to further, more detailed investigations of cluster assembly.

The biosynthesis of $[Fe_4S_4(SR)_4]^{2-}$ clusters, as well as those of the $[Fe_2S_2(SR)_4]^{2-}$ type, remains an open question. The spontaneous occurrence of reactions such as (1) and (4)-(7) makes it obvious that no protein is required to guide the construction of a cluster from simple reactants. Iron is a ubiquitous component of cells, and sulfide has been demonstrated in bacterial, plant, and fungal cells.[19] The possible role of S(0) in protein cluster synthesis has been noted,[36] and 2-Fe ferredoxins have been reconstituted from apoproteins containing S(0) in the presence of a thiol reductant.[43] As noted at the outset cysteinyl peptides can be placed around Fe_4S_4 units by reaction 2. Consequently, one view that must be entertained is that in vivo Fe-S cluster synthesis may occur by reactions the same or similar to those examined here and that cluster insertion into a peptide environment may be a nonenzymatic process. Interception and stabilization of a particular type of unit (1Fe, 2Fe-2S, 4Fe-4S) would then be a function of the selectivity or specificity of the apoprotein. Examples of the instability of an iron site in an "unnatural" peptide[44] and the selectivity of several apoproteins for the "natural" Fe-S clusters,[45] as in the ligand substitution reaction (2) with nR′SH = apoprotein, are available.

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Actinide-Carbon Bonds: Insertion Reactions of Carbon Monoxide, *tert*-Butyl Isocyanide, and *tert*-Butyl Cyanide into $[(Me_3Si)_2N]_2MCH_2Si(Me)_2NSiMe_3$

Stephen J. Simpson and Richard A. Andersen*

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

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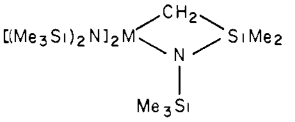
Abstract: The thorium or uranium metallacycles $[(Me_3Si)_2N]_2MCH_2Si(Me)_2NSiMe_3$ (I) react with *tert*-butyl cyanide to give the six-membered ring compounds $[(Me_3Si)_2N]_2MN{=}C(t\text{-}Bu)CH_2Si(Me)_2NSiMe_3$. The metallacycles (I) also react with the isoelectronic molecules *tert*-butyl isocyanide and carbon monoxide to give the unique five-membered ring compounds with exocyclic carbon-carbon double bonds, $[(Me_3Si)_2N]_2MXC({=}CH_2)Si(Me)_2NSiMe_3$, where X is t-BuN or oxygen. The four-membered ring metallacycles (I) give simple coordination complexes of the type $[(Me_3Si)_2N]_2MCH_2Si(Me)_2NSiMe_3(N_3SiMe_3)$ with trimethylsilyl azide.

The four-membered ring metallacycles of thorium or uranium (I) are formed by γ elimination of methane or hydrogen from



I, M = Th or U

$[(Me_3Si)_2N]_3MMe$ or $[(Me_3Si)_2N]_3MH$, respectively.[1] The polarity of the actinide-carbon bond and the ring strain inherent in the four-membered ring suggest that 1,2-dipolar organic molecules will insert into the metallacyclic ring. Insertion of the isoelectronic molecules carbon monoxide, *tert*-butyl isocyanide, and *tert*-butyl cyanide into the actinide-carbon bond has been realized, and the results are described herein.

tert-Butyl cyanide reacts with I (M = Th) to give a 1:1, monomeric, diamagnetic complex. The ν(CN) stretching frequency in the infrared spectrum (1617 cm^{-1}) shows that the complex is not a simple coordination complex but one in which the carbon-nitrogen bond order has been reduced from 3 in the uncomplexed alkylcyanide to 2 in the complex. The nuclear magnetic resonance spectra show that insertion has occurred into the thorium-carbon bond rather than into the thorium-nitrogen bonds. The ^1H and

Table I. ^1H Nuclear Magnetic Resonance Data[a]

compd	$(Me_3Si)_2N$	Me_3SiN	Me_2Si	CH_2	Me_3C
I, M = Th[d]	0.37	0.38	0.56	0.49	
II, M = Th	0.36	0.90	0.33	2.04	1.29
VI, M = Th	0.54	0.44	0.61	5.51 and 5.43[b] (J = 13 Hz)	1.56
IX, M = Th	0.48	0.41	0.63	5.49 and 4.15[b] (J = 13 Hz)	
X, M = Th	0.46	0.64[e] 0.45[e]	0.23	1.04	
I, M = U[d]	−23.3	−9.90	+2.08	−128.6	
II, M = U	−5.85	−19.9	+8.58	+33.6	−11.8
VI, M = U	−3.88	−10.8	+5.91	+8.71[c]	−14.1
IX, M = U	−6.69	−17.0	+2.74	−11.0[c]	
X, M = U	−3.59	−19.6[e] −27.9[e]	−11.8	72.9	

[a] In benzene-d_6 at 28 °C, chemical shifts are expressed in δ units (positive numbers are to high frequency) relative to Me_4Si. [b] A AB spin system, see text. [c] Broadened resonance ($\nu_{1/2}$ is ca. 10 Hz). [d] See ref 1. [e] These equal-area resonances are due to Me_3SiN of the metallacycle and coordinated Me_3SiN_3. Free Me_3SiN_3 resonates at δ 0.20.

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* To whom correspondence should be addressed at the Chemistry Department.

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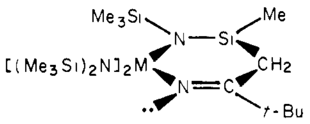
Table II. ^{13}C Nuclear Magnetic Resonance Data[a]

compd	$(Me_3Si)_2N$	Me_3SiN	Me_2Si	CH_2	Me_3CCN	$Me_3\mathit{C}CN$	$Me_3Si\mathit{C}N$
I, M = Th[b]	3.46 (q, J = 117[h])	4.52 (q, J = 117)	5.55 (q, J = 118)	68.8 (t, J = 120)			
II, M = Th	4.10 (q, J = 119)	3.45 (q, J = 118)	4.36 (q, J = 116)	34.4 (t, J = 116)	27.9 (q, J = 127)	43.3 (s)	191.5 (s)
VI, M = Th	4.82 (q, J = 118)	5.16 (q, J = 118)	6.56 (q, J = 118)	110.1[c]	29.8 (q, J = 125)	58.2 (s)	150.0 (s)
IX, M = Th[e]	3.52 (q, J = 117)	4.90 (q, J = 117)	5.75 (q, J = 118)	100.4[d]			
X, M = Th	3.40 (q, J = 119)	4.51 (q,[i] J = 118) 2.01 (q,[i] J = 119)	5.61 (q, J = 118)	68.4 (t, J = 120)			
I, M = U[b]	−40.8 (q, J = 118)	+24.5 (q, J = 118)	+49.6 (q, J = 118)	*f*			
II, M = U	−32.6 (q, J = 118)	−21.4 (q,[g] J = 118)	+6.71 (q, J = 117)	−65.1 (t, J = 116)	17.7 (q,[g] J = 126)	*f*	*f*
VI, M = U	−16.4 (q, J = 118)	−15.7 (q,[g] J = 118)	+8.63 (q, J = 118)	+95.3 (t, J = 155)	21.1 (q, J = 126)	*f*	*f*

[a] In benzene-d_6 at 28 °C, chemical shifts are expressed in δ units (positive numbers to high frequency) relative to Me_4Si. [b] See ref 1. [c] The $^{13}C\{^1H\}$ resonance is at δ 110.1 whereas the gated-decoupled spectrum yields a pair of doublets with coupling constants of 154 and 158 Hz. [d] The $^{13}C\{^1H\}$ resonance is at δ 100.4 whereas the gated-decoupled spectrum yields a pair of doublets with coupling constants of 152 and 154 Hz. [e] The ThO*C*=CH_2 resonance is a singlet at δ 172.6. [f] Not observed. [g] Assigned by heteronuclear decoupling. [h] J is the one-bond C–H coupling constant expressed in hertz. [i] These resonances are due to Me_3SiN of the metallacycle and of coordinated Me_3SiN_3. Free Me_3SiN_3 resonates at δ 2.04 (q, J = 118 Hz).

^{13}C NMR spectra (Tables I and II) reveal that the Me_3Si and Me_2Si groups of the complex are only slightly perturbed relative to metallacycle I (M = Th) though the resonances due to the methylene group are strongly deshielded (^1H) and shielded (^{13}C). Thus insertion has occurred into the thorium–carbon bond giving the six-membered ring complex (II, M = Th). The reduced



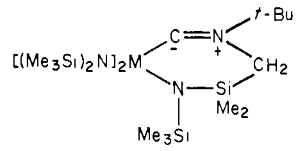
II, M = Th or U

tert-butyl cyanide group is structurally related to an organic azomethine, $R_2C{=}NR$, and the ^{13}C NMR and infrared spectra support this contention. For example, the methine carbon atom of *t*-BuCH=NMe resonates at δ 172.5[2a] and ν(CN) of azomethines falls in the region 1650–1610 cm^{-1}.[3]

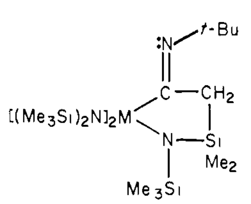
The uranium metallacycle (I, M = U) behaves similarly, giving orange II (M = U). Since it is paramagnetic (μ = 2.67 μ_B at 30 °C in benzene solution), and the ^1H and ^{13}C NMR absorptions are drastically shifted relative to the diamagnetic thorium analogue and do not lend themselves to a straightforward structural interpretation. However, the highly shielded methylene resonance of II relative to I strongly supports the notion that *tert*-butyl cyanide also inserts into the uranium–carbon bond.

The ^1H NMR spectral line shapes (though not the chemical shifts of the uranium species) for both compounds (II) are temperture invariant from +110 to −85 °C. This suggests that the six-membered ring complexes are planar (as drawn in II) or that they are undergoing a rapid fluxional process (inversion at the Me_3SiN group) that causes the Me_2Si and CH_2 protons to be chemically equivalent on the ^1H NMR time scale. The lone pair of electrons on the "azomethine-like" nitrogen atom are, however, stereochemically active since both complexes may be protonated (HBF_4) or methylated (Me_3OBF_4) but the resulting cationic complexes are too insoluble to be purified and therefore properly characterized. The "azomethine-like" nitrogen atom is most likely protonated or alkylated in preference to the other lone pairs of electrons on the nitrogen atoms since the metallacycles (I) cannot be protonated nor methylated.

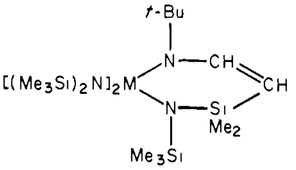
In contrast to the straightforward insertion of *tert*-butyl cyanide into the metal–carbon bond of I, reaction of the isoelectronic and isosteric *tert*-butyl isocyanide takes a different course. Though the thorium metallacycle (I) gives a 1:1, monomeric, diagmagnetic complex with *tert*-butyl isocyanide, it is not isostructural with that of the *tert*-butyl cyanide complex (II, M = Th). At this point it is instructive to consider four structural possibilities (III–VI)



III



IV



V

and to show that the spectroscopy is consistent with only one of them. If insertion occurs at the thorium–carbon bond in a manner similar to that of *tert*-butyl cyanide, then the dipolar complex III will result. If, on the other hand, a normal insertion of an isocyanide into the thorium–carbon bond occurs, then IV will result.[4] Neither of these isomers is consistent with the spectroscopic data. The methylene resonances in the ^1H and ^{13}C NMR spectra of III or IV should be similar to that observed in the *tert*-butyl cyanide complex (II, M = Th), i.e., a singlet at ca. δ 2 and a triplet at ca. δ 35 in the ^1H and ^{13}C NMR spectra, respectively. Further, the quaternary carbon atoms in III and IV will appear as strongly deshielded singlets at ca. δ 250. This is not observed. The methylene protons of the thorium complex show a AB (doublet of doublet) pattern (Table I). The methylene and quaternary carbon atoms in the $^{13}C\{^1H\}$ NMR spectra are singlets at δ 110.1 and 150.0, respectively. The former resonance yields a pair of doublets (J_{CH} = 154 and 158 Hz) in the gated-decoupled ^{13}C spectrum while the latter is a singlet. The chemical shift and coupling constant data are indicative of an olefinic functionality.[5] The carbon–carbon double-bond stretching frequency occurs at 1535 cm^{-1} for the thorium species, typical for olefinic functional groups.[3b] The $^{13}C\{^1H\}$ NMR spectrum rules out isomer V, since it is most unlikely that the two olefinic carbon atoms will have identical chemical shifts. Thus, the only structure that is consistent with all the data is VI.

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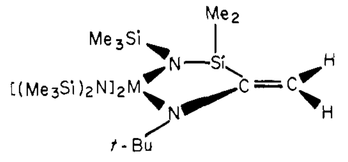
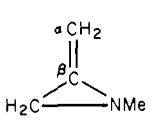
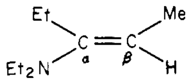


VI, M = Th or U

The *tert*-butyl isocyanide portion of VI is analogous to that of an organic enamine (vinylamine). The ^{13}C NMR chemical shifts are in accord with this contention.[6] Thus, the β-methylene carbon atoms in VII and VIII resonate at δ 82.0 and 98.4, and the α-carbon atoms resonate at δ 138.5 and 148.9, respectively.[2b,6]



VII

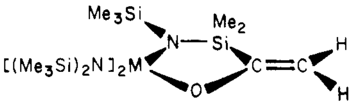


VIII

The uranium metallacycle (I, M = U) reacts with *tert*-butyl isocyanide in a similar manner to give VI (M = U). The orange complex is paramagnetic (μ = 2.69 μ_B, 30 °C in benzene solution), and thus the NMR spectra are not useful as a structural probe, though the spectra are fully consistent with structure VI. Further, the line widths in the ^1H and ^{13}C NMR spectra ($\nu_{1/2}$ = 10 Hz) simplify the coupling pattern of the methylene protons and carbon atoms, respectively.

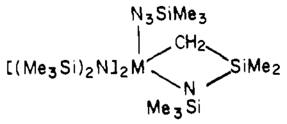
The five-membered ring in VI appears to be rigid on the ^1H NMR time scale since the methylene protons and Me_2Si group protons are shape invariant from +110 to -85 °C. Thus, the molecule must contain, at least on average, a symmetry plane that contains the MNSiCN unit since the two methyl groups on silicon are chemically equivalent and the exocyclic methylene protons are nonequivalent. The chemical equivalence of the methyl groups on the Me_2Si group suggests either that a rapid fluxional process causes the lone pairs of electrons on the nitrogen atoms to be rapidly inverting or that the five-membered ring is, in fact, planar. Support for the latter is derived from the observation that neither the thorium nor uranium complexes can be protonated (HBF_4) nor methylated (Me_3OBF_4). Unfortunately we can say no more about the ring conformation except to point out that planar coordination at three-coordinate nitrogen in five-membered rings has been observed.[7]

The metallacycles (I, M = Th or U) also undergo insertion reactions with carbon monoxide (18 atm, room temperature). The products (IX) are similar to those of the related *tert*-butyl isocyanide insertion products (VI). This follows from the NMR spectroscopy (Tables I and II). The spectroscopy further suggests that the carbon monoxide insertion products may be constructively viewed as a vinyl ether. For example the α- and β-carbon atoms of $CH_2{=}CHOMe$ resonate at δ 153.1 and 85.5, respectively.[5b] Again, the five-membered ring appears to be planar since there is no change in ^1H NMR spectral line shape from +110 to -85 °C.



IX, M = Th or U

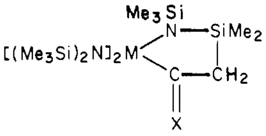
Another dipolar organic molecule that is potentially capable of undergoing insertion reactions is an alkyl azide. However reaction of trimethylsilyl azide with either thorium or uranium metallacycle (I) yields a simple coordination complex (X). This is most readily seen in the diamagnetic thorium compound. The chemical shifts in the ^1H and ^{13}C NMR spectra of the complex are only slightly perturbed relative to those in the uncomplexed metallacycle (Tables I and II). Further, $\nu(N_3)$ in the infrared spectrum (2105 cm^{-1}) is essentially identical with that of the free zide (2118 cm^{-1}). Though the ^1H NMR chemical shifts of the paramagnetic uranium complex do not follow a simple pattern, $\nu(N_3)$ (2103 cm^{-1}) strongly suggests that this complex is isostructural with that of the thorium analogue.



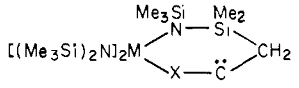
X, M = Th or U

The rather curious formal insertion of *tert*-butyl isocyanide and carbon monoxide into a silicon-carbon rather than into a metal-carbon bond requires some comment. For convenience, the reaction of *t*-BuNC and CO with the metallacycles are factored into two parts—insertion into a metal-carbon bond followed by insertion into a silicon-carbon bond.

Transition-metal alkyls yield metal acyls when exposed to carbon monoxide by a pathway that involves alkyl migration to a coordinated carbon monoxide group rather than by direct insertion of carbon monoxide into a metal-carbon bond.[8] It is likely that carbon monoxide and *tert*-butyl isocyanide follow a similar pathway with the actinide metallacycles, viz., coordination followed by methylene migration to give XI. Isolation of a coordination complex of the metallacycles with trimethylsilyl azide shows that there is sufficient space about the metal atom in the metallacycle for coordination of the sterically small *t*-BuNC and CO ligands. Though no simple coordination complexes of carbon monoxide have been isolated for the actinide metals, matrix isolation experiments have shown that carbon monoxide does indeed yield coordination complexes with some lanthanide metals.[9] Some isocyanide complexes of the lanthanides[10] and actinides[11] have been isolated. Since electropositive metal-oxygen or -nitrogen bonds are thermodynamically more stable than metal-carbon bonds,[12] a metal-heteroatom interaction is likely, giving a η^2-acyl or iminoacyl compound.[13] This could then rearrange to give a carbene intermediate, XII, which is a valence tautomer of XI.



XI



XII

X = O or *t*-BuN

This latter rearrangment has been postulated in a number of carbon monoxide insertion processes observed in the early transition-metal and actinide-metal complexes.[14]

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The carbene-like intermediate XII will insert into the thermodynamically weakest bond, the silicon–carbon bond,[15] giving the observed products VI and IX. This is a typical reaction of organic carbenes.[16] If the carbene intermediate has a sufficient lifetime, then it should be possible to trap XII before it goes on to product. Unfortunately reaction of either metallacycle (I) with carbon monoxide in presence of triethoxysilane[17] with carbon monoxide in presence of triethoxysilane[17] yields the insertion product IX. Hence, the existence of a carbene intermediate is speculative; however it neatly accounts for the observed results.

Experimental Section

All reactions were performed under argon. Analyses were done by the microanalytical laboratory of this department. Infrared spectra were recorded as Nujol mulls by using a Perkin-Elmer 580 machine. Mass spectra were obtained on a AEI-MS-12 instrument equipped with a direct inlet. Proton and carbon NMR spectra were obtained at 89.56 and 22.50 MHz, respectively, on a JEOL-FX90Q instrument. Solution magnetic susceptibilities were determined by Evans' method by using a Varian T-60 spectrometer.[18]

Preparation of $[(Me_3Si)_2N]_2ThN{=}C(t\text{-}Bu)CH_2Si(Me)_2NSiMe_3$. *tert*-Butyl cyanide (0.10 mL, 0.90 mmol) was added to a stirred solution of $[(Me_3Si)_2N]_2ThCH_2Si(Me)_2NSiMe_3$ (0.61 g, 0.86 mmol) in pentane (40 mL) at 0 °C. The colorless solution was stirred for 1 h at 0 °C, and then the pentane was removed under reduced pressure. The residue was extracted with pentane (2 × 30 mL), reduced in volume to ca. 5 mL, and cooled (–70 °C). The waxy, white solid was collected and dried under vacuum. Yield was 0.59 g (87%). Anal. Calcd for $C_{23}H_{62}N_4Si_6Th$: C, 34.8; H, 7.81; N, 7.05. Found: C, 34.5; H, 7.94; N, 7.21. The mass spectrum contained a M^+ ion at 794. The infrared spectrum contained $\nu(CN)$ at 1617 cm^{-1}.

Preparation of $[(Me_3Si)_2N]UN{=}C(t\text{-}Bu)CH_2Si(Me)_2NSiMe_3$. The uranium compound was prepared in a manner similar to that of the thorium analogue and crystallized as an orange, waxy solid in 92% yield. Anal. Calcd for $C_{23}H_{62}N_4Si_6U$: C, 34.5; H, 7.75; N, 7.00. Found: C, 34.2; H, 7.89; N, 7.15. The mass spectrum consisted of a M^+ ion at 800. The infrared spectrum gave $\nu(CN)$ at 1615 cm^{-1}.

Preparation of $[(Me_3Si)_2N]_2ThN(t\text{-}Bu)C({=}CH_2)Si(Me)_2NSiMe_3$. *tert*-Butyl isocyanide (0.80 mL, 0.74 mmol) was added to a stirred solution of $[(Me_3Si)_2N]_2ThCH_2Si(Me)_2NSiMe_3$ (0.48, g, 0.68 mmol) in pentane (50 mL) at 0 °C. The colorless solution was stirred for 30 min, and then the pentane was evaporated under reduced pressure. The residue was extracted with pentane (2 × 30 mL), concentrated to ca. 5 mL, and cooled (–70 °C). The white needles were collected and dried under vacuum. Yield was 0.46 g (85%). Anal. Calcd for $C_{23}H_{62}N_4Si_6Th$: C, 34.8; H, 7.81; N, 7.05. Found: C, 34.4; H, 7.83; N, 7.14. The mass spectrum contained a $(M - CMe_3)^+$ ion at 737 as the highest mass fragment. The infrared spectrum gave $\nu(C{=}C)$ at 1535 cm^{-1}.

Preparation of $[(Me_3Si)_2N]_2UN(t\text{-}Bu)C({=}CH_2)Si(Me)_2NSiMe_3$. This compound was prepared in a manner similar to that of its thorium analogue and crystallized as light orange blocks in 90% yield. Anal. Calcd for $C_{23}H_{62}N_4Si_6U$: C, 34.5; H, 7.75; N, 7.00. Found: C, 34.3; H, 7.66; N, 7.23. The mass spectrum contained a $(M - CMe_3)^+$ ion at 743 as the highest fragmentation ion. The infrared spectrum consisted of $\nu(C{=}C)$ at 1537 cm^{-1}.

Preparation of $[(Me_3Si)_2N]_2ThOC({=}CH_2)Si(Me)_2NSiMe_3$. The metallacycle $[(Me_3Si)_2N]_2ThCH_2Si(Me)_2NSiMe_3$ (0.66 g, 0.93 mmol) in pentane (50 mL) was stirred under carbon monoxide (18 atm) in a thick-walled vessel for 36 h. The pentane was removed under reduced pressure, and the residue was extracted with pentane (2 × 30 mL). The extracts were combined, concentrated to ca. 8 mL, and cooled (–70 °C). The colorless blocks (0.58 g, 84%) were collected and dried under vacuum, mp 124–127 °C. Anal. Calcd for $C_{19}H_{53}N_3OSi_6Th$: C, 30.8; H, 7.17; N, 5.68. Found: C, 30.6; H, 7.00; N, 5.73. The mass spectrum gave M^+ ion at 739, and the infrared spectrum gave $\nu(C{=}C)$ at 1587 cm^{-1}.

Preparation of $[(Me_3Si)_2N]_2UOC({=}CH_2)Si(Me)_2NSiMe_3$. The compound was prepared in a manner analogous to that of its thorium analogue and crystallized as deep orange blocks in 75% yield, mp 135–138 °C. Anal. Calcd for $C_{19}H_{53}N_3OSi_6U$: C, 30.6; H, 7.11; N, 5.64. Found: C, 30.3; H, 7.23; H, 5.77. The mass spectrum yielded M^+ ion at 745, and the infrared spectrum showed an absorption at 1585 cm^{-1} due to $\nu(C{=}C)$. The magnetic moment was found to be 2.73 μ_B at 30 °C in benzene solution.

Preparation of $[(M_3Si)_2N]_2ThCH_2Si(Me)_2NSiMe_3(Me_3SiN_3)$. Trimethylsilyl azide (0.14 mL, 1.1 mmol) was added to a solution of $[(Me_3Si)_2N]_2ThCH_2Si(Me)_2NSiMe_3$ (0.74 g, 1.0 mmol) in pentane (50 mL). The colorless solution was stirred for 1 h, and the pentane was removed under reduced pressure. The residue was extracted with pentane (2 × 30 mL), and the extract was concentrated to ca. 15 mL. Cooling (–70 °C) afforded white blocks (0.81 g, 90% yield) which were collected and dried under vacuum. Anal. Calcd for $C_{21}H_{62}N_6Si_7Th$: C, 30.5; H, 7.51; N, 10.2. Found: C, 30.2; H, 7.28; N, 10.1. The infrared spectrum showed $\nu(N_3)$ at 2105 cm^{-1}.

Preparation of $[(Me_3Si)_2N]_2UCH_2Si(Me)_2NSiMe_3(Me_3SiN_3)$. This adduct was prepared in a manner similar to that of the thorium adduct and crystallized as green-brown blocks from pentane in 80% yield. Anal. Calcd for $C_{21}H_{62}N_6Si_7U$: C, 30.3; H, 7.45; N, 10.1. Found: C, 29.9; H, 7.62; N, 10.3. The infrared spectrum showed $\nu(N_3)$ at 2103 cm^{-1}, and the mass spectrum gave a $(M - 28)^+$ ion at 804.

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