Structure Solution and Refinement. The direct methods program MULTAN[34b] was employed for the solution of the structure and gave the coordinates of the central core atoms (Pd_2Cl_2). Difference Fourier methods[34e] were used in locating the remaining non-hydrogen atoms and in refining the coordinates and isotropic thermal parameters of all non-hydrogen atoms. Full matrix least-squares refinement of the parameters listed in Table IV but with anisotropic thermal parameters (supplementary material) for all Pd and Cl atoms and for C(1) of the solvent gave the reliability indices listed in Table III. At this stage, a test refinement of the occupancies of the non-hydrogen atoms of the solvent molecule led to values within two esd's of 100%; full occupancies therefore were retained. Idealized positions for the 26 hydrogen atoms (C–H = 0.95 Å) were calculated and included (with B_{iso} = 4.0 Å^2) in the final structure factor calculation. The maximum shift/error ratio of any variable parameter in the final cycle was less than 0.1. The maximum residuals on the final difference density synthesis were ±1.2 e Å^{-3} and were in the vicinity of Pd(2). An anisotropic refinement of all non-hydrogen atoms did converge ($R(F_o)$ = 0.060, N_v = 298), but the improvement in the model was not judged to be significant on the basis of Hamilton's confidence test.[35]

Atomic scattering factors and anomalous dispersion correction terms for all atoms were taken from standard tables.[36] Tables of all bond distances and angles, Pd, Cl, and C(1) anisotropic thermal parameters, fixed hydrogen atom positions, least-squares planes, and structure factors are available as supplementary material. Standard computer programs were employed in the data reduction and structure solution and refinement,[34] including Johnson's ORTEP-II for Figures 1–3.[34c]

Acknowledgment. We wish to thank Dr. K. Barkigia for helpful discussions. This research was carried out at Brookhaven National Laboratory under contract with the United States Department of Energy and supported by its Office of Basic Energy Sciences.

Registry No. 1, 91547-45-4; **2**, 91443-56-0; **3c**, 91443-46-8; **3d**, 91443-47-9; **4a**, 91443-48-0; **4b**, 91443-49-1; **4c**, 91443-50-4; **4e**, 82135-64-6; **4f**, 91443-51-5; **4g**, 91443-52-6; **4h**, 91443-53-7; **5c**, 91443-54-8; $Pd(CD_3CN)_2ClNO_2$, 91443-44-6; $Pd(CH_3CN)_2Cl^{15}NO_2$, 91443-45-7; $Pd(CH_3CN)_2Cl_2$, 21264-30-2; $Pd(CD_3CN)_2Cl_2$, 91443-55-9; $PdCl_2$, 7647-10-1; ethylene, 74-85-1; propylene, 115-07-1; isobutylene, 115-11-7; norbornene, 498-66-8; benzonorbornene, 4486-29-7; dicyclopentadiene, 77-73-6; bicyclo[2.2.2]oct-2-ene, 931-64-6; *cis*-2-butene, 590-18-1; allylbenzene, 300-57-2; 2-methyl-1-pentene, 763-29-1; methylenecyclohexane, 1192-37-6; cyclopentene, 142-29-0; cyclohexene, 110-83-8; cycloheptene, 628-92-2; *trans*-cyclooctene, 931-89-5; styrene, 100-42-5; acrylonitrile, 107-13-1; maleic anhydride, 108-31-6; 4,4-dimethyl-2-pentene, 26232-98-4.

Supplementary Material Available: Tables of bond distances, bond angles, anisotropic thermal parameters, fixed hydrogen atom positions, least-squares planes, and structure factors (17 pages). Ordering information is given on any current masthead page.

---

(34) Methods and computer programs in the Brookhaven Crystallographic Computing Library are described by: (a) Coppens, P.; Leiserowitz, L.; Rabinovich, D. *Acta Crystallogr.* **1965**, *18*, 1035–1038. (b) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *27A*, 368. (c) Johnson, C. K. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976. (d) Schlemper, E. O.; Hamilton, W. C.; LaPlaca, S. J. *J. Chem. Phys.* **1971**, *54*, 3990–4000. (e) McMullan, R. K., unpublished work. (f) Lundgren, J.-O. In "Crystallographic Computer Programs", Report UUJC-B13-4-05; Institute of Chemistry, University of Uppsala: Sweden, 1982.

(35) Hamilton, W. C. "Statistics in Physical Science"; Ronald Press: New York, 1964; p 157.

(36) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B. Cromer, D. T. *Ibid.*, Vol. IV, Table 2.3.1.

Structure and Bonding of a Nearly Homoleptic Uranium Phoshoylide Complex

Roger E. Cramer,*[†] Arthur L. Mori,[†] Richard B. Maynard,[†] John W. Gilje,*[†]
Kazuyuki Tatsumi,*[‡] and Akira Nakamura[‡]

Contribution from the Chemistry Department, University of Hawaii, Honolulu, Hawaii 96822, and Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan. *Received February 13, 1984*

Abstract: Golden crystals of $CpU[(CH_2)(CH_2)P(C_6H_5)_2]_3$, I, grown from diethyl ether belong to the space group $P2_1/c$ with the following unit-cell parameters: a = 14.062 (6) Å, b = 26.752 (3) Å, c = 24.220 (5) Å, β = 114.84 (2)°, V = 8268 (3) Å^3, Z = 8. Data collection, the solution of the structure, and refinement of the structural parameters preceeded routinely and converged at R_1 = 0.050 and R_2 = 0.060. The unit cell of I contains two nonsymmetry-related molecules IA and IB. The gross structure of both is pentagonal bipyramidal with a Cp and a CH_2 group occupying axial positions and five CH_2 moieties composing the equatorial plane. This molecule contains more actinide–carbon σ-bonding interactions than any previously characterized organoactinide complex, and they are the longest U–C σ distances, 2.66 (3) Å, yet reported. Extended Hückel molecular orbital calculations indicate significant covalent character to the U–C σ bonds in I, and an analysis of overlap populations provides an explanation for the observed structural parameters. Alternatively, the long U–C σ bonds can be rationalized in terms of an ionic bonding model.

Introduction

Phosphoylides are textbook examples of elimination stabilized alkyls that have been used to prepare homoleptic transition-metal complexes with very stable metal–carbon σ bonds.[1] As part of an ongoing investigation[2-7] of actinide–ylide chemistry, we have sought to exploit this property and have attempted the synthesis of organoactinide complexes containing many carbon–metal σ bonds.

Recently we reported[3] the synthesis of a structurally diverse and chemically interesting series of U(IV) ylide complexes.

[†] University of Hawaii.

[‡] Osaka University.

(1) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley-Interscience: New York, 1980; pp 1123–1140.

(2) Cramer, R. E.; Maynard, R. B.; Paw, J. C.; Gilje, J. W. *Organometallics* **1982**, *1*, 869–871.

(3) Cramer, R. E.; Maynard, R. B.; Gilje, J. W. *Inorg. Chem.* **1981**, *20*, 2466–2470.

(4) Cramer, R. E.; Maynard, R. B.; Gilje, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 5562–5564.

(5) Cramer, R. E.; Maynard, R. B.; Gilje, J. W. *Inorg. Chem.* **1980**, *19*, 2564–2569.

0002-7863/84/1506-5920$01.50/0

Table I. Crystal, Data Collection, and Reduction Parameters

compd	$CpU[(CH_2)(CH_2)P(C_6H_5)_2]_3$
formula	$C_{47}H_{47}P_3U$
fw	1073.028
a, Å	14.062 (6)
b, Å	26.752 (3)
c, Å	24.220 (5)
β, deg	114.84 (2)
V, Å^3	8268 (3)
Z	8
d(calcd), g/cm^3	1.72
space group	$P2_1/c$
cryst dimen, mm	0.08 × 0.14 × 0.48
cryst vol, mm^3	0.0057
radiatn	Mo K*α* (λ = 0.709 30 Å) from graphite monochromator
μ, cm^{-1}	38.65
trans factors	0.58–0.73
scan type	2*θ*
scan range, deg	2.0
2*θ* limits, deg	3.0–45.0
no. of variables	347
unique data measd	11036
unique data used ($F_o^2 > 3\sigma(F_o^2)$)	6590
observns/parameters	19.0
goodness-of-fit	1.46
R_1	0.050
R_2	0.060

Among these are several of formula $CpU[(CH_2)(CH_2)PR_2]_3$, Cp = η-C_5H_5. These complexes contain more metal–carbon σ-bonding interactions than any other reported organoactinide complex, two more than in $(C_6H_5CH_2)_4Th(dmpe)$ and $(C_6H_5CH_2)_3(CH_3)U(dmpe)$ for which X-ray structures have recently been published.[8] In this paper we report the X-ray crystal and molecular structure of $CpU[(CH_2)(CH_2)P(C_6H_5)_2]_3$, I, which is important both for the characterization of the $CpU[(CH_2)(CH_2)PR_2]_3$ class of molecules and for its relevance to the structural chemistry of the actinide–carbon σ bond.

The nature of the chemical bonding in organoactinide complexes is not yet well established. Since ylides are among the most powerful nucleophiles known and are capable of forming complexes with ionic metals (i.e., alkali-metal ions) as well as those which form more covalent bonds (e.g., group 8 metals),[9] their interaction with actinide ions provides an arena in which the concepts of ionic and covalent metal–carbon σ bonding can be tested. We, consequently, have examined the bonding in I from both a molecular orbital and an ionic viewpoint.

Experimental Section

Collection and Reduction of X-ray Data. Compound I was synthesized as previously described.[3] Golden, rod-shaped crystals grew from diethyl ether chilled to −15 °C overnight. A crystal was sealed in a capillary under dry N_2 and immobilized with Corning high-vacuum stopcock grease.

Data collection and reduction parameters are listed in Table I. The instrumentation, procedure, and programs used have been previously described,[6] except that the large data set and large number of atoms required some programs to be redimensioned. The cell constants were determined by least-squares methods from the centered angular coordinates of 15 intense reflections with 2*θ* values between 17.4° and 29.6°.

Atomic scattering factors for U^0, C^0, and P^0 were used.[10] Anomalous dispersion corrections wre made for all three types of atoms.[11] Hydrogen atoms were not included.

Structure Solution and Refinement. Systematic absences indicated space group $P2_1/c$. The two uranium atoms were located from a Patterson map, and all of the remaining atoms were located in subsequent Fourier maps. Refinement, using previously described rigid-group parameters for the aromatic rings,[7] proceeded routinely and converged at $R_1 = 0.050$ and $R_2 = 0.060$. In the last cycle of refinement no parameter shifted more than 4% of its estimated standard deviation. A final difference Fourier with an estimated standard deviation of $N = 0.02$ e/Å^3 showed no peaks larger than 0.7 e/Å^3 except for large ripples near the uranium atoms.

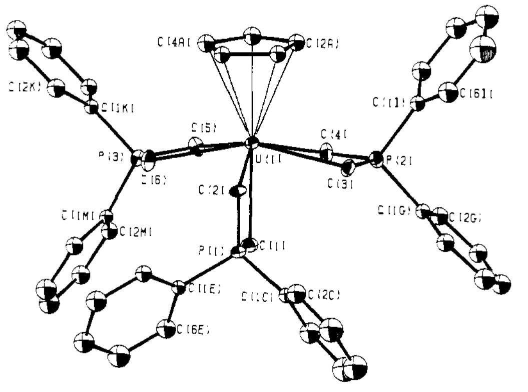


Figure 1. A labeled ORTEP view of $CpU[(CH_2)(CH_2)P(C_6H_5)_2]_3$, IA.

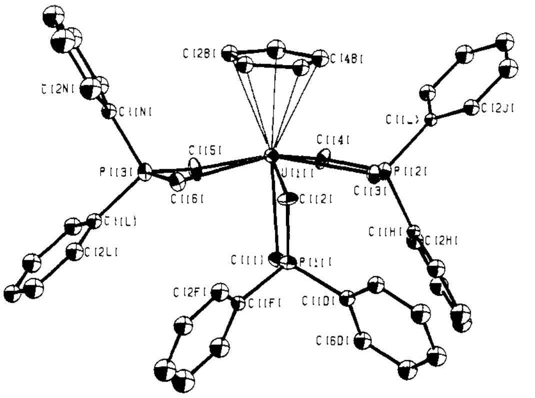


Figure 2. A labeled ORTEP view of $CpU[(CH_2)(CH_2)P(C_6H_5)_2]_3$, IB.

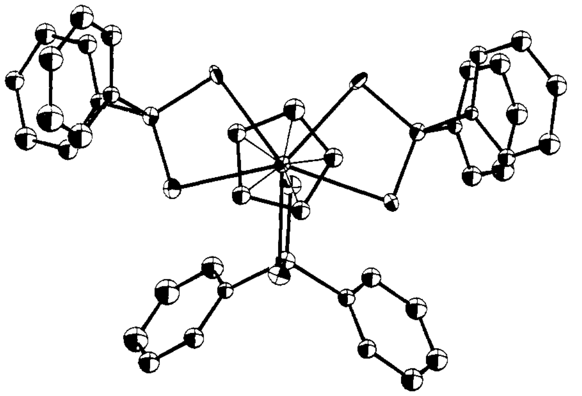


Figure 3. An ORTEP view down the Cp centroid–U axis of $CpU[(CH_2)(CH_2)P(C_6H_5)_2]_3$.

Results and Discussion

The unit cell of I contains two nonsymmetry-related molecules IA and IB. The molecular structures of IA and IB are shown in Figures 1 and 2, and bond angles and distances are listed in Tables II and III. The gross structure of both IA and IB is pentagonal bipyramidal, with the Cp centroid, U, and C(1) for IA or C(11) for IB being nearly linear and defining the axis of the polyhedron. The other five methylene carbon atoms that are bound to each uranium constitute the equatorial pentagon (see Figure 3) and are almost coplanar (Table IV).

While the structures of IA and IB are similar, there are statistically significant differences between them. The most important of these involves the extent to which the UCPC chelate rings are folded. In both IA and IB two are planar, while the third is

---

[6] Cramer, R. E.; Maynard, R. B.; Paw, J. C.; Gilje, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 3589–3590.

[7] Cramer, R. E.; Maynard, R. B.; Paw, J. C.; Gilje, J. W. *Organometallics* **1983**, *2*, 1336–1340.

[8] Edwards, P. G.; Anderson, R. A.; Zalkin, A. *Organometallics* **1984**, *3*, 293–298.

[9] Kaska, W. C. *Coord. Chem. Rev.* **1983**, *48*, 1–58.

[10] "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 78–87.

[11] Reference 10, pp 149–50.

Table II. Bond Angles (deg) for $CpU[(CH_2)(CH_2)P(C_6H_5)_2]_3$[a]

molecule 1A				molecule 1B			
C(1)	U(1)	C(2)	66.9 (4)	C(11)	U(11)	C(12)	66.8 (4)
C(3)	U(1)	C(4)	63.2 (4)	C(13)	U(11)	C(14)	65.7 (4)
C(5)	U(1)	C(6)	64.9 (5)	C(15)	U(11)	C(16)	63.5 (5)
C(1)	U(1)	C(3)	79.4 (4)	C(11)	U(11)	C(13)	76.6 (5)
C(1)	U(1)	C(4)	81.9 (5)	C(11)	U(11)	C(14)	85.1 (5)
C(1)	U(1)	C(5)	82.9 (5)	C(11)	U(11)	C(15)	84.1 (5)
C(1)	U(1)	C(6)	79.4 (5)	C(11)	U(11)	C(16)	79.6 (5)
C(2)	U(1)	C(3)	74.1 (4)	C(12)	U(11)	C(13)	71.7 (5)
C(2)	U(1)	C(6)	71.7 (4)	C(12)	U(11)	C(16)	73.7 (5)
C(4)	U(1)	C(5)	77.8 (4)	C(14)	U(11)	C(15)	77.2 (4)
C(2)	U(1)	C(4)	131.0 (4)	C(12)	U(11)	C(14)	133.2 (5)
C(2)	U(1)	C(5)	130.8 (4)	C(12)	U(11)	C(15)	131.8 (5)
C(3)	U(1)	C(5)	138.9 (5)	C(13)	U(11)	C(15)	139.1 (4)
C(3)	U(1)	C(6)	144.7 (5)	C(13)	U(11)	C(16)	143.6 (5)
C(4)	U(1)	C(6)	139.8 (5)	C(14)	U(11)	C(16)	138.9 (5)
C(1)	U(1)	CP-A	173.5 (4)	C(11)	U(11)	CP-B	170.3 (4)
C(2)	U(1)	CP-A	106.7 (3)	C(12)	U(11)	CP-B	104.4 (4)
C(3)	U(1)	CP-A	100.2 (4)	C(13)	U(11)	CP-B	97.1 (4)
C(4)	U(1)	CP-A	103.7 (4)	C(14)	U(11)	CP-B	99.2 (4)
C(5)	U(1)	CP-A	101.2 (4)	C(15)	U(11)	CP-B	105.3 (4)
C(6)	U(1)	CP-A	97.8 (4)	C(16)	U(11)	CP-B	102.2 (4)
C(1)	P(1)	C(2)	111.0 (6)	C(11)	P(11)	C(12)	111.2 (7)
C(3)	P(2)	C(4)	108.2 (7)	C(13)	P(12)	C(14)	108.8 (7)
C(5)	P(3)	C(6)	110.9 (7)	C(15)	P(13)	C(16)	105.6 (7)
C(1)	P(1)	C(1C)	110.9 (6)	C(11)	P(11)	C(1D)	110.8 (6)
C(1)	P(1)	C(1E)	109.0 (6)	C(11)	P(11)	C(1F)	109.7 (6)
C(2)	P(1)	C(1C)	110.7 (6)	C(12)	P(11)	C(1D)	112.4 (6)
C(2)	P(1)	C(1E)	112.7 (6)	C(12)	P(11)	C(1F)	110.6 (6)
C(1C)	P(1)	C(1E)	102.2 (5)	C(1D)	P(11)	C(1F)	101.8 (5)
C(3)	P(2)	C(1G)	112.1 (7)	C(13)	P(12)	C(1H)	111.0 (7)
C(3)	P(2)	C(1I)	111.0 (8)	C(13)	P(12)	C(1J)	111.4 (7)
C(4)	P(2)	C(1G)	113.4 (7)	C(14)	P(12)	C(1H)	110.7 (7)
C(4)	P(2)	C(1I)	110.0 (7)	C(14)	P(12)	C(1J)	110.1 (7)
C(1G)	P(2)	C(1I)	102.1 (7)	C(1H)	P(12)	C(1J)	104.7 (6)
C(5)	P(3)	C(1K)	109.7 (6)	C(15)	P(13)	C(1L)	114.7 (7)
C(5)	P(3)	C(1M)	111.6 (6)	C(15)	P(13)	C(1N)	109.7 (7)
C(6)	P(3)	C(1K)	110.7 (7)	C(16)	P(13)	C(1L)	113.3 (7)
C(6)	P(3)	C(1M)	110.1 (6)	C(16)	P(13)	C(1N)	110.9 (7)
C(1K)	P(3)	C(1M)	103.5 (5)	C(1L)	P(13)	C(1N)	102.8 (6)
U(1)	C(1)	P(1)	91.2 (6)	U(11)	C(11)	P(11)	90.6 (6)
U(1)	C(2)	P(1)	90.9 (5)	U(11)	C(12)	P(11)	91.4 (6)
U(1)	C(3)	P(2)	93.8 (6)	U(11)	C(13)	P(12)	92.6 (6)
U(1)	C(4)	P(2)	93.3 (6)	U(11)	C(14)	P(12)	92.9 (6)
U(1)	C(5)	P(3)	92.6 (6)	U(11)	C(15)	P(13)	93.5 (6)
U(1)	C(6)	P(3)	91.6 (6)	U(11)	C(16)	P(13)	94.7 (6)

[a] CP-A and CP-B represents the centroid of the η-C_5H_5 group in IA and IB, respectively.

puckered, the folded ring being U(1)–C(3)–C(4)–P(2) in IA and U(11)–C(15)–C(16)–P(13) in IB (Table V). Both planar and folded MC_2P chelate rings have been observed in other metal–ylide complexes,[4] but it is not clear whether a particular conformation results from crystal packing or from some more fundamental electronic effect. In any event, the energy difference between the two conformations is probably small, and the one adopted by an individual ring may well be the result of a number of small, subtle effects. Within the ylide ligands bond angles and distances are normal, being very similar to those in the other uranium–ylide complexes which we have characterized.[4–7]

Both IA and IB are crowded molecules and close contacts are summarized in Table VI. Intramolecular ligand–ligand repulsions clearly influence the structure of I. The uranium lies above the equatorial plane toward the Cp group, 0.55 Å in IA and 0.54 Å in IB (Table IV). This placement may arise from steric repulsion between the Cp and the equatorial CH_2 moieties that displace the equatorial carbon atoms away from the positions they would occupy in the idealized polyhedron (but see below for possible electronic reasons for the observed conformation). Even with this distortion the separation of the centroids of the Cp rings and equatorial pentagons, 3.06 Å in IA and 3.05 Å in IB, is much less than the sum of the radius of an aromatic ring, 1.85 Å, and a CH_2 group, 2.0 Å.[12] As one would expect, the Cp ring is staggered with respect to the equatorial pentagon of CH_2 groups (see Figure 3). All nonbonded interactions between these atoms are short, the smallest being 3.26 Å between C(13) and C(4B) and the longest 3.83 Å between C(15) and C(3B). Similar distortions

Table III. Bond Distances (Å) for $CpU[(CH_2)(CH_2)P(C_6H_5)_2]_3$[a]

molecule 1A			molecule 1B		
U(1)	C(1)	2.26 (1)	U(11)	C(11)	2.65 (1)
U(1)	C(2)	2.64 (1)	U(11)	C(12)	2.63 (1)
U(1)	C(3)	2.70 (1)	U(11)	C(13)	2.68 (1)
U(1)	C(4)	2.68 (1)	U(11)	C(14)	2.63 (1)
U(1)	C(5)	2.67 (1)	U(11)	C(15)	2.67 (1)
U(1)	C(6)	2.70 (1)	U(11)	C(16)	2.67 (1)
U(1)	CP-A	2.512 (7)	U(11)	CP-B	2.511 (7)
P(1)	C(1)	1.77 (2)	P(11)	C(11)	1.76 (2)
P(1)	C(2)	1.76 (1)	P(11)	C(12)	1.76 (1)
P(2)	C(3)	1.71 (2)	P(12)	C(13)	1.75 (2)
P(2)	C(4)	1.77 (1)	P(12)	C(14)	1.80 (1)
P(3)	C(5)	1.75 (1)	P(13)	C(15)	1.79 (1)
P(3)	C(6)	1.75 (2)	P(13)	C(16)	1.74 (2)
P(1)	C(1C)	1.81 (1)	P(11)	C(1D)	1.81 (1)
P(1)	C(1E)	1.797 (9)	P(11)	C(1F)	1.82 (1)
P(2)	C(1G)	1.82 (1)	P(12)	C(1H)	1.82 (1)
P(2)	C(1I)	1.79 (1)	P(12)	C(1J)	1.82 (1)
P(3)	C(1K)	1.81 (1)	P(13)	C(1L)	1.82 (1)
P(3)	C(1M)	1.82 (1)	P(13)	C(1N)	1.81 (1)

[a] CP-A and CP-B represent the centroid of the η-C_5H_5 group in IA and IB, respectively.

---

(12) Weast, R. C., Ed. "CRC Handbook of Chemistry and Physics", 59th ed.; CRC Press: West Palm Beach, FL, 1978; p D-230.

Table IV. Planes and Dihedral Angles in $CpU[(CH_2)(CH_2)P(C_6H_5)_2]_3$

Displacement (Å)	
plane 1:	plane 11:
C(2) = 0.15	C(12) = 0.10
C(3) = −0.15	C(13) = −0.06
C(4) = 0.09	C(14) = −0.01
C(5) = 0.05	C(15) = 0.09
C(6) = −0.15	C(16) = −0.12
U(1) = −0.55[a]	U(11) = −0.54[a]
plane 2:	plane 12:
rigid group A = 0.00	rigid group B = 0.00
U(1) = 2.51[a]	U(11) = 2.51[a]
plane 3:	plane 13:
rigid group C = 0.00	rigid group D = 0.00
P(1) = 0.11[a]	P(11) = 0.08[a]
plane 4:	plane 14:
rigid group E = 0.00	rigid group F = 0.00
P(1) = 0.04[a]	P(11) = 0.09[a]
plane 5:	plane 15:
rigid group G = 0.00	rigid group H = 0.00
P(2) = 0.16[a]	P(12) = 0.07[a]
plane 6:	plane 16:
rigid group I = 0.00	rigid group J = 0.00
P(2) = 0.09[a]	P(12) = 0.03[a]
plane 7:	plane 17:
rigid group K = 0.00	rigid group L = 0.00
P(3) = 0.08[a]	P(13) = 0.08[a]
plane 8:	plane 8:
rigid group M = 0.00	rigid group N = 0.00
P(3) = 0.16[a]	P(13) = 0.01[a]
Dihedral Angle (deg) between Planes	
plane 1/plane 2 = 1.7	plane 11/plane 12 = 4.2

[a] Atoms not used in calculation of the planes.

Table V. Fold Angles (deg) within the U–C–P–C Chelate Ring

atoms defining plane I	atoms defining plane II	fold angle
C(1), U(1), C(2)	C(1), P(1), C(2)	2.9
C(3), U(1), C(4)	C(3), P(2), C(4)	12.8
C(5), U(1), C(6)	C(5), P(3), C(6)	0.9
C(11), U(11), C(12)	C(11), P(11), C(12)	0.1
C(13), U(11), C(14)	C(13), P(12), C(14)	0.6
C(15), U(11), C(16)	C(15), P(13), C(16)	17.7

are evident in $(\eta\text{-}C_6H_6)U[Cl_2AlCl_2]_3$,[13] which also has a pentagonal-bipyramidal structure, and $CpUCl_3.2THF$,[14] in which the uranium is octahedrally coordinated. It is becoming clear from these and related structures[15] that intramolecular, nonbonded interactions often have significant influence on the structures of organoctinide complexes.

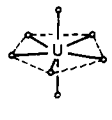
Befitting the interactions between the Cp and the equatorial CH_2 groups, the U–C(Cp) distances are long and are comparable to those in Cp_4U[16] (Table VII). In fact, these distances are long in all the uranium-ylide complexes that have been characterized.[4–7] These complexes are structurally dissimilar, and, when coordination number is defined as the number of electron pairs involved in ligand to metal coordination, the coordination number of the uranium ranges from 9 to 11. Nonetheless, their U–C(Cp) distances are remarkedly similar, 2.79 ± 0.01 Å. If appropriate ionic radii for uranium, calculated by the method outlined by Raymond,[17] are subtracted from the U–C(Cp) distances, effective Cp radii of 1.72 –1.76 Å are obtained for the ylide complexes. This range exceeds the 1.64 ± 0.04 Å radius previously assigned[17] to this group in actinide–Cp complexes and clearly indicates that U–Cp distances are more varied than previously supposed.

Table VII. Uranium(IV)–Carbon Bond Distances in Organouranium Complexes (Å)

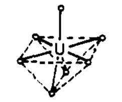
compound	U–C(Cp)	U–C(σ)	ref
$CpU[(CH_2)(CH_2)P(C_6H_5)_2]_3$	2.79 (1)	2.66 (3)	this work
$[Cp_2U]_2[\mu\text{-}CHP(C_6H_5)_2CH_2]_2$	2.78 (1)	2.43 (1) 2.53 (2) 2.66 (3)	4
$CpUCHP(CH_3)_2(C_6H_5)$	2.79 (3)	2.29 (3)	7
$Cp_3U(OCCH)P(CH_3)(C_6H_5)_2$	2.80 (3)	2.37 (2)	2
$Cp_3U(n\text{-}C_4H_9)$	2.74 (8)	2.43 (2)	28
$Cp_3U(CH_2)\text{-}p\text{-}(CH_3C_6H_4)$	2.722 (4)	2.54 (2)	28
$Cp_3U[(CH_2)C(CH_2)(CH_3)]$	2.74 (1)	2.48 (3)	29
$Cp_3UC{\equiv}CH$	2.73 (6)	2.36 (3)	27
$Cp_3UC{\equiv}CC_6H_5$	2.68	2.33 (2)	30
Cp_4U	2.81 (2)		31

The average U–C σ bond distance is 2.66 (3) Å, calculated by using all such bonds in IA and IB. This is the same as the U–CH_2 distance in $[Cp_2U]_2[\mu\text{-}CHP(C_6H_5)_2CH_2]_2$;[7,8] these are the longest U–C σ bonds yet reported. While the uranium–carbon bonds in I are long, normal metal–carbon bond lengths have been observed in cases both where the $[(CH_2)(CH_2)PR_2]^-$ ligand is chelating,[18] $([Me_2P(CH_2)(CH_2)]Ni)_2[\mu\text{-}(CH_2)(CH_2)PMe_2]_2$ and $Co[(CH_2)(CH_2)PMe_2](CH_3)_2(PMe_3)_2$, and nonchelating,[19] $M_2[\mu\text{-}(CH_2)(CH_2)PMe_2]_4$, M = Cr, Mo. However, long metal–carbon distances have been observed not only in I but also in $[Cp_2U]_2[\mu\text{-}CHP(C_6H_5)_2CH_2]_2$[4,5] and $([(CH_2)(CH_2)PMe_2]_2Zr)_2(\mu\text{-}CPMe_3)_2$.[20] It is not clear to us why chelating ylides produce long bonds in some cases and normal bonds in others, but we do note that the reported cases of long bonds involve metals in high oxidation states.

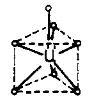
Molecular Orbital Analysis of the Structure. Extended Hückel calculations,[21] using the parameters outlined in the Appendix, were carried out on the simplified model compound $CpU[(CH_2)(CH_2)PH_2]_3$, IC. Our attention was directed to two issues: why molecule I chooses the structure that it possesses and the possibility of an electronic origin of the long U–C σ bonds. Geometrical features characteristic of I are the pentagonal-bipyramidal arrangement of ligands **2** and the displacement of U out of the equatorial plane. Other possible idealized seven-coordinate structures include a tetragonal-face-capped trigonal prism **3**, a trigonal-face-capped prism **4**, a capped octahedron **5**, and a square-base trigonal-cap **6**.[22–24]



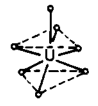
2



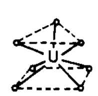
3



4



5



6

We have attempted to roughly optimize the geometry of IC. Of the seven-coordinate structures **4–6** are immediately ruled out

---

(13) Cesari, M.; Pedretti, U.; Zazzetta, A.; Lugli, G.; Marconi, W. *Inorg. Chem. Acta* **1971**, *5*, 439–44.

(14) Ernst, R. D.; Kennelly, W. J.; Day, C. S.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 2656–2664.

(15) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, C. S.; Vollmer, S. H.; Day, V. W. *Organometallics* **1982**, *1*, 170–180.

(16) Burns, J. H. *J. Organomet. Chem.* **1974**, *69*, 225–233.

(17) Raymond, K. N.; Eigenbrot, C. W., Jr. *Acc. Chem. Res.* **1980**, *13*, 276–283.

(18) Schmidbaur, H. *Acc. Chem. Res.* **1975**, *8*, 62–70.

(19) Cotton, F. A.; Hanson, B. E.; Ilsley, W. H.; Rice, G. W. *Inorg. Chem.* **1979**, *18*, 2713–2717.

(20) Rice, G. W.; Ansell, G. B.; Modrick, M. A.; Zentz, S. *Organometallics* **1983**, *2*, 154–157.

(21) (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397–1412. (b) Tatsumi, K.; Hoffmann, R. *Inorg. Chem.* **1980**, *19*, 2656–2658. (c) Tatsumi, K.; Nakamura, A., submitted for publication in *J. Organomet. Chem.*

(22) Hoffmann, R.; Beier, B. F.; Mutterties, E. L.; Rossi, A. R. *Inorg. Chem.* **1977**, *16*, 511–522.

(23) Britton, D.; Dunitz, J. D. *Acta Crystallogr., Sect. A* **1973**, *A29*, 362–371.

(24) King, R. B. *J. Am. Chem. Soc.* **1969**, *91*, 7211–7216.

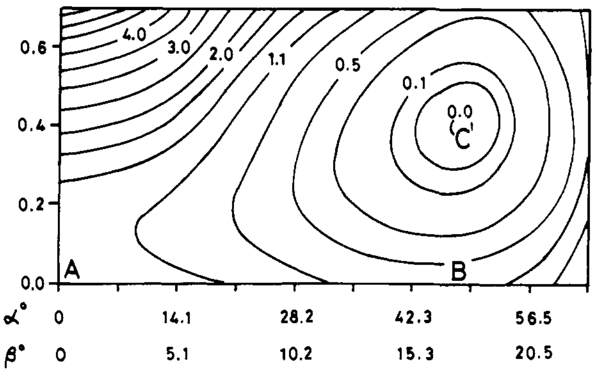
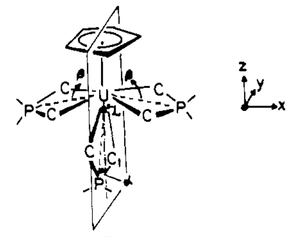


Figure 4. Pontential energy surface for the polytopal change (α, β) and the UCp group moving out of the equatorial plane (L). The geometrical parameters in $CpU[(CH_2)(CH_2)PH_2]_3$ are defined in **7**. The contours are in electronvolt units.

by inspection, simple because none of their coordination sites provides enough room for the Cp group. Thus **2** and **3** are the idealized limiting geometries that the molecule might assume, with Cp occupying the axial site of **2** or the capping site of **3**. To describe the variation between these structures, the parameters α and β were defined as shown in **7**. These define the three U-P vectors with respect to the z and y axes: the P-U-($-z$) angle, α, describes the lower ylide ligand with respect to the yz plane and β denotes the movement of the upper two ylides in the equatorial xy plane. At $\alpha = \beta = 0°$, the molecule assumes the structure **3**. From that point, the parameters were simultaneously varied to $\alpha = 56.5°$ and $\beta = 20.5°$, a geometry near **2** in that five carbon atoms and U are in the xy plane. Starting from this conformation, and while keeping U-C(ylide) and U-C(Cp) fixed at 2.66 and 2.79 Å, respectively, the distance L between U and the equatorial plane was independently varied. As the CpU unit was moved, the planarity of the U-C-P-C linkages was maintained.



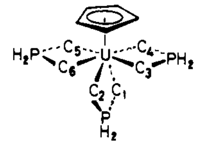
7

Figure 4 shows the computed potential energy surface as a function of α (or β) and L. An energy minimum appears at $\alpha = 48°$ and $L = 0.4$ Å. The tetrangonal-face-capped trigonal prism **3** was calculated to be 1.3 eV less stable. In the optimum structure, which is close to the idealized polyhedron **2**, the five carbon atoms C_2–C_6 are nearly planar and the Cp centroid-U–C_1 angle is 165°. These calculated parameters can be compared with the observed values of L (Table IV) of 0.55 and 0.54 Å and the observed Cp-U–C(1) and Cp-U–C(11) angles of 173.5 (4) and 170.3 (4)°, respectively. Given the approximate nature of the optimization, the agreement with the structure observed for I is very satisfactory.

Consider the three geometries labeled A, B, and C in the potential surface. A corresponds to **3** at $\alpha = \beta = 0°$ and $L = 0$ Å. Motion from A to B rearranges the ligand set, so that the molecule becomes nearly pentagonal bipyramidal with the U atom in the equatorial plane. Finally C is the conformation at the potential minimum. Let us examine how IC is stabilized upon rearrangement from A to B to C. The analysis will consist of an inspection of overlap populations for the U–C(ylide) bonds as well as those for ylide–ylide and ylide–Cp interactions. The evolution of these quantities P(U-C), P(Y-Y), and P(Y-Cp) along the sequence A → B → C is listed in Table VIII.

Focusing on the ligand–ligand repulsive interactions, we see that P(Y–Y) becomes less negative from A to B and likewise for P(Y–Cp) from B to C. The congestion of ligands in A appears to be eased in two distinct ways. The pentagonal-bipyramidal arrangement of ligands minimizes ylide–ylide repulsions and a relief of ylide–Cp nonbonded interactions is achieved by the displacement of U out of the plane. This is a steric rationale of the geometrical choice.

Table VIII. Overlap Population in the Three Geometries of $CpU[(CH_2)(CH_2)PH_2]_3$



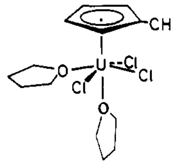
	A[a] $\alpha = 0°$, $L = 0$ Å	B $\alpha = 48°$, $L = 0$ Å	C $\alpha = 48°$, $L = 0.4$ Å
P(Y-Y)[b]	−0.099	−0.042	−0.067
P(Y-Cp)[c]	−0.165	−0.169	−0.053
P(U-C_1)	0.249	0.279	0.269
P(U-C_2)	0.249	0.250	0.251
P(U-C_3)	0.251	0.250	0.247
P(U-C_4)	0.251	0.257	0.258
P(U-C_5)	0.253	0.257	0.259
P(U-C_6)	0.253	0.249	0.249
P(U-C_{all})	1.506	1.542	1.531

[a] Geometries labeled in Figure 1. The parameters α and L are defined in **7**. [b] The sum of all ylide-ylide interactions. [c] The sum of all ylide-cyclopentadienyl interactions.

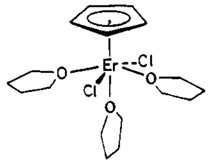
There is, however, another interesting feature in Table VIII. The U-C bonding interactions P(U–C_{all}) grow large at B. From the overlap populations calculated for individual U-C bonds, we can trace this trend to the behavior of P(U–C_1). This is consistent with the tendency of axial bonds to be marginally stronger than equatorial ones in pentagonal-bipyramidal complexes.[22] For IC the U–C_1 bond strength increases as C_1 shifts to a near axial position, while net weakening of the other U-C bonds does not occur. Consequently the movement of one ylide carbon into an axial position stabilizes the molecule.

For C, P(U–C_1) is larger than the other U-C overlap populations, but not by much. If such a difference implies trends in U–C bond lengths, they probably would involve small differences. From our X-ray data there is no statistically significant difference between U-C(axial) and U–C(equatorial) σ bonds in IA and IB. A quick glance at Table III shows that the distances to the ylide containing P_1, U–C_1, and U–C_2 are indistinguishable, but these distances are shorter than the U-C distances to the other two ylides. The average U-C distance to the unique ylide is 2.635 (12) Å, which is about 2σ shorter than the average of the remaining U–C bonds, 2.675 (22) Å. Thus there is some structural support for a view that the bonds to both of the carbons of the unique ylide are shorter than those to the other two ylides.

We should also note that the electronic reasoning used here can be applied only when the number of equatorial ligands is five or more. The molecules $(\eta^5\text{-}CH_3C_5H_4)UCl_3(THF)_2$,[14] **8**, and $CpErCl_2(THF)_3$,[25] **9**, have structures very similar to I but contain only four equatorial ligands. In these cases, the axial bond is not necessarily stronger than the equatorial ones. In particular, Er–O_{ax} is clearly longer than Er–O_{eq}.[25]



8



9

Now we turn to the long U-C(ylide) σ bonds. When viewed within a broader framework of uranium–ylide structural chemistry, one sees that U-C distances are remarkably diverse. They range

---

(25) Day, C. S.; Day, V. W.; Ernst, R. D.; Vollmer, S. H. *Organometallics* **1982**, *1*, 998–1003.

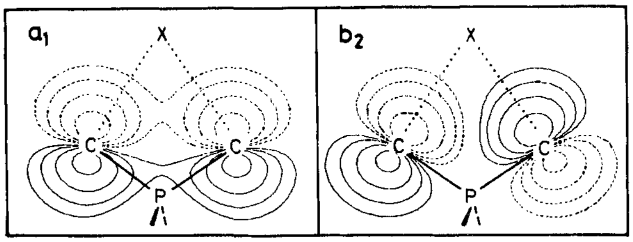


Figure 5. Countour plots of the a_1 and b_2 orbitals of $(CH_2)(CH_2)PH_2$. The countour levels of the wave functions are ±0.025, ±0.05, ±0.10, and ±0.20 in atomic units. The mark X indicates the position of an uranium atom when the ligand is coordinated to it.

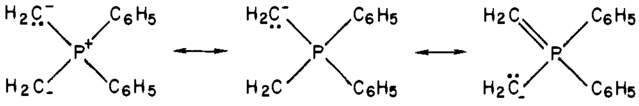
from 2.66 (3) Å in I to 2.29 (3) Å in $Cp_3UCHP(C_6H_5)(CH_3)_2$,[4,5] which is the shortest U–C distance known.[6,7] Table VII summarizes the observed U–C(ylide) bond lengths together with U–C(R) distances in several Cp_3U–R complexes. Steric crowding or ligand–ligand repulsion cannot be the cause of the long U–C(ylide) bond in I, for the U(IV) compounds in Table VII are all crowded molecules. Instead, the variation of distances may reflect differences in covalent bond strengths. The extended Hückel calculations support this view.

The presence of significant covalency in U–C σ bonds has been noted by Tatsumi and Hoffmann.[26] From comparison of the calculated Fe–C(methyl) and U–C(methyl) overlap populations they concluded that covalency of U–C σ bonds is not much less than in Fe–C σ bonds. However, there is a very small overlap population, thus weak covalent character, for U–Cp π bonds. These trends hold true for IC. The U–Cp overlap population is as small as −0.032 in C, while the average of $P(U\text{–}C_n)$ (n = 1–6) is 0.255.

Extended Hückel calculations were performed on Cp_3UCHPH_3 (a model for $Cp_3UCHPPhMe_2$), Cp_3UCH_3 (a model for Cp_3UCH_2R), and $CP_3UC{\equiv}CH$ using U–C bond lengths of 2.4 Å. The U–C overlap populations P(U–C) were computed to be 0.567, 0.397, and 0.596, respectively. The large P(U–C) in Cp_3UCHPH_3 and $Cp_3UC{\equiv}CH$ arise from partial multiple-bond character in their U–C bonds where U–C π interactions contribute 0.151 for Cp_3UCHPH_3 and 0.104 for $Cp_3UC{\equiv}CH$ to P(U–C). On the other hand, P(U–C) for IC is only 0.255 and is even smaller than that in Cp_3UCH_3. The calculated overlap populations, which decrease in the order of $Cp_3UC{\equiv}CH \simeq Cp_3UCHPH_3 > Cp_3UCH_3 > CpU[(CH_2)(CH_2)PH_2]_3$, correlate well with the observed U–C bond lengths, the small value of P(U–C) for IC being associated with the long U–C bond in I.

Why is the overlap population so small in IC? That it is not a result of the long, 2.66-Å, U–C bond in the model compound was proven by calculations on IC with U–C distances of 2.4 Å. At this closer separation, P(U–C) increases only slightly to 0.266. However, the small P(U–C) and the long U–C distances in I do reflect the orientation and spatial extension of a lone pair on each ylide carbon atom. Figure 5 shows contour plots of the a_1 and b_2 molecular orbitals calculated for the free ligand $[(CH_2)(CH_2)PH_2]^-$. These comprise the in-phase and out-of-phase combinations of the two lone-pair orbitals. The mark X indicates the position that U occupies when $[(CH_2)(CH_2)PH_2]^-$ coordinates to it. As can be seen in Figure 5, the orbital lobes deform outward from the lines drawn between X and the carbon atoms, more so for the a_1 orbital. Thus, the ylide lone pairs are unable to assume their best orientation toward a central U atom, resulting in the U–C(ylide) overlap being smaller than that in a U–C(alkyl) bond. Furthermore, molecule I carries five ylide carbon atoms approximately in the xy plane and slight repulsive interactions between the lone pairs on adjacent ylides will further reduce the size of the orbital lobes pointing inward. This may be another reason for the decrease in the U–C(ylide) interactions in I.

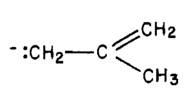
Classical ionic bonding agruments provide a different and interesting perspective on the relationship between the U–C σ bond distances and the formal charge localized on the α-carbon atom of the parent ylide anion. According to Pauling's ionic model[31] interionic distance, R, can be related to the charge of the anion, Z_-, and cation Z_+, by $R\ \alpha[1/Z_-Z_+]^{1/n-1}$. The *ratio* of anion charges within a series of compounds in which *all* factors except Z_- are constant can be calculated from this equation if interionic distances and the Born exponent, n, are known. Table VII summarizes U–C distances in a number of U(IV) compounds. The assignment of charges to the α-C atoms in any of these compounds cannot be precise, but, if the U–C bonds are totally ionic and there is no charge delocalization within a saturated alkyl carbanion, a 1− charge would occur at the α-C atom of $n\text{-}C_4H_9^-$. Using this charge and the U–C distance of 2.43 Å found in $Cp_3UC_4H_9$ as standards,[28] while assuming $n = 9$, then, from the uranium–carbon distances in Table VII, formal negative charges of 0.49− and 1.61− can be calculated for the α-carbon atoms in $(CH_2)(CH_2)P(C_6H_5)_2^-$ and $HCP(CH_3)_2(C_6H_5)^-$, respectively. These lie within the range of negative charges predicted from the resonance structures



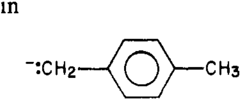
and

$$H\ddot{\underset{..}{C}}{}^{-}\text{—}P^{+}(CH_3)_2(C_6H_5) \longleftrightarrow H\ddot{C}{=}P(CH_3)_2(C_6H_5)$$

Likewise formal negative charges of 0.85− and 0.70− can be estimated for the α-carbons in



and



In both of these ligands charge should delocalize to a greater extent than in $CH_2CH_2CH_2CH_3$. It is satisfying that the calculated charges are in agreement with expected trends. We should point out that, since these values are derived from a ratio, their relative magnitudes will be correct even if some charge delocalization away from the α-carbon atom in $-CH_2CH_2CH_2CH_3$ does occur.

Of course these simple ionic charge agruments are fraught with uncertainties. Not only do they demand the estimation of ionic charge on a particular carbon atom, but also they ignore next nearest-neighbor repulsions and attractions, effects of differing metal coordination number, differences in univalent ligand radii, and the whole question of covalent participation in uranium–carbon bonding.

Acknowledgment. The support of this work by the National Science Foundation through Research Grant CHE 8210244 (J.W.G. and R.E.C.) and a Science Faculty Professional Development Grant (A.L.M.) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Appendix

The extended Hückel parameters are as follows. H_{ii}: U 7s, −5.50 eV; U 7p, −5.50 eV; U 6d, −5.09 eV; U 4f, −9.01 eV; U 6p, −30.03 eV; P 3s, −18.6 eV; P 3p, −14.0 eV; C 2s, −21.4 eV; C 2p, −11.4 eV; H 1s, −13.6 eV. Orbital exponents: U 7s,7p, 1.914; U 6d, 2.581 (0.7608) + 1.207 (0.4126); U 5f 4.943 (0.7844) + 2.106 (0.3908); U 6p, 4.033; P 3s,3p, 1.60; C 2s,2p, 1.625; H 1s, 1.3. Exponents of the Slater-type uranium orbitals were estimated from the relativistic Dirac–Fock wave functions of Desclaux.[32] The U 7s, 7p, and 6p orbitals are of single-ζ type,

---

[26] Tatsumi, K.; Hoffmann, R. *Inorg. Chem.*, in press.

[27] Atwood, J.; Tsutsui, M.; Ely, N.; Gebala, A. E. *J. Coord. Chem.* **1976**, *5*, 209–215.

[28] Perego, G.; Cesari, M.; Farina, F.; Lugli, G. *Acta Crystallogr., Sect. B* **1976**, *B32*, 3034–3039.

[29] Halstead, G. W.; Baker, E. C.; Raymond, K. N. *J. Am. Chem. Soc.* **1975**, *97*, 3049–3055.

[30] Atwood, J. L.; Cesari, M.; Farina, F.; Gebala, A. E. *J. Chem. Soc., Chem. Commun.* **1973**, 452–3.

[31] Pauling, L. "The Nature of the Chemical Bond", 3rd Ed., Cornell University Press: Ithaca, NY, 1960.

[32] Desclaux, J. P. *At. Data Nucl. Data Tables* **1973**, *12*, 311.

5926 *J. Am. Chem. Soc.* **1984**, *106*, 5926-5933

exponents of which were determined from R_{max} radius of maximum radial density, of the U $7s_{1/2}$ function. For the double-ζ paremeters of U 6d and 5f, we used R_{max}, $\langle r \rangle$, and $\langle r^2 \rangle$ of U $6d_{5/2}$ and $6d_{3/2}$ and those of U $5f_{7/2}$ and $5f_{5/2}$, respectively. H_{ii} values were also taken from the Desclaux's functions.[32] In transforming the relativistic functions of U 6d, 5f, and 6p to nonrelativistic ones, weighted averages of each multiplet was used. The parameters for the other elements are standard ones. In the calculations, the weighted H_{ij} formula was used.

Assumed geometries not given in the text are as follows. $CpU[(CH_2)(CH_2)PH_2]_3$: P–C = 1.8 Å; P–H = 1.42 Å; C–C(Cp) = 1.42 Å; C–H = 1.09 Å; C–P–C = 109.47°. $Cp_3UC{\equiv}CH$: C≡C = 1.25 Å.

Registry No. I, 77357-87-0; IC, 91443-30-0.

Supplementary Material Available: Table VI, nonbonded intramolecular contacts of less than 3.5 Å, Table IX, positional parameters for $CpU[(CH_2)(CH_2)P(C_6H_5)_2]_3$, Table X, thermal parameters for $CpU[(CH_2)(CH_2)P(C_6H_5)_2]_3$, Table XI, parameters for the rigid groups, and Table XII, observed and calculated structure factors for $CpU[(CH_2)(CH_2P(C_6H_5)]_3$ (31 pages). Ordering information is given on any current masthead page.

Alkylation of Salts of the Triosmium Anions $[Os_3\{eq\text{-}\eta^1\text{-}C(O)CH_3\}(CO)_{11}]^-$, $[Os_3\{\mu\text{-}O{=}C(CH_3)\}(CO)_{10}]^-$, and $[Os_3\{C(O)R\}\{\mu\text{-}H;\mu\text{-}O{=}C(CH_3)\}(CO)_9]^-$, R = CH_3 or C_6H_5. Crystal and Molecular Structure of $Os_3\{1\text{-}\eta^1\text{-}C(OCH_3)CH_3\}\{1,2\text{-}\mu\text{-}H;1,2\text{-}\mu\text{-}O{=}C(CH_3)\}(CO)_9$

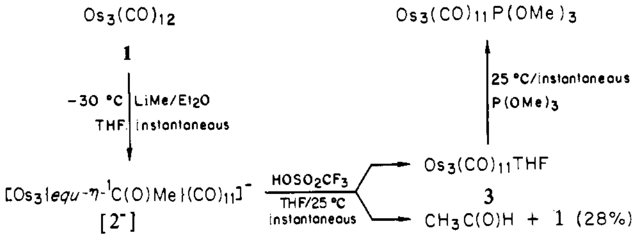
C. M. Jensen, C. B. Knobler, and H. D. Kaesz*

Contribution from the Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024. *Received January 9, 1984*

Abstract: Treatment of $Os_3(CO)_{12}$ with methyl lithium at 0 °C converts it instantly into $[Li][Os_3\{eq\text{-}\eta^1\text{-}C(O)CH_3\}(CO)_{11}]$, [Li][**2a**]. [Li$^+$] or [bis(triphenylphosphine)nitrogen(1+)] *N* salts of [**2a**$^-$] are resistant to alkylation by $CH_3OSO_2CF_3$ in tetrahydrofuran solution. Replacement of THF by $CHCl_3$ is accompanied by loss of CO to give the μ-acyl complex, $[Os_3\{\mu\text{-}O{=}C(CH_3)\}(CO)_{10}{}^-]$, [**4**$^-$]. This anion is slowly alkylated by $CH_3OSO_2CF_3$ in $CHCl_3$ solution to form a highly unstable bis(acyl) complex $Os_3\{C(O)CH_3\}\{\mu\text{-}O{=}C(CH_3)\}(CO)_9$, **5**. Attempts to purify **5** by chromatography on a silica gel column result in its disproportionation to $Os_3\{1\text{-}C(OMe)Me\}\{1,2\text{-}\mu\text{-}H;1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_9$, **7a**, and $Os_3\{1,2\text{-}\mu\text{-}OH;1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_{10}$, **8**. Alkylation of [**4**$^-$] with $CD_3OSO_2CF_3$ produces $Os_3\{C(O)CD_3\}\{\mu\text{-}O{=}C(CH_3)\}(CO)_9$, **5**-$d_3$. Addition of water to a chloroform solution of **5**-d_3 converts it to a mixture of **7a**-d_6, $Os_3\{1\text{-}\eta^1\text{-}C(OCD_3)CD_3\}\{1,2\text{-}\mu\text{-}H;1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_9$ and **8**. Due to the presence of halide salts, small amounts of $Os_3\{1,2\text{-}\mu\text{-}X;1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_{10}$, **6a**, X = Cl, or **6c**, X = I, are obtained as minor byproducts in these systems. Chromatography of **7a**-d_6 on silica gel is accompanied by H/D exchange of the carbene methyl group to give **7a**-d_3, $Os_3\{1\text{-}\eta^1\text{-}C(OCD_3)CH_3\}\{1,2\text{-}\mu\text{-}H;1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_9$. Treatment of $Os_3\{1,2\text{-}\mu\text{-}H;1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_{10}$, **9**, with LiR at −30 °C produces $[Li][Os_3\{\eta^1\text{-}C(O)R\}\{1,2\text{-}\mu\text{-}H;1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_9]$, [Li][**10a** or **10b**] (a, R = Me, **b**, R = Ph). Warming the solution to 25 °C and treating it with a slight excess of $R'OSO_2CF_3$ leads to formation of $Os_3\{1\text{-}\eta^1\text{-}C(OR')R\}\{1,2\text{-}\mu\text{-}H;1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_9$, **7a** (R = R′ = Me), **7b** (R = Me, R′ = Et) and **7c** (R = Ph, R′ = Et) in 68, 80, and 42% yields respectively. A small amount of **6b** (X = Br) is also obtained. The crystal and molecular structure of **7a** was determined at −158 °C: orange crystals are monoclinic of space group $P2_1/n$ with $a = 9.578$ (4) Å, $b = 13.494$ (4) Å, $c = 15.187$ (6) Å, $\beta = 96.30$ (3)°, $V = 1951$ (1) Å^3, $Z = 4$, and $\rho_{calcd} = 3.15$ g cm^{-3} (Mo Kα = 0.71069 Å^3). The structure was solved and refined by using 2728 observed ($I > 3\sigma(I)$) independent reflections measured on a Syntex P$\bar{1}$ automated diffractometer in the range $0° < 2\theta < 50°$. An absorption correction was applied ($\mu = 195.66$ cm^{-1}). Refinement converged at $R = 0.050$ and $R_w = 0.061$. The molecule consists of a triangle of osmium atoms, Os(1)–Os(2) = 2.934 (2) Å, Os(1)–Os(3) = 2.852 (1) Å, and Os(2)–Os(3) = 2.892 (1) Å, bridged on the longest edge by an acetyl group and a hydrogen atom on opposite sides of the trimetal plane. The carbene group is terminally bonded on Os(1) to which is also coordinated the oxygen of the bridging acetyl group.

In the 18 years since the isolation of the first heterocarbene complex by Fischer and Maasböl,[1] there had been no report of the synthesis of such a functional group on a cluster complex prior to recent isolation of $Os_3\{1\text{-}\eta^1\text{-}C(OMe)Me\}\{1,2\text{-}\mu\text{-}H;1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_9$ (**7a**, Scheme I).[2a] Di- and trinuclear complexes containing a μ-C(OMe)Ph group have been formed by reaction of $M\{C(OMe)Ph\}(CO)_5$ (M = Cr or W) with zerovalent platinum complexes;[2b] this involves migration or transfer of the preformed Fischer carbene group. A triiron complex containing the η^1-$CS_2(CH)_2$ group has been obtained in the reaction of 1,3-dithiole-2-thione with $Fe_2(CO)_9$.[2c]

Scheme I



In the present work, acyl anions are formed instantaneously by attack of a nucleophile on a carbonyl group, but subsequent alkylation is slow and fraught with complications.[3] We here report

---

[1] Fischer, E. O.; Maasböl, A. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 580–581.

[2] (a) Jensen, C. M.; Lynch, T. J.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1982**, *104*, 4679–4680. (b) Ashworth, T. V.; Berry, M.; Howard, J. A. K.; Laguna, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1615–1624. (c) Benoit, A.; Le Marouille, J.-Y.; Mahe, C.; Patin, H. *J. Organomet. Chem.* **1982**, *233*, C51–C54.

0002-7863/84/1506-5926$01.50/0