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Author
Turner, H.W.

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

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

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 deutero-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.[2] 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)[3] with one molar equivalent of sodium hexamethyldisilylamide in refluxing tetrahydrofuran yields hydridotris(hexamethyldisilylamido)thorium as white needles from pentane,[4] mp 145-147°C, νThH = 1480 cm^{-1},

^{1}HNMR (PhH) δ0.90 and 0.40 due to the hydride and trimethylsilyl resonances, respectively. The deuteride, $DTh[N(SiMe_3)_2]$, νThD = 1060 cm^{-1} can be prepared by refluxing $ClTh[N(SiMe_3)_2]_3$ and $NaN(SiMe_3)_2$ in perdeutero-tetrahydrofuran. The uranium hydride and deuteride were prepared similarly. Hydridotris(hexamethyldisilylamido)uranium was crystallized from pentane as brown-yellow needles[4], mp 97-98°C, νUH = 1430 cm^{-1}, νUD = 1020 cm^{-1}. We have been unable to locate the hydride signal in the ^{1}HNMR spectrum of this paramagnetic (μ_B = 2.6 B.M. in benzene solution) substance, though the trimethylsilyl groups resonate at δ-19.5. The hydrides can also be prepared from $ClM[N(SiMe_3)_2]_3$ 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 $ClM[N(SiMe_3)_2]_3$, 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 $MeM[N(SiMe_3)]_3$[3], M = Th or U quantitatively. The product from reaction of n-butyllithium with the hydride derivatives affords $HM[(N(SiMe_3)_2]_3$ or $DM[N(SiMe_3)_2]_3$ (M is Th or U) upon addition of trifluoroacetic acid or deutero-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.[5]

References

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3. Turner, H. W.; Andersen, R. A.; Templeton, D. H.; Zalkin, A.; Inorg. Chem., submitted for publication.

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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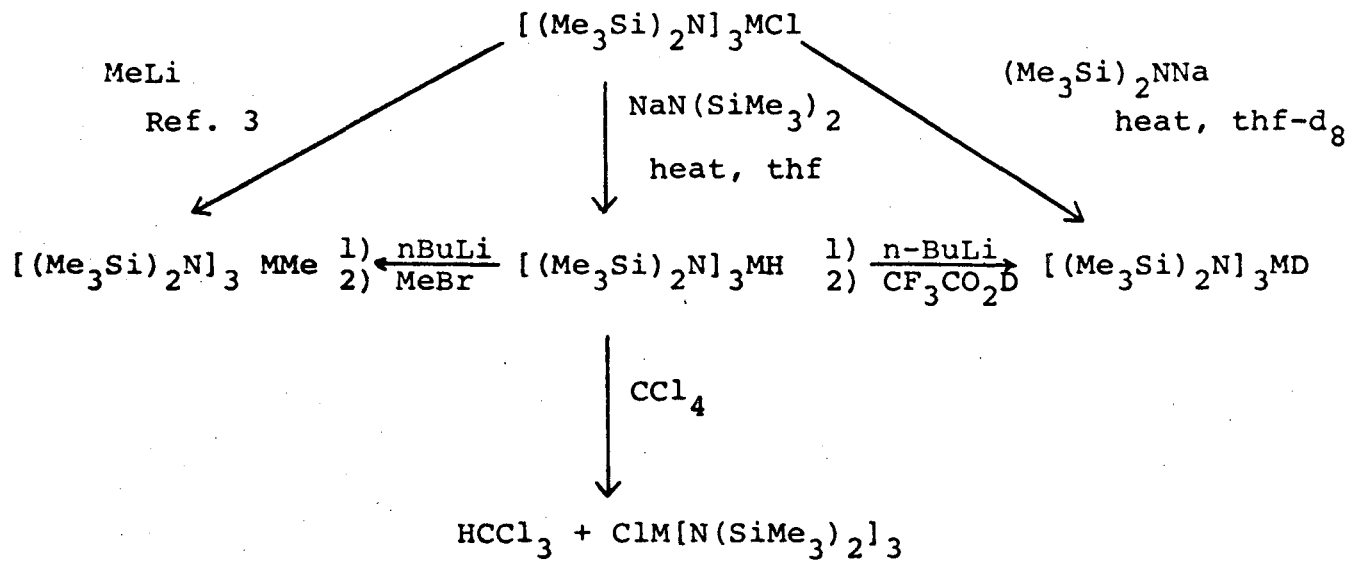
[(Me3Si)2N]3MCl
MeLi
Ref. 3
NaN(SiMe3)2
heat, thf
(Me3Si)2NNa
heat, thf-d8
[(Me3Si)2N]3 MMe
1) nBuLi
2) MeBr
[(Me3Si)2N]3MH
1) n-BuLi
2) CF3CO2D
[(Me3Si)2N]3MD
CCl4
HCCl3 + ClM[N(SiMe3)2]3
M = Th, U

Scheme

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720