uration over the η^3 configuration. Molecular orbital calculations, however, appear to favor the η^2 configuration by ~4 kcal mol^{-1}.

(17) The Al–C_5 ring interaction in **1** may be idealized for electron-counting purposes in at least two ways depending upon whether the C_5 ring is considered to show monohapto or trihapto coordination. With monohapto coordination the electrons could be counted as follows: three electrons from the aluminum atom, one electron from the methyl group, one and one half electrons from each of the two chlorine atoms, and one electron from the ring. With trihapto coordination the aluminum atom would be formally five coordinate and the electron count could be made as follows: three electrons from aluminum atom, one electron from the methyl group, one half electron from each of two chlorine atoms, and three electrons from the ring. Under the second description each Al–Cl–Al bridge bond may be regarded as a three-center–one-electron bond.

(18) Nonbonded interactions listed in Table I no doubt play a role in determining the geometry of **1**. Molecular orbital calculations are in progress which may permit analysis of the relative importance of steric and electronic interactions on the final geometry.

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Hydrogen–Deuterium Exchange: Perdeuteriohydridotris(hexamethyldisilylamido)thorium(IV) and -uranium(IV)

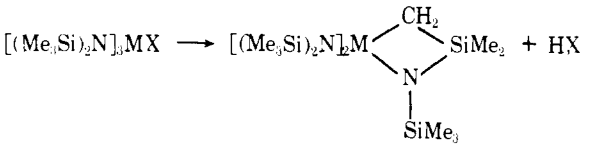
Sir:

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 $HU[N(SiMe_3)_2]_3$ and $HTh[N(SiMe_3)_2]_3$, examples of f^2 and f^0 electronic configurations, respectively.

Stirring a pentane solution of $HU[N(SiMe_3)_2]_3$[3] under deuterium (1 atm, 40 equiv/5 cycles, room temperature) results in complete exchange of all hydrogen atoms for deuterium yielding $DU\{N[Si(CD_3)_3]_2\}_3$, ν_{CD} 2210 and ν_{UD} 1027 cm^{-1}, mp 95–97 °C.[4] Elemental analysis,[5] absence of a ^1H NMR spectrum, and isolation of $[(CD_3)_3Si]_2ND$ after hydrolysis[6] confirm that all 55 hydrogen atoms have been exchanged for deuterium. The exchange reaction is reversible since the perdeuterio compound exchanges with molecular hydrogen to give $HU[N(SiMe_3)_2]_3$. Neither the methyl-, tetrahydroborato-, nor chlorotris(hexamethyldisilylamido)uranium analogue[9] nor the uranium(III) species, $U[N(SiMe_3)_2]_3$,[10] 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, $HTh[N(SiMe_3)_2]_3$, as thorium(VI) is unknown. However, the thorium hydride undergoes complete exchange under similar conditions yielding $DTh\{N[Si(CD_3)_3]_2\}_3$, ν_{CD} 2207 and ν_{ThD} 1060 cm^{-1}, mp 144–147 °C,[11] Elemental analysis[12], lack of a ^1H NMR spectrum, and mass spectroscopic analysis[13] confirm that the f^0 hydride undergoes complete exchange.

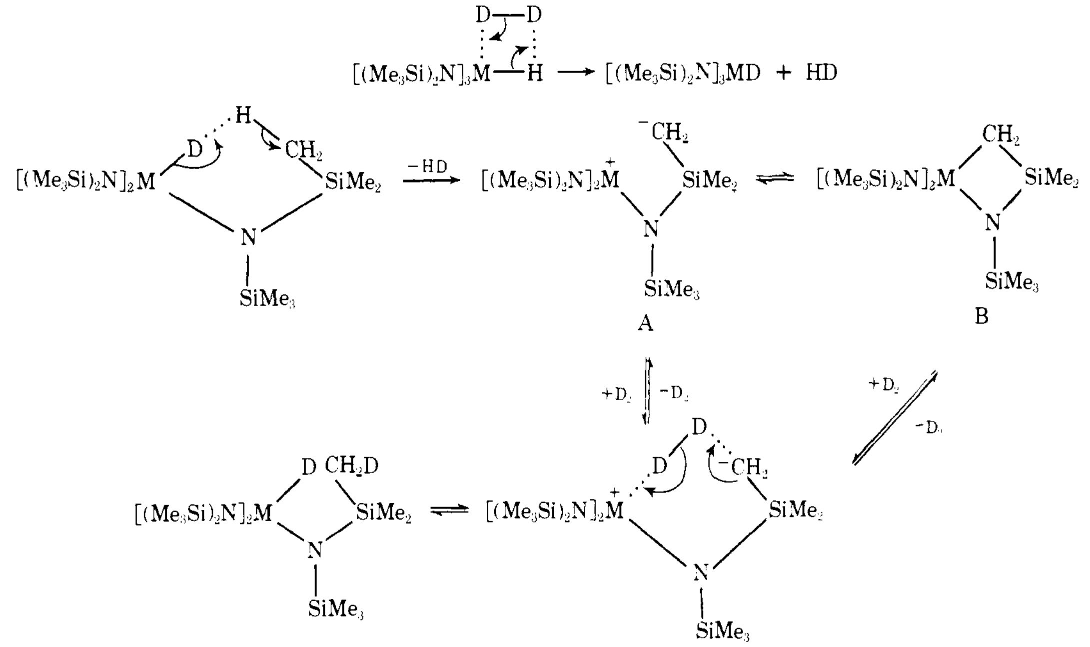
Insight into the mechanism of exchange is assisted by isolation of the four-membered ring metallobutane, $[(Me_3Si)_2N]_2\overline{MN(SiMe_3)(SiMe_2CH_2)}$ where M is thorium or uranium by pyrolysis of the thorium or uranium hydrides (neat, 180–190 °C, 1 atm) or methyls (neat, 150–160 °C, 1 atm).



M = Th or U; X = H or Me

The colorless diamagnetic thorium derivative,[14] 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 an area ratio of 36:9:2:6 due to $(Me_3Si)_2N$, Me_3Si, CH_2, and Me_2Si, respectively. The ^{13}C 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

Scheme I



Hz) due to the carbon atoms of the Me_2Si, Me_3Si, and $(Me_3Si)_2N$ 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 BM at 30 °C by Evans' method) uranium metallocycle,[14] 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 an area ratio of 6:9:36:2 due to Me_2Si, Me_3Si, $(Me_3Si)_2N$, and CH_2 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 perdeuteriothorium or -uranium amides. The uranium metallocycle can also be prepared by reaction of $[(Me_3Si)_2N]_3UCl$ and ethyllithium or trimethylsilylmethyllithium, the organic product being ethane or tetramethylsilane, respectively.

Observation of the facile hydride-metallocycle interconversion suggests the mechanism shown in Scheme I. The first step in Scheme I 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 $Cp_2Zr(H)(R)$.[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 from that proposed by Bercaw to account for formation of perdeuterio-$(Me_5C_5)_2ZrH_2$ which occurs by conventional oxidative-addition, reductive elimination steps, though these authors isolate a compound which is thought to be $(Me_5C_5)ZrMe_3C_5(CH_2)_2$.[17]

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(6) The perdeuterioamide was hydrolyzed with NaOD in D_2O and the amine was transferred under 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 ≥98% deuterated.
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(11) The melting point of the undeuterated hydride is 145–147 °C.[3]
(12) Anal. Calcd for $C_{18}D_{55}N_3Si_6Th$: C, 28.1; D, 14.3; N, 5.49. Found: C, 28.4; D, 13.6; N, 5.54.
(13) The amine is ≥91% deuterated.[6-8]
(14) 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; M^+ (by mass spectrometry), 711. 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; M^+ (by mass spectrometry), 717.
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Sitting-atop Porphyrin Complexes. The Structure of the Bischloromercury(II) Complex of *N*-Tosylaminooctaethylporphyrin

Sir:

Metalloporphyrins in which the metal is bonded to fewer than four nitrogen atoms, sitting-atop complexes, may be considered as models for the initial steps of the metalation of the macrocycle. Such complexes are known for ruthenium and technetium,[1] rhodium,[2] and platinum.[3] Also several examples of mercury complexes have been formulated,[4,5] but no X-ray structural data are available so far. In this communication we describe the molecular structure of a bischloromercury complex of *N*-tosylaminooctaethylporphyrin which represents the first X-ray structural proof for the existence of mercury(II) porphyrin sitting-atop complexes.

The bischloromercury(II) complex of *N*-tosylaminooctaethylporphyrin, $C_{43}H_{51}N_5O_2SCl_2Hg_2$, was prepared from the corresponding base[6] and mercury(II) chloride.[7] Single crystals were grown by slow evaporation from a $CHCl_3$-CH_2Cl_2-CH_3OH solution. The compound crystallizes in the monoclinic space group $P2_1/n$ with a = 17.887 (6), b = 17.121 (6), c = 15.301 (4) Å; β = 113.48 (8)°; Z = 4; F_{000} = 2280; D_c = 1.814 g cm^{-3}. Intensity data were collected on a Philips PW1100 diffractometer and corrected for absorption (Mo Kα radiation, μ = 75.01 cm^{-1}, 2θ < 65°, step scan techniques); 7224 reflections with $I > 4\sigma(I)$ were used in structure refinement and resolution. The structure was solved by the heavy-atom method and anisotropically refined by full-matrix least-square techniques (R_1 = 0.040 and R_2 = 0.058).[8] Figure 1 gives a perspective view of the molecular compound which appears as a sitting-atop complex. Atoms Hg(1) and Hg(2) are located on both sides of the macrocycle and separated by 3.39 Å. The most interesting distances from mercury atoms to the ligand are summarized in Table I. It must be noted that the mercury-nitrogen distances are largely diversified from ~2 to >3 Å. As currently observed even in highly distorted metalloporphyrins the four pyrrole nitrogens N(1)-N(4) are here coplanar within ±0.03 Å. The tosyl nitrogen N(t) is considerably removed from the (4N) plane; its displacement of 1.36 Å is in the same direction that the linked Hg(2) atom, itself displaced by 2.05 Å. Hg(1) is 1.28 Å out of plane in the opposite direction. The porphyrin macrocycle is distorted. Indeed the distortion appears as a result of the *N*-tosyl group. Thus, pyrrole N(1) to which is attached the *N*-tosyl is the most deviate from the (4N) plane, making a dihedral angle of 40.8°, whereas small angles of 1.6, 9.1 and 10.2° occur with pyrroles N(2), N(3), and N(4), respectively. Dihedral angles between pyrroles are 39.6 for N(1)-N(2), 7.5 for N(2)-N(3), 1.1 for N(3)-N(4), and 33.3° for N(4)-N(1). Similar influence on the overall structure, causing the N-substituted pyrrole ring to deviate strongly from the mean plane of the remainder of the porphyrin ligand, has been previously reported in N-substituted metalloporphyrin complexes of cobalt,[9] manganese,[10] zinc,[11] and nickel.[7,12] Distortion of the porphinato core has little or no effect on π-electron delocalization and on bond parameters. The average values for both lengths in the por-

Table I. Interatomic Distances around Mercury Atoms

from Hg(1) to	Å	from Hg(2) to	Å
Cl(1)	2.318 (2)	Cl(2)	2.285 (2)
N(3)	2.194 (5)	N(t)	2.075 (5)
N(4)	2.325 (5)	N(2)	2.597 (5)
N(2)	2.496 (5)	N(3)	2.863 (6)
N(1)	2.829 (5)	N(1)	3.090 (5)
		N(4)	3.264 (5)