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Synthesis and Characterization of Bis(pentamethylcyclopentadienyl)uranium(IV) and -thorium(IV) Compounds Containing the Bis(trimethylsilyl)phosphide Ligand

S. W. Hall,[†,‡] J. C. Huffman,[§] M. M. Miller,[∥] L. R. Avens,[†] C. J. Burns,[*,‡]
D. S. J. Arney,[‡] A. F. England,[‡] and A. P. Sattelberger[‡]

*Nuclear Materials Technology Division, Los Alamos National Laboratory,
Los Alamos, New Mexico 87545, Isotope and Nuclear Chemistry Division,
Los Alamos National Laboratory, Los Alamos, New Mexico 87545, Molecular Structure Center,
Indiana University, Bloomington, Indiana 47405, and Department of Chemistry,
Colorado State University, Fort Collins, Colorado 80523*

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A series of bis(pentamethylcyclopentadienyl)uranium and thorium bis(trimethylsilyl)phosphide compounds, $Cp^*_2An(X)[P(SiMe_3)_2]$, has been synthesized, where X = Cl [An = U (**1a**), Th (**1b**)] or CH_3 [An = U (**2a**), Th (**2b**)]. Thermal decomposition of **2a,b** results in the formation of the metallacycle complexes $Cp^*_2\overline{An[P(Si(CH_3)_3)Si(CH_3)_2C}H_2]$ [An = U (**3a**), Th (**3b**)], accompanied by the liberation of methane. The compounds **1a**, **2b**, and **3a** have been characterized by single crystal X-ray structural analysis. Crystal data: for **1a**, space group $P2_1/a$, $a = 12.025$ (2) Å, $b = 16.821$ (4) Å, $c = 15.156$ (3) Å, $\beta = 95.85$ (1)°, $V = 3049.7$ (7) Å^3, $Z = 4$, $R = 0.059$; for **2b**, space group $P2_1/c$, $a = 15.296$ (3) Å, $b = 16.870$ (3) Å, $c = 12.137$ (2) Å, $\beta = 96.07$ (3)°, $V = 3114.1$ (10) Å^3, $Z = 4$, $R = 0.040$; for **3a**, space group $P2_1/n$, $a = 8.632$ (2) Å, $b = 18.809$ (9) Å, $c = 19.063$ (10) Å, $\beta = 100.66$ (4)°, $V = 3042$ (2) Å^3, $Z = 4$, $R = 0.073$.

Introduction

The chemistry of organoactinide complexes containing metal–heteroatom bonds, particularly those with functional groups such as oxides and imides capable of engaging in multiple bonding, is of great interest due to the inherently large ligand–metal charge separation in complexes of electropositive metals. Although there are several well-characterized uranium organoimido complexes,[1] few examples exist of actinide phosphide complexes,[2] and there is only one report of an actinide phosphinidene complex.[3] The first reported stable terminal phosphinidene complex of a transition metal was reported by Lappert et al.,[4] who utilized the Cp_2M (Cp = C_5H_5) framework and bulky phosphorus alkyl or aryl substituents to kinetically stabilize metal–phosphorus multiple bonding. Marks and co-workers[5] pioneered the use of the analogous sterically encumbered metal framework Cp^*_2An ($Cp^* = C_5Me_5$, An = U, Th) to prevent ligand redistribution and aggregation in actinide chemistry. This framework will support actinide–phosphorus bonding in metal phosphide complexes.[2a,b] We have attempted the preparation of actinide phosphinidene complexes via loss of trimethylsilyl groups from the functionalized phosphide ligand, bis(trimethylsilyl)phosphide anion. This anion has been successfully employed in the preparation of transition-metal–phosphorus bonds,[6,7] and Weber et al. have further demonstrated that phosphorus–silicon bond cleavage can occur in related main-group complexes with elimination of chlorotrimethylsilane to yield multiply bonded diphosphene complexes.[6]

We have discovered, however, that the monosubstituted complexes $Cp^*_2An(Cl)[P(SiMe_3)_2]$ (An = U, Th) exhibit remarkable thermal stability and sho no evidence of elimination reactions. The corresponding methyl derivatives $Cp^*_2An(Me)[P(SiMe_3)_2]$ decompose thermally to liberate methane and yield the phosphametallacycle compounds $Cp^*_2\overline{An[P(Si(CH_3)_3)Si(CH_3)_2C}H_2]$. We report here the preparation and structural characterization of these complexes.

Experimental Section

General Considerations. The compounds $Cp^*_2AnCl_2$,[5] $Cp^*_2An(Cl)CH_3$[5] (An = U, Th; Cp* = pentamethylcyclopentadienyl),

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[†] Nuclear Materials Technology Division, Los Alamos National Laboratory.

[‡] Isotope and Nuclear Chemistry Division, Los Alamos National Laboratory.

[§] Indiana University.

[∥] Colorado State University.

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Table I. Crystal Data Collection and Refinement Parameters for 1a, 2b, and 3a

	1a	2b	3a
formula	$UC_{26}H_{48}ClPSi_2$	$ThC_{27}H_{51}PSi_2$	$UC_{26}H_{47}PSi_2$
lattice type	monoclinic	monoclinic	monoclinic
space group	$P2_1/a$	$P2_1/c$	$P2_1/n$
a, Å	12.025 (2)	15.296 (3)	8.632 (2)
b, Å	16.821 (4)	16.870 (3)	18.809 (9)
c, Å	15.156 (3)	12.137 (2)	19.063 (10)
β, deg	95.85 (1)	96.07 (3)	100.66 (4)
V, $Å^3$	3049.8 (19)	3114.1 (10)	3042 (2)
Z	4	4	4
d_{calc}, g cm^{-3}	1.571	1.482	1.495
μ, cm^{-1}	52.748	50.93	52.00
cryst dim, mm	0.10 × 0.12 × 0.08	0.40 × 0.22 × 0.30	0.40 × 0.60 × 0.02
collectn temp, °C	−155	−100	25
2θ range, deg	6–45	2–45	2–45
no. of rflns read	4442	4469	4314
no. of unique rflns obsd	3416 ($2.33\sigma(F)$)	2304 ($6.0\sigma(F)$)	2929 ($2.5\sigma(F)$)
no. of params	280	280	222
R_{int}, %	7.50	4.02	8.40
$R(F)$, %	5.94	4.02	7.33
$R_w(F)$, %	5.80	4.81	9.34
GOF	1.506	1.05	1.01
max Δ/σ, e $Å^{-3}$	0.25	0.02	0.45
	1.08	2.90	1.84
structure soln	MULTAN78	Patterson	Patterson
abs cor	none	empirical	empirical

and $Li[P(Si(CH_3)_3)_2]\cdot 2THF$[8] were prepared by literature methods. The purity of the compounds was verified by ^1H NMR. ^1H and ^{31}P NMR spectra were recorded on a Varian Unity 300 NMR (^1H, 300 MHz; ^{31}P, 122 MHz) spectrometer, in C_6D_6, at room temperature. ^1H NMR chemical shifts were referenced to residual protio-solvent signal, and ^{31}P NMR chemical shifts were referenced to external 85% H_3PO_4. The tetrahydrofuran, hexane, and benzene-d_6 solvents were purchased from Aldrich Chemical Company, dried over Na/K alloy, and distilled under argon prior to use. Pyridinium hydrochloride was purchased from Aldrich Chemical Company, and silver(I) fluoride was purchased from Strem Chemicals; both were used as received. All manipulations were carried out in an inert-atmosphere (He) glovebox.

$K[P(Si(CH_3)_3)_2]$. Preparation of the potassium phosphide from the lithium phosphide follows the general procedure for such reactions as given by Lochmann et al.[9] A hexane solution of KO^tBu (1.12 g, 9.99 mmol, 50 mL hexane) was added with stirring to a hexane solution of $Li[P(Si(CH_3)_3)_2]\cdot 2THF$ (3.28 g, 9.99 mmol, 100 mL hexane). A white precipitate, $K[P(Si(CH_3)_3)_2]$, formed immediately upon mixing. The mixture was stirred at room temperature for 2 h and then filtered. The product was dried under vacuum. Yield: 90%.

$Cp^*{}_2U(Cl)[P(Si(CH_3)_3)_2]$ (1a). A colorless tetrahydrofuran solution of $K[P(Si(CH_3)_3)_2]$ (0.432 g, 2.00 mmol, 25 mL THF) was added dropwise to a stirred, bright red tetrahydrofuran solution of $Cp^*{}_2UCl_2$ (1.158 g, 2.00 mmol, 50 mL THF) over a period of 10 min. No color change was apparent, but a white precipitate formed immediately upon addition of the potassium phosphide to the actinide solution. The mixture was stirred at room temperature for 2 h. Removal of all volatiles under vacuum left a bright red solid. Extraction into hexane and filtration through Celite to remove any insoluble material resulted in a clear red solution. Reduction in volume of the hexane and storage at −40 °C resulted in a red crystalline product. Yield: 80%.

The thorium compound $Cp^*{}_2Th(Cl)[P(Si(CH_3)_3)_2]$ (**1b**) was prepared in an analogous manner, and a similar method was used to prepare the methyl derivatives of uranium $Cp^*{}_2U(CH_3)[P(Si(CH_3)_3)_2]$ (**2a**) and thorium $Cp^*{}_2Th(CH_3)[P(Si(CH_3)_3)_2]$ (**2b**), using $Cp^*{}_2An(Cl)(CH_3)$ as the starting actinide complexes. Yields range from 80 to 90%.

$Cp^*{}_2U[P(Si(CH_3)_3)Si(CH_3)_2CH_2]$ (3a). In a sealed, thick-walled NMR tube, with benzene-d_6 as the solvent, a sample of $Cp^*{}_2U(CH_3)P(Si(CH_3)_3)_2$ was heated to 120 °C and the reaction monitored by ^1H NMR spectroscopy. Approximately 3 h was required for completion of the reaction. No other products were observed in the NMR spectrum. The contents were removed from the NMR tube in an inert-atmosphere (He) glovebox and volatiles removed by vacuum. The red solids were dissolved in hexane and stored at −40 °C, producing X-ray-quality crystals.

A similar method was used to prepare the analogous thorium compound $Cp^*{}_2Th[P(Si(CH_3)_3)Si(CH_3)_2CH_2]$ (**3b**).[10]

X-ray Structure Determination for 1a, 2b, and 3a. 1a. A suitable crystal was located, transferred to the Picker four-circle goniometer of a diffractometer designed and constructed at the Molecular Structure Center at Indiana University, and cooled to −155 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to the unique monoclinic space group $P2_1/a$ (alternate setting of $P2_1/c$). Subsequent solution and refinement of the structure confirmed this choice. Final cell parameters are given in Table I, as are other crystallographic data. Reflections were collected using a continuous θ–2θ scan with fixed backgrounds, at a scan rate of 6.0° min^{-1}. A total of 4442 reflections were collected. The data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects. No absorption correction was applied. The data were averaged over $P2/m$ symmetry (R_{int} = 7.5%). The structure was solved by direct methods and refined via standard least-squares and Fourier techniques. All non-hydrogen atoms were refined anisotropically. A difference Fourier synthesis revealed the location of some, but not all, hydrogen atoms. The hydrogen atoms were added to the structure factor calculation in idealized positions without refinement (C–H fixed at 0.95 Å). The final residuals for 280 variables refined against 3416 unique reflections were $R = 0.059$, $R_w = 0.058$, and GOF = 1.51. The highest peak in the final difference Fourier map had a height of 1.08 e/$Å^3$ and was associated with the uranium atom.

2b. A suitable crystal was isolated, mounted in a quartz capillary, flame-sealed, transferred to the goniostat of an Enraf-

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(10) In our hands, inconsistent results are frequently obtained when attempting to characterize silylphosphide-containing complexes by combustion elemental analysis. We have obtained satisfactory analyses of a representative member of each of the three classes of compounds described, however. Anal. Calcd for $C_{26}H_{48}PSi_2ClTh$ (**1b**): C, 43.66; H, 6.76. Found: C, 43.30; H, 6.77. Calcd for $C_{27}H_{51}PSi_2U$ (**2a**): C, 46.27; H, 7.33. Found: C, 46.23; H, 7.33. Calcd for $C_{26}H_{47}PSi_2U$ (**3a**): C, 45.60; H, 6.92. Found: C, 46.17; H, 7.10.

Table II. ^1H **and** $^{31}P\{^1H\}$ **NMR Data for Compounds 1–3 (Chemical Shift in ppm (δ))**

^1H NMR

	1a	**1b**	**2a**	**2b**	**3a**	**3b**
Cp*	13.26 (s)	2.11 (s)	12.63 (s)	1.96 (s)	6.46 (s)	2.04 (s)
CH_3			−208.70 (s)	0.22 (s)		
$SiCH_2$					−201.60 (s)	1.11 (d), $^3J_{PH}$ = 5.4 Hz
$Si(CH_3)_3$	−12.98 (s)	0.58 (d), $^3J_{PH}$ = 4.7 Hz	−15.63 (s)	0.42 (d), $^3J_{PH}$ = 5.4 Hz	−7.52 (s)	0.50 (d), $^3J_{PH}$ = 5.6 Hz
$Si(CH_3)_3$	−20.91 (s)	0.53 (d), $^3J_{PH}$ = 4.7 Hz	−24.36 (s)	0.39 (d), $^3J_{PH}$ = 4.5 Hz		
$Si(CH_3)_2$					−7.55 (s)	0.73 (d), $^3J_{PH}$ = 2.6 Hz

$^{31}P\{^1H\}$ NMR

1b	**2b**	**3b**
109.0 (s)	115.22 (s)	95.88 (s)

Nonius CAD-4 diffractometer, and cooled to −100 °C. Cell constants and an orientation matrix were obtained by least-squares refinement, using the setting angles of 25 reflections in the range $8 < \theta < 14°$. Final cell parameters are given in Table I, as are other crystallographic data. Data were collected utilizing the θ–2θ scan mode, at a fixed scan rate of 5.5° min^{-1} in ω. A total of 4469 reflections ($\pm h,k,l$) were collected. The systematic absences uniquely determined the space group as $P2_1/c$; this choice was verified by satisfactory solution and refinement of the structure. The data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects. An empirical absorption correction based on the averaged relative intensity curve of azimuthal scan data was applied. The data were averaged over $P2/m$ symmetry (R_{int} = 4.4%). The structure was solved by direct methods and refined via standard least-squares and Fourier techniques. All non-hydrogen atoms were refined anisotropically. A difference Fourier synthesis revealed the location of some, but not all, hydrogen atoms. The hydrogen atoms were added to the structure factor calculation in idealized positions without refinement (C–H fixed at 0.95 Å). There was evidence of secondary extinction in the low-angle, high-intensity data, and a secondary extinction correction was applied to the data. The final residuals for 280 variables refined against 2304 unique reflections were R = 0.040, R_w = 0.048, and GOF = 1.05. The highest peak in the final difference Fourier map had a height of 2.90 e/Å^3 and was associated with the thorium atom. All calculations were performed using the SHELXTL PLUS software package licensed by Siemens Analytical X-Ray Corporation.

3a. A suitable crystal was isolated, mounted in a quartz capillary, flame-sealed, and transferred to the goniostat of a Siemens R3m/V diffractometer at room temperature. Cell constants and an orientation matrix were obtained by least-squares refinement, using the setting angles of 25 reflections in the range $5 < 2\theta < 25°$. Final cell parameters are given in Table I, as are other crystallographic data. Data were collected utilizing the θ–2θ scan mode, with a variable scan rate 1.50–15.00° min^{-1} in ω. A total of 4314 reflections ($\pm h,k,l$) were collected. The systematic absences uniquely determined the space group as $P2_1/n$; this choice was verified by satisfactory solution and refinement of the structure. The data were scaled for linear decay (maximum correction 0.58), and an empirical absorption correction based on the averaged relative intensity curve of azimuthal scan data was applied. The data were averaged over $P2/m$ symmetry (R_{int} = 8.4%). The structure was solved by direct methods and refined via standard least-squares and Fourier techniques. All non-hydrogen atoms were refined anisotropically, except for the 10 methyl carbons of the pentamethylcyclopentadienyl groups. A difference Fourier synthesis revealed the location of some, but not all, hydrogen atoms. The hydrogen atoms were added to the structure factor calculation in idealized positions without refinement (C–H fixed at 0.95 Å). There was evidence of secondary extinction in the low-angle, high-intensity data, and a secondary extinction correction was applied to the data. The final residuals for 222 variables refined against 2929 unique reflections were R = 0.073, R_w = 0.093, and GOF = 1.01. The highest peak in the final difference Fourier map had a height of 1.84 e/Å^3 and was associated with the uranium atom. All calculations were performed using the SHELXTL PLUS software package licensed by Siemens Analytical X-Ray Corporation.

Results and Discussion

The silylphosphide complexes **1a** and **1b** may be conveniently prepared in high yield by reaction of $Cp^*_2AnCl_2$[5] (An = U and Th, respectively) with the potassium salt of the bis(trimethylsilyl)phosphide anion, as shown in eq 1. The thorium compound **1b** may also be prepared utilizing the analogous lithium salt. Reaction of $Cp^*_2UCl_2$ with $LiP(SiMe_3)_2{\cdot}2THF$, however, results in the isolation of a dark green crystalline material identified by ^1H NMR spectroscopy as the known U(III) complex Cp^*_2UCl.[5] The ability of the lithium salt of bis(trimethylsilyl)phosphide to act as a reducing agent toward uranium has been demonstrated previously.[11]

$$Cp^*_2AnCl_2 + KP(Si(CH_3)_3)_2 \xrightarrow{THF} \underset{\mathbf{1}}{Cp^*_2An(Cl)P(Si(CH_3)_3)_2} \quad (1)$$

1a: An = U; dark red needles

1b: An = Th; yellow needles

The ^1H NMR spectra of **1a** and **1b** (Table II) display resonances for two inequivalent trimethylsilyl groups, indicating restricted rotation about the actinide–phosphorus bond, as well as the lack of a mirror plane of symmetry relating the two trimethylsilyl groups in the solution structure. The bis(trimethylsilyl)phosphide ligand in these complexes remains "locked" even at elevated temperatures; coalescence is not reached at temperatures up to 120 °C. The origin of this restricted rotation appears to be the steric encumbrance of the molecules. This crowding further restricts the reactivity of the complexes. Unlike the analogous bis(cyclopentadienyl)zirconium and -hafnium compounds,[6,7] the bis(bis(trimethylsilylphosphide)) bis(pentamethylcyclopentadienyl) complexes of uranium and thorium could not be prepared, presumably due to the increased size of the substituted cyclopentadienyl ring. Complexes **1a** and **1b** fail to react in the presence of excess $KP(SiMe_3)_2$ to give the disubstituted product even after 48 h at room temperature. Despite this evident steric crowding, attempts to pyrolyze the compounds did not result in the elimination of chlorotrimethylsilane. Both the uranium and thorium com-

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plexes, while sensitive to oxygen and water, are very stable thermally. Samples of **1a** and **1b** heated to 230 °C (sealed NMR tube, benzene-d_6) for 168 h do not appear to undergo any further reaction or thermal decomposition, as evidenced by their ^{1}H NMR spectra. Attempts to replace the chloride with a fluoride were carried out by treatment of **1a** and **1b** with silver fluoride, in hopes that fluorotrimethylsilane might be eliminated. In tetrahydrofuran, stirred samples of **1a** and **1b** in the presence of AgF heated to 50 °C for 12 h showed no reaction, however.

The synthesis of **2a** and **2b** (eq 2) is similar to that of **1a** and **1b**, with yields of 83 and 87%, respectively. The

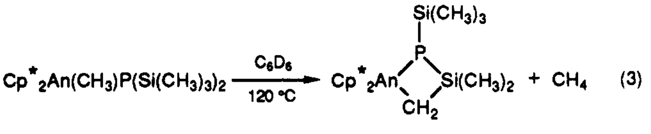
$$Cp^*_2An(CH_3)Cl + KP(Si(CH_3)_3)_2 \xrightarrow{THF} Cp^*_2An(CH_3)P(Si(CH_3)_3)_2 \quad (2)$$

2

2a: An = U; dark red needles

2b: An = Th; yellow needles

^{1}H NMR spectra of **2a** and **2b** (Table II) again show two distinct resonances for the trimethylsilyl groups, indicating similar steric crowding in the molecule. The methyl compounds do not possess the thermal stability exhibited by **1a** and **1b**, however. Although **2a** and **2b** appear to be stable indefinitely in the solid state and **2a** does not appear to decompose in solution in the absence of air and moisture, solutions of **2b** in C_6D_6 decompose over a period of months at room temperature by elimination of methane. The decomposition is greatly accelerated at higher temperatures; heating samples of either **2a** or **2b** in sealed thick-walled NMR tubes (C_6D_6) to 120 °C for 3 h results in their quantitative conversion to the metallacycle compounds **3a** and **3b**, respectively. The thermal syntheses of **3a** and **3b** (eq 3) from **2a** and **2b** are very clean elimination reactions, proceeding in quantitative yield, as monitored by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra of **3a** and **3b** (Table II) show distinct resonances for the trimethylsilyl and for the dimethyl(methylene)silyl groups. This reaction may be described as an *intra*molecular alkanolysis reaction of a type not unusual in actinide chemistry. Andersen et al. have demonstrated that methane is readily eliminated from tris[bis(trimethylsilyl)amido]methyluranium,[12] yielding the analogous nitrogen-containing metallacycle, and Marks et al. have produced a number of thoracyclobutanes by thermolysis of neopentyl- and ((trimethylsilyl)methyl)thorium compounds.[13]



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3a: An = U; dark brown needles
3b: An = Th; amber needles

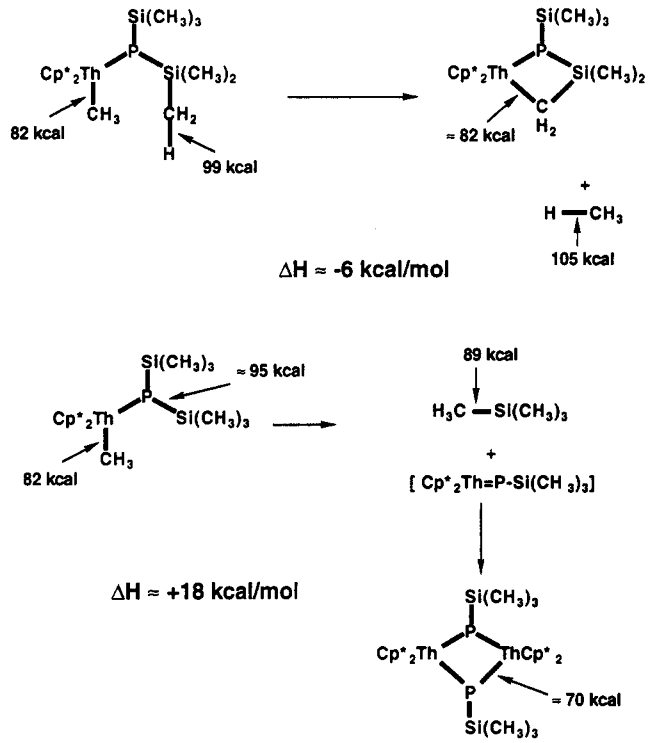
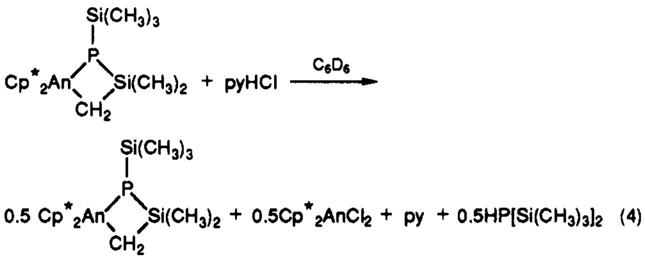


Figure 1. Estimation of reaction enthalpies.

As in related metallacycle formation reactions,[13] the elimination of either methane or tetramethylsilane is favored entropically. The formation of the metallacycle through the loss of methane, rather than the formation of a dimer of the phosphinidene–metal complex, through the loss of tetramethylsilane, can be attributed to the thermodynamic bond strengths of the reaction (Figure 1).[14] The formation of the metallacycle has an estimated ΔH of approximately −6 kcal/mol, whereas the formation of a dimer of the phosphinidene–metal complex has an estimated ΔH of approximately +18 kcal/mol (neglecting ΔH of dimerization); thus, the formation of the metallacycle is favored by approximately 24 kcal/mol. This energy difference is sufficient to dictate the path of the decomposition reaction.

In attempts to convert the metallacycles **3a** and **3b** to **1a** and **1b** through the use of pyridinium hydrochloride, it was found that the major products were unreacted metallacycle and bis(pentamethylcyclopentadienyl)metal dichloride (eq 4).



X-ray Structure Analysis of 1a, 2b, and 3a. Compounds **1a** and **2b** are isomorphous and display similar structural features (Figures 2 and 3, Tables III, IV and VI,

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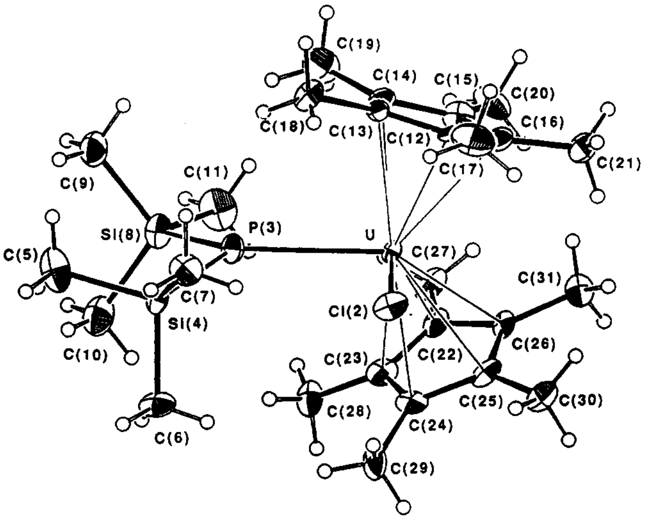

Figure 2. View (ORTEP) of **1a** with atomic numbering scheme.

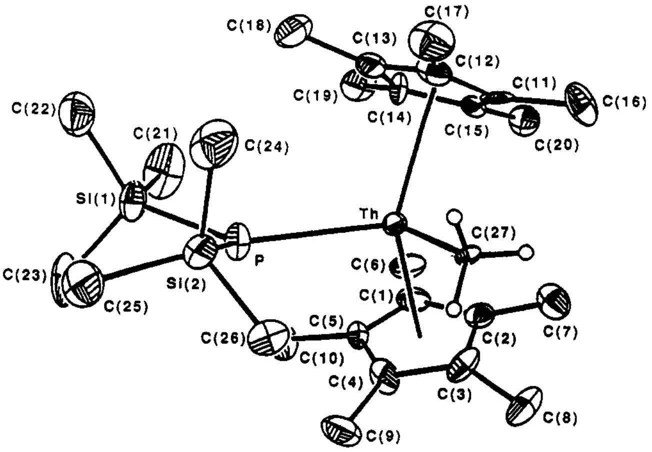

Figure 3. View (ORTEP) of **2b** with atomic numbering scheme.

Table III. Selected Bond Lengths (Å) for Compound 1a

U–Cl	2.570 (4)	P–Si(4)	2.230 (5)
U–P	2.789 (4)	P–Si(8)	2.225 (6)

Table IV. Selected Bond Lengths (Å) for Compound 2b

Th–CH_3	2.510 (13)	P–Si(1)	2.220 (6)
Th–P	2.888 (4)	P–Si(2)	2.213 (6)

Table V. Selected Bond Lengths (Å) for Compound 3a

U–CH_2	2.415 (20)	P–Si(2)	2.209 (9)
U–P	2.656 (6)	Si(1)–CH_2	1.888 (22)
P–Si(1)	2.234 (9)		

Table VI. Selected Bond Angles (deg) for Compound 1a

P–U–Cl	93.92 (12)	Si(8)–P–U	129.88 (18)
Si(4)–P–Si(8)	105.86 (21)	Cp*$_a$–U–Cp*$_b$	134.5
Si(4)–P–U	121.93 (18)		

Table VII. Selected Bond Angles (deg) for Compound 2b

Pt–Th–CH_3	94.8 (3)	Si(2)–P–Th	122.6 (2)
Si(1)–P–Si(2)	106.3 (2)	Cp*$_a$–Th–Cp*$_b$	134.2
Si(1)–P–Th	126.3 (2)		

Table VIII. Selected Bond Angles (deg) for Compound 3a

P–U–CH_2	78.7 (5)	CH_2–Si(1)–P	102.4 (7)
Si(1)–P–Si(2)	113.7 (4)	Si(1)–CH_2–U	47.9 (7)
Si(1)–P–U	82.2 (3)	Cp*$_a$–U–Cp*$_b$	132.8
Si(2)–P–U	163.5 (3)		

VII). Both compounds exhibit typical pseudotetrahedral Cp_2AnX_2 coordination geometry, with averaged metal–carbon (ring) distances of 2.460 and 2.532 Å for the uranium and thorium compounds, respectively. The ring centroid–metal–ring centroid angles of 134.5° for **1a** and 134.2° for **2b** are nearly identical and are well within the range typically found for bis(cyclopentadienyl)actinide(IV) complexes.[2a,13,15,17–19,22] The steric repulsion of the pentamethylcyclopentadienyl rings results in a compression of the phosphorus–metal–X angle from tetrahedral values (**1a**, P–U–Cl = 93.92 (12)°; **2b**, P–Th–CH_3 = 94.8 (3)°). The uranium–chloride distance in **1a** is 2.570 (4) Å, which is short in comparison to previously reported bis(pentamethylcyclopentadienyl)uranium(IV)–Cl bond lengths (2.65–2.73 Å),[16–18] and comparable to those found in six-coordinate uranium(IV) complexes of the type UCl_4L_2 (2.58–2.63 Å).[19] The distance is nearly identical to that determined for $(C_5H_5)_3UCl$ (2.56 (2) Å),[20] suggesting that the relatively small halide ligand may not be as affected by intramolecular repulsions in bulky coordination environments, and therefore displays less metal–ligand bond lengthening as a function of increasing coordination number. In contrast, the thorium–carbon (methyl) distance in **2b** is 2.510 (13) Å; this value is well within the range typically found for other Th–C σ bonds (2.44–2.55 Å).[13a,c,21,22]

The most interesting structural feature of complexes **1a** and **2b** is the bis(trimethylsilyl)phosphide ligand. The coordination geometry about the phosphorus is approximately planar in both complexes, with the angles about the phosphorus summing to 357.7° and 355.2° in **1a** and **2b**, respectively. The metal–phosphorus distances (U–P = 2.789 (4) Å; Th–P = 2.888 (4) Å) compare well with the few reported examples of actinide–phosphorus distances; the uranium–phosphinidine distance in $[Cp^*_2U(OMe)]_2(\mu\text{-}PH)$ is 2.743 (1) Å,[3] while the average thorium–phosphide distance in $Cp^*_2Th(PPh_2)_2$ is 2.874 (7) Å.[2a] The difference in the metal–phosphorus distances is slightly larger than the difference in the ionic radii of uranium and thorium in eight-coordination, which could be a reflection of the slightly larger size of the methyl ligand in the thorium compound. The lack of an electronic origin for this difference is supported by the fact that the average phosphorus–silicon distance is the same in both compounds (**1a**, Si–P(av) = 2.228 (6) Å; **2b**, Si–P(av) = 2.217 (6) Å).

The dihedral angle formed by the P-An-X and Si-P-Si planes is 13.4° in compound **1a** and 19.3° in compound **2b**. The steric crowding which inhibits free rotation of the bis(trimethylsilyl)phosphide ligand is evident in both complexes (Figures 2 and 3). Both structures exhibit nonbonding contacts between one silylphosphide methyl ligand and two methyl substituents on the cyclopenta-

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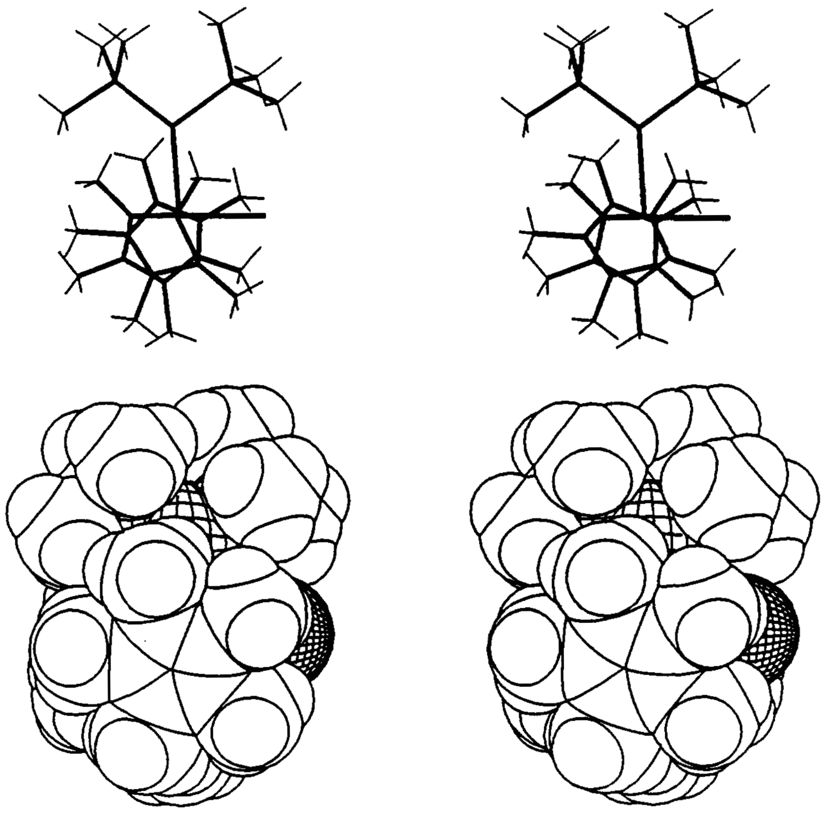

Figure 4. Stereoview of **1a**.

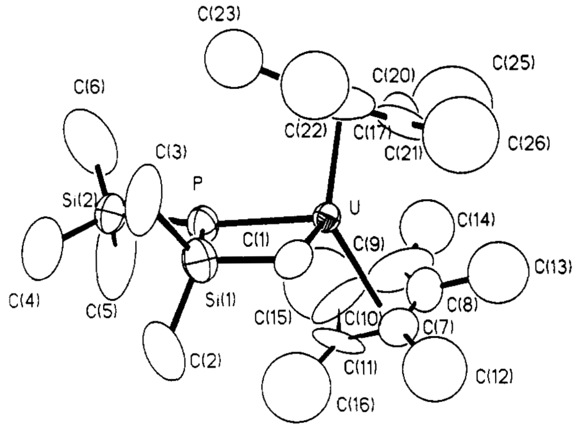

Figure 5. View (ORTEP) of **3a** with atomic numbering scheme.

dienyl rings (**1a**, C(11)···C(19) = 3.842 Å, C(11)···C(28) = 3.872 Å; **2b**, C(21)···C(10) = 3.877 Å, C(21)···C(18) = 3.879 Å), as well as between a different methyl group and the "X" ligand (**1a**, C(26)···C(27) = 3.844 Å; **2b**, C(7)···Cl(2) = 3.709 Å). This restricts further rotation and leads to inequivalent signals in the ^{1}H NMR spectra of both compounds. The space-filling model stereoview of **1a** (Figure 4) clearly illustrates the crowding around the uranium center.

The results of a single-crystal structural analysis of compound **3a** are shown in Figure 5, while important bond distances and angles are provided in Tables V and VIII. The compound possesses the expected Cp_2AnX_2 structure, with a ring centroid–metal–ring centroid angle of 132.8°. The elimination of methane from **2a** gives rise to the observed metallacycle containing uranium, phosphorus, silicon, and carbon. The largest deviation from planarity in the metallacycle unit is 0.01 Å. The observed uranium–phosphide bond distance of 2.656 (6) Å is significantly shorter than that found in **1a**, presumably due to decreased intramolecular steric crowding in the coordination sphere of the metal. The phosphorus–silicon distances (P–Si(1) = 2.234 (9) Å, P–Si(2) = 2.208 (9) Å) are virtually unchanged from those determined in **1a** and **2b**. The U–C(1) bond distance of 2.415 (20) Å is within the range of values (2.42 Å to 2.6 Å) determined for other crystallographically characterized examples of uranium–carbon σ-bonds.[20,21,23,24]

Conclusions

We have prepared a series of bis(pentamethylcyclopentadienyl)uranium and -thorium bis(trimethylsilyl)phosphide compounds and investigated their thermal stability. Both the chloride and methyl derivatives display a high degree of steric crowding both in the solid state and in solution; no rotation of the bis(trimethylsilyl)phosphide ligand is observed on the NMR time scale to 120 °C. Prolonged heating of $Cp^*_2An(Me)[P(SiMe_3)_2]$, however, results in elimination of methane to form a phosphametallacycle complex; qualitative thermodynamic estimates suggest that this pathway is enthalpically favored over elimination of tetramethylsilane. Although we were not successful in our attempts to synthesize an actinide–phosphorus multiple bond, we have shown that it is possible to prepare an actinide–phosphorus species which displays unusual reactivity due to its steric congestion. Further metathesis reactions employing $Cp^*_2An(Cl)[P(SiMe_3)_2]$ will be investigated to examine whether additional interligand reactions of this type can be effected. Finally, the use of similarly functionalized, bulkier phos-

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phorus moieties without γ-protons may provide compounds containing actinide–phosphorus multiple bonds.

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Supplementary Material Available: Tables of atomic coordinates and isotropic thermal parameters, bond distances, bond angles, and anisotropic thermal parameters (21 pages). Ordering information is given on any current masthead page.

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