.47(4) N(1)-Th(1)-Cl(2) = 67.66(11) Cl(1)-Th(1)-Cl(2) = 92.53(4)

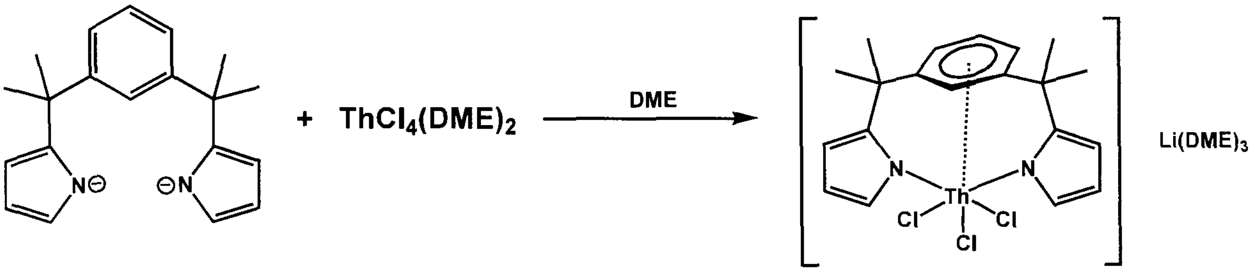
Table 6.2 (contd.). Selected bonds distances (Å) and angles (deg) for complexes **6.3**, **6.4** and **6.5**

6.3	6.4	6.5
Th(1)-N(1) = 2.474(5) Th(1)-Cl(2) = 2.7350(17) Th(1)-Cl(1) = 2.764(2) Th(1)-C(10) = 2.790(7) Th(1)-C(8) = 2.914(6) Th(1)-K(1) = 4.5815(16) N(1)-Th(1)-N(1A) 83.0(2) N(1)-Th(1)-Cl(2) = 93.85(13) Cl(2A)-Th(1)-Cl(2) = 86.39(9) N(1)-Th(1)-Cl(1) = 85.41(14) Cl(2)-Th(1)-Cl(1) = 81.69(5) N(1)-Th(1)-C(8) = 61.0(2) Cl(2)-Th(1)-C(8) = 94.36(17) Cl(1)-Th(1)-C(8) = 145.9(2) N(1)-Th(1)-K(1) = 42.23(12) Cl(2)-Th(1)-K(1) = 136.08(5) Cl(1)-Th(1)-K(1) = 92.54(5) C(8)-Th(1)-K(1) = 67.00(13) K(1B)-Th(1)-K(1) = 141.684(9)	Th(1)-N(3) = 2.435(5) Th(1)-N(4) = 2.442(5) Th(1)-N(2) = 2.458(5) Th(1)-N(1) = 2.464(5) N(3)-Th(1)-N(4) = 82.84(16) N(3)-Th(1)-N(2) = 95.89(16) N(4)-Th(1)-N(2) = 104.81(16) N(3)-Th(1)-N(1) = 83.56(17) N(4)-Th(1)-N(1) = 163.02(16) N(2)-Th(1)-N(1) = 86.66(16)	Th(1)-N(4) = 2.309(6) Th(1)-N(3) = 2.466(6) Th(1)-N(1) = 2.498(6) Th(1)-N(2) = 2.534(6) Th(1)-Cl(1) = 2.725(2) Th(1)-Cl(2) = 2.790(2) N(4)-Th(1)-N(3) = 35.53(19) N(4)-Th(1)-N(1) = 79.79(19) N(3)-Th(1)-N(1) = 115.26(19) N(4)-Th(1)-N(2) = 159.85(19) N(3)-Th(1)-N(2) = 161.61(18) N(1)-Th(1)-N(2) = 81.15(19) N(4)-Th(1)-Cl(1) = 84.82(15) N(3)-Th(1)-Cl(1) = 81.46(14) N(1)-Th(1)-Cl(1) = 93.09(14) N(2)-Th(1)-Cl(1) = 89.75(14) N(4)-Th(1)-Cl(2) = 116.27(15) N(3)-Th(1)-Cl(2) = 80.75(13) N(1)-Th(1)-Cl(2) = 163.74(14) N(2)-Th(1)-Cl(2) = 82.60(14) Cl(1)-Th(1)-Cl(2) = 86.28(7)

Results and Discussion

Deprotonation of the dipyrrole-benzene ligand 1,3-[(2-C_4H_3N)$(CH_3)_2C]_2C_6H_4$} was carried out in diethyl ether with MeLi affording the corresponding di-lithium salt {1,3-[(2-C_4H_3N)$(CH_3)_2C]_2C_6H_4$} $Li_2\cdot(Et_2O)_{0.5}$ in high yield. The ^{1}H-NMR consists of eight resonances situated in the range of 8 – 1 ppm. The most intense is located at 1.89 ppm and accounts for the twelve protons of the four methyl groups. The interstitial ether solvent resonances are visible at 1.22 ppm and 3.46 ppm while all the other signals appear in the typical aromatic region. The phenyl ring proton located between the two attachments is visible as a single resonance at 7.92 ppm. The three remaining protons on the central phenyl ring of the ligand are present as one multiplet at 7.42 ppm with the expected intensity. The three peaks at 7.36 ppm 6.79 ppm and 6.36 ppm with relative intensity 2:2:2 are attributed to the protons of two pyrrolide-anion rings.

The reaction of $ThCl_4(DME)_2$ with the ligand dilithium salt {1,3-[(2-C_4H_3N)$(CH_3)_2C]_2C_6H_4$} $Li_2\cdot(Et_2O)_{0.5}$ proceeded rapidly with visible color change as well as initial solubilization of all the materials. Complex **6.1** was isolated in crystalline form and high yield after work up (Scheme 6.1).



6.1

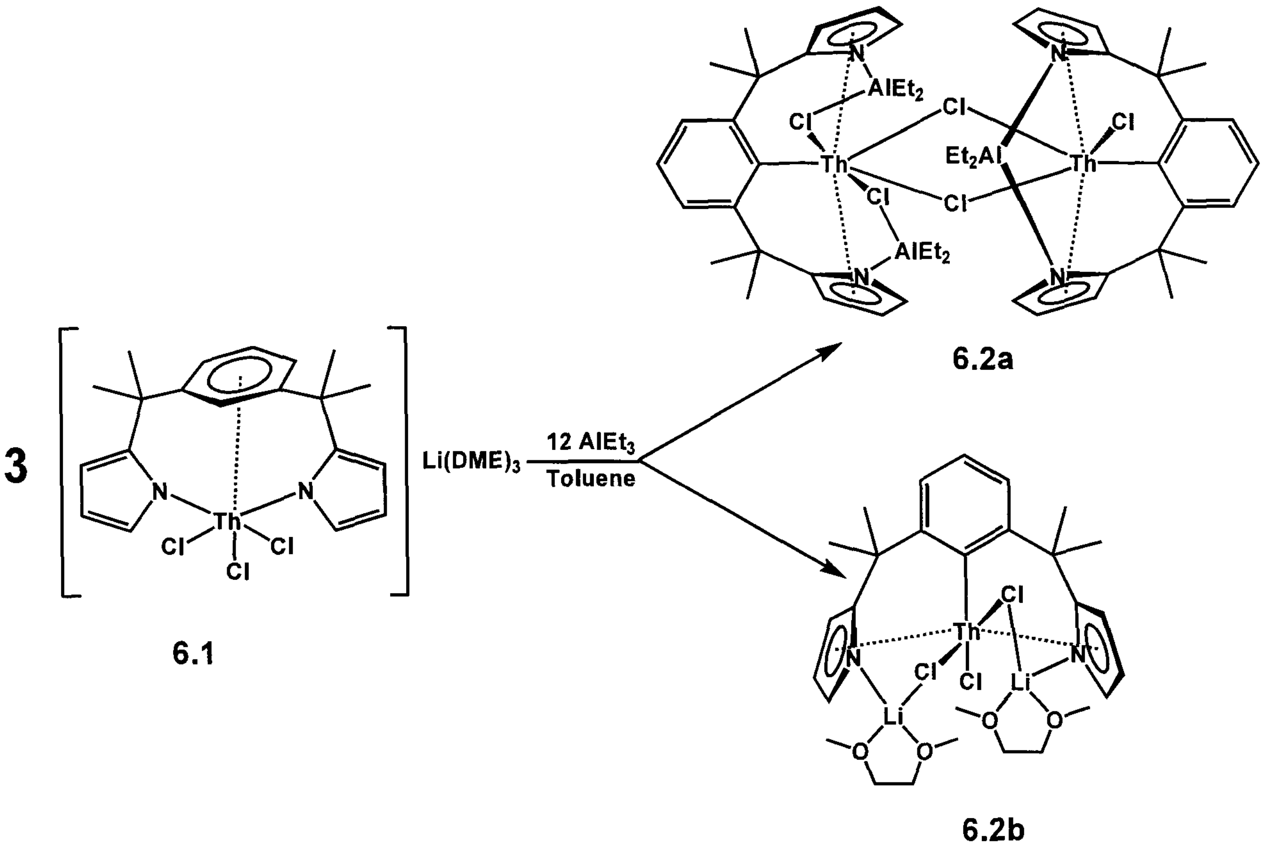
Scheme 6.1.

The ionic structure of complex **6.1**, as revealed by the X-ray structure, showed the expected arrangement with the pyrrolide rings adopting the σ-bonding mode with thorium and the central aromatic ring capping the metal in an apparent π-interaction. The ^{1}H-NMR spectrum was as expected showing four aromatic rings protons with relative intensity 2:1:1 located at 8.05 ppm, 7.87 ppm and

7.77 ppm respectively. The broad singlet at 7.87 is attributed to the hydrogen at the ring position between the two substituents. The resonances of the pyrrolide ring H_α-protons are slightly down-field shifted to 7.17 ppm with the two other resonances located in the normal range at 5.72 ppm and 5.36 ppm, all with the expected intensity ratio. The peak of the four methyl groups experienced a slight up-field shift, appearing at 1.65 ppm. The resonances of DME bonded to lithium are also observed in the normal range at 3.39 and 3.22 ppm.

The π-interaction between thorium and the phenyl ring visible in complex **6.1** might be simply matter of pure steric constraint. Nonetheless, it is also possible that it might the result of a significant chemical interaction, hopefully beneficial for preparing low-valent synthons. Our recent work in uranium chemistry of the 1,3-bis-iminobenzene ligand system, also having a similarly constrained phenyl ring in the bonding range, has shown that the ring hydrogen atom located between the two attachments may be readily deprotonated. In turn, this switched the bonding mode from π- to σ- and affected the stability of the reduced species. To probe the ability of the ring in this case to be involved in the reactivity of the metal center we have attempted the reaction with alkyl aluminum reagents. The basic idea was that initial alkylation at the Th center may be a prelude to ring deprotonation via an internal C-H σ-bond metathesis reaction. It is also possible that the Al containing residue might switch the bonding mode of the pyrrolide rings in turn providing the metal with additional and more robust π-interactions.

The reaction of **6.1** with three equivalents of $AlEt_3$ afforded a mixture of two complexes **6.2a** and **6.2b** which have been readily separated and purified by fractional crystallization (Scheme 6.2). The first complex was formulated as $\{[\{1,3\text{-}[(\eta^5\text{-}2\text{-}C_4H_3N)(CH_3)_2C]_2C_6H_4\}Th(\mu\text{-}Cl\text{-}AlEt_2)_2](\mu\text{-}Cl)_2[\{1,3\text{-}[(\eta^5\text{-}2\text{-}C_4H_3N)(CH_3)_2C]C_6H_4\}Th]\ (\mu\text{-}AlEt_2)Cl]\}\cdot(C_7H_8)_{0.5}$ (**6.2a**) on the basis of the X-ray crystal structure. The salient feature of this species, besides the dinuclear structure, is the expected deprotonation of the phenyl ring and consequent switching of bonding mode from π- to σ–. In turn, the pyrrolide rings also have switched the bonding mode from σ– to π- as a result of the retention of the Al residues σ-bonded to the pyrrolide N atoms. The ^{1}H-NMR spectrum of **6.2a** in d^8-THF showed only one type of ligand system, indicating symmetrization in solution and formation of only one type of Th complex. All aromatic protons of the phenyl ring as well as two pyrrolide moieties experienced a minor up-field shift. Three signals with the relative intensity of 2:2:2 positioned at 6.30 ppm, 5.46 ppm, and 5.26 ppm could be attributed to the protons of the two pyrrole rings. Two other signals in higher ppm region at 7.31 ppm and 6.51 ppm with the intensities of 1:2 could be assigned to the central phenyl ring of the ligand. Four methyl groups of the ligand produce an intense singlet at 1.35 ppm with the expected relative intensity. The remaining quartets at 1.01 ppm and triplets at 0.14 ppm are attributed to the two ethyl groups of the diethylaluminum units.



Scheme 6.2.

The byproduct of the formation of **6.2a** is formulated as $\{[\{1,3\text{-}[(\eta^5\text{-}2\text{-}C_4H_3N)(CH_3)_2C]_2C_6H_4\}ThCl(\mu\text{-}Cl)_2[Li(DME)]_2$ (**6.2b**) The feature in common with **6.2a** is the deprotonation of the central phenyl ring and consequent adoption of the σ-bonding mode. The lithium counter-cations play in this case the role similar to some extent to the one of Al in **6.2a** enforcing the σ/π switching of the bonding mode of the pyrrolide rings. The major difference in this case is the absence of $AlEt_2$ residues, which is most likely the result of the original stoichiometry employed in this reaction. Once crystallized the complex **6.2b** displayed rather poor solubility in hydrocarbon and solvents as THF-d^8 which prevented full NMR characterization. It is interesting to observe that in both cases the deprotonation of the central ring of **6.1** resulted in switching of the bonding mode of the pyrrolide rings with or mwithout the intervention of a potent Lewis acid such as Al.

An attempt to reduce the oxidation state of the Th metal center and to probe the ability of this ligand system to support reduced thorium complexes was carried out by reacting **6.1** in THF with metallic potassium. The reaction proceeded slowly until complete consumption of metallic potassium affording $[\{\eta^5\text{-}1,3\text{-}[(\eta^5\text{-}2\text{-}C_4H_3N)(CH_3)_2C]_2C_6H_4\}ThK(\mu\text{-}Cl)_3][Li(DME)_3]$ **(6.3)** as very dark-purple crystalline material. The structure is closely related to **6.1** still showing one ligand surrounding a $ThCl_3$ unit. The difference from **6.1** is that one potassium cation is retained as a part of the structure in addition to the pre-existing $Li(DME)_3$ counter-cation. Thus the connectivity in principle might be indicative of the presence of an extremely rare case of a trivalent thorium species. In further agreement, **6.3** is paramagnetic with the NMR spectrum showing very broad and overlapping lines. The room temperature EPR spectrum showed a broad single wave signal centered at $g = 1.996$ of the A band [337.243]. The lack of hyperfine coupling may be ascribed to the spin-orbit couplings probably rather significant in the case of thorium. The previously reported data, obtained by Cloke and coworkers[11c] provided the single wave spectrum with the value of $g = 1.916$. A similar value of $g = 1.915$ was also reported by Lappert[11e] for Th(III) compound supported by bulky cyclopentadienyl ligands. The discrepancy between the values could be easily attributed to the different Th atomic orbitals which are involved in the electron density distribution in previously reported cases. Both previously reported compounds demonstrated considerable involvement of 6dz^2 Th AO, whereas in the presented case the only small amount of electronic density resides on the 7s-6d orbital mix of the Th metal center (*vide infra*).

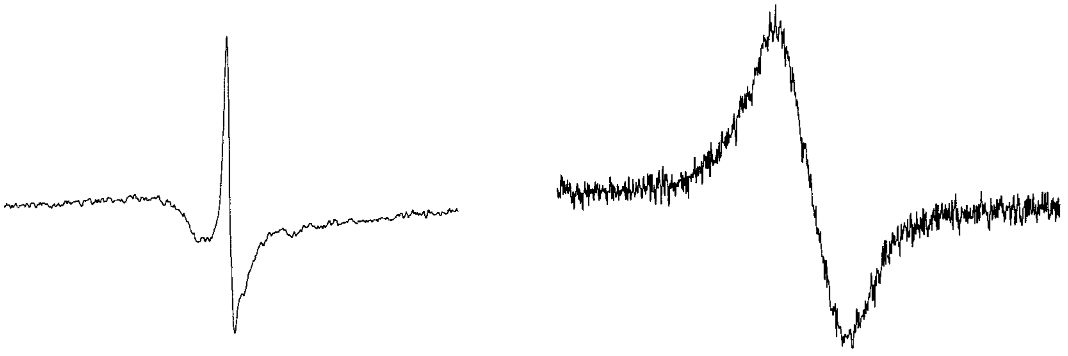
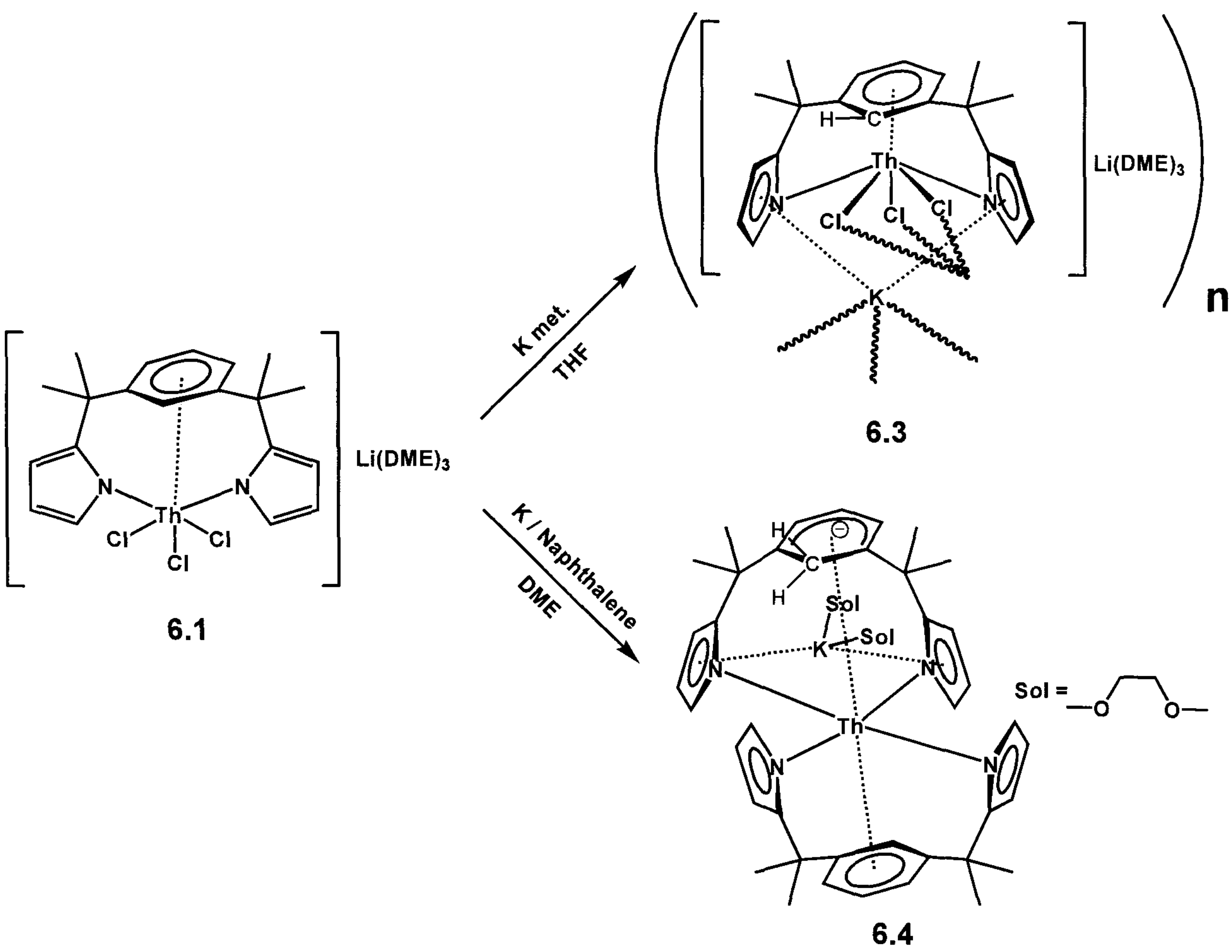


Figure 6.7. EPR spectrum of complex **3** in dioxane at 113.2 K (g = 1.9991) and 273.2 K (g = 2.0012)

Furthermore, the phenyl ring shows a very substantial deviation from planarity with the carbon atom located between the two pyrrolylmethyl attachments pointing away from the molecular core. The consequent breakup of ring conjugation causes this C atom forming long bonding distances (in the C-C single bond range) with the two neighboring carbon atoms. These features strongly suggest that the phenyl ring has been transformed into a radical anion while the thorium metal center preserves in this case it tetravalent state. Also the geometric deformation of that particular carbon atom might be indicative that spin density is substantially localized there. This idea is well substantiated by DFT calculation (see below). Although in a totally different ligand contest, complex **6.3** show the same basic feature observed in the other two documented trivalent synthons based on thorium cyclooctateraene[11c] and thorium tris-cyclopentadienyl[11d] ligand systems. In all these species the thorium center is participating in very substantial charge-transfer to the π-system of the ligand.

When a similar reduction was carried out in DME with K/Naphthalene, the reaction resulted also in the sudden formation of an intensely purplish-red color which, however, gradually faded in the range of 24 hours at room temperature. A new complex formulated as $\{\eta^6\text{-1,3-[(2-}C_4H_3N)(CH_3)_2C]_2C_6H_4\}Th\{\mu\text{-}\eta^5\text{-1,3-[(}\eta^5\text{-2-}C_4H_3N)(CH_3)_2C]_2C_6H_5\}K(DME)_2$ (**6.4**) was obtained in moderate yield (Scheme 6.3). The formation of **6.4** is the result of a complex transformation since in the process the thorium center has acquired one additional ligand, the fate of the corresponding thorium atom remaining unknown. One potassium atom is also retained in the structure.

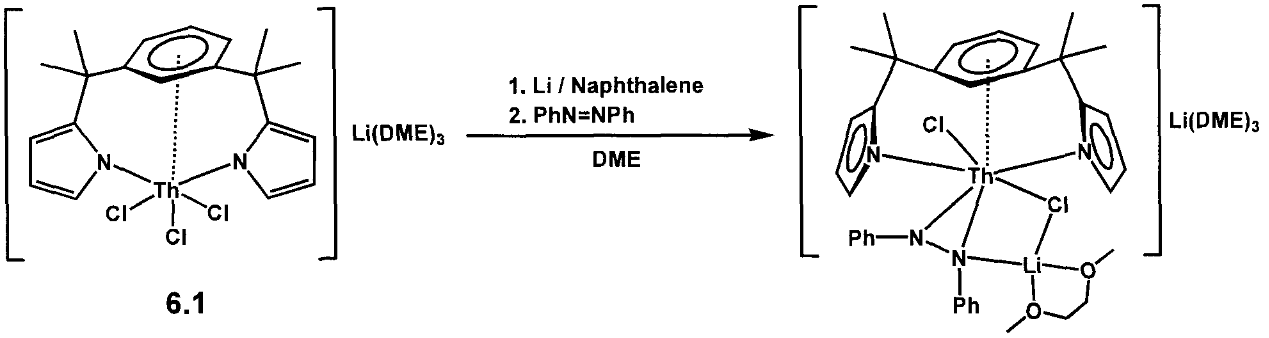


Scheme 6.3.

Of the two ligand systems, one is virtually unchanged showing the two pyrrolide rings normally σ-bonded, and the central phenyl ring π-bonded as in the case of **6.1.** The second ligand system has instead the central π-bonded phenyl ring showing the same sort of deformation visible in **6.3**. Different from **6.3** however, the pale color and diamagnetism gave a clear indication of the metal center tetravalent state and absence of unpaired electrons. This implies that the aromatic ring is anionic and which in turn implies that the particular carbon atom pointing away from the molecular core has acquired one additional hydrogen atom. Therefore, during the reduction and subsequent slow reoxidation the central phenyl ring has been transformed into a cyclohexadienyl anion. The ^{1}H-NMR is clearly supporting this proposal. The intact ligand system exhibit chemical shifts very similar to those of **6.1** and of the ligand dilithium salt. Three signals in the aromatic region of the spectrum appearing at 7.45 ppm, 7.33 ppm, 7.23 ppm have relative intensity 1:2:1 could be assigned to the un-altered phenyl ring coordinated to Th atom. Three resonances at 6.79 ppm, 6.48 ppm and 6.40 ppm with integration of 2:2:2 are assigned to the pyrrolide fragments of the same ligand. Finally one strong peak at 1.80 integrated to 12 protons could be attributed to the methyl protons. The second ligand system shows the resonances of the pyrrolide protons slightly shifted to 6.73 ppm, 6.23 ppm and 5.72 ppm as a possible result of the π-coordination to the potassium cation. The methyl groups of this second tris anionic ligand system are also significantly shifted to 0.43 ppm. The most interesting features are visible for the cyclohexadienly ring. Two resonances with relative intensity of 1:2 are located at 7.31 ppm and 7.20 ppm respectively accounting for the three coplanar H atoms. The ring CH_2 group displays two doublets coupled to each other at 3.77 ppm and 2.60 ppm for the *endo* and *exo* hydrogen atoms with the expected intensity.

Questions arise about the formation of **6.4**. While the formation of **6.3** is an electron transfer reaction from the reductant to the aromatic ring of **6.1**, the formation of **6.4** implies a subsequent hydrogen atom abstraction. Cleavage of ethers and particularly of THF and DME are widely precedented in both lanthanide and actinide chemistry.[2o,t,6l,7k,n,8l,h,9o,21] Furthermore even multiple hydrogen atom abstraction during reduction of thorium has been observed before.[3r,9n] Therefore, a possible higher lability of DME comparing to THF with respect to undergoing radical attack is responsible for the remarkable difference of behavior observed for the reactions carried out in the two solvents. However, the fact that **6.3** does not generate **6.4** upon dissolution in DME may suggest that the naphthalene electron transfer agent may play a role.

We have observed that reduction with Li naphthalenide in DME follows the same trend of color change as during the formation of **6.4**. The immediate color deepening and change observed upon mixing was followed even in this case by a slow color fading. Since attempts to characterize this deeply colored reduced species failed in this case, we have attempted to trap these intermediates via *in situ* reaction with mild oxidizing agents. The most successful combination was the reduction of **6.1** in DME by Li/Naphthalene followed by the addition of azobenzene affording the tetravalent and diamagnetic $[\{\eta^6\text{-}1,3\text{-}[(\eta^5\text{-}2\text{-}C_4H_3N)(CH_3)_2C]_2C_6H_4\}Th(\mu\text{-}\eta^2\text{-}PhNNPh)(\mu\text{-}Cl)(Cl)Li(DME)][Li(DME)_3]$ (**6.5**) (Scheme 6.4). NMR data were in complete agreement with this formulation and did not display any particularly significant feature.



6.1

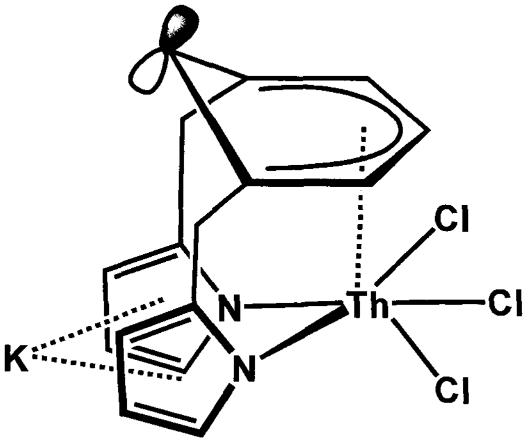
6.5

Scheme 6.4.

Complex **6.5** contains tetravalent thorium and is clearly the result of a two-electron oxidative addition to azobenzene by a transient reduced species. Although the two electrons necessary for the reduction of azobenzene might still be provided by the cooperative action of two one-electron reduced thorium units, at this stage we cannot rule out the possibility that in DME and by using alkali naphthalene reductants two electron synthons might be produced. In turn, the substantially stronger reducing power may somehow be responsible for hydrogen atom abstraction.

Electronic Structure.

To elucidate the radical nature of **6.3**, DFT calculations were performed on the crsytallographic atomic coordinates of truncated models of the monomeric anionic unit (Scheme 6.5). The presence of the mirror plane symmetry element in the x-ray crystal structure, results in a symmetrical distribution of the electron density and equal numbers for bond orders and charges of the symmetry related atoms.



Scheme 6.5. Simplification of the structure for complex **6.3.** Model compound for DFT calculation shown.

Calculations were performed for doublet state corresponding to an hypothetical Th(III) f^1 metal center obtaining computationally stable model in agreement with the charge transfer hypothesis. The singly occupied highest molecular orbital is located mostly on the phenyl ring of the ligand (Fugure 6.8) and is energetically well separated from both HOMO-1 (ΔE = - 2.33 eV) and LUMO (ΔE = 1.21eV).

The computational results also clarified the visible ring distortion of **6.3**. Mulliken population analysis (MPA) indicated that the spin density is concentrated mostly on the ring carbon atom above the ring plane (C(24) = 69.8%). Moreover the orbital contribution of this carbon atom into the formation of the molecular orbital is of pure π-character. Such concentration of electron density on one part of the ring leads to the observed distortion of the phenyl aromatic fragment and C-C bond elongation. Such *p*-orbital of the carbon atom in *para* position to the "radicalic" carbon with an overall contribution of 16.3% (Figure 6.9).

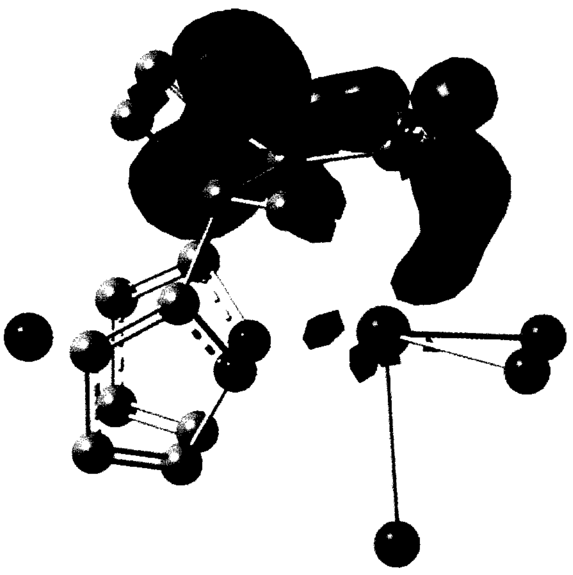
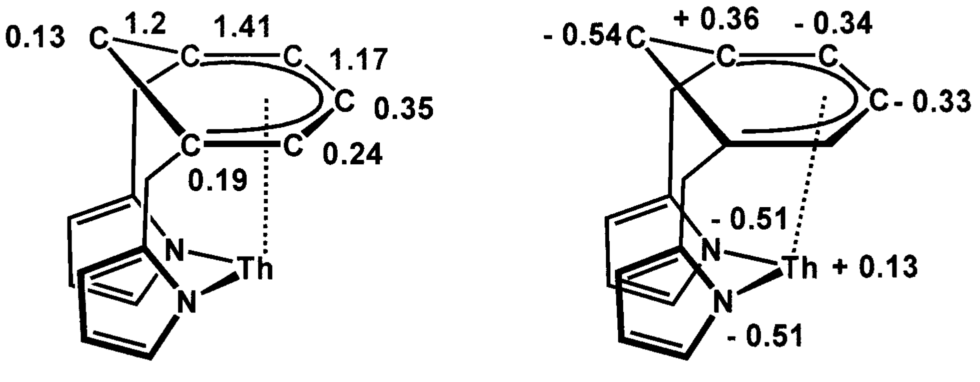


Figure 6.9. Spin density distribution for the simplified model structure of complex **6.3**. Isosurface contour value of 0.003 e□Å^{-3}.



I II

Scheme 6.7. Mayer bond orders (in red – ligand to Th bonds, in green – bonds within the arene subsystem) and MPA-derived atomic charges (a.u., in blue) of the π-bonded arene fragment for model of complex **6.3**.

The valence indexes for the Th metal center and for "radicalic carbon" equal 6.3 and 3.67 respectively. These values confirm once again that the electron, acquired during the reduction, is generating a free valence on the carbon atom, leaving the electronic arrangement of Th metal center practically undisturbed.

In summary, calculations substantiate the initial assignment of the oxidation state of the thorium center in this species as mainly tetravalent with the ligand playings the role of electron density storage. The presence of an additional electron on the arene delocalized π-orbital results in a ring distortion. These features lead to the change in ligand to Th bond-order character illustrated in Scheme 6.7-**I**, while the overall charge distribution is depicted in Scheme 6.7-**II**.

Conclusions

In this work we have reported the preparation of the third case of a Th(III) synthon which to the best of our knowledge is the first for a non-Cp based system. Similarly to the case of the other two existing synthons, the metal engaged in a substantial charge transfer with the ligand aromatic ring. The possibility that the organic radical so generated may perform hydrogen abstraction reactions opens interesting perspectives for the use of this ligand to generate low-valent synthons and for further reactivity studies.

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Chapter Seven

Conclusions

The original goal of this thesis was rather simple. It was an exploration aiming at further developing the reactivity of *f*-block metals, in combination with different ligands. The ultimate goal was the discovery of the factors responsible for stabilization the low oxidation state of the metal center.

The initial attempts to utilize the bulky σ-bonding molecules led to the isolation of several unprecedented cluster compounds with multiple γ-deprotonation of the ligand system. Such reactivity strongly suggests that aggregation of several metal centers upon halogen removal was the most favorable transformation pathway. Similarly, the reactions of reductive halogen elimination could also proceed through the formation of multimetal conglomerates. It was found in the course of the research work that reduction reaction afforded the formation of species with the oxidation state of the metal being higher in the product then in the starting materials. Moreover, the ligand to metal ratio in the final products was clearly different, indicating ligand migration during the reaction. Even assuming the presence of the low-valent intermediate in the reaction mixture, the steric configuration of the ligand, prevented the reaction with any substrate and led to the collapse of the clusters and re-oxidation of the metal center. All these findings were suggesting that the role of ligand system is far from being sole spectator. From the other point of view it became clear that the simple σ-bonding bulky amido-molecules had a very limited potential in the stabilization of the low oxidation states. The presence of π-interaction between the ligand and the metal center became one of the necessary prerequisites in the hunt for the low oxidation state.

Different ways of inducing π-bonding of the ligand were explored in the course of this research work. Following the initial discovery that the addition of strong Lewis acid to the complex led to the σ- to π-coordination, several new compounds were prepared employing similar approach. It was quickly learned that the presence of the π-system in the ligand molecule could be beneficial to the stabilization of the low oxidation state metal center. Remarkably, the ligand π-system not necessarily had to bear a negative charge in order to interact with the *f*-block metal center. Thus the treatment of σ-coordinated aryloxide samarium complexes with aluminum alkyls resulted in the appearance of strong π-bonding interaction between the phenyl rings and the samarium metal center. Interestingly enough, the stability of the low valent metal center in this surroundings was significantly increased, even to the point that rare spontaneous reduction of samarium to the lower oxidation state was discovered. The over-stabilization through π-coordination effect was so strong that even mild oxidation agents were not capable to induce red-ox transformation, displaying different reactivity pathways.

Similar π-coordination induction approach was used to explore the chemistry of less known thulium metal center. This time it was discovered that spontaneous reduction is not present, which came as no surprise, due to the significantly increased reduction potential of thulium metal. Nevertheless, the presence of the Lewis acidic aluminum alkyl provoked a series of rather unusual transformations. The close resemblance with the *ansa*-cyclopentadienyl compounds calls for more detail exploration, giving the promises for the unconventional reactivity patterns. However, the explored ligand system was prone to rearrangement and migration which was detrimental for the stabilization of the low valent oxidation states. Therefore a different approach was employed in order to induce the π-bonding of the ligand to the metal center.

The ligands with the large delocalized non-bonded π-system positioned in the close proximity to the metal center were found to be more successful in preserving the low oxidation state metal centers. It was discovered in the process that low valent intermediates produced through the *in situ* reduction possessed long enough lifetime to participate in the reactivity with substrates and the solvent media. Moreover it was discovered that the ligand system could act as electron storage, accepting electrons from the reducing agents. It was later discovered that ligand-localized spin density could be delivered back to the metal center, providing the expected red-ox reactivity. Attempts to go beyond the limit of the known oxidation state often led to partial decomposition of the materials. However in several cases extra-low formal oxidation states compounds has beenobtained, building on the same electron-storage principles. The reverse of the medal was the complete lack of control of the reactivity of these compounds.

Yet another approach to involve the ligand π-system in the interaction with the metal center was explored in the case of thorium compounds. These complexes were prepared with the ligand whose aromatic π-system was forced to interact with the metal center by the steric constrains. Initial attempts to lower the oxidation state of Th afforded several re-oxidation products, indicating the presence of the reactive low valent intermediate. After experimenting with the reaction conditions and the reducing agents it was possible to isolate a complex with the rare formal low valent oxidation state of thorium metal center. Detailed investigation, however, clarified the electronic arrangement of the complex. The key to this success was once again the electron storage capability, provided by the ligand. One more time it was proved that on demand this electron density could be transferred back to the metal center and further to the coordinated substrates, therefore creating another low-valent synthon, based on *f*-block metal.

In conclusion, walking the fine line between the completely quenched reactivity and incontrollable decomposition of the low valent complex was a very challenging task. The proper combination of many factors was necessary in order to create just the right mix of stability and reactivity. Even these days the field of the *f*-block elements chemistry somewhat reminds the work of the alchemists, with experiments with known species and starting materials leading to absolutely unprecedented results. This chemistry is very often difficult to handle but also unpredictable, surprising and always very rewarding. Despite the growing interest the results are still scattered and there are a lot of great wonders still to be uncovered in the area of *f*-chemistry.