Synthesis and Structure of $Cp_3U=CHPMe_3$: A Compound with a U=C Multiple Bond

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Received August 27, 1987

Green, crystalline $Cp_3U=CHPMe_3$ has been synthesized by the reaction of Cp_3UCl with $Li[CH_2]_2PMe_2$ or $CH_2=PMe_3$. Its crystal structure has been determined by single crystal X-ray diffraction. The short U=CH bond distance, 2.274(8) Å, and large U–C–P angle, 143.5(5)°, indicate uranium-carbon multiple bond character. The $^1J(^{13}C^1H)$ coupling constants within the CH group between uranium and phosphorus in $Cp_3U=CHPMe_3$ (95 Hz), $Cp_3U=CHPMe_2Ph$ (100 Hz), and $Cp_3U=CHPPh_2Me$ (113 Hz) are surprisingly small, but no agostic interaction UCHP can be derived from the structural data.

Synthese und Struktur von $Cp_3U=CHPMe_3$: Eine Verbindung mit U=C-Mehrfachbindung

Grünes, kristallines $Cp_3U=CHPMe_3$ wurde durch Umsetzung von Cp_3UCl mit $Li[CH_2]_2PMe_2$ oder $H_2C=PMe_3$ dargestellt. Seine Kristallstruktur wurde durch Röntgenbeugungsanalyse an Einkristallen bestimmt. Der kurze U=CH-Abstand von 2.274(8) Å und der große Winkel U–C–P von 143.5(5)° deuten Uran-Kohlenstoff-Mehrfachbindungscharakter an. Die $^1J(^{13}C^1H)$-Kopplungskonstanten in den CH-Gruppen zwischen Uran und Phosphor von $Cp_3U=CHPMe_3$ (95 Hz), $Cp_3U=CHPMe_2Ph$ (100 Hz) und $Cp_3U=CHPPh_2Me$ (113 Hz) sind auffallend klein. Den Strukturdaten kann aber keine agostische UCHP-Wechselwirkung entnommen werden.

Several years ago we reported[1)] the synthesis of $Cp_3U=CHPMePh_2$ and $Cp_3U=CHPMe_2Ph$, Cp = η^5-$C_5H_5^-$. Based on the structure of $Cp_3U=CHPMe_2Ph$, which contains the shortest known uranium-carbon bond and a large U–C–P angle, we postulated these were the first compounds to contain f-element-carbon multiple bonds[2,3)]. This assignment was further supported by EHMO calculations[4)]. As part of an ongoing effort to characterize the chemistry[5)] and the nature[6,7)] of actinide-ligand bonding we have now prepared $Cp_3U=CHPMe_3$, which is the simplest $Cp_3U=CHPMeRR'$ compound, and have found that the ^{13}C-H coupling constants for the alpha CH group in the compounds of this series are small. To search for a structural reason for these low values we determined the crystal structure of $Cp_3U=CHPMe_3$.

Results and Discussion

$Cp_3U=CHPMe_3$ can be obtained in good yield by reaction (1)

$$Cp_3UCl + LiCH_2CH_2PMe_2 \rightarrow Cp_3U=CHPMe_3 + LiCl \qquad (1)$$

using the same procedure originally developed for $Cp_3U=CHPMe_2Ph$ and $Cp_3U=CHPMePh_2$[1)]. It can also be prepared by the direct reaction of $H_2C=PMe_3$ with Cp_3UCl:

$$Cp_3UCl + 2\,H_2C=PMe_3 \rightarrow Cp_3U=CHPMe_3 + [PMe_4][Cl] \qquad (2)$$

$Cp_3U=CHPMe_3$ is an air and moisture sensitive, pyrophoric green solid which is soluble in THF and aromatic solvents, but virtually insoluble in aliphatic hydrocarbons.

Within the $Cp_3U=CHPMeRR'$ series of compounds the ^{13}C-H coupling constants of the CH group attached to uranium decrease with increasing Me substitution: $Cp_3U=CHPMePh_2$, 113 Hz; $Cp_3U=CHPMe_2Ph$, 100 Hz; and $Cp_3U=CHPMe_3$, 95 Hz. The 95-Hz coupling is particularly notable since it lies in the range encountered in electron deficient alkylidene complexes which contain agostic metal-hydrogen interactions[8)]. In line with this trend the ^{13}C-H coupling constants of the related compounds, $Cp_2ClZr=CHPPh_3$: 122 Hz[9)]; $Cp_2PhZr=CHPPh_3$: 117 Hz[10)], $Cp_2PhTi=CHPPh_3$: 122 Hz[11)], are somewhat greater than those in $Cp_3U=CHPMeRR'$. Hydrogens were located in the X-ray crystal structures of each of these compounds[9–11)] and, even though the metal-carbon bonds are short, there are no indications of unusual metal-hydrogen interactions.

Since there are 1 – 2% standard deviations on the metrical parameters in the published structure of $Cp_3U=CHPMe_2Ph$[2,3)] it is impossible to determine if there are structural effects which may explain the low ^{13}C-H couplings within the uranium series. Consequently, we examined $Cp_3U=CHPMe_3$, the compound with the lowest ^{13}C-H coupling, using very good quality crystals and obtained a crystal structure which is much more precise than that of $Cp_3U=CHPMe_2Ph$.

The molecular structure of $Cp_3UCHPMe_3$ is shown in Figure 1, and the bond distances and angles are summarized in Table 1. As typical for a Cp_3U-X type molecule the geometry about the uranium is trigonal pyramidal with the three Cp centroids defining the base and the $[CHPMe_3]^-$ ligand occupying the apical site.

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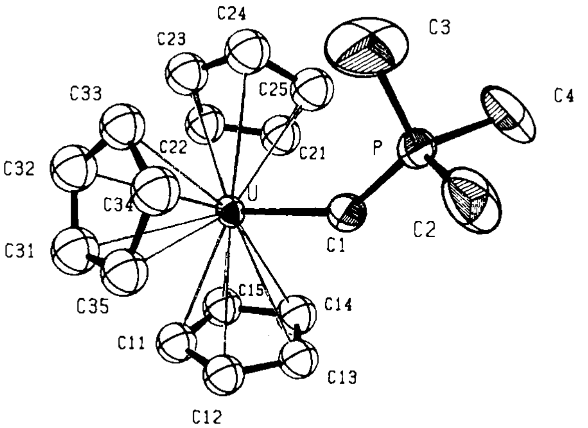


Figure 1. ORTEP drawing of $Cp_3UCHPMe_3$

Table 1. Selected bond lengths and angles for $Cp_3UCHPMe_3$ (Cp represents the centroid of a cyclopentadienide group)

Distances (Angstrøms)

Atom	Atom	Distance	Atom	Atom	Distance
U	- C1	2.274(8)	U	- C23	2.820(6)
P	- C1	1.696(8)	U	- C24	2.813(8)
P	- C2	1.78(1)	U	- C25	2.786(8)
P	- C3	1.77(1)	U	- C31	2.800(8)
P	- C4	1.80(1)	U	- C32	2.781(8)
U	- C11	2.781(8)	U	- C33	2.777(8)
U	- C12	2.799(8)	U	- C34	2.794(8)
U	- C13	2.820(8)	U	- C35	2.807(8)
U	- C14	2.816(8)	U	- Cp1	2.53
U	- C15	2.792(8)	U	- Cp2	2.62
U	- C21	2.777(6)	U	- Cp3	2.51
U	- C22	2.798(8)			

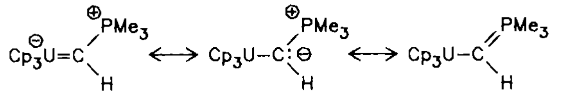
Angles (Degrees)

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
C2	- P	- C1	115.0(5)	C1	- U	- Cp1	100
C3	- P	- C1	112.3(6)	C1	- U	- Cp2	107
C3	- P	- C2	105.4(8)	C1	- U	- Cp3	104
C4	- P	- C1	116.1(6)	Cp1	- U	- Cp2	116
C4	- P	- C2	101.1(6)	Cp2	- U	- Cp3	114
C4	- P	- C3	105.6(8)	Cp3	- U	- Cp1	113
P	- C1	- U	143.5(5)				

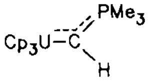
The metrical parameters in $Cp_3UCHPMe_3$ are very similar to, but much more precise than those in $Cp_3UCHPMe_2Ph$. For the most part, uncertainties in bond distances and angles for $Cp_3UCHPMe_3$ are 1/3 to 1/4 of those for $Cp_3UCHPMe_2Ph$. Particularly significant are the U–C(1) distance of 2.274(8) Å and the U–C(1)–P angle of 143.5(5)°. These values can be compared with the corresponding U–C distance, 2.29(3) Å, and U–C–P angle, 142(1)°, for $Cp_3UCHPMe_2Ph$ which have nearly the same absolute values, but with 3σ uncertainties of $\pm$.0.09 Å in the U–C bond distance and $\pm 3°$ in the U–C–P angle. Thus our results for $Cp_3UCHPMe_3$ more firmly establish these phosphoylide complexes as having the shortest uranium-carbon bonds yet measured.

The phosphorus atom is nearly tetrahedral. The $P-CH_3$ distances are normal for P–C(alkyl) bonds, about 1.80 Å. The C(1)–P separation, 1.696(9) Å, is significantly shorter than a normal single bond, but is longer than the 1.640(6) Å CH_2-P bond in CH_2PMe_3[12], and is the same as those in $Cp_2ClZr=CHPPh_3$, 1.708(6) Å[9], $Cp_2PhZr=CHPPh_3$: 1.689(4) Å[10], and $Cp_2PhTi=CHPPh_3$: 1.689(4) Å[11]. In $[Cp(OC)_2ReC(Ph)PMe_3]^+[BF_4]^-$, where a full Re=C double bond is assigned[13], the analogous C–P distance, 1.79 Å, is considerably greater.

As we have discussed before[2,3] such short uranium-carbon distances combined with wide U–C–P angles indicate multiple uranium-carbon bonding which can be formulated in terms of several resonance structures as given in (3).



(3)



(4)

A combination of these resonance forms, (4), accounts for the short U–C(1) and P–C(1) bonds.

One of the motivations for undertaking the structure determination on $Cp_3U=CHPMe_3$ was to seek a rational for the differences in ^{13}C-H coupling constants at the alpha carbon atom within the $Cp_3UCHPMe_nPh_{3-n}$ series. During later cycles of refinement on the structure of $Cp_3UCHPMe_3$ hydrogen atoms appeared in difference Fourier maps. At this point, the Cp and methyl groups were refined as rigid groups containing hydrogens at calculated positons. A peak near C(1), however, was refined as H(111) with independent positional and thermal parameters. This resulted in a C(1)–H(111) distance of 0.6(2) Å and a U–H(111) separation of 2.3(2) Å. The standard deviations on the bond angles were large, and the HCUP unit did not appear to be planar. Since light atoms contribute most to the intensity of low angle reflections[14], the position of H(111) was refined using only data up to $2\Theta = 25°$. The final metrical parameters obtained after convergence of least squares refinement using the low angle data are C(1)–H(111): 0.90(1) Å, U–H(111): 2.77(12) Å, H(111)–C(1)–P: 102(8)°, H(111)–C(1)–U: 115(8)°, and P–C(1)–U: 143.5(5)°. Notice that the sum of the angles around C(1) is 360° so that this atom is planar. On the basis of these data there is no indication of an agostic interaction between H(111) and U. However, in view of the difficulties associated with the location of hydrogen atoms in the presence of heavy atoms and the large standard deviations on the refined metrical parameters involving H(111), firm conclusions on the locations of this atom must await a neutron diffraction study.

The support of this work by the *National Science Foundation*, Grant # CHE 85-19289 (JWG and REC), by the *Petroleum Research Fund*, administered by the *American Chemical Society* (REC and JWG), and by *NATO Grant* # 902/83 (HS and JWG) is gratefully acknowledged. The support of the *Alexander von Humboldt-Stiftung* through a *Feodor-Lynen-Stipendium* (FE) is also gratefully acknowledged.

Experimental

All manipulations were carried out under dry nitrogen using a Vacuum Atmospheres Dry Box or standard Schlenck techniques.

Solvents were dried by refluxing over sodium benzophenone and were distilled under dry nitrogen before use. Cp_3UCl[15], $Cp_3U=CHPMe_2Ph$[1,16], and $Cp_3U=CHPMePh_2$[1,16] were synthesized as described in the literature, and $LiCH_2CH_2PMe_2$ was prepared from Me_4PI by the procedure reported[16,17] for $LiCH_2CH_2PMePh$ and $LiCH_2CH_2PPh_2$. Preparation of $Me_3P=CH_2$ and its lithiation are further described in ref.[18,19].

Microanalyses: Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim. — Diffraction data: Recorded at ambient temperature, Syntex $P\bar{1}$ diffractometer, crystallographic calculations performed on an IBM 3081 D computer. — NMR spectra: Nicolet NM-300 spectrometer, Fourier transform mode. ^{13}C-H coupling constants were determined for the $CH-PR_3$ groups of $Cp_3U=CHPMe_3$, $J_{C,H}$ = 95 Hz, $Cp_3U=CHPMe_2Ph$, 100 Hz, and $Cp_3U=CHPMePh_2$, 113 Hz, from satellite peaks about the C−H resonance in the ^1H spectrum.

Tris(cyclopentadienyl)(trimethylmethylenephosphorane)uranium, $Cp_3U=CHPMe_3$: Over a 30 min period 1.15 g (11.9 mmol) of $LiCH_2CH_2PMe_2$, dissolved in 30 ml of THF, was added to a 25-ml THF solution containing 4.88 g (10.4 mmol) of Cp_3UCl, which had been cooled to −78°C. After the addition was complete the resulting mixture was stirred for an additional 5 h, during which the temperature was slowly raised to 0°C. During this time the color of the solution changed from brown to a very dark green color. Volatile components were evaporated in vacuo at 0°C leaving a dark mass which was extracted with three 15-ml portions of benzene. The resulting dark green benzene solution was filtered through a medium-porosity glass filter frit using Celite as a filter aid. The green powder which remained after evaporation of the benzene in vacuo was recrystallized from toluene to yield 3.74 g (68% yield) of the dark green, crystalline $Cp_3U=CHPMe_3$. — NMR (C_6D_6): ^1H; δ (ppm from TMS) = −3.025 (d, 9H, $J_{P,H}$ = 11.4 Hz, PCH_3), −13.195 (s, 15H, Cp), −106.331 (d, 1H, $J_{P,H}$ = 13.6, $J_{C,H}$ = 95 Hz, CHP). — ^{31}P: −217.96 ppm from 85% H_3PO_4.

$C_{19}H_{25}PU$ (522.4)	Calcd.	C 43.68	H 4.82
	Found	C 43.44	H 4.90

The reaction of Cp_3UCl with 2 equivalents of $H_2C=PMe_3$ using a procedure similar to that described above is an alternate preparation of $Cp_3U=CHPMe_3$. In our hands the use of the solid, $LiCH_2CH_2PMe_2$, is more satisfactory because it can be prepared, purified, and handled more easily than $H_2C=PMe_3$.

X-Ray Crystallography: Crystals of $Cp_3U=CHPMe_3$ were grown from a saturated toluene solution and mounted and sealed in thin walled capillaries under dry N_2. Crystal, data collection, and refinement parameters are summarized in Table 2. Cell constants were determined by least squares methods from the centered angular coordinates of 15 intense reflections with 2-Θ values between 14.2° and 27.9°. Atomic scattering factors for P^0, N^0, C^0 and H^0 were supplied by SHELX-76[20]. The atomic scattering factor including the anomalous dispersion correction for U^0 was taken from the literature[21]. The data were corrected for absorption using the program PROCESS[22] and measured ψ scans for 6 reflections with χ values near 90°.

Structure Solution and Refinement: Since the cell constants indicated a triclinic unit cell, $P\bar{1}$ was assumed. Use of this space group led to the successful solution of the structure. The position of the uranium atom was determined by Patterson methods, and the remaining atoms were located in a straightforward fashion in a series of difference Fourier maps and least squares refinements using SHELX-76. The uranium, phosphorus, and non-ring carbon atoms were refined anisotropically. Using the parameters in SHELX-76 and 0.95 Å C−H bond distances, the cyclopentadienide groups were treated as rigid bodies with hydrogens attached at calculated positions and the hydrogens on the methyl groups as a fixed group. Refinement converged at R_1 = 0.042 and R_g = 0.048. In the final

Table 2. Crystal, data collection, and reduction parameters for $Cp_3UCHPMe_3$

Formula $(C_5H_5)_3UCHP(CH_3)_3$	Mol. mass 522.41
Space Group (and No.): $P\bar{1}$ (No. 2)	Crystal System: Triclinic
Lattice Constants with esd's:	
a = 10.552(3) Å	α = 90.97(2)°
b = 11.643(3) Å	β = 92.39(2)°
c = 8.276(1) Å	γ = 63.98(2)°
Number of Molecules per Unit Cell: Z = 2	V = 910.4(4) $Å^3$
Crystal dimension: 0.4 × 0.5 × 0.3 mm	Crystal shape: Rect. Parallelepipede
Crystal volume 0.06 mm^3	Crystal color: Green
Calculated density 1.8354 g/cm^3	
Absorption coefficient, μ = 85.90 cm^{-1}	
Absorption correction range: 1.01 − 1.80	
Radiation: Mo-K_α, graphite monochromator	Wavelength 0.71073 Å
Scan type: 2Θ, Scan Rate 2−24°/min,	
2Θ Range: 3−60	
Total observations: 4968	Number of data used in refinement: 4046
Criteria for selecting data used in refinement: $I > 3\sigma(I_o)$	
Number of parameters: 108	Overdetermination ratio: 37.5
Final R: 0.042	R_g − 0.048

Table 3. Positional parameters for $Cp_3UCHPMe_3$

Atom	X	Y	Z
U	0.11192(3)	0.21467(3)	0.20606(3)
P	0.3803(2)	0.3431(2)	0.2954(4)
C1	0.2203(9)	0.3409(9)	0.274(1)
C2	0.385(1)	0.485(1)	0.227(2)
C3	0.512(1)	0.217(2)	0.189(3)
C4	0.451(1)	0.333(2)	0.499(2)
C11	−0.1812(8)	0.3086(7)	0.1930(7)
C12	−0.1583(8)	0.4195(7)	0.1809(7)
C13	−0.1028(8)	0.4389(7)	0.3328(7)
C14	−0.0915(8)	0.3399(7)	0.4388(7)
C15	−0.1399(8)	0.2594(7)	0.3524(7)
C21	0.1785(7)	0.0592(7)	0.4776(8)
C22	0.1506(7)	−0.0134(7)	0.3537(8)
C23	0.2617(7)	−0.0526(7)	0.2433(8)
C24	0.3582(7)	−0.0043(7)	0.2990(8)
C25	0.3068(7)	0.0649(7)	0.4439(8)
C31	0.0099(6)	0.2065(7)	−0.110(1)
C32	0.1309(6)	0.0877(7)	−0.086(1)
C33	0.2522(6)	0.1116(7)	−0.076(1)
C34	0.2062(6)	0.2452(7)	−0.094(1)
C35	0.0564(6)	0.3039(7)	−0.114(1)

Table 4. Thermal parameters for $Cp_3UCHPMe_3$

Anisotropically Refined Atoms

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U	0.0329(1)	0.0380(1)	0.0265(1)	−0.0001(1)	−0.0001(1)	−0.0161(1)
P	0.036(1)	0.051(1)	0.094(2)	−0.023(1)	0.000(1)	−0.021(1)
C1	0.038(4)	0.053(5)	0.070(6)	−0.014(4)	0.003(4)	−0.020(4)
C2	0.072(8)	0.11(1)	0.13(1)	0.024(9)	−0.019(8)	−0.062(8)
C3	0.063(8)	0.16(2)	0.29(3)	−0.15(2)	0.07(1)	−0.06(1)
C4	0.067(8)	0.13(1)	0.12(1)	0.021(9)	−0.043(8)	−0.054(8)

Isotropically Refined Atoms

ATOM	U	ATOM	U	ATOM	U
C11	0.067(3)	C21	0.069(3)	C31	0.078(3)
C12	0.065(3)	C22	0.071(3)	C32	0.076(3)
C13	0.059(2)	C23	0.076(3)	C33	0.066(2)
C14	0.067(3)	C24	0.080(3)	C34	0.072(3)
C15	0.065(3)	C25	0.075(3)	C35	0.068(3)

cycle of refinement, the maximum shift/esds were 1.0 and 0.8 for rotational parameters associated with two of the fixed methyl groups. For the remaining parameters, shift/esd values were between 0.4 and 0.001. A final difference Fourier map showed maximum peaks of 1.4 $e/\text{Å}^3$ to 1.7 $e/\text{Å}^3$ near the uranium atom.

The positional and thermal parameters of the non-hydrogen atoms are in Tables 3 and 4, respectively[23].

CAS Registry Numbers

Cp3UCHPMe$_3$: 111209-58-6 / Cp$_3$UCl: 1284-81-7 / LiCH$_2$CH$_2$-PMe$_2$: 74952-82-2 / H$_2$CPMe$_3$: 14580-91-7

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Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie Physik Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-52800, the names of authors, and the journal citation.

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