## Title

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# Preparation of the First Molecular Carbon Monoxide Complex of Uranium, $(Me_3SiC_5H_4)_3UCO$.

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Abstract

The trivalent uranium metallocene $(Me_3SiC_5H_4)_3U$ reversibly adsorbs 1.0 ± 0.05 equivalents of carbon monoxide in hydrocarbon solution at room temperature. The solution infrared spectrum with $^{12}CO$, $^{13}CO$, and $C^{18}O$ contain $\nu_{CO}$ stretching frequencies of 1976, 1935, and 1932 $cm^{-1}$ respectively. The metallocene also adsorbs CO in the solid state, with measured CO stretching frequencies 1969 ($^{12}CO$) and 1922 ($^{13}CO$) $cm^{-1}$. The structure of the isoelectronic isocyanide complex $(Me_3SiC_5H_4)_3UCNEt$ contains a near linear U-C-N angle, 173.6(2.0)$^{o}$, and C-N-C angle, 170.2(2.2)$^{o}$. The U-C (CNEt) distance is 2.57(3)Å.

Migratory insertion of an anionic group onto coordinated carbon monoxide or an isocyanide is an important mechanistic postulate in organoactinide chemistry[1]. In contrast to transition metals, where carbon monoxide complexes abound, only three examples of carbon monoxide coordination to a uranium have been observed in matrix isolation studies at cyrogenic temperatures. These studies showed that $U(CO)_6$ can exist below ca. 20K and that $\nu_{CO}$ of 1961 $cm^{-1}$ is similar to that found for $W(CO)_6$, $\nu_{CO}$ is 1987 $cm^{-1}$ under similar conditions[2a,b]. The $\nu_{CO}$ is lowered substantially from gaseous CO ($\nu$ = 2145 $cm^{-1}$) which implies that uranium metal is a $\pi$ donor, though the bonds are either kinetically labile, thermodynamically weak, or both. In $UF_4(CO)$ the $\nu_{CO}$ of 2182 $cm^{-1}$ at 20K[2c] shows that the tetravalent compound does not engage in $\pi$-backbonding to CO[3]. In another study, $UO_2$ has been shown to absorb CO at temperatures below 20K; the CO stretching frequency was not measured[2d]. In this note, we give evidence for $(Me_3SiC_5H_4)_3UCO$, the first molecular actinide complex of carbon monoxide, in solution and solid phase.

We have determined, on the basis of equilibrium constant measurements, that the ligand displacement series towards $(MeC_5H_4)_3U$ is $PMe_3 \approx P(OMe)_3 >$ pyridine> tetrahydrothiophene> tetrahydrofuran and towards $(Me_3SiC_5H_4)_3U$ the series is EtNC > EtCN[4a]. The observation that phosphite and isocyanide ligands, which are generally classified as $\pi$-acceptor ligands[4b], are good ligands toward the trivalent uranium metallocenes suggests that the uranium center can act as a $\pi$ donor. The extent of $\pi$ acceptance is difficult to judge on the basis of the infrared spectrum[5] as $\nu_{CN}$ of 2160 $cm^{-1}$ in $(Me_3SiC_5H_4)_3UCNEt$[6a] is slightly higher in energy than that in free CNEt of 2151 $cm^{-1}$. In $Cp_3UCN(cyclohexyl)$[6c], $\nu_{CN}$ increases by 25 $cm^{-1}$ on

coordination. The purported π donating character of $(RC_5H_4)_3U$ lead us to expose $(Me_3SiC_5H_4)_3U$ to one of the best π acids known, carbon monoxide.

The deep green solution of $(Me_3SiC_5H_4)_3U$ in either pentane or hexane turned purple on exposure to carbon monoxide at 1 atm and 20°C. Volumetric studies showed that the metallocene absorbs 1.0 ± 0.05 molar equivalents of carbon monoxide at 25°C. Exposure of the red carbon monoxide complex to either vacuum or purging the solution with argon regenerates the green, carbon-monoxide free, $(Me_3SiC_5H_4)_3U$. The carbon monoxide, vacuum cycle may be repeated several times without detectable decomposition. In addition, the red solution may be stored for at least two years at -80°C. Clearly, $(Me_3SiC_5H_4)_3U$ reversibly adsorbs a molar equivalent of carbon monoxide in hydrocarbon solution. Examination of the infrared spectrum of the red solution with $^{12}CO$ shows $\nu_{CO}$ at 1976 $cm^{-1}$, with $^{13}CO$ $\nu_{CO}$ is 1935 $cm^{-1}$, and with $C^{18}O$ $\nu_{CO}$ is 1932 $cm^{-1}$. The predicted values for $\nu$ $^{13}CO$ and $C^{18}O$ are 1931 and 1930 $cm^{-1}$ respectively[7].

The $(Me_3SiC_5H_4)_3U$ also reversibly absorbs $^{12}CO$ in the solid state. Exposure of $(Me_3SiC_5H_4)_3U$ in a KBr wafer to $^{12}CO$ at 1 atm results in the appearance of an absorption at 1969 $cm^{-1}$ which completely disappears when the sample is evacuated for 1.5 h. Using $^{13}CO$ (99%) causes the absorption to shift to 1922 $cm^{-1}$.

We assume that the complex is carbon bonded, as are all CO complexes, and the U-C-O unit is linear. Some support for this is derived from the X-ray crystal structure determination of $(Me_3SiC_5H_4)_3UCNEt$[8]. The averaged U-C (Cp) distance is 2.81 ± 0.03Å, the U-Cp ring centroid distance is 2.53Å, the U-C (CNEt) distance is 2.57(3)Å, the ring centroid-U-ring centroid angle is 118.6°, the ring centroid-U-C (CNEt) angle is 97°, and most importantly, the U-C-N angle is 173.6(2.0)° and the C-N-C (Et) angle is 170.2(2.6)°.

A very crude molecular orbital model, based upon the symmetry orbitals, may be constructed that accounts for the reduction in the C-O stretching frequency in the complex. Assume that the molecule has $C_{3v}$ symmetry. The $e_1$ and a $p\pi$ SALC'S for $(Cp)_3$ transform as $2a_1 + a_2 + 3e$. In $C_{3v}$ symmetry the metal AO's transform as $a_1[s, z, z^2, z^3, x(x^2-3y^2)]$, $a_2[y(3x^2-y^2]$, $e[x, y, x^2-y^2, xy, xz, yz, xz^2, yz^2, xyz$, and $z(x^2-y^2)]$. If we let the nine Cp orbitals overlap with the available metal AO's then we have left over $3a_1$ + 2e symmetry orbitals that contain three electrons to overlap with the filled σ-orbitals and the empty π-orbitals on CO. Since the π-orbitals on CO are C-O antibonding, population of these orbitals results in lowering of ν CO. The lowering of $\nu_{CO}$ may be expressed in valence bond language by the two resonance structures.

$$Cp_3U{\leftarrow}\overset{+}{C}{\equiv}\overset{-}{O} \;\text{<-------->}\; Cp_3U{=}C{=}O$$

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**Supplementary Material Avaliable.** Listing of positional parameters, general temperature factors and RMS amplitudes of thermal vibration, ORTEP diagrams of the four molecules in the unit cell, tables of bond lengths and angles, crystal data and method of solution, and structure factor tables (46 pages)

for $(Me_3SiC_5H_4)_3UCNEt$. Ordering information is given on any current masthead.

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6. (a) Red crystals of $(Me_3SiC_5H_4)_3U(CNEt)$ can be isolated from the reaction of $(Me_3SiC_5H_4)_3U$[5b] and the isocyanide in hexane, m.p. 112-5°C. Anal. Calcd. for $C_{27}H_{44}NSi_3U$: C, 46.0; H, 6.29; N, 1.99. Found: C, 45.9; H, 6.31; N, 1.93. (b) Brennan, J.G.; Andersen, R.A.; Zalkin, A. submitted for publication. (c) Kanellakopulos, B.; Fischer, E.O.; Dornberger, E.; Baumgartner, F. J. Organomet. Chem. **1970**, 24, 507-514.

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8. The details are given in the Supplimentary Material.

Supplimentary Material for

Preparation of the First Molecular Carbon Monoxide Complex of Uranium.

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1. Positional Parameters for $(Me_3SiC_5H_4)_3UCNEt$.
2. General Temperature factors and RMS amplitudes of thermal vibration.
3. ORTEP Diagrams of the four molecules in the unit cell.
4. Tables of Bond Lengths and Angles.
5. Crystal Data and method of solution.
6. Structure factor tables.

# TABLE I

## Crystal and Data Collection Parameters

Compound: $(C_5H_4\text{-}Si(CH_3)_3)_3U\text{-}CN\text{-}C_2H_5$

A) Crystal Parameters at 25°C [a,b]

| | |
|---|---|
| a = 24.136(10) Å | Space Group: $P\bar{1}$ |
| b = 24.456(8) Å | Formula Weight = 705.0 amu |
| c = 11.304(6) Å | Z = 8 |
| $\alpha$ = 91.30(4) ° | $d_c$ = 1.44 g $cm^{-3}$ |
| $\beta$ = 76.98(4) ° | $d_o$ = _____ |
| $\gamma$ = 92.35(3) ° | $\mu$ (calc.)= 48.6 $cm^{-1}$ |
| V = 6495(7) $Å^3$ | |

Size of crystal : 0.09 x 0.35 x 0.40 mm

B) Data Measurement Parameters [8]

Radiation : Mo K$\alpha$ ($\lambda$ = 0.71073 Å)

Monochromator: Highly-oriented graphite (2$\theta$ = 12.2°)

Detector: Crystal scintillation counter, with PHA.

Reflections measured: + h, ± k, ± l

2$\theta$ Range: 2.2 ° -> 45° Scan Type : $\theta$-2$\theta$

Scan width: $\Delta\theta$ = 0.75 + .347 tan($\theta$)

Scan speed: 1.0 -> 4.0 ($\theta$, °/min)

Background : Measured over 0.10°($\theta$) added to each end of the scan.
Measured for a total of 0.25 of the scan time.

No. of reflections collected: 19494

No. of unique reflections: 16896

Intensity standards: (700), (030), (003); measured after every 250 intensity measurements. Over the data collection period a 16 % decrease in intensity was observed.

Orientation: Reorientation was not needed during data collection.

[a] Unit cell parameters and their esd's were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components of 21 reflections with 2θ 20.0° to 29.0°.

[b] In this and all subsequent tables the esd's of all parameters are given in parentheses, right-justified to the least significant digit(s) given.

The structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques. Refinement was started using LBL programs, then transferred to the CHEXRAY computer system and completed there [2,3].

Due to the paucity of good data (only 5086 of 16896 data were observed) and the essentially low-resolution nature of these data, constraints were applied to some of the distances and angles in the known portions of the structure. It was necessary to do this to obtain reasonable distances and angles, and in some cases to even locate the atoms. Disorder of the methyl groups attached to Si1 and Si2 was clearly indicated on difference Fourier maps, and this disorder was included with suitable constraints. The thermal parameters of C94 and C95 are clear indication of some problem with the methyl groups attached to Si12, but no clear model emerged from inspection of peaks in the last difference Fourier map, so they were left "as is". Constraints were weighted by inverse esd**2, with esd's for angles assigned as 0.5 deg and for distances as 0.005 A. The following constraints were imposed on the CpSiMe3 ligands: 1)Internal ring angles of 108 deg. 2) External angles to the Si of 125.5 deg. 3)C-Si-C angles of 109.5 deg. 4) Si-C(methyl) distances of 1.90 A. 5) C-C bonds in the rings were set to equal each other in groups of 15 (i.e. one distance per molecule), but the rings were allowed to "breathe". The following constraints were applied to the isocyanide ligands: 1) N-C(methylene) and C-C distances of 1.50 A. 2) N-C-C angles of 110 deg. In all there were 282 constraints applied.

Given the nature of the refinement it is not surprising that no evidence of the hydrogen atoms was found in the final difference Fourier.

The final residuals [5] for 617 variables refined against the 282 constraints and the 5086 data for which F**2 > 3 sigma(F**2) were R = 5.83 %, wR = 6.73 % and GOF

= 1.628. The R value for all 16896 data was 26.2 %. The maximum shifts were 2 times their esds and applied to the atoms of the isocyanide ligand of molecule 1 and the methyl carbons of Si12. All other shifts were less than Ø.6 times their esd.

The quantity minimized by the least squares program was w(|Fo|-|Fc|)**2, where w is the weight of a given observation. The p-factor [5], used to reduce the weight of intense reflections, was set to Ø.Ø5 throughout the refinement. The analytical forms of the scattering factor tables for the neutral atoms were used [6] and all non-hydrogen scattering factors were corrected for both the real and imaginary components of anomalous dispersion [7].

Inspection of the residuals ordered in ranges of sin(theta)/lambda, |Fo|, and parity and value of the individual indexes showed no unusual features or trends. There was no evidence of secondary extinction in the low-angle, high-intensity data. The largest peak in the final difference Fourier map had an electron density of 1.Ø e-/A3 and was located near U2.

The positional and thermal parameters of the non-hydrogen atoms are given in Table II. A listing of the values of Fo and Fc are available as supplementary material.

## Notes on the Figures

All Figures are ORTEP [9] stereopair drawings. In each Figure the stereopair is set up for cross-eyed viewing, with the left- and right-eye views interchanged -- I(R) (L)I. Before submitting the Figures for photographic reduction, the two images should be restored to their correct positions for viewing with a stereopticon -- I(L) (R)I. The correct distance between the centers of the drawings after reduction is 2 1/4 inches or 55 mm.

In Figures 1-4 the ellipsoids are scaled to represent the 50% probability surface.

Figure 1 - Labeling diagram for Molecule 1.

Figure 2 - Labeling diagram for Molecule 2.

Figure 3 - Labeling diagram for Molecule 3.

Figure 4 - Labeling diagram for Molecule 4.

All figures are viewed from the same direction as defined by the U-C(isocyanide) and U-Cp (trans) vectors, in order to show the similarities and differences between them.

There are four independent molecules in the asymmetric unit of the structure and they are shown in Fig 1 - 4. Distances, angles planes and torsion angles are given in the tables.

The molecules are unique and not related by symmetry in any way. Differences can be seen in the orientation of the SiMe3 "lumps" on the Cp ligands and in the orientation of the ethyl groups of the isocyanide ligands. Similarities are also present, as shown by the Figures. Each U is coordinated by two Cp ligands with their SiMe3 groups pointed more or less in the same direction as the isocyanide and one which is oriented approximately trans to the isocyanide. The ligands are coordinated in a true pentahapto fashion in all cases. The SiMe3 group is pushed out of the plane of the Cp ring by from Ø.22 to Ø.62 A, with the unique SiMe3 in each molecule being the least distorted from planarity. The isocyanide ligands are coordinated in an end-on fashion with U-C-N angles ranging from 17Ø.5 to 177.2 deg, and C-N-C angles from 167.3 to 174.6 deg. Since these were not constrained there is every reason to trust them in a qualitative fashion. The U-C(isocyanide) distances range from 2.53(4) to 2.6Ø(4) A.

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1b R. B. Roof, Jr., "A Theoretical Extension of the Reduced-Cell Concept in Crystallography", Publication LA-4038, Los Alamos Scientific Laboratory, Los Alamos, New Mexico, 1969.

2) All calculations were performed on a PDP 11/60 equipped with 128 kilowords of memory, twin RK07 28 MByte disk drives, Versatec printer/plotter and TU10 tape drive using locally-modified Nonius-SDP[3] software operating under RSX-11M.

3) Structure Determination Package User's Guide, 1982, B.A. Frenz and Associates, College Station, TX 77840.

4) The data reduction formulae are:

$$F_o^2 = \frac{\omega}{Lp}(C-2B) \qquad \sigma_o(F_o^2) = \frac{\omega}{Lp}(C + 4B)^{1/2}$$

$$F_o = \sqrt{F_o^2} \qquad \sigma_o(F) = \frac{\sigma_o(F_o^2)}{2F_o}$$

where C is the total count in the scan, B the sum of the two background counts, $\omega$ the scan speed used in deg/min, and

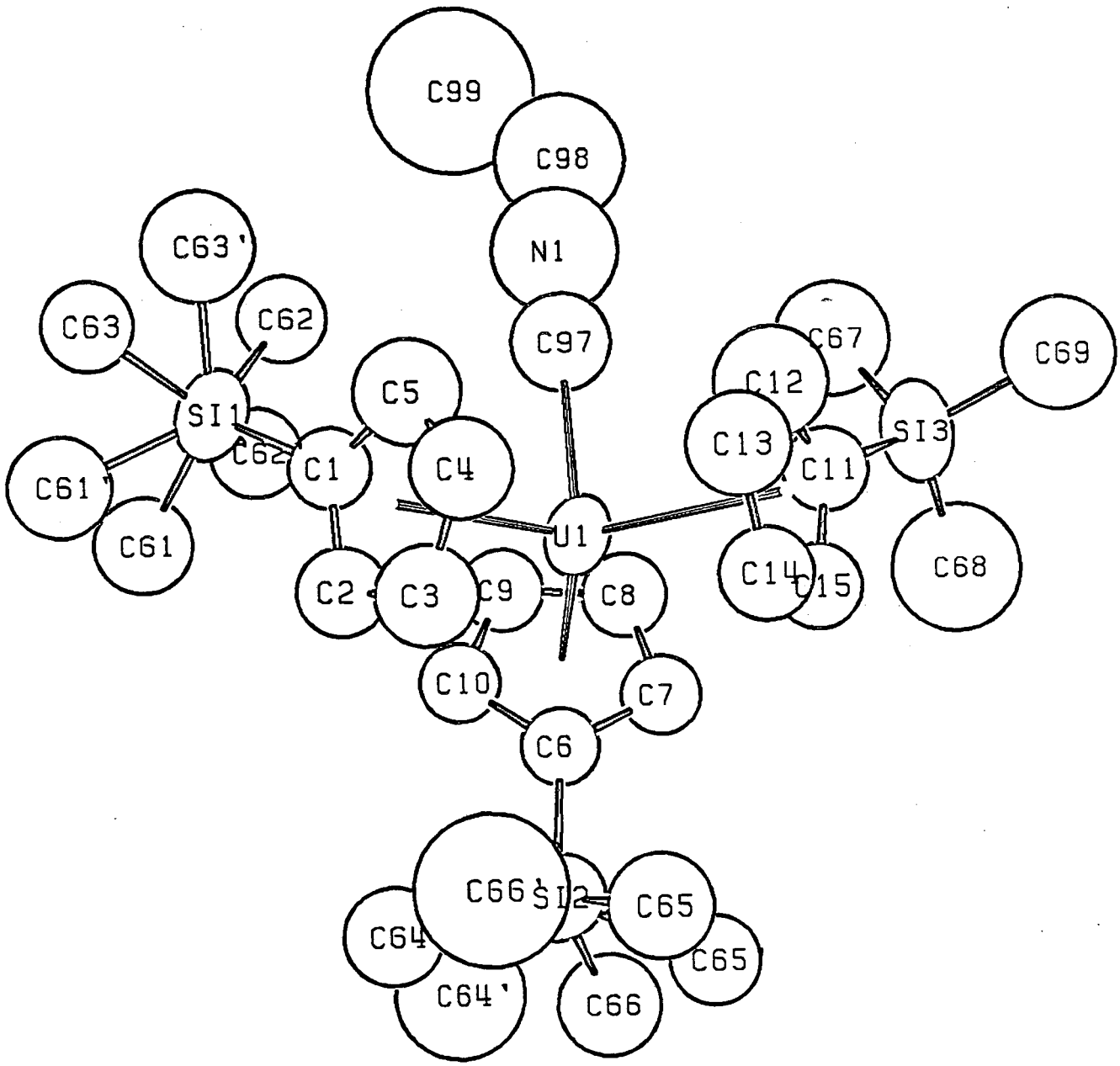
$$\frac{1}{Lp} = \frac{\sin 2\theta\ (1 + \cos^2 2\theta_m)}{1 + \cos^2 2\theta_m - \sin^2 2\theta}$$

is the correction for Lorentz and polarization effects for a reflection with scattering angle $2\theta$ and radiation monochromatized with a 50% perfect single-crystal monochrometer with scattering angle $2\theta_m$.

5) $$R = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|} \qquad wR = \left\{\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma wF_o^2}\right\}^{1/2}$$

$$GOF = \left\{\frac{\Sigma w(|F_o| - |F_c|)^2}{(n_o - n_v)}\right\}^{1/2}$$

where $n_o$ is the number of observations.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C61
C14
C15
C68
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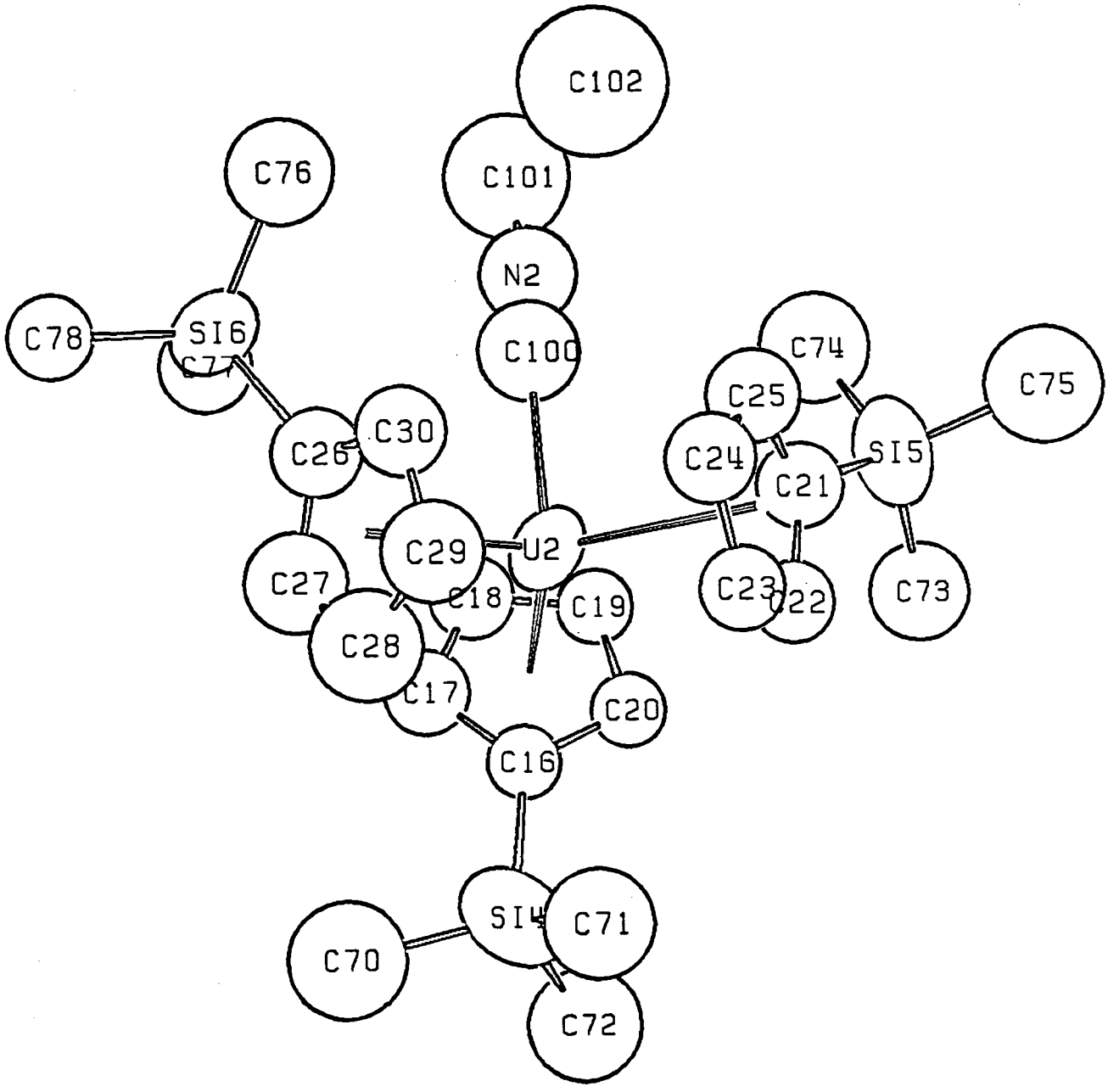
C65
C64'
C66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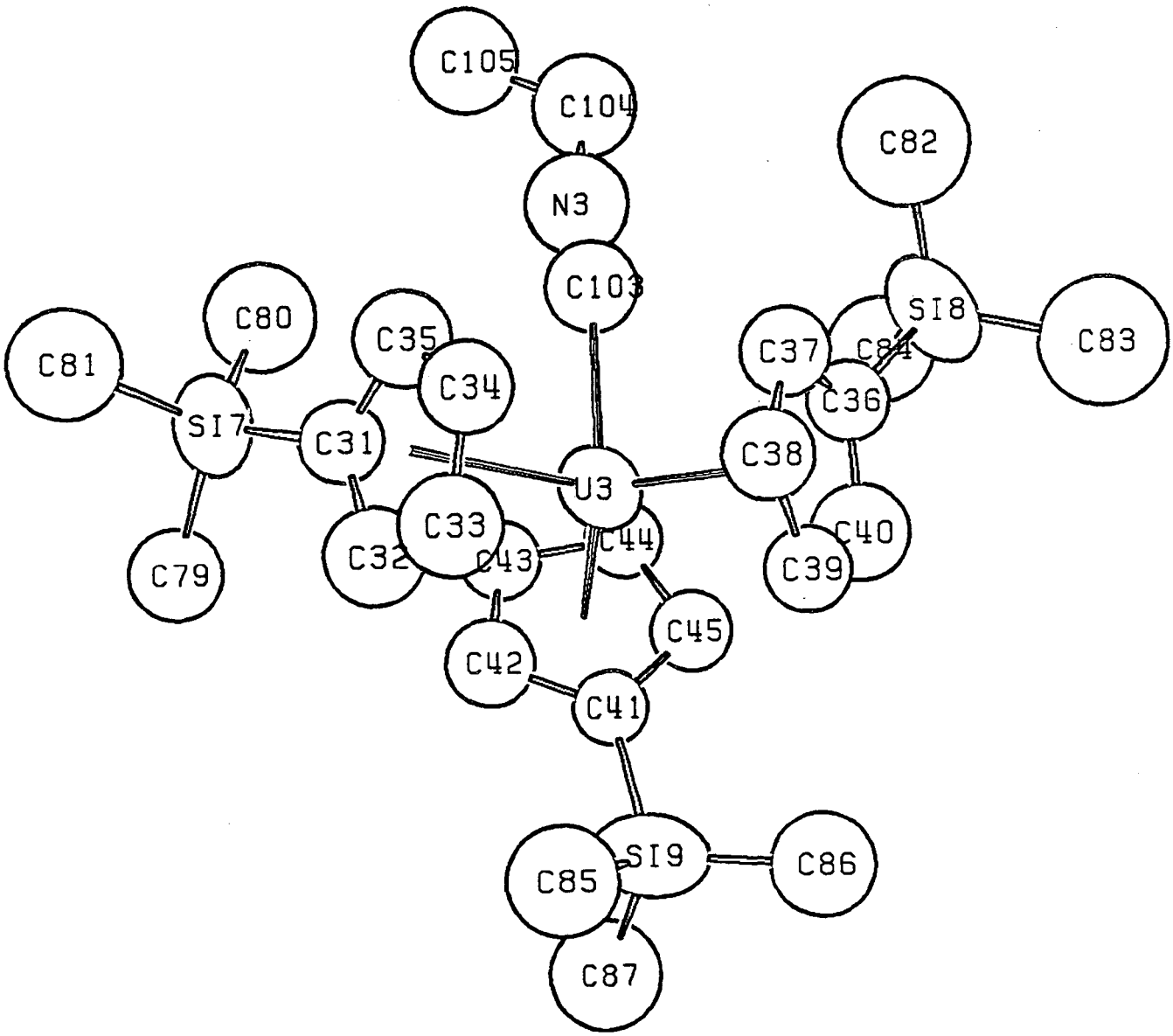
SI4
C71
C70
C72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SI9
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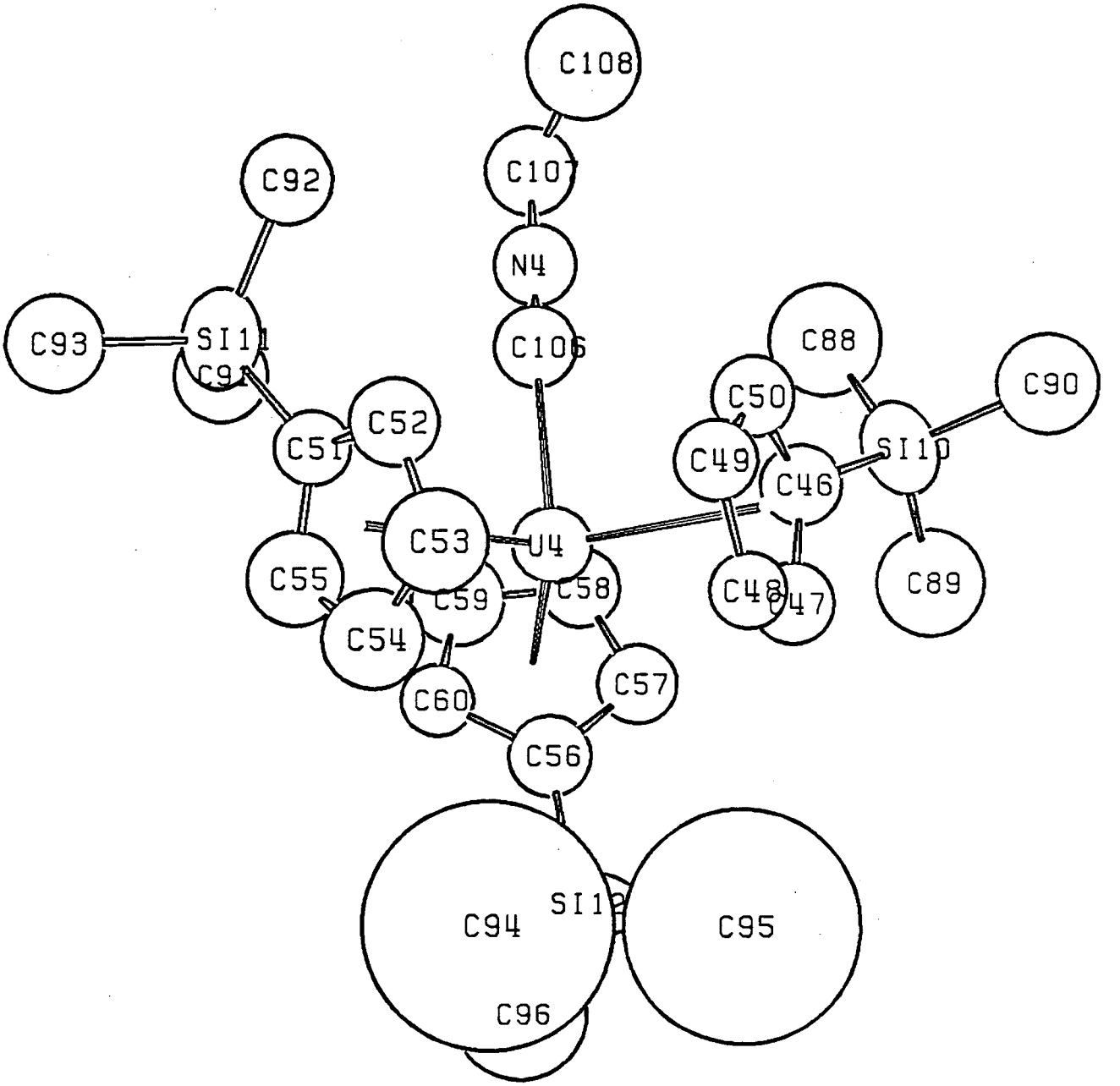
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C49
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SI10
C53
U4
C55
C59
C58
C48
C47
C89
C54
C57
C60
C56
C94
SI12
C95
C96

Intramolecular Distances

| ATOM 1 | ATOM 2 | DISTANCE |
|---|---|---|
| U1 | C97 | 2.60(4) |
| U1 | C1 | 2.86(2) |
| U1 | C2 | 2.81(2) |
| U1 | C3 | 2.73(3) |
| U1 | C4 | 2.79(3) |
| U1 | C5 | 2.78(3) |
| U1 | CP1 | 2.515 |
| U1 | C6 | 2.75(2) |
| U1 | C7 | 2.83(2) |
| U1 | C8 | 2.79(2) |
| U1 | C9 | 2.82(2) |
| U1 | C10 | 2.80(2) |
| U1 | CP2 | 2.520 |
| U1 | C11 | 2.84(2) |
| U1 | C12 | 2.82(3) |
| U1 | C13 | 2.83(3) |
| U1 | C14 | 2.76(3) |
| U1 | C15 | 2.75(2) |
| U1 | CP3 | 2.520 |
| U2 | C100 | 2.53(4) |
| U2 | C16 | 2.82(2) |
| U2 | C17 | 2.83(2) |
| U2 | C18 | 2.83(2) |
| U2 | C19 | 2.81(2) |
| U2 | C20 | 2.86(2) |
| U2 | CP4 | 2.556 |
| U2 | C21 | 2.85(2) |
| U2 | C22 | 2.77(2) |
| U2 | C23 | 2.75(2) |
| U2 | C24 | 2.76(2) |
| U2 | C25 | 2.87(2) |
| U2 | CP5 | 2.525 |
| U2 | C26 | 2.82(2) |
| U2 | C27 | 2.83(3) |
| U2 | C28 | 2.79(3) |
| U2 | C29 | 2.77(3) |
| U2 | C30 | 2.78(2) |
| U2 | CP6 | 2.522 |

Intramolecular Distances

| ATOM 1 | ATOM 2 | DISTANCE |
|---|---|---|
| U3 | C103 | 2.59(3) |
| U3 | C31 | 2.83(2) |
| U3 | C32 | 2.73(3) |
| U3 | C33 | 2.79(3) |
| U3 | C34 | 2.89(2) |
| U3 | C35 | 2.86(3) |
| U3 | CP7 | 2.539 |
| U3 | C36 | 2.84(2) |
| U3 | C37 | 2.75(2) |
| U3 | C38 | 2.82(2) |
| U3 | C39 | 2.80(2) |
| U3 | C40 | 2.85(3) |
| U3 | CP8 | 2.531 |
| U3 | C41 | 2.82(2) |
| U3 | C42 | 2.82(2) |
| U3 | C43 | 2.84(2) |
| U3 | C44 | 2.82(2) |
| U3 | C45 | 2.85(2) |
| U3 | CP9 | 2.547 |
| U4 | C106 | 2.58(3) |
| U4 | C46 | 2.82(2) |
| U4 | C47 | 2.75(2) |
| U4 | C48 | 2.82(2) |
| U4 | C49 | 2.80(2) |
| U4 | C50 | 2.83(2) |
| U4 | CP10 | 2.521 |
| U4 | C51 | 2.92(2) |
| U4 | C52 | 2.91(2) |
| U4 | C53 | 2.79(3) |
| U4 | C54 | 2.77(3) |
| U4 | C55 | 2.90(3) |
| U4 | CP11 | 2.581 |
| U4 | C56 | 2.82(2) |
| U4 | C57 | 2.82(2) |
| U4 | C58 | 2.80(2) |
| U4 | C59 | 2.82(3) |
| U4 | C60 | 2.77(2) |
| U4 | CP12 | 2.523 |

CPnn are the centroids of the Cp rings.

Intramolecular Distances

| ATOM 1 | ATOM 2 | DISTANCE |
|---|---|---|
| C97 | N1 | 1.25(4) |
| C100 | N2 | 1.12(4) |
| C103 | N3 | 1.14(3) |
| C106 | N4 | 1.17(3) |
| C98 | N1 | 1.503(6) |
| C101 | N2 | 1.500(6) |
| C104 | N3 | 1.504(6) |
| C107 | N4 | 1.497(6) |
| C98 | C99 | 1.496(6) |
| C101 | C102 | 1.494(6) |
| C104 | C105 | 1.497(6) |
| C107 | C108 | 1.497(6) |

Intramolecular Angles

| ATOM 1 | ATOM 2 | ATOM 3 | ANGLE |
|---|---|---|---|
| C97 | U1 | CP1 | 97.6 |
| C97 | U1 | CP2 | 94.7 |
| C97 | U1 | CP3 | 96.5 |
| CP1 | U1 | CP2 | 120.9 |
| CP1 | U1 | CP3 | 114.4 |
| CP2 | U1 | CP3 | 121.2 |
| C100 | U2 | CP4 | 96.6 |
| C100 | U2 | CP5 | 95.3 |
| C100 | U2 | CP6 | 99.3 |
| CP4 | U2 | CP5 | 120.1 |
| CP4 | U2 | CP6 | 119.7 |
| CP5 | U2 | CP6 | 115.7 |
| C103 | U3 | CP7 | 97.0 |
| C103 | U3 | CP8 | 98.4 |
| C103 | U3 | CP9 | 96.9 |
| CP7 | U3 | CP8 | 115.8 |
| CP7 | U3 | CP9 | 120.6 |
| CP8 | U3 | CP9 | 118.7 |
| C106 | U4 | CP10 | 96.7 |
| C106 | U4 | CP11 | 99.5 |
| C106 | U4 | CP12 | 95.2 |
| CP10 | U4 | CP11 | 115.4 |
| CP10 | U4 | CP12 | 120.6 |
| CP11 | U4 | CP12 | 119.5 |
| U1 | C1 | SI1 | 131.6(8) |
| U1 | C6 | SI2 | 123.9(8) |
| U1 | C11 | SI3 | 130.9(8) |
| U2 | C16 | SI4 | 122.2(8) |
| U2 | C21 | SI5 | 131.6(8) |
| U2 | C26 | SI6 | 131.7(7) |
| U3 | C31 | SI7 | 132.9(7) |
| U3 | C36 | SI8 | 131.6(8) |
| U3 | C41 | SI9 | 123.0(7) |
| U4 | C46 | SI10 | 134.3(7) |
| U4 | C51 | SI11 | 128.9(7) |
| U4 | C56 | SI12 | 123.3(9) |

Intramolecular Angles

| ATOM 1 | ATOM 2 | ATOM 3 | ANGLE |
|---|---|---|---|
| U(1) | C97 | N1 | 177.2(32) |
| U(2) | C100 | N2 | 170.5(31) |
| U(3) | C103 | N3 | 173.5(27) |
| U(4) | C106 | N4 | 173.2(23) |
| C97 | N1 | C98 | 167.7(43) |
| C100 | N2 | C101 | 171.0(36) |
| C103 | N3 | C104 | 167.3(31) |
| C106 | N4 | C107 | 174.6(24) |
| N1 | C98 | C99 | 109.7(6) * |
| N2 | C101 | C102 | 109.6(6) * |
| N3 | C104 | C105 | 109.8(6) * |
| N4 | C107 | C108 | 109.6(6) * |

* These angles were constrained in refinement.

Table of Positional Parameters and Their Estimated Standard Deviations

| Atom | x | y | z | $B(A^2)$ |
|---|---|---|---|---|
| U1 | -0.16308(5) | -0.03889(6) | 0.2197(1) | 4.73(4) |
| U2 | -0.08949(6) | 0.36805(6) | 0.1647(1) | 5.53(4) |
| U3 | 0.36705(5) | 0.32511(6) | 0.1937(1) | 5.54(4) |
| U4 | 0.35065(5) | -0.18900(6) | 0.2529(1) | 5.15(4) |
| SI1 | -0.1919(2) | -0.0730(2) | -0.1376(5) | 7.2(3) |
| SI2 | -0.1092(2) | -0.1838(2) | 0.3241(4) | 8.7(4) |
| SI3 | -0.0849(3) | 0.0915(2) | 0.3948(5) | 8.5(4) |
| SI4 | 0.0537(2) | 0.3076(3) | 0.2561(5) | 9.8(4) |
| SI5 | -0.1424(2) | 0.5042(3) | 0.4095(5) | 9.6(4) |
| SI6 | -0.1118(2) | 0.3406(2) | -0.2017(6) | 6.9(3) |
| SI7 | 0.4154(2) | 0.1967(3) | 0.3993(5) | 8.2(4) |
| SI8 | 0.3285(2) | 0.3407(2) | -0.1579(6) | 9.3(4) |
| SI9 | 0.4612(2) | 0.4627(3) | 0.2590(5) | 9.9(4) |
| SI10 | 0.3239(2) | -0.1630(2) | -0.1089(6) | 6.5(3) |
| SI11 | 0.3611(2) | -0.3379(3) | 0.4358(5) | 7.5(3) |
| SI12 | 0.4396(2) | -0.0452(3) | 0.2890(5) | 12.2(5) |
| N1 | -0.1201(8) | 0.0829(4) | 0.005(1) | 17(1)* |
| N2 | -0.1344(6) | 0.4780(4) | 0.001(1) | 9.5(9)* |
| N3 | 0.373(1) | 0.1993(4) | -0.0002(9) | 10(1)* |
| N4 | 0.3656(6) | -0.3208(4) | 0.076(1) | 6.8(7)* |
| C1 | -0.2175(4) | -0.0724(2) | 0.0282(6) | 6.3(9)* |
| C2 | -0.2201(5) | -0.1190(3) | 0.1043(7) | 8(1)* |
| C3 | -0.2559(5) | -0.1065(3) | 0.2205(7) | 9(1)* |
| C4 | -0.2776(5) | -0.0533(3) | 0.2141(7) | 9(1)* |
| C5 | -0.2507(6) | -0.0306(3) | 0.0983(7) | 11(1)* |
| C6 | -0.0889(4) | -0.1200(3) | 0.2313(5) | 6.1(9)* |
| C7 | -0.0597(5) | -0.0725(3) | 0.2681(6) | 6.6(9)* |
| C8 | -0.0442(6) | -0.0366(3) | 0.1665(6) | 8(1)* |
| C9 | -0.0583(6) | -0.0646(3) | 0.0635(6) | 7(1)* |
| C10 | -0.0858(6) | -0.1163(3) | 0.1033(6) | 6.5(9)* |
| C11 | -0.1472(3) | 0.0438(3) | 0.3909(7) | 6.9(9)* |
| C12 | -0.1970(3) | 0.0580(3) | 0.351(1) | 12(1)* |
| C13 | -0.2415(3) | 0.0185(3) | 0.398(1) | 10(1)* |
| C14 | -0.2183(3) | -0.0225(3) | 0.459(1) | 8(1)* |
| C15 | -0.1595(3) | -0.0073(3) | 0.453(1) | 7.0(9)* |
| C16 | 0.0242(5) | 0.3678(3) | 0.1885(5) | 5.3(8)* |
| C17 | 0.0289(6) | 0.3765(3) | 0.0623(6) | 7(1)* |
| C18 | 0.0089(6) | 0.4293(3) | 0.0491(6) | 7(1)* |
| C19 | -0.0082(6) | 0.4533(3) | 0.1671(6) | 5.9(8)* |
| C20 | 0.0037(6) | 0.4163(3) | 0.2525(6) | 5.5(8)* |
| C21 | -0.1502(3) | 0.4307(3) | 0.3645(7) | 7.1(9)* |
| C22 | -0.1256(3) | 0.3866(3) | 0.4120(8) | 6.2(9)* |
| C23 | -0.1542(3) | 0.3371(3) | 0.3876(8) | 6.3(9)* |
| C24 | -0.1944(3) | 0.3502(3) | 0.3189(8) | 7.2(9)* |
| C25 | -0.1938(3) | 0.4082(3) | 0.3093(9) | 8(1)* |

Table of Positional Parameters and Their Estimated Standard Deviations (cont.)

| Atom | x | y | z | B(Å$^2$) |
|---|---|---|---|---|
| C26 | -0.1072(2) | 0.3137(4) | -0.0475(7) | 7(1)* |
| C27 | -0.0585(3) | 0.2891(4) | -0.0228(7) | 10(1)* |
| C28 | -0.0761(3) | 0.2595(5) | 0.0870(7) | 11(1)* |
| C29 | -0.1357(3) | 0.2651(4) | 0.1297(7) | 9(1)* |
| C30 | -0.1549(3) | 0.2989(4) | 0.0471(7) | 7.1(9)* |
| C31 | 0.3653(3) | 0.2482(3) | 0.3783(8) | 6.2(9)* |
| C32 | 0.3619(3) | 0.3026(3) | 0.432(1) | 9(1)* |
| C33 | 0.3059(3) | 0.3221(3) | 0.435(1) | 9(1)* |
| C34 | 0.2752(3) | 0.2805(3) | 0.380(1) | 7(1)* |
| C35 | 0.3128(3) | 0.2360(3) | 0.340(1) | 8(1)* |
| C36 | 0.3167(3) | 0.3605(3) | 0.0060(6) | 6.0(8)* |
| C37 | 0.2722(4) | 0.3378(3) | 0.1014(7) | 7.0(9)* |
| C38 | 0.2633(4) | 0.3759(3) | 0.2021(7) | 7.2(9)* |
| C39 | 0.3068(4) | 0.4188(4) | 0.1752(7) | 6.4(9)* |
| C40 | 0.3388(4) | 0.4102(3) | 0.0524(7) | 9(1)* |
| C41 | 0.4642(5) | 0.3938(3) | 0.1865(5) | 5.3(8)* |
| C42 | 0.4763(7) | 0.3439(3) | 0.2402(6) | 8(1)* |
| C43 | 0.4841(7) | 0.3018(3) | 0.1476(6) | 6.3(9)* |
| C44 | 0.4759(7) | 0.3252(3) | 0.0372(6) | 6.0(8)* |
| C45 | 0.4654(7) | 0.3825(3) | 0.0602(6) | 6.5(9)* |
| C46 | 0.3005(4) | -0.1609(3) | 0.0616(7) | 6.2(9)* |
| C47 | 0.3030(5) | -0.1124(3) | 0.1361(7) | 6.2(9)* |
| C48 | 0.2609(5) | -0.1193(3) | 0.2484(8) | 5.1(8)* |
| C49 | 0.2367(5) | -0.1740(3) | 0.2486(7) | 5.9(8)* |
| C50 | 0.2597(5) | -0.1992(3) | 0.1321(7) | 6.1(9)* |
| C51 | 0.3386(2) | -0.2691(3) | 0.446(1) | 5.2(8)* |
| C52 | 0.2813(3) | -0.2531(3) | 0.450(1) | 6.8(9)* |
| C53 | 0.2777(3) | -0.1958(3) | 0.482(1) | 9(1)* |
| C54 | 0.3321(3) | -0.1769(3) | 0.503(1) | 9(1)* |
| C55 | 0.3691(3) | -0.2227(3) | 0.484(1) | 8(1)* |
| C56 | 0.4439(4) | -0.1136(3) | 0.2218(5) | 6.8(9)* |
| C57 | 0.4385(6) | -0.1272(3) | 0.0997(6) | 6.5(9)* |
| C58 | 0.4527(5) | -0.1838(3) | 0.0760(6) | 6.7(9)* |
| C59 | 0.4685(6) | -0.2045(3) | 0.1819(6) | 9(1)* |
| C60 | 0.4608(6) | -0.1619(3) | 0.2739(6) | 5.2(8)* |
| C61 | -0.1504(6) | -0.1372(4) | -0.186(2) | 10(2)*$ |
| C62 | -0.1430(5) | -0.0107(4) | -0.187(2) | 8(2)*$ |
| C63 | -0.2545(4) | -0.0724(9) | -0.214(1) | 8(2)*$ |
| C61' | -0.2184(6) | -0.1385(4) | -0.203(1) | 10(2)*$ |
| C62' | -0.1112(3) | -0.0688(9) | -0.180(2) | 9(2)*$ |
| C63' | -0.2206(6) | -0.0116(4) | -0.201(1) | 13(3)*$ |
| C64 | -0.1409(6) | -0.2375(5) | 0.232(1) | 9(2)*$ |
| C65 | -0.1626(6) | -0.1677(8) | 0.4705(9) | 11(2)*$ |
| C66 | -0.0427(4) | -0.2115(6) | 0.361(1) | 11(3)*$ |
| C64' | -0.0673(6) | -0.2434(4) | 0.244(1) | 17(4)*$ |
| C65' | -0.0931(6) | -0.1720(8) | 0.4799(7) | 8(2)*$ |
| C66' | -0.1883(3) | -0.2001(8) | 0.343(2) | 22(5)*$ |
| C67 | -0.0533(8) | 0.1199(6) | 0.2379(8) | 14(2)* |
| C68 | -0.0281(4) | 0.0531(5) | 0.447(1) | 18(2)* |
| C69 | -0.1082(8) | 0.1499(4) | 0.506(1) | 13(2)* |

Table of Positional Parameters and Their Estimated Standard Deviations (cont.)

| Atom | x | y | z | $B(A^2)$ |
|---|---|---|---|---|
| C70 | 0.0871(7) | 0.2586(5) | 0.130(1) | 14(2)* |
| C71 | -0.0058(5) | 0.2704(6) | 0.368(1) | 11(1)* |
| C72 | 0.1100(4) | 0.3342(7) | 0.338(1) | 13(1)* |
| C73 | -0.0755(4) | 0.5142(8) | 0.471(1) | 10(1)* |
| C74 | -0.1375(8) | 0.5506(5) | 0.2748(9) | 13(1)* |
| C75 | -0.2067(5) | 0.5230(7) | 0.533(1) | 14(2)* |
| C76 | -0.1827(4) | 0.3735(6) | -0.191(2) | 11(1)* |
| C77 | -0.0511(4) | 0.3922(5) | -0.258(2) | 9(1)* |
| C78 | -0.1065(7) | 0.2805(4) | -0.313(1) | 6.5(9)* |
| C79 | 0.4815(4) | 0.2312(6) | 0.437(1) | 8(1)* |
| C80 | 0.4366(8) | 0.1540(5) | 0.2547(9) | 12(1)* |
| C81 | 0.3796(7) | 0.1505(5) | 0.529(1) | 11(1)* |
| C82 | 0.2821(5) | 0.2777(4) | -0.174(2) | 16(2)* |
| C83 | 0.3082(6) | 0.3992(4) | -0.246(1) | 16(2)* |
| C84 | 0.4060(4) | 0.3253(7) | -0.222(2) | 12(1)* |
| C85 | 0.4130(6) | 0.4594(8) | 0.4167(8) | 11(1)* |
| C86 | 0.4321(5) | 0.5127(4) | 0.164(1) | 10(1)* |
| C87 | 0.5358(4) | 0.4868(7) | 0.270(1) | 12(1)* |
| C88 | 0.3549(6) | -0.2319(4) | -0.161(2) | 14(2)* |
| C89 | 0.3795(5) | -0.1063(4) | -0.162(2) | 12(1)* |
| C90 | 0.2598(4) | -0.1525(7) | -0.176(1) | 10(1)* |
| C91 | 0.4363(4) | -0.3422(8) | 0.338(1) | 9(1)* |
| C92 | 0.3104(4) | -0.3832(5) | 0.367(1) | 7(1)* |
| C93 | 0.3603(7) | -0.3622(6) | 0.5948(7) | 9(1)* |
| C94 | 0.3959(7) | -0.0482(9) | 0.4512(8) | 59(9)* |
| C95 | 0.4038(5) | 0.0007(5) | 0.198(1) | 56(8)* |
| C96 | 0.5134(4) | -0.0158(7) | 0.289(2) | 19(2)* |
| C97 | -0.133(2) | 0.043(2) | 0.072(4) | 10(1)* |
| C98 | -0.0924(4) | 0.1300(4) | -0.0730(7) | 19(2)* |
| C99 | -0.1144(6) | 0.131(1) | -0.1865(8) | 30(4)* |
| C100 | -0.124(2) | 0.441(2) | 0.047(4) | 10(1)* |
| C101 | -0.1446(4) | 0.5228(4) | -0.0791(9) | 17(2)* |
| C102 | -0.2002(4) | 0.5478(7) | -0.025(2) | 24(3)* |
| C103 | 0.369(1) | 0.239(1) | 0.055(3) | 8(1)* |
| C104 | 0.3811(8) | 0.1549(3) | -0.0959(7) | 11(1)* |
| C105 | 0.3923(9) | 0.1022(4) | -0.042(1) | 12(1)* |
| C106 | 0.359(1) | -0.282(1) | 0.138(3) | 6.7(9)* |
| C107 | 0.3802(3) | -0.3702(4) | -0.004(1) | 8(1)* |
| C108 | 0.3271(4) | -0.3962(7) | -0.031(2) | 14(2)* |

* -- Atoms refined with isotropic thermal parameters.
$ -- Atoms refined at occupancy of 1/2.

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:

$$(4/3) * [a^2*B(1,1) + b^2*B(2,2) + c^2*B(3,3) + ab(\cos gamma)*B(1,2)$$

$$+ ac(\cos beta)*B(1,3) + bc(\cos alpha)*B(2,3)]$$

Positions of the Centroids of the Cyclopentadienide rings.

| Atom | x | y | z |
|---|---|---|---|
| CP1 | -0.2444 | -0.0764 | 0.1331 |
| CP2 | -0.0674 | -0.0820 | 0.1665 |
| CP3 | -0.1927 | 0.0181 | 0.4103 |
| CP4 | 0.0115 | 0.4086 | 0.1439 |
| CP5 | -0.1637 | 0.3826 | 0.3585 |
| CP6 | -0.1065 | 0.2853 | 0.0387 |
| CP7 | 0.3242 | 0.2779 | 0.3930 |
| CP8 | 0.2996 | 0.3806 | 0.1074 |
| CP9 | 0.4732 | 0.3494 | 0.1343 |
| CP10 | 0.2722 | -0.1532 | 0.1654 |
| CP11 | 0.3198 | -0.2235 | 0.4730 |
| CP12 | 0.4529 | -0.1582 | 0.1707 |

## Table of General Temperature Factor Expressions - B's

| Name | B(1,1) | B(2,2) | B(3,3) | B(1,2) | B(1,3) | B(2,3) | Beqv |
|---|---|---|---|---|---|---|---|
| U(1) | 4.18(6) | 6.45(8) | 3.20(6) | -0.31(6) | -0.18(5) | -0.14(6) | 4.73(4) |
| U(2) | 6.89(7) | 5.43(8) | 4.21(6) | -1.17(6) | -1.29(5) | 0.70(7) | 5.53(4) |
| U(3) | 4.68(6) | 7.20(9) | 4.39(6) | 0.98(6) | -0.17(5) | -0.73(7) | 5.54(4) |
| U(4) | 5.33(7) | 5.69(8) | 3.90(6) | 0.12(6) | 0.02(5) | -0.38(7) | 5.15(4) |
| SI1 | 7.6(6) | 8.9(8) | 5.4(5) | 1.1(6) | -2.3(4) | -1.1(6) | 7.2(3) |
| SI2 | 9.4(7) | 8.3(8) | 8.2(7) | -1.1(6) | -1.9(6) | 1.7(7) | 8.7(4) |
| SI3 | 10.7(7) | 8.0(8) | 6.3(6) | -1.9(6) | -1.2(6) | -1.3(6) | 8.5(4) |
| SI4 | 8.5(7) | 7.9(8) | 12.4(9) | 1.0(6) | -0.8(7) | 0.9(8) | 9.8(4) |
| SI5 | 10.5(8) | 8.3(8) | 8.6(7) | 1.0(7) | 0.2(7) | -2.1(7) | 9.6(4) |
| SI6 | 7.2(6) | 8.2(8) | 5.5(5) | -0.6(5) | -1.9(4) | 1.0(6) | 6.9(3) |
| SI7 | 9.4(7) | 9.3(8) | 6.0(6) | 0.6(6) | -1.8(5) | 1.6(6) | 8.2(4) |
| SI8 | 8.7(7) | 13(1) | 6.8(6) | 1.8(7) | -3.0(5) | -0.8(7) | 9.3(4) |
| SI9 | 10.3(8) | 9.5(9) | 9.5(7) | -0.6(7) | -1.8(6) | -3.1(7) | 9.9(4) |
| SI10 | 5.6(5) | 9.4(8) | 4.3(5) | 1.2(5) | -0.6(4) | -0.2(6) | 6.5(3) |
| SI11 | 7.3(6) | 8.9(8) | 6.0(6) | 1.0(6) | -0.7(5) | 1.6(6) | 7.5(3) |
| SI12 | 10.6(8) | 8.5(8) | 17(1) | -1.4(7) | -3.4(8) | -5.4(8) | 12.2(5) |

The form of the anisotropic thermal parameter is:

$\exp[-0.25(h^2 a^{*2} B(1,1) + k^2 b^{*2} B(2,2) + l^2 c^{*2} B(3,3)' + 2hka^*b^*B(1,2) + 2hla^*c^*B(1,3)$

$+ 2klb^*c^*B(2,3))]$ , where a*,b*, and c* are reciprocal lattice constants.

Table of Root-Mean-Square Amplitudes of Thermal Vibration in Angstroms.

| Atom | Min. | Int'med. | Max. | Atom | Min. | Int'med. | Max. |
|---|---|---|---|---|---|---|---|
| U(1) | 0.195 | 0.239 | 0.291 | SI5 | 0.271 | 0.353 | 0.407 |
| U(2) | 0.223 | 0.249 | 0.314 | SI6 | 0.254 | 0.292 | 0.335 |
| U(3) | 0.212 | 0.267 | 0.307 | SI7 | 0.260 | 0.341 | 0.358 |
| U(4) | 0.210 | 0.265 | 0.285 | SI8 | 0.271 | 0.329 | 0.416 |
| SI1 | 0.245 | 0.303 | 0.348 | SI9 | 0.278 | 0.356 | 0.414 |
| SI2 | 0.287 | 0.336 | 0.366 | SI10 | 0.229 | 0.269 | 0.349 |
| SI3 | 0.258 | 0.308 | 0.404 | SI11 | 0.260 | 0.299 | 0.356 |
| SI4 | 0.306 | 0.328 | 0.414 | SI12 | 0.249 | 0.380 | 0.509 |

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