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Uranium−Sulfilimine Chemistry: Synthesis and Characterization of $Cp^*_2UCl(NSPh_2)$ and $Cp^*_2U(NSPh_2)_2$

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Two imido derivatives of U(IV), $Cp^*_2UCl(NSPh_2)$ (**1**; Cp* = pentamethylcyclopentadienyl) and $Cp^*_2U(NSPh_2)_2$ (**2**), have been prepared in high yield from $Cp^*_2UCl_2$ and $LiNSPh_2$. Alternatively, **1** and **2** can be synthesized by treating $Cp^*_2UCl[(CH_2)_2PPh_2]$ with anhydrous $HNSPh_2$. $Cp^*_2U(NSPh_2)_2$ is the first structurally characterized uranium bis(sulfilimide) complex. Its short U−N distance suggests significant uranium−imido multiple-bond character.

Introduction

Early-transition-metal−imido complexes have been of great interest.[1−3] Many of these complexes belong to the bent-metallocene family.[4−11] Although a broad range of transition-metal imido complexes are known, only a few f-element imido complexes have been reported.[12−18] While the set of compounds is limited, the Cp^*_2An (An = actinide) bent-metallocene framework is able to support imido complexes.[12−18] The ability of the Cp^*_2-An fragment to form stable complexes has been attributed to factors such as the high polarity of the actinide-element bonds that it forms, the enhanced coordinative flexibility of the 5f ions, and the tendency of the f orbitals to take part in bonding.[19−21]

The sulfilimide ion $[NSPh_2]^-$ is electronically very similar to the $[CHPR_3]^-$ and $[NPPh_3]^-$ ligands whose organo-actinide chemistry we have reported.[22−38] Although several transition-metal−sulfilimide complexes are known,[39,40] only a single structurally characterized uranium sulfilimide complex has been reported.[41] The synthesis of stable sulfilimide complexes using the

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Cp*$_2$U framework appeared to us as a sensible target. In a previous paper we described the synthesis and structural characterization of Cp*$_2$UCl$_2$(HNSPh$_2$), where the imino hydrogen of HNSPh$_2$ is hydrogen-bonded to a chloro ligand.[42] Since our initial attempts to produce the sulfilimide complex Cp*$_2$UCl(NSPh$_2$) by dehydrochlorination of Cp*$_2$UCl$_2$ were unsuccessful, we looked into alternative routes for its synthesis.[43] Although Me$_3$Si derivatives are commonly used in transition-metal chemistry for replacing coordinated halides with other anions, in our hands no reaction occurred between Me$_3$SiNSPh$_2$ and Cp*$_2$UCl$_2$.[43] However, the two organouranium imido complexes Cp*$_2$UCl(NSPh$_2$) (**1**) and Cp*$_2$U(NSPh$_2$)$_2$ (**2**) could be obtained by the treatment of LiNSPh$_2$ with Cp*$_2$UCl$_2$ and from reactions of HNSPh$_2$ with Cp*$_2$UCl(CH$_2$)$_2$PPh$_2$. Compounds **1** and **2** are the only Cp*$_2$U−sulfilimide complexes currently known. In this paper we present their synthesis and characterization.

Experimental Section

All reactions were carried out under a dinitrogen atmosphere using normal Schlenk, glovebox, and vacuum techniques. Solvents were dried and deoxygenated over sodium−benzophenone and were distilled prior to use. Cp*$_2$UCl$_2$ and Cp*$_2$UCl(CH$_2$)$_2$P(Ph)$_2$ were prepared by using literature methods, and HNSPh$_2$ was purchased from Aldrich Chemical Co. as HNSPh$_2$·H$_2$O, which was dehydrated under high vacuum for 3 days at room temperature.[44,45] LiNSPh$_2$ was synthesized by reacting HNSPh$_2$ with n-BuLi in tetrahydrofuran at −78 °C and recrystallizing from tetrahydrofuran. NMR spectra were obtained using a Nicolet QE 300 MHz spectrometer, and samples were prepared in d_6-benzene, d_8-toluene, or d_8-tetrahydrofuran. IR spectra were recorded on a Perkin-Elmer 1430 spectrometer or a Nicolet-740 IR spectrometer operating in the Fourier transform mode. Microanalyses were performed by Oneida Research Services Inc., Whitesboro, NY.

Reactions of LiNSPh$_2$ with Cp*$_2$UCl$_2$. A. Preparation of Cp*$_2$UCl(NSPh$_2$) (1). A solution of 84 mg (0.40 mmol) of LiNSPh$_2$ in 25 mL of toluene was added slowly to 230 mg (0.40 mmol) of Cp*$_2$UCl$_2$ dissolved in 25 mL of toluene and stirred at −78 °C for 3 h. The dark red solution was warmed slowly to room temperature over 6 h, filtered through a medium-porosity frit, and evaporated to dryness under vacuum to yield 127 mg (72%) of red-orange Cp*$_2$UCl(NSPh$_2$). ^{1}H NMR (d_8-toluene; ppm): 2.27 (s, 30H, Cp*), 8.37 (t, 2H, J = 7 Hz, p-C$_6$H$_5$), 8.48 (t, 4H, J = 7 Hz, m-C$_6$H$_5$), 14.12 (d, 4H, J = 7 Hz, o-C$_6$H$_5$). In addition, weak NMR resonances arising from trace amounts of Cp*$_2$U(NSPh$_2$)$_2$ were observed at −0.2, 3.9, 5.9, and 6.2 ppm. IR (cm^{-1}): 3010 m, 3000 m, 2975 m, 2820 m, 2690 w, 1555 w, 1475 w, 1450 w, 1360 m, 1270 w, 1025 s, 800 vs, 750 s, 695 s. Dark red prismatic crystallographic quality crystals were obtained from a concentrated toluene solution of **1** after the addition of pentane. These were washed with 2 × 0.5 mL of pentane and dried under vacuum.

B. Preparation of Cp*$_2$U(NSPh$_2$)$_2$ (2). The procedure described above was repeated by using 168 mg (0.8 mmol) of LiNSPh$_2$ and 230 mg (0.40 mmol) of Cp*$_2$UCl$_2$ to yield 224 mg (62%) of Cp*$_2$U(NSPh$_2$)$_2$. ^{1}H NMR (d_8-toluene; ppm): −0.24 (s, 30H, Cp*), 3.93 (d, 8H, J = 7 Hz, o-C$_6$H$_5$), 5.93 (t, 4H, J = 7 Hz, m-C$_6$H$_5$), 6.18 (t, 4H, J = 7 Hz, p-C$_6$H$_5$). IR (cm^{-1}): 3075 m, 3010 m, 2890 m, 2860 m, 2300 w, 1965 w, 1585 w, 1465 w, 1425 m, 1300 w, 1080 s, 1000 vs, 990 s. Anal. Calcd for C$_{44}$H$_{50}$N$_2$S$_2$U: C, 58.13; H, 5.54; N, 3.08. Found: C, 57.10; H, 5.40; N, 2.77.

A saturated solution of Cp*$_2$U(NSPh$_2$)$_2$ in tetrahydrofuran produced dark red prismatic crystals upon standing at room temperature for several weeks. These were washed with 2 × 0.5 mL of pentane and dried under vacuum.

Reactions of HNSPh$_2$ with Cp*$_2$UCl(CH$_2$)$_2$PPh$_2$. A. Preparation of Cp*$_2$UCl(NSPh$_2$) (1). To a solution of 304 mg (0.40 mmol) of Cp*$_2$UCl(CH$_2$)$_2$PPh$_2$ in 25 mL of toluene was added 80 mg (0.40 mmol) of solid anhydrous HNSPh$_2$ slowly with stirring at room temperature. A yellow precipitate began to form as soon as the addition of HNSPh$_2$ was started. Stirring was continued for a further 3 h, and the yellow precipitate was removed from the dark red solution by filtering through a medium-porosity frit. The solution was evaporated to dryness, rinsed with 2 mL of pentane, and dried under vacuum to yield 193 mg (64%) of Cp*$_2$UCl(NSPh$_2$). The Cp*$_2$UCl(NSPh$_2$) was always contaminated by a small amount of Cp*$_2$U(NSPh$_2$)$_2$. Proton NMR spectra indicated this to be <5%, providing no evidence of equilibrium between the two species. Due to this impurity and traces of solvent that remained after drying under vacuum, elemental analysis of Cp*$_2$UCl(NSPh$_2$) was not successful.

B. Preparation of Cp*$_2$U(NSPh$_2$)$_2$ (2). The above procedure was repeated by using 168 mg (0.80 mmol) of anhydrous HNSPh$_2$ and 304 mg (0.40 mmol) of Cp*$_2$UCl(CH$_2$)$_2$PPh$_2$ to yield 254 mg (71%) of Cp*$_2$U(NSPh$_2$)$_2$.

Reactions of Me$_3$SiNSPh$_2$ with Cp*$_2$UCl$_2$. Two NMR samples were prepared in toluene-d_8 using 29 mg (0.05 mol) of Cp*$_2$UCl$_2$/14 mg (0.05 mol) of Me$_3$SiNSPh$_2$ and 29 mg (0.05 mol) of Cp*$_2$UCl$_2$/28 mg (0.10 mol) of Me$_3$SiNSPh$_2$. The ^{1}H NMR spectra were recorded before and after heating the two samples at 100 °C for 12 h. Finally, the samples were exposed to UV light for 12 h and the ^{1}H NMR spectra were re-recorded. No evidence of any chemical reactions was observed under any of the conditions employed.

Data Collection and Reduction of X-ray Data. Single crystals of **1** and **2** were selected and mounted and sealed in thin-walled glass capillaries under dinitrogen. A Nicolet R3 computer-controlled diffractometer with graphite-monochromated Mo Kα radiation (Kα_1 = 0.709 30 Å, Kα_2 = 0.713 59 Å) and a scintillation detector with pulse height analyzer was used for the measurement of diffraction intensities. During data collection, the intensities of 3 standard reflections were remeasured every 97 reflections in each data set. Data manipulation, structure solution, and refinement were carried out using the SHELXL 97-2 program system.[46] Data were corrected for Lorentz and polarization effects and for decay of the intensities of check reflections during data collection, and an empirical absorption correction was applied to each data set. The structure of **1** belongs to the monoclinic space group $P2_1/n$ with unit cell parameters a = 12.120(5) Å, b = 13.249(6) Å, c = 21.644(8) Å, β = 95.57(3)°, V = 3445(2) Å^3, and Z = 4. While the structure could not be satisfactorily refined due to disordered Cp* groups and detailed metrical data could not be obtained, the molecular connectivity could be determined.

The structure of **2** belongs to the monoclinic space group $C2/c$. The position of the uranium was determined by Patterson methods, and the remaining atoms were located in subsequent difference Fourier maps and least-squares refinements. All non-hydrogen atoms were refined anisotropically. During the first few least-squares refinements all non-hydrogen atoms were revealed. After an empirical absorption correction, the R and R_g values were found to be 6.52% and 7.67%, respectively. H atoms were added at calculated positions to the Cp*

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Table 1. Crystallographic Data for 2

empirical formula	$C_{44}H_{50}N_2S_2U$
fw	909.01
temp	293(2) K
wavelength	0.710 73 Å
cryst syst	monoclinic
space group	*C*2/*c*
unit cell dimens	
a	15.699(12) Å
b	12.999(10) Å
c	19.126(12) Å
α	90°
β	92.98(6)°
γ	90°
V	3898(5) $Å^3$
Z	4
density (calcd)	1.549 Mg/m^3
abs coeff	4.304 mm^{-1}
$F(000)$	1808
cryst size	$0.5 \times 0.5 \times 0.5$ mm^3
θ range for data collecn	2.04−32.61°.
index ranges	$0 \le h \le 23$, $0 \le k \le 19$, $-28 \le l \le 28$
no. of rflns collected	7482
no. of indep rflns	7048 (R(int) = 0.0123)
completeness to $\theta = 32.61°$	98.9%
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	7048/0/229
goodness of fit on F^2	1.053
final R indices ($I > 2\sigma(I)$)	R1 = 0.0373, wR2 = 0.0937
R indices (all data)	R1 = 0.0459, wR2 = 0.0988
largest diff peak and hole	1.509 and −2.030 e $Å^{-3}$

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 2

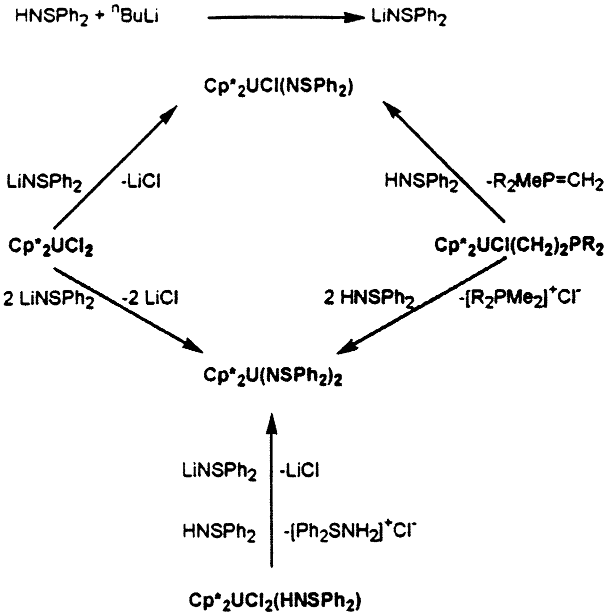
U−N	2.143(3)	U−C(32)	2.792(4)
S−N	1.552(4)	U−C(33)	2.785(4)
S−C(11)	1.814(5)	U−C(34)	2.830(4)
S−C(21)	1.822(5)	U−C(35)	2.806(4)
U−C(31)	2.808(4)		
U−N−S	152.2(2)	N−U−N(A)	96.0(2)
N−S−C(11)	109.1(2)	C(11)−S-C(21)	98.7(2).
N−S−C(21)	107.6(2)		

methyl and phenyl groups, and final refinement yielded the following R values: R1 = 3.73%, wR2 = 9.41% ($I > 2\sigma(I)$); R1 = 4.59%, wR2 = 9.93% (all data). The crystal data and data collection and refinement details for **2** are summarized in Table 1, and important bond lengths and bond angles in Table 2.

Results and Discussion

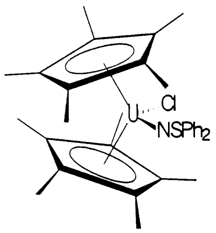
Two methodologies have been developed for the preparation of **1** and **2**. They are summarized in Scheme 1. The failure of $Me_3SiNSPh_2$ to yield **1** and **2** from the treatment with $Cp^*{}_2UCl_2$ is in contrast with the successful synthesis of $[Ph_4P]^+[OUCl_4NSPh_2]^-$ by the reaction of $[Ph_4P]^+[OUCl_5]^-$ with $Me_3SiNSPh_2$.[41] The reactions of $Cp^*{}_2UCl_2$ with $LiNSPh_2$ are analogous to those of $Cp^*{}_2UCl_2$ with $LiNPPh_3$ that produce $Cp^*{}_2UCl(NPPh_3)$ and $Cp^*{}_2U(NPPh_3)_2$.[47] In the reaction between $Cp^*{}_2UCl(CH_2)_2PPh_2$ and $HNSPh_2$, the precooordinated phosphoylide ligand abstracts the imino hydrogen of sulfilimine and leaves as the free ylide, while the $[NSPh_2]^-$ moiety coordinates to uranium. This behavior is similar to the reaction between $Cp_3U{=}CHPR_3$ and $HNSPh_2$, which yields Cp_3UNSPh_2.[48] A second equivalent of sulifilimine replaces the chloride of complex **1** with the $[NSPh_2]^-$ ligand, producing the phosphonium salt $[Me_2Ph_2P]^+Cl^-$ and the complex **2**. Furthermore, $Cp^*{}_2UCl_2(HNSPh_2)$ was found to react with $LiNSPh_2$ in the presence of $HNSPh_2$ to produce **2**.[43] These reactions are summarized in Scheme 1.

Scheme 1. Summary of Reactions Involved in the Synthesis of 1 and 2



Both **1** and **2** dissolve in organic solvents such as toluene, benzene, and tetrahydrofuran to form dark red solutions and rapidly decompose upon exposure to moisture and air. The ^1H NMR spectra of **1** and **2** appear in the same general region with paramagnetic effects of uranium on the chemical shifts and considerable variations in the positions of the Cp* and phenyl protons.

The asymmetric unit in the crystal structure of **1** contains a molecule of **1** and half a pentane molecule that lies at a center of inversion. Therefore, the unit cell contains four molecules of **1** and two pentane molecules. Due to disorder in the Cp* groups, the structure of **1** could not be refined to satisfactory error indices and the metrical parameters could not be determined with certainty. Nonetheless, the overall connectivity the molecule is clearly established as



In contrast, the structure of complex **2** is well-behaved. In the unit cell of **2**, the molecule lies on a 2-fold axis of symmetry so that the asymmetric unit contains one unique sulfilimido group and one unique pentamethylcyclopentadienyl group. A perspective drawing of **2** is given in Figure 1, and the bond lengths and angles of **2** are summarized in Table 1.

Both complexes belong to the bent-metallocene family with pseudotetrahedral coordination about uranium. The ring centroid−U−ring centroid angle of 133.2° and

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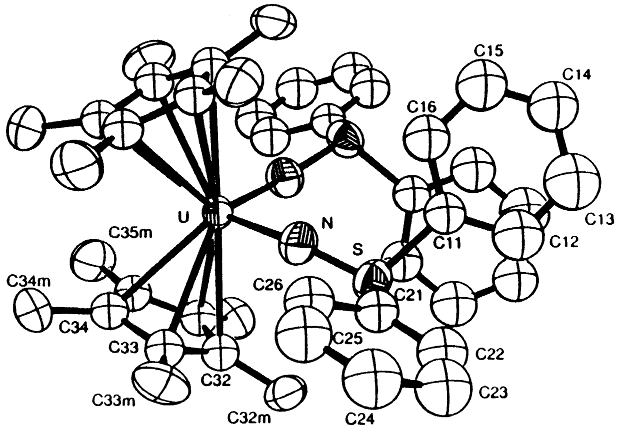

Figure 1. Ortep diagram of the non-hydrogen atoms of **2** showing the atom-labeling scheme.

the average U−Cp* distance of 2.804(4) **Å** in **2** are in the same ranges found for other Cp^*_2U complexes.[49] The U−N−S angle of 152.2(2)° in **2** is considerably larger than that in $Cp^*_2UCl_2(HNSPh_2)$, 134(1)°, and similar to that in $[Ph_4P]^+[OUCl_4NSPh_2]^-$, 157.5(2)°. This angle is well within the range of corresponding M−N−S angles seen among transition-metal sulfilimide complexes.[50] The N−U−N equatorial angle of 96.8(3)° in **2** is significantly narrower than the Cl−U−Cl angle in $Cp^*_2UCl_2(HNSPh_2)$, 145.9(3)° , and lies in the same range found for the corresponding angles in the analogous U(VI) complexes $Cp^*_2U(NPh)_2$ and $Cp^*_2U[N(1\text{-adamantyl})]_2$.[13,21]

The most interesting structural feature is the U−N bond distance in **2**, 2.143(3) Å, which is much shorter than that in $Cp^*_2UCl_2(HNSPh_2)$, 2.44(3) Å, and on the long end of the range observed in uranium imides.[51] Previously, we have argued that a similarly short U−N distance in Cp_3UNPPh_3 implies U−N multiple bonding,[29] and the U−N bond in the recently reported ketimido complex $Cp^*_2U(N{=}CPh_2)_2$, where the U−N distances are 2.179(6) and 2.185(5) Å, has been described as containing significant π-bonding.[52] DFT calculations on $[Ph_4P]^+[OUCl_4NPPh_3]^-$, whose structure and U−N separation are very similar to those in $[Ph_4P]^+[OUCl_4NSPh_2]^-$,[41] indicate that the U−N bond order is best described as 3.[53] However, the difference between the U−N distance in **2** and in $[Ph_4P]^+[OUCl_4NSPh_2]^-$ (1.920(3) Å)[41] of 0.22 Å exceeds the approximate 0.14 Å expected between U(IV) and U(VI) on the basis of ionic radii.[54] Thus, consistent with the realization that transition-metal−imide bond orders are often variable and lie between 2 and 3,[55] the U−N bond in **2** is likely to be best described by a combination of resonance structures containing both double- and triple-bonded canonical forms.

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Supporting Information Available: Tables of crystal data and data collection and refinement parameters and interatomic distances and angles for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[49] Cp*−U distances: $Cp^*_2U(N\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2)$, 2.790(12) Å;[19] $[Li(TMED)][Cp^*_2U(NC_6H_5)Cl]$, 2.767(2) Å;[19] $Cp^*_2U(NPh)_2$, 2.718(10) Å;[13] $Cp^*_2U(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(O)$, 2.730(6) Å;[12] $Cp^*_2UCl_2(HNSPh_2)$, 2.77(2) Å.[42]

[50] M−N−S angles of sulfilimide complexes: $F_4W(NSPh_2)_2$, 171.7(3), 138.4(3)°;[39] $Cl_2VO(NSPh_2)$, 134.5(4), 141.9(4)°;[40] $[Cl_2Fe(NSPh_2)]_2$, 138.3(5), 129.6(3)°.[40]

[51] Short U−N bond distances of uranium imido complexes: $Cp^*_2U(N\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2)$, 1.952(12) Å;[19] $[Li(TMED)][Cp^*_2U(NC_6H_5)Cl]$, 2.051(14) Å;[19] $(MeC_5H_4)_3UNPh$, 2.019 Å;[20] $[(NSiMe_3)_2]_3U(NSiMe_3)F$, 1.854(23) Å;[14] $[(NSiMe_3)_2]_3U(NPh)F$, 1.979(8) Å;[14] $Cp^*_2U(NPh)_2$, 1.952(7) Å;[13] $Cp^*_2U(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(O)$, 1.988(4) Å;[12] Cp_3UNPPh_3, 2.07(2) Å;[38] $Cp^*_2U[N(1\text{-adamantyl})_2]$, 1.94(2), 1.96(2) Å;[21] $[Ph_4P]^+[OUCl_4NSPh_2]$, 1.920(3) Å.[41]

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