and benzene were vacuum transferred from sodium/benzophenone ketyl solutions while CD_2Cl_2 was vacuum transferred from Linde 4-Å molecular sieves and degassed through four freeze-pump-thaw cycles on a vacuum line.

NMR experiments were carried out as follows. A standard NMR tube fused to a 14/20 ground-glass joint was loaded with the desired compounds in the drybox, capped with a Teflon needle valve, placed on a vacuum line, and evacuated at −196 °C. The tube was charged with the desired amount of solvent by vacuum transfer out of a graduated tube of solvent. The NMR tube was sealed and carefully thawed before any heating cycles were undertaken. All heating was accomplished in a Precision Scientific model H-11 constant-temperature bath.

The phosphine inhibition experiment was set up by dissolving equal amounts of **1** (17.0 mg, 0.0397 mmol) and **2** (25.0 mg, 0.0386 mmol) into NMR tubes with joints. Into one tube was weighed 104 mg of PPh_3-d_{15} (0.376 mmol). The two tubes were then charged with toluene-d_8 solvent to bring the volume of the solutions to 600 μL. The tubes were sealed as before.

After completion of a reaction, the volatile components were vacuum transferred into another tube, under inert conditions, and analyzed by standard NMR, IR, VPC, and mass spectral methods. The nonvolatile components were then similarly isolated and analyzed by standard methods. Nonvolatile products of the iron reactions were analyzed as a mixture by NMR and IR comparisons to known compounds. Mixtures of cobalt alkyls were purified by air-free column chromatography on silica gel using benzene/hexane as the eluant. The mixture was recrystallized from benzene/hexane.

Acknowledgment. We are grateful for financial support of this work from the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract No. W-7405-48. H.E.B. was supported by a Fannie and John Hertz Foundation Fellowship.

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Preparation and Hydrogen-Deuterium Exchange of Alkyl and Hydride Bis(trimethylsilyl)amido Derivatives of the Actinide Elements

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Received February 5, 1981

The monomeric, hydrocarbon-soluble monohydrides and monodeuterides of the actinide metals (thorium or uranium) of the type $HM[N(SiMe_3)_2]_3$ have been prepared. Their reaction chemistry—*n*-BuLi followed by MeBr yields $MeM[N(SiMe_3)_2]_3$ and borane in tetrahydrofuran yields $BH_4M[N(SiMe_3)_2]_3$—suggests that the hydrogen atom is hydridic. Pyrolysis of the hydrides yields the novel, four-membered ring metallacycle $[(Me_3Si)_2N]_2\overline{MCH_2Si(Me)_2N}SiMe_3$ where M is Th or U. These metallacycles are the key intermediates in the hydrogen-deuterium exchange reaction that yields $\{[(CD_3)_3Si]_2N\}_3MD$.

Metal alkyl and hydride derivatives are important compounds in inorganic and organometallic chemistry.[1a] These functional groups are of interest in their own right as well as for their utility in organic synthesis.[1b,c] 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 Cp_3MR where M is an actinide element or Cp_2MR where M is a lanthanide element.[2] In contrast to the rather extensive alkyl chemistry, only two hydride derivatives, $(Me_5C_5)_4M_2H_4$ (M = Th or U), are known[3a,b] though attempts at their preparation have been described.[3c,d]

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. For preparation of low-coordination-number, volatile, and hydrocarbon-soluble compounds of these metals, sterically bulky ligands are required. The bis(trimethylsilyl)amido ligand, $(Me_3Si)_2N$, is ideally suited for this task.[4] The steric bulk of this amide is shown, by way of example, by the observation that the uranium(III) species $[(Me_3Si)_2N]_3U$ is monomeric and three coordinate.[5] Further, the tetravalent methyl and tetrahydroborate derivatives $RM[N(SiMe_3)_2]_3$ where R is Me or BH_4 and M is Th or U are also monomeric.[6] Since the simple methyls and tetrahydroborates can be prepared readily there is no reason why the simple hydride species should not exist.[7]

Refluxing a tetrahydrofuran solution of 4 molar equiv of sodium bis(trimethylsilyl)amide and uranium or thorium tetrachloride yields the hydrides $HM[N(SiMe_3)_2]_3$, M = Th or U. The hydrides may also be prepared from $ClM[N(SiMe_3)_2]_3$ and 1 molar equiv of $NaN(SiMe_3)_2$ 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 $ClM[N(SiMe_3)_2]_3$ is recovered quantitatively. This inference is substantiated by using perdeuteriotetrahydrofuran as reaction solvent. In this solvent the deuteride $DM[N(SiMe_3)_2]_3$, M = Th or U, is isolated. The observation that tetrahydrofuran is the source of the hydrogen atom is not unique, as it has been observed previously.[8]

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(1) (a) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; Wiley: New York, 1980; pp 1113-1182. (b) *Ibid.*; pp 1234-1309. (c) Parshall, G. W. "Homogeneous Catalysis"; Wiley: New York, 1980.

(2) (a) Marks, T. J. *Prog. Inorg. Chem.* **1978**, *24*, 51-107. (b) *Ibid.* **1979**, *25*, 223-333. (c) Cotton, S. A. *J. Organomet. Chem. Libr.* **1977**, *3*, 189-222. (d) Raymond, K. N. In "Organometallics of the f-Elements"; Marks, T. J., Fischer, R. D., Eds.; Reidel Publishing Co.: Dordrecht, Holland, 1979; pp 249-280.

(3) (a) Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3939-3941. (b) Broach, R. W.; Schultz, A. J.; Williams, J. M.; Brown, G. M.; Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *Science (Washington, D.C.)* **1979**, *203*, 172-174. (c) Zanella, P.; Rosetto, G.; DePaoli, G.; Traverso, O. *Inorg. Chim. Acta* **1980**, *44*, L155-L156. (d) McLaren, A. B.; Kanellakopulos, B.; Dornberger, E. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 233-235.

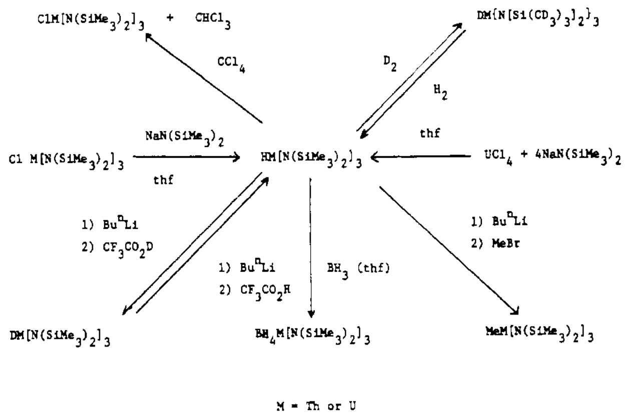
(4) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. "Metal and Metalloid Amides"; Halsted Press: New York, 1980.

(5) Andersen, R. A. *Inorg. Chem.* **1979**, *18*, 1507-1509.

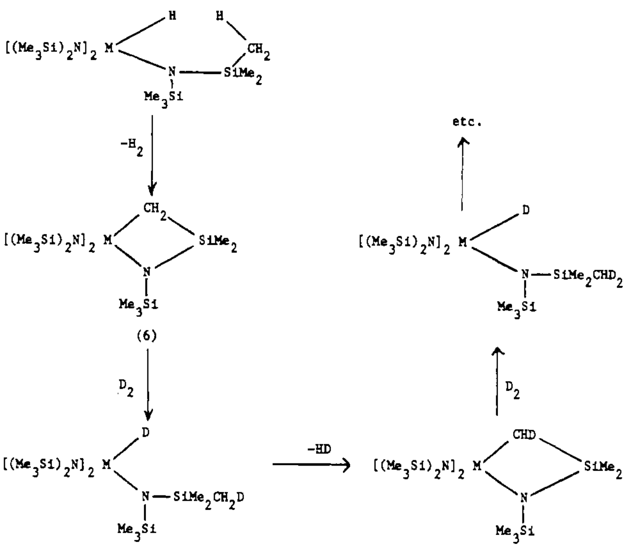
(6) Turner, H. W.; Andersen, R. A.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1979**, *18*, 1221-1224.

(7) Two communications have appeared: (a) Turner, H. W.; Simpson, S. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 2782-2782. (b) Simpson, S. J.; Turner, H. W.; Andersen, R. A. *Ibid.* **1979**, *101*, 7728-7729.

Scheme I



Scheme II



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 ($\mu = 2.62\ \mu_B$) and soluble in pentane. Both hydrides may be sublimed under 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.[9] The thorium hydride has a Th–H stretching frequency in the infrared spectrum at 1480 cm^{-1}, and the deuteride absorbs at 1060 cm^{-1}. The uranium–hydrogen stretching frequency occurs at 1430 cm^{-1} and that of the deuteride occurs at 1020 cm^{-1}. The low terminal metal–hydrogen stretching frequency is rather surprising.[10] However, the metal–hydrogen stretching frequency in $(Me_5C_5)_2TiH_2$ and $(Me_5C_5)_2ZrH_2$ appear at 1560 and 1555 cm^{-1}, respectively.[11,12] Further, the zinc–hydride stretching frequency in the dimeric amidozinc hydride $(Me_2NCH_2CH_2NMeZnH)_2$ 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, $(Me_5C_5)_4M_2H_4$, 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 ^1H nuclear magnetic resonance spectrum of the diamagnetic thorium hydride shows two absorptions at δ 0.63 and 0.37, the former being due to the unique hydride and the latter due to the $(Me_3Si)_2N$ ligand. The δ 0.63 absorption is absent in the deuteride. The ^{13}C NMR spectrum is a quartet centered at δ 6.80 ($^1J_{CH}$ = 118 Hz). We have been unable to find the hydride signal for the paramagnetic (f^2) uranium species though the $(Me_3Si)_2N$ protons and carbons resonate at δ −19.5 and −40.8, respectively. By way of comparison the ^{13}C NMR spectrum of the uranium(III) species, $U[N(SiMe_3)_2]_3$ yields a quartet centered at δ −71.9 (J_{CH} = 118 Hz, 28 °C, $\nu_{1/2}$ = 3 Hz). The chemical shift of the Th–H resonance (δ 0.63) in $HTh[N(SiMe_3)_2]_3$ is not unusual since the hydride resonances in $(Me_5C_5)_2MH_2$ (M = Ti, Zr, or Hf) appear at δ 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 $ClM[N(SiMe_3)_2]_3$ and chloroform (detected by ^1H NMR spectroscopy), a well-known reaction of transition–metal hydrides.[14] The hydrides may also be converted to the tetrahydroborate derivatives by reaction of borane in tetrahydrofuran.[15] In this sense, the actinide hydrides might be profitably viewed as a hydrocarbon soluble source of sodium hydride. On the other hand, the hydrogen atom can be removed by butyllithium.[16] Though we have been unable to isolate the lithium containing compounds, they may be converted to $MeM[N(SiMe_3)_2]_3$ or $DM[N(SiMe_3)_2]_3$ by further reaction with MeBr or CF_3CO_2D, respectively. In this sense, the hydrogen atom is not hydridic but protonic. Thus, the actinide hydrides appear to be amphoteric.

Another characteristic reaction of transition-metal hydrides is their ability to undergo exchange reactions with deuterium.[17] Exposure of the hydrides to deuterium results not only in exchange of the hydridic hydrogen atom but in exchange of all 55 hydrogen atoms in the molecule (Scheme I). Not surprisingly this process is reversible, viz., exposure of the perdeuteriometal deuteride to hydrogen yields the hydride. The extent of deuteration was determined by hydrolyzing the compound (NaOD in D_2O) and analyzing the $[(CD_3)_3Si]_2ND$ 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.[17] 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

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(8) (a) Wailes, P. C.; Weingold, H. *J. Organomet. Chem.* **1970**, *14*, 405–411. (b) Domaille, P. J.; Foxman, B. M.; McNeese, T. J.; Wreford, S. S. *J. Am. Chem. Soc.* **1980**, *102*, 4114–4120 and references therein.

(9) Andersen, R. A.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1981**, *20*, 622.

(10) (a) Kaesz, H. D.; Saillant, R. B. *Chem. Rev.* **1972**, *72*, 231–281. (b) Schunn, R. A. In "Transition Metal Hydrides"; Muetterties, E. L., Ed.; Dekker: New York, 1971; pp 203–269.

(11) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219–1238.

(12) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716–2724.

(13) (a) Bell, N. A.; Coates, G. E. *J. Chem. Soc. A* **1968**, 823–826. (b) Bell, N. A.; Moseley, P. T.; Shearer, H. M. M.; Spencer, C. B. *J. Chem. Soc., Chem. Commun.* **1980**, 359–360.

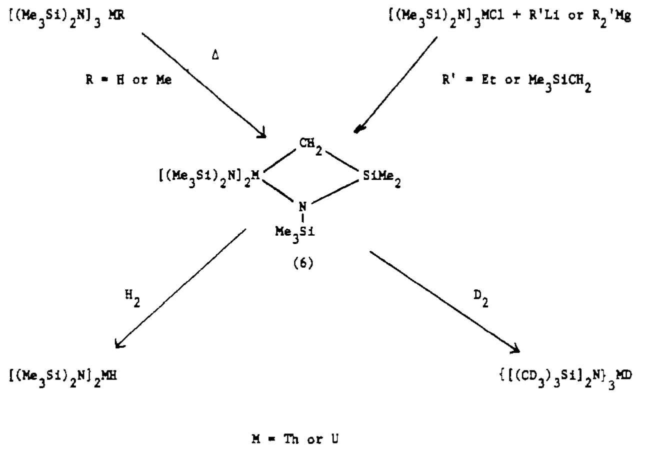
(14) (a) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104–124. (b) Cooper, R. L.; Green, M. L. H. *Z. Naturforsch.* **1964**, *B19*, 652–652.

(15) (a) Schlesinger, H. I.; Brown, H. C.; Hoekstra, H. R.; Rapp, L. R. *J. Am. Chem. Soc.* **1953**, *75*, 199–204. (b) James, B. D.; Wallbridge, M. L. H. *Prog. Inorg. Chem.* **1970**, *11*, 99–231.

(16) (a) Cooper, R. L.; Green, M. L. H.; Moelwyn-Hughes, J. T. *J. Organomet. Chem.* **1962**, *3*, 261–268. (b) Francis, B. R.; Green, M. L. H.; Luong-Thi, T.; Moser, G. A. *J. Chem. Soc., Dalton Trans.* **1976**, 1339–1345. (c) Green, M. L. H.; Simpson, S. J. *J. Organomet. Chem.* **1979**, *173*, 287–292.

(17) (a) Strathdee, G.; Given, R. *Can. J. Chem.* **1974**, *52*, 2216–2215. (b) *Ibid.* **1975**, *53*, 1402–1409. (c) Parshall, G. W. *Acc. Chem. Res.* **1970**, *3*, 139–144. (d) *Ibid.* **1975**, *8*, 113–117. (e) Webster, D. E. *Adv. Organomet. Chem.* **1977**, *15*, 147–186.

Scheme III

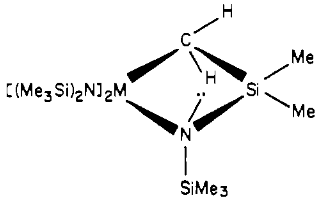


cycles, is worthy of consideration. Though neither thorium(II) nor uranium(II) compounds have been isolated, they in principle could exist as transition states. This possible pathway has its origins in cyclopentadienyl- and (pentamethylcyclopentadienyl)metal chemistry.[18] Thus, a reductive elimination of $(Me_3Si)_2NH$ would give a divalent species which could undergo an oxidative addition of a γ-hydrogen atom giving tetravalent metallacycle hydride. There is precedent for this process.[19] Another reductive elimination of $(Me_3Si)_2NH$ followed by oxidative addition of deuterium and insertion of deuterium into the metal–carbon bond of the metallacycle will generate a species that has deuterium in the silylamide ligand. Repeating this process will generate the fully deuterated compound.

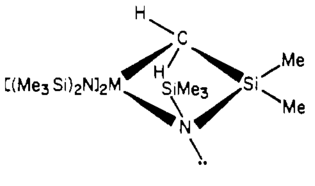
The key tenet of this mechanism is reductive elimination of silylamine, $(Me_3Si)_2NH$. Thus the hydrides $HM[N(SiMe_3)_2]_3$ should exchange with perdeuteriosilylamine, $[(CD_3)_3Si]_2ND$, giving a metal-containing product containing deuterium since the equilibrium constant for the exchange of the amine with perdeuterioamine is unlikely to be zero. Stirring a solution of either (M = Th or U) undeuterated hydride with perdeuteriosilylamine 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 is Scheme II. This pathway involves the elimination of a γ-hydrogen atom of the silylamide as dihydrogen, yielding the four-membered ring metallacycle **6**. This process could occur by a variety of processes that are discussed later. The key tenant of this mechanistic suggestion is the postulate of metallacycle **6** as the key intermediate and that the metallacycle will undergo hydrogen for deuterium exchange. Thus, a synthetic route to the metallacycle is required. Some related metallacycles, $Cp_2TiCH_2Si(Me)_2NSiMe_3$[20] and $[Et_2N]_3TaCH(Me)NEt$,[21] have been prepared. The observation that thermal decomposition of $(R_2N)_3TiMe$ gives methane,[22] and presumably a metallacycle, suggests that thermal decomposition of the hydrides will afford the metallacycle (**6**) and dihydrogen. This has been observed; pyrolysis of the thorium or uranium hydrides or methyls yields the metallacycles and hydrogen or methane, respectively (Scheme III). The uranium metallacycle may also be obtained from ethyl- or [(trimethylsilyl)methyl]lithium and the monochloride $ClU[N(SiMe_3)_2]_3$. The thorium metallacycle can be made from the analogous dialkylmagnesium derivatives. In each case, ethane or tetramethylsilane, respectively, are the only gases liberated. It is noteworthy that the hypothetical ethyl derivative $EtM[N(SiMe_3)_2]_3$ does not undergo β-hydrogen elimination to give ethylene and the hydride but the ethyl group abstracts a γ-hydrogen atom. The absence of a thermal β-hydrogen elimination process has been observed previously in organoactinide chemistry.[23] The metallacycles **6** do indeed react with hydrogen or deuterium to yield the hydride or the perdeuteriodeuteride, respectively. Thus our postulate that the metallacycle is a key intermediate in the hydrogen for deuterium exchange is supported. It is noteworthy that neither the chloro nor the tetrahydroborate species $XM[N(SiMe_3)_2]_3$ ($X = Cl, BH_4$; M = Th or U) undergoes the hydrogen-deuterium exchange. Although the methyl derivatives $MeM[N(SiMe_3)_2]_3$ 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 metallocycles at room temperature, as shown by monitoring the elimination of methane by ^1H NMR spectroscopy. Further, the uranium(III) species $[(Me_3Si)_2N]_3U$ does not undergo exchange with deuterium. These observations reinforce the pathway shown in Scheme II.

The conformation of the four-membered ring of the metallacycle is of considerable interest. The ^{13}C 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 sp^3-hydridized 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 to +100 °C, indicative of a planar ring. The apparently planarity could be due to a rapid interconversion (**7a** $\rightleftarrows$ **7b**) since the methylene protons and methyl groups of the Me_2Si unit in either **7a** or **7b** are chemically nonequivalent. If this process was rapid on the NMR time scale, 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 spirocycle compounds $[t\text{-}BuNSi(Me)_2(t\text{-}Bu)N]_2M$, where M is titanium or zirconium, have planar four-membered rings.[24] Fur-



7a



7b

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[18] (a) Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1324–1331. (b) Cannillo, E.; Prout, K. *Acta Crystallogr., Sect. B* **1977**, *B33*, 3916–3918. (c) McAlister, D. R.; Erwin, D. K.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 5966–5968. (d) Davies, S. G.; Felkin, H.; Watts, O. *J. Chem. Soc., Chem. Commun.* **1980**, 159–160.

[19] (a) Foley, P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1979**, *101*, 2732–2733. (b) Andersen, R. A.; Jones, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1978**, 446–453.

[20] Bennett, C. R.; Bradley, D. C. *J. Chem. Soc., Chem. Commun.* **1974**, 29–30.

[21] (a) Takahashi, Y.; Onoyama, N.; Ishikawa, Y.; Motojima, S.; Sigiyama, K. *Chem. Lett.* **1978**, 525–528. (b) Airoldi, C.; Bradley, D. C.; Vuru, G. *Transition Met. Chem.* **1979**, *4*, 64–65.

[22] Bürger, H.; Neese, H. J. *J. Organomet. Chem.* **1970**, *21*, 381–388.

[23] (a) Marks, T. J.; Seyam, A. M.; Kolb, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 5529–5539. (b) Marks, T. J.; Wachter, W. A. *J. Am. Chem. Soc.* **1976**, *98*, 703–710.

[24] Brauer, D. J.; Bürger, H.; Essig, E.; Geschwandtner, W. *J. Organomet. Chem.* **1980**, *190*, 343–351.

ther, all crystal structures of $[(Me_3Si)(R)N]_xM$ compounds contain planar $MN(R)(SiMe_3)$ units.[4]

Having shown that the metallacycle 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 as follows: (a) the metallacycle can be prepared from the hydride by pyrolysis (ca. 200 °C) of the neat solid; (b) no detectable concentration of the metallacycle is observed by ^1H NMR spectroscopy of the uranium hydride even on heating in toluene-d_8 at 90 °C for 20 h; (c) stirring a pentane solution of the hydrides with deuterium at room temperature for 10 min leads to significant deuterium incorporation, as judged by IR spectroscopy. Taken together these observations suggest that metallacycle 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 with use of 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 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 susceptabilities were determined by Evans' method using a Varian T-60 spectrometer.[26] Gas chromatographic analyses were performed on a Varian Moduline Series 2700 instrument equipped with a thermal conductivity detector. The columns used were 10 ft. × 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 and allowed to settle, and the supernatant was decanted. The residue was extracted with tetrahydrofuran (2 × 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 × 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 $C_{18}H_{55}N_3Si_6Th$: 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. ^1H NMR consists of singlets at δ 0.63 and 0.37 due to ThH and $Th[N(SiMe_3)_2]_3$, respectively. The ^{13}C NMR consists of a quartet centered at δ 6.80 (J_{CH} = 118 Hz).

(b) From $ClTh[(SiMe_3)_2]_3$. 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 being stirred at 60 °C for 2 h, tetrahydrofuran was removed under reduced pressure and the residue was exposed to vacuum at 50° C for 2 h. Extraction of the dry solid with pentane (2 × 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 $HTh[N(SiMe_3)_2]_3$ by IR and mp.

Hydridotris[bis(trimethylsilyl)amido]uranium. From 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 h and cooled to room temperature, and tetrahydrofuran was removed under reduced pressure. The sticky brown mass was exposed to vacuum at 50 °C for 4 h and then extracted with pentane (4 × 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 under vacuum; mp 97–98 °C. Anal. Calcd for $C_{18}H_{55}N_3Si_6U$: 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 μ_B. The ^1H NMR spectrum consisted of a singlet at δ –19.5 ($\nu_{1/2}$ = 9 Hz), and the ^{13}C NMR spectrum consisted of a quartet centered at δ –40.8 (J_{CH} = 118 Hz). The half-width of the $^{13}C\{^1H\}$ resonance was 4 Hz. The uranium hydride was also prepared from $ClU[N(SiMe_3)_2]_3$ 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. (a) With Carbon Tetrachloride. Thorium hydride (0.37 g, 0.0052 mol) in pentane (40 mL) was treated with carbon tetrachloride (6.0 × 10^{-3} mL, 0.62 mmol). After the solution was stirred for 15 min, the volatile material was removed under reduced pressure and the residue was extracted with pentane (2 × 30 mL). The extracts were combined, concentrated to ca. 10 mL and cooled (–20 °C). The colorless prisims were collected, dried under vacuum, and shown to be $ClTh[N(SiMe_3)_2]_3$ by IR and mp. the 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 similarily; the yield of $ClU[N(SiMe_3)_2]_3$ was 70%.

(b) With Butyllithium and Methyl Bromide. 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, 0.000 28 mol) in pentane (35 mL) at 35 °C. The dark red solution was stirred for 2 min and then rapidly cooled to 0 °C. Methyl bromide 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 $MeU[N(SiMe_3)_2]_3$ by comparison of their IR and mp with those of an authentic specimen.[6] The methylthorium analogue $MeTh[N(SiMe_3)_2]_3$ was prepared in 50% yield in an analogous manner.

(c) With 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 the colorless solution was stirred for 15 h at 0 °C, 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 $BH_4Th[N(SiMe_3)_2]_3$ by IR and mp.[6] The uranium analogue was prepared similarly in 60% yield.

Deuteriotris[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 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 and then treated with deuteriotrifluoroacetic acid (2.3 × 10^{-3} mL, 0.30 mmol). The volatile material was immediately removed under reduced pressure, and the white residue was recrystallized as white needles from pentane (0.17 g, 85%); mp 144–146 °C. Anal. Calcd for $C_{18}H_{54}DN_3Si_6Th$: 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 ^1H NMR spectrum consisted of a singlet at δ 0.38. The deuteride was also prepared (85% yield) from $ClTh[N(SiMe_3)_2]_3$ and $NaN(SiMe_3)_2$ in refluxing tetrahydrofuran-d_8.

Deuteriotris[bis(trimethylsilyl)amido]uranium. 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 deuteriotrifluoroacetic acid (3.0 × 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 $C_{18}H_{54}DN_3Si_6U$: 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 ^1H

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(25) (a) Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1978**, *100*, 3246–3248. (b) Brintzinger, H. H. *J. Organomet. Chem.* **1979**, *171*, 337–344. (c) Schwartz, J. *Pure Appl. Chem.* **1980**, *52*, 733–740.

(26) Evans, D. F. *J. Chem. Soc.* **1958**, 2003–2005.

NMR spectrum was a singlet at δ −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 $[(Me_3Si)_2N]_2\overline{ThCH_2Si(Me)_2N}SiMe_3$. (a) From $MeTh[N(SiMe_3)_2]_3$. Methyltris[bis(trimethylsilyl)amido]thorium (1.34 g, 0.001 84 mol) contained in a Schlenk tube (175-mL capacity) under 1 atm of argon was heated to 140 °C over 45 min with an oil bath. The colorless melt was carefully run into a thin film around 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 $C_{18}H_{53}N_3Si_6Th$: 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 *m/e* 711 in the mass spectrometer. The ^1H 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 $[(Me_3Si)_2N]_2Th$, Me_3SiNTh, CH_2Th, and Me_2SiCH_2Th, respectively. The ^{13}C NMR spectrum consisted of quartets centered at δ 3.46 (J_{CH} = 117 Hz), 4.52 (J_{CH} = 117 Hz), and 5.55 (J_{CH} = 118 Hz) due to $[(Me_3Si)_2N]_2Th$, Me_3SiN, and Me_2SiCH_2Th, respectively, and a triplet centered at δ 68.8 (J_{CH} = 120 Hz) due to $Me_2Si\mathit{CH}_2Th$. In a separate experiment, the gases formed upon pyrolysis were examined by gas chromatography and shown to be only methane. The metallacycle 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_2Mg. 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, 0.000 51 mol) in diethyl ether (100 mL) 0 °C. After the solution was stirred 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 × 50 mL) and filtered, and the filtrate was concentrated to ca. 5 mL and cooled (−70 °C). The colorless blocks were collected and dried under vacuum. The 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 workup showed that ethane was the only hydrocarbon present. Reaction of the chloroamide with $(Me_3SiCH_2)_2Mg$ under similar conditions gives the metallacycle and tetramethylsilane.

Preparation of $[(Me_3Si)_2N]_2\overline{UCH_2Si(Me)_2N}SiMe_3$. (a) From $MeU[N(SiMe_3)_2]_3$. The uranium metallacycle was prepared in manner similar to that of the thorium metallacycle 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 $C_{18}H_{53}N_3Si_6U$: 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 *m/e* 717. The magnetic susceptibility in benzene solution (30 °C) was 2.71 μ_B. The ^1H NMR spectrum (28 °C) consists of singlets at δ 2.08, −9.90, −23.3, and −128.6 in area ratio 6:9:36:2 due to Me_2SiCH_2U, Me_3SiNU, $[(Me_3Si)_2N]U$ and $Me_2Si\mathit{CH}_2U$, respectively. The ^{13}C NMR spectrum (28 °C) afforded quartets centered at δ 49.6 (J_{CH} = 118 Hz), 24.5 (J_{CH} = 118 Hz), and −40.8 (J_{CH} = 118 Hz) due to Me_2SiCH_2U, Me_3SiNU, and $[(Me_3Si)_2N]_2U$, respectively. The methylene carbon atom could not be observed. Gas chromatograpic analysis of the gases above the melt indicated that methane was the only organic hydrocarbon present.

(b) From $ClU[N(SiMe_3)_2]_3$ and EtLi. Ethyllithium (6.0 mL of a 0.47 M toluene solution, 2.8 mmol) was added to a solution of chlorotris[bis(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, and 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 × 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 Me_3SiCH_2Li in hexane rather than EtLi yielded the metallacycle in 60% yield and tetramethylsilane as the sole gaseous product.

Preparation of $\{[(CD_3)_3Si]_2N\}_3UD$. Hydridotris[bis(trimethylsilyl)amido]uranium (0.76 g, 0.000 11 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. The yield was 0.52 g (64%); mp 95–97 °C. Anal. Calcd for $C_{18}D_{55}N_3Si_6U$: 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, we finely ground the deuterated specimen (0.30 g, 0.000 42 mol) and exposed it to vacuum for 3 h at 50 °C. The flask was cooled to 0 °C, and a solution of sodium deuterioxide in deuterium oxide (0.5 mL of a 4 M 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 (4×) 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 and 70 eV. Analysis of the envelope from *m/e* 160 to 180 by standard methods revealed that the amine was ≥97% deuterated.[27] The metallacycle $[(Me_3Si)_2N]_2\overline{UCH_2Si(Me)_2N}SiMe_3$ was deuterated in an analogous fashion to that of its thorium analogue, described above. The isolated yield was 60%; mp 144–147 sC. Anal. Calcd for $C_{18}D_{55}N_3Si_6Th$: 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 $[(CD_3)_3Si]_2ND$ (pentane solution at room temperature for 24 h). Neither $(Me_3Si)_2NH$, $NaN(SiMe_3)_2$, $U[N(SiMe_3)_2]_3$, 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-- period.

Acknowledgment. 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.

Registry No. $HTh[N(SiMe_3)_2]_3$, 70605-07-1; $HU[N(SiMe_3)_2]_3$, 70605-08-2; $ClTh[N(SiMe_3)_2]_3$, 51700-07-3; $ClU[N(SiMe_3)_2]_3$, 69517-42-6; $MeU[N(SiMe_3)_2]_3$, 69517-44-8; $MeTh[N(SiMe_3)_2]_3$, 69517-43-7; $BH_4Th[N(SiMe_3)_2]_3$, 69532-06-5; $BH_4U[N(SiMe_3)_2]_3$, 69532-07-6; $DTh[N(SiMe_3)_2]_3$, 70605-09-3; $DU[N(SiMe_3)_2]_3$, 70605-10-6; $[(Me_3Si)_2N]_2\overline{ThCH_2Si(Me)_2N}SiMe_3$, 72557-95-0; $[(Me_3Si)_2N]_2\overline{UCH_2Si(Me)_2N}SiMe_3$, 72472-77-6; $\{[(CD_3)_3Si]_2N\}_3UD$, 72472-78-7; $\{[(CD_3)_3Si]_2N\}_3ThD$, 72472-79-8.

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[27] (a) Tamas, J.; Ujszazy, K.; Szekely, T.; Bujjas, G. *Acta Chim. Acad. Sci. Hung.* **1969**, *62*, 335–355. (b) Budzikiewicz, H.; Djerassi, C.; Williams, D. H. "Structural Elucidation of Natural Compounds by Mass spectrometry"; Holden-Day: San Francisco, 1961; Vol. 1, pp 34–36.