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

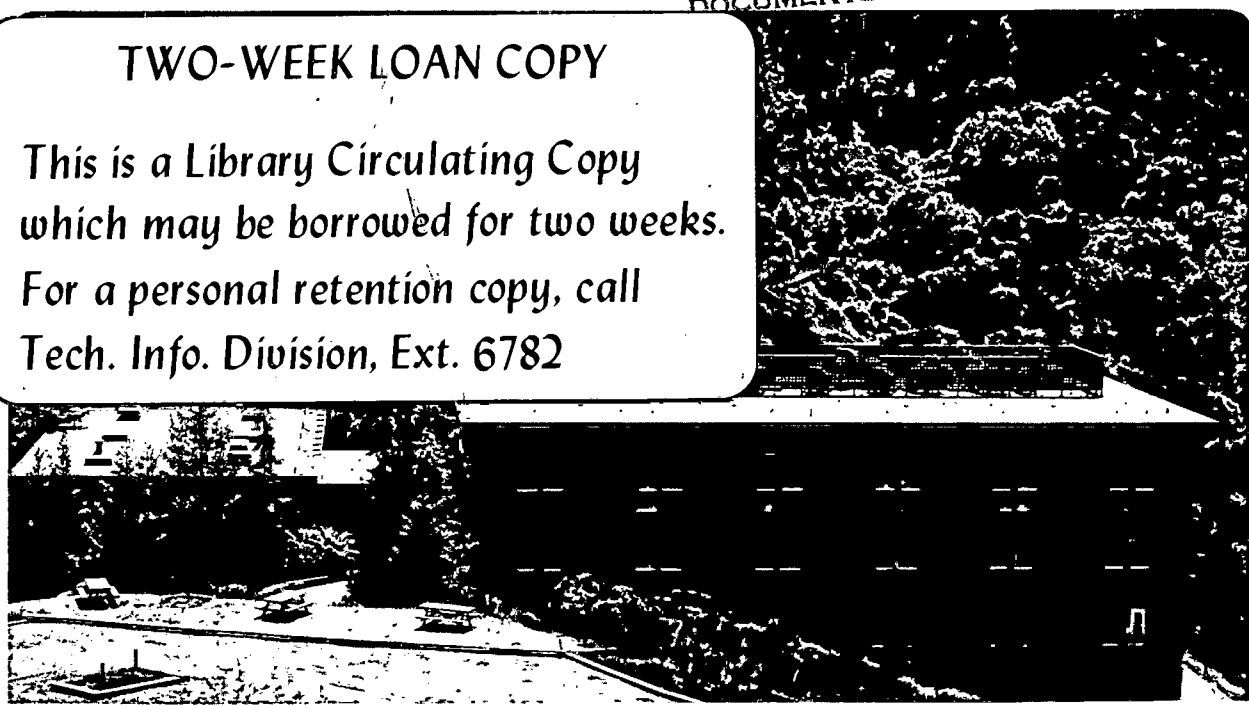
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Hydrogen-Deuterium Exchange; Perdeutero-HydridoTris(hexamethyl-
disilyl)amido-Thorium(IV) and -Uranium(IV)

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

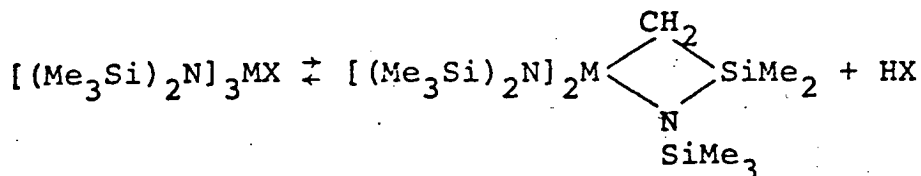
Abstract: The hydrides, $\text{HM}[\text{N}(\text{SiMe}_3)_2]_3$ where M is thorium or uranium, react with deuterium (1 atm, room temperature in pentane) to give the perdeutero-derivatives, $\text{DM}[\text{N}[\text{Si}(\text{CD}_3)_3]_2]_3$. The mechanism for exchange of 55-hydrogen atoms with deuterium is suggested to proceed by way of a metallocyclic intermediate $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{MN}(\text{SiMe}_3)-(\text{SiMe}_2)\text{CH}_2$, which has been isolated and characterized.

Sir: Hydrogen-deuterium exchange is a topic of current interest relative to hydrocarbon C-H-bond activation.^{1,2} The mechanism of these transition-metal assisted processes is thought to proceed by way of oxidative-addition, reductive-elimination sequences and is therefore applicable to metals which can shuttle between two accessible oxidation states. In this communication we describe a novel H-D exchange process in $\text{HU}[\text{N}(\text{SiMe}_3)_2]_3$ and $\text{HTh}[\text{N}(\text{SiMe}_3)_2]_3$, examples of f^2 and f^0 electronic configuration, respectively.

Stirring a pentane solution of $\text{HU}[\text{N}(\text{SiMe}_3)_2]_3^3$ under deuterium (1 atm, 40 equivalents/5 cycles, room temperature) results in complete exchange of all hydrogen atoms for deuterium yielding $\text{DU}\{\text{N}[\text{Si}(\text{CD}_3)_3]_2\}_3$, $\nu_{\text{CD}} = 2210 \text{ cm}^{-1}$, $\nu_{\text{UD}} = 1027 \text{ cm}^{-1}$, mp, 95-97 °C.⁴ Elemental analysis⁵, absence of a ^1H NMR spectrum, and isolation of $[(\text{CD}_3)_3\text{Si}]_2\text{ND}$ after hydrolysis⁶ confirms that all fifty-five hydrogen atoms have been exchanged for deuterium. The exchange reaction is reversible since the perdeutero-compound exchanges with molecular hydrogen to give $\text{HU}[\text{N}(\text{SiMe}_3)_2]_3$. Neither the methyl-, tetrahydroborato-, chloro-tris(hexamethyldisilyl)amido uranium analogues⁷ nor the uranium (III) species, $\text{U}[\text{N}(\text{SiMe}_3)_2]_3^8$, exchange with deuterium under similar conditions.

The observation of H-D exchange in the uranium (IV) species might be rationalized by a series of oxidative-addition, reductive elimination cycles since uranium (VI) is a well-known oxidation state. This mechanism would be implicated by the lack of H-D exchange in the corresponding thorium derivative, $\text{HTh}[\text{N}(\text{SiMe}_3)_2]_3$, as thorium (VI) is unknown. However, the thorium hydride undergoes complete exchange under similar conditions yielding $\text{DTh}\{\text{N}[\text{Si}(\text{CD}_3)_3]_2\}_3$, $\nu_{\text{CD}} = 2207 \text{ cm}^{-1}$, $\nu_{\text{ThD}} = 1060 \text{ cm}^{-1}$, mp, 144-147 °C.¹¹ Elemental analysis¹², lack of a ^1H NMR spectrum, and mass spectroscopic analysis¹³ confirms that the f^0 -hydride undergoes complete exchange.

Insight into the mechanism of exchange is assisted by isolation of the four-membered ring metallobutane, $[(\text{Me}_3\text{Si})_2\text{N}]_2\overline{\text{MN}(\text{SiMe}_3)-(\text{SiMe}_2\text{CH}_2)}$ where M is thorium or uranium by pyrolysis of the thorium or uranium hydrides (neat, 180-190°C, 1 atm) or methyls (neat, 150-160°C, 1 atm). The colorless diamagnetic thorium deriva-



M = Th or U; X = H or Me

tive¹⁴ mp, 109-111°C, yields a ¹H NMR spectrum (which is temperature independent to -85°C) at 180 MHz which consists of four single resonances at δ 0.37, 0.38, 0.49, and 0.56 in area ratio 36:9:2:6 due to (Me₃Si)₂N, Me₃Si, CH₂, and Me₂Si respectively. The ¹³C NMR spectrum proves the metallocycle formation since it consists of three quartets centered at δ 5.55 (J_{CH} = 118 Hz), 4.52 (J_{CH} = 117 Hz), and 3.46 (J_{CH} = 117 Hz) due to the carbon atoms of Me₂Si, Me₃Si, and (Me₃Si)₂N groups respectively and a triplet centered at δ 68.8 (J_{CH} = 120 Hz) due to the methylene carbon atom. The bright yellow, paramagnetic (μ_B = 2.7 B.M. at 30°C by Evans' method) uranium metallocycle¹⁴ mp, 126-129°C was further characterized by its ¹H NMR spectrum which consists of four singlets at δ +2.08, -9.90, -23.3, and -128.6 in area ratio 6:9:36:2 due to Me₂Si, Me₃Si, (Me₃Si)₂N, and CH₂ groups, respectively. An X-ray analysis is in progress.¹⁵ The only volatile, organic product isolated from pyrolysis of the hydrides is hydrogen and methane from pyrolysis of the methyl derivatives. The transformation is reversible in the case of X = H since exposure of the metallocycles to an atmosphere of molecular hydrogen yields the hydrides. Further, exposure of the metallocycles to deuterium yields the per-deutero-thorium or uranium amides. The uranium metallocycle can also be prepared by reaction of [(Me₃Si)₂N]₃UCl and ethyllithium or trimethylsilylmethyl lithium, the organic product being ethane or tetramethylsilane, respectively.

Observation of the facile hydride-metallocycle interconversion suggests the mechanism shown in the Scheme. The first step

in the Scheme proposes that metal-hydride-deuterium exchange occurs by way of a four-center interaction similar to that proposed by Schwartz to account for metal H-D exchange in $\text{Cp}_2\text{Zr(H)(R)}$.¹⁶ The next step is elimination of HD yielding the ylide (A) or its valence tautomer, the fully-developed metallocycle (B). This intermediate is the key to the mechanistic proposal since it allows incorporation of the deuterium label into the silylamido ligands. This scrambling mechanism is rather different than that proposed by Bercaw to account for formation of perdeutero- $(\text{Me}_5\text{C}_5)_2\text{ZrH}_2$ which occurs by conventional oxidative-addition, reductive elimination steps though these authors isolate a compound which is thought to be $(\text{Me}_5\text{C}_5)\overline{\text{ZrMe}_3\text{C}_5(\text{CH}_2)_2}$.¹⁷

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2. Webster, D. E. Adv. Organomet. Chem. 1977, 15, 147-186.
3. Turner, H. W.; Simpson, S. J.; Andersen, R. A. J. Am. Chem. Soc. 1979, 101, 2782-2782.
4. Melting point of the undeuterated hydride is 97-98°C.³
5. Analysis of $C_{18}D_{55}N_3Si_6U$ requires C, 27.9; D, 14.2; N, 5.43%. Found: C, 27.8; D, 13.7; N, 5.34%.
6. The perdeutero-amide was hydrolyzed with NaOD in D_2O and the amine was transferred in vacuum to a vessel which was connected to a mass spectrometer. Analysis of the fragmentation pattern relative to that of undeuterated amine^{7,8} showed that the amine was $\geq 98\%$ deuterated.
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11. Melting point of the undeuterated hydride is 145-147°C.³
12. Analysis of $C_{18}D_{55}N_3Si_6Th$ requires C, 28.1; D, 14.3; N, 5.49%. Found: C, 28.4; D, 13.6; N, 5.54%.
13. The amine is $\geq 91\%$ deuterated.^{6,7,8}
14. Satisfactory C,H and N analysis and a monomeric molecular ion by

mass spectrometry were obtained.

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