unfavorable $\Delta S^{\ddagger}$. For the slower reaction $\Delta H^{\ddagger}$ is less favorable because overlap with the π system cannot readily occur. Restrictions must also be relaxed on the angle of approach of the base in the slow reaction because $\Delta S^{\ddagger}$ is not so unfavorable as in the rapid reaction.

For enzymes, the potential significance of the activation parameters for the fast reaction is substantial and the following speculation is therefore warranted. Correct positioning of an auxiliary base at the active site of the enzyme could make $\Delta S^{\ddagger}$ much less negative. For the low value of $\Delta H^{\ddagger}$ observed by us and $\Delta S^{\ddagger} = 0$, the reaction would occur at a rate more rapid than is generally observed for reactions catalyzed by vitamin B_6 enzymes. It appears that the Dunathan hypothesis not only can explain the selectivity of vitamin B_6 enzymes but also may explain the magnitude of the rate enhancements observed with these enzymes.

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(4) Evidence for different environments of the two protons comes from NMR studies. The glycine moiety's CH_2 proton resonance appears as an AB pattern, consistent with different environments for the two protons. For each, the pseudo-allylic 4-bond coupling could be measured to the azomethine C–H proton. These couplings were $J = 1.85$ and 0.95 Hz. The larger coupling constant is consistent with the greatest angle to the plane of the π system (M. Barfield et al., *J. Am. Chem. Soc.*, **97**, 1482 (1975)) and it is this proton which exchanges most rapidly. NMR spectra showing these changes were supplied to the referees.

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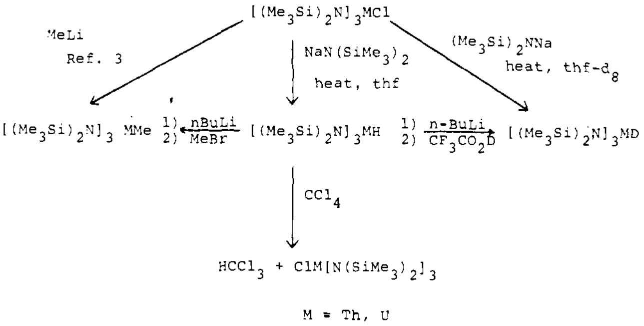
Hydrido[tris(hexamethyldisilylamido)]thorium(IV) and -uranium(IV)

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 describe here the first monomeric, monohydride derivatives of these metals, viz., $HTh[N(SiMe_3)_2]_3$ and $HU[N(SiMe_3)_2]_3$.

Reaction of chloro[tris(hexamethyldisilylamido)]thorium(IV)[3] with 1 molar equiv of sodium hexamethyldisilylamide in refluxing tetrahydrofuran yields hydrido[tris(hexamethyldisilylamido)]thorium as white needles from pentane:[4] mp 145–147 °C; IR ν_{ThH} 1480 cm^{-1}; ^1H NMR (PhH) δ 0.90 and 0.40 due to the hydride and trimethylsilyl resonances, respectively. The deuteride, $DTh[N(SiMe_3)_2]$, ν_{ThD} 1060 cm^{-1}, can be prepared by refluxing $ClTh[N(SiMe_3)_2]_3$ and $NaN(SiMe_3)_2$ in perdeuteriotetrahydrofuran. The uranium hydride and deuteride were prepared similarly. Hydrido[tris(hexamethyldisilylamido)]uranium was crystallized from pentane as brown-yellow needles:[4] mp 97–98 °C; IR ν_{UH} 1430 cm^{-1}, ν_{UD} 1020 cm^{-1}. We have been unable to locate the hydride signal in the ^1H NMR spectrum of this paramagnetic ($\mu_B = 2.6$ BM 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.

Scheme I



The metal-bound hydrides were further characterized by their reaction chemistry; see Scheme I. 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 melting point, mixture melting point, and IR and NMR spectra. Further, addition of *n*-butyllithium to a pentane solution of the hydrides, followed by methyl bromide, 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 = Th or U) upon addition of trifluoroacetic acid or deuteriotrifluoroacetic 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]

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A New Approach toward the Synthesis and Chemistry of Fluoroxy Compounds

Sir:

Since the pioneering investigations of Barton and Hesse[1] in which electrophilic fluorination was developed, work in this new area has been restricted to the use of fluoroxytrifluoromethane (CF_3OF).[2,3] Recently reactions have been developed in which a fluorine molecule acts as an electrophile, replacing tertiary hydrogens in organic substrates.[4]

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