

pentadienyl moieties and transamination, are often plagued by ligand redistribution reactions and concurrent formation of $\text{Cp}_3\text{U}(\text{NR}_2)$. $\text{Cp}_3\text{U}(\text{NEt}_2)$ also forms when $\text{Cp}_2\text{U}(\text{NEt}_2)_2$ is further reacted with cyclopentadiene. Thermal stability also appears to favor the tricyclopentadienyl derivatives since attempted sublimation of some of the products produced $\text{Cp}_3\text{U}(\text{NR}_2)$ -type compounds. It is clear that steric factors are of utmost importance in this area of chemistry. The combination of two cyclopentadienyl groups and two amide moieties is sometimes sufficient to saturate the coordination sphere of uranium(IV) and stabilize the so formed Cp_2UX_2 species. However, given a chance, even those species rearrange or react to give the more favored Cp_3U containing complexes. $\text{Cp}_2\text{U}[\text{NC}_4\text{Me}_3(\text{COOEt})]_2$ appears to be an exception. In this case, the postulated interaction between oxygen of the carboxylate functionality and uranium may account for the added stability. Indeed, as will be seen in the following papers, replacement of the amido group by potentially bidentate ligands results in the synthesis of relatively stable Cp_2UX_2 (X

$= \text{R}_2\text{NCS}_2, \text{R}_2\text{NCOS}, \text{R}_2\text{NCO}_2, \text{RCO}_2, \text{RCOS}$) compounds.

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Registry No. $\text{U}(\text{NMe}_2)_4$, 53091-47-7; $\text{U}(\text{NEt}_2)_4$, 40678-59-9; $\text{U}(\text{NPr}_2)_4$, 63833-51-2; $\text{U}(\text{NPh}_2)_4$, 61900-16-1; $\text{Cp}_2\text{U}(\text{NEt}_2)_2$, 54068-37-0; $\text{Cp}_2\text{U}(\text{NPr}_2)_2$, 77507-87-0; $\text{Cp}_2\text{U}(\text{NPh}_2)_2$, 77507-88-1; $\text{Cp}_2\text{U}(\text{NMe}_2)_2$, 77507-86-9; $\text{Cp}_2\text{U}(\text{NEt}_2)(\text{NPh}_2)$, 77507-89-2; $\text{Cp}_2\text{U}[\text{NC}_4\text{Me}_3(\text{COOEt})]_2$, 77507-90-5; $\text{Cp}_2\text{U}(\text{NEt}_2)(\text{NC}_4\text{H}_2\text{Me}_2)$, 77507-91-6; $\text{Cp}_3\text{U}(\text{NEt}_2)$, 77507-92-7; $\text{Cp}_2\text{U}(\text{NC}_4\text{H}_4)_2$, 77507-93-8; $\text{Cp}_3\text{U}(\text{NC}_4\text{H}_4)$, 77507-94-9; $\text{Cp}_3\text{U}(\text{NMe}_2)$, 77507-95-0.

Supplementary Material Available: Listings of characteristic infrared frequencies (Table II), mass spectral data (Tables III and IV), and the optical spectra (Table V) (4 pages). Ordering information is given in any current masthead page.

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Reactivity of Dicyclopentadienylbis(diethylamido)uranium(IV). Insertion Reactions

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$\text{Cp}_2\text{U}(\text{NEt}_2)_2$ reacts with CS_2 , COS , and CO_2 to give insertion-type compounds of the formula $\text{Cp}_2\text{U}(\text{XYCNET}_2)_2$ ($X, Y = \text{O}$ or $\text{S}; X = \text{O}, Y = \text{S}$). Molecular weight data show that $\text{Cp}_2\text{U}(\text{S}_2\text{CNET}_2)_2$ and $\text{Cp}_2\text{U}(\text{OSCNET}_2)_2$ are monomeric in benzene; for $\text{Cp}_2\text{U}(\text{O}_2\text{CNET}_2)_2$, polymeric behavior is indicated. Spectroscopic data are consistent with a bidentate coordination mode of the carbamate ligands and η^5 -cyclopentadienyl moieties. The coordination geometry around the uranium can be described as pseudooctahedral with cyclopentadienyl groups occupying mutually cis positions. The variable-temperature ^1H NMR spectra of the molecules are indicative of dynamic solution behavior. It is shown that a combination of rapid metal-centered rearrangement with slow $\text{C}-\text{N}$ bond rotation can adequately explain the observed spectra.

Introduction

The reactivity of the metal–nitrogen σ bond continues to occupy a central place in the chemistry of amido derivatives of the early transition metals, $\text{M}(\text{NR}_2)_n$.¹ These compounds have been shown to undergo substitution reactions with protic reagents and insertion reactions with molecules containing polar multiple bonds, thus providing unique synthetic intermediates for a wide variety of complexes of these transition elements. In contrast to this, the reactivity of actinide amides has remained largely unexplored even though initial work on their preparation was reported by Gilman as early as 1956.² However, as a result of renewed interest in the chemistry of actinide amides,³ rapid progress in this field can be anticipated. Indeed the few reports already existing in the literature presage a chemistry comparable in diversity to that found with the analogous transition-metal compounds.

Insertion of CX_2 ($X = \text{O}, \text{S}, \text{Se}$) into the metal–nitrogen σ bonds of the tetrakis(amido)actinide(IV) complexes has been described by Bagnall and Yanir⁴ as a means of obtaining thorium and uranium carbamates. We have shown that the tetrakis(amido) species, $\text{U}(\text{NEt}_2)_4$, will react with the weakly

acidic hydrocarbon cyclopentadiene to yield the complex $\text{Cp}_2\text{U}(\text{NEt}_2)_2$.^{5,6} This molecule, which contains labile uranium–nitrogen bonds, was expected to provide a versatile entry into the so far elusive organouranium chemistry containing the “ Cp_2U ” fragment.

In this first report on the reactivity on $\text{Cp}_2\text{U}(\text{NEt}_2)_2$, we detail our work on the insertion of CS_2 , COS , and CO_2 into the uranium–nitrogen bonds, a reaction which produces the expected carbamates $\text{Cp}_2\text{U}(\text{XYCNET}_2)_2$.

Experimental Section

Reagents and General Techniques. All reactions and operations were performed with the use Schlenk techniques under a static atmosphere of rigorously purified nitrogen.

Toluene, benzene, hexane, and pentane were dried by refluxing under purified nitrogen with the appropriate drying agent and were distilled prior to use. Pentane was also freeze–thaw–degassed before use. The compound $\text{Cp}_2\text{U}(\text{NEt}_2)_2$ was synthesized and purified according to published procedures.⁶ Carbon disulfide (reagent grade, Anachemia) was refluxed over P_2O_5 and distilled. Dissolved oxygen was displaced by vigorously bubbling nitrogen through the liquid. Carbonyl sulfide (Matheson) was purified of H_2S contaminant by reaction with lead acetate. Carbon dioxide (glass flask assayed, research purity, Airco) was used as received.

Physical Measurements. Infrared spectra were recorded in the region $4000\text{--}250\text{ cm}^{-1}$ with a Perkin-Elmer 467 grating spectrometer. The complexes were studied as Nujol and Fluorolube mulls between potassium bromide plates. The samples were prepared in a glovebag filled with purified nitrogen.

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Table I. Mass Spectral Data for $\text{Cp}_2\text{U}(\text{XYCNEt}_2)_2^a$

assignt	$\text{Cp}_2\text{U}(\text{S}_2\text{CNEt}_2)_2^b$		$\text{Cp}_2\text{U}(\text{OSCNEt}_2)_2^c$		$\text{Cp}_2\text{U}(\text{O}_2\text{CNEt}_2)_2^d$	
	<i>m/e</i>	rel abundance	<i>m/e</i>	rel abundance	<i>m/e</i>	rel abundance
P*	664	20.6	632	25.6	600	23.2
[P - Cp]*	599	100	567	100	535	100
[P - Cp - H ₂ CXY]*	521	18.6	505	18.2	489	29.0
[P - (XYCNEt ₂)]*	516	13.4	500	4.0	484	12.0
[P - Cp - (XYCNEt ₂)]*	451	12.4	435	11.6	419	13.4
[CpU(NEtC ₂ H ₃) ₂]*	443	0.2	443	0.6	443	19.4
[Cp ₂ U{NEt(C ₂ H ₃)}]*	438	2.0	438	1.4	438	4.8
Cp ₂ U*	368	7.2	368	2.5	368	7.4
CpUS*	367	21.6	367	1.2	367	
CpUSH*	336	10.3	336		336	
CpUS, CpUO ₂ *	335	22.7	335	4.0	335	0.1
CpUOH*			320	0.9	320	1.2
CpUO*			319	11.6	319	15.2

^a Not corrected for ¹³C. ^b *T* = 160 °C. ^c *T* = 100 °C. ^d *T* = 100 °C.

Table II. Major Fragmentation Processes for $\text{Cp}_2\text{U}(\text{XYCNEt}_2)_2$

process	metastable peaks					
	CS ₂ ^a		COS ^b		CO ₂ ^c	
	calcd	obsd	calcd	obsd	calcd	obsd
$\text{Cp}_2\text{U}(\text{XYCNEt}_2)_2^+ \rightarrow \text{CpU}(\text{XYCNEt}_2)_2^+ + \text{Cp}$	540.4	541	508.7	509	477.0	477.2
$\text{CpU}(\text{XYCNEt}_2)_2^+ \rightarrow \text{CpU}(\text{XYCNEt}_2)(\text{NEtC}_2\text{H}_3)^+ + \text{H}_2\text{CXY}$	453.2	453.5	449.8	450	447.0	447
$\text{CpU}(\text{XYCNEt}_2)(\text{NEtC}_2\text{H}_3)^+ \rightarrow \text{CpU}(\text{NEtC}_2\text{H}_3)_2^+ + \text{H}_2\text{CXY}$ $\rightarrow \text{CpU}(\text{XYCNEt}_2)^+ + \text{NEtC}_2\text{H}_3$	390.4	391	388.6	389	401.3	401.5

^a $\text{Cp}_2\text{U}(\text{S}_2\text{CNEt}_2)_2$. ^b $\text{Cp}_2\text{U}(\text{OSCNEt}_2)_2$. ^c $\text{Cp}_2\text{U}(\text{O}_2\text{CNEt}_2)_2$.

Proton magnetic resonance spectra were obtained on a Perkin-Elmer R-32 NMR spectrometer (35 °C) or a Varian HA-100 (32 °C) or a Varian A-60 (44 °C). Variable-temperature spectra were recorded on either the Perkin-Elmer or Varian HA-100 machine, with use of sealed NMR tubes. Ambient-temperature NMR spectra were obtained with use of serum-stoppered NMR tubes.

Mass spectra of the $\text{Cp}_2\text{U}(\text{XYCNEt}_2)_2$ complexes were recorded on an AEI-MS12 mass spectrometer operating at 70 eV and at temperatures between 100 and 160 °C. Each sample was sealed in a capillary under nitrogen and admitted into the spectrometer by using a direct-probe technique.

Analyses were performed by Analytische Laboratorien, D-5250, Engelskirchen, West Germany. Abbreviations used are as follows: Cp = $\eta^5\text{-C}_5\text{H}_5$, Et = CH_2CH_3 , Me = CH_3 , Ph = C_6H_5 , and *i*-Pr = $\text{CH}(\text{CH}_3)_2$.

Preparation of $\text{Cp}_2\text{U}(\text{S}_2\text{CNEt}_2)_2$. Carbon disulfide (2.6 mL, 43.1 mmol) was added to 10 mL of pentane, and this solution was added dropwise at room temperature to a solution of $\text{Cp}_2\text{U}(\text{NEt}_2)_2$ (1.84 g, 3.6 mmol) in 30 mL of pentane. After the addition, the dropping funnel was rinsed with 10 mL of pentane and 30 mL of benzene. After 3 h, the color of the solution was orange-red and there was a reddish precipitate. The solution was stirred for an additional 18 h. The precipitated red solid was filtered and dried to give analytically pure $\text{Cp}_2\text{U}(\text{S}_2\text{CNEt}_2)_2$. Anal. Calcd for $\text{C}_{20}\text{H}_{30}\text{N}_2\text{S}_4\text{U}$: C, 36.14; H, 4.55; N, 4.21; U, 35.81. Found: C, 35.91; H, 4.40; N, 4.11; U, 35.49. Molecular weight for $\text{C}_{20}\text{H}_{30}\text{N}_2\text{S}_4\text{U}$: calcd, 665; found, 682 (osmometry in benzene).

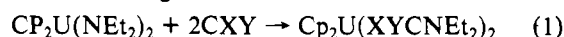
Preparation of $\text{Cp}_2\text{U}(\text{OSCNEt}_2)_2$. $\text{Cp}_2\text{U}(\text{NEt}_2)_2$ (0.489 g, 0.954 mmol) was dissolved in 12 mL of pentane and then placed in a liquid-N₂ bath. Carbonyl sulfide (0.218 g, 3.64 mmol) was transferred to the frozen bulb by trap-to-trap distillation. The bulb was allowed to warm to room temperature, during which time a brown precipitate formed; the reaction solution was stirred for a further 2 h at room temperature. The excess COS and pentane were removed under vacuum, and the resulting gold-brown solid was collected. Anal. Calcd for $\text{C}_{20}\text{H}_{30}\text{N}_2\text{O}_2\text{S}_2\text{U}$: C, 37.97; H, 4.78; N, 4.43; S, 10.14; U, 37.63. Found: C, 37.69; H, 4.66; N, 4.33; S, 10.91; U, 37.44. Molecular weight of $\text{C}_{20}\text{H}_{30}\text{N}_2\text{O}_2\text{S}_2\text{U}$: calcd, 634; found, 664 (osmometry in benzene).

Preparation of $\text{Cp}_2\text{U}(\text{O}_2\text{CNEt}_2)_2$. $\text{Cp}_2\text{U}(\text{NEt}_2)_2$ (1.83 g, 3.57 mmol) was dissolved in 50 mL of pentane and cooled to -78 °C. Carbon dioxide (8.4 mmol) was condensed onto this solution. The flask was then allowed to warm to room temperature, and the solution was stirred for an additional 5 h. During this time, a dark green solid precipitated

from solution. The solid was isolated by filtration and dried. Recrystallization from a toluene/hexane mixture gave analytically pure $\text{Cp}_2\text{U}(\text{O}_2\text{CNEt}_2)_2$. Anal. Calcd for $\text{C}_{20}\text{H}_{30}\text{N}_2\text{O}_4\text{U}$: C, 40.00; H, 5.04; O, 10.66; N, 4.66. Found: C, 39.74; H, 4.91; O, 10.44; N, 4.70. Molecular weight of $\text{C}_{20}\text{H}_{30}\text{N}_2\text{O}_4\text{U}$: calcd, 600; found, 7200, 4900 (osmometry in benzene), 1790 (osmometry in CH_2Cl_2).

Results and Discussion

Synthesis. Hydrocarbon solutions of $\text{Cp}_2\text{U}(\text{NEt}_2)_2$ react rapidly with CO₂, CS₂, and COS to give the corresponding carbamates according to reaction 1. In cases where excess



reagent, CXY, is used, the insertion occurs only into the uranium-nitrogen bonds. The reactions are quite rapid and give almost quantitative yield of the anticipated product. The cyclopentadienyl ring in the formed carbamates retains its pentahapto bonding mode as determined by the characteristic bands for a $\eta^5\text{-C}_5\text{H}_5$ ring seen in the IR spectra of the complexes.⁷ The observation of a single sharp line, assignable to the cyclopentadienyl protons in the ¹H NMR spectra, is also consistent with this formulation. Molecular weight determinations show that both $\text{Cp}_2\text{U}(\text{S}_2\text{CNEt}_2)_2$ and $\text{Cp}_2\text{U}(\text{OSCNEt}_2)_2$ are monomeric in benzene; the variable results obtained for $\text{Cp}_2\text{U}(\text{O}_2\text{CNEt}_2)_2$, however, indicate polymeric behavior which is both solvent and concentration dependent. Although the apparent high degree of polymerization found for $\text{Cp}_2\text{U}(\text{O}_2\text{CNEt}_2)_2$ in benzene compared to the other inserted product is surprising, the tendency for association is nevertheless as expected on the basis of variations in the ligands bite sizes: carbamate < thiocarbamate < dithiocarbamate.⁸ Of course, aggregate formation in carbamate complexes has been seen before. Examples are provided by the monothio-carbamates of the late transition metals,⁹ $\text{M}(\text{OSCNr}_2)$ (M

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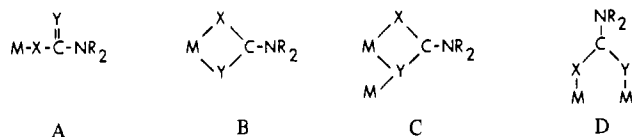
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= Cu, Ag; R = alkyl), and by the tin carbamate complex, $\text{Me}_3\text{Sn}(\text{O}_2\text{CNMe}_2)$.^{10,11}

The mass spectra of the three compounds and their major fragmentation patterns are given in Tables I and II. The results indicate that $\text{Cp}_2\text{U}(\text{S}_2\text{CNET}_2)_2$ and $\text{Cp}_2\text{U}(\text{OSCNET}_2)_2$ are possibly monomeric in the gas phase as well. Attempts to observe polymeric fragments for $\text{Cp}_2\text{U}(\text{O}_2\text{CNET}_2)_2$ by varying the probe temperature met with failure. The mass spectral assignments are speculative since they are not confirmed by high-resolution data; however, the assignments are chemically reasonable. The parent ion is observed in all three cases in approximately the same relative abundance. There appears to be a slight amount of thermal decomposition occurring since very small amounts (less than 1%) of $\text{CpU}(\text{X}_2\text{CNET}_2)_3$ and $\text{Cp}_3\text{U}(\text{X}_2\text{CNET}_2)$ appear in the mass spectra; these however are not observed in the NMR spectra of the compounds. In addition elemental analyses indicate pure compounds. The major breakdown from the parent ion involves loss of a cyclopentadienyl moiety. The loss of a carbamate ligand is a much less favorable process. Another major fragmentation mode is loss of H_2CXY , being most facile in the carbamate complex. A comparison of transition metal tris(dialkyldithiocarbamate) complexes to the uranium compounds indicates that loss of S_2CNR_2 is more significant in the former.¹² This observation may suggest that a ligand will be lost to decrease steric congestion around the transition metal. For the uranium compounds the U-Cp bond is more easily broken.

Coordination Mode of the Carbamate Moieties. The great interest in carbamate complexes is a result of some unique characteristics of the R_2NCX_2 ligand. This moiety can bond in a variety of fashions (A-D), the most common modes being either A (monodentate) or B (terminal bidentate).



Crystal structure determinations of a number of dithiocarbamate and monothiocarbamate complexes have shown all four bonding modes. The compound $\text{Sn}(\text{S}_2\text{CNET}_2)_4$ ¹³ possesses two terminal bidentate and two monodentate ligands. Another compound containing mixed coordination modes is $[\text{Ru}(\text{NO})(\text{S}_2\text{CNMe}_2)_3]$,¹⁴ which has one monodentate dithiocarbamate and two terminal bidentate moieties. The ligating mode C is observed in the iron dimer $[\text{Fe}(\text{S}_2\text{CNET}_2)_2]_2$ ¹⁵ where each iron is bonded to a bridging sulfur atom which itself is part of a terminal bidentate ligand. The hexameric structure of $[\text{AgSOCN}(i\text{-Pr})_2]_6$ also involves bonding of type C.¹⁶ Simple bridging mode D has been established, for instance, in $\text{Zn}(\text{S}_2\text{CNET}_2)_2$ ¹⁷ and $\text{U}_4\text{O}_2(\text{O}_2\text{CNET}_2)_{12}$.¹⁸

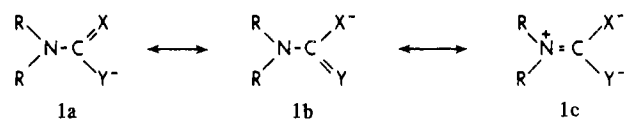
In the absence of structural information, the infrared spectra of these complexes proved to be valuable, although not infallible, in distinguishing between the monodentate and bidentate bonding modes of the carbamate moieties. In the case of a dithiocarbamate ligand, the criteria for monodentate coordination has been the presence of two $\nu(\text{C}\rightarrow\text{N})$ and two

Table III. Characteristic Infrared Absorptions (cm^{-1}) of $\text{Cp}_2\text{U}(\text{XYCNET}_2)_2$ Complexes

	$\text{Cp}_2\text{U}(\text{S}_2\text{CNET}_2)_2$	$\text{Cp}_2\text{U}(\text{OCSNET}_2)_2$	$\text{Cp}_2\text{U}(\text{O}_2\text{CNET}_2)_2$
$\nu(\text{OCN})$		1537 m 1521 m 1514 m	1549 m 1512 s 1503 s
$\nu(\text{C-N})$	1484 s		
$\delta(\text{C-H})^a$	1017 m 1012 m	1019 m	1030 m
$\nu(\text{C-S})$	915 m	946 w	
$\gamma(\text{C-H})^a$	805 sh 792 vs	791 vs 783 vs	796 sh 785 vs

^a Cyclopentadienyl group absorptions.

$\nu(\text{C}\rightarrow\text{S})$ absorptions around 1500 and 1000 cm^{-1} , respectively.^{19,20} The bidentate moiety exhibits single $\nu(\text{C}\rightarrow\text{N})$ and $\nu(\text{C}\rightarrow\text{S})$ bands where the $\text{C}\rightarrow\text{N}$ stretching frequency is in the range of 1480–1550 cm^{-1} . A rationale for the variable position of this absorption is easily obtained by making reference to the possible resonance structures of the carbamate ligands (**1a-c**). Increased importance of form **1c** is seen to cause a



concomitant increase in $\nu(\text{C}\rightarrow\text{N})$. The value of the $\text{C}\rightarrow\text{N}$ stretching frequency has been correlated with the nature of the substituents R on the nitrogen atom of the carbamate ligand and with that of the ancillary ligands on the central metal atom. The $\nu(\text{C}\rightarrow\text{S})$ stretching frequency is not as sensitive to differing R groups.²¹ X-ray analyses of the compounds $\text{Ti}(\text{S}_2\text{CNET}_2)_4$ ²² and $\text{Ti}(\text{S}_2\text{CNMe}_2)_3\text{Cl}$ ²³ have shown that both possess bidentate dithiocarbamate groups. These complexes exhibit a single $\nu(\text{C}\rightarrow\text{N})$ band at 1493¹⁹ and 1526 cm^{-1} ,²⁴ respectively; however, the latter also has two $\nu(\text{C}\rightarrow\text{S})$ bands at 990 and 981 cm^{-1} .²⁴ Fay et al.²⁵ have noted that sometimes two $\nu(\text{C}\rightarrow\text{N})$ bands are observed even though an X-ray analysis has shown bidentate coordination. They suggest that in most monodentate coordination systems, the two $\nu(\text{C}\rightarrow\text{N})$ bands are separated by greater than 20 cm^{-1} . The same argument could hold for the $\nu(\text{C}\rightarrow\text{S})$ stretch region also. For monothiocarbamate complexes, bidentate coordination has been associated with $\nu(\text{C}\rightarrow\text{O})$ values between 1500–1580 cm^{-1} and a strong $\nu(\text{C}\rightarrow\text{N})$ band around 1500–1550 cm^{-1} as in the dithiocarbamate case. The bidentate monothiocarbamate complex $\text{Ti}(\text{OSCNET}_2)_4$ has $\nu(\text{C}\rightarrow\text{O})$ and $\nu(\text{C}\rightarrow\text{N})$ bands at 1547 and 1530 cm^{-1} , respectively,²⁶ and similarly $\text{Fe}(\text{SOCNMe}_2)_3$ exhibits bidentate coordination²⁷ and has a $\nu(\text{C}\rightarrow\text{N})$ band at 1540 cm^{-1} .²⁸ Examples of monodentate coordination are the compound $\text{Pd}(\text{PPh}_3)(\text{SSeCNMe}_2)(\text{SOCNMe}_2)$ which has a $\nu(\text{C}=\text{O})$ band around 1600 cm^{-1} .²⁹

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and $\text{Me}_3\text{Sn}(\text{OSCNMe}_2)$ with a band at 1621 cm^{-1} .¹¹ Chisholm and Extine have studied a series of carbamate compounds quite extensively and have determined, through an analysis of infrared and structural data, that a strong band in the region of $1550\text{--}1600\text{ cm}^{-1}$ would be characteristic of a $\nu(\text{O}_2\text{CN})$ for a bidentate ligand.^{8a,30} The compound $\text{Ti}(\text{OiPr})_3(\text{O}_2\text{CNEt}_2)$ is also assumed to have a bidentate ligand based on an infrared spectrum that shows strong bands at $1560\text{--}1475\text{ cm}^{-1}$.³¹ A monodentate carbamate group has a $\nu(\text{O}_2\text{CN})$ band above 1620 cm^{-1} as in the species $\text{W}(\text{NMe}_2)_3(\text{O}_2\text{CNMe}_2)_3$ which has a band at 1636 cm^{-1} .^{30b}

Characteristic infrared frequencies for the new cyclopentadienyluranium carbamates are listed in Table III. On the basis of the foregoing literature survey, the data are clearly consistent with a bidentate bonding mode of the carbamate ligands in these molecules. Further corroboration of this point comes from a comparison of our results with those of other carbamate complexes of uranium where bidentate behavior of the ligands was also suggested or, as is the case with $\text{U}(\text{S}_2\text{CNEt}_2)_4$, conclusively established by X-ray structure determination.³² The observed values are 1494 and 996 cm^{-1} for $\nu(\text{C}\text{--}\text{N})$ and $\nu(\text{C}\text{--}\text{S})$ in $\text{U}(\text{S}_2\text{CNEt}_2)_4$,⁴ $1515\text{--}1520\text{ cm}^{-1}$ for $\nu(\text{OCN})$ in $\text{U}(\text{OSCNEt}_2)_4$,⁴ and 1510 cm^{-1} for $\nu(\text{OCN})$ in $\text{U}(\text{O}_2\text{CNEt}_2)_4$.^{4,33} With the exception of $\nu(\text{C}\text{--}\text{S})$, these frequencies are indeed rather similar to the values listed in Table III. No special significance is to be attached to the discrepancy in $\nu(\text{C}\text{--}\text{S})$ since, due to an absorption from the Cp ligand system in the 1000-cm^{-1} region, the assignment of the $\nu(\text{C}\text{--}\text{S})$ is the least secure in our compounds. Of course the bidentate bonding mode of the carbamate ligand is also consistent with the known preference of uranium for high coordination number. The increase in formal coordination number on going from the starting material to final products could in fact account in part for the observed enhanced stability of the $\text{Cp}_2\text{U}(\text{XYCNEt}_2)_2$ complexes over $\text{Cp}_2\text{U}(\text{NEt}_2)_2$. The ability of uranium to achieve high coordination number almost seems to be a prerequisite for the formation of this type of compound. Indeed, whereas transition metals are known to form a plethora of Cp_2ML_2 derivatives containing monodentate ligands,³⁴ complexes with two η^5 -cyclopentadienyl ligands in conjunction with two bidentate ligands are conspicuous by their absence. $\text{Cp}_2\text{Hf}(\text{BH}_4)_2$ ³⁵ appears to be the only transition-metal example so far identified.

The other frequencies listed in Table III are characteristic of the cyclopentadienyl moiety. The appearance of only a few bands assignable to this group is consistent with the presence of $\eta^5\text{-C}_5\text{H}_5$ rings.^{7,36} The out-of-plane deformation mode, $\delta(\text{C}\text{--}\text{H})$, around 800 cm^{-1} has been used to draw conclusion about the nature of the $\text{M}\text{--}\text{Cp}$ bond. According to Fritz,⁷ shifts to lower frequency indicate increased ionicity of this bond. The $\gamma(\text{C}\text{--}\text{H})$ value for the carbamate complexes decreases from 792 cm^{-1} for $\text{Cp}_2\text{U}(\text{S}_2\text{CNEt}_2)_2$, to 787 cm^{-1} (average) for $\text{Cp}_2\text{U}(\text{OSCNEt}_2)_2$ and 785 cm^{-1} for $\text{Cp}_2\text{U}(\text{O}_2\text{CNEt}_2)_2$. These values are higher than the value of $\sim 770\text{ cm}^{-1}$ for $\text{Cp}_2\text{U}(\text{NEt}_2)_2$. Within the series, it seems that complexes with oxygen-containing ligands have more ionic uranium-cyclopentadienyl bonds.

Table IV. ¹H NMR Data for $\text{Cp}_2\text{U}(\text{XYCNEt}_2)_2$ Complexes^a

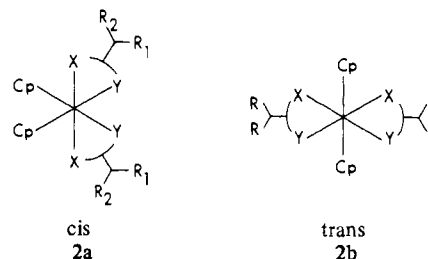
	$\text{Cp}_2\text{U}(\text{S}_2\text{CNEt}_2)_2$	$\text{Cp}_2\text{U}(\text{OSCNEt}_2)_2$	$\text{Cp}_2\text{U}(\text{O}_2\text{CNEt}_2)_2$
Cp	-7.7 s	-4.4 s	0.49 s
CH_2	4.1 br	-12.5 q, 6.4 q	0.83 q
CH_3	3.6 br	-8.1 t, 4.6 t	1.3 t

^a Given in ppm from Me_4Si ; downfield shift is negative (solvent benzene) $T\ 35^\circ\text{C}$; s, singlet; t, triplet; q, quartet; br, broad.

Coordination Geometry. Having given a reasonable account of the bonding modes of the ligands in these complexes, we next turn our attention to the coordination geometry about the central uranium atom. A commonly used practice in describing the basic geometry of Cp_xML_n -type compounds is to count the Cp ligands as occupying one coordination site. With this convention, the compounds can be considered as pseudo-six-coordinate molecules. The basic geometry for six-coordination is octahedral, and within this framework there can be two geometrical forms, either cis (**2a**) or trans (**2b**) as far as the Cp ligands are concerned; the situation is of course more complicated when $X \neq Y$.

As we have mentioned before, compounds of the type Cp_2ML_2 (where L = monodentate) are quite numerous and have well-known tetrahedral geometry, containing the angular Cp_2M moiety. However compounds of the type $\text{Cp}_2\text{M}(\text{chelate})_2$ are very rare. A very recent structure of Marks et al.,³⁵ of $(\eta^5\text{-MeC}_5\text{H}_4)_2\text{Hf}(\text{BH}_4)_2$ has shown that the $(\text{MeCp})_2\text{Hf}$ fragment retains the angular cisoid arrangement. As well, the preliminary X-ray analysis of the compound $\text{Cp}_2\text{U}(\text{BH}_4)_2$ ³⁷ suggests a structure consisting of a tetrahedral arrangement of the Cp and BH_4 ligands around the uranium center. We have also shown that the solid-state structure of $\text{Cp}_2\text{U}[\text{cis}(\text{OC})_4\text{Re}(\text{MeCO})_2]_2$ can be described as distorted octahedral containing cis positioned η^5 -cyclopentadienyl groups.³⁸

Of course there exists a large number of compounds of the type $\text{M}(\text{chelate})_2\text{XY}$ both for main-group and transition metals. Interestingly for group 4 metals the cis configuration about the metal center seems to be the preferred geometrical form. This has been shown for $\text{Sn}(\text{acac})_2\text{X}_2$ ($X = \text{Cl}, \text{Br}, \text{I}$),³⁹ $\text{Sn}(\text{acac})_2\text{RCl}$,⁴⁰ and a variety of $\text{Ti}(\text{chelate})_2\text{XY}$ compounds (chelate = dithiocarbamate,²⁴ acetylacetonate⁴¹). Based on these examples, in particular by analogy with the known $\text{Cp}_2\text{M}(\text{chelate})_2$ complexes, it would be reasonable to state that the present compounds also possess the cis octahedral geometry **2a**.



We hoped to corroborate this assignment by analyzing the NMR spectra of the Cp_2 compounds. The ambient temperature results are summarized in Table IV. As expected for compounds containing a paramagnetic metal ion ($\text{U}(\text{IV}), 5f^2$), the resonances exhibit large shifts from the expected dia-

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Table V. Predicted Number of Resonances for the Cp and R Groups Respectively in $\text{Cp}_2\text{U}(\text{XYCNR}_2)_2$ for Various Rearrangement Possibilities

	symmetry	A	B	C	D
$\text{Cp}_2\text{U}(\text{X}_2\text{CNR}_2)_2$	C_2	1, 2	1, 1	1, 1	1, 1
$\text{Cp}_2\text{U}(\text{OSCNR}_2)_2$	C_2^a	1, 2	1, 1	1, 2	1, 1
	C_2^a	1, 2	1, 1	1, 2	1, 1
	C_1^b	2, 4	2, 2	2, 2	2, 1

^a Sulfur or oxygen of monothiocarbamate trans to each other.

^b All cis compound.

magnetic positions.⁴² The upfield shifts observed for the Cp rings in $\text{Cp}_2\text{U}(\text{O}_2\text{CNET}_2)_2$ and $\text{Cp}_2\text{U}(\text{OSCNET}_2)_2$ are in line with previous observations on cyclopentadienyl-containing uranium compounds,^{42,43} however, the downfield shift seen in $\text{Cp}_2\text{U}(\text{S}_2\text{CNET}_2)_2$ appears to be so far unprecedented. Since it is known that both dipolar and contact terms are important in determining the observed isotropic shifts, variations in either could account for the trend observed in the present series. The single sharp lines obtained for the Cp groups indicate equivalence of the attached hydrogen atoms, consistent with the assigned η^5 bonding mode for these ligands. Equivalence of the ethyl groups may also be indicated by the observation of one set of quartet (CH_2) and triplet (CH_3) resonances in the symmetric CS_2 - and CO_2 -inserted compounds. The monothiocarbamate derivative exhibits two equal-intensity ethyl resonances, although there is still only one cyclopentadienyl peak. The significance of a simple ^1H NMR spectrum obtained for $\text{Cp}_2\text{U}(\text{O}_2\text{CNET}_2)_2$ is obscured by the probably fast intermolecular exchange between different polymeric aggregates. In what follows we will restrict our discussion to the behavior of the dithio- and monothiocarbamate complexes whose monomeric nature in benzene has been established.

Clearly the ambient-temperature ^1H NMR spectra are not consistent with the static structure **2a**. For instance, two ethyl resonances are expected for $\text{Cp}_2\text{U}(\text{S}_2\text{CNET}_2)_2$. A number of possible reasons exist for these apparently simplified spectra. It is known that the chemical shifts of paramagnetic compounds are temperature dependent so that accidental chemical shift equivalence of some ligand resonances may be responsible for the observed spectra at room temperature. Another factor pertinent to these complexes is the fact that stereochemical nonrigidity is common among metal carbamates. Indeed it is well-known that the NMR line shapes of metal carbamates are often affected by two main kinetic processes:⁴⁴ (i) metal-centered rearrangement; (ii) $\text{C}\equiv\text{N}$ bond rotation. The observation of metal-centered rearrangement in related $\text{Cp}_2\text{U}[\text{cis}-(\text{OC})_4\text{Re}(\text{MeCO})_2]_2$ ³⁸ is further support for considering nonrigidity in the present case.

Four situations must be considered involving various combinations of metal-centered rearrangement and $\text{C}\equiv\text{N}$ bond rotation that can be either fast or slow on the NMR time scale. The predicted number of resonances for the Cp and R groups in $\text{Cp}_2\text{U}(\text{XYCNR}_2)_2$ are indicated in Table V for the following cases: (A) metal-centered rearrangement and $\text{C}\equiv\text{N}$ bond rotation are both slow on the NMR time scale; (B) metal-centered rearrangement is slow, but $\text{C}\equiv\text{N}$ bond rotation is fast; (C) metal-centered rearrangement is fast, but $\text{C}\equiv\text{N}$ bond rotation is slow; and (D) both processes are fast. A few explanatory notes are in order concerning Table V. A full permutational analysis of the metal-centered rearrangement process in $\text{cis-M}(\text{AA})_2\text{X}_2$ and $\text{cis-M}(\text{AB})_2\text{X}_2$ has been carried

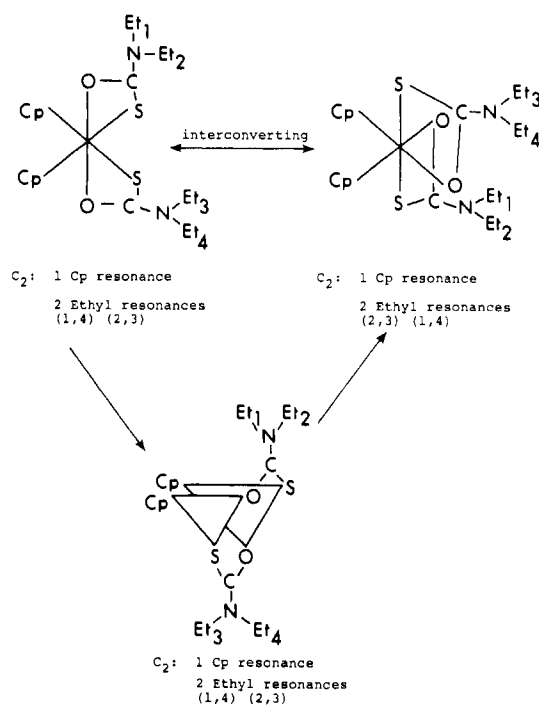
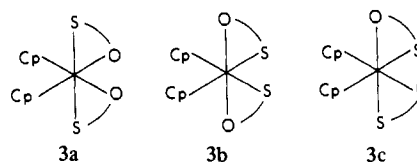


Figure 1. Intramolecular nonbond-rupture mechanism for interconverting one set of isomers of $\text{Cp}_2\text{U}(\text{OSCNET}_2)_2$.

out by Serpone and Bickley.⁴⁵ These authors have considered the effects of the trigonal twist about each of the four imaginary C_3 axes of **2a**, as well as the possibility of metal-chelate bond cleavage and subsequent rearrangements of the so produced five-coordinate intermediate. Obviously the possibilities are numerous, and the delineation of probable physical pathway for rearrangement in this class of molecules, as in others, requires carefully designed molecules undergoing specific line collapses. Our molecules do not satisfy these stringent requirements, and in constructing the table we have taken into account only the chemically most reasonable rearrangement pathway. This pathway is that of a trigonal-twist motion which converts the starting octahedron to a prismatic intermediate, with the two chelating ligands situated along the rectangular edges, a Bailar-twist-type motion. Keeping the foregoing discussion of the rearrangement in mind, the entries in Table V for the symmetric $\text{Cp}_2\text{U}(\text{X}_2\text{CNET}_2)_2$ cases become self-explanatory; however, the many possibilities appearing against $\text{Cp}_2\text{U}(\text{OSCNET}_2)_2$ may still require some comments. This molecule can actually exist as three distinct cis-geometrical isomers once the location of the O and S donor functions are taken into account (**3a-c**). Under static conditions, iso-



mers **3a** and **3b** should each exhibit one Cp and two ethyl resonances. However, a rapid Bailar-twist would interconvert the two isomers (Figure 1), thus resulting in the observation of an averaged Cp and two sets of averaged ethyl resonances (entries 1, 2 under case C). Of course $\text{C}\equiv\text{N}$ bond rotation would further average the ethyl resonances to finally give one Cp and one ethyl signal (entries 1, 1 under case D). In a

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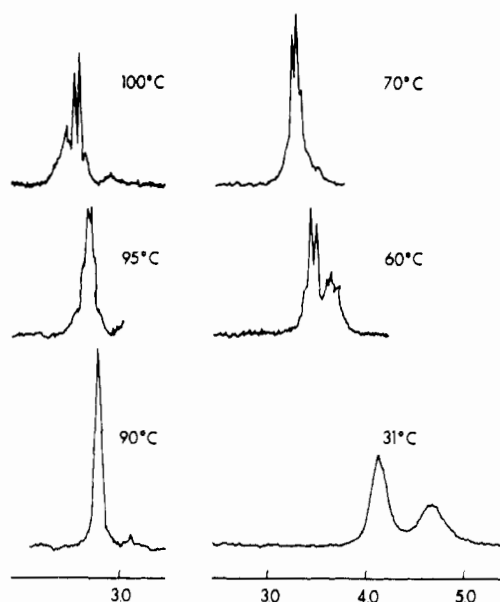


Figure 2. Variable-temperature ^1H NMR spectra of $\text{Cp}_2\text{U}(\text{S}_2\text{CNEt}_2)_2$. Chemical shifts are given in ppm relative to Me_4Si ; positive shift is an upfield shift (solvent cyclohexane).

similar manner the entries for isomer **3c**, symmetry C_1 , can be obtained. In principle then from $\text{Cp}_2\text{U}(\text{OSCNEt}_2)_2$ we could expect to see twelve sets of resonances, four Cp and eight ethyl group signals, under static condition.

In order to distinguish between the possibilities listed above, the variable-temperature NMR data were collected for the compounds $\text{Cp}_2\text{U}(\text{OSCNEt}_2)_2$ and $\text{Cp}_2\text{U}(\text{S}_2\text{CNEt}_2)_2$ in the solvent toluene. For the monothiocarbamate complex, cooling the sample down to -90°C caused broadening of the ethyl resonances; however, the Cp resonance remained sharp. Warming the sample up to $+92^\circ\text{C}$ produced almost the same effect, a sharp Cp resonance and only slightly broadened ethyl resonances. The ^1H NMR spectrum of $\text{Cp}_2\text{U}(\text{S}_2\text{CNEt}_2)_2$ at -60°C also showed a sharp Cp resonance and broad ethyl resonances. As the temperature was raised, the ethyl resonances sharpened, "coalesced" to a singlet at 90°C , and separated again at higher temperature. That the "coalescence" was really a merging of peaks due to the different temperature dependence of the methylene and methyl chemical shifts can be seen in Figure 2 or more clearly Figure 3 which shows the variation of the chemical shifts as a function of temperature. The linear behavior found is commonly observed with organouranium(IV) compounds. The temperature-invariant line shapes in the NMR spectra was disappointing. However, it is highly improbable that accidental chemical shift equivalence would account for the pattern of Cp and ethyl resonances observed. As we have already mentioned, the presence of the paramagnetic U(IV) ion has the effect of amplifying the chemical shift differences between groups; this should diminish the chance of accidental equivalence compared to diamagnetic compounds. Furthermore, as can be seen in Figures 2 and 3, the chemical shifts in paramagnetic compounds are temperature dependent as well, thus the accidentally overlapping resonances would also have to have identical temperature dependent chemical shifts in order to maintain the simple spectrum at all temperatures. This situation for the complicated spectrum expected for $\text{Cp}_2\text{U}(\text{OSCNEt}_2)_2$ seems indeed virtually impossible.

If we assume that rearrangement processes are responsible for the observed NMR spectra, we see that in the case of $\text{Cp}_2\text{U}(\text{S}_2\text{CNEt}_2)_2$ several possibilities could account for the experimental spectra. More discrimination is offered however by the monothiocarbamate complex. Indeed, any assumed

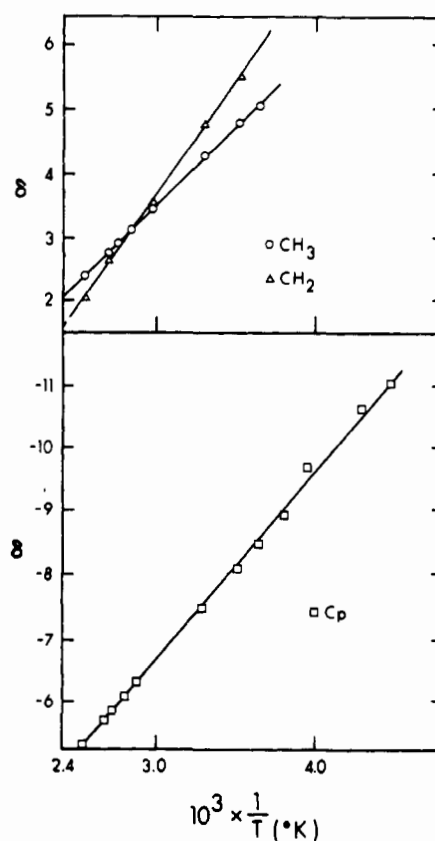


Figure 3. Chemical shift of protons of $\text{Cp}_2\text{U}(\text{S}_2\text{CNEt}_2)_2$ vs. $1/T$. Chemical shifts are given in ppm relative to Me_4Si .

mechanism must maintain two ethyl groups distinct during the rearrangement process. Reference to Table V shows that an attractive possibility for this, as long as the ground-state geometry is the symmetric structure **3a** and/or **3b**, is case C where rapid metal-centered rearrangement but slow $\text{C}^{\ominus}\text{N}$ bond rotation is occurring. Precedent for fast metal-centered rearrangement down to the lowest accessible temperatures (-90°C) in similar complexes, *cis*- $\text{Ti}(\text{S}_2\text{CNR}_2)_2\text{Cl}_2$, has been obtained by Fay et al.,²⁴ whereas Chisholm^{30b} and Bagnall⁴ have reported that in $\text{Ti}(\text{OSCNMe}_2)_4$ and $\text{Th}(\text{OSCNMe}_2)_4$, $\text{C}^{\ominus}\text{N}$ bond rotation is slow on the NMR time scale at 40 and 50°C , respectively. Comparison of the $\text{C}^{\ominus}\text{N}$ stretching frequency of the thorium complex, 1915 cm^{-1} , with the almost identical values of $\text{Cp}_2\text{U}(\text{OSCNMe}_2)_2$ (Table III) suggests that $\text{C}^{\ominus}\text{N}$ bond rotation should also be slow in this complex. By analogy we assume possibility C is operational in the dithiocarbamate complex as well. Although consistent with the NMR data obtained, the combination Bailar twist and hindered $\text{C}^{\ominus}\text{N}$ bond rotation requires the presence of only symmetric thiocarbamate complexes in solution. The presence of a sharp single Cp resonance would suggest that not all three isomers, **3a-c**, are present at the same time, since it would be unlikely that the Cp resonances would all have the same chemical shifts over the temperature range studied. However, whether only **3a** and **3b** exist or only **3c**, the asymmetric compound undergoing more complicated nonrigid behavior in solution must await the result of X-ray structural work which we have planned for the future.

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Registry No. $\text{Cp}_2\text{U}(\text{S}_2\text{CNEt}_2)_2$, 77507-05-2; $\text{Cp}_2\text{U}(\text{OSCNMe}_2)_2$, 77495-57-9; $\text{Cp}_2\text{U}(\text{O}_2\text{CNEt}_2)_2$, 77495-58-0; $\text{Cp}_2\text{U}(\text{NEt}_2)_2$, 54068-37-0; CS_2 , 75-15-0; COS, 463-58-1; CO_2 , 124-38-9.