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Contribution from the Department of Chemistry,
University of Hawaii, Honolulu, Hawaii 96822

Organoactinide–Phosphoylide Chemistry. Crystal and Molecular Structure of $[(\mu\text{-CH})(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2\cdot 0.5(C_2H_5)_2O$ and M-$[(\mu\text{-}S\text{-CH})(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2\cdot C_5H_{12}$

ROGER E. CRAMER,* RICHARD B. MAYNARD, and JOHN W. GILJE*

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The addition of 2 equiv of $Li[(CH_2)(CH_2)P(C_6H_5)_2]$ to 1 equiv of $(C_5H_5)_3UCl$ in diethyl ether under an inert atmosphere produces, after standing for several days, deep red crystals of $[(\mu\text{-CH})(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2\cdot 0.5(C_2H_5)_2O$ (I) belonging to the monoclinic space group $P2_1/c$ with a = 12.676 (8) Å, b = 15.462 (8) Å, c = 25.837 (25) Å, β = 124.43 (5)°, and Z = 4. A total of 249 parameters were refined for 3993 unique observed ($I > 3\sigma(I)$) reflections to R_1 = 0.091 and R_2 = 0.110. Soxhlet extraction of the product with pentane yields deep red crystals of M-$[(\mu\text{-}S\text{-CH})(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2\cdot C_5H_{12}$ (II) belonging to the orthorhombic space group $P2_12_12_1$ with a = 16.026 (12) Å, b = 23.453 (13) Å, c = 12.679 (3) Å, and Z = 4. A total of 269 parameters were refined for 1874 unique observed ($I > 3\sigma(I)$) reflections to R_1 = 0.047 and R_2 = 0.052. The complex is a bis(cyclopentadienyl)uranium(IV) dimer bridged by two phosphoylide ligands. Each phosphorus ylide bridges the uranium atoms with a methine carbon atom (C(2)) and chelates one uranium atom via (C(2)) and a methylene carbon atom (C(1)). Average uranium–carbon bond lengths are U–C(cyclopentadienyl) = 2.78 (1) Å (I) and 2.776 (7) Å (II), U_1–C_1 = 2.66 (4) Å (I) and 2.66 (3) Å (II), U_1–C_2 = 2.52 (4) Å (I) and 2.55 (3) Å (II), and U_2–C_2 = 2.43 (4) Å (I) and 2.42 (2) (II) Å.

Introduction

During the past several years there has been a growing interest[1] in the synthesis of stable f-element organometallic complexes containing metal–carbon σ bonds. Complexes containing metal–carbon σ bonds and such coligands as the cyclopentadienide ion and its derivatives[2,4] are often stable well above room temperature. Phosphorus ylides have been shown[5] to possess an extensive coordination chemistry with main-group and transition-metal atoms and to form metal–carbon σ bonds of unusual stability. A recently prepared series[6] of uncharged complexes of various lanthanide ions with bis[(dimethylphosphoniumylidene)bis(methylene)], $M[(CH_2)(CH_2)P(CH_3)_2]_2$, where M = La, Pr, Nd, Sm, Gd, Ho, Er, and Lu, indicates that ylide f-element organometallics also may be thermally stable. Accordingly, we have begun an investigation of phosphorus ylides as ligands toward actinides. We report here the preparation and molecular structure of the first actinide phosphoylide complex, $[(\mu\text{-CH})(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2$. A preliminary report[7] of this work has been published.

Experimental Section

All reactions were carried out in a dry nitrogen atmosphere by using Schlenk techniques, a Vacuum Atmospheres glovebox equipped with a HE-493 Dri-train, or a high-vacuum line.

Uranium tetrachloride and 1.7 M $LiCH_3$ were obtained from Research Organic/Inorganic Corp. Thallous cyclopentadienide was obtained from Aldrich Chemical Co. All of the above materials were used as received. The reagents, $(C_5H_5)_3UCl$ and $Li[(CH_2)(CH_2)P(C_6H_5)_2]$, were prepared by literature procedures.[8,9] Diethyl ether and benzene were dried by reflux over sodium–benzophenone ketyl, and pentane was dried by reflux over calcium hydride.

Preparation of $[(\mu\text{-CH})(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2$. A reaction vessel similar to that used to prepare uranocene[10] was charged with 0.490 g (1.04 mmol) of $(C_5H_5)_3UCl$ and 0.458 g (2.08 mmol) of $Li[(CH_2)(CH_2)P(C_6H_5)_2]$. After the system was cooled to −50 °C, 100 mL of diethyl ether was added, and the mixture was stirred for 1 h and then allowed to warm to room temperature. After standing for several days, the solution formed deep red crystals of $[(\mu\text{-CH})(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2\cdot 0.5(C_2H_5)_2O$ (I) which were filtered from the remaining brownish red solution. Diethyl ether was removed in vacuo. This solid was extracted with 50 mL of benzene and filtered and the benzene removed in vacuo. A portion of this product was placed in a Soxhlet extractor and extracted with ca. 30 mL of pentane for 24 h whereupon very deep red crystals of $[(\mu\text{-CH})(CH_2)P(C_6H_5)_2U(C_5H_5)_2]\cdot C_5H_{12}$ (II) appeared.

A high-resolution mass spectrum run on a Varian MAT-311 mass spectrometer using crystals of I, which had been washed with a large amount of hexane and dried under vacuum for 12 h at 30 °C, did not show a parent ion but contained fragments resulting from the loss of one or more cyclopentadienyl groups. The formulation of the compound as an ether solvate was indicated by the presence of $C_4H_{10}O^+$ (m/e 74.0732 (calcd), 74.0728 (obsd)) and $C_3H_7O^+$ (m/e 59.0497 (calcd), 59.0497 (obsd)). NMR spectra obtained by dissolving crystals of I in C_6D_6 also indicated the presence of diethyl ether. The ^1H NMR spectrum is in complete accord with the structure described here. It is temperature dependent and will be discussed in a forthcoming publication.

Collection and Reduction of X-ray Data. Crystals of I and II were mounted with Corning high-vacuum stopcock grease in thin-walled glass capillaries under nitrogen. A platelike crystal of I measuring 0.39 mm × 0.29 mm × 0.06 mm and a crystal of II with 0.26 mm × 0.22 × 0.15 mm dimensions were selected by microscopic examination and found to be suitable for X-ray diffraction.

A Syntex four-circle computer-controlled diffractometer with graphite-monochromatized Mo Kα radiation (Kα_1, λ = 0.709 30 Å; Kα_2, λ = 0.713 59 Å) and a scintillation detector with pulse-height analyzer was used for preliminary experiments and the measurement of diffraction intensities. The cell constants were determined by least-squares methods from the centered angular coordinates of 15 intense reflections with 2θ values between 4 and 17° for I and between 4 and 19° for II. Except as otherwise noted, the procedure used has previously been reported.[11,12] Crystal data, data collection, and

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Table I. Summary of Crystal Data, Data Collection, and Refinement

	structure I	structure II
compd	$[(\mu\text{-CH})(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2\cdot 0.5(C_2H_5)_2O$	$M\text{-}[(\mu\text{-}S\text{-CH})(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2\cdot C_5H_{12}$
fw	1235.01	1233.11
	monoclinic	orthorhombic
space group	$P2_1/c$ (No. 14)	$P2_12_12_1$ (No. 19)
a, Å	12.676 (8)	16.026 (12)
b, Å	16.462 (8)	23.453 (13)
c, Å	25.837 (25)	12.679 (3)
β, deg	124.43 (5)	
vol, $Å^3$	4447 (6)	4799 (4)
Z	4	4
calcd density, g/cm^3	1.84	1.71
absorption grid		6 × 10 × 4
μ, cm^{-1}	70.37	64.83
transmissn coeff		0.428–0.527
scan rate, deg/min	5–24	5–24
2θ range, deg	3–50	3–40
total no. of observns	8126	2584
data with $I_o > 3(\sigma_I)$ (*m*)	3993	1874
P	0.05	0.05
R_1	0.091	0.047
R_2	0.110	0.052
goodness-of-fit	2.44	1.29
parameters (*s*)	249	269
overdetermination ratio (*m*/*s*)	13.6	7.0

refinement parameters are listed in Table I.

Atomic scattering factors for U, P, and C were used.[13] Anomalous dispersion corrections[14] to the scattering factors were made for all nonhydrogen atoms.

Solution and Refinement of Structure I. A three-dimensional Patterson map[15] yielded the coordinates for the uranium atoms. Subsequent Fourier maps and full-matrix least-squares refinement with anisotropic thermal parameters for uranium and phosphorus and isotropic thermal parameters for the carbon atoms converged at $R_1 = 0.095$ and $R_2 = 0.115$. Although absorption is undoubtedly important in this structure, orientation of the crystal was lost and an absorption correction was not possible. At this point a difference Fourier map revealed a diethyl ether solvate. Since the solvate position is only 0.4 Å from the inversion center at 0, 0, $^1/_2$, it can only be half-occupied. These solvate atoms lowered the error indices to $R_1 = 0.091$ and $R_2 = 0.110$. No attempt was made to locate hydrogen atoms.

Examination of the final difference Fourier with an estimated standard deviation of $\simeq 0.4$ e/Å^3 showed that the largest peak has a height of 1.0 e/Å^3 and is associated with one of the solvate atoms. All others with the exception of ripples around the uranium atom are less than 0.9 e/Å^3. The final cycle of least-squares refinement yielded shifts less than 30% of their estimated standard deviations.

Solution and Refinement of Structure II. The structure was routinely solved by heavy-atom methods. However, since $P2_12_12_1$ is a noncentric space group, it was necessary to determine the correct enantiomer for the crystal examined. Refinement with anisotropic thermal parameters for uranium and phosphorus and isotropic thermal parameters for the carbon atoms of the original, arbitrarily chosen, enantiomer converged at $R_1 = 0.049$ and $R_2 = 0.056$. Refinement of the other enantiomer yielded $R_1 = 0.055$ and $R_2 = 0.063$. The *R* factor ratio is 1.12 and is greater than the limiting value of 1.07 calculated for a 99% confidence level.[16] Thus the initial enantiomer chosen was judged to be correct.

Finally, the four carbon atoms bound to both uranium and phosphorus were given anisotropic thermal parameters, and all atoms were allowed to refine for three more cycles, producing final values of $R_1 = 0.047$ and $R_2 = 0.052$. No attempt was made to locate hydrogen atoms. A final difference Fourier with an estimated standard deviation of $\simeq 0.2$ e/Å^3 showed no peaks greater than 0.5 e/Å^3 or roughly 25% of a carbon atom other than noise peaks in the region of the uranium atoms. The final cycle of least-squares refinement yielded shifts no greater than 10% of their estimated standard deviations, except for those of the pentane carbons which were less than 50% of their estimated standard deviations.

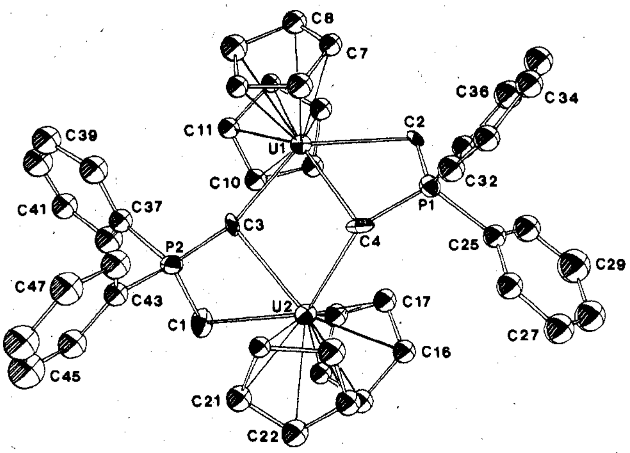

Figure 1. Perspective view of the $M\text{-}[(\mu\text{-}S\text{-CH})(CH_2)P(C_6H_5)U(C_5H_5)_2]_2$ molecule (thermal ellipsoids as drawn by ORTEP-II at the 20% probability level).

The final positional and thermal parameters for structures I and II are listed in Tables II and III. The bond lengths and bond angles are shown in Tables IV–VI. The cyclopentadienyl and phenyl C–C bond distances and angles are given in Tables VIII and IX,[17] and observed and calculated structure factors are given in Table X and XI.[17]

Description of the Structure

Since the molecular structures of I and II are almost identical, the bond distances and angles to be discussed here were obtained by averaging corresponding parameters in the two structures as well as those which are made equivalent by the approximate C_2 site symmetry of the molecule.

A perspective drawing $[(\mu\text{-CH})(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2$ is shown in Figure 1. The structure contains several inter-

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(17) Supplementary material.

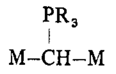
Table II. Positional and Thermal Parameters[a] with Standard Deviations for $[(\mu\text{-CH})(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2\cdot 0.5(C_2H_5)_2O$

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
U(1)	0.03844 (12)	0.33792 (8)	0.39289 (6)	73.6 (14)	19.6 (5)	22.1 (4)	−18.0 (15)	60.4 (12)	−5.4 (8)
U(2)	−0.20680 (12)	0.24506 (8)	0.23328 (6)	69.7 (13)	24.1 (6)	22.3 (4)	1.6 (16)	54.4 (11)	−3.8 (8)
P(1)	0.1692 (8)	0.2751 (5)	0.3259 (4)	72 (9)	23 (4)	22 (2)	−8 (9)	58 (8)	−4 (5)
P(2)	−0.3143 (8)	0.2634 (5)	0.3178 (4)	65 (9)	26 (4)	27 (3)	−2 (9)	62 (8)	−2 (5)

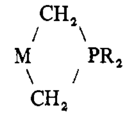
atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(1)	−0.393 (3)	0.301 (2)	0.242 (1)	2.7 (6)	C(27)	0.145 (4)	0.213 (2)	0.163 (2)	5.0 (9)
C(2)	0.198 (4)	0.370 (2)	0.359 (2)	4.6 (9)	C(28)	0.200 (4)	0.281 (3)	0.157 (2)	5.1 (9)
C(3)	−0.158 (3)	0.257 (2)	0.340 (2)	4.1 (7)	C(29)	0.234 (3)	0.347 (3)	0.196 (2)	4.9 (8)
C(4)	0.021 (3)	0.243 (2)	0.310 (1)	3.0 (6)	C(30)	0.228 (3)	0.352 (2)	0.248 (2)	4.0 (7)
C(5)	0.232 (4)	0.345 (3)	0.517 (2)	5.8 (10)	C(31)	0.296 (3)	0.200 (2)	0.375 (1)	2.3 (6)
C(6)	0.121 (4)	0.323 (3)	0.515 (2)	5.6 (9)	C(32)	0.268 (3)	0.124 (2)	0.382 (1)	3.4 (7)
C(7)	0.091 (4)	0.242 (3)	0.492 (2)	5.3 (9)	C(33)	0.364 (4)	0.065 (3)	0.417 (2)	5.4 (9)
C(8)	0.181 (4)	0.214 (2)	0.478 (2)	4.4 (8)	C(34)	0.492 (4)	0.093 (3)	0.450 (2)	5.3 (9)
C(9)	0.265 (4)	0.287 (3)	0.494 (2)	6.4 (11)	C(35)	0.522 (4)	0.167 (3)	0.443 (2)	5.0 (8)
C(10)	0.054 (3)	0.506 (2)	0.390 (2)	3.3 (7)	C(36)	0.424 (4)	0.222 (2)	0.405 (2)	4.4 (8)
C(11)	0.036 (4)	0.493 (3)	0.440 (2)	5.3 (9)	C(37)	−0.379 (3)	0.167 (2)	0.325 (1)	3.1 (6)
C(12)	−0.102 (3)	0.465 (2)	0.400 (2)	3.8 (7)	C(38)	−0.513 (3)	0.158 (2)	0.288 (2)	4.5 (8)
C(13)	−0.150 (3)	0.458 (2)	0.335 (2)	3.7 (7)	C(39)	−0.568 (4)	0.081 (3)	0.289 (2)	5.7 (10)
C(14)	−0.050 (3)	0.488 (2)	0.330 (2)	3.7 (7)	C(40)	−0.491 (4)	0.022 (3)	0.324 (2)	5.0 (9)
C(15)	−0.345 (4)	0.352 (3)	0.134 (2)	5.2 (9)	C(41)	−0.356 (4)	0.028 (2)	0.363 (2)	4.9 (9)
C(16)	−0.303 (4)	0.296 (3)	0.105 (2)	5.8 (10)	C(42)	−0.304 (3)	0.106 (2)	0.360 (2)	4.2 (8)
C(17)	−0.168 (4)	0.306 (3)	0.146 (2)	5.7 (10)	C(43)	−0.339 (3)	0.321 (2)	0.368 (2)	4.3 (8)
C(18)	−0.135 (3)	0.374 (3)	0.190 (2)	5.0 (9)	C(44)	−0.259 (3)	0.311 (2)	0.438 (2)	4.2 (8)
C(19)	−0.247 (4)	0.398 (2)	0.184 (2)	4.5 (8)	C(45)	−0.275 (4)	0.355 (2)	0.480 (2)	4.8 (8)
C(20)	−0.155 (4)	0.084 (3)	0.219 (2)	5.4 (9)	C(46)	−0.364 (4)	0.417 (3)	0.453 (2)	5.4 (9)
C(21)	−0.228 (4)	0.075 (3)	0.249 (2)	5.3 (9)	C(47)	−0.438 (4)	0.432 (3)	0.391 (2)	5.2 (9)
C(22)	−0.349 (4)	0.100 (3)	0.207 (2)	5.1 (9)	C(48)	−0.429 (3)	0.388 (2)	0.344 (2)	4.3 (8)
C(23)	−0.363 (4)	0.124 (3)	0.152 (2)	6.6 (11)	O	−0.015 (2)	0.031 (4)	0.488 (3)	7.6 (17)
C(24)	−0.245 (5)	0.115 (3)	0.160 (2)	6.6 (11)	C(E1)	0.03 (2)	−0.04 (1)	0.464 (8)	11.9 (49)
C(25)	0.179 (3)	0.284 (2)	0.258 (1)	2.8 (6)	C(E2)	0.07 (2)	−0.01 (1)	0.430 (8)	14.7 (53)
C(26)	0.141 (3)	0.208 (2)	0.219 (2)	3.7 (7)	C(E3)	−0.05 (2)	−0.01 (1)	0.526 (8)	12.0 (48)
					C(E4)	−0.11 (2)	0.07 (1)	0.538 (7)	13.0 (45)

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. Thermal parameters ×10^4 are given.

esting features, the most obvious being the manner in which the ylide is incorporated into the molecule. Each ylide is bonded to both uranium atoms, chelating one and bridging to the second with a single carbon. This mode of ylide attachment is unique in phosphorus ylide chemistry but might be considered as a hybrid of A and B, which are bonding schemes seen in other metal–ylide complexes.[5]



A



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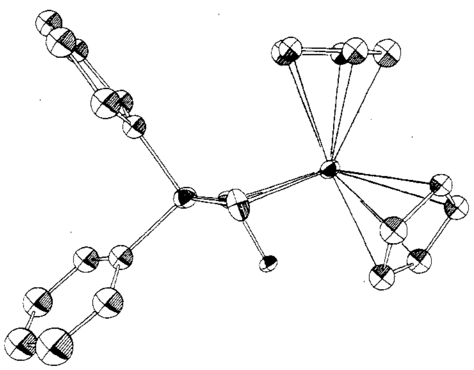

Figure 2. A view showing the fold angle about the C–U–C and C–P–C planes. A portion of the molecule has been removed for clarity. Ellipsoids of 20% probability are shown.

The U–C bonds in the U–C–U bridge, 2.43 (1) and 2.53 (2) Å, are both within the range found for U–C σ bonds in several tris(cyclopentadienyl)uranium–alkyl complexes: $(C_5H_5)_3U\text{-}(CH_2)_2CCH_3$,[18] 2.48 (3) Å; $(C_5H_5)_3U\text{-}C_4H_9$,[19] 2.426 (23) Å; $(C_5H_5)_3U\text{-}CH_2(p\text{-}CH_3C_6H_4)$,[19] 2.541 (15) Å. Thus, the bridging carbon can be considered to be σ bonded to both uranium atoms. Such an arrangement is unique in organoactinide chemistry. The most similar case is $[\eta^5\text{-}(C_5H_5)_2Th(\eta^5,\eta^1\text{-}C_5H_4)]_2$[26] where a cyclopentadienyl group bridges between two Th atoms, being bonded to one via a C–Th σ bond but to the second in a η^5 fashion. In contrast to the uranium–methine bonds, the U bond to the nonbridging methylene group is somewhat longer, 2.662 (5) Å, and, in fact, is closer to the bond length observed between uranium and η^5-cyclopentadienyl groups (range 2.68–2.74 Å, Table VII).

The conformation of the U-C-P-C ring is also significant with respect to the nature of the uranium–methylene bond. As shown in Figure 2, the C–U–C plane is folded with respect to the C–P–C plane. The fold angles in these two structures range from 25 to 28°, averaging 27 (1)°. Such folding has been observed before in a nickel complex[27] where the fold angle

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Table III. Positional and Thermal Parameters[a] with Standard Deviations for $[(\mu\text{-CH})(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2 \cdot C_2H_{12}$

atom	*x*	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
U(1)	0.13013 (8)	0.15453 (4)	0.23341 (9)	3.98 (6)	1.20 (2)	6.35 (11)	6.8 (7)	−4.9 (15)	−4.9 (8)
U(2)	0.29331 (8)	0.16871 (5)	0.45035 (10)	5.06 (7)	1.20 (2)	5.98 (10)	−5.3 (7)	−8.5 (15)	−9.1 (9)
P(1)	0.0912 (6)	0.0722 (4)	0.4223 (8)	4.3 (5)	1.9 (2)	7.6 (8)	−0.6 (5)	0.6 (10)	−0.7 (7)
P(2)	0.3529 (6)	0.2263 (3)	0.2377 (8)	5.0 (5)	2.2 (2)	6.9 (8)	−1.7 (5)	−3.0 (12)	0.7 (7)
C(1)	0.358 (2)	0.262 (1)	0.360 (3)	9 (3)	1 (1)	10 (3)	−3 (2)	4 (5)	0 (2)
C(2)	0.016 (1)	0.115 (1)	0.365 (2)	1 (1)	3 (1)	7 (3)	−2 (2)	−2 (4)	3 (3)
C(3)	0.280 (1)	0.174 (1)	0.250 (2)	4 (1)	1 (0)	8 (3)	−2 (2)	1 (4)	3 (2)
C(4)	0.190 (2)	0.102 (1)	0.389 (2)	4 (2)	3 (1)	3 (2)	0 (2)	−7 (3)	−2 (2)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
C(5)	0.196 (2)	0.092 (1)	0.070 (2)	4.3 (7)	C(30)	0.004 (2)	0.085 (1)	0.616 (3)	7.4 (11)
C(6)	0.158 (2)	0.052 (1)	0.133 (3)	5.8 (9)	C(31)	0.081 (2)	−0.004 (1)	0.385 (2)	4.7 (7)
C(7)	0.071 (2)	0.061 (1)	0.124 (2)	4.6 (8)	C(32)	0.149 (2)	−0.036 (1)	0.378 (3)	5.9 (9)
C(8)	0.048 (2)	0.106 (1)	0.062 (3)	5.5 (8)	C(33)	0.142 (2)	−0.098 (1)	0.358 (2)	5.2 (8)
C(9)	0.131 (2)	0.127 (1)	0.025 (3)	6.8 (9)	C(34)	0.060 (2)	−0.118 (1)	0.342 (3)	5.9 (9)
C(10)	0.132 (2)	0.272 (1)	0.255 (2)	5.4 (7)	C(35)	−0.011 (2)	−0.087 (1)	0.345 (3)	6.9 (10)
C(11)	0.112 (2)	0.265 (1)	0.146 (2)	5.0 (8)	C(36)	−0.007 (2)	−0.025 (1)	0.373 (3)	7.1 (10)
C(12)	0.030 (2)	0.237 (1)	0.136 (2)	4.1 (7)	C(37)	0.333 (2)	0.276 (1)	0.131 (3)	5.5 (9)
C(13)	0.000 (2)	0.230 (1)	0.237 (3)	5.8 (8)	C(38)	0.327 (2)	0.249 (1)	0.029 (3)	7.7 (11)
C(14)	0.059 (2)	0.252 (1)	0.310 (2)	5.5 (9)	C(39)	0.321 (2)	0.294 (1)	−0.062 (3)	8.2 (11)
C(15)	0.290 (2)	0.214 (1)	0.657 (2)	5.6 (8)	C(40)	0.321 (2)	0.347 (2)	−0.039 (3)	8.9 (11)
C(16)	0.211 (2)	0.180 (1)	0.640 (2)	5.4 (8)	C(41)	0.325 (2)	0.369 (1)	0.056 (3)	7.2 (10)
C(17)	0.158 (2)	0.206 (1)	0.566 (3)	5.7 (8)	C(42)	0.331 (2)	0.334 (2)	0.152 (3)	8.1 (11)
C(18)	0.196 (2)	0.258 (1)	0.538 (3)	5.9 (8)	C(43)	0.455 (2)	0.200 (1)	0.197 (2)	5.0 (8)
C(19)	0.276 (2)	0.260 (1)	0.590 (2)	5.1 (8)	C(44)	0.528 (2)	0.236 (1)	0.213 (3)	7.1 (10)
C(20)	0.422 (2)	0.096 (1)	0.395 (2)	3.7 (7)	C(45)	0.606 (3)	0.213 (2)	0.184 (4)	10.6 (15)
C(21)	0.462 (2)	0.144 (1)	0.448 (3)	5.6 (8)	C(46)	0.611 (2)	0.157 (2)	0.133 (3)	9.3 (12)
C(22)	0.439 (2)	0.144 (1)	0.559 (3)	6.2 (8)	C(47)	0.537 (3)	0.127 (1)	0.117 (3)	8.1 (11)
C(23)	0.386 (2)	0.094 (1)	0.568 (3)	5.5 (8)	C(48)	0.459 (2)	0.146 (1)	0.149 (3)	6.8 (9)
C(24)	0.373 (2)	0.067 (1)	0.476 (3)	6.2 (8)	C(P1)	0.746 (9)	0.069 (6)	0.370 (2)	28.5 (64)
C(25)	0.074 (2)	0.063 (1)	0.565 (3)	5.2 (8)	C(P2)	0.674 (8)	0.054 (5)	0.394 (11)	30.8 (55)
C(26)	0.135 (2)	0.035 (1)	0.624 (3)	6.4 (9)	C(P3)	0.729 (8)	0.078 (5)	0.510 (10)	26.1 (44)
C(27)	0.130 (3)	0.026 (1)	0.735 (3)	8.3 (10)	C(P4)	0.644 (6)	0.056 (4)	0.557 (9)	24.2 (39)
C(28)	0.060 (3)	0.045 (2)	0.782 (4)	9.3 (13)	C(P5)	0.711 (8)	0.043 (4)	0.648 (9)	28.5 (47)
C(29)	−0.004 (3)	0.074 (2)	0.723 (4)	11.3 (15)					

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. Thermal parameters $\times 10^3$ are given.

Table IV. Bond Lengths for $[(\mu\text{-CH})(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2$

atoms	dist, A		atoms	dist, A	
	I	II		I	II
U(1)–C(2)	2.67 (4)	2.65 (3)	U(2)–C(19)	2.73 (4)	2.79 (3)
U(1)–C(3)	2.44 (4)	2.45 (2)	U(2)–C(20)	2.81 (4)	2.77 (3)
U(1)–C(4)	2.55 (3)	2.53 (3)	U(2)–C(21)	2.86 (4)	2.77 (3)
U(2)–C(1)	2.66 (3)	2.67 (3)	U(2)–C(22)	2.83 (4)	2.78 (3)
U(2)–C(3)	2.48 (3)	2.57 (3)	U(2)–C(23)	2.75 (5)	2.74 (3)
U(2)–C(4)	2.41 (3)	2.40 (3)	U(2)–C(24)	2.71 (5)	2.74 (3)
U(1)–C(5)	2.72 (4)	2.77 (3)	P(1)–C(2)	1.73 (4)	1.74 (3)
U(1)–C(6)	2.72 (4)	2.77 (3)	P(1)–C(4)	1.76 (3)	1.79 (3)
U(1)–C(7)	2.74 (4)	2.78 (3)	P(1)–C(25)	1.83 (3)	1.86 (3)
U(1)–C(8)	2.79 (4)	2.80 (3)	P(1)–C(31)	1.85 (3)	1.85 (3)
U(1)–C(9)	2.70 (5)	2.74 (4)	P(2)–C(1)	1.73 (3)	1.78 (3)
U(1)–C(10)	2.78 (3)	2.77 (2)	P(2)–C(3)	1.73 (4)	1.70 (2)
U(1)–C(11)	2.84 (4)	2.83 (3)	P(2)–C(37)	1.83 (3)	1.82 (3)
U(1)–C(12)	2.82 (3)	2.80 (3)	P(2)–C(43)	1.79 (4)	1.83 (4)
U(1)–C(13)	2.79 (3)	2.73 (3)	groups[a]		
U(1)–C(14)	2.81 (4)	2.73 (3)	U(1)–11	2.53	2.49
U(2)–C(15)	2.76 (4)	2.84 (3)	U(1)–12	2.46	2.49
U(2)–C(16)	2.92 (4)	2.77 (3)	U(2)–21	2.51	2.52
U(2)–C(17)	2.76 (4)	2.76 (3)	U(2)–22	2.52	2.47
U(2)–C(18)	2.79 (4)	2.84 (3)			

[a] Group 11 = cp ring C(5)–C(9), group 12 = cp ring C(10)–C(14), group 21 = cp ring C(15)–C(19), and group 22 = cp ring C(20)–C(24).

is 44°, and the ylide was described as bonding in a "pseudophosphaallyl" fashion. The P–C methine and P–C methylene bonds are both 1.74 (1) Å, typical for such groups in other ylides, and are shorter than the typcial 1.87 Å P–C single-bond length in phosphorus alkyls[28] and the 1.83 (1) Å P–C bonds to the phenyl rings. Thus it is likely that the U–C methylene bond should not be considered as a σ bond but rather to have formed via interaction of metal orbitals with a π system on the ylide. The disparity in fold angles between I and II and the nickel complex mentioned above is probably the result of steric interactions between C_5H_5 and phenyl groups which preclude the formation of a more acute angle in I and II.

Within the uranium ylide chelate ring most of the bond angles and distances are similar to those found in transition-metal phosphoylide structures.[5] The main exception is the C–U–C angle (64.6 (6)°) which is about 15° less than typcial values in other chelating structures. This probably is the result of the larger size of the actinide and, perhaps, of steric interactions between cyclopentadienyl and phenyl moieties which prevent a closer approach of the ylide. The C(phenyl)–P–C(phenyl) angle (98.8 (1)°) is less than tetrahedral and may indicate such a steric interaction. It is also noteworthy that the U–C(methine)–P angle is highly distorted from tetrahedral to an average value of 142.5 (8)°.

The average U–C(cyclopentadienyl) distance is 2.78 (1) Å in I and 2.776 (7) Å in II. These are somewhat longer than the average U–C bond in the tris(cyclopentadienyl)uranium complexes (Table VII) and may also reflect large steric interactions within the molecule. However, they are shorter than the 2.81-Å U–C bond length in $U(C_5H_5)_4$,[25] a severely crowded molecule. The average ring centroid–U–ring centroid angle of 118° is essentially the same as that found in the tris(cyclopentadienyl) complexes[18-23] and indicates that steric strains are not relieved by compression of these groups.

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Table V. Selected Bond Angles for $[(\mu\text{-CH})(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2$

atoms	angles, deg I	angles, deg II	atoms	angles, deg I	angles, deg II	groups[a]	angles, deg I	angles, deg II
C(2)-U(1)-C(3)	130 (1)	133.4 (9)	C(2)-P(1)-C(4)	106 (2)	107 (1)	11-U(1)-12	119	119
C(4)-U(2)-C(1)	130 (1)	131 (1)	C(3)-P(2)-C(1)	103 (2)	106 (1)	11-U(1)-C(2)	104	103
C(2)-U(1)-C(4)	65 (1)	66.4 (9)	C(2)-P(1)-C(31)	114 (2)	113 (1)	11-U(1)-C(3)	106	104
C(1)-U(2)-C(3)	63 (1)	64.2 (8)	C(1)-P(2)-C(43)	114 (2)	112 (2)	11-U(1)-C(4)	112	109
C(4)-U(1)-C(3)	68 (1)	69.4 (9)	C(4)-P(1)-C(25)	116 (2)	114 (1)	12-U(1)-C(2)	95	95
C(4)-U(2)-C(3)	70 (1)	69.5 (8)	C(3)-P(2)-C(37)	114 (2)	114 (1)	12-U(1)-C(3)	103	104
U(2)-C(3)-U(1)	101 (1)	99.2 (9)	C(25)-P(1)-C(31)	102 (1)	98 (1)	12-U(1)-C(4)	128	131
U(2)-C(4)-U(1)	100 (1)	102 (1)	C(37)-P(2)-C(43)	96 (2)	99 (1)	21-U(2)-22	116	119
P(1)-C(4)-U(1)	93 (1)	92 (1)	C(2)-P(1)-C(25)	107 (2)	112 (1)	21-U(2)-C(1)	96	94
P(2)-C(3)-U(2)	96 (2)	94 (1)	C(1)-P(2)-C(37)	114 (2)	112 (1)	21-U(2)-C(3)	134	133
P(1)-C(4)-U(2)	144 (2)	142 (1)	C(4)-P(1)-C(31)	111 (1)	113 (1)	21-U(2)-C(4)	104	106
P(2)-C(3)-U(1)	140 (2)	143 (1)	C(3)-P(2)-C(43)	115 (2)	114 (1)	22-U(2)-C(1)	105	104
P(1)-C(2)-U(1)	90 (2)	89 (1)				22-U(2)-C(3)	108	107
P(2)-C(1)-U(2)	90 (1)	89 (1)				22-U(2)-C(4)	105	104

[a] See footnote in Table IV.

Table VI. Bond Lengths and Angles for the Solvate Molecules

atoms	dist, Å	atoms	angle, deg
		Pentane	
C(P1)-C(P2)	1.2 (2)	C(P1)-C(P2)-C(P3)	70 (11)
C(P2)-C(P3)	1.8 (2)	C(P2)-C(P3)-C(P4)	78 (8)
C(P3)-C(P4)	1.6 (2)	C(P3)-C(P4)-C(P5)	76 (8)
C(P4)-C(P5)	1.6 (2)		
		Diethyl Ether	
C(E4)-C(E3)	1.6 (3)	C(E4)-C(E3)-O	100 (13)
C(E3)-O	1.4 (2)	C(E3)-O-C(E1)	100 (11)
C(E1)-O	1.6 (2)	O-C(E1)-C(E2)	100 (14)
C(E2)-C(E2)	1.4 (2)		

Table VII. Average Uranium-Cyclopentadienyl Carbon Bond Distances (Å) for Several (η^5-Cyclopentadienyl)uranium(IV) Complexes

compd	distance	ref
$[(\mu\text{-CH})(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2$ (I)	2.78 (1)	this work
M-$[(\mu\text{-}S\text{-CH})(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2$ (II)	2.776 (7)	this work
$(C_5H_5)_3U[CH_3C(CH_2)_2]$	2.74 (1)	18
$(C_5H_5)_3U(n\text{-}C_4H_9)$	2.736 (8)	19
$(C_5H_5)_3U[CH_2(p\text{-}CH_3C_6H_4)]$	2.722 (4)	19
$(C_5H_4CH_2C_6H_5)_3UCl$	2.733 (1)	20
$(C_5H_5)_3U(C_2H)$	2.73 (5)	33
$(C_5H_5)_3U(C_2C_6H_5)$	2.68	21
$(C_5H_5)_3UF$	2.74	22
$(C_5H_5)_3UCl$	2.74	23
$LiU_2Cl_5[CH_2(C_5H_4)_2]_2\cdot 2THF$	2.72	24
$(C_5H_5)_4U$	2.81	25

The overall geometry about each uranium is approximately tetrahedral if the two η^5-C_5H_5 groups, the chelating ylide, and the bridging methine carbon atom on the remaining ylide are considered to define the vertices of a polyhedron. The U–U separation (3.810 (2) in I, 3.824 (2) Å in II) is at the limit of van der Waals interactions[29] for neutral uranium atoms, 3.8 Å, indicating that a U–U bond is highly unlikely. Thus if each cyclopentadienyl group is considered to occupy three coordination sites, the chelating phosphoylide to occupy two, and the bridging methine to occupy one, each uranium is nine-coordinate. This is the first example of a nine-coordinate U(IV) organometallic compound. This is noteworthy because organoactinides tend to be ten-coordinate.[3,30] Consequently we consider this molecule to be coordinatively unsaturated.

The complex is chiral. The space group of I, however, is achiral and the crystal is thus racemic. On the other hand, crystals of II contain only a single enantiomer, and the one present in the crystal studied here is shown in Figure 1. Both methine carbon atoms are centers of chirality and are of the same absolute configuration. Using standard sequence-rule procedures,[31,32] we have been unable to assign relative priorities to the two uranium-containing substituents, even though, relative to an individual methine carbon atom, they are clearly distinct in a topological sense. We have therefore assigned the uranium atom that is *not* chelated by the ylide containing the carbon atom whose configuration is being sought a *higher*

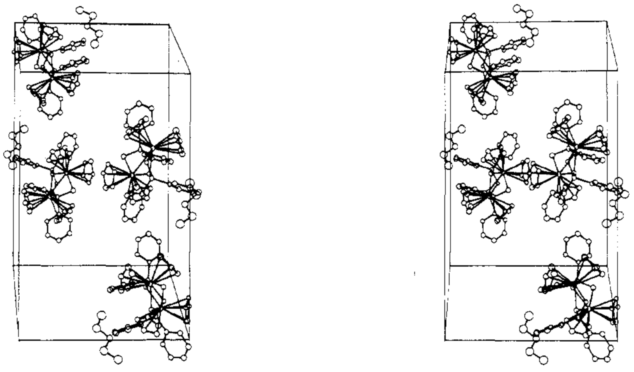

Figure 3. A stereoview (ORTEP-II) of the contents of a unit cell of $[(\mu\text{-CH})(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2\cdot 0.5(C_2H_5)_2O$. The b axis is horizontal, the c axis is vertical, and the view is along the a axis. Ellipsoids of 20% probability are used.

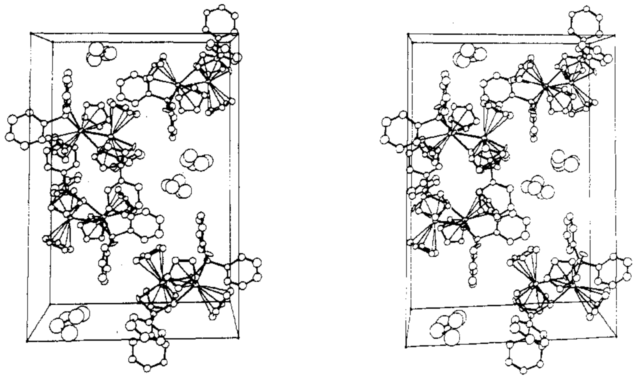

Figure 4. A stereoview (ORTEP-II) of the contents of a unit cell of M-$[(\mu\text{-}S\text{-CH})(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2\cdot C_5H_{12}$. The a axis is horizontal, the b axis is vertical, and the view is along the c axis. Ellipsoids of 20% probability are used.

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Inorg. Chem. **1980**, *19*, 2569–2573

priority than the one that is chelated by this ylide. Making this assignment gives both methine carbons an *S* configuration. There is also a helical axis of chirality collinear with the molecular twofold axis. The helix is left-handed and therefore *M*.

The solvate molecule in both structures does not associate with the uranium dimer. This can be seen in the stereoviews of the two structures in Figure 3 and 4. In structure I the closest interatomic contact of the diethyl ether solvate within the asymmetric unit is a 4.45 Å distance to a phenyl carbon. The closest contact to the dimer in an adjacent cell is 3.55 Å to a cyclopentadienyl carbon. In structure II the pentane molecule would not be expected to interact with the dimer and is not found to do so. The closest contact is 3.88 Å with a cyclopentadienyl carbon. Both of the solvate molecules are poorly determined with high thermal parameters. As a result their structural parameters are characterized by large errors and are of little merit.

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Registry No. I, 67771-71-5; II, 71685-94-4; $(C_5H_5)_3UCl$, 1284-81-7.

Supplementary Material Available: Listings of structure factor amplitudes and cyclopentadienyl and phenyl C–C bond distances and angles (Tables VIII–XI) (27 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, The Pennsylvania State University,
University Park, Pennsylvania 16802, and The University of Wisconsin, Madison, Wisconsin 53706

Synthesis and Spectroscopic Characterization of $H_3CoRu_3(CO)_{12}$. Crystal and Molecular Structure of the C_{3v} Isomer

WAYNE L. GLADFELTER,[1a] GREGORY L. GEOFFROY,*[1a] and JOSEPH C. CALABRESE[1b]

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The reaction of $HCoRu_3(CO)_{13}$ with H_2 in refluxing hexane gives the new cluster $H_3CoRu_3(CO)_{12}$ in 75% yield. Infrared and ^1H NMR spectra indicate that the cluster exists in two isomeric forms. The structure of one isomer has been determined by single-crystal X-ray diffraction. It crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.204$ (2) Å, $b = 13.615$ (4) Å, $c = 8.318$ (2) Å, $\alpha = 100.49$ (2)°, $\beta = 111.51$ (2)°, $\gamma = 81.78$ (2)°, $V = 950.1$ Å^3, and $Z = 2$. The structure was determined by the heavy-atom method and refined to $R_1 = 2.3\%$ and $R_2 = 3.6\%$. The $CoRu_3$ core of the molecule defines a distorted tetrahedron with three carbonyls terminally bound to each metal atom. The hydride ligands were located by difference Fourier techniques and bridge the three Ru–Ru bonds. The overall symmetry of the cluster is approximately C_{3v}. Spectral evidence indicates that the second isomer contains a bridging CO ligand and three nonequivalent hydrogens. The interconversion of the two isomers and the various hydrogen-exchange processes have been monitored by ^1H NMR spectroscopy, and the exchange mechanisms are discussed.

Comparison across a series of isoelectronic mixed-metal clusters with systematic metal variation can often provide valuable insight into the factors which affect bonding, stereochemistry, and stereochemical nonrigidity.[2,3] Mixed-metal clusters involving metals of neighboring groups are especially interesting since the change in the number of electrons contributed by each metal is usually accompanied by a change in the number of hydride ligands so as to maintain the proper electron count. The clusters $Co_4(CO)_{12}$,[4,5] $HCo_3Os(CO)_{12}$,[6] $H_2Co_2Os_2(CO)_{12}$,[7] $H_3CoOs_3(CO)_{12}$,[8] and $H_4Os_4(CO)_{12}$[9–11] constitute a Co–Os series of this type.

For the analogous Co–Ru series only $Co_4(CO)_{12}$, $HCo_3Ru(CO)_{12}$,[12,13] and $H_4Ru_4(CO)_{12}$[9,14] have been previously described. We recently reported the high-yield preparation of $HCoRu_3(CO)_{13}$[15] and have since found that treatment of this cluster with H_2 cleanly yields $H_3CoRu_3(CO)_{12}$, one of the remaining members of the Co–Ru series. Described herein are details of the synthesis of this compound, its spectroscopic

Table I. Data for the X-ray Diffraction Study of $H_3CoRu_3(CO)_{12}$

Crystal Parameters

cryst system: triclinic
space group: $P\bar{1}$
$V = 950.1$ Å^3
$Z = 2$
calcd density = 2.451 g cm^{-3}
temp = 22 °C

$a = 9.204$ (2) Å
$b = 13.615$ (4) Å
$c = 8.318$ (2) Å
$\alpha = 100.49$ (2)°
$\beta = 111.51$ (2)°
$\gamma = 81.78$ (2)°

Measurement of Intensity Data

diffractometer: Syntex $P\bar{1}$
radiation: Mo Kα (λ 0.710 73 Å)
monochromator: graphite crystal
scan method: θ–2θ (fixed background; background/scan time = 67)
scan speed: variable, 2–24°/min
scan range: 2°
takeoff angle: 4°
std reflctns: 2/50, 1% variation
data limits: $3° \leqslant 2\theta \leqslant 50°$
unique data: 3347
nonzero data: 3089 ($I \geqslant 2\sigma(I)$)
$p = 0.055$

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(1) (a) The Pennsylvania State University. (b) The University of Wisconsin.

(2) Such comparison has been made by utilizing the series $M_xM'_{4-x}(CO)_{12}$ (M, M′ = Co, Rh, Ir): Martinengo, S.; Chini, P.; Albano, V. G.; Cariati, F.; Salvatori, T. *J. Organomet. Chem.* **1973**, *59*, 379. Chini, P.; Heaton, B. T. *Top. Curr. Chem.* **1977**, *71*, 1.

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