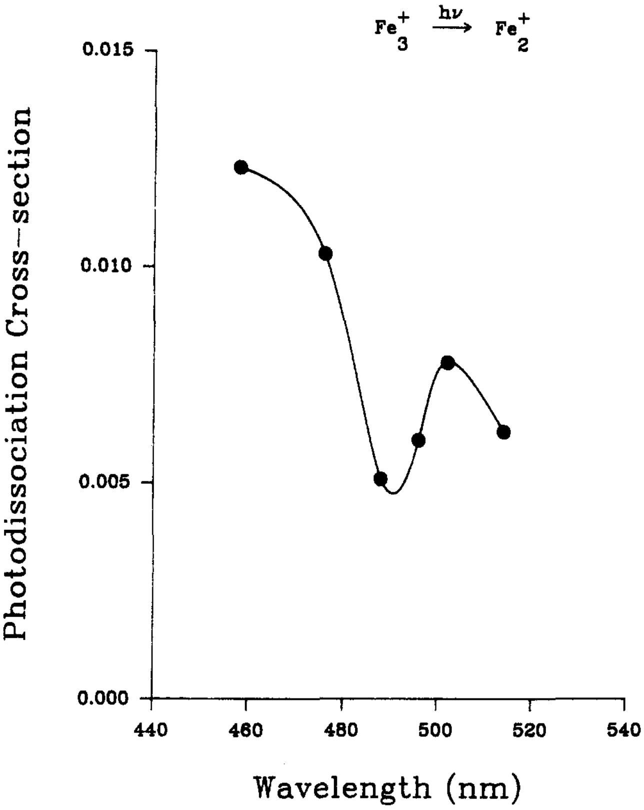

Figure 9. Photodissociation cross section as a function of laser wavelength for $Fe_3^+ \rightarrow Fe_2^+$.

bond, then no Fe^+ photoproduct ions will be observed. As the photon energy is increased, the rate for photodissociation may become comparable to the rate for emission of a photon. This will also lead to anomalously high values for the measured Fe_2^+ bond strength. Competitive radiative decay/photodissociation pathway may explain why the photodissociation cross sections steadily decrease on going from the $Fe_2(CO)_5^+$ ion to the Fe_2^+ ion (see Table I), i.e., slow radiative decay processes at low M/L ratios and fast radiative decay processes at high M/L ratios. Additional studies are underway which hopefully will resolve some of these questions.

Conclusions

The high-resolution and large dynamic range capabilities of the laser–ion beam mass apparatus allow the electronic and thermodynamic properties of novel ionic transition-metal cluster fragments to be studied without complicating solvation effects. Although much higher mass resolutions (R = 100 000–150 000) are obtainable by using a double-focusing mass spectrometer of the sort described herein, these resolutions result in poor ion transmission efficiencies. As a result, laser–ion beam photodissociation methods may be limited to moderate resolutions (5 000–50 000) since data acquisition times become prohibitively long at higher mass resolutions.

Acknowledgment. We wish to express our appreciation to one of the reviewers for bringing ref 29 to our attention. This work was supported by grants from the U.S. Department of Energy, Office of Basic Energy Sciences (DE-AS05-82ER13023), and the National Science Foundation (CHE-8418457).

Registry No. $Fe_3(CO)_{12}$, 17685-52-8; Fe_3^+, 73145-64-9; Fe_2^+, 61674-68-8; $Fe(CO)_4^+$, 35038-17-6; $Fe(CO)_3^+$, 35038-16-5; $Fe(CO)_2^+$, 35038-15-4; $Fe(CO)^+$, 35038-14-3.

Mono(cyclooctatetraenyl) Actinide Complexes. 1. Preparation of the Diamides $(C_8H_8)An[N(SiMe_3)_2]_2$ (An = Th, U) and the Structure of $(C_8H_8)Th[N(SiMe_3)_2]_2$

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Received April 7, 1988

An improved synthesis of the mono(cyclooctatetraenyl)thorium ("half-sandwich") complex $(C_8H_8)ThCl_2(THF)_2$ (**1a**) is reported. Although treatment of **1a** or the uranium analogue $(C_8H_8)UCl_2(THF)_2$ (**1b**) with alkyllithium or Grignard reagents leads to intractable products, metathesis of the chloride ligands of **1a** or **1b** with 2 equiv of $NaN(SiMe_3)_2$ cleanly gives the pseudo-seven-coordinate diamide complexes $(C_8H_8)An[N(SiMe_3)_2]_2$ (An = Th, **2a**; An = U, **2b**). A single-crystal X-ray diffraction study of $(C_8H_8)Th[N(SiMe_3)_2]_2$ (T = 298 K, monoclinic, $P2_1/a$, a = 12.071 (2) Å, b = 13.160 Å, c = 18.113 Å, β = 90.96°, V = 2876.9 Å^3, Z = 4) revealed that one carbon of each silyl amide ligand is directed toward the thorium in such a way as to mimic a four-legged piano stool with trans nitrogen atoms and trans carbon atoms. This result is ascribed to the coordination number deficiency at the metal center. The amide complex **2a** does not react with H_2 even at elevated temperatures.

Introduction

In 1980, the first mono(cyclooctatetraenyl)thorium ("half-sandwich") complexes were reported. The parent compound $(C_8H_8)ThCl_2(THF)_2$ (**1a**) was prepared by prolonged (ca. 1 week) reaction of thorocene with thorium tetrachloride in refluxing THF (eq 1) and its structure

$$(C_8H_8)_2Th + ThCl_4 \xrightarrow[\Delta]{THF} \underset{\textbf{1a}}{2(C_8H_8)ThCl_2(THF)_2} \quad (1)$$

determined by single-crystal X-ray diffraction.[1,2] In the

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solid state **1a** is a four-legged piano stool with trans chloride and trans THF ligands. Reaction 1 does not work with analogous uranium species, but $(C_8H_8)UCl_2(THF)_2$ (**1b**) can be prepared via electron transfer from uranium trichloride to neutral cyclooctatetraene in THF (eq 2).[3] In

$$2UCl_3 + C_8H_8 \xrightarrow{THF} \underset{\textbf{1b}}{(C_8H_8)UCl_2(THF)_2} + UCl_4 \quad (2)$$

contrast to **1a**, which is stable toward solvent loss at ambient temperature, one THF ligand dissociates rapidly from the metal center upon removal of **1b** from the mother liquor.

As the reactivities and spectroscopic properties of this class of compounds remain largely unexplored,[3b,4] we undertook a series of derivitization experiments designed to investigate the metathetical characteristics of the chloride ligands. We report a large scale synthesis of the thorium dichloride **1a**, the successful preparation of the mono(cyclooctatetraenyl)thorium and uranium diamides $(C_8H_8)An[N(SiMe_3)_2]_2$ (An = Th, U), and a single-crystal X-ray diffraction study of the seven-coordinate thorium diamide $(C_8H_8)Th[N(SiMe_3)_2]_2$.

Experimental Section

General Data. All reactions and manipulations were performed in oven-dried glassware under an inert atmosphere employing either standard Schlenk and vacuum line techniques or a helium-filled Vacuum Atmospheres drybox equipped with an MO 40-2 gas purification system. Solid reagents were routinely stored in the drybox. THF, diethyl ether, toluene, hexane, and heptane were distilled under nitrogen from either molten potassium or sodium–potassium alloy and were stored both in the drybox and in bulbs on the vacuum line. $ThCl_4$ (Strem) was sublimed at 600 °C ($<10^{-4}$ Torr). $NaN(SiMe_3)_2$ was prepared by a modification of the literature method, employing NaH instead of $NaNH_2$.[5] Cyclooctatetraene (Aldrich) was vacuum transferred from 4-Å molecular sieves and stored frozen in the drybox. It was derivatized to solid $K_2C_8H_8$ by potassium metal reduction in THF, filtration of the resultant solution, evaporation of solvent, trituration with hexane, filtration of the off-white solid, and vacuum drying. (*Caution*: Desolvated $K_2C_8H_8$ explodes violently upon contact with air.) Thorocene, $(C_8H_8)_2Th$, was prepared by the method of Streitwieser and co-workers[6] and purified by Soxhlet extraction with toluene followed by sublimation at 200 °C ($\leq 10^{-4}$ Torr). (^1H NMR (CD_2Cl_2): δ 6.63 (s, C_8H_8).)

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on either a Bruker AM-200 or an IBM NR-250/AF instrument. Chemical shifts are reported in parts per million relative to tetramethylsilane (δ 0.0). IR spectra were recorded on a Perkin-Elmer 683 spectrometer as Nujol mulls sealed in KBr plates; only bands in the region 1300–600 cm^{-1} are reported. Elemental analyses were performed by Mr. V. Tashinian, Microanalytical Laboratory, Department of Chemistry, University of California, Berkeley.

$(C_8H_8)ThCl_2(THF)_2$ (1a). Inside the drybox, a rapidly stirred slurry of $ThCl_4$ (11.0 g, 29.4 mmol) in 100 mL of THF in a 250-mL one-neck Schlenk vessel (equipped with a Teflon stopcock) was treated with $K_2C_8H_8$ (5.37 g, 29.4 mmol) in small portions. A mixture of white (KCl) and yellow (thorocene) precipitates formed rapidly. Following the addition of $K_2C_8H_8$ the slurry was stirred for 2 h. The vessel was then removed from the drybox, partially evacuated, and sealed and the contents were heated to 100 °C. The latter operation was routinely performed behind a safety shield. Over a period of ca. 5 h, the yellow precipitate dissolved and the slurry turned white. The hot slurry was returned to the drybox, where it was filtered through Celite packed in a 150-mL coarse sintered glass frit and washed with 4 × 75 mL of hot THF. The combined filtrate and washings were evaporated in vacuo to the cloud point and cooled to −40 °C overnight. White crystals of the complex were then separated by filtration, washed with −40 °C THF, and dried in vacuo. Concentration of the mother liquor and recooling provided a second crop of product. Total yield: 14.85 g (91%).

This material can also be prepared in comparable yield by heating a THF slurry of purified $(C_8H_8)_2Th$ and $ThCl_4$ to 100 °C for 5 h, followed by filtration and workup as indicated above.

^1H NMR (CD_2Cl_2): δ 6.77 (s, C_8H_8); 4.03, 1.92 (both m, THF). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 102.4 (s, C_8H_8); 71.8, 25.9 (both s, THF).

$(C_8H_8)UCl_2(THF)_2$ (1b). This complex was prepared and purified by the method of Moore.[3b]

$(C_8H8)Th[N(SiMe_3)_2]_2$ (2a). Solid $(C_8H_8)ThCl_2(THF)_2$ (1.21 g, 2.19 mmol) and $NaN(SiMe_3)_2$ (845 mg, 4.6 mmol) were placed in a 100-mL Schlenk flask capped with a vacuum stopcock. Toluene (50 mL) was added by vacuum transfer at −196 °C. The reaction mixture was slowly warmed to room temperature and stirred overnight. The solvent was evaporated in vacuo, and the white solid was dried under high vacuum for 4 h. Heptane (20 mL) was then added by vacuum transfer, and the resulting slurry was heated to 85 °C. The pale yellow solution was filtered and cooled to −78 °C. After 2 h, the white microcrystalline solid was filtered and dried in vacuo. Yield: 1.04 g (72%).

^1H NMR ($C_6D_5CD_3$): δ 6.58 (s, 8 H, C_8H_8); 0.21 (s, 36 H, Me). ^1H NMR (1:1 $C_6D_5CD_3$/THF-d_8, −120 °C): δ 6.56 (s, 8 H, C_8H_8); 0.10 (s, 36 H, Me). ^{13}C NMR ($C_6D_5CD_3$): δ 102.8 (d, J_{CH} = 160 Hz, C_8H_8); 4.5 (q, J_{CH} = 117 Hz, Me). IR (Nujol): ν 1249 (s), 936 (vs), 875 (s), 847 (vs), 773 (m), 716 (s); 670 (br, m), 610 (m) cm^{-1}. Anal. Calcd for $C_{20}H_{44}N_2Si_4Th$: C, 36.57; H, 6.75; N, 4.26. Found: C, 36.23; H, 6.79; N, 4.30.

$(C_8H_8)U[N(SiMe_3)_2]_2$ (2b). Freshly prepared $(C_8H_8)UCl_2(THF)_2$ (1.11 g, 2.00 mmol) was placed in a 50-mL Erlenmeyer flask in the drybox and slurried in toluene (40 mL). $NaN(SiMe_3)_2$ (734 mg, 4.0 mmol) was added in small portions with stirring. After stirring overnight, the red solution was filtered to remove NaCl. The solution was concentrated to ca. 10 mL and then cooled to −40 °C overnight. The resultant dark red crystals were filtered, washed with cold hexane and dried. A second crop was obtained by concentrating the mother liquor to 1 mL and recooling. Total yield: 1.01 g (76%).

^1H NMR (C_6D_6): δ −33.4 (s, 8 H), C_8H_8); −11.0 (s, 36 H, Me). ^1H NMR (1:1 $C_6D_5CD_3$/THF-d_8, 0 °C): δ −37.9 (s, C_8H_8); −12.1 (s, Me). ^1H NMR (1:1 $C_6D_5CD_3$/THF-d_8, −120 °C): δ −67.7 (s, C_8H_8). ^{13}C NMR (1:1 $C_6D_5CD_3$/THF-d_8, 0 °C): δ 220.5 (d, J_{CH} = 163 Hz, C_8H_8); −18.7 (q, J_{CH} = 117 Hz, Me). $^{13}C\{^1H\}$ NMR (1:1 $C_6D_5CD_3$/THF-d_8, −120 °C): δ 299.3 (s, C_8H_8). IR (Nujol): ν 1249 (s), 930 (vs), 871 (s), 846 (vs), 775 (m), 720 (s), 660 (m), 611 (m) cm^{-1}. Anal. Calcd for $C_{20}H_{44}N_2Si_4U$: C, 36.23 H, 6.69; N, 4.23. Found: C, 35.90; H, 6.62; N, 4.19.

X-ray Crystallography. Single crystals of $(C_8H_8)Th[N(SiMe_3)_2]_2$ suitable for diffraction studies were grown from heptane at −40 °C. Samples were brought from the drybox under a layer of fluorolube to facilitate microscopic inspection and crystal mounting. An irregularly shaped crystal was wedged into a 0.2-mm glass capillary, which was then flame sealed. The crystal was mounted on an Enraf-Nonius CAD-4 diffractomter and centered in the X-ray beam. Automatic peak search and indexing procedures yielded a monoclinic reduced primitive cell. Cell constants and data collection parameters are given in Table I.

Data were collected at ambient temperature by using variable speed θ–2θ scans. Two standard reflections were monitored every 2 h of X-ray exposure time. Two orientation standards were checked every 200 reflections, and the crystal orientation redetermined if either of the reflections deviated more than 0.1° from the calculated position; reorientation was required twice during data collection. Systematic absences indicated the monoclinic space group as $P2_1/a$.

The raw intensity data were converted to structure factor amplitudes and their esds by correction for scan speed, background, and Lorentz and polarization effects. Inspection of the intensity standards showed a slight anisotropic decay and the data were corrected for this decay. Inspection of the averaged curve

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(1) LeVanda, C.; Solar, J. P.; Streitwieser, A. *J. Am. Chem. Soc.* **1980**, *102*, 2128.

(2) Zalkin, A.; Templeton, D. H.; LeVanda, C.; Streitwieser, A. *Inorg. Chem.* **1980**, *19*, 2560.

(3) (a) Streitwieser, A., personal communication. (b) Moore, R. M. Ph.D. Thesis, University of California, Berkeley, 1985.

(4) Smith, K. A. Ph.D. Thesis, University of California, Berkeley, 1984.

(5) Kruger, C. R.; Niederprum, H. *Inorg. Synth.* **1966**, *8*, 15.

(6) Streitwieser, A.; Yoshida, N. *J. Am. Chem. Soc.* **1969**, *91*, 7528.

Table I. Crystal Data and Data Collection Parameters for 2a

formula	$C_{20}H_{44}N_2Si_4Th$
fw	656.97
cryst color	colorless
cryst system	monoclinic
space group	$P2_1/a$
temp, °C	23
a, Å	12.071 (2)[a]
β, Å	13.160 (2)
c, Å	18.113 (5)
β, deg	90.96 (2)
V, Å^3	2876.9
Z	4
ρ_{calcd}, g cm^{-3}	1.517
linear abs coeff, cm^{-1}	55.36
abs corrctn method	$\phi \times$ sphere
sphere radius, mm	0.2
transmissn (max, min)	0.223, 0.145
radiatn, λ	Mo $K\alpha_1$, 0.709 30 Å
av ω peak width, deg	0.7
scan method	θ–2θ
scan rate	variable
2θ limits, deg	0–45
target $\sigma(I)/I$	0.015
reflctns measd	$\pm h,+k,+l$
data collected	4185
unique data	3758
unique data with $I > 2\sigma(I)$	2155
no. of refined parameters	245
$R(F)$, obsd reflctns	0.037
$R_w(F)$, obsd reflctns	0.043

[a] Unit cell parameters and their esds were derived by a least-squares fit to the setting angles of the unresolved Mo $K\alpha$ components of 25 reflections with 2θ near 30°.

from an azimuthal scan of a reflection near $\chi = 90°$ and its Friedel pair (measured at 10° increments about ψ) showed a variation of $I_{min}/I_{max} = 0.66$. An absorption correction based on these data, multiplied by the calculated factor for a sphere, was applied to the intensities. Removal of systematically absent reflections and averaging of redundant data ($R(I) = 2.8\%$) left 3758 unique data.

The structure was solved by Patterson methods and refined by using standard least-squares and Fourier techniques. The refinements were carried out by using neutral atom scattering factors and appropriate anomalous scattering terms and a secondary extinction parameter.[7,8] All non-hydrogen atoms were refined with anisotropic thermal parameters. A final difference Fourier map revealed the positions of some of the hydrogen atoms, but no attempt was made to include or refine these. Positional and equivalent isotropic thermal parameters are given Table II.

Results and Discussion

The original synthesis of $(C_8H_8)ThCl_2(THF)_2$ (**1a**), required the independent preparation and purification of thorocene, $(C_8H_8)_2Th$, followed by ring exchange with $ThCl_4$ in refluxing THF (bp 67 °C at 760 Torr) over the course of 1 week.[1,2] We have discovered that when the reaction is performed in a sealed vessel at temperatures ≥100 °C, the time required the synthesis of **1a** is reduced to approximately 5 h. We have also found that it is not necessary to isolate and purify thorocene for the ring exchange reaction with $ThCl_4$. Treatment of $ThCl_4$ with 1 equiv of $K_2C_8H_8$ in THF, followed by heating to 100 °C, provides **1a** in comparable yield (≥90%). The latter reaction is typically carried out on a 30-mmol scale in our laboratory, providing ca. 15 g of pure, crystalline **1a** in 1 day.

Table II. Fractional Coordinates and Isotropic Thermal Parameters[a] for 2a

atom	x	y	z	B_{ISO}, Å^2
Th(1)	0.14068 (4)	0.05680 (4)	0.25119 (3)	3.48
N(1)	0.197 (1)	−0.032 (1)	0.148 (1)	3.4
Si(1)	0.1240 (3)	−0.1451 (3)	0.1385 (2)	4.2
C(1)	0.215 (1)	−0.263 (1)	0.137 (1)	7.0
C(2)	0.022 (1)	−0.146 (1)	0.057 (1)	6.5
C(3)	0.036 (1)	−0.159 (1)	0.224 (1)	5.5
Si(2)	0.2983 (4)	−0.0054 (4)	0.0820 (2)	4.6
C(4)	0.315 (1)	0.136 (1)	0.069 (1)	6.4
C(5)	0.438 (1)	−0.062 (1)	0.109 (1)	6.8
C(6)	0.264 (1)	−0.055 (1)	−0.015 (1)	7.6
N(2)	0.234 (1)	−0.028 (1)	0.348 (1)	3.7
Si(3)	0.3652 (3)	0.0230 (3)	0.3534 (2)	4.2
C(7)	0.388 (1)	0.107 (1)	0.436 (1)	6.2
C(8)	0.386 (1)	0.106 (1)	0.269 (1)	4.6
C(9)	0.480 (1)	−0.075 (1)	0.347 (1)	6.1
Si(4)	0.1951 (4)	−0.1208 (4)	0.4098 (3)	5.3
C(10)	0.255 (1)	−0.103 (1)	0.506 (1)	7.8
C(11)	0.039 (1)	−0.124 (1)	0.426 (1)	5.9
C(12)	0.242 (1)	−0.252 (1)	0.375 (1)	7.7
C(13)	0.144 (2)	0.254 (2)	0.296 (2)	9.9
C(14)	0.142 (1)	0.259 (2)	0.224 (2)	7.7
C(15)	0.071 (2)	0.221 (2)	0.165 (1)	9.0
C(16)	−0.019 (2)	0.153 (2)	0.164 (1)	7.7
C(17)	−0.076 (1)	0.095 (1)	0.221 (1)	7.5
C(18)	−0.070 (2)	0.089 (1)	0.299 (1)	7.3
C(19)	−0.008 (2)	0.134 (2)	0.352 (1)	8.0
C(20)	0.082 (2)	0.203 (2)	0.353 (1)	8.6

[a] $B_{ISO} = 10^2[(U(11) + U(22) + U(33)/3]$.

Neither the ring exchange method nor the addition of 1 equiv of $K_2C_8H_8$ to UCl_4 in THF provide appreciable quantities of **1b**. Uranocene, $(C_8H_8)_2U$, and unreacted UCl_4 are the primary products. The Streitwieser group has recently isolated **1b** via an elegant preparation employing electron-transfer methods.[3] Their straightforward method provides **1b** in high yield and high purity.

Previous attempts to metathesize the halide ligands of **1a** or **1b** with alkylating agents failed to provide stable $(C_8H_8)AnR_2$ complexes.[3,4] We confirmed some of these results and found that the stability of the alkylation products were related to the steric bulk of the alkyl ligand. For example, the product obtained upon treatment of **1a** with 2 equiv of $LiCH_2SiMe_3$ in diethyl ether decomposed qualitatively more rapidly than the product obtained with $LiCH(SiMe_3)_2$.

Recent work from the Marks group[10] indicates that actinide–nitrogen bonds are ca. 15 kcal stronger than actinide-carbon bonds. Anticipating that a half-sandwich diamide would be isolable, we reacted (eq 3) **1a** and **1b** in

$$(C_8H_8)AnCl_2(THF)_2 + 2\,NaN(SiMe_3)_2 \xrightarrow{PhCH_3} (C_8H_8)An[N(SiMe_3)_2]_2 + 2NaCl \quad (3)$$

2a: An = Th
2b: An = U

toluene with 2 equiv of $NaN(SiMe_3)_2$. these reactions provide the heptane-soluble, air-sensitive diamide complexes $(C_8H_8)An[N(SiMe_3)_2]_2$ (An = Th, **2a**; An = U, **2b**) in ca. 70% isolated yield. Spectroscopic data are consistent with a pseudo seven-coordinate formulation.[11] The ^1H NMR spectrum of **2b** shows a surprising, although not unprecedented,[12] shift of the silyl methyl protons to high

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(7) (a) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Table 2.2 A. (b) Cromer, D. T. *Ibid*, Table 2.3.1.

(8) (a) Zachariasen, W. H. *Acta Crystallogr.* **1967**, *23*, 558. (b) Larson, A. C. *Ibid.* **1967**, *23*, 664.

(9) LeVanda, C.; Streitwieser, A. *Inorg. Chem.* **1981**, *20*, 656.

(10) Bruno, J. W.; Marks, T. J.; Morss, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 6824.

(11) By analogy with the cyclopentadienyl anion (a six-electron donor) which is normally considered to occupy three coordination sites, the cyclooctatetraenyl dianion, a ten-electron donor, is considered to occupy five coordination sites. See: Baker, E. C.; Halstead, G. N.; Raymond, K. N. *Struct. Bonding (Berlin)* **1976**, *25*, 23.

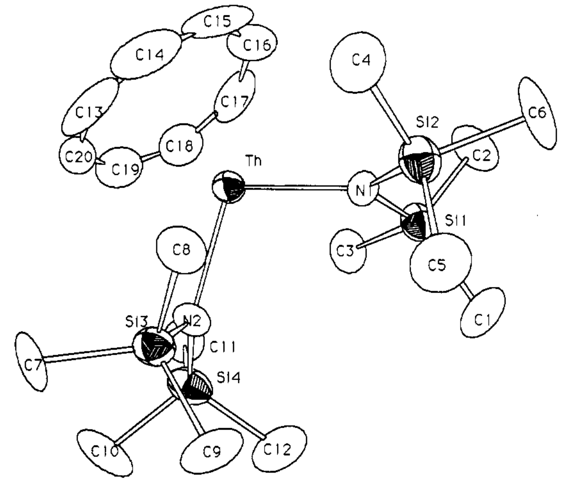

Figure 1. ORTEP drawing of $(C_8H_8)Th[N(SiMe_3)_2]_2$, showing the atomic labeling scheme.

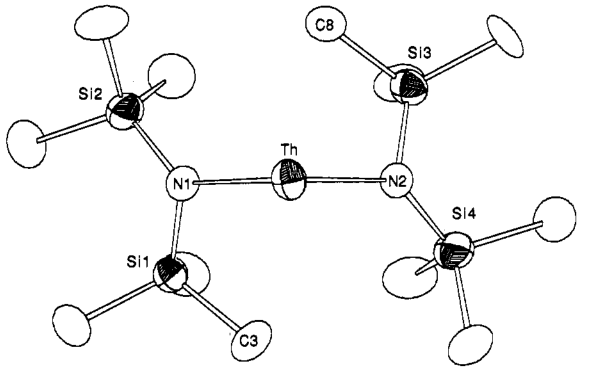

Figure 2. ORTEP drawing (partial labeling) of $(C_8H_8)Th[N(SiMe_3)_2]_2$, viewed down the ring centroid–metal axis. The carbon atoms of the cyclooctatetraene ring have been removed for clarity.

field (δ −11.0). The infrared spectra of **2a** and **2b** are virtually superimposable, with a number of bands in the region 1300–600 cm^{-1} attributable to the amide ligands, and a strong band near 720 cm^{-1}, which appears to be characteristic of mono(cyclooctatetraenyl)actinide(IV) linkages.[13]

We were particularly interested in the structural characterization of one of these compounds because of their low formal coordination numbers. A single-crystal X-ray diffraction study of **2a** confirmed the $(C_8H_8)Th[N(SiMe_3)_2]_2$ stoichiometry and revealed an interesting facet of the solid-state coordination geometry. ORTEP drawings of the complex appear in Figures 1 and 2; selected bond distances and angles appear in Table III.

The carbon atoms of the cyclooctatetraenyl ring are planar to within 0.05 Å. The thorium atom lies 2.04 Å from the centroid of the ring, with an average metal-to-ring carbon distance of 2.75 (2, 3, 8) Å.[14] The thorium atom is also bound to two amide ligand nitrogen atoms at an average distance of 2.34 (1) Å. All of these values are similar to those observed previously in other thorium(IV) cyclooctatetraenyl and/or silyl amide systems.[2,12a,15,16]

Table III. Selected Distances (Å) and Angles (deg) for 2a

A	B	distance	A	B	distance
Th	C3	3.146 (15)	Th	C8	3.041 (13)
Th	C13	2.72 (2)	Th	C14	2.71 (2)
Th	C15	2.79 (2)	Th	C16	2.77 (2)
Th	C17	2.711 (15)	Th	C18	2.74 (2)
Th	C19	2.78 (2)	Th	C20	2.76 (2)
Th	N1	2.32 (1)	Th	N2	2.35 (1)
N1	Si1	1.73 (1)	N1	Si2	1.76 (1)
N2	Si3	1.73 (1)	N2	Si4	1.73 (1)
Si1	C1	1.898 (15)	Si2	C4	1.890 (16)
Si1	C2	1.904 (15)	Si2	C5	1.901 (15)
Si1	C3	1.908 (14)	Si2	C6	1.914 (15)
Si3	C7	1.886 (15)	Si4	C10	1.886 (16)
Si3	C8	1.896 (15)	Si4	C11	1.907 (15)
Si3	C9	1.898 (14)	Si4	C12	1.924 (17)

A	B	C	angle	A	B	C	angle
N1	Th	N2	102.5 (4)	Si1	N1	Si2	117.8 (6)
C3	Th	C8	126.8 (4)	Si3	N2	Si4	119.7 (6)
Th	N1	Si1	110.8 (5)	Th	N2	Si3	106.6 (5)
Th	N1	Si2	131.5 (5)	Th	N2	Si4	133.6 (6)
C1	Si1	C2	110.5 (8)	C4	Si2	C5	108.9 (8)
C1	Si1	C3	105.4 (8)	C4	Si2	C6	104.4 (8)
C2	Si1	C3	105.5 (7)	C5	Si2	C6	106.2 (8)
C7	Si3	C8	106.3 (7)	C10	Si4	C11	103.2 (8)
C7	Si3	C9	110.5 (8)	C10	Si4	C12	107.6 (9)
C8	Si3	C9	103.9 (7)	C11	Si4	C12	108.9 (7)
N1	Si1	C1	113.8 (6)	N1	Si2	C4	110.8 (6)
N1	Si1	C2	113.7 (6)	N1	Si2	C5	111.7 (6)
N1	Si1	C3	107.2 (6)	N1	Si2	C6	114.4 (6)
N2	Si3	C7	113.7 (7)	N2	Si4	C10	113.9 (7)
N2	Si3	C8	108.1 (6)	N2	Si4	C11	113.1 (6)
N2	Si3	C9	110.5 (8)	N2	Si4	C12	109.8 (7)

As shown in Figure 2, the amide ligands are skewed and the 12 silyl carbon atoms are not chemically equivalent. Inspection of the coordination geometry around the metal center shows that one carbon atom (C(3) and C(8)) of each silyl amide ligand is directed toward the thorium in such a way as to mimic a four-legged piano stool with trans nitrogen atoms and trans carbon atoms. The distances from thorium to the directed carbons are 3.147 (15) Å (C(3)) and 3.041 (13) Å (C(8)), while the distances to the other amide carbon atoms are all greater than 4.07 Å. Several amide-based ligand angles contract as a result of these interactions: the N(1)-Si(1)-C(3) and N(2)–Si(3)–C(8) angles are 107.2 (6)° and 108.1 (6)°, respectively, while the other N–Si–C angles average 112.9 (6, 15, 10)°; the Th–N(1)–Si(1) and Th–N(2)–Si(3) angles average 108.7 (5)°, while the Th–N(1)–Si(2) and Th–N(2)–Si(4) angles average 132.6 (5)°. The dihedral angle between the plane containing thorium and the two nitrogen atoms and the plane containing thorium and the two silyl carbon atoms is 76.4°.

We found evidence for some of the hydrogen atoms of the amide ligands in difference Fourier maps but did not include them in the refinement due to the rather large thermal motion associated with the ring and amide carbon atoms. Placement of methyl hydrogen atoms into idealized tetrahedral positions on C3 and C8 indicates that the closest approach of these hydrogens to the thorium center ranges from 2.77 to 2.88 Å. On the basis of numerous cases of "agostic" metal-to-C–H bond interactions discerned in other diffraction studies,[15,17-20] including one involving silyl

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[12] The silyl methyl protons of [bis(trimethylsilyl)amido]uranium(IV) complexes typically resonate between δ 0 and δ −2 in the ^{1}H NMR spectrum, but a chemical shift of δ −19.5 is reported for these protons in the hydride $UH[N(SiMe_3)_2]_3$. See: (a) Turner, H. W.; Andersen, R. A.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1979**, *18*, 1221. (b) McCullough, L. G.; Turner, H. W.; Andersen, R. A.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1981**, *20*, 2869. (c) Simpson, S. J.; Turner, H. W.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 2991.

[13] Solar, J. P.; Streitwieser, A.; Edelstein, N. Lawrence Berkeley Laboratory Report 10348, December, 1979; p 3.

[14] For averages of crystallographic data, values in parentheses are the mean value of the esds, the standard deviation of the individual determinations of a datum from the average value (calculated as $[\sum(x_i - x)^2/(N-1)]^{1/2}$), and the number of individual determinations, respectively.

[15] Gilbert, T. M.; Ryan, R. R.; Sattelberger, A. P. *J. Am. Chem. Soc.*, submitted for publication.

[16] Avdeef, A.; Raymond, K. N.; Hodgson, K. O.; Zalkin, A. *Inorg. Chem.* **1972**, *11*, 1083.

amide ligands,[21] it is clear that the thorium atom is interacting with the C(3)–H and C(8)–H bonds of the amide ligands in order to minimize coordinative/electronic unsaturation.

Frequently, "agostic" M···H–C interactions manifest themselves in infrared and NMR spectra.[17] The infrared spectra show low-energy C–H stretching vibrations in the region 2700–2350 cm^{-1}. These characteristic vibrations are absent in the IR spectra of **2a** and **2b**. In the ^{13}C NMR spectra of complexes with static M···H–C interactions, values of $^1J_{\text{CH}}$ for sp^3 C–H bonds range from 75 to 100 Hz. We attempted to "freeze out" the asymmetric conformation of **2a** and have recorded ^{1}H and ^{13}C NMR spectra down to −120 °C in a 1:1 toluene-d_8/THF-d_8 mixture. At −120 °C, the resonances corresponding to the silyl methyl groups in both spectra have broadened, but the peak positions and the carbon–hydrogen coupling constant are unexceptional. We propose that the silyl methyl groups interconvert rapidly on the NMR time scale, leading to an averaged $^1J_{\text{CH}}$ value close to that of a noninteracting SiMe_3 group. A similar proposal has been advanced by Teuben and co-workers to explain the solution NMR behavior of the yttrium(III) complex $(\text{C}_5\text{Me}_5)_2\text{Y}[\text{N}(\text{SiMe}_3)_2]$, which also exhibits a γ-C–H···M interaction in the solid state.[19] We also obtained the ^{1}H and ^{13}C NMR spectra of paramagnetic **2b**, hoping that a greater chemical shift difference between "coordinated" and "uncoordinated" silyl methyl groups would raise the coalescence temperature above −120 °C. In fact, the silyl methyl resonances of **2b** coalesce[22] at −120 °C; extremely broad features were observed in the appropriate regions of the ^{1}H and ^{13}C{^{1}H} NMR spectra. A rough calculation,[23] assuming three equivalent methyl sites and a large chemical shift difference (>500 Hz), leads to $\Delta G^{\ddagger}_{153} \approx 7$–8 kcal for exchange of silyl methyl groups.

In the thermochemical study noted above,[10] the thorium–nitrogen and thorium–hydrogen bonds were shown to be of nearly equal strength, with the thorium–nitrogen bond perhaps slightly stronger. In keeping with this result, we find that amide complex **2a** does not react with H_2, even at elevated temperatures.

Conclusion

We have shown that the chloride ligands of thorium and uranium "half-sandwich" $(\text{C}_8\text{H}_8)\text{AnCl}_2(\text{THF})_2$ complexes can be metathesized to provide base-free $(\text{C}_8\text{H}_8)\text{An}[\text{N}(\text{SiMe}_3)_2]_2$ compounds. The diffraction study of **2a** indicates a remarkable feature of this class: rather than exist as "simple" seven-coordinate monomers, the metal center attracts electron density from remote C–H bonds to complete its coordination sphere. Because the solution NMR data indicates that this interaction is a weak one, **2a**, **2b**, and analogous diamide derivatives should be highly reactive species. Further studies are in progress.

Acknowledgment. This work was performed under the auspices of the U.S. Department of Energy, and, in part, under the auspices of the Division of Chemical Energy Sciences, Office of Basic Energy Sciences, Department of Energy. We thank Kenneth Salazar for skilled technical assistance.

Registry No. **1a**, 73652-04-7; **1b**, 117097-69-5; **2a**, 117097-70-8; **2b**, 117097-71-9; ThCl_4, 10026-08-1; $\text{K}_2\text{C}_8\text{H}_8$, 59391-85-4; $\text{NaN}(\text{SiMe}_3)_2$, 1070-89-9.

Supplementary Material Available: Anisotropic thermal parameters (Table S1) for **2a** (2 pages); a listing of F_o and F_c (Table S2) for **2a** (10 pages). Ordering information is given on any current masthead page.

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[22] (a) One reviewer objects to our use of this term and comments that the disappearance of the silyl methyl resonance at −120 °C does not necessarily mean that the silyl methyl groups are undergoing chemical exchange coalescence and that other (unspecified) explanations are possible. While we are in agreement that caution must be exercised in the interpretation of any system where a low-temperature-limiting spectrum cannot be reached, we believe our observation that the line shape of the C_8H_8 resonance of **2b** remains relatively unperturbed as the temperature is lowered while the SiMe_3 resonance disappears into the base line argues for chemical exchange coalescence.

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