Title

ELECTRON-TRANSFER REACTIONS OF TRIVALENT URANIUM; PREPARATION AND STRUCTURE OF (MeC5H4) 3U=NPh AND [(MeC5H4) 3U]2[u-n1, n2-PhNCO].

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Publication Date

1984-09-01

UC-4
LBL-18353
Preprint c.1

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

Submitted to the Journal of the American Chemical Society

ELECTRON-TRANSFER REACTIONS OF TRIVALENT URANIUM; PREPARATION AND STRUCTURE OF $(MeC_5H_4)_3U{=}NPh$ AND $[(MeC_5H_4)_3U]_2[\mu\text{-}\eta^1,\eta^2\text{-}PhNCO]$

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September 1984

LBL-18353
c.1

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

LBL-18353

Electron-Transfer Reactions of Trivalent Uranium; Preparation and Structure of $(MeC_5H_4)_3U{=}NPh$ and $[(MeC_5H_4)_3U]_2[\mu\text{-}\eta^1,\eta^2\text{-}PhNCO]$

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Abstract:

Reaction of either $Cp_3U(thf)$ or $(MeC_5H_4)_3U(thf)$ with PhN_3 or Me_3SiN_3 yields the organoimides, $Cp_3U{=}NSiMe_3$ or $(MeC_5H_4)_3U{=}NR$ (R is Ph or Me_3Si) and N_2. The crystal structure of $(MeC_5H_4)_3U{=}NPh$ is described. In contrast, PhNCO reacts with $(MeC_5H_4)_3U(thf)$ to give the coordination complex $[(MeC_5H_4)_3U]_2$-[μ-η^1,η^2-PhNCO], the result of electron transfer since the uranium atoms are tetravalent. The complex was characterized by X-ray crystallography.

In contrast to the large number of d-metal organoimides,[1] $\overset{+}{M}-\underset{\cdot\cdot}{\bar{N}}-R \longleftrightarrow M{=}\underset{\cdot\cdot}{N}-R \longleftrightarrow \bar{M}{\equiv}\overset{+}{N}-R$, only one f-metal organoimide, $Cp_3UNC(Me)C(H)PPh_2Me$[2a] prepared by insertion of acetonitrile into $Cp_3U(CH)PPh_2Me$,[2b] has been reported. The U-N distance of 2.06(1) Å and the U-N-C angle of 163(1)° suggests that the U-N bond order is between two and three. Organoimides are of considerable interest relative to structure[3] and reactivity studies[4] and rational synthetic reactions need to be developed before the reaction chemistry can be explored systematically. Reaction of a trivalent uranium compound with either an organic azide or isocyanate to give a pentavalent uranium organoimide derivative with evolution of either nitrogen or carbon monoxide, respectively, is a rational and potentially general synthetic reaction for these interesting complexes.[1,5] In this communication we describe the reaction of $U(C_5H_4Me)_3thf$ with organic azides to give $U(C_5H_4Me)_3NR$, or organoisocyanates to give $[U(C_5H_4Me)_3]_2[PhNCO]$.

The uranium metallocene, $U(C_5H_4Me)_3(thf)$,[6] reacts with Me_3SiN_3 or PhN_3 in diethyl ether at room temperature with evolution of nitrogen over 30 minutes to give red $U(C_5H_4Me)_3UNR$, R = Me_3Si[8] or Ph,[9] on crystallization from hexane in _ca._ 50% isolated yield. The $Cp_3UNSiMe_3$ was prepared similarly and crystallized from diethyl ether.[10] An ORTEP diagram for the phenylimide complex is shown in Figure I. The most important feature is the presence of the imido functional group with a U-N distance of 2.019(6) Å and a U-N-C(1) angle of 167.4(6)°. The U-N distance is the shortest U-N distance ever reported. The U-N (single) bond distance in triscyclopentadienyluranium complexes ranges from 2.29(1) Å in Cp_3UNPh_2[11a] to an average of 2.38(1) Å in Cp_3U (pyrazolate).[11b] If we assume a standard U-N single bond distance of 2.30 Å, then the U-N distance in the organoimide of 2.02 Å is 0.28 Å or 12% shorter. Similar shortening is observed in comparing $M-NR_2$ relative to M=NR or M≡NR distances in the transition metal series.[1,12] The essentially linear UNC angle suggests that both lone-pairs of electrons on the nitrogen atom are involved in bonding to uranium and the U-N bond is best viewed as a triple bond.

We can account for the bonding in a very crude symmetry orbital picture in the following way.[13] Assume that the molecule has C_{3v} symmetry and that the 5f, 6d, and 7s orbitals on uranium are available for bonding to the Cp and NR functional groups. Assume further that the 7p orbitals are too high in energy for useful bonding interactions.[13c,d] The e_1 ($p\pi$) orbitals of the 3 Cp rings give rise to four SALC's that transform as a_1, a_2, 2 x e and the $a_1(p\pi)$ orbitals of the 3 Cp rings give rise to two SALC's that transform a_1 and e. The metal AO's transform as a_1 [s, z^2, z^3, and $x(x^2-3y^2)$], a_2 [$y(3x^2-y^2)$], and e [xy, x^2-y^2, xz, yz, xz^2, yz^2, xyz, $z(x^2-y^2)$]. If we let the 9 Cp orbitals overlap with the a_1 [s, z^2, $x(x^2-3y^2)$], a_2 and e [xy, x^2-y^2, xz, yz, xyz, $z(x^2-y^2)$] metal AO's, then we have left over the $2a_1$ + e AO's to overlap with the a_1 + e set on the -NR fragment. In this way we can account for the M-NR triple bond since the 6 electrons on the $(NR)^{2-}$ unit are donated into the $2a_1$ + e AO's of the $(Cp_3U)^{2+}$ unit which contains one electron.

In contrast to the reaction of the organoazides with the trivalent metallocene, $U(C_5H_4Me)_3(thf)$, reaction of phenylisocyanate does not give the phenylimide with evolution of carbon monoxide, but gives the red 2:1 complex, $[(C_5H_4Me)_3U]_2[[\mu-\eta^1,\eta^2-PhNCO]]$.[14] An ORTEP drawing is shown in Figure II. The structural feature of most interest is the $[PhNCO]^{2-}$ unit that is bridging the two tetravalent uranium, $U(C_5H_4Me)_3$, fragments in a η^1[U(2) - O], η^2[U(1)NC(1)] fashion. The U(1) - N distance of 2.36(2) Å is similar to that found in Cp_3U (pyrazolate)[11b] of 2.38(1) Å, the U(1) - C(1) distance of 2.42(2) Å is similar to that found in Cp_3U (n-Bu) of 2.43(2) Å[15a] and the U(2)

- O distance of 2.11(1) Å is similar to that found in $[(Me_5C_5)_2U(OMe)]_2PH$ of 2.05(1) Å.[15b] The bond length data support the view that the uranium atoms in the $U(C_5H_4Me)_3$ units are tetravalent and that the bridging phenylisocyanate is best represented by the valence bond structure, $Ph\bar{N}{=}\bar{C}{-}O^{-}$, the result of a one electron-transfer from each $(MeC_5H_4)_3U$ molecule. The PhNCO complex does not liberate CO on heating to 80°C, nor do the nonequivalent MeC_5H_4 groups undergo site exchange.

Acknowledgments 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 DEAC-03-76SF00098. We also thank Dr. F.J. Hollander, staff crystallographer of the U.C. Berkeley, College of Chemistry X-ray facility (CHEXRAY) for doing both crystal structures. The CHEXRAY facility was set up by a departmental grant from N.S.F.

Supplementary Material. Complete listing of bond lengths and angles for both crystal structures and positional and thermal parameters. Ordering information is given in any current masthead page (13 pages).

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(6) Prepared from UCl_3[7] and NaC_5H_4Me in thf, followed by crystallization from hexane: thf (50:1) as dark (black) needles in 33% yield, mp 136-140°C. *Anal.* Calcd for $C_{22}H_{29}OU$: C, 48.3; H, 5.33. Found: C, 47.9; H, 5.31. ^{1}HNMR (C_6D_6, δ7.15, 27.5°C): δ - 11.6(bH)6H), - 14.0 (4H), -14.4(6H), -15.6 (9H), -31.1 (4H). The second and fifth resonances undergo exchange with added thf showing that these resonances are due to coordinated thf.

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(8) *Anal.* Calcd for $C_{21}H_{30}NSiU$: C, 44.8; H, 5.38; N, 2.49. Found: C, 45.2; H, 5.39; N, 2.30 mp. 132-140°C. ^{1}HNMR (C_6D_6 36°C): δ6.72 (9H) $\nu_{1/2}$=11 Hz, 3.03 $\nu_{1/2}$=10 Hz (9H), -1.96 $\nu_{1/2}$=37Hz (6H), -10.4 $\nu_{1/2}$=29 Hz (6H). $^{13}C\{^1H\}$: δ121.0, 117.4, 100.9, 73.26, -2.28. The first three resonances and the last resonance are due to the MeC_5H_4 carbon atoms.

(9) *Anal.* Calcd for $C_{24}H_{26}NU$: C, 50.9; H, 4.63; N, 2.47. Found: C, 50.1; H,

4.77; N, 2.07. M^+, 566 amu, mp 108-110°C. ^{1}HNMR (C_6D_6 +32°C): δ18.5 $\nu_{1/2}$=15 Hz (2H), 4.20 $\nu_{1/2}$=2 Hz,t,J=7 Hz (1H), 3.67 $\nu_{1/2}$=19Hz (9H), -2.40 $\nu_{1/2}$=8 Hz (2H), -3.39 $\nu_{1/2}$=45 Hz (6H), -10.8 $\nu_{1/2}$=45 Hz (6H). $^{13}C\{^1H\}$: The methylcyclopentadienyl carbons appear at δ118, 99.3, 82.0, -3.9 and the phenyl carbons appear at δ122.7, 97.6, 108.4 and the ipso carbon resonance was not observed. Crystal Data (-95 ± 5°C): orthorhombic, a = 8.4113(14), b = 10.0701(19), c = 22.9639(33) Å, Space Group, $P2_12_12_1$, F_w = 566.5, V = 1945.1(10) $Å^3$, ρ(calc) = 1.93 g cm^{-3}, Z =4, $\mu(Mo\text{-}K_\alpha)$ = 79.2 cm^{-1}, λ = 0.71073 Å, The 1505 raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects. Inspection of the azimuthal scan data showed a variation I min $(I\ max)^{-1}$ = 0.51 for the average curve. An empircal correction for absorption, based on the azimuthal scan data, was applied to the intensities since the crystal did not have well-developed faces, crystal size was 0.15 x 0.28 x 0.42 mm. Removal of systematically absent data left 1484 unique data. The structure was solved by Patterson methods and refined by least squares and Fourier techniques. One of the C_5H_4Me groups, C19-C24, refined poorly and it was constrained to have C-C distances of 1.40 Å in the ring, a Me-C distance of 1.50 Å and an internal angle of 108°. Refinement with this model revealed an alternate orientation of the ring, which was also refined with constrained distances and angles and it's occupancy was linked to the first ring so that they summed to one full ligand. Refinement of the enantiomeric structure dropped R by 1.2%. In the difference Fourier map calculated following this refinement, peaks corresponding to the expected positions of most of the hydrogen atoms were found. The hydrogens were included in the structure factor calculations for the ordered ligands in their expected positions based upon idealized bonding geometry but not refined in least squares. The final residuals for 231 variables refined against 26 constraints and the 1405 data for which $F^2 > 3\sigma(F^2)$ were R = 0.0212, R_w = 0.0293 and GOF = 1.803. The R-value for all 1484 data was 0.0248. The occupancy factor of the majority component of Cp (3) refined to 0.63.

(10) Anal. Calcd for $C_{18}H_{24}NSiU$: C, 41.4; H, 4.65; N, 2.69. Found: C, 41.5; H, 4.80; N, 2.56. M^+ = 520 amu, mp = 207-208°C, μ=1.98 B.M. (4-300K). ^{1}HNMR (C_6D_6, 32°C): δ6.96 $\nu_{1/2}$=8 Hz (9H) and -6.47 $\nu_{1/2}$=30 Hz (15H). $^{13}C\{^1H\}$: δ108.1 (d, J = 150 Hz), 72.27 (q, J = 118 Hz.).

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(14) Anal. Calcd for $C_{43}H_{47}NOU$: C, 48.3; H, 4.43, N, 1.31. Found: C, 47.8; H, 4.37; N, 1.33, μ=3.58 B.M. (90-300K) per molecule. ^{1}HNMR (C_7D_8, 29°C), Inequivalent C_5H_4Me resonances: δ12.6 (6H), 4.39 (6H), -3.14 (9H), -7.86 (6H), -18.6 (6H), and -21.7 (9H); phenyl resonances: 6.40 (1H, t, J=7 Hz), 3.06 (2H, m) -24.9 (2H, d, J = 7 Hz). The width at half-height is

1-2 Hz for allof the resonances. <u>Crystal data</u> (25°C): monoclinic, a = 17.596 (6), b = 13.882 (3), C = 16.312(6) Å, β = 113.11(3)°, Space Group $P2_{1/c}$ (No. 14), F_w = 1069.9, V = 3665(4) $Å^3$, ρ (calc) = 1.94 g cm^3, Z = 4, μ(Mo-K_α = 84.0 cm^{-1}, λ = 0.71073 Å, crystal size: 0.09 x 0.21 x 0.25 mm. The data were collected on a Picker FACS-1 diffractometer and corrected for Lorentz and polarization effects and crystal decomposition. Systematic absences were consistent only with space group $P2_{1/c}$ and these reflections were removed from the data set. The 9636 data were averaged before absorption correction with residuals R(I) = 0.106 for all 4810 unique data. An absorption corrections based upon the measured size and shape of the crystal and an 6 x 10 x 12 Gaussian grid of internal points was applied to the data after solution of the structure confirmed the contents of the unit cell, T_{max} = 0.589, T_{min} = 0.195. After absorption correction the averaged residual was 0.056 and no reflections were more than 3 esds away from their average. The structure was solved by Patterson methods and refined by least squares and Fourier techniques. Refinement of all non-hydrogen atoms with isotopic thermal parameters converged to R = 0.10. Refinement of the uranium atoms with anisotropic thermal parameters (all others isotropic) gave a residual of 0.044. Attempts to refine the remaining non-hydrogen atoms with anisotropic thermal parameters initially reduced the residuals, but failed to converge. In the final cycles of least squares the uranium atoms were refined with anisotropic thermal parameters and all other atoms with isotropic thermal parameters. The final residuals for 199 variables refined against 2089 data for which $F^2 > 3\sigma(F^2)$ were R = 0.0435, R_w = 0.0483, and GOF = 1.254. The R-value for all of the 4810 data was 0.124.

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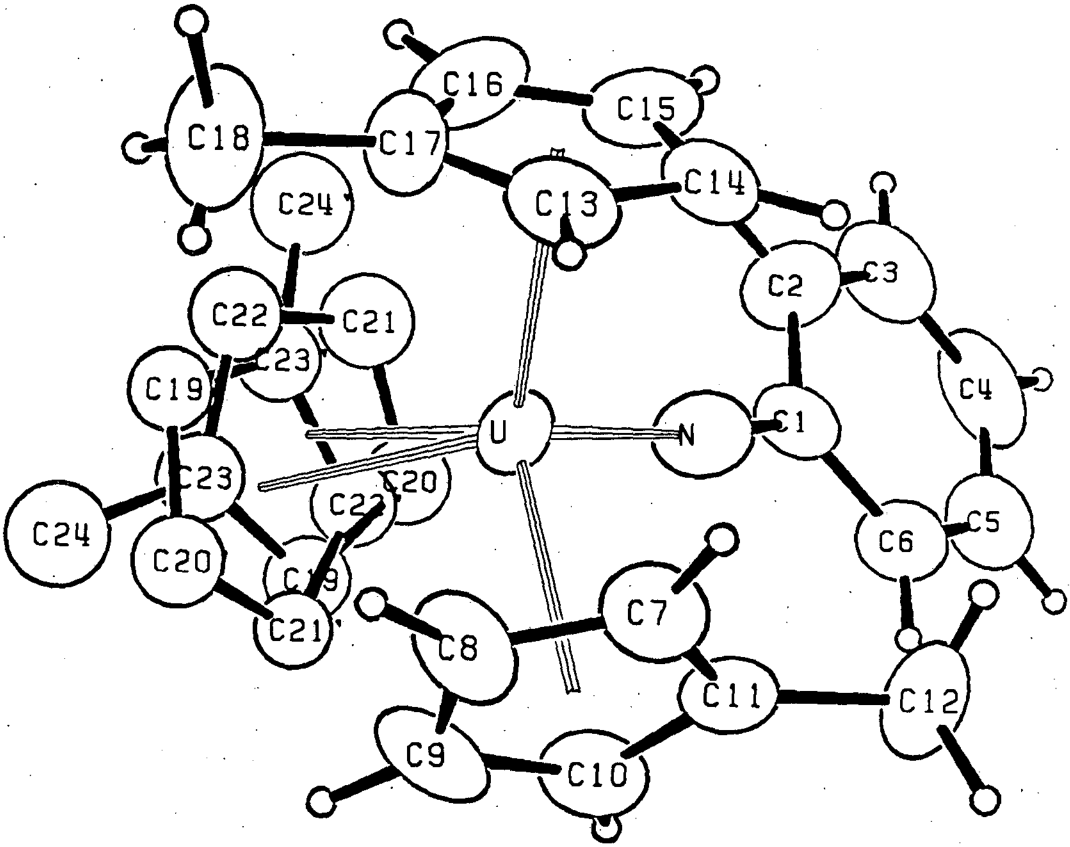
Figure I

An ORTEP diagram for $(MeC_5H_4)_3UNPh$. One MeC_5H_4 ring is disordered, see footnote 9. The averaged U-C (7-11) = 2.758 ± 0.024 Å, U-C (13-17) = 2.734 ± 0.023 Å, and U-C (19-23) = 2.759 ± 0.036 Å (for the 63% occupancy ring). The averaged U-ring centroid distance is 2.48 Å. There is no bond between C(2) and C(14), the line from C(2) is the bond to hydrogen.

Figure II

An ORTEP diagram for $[(MeC_5H_4)_3U]_2[PhNCO]$. MeC_5H_4 groups are labelled Cp (1...6) for clarity. The averaged U(1) - C (Cp 1, 2, 3) and U(2) - C (Cp 4, 5, 6) distance is 2.80(3) Å and 2.76(2) Å, respectively. The averaged U(1) - ring centroid (Cp 1, 2, 3) and U(2) - ring centroid (Cp 4, 5, 6) distance is 2.53 Å and 2.48 Å, respectively, and the averaged ring centroid - U(1) - ring centroid and ring centroid - U(2) - ring centroid angle is 113.8° and 116.5°, respectively. C(1)-N(1) = 1.31(2) Å, C(1)-O = 1.36(2) Å, U(1)-N-C(2) = 152.5(13)°, C(1)-N-C(2) = 130.1(16)°, N(1)-C(1) - O = 118.9(16)°, U(1)-C(1) - O = 168.1(13)°, C(1)-O-U(2) = 164.0(12)°. The torsional angles between Cp(1)-U(1)-U(2)-Cp(4) is 176.0° and between C(2)-N-U(1)-Cp(1) is -8.7°.



XBL 847-3151

Figure I

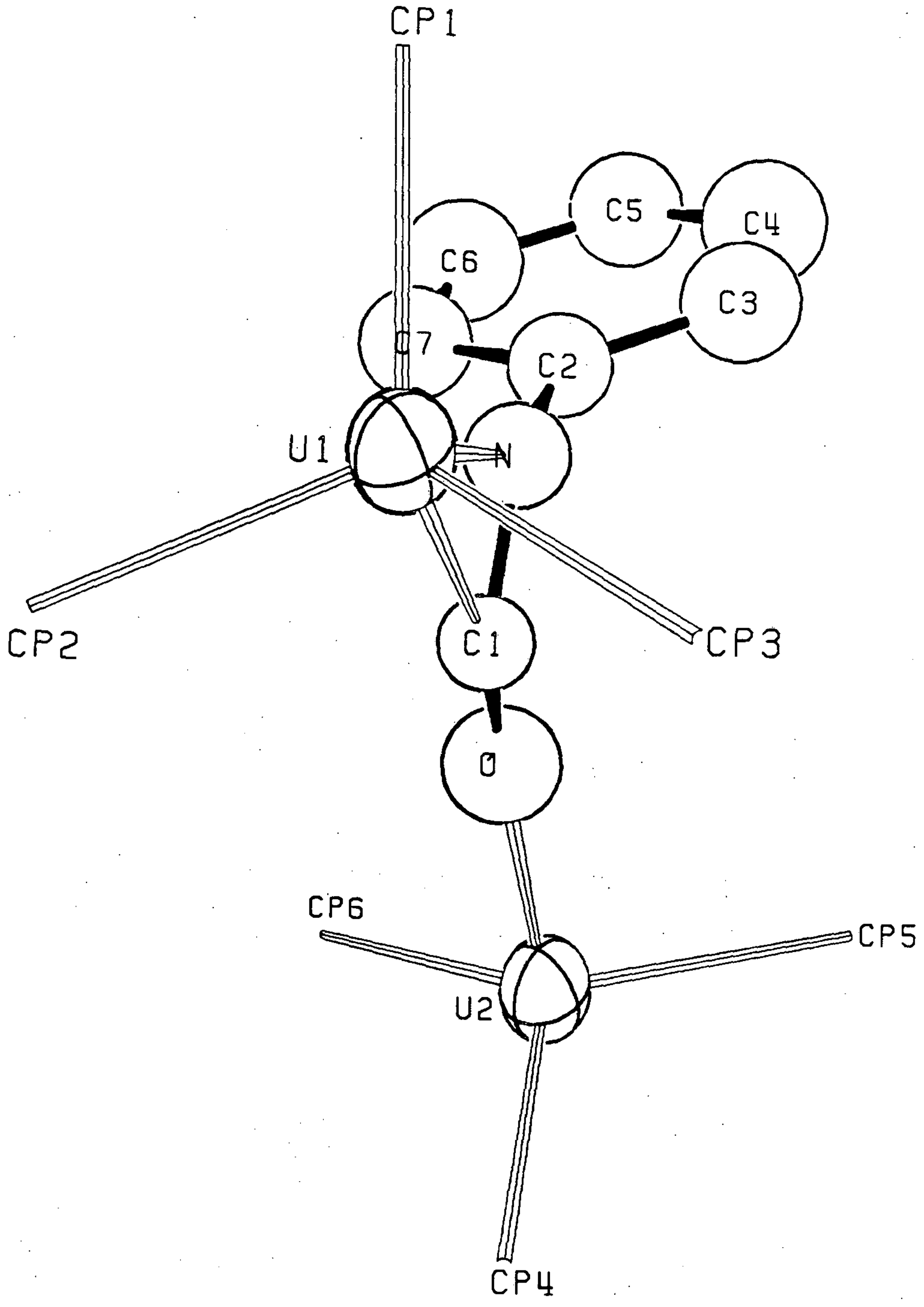


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Figure II

Supplementary Material for

Electron-Transfer Reactions of Trivalent Uranium; Preparation and Structure of $(MeC_5H_4)_3U = NPh$ and $[(MeC_5H_4)_3U]_2[\mu-\eta^1,\eta^2 - PhNCO]$

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Positional and Thermal Parameters for $(MeC_5H_4)_3UNPh$

Atom	x	y	z	$B(\AA^2)$
U	0.22638(4)	0.40291(3)	0.35853(1)	2.774(6)
N	0.0795(9)	0.5432(8)	0.3909(3)	3.7(2)
C1	-0.043(1)	0.6156(9)	0.4133(3)	3.1(2)
C2	-0.137(1)	0.563(1)	0.4575(4)	4.2(2)
C3	-0.257(1)	0.638(1)	0.4830(4)	4.9(2)
C4	-0.283(1)	0.765(1)	0.4634(4)	5.9(3)
C5	-0.190(2)	0.817(1)	0.4186(4)	5.4(3)
C6	-0.074(1)	0.7448(9)	0.3947(4)	4.0(2)
C7	0.499(1)	0.541(1)	0.3305(4)	4.0(2)
C8	0.490(1)	0.436(1)	0.2910(4)	4.2(2)
C9	0.362(1)	0.463(1)	0.2531(4)	4.7(3)
C10	0.290(1)	0.583(1)	0.2720(4)	4.0(2)
C11	0.380(1)	0.6320(9)	0.3183(4)	3.2(2)
C12	0.348(1)	0.765(1)	0.3482(4)	5.0(2)
C13	0.480(1)	0.337(1)	0.4285(4)	3.9(2)
C14	0.385(1)	0.428(1)	0.4606(4)	3.7(2)
C15	0.249(1)	0.363(1)	0.4746(4)	4.3(2)
C16	0.256(1)	0.238(1)	0.4522(5)	5.5(3)
C17	0.400(1)	0.2182(9)	0.4219(4)	4.6(2)
C18	0.456(2)	0.097(1)	0.3922(6)	9.0(4)
C19 (a)	0.0125(3)	0.3280(2)	0.27654(7)	3.8(3)*
C20	-0.0849(3)	0.3611(2)	0.32382(7)	4.2(3)*
C21	-0.0617(3)	0.2657(2)	0.36734(7)	4.9(4)*
C22	0.0454(3)	0.1709(2)	0.34609(7)	4.4(4)*
C23	0.0947(2)	0.2114(1)	0.29061(6)	3.9(3)*
C24	0.2069(3)	0.1376(3)	0.2515(1)	5.2(4)*
C19' (b)	0.1149(2)	0.1558(2)	0.31245(8)	3.4(5)*
C20'	0.1544(2)	0.2289(2)	0.26264(8)	4.1(6)*
C21'	0.0510(2)	0.3376(2)	0.25922(8)	2.9(5)*
C22'	-0.0518(2)	0.3321(2)	0.30709(8)	3.9(6)*
C23'	-0.0137(2)	0.2188(1)	0.33958(6)	3.7(5)*
C24'	-0.0987(4)	0.1712(3)	0.3931(1)	5.7(7)*

(a) C19-C24 have occupancies of 0.634.
(b) C19'-C24' have occupancies of 0.366.
(a) and (b) - constraints were applied to force idealized geometry.
* -- Atoms refined with isotropic thermal parameters.

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

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

Atom	x	y	z	$B(\AA^2)$
H2	-0.1195	0.4744	0.4703	5.0**
H3	-0.3194	0.6029	0.5139	6.0**
H4	-0.3646	0.8180	0.4803	7.0**
H5	-0.2098	0.9042	0.4050	6.0**
H6	-0.0115	0.7819	0.3643	5.0**
H7	0.5758	0.5496	0.3608	5.0**
H8	0.5571	0.3592	0.2899	5.0**
H9	0.3297	0.4115	0.2206	6.0**
H10	0.1971	0.6223	0.2561	5.0**
H12A	0.4088	0.8324	0.3298	7.0**
H12B	0.2385	0.7853	0.3455	7.0**
H12C	0.3781	0.7587	0.3881	7.0**
H13	0.5829	0.3549	0.4139	5.0**
H14	0.4109	0.5172	0.4704	5.0**
H15	0.1629	0.3978	0.4964	6.0**
H16	0.1758	0.1722	0.4570	7.0**
H18A	0.5136	0.0439	0.4190	10.0**
H18B	0.3683	0.0494	0.3775	10.0**
H18C	0.5245	0.1221	0.3609	10.0**

** -- Atoms included but not refined.

Table of General Temperature Factor Expressio

$(MeC_5H_4)_3UNPh$

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)	Beqv
U	2.18(1)	2.35(1)	3.79(1)	0.08(1)	-1.02(1)	0.20(1)	2.774(6)
N	2.2(3)	4.6(4)	4.3(3)	0.4(3)	0.5(3)	0.7(3)	3.7(2)
C1	2.4(3)	4.4(5)	2.6(3)	0.3(4)	-0.2(3)	-0.1(4)	3.1(2)
C2	2.3(4)	4.8(5)	5.6(4)	-0.5(4)	-0.4(4)	1.1(4)	4.2(2)
C3	2.2(4)	7.9(6)	4.5(4)	-1.0(5)	0.3(4)	-1.2(4)	4.9(2)
C4	5.0(5)	7.0(6)	5.6(5)	3.4(5)	-1.4(5)	-3.1(4)	5.9(3)
C5	6.9(6)	4.5(5)	4.8(4)	2.1(5)	-1.0(5)	-0.7(4)	5.4(3)
C6	3.9(5)	4.3(5)	3.8(4)	0.8(4)	-0.6(4)	0.3(4)	4.0(2)
C7	3.2(4)	5.0(5)	3.8(4)	-0.8(4)	-0.3(4)	0.2(4)	4.0(2)
C8	3.2(4)	5.7(6)	3.8(4)	1.2(4)	0.8(4)	-1.1(4)	4.2(2)
C9	4.7(5)	7.2(6)	2.3(3)	0.5(5)	0.1(4)	-0.5(4)	4.7(3)
C10	3.3(4)	5.1(5)	3.6(4)	1.3(5)	-0.1(3)	0.8(4)	4.0(2)
C11	2.8(4)	3.9(5)	3.0(3)	-0.4(4)	-0.1(3)	0.9(3)	3.2(2)
C12	5.1(5)	3.4(4)	6.7(5)	-1.2(4)	3.5(4)	-1.2(4)	5.0(2)
C13	3.0(4)	5.6(5)	3.2(4)	0.3(4)	-0.9(4)	0.5(4)	3.9(2)
C14	3.8(4)	4.6(5)	2.5(3)	0.5(4)	-0.2(3)	-0.1(4)	3.7(2)
C15	3.6(5)	5.3(5)	3.9(4)	0.8(4)	0.8(4)	1.7(4)	4.3(2)
C16	5.7(6)	4.5(5)	6.2(5)	-1.8(5)	-1.4(5)	2.2(4)	5.5(3)
C17	6.0(5)	3.1(4)	4.6(4)	2.2(4)	-1.8(4)	-0.7(4)	4.6(2)
C18	13.5(9)	5.1(5)	8.3(6)	5.9(6)	-5.2(6)	-2.0(6)	9.0(4)

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.

Bond Lengths and Angles for $(MeC_5H_4)_3UNPh$

Intramolecular Distances

ATOM 1	ATOM 2	DISTANCE
C7	C8	1.397(11)
C8	C9	1.417(12)
C9	C10	1.414(12)
C10	C11	1.398(11)
C11	C7	1.384(12)
C11	C12	1.531(10)
C13	C14	1.423(12)
C14	C15	1.360(12)
C15	C16	1.360(12)
C16	C17	1.406(14)
C17	C13	1.379(12)
C17	C18	1.475(12)
C19	C20	1.400(1) *
C23	C24	1.500(1) *
C19'	C20'	1.400(1) *
C23'	C24'	1.500(1) *

* Distances in Cp3 and Cp3' were fixed.

ATOM 1	ATOM 2	DISTANCE
U	N	2.019(6)
U	CP1	2.485(1)
U	CP2	2.470(1)
U	CP3	2.489(1)
U	CP3'	2.541(1)
N	C1	1.363(10)
C1	C2	1.392(11)
C2	C3	1.391(12)
C3	C4	1.372(12)
C4	C5	1.390(14)
C5	C6	1.337(12)
C6	C1	1.394(10)
U	C7	2.762(8)
U	C8	2.727(8)
U	C9	2.744(8)
U	C10	2.740(7)
U	C11	2.803(8)
U	C13	2.751(8)
U	C14	2.709(7)
U	C15	2.703(7)
U	C16	2.732(8)
U	C17	2.775(8)
U	C19	2.711(14)
U	C20	2.769(14)
U	C21	2.797(13)
U	C22	2.803(13)
U	C23	2.717(11)
U	C19'	2.862(20)
U	C20'	2.878(21)
U	C21'	2.794(20)
U	C22'	2.717(23)
U	C23'	2.776(20)

CP1,etc. are the centroids of the five-carbon cyclopentadiene rings.

Intramolecular Angles

ATOM 1	ATOM 2	ATOM 3	ANGLE
N	U	CP1	103.24(18)
N	U	CP2	101.92(18)
N	U	CP3	92.63(19)
N	U	CP3'	105.28(19)
CP1	U	CP2	115.07(1)
CP1	U	CP3	122.17(1)
CP1	U	CP3'	108.25(1)
CP2	U	CP3	115.17(1)
CP2	U	CP3'	120.82(1)
CP3	U	CP3'	16.34(1)
U	N	C1	167.4(6)
N	C1	C2	120.1(7)
N	C1	C6	121.6(7)
C6	C1	C2	118.3(8)
C1	C2	C3	120.8(8)
C2	C3	C4	119.0(8)
C3	C4	C5	120.0(8)
C4	C5	C6	120.9(8)
C5	C6	C1	121.0(8)

CP1, etc. are the centroids of the five-carbon cyclopentadiene rings.

Intramolecular Angles

ATOM 1	ATOM 2	ATOM 3	ANGLE
C11	C7	C8	109.3(7)
C7	C8	C9	107.0(8)
C8	C9	C10	107.6(7)
C9	C10	C11	107.7(7)
C7	C11	C10	108.2(7)
C7	C11	C12	128.1(7)
C10	C11	C12	123.7(8)
C17	C13	C14	110.0(8)
C13	C14	C15	106.3(8)
C14	C15	C16	108.7(9)
C15	C16	C17	110.8(9)
C13	C17	C16	104.1(7)
C13	C17	C18	127.4(10)
C16	C17	C18	128.4(11)
C23	C19	C20	108.02(9) *
C19	C23	C24	126.00(11) *
C23'	C19'	C20'	108.00(9) *
C19'	C23'	C24'	126.00(11) *

* Angles in Cp3 and Cp3' were fixed.

TABLE I

Crystal and Data Collection Parameters

Compound: $(C_5H_4\text{-}CH_3)_3U{=}N\text{-}C_6H_5$

A) Crystal Parameters at -95±5°C [a,b]

a = 8.4113(14) Å	Space Group: $P2_12_12_1$
b = 10.0701(19) Å	Formula Weight = 566.5 amu
c = 22.9639(33) Å	Z = 4
V = 1945.1(10) Å^3	
d_c = 1.93 g cm^{-3}	d_o = ________

μ (calc.)= 79.2 cm^{-1}

Size of crystal : 0.15 x 0.28 x 0.42 mm

B) Data Measurement Parameters [8]

Radiation : Mo Kα (λ = 0.71073 Å)

Monochromator: Highly-oriented graphite (2θ = 12.2°)

Detector: Crystal scintillation counter, with PHA.

Reflections measured: + h, + k, + ℓ

2θ Range: 3 ° -> 45° Scan Type : θ-2θ

Scan speed: 0.72 -> 6.7 (θ, °/min)

Scan width: Δθ = 0.6 + .347 tan(θ)

Background : Measured over 0.25(Δθ) added to each end of the scan.

Aperture -> crystal = 173 mm Vertical aperture = 3.0 mm

Horizontal aperture = 2.0 + 1.0 tan(θ) mm (variable).

No. of reflections collected: 1505

No. of unique reflections: 1484

Intensity standards: (264), (535), (0,0,14); measured every 2 hours of x-ray exposure time. Over the data collection period no decrease in intensity was observed.

Orientation: 3 reflections were checked after every 250 measurements. Crystal orientation was redetermined if any of the reflections were offset from their predicted positions by more than 0.1 °. 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 24 reflections with 2θ between 27° and 30°.

[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.

Positional and Thermal Parameters of $[(MeC_5H_4)_3U]_2[PhNCO]$

Atom	x	y	z	B(Å^2)
U1	0.27304(5)	0.25308(7)	0.02673(4)	4.22(2)
U2	0.26664(5)	0.66903(7)	0.00873(5)	4.60(2)
O	0.2463(8)	0.520(1)	-0.0146(8)	5.5(4)*
N	0.1828(9)	0.374(1)	-0.0609(9)	4.1(4)*
C1	0.245(1)	0.423(1)	-0.005(1)	3.4(4)*
C2	0.113(1)	0.405(2)	-0.137(1)	4.4(5)*
C3	0.034(1)	0.412(2)	-0.135(1)	6.1(6)*
C4	-0.035(1)	0.443(2)	-0.213(2)	7.2(7)*
C5	-0.022(1)	0.465(2)	-0.287(1)	6.1(6)*
C6	0.052(1)	0.459(2)	-0.294(2)	7.2(7)*
C7	0.125(1)	0.427(2)	-0.215(1)	5.6(6)*
C8	0.184(1)	0.080(2)	0.004(1)	5.9(6)*
C9	0.241(1)	0.067(2)	-0.037(1)	5.9(6)*
C10	0.220(1)	0.123(2)	-0.112(1)	5.7(6)*
C11	0.150(1)	0.173(2)	-0.123(1)	5.4(5)*
C12	0.126(1)	0.140(2)	-0.052(1)	6.2(6)*
C13	0.044(2)	0.172(2)	-0.040(2)	9.2(8)*
C14	0.440(1)	0.293(2)	0.089(1)	6.4(6)*
C15	0.404(1)	0.350(1)	0.011(1)	4.4(5)*
C16	0.375(1)	0.286(2)	-0.060(1)	5.6(6)*
C17	0.398(1)	0.188(2)	-0.030(1)	6.8(6)*
C18	0.435(1)	0.199(2)	0.062(1)	6.7(7)*
C19	0.474(2)	0.101(3)	0.110(2)	12(1)*
C20	0.317(1)	0.337(2)	0.198(1)	4.6(5)*
C21	0.350(1)	0.243(2)	0.213(1)	6.1(6)*
C22	0.286(1)	0.173(2)	0.189(1)	5.9(6)*
C23	0.210(1)	0.229(2)	0.159(1)	5.3(5)*
C24	0.231(1)	0.326(2)	0.166(1)	5.5(5)*
C25	0.171(2)	0.404(2)	0.150(2)	9.3(8)*
C26	0.356(1)	0.715(2)	0.185(1)	6.2(6)*
C27	0.352(1)	0.616(2)	0.181(1)	7.1(7)*
C28	0.399(1)	0.582(2)	0.141(1)	6.5(6)*
C29	0.433(1)	0.658(2)	0.112(1)	6.0(6)*
C30	0.406(1)	0.745(2)	0.139(1)	6.2(6)*
C31	0.422(2)	0.851(2)	0.138(2)	13(1)*
C32	0.138(1)	0.798(2)	-0.017(1)	6.1(6)*
C33	0.174(1)	0.781(2)	0.074(1)	6.1(6)*
C34	0.159(1)	0.681(2)	0.089(1)	6.0(6)*
C35	0.112(1)	0.635(2)	0.011(1)	5.4(6)*
C36	0.098(1)	0.710(2)	-0.053(1)	5.9(6)*
C37	0.040(2)	0.697(2)	-0.157(2)	8.4(8)*
C38	0.359(1)	0.725(2)	-0.087(1)	5.4(6)*
C39	0.302(1)	0.806(2)	-0.097(1)	7.1(7)*
C40	0.224(1)	0.769(2)	-0.151(1)	6.7(6)*
C41	0.227(1)	0.668(2)	-0.171(1)	5.9(6)*
C42	0.313(1)	0.645(2)	-0.133(1)	7.1(7)*
C43	0.360(2)	0.558(2)	-0.140(2)	12(1)*

---

* -- Atoms refined with isotropic thermal parameters.

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

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

CP1	0.1842	0.1164	-0.0640	**
CP2	0.4105	0.2633	0.0144	**
CP3	0.2786	0.2616	0.1848	**
CP4	0.3892	0.6633	0.1516	**
CP5	0.1361	0.7212	0.0208	**
CP6	0.2851	0.7226	-0.1277	**

** -- Centroids of the five-membered cyclopentadiene rings.

Bond Lengths and Angles for $[(MeC_5H_4)_3U]_2[PhNCO]$

Intramolecular Distances

ATOM 1	ATOM 2	DISTANCE
U1	N	2.364(15)
U1	C1	2.422(19)
U1	CP1	2.533 *
U1	CP2	2.508 *
U1	CP3	2.544 *
U2	O	2.106(14)
U2	CP4	2.479 *
U2	CP5	2.488 *
U2	CP6	2.486 *
O	C1	1.36(2)
C1	N	1.31(2)
N	C2	1.44(2)
C2	C3	1.41(2)
C3	C4	1.43(3)
C4	C5	1.34(3)
C5	C6	1.35(3)
C6	C7	1.49(3)
C7	C2	1.40(2)

* CPn (n=1,6) are the centroids of the cyclopentadienide rings.

Intramolecular Distances

ATOM 1	ATOM 2	DISTANCE
U1	C8	2.82(2)
U1	C9	2.76(2)
U1	C10	2.76(2)
U1	C11	2.78(2)
U1	C12	2.86(2)
U1	C14	2.76(2)
U1	C15	2.766(19)
U1	C16	2.73(2)
U1	C17	2.84(2)
U1	C18	2.79(2)
U1	C20	2.839(19)
U1	C21	2.80(2)
U1	C22	2.79(2)
U1	C23	2.81(2)
U1	C24	2.83(2)
U2	C26	2.76(2)
U2	C27	2.72(2)
U2	C28	2.76(2)
U2	C29	2.75(2)
U2	C30	2.75(2)
U2	C32	2.79(2)
U2	C33	2.75(2)
U2	C34	2.71(2)
U2	C35	2.77(2)
U2	C36	2.80(2)
U2	C38	2.77(2)
U2	C39	2.79(2)
U2	C40	2.78(2)
U2	C41	2.73(2)
U2	C42	2.75(2)

Intramolecular Distances

ATOM 1	ATOM 2	DISTANCE
C8	C9	1.42(3)
C9	C10	1.37(3)
C10	C11	1.36(2)
C11	C12	1.46(3)
C12	C8	1.35(3)
C12	C13	1.60(3)
C14	C15	1.42(3)
C15	C16	1.39(2)
C16	C17	1.44(3)
C17	C18	1.39(3)
C18	C14	1.38(3)
C18	C19	1.58(4)
C20	C21	1.41(3)
C21	C22	1.42(3)
C22	C23	1.46(3)
C23	C24	1.39(3)
C24	C20	1.39(2)
C24	C25	1.47(3)
C26	C27	1.39(3)
C27	C28	1.34(3)
C28	C29	1.38(3)
C29	C30	1.43(3)
C30	C26	1.42(3)
C30	C31	1.49(4)
C32	C33	1.38(3)
C33	C34	1.45(3)
C34	C35	1.38(3)
C35	C36	1.42(3)
C36	C32	1.41(3)
C36	C37	1.61(3)
C38	C39	1.47(3)
C39	C40	1.41(3)
C40	C41	1.45(3)
C41	C42	1.42(3)
C42	C38	1.40(3)
C42	C43	1.49(3)

$[(MeC_5H_4)_3U][PhNCO]$

Intramolecular Angles

ATOM 1	ATOM 2	ATOM 3	ANGLE
C12	C8	C9	104.3(21)
C8	C9	C10	110.7(21)
C9	C10	C11	109.0(20)
C10	C11	C12	104.7(19)
C11	C12	C8	111.0(22)
C8	C12	C13	124.6(23)
C11	C12	C13	124.4(21)
C18	C14	C15	106.5(21)
C14	C15	C16	106.8(20)
C15	C16	C17	110.5(19)
C16	C17	C18	102.7(22)
C17	C18	C14	113.3(24)
C14	C18	C19	134.3(25)
C17	C18	C19	112.0(24)
C24	C20	C21	105.9(20)
C20	C21	C22	111.2(20)
C21	C22	C23	104.1(20)
C22	C23	C24	107.9(20)
C23	C24	C20	110.9(22)
C20	C24	C25	126.2(23)
C23	C24	C25	122.7(22)
C30	C26	C27	107.6(24)
C26	C27	C28	109.8(24)
C27	C28	C29	109.1(23)
C28	C29	C30	107.9(20)
C29	C30	C26	105.4(23)
C26	C30	C31	116.7(26)
C29	C30	C31	137.6(25)
C36	C32	C33	104.9(21)
C32	C33	C34	107.6(20)
C33	C34	C35	111.4(20)
C34	C35	C36	102.3(20)
C35	C36	C32	113.7(20)
C32	C36	C37	123.6(21)
C35	C36	C37	122.6(21)
C42	C38	C39	109.1(22)
C38	C39	C40	103.8(21)
C39	C40	C41	112.3(21)
C40	C41	C42	104.1(21)
C41	C42	C38	110.4(24)
C38	C42	C43	118.0(25)
C41	C42	C43	131.3(26)

Intramolecular Angles

ATOM 1	ATOM 2	ATOM 3	ANGLE
N	U1	CP1	93.6 *
N	U1	CP2	110.6 *
N	U1	CP3	109.2 *
C1	U1	CP1	125.2 *
C1	U1	CP2	93.0 *
C1	U1	CP3	95.3 *
C1	U1	N	31.7(5)
CP1	U1	CP2	112.9 *
CP1	U1	CP3	113.4 *
CP2	U1	CP3	115.0 *
O	U2	CP4	99.3 *
O	U2	CP5	101.7 *
O	U2	CP6	101.8 *
CP4	U2	CP5	115.1 *
CP4	U2	CP6	118.7 *
CP5	U2	CP6	115.6 *
U1	N	C2	152.5(13)
U1	C1	O	168.1(13)
U2	O	C1	164.0(12)
O	C1	N	118.9(16)
C1	N	C2	130.1(16)
N	C2	C3	121.2(18)
N	C2	C7	117.9(18)
C7	C2	C3	120.9(19)
C2	C3	C4	119.1(21)
C3	C4	C5	119.3(23)
C4	C5	C6	124.8(24)
C5	C6	C7	118.3(21)
C6	C7	C2	117.5(19)

* CPn (n=1,6) are the centroids of the cyclopentadienide rings.

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