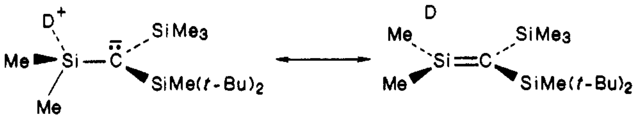

A B

zwitterionic contribution to the bonding in 2 was previously proposed on a tentative basis to account for the peculiar structure of 2.[3] With increasing Lewis basicity of the donor D (D = THF < F^-) toward the Lewis acidic center Si1, the weight of the zwitterionic form A is expected to increase. In other words, the Si–C bond length changes observed upon going from "free" 1 to the THF adduct 2 to the fluoride adduct 5 result from an increased negative charge buildup at the former olefinic C atom C1 which causes the Si=C bond to lengthen (by increasingly less p orbital overlap) and the C1–Si2/Si3 bonds to shorten (mainly because of their greater polarity).

In summary, the structures of the silaethene 1 and its Lewis base adducts 2 and 5 form a concise picture of the silicon–carbon double bond in that (a) 1 closely resembles in reactivity and structure short-lived silaethenes, (b) 1 forms stable adducts with even weak donor molecules such as THF, whose structures show resemblances to that of 1. They are best described by a zwitterionic/π-bonding model with the charge separation increasing with increasing donor character of the Lewis base toward the olefinic Si atom. The increased charge separation leads to an elongation of the former Si=C p_π–p_π bonds due to reduced p orbital overlap. They are still significantly shorter than Si–C single bonds, however, because of their high polarity (bond ionicity) as is best seen in the fluoride adduct 5. The structures of the trimethylamine and pyridine adducts 3 and 4 are expected to be intermediate between 2 and 5. A prerequisite for adduct formation seems to be a polar Si=X double bond as neither Brook's sila enol ether $(Me_3Si)_2Si{=}C(OSiMe_3)$(1-adamantyl), which has a largely nonpolar silicon–carbon double bond,[4] nor West's[17] or Masamune's[18] (symmetrical) disilenes have been reported to form stable adducts.

Acknowledgment. Support of this work by Deutsche Forschungsgemeinschaft (to N.W. and G.M.) is gratefully acknowledged. We are grateful to Mr. G. Bernhardt and Ms. H.-S. Hwang (Universität München) for the thermolysis studies of 2 and 3 and to Prof. B. Wrackmeyer for recording NMR spectra. G.M. is grateful to Prof. C. Krüger and Ms. U. Bartsch (MPI für Kohlenforschung, Mülheim a.d. Ruhr) for providing VAX-780 versions of the refinement programs.

Registry No. 1, 87937-47-1; 2, 93228-68-3; 3, 105253-42-7; 4, 105253-43-8; 5, 105369-28-6; 6, 105280-95-3; 8, 100207-12-3; 9, 100207-13-4; 10, 105280-97-5; 11, 87937-50-6; 12, 100207-16-7; 13, 87937-52-8; 14, 87937-51-7; 15, 87937-53-9; 17, 100229-17-2; 18, 87937-49-3; 19, 105280-96-4; $Me_2SiFCLi(SiMe_3)(SiMe\text{-}t\text{-}Bu_2)$, 87937-48-2.

Supplementary Material Available: Complete tables of atomic and thermal parameters for 5 (10 pages); a listing of observed and calculated structure factor amplitudes (28 pages). Ordering information is given on any current masthead page.

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Uranium–Carbon Multiple-Bond Chemistry. 7.[1] The Reaction of $Cp_3UCHP(CH_3)(C_6H_5)_2$ with Diphenylamine and the Structure of $Cp_3UN(C_6H_5)_2$

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The reaction between $Cp_3U{=}CHP(CH_3)(C_6H_5)_2$ and $HN(C_6H_5)_2$ produces $Cp_3UN(C_6H_5)_2$ in good yield. The X-ray structure of this product, which is the first Cp_3U amide to be structurally characterized (space group $P2_1$, a = 8.875 (1) Å, b = 8.402 (1) Å, c = 14.280 (1) Å, β = 99.68 (1)°, V = 1049 (1) Å^3, and Z = 2, R_1 = 0.054 and R_2 = 0.065), shows the U–N bond distance to be 2.29 (1) Å and indicates a U–N bond order near 2.

While the Cp_3U^+ moiety (Cp = η-$C_5H_5^-$) is common in organouranium chemistry and the first uranium amides were characterized during the 1940s by Gilman's group,[2] no Cp_3U amides were known until several were mentioned[3] as byproducts in the preparation of $Cp_2U(NR_2)_2$. $Cp_3UN(C_2H_5)_2$ and $Cp_3UN(C_6H_5)_2$ were further reported in 1985.[4] It has been noted[4] that the synthesis of the amides is not as straightforward as that of most other Cp_3U–X systems. For example $Cp_3UN(C_6H_5)_2$ was obtained via an acid–base reaction

$$Cp_3UP(C_6H_5)_2 + HN(C_6H_5)_2 \rightarrow Cp_3UN(C_6H_5)_2 + HP(C_6H_5)_2$$

using $Cp_3UP(C_6H_5)_2$, which itself is not easily prepared.[4] An analogous reaction between $Cp_3UN(C_2H_5)_2$ and $HN(C_6H_5)_2$ failed to produce $Cp_3UN(C_6H_5)_2$, even though $HN(C_6H_5)_2$ is a stronger acid than $HN(C_2H_5)_2$[4] and the reaction of $U[N(C_2H_5)_2]_4$ with $HN(C_6H_5)_2$ has been used to synthesize $U[N(C_6H_5)_2]_4$.[5]

(1) Part 6 in this series: Cramer, R. E.; Panchanatheswaran, K.; Gilje, J. W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 912–913.
(2) Jones, R. J.; Karmas, G.; Martin, G. A.; Gilman, H. *J. Am. Chem. Soc.* **1956**, *78*, 4285.
(3) Arduini, A. L.; Edelstein, N. M.; Jamerson, J. D.; Reynolds, J. G.; Schmid, K.; Takats, J. *Inorg. Chem.* **1981**, *20*, 2470–2474. The isolation and/or detection of several Cp_3U amides was mentioned, but, with the exception of the NMR spectrum of $Cp_3UN(C_2H_5)_2$, no details of their chemical or spectral characterization were published.
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Table I. Cell, Data Collection, and Refinement Parameters for $Cp_3UN(C_6H_5)_2$

formula	$C_{27}H_{25}UN$
fw	601.53
space group	$P2_1$
a, Å	8.875 (1)
b, Å	8.402 (1)
c, Å	14.280 (1)
β, deg	99.68 (1)
V, Å^3	1049 (1)
Z	2
μ, cm^{-1}	85.0
D(calcd), g/cm^3	1.903
cryst dimens, mm	0.29 × 0.44 × 0.76
cryst volume, mm^3	0.071
cryst shape	hexagonal
absorptn grid	4 × 6 × 10
trans coeff range	0.0562–0.1211
radiatn	Mo Kα, 0.71073 Å
scan rate, deg/min	4.0–24.0
2-θ range, deg	3–60
total observns	3347
no. of obsd ($I > 3\sigma(I)$)	2845
no. of variables	70
R_1	0.054
R_2	0.065

We have recently characterized a class of compounds, $Cp_3U{=}CHP(CH_3)(C_6H_5)R$, R = CH_3 or C_6H_5, which contain actinide–carbon multiple bonds.[6] Both the nature of the U=C bond[6] and the chemistry[7,8] of $Cp_3U{=}CHP(CH_3)(C_6H_5)R$ suggest that the α-carbon atom is a nucleophilic center capable of interacting with electrophiles. In this paper we report that $Cp_3U{=}CHP(CH_3)(C_6H_5)_2$ yields $Cp_3UN(C_6H_5)_2$ when allowed to react with $HN(C_6H_5)_2$. In addition to reflecting the polar nature of the U=C bond, this establishes $Cp_3U{=}CHP(CH_3)(C_6H_5)R$ as a reagent for the preparation of organouranium complexes of conjugate bases of weak Brønsted acids.

Experimental Section

Reaction of $Cp_3U{=}CHP(CH_3)(C_6H_5)_2$ and $HN(C_6H_5)_2$. A solution of 0.42 g (0.65 mmol) of $Cp_3U{=}CHP(CH_3)(C_6H_5)_2$ in 20 mL of toluene was added to 1.11 g (6.59 mmol) of diphenylamine under a nitrogen atmosphere at room temperature. The solution immediately changed from green to red, and a precipitate slowly formed. After 2 days red-brown crystals were separated by filtration and washed with a small amount of toluene to yield 0.32 g (80% based on uranium) of $Cp_3UN(C_6H_5)_2$. A crystal of approximate dimensions 0.29 mm × 0.44 mm × 0.76 mm was selected from this material, mounted in a thin walled glass capillary under nitrogen, and used for X-ray structure determination. Electron-impact mass spectra of $Cp_3UN(C_6H_5)_2$ taken at 70 eV show peaks for $Cp_3UN(C_6H_5)_2^+$, $Cp_2UN(C_6H_5)_2^+$, Cp_3U^+, Cp_2U^+, CpU^+, and $N(C_6H_5)_2^+$. The NMR corresponds to the reported spectrum.[4]

X-ray Crystallography. Routine 2θ data collection between 4° and 60° was carried out by using Mo Kα radiation ($K\alpha_1$, λ = 0.70930 Å; $K\alpha_2$, λ = 0.71359 Å). The cell constants were determined from the centered angular coordinates of 15 intense reflections by linear least-squares methods. Crystal data: space group $P2_1$, a = 8.875 (1) Å, b = 8.402 (1) Å, c = 14.280 (1) Å, β = 99.68 (1)°, V = 1049 (1) Å^3, and Z = 2. A total of 3347 unique reflections were collected of which 2845 were of 3σ sgnificance level. The programs used in the data reduction have been described previously.[6,9] A three-dimensional Patterson map yielded the x and z coordinates of the uranium atom, while the y coordinate was arbitrarily fixed at 0.25. Full-matrix least-squares refinement of the x and z coordinates of the uranium and the isotropic thermal parameter gave an R_1 value of 0.118. With considerable difficulty the carbon and nitrogen atoms were located in subsequent difference Fourier maps and confirmed by full-matrix least-squares refinements. Error indices of R_1 = 0.061 and R_2 = 0.076 were obtained with anisotropic refinement of the uranium and with the cyclopentadienyl and phenyl rings as rigid groups containing hydrogen atoms and fixed 1.0-Å C–H bond lengths. After absorption correction, final converged values of R_1 = 0.056 an R_2 = 0.068 were obtained. Refinement of the enantiomer resulted in lower final values of R_1 = 0.054 and R_2 = 0.065. The asymmetry of the molecule is the result of a propeller-like orientation of the phenyl rings (see Figures 1 and 2). Since enantiomerization can occur by rotation about the N-phenyl single bonds, which should be a low energy process, the molecule's chirality should be of limited chemical significance in solution.

Table II. Positional and Isotropic Thermal Parameters for Atoms Refined as Rigid Groups

atoms	x	y	z	B, Å^2
C(1)	−0.061 (1)	0.015 (2)	0.2020 (8)	2.0 (2)
C(2)	−0.181 (2)	0.036 (1)	0.1280 (6)	3.4 (3)
C(3)	−0.318 (1)	−0.044 (2)	0.1280 (8)	4.0 (4)
C(4)	−0.333 (1)	−0.146 (2)	0.2019 (8)	3.6 (4)
C(5)	−0.212 (2)	−0.167 (1)	0.2759 (8)	4.0 (4)
C(6)	−0.076 (1)	−0.087 (2)	0.2760 (8)	3.1 (3)
C(7)	0.137 (1)	0.055 (1)	0.1116 (6)	2.8 (3)
C(8)	0.234 (1)	−0.074 (1)	0.1100 (7)	2.9 (3)
C(9)	0.290 (1)	−0.110 (1)	0.0280 (9)	3.8 (4)
C(10)	0.250 (1)	−0.017 (1)	−0.0524 (6)	4.2 (4)
C(11)	0.153 (1)	0.111 (1)	−0.0508 (7)	3.5 (4)
C(12)	0.097 (1)	0.147 (1)	0.0312 (8)	2.9 (3)
C(13)	−0.033 (3)	0.272 (3)	0.392 (1)	5.7 (5)
C(14)	0.080 (2)	0.362 (2)	0.4535 (9)	5.3 (5)
C(15)	0.114 (3)	0.501 (3)	0.403 (1)	5.4 (5)
C(16)	0.022 (3)	0.497 (2)	0.311 (1)	7.6 (8)
C(17)	−0.069 (2)	0.355 (3)	0.3041 (9)	4.8 (5)
C(18)	0.318 (2)	−0.047 (2)	0.386 (1)	4.0 (4)
C(19)	0.455 (2)	0.025 (2)	0.366 (1)	4.7 (5)
C(20)	0.493 (2)	0.155 (2)	0.431 (1)	4.2 (4)
C(21)	0.379 (2)	0.162 (2)	0.491 (1)	3.7 (4)
C(22)	0.271 (1)	0.038 (2)	0.463 (1)	3.4 (4)
C(23)	0.336 (3)	0.534 (2)	0.249 (1)	6.4 (7)
C(24)	0.474 (2)	0.458 (2)	0.293 (1)	6.7 (7)
C(25)	0.501 (2)	0.325 (2)	0.236 (1)	5.7 (6)
C(26)	0.380 (2)	0.319 (2)	0.1561 (9)	3.6 (4)
C(27)	0.277 (2)	0.447 (2)	0.164 (1)	5.1 (5)
H(2)	−0.170 (2)	0.110 (2)	0.0745 (8)	4.5
H(3)	−0.404 (1)	−0.029 (3)	0.074 (1)	4.5
H(4)	−0.431 (1)	−0.204 (4)	0.202 (1)	4.5
H(5)	−0.223 (2)	−0.241 (2)	0.3294 (9)	4.5
H(6)	0.011 (1)	−0.102 (3)	0.329 (1)	4.5
H(8)	0.263 (2)	−0.141 (2)	0.1682 (8)	4.5
H(9)	0.361 (2)	−0.203 (2)	0.027 (1)	4.5
H(10)	0.291 (2)	−0.044 (2)	−0.1117 (9)	4.5
H(11)	0.124 (2)	0.178 (2)	−0.1090 (8)	4.5
H(12)	0.027 (2)	0.240 (2)	0.032 (1)	4.5
H(13)	−0.078 (6)	0.169 (4)	0.408 (2)	4.5
H(14)	0.127 (3)	0.333 (3)	0.520 (1)	4.5
H(15)	0.188 (5)	0.587 (4)	0.428 (2)	4.5
H(16)	0.020 (5)	0.579 (3)	0.260 (1)	4.5
H(17)	−0.144 (3)	0.321 (4)	0.248 (1)	4.5
H(18)	0.264 (4)	−0.140 (3)	0.352 (2)	4.5
H(19)	0.514 (3)	−0.009 (2)	0.316 (1)	4.5
H(20)	0.583 (3)	0.227 (4)	0.434 (2)	4.5
H(21)	0.376 (3)	0.241 (2)	0.543 (1)	4.5
H(22)	0.179 (2)	0.014 (3)	0.493 (2)	4.5
H(23)	0.288 (4)	0.630 (3)	0.273 (2)	4.5
H(24)	0.540 (3)	0.493 (3)	0.353 (1)	4.5
H(25)	0.590 (3)	0.250 (4)	0.249 (2)	4.5
H(26)	0.368 (4)	0.238 (2)	0.104 (1)	4.5
H(27)	0.181 (2)	0.472 (4)	0.119 (2)	4.5

(5) Reynolds, J. G.; Zalkin, A.; Templeton, D. H.; Edelstein, N. M. *Inorg. Chem.* **1977**, *16*, 1090–1096.

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(7) Gilje, J. W.; Cramer, R. E.; Bruck, M. A.; Higa, K. T.; Panchanatheswaran, K. *Inorg. Chim. Acta* **1985**, *110*, 139–143.

(8) (a) Higa, K. T. Ph.D. Thesis, University of Hawaii, 1984. (b) Panchanatheswaran, K. Ph.D. Thesis, University of Hawaii, 1984.

(9) Cramer, R. E.; VanDoorne, W.; Dubois, R. *Inorg. Chem.* **1975**, *14*, 2462–2466.

Table III. Positional and Thermal Parameters for Anisotropically Refined Atoms of $Cp_3UN(C_6H_5)_2$

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
U	0.23065 (5)	0.25	0.31123 (3)	0.00965 (6)	0.00881 (6)	0.00272 (2)	−0.0010 (2)	0.00015 (2)	0.0006 (1)
N	0.084 (1)	0.093 (2)	0.2008 (2)	0.009 (1)	0.009 (2)	0.0026 (5)	0.000 (1)	0.0008 (3)	0.0010 (8)

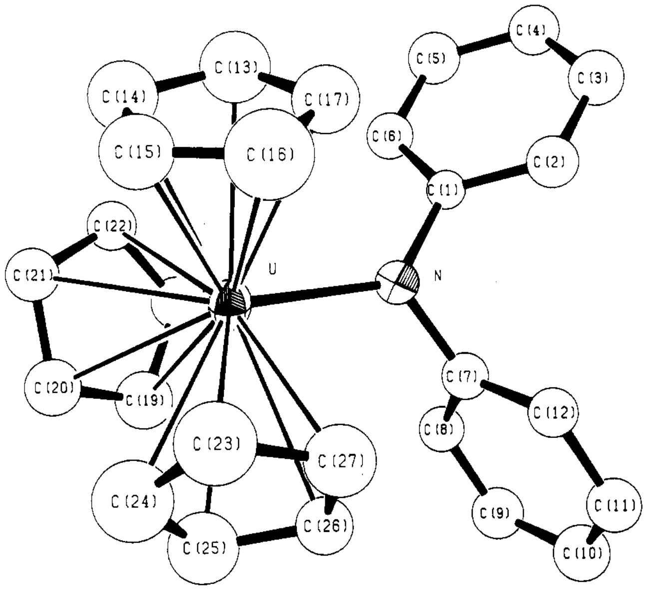

Figure 1. An ORTEP perspective drawing of $Cp_3UN(C_6H_5)_2$.

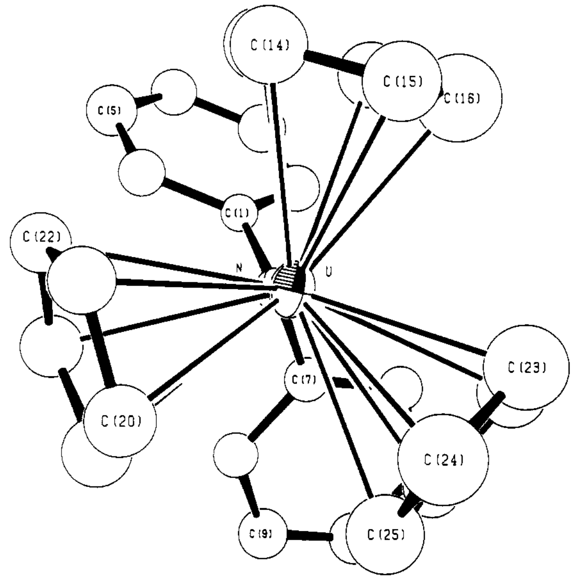

Figure 2. An ORTEP perspective drawing of $Cp_3UN(C_6H_5)_2$ looking down the U–N bond.

A summary of crystal data, data collection, and refinement parameters are listed in Table I. The positional and thermal parameters for $Cp_3UN(C_6H_5)_2$ are listed in Tables II and III.

Results and Discussion

The formation of $Cp_3UN(C_6H_5)_2$ from the reaction of $Cp_3U{=}CHP(CH_3)(C_6H_5)_2$ and $HN(C_6H_5)_2$ reveals that the α-carbon in the U=C bond is sufficiently basic to deprotonate weak Brønsted acids. Since both this and the earlier preparation[4] of $Cp_3UN(C_6H_5)_2$ utilize deprotonation of diphenylamine, a weak acid, by Cp_3U^+ complexes of strong bases, it is tempting to asssume that analogous reactions could be employed so long as $HN(C_6H_5)_2$ is a stronger acid than the conjugate acid of the ligand coordinated to the Cp_3U^+ moiety. In fact this does not appear to be the case. Carbanions are very strong bases and from a thermodynamic standpoint Cp_3U alkyls should be good reagents from which to prepare Cp_3U^+ derivatives of weak acids. In fact, the reaction of Cp_3UCH_3 with ROH does produce Cp_3UOR and CH_4.[10,11] However, we have been unable to obtain $Cp_3UN(C_6H_5)_2$ from the reaction of $HN(C_6H_5)_2$ with Cp_3UCH_3, and NMR spectra of mixtures of these two materials dissolved in benzene show no reaction after several days. This failure to obtain $Cp_3UN(C_6H_5)_2$ was somewhat surprising, but we note that, even though some product can be detected, the reaction of Cp_3UCH_3 with $HP(C_6H_5)_2$ is not a good route to $Cp_3UP(C_6H_5)_2$.[4] With these observations in mind, $Cp_3U{=}CHP(CH_3)(C_6H_5)_2$, which can be prepared in sizable quantities and stored under an inert atmosphere for long periods,[6] should be considered as a reagent for the preparation of Cp_3U^+ derivatives via reactions with Brønsted acids.

Table IV. Bond Distances (Å) for $Cp_3UN(C_6H_5)_2$[a]

U–N	2.29 (1)	U–C(22)	2.79 (2)
U–C(13)	2.78 (2)	U–Cp(2)	2.48
U–C(14)	2.78 (1)	U–C(23)	2.76 (2)
U–C(15)	2.78 (2)	U–C(24)	2.83 (2)
U–C(16)	2.79 (2)	U–C(25)	2.87 (2)
U–C(17)	2.79 (2)	U–C(26)	2.82 (2)
U–Cp(1)	2.49	U–C(27)	2.76 (2)
U–C(18)	2.77 (2)	U–Cp(3)	2.53
U–C(19)	2.76 (2)	N–C(1)	1.44 (2)
U–C(20)	2.77 (2)	N–C(7)	1.47 (2)
U–C(21)	2.78 (1)		

[a] The cyclopentadienyl and phenyl rings were refined as rigid groups with C-C distances fixed at 1.430 and 1.383 Å, respectively. U–Cp represents the distance from uranium to the centroid of the respective cyclopentadienide ring.

Table V. Bond Angles (deg) for $Cp_3UN(C_6H_5)_2$

U–N–C(1)	131.1 (8)	Cp(1)–U–N	99
U–N–C(7)	119.8 (8)	Cp(2)–U–N	106
C(1)–N–C(7)	109 (1)	Cp(3)–U–N	106
C(2)–C(1)–N	120 (1)	Cp(1)–U–Cp(2)	116
C(6)–C(1)–N	120 (1)	Cp(1)–U–Cp(3)	115
C(8)–C(1)–N	119 (1)	Cp(2)–U–Cp(3)	113
C(12)–C(7)–N	121 (1)		

While $Cp_3UN(C_6H_5)_2$ has already been characterized by chemical and spectroscopic means,[4] there has been no structure reported for it or for any Cp-substituted actinide amide. Therefore, to add to the body of structural data on Cp_3U–X molecules which is being utilized, among other things, to evaluate the nature of ligand–actinide bonding,[12] we have determined the structure of $Cp_3UN(C_6H_5)_2$. ORTEP drawings of $Cp_3UN(C_6H_5)_2$ are shown in Figures 1 and 2, and bond distances and angles are summarized in Tables IV and V. As is common in most Cp_3U–X molecules the uranium is roughly tetrahedral. In this case the coordination sphere is composed of the three Cp groups and the nitrogen atom. The average U–C(Cp) distance, 2.79 (3) Å, is comparable with that found in other Cp–U complexes.[6]

The nitrogen is planar with U, N, C(1), and C(7) deviating less than 0.01 Å from a least-squares plane. While there are no other Cp_3U amides to which comparisons can be made, data for other uranium-nitrogen bonds are sum-

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Table VI. List of Uranium-Nitrogen Bond Lengths

compd	U–N dist, Å	ref
Cp_3UNPh	2.019 (6)	*a*
$Cp_3UNC(Me)CHPMePh_2$	2.06 (1)	*b*
Cp_3UNPPh_3	2.07 (2)	*c*
$(ArO)_3UNEt_2$	2.162 (5)	*d*
$[U(NEt_2)_4]_2$	terminal 2.21 (1), 2.22 (1), 2.24 (1) bridging 2.46 (1), 2.57 (1)	*e*
$U[NPh_2]_4$	2.21 (2), 2.25 (2), 2.27 (2), 2.35 (2)	*f*
$U_3[MeNCH_2CH_2NMe]_6$	terminal 2.19 (2), 2.21 (2), 2.24 (2) bridging 2.37 (2), 2.38 (2), 2.60 (2), 2.55 (2), 2.57 (2)	*g*
$U_4(MeNCH_2CH_2NMe)_8$	terminal 2.23 (4), 2.32 (5) bridging 2.44 (4), 2.50 (4), 2.51 (4), 2.53 (4)	*h*
$(MeOCH_2CH_2OMe)Cl_2U[N(SiMe_3)_2]_2$	2.231 (8)	*i*
$HU[N(SiMe_3)_2]_3$	2.237 (9)	*j*
Cp_3UNPh_2	2.29 (1)	*k*
$Cp_3U[\eta^2\text{-}N(C_6H_{11})C{=}CHPMePh_2]$	2.31 (2)	*l*
$[(Ph_2N)_3UO\text{-}Li\cdot OEt_2]_2$	2.33 (1), 2.34 (1), 2.44 (1)	*f*
$Cp^*_2UCl(\eta^2\text{-}N_2C_3H_3)$	2.349 (5), 2.351 (5)	*m*
$Cp^*_2U(\eta^2\text{-}N_2C_3H_3)_2$	2.360 (5), 2.403 (4), 2.363 (5), 2.405 (5)	*m*
$Cp_3U(\eta^2\text{-}N_2C_3H_3)$	2.36 (1), 2.40 (1)	*n*
$Cp_3U[\eta^2\text{-}N(Ph)C(OUCp_3)]$	2.36 (2)	*a*
$Cp_3U[\eta^2\text{-}N(C_6H_{11})CMe]$	2.40 (2)	*o*
bis(phthalocyaninato)uranium	2.43	*p*
$Cp_3U(NCS)_2^-$	2.50 (1), 2.46 (1)	*q*
$U(NO_4C_7H_3)_3$	2.52 (3)	*r*
$U(C_6H_3ON_2F_6)_4$	2.539 (5), 2.574 (5), 2.589 (5), 2.593 (5)	*s*
$Cp^*_2UCl_2(\eta^1\text{-}N_2C_3H_4)$	2.607 (8)	*m*
$Cp_3U(NCMe)_2^+$	2.61 (2), 2.58 (2)	*t*
$U(BH_4)_3(NC_5H_4PPh_2)_2$	2.659 (4)	*u*
$Cp_3U(NCS)(NCMe)$	U–NCMe, 2.678 (16) U–NCS, 2.407 (15)	*v*
$[CH_2(C_5H_4)_2]UCl_2\cdot bpy$	2.68 (2)	*w*

Me = CH_3, Et = C_2H_5, Ph = C_6H_5, Cp = C_5H_5, Cp* = C_5Me_5, Ar = $OC_6H_3(CMe_3)_2$, bpy = $N_2C_{10}H_8$

[a] Brennan, J. G.; Anderson, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 514–516. [b] Cramer, R. E.; Panchanatheswaran, K.; Gilje, J. W. *J. Am. Chem. Soc.* **1984**, *106*, 1853–1854. [c] Cramer, R. E.; Mori, A.; Edelmann, F.; Gilje, J. W., unpublished results. [d] Hitchcock, P. B.; Lappert, M. F.; Singh, A.; Taylor, R. G.; Brown, D. *J. Chem. Soc., Chem. Commun.* **1983**, 561–563. [e] Reynolds, J. G.; Zalkin, A.; Templeton, D. H.; Edelstein, N. M.; Templeton, L. K. *Inorg. Chem.* **1976**, *15*, 2498–2502. [f] Reynolds, J. G.; Zalkin, A.; Templeton, D. H.; Edelstein, N. M. *Inorg. Chem.* **1977**, *16*, 1090–1096. [g] Reynolds, J. G.; Zalkin, A.; Templeton, D. H.; Edelstein, N. M. *Inorg. Chem.* **1977**, *16*, 599–603. [h] Reynolds, J. G.; Zalkin, A.; Templeton, D. H.; Edelstein, N. M. *Inorg. Chem.* **1977**, *16*, 1858–1861. [i] McCullough, L. G.; Turner, H. W.; Anderson, R. A.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1981**, *20*, 2869–2871. [j] Anderson, R. A.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1981**, *20*, 622–623. [k] This work. [l] Cramer, R. E.; Panchanatheswaran, K.; Gilje, J. W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 912–913. [m] Eigenbrot, C. W., Jr.; Raymond, K. N. *Inorg. Chem.* **1982**, *21*, 2653–2660. [n] Eigenbrot, C. W., Jr.; Raymond, K. N. *Inorg. Chem.* **1981**, *20*, 1553–1556. [o] Zanella, P.; Paolucci, G.; Rosetto, G.; Benetollo, F.; Polo, A.; Fischer, R. D.; Bombieri, G. *J. Chem. Soc., Chem. Commun.* **1985**, 96–98. [p] Gierien, A.; Hope, W. *J. Chem. Soc., Chem. Commun.* **1971**, 413–414. [q] Bombieri, G.; Benetollo, F.; Bagnall, K. W.; Plews, M. J.; Brown, D. *J. Chem. Soc., Dalton Trans.* **1983**, 45–49. [r] Baracco, L.; Bombieri, G.; Degetto, S.; Forsellini, E.; Graziani, R.; Marangoni, G. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 1045–1050. [s] Volz, K.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1976**, *15*, 1827–1831. [t] Bombieri, G.; Benetello, F.; Klaehne, E.; Fischer, R. D. *J. Chem. Soc., Dalton Trans.* **1983**, 1115–1121. [u] Wasserman, H. J.; Moody, D. C.; Paine, R. T.; Ryan, R. R.; Salazar, K. V. *J. Chem. Soc., Chem. Commun.* **1984**, 533–534. [v] Fischer, R. D.; Klaehne, E.; Kopf, J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1393–1397. [w] Quoted in: Marks, T. J. *J. Organomet. Chem.* **1977**, *138*, 125–156.

marized in Table VI. It can be seen that the U–N bond in $Cp_3UN(C_6H_5)_2$, 2.29 (1) Å, is within the range of U–N distances for terminally coordinated NR_2 groups. It can also be noted that a wide range of U–N bond lengths occurs, with the distance in $Cp_3UN(C_6H_5)_2$ lying between the short distances of 2.06 (1) Å in $Cp_3UN(CH_3)CCHP(CH_3)(C_6H_5)_2$,[13] 2.019 (6) Å in $Cp_3UN(C_6H_5)$,[14] and 2.07 (2) Å in $Cp_3UNP(C_6H_5)_3$,[15] where uranium–nitrogen bond orders are near 3, and the longer distances in a number of compounds containing a uranium–nitrogen single bond. These relationships are consistent with the nearly double metal–nitrogen bond character frequently assigned when a metal is coordinated to a planar amide group.[16]

The angles about nitrogen, U–N–C(1) = 131.1 (8)°, U–N–C(7) = 119.8 (8)°, and C(1)–N–C(7) = 109 (1)°, deviate from the idealized value of 120° for a trigonal-planar nitrogen atom, with the difference between the two U–N–C angles being of particular interest. The two phenyl groups which are attached to nitrogen occupy similar positions relative to the Cp_3U moiety (Figure 2), and there are no close inter- or intramolecular contacts which would indicate that steric effects or crystal packing is responsible for the difference. In fact, similar inequalities in M–N–C angles are encountered in many, but not all, dialkyl- or diarylamides of the actinides and transition metals,[17] and underlying electronic effects may be responsible for these differences. In this regard interactions of filled bonding orbitals of alkyl or alkylidene ligands with empty metal orbitals have been proposed[20,21] to explain bent metal

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(17) See, for example, $[U[N(C_2H_5)_2]_4]_2$ where the differences in U–N–C angles within the three independent terminal amide groups are 27°, 15°, and 4°,[18] $U[N(C_6H_5)_2]_4$ with differences of 55°, 36°, 34°, and 31° in four different terminal $UN(C_6H_5)_2$ groups,[19] and $[U[N(C_6H_5)_2]_3\cdot O\cdot Li\cdot O(C_2H_5)_2]_2$ where the U–N–C angles are all the same.[19]

(18) Reynolds, J. G.; Zalkin, A.; Templeton, D. H.; Edelstein, N. M.; Templeton, L. K. *Inorg. Chem.* **1976**, *15*, 2498–2502.

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alkyls or alkylidenes. A similar effect could be responsible for the M–N–C inequalities in the amides.

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Registry No. $Cp_3U{=}CHP(CH_3)(C_6H_5)_2$, 77357-86-9; $Cp_3UN(C_6H_5)_2$, 98703-43-6; $HN(C_6H_5)_2$, 122-39-4.

Supplementary Material Available: A listing of observed and calculated structure factors for $Cp_3UN(C_6H_5)_2$ (15 pages). Ordering information is given on on any current masthead page.

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The Coupling of Cumulenes to an Alkyne Ligand in an Osmium Cluster Complex. The Reactions of $Os_4(CO)_{11}(\mu_4\text{-}HC_2CO_2Me)(\mu_4\text{-}S)$ with Allene and Methyl Isocyanate

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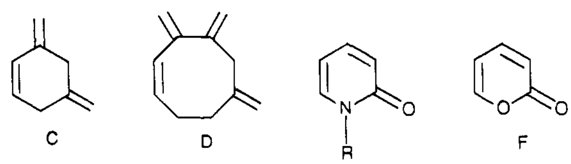
The reactions of $Os_4(CO)_{11}(\mu_4\text{-}HC_2CO_2Me)(\mu_4\text{-}S)$ (1) with allene and methyl isocyanate have been studied. Compound 1 reacts with allene at 25 °C by the addition of 2 mol equiv of allene to yield the new cluster complex $Os_4(CO)_{11}[\mu\text{-}C(CH_2)_2][\mu_3\text{-}\eta^5\text{-}(CH_2)_2CC(H)C(CO_2Me)](\mu_3\text{-}S)$ (2) in 46% yield. Compound 2 was characterized by a single-crystal X-ray diffraction analysis; space group $P\bar{1}$, $a = 15.047$ (3) Å, $b = 11.472$ (2) Å, $c = 9.444$ (2) Å, $\alpha = 103.85$ (2)°, $\beta = 89.10$ (2)°, $\gamma = 77.20$ (1)°, $Z = 2$, $\rho_{calcd} = 2.82$ g/cm^3. The structure was solved by direct methods and was refined (3609 reflections, $F^2 \geq 3.0\sigma(F^2)$) to the final values of the residuals, $R = 0.050$ and $R_w = 0.057$. The molecule consists of a group of three osmium atoms joined by metal–metal bonds and bridging ligands. The fourth metal atom is held to the molecule by bridging ligands alone. The bridging ligands include a sulfido ligand, an allene ligand, a carbonyl group, and 1-carbomethoxy-2-allylvinyl group that was formed by addition of an allene molecule to the unsubstituted end of the alkyne ligand in 1. When reacted with methyl isocyanate at 25 °C, compound 1 adds 1 mol of methyl isocyanate, loses an $Os(CO)_2$ fragment, and forms the product $Os_3(CO)_9[\mu_3\text{-}\eta^3\text{-}MeNC(O)C(H)C(CO_2Me)](\mu_3\text{-}S)$ (3) in 71% yield. Compound 3 was characterized by a single-crystal X-ray diffraction analysis: space group $P2_1/c$, $a = 12.318$ (2) Å, $b = 14.550$ (2) Å, $c = 13.500$ (2) Å, $\beta = 116.482$ (9)°, $Z = 4$, $\rho_{calcd} = 3.05$ g/cm^3. The structure was solved by direct methods and was refined (2947 reflections, $F^2 \geq 3.0\sigma(F^2)$) to the final values of the residuals, $R = 0.046$ and $R_w = 0.055$. The molecule consists of an open triangular cluster of three metal atoms with only one metal–metal bond and a triply bridging sulfido ligand. The isocyanate molecule was added to the alkyne ligand at the unsubstituted carbon atom by the formation of a carbon–carbon bond.

Introduction

The use of metal complexes to promote the formation of carbon–carbon bonds between unsaturated organic molecules has been one of the greatest triumphs to emerge from the study of organometallic compounds.[1,2] Recently, interest has been focused on the use of metal complexes to activate allenes, A, and heteroallenes, B, X, Y = NR,

$$\underset{A}{R_2C{=}C{=}CR_2} \qquad \underset{B}{X{=}C{=}Y}$$

O, or S, which belong to the general class of 1,2-diunsaturated compounds known as cumulenes.[3,4] The metal-catalyzed cooligomerization of alkynes with allenes, alkyl isocyanates, and carbon dioxide yields *exo*-methylenecyclohexene, C, or -cyclooctene, D, derivatives,[5] 2-pyridones, E[6], and pyrones, F,[4] respectively.



C D E F

We have recently synthesized the unsaturated osmium cluster complex $Os_4(CO)_{11}(\mu_4\text{-}HC_2CO_2Me)(\mu_4\text{-}S)$ (1).[7] This complex readily adds donors and unsaturated hydrocarbons. In this report is described the results of our studies of the reactions of compound 1 with allene and methyl isocyanate. A preliminary report has been published.[8]

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