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HYDRIDO(TRIS(HEXAMETHYLDISILYLAMIDO))-THORIUM(IV) AND -URANIUM(IV)

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and Richard A. Andersen

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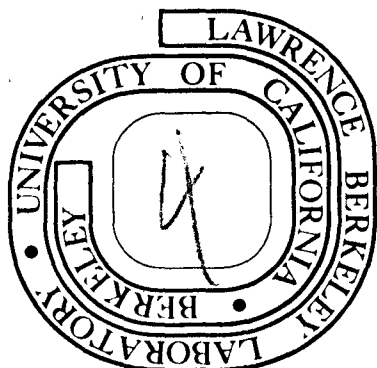
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Hydrido[Tris(hexamethyldisilylamido)]-Thorium(IV) and -Uranium(IV)

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

Abstract: Reaction of chlorotris(hexamethyldisilylamido)-thorium(IV) or uranium(IV) and sodium hexamethyldisilylamide in refluxing tetrahydrofuran or perdeuterotetrahydrofuran yields monomeric hydrido-[tris(hexamethyldisilylamido)]-thorium(IV) or -uranium(IV), or its deuteride, respectively. The hydrides react with carbon tetrachloride yielding chloroform and  $ClM[N(SiMe_3)_2]_3$  where M is thorium or uranium. Further, the hydrides with n-butyllithium followed by methylbromide or deuterio-trifluoroacetic acid afford  $MeM[N(SiMe_3)_2]_3$  or  $DM[N(SiMe_3)_2]_3$ , respectively, M = Th or U.

Sir: Metal hydrides are known for most of the metals. The 4f- and 5f-block metals, except those of the man-made ones, form rather stable metallic, binary hydrides of the type  $MH_2$  and  $MH_3^1$ . In contrast, only one molecular hydride of the f-block metals has been described, viz.,  $(Me_5C_5)_4M_2H_4$  where M is thorium or uranium.<sup>2</sup> We wish to describe the first monomeric, mono-hydride derivatives of these metals, viz.,  $HTh[N(SiMe_3)_2]_3$  and  $HU[N(SiMe_3)_2]_3$ .

Reaction of chlorotris(hexamethyldisilylamido)thorium(IV)<sup>3</sup> with one molar equivalent of sodium hexamethyldisilylamide in refluxing tetrahydrofuran yields hydridotris(hexamethyldisilylamido)thorium as white needles from pentane,<sup>4</sup> mp 145-147°C,  $\nu_{ThH} = 1480 \text{ cm}^{-1}$ ,

$^1\text{HNMR}$  (PhH)  $\delta$ 0.90 and 0.40 due to the hydride and trimethylsilyl resonances, respectively. The deuteride,  $\text{DTh}[\text{N}(\text{SiMe}_3)_2]$ ,  $\nu_{\text{ThD}} = 1060 \text{ cm}^{-1}$  can be prepared by refluxing  $\text{ClTh}[\text{N}(\text{SiMe}_3)_2]_3$  and  $\text{NaN}(\text{SiMe}_3)_2$  in perdeutero-tetrahydrofuran. The uranium hydride and deuteride were prepared similarly. Hydridotris(hexamethylidisilylamido)uranium was crystallized from pentane as brown-yellow needles<sup>4</sup>, mp 97-98°C,  $\nu_{\text{UH}} = 1430 \text{ cm}^{-1}$ ,  $\nu_{\text{UD}} = 1020 \text{ cm}^{-1}$ . We have been unable to locate the hydride signal in the  $^1\text{HNMR}$  spectrum of this paramagnetic ( $\mu_{\text{B}} = 2.6 \text{ B.M.}$  in benzene solution) substance, though the trimethylsilyl groups resonate at  $\delta$ -19.5. The hydrides can also be prepared from  $\text{ClM}[\text{N}(\text{SiMe}_3)_2]_3$  and tert-butyllithium or lithium triethylhydridoborate in pentane.

The metal-bound hydrides were further characterized by their reaction chemistry, see scheme. The hydrides react with carbon tetrachloride yielding chloroform (identified by its NMR spectrum) and  $\text{ClM}[\text{N}(\text{SiMe}_3)_2]_3$ , M is thorium or uranium. The latter were identified by mp, mixed mp, ir, and NMR spectra. Further, addition of n-butyllithium to a pentane solution of the hydrides followed by methylbromide yields  $\text{MeM}[\text{N}(\text{SiMe}_3)]_3^3$ , M = Th or U quantitatively. The product from reaction of n-butyllithium with the hydride derivatives affords  $\text{SHM}[\text{N}(\text{SiMe}_3)_2]_3$  or  $\text{DM}[\text{N}(\text{SiMe}_3)_2]_3$  (M is Th or U) upon addition of trifluoroacetic acid or deuterio-trifluoroacetic acid, respectively.

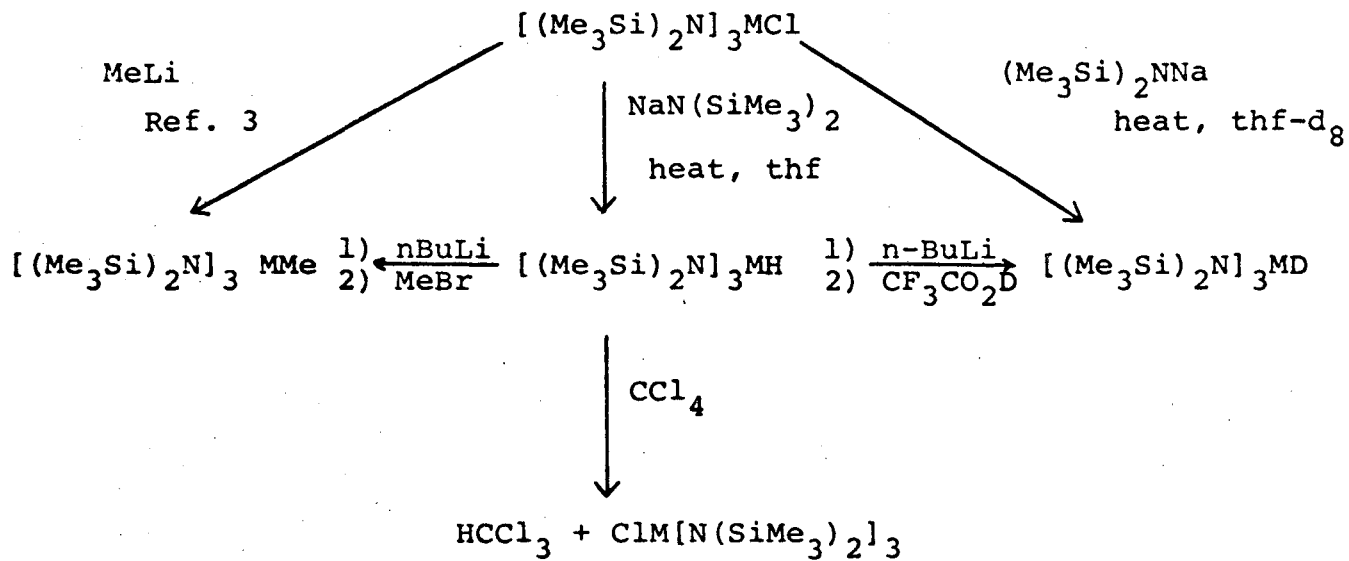
The uranium and thorium hydrides have also been characterized by a single crystal X-ray analysis, though the hydrogen atom was not located.<sup>5</sup>

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4. All new compounds gave satisfactory elemental analysis for C, H, and N and molecular ions (M-2) in the mass spectrometer.
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M = Th, U

Scheme



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