larger the greater the value of the pentane/guest ratio, suggesting that the fractionation of deuterium would be more effective the more the system is diluted with pentane. The data also indicate that the preference of the host for the deuterated isotopomer over the protonated is greater in the *p*-xylene systems than in the naphthalene, and nearly the same for the two *p*-xylene systems. The explanation for these preferences is not yet clear.

Further work is being conducted to extend the concentration ranges and to apply the phenomenon to the liquid chromatographic fractionation of isotopomers where the effects of the differential inclusion are cumulative and prospects for practical applications are emerging.

Acknowledgment. We express our thanks to Margaret J. Legg and Albert P. Mortola[7] for their assistance, to Dr. D. J. Hennessy of our department for advice and helpful discussions, and to the Fordham University Office of Research Services for a grant—all in the early stages of this project. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the major support of this research.

References and Notes

(1) Schaeffer, W. D.; Dorsey, W. S.; Skinner, D. A.; Christian, C. G. *J. Am. Chem. Soc.* **1957**, *79*, 5870–5876.
(2) Allison, S. A.; Barrer, R. M. *J. Chem. Soc. A* **1969**, 1717–1723.
(3) Andreetti, G. D.; Bocelli, G.; Sgarabotto, P. *Cryst. Struct. Commun.* **1972**, *1*, 51–53.
(4) de Gil, E. R.; Kerr, I. S. *Appl. Crystallogr.* **1977**, *10*, 315–320.
(5) Minton, M. J.; Smith, N. O. *J. Phys. Chem.* **1967**, *71*, 3618–3622.
(6) Logan, A. V.; Carle, D. W. *J. Am. Chem. Soc.* **1952**, *74*, 5224–5225.
(7) Deceased.

Samuel E. Ofodile, Richard M. Kellett, Norman O. Smith*
Department of Chemistry, Fordham University
New York, New York 10458

Received July 20, 1979

Synthesis, Characterization, and Molecular Structure of an Aluminum Pentamethylcyclopentadienyl Complex, $[\eta^3\text{-}(CH_3)_5C_5Al(Cl)CH_3]_2$: An Organometallic Analogue of Benzvalene

Sir:

Several organoaluminum compounds play an important role in commercial olefin polymerization processes;[1,2] yet the fundamental structural chemistry, bonding, and rearrangement dynamics of discrete organoaluminum–olefin complexes remain incompletely defined and systematized. The chemistry of aluminum–olefin complexes has recently piqued our interest, and we report here on the formation and molecular structure of an unusual aluminum addition complex of pentamethylcyclopentadiene, $[\eta^3\text{-}(CH_3)_5C_5Al(Cl)CH_3]_2$ (**1**).

Compound **1** was prepared by combination of a toluene solution containing 1.95 g (10 mmol) of pentamethylcyclopentadienylmagnesium chloride[3] with 0.92 g (5 mmol) of $[(CH_3)_2AlCl]_2$ under a dry nitrogen atmosphere. The resulting yellow-white solid was extracted with hexane from which colorless crystals were obtained upon vacuum evaporation of the solvent (50% yield after crystallization).[4] The compound is extremely air and moisture sensitive; the solid material and the solutions turn dark purple upon exposure to protic sources. The mass spectrum (70 eV) of **1** displays a fragmentation pattern typical of $[RR'AlCl]_2$ compounds;[5] the most intense ions include *m/e* 232 ($^{35}Cl_2AlC_5(CH_3)_5^+$), 212 ($^{35}ClAlC_5(CH_3)_5(CH_3)^+$), 197 ($^{35}ClAlC_5(CH_3)_5^+$), and 177 ($CH_3AlC_5(CH_3)_5^+$). The 60-MHz ^{1}H NMR spectrum (32 °C, Me_4Si standard) of **1** in benzene shows a singlet at 1.60 ppm (area 5) which can be assigned to the protons on five equivalent cyclopentadienyl ring methyl groups, and a singlet at −0.85 ppm (area 1) which can be assigned to the equivalent protons of a methyl group bonded to the aluminum atom. The 25.2-MHz $^{13}C\{^1H\}$ NMR spectrum (32 °C, Me_4Si standard) shows a singlet at 10.74 ppm assigned to the ring methyl carbon atoms and a singlet at 115.36 ppm assigned to the ring framework carbon atoms. The resonance for the methyl group bonded directly to the aluminum atom is not observed.[6] The stoichiometry involved in the synthesis of **1** and the mass spectrometric and NMR data are consistent with a reaction pathway involving the exchange of pentamethylcyclopentadienyl groups for two of the terminal methyl groups on the parent dimer $[(CH_3)_2AlCl]_2$. Upon first examination, the room temperature NMR spectra suggest that in solution the molecular structure of **1** contains fluxional monohapto $(CH_3)_5C_5$–Al units as are found in $(CH_3)_3Ge[(CH_3)_5C_5]$ and $(CH_3)_3Sn[(CH_3)_5C_5]$.[7] However, these data are inconclusive, and a single-crystal X-ray diffraction analysis has been carried out to provide the necessary structural description.

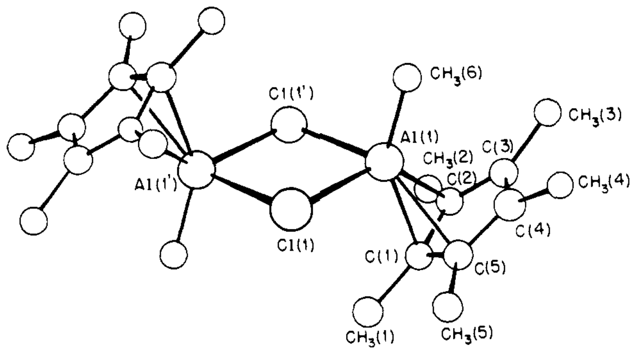


Figure 1. Molecular structure of $[\eta^3\text{-}(CH_3)_5C_5Al(Cl)CH_3]_2$.

Compound **1** crystallizes in a monoclinic cell, $P2_1/c$, with two molecules per unit cell. Crystal data are as follows: a = 8.657 (2), b = 8.914 (2), c = 16.208 (2) Å; β = 104.95 (1)°; V = 1208.4 (4) Å^3; Z = 2; ρ_{calcd} = 1.17 g cm^{-1}; Cu Kα radiation (λ = 1.5418 Å); μ (Cu Kα) = 10.8 cm^{-1}; $F(000)$ = 424.[8] Each dimeric molecule of **1** possesses crystallographic C_i-$\bar{1}$ site symmetry and the molecule nearly conforms to an idealized C_{2h}-$2/m$ geometry. The molecular structure of **1** is shown in Figure 1, and the significant intramolecular bond angles and distances are summarized in Table I. Each alumi-

Table I. Selected Interatomic Distances (Ångstroms) and Angles (Degrees)

	Contact Distances		
Al(1)–Cl(1)	2.378 (3)	C(1)–C(2)	1.43 (1)
Al(1)–Cl(1′)	2.398 (2)	C(1)–C(5)	1.44 (1)
Al(1)–C(1)	2.095 (7)	C(2)–C(3)	1.39 (1)
Al(1)–C(2)	2.254 (8)	C(3)–C(4)	1.37 (1)
Al(1)–C(5)	2.279 (8)	C(4)–C(5)	1.38 (1)
Al(1)–CH_3(6)	1.916 (7)		
	Nonbonded Distances		
Al(1)–C(3)	2.499 (6)	CH_3(6′)–CH_3(2)	>5.0
Al(1)–C(4)	2.517 (7)	Al(1)–Al(1′)	3.561 (3)
CH_3(1)–Cl(1)	3.878 (8)	Cl(1)–Cl(1′)	3.182 (2)
CH_3(2)–Cl(1)	3.406 (10)	CH_3(6)–CH_3(3)	3.685 (10)
CH_3(6′)–CH_3(1)	3.879 (11)	CH_3(6)–CH_3(4)	3.572 (11)
	Bond Angles		
Cl(1)–Al(1)–Cl(1′)	83.56 (8)	C(5)–C(1)–C(2)	107.1 (6)
Al(1)–Cl(1)–Al(1′)	96.44 (9)	C(1)–C(2)–C(3)	106.9 (6)
Cl(1)–Al(1)–CH_3(6)	101.5 (2)	C(2)–C(3)–C(4)	109.1 (6)
Cl(1′)–Al(1)–CH_3(6)	101.1 (2)	C(3)–C(4)–C(5)	110.4 (6)
Al(1′)–Al(1)–C(1)	104.6 (2)	C(4)–C(5)–C(1)	106.5 (6)
Al(1′)–Al(1)–CH_3(6)	105.2 (2)		

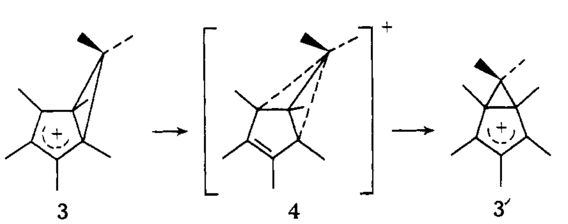
0002-7863/79/1501-7726$01.00/0

num atom in the dimeric unit is bonded to a terminal methyl group, two bridging chlorine atoms, and a pentamethylcyclopentadienyl ring. The Al_2Cl_2 ring is planar and slightly asymmetric. The nonbonding distance, Cl(1)-Cl(1′) = 3.182 Å, is comparable with the same nonbonding distance in $[CH_3AlCl_2]_2$, 3.16 Å,[10] $[(CH_3)_2AlCl]_2$, ~3.2 Å,[11] and a variety of four-membered transition metal-chlorine ring compounds.[12] The Al-Cl bridge bond distances in **1**, Al(1)-Cl(1) = 2.378 and Al(1)-Cl(1′) = 2.398 Å, on the other hand, are long compared with the Al-Cl bridge distances in $[CH_3AlCl_2]_2$, 2.25 and 2.26 Å,[10] and in $[(CH_3)_2AlCl]_2$, 2.31 Å.[11] The ring angle, Al(1)-Cl-Al(1′) = 96.44°, in **1** is enlarged over the same angle in $[CH_3AlCl_2]_2$, 91.1°.[10] The Al(1)-Al(1′) distance, 3.561 Å, is also long compared with the same distance in $[CH_3AlCl_2]_2$, 3.22 Å, and in trialkylaluminum dimer molecules.[13] Consequently, the ring bond angles and the elongated Al-Cl bridge distances in **1** are consistent with a weak interaction between the two monomeric units.

The stereochemistry involving the aluminum atom and the pentamethylcyclopentadienyl ring is of central interest. The C_5 ring framework is planar, and there are three short aluminum atom-ring carbon atom distances: Al-Cl(1) = 2.095, Al-C(2) = 2.254, and Al-C(5) = 2.279 Å. These distances fall within a range expected for Al-C(terminal) and Al-C(electron-deficient bridge) bonding interactions in alkylaluminum compounds.[10,11,13] The distances Al-C(3), 2.499 Å, and Al-C(4), 2.517 Å, are long, and they may be considered to be nonbonding distances. Within the pentamethylcyclopentadienyl ring the C(1)-C(2), 1.43, and C(1)-C(5), 1.44 Å, bond distances are significantly longer than the distances C(2)-C(3), 1.39, C(3)-C(4), 1.37, and C(4)-C(5), 1.38 Å. By comparison, the (ring C)-(ring C) distances in $[\eta^5\text{-}(CH_3)_5C_5]_2Fe$ are essentially equivalent with a mean value of 1.419 Å.[14] Apparently in response to small nonbonded interactions the ring methyl groups deviate only slightly from the C_5 ring plane; $CH_3(1)$, $CH_3(2)$, and $CH_3(5)$ are displaced 0.13, 0.09, and 0.12 Å, respectively, away from the aluminum atom. The $CH_3(3)$ and $CH_3(4)$ groups are displaced 0.03 and 0.04 Å toward the aluminum atom.

An interesting structural comparison may be made between the solid-state structure of **1** and the gas-phase structure of the seemingly related monomeric compound $[(CH_3)_2Al(C_5H_5)]$ (**2**). Based upon electron-diffraction data[15] and molecular orbital calculations,[16] Haaland and co-workers proposed that **2** has a dihapto Al-Cp interaction with Al-C(3) and Al-C(4) distances of 2.21 and nonbonding Al-Cp distances of 2.75 and 3.04 Å to the remaining three framework carbon atoms. The Al-Cp interaction is suggested to involve a Al-C two-center-two electron σ bond and an olefin-aluminum π bond. Formal electron counting for **1** is not unambiguous,[17] and a clear-cut distinction between an assignment of monohapto or trihapto Al-C_5 ring coordination is not possible. We favor an assignment of formal trihapto coordination based upon the observed enlarged four-membered Al_2Cl_2 ring geometry, the short Al-C(2) and Al-C(5) bond distances, and the alteration of the ring C-C bond distances.[18] The structure is clearly distinct from the structure of **2** and molecular orbital calculations now in progress may reveal the nature of the bonding differences between **1** and **2.**

An intriguing structural comparison of **1** and **2** with benzvalene,[19] bicyclo[3.1.0]hex-3-en-2-yl cation (**3**), and its rearrangement transient (**4**) is also possible.[20] Using the framework shown in eq 1 and orbital and electron counting conventions proposed by Wade[21] and Williams,[22] the carbocation **3** may be described as isoelectronic with **2** and indeed they are also structurally related. Likewise, **4** appears related to the new compound **1.** This correspondence is not entirely unexpected. Spielvogel and co-workers[23] and Noth and Wrackmeyer[24] noted an isoelectronic relationship between carbenium ions and their trigonal boron analogues, and they have successfully correlated ^{13}C and ^{11}B NMR data in isoelectronic compounds. Williams[22] extended the isoelectronic organizing principles in a more generalizing fashion to include boron hydrides, carboranes, and nonclassical carbocations, and ^{13}C and ^{11}B NMR chemical shift data also have been correlated.[25] Our work suggests that isoelectronic and isostructural relationships between organoaluminum compounds and carbocations exist; this in turn suggests that ^{27}Al and ^{13}C chemical shift correlations may be found. Lastly, it is worth noting that the electron-deficient aluminum atom in **1** is apparently capable of stabilizing a configuration which has only a fleeting existence in the organic carbocation analogue. Further details of temperature-dependent NMR spectra, a low-temperature X-ray structure determination, and molecular orbital calculations will be reported in the near future.



3 **4** **3′** (1)

Acknowledgment. The authors recognize the NSF Grant, CHE-7802921, which facilitated the purchase of the X-ray diffractometer. R.T.P acknowledges partial support of this research by the Research Corporation. We also thank Dr. R. E. Williams, Chemical Systems, Inc., and the Institute of Hydrocarbon Chemistry, University of Southern California, and Professor R. W. Holder, University of New Mexico, for several helpful discussions on the carbocation analogy.

References and Notes

(1) Reviews on the topic of carboalumination: Mole, T.; Jeffery, E. A. "Organoaluminum Compounds"; Elsevier: Amsterdam, 1972. Eisch, J. J. *Adv. Organomet. Chem.* **1977,** *16,* 67. Oliver, J. P. *Ibid.* **1977,** *16,* 111. Ziegler, K. *ACS Monograph Ser.* **1960,** No. 147, Chapter 5.

(2) Kennedy, J. P. "Cationic Polymerization of Olefins: A Critical Inventory"; Wiley-Interscience: New York, 1975. Koster, R.; Binger, R. *Adv. Inorg. RadioChem.* **1965,** *7,* 263. Haines, R. J.; Leigh, G. J. *Chem. Soc. Rev.* **1975,** *4,* 155. Caunt, A. D. "Catalysis"; Chemical Society: London, **1977;** Vol. 1. Richards, D. H. *Chem. Soc. Rev.* **1977,** *6,* 235.

(3) Solvent free pentamethylcyclopentadienylmagnesium chloride was prepared by addition of pentamethylcyclopentadiene to a boiling solution of isopropylmagnesium chloride in toluene. The $(CH_3)_5C_5H$ was prepared according to a literature recipe: Threlkel, R. S.; Bercaw, J. E. *J. Organomet. Chem.* **1977,** *136,* 1.

(4) The complex was recrystallized from cold hexane. The solid sublimes at ~80 °C (10^{-3} Torr); it is slightly soluble in benzene, toluene, and hexane.

(5) Tanaka, J.; Smith, S. R. *Inorg. Chem.* **1969,** *8,* 265. Litzow, M. R.; Spalding, T. R. "Mass Spectrometry of Inorganic and Organometallic Compounds"; Elsevier: Amsterdam, 1973; and references therein specific to organoaluminum compounds. The parent dimer ion $[(CH_3)_5C_5Al(Cl)CH_3]_2^+$ is not detected under high ionization energy conditions and ion source temperatures of 110 °C. Dimer fragment ions are observed with low relative intensities.

(6) The ^{13}C NMR resonance for the methyl groups in $[(CH_3)_2AlCp]$ has not been detected: Fisher, P.; Stadelhofer, J.; Weidlein, J. *J. Organomet. Chem.* **1976,** *116,* 65.

(7) Davison, A.; Rakita, P. E. *Inorg. Chem.* **1970,** *9,* 289.

(8) X-Ray intensity data were collected at 298 K by the θ-2θ technique with Ni-filtered Cu Kα radiation on a Syntex P3 automated diffractometer equipped with a scintillation counter and a pulse height analyzer. Of a total of 1242 independent reflections examined with $3° \leq 2\theta \leq 55°$, 1053 had $I > 3\sigma(I)$ and these were used in the structure determination and refinement. The structure was solved using MULTAN and refined by anisotropic least-squares techniques[9] to yield $R_1(F) = 6.7$ and $R_2(F) = 7.3\%$ at the present stage of refinement.

(9) All X-ray structure calculations were carried out using the Syntex R3/XTL structure determination system.

(10) Allegra, G.; Perego, G.; Immirzi, A. *Makromol. Chem.* **1963,** *61,* 69.

(11) Brockway, L. O.; Davidson, N. R. *J. Am. Chem. Soc.* **1941,** *63,* 3287.

(12) Ross, F. K.; Stucky, G. D. *J. Am. Chem. Soc.,* **1970,** *92,* 4538.

(13) A range of Al-Al bond distances may be taken as 2.60-2.68 Å: Oliver, J. P. *Adv. Organomet. Chem.* **1977,** *15,* 235, and references therein.

(14) Freyberg, D. P.; Robbins, J. L.; Raymond, K. N.; Smart, J. C. *J. Am. Chem. Soc.* **1979,** *101,* 892.

(15) Drew, D. A.; Haaland, A. *Acta Chem. Scand.* **1973,** *27,* 3725.

(16) Gropen, O.; Haaland, A. *J. Organomet. Chem.* **1975,** *92,* 157. The electron-diffraction data do not unambiguously favor the η^2 structural config-

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.

(19) Reports on the structure of benzvalene and **3:** Katz, T. J.; Wong, E. G.; Acton, H. *J. Am. Chem. Soc.* **1971,** *93*, 3782. Wilzbach, K. E.; Ritscher, J. S.; Kaplan, L. *Ibid.* **1967,** *89*, 1031. Kaplan, L.; Wilzbach, K. E. *Ibid.* **1968,** *90*, 1085. Katz, T. J.; Wang, E. J.; Acton, N. *Ibid.* **1971,** *93*, 3782. Suenram, R. D.; Harmond, M. D. *Ibid.* **1972,** *94*, 5915; **1973,** *95*, 4506. Berson, J. A.; Jenkins, J. A. *Ibid.* **1974,** *94*, 8907. Hehre, W. J. *Ibid.* **1972**, *94*, 8909. Hehre, W. J. *Ibid.* **1974,** *96*, 5207.

(20) **4** may be considered to be the protonated form of benzvalene.

(21) Wade, K. *Adv. Inorg. Radiochem.* **1976,** *18*, 1.

(22) Williams, R. E. *Adv. Inorg. Radiochem.* **1976,** *18*, 67.

(23) Spielvogel, F. G.; Nutt, W. R.; Izydore, R. A. *J. Am. Chem. Soc.*, **1975,** *97*, 1609.

(24) Nöth, H.; Wrackmeyer, B. *Chem. Ber.* **1974,** *107*, 3089.

(25) Williams, R. E. Abstracts, 3rd International Meeting on Boron Chemistry, Garmisch, Germany, 1976.

P. R. Schonberg, R. T. Paine,* C. F. Campana*
Department of Chemistry, University of New Mexico
Albuquerque, New Mexico 87131

Received June 7, 1979

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

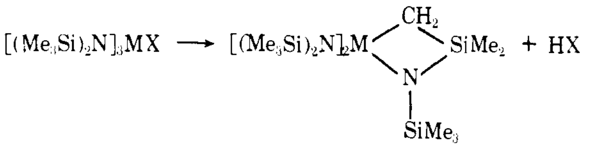
Sir:

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.

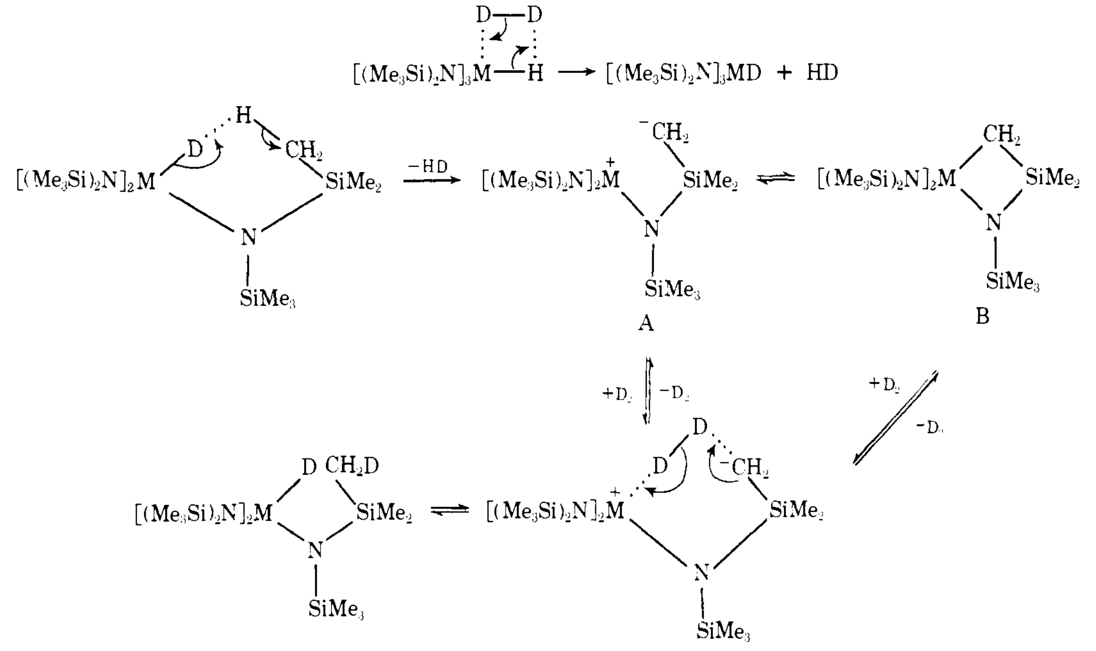
The observation of H–D exchange in the uranium(IV) species might be rationalized by a series of oxidative-addition, reductive-elimination cycles since uranium(VI) is a well-known oxidation state. This mechanism would be implicated by the lack of H–D exchange in the corresponding thorium derivative, $HTh[N(SiMe_3)_2]_3$, 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, $[(Me_3Si)_2N]_2\overline{MN(SiMe_3)(SiMe_2C}H_2)$ 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 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



M = Th or U; X = H or Me

Scheme I



0002-7863/79/1501-7728$01.00/0