Title
ALKYL AND HYDRIDE BIS (TRIMETHYLSIYL)AMIDO DERIVATIVES OF THE ACTINIDE ELEMENTS: PREPARATION AND HYDROGEN-DEUTERIUM EXCHANGE

Permalink
https://escholarship.org/uc/item/75r6x74t

Author
Simpson, Stephen J.

Publication Date
2013-09-09
Submitted to the Journal of the American Chemical Society

ALKYL AND HYDRIDE BIS(TRIMETHYLSILYL)AMIDO DERIVATIVES OF THE ACTINIDE ELEMENTS; PREPARATION AND HYDROGEN-DEUTERIUM EXCHANGE

Stephen J. Simpson, Howard W. Turner, and Richard A. Andersen

September 1980

TWO-WEEK LOAN COPY
This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 6782.

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

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
Alkyl and Hydride Bis(trimethylsilyl)Amido Derivatives of the Actinide Elements; Preparation and Hydrogen-Deuterium Exchange

Stephen J. Simpson, Howard W. Turner, and Richard A. Andersen*

Contribution from Chemistry Department and Materials and Molecular Research Division of Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

Abstract

The monomeric, hydrocarbon-soluble monohydrides and monodeuterides of the actinide metals (thorium or uranium) of the type HM[N(SiMe₃)₂]₃ have been prepared. Their reaction chemistry, n-BuLi followed by MeBr yields MeM[N(SiMe₃)₂]₃ and borane in tetrahydrofuran yields BH₄M[N(SiMe₃)₂]₃, suggests that the hydrogen atom is hydridic. Pyrolysis of the hydrides yields the novel, four-membered ring metallocycle, [(Me₃Si)₂N]₂ - MCH₂Si(Me)₂NSiMe₃ where M is Th or U. These metallocycles are the key intermediates in the hydrogen-deuterium exchange reaction that yields 

\{[(CD₃)₃Si]₂N\}_₃MD.

*Chemistry Department, UCB.
Metal alkyl and hydride derivatives are important compounds in inorganic and organometallic chemistry. These functional groups are of interest in their own right as well as for their utility in organic synthesis. Though the organometallic and hydride derivatives of the p- and d-block elements are extensive, those of the f-block elements have been rather less extensively explored. The latter compounds are generally of the type \( \text{Cp}_3 \text{MR} \) where \( M \) is an actinide element or \( \text{Cp}_2 \text{MR} \) where \( M \) is a lanthanide element. In contrast to the rather extensive alkyl chemistry, only two hydride derivatives, \( \left( \text{Me}_5 \text{C}_5 \right)_4 \text{M}_2 \text{H}_4 \) (\( M = \text{Th} \) or \( \text{U} \)) are known though attempts at their preparation have been described.

The large size and "hard" acid character of the actinide elements affords, as a natural consequence, compounds with high coordination numbers with nitrogen or oxygen ligands. In order to prepare low-coordination number, volatile, and hydrocarbon soluble compounds of these metals, sterically bulky ligands are required. The bis(trimethylsilyl)amido ligand, \( \left( \text{Me}_3 \text{Si} \right)_2 \text{N} \), is ideally suited for this task. The steric bulk of this amide is shown, by way of example, by the observation that the uranium (III) species, \( \left[ \left( \text{Me}_3 \text{Si} \right)_2 \text{N} \right]_3 \text{U} \), is monomeric and three coordinate. Further, the tetravalent methyl and tetrahydroborate derivatives, \( \text{RM}[\text{N(SiMe}_3)_2]_3 \) where \( R \) is \( \text{Me} \) or \( \text{BH}_4 \) and \( M \) is \( \text{Th} \) or \( \text{U} \), are also monomeric. Since the simple methyls and tetrahydroborates can be prepared readily there is no reason why the simple hydride species should not exist.
Refluxing a tetrahydrofuran solution of four molar equivalents of sodium bis(trimethylsilyl)amide and uranium or thorium tetrachloride yields the hydrides, $\text{HM}[\text{N(SiMe}_3\text{)}_2]_3$, $M = \text{Th}$ or $\text{U}$. The hydrides may also be prepared from $\text{ClM}[\text{N(SiMe}_3\text{)}_2]_3$ and one molar equivalent of $\text{NaN(SiMe}_3\text{)}_2$ in refluxing tetrahydrofuran. Tetrahydrofuran is implicated as the hydrogen atom source since if the latter reaction is conducted in refluxing diethyl ether, benzene, or isooctane, the starting chloro-species, $\text{ClM}[\text{N(SiMe}_3\text{)}_2]_3$ is recovered quantitatively. This inference is substantiated by using perdeuterotetrahydrofuran as reaction solvent. In this solvent the deuteride, $\text{DM}[\text{N(SiMe}_3\text{)}_2]_3$, $M = \text{Th}$ or $\text{U}$, is isolated.

The observation that tetrahydrofuran is the source of the hydrogen atom is not unique, as it has been observed previously.\textsuperscript{8} The thorium hydride is colorless and diamagnetic. It is soluble in pentane from which it may be crystallized. The uranium hydride is brown-yellow, paramagnetic (μ\textsubscript{B} = 2.62 B.M.), and soluble in pentane. Both hydrides may be sublimed in vacuum at ca. 80-100°C, and afford monomeric molecular ions (M-2) in the mass spectrometer. They are also monomeric in the solid state.\textsuperscript{9} The thorium hydride has a Th-H stretching frequency in the infrared spectrum at 1480 cm\textsuperscript{-1} and the deuteride absorbs at 1060 cm\textsuperscript{-1}. The uranium-hydrogen stretching frequency occurs at 1430 cm\textsuperscript{-1} and that of the deuteride occurs at 1020 cm\textsuperscript{-1}. The low terminal metal-hydrogen stretching frequency is rather surprising.\textsuperscript{10} However, the metal-hydrogen stretching frequency in ($\text{Me}_5\text{C}_5\text{)}_2\text{TiH}_2$ and ($\text{Me}_5\text{C}_5\text{)}_2\text{ZrH}_2$ appear at 1560 and 1555 cm\textsuperscript{-1} respectively.\textsuperscript{11,12} Further, the zinc-hydride stretching frequency
in the dimeric amidozinc hydride, \((\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMeZnH})_2\)\(^2\), with terminal zinc hydrogen bonds, appears at 1695 cm\(^{-1}\).\(^{13}\) In the only other molecular hydrides that have been described for the actinide elements, \((\text{MeC}_5)_4\text{M}_2\text{H}_4\), where M is thorium or uranium, the absorptions associated with the thorium-hydrogen bond occur at 1406, 1361, 1215, and 1114 cm\(^{-1}\).\(^{3a}\)

The \(^1\text{H}\) nuclear magnetic resonance spectrum of the diamagnetic thorium hydride shows two absorptions at \(\delta \) 0.63 and \(\delta \) 0.37, the former being due to the unique hydride and the latter due to the \((\text{Me}_3\text{Si})_2\text{N}\) ligand. The \(\delta \) 0.63 absorption is absent in the deuteride. The \(^{13}\text{C}\) NMR spectrum is a quartet centered at \(\delta \) 6.80 (\(\text{J}_{\text{CH}} = 118\) Hz). We have been unable to find the hydride signal for the paramagnetic (\(f^2\)) uranium species though the \((\text{Me}_3\text{Si})_2\text{N}\) protons and carbons resonate at \(\delta \) -19.5 and \(\delta \) -40.8, respectively. By way of comparison the \(^{13}\text{C}\) NMR spectrum of the uranium (III) species, \(\text{U}[\text{N(SiMe}_3)_2]\)\(_3\) yields a quartet centered at \(\delta \) -71.9 (\(\text{J}_{\text{CH}} = 118\) Hz, 28°C, \(\nu_2 = 3\) Hz). The chemical shift of the Th-H resonance (\(\delta \) 0.63) in \(\text{HTh}[\text{N(SiMe}_3)_2]\)\(_3\) is not unusual since the hydride resonances in \((\text{Me}_5\text{C}_5)_2\text{MH}_2\) (M = Ti, Zr, or Hf) appear at \(\delta \) 0.28,\(^{11}\) 7.46,\(^{12}\) and 15.6\(^{12}\) respectively.

The spectroscopy indicates that the hydrides are indeed authentic mononuclear compounds with actinide-hydrogen bonds. This conclusion is further supported by chemical reactions (Scheme I). The hydrides can be converted quantitatively into the chloro-species \(\text{ClM}[\text{N(SiMe}_3)_2]\)\(_3\) and chloroform (detected by \(^1\text{H}\) NMR spectroscopy), a well-known reaction of transition metal hydrides.\(^{14}\) The hydrides may also be converted to the tetra-
\[
\text{ClM}[\text{N(SiMe}_3\text{)}_2]_3 \quad + \quad \text{CHCl}_3
\]

\[
\text{CCl}_4 \quad \text{D}_2 \quad \text{H}_2 \quad \text{thf}
\]

\[
\text{ClM}[\text{N(SiMe}_3\text{)}_2]_3 \quad \xrightarrow{\text{thf}} \quad \text{HM}[\text{N(SiMe}_3\text{)}_2]_3 \quad \xleftarrow{\text{UCl}_4 + \text{4NaN(SiMe}_3\text{)}_2} \quad \text{DM}[\text{N(Si(OD}_3\text{)}_2]_3
\]

\[
1) \text{Bu}^n\text{Li} \quad 2) \text{CF}_3\text{CO}_2\text{D} \quad 1) \text{Bu}^n\text{Li} \quad 2) \text{MeBr}
\]

\[
\text{DM}[\text{N(SiMe}_3\text{)}_2]_3 \quad \xrightarrow{2) \text{CF}_3\text{CO}_2\text{H}} \quad \text{BH}_4[\text{N(SiMe}_3\text{)}_2]_3 \quad \xrightarrow{1) \text{Bu}^n\text{Li}} \quad \text{MeM}[\text{N(SiMe}_3\text{)}_2]_3
\]

\[M = \text{Th or U}\]

**Scheme I**
hydroborate derivatives by reaction of borane in tetrahydrofuran. Further, the hydrogen atom can be removed by n-butyllithium. Though we have been unable to isolate the lithium-containing compounds, they may be converted to MeM[N(SiMe3)2]3 or DM[N(SiMe3)2]3 by further reaction with MeBr or CF3CO2D, respectively. Thus, the hydrogen atom in these actinide compounds is hydridic as is to be expected for a hydrogen atom bonded to an electropositive metal atom. Indeed, these actinide hydrides might be viewed profitably as a hydrocarbon soluble source of sodium hydride.

Another characteristic reaction of transition metal hydrides is their ability to undergo exchange reactions with deuterium. Exposure of the hydrides to deuterium results not only in exchange of the hydridic hydrogen atom but in exchange of all fifty-five hydrogen atoms in the molecule (Scheme I). Not surprisingly this process is reversible, viz., exposure of the perdeuterometal-deuteride to hydrogen yields the hydride. The extent of deuteration was determined by hydrolyzing the compound (NaOD in D2O) and analyzing the [(CD3)3Si]2ND by mass spectrometry. In the case of uranium, the extent of deuteration was > 97% and that for thorium was > 93%.

The mechanism of this exchange process is of obvious interest. Hydrogen for deuterium exchange processes are generally explained by a series of oxidative-addition, reductive-elimination cycles. This type of a mechanism can be invoked for uranium (IV) since the hexavalent oxidation state is well-known; however, thorium (VI) is unknown. The reverse process, a series of reductive-elimination,
oxidative-addition cycles, is worthy of consideration. Though neither thorium (II) nor uranium (II) compounds have been isolated, they in principle could exist as transition states. This pathway, shown in Scheme II, has its origins in cyclopentadienyl- and pentamethylcyclopentadienylmetal chemistry.\textsuperscript{18}

The first step is a reductive-elimination of bis(trimethylsilyl)amine giving (1) which undergoes an oxidative-addition of the $\gamma$-hydrogen atom giving metallocycle (2).\textsuperscript{19} Another reductive-elimination of bis(trimethylsilyl)amine gives (3) which undergoes oxidative-addition of deuterium yielding (4). Insertion of deuterium into the metal-carbon bond of the metallocycle giving (5) will generate a species that has a deuterium in the silylamide ligand. The remaining steps in the cycle will generate mono-deutero-[(Me\textsubscript{3}Si)\textsubscript{2}N]\textsubscript{3}MH. Repeating this process will generate the fully deuterated compound.

The key tenant of Scheme II is reductive-elimination of silylamine, (Me\textsubscript{3}Si)\textsubscript{2}NH. Thus the hydrides, HM[N(SiMe\textsubscript{3})\textsubscript{2}]\textsubscript{3}, should exchange with perdeutero silylamine, [(CD\textsubscript{3})\textsubscript{3}Si]\textsubscript{2}ND, giving a metal-containing product containing deuterium, since the equilibrium constant for the exchange of the amine with perdeuterosilylamine is unlikely to be zero. Stirring a solution of either (M = Th or U) undeuterated hydride with perdeuterosilylamine leads to recovery of the hydride compound with no deuterium incorporation. Thus, another mechanism is required to explain the results.

Such a mechanism is shown in Scheme III. This pathway involves the elimination of a $\gamma$-hydrogen atom of the silylamide as dihydrogen, yielding the four-membered ring metallocycle (6).
\[
\begin{align*}
\text{Scheme II}
\end{align*}
\]
Scheme III
This process could occur by a variety of processes that are discussed later. The key tenant of this mechanistic suggestion is the postulate of the metallocycle (6) as the key intermediate and that the metallocycle will undergo hydrogen for deuterium exchange. Thus, a synthetic route to the metallocycle is required. Some related metallocycles, \( \text{Cp}_2\text{TiCH}_2\text{Si(Me)}_2\text{NSiMe}_3^{20} \) and \([\text{Et}_2\text{N}]_3\text{TaCH(Me)NEt}^{21}\) have been prepared. The observation that thermal decomposition of \((\text{R}_2\text{N})_3\text{TiMe}\) gives methane, \(^{22}\) and presumably a metallocycle, suggests that thermal decomposition of the hydrides will afford the metallocycle (6) and dihydrogen. This has been observed, pyrolysis of the thorium or uranium hydrides or methyls yields the metallocycles and hydrogen or methane, respectively (Scheme IV). The uranium metallocycle may also be obtained from ethyl- or trimethylsilylmethyl-lithium and the mono-chloride, \(\text{ClU}[\text{N(SiMe}_3]_2\]_3\). The thorium metallocycle can be made from the analogous dialkyl-magnesium derivatives. In each case, ethane or tetramethylsilane, respectively, are the only gases liberated. It is noteworthy that the hypothetical ethyl derivative, \(\text{EtM}[\text{N(SiMe}_3]_2\]_3\), does not undergo \(\beta\)-hydrogen elimination to give ethylene and the hydride but the ethyl group abstracts a \(\gamma\)-hydrogen atom. The absence of a thermal \(\beta\)-hydrogen elimination process has been observed previously in organoactinide chemistry. \(^{23}\) The metallocycles (6) do indeed react with hydrogen or deuterium to yield the hydride or the perdeuterodeuteride, respectively. Thus our postulate that the metallocycle is a key intermediate in the hydrogen for deuterium exchange is supported. It is noteworthy that neither the chloro, nor the tetrahydroborate species, \(\text{XM}[\text{N(SiMe}_3]_2\]_3\) \((X = \text{Cl, BH}_4; M = \text{Th or U})\) undergo the
Scheme IV

\[
\begin{align*}
[\text{Me}_3\text{Si}]_2\text{N} \quad &\text{MR} \\
&\quad \Delta \\
&\quad \text{R} = \text{H or Me} \\
\uparrow &\quad \text{CH}_2 \\
\quad &\quad \text{SiMe}_2 \\
\quad &\quad \text{Me}_3\text{Si} \\
\quad &\quad \text{Me}_3\text{Si} \\
\quad &\quad \text{H}_2 \\
\quad &\quad \text{D}_2 \\
\quad &\quad \text{[(Me}_3\text{Si}]_2\text{N} \text{M} \\
\quad &\quad \text{[(CD}_3\text{Si}]_2\text{N} \text{MD}} \\
\quad &\quad \text{[Me}_3\text{Si}]_2\text{N} \text{Cl + R'}\text{Li or R}_2\text{'Mg} \\
&\quad \text{R'} = \text{Et or Me}_3\text{SiCH}_2
\end{align*}
\]

\( M = \text{Th or U} \)
hydrogen-deuterium exchange. Although the methyl derivatives
MeM[N(SiMe₃)₂]₃ do not undergo exchange with deuterium at 0°C,
they undergo slow exchange at room temperature. This is due to
the slow decomposition of the methyls to their respective metallo­
cycles at room temperature, as shown by monitoring the elimi­
nation of methane by ¹H NMR spectroscopy. Further, the uranium
(III) species, [(Me₃Si)₂N]₃U, does not undergo exchange with deu­
terium. These observations reinforce the pathway shown in Scheme III.

The conformation of the four-membered ring of the metallo­
cycle is of considerable interest. The ¹³C NMR spectrum of the
methylene resonance is a triplet centered at δ 68.8 with ¹J_CH equal to
120 Hz for the thorium compound. The coupling constant is normal
for a sp³-hybridized carbon atom. The methylene-carbon resonance
for the uranium species could not be observed, though the MeSi
resonances were observable. The ¹H nuclear magnetic resonance
spectrum of the thorium or uranium derivatives is temperature
independent from -85°C to +100°C, indicative of a planar ring. The
apparent planarity could be due to a rapid interconversion
(7a ⇌ 7b) since the methylene protons and methyl groups of the
Me₂Si unit in either 7a or 7b are chemically non-equivalent. If
this process was rapid on the NMR timescale, the proton and carbon
atoms would appear equivalent. It is unlikely that these protons
are chemical shift degenerate in the paramagnetic uranium compound,
since the chemical shifts of the other protons differ greatly.
On the other hand, the ring might be planar. X-ray crystallography
is the only way to answer this question, but we have been unable
to obtain suitable single crystals for such an analysis. In this
regard, the spirocyclic compounds, \([\text{t-BuNSi(Me)}_2 \text{(t-Bu)N}]_2 M\), where \(M\) is titanium or zirconium, have planar four-membered rings.\(^{24}\)

Further, all crystal structures of \([\text{(Me}_3\text{Si})(R)\text{N}]_x M\) compounds contain planar \(\text{MN(R)(SiMe}_3\) units.\(^4\)

Having shown that the metallocycle is a key intermediate in the hydrogen-deuterium exchange process, it is of interest to inquire into the pathway by which it is formed. Relevant experimental observations are, (a) the metallocycle can be prepared from the hydride by pyrolysis (ca. 200°C) of the neat solid; (b) no detectable concentration of the metallocycle is observed by \(^1\text{H NMR spectroscopy of the uranium hydride even on heating in toluene-d}_8\) at 90°C for 20 hours; (c) stirring a pentane solution of the hydrides with deuterium at room temperature for ten minutes leads to significant deuterium incorporation, as judged by infrared spectroscopy. Taken together these observations suggest that metallocycle formation is assisted by hydrogen (deuterium). These results are in accord with the findings of Schwartz and Brintzinger\(^{25}\) and they form a unified view of hydrogen activation in metal systems that are unable to undergo oxidative-addition reactions.
Experimental Section

All reactions were carried out under argon. Analyses were performed by the microanalytical laboratory of this department. Infrared spectra were recorded as Nujol mulls using a Perkin-Elmer 580 instrument. Mass spectra were obtained on a AEI-MS-12 machine equipped with a direct inlet. Proton and carbon NMR spectra were obtained at 89.56 MHz and 22.50 MHz respectively on a JEOL-FX 90 Q instrument in benzene-d$_6$ solution. The chemical shifts are expressed in δ-units relative to tetramethylsilane. Solution magnetic susceptibilities were determined by Evans' method using a Varian T-60 spectrometer. Gas chromatographic analyses were performed on a Varian Moduline Series 2700 instrument equipped with a thermal conductivity detector. The columns used were 10 ft. x 0.25 in. stainless steel containing either 50-80 mesh Porapak Q or 10% propylene carbonate on 80-100 mesh Chromsorb Q.

Hydridotris[bis(trimethylsilyl)amido]Thorium. (a) From Thorium Tetrachloride. Sodium bis(trimethylsilyl)amide (17.1 g, 0.0935 mol) in tetrahydrofuran (200 mL) was added to thorium tetrachloride (8.69 g, 0.0232 mol) suspended in tetrahydrofuran (200 mL). The suspension was refluxed for 84 h, allowed to settle, and the supernatant was decanted. The residue was extracted with tetrahydrofuran (2 x 40 mL) and the extracts were combined with the supernatant. The solvent was removed from the extracts under reduced pressure and the sticky mass was extracted with pentane (4 x 50 mL). The extracts were combined, concentrated to ca. 40 mL and cooled (-70°C). The white needles (9.8 g, 60%) were collected and dried under vacuum, mp 145-147°C. Anal. Calcd for C$_{18}$H$_{55}$N$_3$Si$_6$Th:
C, 30.3; H, 7.71; N, 5.89. Found: C, 30.2; H, 7.83; N, 5.94.
The mass spectrum shows a (M-2)$^+$ ion at 711. The Th-H absorption is at 1480 cm$^{-1}$ in the IR spectrum. $^1$H NMR consists of singlets at $\delta$ 0.63 and 0.37 due to $^{14}$N and $^{15}$N, respectively. The $^{13}$C NMR consists of a quartet centered at $\delta$ 6.80 ($J_{CH} = 118$ Hz).

(b) From $\text{ClTh}[\text{N(SiMe}_3\text{)}_2]$\textsubscript{3}. Sodium bis(trimethylsilyl)amide (0.21 g, 0.0013 mol) in tetrahydrofuran (30 mL) was added to chlorotris[bis(trimethylsilyl)amido]thorium (0.88 g, 0.0012 mol) in tetrahydrofuran (20 mL). After stirring at 60°C for 2 hr, the tetrahydrofuran was removed under reduced pressure and the residue was exposed to vacuum at 50°C for 2 hr. Extraction of the dry solid with pentane (2 x 30 mL) followed by filtration and concentration of the filtrate to ca. 6 mL gave white needles (0.75 g, 89%) on cooling (-70°C). The needles were shown to be $\text{HTh}[\text{N(SiMe}_3\text{)}_2]$\textsubscript{3} by IR and mp.

**Hydridotris[bis(trimethylsilyl)amido]Uranium.** (a) From $\text{Uranium Tetrachloride}$. Sodium bis(trimethylsilyl)amide (16.4 g, 0.0897 mol) in tetrahydrofuran (200 mL) was added to a solution of uranium tetrachloride (8.44 g, 0.0222 mol) in tetrahydrofuran (200 mL). The brown-green solution was refluxed for 20 hr., cooled to room temperature and the tetrahydrofuran was removed under reduced pressure. The sticky brown mass was exposed to vacuum at 50°C for 4 hr., then extracted with pentane (4 x 100 mL). The combined extracts were filtered, concentrated to ca. 40 mL and cooled (-70°C). The light brown needles (7.8 g, 48%) were collected and dried in vacuum, mp 97-98°C. Anal. Calcd for $\text{C}_{18}\text{H}_{55}\text{N}_3\text{Si}_6\text{U}$: C, 30.0; H, 7.64; N, 5.83. Found: C, 29.8; H, 7.74; N, 5.91.
The mass spectrum contained a (M-2)$^+$ at 717. The U-H stretching frequency was at 1430 cm$^{-1}$ in the infrared. The solution (benzene) magnetic moment at 31°C was 2.62 B.M. The $^1$H NMR spectrum consisted of a singlet at $\delta$-19.5 ($v_{1^H}$ = 9 Hz) and the $^{13}$C NMR spectrum consisted of a quartet centered at $\delta$ -49.8 ($J_{CH} = 118$ Hz). The half-width of the $^{13}$C($^1$H) resonance was 4 Hz. The uranium hydride was also prepared from ClU[N(SiMe$_3$)$_2$], and NaN(SiMe$_3$)$_2$ in refluxing tetrahydrofuran in a manner similar to that of HTh[N(SiMe$_3$)$_2$]$_3$ in 75% yield.

Reactions of Hydridotris[bis(trimethylsilyl)amido]Actinides with (a) Carbon Tetrachloride. The thorium hydride (0.37 g, 0.0052 mol) in pentane (40 mL) was treated with carbon tetrachloride (6.0 x 10$^{-3}$ mL, 0.62 mmol). After stirring for 15 min. the volatile material was removed under reduced pressure and the residue was extracted with pentane (2 x 30 mL). The extracts were combined, concentrated to ca. 10 mL and cooled (-20°C). The colorless prisms were collected, dried under vacuum, and shown to be ClTh[N(SiMe$_3$)$_2$]$_3$ by IR and mp. Yield was 0.24 g (62%). In a separate experiment, carbon tetrachloride was added to the hydride in tetrahydrofuran-d$_8$ in a NMR tube. Chloroform was the only organic product observed by NMR. The uranium hydride behaves similarly; the yield of ClU[N(SiMe$_3$)$_2$]$_3$ was 70%. (b) n-Butyllithium and Methylbromide. n-Butyllithium (0.12 mL of a 2.4 M hexane solution, 0.29 mmol) was added to a solution of hydridotris[bis(trimethylsilyl)amido]uranium (0.20 g, 0.00028 mol) in pentane (35 mL) at 35°C. The dark red solution was stirred for 2 min., then rapidly cooled to 0°C. Methylbromide was bubbled through the solution
for 2 min., and the light brown solution was stirred for 10 min. (0°C). The solution was filtered and the volatile material was removed under reduced pressure. Crystallization of the brown residue from pentane (-20°C) yielded brown-yellow crystals which were collected and dried under vacuum. The crystals (0.16 g, 78%) were identified as MeU[NSiMe3]3 by comparison of their IR and mp with those of an authentic specimen. The methylthorium analogue, MeTh[NSiMe3]3, was prepared in 50% yield in an analogous manner. (c) Borane in Tetrahydrofuran. The tetrahydrofuran complex of borane (1 mL of a 1.0 M tetrahydrofuran solution, 1.0 mmol) was added to hydridotris[bis(trimethylsilyl)amido]thorium (0.21 g, 0.29 mmol) in tetrahydrofuran (50 mL) at 0°C. After stirring the colorless solution for 15 h at 0°C, the tetrahydrofuran was evaporated and pentane (50 mL) was added to the sticky residue. Filtration, followed by concentration of the filtrate to ca. 15 mL and cooling (-20°C) yielded colorless prisms (0.12 g, 57%) which were collected and dried under vacuum. The crystals were identified as BH4Th[NSiMe3]3 by IR and mp.6 The uranium analogue was prepared similarly in 60% yield.

Deuterotris[bis(trimethylsilyl)amido]Thorium. A solution of hydridotris[bis(trimethylsilyl)amido]thorium (0.20 g, 0.28 mmol) in pentane (40 mL) was maintained at 35°C while a solution of n-butyllithium (0.12 mL of a 2.4 M hexane solution, 0.29 mmol) was added. The pale yellow solution was stirred for 2 min., then treated with monodeutero-trifluoroacetic acid (2.3 x 10^-3 mL, 0.30 mmol). The volatile material was immediately removed under reduced pressure and the white residue was crystallized as white
needles from pentane (0.17 g, 85%), mp 144-146°C. Anal. Calcd for C_{18}H_{54}N_{3}Si_{6}Th: C, 30.3; H, 7.83; N, 5.89. Found: C, 30.1; H, 7.66; N, 5.92. The Th-D stretching frequency in the infrared was observed at 1060 cm\(^{-1}\). The \(^1\)H NMR spectrum consisted of a singlet at \(\delta\ 0.38\). The deuteride was also prepared (85% yield) from ClTh[N(SiMe\(_3\)]\(_3\) and NaN(SiMe\(_3\))\(_2\) in refluxing tetrahydrofuran-d\(_8\).

Deuterotris[bis(trimethylsilyl)amido]uranium. n-Butyllithium (0.16 mL of a 2.4 M hexane solution, 0.38 mmol) was added to a solution of hydridotris[bis(trimethylsilyl)amido]uranium (0.28 g, 0.39 mmol) in pentane (60 mL) maintained at 35°C. The dark red solution was immediately treated with mono-deuterotri-fluoroacetic acid (3.0 x 10\(^{-3}\) mL, 0.39 mmol). The volatile material was immediately removed under reduced pressure from the brown-green solution. The brown residue was crystallized as light brown needles from pentane (-20°C) in 90% (0.25 g) yield, mp 98-99°C. Anal. Calcd for C_{18}H_{54}N_{3}Si_{6}U: C, 30.0; H, 7.78; N, 5.83. Found: C, 30.1; H, 7.59; N, 5.90. The U-D stretching frequency was observed at 1020 cm\(^{-1}\) in the IR. The \(^1\)H NMR spectrum was a singlet at \(\delta\ -19.4\ (28°C)\) with \(\nu_{1/2} = 10\) Hz. The deuteride was also prepared from ClU[N(SiMe\(_3\)]\(_2\)\(_3\) and NaN(SiMe\(_3\))\(_2\) in refluxing tetrahydrofuran-d\(_8\) in 90% yield.

Preparation of [(Me\(_3\)Si\(_2\)]\(_2\)ThCH\(_2\)Si(Me\(_2\)NSiMe\(_3\)]\(_2\). (a) From MeTh[N(SiMe\(_3\)]\(_2\)\(_3\). Methyltris[bis(trimethylsilyl)amido]thorium (1.34 g, 0.00184 mol) contained in a Schlenk tube (175 mL capacity) under one atmosphere of argon was heated to 140°C over 45 min. using an oil bath. The colorless melt was carefully run into a
thin film round the bottom of the Schlenk tube and heated at 150-160°C for 10 min (until sublimation was evident). The melt was then allowed to cool to room temperature and purified either by vacuum sublimation (100°C) in ca. 60% yield or crystallized from pentane (-70°C) in ca. 60% yield. The colorless needles melted at 109-111°C. Anal. Calcd for C_{18}H_{53}N_{3}Si_{6}Th: C, 30.3; H, 7.45; N, 5.90. Found: C, 30.0; H, 7.14; N, 5.69. A molecular ion, M^+, was observed at 711 in the mass spectrometer. The $^1$H NMR spectrum consisted of singlets at δ 0.37, 0.38, 0.49, and 0.56 in area ratio 36:9:2:6 due to [(Me$_3$Si)$_2$N]$_2$Th, Me$_3$SiNTh, CH$_2$Th, and Me$_2$SiCH$_2$Th, respectively. The $^{13}$C NMR spectrum consisted of quartets centered at δ 3.46 ($J_{CH} = 117$ Hz), 4.52 ($J_{CH} = 117$ Hz), 5.55 ($J_{CH} = 118$ Hz) due to [(Me$_3$Si)$_2$N]$_2$Th, Me$_3$SiN, and Me$_2$SiCH$_2$Th, respectively, and a triplet centered at δ 68.8 ($J_{CH} = 120$ Hz) due to Me$_2$SiCH$_2$Th. In a separate experiment, the gases formed upon pyrolysis were examined by gas chromatography and shown to be only methane. The metallocycle may be obtained by pyrolysis of HTh[N(SiMe$_3$)$_2$]$_3$ in a similar fashion to a final temperature of 180-190°C in 20% yield. (b) From ClTh[N(SiMe$_3$)$_2$]$_3$ and Et$_2$Mg.

Diethylmagnesium (0.30 mL of a 0.88 M diethyl ether solution, 0.26 mmol) was added to a solution of chlorotris[bis(trimethylsilyl)-amido]thorium (0.38 g, 0.00051 mol) in diethyl ether (100 mL) 0°C. After stirring at 0°C for 24 h the solvent was removed under reduced pressure at 0°C. The pale yellow residue was extracted with pentane (2 x 50 mL), filtered, and the filtrate was concentrated to ca. 5 mL and cooled (-70°C). The colorless blocks were collected and dried under vacuum. Yield was 0.28 g
(77%). The compound was identified by comparison of its IR and mp with an authentic specimen. Gas chromatographic analysis of the vapor above the reaction mixture prior to commencement of the work-up showed that ethane was the only hydrocarbon present. Reaction of the chloro-amide with \((\text{Me}_3\text{SiCH}_2)_2\text{Mg}\) under similar conditions gives the metallocycle and tetramethylsilane.

Preparation of \([\text{Me}_3\text{Si}]_2\text{N}_2\text{CH}_2\text{Si(Me)}_2\text{NSiMe}_3\). (a) From \(\text{MeU[N(SiMe}_3)_2\text{]}\). The uranium metallocycle was prepared in a similar manner as that of the thorium metallocycle just described in ca. 85% yield. The compound was isolated either by vacuum sublimation (110°C) or crystallization from pentane (-70°C) as yellow needles, mp 126-129°C. Anal. Calcd for \(\text{C}_{18}\text{H}_{53}\text{N}_3\text{Si}_6\text{U}\): C, 30.1; H, 7.39; N, 5.86. Found: C, 29.8; H, 7.14; N, 5.77. The mass spectrum contained a \(M^+\) ion at 717. The magnetic susceptibility in benzene solution (30°C) was 2.71 B.M. The \(^1H\) NMR spectrum (28°C) consists of singlets at \(\delta\) 2.08, -9.90, -23.3, and -128.6 in area ratio 6:9:36:2 due to \(\text{Me}_2\text{SiCH}_2\text{U}\), \(\text{Me}_3\text{SiNU}\), \([\text{Me}_3\text{Si}]_2\text{N}\text{U}\) and \(\text{Me}_2\text{SiCH}_2\text{U}\), respectively. The \(^{13}C\) NMR spectrum (28°C) afforded quartets centered at \(\delta\) 49.6 (\(J_{\text{CH}} = 118\text{ Hz}\)), 24.5 (\(J_{\text{CH}} = 118\text{ Hz}\)), and -40.8 (\(J_{\text{CH}} = 118\text{ Hz}\)) due to \(\text{Me}_2\text{SiCH}_2\text{U}\), \(\text{Me}_3\text{SiNU}\), and \([\text{Me}_3\text{Si}]_2\text{N}\text{U}\), respectively. The methylene carbon atoms could not be observed. Gas chromatographic analysis of the gases above the melt indicated that methane was the only organic hydrocarbon present. (b) From \(\text{ClU[N(SiMe}_3)_2\text{]}_3\) and \(\text{EtLi}\). Ethyllithium (6.0 mL of a 0.47 M toluene solution, 2.8 mmol) was added to a solution of chlorotris[trimethylsilyl]amido]uranium (2.1 g, 0.0028 mol) in pentane (150 mL) at 0°C. The resulting dark yellow solution was stirred at 0°C for
16 h, then the volatile material was removed under reduced pressure at 0°C. The brown mass was exposed to vacuum for 3 h. Extraction of the dry residue with pentane (2 x 40 mL) followed by filtration and concentration of the filtrate to ca. 20 mL and cooling (-70°C) yielded bright yellow needles. The needles (1.8 g, 90%) were collected and dried under vacuum. The needles were identified by IR and mp. The gases above the reaction mixture were shown to be ethane by gas chromatographic analysis. The analogous reaction using Me₃SiCH₂Li in hexane rather than EtLi yielded the metallocycle in 60% yield and tetramethylsilane as the sole gaseous product.

Preparation of [((CD₃)₃Si]₂N]UD. Hydridotris[bis(trimethylsilyl)amido]uranium (0.76 g, 0.00011 mol) in pentane (80 mL) was stirred under deuterium in a thick-walled bottle (100 mL) fitted with a pressure-cap at a total pressure of 15 atm for 48 h. The gas above the solution was vented and the bottle was recharged. After a further 48 h the process was repeated three additional times using reaction times of 24 h. Finally the solution was transferred to a Schlenk tube and the solvent was removed under reduced pressure. Crystallization of the brown residue from pentane (-70°C) gave light brown blocks which were collected and dried under vacuum. Yield was 0.52 g (64%), mp 95-97°C. Anal. Calcd for C₁₈D₅₅N₃Si₆U: C, 27.9; D, 14.2; N, 5.43. Found: C, 27.8; D, 13.8; N, 5.34. The infrared spectrum contained C-D and U-D stretching frequencies at 2210 and 1027 cm⁻¹, respectively. In order to assay the extent of deuteration, the deuterated specimen (0.30 g, 0.00042 mol) was finely ground and exposed to vacuum
for 3 h at 50°C. The flask was cooled to 0°C and a solution of sodium deuteroxide in deuterium oxide (0.5 mL of a 4M solution, 2.0 mmol) was added. The closed system was stirred for 1 min. at 30°C and the volatile material was distilled into a cooled (-196°C) receiver under vacuum. The distillate was allowed to stand over molecular sieves (4X) for 30 min. and the clear organic product (ca. 0.2 mL) was decanted into a dry capillary tube. The mass spectrum of the liquid was recorded at 15 eV and 70 eV. Analysis of the envelope from m/e 160-180 by standard methods revealed that the amine was > 97% deuterated. 27 The metallocycle,

\[
[(\text{Me}_3\text{Si})_2\text{N}]_2\text{UCH}_2\text{Si(Me)}_2\text{NSiMe}_3,
\]

was deuterated in an analogous fashion to that of its thorium analogue, described above. The isolated yield was 60%, m.p. 144-147°C. Anal. Calcd for C\(_{18}\)D\(_{55}\)N\(_3\)Si\(_6\)Th: C, 28.1; D, 14.3; N, 5.49. Found: C, 28.4; D, 13.7; N, 5.54. The deuterium content of the amine upon deuterolysis was > 91%, statistically distributed.

Other Deuteration Studies. The hydrides do not exchange with benzene-d\(_6\) (refluxing, 24 h) nor with [(CD\(_3\))\(_3\)Si]\(_2\)ND (pentane solution at room temperature for 24 h). Neither (Me\(_3\)Si)\(_2\)NH, NaN(SiMe\(_3\))\(_2\), U[N(SiMe\(_3\))\(_2\)]\(_3\) nor the derivatives XM[N(SiMe\(_3\))\(_2\)]\(_3\), where X is Cl or BH\(_4\) and M is Th or U, exchange with deuterium (1-20 atm) at room temperature for periods of 24-36 h. The methyl derivatives, MeM[N(SiMe\(_3\))\(_2\)]\(_3\) where M is Th or U, do not exchange with deuterium (1-20 atm) in pentane at 0°C over a 36 h period.
Acknowledgement  This work was supported by the Division of Nuclear Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under Contract W-7405-ENG-48.
References


