LBL-26270
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Chemical Sciences Division

RECEIVED
LAWRENCE
BERKELEY LABORATORY

JAN 25 1989

LIBRARY AND
DOCUMENTS SECTION

Submitted to Acta Crystallographica C

Structure of Bis(bis(trimethylsilyl)cyclopentadienyl)(chloro)uranium(III) (bis(t-butylisocyanide)) and Bis(bis(trimethylsilyl)cyclopentadienyl)(chloro)uranium(III) (bis(t-butylcyanide))

S. Beshouri and A. Zalkin

November 1988

Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

LBL-26270 c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-26270

Structure of Bis(bis(trimethylsilyl)cyclopentadienyl)(chloro)uranium(III) (bis(t-butylisocyanide)) and Bis(bis(trimethylsilyl)cyclopentadienyl)(chloro)uranium(III) (bis(t-butylcyanide))

Sharon Beshouri and Allan Zalkin

Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory
1 Cyclotron Road
Berkeley, California 94720
USA

November 1988

Materials and Molecular Research Division, Lawrence Berkeley Laboratory
University of California, Berkeley, California 94720 USA

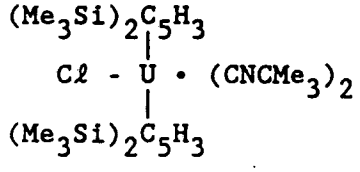
Structure of Bis(bis(trimethylsilyl)cyclopentadienyl)(chloro)uranium(III) (bis(t-butylisocyanide)) and Bis(bis(trimethylsilyl)cyclopentadienyl)(chloro)uranium(III) (bis(t-butylcyanide))

By Sharon Beshouri & Allan Zalkin

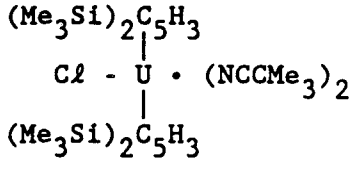
Abstract. (I) $[(Me_3Si)_2C_5H_3]_2C\ell U{\cdot}CNCMe_3$, (II) $[(Me_3Si)_2C_5H_3]_2C\ell U{\cdot}NCCMe_3$; M_r = 858.67, monoclinic, $P2_1/n$, Z=4; (I) a = 22.211(3), b = 11.484(2), c = 18.026(3) Å, β = 110.43(2)°, V = 4308.7(12) $Å^3$, D_x= 1.324 g cm^{-3}; (II) a = 22.206(4), b = 11.457(2), c = 18.030(3) Å, β = 110.46(2)°, V = 4297.7(13) $Å^3$, D_x= 1.327 g cm^{-3}; (I,II) λ(MoKα) = 0.71073 Å, μ = 37.7 cm^{-1}, F(000) = 1724, T = 296 K; (I) R = 0.030 for 3271 data [$F^2>3\sigma(F^2)$], (II) 0.033 for 3090 data [$F^2>3\sigma(F^2)$. The uranium(III) atom is in a plane with chlorine and the centroids of two cyclopentadienyl rings; the two coordinating groups (t-butylcyanide in I, t-butylisocyanide in II) lie above and below this plane. Distances: <U-Cp> (I) 2.51, (II) 2.53; <U-C(Cp) (I) 2.79(2), (II) 2.80(2); U-Cℓ (I) 2.694(3), (II) 2.698(3); <U-C(isocyanide)> 2.66(1); <U-N(cyanide) 2.62(1).

Introduction. The synthesis and structure of the uranium(III) chloro-bridged dimer $\langle Cp''_2UC\ell\rangle_2$, [Cp" = $C_5H_3(SiMe_3)_2$] has been reported (Blake, Lappert, Taylor, Atwood, Hunter & Zhang, 1986). In an attempt to explore the lability of this species toward Lewis bases, reactions were undertaken using <u>tert</u>-butylcyanide [NC-C(CH_3)$_3$] and <u>tert</u>-butylisocyanide [CN-C(CH_3)$_3$]. We find that reaction of $\langle Cp''_2UC\ell\rangle_2$ with these ligands (L) is facile, forming five coordinate uranium(III) complexes of the general formula $Cp''_2UC\ell\cdot 2L$. The structural representations of these two complexes are shown below.

(I)



(II)



Experimental. Both complexes were prepared via the same synthetic procedure. $\langle Cp''_2UC\ell\rangle_2$ was dissolved in diethyl ether under an N_2 atmosphere. CN-CMe_3 or NC-CMe_3 was added via syringe. The color of the solution immediately darkened (I brown; II green-black). Stirring was continued several hours, then solvent was removed under vacuum. The residue was extracted with hexanes, filtered, then cooled at -20°C. Dark crystals were isolated after several days and sealed inside thin-walled quartz capillaries under an inert and dry atmosphere of argon. Crystal size (I) 0.13x0.17x0.33 mm, (II) 0.06x0.21x0.45 mm. X-ray diffraction intensities (θ-2θ scans) were obtained using a modified Picker FACS-I automatic diffractometer equipped with a graphite monochromator. Cell dimensions from 31 reflections, $20° < 2\theta < 30$; analytical absorption correction, range (I) 1.4 to 2.2 (II) 1.2 to 2.0; max $\sin\theta/\lambda$ 0.54 cm^{-1}, h -23 to 23, k 0 to 12, ℓ -19 to 19; three

standard reflections, (I) 1.3%, 0.8%, 0.9% (II) 1.6%, 1.9%, 1.1% variation in standards intensities from average, intensities adjusted isotropically; (I) 11283 data, 5648 unique (of which 2377, $F^2<3\sigma(F^2)$), R_{int}= 0.04, (II) 11371 data, 5696 unique (of which 2606, $F^2<3\sigma(F^2)$), R_{int}= 0.05; structure solved by Patterson and Fourier methods; refined on F, 350 parameters. Anisotropic thermal parameters were assigned to all of the non-hydrogen atoms with the exception of the methyl carbon atoms on the t-butyl groups which, because of their unsatisfactory thermal parameters when refined anisotropically, were refined with isotropic values. The parameters of the six hydrogen atoms of the cyclopentadienyl rings were included in the least-squares refinement with a single global isotropic thermal parameter; the atomic parameters of the remaining hydrogen atoms of the structure were included with fixed positional and isotropic-thermal parameters but not varied. R (all the data) = 0.080 (I), 0.091 (II); R ($F^2 > 3\sigma(F^2)$) = 0.030 (I), 0.033 (II); wR= 0.034 (I), 0.037 (II); S = 1.07 (I), 1.08 (II); w = $4F^2[\sigma^2(F^2)+(0.04F^2)^2]^{-1}$; max (shift/$\sigma$) = < 0.02; extinction correction $F_{obs}(1+3.8\times10^{-8})I$ (I), $F_{obs}(1+3.7\times10^{-8})I$ (II); max & min of ΔF synthesis 1.0,-0.9 e/Å^3(I), 1.1,-1.2 e/Å^3 (II); atomic f for neutral U, Cℓ, Si, C & N atoms from International Tables (1974); local unpublished programs and ORTEP (Johnson, 1965).

Atomic parameters are listed in Table 1,* and distances and angles are listed in Table 2. Figures 1 and 2 shows schematics of the structures.

---

*Lists of structure factors, anisotropic thermal parameters, hydrogen positions, distances and angles, and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication 00000 (30 pp). Copies may be obtained through the Executive

Secrtetary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The uranium(III) chloro-bridged dimer, $\langle Cp''_2UC\ell\rangle_2$, is cleaved by reaction with four equivalents of L [L = $CN\text{-}C(CH_3)_3$ or $NC\text{-}C(CH_3)_3$]. The resultant monomeric product, $Cp''_2UC\ell\cdot 2L$, is isolated as a dark, crystalline solid. The molecule adopts a five coordinate, distorted trigonal bipyramidal structure, where the donor L ligands occupy the axial sites.

The ability of the isocyanide and cyanide ligands to act as good coordinating ligands toward uranium centers has been reported (Andersen, Brennan & Robbins, 1986; Kanellakopulos, Fisher, Dornberger & Baumgartner, 1970). While cyanides and isocyanides can act as pure σ-donors, isocyanides also have the ability to act as π-acceptor ligand in a uranium system. This should be reflected in a shortening of the bond distance relative to its cyanide analog. In the $Cp''_2UC\ell\cdot 2L$ system, the U-L bond distances are virtually identical. For (I), $U\text{-}C(CNC(CH_3)_3)$=2.662(11), 2.657(10)Å; for (II), $U\text{-}N(NCC(CH_3)_3$ = 2.632(10), 2.606(10)Å. This similarity in U-L bond distances, regardless of the L ligand, suggests that the amount of π-acceptance form U to isocyanide is very small.

Other complexes, also of formula $Cp''_2UX\cdot 2L$, have been prepared, where X = $C\ell$ or Br, L = cyanide or isocyanide. These complexes exhibit similar structural properties and comparable bond distances. In $Cp''_2UC\ell\cdot 2CN$-(2,6-dimethylphenyl) (Zalkin & Beshouri, 1988a), U-C(CN-xylyl) = 2.681(9), 2.654(9) Å, while in $Cp''_2UBr\cdot 2(CNCCH_3)_3$ (Beshouri & Zalkin, 1988), U-C(CN-CCH_3) = 2.662(8), 2.697(7)Å. These distances are in good agreement with the comparable distances in (I) (Table 2). The cyanide complex $Cp''_2UC\ell\cdot 2NC\text{-}SiMe_3$

(Zalkin & Beshouri, 1988b) has also been structurally characterized, with U-N(NC-$SiMe_3$) = 2.592(11), 2.619(10) Å, and are similar to the distances in (II).

Distortion from trigonal bipyramidal geometry is also observed in the collapsing of the L-U-L angles, where <C-U-C = 147.4° in (I) and <N-U-N = 151.7(3)° in (II). The Cp"-U-Cp" angles are opened up, presumbaly to accomodate the bulky $SiMe_3$ groups on the cyclopentadienyl ring: <Cp"-U-Cp" = 134.2° in (I) and 133.7° in (II).

Aknowledgement. Helpful discussions with Professor R. A. Andersen are appreciated. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

References.

Andersen, R. A., Brennan, J. G. & Robbins, J. L. (1986). J. Am. Chem. Soc., 108, 335-336.

Beshouri, S. M. & Zalkin, A. (1988) Submitted to Acta Crystallographica.

Blake, P. C., Lappert, M. F., Taylor, R. G., Atwood, J. L., Hunter, W. E. & Zhang, H. (1986). J. Chem. Soc., Chem. Comm., 1394-1395.

International Tables for X-ray Crystallography (1974). Vol. IV, Table 2.2, pp. 71-102. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Johnson, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Kanellakopulos, B., Fisher, E. O., Dornberger, E. & Baumgartner, F. (1970). J. Organomet. Chem., 24, 507-514.

Zalkin, A., Beshouri, S. M. (1988a) Submitted to Acta Crystallographica.

Zalkin, A., Beshouri, S. M. (1988b) Submitted to Acta Crystallographica.

Table 1. Positional and Thermal Parameters

$$B_{eq} = \sum B_{ij})a_i^* a_j^* \; a_i \cdot a_j/3$$

Atom	x	y	z	B/B_{eq}
		(I) (isocyanide complex)		
U	0.18783(1)	-0.01339(3)	0.46132(2)	3.28(1)
Cℓ	0.26143(12)	0.02504(26)	0.61354(14)	6.70(9)
Si1	0.09042(13)	0.16284(25)	0.24771(17)	4.8(1)
Si2	0.10736(14)	0.21845(26)	0.57406(19)	5.2(1)
Si3	0.12599(13)	-0.32839(24)	0.32672(17)	4.66(9)
Si4	0.37017(12)	-0.15842(26)	0.53523(18)	5.1(1)
N1	0.2964(4)	0.2456(7)	0.4657(5)	4.8(3)
N2	0.1408(4)	-0.2191(7)	0.5949(5)	5.1(3)
C1	0.1158(4)	0.1898(9)	0.4167(6)	4.3(4)
C2	0.0934(4)	0.1210(8)	0.3483(6)	4.2(3)
C3	0.0603(4)	0.0278(9)	0.3695(6)	4.5(4)
C4	0.0624(4)	0.0411(8)	0.4480(6)	3.9(3)
C5	0.0980(4)	0.1449(8)	0.4779(5)	3.8(3)
C6	0.2389(5)	-0.2307(8)	0.4468(6)	4.3(4)
C7	0.1877(4)	-0.2161(7)	0.3726(5)	3.5(3)
C8	0.2081(5)	-0.1244(9)	0.3361(6)	4.1(3)
C9	0.2687(5)	-0.0868(8)	0.3851(6)	4.3(4)
C10	0.2898(4)	-0.1523(8)	0.4571(6)	4.0(4)
C11	0.2637(5)	0.1660(10)	0.4610(6)	5.3(4)
C12	0.1476(5)	-0.1631(9)	0.5464(6)	4.7(4)
C13	0.3360(5)	0.3481(9)	0.4770(7)	5.8(4)
C14	0.1436(6)	-0.2854(10)	0.6650(7)	6.6(5)
C15	0.0388(6)	0.2951(10)	0.2164(7)	7.3(5)
C16	0.1716(5)	0.1978(11)	0.2455(6)	7.3(5)
C17	0.0532(5)	0.0439(9)	0.1756(6)	6.3(4)
C18	0.1126(5)	0.1095(10)	0.6522(6)	6.5(4)
C19	0.1790(5)	0.3155(9)	0.6025(7)	6.7(4)
C20	0.0358(6)	0.3130(11)	0.5586(8)	8.3(5)
C21	0.1206(5)	-0.4297(9)	0.4036(7)	6.2(4)
C22	0.1535(6)	-0.4082(10)	0.2534(7)	7.4(5)
C23	0.0440(5)	-0.2714(9)	0.2696(7)	7.6(5)

C24	0.3631(5)	-0.2309(10)	0.6254(7)	7.0(4)
C25	0.4083(5)	-0.0147(11)	0.5585(8)	8.4(5)
C26	0.4237(5)	-0.2499(12)	0.5007(8)	8.4(5)
C27	0.3498(9)	0.3929(16)	0.5581(12)	13.8(6)*
C28	0.3033(8)	0.4355(15)	0.4177(10)	12.0(5)*
C29	0.3990(8)	0.3156(14)	0.4705(10)	11.4(5)*
C30	0.2039(9)	-0.3584(17)	0.6853(11)	14.2(6)*
C31	0.1497(8)	-0.2079(16)	0.7301(11)	13.4(5)*
C32	0.0930(10)	-0.3711(18)	0.6450(13)	15.4(6)*
		(II) (cyanide complex)		
U	0.18741(2)	-0.01196(3)	0.46238(2)	3.26(1)
Cℓ	0.26018(14)	0.0243(3)	0.61545(17)	6.8(1)
Si1	0.09072(15)	0.16287(29)	0.24681(19)	4.8(1)
Si2	0.10706(17)	0.2246(3)	0.57276(22)	5.0(1)
Si3	0.12549(15)	-0.32783(28)	0.32719(20)	4.6(1)
Si4	0.37012(15)	-0.1575(3)	0.53578(21)	5.1(1)
N1	0.2627(5)	0.1638(9)	0.4585(7)	5.7(4)
N2	0.1433(5)	-0.1627(8)	0.5390(6)	5.3(4)
C1	0.1155(5)	0.1931(10)	0.4149(7)	4.1(4)
C2	0.0931(5)	0.1239(10)	0.3479(6)	3.9(4)
C3	0.0591(5)	0.0321(9)	0.3693(7)	4.1(4)
C4	0.0618(5)	0.0453(11)	0.4461(6)	4.5(4)
C5	0.0971(5)	0.1480(10)	0.4774(6)	3.8(4)
C6	0.2389(7)	-0.2295(10)	0.4469(7)	4.5(5)
C7	0.1878(5)	-0.2155(9)	0.3729(6)	3.4(3)
C8	0.2086(5)	-0.1233(10)	0.3367(7)	4.1(4)
C9	0.2691(5)	-0.0840(10)	0.3861(7)	4.3(4)
C10	0.2895(5)	-0.1509(9)	0.4567(6)	3.9(4)
C11	0.2949(5)	0.2408(11)	0.4668(7)	4.6(4)
C12	0.1409(6)	-0.2130(10)	0.5905(8)	5.1(5)
C13	0.3354(6)	0.3461(11)	0.4779(8)	5.6(5)
C14	0.1434(7)	-0.2756(11)	0.6632(7)	6.4(5)
C15	0.0379(7)	0.2945(11)	0.2145(8)	7.4(6)
C16	0.1716(6)	0.1980(13)	0.2447(7)	7.5(5)
C17	0.0541(6)	0.0421(10)	0.1752(7)	6.1(4)
C18	0.1118(6)	0.1172(12)	0.6521(7)	6.8(5)

C19	0.1784(6)	0.3210(10)	0.5993(7)	6.6(5)
C20	0.0350(6)	0.3191(13)	0.5573(8)	7.7(6)
C21	0.1212(5)	-0.4307(10)	0.4045(8)	6.0(5)
C22	0.1524(6)	-0.4063(12)	0.2534(8)	7.3(6)
C23	0.0439(5)	-0.2703(11)	0.2722(8)	7.7(5)
C24	0.3627(6)	-0.2283(12)	0.6250(8)	7.6(5)
C25	0.4079(5)	-0.0126(13)	0.5604(9)	9.0(5)
C26	0.4244(6)	-0.2494(13)	0.5019(8)	7.7(6)
C27	0.3505(10)	0.3909(18)	0.5582(14)	13.5(6)*
C28	0.3030(9)	0.4342(16)	0.4163(12)	11.6(5)*
C29	0.3993(8)	0.3156(15)	0.4679(10)	10.4(5)*
C30	0.2051(11)	-0.3480(21)	0.6823(14)	15.3(7)*
C31	0.1512(10)	-0.1989(19)	0.7295(13)	13.8(7)*
C32	0.0932(12)	-0.3666(23)	0.6474(15)	17.3(8)*

* Thermal parameters refined isotropically.

Table 2. Selected Distances (Å) and Angles (°)

(I)		(II)	
Cp1 - U	2.518	U - Cp1	2.535
Cp2 - U	2.510	U - Cp2	2.523
C11 - U	2.662(11)	N1 - U	2.632(10)
C12 - U	2.657(10)	N2 - U	2.606(10)
Cℓ - U	2.6935(24)	Cℓ - U	2.6977(28)
C1 - U	2.782(9)	C1 - U	2.800(10)
C2 - U	2.817(9)	C2 - U	2.835(10)
C3 - U	2.775(9)	C3 - U	2.800(9)
C4 - U	2.782(9)	C4 - U	2.778(11)
C5 - U	2.790(8)	C5 - U	2.797(10)
C6 - U	2.789(9)	C6 - U	2.796(12)
C7 - U	2.822(8)	C7 - U	2.836(9)
C8 - U	2.762(10)	C8 - U	2.779(11)
C9 - U	2.747(9)	C9 - U	2.757(11)
C10 - U	2.791(9)	C10 - U	2.800(11)
C11 - N1	1.151(11)	C11 - N1	1.113(12)
C12 - N2	1.135(11)	C12 - N2	1.110(13)
C13 - N1	1.440(12)	C11 - C13	1.476(16)
C14 - N2	1.457(13)	C12 - C14	1.478(17)
<U - C(Cp)>	2.786(22)	<U - C(Cp)>	2.798(24)
Cℓ - U - Cp1	114.89	Cℓ - U - Cp1	115.35
Cℓ - U - Cp2	110.87	Cℓ - U - Cp2	110.98
Cℓ - U - C11	73.53(24)	Cℓ - U - N1	75.57(25)
Cℓ - U - C12	74.02(23)	Cℓ - U - N2	76.23(24)
C11- U - C12	147.4(3)	N1 - U - N2	151.7(3)
C11- U - Cp1	94.21	N1 - U - Cp1	93.95
C11- U - Cp2	98.14	N1 - U - Cp2	96.55
C12- U - Cp1	96.34	N2 - U - Cp1	95.73
C12- U - Cp2	96.34	N2 - U - Cp2	95.83
Cp1- U - Cp2	134.23	Cp1- U - Cp2	133.66
C11- N1 - C13	175.4(11)	N1 - C11- C13	177.5(13)
C12- N2 - C14	170.0(11)	N2 - C12- C14	174.8(15)
U - C11- N1	175.4(10)	U - N1 - C11	170.8(11)
U - C12- N2	166.3(9)	U - N2 - C12	157.6(11)

Figure 1. ORTEP drawing of (I) showig atomic numbering; 50% probability ellipsoids.

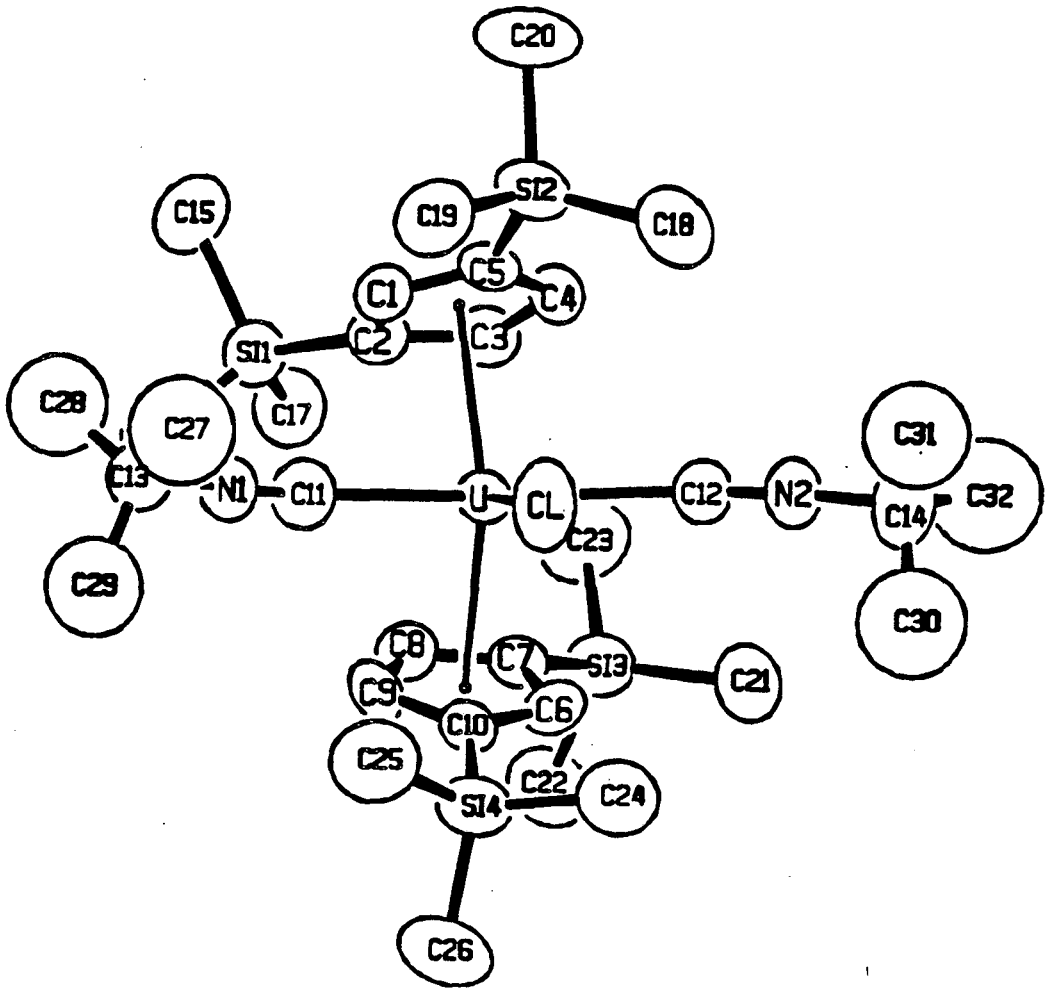
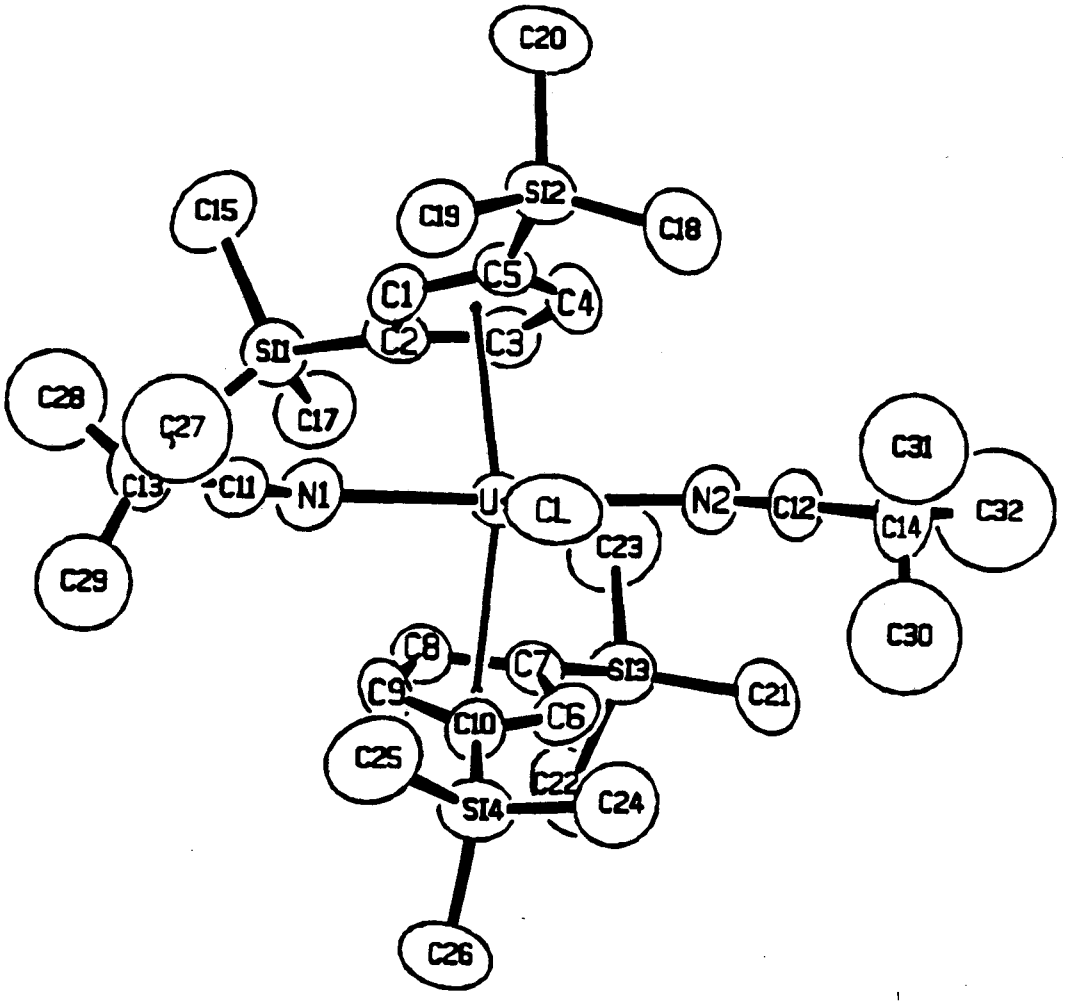


Figure 2. ORTEP drawing of (II) showng atomic numbering; 50% probability ellipsoids.



SUPPLEMENTARY MATERIALS

Materials and Molecular Research Division, Lawrence Berkeley Laboratory
University of California, Berkeley, California 94720 USA

Structure of Bis(bis(trimethylsilyl)cyclopentadienyl)(chloro)uranium(III) (bis(t-butylisocyanide)) and Bis(bis(trimethylsilyl)cyclopentadienyl)(chloro)uranium(III) (bis(t-butylcyanide))

By Sharon Beshouri & Allan Zalkin

Abstract. (I) $[(Me_3Si)_2C_5H_3]_2C\ell U{\cdot}CNCMe_3$, (II) $[(Me_3Si)_2C_5H_3]_2C\ell U{\cdot}NCCMe_3$; M_r = 858.67, monoclinic, $P2_1/n$, Z=4; (I) a = 22.211(3), b = 11.484(2), c = 18.026(3) Å, β = 110.43(2)°, V = 4308.7(12) $Å^3$, D_x = 1.324 g cm^{-3}; (II) a = 22.206(4), b = 11.457(2), c = 18.030(3) Å, β = 110.46(2)°, V = 4297.7(13) $Å^3$, D_x = 1.327 g cm^{-3}; (I,II) λ(MoKα) = 0.71073 Å, μ = 37.7 cm^{-1}, F(000) = 1724, T = 296 K; (I) R = 0.030 for 3271 data [$F^2>3\sigma(F^2)$], (II) 0.033 for 3090 data [$F^2>3\sigma(F^2)$. The uranium(III) atom is in a plane with chlorine and the centroids of two cyclopentadienyl rings; the two coordinating groups (t-butylcyanide in I or t-butylisocyanide in II) lie above and below this plane. Distances: <U-Cp> (I) 2.51, (II) 2.53; <U-C(Cp) (I) 2.79(2), (II) 2.80(2); U-Cℓ (I) 2.694(3), (II) 2.698(3); <U-C(isocyanide)> 2.66(1); <U-N(cyanide) 2.62(1).

Supplementary Table 1. Thermal Parameters

isocyanide(I)

Atom	B11	B22	B33	B12	B13	B23
U	3.210(14)	3.500(16)	3.144(14)	-0.047(18)	1.116(10)	-0.202(19)
Cℓ	5.97(13)	8.74(18)	4.20(12)	1.13(13)	0.31(10)	-2.29(13)
Si1	4.90(14)	5.36(15)	4.09(14)	0.50(12)	1.42(12)	0.69(12)
Si2	4.79(16)	5.96(16)	5.08(18)	0.30(12)	2.08(14)	-1.54(13)
Si3	4.11(13)	4.73(14)	4.84(15)	-0.23(11)	1.20(12)	-0.89(12)
Si4	3.21(12)	6.06(16)	5.40(17)	0.42(11)	0.72(11)	-0.63(13)
N1	3.8(4)	4.2(4)	6.4(5)	-0.8(4)	1.8(4)	0.4(4)
N2	6.7(5)	5.1(5)	4.1(5)	-0.1(4)	2.7(4)	0.6(4)
C1	4.6(5)	3.4(5)	5.4(6)	0.2(4)	2.2(5)	0.2(5)
C2	4.0(5)	4.3(5)	4.2(5)	0.5(4)	1.3(4)	0.0(4)
C3	3.4(4)	4.6(6)	5.3(6)	-0.2(4)	1.3(4)	-0.4(5)
C4	3.8(4)	4.0(5)	4.2(5)	-0.3(4)	1.7(4)	0.0(4)
C5	3.4(4)	4.4(5)	3.9(5)	1.0(4)	1.5(4)	-0.1(4)
C6	4.9(6)	3.8(5)	4.1(6)	1.2(5)	1.5(5)	0.4(4)
C7	3.2(4)	3.7(4)	3.4(5)	0.2(3)	1.1(4)	-0.5(4)
C8	4.4(5)	4.6(5)	3.0(5)	0.8(4)	1.0(4)	0.1(4)
C9	4.4(5)	4.4(5)	5.0(6)	-0.9(4)	2.9(5)	-0.7(5)
C10	3.8(5)	4.3(5)	4.5(6)	0.7(4)	2.2(4)	0.3(4)
C11	4.0(6)	5.4(6)	6.0(7)	-0.7(5)	1.1(5)	0.3(5)
C12	5.9(6)	4.5(5)	4.4(6)	0.2(4)	2.5(5)	0.3(5)
C13	5.0(6)	5.5(6)	6.9(7)	-0.2(5)	2.0(5)	0.6(5)
C14	9.2(8)	6.3(6)	4.3(6)	-1.1(6)	2.4(6)	0.5(5)
C15	9.3(8)	7.0(7)	5.2(7)	2.1(6)	2.3(6)	1.8(5)
C16	6.6(6)	10.4(8)	4.7(6)	0.0(6)	1.6(5)	2.1(6)
C17	7.1(6)	7.7(7)	3.6(5)	0.5(5)	1.2(4)	0.4(5)
C18	7.3(7)	8.7(7)	3.9(5)	-0.5(6)	2.4(5)	-1.1(5)
C19	8.8(7)	5.1(6)	6.1(7)	-0.3(5)	2.4(6)	-1.8(5)
C20	7.3(7)	9.4(8)	8.1(8)	2.9(6)	2.5(6)	-3.2(7)
C21	5.9(6)	5.9(6)	7.0(7)	-1.4(5)	2.7(5)	-0.3(5)
C22	8.7(8)	7.0(7)	7.4(8)	-1.5(6)	4.1(6)	-3.0(6)
C23	4.9(6)	6.6(7)	9.3(9)	-0.7(5)	-0.1(6)	-0.5(6)
C24	5.4(6)	9.5(8)	5.4(6)	1.4(6)	0.9(5)	1.1(6)
C25	4.2(5)	8.8(8)	10.6(9)	-0.6(6)	0.6(5)	-0.1(8)
C26	4.9(6)	12.1(10)	8.3(8)	1.8(6)	2.2(6)	-0.4(7)

Atom	B (Å)
C27	13.8(6)
C28	12.0(5)
C29	11.4(5)
C30	14.2(6)
C31	13.4(5)
C32	15.4(6)

H1 - H6 B = 2.1(7)

H7 - H60 B = 10.0

Supplemental Table 1 (continued)

cyanide(II)

Atom	B11	B22	B33	B12	B13	B23
U	3.137(15)	3.353(19)	3.151(16)	-0.027(22)	0.925(11)	-0.160(23)
Cℓ	6.05(15)	8.91(22)	4.37(14)	1.52(16)	0.36(12)	-2.27(16)
Si1	4.80(16)	5.40(17)	3.88(16)	0.35(14)	1.29(13)	0.54(14)
Si2	4.61(18)	5.51(18)	5.01(20)	0.21(15)	1.93(16)	-0.93(15)
Si3	3.80(15)	4.51(16)	5.03(17)	-0.30(12)	0.92(13)	-0.82(14)
Si4	3.30(14)	5.80(19)	5.34(19)	0.41(13)	0.46(13)	-0.57(15)
N1	4.9(6)	4.2(6)	7.9(8)	-0.9(5)	2.0(5)	0.3(5)
N2	7.0(6)	4.4(5)	5.2(6)	0.4(5)	3.3(5)	0.8(5)
C1	3.9(6)	3.1(5)	4.9(6)	0.0(4)	1.1(5)	0.3(5)
C2	2.9(5)	4.9(6)	3.6(5)	0.6(4)	0.8(4)	-0.4(5)
C3	2.9(5)	4.1(6)	4.8(7)	-0.5(4)	0.6(4)	-0.5(5)
C4	4.8(6)	6.0(8)	3.2(6)	-0.2(5)	1.9(5)	0.6(5)
C5	3.2(5)	4.3(6)	3.9(6)	0.7(4)	1.2(5)	0.2(5)
C6	5.5(7)	3.7(7)	3.7(7)	0.9(6)	1.0(6)	-0.1(5)
C7	3.3(5)	3.7(5)	3.4(5)	0.0(4)	1.4(4)	-0.6(4)
C8	3.5(6)	5.0(6)	3.4(6)	0.8(5)	0.8(5)	0.7(5)
C9	4.3(6)	4.4(6)	4.8(6)	-0.7(5)	2.5(5)	0.1(5)
C10	4.0(6)	3.8(6)	3.8(6)	-0.2(5)	1.1(5)	-0.2(5)
C11	4.0(6)	4.1(6)	5.6(7)	0.4(5)	1.7(5)	0.6(5)
C12	6.4(8)	4.4(6)	5.3(8)	-0.6(5)	3.1(7)	0.3(6)
C13	5.0(6)	6.1(7)	5.7(7)	-1.2(6)	1.8(6)	0.4(6)
C14	9.2(9)	5.8(7)	4.1(6)	-2.1(7)	2.1(6)	0.4(6)
C15	8.7(9)	6.2(7)	5.9(8)	1.4(7)	0.9(7)	1.2(6)
C16	7.0(8)	10.8(10)	4.9(7)	-0.3(7)	2.4(6)	2.4(7)
C17	7.0(7)	6.5(7)	3.8(5)	0.5(5)	0.8(5)	-0.6(5)
C18	8.2(8)	9.1(9)	3.5(6)	-0.4(7)	2.5(6)	-0.8(6)
C19	8.4(8)	5.5(7)	5.9(7)	0.0(6)	2.3(7)	-1.3(6)
C20	6.6(8)	9.8(10)	6.3(8)	2.2(7)	1.7(6)	-2.0(7)
C21	5.7(7)	5.3(6)	8.0(8)	-1.6(5)	3.7(6)	-0.7(6)
C22	8.2(8)	8.0(8)	6.4(8)	-3.2(7)	3.6(7)	-3.7(7)
C23	4.1(6)	7.2(8)	8.8(10)	-1.1(6)	-1.6(7)	-0.7(7)
C24	5.6(7)	9.8(9)	5.8(8)	1.2(7)	-0.1(6)	2.0(7)
C25	3.7(5)	8.5(9)	11.8(10)	-0.6(7)	-1.0(6)	0.3(9)
C26	4.3(6)	10.0(10)	8.2(9)	1.5(7)	1.5(6)	-0.7(8)

Atom	B (Å)
C27	13.5(6)
C28	11.6(5)
C29	10.4(5)
C30	15.3(7)
C31	13.8(7)
C32	17.3(8)

H1 - H6 B = 1.6(8)

H7 - H60 B = 10.0

The temperature factor has the form: $\exp[-(B_{11}\ h^2a^{*2} + 2B_{12}hka^*b^* + \ldots)/4]$ or $\exp(-B\sin\theta/\lambda)^2$.

Supplemental Table 2. Hydrogen atomic coordinates

Isocyanide Complex (I)

H1	0.135(3)	0.261(6)	0.421(4)	H31	0.046	-0.2218	0.2262
H2	0.039(3)	-0.025(6)	0.344(4)	H32	0.0280	-0.2257	0.3047
H3	0.038(3)	-0.015(5)	0.475(4)	H33	0.0148	-0.3368	0.2476
H4	0.240(3)	-0.287(6)	0.477(4)	H34	0.3463	-0.3101	0.6118
H5	0.192(3)	-0.097(6)	0.291(4)	H35	0.3338	-0.186	0.6443
H6	0.289(3)	-0.038(6)	0.371(4)	H36	0.4056	-0.2346	0.6672
H7	0.0573	0.3588	0.2538	H37	0.3814	0.037	0.5770
H8	-0.0045	0.2777	0.2158	H38	0.4134	0.0184	0.5108
H9	0.0367	0.3186	0.1633	H39	0.4507	-0.0226	0.600
H10	0.1995	0.1295	0.2624	H40	0.4273	-0.216	0.4525
H11	0.190	0.2630	0.2815	H41	0.4060	-0.3287	0.4895
H12	0.168	0.2194	0.1916	H42	0.4665	-0.2533	0.542
H13	0.0093	0.0295	0.1743	H43	0.3723	0.3330	0.5966
H14	0.0787	-0.0274	0.1918	H44	0.3092	0.4126	0.5656
H15	0.0519	0.0671	0.1227	H45	0.3767	0.4626	0.5662
H16	0.1498	0.0587	0.6599	H46	0.2622	0.4561	0.4231
H17	0.0733	0.0624	0.6361	H47	0.2954	0.4039	0.3645
H18	0.1175	0.1498	0.7020	H48	0.3302	0.5053	0.4253
H19	0.1733	0.3745	0.5614	H49	0.3920	0.2826	0.418
H20	0.2175	0.2692	0.6085	H50	0.4204	0.2576	0.5112
H21	0.1839	0.354	0.6529	H51	0.4263	0.3850	0.4782
H22	-0.0032	0.265	0.5416	H52	0.2413	-0.3071	0.6959
H23	0.033	0.3713	0.5179	H53	0.2008	-0.4098	0.6407
H24	0.0397	0.3524	0.6084	H54	0.2086	-0.4054	0.7323
H25	0.1087	-0.3865	0.4433	H55	0.1125	-0.1553	0.7159
H26	0.1624	-0.4675	0.4292	H56	0.1892	-0.1617	0.7422
H27	0.0880	-0.4891	0.3793	H57	0.1516	-0.2533	0.7770
H28	0.1955	-0.444	0.2810	H58	0.0978	-0.4246	0.605
H29	0.1572	-0.3533	0.2135	H59	0.0511	-0.3319	0.6236
H30	0.1222	-0.469	0.2274	H60	0.0953	-0.4152	0.6925

Supplemental Table 2. (continued)

Cyanide Complex (II)

H1	0.134(3)	0.265(6)	0.420(4)	H31	0.0455	-0.2199	0.229
H2	0.043(4)	-0.037(6)	0.343(5)	H32	0.0285	-0.2251	0.3083
H3	0.048(3)	0.000(7)	0.474(4)	H33	0.0144	-0.3356	0.2503
H4	0.241(5)	-0.275(7)	0.472(5)	H34	0.3457	-0.3075	0.6116
H5	0.188(4)	-0.090(6)	0.295(5)	H35	0.3334	-0.1828	0.6436
H6	0.294(3)	-0.026(6)	0.371(4)	H36	0.4051	-0.232	0.6669
H7	0.0558	0.3590	0.2515	H37	0.3805	0.0382	0.5789
H8	-0.0054	0.276	0.214	H38	0.413	0.0215	0.5131
H9	0.0355	0.3176	0.1612	H39	0.4501	-0.0206	0.6021
H10	0.1998	0.1302	0.2627	H40	0.4283	-0.2154	0.4539
H11	0.1895	0.2644	0.2797	H41	0.4065	-0.3283	0.4903
H12	0.1681	0.218	0.1905	H42	0.4669	-0.2529	0.5435
H13	0.0101	0.0278	0.1735	H43	0.3737	0.3312	0.5964
H14	0.0798	-0.029	0.1923	H44	0.3105	0.4109	0.5669
H15	0.0533	0.0645	0.1224	H45	0.3774	0.4609	0.5652
H16	0.1487	0.0654	0.6602	H46	0.2616	0.4555	0.4206
H17	0.0722	0.0708	0.6365	H47	0.2960	0.4014	0.3638
H18	0.1170	0.1588	0.7015	H48	0.3302	0.5039	0.4241
H19	0.1725	0.3788	0.5573	H49	0.391	0.2844	0.4147
H20	0.2168	0.274	0.6054	H50	0.422	0.257	0.5074
H21	0.1837	0.361	0.6492	H51	0.4259	0.3861	0.4754
H22	-0.0038	0.2706	0.5415	H52	0.2418	-0.2959	0.6906
H23	0.0317	0.3764	0.5157	H53	0.2011	-0.4008	0.6380
H24	0.0394	0.3600	0.6068	H54	0.2115	-0.394	0.7303
H25	0.1099	-0.3878	0.4449	H55	0.1149	-0.1446	0.716
H26	0.163	-0.4687	0.4291	H56	0.1914	-0.1553	0.7416
H27	0.0883	-0.4900	0.3804	H57	0.1525	-0.2456	0.7756
H28	0.1945	-0.4423	0.2805	H58	0.099	-0.4242	0.610
H29	0.1558	-0.3508	0.2137	H59	0.0506	-0.3309	0.6244
H30	0.121	-0.467	0.2273	H60	0.0965	-0.4061	0.6970

Supplemental Table 3. Distances (Å)

Isocyanid Complex (I)

Cp1-U	2.518	C2 -SI1	1.855(10)	C24-SI4	1.879(12)	C10-C9	1.431(13
Cp2-U	2.510	C16-SI1	1.860(11)	C11-N1	1.151(11)	C28-C13	1.460(18
CL -U	2.694(3)	C15-SI1	1.866(11)	C13-N1	1.440(12)	C27-C13	1.476(20
C11-U	2.662(11)	C17-SI1	1.866(11)	C12-N2	1.135(11)	C29-C13	1.492(17
C12-U	2.657(10)	C18-SI2	1.856(11)	C14-N2	1.457(13)	C32-C14	1.441(21
C1 -U	2.782(9)	C19-SI2	1.861(11)	C5 -C1	1.395(12)	C31-C14	1.442(19
C2 -U	2.817(9)	C20-SI2	1.863(11)	C2 -C1	1.400(13)	C30-C14	1.510(20
C3 -U	2.775(9)	C5 -SI2	1.872(9)	C3 -C2	1.423(12)	C1 -H1	0.92(6)
C4 -U	2.782(9)	C21-SI3	1.845(11)	C4 -C3	1.407(13)	C3 -H2	0.80(6)
C5 -U	2.790(8)	C7 -SI3	1.852(9)	C5 -C4	1.426(12)	C4 -H3	1.07(6)
C6 -U	2.789(9)	C23-SI3	1.869(10)	C10-C6	1.405(13)	C6 -H4	0.84(6)
C7 -U	2.822(8)	C22-SI3	1.876(11)	C7 -C6	1.431(12)	C8 -H5	0.82(7)
C8 -U	2.762(10)	C25-SI4	1.835(12)	C8 -C7	1.396(12)	C9 -H6	0.82(6)
C9 -U	2.747(9)	C10-SI4	1.848(10)	C9 -C8	1.395(13)	(C15-C32)-H	0.98
C10-U	2.791(9)	C26-SI4	1.850(12)				

Cyanide Complex (II)

Cp1-U	2.535	C2 -SI1	1.858(11)	C26-SI4	1.856(13)	C10-C9	1.417(14)
Cp2-U	2.523	C15-SI1	1.874(13)	C11-N1	1.113(12)	C27-C13	1.460(23)
CL -U	2.6977(3)	C16-SI1	1.852(13)	C12-N2	1.110(13)	C28-C13	1.486(20)
N1 -U	2.632(10)	C17-SI1	1.872(11)	C13-C11	1.476(16)	C29-C13	1.532(19)
N2 -U	2.606(10)	C5 -SI2	1.873(11)	C14-C12	1.478(17)	C31-C14	1.442(22)
C1 -U	2.800(10)	C18-SI2	1.861(13)	C2 -C1	1.384(14)	C32-C14	1.478(26)
C2 -U	2.835(10)	C19-SI2	1.851(13)	C5 -C1	1.421(14)	C30-C14	1.534(24)
C3 -U	2.800(9)	C20-SI2	1.870(13)	C3 -C2	1.425(14)	C1 -H1	0.91(7)
C4 -U	2.778(11)	C7 -SI3	1.857(10)	C4 -C3	1.373(14)	C3 -H2	0.92(7)
C5 -U	2.797(10)	C21-SI3	1.853(13)	C5 -C4	1.417(14)	C4 -H3	0.85(7)
C6 -U	2.796(12)	C22-SI3	1.869(12)	C10-C6	1.401(16)	C6 -H4	0.69(8)
C7 -U	2.836(9)	C23-SI3	1.856(11)	C7 -C6	1.427(15)	C8 -H5	0.83(7)
C8 -U	2.779(11)	C10-SI4	1.859(11)	C8 -C7	1.403(14)	C9 -H6	0.96(7)
C9 -U	2.757(11)	C24-SI4	1.859(14)	C9 -C8	1.400(14)	(C15-C32)-H	0.98
C10-U	2.800(11)	C25-SI4	1.842(14)				

Supplemental Table 4. Angles (°)

Isocyanide Complex (I)

CL -U -C11	73.5(3)	C7 -SI3-C22	106.4(4)	SI3-C7 -C6	123.9(7)
CL -U -C12	74.0(3)	C7 -SI3-C23	115.4(4)	SI3-C7 -C8	128.7(7)
C11-U -C12	147.4(3)	C21-SI3-C22	110.1(5)	C6 -C7 -C8	104.2(8)
CL -U -Cp1	114.89	C21-SI3-C23	109.2(5)	C7 -C8 -C9	109.6(9)
CL -U -Cp2	110.87	C22-SI3-C23	106.1(6)	C8 -C9 -C10	110.4(9)
C11-U -Cp1	94.21	C10-SI4-C24	109.0(5)	SI4-C10-C6	126.5(8)
C11-U -Cp2	98.14	C10-SI4-C25	112.7(5)	SI4-C10-C9	129.3(8)
C12-U -Cp1	96.34	C10-SI4-C26	109.2(5)	C6 -C10-C9	102.9(9)
C12-U -Cp2	96.34	C24-SI4-C25	111.8(6)	U -C11-N1	175.4(10)
Cp1-U -Cp2	134.23	C24-SI4-C26	107.3(6)	U -C12-N2	166.3(9)
C2 -SI1-C15	108.3(5)	C25-SI4-C26	106.7(6)	N1 -C13-C27	109.2(11)
C2 -SI1-C16	111.9(5)	C11-N1 -C13	175.4(11)	N1 -C13-C28	109.5(10)
C2 -SI1-C17	110.3(5)	C12-N2 -C14	170.0(11)	N1 -C13-C29	109.2(10)
C15-SI1-C16	108.3(6)	C2 -C1 -C5	112.0(9)	C27-C13-C28	111.3(13)
C15-SI1-C17	108.0(5)	SI1-C2 -C1	126.5(8)	C27-C13-C29	106.9(12)
C16-SI1-C17	109.8(5)	SI1-C2 -C3	127.7(8)	C28-C13-C29	110.7(12)
C5 -SI2-C18	110.8(5)	C1 -C2 -C3	104.3(9)	N2 -C14-C30	105.4(12)
C5 -SI2-C19	109.5(5)	C2 -C3 -C4	110.4(9)	N2 -C14-C31	110.3(11)
C5 -SI2-C20	108.1(5)	C3 -C4 -C5	106.8(8)	N2 -C14-C32	110.2(12)
C18-SI2-C19	111.9(5)	SI2-C5 -C1	126.5(8)	C30-C14-C31	108.8(13)
C18-SI2-C20	109.2(6)	SI2-C5 -C4	126.5(7)	C30-C14-C32	103.2(13)
C19-SI2-C20	107.1(5)	C1 -C5 -C4	106.4(9)	C31-C14-C32	117.8(15)
C7 -SI3-C21	109.6(5)	C7 -C6 -C10	112.8(9)		

Cyanide Complex (II)

CL -U -N1	75.6(3)	N1 -C11-C13	177.5(13)	SI3-C7 -C6	124.3(8)
CL -U -N2	76.2(3)	N2 -C12-C14	174.8(15)	SI3-C7 -C8	129.1(8)
N1 -U -N2	151.7(3)	C7 -SI3-C22	106.0(5)	C6 -C7 -C8	103.6(10)
CL -U -Cp1	115.35	C7 -SI3-C23	115.3(5)	C7 -C8 -C9	110.2(10)
CL -U -Cp2	110.98	C21-SI3-C22	110.0(6)	C8 -C9 -C10	109.4(10)
N1 -U -Cp1	93.95	C21-SI3-C23	109.3(6)	SI4-C10-C6	125.8(9)
N1 -U -Cp2	96.55	C22-SI3-C23	106.6(7)	SI4-C10-C9	129.0(9)
N2 -U -Cp1	95.73	C10-SI4-C24	109.2(5)	C6 -C10-C9	104.1(10)
N2 -U -Cp2	95.83	C10-SI4-C25	112.5(5)	U -N1 -C11	170.8(11)
Cp1-U -Cp2	133.66	C10-SI4-C26	109.4(6)	U -N2 -C12	157.6(11)
C2 -SI1-C15	107.3(6)	C24-SI4-C25	110.8(7)	C11-C13-C27	109.9(13)
C2 -SI1-C16	112.1(5)	C24-SI4-C26	107.5(6)	C11-C13-C28	110.0(11)
C2 -SI1-C17	110.8(5)	C25-SI4-C26	107.3(7)	C11-C13-C29	110.0(12)
C15-SI1-C16	108.9(6)	C2 -C1 -C5	111.7(10)	C27-C13-C28	112.6(14)
C15-SI1-C17	107.9(6)	SI1-C2 -C1	126.7(9)	C27-C13-C29	107.2(13)
C16-SI1-C17	109.7(6)	SI1-C2 -C3	127.3(8)	C28-C13-C29	107.0(13)
C5 -SI2-C18	110.6(5)	C1 -C2 -C3	104.4(10)	C12-C14-C30	102.4(14)
C5 -SI2-C19	109.4(6)	C2 -C3 -C4	110.5(10)	C12-C14-C31	113.3(13)
C5 -SI2-C20	108.3(5)	C3 -C4 -C5	108.4(10)	C12-C14-C32	112.2(14)
C18-SI2-C19	112.5(6)	SI2-C5 -C1	125.6(9)	C30-C14-C31	107.7(15)
C18-SI2-C20	108.2(7)	SI2-C5 -C4	128.7(9)	C30-C14-C32	102.4(15)
C19-SI2-C20	107.6(6)	C1 -C5 -C4	105.0(10)	C31-C14-C32	117.0(17)
C7 -SI3-C21	109.4(5)	C7 -C6 -C10	112.8(10)		

Plane No. 1

Isocyanide (I)				Cyanide (II)			
Equation of the Plane:							
17.37369x-6.10558y+0.52648z=1.06965				17.24748x-6.18004y+0.57943z=1.03958			
Distance (Å) to the Plane From the Atoms							
Forming Plane		Not Forming Plane		Forming Plane		Not Forming Plane	
C1	0.003(12)	U	2.518(5)	C1	-0.000(16)	U	2.535(5)
C2	-0.003(13)	SI1	-0.364(17)	C2	0.003(14)	SI1	-0.338(19)
C3	0.003(14)	SI2	-0.237(17)	C3	-0.005(15)	SI2	-0.249(20)
C4	-0.001(13)	H1	-0.094(73)	C4	0.005(15)	H1	-0.127(81)
C5	-0.001(12)	H2	-0.056(78)	C5	-0.003(15)	H2	0.131(84)
		H3	-0.079(65)			H3	0.067(80)

Plane No. 2

Isocyanide (I)				Cyanide (II)			
Equation of the Plane:							
-13.82153x+7.55973y+11.05197z=-0.10755				-13.90325x+7.50211y+11.08487z=-0.09266			
Distance (Å) to the Plane From the Atoms							
Forming Plane		Not Forming Plane		Forming Plane		Not Forming Plane	
C6	-0.000(14)	U	2.509(4)	C6	0.003(18)	U	2.522(5)
C7	-0.003(12)	SI3	-0.506(17)	C7	-0.001(14)	SI3	-0.485(19)
C8	0.006(13)	SI4	-0.291(17)	C8	-0.000(15)	SI4	-0.296(20)
C9	-0.007(14)	H4	-0.105(76)	C9	0.001(15)	H4	-0.087(102)
C10	0.004(13)	H5	-0.058(76)	C10	-0.002(15)	H5	0.083(84)
		H6	-0.083(75)			H6	-0.082(73)

Angle Between the Planes:

(I)	(II)
-45.4(4)°	-45.3(5)

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720