LBL-10377

CONF-790917--20

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## Materials & Molecular Research Division

Presented at the 1979 Annual Meeting of the American Chemical Society on The Chemistry of the Lanthanides and Actinides, Washington, DC, September 10-14, 1979

MASTER

# ALKYL, HYDRIDE, AND RELATED BIS(TRIMETHYLSILYL)-AMIDE DERIVATIVES OF THE 4f- and 5f- BLOCK METALS

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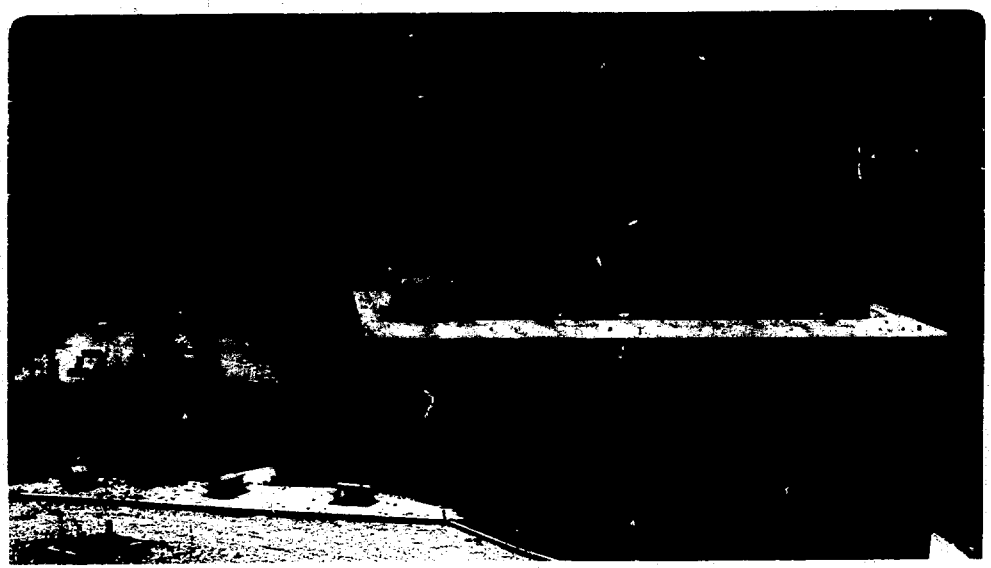
December 1979



Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

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# Alkyl, Hydride, and Related Bis(trimethylsilyl)-Amide Derivatives of the 4f- and 5f- Block Metals

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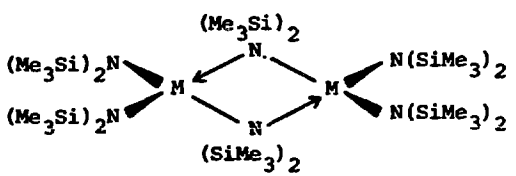
## Introduction

Metal derivatives of the bis(trimethylsilyl)amido ligand, $[(Me_3Si)_2N]$, have been extensively investigated for the p- and first-row d-block elements. An exhaustive review by Harris and Lappert, concentrating upon synthetic chemistry, has recently appeared (1). A review of the molecular and electronic structure of three-coordinate and related $(Me_3Si)_2N$-derivatives, which reports a number of unpublished results has appeared (2). A rather more general review of the transition metal derivatives also has been published (3).

One area of silylamide (this short-hand abbreviation will be used for $(Me_3Si)_2N$) chemistry that has been largely ignored is the f-block element derivatives. The silylamide ligand is potentially a very valuable ligand in this part of the Periodic Table principally due to its size. Association by way of dative bonding (I) is prevented, since in a hypothetical tri-




I

valent, binary derivative (with coordination number of four) the steric congestion about the metal atom is far too great. Further, the lone-pair of electrons on the nitrogen atom is considerably less basic relative to an analogous dialkylamide, (a $(Me_3Si)_2N$) group is electron-withdrawing relative to a $Me_3C$ group, silicon being less electronegative and/or possessing low-lying $d_\pi$-orbitals for electron-delocalization) (II). The resulting decrease in basicity of the nitrogen lone pair minimizes its ability to act as a two electron donor to the metal atom. Thus, the large size and electron-withdrawing



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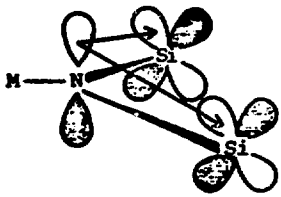



II

ability of the trimethylsilyl group prevents association and monomeric, hydrocarbon soluble, volatile derivatives are to be expected. In addition the extreme simplicity of the nuclear magnetic resonance and vibrational spectra greatly simplifies analysis.

In light of these considerations it is surprising that the f-block metal derivatives of this readily accessible ligand have not been explored. In this review we describe some results which begin to rectify this deficiency.

## Trivalent Lanthanide and Actinide Derivatives

Compounds of the type $[(Me_3Si)_2N]_3M$ have been prepared for all of the lanthanide elements except Pm, Tb, Dy, Tm, and Er (4). The synthetic method used in their preparation is nucleophilic substitution with three molar equivalents of lithium - or sodium - bis(trimethylsilyl)amide on the metal trichlorides in tetrahydrofuran. The compounds are rather high melting solids (145-170°C) which can be isolated by crystallization from pentane as long needles or by vacuum sublimation (80-100°C). The binary silylamides are monomeric in refluxing benzene solution, in the gas phase (by mass spectrometry), and in the solid state (by x-ray crystallography, see below). Thus, these compounds are three-coordinate, a unique coordination number for the lanthanide elements.

The colors of the silylamides closely parallel those of the metal ions in aqueous solution, i.e., $Nd[N(SiMe_3)_2]_3$ is pale blue, $Eu[N(SiMe_3)_2]_3$ is orange, and $Yb[N(SiMe_3)_2]_3$ is pale yellow. The optical spectra of the praesodymium and neodymium derivatives have been studied in gaseous, solution ($CCl_4$), and low temperature (4 K) solid phases (5). The spectra are very similar (number and intensity of absorptions) which indicates that the symmetry is identical in all phases. Further, the silylamide ligand does not greatly perturb the energy levels of the free ion since the observed spectra are very similar to the trivalent metal ions in aqueous solution.

Low temperature magnetic susceptibility measurements (the binary derivatives are all paramagnetic, except those with closed-shell $f^0$ or $f^{14}$ electronic configuration) also closely

parallel the trivalent metal ion values in aqueous solution, for those silylamide derivatives which have been examined (Table 1). An exception is $Eu[N(SiMe_3)_2]_3$ which is a temperature independent paramagnet (T.I.P.), the temperature independent susceptibility being ca. 0.4 B.M. consistent with the $^7F_0$ ground state found for Eu (III).

Table I
Magnetic Susceptibilities of $M[N(SiMe_3)_2]_3$

| M | $\mu_B$(B.M.) | Temp. range (K) | $\Theta$ (K) | $C_M$ | Ref. |
|---|---|---|---|---|---|
| Nd | 3.27 | 4.2-90 | 12 | 1.33 | 6 |
| Gd | 7.94 | 98-298 | -- | -- | 4 |
| Yb | 3.10 | 5.1-46 | 0 | 1.09 | 7 |
| U | 2.51 | 10-70 | -10.5 | 1.64 | 13 |

$$X_M = C_M(T+\Theta)^{-1};\ \mu_{eff} = 2.837\sqrt{X_M}$$

The crystal structure of three representative [Nd (6), Eu (8), and Yb (2)] amides have been determined. The compounds are monomeric and there is no indication of molecular association in the solid state. The $(Me_3Si)_2N$ groups are neither coplanar nor orthogonal to the $MN_3$ unit but half-way between, such that the dihedral angle (defined by the $Si_2NM$ and $MN_3$ planes) are ca. 50° (Figure 1). The molecules are thus molecular propellers and chiral. Therefore, two enantiomeric forms may exist which differ only in their sense of twist. This is the conformation that is expected on the basis of steric arguments, the trimethylsilyl groups pack in the crystalline lattice in such a fashion to minimize Van der Waals contact between them.

A curious feature of the solid-state structural results is that the $MN_3$ unit is not coplanar as found in the first-row transition or Group IIIA series (2) but pyramidal, the metal atom being out of a plane defined by the three nitrogen atoms by ca. 0.4 Å. Since the molecules have no dipole moment in solution (2) the geometry could well be due to packing forces in the solid state.

An interesting feature of the binary, trivalent silylamides is the way that they pack in the crystalline lattice. Six $[(Me_3Si)_2N]_3M$ units are orientated about a six-fold rotation axis such that a cylindrical channel, large enough to include a benzene ring, is formed. This phenomenon has been described in some detail (9a). The existence of the hollow cavity accounts for the low density of the solid (ca. 1g $cm^{-3}$). A single crystal, when viewed under a microscope, appears to contain a hole in the center, the macroscopic structure apparently mirrors the microscopic array (9b). The molecular packing shows that the molecules are three-dimensional molec-

ular sieves.

Consideration of metal-nitrogen bond lengths in light of the ionic-bonding model advanced by Raymond (10) leaves little doubt that the bonding in the binary silylamide derivatives of the lanthanide elements is predominantly ionic (11). Indeed, all of the tris-silylamide derivatives of the p-, d-, and f-block elements can be viewed as being mainly ionic.

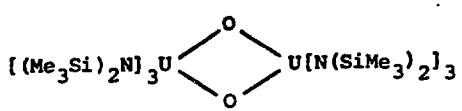
Synthesis of a trivalent uranium silylamide derivative is of considerable interest. The principal synthetic difficulty is the lack of a suitable, large-scale preparation of uranium trichloride (12). We have devleoped an in situ preparation of uranium trichloride by reducing commercially available uranium tetrachloride with one molar equivalent of sodium napthalene in tetrahydrofuran (13). Though we have not characterized this species Moody has recently isolated some coordination complexes of $UCl_3$, prepared by sodium hydride reduction of $UCl_4$ (14, 15). A trivalent tris-silylamide of uranium $U[N(SiMe_3)_2]_3$ can be readily prepared in good yield from $UCl_3$ in situ and sodium bis(trimethylsilyl)amide in tetrahydrofuran. The deep red, paramagnetic (Table I) needles (m.p. 137-140°C) crystallize from pentane. The compound is volatile (sublimation temperature 80-100°/$10^{-3}$ torr) and monomeric in gas phase (by mass spectrometry) (13).

The structure of this unique uranium (III) derivative is of much interest. Unfortunately we have been unable to obtain crystals satisfactory for an X-ray analysis. The compound is most likely similar to that of the binary, trivalent lanthanide derivatives, e.g., pyramidal rather than planar, on the basis of infrared spectroscopy. Planar $M[N(SiMe_3)_2]_3$ show bands due to $\nu as\ MNSi_2$ at 900 $cm^{-1}$ whereas pyramidal ones absorb at 990 $cm^{-1}$. Since $U[N(SiMe_3)_2]_3$ has its $\nu as\ UNSi_2$ absorption band at 990 $cm^{-1}$ it is most likely pyramidal in the solid state. Not surprisingly the analogous thorium (III) derivative cannot be prepared in a similar fashion.

Coordination Chemistry. The coordinative unsaturation of the three-coordinate derivatives suggests that these molecules should have a rich coordination chemistry. This has not been found, doubtless due to the steric congestion about the metal atom. Neodymium tris[bis(trimethylsilyl)amide] forms pale blue 1:1 coordination complexes with the sterically small Lewis bases $Bu^tNC$ and $Bu^tCN$. Triphenylphosphine oxide yields a 1:1 complex with the silylamides of La, Eu, and Lu (16). A crystal structure of the lanthanum derivative has also been described. The dissociation pressure in gas phase of $Ph_3PO$ complex is appreciable as the base-free compound sublimes when heated in vacuum at 80-100°C. In contrast, the uranium tris-silylamide does not yield isolable complexes with $Bu^tNC$, $Bu^tCN$, pyridine, or trimethylphosphine oxide (13). The inability to isolate coordination complexes with a variety of Lewis bases is rather surprising since uranium (III) is larger

than to its cogenic, neodymium (III) (17). Thus, the steric congestion about the lighter f-metal must be greater than about its heavier derivative. However, Nd(III) is more electropositive (by ca. 0.5 units) than that of U(III) and the coordinative affinity of uranium to a reference acid is therefore considerably less.

One attempt to isolate a U(III) complex of trimethylamineoxide resulted in oxidation of $[(Me_3Si)_2N]_3U$ to the pentavalent oxide $[(Me_3Si)_2N]_3UO$. The oxide could be prepared rather more simply from the tris-silylamide and molecular oxygen. The oxide is involatile and is not soluble enough in suitable solvents for a solution molecular weight determination. Thus, its degree of association in solution is unknown. It could be a coordination oligomer (IV), as suggested by its relative insolubility, or a discrete monomer (V). The U=O




IV

$[(Me_3Si)_2N]_3U{=}O$

V

stretching frequency (930 $cm^{-1}$) is similar to that found in monomeric $O_2U[N(SiMe_3)_2]_2(thf)_2$ (938 $cm^{-1}$) (18a). This suggests that the uranium-oxygen bond order is the same in both examples and that $[(Me_3Si)_2N]_3UO$ is a monomer (V). A weak intermolecular interaction which would account for the poor solubility in hydrocarbon solvents in solid-state cannot be ruled out.

## Divalent Lanthanide Derivatives

The divalent oxidation state of the lanthanide elements is commonly found for europium and ytterbium, though some simple salts have been prepared for most of the 4f-series (12). Only a few molecular compounds have been described and these have been mainly with cyclopentadienyl and cyclooctateraene ligands (18b). None have been characterized by X-ray methods since the compounds are generally insoluble and nonvolatile an observation that is consistent with a polymeric constitution. The compounds doubtless polymerize in an attempt to increase their coordination number to a maximum value while maintaining satisfactory metal-ligand interactions.

Since the silylamide ligands occupy considerable volume about a metal atom and the low basicity of the lone pair of electrons on the nitrogen atom will minimize intermolecular association, divalent species, $[(Me_3Si)_2N]_2M$, are likely. The structural and magnetic properties of these molecular compounds are of considerable interest.

The most useful preparative method for the europium derivative is shown (7). The chloroamide of europium (III) is

$$2\ Eu[N(SiMe_3)_2]_3 + EuCl_3 \xrightarrow{thf} 3\ ClEu[N(SiMe_3)_2]_2$$

$$ClEu[N(SiMe_3)_2]_2 + Na\ Napthalene \xrightarrow{thf} Eu[N(SiMe_3)_2]_2(thf)_2$$

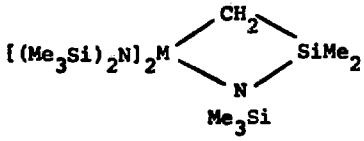
not isolated but is reduced in situ. The 1:2 tetrahydrofuran complex is yellow, paramagnetic ($\mu_B$ = 7.8 B.M.), and soluble in toluene. The tetrahydrofuran can be displaced by pyridine or 1,2-dimethoxyethane giving 1:2 complexes or by bipyridine giving a 1:1 complex. The 1:2 complexes with monodentate ligands and the 1:1 complex with bipyridine are most likely four coordinate complexes with a distorted tetrahedral geometry. The complex with 1,2-dimethoxyethane, however, must be six coordinate. Since the latter complex crystallizes as long, yellow needles from pentane, a crystal structure analysis was done (Figure II) (9b).

The amide is six coordinate but it does not conform to any regular polytopal form since the N-Eu-N bond angle is 135°. The Eu-N bond length is 2.52 Å.

## Tetravalent Actinide Derivatives

The monochlorotris-silylamides, $[(Me_3Si)_3N]_3MCl$, of the two most readily accessible actinide elements, thorium and uranium, have been prepared by reaction of three molar equivalents of sodium bis(trimethylsilyl)amide and the metal chloride in tetrahydrofuran. The thorium derivative is a colorless, diamagnetic, pentane soluble compound which is monomeric in the gas phase (by mass spectrometry) (19, 20). The tan uranium analogue is paramagnetic ($\mu_B$ = 2.8 B.M.) (20).

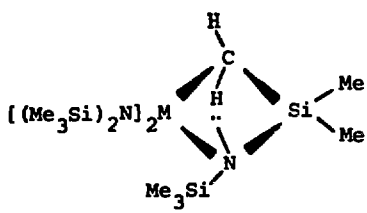
The chloride ligand in both derivatives can be replaced by a methyl group upon reaction with methyllithium in the case of uranium and dimethylmagnesium in the case of thorium (20). The reactions of the chloro-derivatives are summarized in Scheme I. Both methyl derivatives are readily soluble in pentane from which they can be crystallized. They are thermally stable to ca. 130°C. Heating the methyls to ca. 20°C above their respective melting point results, in each case, in elimination of methane and formation of the unique metallocycle VI (21).



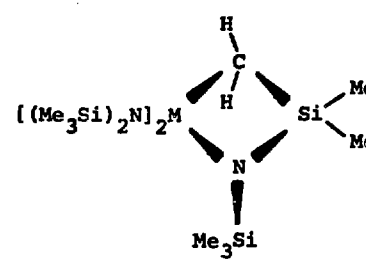

VI

The diamagnetic, monomeric thorium derivative has been completely characterized by its $^1H$ and $^{13}C$ nuclear magnetic resonance spectra. Data are shown in Table II. In particular the $^{13}C$ NMR spectrum, proton-coupled, shows a triplet pattern clearly due to splitting by two equivalent hydrogen atoms. The uranium metallocycle is paramagnetic ($\mu_B$ = 2.7 B.M.) and we have only observed its $^1H$ NMR spectrum. A titanium metallocycle, $Cp_2TiN(SiMe_3)(SiMe_2)(CH_2)$, has been previously described (22).

Some interest is attached to the conformation of the metallocycle in solution, as either conformation VII or VIII are possible. In the former (VII), there is no symmetry plane plane containing the MCSiN-four membered ring, the methylene and $Me_2Si$ protons are chemically nonequivalent. In the latter case, (VIII), there is such a symmetry plane and the methylene and $Me_2Si$ protons are chemically equivalent. The room temperature and -80°C $^1H$ nuclear magnetic resonance spectrum is consistent with VIII. However, conformation (VII) could be present in solution if the molecule were fluxional even at -80°C. A single crystal X-ray examination, which is in progress, will prove which conformation exists in the solid-state (9b).

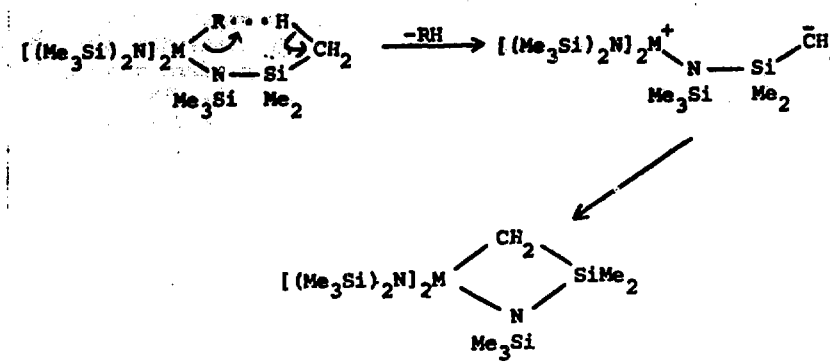



VII




VIII

The high thermal stability of the metal-carbon bond in the actinide methyl derivatives suggests that a series of alkyl derivatives can be made. This does not prove to be the case. Reaction of $ClM[N(SiMe_3)_2]_3$, where M is thorium or uranium, with either ethyllithium or trimethylsilylmethyllithium at room temperature in diethyl ether yields the metallocycle (VI) and ethane or tetramethylsilane. A mechanism for this transformation, which involves a γ-proton abstraction, is shown below. The γ-abstraction process from trimethylsilylmethyl (23) or neopentyl (24) groups is known. The proposed pathway goes by way of the ylide (IX). The ylide could be either a transition state or an intermediate depending upon whether the reaction is concerted or not. A curious facet of the abstraction reaction is that the methyl and hydride derivatives can be isolated and converted into the metallocycle by heating, whereas attempts to prepare alkyls with larger organic groups gives the

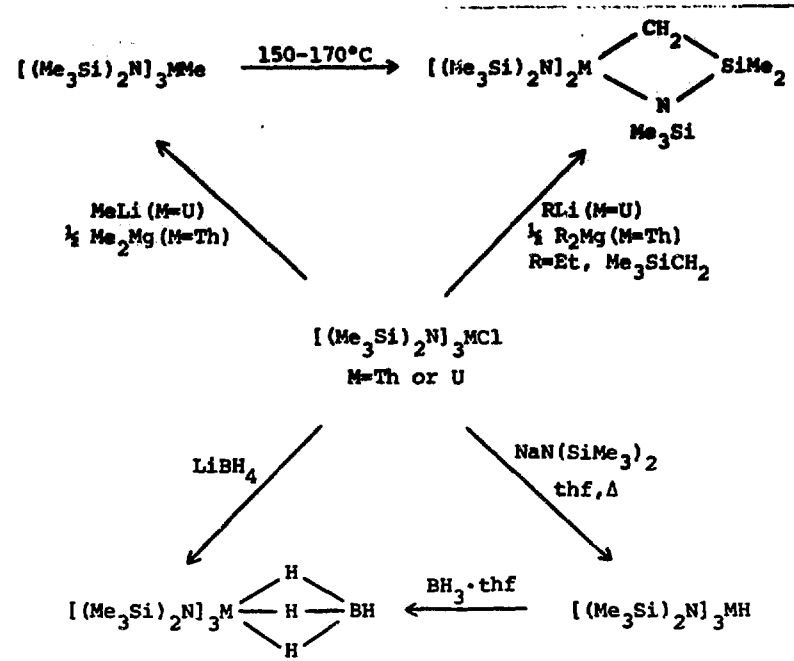


metallocycle straightaway. This is most reasonably ascribed to a steric effect. In hypothetical $[(Me_3Si)_2N]_3MCH_2SiMe_3$ the steric congestion about the metal atom is too great and the molecule relieves itself of the congestion by elimination of tetramethylsilane.

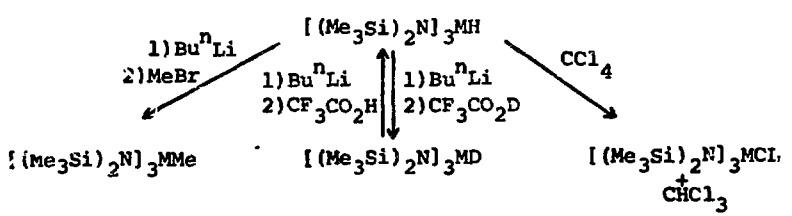
The chloro-tris(silylamido) derivatives also react with lithium borohydride giving $[(Me_3Si)_2N]_3MBH_4$. The infrared spectra and a crystal structure analysis of the thorium derivative shows that the borohydride group is tridentate, that is the metal atoms are six coordinate as they are bonded to three nitrogen atoms and three hydrogen atoms. The $^1H$ nuclear magnetic resonance spectrum of the diamagnetic thorium and paramagnetic uranium derivative indicate that they are fluxional, a 1:1:1:1 quartet being observed even at -80°C (20).

In an attempt to prepare a tetrasilylamide we allowed $[(Me_3Si)_2N]_3MCl$ to react with an equivalent of sodium bis(trimethylsilyl)amide in refluxing tetrahydrofuran (25). In each case, Th or U, we isolated the unique hydride, $[(Me_3Si)_2N]_3MH$. The colorless, diamagnetic thorium hydride (m.p. 145-147°C) shows an ThH absorption in the infrared spectrum at 1480 $cm^{-1}$ which shifts to 1060 $cm^{-1}$ in the deuteride. The paramagnetic ($\mu_B$ = 2.6 B.M.), brown-yellow uranium hydride (m.p. 97-98°C) shows a similar pattern, $\nu$UH = 1430 $cm^{-1}$ and $\nu$UD = 1020 $cm^{-1}$. The proton nuclear magnetic resonance spectrum of the thorium hydride shows a resonance at $\delta$ 0.90 due to the hydride. The source of the hydride has been shown to be one of the hydrogen atoms of tetrahydrofuran since conducting the reaction in perdeuterotetrahydrofuran yields the monodeuteride. Tetrahydrofuran is essential since boiling $ClM[N(SiMe_3)_2]_3$ with $NaN(SiMe_3)_2$ in benzene, toluene, isooctane, or diethyl ether results in isolation of unreacted $ClM[N(SiMe_3)_2]_3$.

The chemical nature of the hydride is clearly demonstrated by some of its reactions shown in Scheme II. In particular the hydrogen-atom abstraction with the strong base n-BuLi is noteworthy. We have not been able, as yet, to isolate the




Scheme I




Scheme II

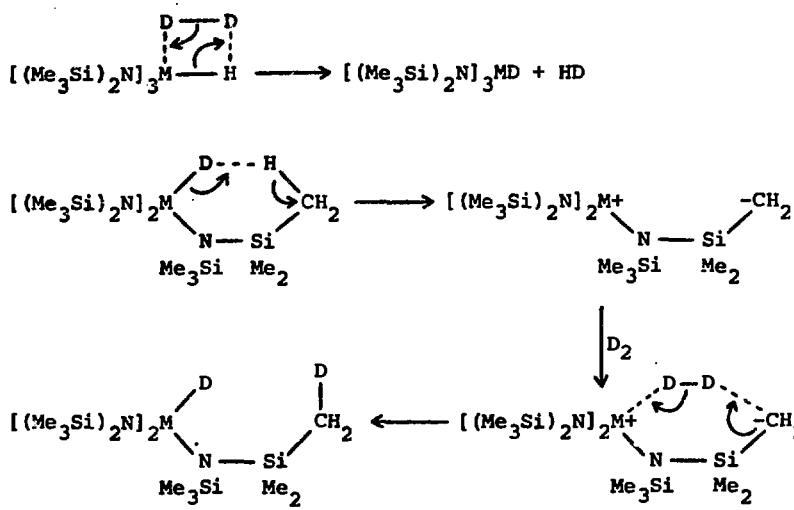
lithium-containing species. The hydridic nature is further illustrated by its reaction with borane in tetrahydrofuran giving the borohydride (Scheme I). In effect, the actinide hydrides act as a soluble source of sodium hydride. This is not unexpected since the actinide elements are quite electropositive.

Possibly the most fascinating reaction of the hydrides so far discovered is their facile exchange of all fifty-five hydrogen atoms with deuterium under one atmosphere of deuterium pressure at room temperature in pentane (21). The conversion

$$[(Me_3Si)_2N]_3MH + D_2 \longrightarrow DM\{N[Si(CD_3)_3]_2\}_3$$

is 92-97% complete. Neither the methyl, chloro, borohydride derivatives nor the uranium (III) derivative, $[(Me_3Si)_2N]_3U$, undergo exchange with deuterium under similar conditions.

The mechanism of this unique H-D exchange is of considerable importance. The usual mechanism proposed for H-D exchange in d-block transition metals involves a series of reductive-elimination, oxidative-addition cycles. The prerequisite in this type of process is the ability of the metal atom to shuttle between two readily available oxidation states. This type of mechanism could be invoked to explain the exchange reaction in the uranium hydride since uranium (VI) is a well-known oxidation state. The observation that the thorium hydride also undergoes exchange at a comparable rate shows that such a process is not viable as thorium (VI) is unknown. Scheme III outlines an



Scheme III

alternative mechanism. The first step is hydride for deuteride exchange by way of a four-center transition state, so common in early p- and d-block chemistry (26, 27). Elimination of HD to form the ylide or its valence tautomer, the fully-developed metallocycle, then occurs. The ylide reacts or the metallocycle opens in the presence of deuterium yielding the di- deutero-compound which then reenters the cycle. The cyclic pathway is followed until all of the hydrogen atoms are exchanged by deuterium. The key to the mechanistic scheme is formation and opening of the metallocycle. Isolation of the metallocycle and

reaction of it with deuterium to yield the perdeutero-d strongly implies that the mechanistic scheme is essenti rect. The observation that the hydrides, $[(Me_3Si)_2N]_3M$ extrude hydrogen and form the metallocycle is added sup the essential validity of the proposed mechanism. Hydr activation of a related type has been shown for zirconi thorium or uranium (29).

Acknowledgement. I thank Dr. S. J. Simpson, Mr. H. W. and Mr. T. D. Tilley for providing the experimental res from which this account was constructed. I also thank Zalkin and Dr. D. H. Templeton for the crystal structur analysis, and Dr. N. M. Edelstein for much valuable ins into the electronic and magnetic properties of the f-bl elements. This work was supported by the Division of N Sciences, Office of Basic Energy Sciences, U. S. Depa of Energy.

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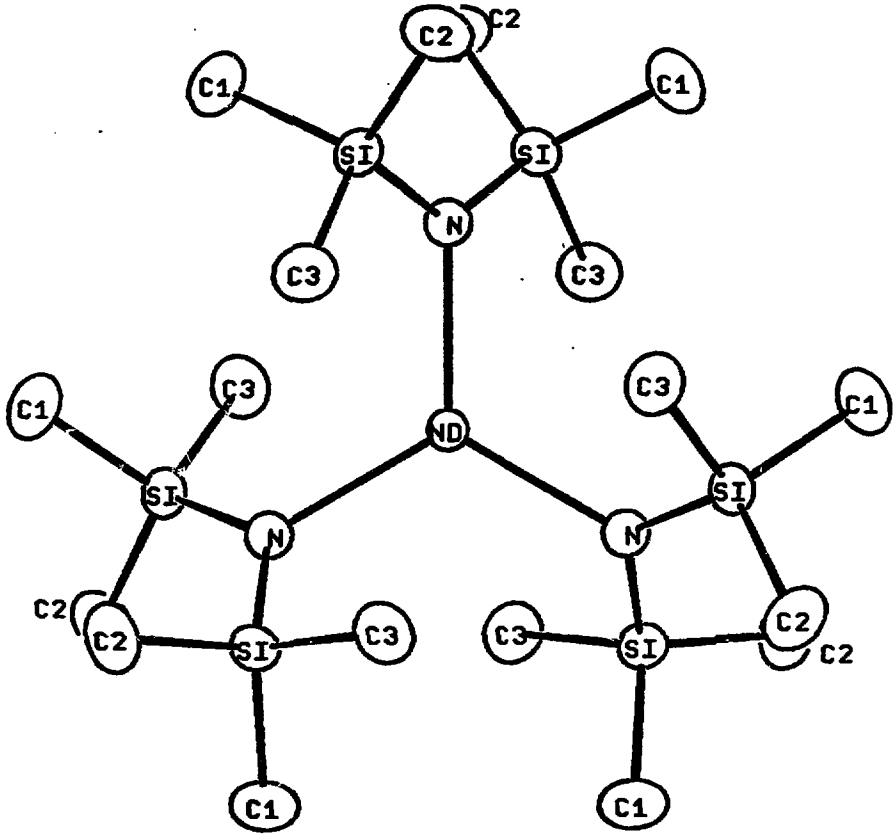
**Table II**
**Nuclear Magnetic Resonance Data**

| | | $^1$H NMR (δ) | $^{13}$C NMR (δ) |
|---|---|---|---|
| $[(Me_3Si)_2N]_2\overline{ThN(SiMe_3)SiMe_2CH_2}$ | | | |
| | $(Me_3Si)_2N$ | 0.37 | 3.46 q J=117 Hz |
| | $Me_3SiN$ | 0.38 | 4.52 q J=117 Hz |
| | $Me_2SiN$ | 0.56 | 5.55 q J=118 Hz |
| | $CH_2$ | 0.46 | 68.8 t J=120 Hz |
| $[(Me_3Si)_2N]_3ThMe$ | | | |
| | $(Me_3Si)_2N$ | 0.57 | 4.17 |
| | Me | 0.85 | 73.6 |
| $[(Me_3Si)_2N]_2\overline{UN(SiMe_3)SiMe_2CH_2}$ | | | |
| | $(Me_3Si)_2N$ | -23.3 | |
| | $Me_3SiN$ | -9.90 | |
| | $Me_2SiN$ | +2.08 | |
| | $CH_2$ | -128.6 | |
| $[(Me_3Si)_2N]_3UMe$ | | | |
| | $(Me_3Si)_2N$ | -1.49 | |
| | Me | -224 | |

**Figure Captions**

**Figure I** Molecular Structure of $Nd[N(SiMe_3)_2]_3$

**Figure II** Molecular Structure of $Eu[N(SiMe_3)_2]_2[MeOCH_2CH_2OMe]_2$; $N = N(SiMe_3)_2$, $O = MeOCH_2CH_2OMe$.




$ND(N(SI(CH_3)_3)_2)_3$

XBL 782-7162

Figure I

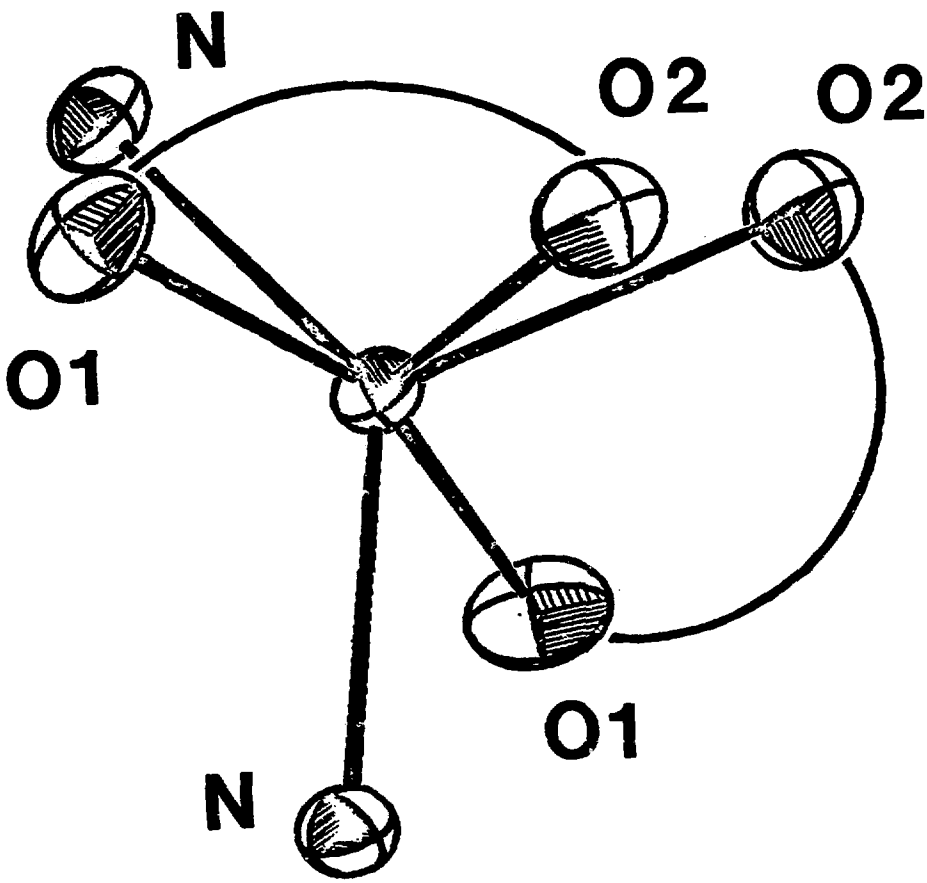



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Figure II