iments, Professor Lloyd Jackman for helpful discussions, and Thomas Neenan and Richard Fitzpatrick for supplying the benzo-15-crown-5.

Registry No. 15-crown-5, 33100-27-5; [15-crown-5][Me_3Al], 114491-48-4; [15-crown-5][Et_3Al], 114491-49-5; Et_2AlBr, 760-19-0; Et_2AlI, 2040-00-8; Pr_2AlI, 53211-90-8; Me_2AlBr, 3017-85-4; Me_2AlI, 2938-72-9; $Et_2AlBr_2^-$, 88873-39-6; $Et_2AlI_2^-$, 114491-50-8; [Pr_2Al(15-crown-5)]$^+$[Pr_2AlI_2]$^-$, 114491-53-1; Me_2Al(benzo-15-crown-5)$^+Br^-$, 114504-78-8; Me_2Al(benzo-15-crown-5)$^+I^-$, 114504-79-9; EtAlBr(15-crown-5)$^+$, 114504-77-7; EtAlI(15-crown-5)$^+$, 114491-54-2.

Crystal and Molecular Structure of an Oxo-Centered Bis[(pentamethylcyclopentadienyl)uranium]magnesium Phosphoylide Complex

Roger E. Cramer,* Michael A. Bruck, and John W. Gilje*

Chemistry Department, University of Hawaii, Honolulu, Hawaii 96822

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The crystal and molecular structure of a novel oxo-centered trimetal cluster of two uraniums and one magnesium has been determined by X-ray diffraction in the hexagonal space group $P6_522$ (No. 179); cell parameters: $a = b = 17.578$ (5) Å, $c = 46.813$ (7) Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 12527$ (5) Å^3, with $R = 0.0634$, $R_w = 0.0575$, and $R_G = 0.0641$. A Cp* is coordinated to each of the two uraniums, and the two are connected by two bridging $[CH_2P(Ph)_2CH_2]^-$ ligands. Chlorides bridge between each uranium and the magnesium, and the coordination sphere about magnesium is completed by two $CH_2{=}PMePh_2$ molecules. In addition to the μ_3-oxo ligand, the two uraniums are also bridged by a μ_2-oxide.

Organo-f-element oxo complexes are rare. Among the actinides, several complexes in which Cp_3An^+ (An = U or Th)[1] or Cp_2U^{2+} groups[2] are coordinated to polyoxoanions have been structurally characterized. In addition, mixed oxyhydroxides containing CpU fragments may have been prepared, and $[Cp_3U]_2O$ has been mentioned, but no complete characterization of any of these species has yet appeared.[3] A few organolanthanide complexes containing an oxo ligand are known,[7] including one which contains a μ_5-O.[8] In addition, catalysts that are postulated to contain organo-f-element fragments bound to a support through oxide bridges have been reported.[9] To add to this body of data, we report the structure of a novel compound, $\{Cp^*U[\mu\text{-}(CH_2)P(Ph)_2(CH_2)]\}_2Mg[CH_2PMePh_2]_2(\mu_3\text{-}O)(\mu_2\text{-}O)(\mu_2\text{-}Cl)_2$ (**1**; Cp* = $(CH_3)_5C_5^-$, Me = CH_3, Ph = C_6H_5), in which two organouranium moieties and an organomagnesium group are linked by μ_2- and μ_3-oxides.

Table I. Crystal, Data Collection, and Reduction Parameters for 1

formula	$C_{76}H_{88}Cl_2MgO_2P_4U_2{}^a$
fw	1728.71^a
space group	$P6_522$ (No. 179)
$a = b$, Å	17.578 (5)
c, Å	46.813 (7)
$\alpha = \beta$, deg	90
γ, deg	120
V, Å^3	12527 (5)
Z	6
D(calcd), g/cm^3	1.32
μ, cm^{-1}	39.03
transmissn coeff	0.81–1.08
radiatn	Mo Kα, λ = 0.71073 Å
scan type	Ω
scan rate, deg/min	2–24
2θ range, deg	3–35
total observns	8859
unique observns	4661
unique data with $I > 3\sigma(I)$	1590
no. of parameters	161
R^b	0.0634
$R_w{}^b$	0.0575
$R_G{}^b$	0.0641

^{a}Excludes solvent molecule. $^b R = \sum(|F_o - F_c|)/\sum(F_o)$, $R_w = \sum(|F_o - F_c|(w)^{1/2}/\sum(F_o(w)^{1/2})$, and $R_G = [\sum(|F_o - F_c|^2)/\sum(F_o)^2]^{1/2}$, where $w = 1/\sigma^2(F)$.

In contrast to a well-documented transition-metal chemistry,[10] oxo-centered trimetallic clusters of the f-elements are very rare. In addition to μ_3-oxides in several minerals and oxyhalides,[11] only $(UO_2)_2U_2O_2(OC_6H_5)_{10}(THF)_4$[12] and $U_4O_2(O_2CNEt_2)_4$,[13] which contain two U_3O units

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[3] While $[Cp_3U]_2O$ has been mentioned in the secondary literature,[4] its characterization and properties are not reported in the primary literature or in the habilitation thesis[5] where its synthesis is described. An incompletely characterized bright green precipitate, which is postulated to be an oxyhydroxide, forms in basic aqueous solutions of Cp_3UCl.[6]

[4] See, for example: Kanellakopulos, B. In *Organometallics of the f-Elements*; Marks, T. J., Fischer, R. D., Eds.; D. Reidel: Boston, 1978; pp 1–35.

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Table II. Bond Distances (Å) for 1[a]

Cl–U	2.928 (9)	C1–U	2.85 (2)
C2–U	2.87 (3)	C3–U	2.86 (2)
C4–U	2.83 (2)	C5–U	2.82 (3)
C11–U	2.67 (3)	C12′–U	2.60 (3)
O1–U	2.13 (2)	O2–U	2.18 (2)
U–U	3.437 (3)	Cl–Mg	2.79 (1)
O2–Mg	1.94 (4)	C41–Mg	2.23 (4)
C11–P1	1.72 (3)	C12–P1	1.73 (3)
C21–P1	1.82 (3)	C31–P1	1.88 (2)
C41–P2	1.75 (4)	C42–P2	1.84 (4)
C51–P2	1.85 (2)	C61–P2	1.82 (2)
C6–C1	1.50 (5)	C7–C2	1.60 (5)
C8–C3	1.57 (4)	C9–C4	1.57 (5)
C10–C5	1.53 (4)	Cp–U	2.58

[a] Cp represents the centroid of the pentamethylcyclopentadienide group.

joined by a shared triangle edge, $U_3(O)(OCMe_3)_{10}$,[14] which contains an isolated M_3O unit, and a polyoxoanion complex, $[Cp_2U]_2[OTiW_5O_{19}]_2^{4-}$,[2] have been previously reported.

Experimental Section

During our investigations of phosphoylide–actinide chemistry[15] we have examined the reactions of $Cp^*{}_2AnCl_2$ with $Li(CH_2)(CH_2)PR_2$. In 1:1 molar ratios $Cp^*{}_2An(Cl)[(CH_2)(CH_2)PR_2]$ forms in good yield.[16] However, during one experiment a single crystal, which was subsequently shown to be 1, grew in an NMR tube containing $Cp^*{}_2UCl_2$ and $Li(CH_2)(CH_2)Ph_2$ in THF-d_8. Since this crystal did not resemble $Cp^*{}_2U(Cl)[(CH_2)(CH_2)PPh_2]$, we determined its structure by X-ray crystallography. We have subsequently attempted to prepare 1 by the careful hydrolysis of $Cp^*{}_2U(Cl)[(Ch_2)(CH_2)PPh_2]$ in the presence of $MgCl_2$ or Cp*MgCl. While we are continuing our efforts, we have not yet been able to develop a rational synthesis of 1.

The crystal of 1 was mounted in a thin-walled glass capillary under dinitrogen. Crystal, data collection, and refinement parameters are listed in Table I. The instrumentation, procedures, and programs used have been previously described.[17] Atomic scattering factors for C^0, H^0, Cl^0, O^0, P^0, and Mg^0 were supplied by SHELX-76[18] and that for U^0 was taken from the literature.[19] Cell constants were determined by least-squares methods from the centered angular coordinates of 15 intense reflections with 2θ values between 15° and 21°. Data were corrected for absorption based on a single psi scan.

Due to the low quality of the crystal a large, high-quality data set could not be obtained. (Data could only be obtained to $2\theta = 35°$, and of the 4661 unique data only 34% were larger than 3σ.) In addition the very long c axis and large unit cell caused some overlapping peaks. An instrumental problem caused "spiking" in some peaks, and 19 reflections were removed from the data set for that reason. As a result of these problems a merging R of 0.077 was obtained, and the resulting metrical parameters are of low accuracy.

Systematic absences indicated space group $P6_522$ or $P6_122$. The uranium position was deduced from the Patterson map and yielded $R = 0.1949$. A Fourier map revealed the location of four second-row atoms. When all four of these atoms were input as phosphorus, an R of 0.1479 resulted in space group $P6_522$. After many Fourier maps the remaining atoms were located and the phenyl and Cp* ring carbons were refined as rigid groups by using the parameters in SHELX-76 to yield $R = 0.0767$. At this point the enantiomeric space group $P6_122$ was evaluated but found to yield a higher R of 0.0871.

After absorption correction, a series of calculations were carried out to establish the identities of the oxygen, magnesium, and chlorine atoms. First the structure was converged with all first-row atoms input as carbon and all second-row atoms as phosphorus, yielding R = 0.0734. Two atoms, identified as O1 and O2 in the final structure, were between 2.1 and 2.2 Å from uranium. Since negative thermal parameters were obtained when these two atoms were refined as carbons and since their separation from uranium is short for a U–C bond, they were input as oxygen. As a result of the lower $R = 0.0729$ and reasonable thermal parameters the assignment of these atoms as oxygens was retained. We assume that oxygen resulted from contamination of the reaction by water. Deprotonation of H_2O by $[(CH_2)(CH_2)PPh_2]^-$ would also produce the CH_2PMePh_2 ligands which are coordinated to the Mg ion.

Connectivity indicated that the atom which is identified as Cl is not a phosphorus. In addition, when it was refined as phosphorus, its thermal parameters were the smallest of all of the second-row atoms, suggesting that it is a heavier atom than phosphorus. Refining this atom as a chlorine resulted in a lower R of 0.0721 and reasonable thermal parameters. Since $Cp^*{}_2UCl_2$ was a starting material, the presence of Cl is reasonable.

As the thermal parameters of the atom identified as Mg were large when it was refined as a phosphorus and since the connectivity would be quite unusual if it is a phosphorus, alternative atoms were considered. Assuming U^{4+} and the identities of the other atoms in the structure, a divalent ion is necessary for charge balance. The separation of this atom from both oxygen and chlorine is correct for magnesium (see Results and Discussion), and when it was refined as Mg, the R value dropped to 0.0717 and the thermal parameters decreased to those shown in Table V. Since $Cp^*{}_2UCl_2$ was synthesized with a Grignard reagent, the presence of some magnesium is plausible. In summary, all atoms identified in this structure could result from the starting materials and water. The connectivity and distances are reasonable for the structure presented, the charge balance is correct, and all atom assignments are supported by decreases in the error index and improvements in thermal parameters.

The unit cell volume suggested the presence of a solvent molecule, and six weak peaks could be located in a difference map. It was not possible through various refinements to identify whether these atoms were carbon or oxygen, nor to identify the molecule conclusively. It was necessary to refine the solvent molecule with a common thermal parameter for all six atoms. Atom O76 would not refine as a full atom, and occupancy refinement led to an occupancy of about $^1/_3$. The final model is that of ether with the oxygen atom disordered over two sites, O71 and O76. A single variable, X, was refined for the occupancy of O71, with the occupancy of O76 refined as $1 - X$. X refined to 0.66 (9). Including the solvent molecule significantly lowered R to 0.0634. In the last cycle of refinement, no parameter shifted by more than 25% of its estimated standard deviation, except for some of the solvent parameters which shifted by as much as 1.3σ and were oscillating. The final difference map was noisy with peaks and holes about 1 e/Å^3. Attempted refinement of several of the largest of these peaks failed. At this point we concluded that the structure was complete.

Results and Discussion

The molecule of 1 contains a crystallographic twofold axis that passes through the three unique atoms O1, O2, and Mg. The molecule is chiral because of the orientation of the phosphoylide groups bound to Mg which destroy the symmetry plane which contains the three metal ions (Figure 2). Rotation about the Mg–C41 bond, which would be expected to be rapid in solution, would yield a time-averaged nonchiral configuration.

The basic structural feature of 1 is an oxo-centered trimetal cluster composed of two uraniums and a magnesium. The two uraniums, the magnesium, and the oxygen

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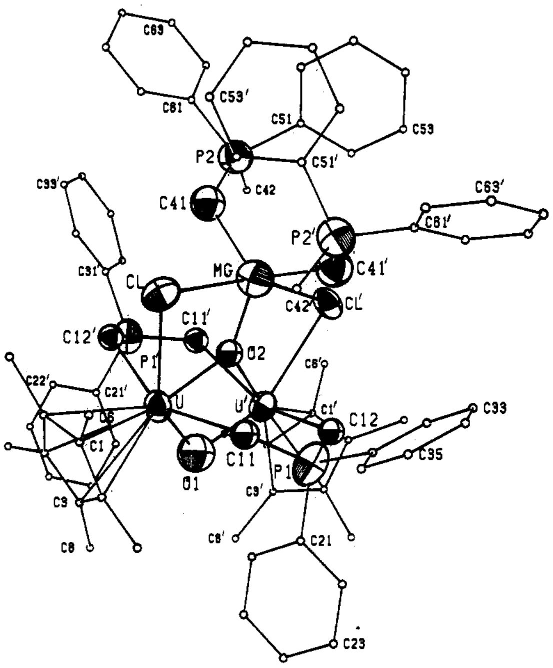

Figure 1. A labeled ORTEP drawing of 1.

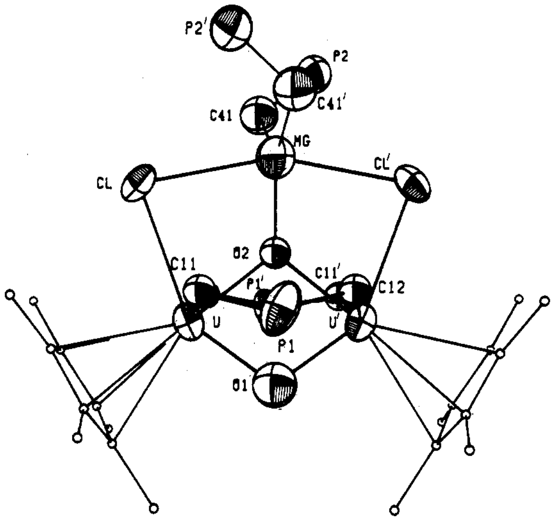

Figure 2. A labeled ORTEP drawing of 1 viewed approximately perpindicular to the U_2MgO triangle. The substituents on the phosphorus atoms have been omitted for clarity.

atom, which compose the triangular U_2MgO unit, the two chlorides and the oxide, which bridge the triangular edges, and the centroids of the two Cp^{*-} groups, which are coordinated to the uraniums, are coplanar (Table VII, supplementary material).

The coordination sphere about each uranium is an irregular octahedron composed of Cp^{*-}, chloride, the μ_2-oxide, two $-CH_2PPh_2CH_2-$ ligands, which bridge the two uraniums, and the μ_3-oxide, which centers the three metals. While constraints imposed by the bridging ligands severely distort the angles about uranium (see Table III), the bond distances to uranium are normal. The U–Cp* separation, 2.85 (2) Å, is the range observed for other complexes.[20] The U–CH_2 bond lengths, 2.67 (3) and 2.60 (3) Å, are among the longest uranium–carbon σ bonds, but indistinguishable from those in $CpU[(CH_2)(CH_2)PPh_2]_3$ where the $(CH_2)(CH_2)PPh_2^-$ is a chelating ligand.[21] While the U–Cl distance, 2.93 (1) Å, is longer than a terminal chloride, where the bond distance is normally about 2.6 Å,[22] it is typical of a bridging chloride[22] and, consequently, implies a significant U–Cl–Mg interaction. U–O1, 2.13 (2) Å, and U–O2, 2.18 (2) Å, are near the sum of the Shannon crystal radii[23] of 1.03 Å for six-coordinate U^{4+} and 1.21 and 1.22 Å for two- and three-coordinate O^{2-}, respectively. For comparison, in $U_4O_2(O_2CNEt_2)_4$, which contains two planar, edge-linked μ_3-OU_3 units, U–O distances are 2.239 (7), 2.294 (7), and 2.147 (7) Å,[11] and in $U_3(O)(O\text{-}t\text{-}Bu)_n$, whose structure differs from 1 in that the oxygen atom is not in the plane of the three metals, the U–O distance is 2.27 (3) Å.[14]

Table III. Bond Angles (deg) for 1[a]

O2-U-O1	74.1 (8)	C12-P1-C11	112 (2)
C11-U-Cl	81.1 (6)	C21-P1-C11	109 (2)
C12'-U-Cl	79.7 (6)	C21-P1-C12	109 (1)
O1-U-Cl	146.4 (8)	C31-P1-C11	106 (2)
O1-U-C12'	92.8 (6)	C31-P1-C12	112 (2)
O1-U-C11	91.9 (6)	C31-P1-C21	107 (2)
O2-U-Cl	72.3 (6)	C42-P2-C41	112 (2)
O2-U-C11	77.8 (6)	C51-P2-C41	114 (2)
O2-U-C12'	76.7 (6)	C51-P2-C42	108 (2)
C11-U-C12'	151 (1)	C61-P2-C41	113 (2)
Cl-Mg-Cl	158 (1)	C61-P2-C42	105 (1)
Cl-Mg-O2	78.9 (5)	C61-P2-C51	104 (2)
C41-Mg-Cl	86 (1)	P1-C11-U	122 (2)
C41-Mg-O2	120 (1)	Mg-C41-P2	122 (2)
C41-Mg-C41'	120 (2)	Cp-U-Cl	102
U-Cl-Mg	80.8 (5)	Cp-U-C11	101
U-O1-U	108 (1)	Cp-U-C12'	104
U-O2-U	104 (1)	Cp-U-O1	111
Mg-O2-U	128.0 (6)	Cp-U-O2	174

[a] Cp represents the centroid of the pentamethylcyclopentadienide group.

In view of a suggestion that bridging ylides may be particularly good ligands to stabilize metal–metal bonds between actinides,[24] the possibility of a U–U bond in 1 should be considered. In 1 the uranium–uranium separation, 3.437 (3) Å, is the shortest yet reported and can be compared to the average 3.82 (1) Å in $[Cp_2U]_2[(CH)P(Ph)_2(CH_2)]_2$,[25] 3.782 (2) Å in $[Cp_2U]_2[OTiW_5O_{19}]_2^{4-}$,[2] 3.573 (1) Å in $U_3(O)(OCMe_3)_{10}$,[14] and 3.702 (1), 3.777 (1), and 4.021 (1) Å in $U_4O_2(O_2CNEt_2)_4$.[13] Nonetheless, this distance is significantly longer than twice the metallic radius of uranium, 1.426 Å.[26] In fact, a repulsive, rather than an attractive U–U interaction is indicated by the wide U–O1–U', 108 (1)°, and U–O2–U', 104 (1)°, and narrow O1–U–O2, 74.1 (8)°, angles which serve to maximize the U–U separation while forcing an O1–O2 contact, 2.60 (4) Å, which approaches the sum of their crystal radii, 2.43 Å.[23] Consequently, as in other complexes in which uranium metals are held in close proximity by bridging ligands,[25,27] there appears to be no metal–metal bonding.

The geometry about the magnesium is distorted trigonal-bipyramidal with the equatorial coordination sites being occupied by O2 and the two $CH_2{=}PMePh_2$ ligands.

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Table IV. Atomic Positions for 1

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
U	0.2300 (1)	0.6348 (1)	−0.11930 (3)	C34	0.427 (2)	1.118 (2)	−0.060 (1)
P1	0.2453 (9)	0.8146 (7)	−0.0677 (2)	C35	0.370 (2)	1.082 (2)	−0.083 (1)
Cl	0.4105 (6)	0.7369 (6)	−0.1405 (2)	C36	0.312 (2)	0.992 (2)	−0.084 (1)
P2	0.5816 (7)	0.6309 (8)	−0.0769 (2)	O1[a]	0.148 (2)	0.574 (1)	−1/12
Mg[a]	0.446 (1)	0.7229 (7)	−1/12	O2[a]	0.318 (2)	0.6591 (9)	−1/12
C1	0.196 (2)	0.688 (1)	−0.1729 (5)	C41	0.518 (2)	0.658 (2)	−0.0993 (8)
C2	0.121 (2)	0.671 (1)	−0.1561 (5)	C42	0.513 (2)	0.546 (2)	−0.0508 (7)
C3	0.072 (2)	0.579 (1)	−0.1511 (5)	C51	0.669 (2)	0.725 (2)	−0.0570 (8)
C4	0.116 (2)	0.539 (1)	−0.1647 (5)	C52	0.648 (2)	0.756 (2)	−0.0323 (8)
C5	0.192 (2)	0.607 (1)	−0.1781 (5)	C53	0.713 (2)	0.833 (2)	−0.0192 (8)
C6	0.264 (3)	0.778 (3)	−0.183 (1)	C54	0.797 (2)	0.878 (2)	−0.0307 (8)
C7	0.090 (3)	0.739 (3)	−0.1476 (9)	C55	0.817 (2)	0.847 (2)	−0.0554 (8)
C8	−0.013 (3)	0.525 (3)	−0.1327 (9)	C56	0.753 (2)	0.771 (2)	−0.0685 (8)
C9	0.080 (2)	0.438 (3)	−0.1682 (8)	C61	0.640 (2)	0.586 (2)	−0.0961 (7)
C10	0.256 (2)	0.592 (3)	−0.1964 (8)	C62	0.685 (2)	0.552 (2)	−0.0811 (7)
C11	0.266 (2)	0.794 (2)	−0.1020 (7)	C63	0.727 (2)	0.514 (2)	−0.0960 (7)
C12	0.270 (2)	0.758 (2)	−0.0425 (7)	C64	0.723 (2)	0.509 (2)	−0.1257 (7)
C21	0.130 (2)	0.782 (3)	−0.0648 (7)	C65	0.677 (2)	0.543 (2)	−0.1407 (7)
C22	0.104 (2)	0.837 (3)	−0.0524 (7)	C66	0.636 (2)	0.581 (2)	−0.1258 (7)
C23	0.015 (2)	0.811 (3)	−0.0500 (7)	O71	0.95 (1)	0.91 (1)	0.219 (3)
C24	−0.049 (2)	0.728 (3)	−0.0600 (7)	C72	0.930 (8)	0.962 (9)	0.195 (3)
C25	−0.023 (2)	0.672 (3)	−0.0725 (7)	C75	0.92 (1)	0.81 (1)	0.200 (4)
C26	0.066 (2)	0.699 (3)	−0.0749 (7)	C74	0.84 (1)	0.79 (1)	0.179 (3)
C31	0.311 (2)	0.937 (2)	−0.063 (1)	C73	0.84 (1)	0.91 (1)	0.207 (3)
C32	0.368 (2)	0.972 (2)	−0.040 (1)	O76	0.85 (2)	0.85 (2)	0.194 (7)
C33	0.426 (2)	1.062 (2)	−0.038 (1)				

[a] These atoms are located on a two-fold axis at $2x, x, -^1/_{12}$.

Table V. Thermal Parameters for 1

Anisotropic Thermal Parameters

atom	*U*(11)	*U*(22)	*U*(33)	*U*(23)	*U*(13)	*U*(12)
U	0.052 (1)	0.050 (1)	0.0371 (9)	−0.003 (1)	−0.009 (1)	0.028 (1)
P1	0.09 (1)	0.037 (8)	0.051 (8)	0.014 (7)	0.026 (9)	0.029 (8)
Cl	0.053 (8)	0.052 (8)	0.045 (6)	0.015 (6)	0.017 (6)	0.022 (6)
P2	0.06 (1)	0.08 (1)	0.06 (1)	0.004 (8)	0.002 (8)	0.040 (9)
Mg	0.06 (2)	0.07 (1)	0.06 (1)	0.01 (1)	0	0.030 (8)

Isotropic Thermal Parameters

atom	*U*	atom	*U*	atom	*U*	atom	*U*
C1	0.05 (1)	C21	0.09 (2)	O1	0.06 (1)	C62	0.12 (2)
C2	0.04 (1)	C22	0.16 (3)	O2	0.04 (1)	C63	0.07 (1)
C3	0.07 (1)	C23	0.31 (5)	C41	0.06 (1)	C64	0.11 (2)
C4	0.05 (1)	C24	0.18 (3)	C42	0.03 (1)	C65	0.09 (2)
C5	0.04 (1)	C25	0.10 (2)	C51	0.06 (1)	C66	0.12 (2)
C6	0.10 (2)	C26	0.10 (2)	C52	0.09 (2)	O71	0.40 (4)
C7	0.09 (2)	C31	0.07 (2)	C53	0.15 (2)	C72	0.40 (4)
C8	0.07 (2)	C32	0.16 (2)	C54	0.14 (2)	C75	0.40 (4)
C9	0.07 (1)	C33	0.21 (3)	C55	0.17 (3)	C74	0.40 (4)
C10	0.08 (1)	C34	0.16 (3)	C56	0.15 (2)	C73	0.40 (4)
C11	0.04 (1)	C35	0.13 (2)	C61	0.05 (1)	O76	0.40 (4)
C12	0.03 (1)	C36	0.10 (2)				

The Mg–O distance, 1.94 (4) Å, is the near the sum of the ionic radii of Mg^{2+} and O^{2-},[28] and the Mg–CH_2 bond length, 2.23 (4) Å, falls into the range of other Mg–C bonds.[29] The axial sites are occupied by chlorides at 2.787 (8) Å. This is about 1.2 times the sum of the Mg^{2+} and Cl^- ionic radii[23] and implies a weak interaction between these atoms.

While the geometry within the ylide ligands is normal, the complex is notable in terms of ylide chemistry. It is the first structurally characterized monodentate ylide complex of a group 2 metal. In addition, it is the first complex in which two f-elements are bridged by a $-CH_2PR_2CH_2-$ group. The molecule is of interest for several other reasons. To our knowledge, it is the first oxo-centered trimetallic complex which contains a group 1 or 2 metal ion and one of only a few which contain two different metals ions.[30] It contains seven different elements, which is an unusually large number and demonstrates the diversity which can be encountered in the organometallic chemistry of the electropositive metals.

The structural characterization of 1 and the earlier determinations of $(UO_2)_2U_2O_2(OC_6H_5)_{10}(THF)_4$,[12] $U_4O_2(O_2CNEt_2)_4$,[13] and $U_3(O)(OCMe_3)_{10}$[14] reveal that the oxo-centered trimetal clusters of actinide elements is a varied class. On the basis of analogy to the transition metals,[10] these compounds should possess a rich chemistry. However, their preparations were all serendipitous,[12-14] and, to date, only $(UO_2)_2U_2O_2(OC_6H_5)_{10}(THF)_4$ has been syn-

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(28) The ionic radius of five-coordinate Mg^{2+} is not given in ref 23. Interpolation between the value for six-coordination, 0.86 Å, and that for four-coordination, 0.71 Å, using the procedure employed by Shannon[23] gives 0.79 Å. Adding this value to 1.22 Å for three-coordinate O^{2-}[23] gives a predicted Mg–O separation of 2.01 Å.

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thesized reproducibly.[12] Consequently, further studies of these molecules await the development of rational syntheses that will produce them in good yield. Experiments toward this goal are now underway.

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Supplementary Material Available: Table VII, least-squares plane calculation for 1 (1 page); Table VI, observed and calculated structure factors for 1 (8 pages). Ordering information is given on any current masthead page.

Assembly, Disassembly, and Reassembly of a Large Mercury Cobalt Carbonyl Cluster, $Hg_9Co_6(CO)_{18}$

Joseph M. Ragosta and James M. Burlitch*

Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853

Received June 9, 1987

The reaction of an aqueous basic solution of $Hg(CN)_2$ with $Hg[Co(CO)_4]_2$ in methanol/water formed the largest mercury-containing cluster yet reported, $Hg_9Co_6(CO)_{18}$ (1). A single-crystal X-ray structure determination on the bis(acetone) solvate, $Hg_9Co_6(CO)_{18}\cdot 2(CH_3)_2CO$ [$P2_1/c$; a = 14.339 (5) Å, b = 21.024 (6) Å, c = 18.535 (8) Å, β = 94.48 (3)°; V = 5570 (36) Å^3; Z = 4; R_1 = 8.1%, R_2 = 12.0%], showed 1 to have *fac*-$(CO)_3Co$ fragments at the corners of a rectangular trigonal prism with a mercury atom at the center of each edge. In addition to forming a 1:3 adduct with $Et_4N^+I^-$, cluster 1 reacted with HgX_2 compounds forming monocobalt compounds $(CO)_3Co(HgX)_3$ (X = I (2), Cl (3), CF_3CO_2). The chloro derivative 3 re-formed 1 in high yield when treated with Ph_3P. Possible mechanisms are discussed. Compound 2 was used to form analogous derivatives, $(CO)_3Co(HgY)_3$: Y = p-$CH_3C_6H_4SO_3$ with silver toluenesulfonate and Y = Ph with phenyllithium. It also formed an 1:1 adduct with n-Bu_4NI.

Introduction

When an attempt was made to recover the starting material from an aborted preparation of $Na^+Co(CO)_4^-$ from $Hg[Co(CO)_4]_2$ and sodium amalgam in methanol, a small quantity of a dark red solid was obtained from the reaction mixture after it had been quenched with aqueous $Hg(CN)_2$. Elemental analysis established the empirical formula as $Hg_3Co_2(CO)_6$, and the simplicity of the infrared spectrum suggested a highly symmetrical structure.

In this paper, we report an improved preparation of this compound, $Hg_9Co_6(CO)_{18}$ (1) the largest mercury-containing cluster yet prepared, and describe some of its reactions.[1] Those with compounds of type HgX_2 provide the first entry point to the chemistry of $(CO)_3CoHgX_3$ compounds from which 1 may be regenerated with surprising efficiency.

Large clusters containing mercury are relatively rare. Prior to preliminary reports of this work,[2,3] the only known mixed-metal clusters containing more than two mercury atoms were $Cp_2Nb[HgS_2CN(Et)_2]_3$,[4] $Hg[NiCp(GePh_3)HgGePh_3]_2$,[5] $Hg_6Rh_4[P(Me)_3]_{12}$,[6] $[Os_3(CO)_{11}Hg]_3$,[7] $[Cp(CO)_3MoHgMo]_4$,[8] $[(MeCp)(CO)_2MgHg]_4$,[9] and $[Cp(CO)_2ReHg]_4$.[10] Except for the last named compound, the structures of these compounds are known; their chemistry has not been reported.

Experimental Section

Unless stated otherwise, all operations were carried out in flame-dried glassware under a purified argon atmosphere, using apparatus and techniques described elsewhere.[11,12] Weighing and preparation of analytical and spectroscopic samples of air-sensitive solids were done in a Vacuum Atmospheres Corp. drybox under prepurified nitrogen. Melting points were observed in sealed capillaries under argon. Molecular weights were determined cryoscopically on freshly prepared samples by using sulfolane as solvent and benzophenone as a standard.[13] Thin-layer chromatography (TLC) was done by using Whatman KC18F plates (200-μm C-18 adsorbant on glass).

Infrared (IR) spectra were obtained on a Perkin-Elmer Model 337 spectrometer, calibrated with the 1944 cm^{-1} line of polystyrene. Unless stated otherwise, elemental analyses were carried out by Galbraith Laboratories, Knoxville, TN, or Analytische Laboratorien, Elbach, Germany. Alternatively, freshly prepared sampes were decomposed by treatment with nitric acid and analyzed for Co and Hg by inductively coupled plasma emission spectroscopy using a Jarrell-Ash 975 spectrophotometer; such analyses were performed by the analytical laboratory of the Cornell University Department of Pomology. Iodide analyses were carried out on similarly prepared samples by the Volhard method.[14a] Proton

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(1) 1,2;2,3;1,3;1,4;2,5;3,6;4,5;5,6;4,6-Nonakis(μ_2-mercurio)-*trigonal-prismato*-hexakis[*fac*-(tricarbonato)cobalt].

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