

# The Synthesis, Crystal Structure, and Reactions of an Actinide Metallocarborane Complex, Bis( $\eta^5$ -(3)-1,2-dicarbollyl)dichlorouranium(IV) Dianion, $[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2]^{2-}$ 1a

Frank R. Fronczek,<sup>1b</sup> Gordon W. Halstead,<sup>1b,c</sup> and Kenneth N. Raymond\*<sup>1b,c</sup>

Contribution from the Department of Chemistry and the Molecular Materials Research Division of the Lawrence Berkeley Laboratory,<sup>1d</sup> University of California, Berkeley, California 94720. Received July 21, 1976

**Abstract:** The reaction of  $\text{UCl}_4$  with the  $\text{C}_2\text{B}_9\text{H}_{11}^{2-}$  anion in tetrahydrofuran solution under inert atmosphere conditions has led to the formation of the complex anion  $[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2]^{2-}$ , which has been isolated as several air-sensitive crystalline salts. The salt  $[\text{Li}(\text{OC}_4\text{H}_8)_4]_2[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2]$  has been subjected to an x-ray crystal structure determination using counter intensity data. The complex anion is found to exhibit approximate  $C_{2v}$  symmetry, with the ligands arranged in a distorted tetrahedral array about uranium. The average U-B distance to the pentahapto-bonded dicarbollide ligands is 2.73 (2) Å, and the average U-Cl distance is 2.599 (6) Å. The Cl-U-Cl angle is 90.3 (5)°, and the dicarbollide bonding face centroids form an angle of 137° about the uranium atom. Refinement in space group  $Cc$  fitting 2020 data by 322 parameters led to agreement indices  $R = 0.058$  and  $R_w = 0.061$ . Unit cell dimensions are  $a = 26.410$  (7) Å,  $b = 11.248$  (5) Å,  $c = 20.163$  (6) Å,  $\beta = 102.35$  (1)°, and the calculated density is  $1.32 \text{ g cm}^{-3}$  for  $Z = 4$ . The lithium cations are coordinated tetrahedrally by tetrahydrofuran molecules, with an average Li-O distance of 1.92 (3) Å. The  $[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2]^{2-}$  anion reacts with  $\text{C}_8\text{H}_8$  to yield uranocene,  $\text{U}(\text{C}_8\text{H}_8)_2$ , and reacts with  $\text{C}_5\text{H}_5^-$  to produce products which are apparently mixed ligand complexes of dicarbollide and cyclopentadienide. In actinide complexes, the dicarbollide dianion seems to have ligating properties which are intermediate between those of the cyclooctatetraene dianion and cyclopentadienide.

The organometallic chemistry of the lanthanides and actinides has dealt primarily with derivatives of the cyclopentadienide ion,  $\text{C}_5\text{H}_5^-$ , although in recent years other complexes, especially of cyclooctatetraene anion, have been prepared. Significant advances have now been made toward the understanding of the structure, bonding, and reactivity of these compounds.<sup>2</sup> The (3)-1,2-dicarbollide ion,  $\text{C}_2\text{B}_9\text{H}_{11}^{2-}$ , has been shown to have an extensive coordination chemistry with transition metal ions analogous to metallocenes of cyclopentadienide,<sup>3-5</sup> but complexes of carborane ions with the f series transition metals have not been reported. There are several reasons to expect that carborane ligands should enhance the stability of complexes with the actinides. The dicarbollide ion possesses an open pentagonal face (which includes the two carbon atoms) and thus can act as a six  $\pi$ -electron donor isoelectronic with  $\text{C}_5\text{H}_5^-$ . This bonding face, however, is substantially larger than that of cyclopentadienide, and possesses a higher formal negative charge. Both these differences should be favorable to the stability of an actinide complex, due to the large coordination numbers and high formal metal oxidation states normally found in actinide organometallic chemistry. These properties of the dicarbollide ion have been used to stabilize the unusually high oxidation state of Ni(IV) in the complex  $[\text{Ni}(\text{C}_2\text{B}_9\text{H}_{11})_2]$ .<sup>6</sup> Sterically hindered derivatives of the large, highly charged  $\text{C}_8\text{H}_8^{2-}$  ligand have recently yielded an air-stable uranocene,<sup>7</sup> and similar behavior might be anticipated for carborane ligands. Accordingly, we have successfully prepared, characterized, and studied several key reactions of the first actinide metallocarborane complex, the anion  $[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2]^{2-}$ . A preliminary report of the preparation and structure of this compound has been made.<sup>8</sup>

## Experimental Section

All reactions were carried out under an inert atmosphere of high-purity nitrogen or argon on a vacuum line. Transfer and handling of the organometallic complexes and their solutions were facilitated by the use of Schlenk techniques or a Vacuum Atmospheres HE 93-A inert atmosphere glove box having an oxygen- and moisture-free ni-

trogen atmosphere. Crystalline samples for the x-ray diffraction experiments were handled in a horizontal format glove box equipped with a binocular microscope. A saturated THF atmosphere was maintained in this drybox by continuous recirculation through Radox oxygen scavenger beads and Linde 3A molecular sieves. Infrared spectra were measured with a Perkin-Elmer Model 337 spectrophotometer and a Cary Model 14 automatic recording spectrophotometer was used to record the electronic spectra.

**Materials.** Dried and degassed solvents were used in all syntheses and further characterizations. Toluene, benzene, diglyme, dioxane, dimethoxyethane (DME), and THF were dried by reflux over sodium-benzophenone ketyl while hexane was dried by distillation from phosphorus pentoxide. Small quantities of acetone were dried with 13A molecular sieves. All solvents were degassed under vacuum prior to use.

Uranium tetrachloride was prepared from a published procedure.<sup>9</sup> Thorium tetrachloride was purchased from ROC/RIC and dried with thionyl chloride,<sup>10</sup>  $[\text{Na}(\text{DME})][\text{C}_5\text{H}_5^-]$  was synthesized from cyclopentadiene monomer and NaH and was recrystallized from DME.<sup>11</sup> Solutions of dipotassium cyclooctatetraene were obtained from the reaction of potassium naphthalide with cyclooctatetraene.<sup>12</sup> The trimethylammonium salt of the dicarbododecahydroundecarborate(-1) ion,  $[(\text{CH}_3)_3\text{NH}][(\text{3-1,2-C}_2\text{B}_9\text{H}_{11})_2]$ , was obtained as a gift from Dr. Chris Salentine or prepared from orthocarborane as previously described.<sup>13</sup> Further deprotonation of  $[(\text{CH}_3)_3\text{NH}][1,2\text{-C}_2\text{B}_9\text{H}_{11}]$  with NaH by a literature procedure<sup>14</sup> yielded the disodium salt of the 1,2-dicarbollide dianion,  $\text{Na}_2[(\text{3-1,2-C}_2\text{B}_9\text{H}_{11})_2]$ . Sodium hydride was washed with hexane to remove its mineral oil coating and stored in the drybox.

**$\text{Na}_2[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2] \cdot x\text{THF}$ .** By refluxing 0.75 g (0.031 mol) of NaH with 3.00 g (0.0155 mol) of  $[(\text{CH}_3)_3\text{NH}][(\text{3-1,2-C}_2\text{B}_9\text{H}_{11})_2]$  in 100 ml of dried degassed THF for 3 h,  $\text{Na}_2[(\text{3-1,2-C}_2\text{B}_9\text{H}_{11})_2]$  was prepared. The solution was cooled to room temperature and then concentrated to ca. 50 ml in order to remove the volatile  $\text{N}(\text{CH}_3)_3$  formed during the reaction. The solution was filtered through a medium fritted funnel to remove any excess NaH and the filter was washed with two 15-ml portions of THF. The filtrate and washings were combined in a reaction flask and were cooled to and maintained at  $-20^\circ\text{C}$ . A solution of 2.95 g (0.00777 mol) of  $\text{UCl}_4$  in 25 ml of THF was added dropwise over a period of 30 min. The reaction proceeded rapidly at  $-20^\circ\text{C}$  and produced an orange-brown solution with an evident precipitate of NaCl. The reaction mixture was allowed to warm to room temperature and stirred for 3 h. The volume was then reduced to ca. 75 ml and the precipitate allowed to settle. The super-

**Table I.** Summary of Vibrational and Electronic Spectral Data for  $[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2]^{2-}$ <sup>a</sup>

$\lambda$ (nm)	$\epsilon$ (L cm <sup>-1</sup> mol <sup>-1</sup> )	$\lambda$ (nm)	$\epsilon$ (L cm <sup>-1</sup> mol <sup>-1</sup> )
1797	10	951	9
1653 sh	13	912	17
1594	24	869	15
1452	20	838 sh	13
1172	36	676	57
1102	25	652	23
1056 sh	19	623	9
973	10		
B-H(terminal), <sup>b</sup> $\nu$ 2488(s, br) <sup>c</sup> cm <sup>-1</sup>			

<sup>a</sup> Infrared data collected on a  $\sim 0.01$  M THF solution of the Na salt; near-infrared and visible data collected on a  $1.67 \times 10^{-2}$  M solution of the Na salt. <sup>b</sup> Weak bands normally occurring below  $1300$  cm<sup>-1</sup> were not observed due to solvent absorption. <sup>c</sup> Key: s, strong; br, broad; sh, shoulder.

nantant solution was removed via syringe and filtered through a fine fritted ( $5 \mu$ ) filter funnel and then diluted to 100 ml in a volumetric flask. (Attempts to filter the reaction mixture directly were extremely slow and failed to remove all the NaCl.) Yield was estimated to be in excess of 75%.<sup>15</sup> Due to the instability of the complex with respect to loss of solvent, it was left in solution in the volumetric flask and used as a stock solution. Uranium and chlorine analyses were used to determine the concentration of this solution and the stoichiometry. Anal. Calcd for  $\text{UCl}_4\text{B}_{18}\text{H}_{22}\text{Cl}_2$ ; U:Cl, 1:2. Found: U:Cl, 1:2.09.<sup>16</sup>

The electronic spectrum of  $\text{Na}_2[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2]$  (which will appear in the supplementary material of this journal) was measured in THF from 2200 to 500 nm in 1-cm quartz cells employing greased ground glass stoppers to protect the air-sensitive solutions. The concentration was 0.0167 M based on total uranium present in the solution.<sup>16</sup> The infrared data were collected on a ca. 0.01 M THF solution of the sodium salt. A summary of the results is tabulated in Table I.

**Lithium, Potassium, Barium, and Tetraalkylammonium Salts of  $[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2]^{2-}$ .** Salts of  $\text{K}^+$ ,  $\text{Li}^+$ , and  $\text{Ba}^{2+}$  were obtained in a manner analogous to the sodium salt by utilizing the appropriate dicarbollide salt. A tetrahydrofuran solution of  $\text{K}_2\text{C}_2\text{B}_9\text{H}_{11}$  was obtained by reaction of 2 equiv of KH with 1 equiv of  $[(\text{CH}_3)_3\text{NH}][(\text{3-1,2-C}_2\text{B}_9\text{H}_{11})_2]$  using the method described above. The lithium salt,  $\text{Li}_2\text{C}_2\text{B}_9\text{H}_{11}$ , was prepared by the reaction of 2 equiv of *n*-butyllithium with 1 equiv of  $[(\text{CH}_3)_3\text{NH}][(\text{3-1,2-C}_2\text{B}_9\text{H}_{11})_2]$  at  $-20^\circ\text{C}$  in THF. Preparation of  $\text{Ba}(\text{C}_2\text{B}_9\text{H}_{11})_2$  was effected by reaction of  $[(\text{CH}_3)_3\text{NH}][(\text{3-1,2-C}_2\text{B}_9\text{H}_{11})_2]$  with an excess of barium metal in refluxing THF for 45 h. No reaction was observed in a similar attempt with calcium metal. Many tetraalkylammonium salts were tested for the desired solubility in THF but only tetra-*n*-butylammonium bromide appeared promising. A metathesis reaction in THF between  $\text{Na}_2[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2] \cdot x\text{THF}$  and  $(n\text{-C}_4\text{H}_9)_4\text{NBr}$  produced insoluble NaBr and  $[\text{n-Bu}_4\text{N}][\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2]$ . This salt was not substantially different in its solubility in THF from those of the 1A and 2A metal ions. All were found to be soluble in diglyme, dimethoxyethane, and THF, and were insoluble or slightly soluble in hexane, toluene, benzene, and dioxane. Decomposition occurs in acidic solvents including acetone and water.

**Attempted Preparation of the Thorium(IV) Analogue.** A THF solution of  $\text{Na}_2[(\text{3-1,2-C}_2\text{B}_9\text{H}_{11})_2]$  was prepared as described above by reacting 0.50 g ( $2.6 \times 10^{-3}$  mol) of  $[(\text{CH}_3)_3\text{NH}][(\text{3-1,2-C}_2\text{B}_9\text{H}_{11})_2]$  in 60 ml of THF with 0.13 g ( $5.4 \times 10^{-3}$  mol) of NaH. A slurry of 0.48 g ( $1.3 \times 10^{-3}$  mol) of  $\text{ThCl}_4$  in 40 ml of THF was added via syringe to the  $\text{Na}_2[(\text{3-1,2-C}_2\text{B}_9\text{H}_{11})_2]$  at  $0^\circ\text{C}$ . The gray-white suspension was allowed to warm to room temperature and was stirred for 12 h. No apparent reaction had occurred so the reaction mixture was refluxed for a further 6 h. The reaction mixture was cooled to room temperature and the suspension was filtered through a medium-fritted filter. The precipitate weighed 0.53 g after drying. An infrared spectrum of the precipitate showed the presence of a weak band at  $2520$  cm<sup>-1</sup> typical of a B-H stretching frequency and several other bands attributed to coordinated THF.<sup>17</sup> After washing three times with ca. 10 ml of THF (total) the band at  $2520$  cm<sup>-1</sup> disappeared while the bands typical of  $\text{ThCl}_4 \cdot 3\text{THF}$ <sup>18</sup> were still present. No other thorium-containing species

**Table II.** Summary of Crystal Data

Chemical formula	$[\text{Li}(\text{OC}_4\text{H}_8)_4]_2[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2]$
Formula weight	1164.49
Space group	$Cc(C_2)$
Cell constants at $24^\circ\text{C}$	
<i>a</i>	26.410 (7) Å
<i>b</i>	11.248 (5) Å
<i>c</i>	20.163 (6) Å
$\beta$	$102.35 (1)^\circ$
<i>V</i>	5851 (3) Å <sup>3</sup>
<i>Z</i>	4
Calculated density	1.32 g cm <sup>-3</sup>
Crystal dimensions	$0.13 \times 0.48 \times 0.31$ mm
Linear absorption coefficient $\mu_{\text{MoK}\alpha}$	$41.7$ cm <sup>-1</sup>

evidencing the B-H stretching frequency typical of carborane complexes could be isolated from the filtrate.

**Reaction with the Cyclopentadiene Anion.** A 0.40 M stock solution of  $\text{C}_5\text{H}_5^-$  was prepared by dissolving 0.71 g of  $[\text{Na}(\text{DME})]\text{C}_5\text{H}_5$  in 10 ml of THF. The concentration of the  $\text{Na}_2[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2]$  solution used was 0.0556 M. To 2.00 ml of  $[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2]^{2-}$  (0.111 mmol) in a 25-ml volumetric flask was added via syringe 1.11 ml of 0.40 M (0.44 mmol)  $\text{C}_5\text{H}_5^-$ . The yellow  $[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2]^{2-}$  solution turned deep red immediately upon addition of the 4 equiv of  $\text{C}_5\text{H}_5^-$  at room temperature. The visible spectrum between 600 and 800 nm exhibited bands at 673 ( $\epsilon$  140), 687 sh, 717, 751, and 787 nm. Reaction of 1 equiv of  $[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2]^{2-}$  with 2 and 3 equiv of  $\text{C}_5\text{H}_5^-$  produced identical results. However, when 1 equiv of  $\text{C}_5\text{H}_5^-$  was reacted with 1 equiv of  $[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2]^{2-}$  the solution remained yellow and was characterized by relatively less intense bands at 648, 667, and 692 nm. Comparison of the spectra and solubility properties of the red product with those of  $\text{U}(\text{C}_5\text{H}_5)_4$ <sup>19</sup> and  $\text{U}(\text{C}_5\text{H}_5)_3\text{Cl}$ <sup>20</sup> indicated that neither of the latter two complexes is formed in the reaction.

**Reaction with the Cyclooctatetraene Dianion.** A solution of  $\text{K}_2\text{C}_8\text{H}_8$  was prepared by the reaction of 2.8 mmol of K naphthalide with a twofold excess (3.1 mmol, 0.35 ml) of cyclooctatetraene at  $-20^\circ\text{C}$  in 50 ml of THF. The K naphthalide was obtained from the reaction of 0.11 g (2.8 mmol) of K metal and 0.38 g (3.0 mmol) of naphthalene at room temperature in THF. When an excess of  $\text{C}_8\text{H}_8^{2-}$  was added to  $[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2]^{2-}$  in THF at room temperature, a green solution immediately resulted. Spectral analysis of the solution in the region 600–800 nm confirmed that uranocene,  $\text{U}(\text{C}_8\text{H}_8)_2$ , was produced in nearly quantitative yield (based on  $\epsilon$  1850,  $\lambda$  615 nm, and 0.0556 M  $[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2]^{2-}$  stock solution).<sup>21</sup> Even when as little as 0.5 equiv of  $\text{C}_8\text{H}_8^{2-}$  is reacted with  $[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2]^{2-}$ , a yield of ca. 80% of the expected uranocene (based on  $\text{C}_8\text{H}_8^{2-}$ ) is indicated from the spectrophotometric results.

**Crystallization and Diffraction Studies.** As noted, group 1A and 2A metal salts of  $[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2]^{2-}$  tend to be extremely soluble in ethereal solvents and quite insoluble in nonpolar solvents. Thus growth of diffraction quality crystals was difficult and was further complicated by the fact that the cation etherate complexes resulting from crystallization from ethers are generally quite unstable. Such crystals lose solvent readily when exposed to dry inert atmospheres. Crystallization attempts of the  $\text{K}^+$  salt from THF, dioxane, and diglyme yielded intractable oils. Complexation of the  $\text{K}^+$  ion with the non-volatile "crown" ether<sup>22</sup> dibenzo-18-crown-6 led to a precipitate insoluble in THF. Crystallization of the  $\text{Na}^+$  salt from THF at  $-78^\circ\text{C}$  yielded a crystalline material with very poor crystal formation. Crystals of the barium salt grown in the same manner from THF solutions are so unstable with respect to loss of solvent as to preclude manipulation and mounting for diffraction experiments. The  $[\text{N}(\text{n-Bu})_4]^+$  salt formed an oil from THF solution upon evaporation. Only the lithium salt (from THF solutions) proved to be suitable as diffraction-quality crystals.

Crystals of  $[\text{Li}(\text{THF})_4]_2[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2]$  were grown from tetrahydrofuran by cooling a concentrated dark brown solution to dry ice temperature ( $-78^\circ\text{C}$ ) for several days. The yellow-orange crystals could not be suction filtered or washed without destroying their crystallinity, and thus they were simply allowed to drain for several

**Table III.** Positional and Thermal<sup>a</sup> Parameters ( $\times 10^4$ ) for Anisotropically Refined Atoms

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
U	0	0.27646 (8)	1/4	18.2 (2)	148.7 (12)	46.8 (4)	-11.8 (12)	7.2 (2)	-6.0 (20)
Cl(1)	-0.0142 (4)	0.2310 (11)	0.3710 (5)	37 (3)	516 (26)	46 (4)	8 (6)	14 (2)	4 (7)
Cl(2)	0.0033 (7)	0.5030 (8)	0.2765 (9)	33 (3)	174 (10)	179 (13)	-9 (6)	26 (6)	-96 (9)
O(1)	-0.1538 (11)	0.2217 (23)	0.7596 (15)	43 (8)	202 (31)	53 (11)	27 (14)	4 (7)	9 (15)
O(2)	-0.1579 (12)	0.0886 (24)	0.8939 (18)	31 (7)	155 (33)	106 (18)	22 (10)	24 (9)	32 (17)
O(3)	-0.1514 (11)	0.3737 (21)	0.8826 (18)	43 (7)	172 (32)	107 (17)	1 (11)	31 (9)	-34 (17)
O(4)	-0.0523 (22)	0.2085 (44)	0.8810 (25)	40 (10)	475 (83)	84 (17)	7 (23)	20 (11)	-15 (3)
O(5)	0.1468 (9)	0.2741 (22)	0.6916 (15)	26 (5)	264 (35)	53 (10)	9 (10)	12 (6)	18 (17)
O(6)	0.1462 (13)	0.1207 (27)	0.5530 (19)	38 (8)	195 (38)	106 (20)	-6 (12)	25 (11)	-1 (20)
O(7)	0.1351 (13)	0.3926 (25)	0.5533 (16)	64 (10)	268 (41)	42 (12)	-20 (13)	13 (9)	9 (15)
O(8)	0.0474 (18)	0.2398 (22)	0.5867 (29)	31 (9)	88 (29)	173 (3)	11 (10)	40 (14)	-5 (18)

<sup>a</sup> The form of the anisotropic temperature factor is  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ .

days while kept at  $-78^\circ\text{C}$ . This procedure yielded a product which, while slightly moist, could be slowly warmed to room temperature without redissolving in residual solvent. Crystal mounting was facilitated by preparing a recirculating oxygen- and water-free nitrogen atmosphere which was approximately saturated with THF. The prismatic and fairly equant crystals were mounted in this atmosphere in thin-walled glass capillaries.

Precession and Weissenberg photographs demonstrated these crystals to be monoclinic, with systematic absences  $hkl$  with  $h + k$  odd, and  $h0l$  with  $l$  odd, consistent with the centrosymmetric space group  $C2/c$  and the noncentric space group  $Cc$ .<sup>23</sup> A crystal of dimensions  $0.13 \times 0.48 \times 0.31$  mm was mounted with its long axis  $b$  inclined slightly from the  $\phi$  axis of a Picker automated four-circle diffractometer.<sup>24</sup> Graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda_{\text{Mo}K\alpha_1} = 0.709261$  Å) was used for precise measurement of the cell constants and for data collection. Cell dimensions obtained from a least-squares fit of coordinates measured for 20 reflections within the  $2\theta$  range  $22$ – $29^\circ$  are given in Table II, along with other pertinent crystal data.

Intensity data were collected by the  $\theta$ - $2\theta$  scan technique at a constant scan rate of  $1$  deg  $\text{min}^{-1}$  from  $0.75^\circ$  below the  $K\alpha_1$  peak to  $0.75^\circ$  above the  $K\alpha_2$  peak, and stationary background counts of 20 s were made at each extreme of the scan. Copper foil attenuators were inserted in the diffracted beam to prevent the counting rate from exceeding  $10^3$   $\text{s}^{-1}$ . Three standard reflections were remeasured every 50 measurements as an index of crystal and instrument stability, and the intensities of these standards decreased smoothly to about 91% of their original values during the course of the 350 h of x-ray exposure. All reflections within the hemisphere  $\pm h$ ,  $\pm k$ ,  $l$  having  $2\theta$  values less than  $45^\circ$  were measured at least once.

The 8792 individual data thus collected were reduced to  $F^2$  and  $\sigma(F^2)$  values by normal procedures, with a parameter  $p$ , introduced to avoid overweighting of the strong reflections, chosen as 0.04.<sup>25</sup> Absorption corrections were calculated by an analytical integration method,<sup>26</sup> and correction factors ranged from 1.65 to 3.12. Equivalent data were averaged and placed on an approximately absolute scale by the method of Wilson,<sup>27</sup> yielding a set of 3570 independent data, of which 2020 had  $F_o^2 > 3\sigma(F_o^2)$ .

**Structure Solution and Refinement.** Preliminary examination of the intensity distribution indicated that the high angle data, which contain significant contributions from essentially only the uranium atom, show a pattern of pseudo-extinctions  $hkl$  with  $h + l$  odd (B centering) and  $hkl$  with  $k + l$  odd (A centering) in addition to the crystallographic C centering extinctions. It was thus correctly assumed that the uranium atoms lie very nearly in a face-centered array. In the centrosymmetric space group  $C2/c$ , this array is only possible for  $Z = 4$  if the uranium atom lies upon the twofold axis  $0, y, 1/4$  at a  $y$  coordinate near  $1/4$ . Thus a Patterson map was examined for evidence of coordinated chloride ligands related by the twofold axis. Since the 12 bonds of types U-Cl, U-B, and U-C are of approximately equal length, the resulting 48 vectors cause much overlap in the Patterson function at a distance of about  $2.5$  Å from the origin, but it was clear that a  $\text{UCl}_2$  unit having twofold symmetry is an incorrect interpretation. As any other orientation necessitates twofold disorder in the centrosymmetric space group, the structure was solved in the noncentric group  $Cc$ , and this choice was confirmed by successful refinement.

Since a face-centered array of uranium atoms is centrosymmetric, it provided no useful phase information. Positions for the two chlorine

atoms and one entire carborane cage were deduced from a sharpened Patterson map, and these eventually led to completion of the structure by standard difference Fourier techniques. This process was very difficult, however, because of the pseudosymmetry, which was not completely broken until the  $[\text{Li}(\text{THF})_4]^+$  cations were correctly placed based upon packing considerations. The lithium atoms were located at the centers of oxygen tetrahedra as peaks of density  $1.2$  e  $\text{\AA}^{-3}$ .

Refinement of the resulting structure was performed by full-matrix least-squares methods in space group  $Cc$ , minimizing the function  $\Sigma w(|F_o| - |F_c|)^2$ , where the weights are  $w = 4F_o^2/\sigma^2(F_o^2)$ . Only the data for which  $F_o^2 > 3\sigma(F_o^2)$  were used in the refinement. Atomic scattering factors for neutral U, B, C, Cl, O, and Li were those tabulated by Cromer and Mann,<sup>28</sup> and both the real and imaginary terms of anomalous dispersion by the uranium atom were taken into account in the calculations.<sup>29</sup> Machine computations were performed on CDC 6400 and CDC 7600 computers using a variety of programs.<sup>30</sup> Positions for hydrogen atoms could not be discerned from difference maps, and no attempt was made to account for them with calculated positions. The U, Cl, and O atoms were refined with anisotropic thermal parameters, but due to the limited number of significantly intense data available, all other atoms were treated isotropically. Carbon atoms of the carborane ligands could not be definitively distinguished from boron, and all were treated as boron. Refinement of 322 parameters led to convergence with  $R = 0.059$ ,  $R_w = 0.061$ , and the error in an observation of unit weight of 1.93.<sup>31</sup> Refinement of the alternate enantiomorph led to the corresponding indices 0.058, 0.061, and 1.91. While not a dramatic improvement, the second model yielded statistically equivalent U-Cl distances and a fairly narrow range of U-B distances, while the first model yielded a somewhat wider range and chemically equivalent U-Cl distances differing by  $0.05$  Å ( $4\sigma$ ). We thus feel that the second model is correct, and refined parameters for it are listed in Tables III and IV. A list of observed and calculated structure factors is available.<sup>32</sup>

### Structure Description

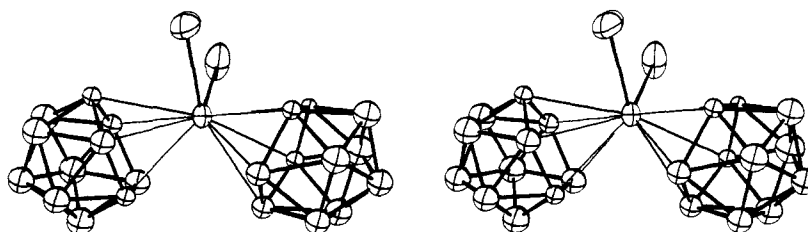
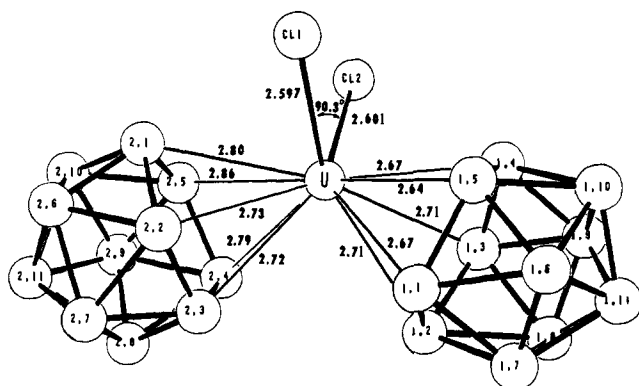
The complex ion  $[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2]^{2-}$  is similar in structure to "bent" metallocenes of the type  $(\pi\text{-C}_5\text{H}_5)_2\text{MX}_2$ . Crystallographically asymmetric, it has approximate symmetry  $C_{2v}$  when the dicarbollide ligands are considered as "pots," and very nearly  $C_2$  symmetry when their rotational conformations are taken into account. The coordination geometry may be described as a distorted tetrahedron with pentahapto-bonded dicarbollide ligands. A stereoscopic representation of this ion is shown in Figure 1, and the numbering scheme is illustrated in Figure 2, along with distances within the coordination sphere.

The pentahapto coordination mode of the dicarbollide ligands is clearly demonstrated by the range of U-B distances  $2.64$  (3) to  $2.86$  (3) Å. The average value of  $2.73$  (2) Å is similar to typical U-C distances found in U(IV) cyclopentadienyl complexes,<sup>33</sup> in harmony with the fact that M-C and M-B distances are almost identical in mixed Cp-dicarbollide complexes of transition metals.<sup>34</sup>

The two U-Cl bond lengths are experimentally identical, and average  $2.599$  (6) Å, in good agreement with values found

Table IV. Positional and Thermal Parameters for Isotropically Refined Atoms

Atom	x	y	z	B	Atom	x	y	z	B
B(1,1)	0.062 (1)	0.090 (3)	0.243 (2)	6.2 (8)	B(2,1)	-0.108 (1)	0.282 (3)	0.236 (2)	4.4 (7)
B(1,2)	0.065 (1)	0.188 (2)	0.174 (2)	6.0 (7)	B(2,2)	-0.085 (1)	0.133 (4)	0.219 (2)	6.9 (10)
B(1,3)	0.090 (1)	0.324 (2)	0.213 (1)	3.9 (6)	B(2,3)	-0.065 (1)	0.162 (2)	0.147 (1)	4.3 (6)
B(1,4)	0.101 (1)	0.313 (3)	0.292 (2)	2.8 (6)	B(2,4)	-0.066 (1)	0.321 (3)	0.124 (2)	8.2 (10)
B(1,5)	0.087 (1)	0.177 (3)	0.313 (2)	3.9 (7)	B(2,5)	-0.096 (1)	0.376 (3)	0.181 (2)	5.3 (7)
B(1,6)	0.130 (2)	0.073 (3)	0.292 (2)	8.2 (10)	B(2,6)	-0.153 (2)	0.189 (5)	0.194 (3)	8.8 (18)
B(1,7)	0.118 (1)	0.076 (3)	0.207 (2)	6.8 (8)	B(2,7)	-0.127 (2)	0.111 (3)	0.133 (2)	7.9 (9)
B(1,8)	0.136 (2)	0.233 (3)	0.183 (2)	8.6 (10)	B(2,8)	-0.115 (2)	0.226 (3)	0.076 (2)	9.4 (10)
B(1,9)	0.152 (2)	0.307 (4)	0.254 (3)	10.4 (12)	B(2,9)	-0.136 (2)	0.363 (4)	0.103 (2)	9.8 (11)
B(1,10)	0.156 (2)	0.199 (4)	0.328 (3)	8.4 (15)	B(2,10)	-0.161 (2)	0.332 (4)	0.176 (2)	9.6 (11)
B(1,11)	0.172 (2)	0.156 (3)	0.256 (2)	7.4 (8)	B(2,11)	-0.175 (2)	0.232 (3)	0.109 (2)	8.6 (10)
Li(1)	-0.126 (3)	0.221 (7)	0.862 (6)	11.8 (20)	Li(2)	0.117 (2)	0.254 (5)	0.602 (3)	6.7 (12)
C(1,1)	-0.203 (2)	0.158 (4)	0.724 (2)	11.6 (11)	C(5,1)	0.111 (2)	0.306 (4)	0.740 (3)	13.5 (15)
C(1,2)	-0.215 (2)	0.195 (4)	0.651 (2)	13.0 (12)	C(5,2)	0.157 (2)	0.327 (4)	0.805 (2)	12.1 (12)
C(1,3)	-0.172 (2)	0.270 (4)	0.641 (3)	14.3 (14)	C(5,3)	0.201 (3)	0.278 (5)	0.806 (4)	18.2 (19)
C(1,4)	-0.136 (3)	0.266 (5)	0.702 (3)	14.2 (15)	C(5,4)	0.199 (2)	0.251 (4)	0.728 (3)	13.3 (13)
C(2,1)	-0.208 (2)	0.070 (4)	0.898 (2)	10.5 (12)	C(6,1)	0.202 (2)	0.103 (4)	0.567 (3)	11.8 (15)
C(2,2)	-0.219 (3)	-0.026 (4)	0.967 (3)	25.1 (30)	C(6,2)	0.201 (2)	-0.026 (5)	0.545 (3)	13.0 (17)
C(2,3)	-0.168 (2)	-0.104 (5)	0.932 (3)	16.7 (17)	C(6,3)	0.155 (2)	-0.055 (4)	0.498 (3)	13.7 (13)
C(2,4)	-0.129 (2)	-0.027 (4)	0.899 (3)	15.0 (15)	C(6,4)	0.114 (1)	0.021 (3)	0.514 (2)	9.7 (9)
C(3,1)	-0.194 (2)	0.407 (4)	0.911 (2)	10.4 (11)	C(7,1)	0.127 (2)	0.390 (4)	0.485 (3)	15.3 (16)
C(3,2)	-0.184 (2)	0.514 (5)	0.918 (2)	12.1 (12)	C(7,2)	0.139 (2)	0.502 (6)	0.454 (4)	19.8 (20)
C(3,3)	-0.154 (4)	0.562 (7)	0.907 (5)	21.2 (26)	C(7,3)	0.159 (2)	0.570 (5)	0.521 (4)	17.3 (18)
C(3,4)	-0.112 (2)	0.492 (5)	0.916 (2)	22.9 (27)	C(7,4)	0.184 (3)	0.513 (8)	0.581 (4)	20.0 (20)
C(4,1)	-0.026 (2)	0.179 (3)	0.832 (2)	10.4 (10)	C(8,1)	0.014 (2)	0.148 (4)	0.564 (2)	11.1 (11)
C(4,2)	0.030 (2)	0.198 (4)	0.880 (3)	12.8 (13)	C(8,2)	-0.019 (2)	0.184 (5)	0.572 (3)	16.1 (18)
C(4,3)	0.025 (2)	0.207 (5)	0.946 (3)	14.7 (14)	C(8,3)	-0.040 (2)	0.309 (4)	0.579 (3)	14.4 (14)
C(4,4)	-0.027 (3)	0.284 (6)	0.923 (3)	15.2 (15)	C(8,4)	0.013 (2)	0.350 (5)	0.565 (2)	12.2 (14)

Figure 1. Thermal ellipsoids of the  $[U(C_2B_9H_{11})_2Cl_2]^{2-}$  ion in stereopair, drawn at the 20% probability level.Figure 2. Atom numbering scheme and coordination-sphere distances within the  $[U(C_2B_9H_{11})_2Cl_2]^{2-}$  ion. Estimated standard deviations are 0.009 Å for U-Cl, 0.03 Å for U-B, and 0.5° for Cl-U-Cl.

in similar cyclopentadienyl complexes: 2.559 (16) Å in  $U(C_5H_5)_3Cl$ ,<sup>35</sup> 2.627 (2) Å in  $U(C_5H_4CH_2Ph)_3Cl$ ,<sup>36</sup> and 2.593 (3) Å in  $U(C_9H_7)_3Cl$ .<sup>37</sup> The angle which the chloro ligands make about uranium is 90.3 (5)°. This value is intermediate between the ranges 85–88° found for  $d^1$  and 94–97° for  $d^0$  transition metal complexes<sup>38</sup> of the type  $Cp_2MX_2$ , which are similar in structure to  $[U(C_2B_9H_{11})_2Cl_2]^{2-}$ .

The centroids of the dicarbollide bonding faces form an angle of 137° about the uranium atom. This value is considerably larger than the usual values 126–132° found in  $Cp_2MCl_2$  complexes,<sup>38</sup> and presumably reflects the steric requirements of the large carborane ligand, even when coordinated to the large uranium(IV) metal center. All four centroid-U-Cl angles have essentially the tetrahedral value.

The 1,2-dicarbollide ligands have normal geometries, exhibiting approximate symmetry  $C_{5v}$  (neglecting the difference between C and B) expected of this icosohedral fragment. The 50 distances between nearest neighbor atoms<sup>39</sup> within the carborane cages range from 1.58 (4) to 1.94 (6) Å, and average 1.77 (1) Å. Individual values are listed in Table V. These values are consistent with more precisely determined distances found in other complexes of the dicarbollide ligand. For example, in the structure<sup>40</sup> of  $Cs[Re(C_2B_9H_{11})(CO)_3]$ , the identities of the carbon atoms are unambiguous, and the average intraligand distances within the carborane are 1.78 Å for B-B, 1.72 Å for C-B, and 1.61 Å for C-C; the weighted mean of these values is 1.76 Å.

Unfortunately, our standard deviations in bond lengths are not sufficiently low to distinguish between the expected B-B, B-C, and C-C bond lengths. Thus we cannot unambiguously identify the positions of the carborane carbon atoms. This is a result of the high thermal motion present in the structure; isotropic thermal parameters for the carborane atoms vary over

**Table V.** Individual Bond Distances Within the 1,2-Dicarbollide Ligands

Carborane 1		Carborane 2	
Atoms	Distance (Å)	Atoms	Distance (Å)
B(1,1)–B(1,2)	1.79 (4)	B(2,1)–B(2,2)	1.84 (5)
B(1,1)–B(1,5)	1.73 (5)	B(2,1)–B(2,5)	1.62 (5)
B(1,1)–B(1,6)	1.88 (5)	B(2,1)–B(2,6)	1.68 (6)
B(1,1)–B(1,7)	1.80 (4)	B(2,1)–B(2,10)	1.74 (6)
B(1,2)–B(1,3)	1.78 (4)	B(2,2)–B(2,3)	1.67 (5)
B(1,2)–B(1,7)	1.89 (5)	B(2,2)–B(2,6)	1.88 (7)
B(1,2)–B(1,8)	1.93 (5)	B(2,2)–B(2,7)	1.87 (6)
B(1,3)–B(1,4)	1.58 (4)	B(2,3)–B(2,4)	1.84 (5)
B(1,3)–B(1,8)	1.79 (5)	B(2,3)–B(2,7)	1.69 (5)
B(1,3)–B(1,9)	1.67 (5)	B(2,3)–B(2,8)	1.88(5)
B(1,4)–B(1,5)	1.65 (4)	B(2,4)–B(2,5)	1.66 (4)
B(1,4)–B(1,9)	1.68 (6)	B(2,4)–B(2,8)	1.80 (6)
B(1,4)–B(1,10)	1.94 (6)	B(2,4)–B(2,9)	1.88 (6)
B(1,5)–B(1,6)	1.74 (5)	B(2,5)–B(2,9)	1.68 (5)
B(1,5)–B(1,10)	1.77 (6)	B(2,5)–B(2,10)	1.75 (6)
B(1,6)–B(1,7)	1.67 (5)	B(2,6)–B(2,7)	1.78 (7)
B(1,6)–B(1,10)	1.66 (6)	B(2,6)–B(2,10)	1.64 (7)
B(1,6)–B(1,11)	1.71 (5)	B(2,6)–B(2,11)	1.75 (7)
B(1,7)–B(1,8)	1.91 (5)	B(2,7)–B(2,8)	1.80 (5)
B(1,7)–B(1,11)	1.78 (5)	B(2,7)–B(2,11)	1.86 (5)
B(1,8)–B(1,9)	1.62 (6)	B(2,8)–B(2,9)	1.77 (6)
B(1,8)–B(1,11)	1.78 (5)	B(2,8)–B(2,11)	1.83 (6)
B(1,9)–B(1,10)	1.92 (7)	B(2,9)–B(2,10)	1.76 (6)
B(1,9)–B(1,11)	1.77 (6)	B(2,9)–B(2,11)	1.80 (6)
B(1,10)–B(1,11)	1.68 (7)	B(2,10)–B(2,11)	1.74 (6)
Average = 1.76 <sub>5</sub> (2) Å <sup>a</sup>		Average = 1.77 (2) Å	

<sup>a</sup> The average values reported here and elsewhere in this paper for four or more observations are computed as  $\bar{x} = (\sum_{i=1}^n x_i)/n$  with an associated standard deviation computed as  $\sigma(\bar{x}) = [1/n(n-1) \cdot \sum_{i=1}^n (x_i - \bar{x})^2]^{1/2}$ . When averaging fewer than four observations, the standard deviation of the mean was computed from the individual standard deviations via  $1/\sigma^2(\bar{x}) = \sum_{i=1}^n 1/\sigma_i^2(x_i)$ .

a range of 2.6 (6)–12 (1) Å<sup>2</sup>, and these are small in comparison to those of the THF carbon atoms, which are typically 10–20 Å<sup>2</sup>. In spite of uncertainty in individual distances, the pattern of average distances to atoms of the bonding faces and of isotropic temperature factors obtained when all atoms are refined as boron suggest carbon positions which, while not totally conclusive, are plausible and, to us, convincing.

Based upon the expected individual distances (averages in [Re(C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)(CO)<sub>3</sub>]<sup>−</sup>), the mean of the four bonds to an atom of the bonding face varies according to its identity in the following manner:  $C = 1.69$  Å,  $B_{\text{adjacent}} = 1.77$  Å,  $B_{\text{remote}} = 1.78$  Å,  $1/2(B + C) = 1.73$  Å. The last entry corresponds to a position half-populated by a carbon atom and half-populated by a boron atom adjacent to a carbon atom; this type of site is caused by rotational disorder of the carborane cage about its axis. Average values and temperature factors are listed for all bonding-face atoms in Table VI, and atom types postulated from these data are given.

Thus, if this model is correct, the [U(C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>Cl<sub>2</sub>]<sup>2−</sup> ion exists in this crystal as an equally populated mixture of ions of idealized symmetries  $C_2$  and  $C_1$ , one having carbon atom positions related by a twofold axis and the other derived from it by rotation of one dicarbollide ligand by one position. Such disorder has previously been observed in a dicarbollide complex,<sup>41</sup> [(C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)Co]<sub>2</sub>(C<sub>2</sub>B<sub>8</sub>H<sub>10</sub>)<sup>2−</sup>. It should be noted that this model places the carbon atoms of the two cages far apart, as is the case in ferrocene-type metallocarborane complexes, which normally adopt a *transoid* configuration.<sup>5</sup> It also happens that this model places the carbon atoms (which have the least formal negative charge of the face atoms) closest to the coordinated chloride ligands.

**Table VI.** Average Distances to Bonding Face Atoms

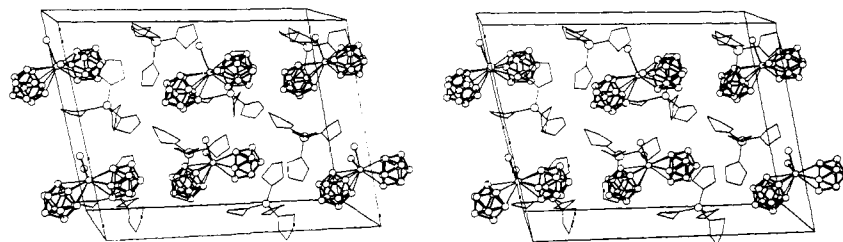
Atom	$B_{\text{iso}}$ (Å <sup>2</sup> )	Av distance (Å)	Theor av (Å)	Atom type assignment
B(1,1)	6.2 (8)	1.80 (3)	1.77	B
B(1,2)	6.0 (7)	1.85 (4)	1.77	B
B(1,3)	3.9 (6)	1.71 (5)	1.73	1/2(B + C)
B(1,4)	2.8 (6)	1.71 (8)	1.69	C
B(1,5)	3.9 (7)	1.72 (3)	1.73	1/2(B + C)
B(2,1)	4.4 (7)	1.72 (5)	1.69	C
B(2,2)	7 (1)	1.82 (5)	1.77	B
B(2,3)	4.3 (6)	1.77 (5)	1.78	B
B(2,4)	8 (1)	1.80 (5)	1.77	B
B(2,5)	5.3 (7)	1.68 (3)	1.69	C

**Table VII.** Lithium Coordination Geometry

Atoms	Distance (Å)	Atoms	Angle (deg)
Li(1)–O(1)	2.05 (11)	O(1)–Li(1)–O(2)	107 (5)
–O(2)	1.88 (8)	O(1)–Li(1)–O(3)	96 (4)
–O(3)	1.91 (8)	O(1)–Li(1)–O(4)	109 (5)
–O(4)	1.90 (10)	O(2)–Li(1)–O(3)	115 (5)
		O(2)–Li(1)–O(4)	116 (6)
		O(3)–Li(1)–O(4)	111 (4)
Li(2)–O(5)	1.88 (6)	O(5)–Li(2)–O(6)	116 (3)
–O(6)	2.02 (6)	O(5)–Li(2)–O(7)	107 (3)
–O(7)	1.92 (6)	O(5)–Li(2)–O(8)	113 (3)
–O(8)	1.86 (7)	O(6)–Li(2)–O(7)	101 (3)
		O(6)–Li(2)–O(8)	110 (3)
		O(7)–Li(2)–O(8)	110 (3)

The lithium counterions occur as discrete tetrahedral Li(OC<sub>4</sub>H<sub>8</sub>)<sub>4</sub><sup>+</sup> units. Diagrams of these ions are included in the supplementary material. The Li–O contacts average 1.93 (2) Å in length, and the O–Li–O angles average 109 (2)°. Individual distances and angles involving the lithium coordination are listed in Table VII. Carbon atom positions in the cations are less precise, hence no detailed description will be given of THF molecule conformations. Large thermal parameters and possible disorder of the THF molecules prevented isotropic-atom refinement from yielding totally satisfactory geometries for these solvent molecules. Since the crystals are 51% tetrahydrofuran by weight and only 20% uranium, this effect limits the angular extent of the x-ray scattering and the precision of the overall determination. Attempts to circumvent this problem by collection of a low-temperature data set were abandoned, as crystals invariably cracked and disintegrated in minutes when cooled in a cold nitrogen stream. The cell constants measured at 100 ± 5 K are as follows:  $a = 26.41$  (3),  $b = 10.82$  (2),  $c = 19.80$  (3) Å;  $\beta = 103.3$  (1)°. Thus in cooling from room temperature to 100 °C, the  $b$  and  $c$  axes decrease in length several tenths of an Angstrom, while  $a$  is unaffected. This anisotropic thermal contraction may cause destruction of the sample.

The crystal packing is illustrated in stereopair in Figure 3. The pseudo-face centering is evident in this diagram, and the carborane cages as well as the uranium atoms are seen to conform to this arrangement. The structure may be thought of as derived from the simple AB<sub>2</sub> arrangement of CaF<sub>2</sub>.<sup>42</sup> Each uranium carborane anion is surrounded by eight Li(THF)<sub>4</sub><sup>+</sup> cations which are distributed prismatically about it, and each cation is surrounded tetrahedrally by [U(C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>Cl<sub>2</sub>]<sup>2−</sup> anions. The cation presents a tetrahedral face to the anion. No unusually close interionic contacts are present in the structure.



**Figure 3.** Unit cell contents of  $[\text{Li}(\text{THF})_4]_2[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2]$ , in stereopair. The view is slightly oblique to the  $b$  axis, and  $a$  is horizontal. All atoms are drawn with arbitrary sizes.

## Discussion of Results

The electronic and steric requirements of the d-transition metals are satisfied by the formation of bis-1,2-dicarbollide complexes resembling ferrocene in structure.<sup>3-5</sup> However, the larger size and higher ionic character of the actinide ions allow them to accommodate more ligands without such stringent requirements upon electron count. Thus, in the  $[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2]^{2-}$  complex, U(IV) retains two coordinated chloride ligands in addition to the two  $(\eta^5)$ -1,2-dicarbollide ligands present. This structure is unprecedented for metallo-carborane complexes and is reminiscent of the cyclopentadienyl complexes of the early transition metals.<sup>38</sup>

The formal coordination number of  $[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2]^{2-}$  is eight (counting coordinating electron pairs). Thus it might be considered coordinatively unsaturated, since the usual coordination number found in actinide organometallic complexes is ten.<sup>2</sup> The  $[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2]^{2-}$  ion does not, however, react with excess  $[\text{C}_2\text{B}_9\text{H}_{11}]^{2-}$ ; the product of the reaction of  $\text{UCl}_4$  with 3 or more equiv of dicarbollide dianion is invariably the disubstituted complex. (This may be attributed partly to the rapid buildup of charge accompanying chloride substitution by dicarbollide, but it is primarily due to the steric bulk of the dicarbollide anions.) The centroid-U-centroid angle in  $[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2]^{2-}$  is quite large,  $137^\circ$ , and even with the observed staggered arrangement of the two dicarbollide ligands, the contact between them is  $3.37 \text{ \AA}$  [ $\text{B}(1,2) \cdots \text{B}(2,3)$ ], only slightly larger than the closest C  $\cdots$  C contacts found in  $\text{U}(\text{C}_5\text{H}_4\text{CH}_2\text{Ph})_3\text{Cl}$ .<sup>2</sup> The maximum possible angle between the centroids in a trisdicarbollide complex is  $120^\circ$ , which seems impossibly small.

Addition of the carbocyclic ligands,  $\text{C}_5\text{H}_5^-$  and  $\text{C}_8\text{H}_8^{2-}$ , to  $[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2]^{2-}$  gives several interesting results. Uranocene,  $\text{U}(\text{C}_8\text{H}_8)_2$ , was produced immediately when  $[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2]^{2-}$  was combined with excess  $\text{K}_2\text{C}_8\text{H}_8$ . Considerable amounts of uranocene were detected even with less than stoichiometric quantities of  $\text{C}_8\text{H}_8^{2-}$ . Addition of an excess of cyclopentadienide to the dicarbollide complex gave a red product; spectral results indicated that a minimum of 2 equiv of  $\text{C}_5\text{H}_5^-$  is necessary for the formation of this product. Electronic spectra and solubility properties have shown that the red product contains no  $\text{U}(\text{C}_5\text{H}_5)_4$  or  $\text{U}(\text{C}_5\text{H}_5)_3\text{Cl}$ . In contrast to the cyclooctatetraene dianion, it is clear that even an excess of  $\text{C}_5\text{H}_5^-$  cannot completely displace the 1,2-dicarbollide dianion from  $[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2]^{2-}$ . Despite the unsuccessful attempts in the past by other workers to synthesize mixed  $\text{C}_8\text{H}_8^{2-}$  and  $\text{C}_5\text{H}_5^-$  complexes or uranium, apparently mixed ligand complexes of cyclopentadienide and the dicarbollide dianions (similar to those of the d-transition metals) can be prepared although they have as yet not been isolated.

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**Supplementary Material Available:** A listing of structure factor amplitudes, the visible spectrum of the  $[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2]^{2-}$  ion, and perspective drawings of the  $\text{Li}(\text{OC}_4\text{H}_8)_2^+$  ions (17 pages). Ordering information is given on any current masthead page.

## References and Notes

- (1) (a) Supported in part by the National Science Foundation, Grant GP 36977X. (b) University of California. (c) Lawrence Berkeley Laboratory. (d) Work performed under the auspices of the U.S. Energy Research and Development Administration.
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- (16) After degradation of aliquots of the stock solution, uranium was determined gravimetrically as  $\text{UO}_2(\text{C}_9\text{H}_6\text{ON})_2 \cdot 2\text{C}_9\text{H}_7\text{ON}$  and chlorine was determined gravimetrically as  $\text{AgCl}$ .
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- (31) Definitions of indicators are:  $R = \sum |F_o| - |F_c| / \sum |F_o|$ ,  $R_w = \{ \sum w(F_o - F_c)^2 / \sum w F_o^2 \}^{1/2}$ , error in an observation of unit weight =  $\{ \sum w(F_o - F_c)^2 / (N_o - N_r) \}^{1/2}$  where  $N_o$  is the number of observations and  $N_r$  is the number of refined variables.
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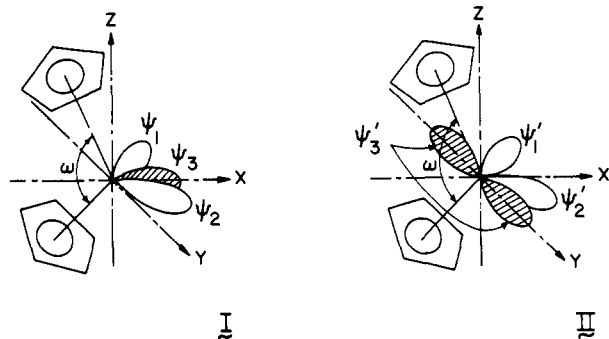
## X-Ray and Neutron Diffraction Studies on $\text{H}_3\text{Nb}(\text{C}_5\text{H}_5)_2$ and $\text{H}_3\text{Ta}(\text{C}_5\text{H}_5)_2$ <sup>1</sup>

Robert D. Wilson,<sup>2a</sup> Thomas F. Koetzle,\*<sup>2b</sup> Donald W. Hart,<sup>2a</sup> Åke Kvick,<sup>2c</sup>  
 Donald L. Tipton,<sup>2a</sup> and Robert Bau\*<sup>2a,3</sup>

Contribution from the Department of Chemistry, University of Southern California, Los Angeles, California 90007, the Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973, and the Institute of Chemistry, Uppsala University, 21 Uppsala 1, Sweden. Received August 17, 1976

**Abstract:** The molecular structures of  $\text{H}_3\text{Nb}(\text{C}_5\text{H}_5)_2$  and  $\text{H}_3\text{Ta}(\text{C}_5\text{H}_5)_2$  have been analyzed by x-ray and neutron diffraction techniques, respectively. In both compounds the central  $\text{H}_3\text{M}$  fragment is planar within experimental error and defines a non-crystallographic mirror plane for the molecule. The three hydridic atoms are essentially equidistant from the metal atom and are arranged with the central M-H bond in a bisecting position. From the x-ray diffraction analysis of  $\text{H}_3\text{Nb}(\text{C}_5\text{H}_5)_2$ , Nb-H = 1.65 (6), 1.65 (6), and 1.76 (7) Å, and H-Nb-H = 65 (3) and 61 (3)°. More accurate distances and angles were obtained from the neutron diffraction analysis of  $\text{H}_3\text{Ta}(\text{C}_5\text{H}_5)_2$ : Ta-H = 1.769 (8), 1.775 (9), and 1.777 (9) Å; H-Ta-H = 62.8 (5) and 63.0 (4)°. Other important molecular parameters are as follows: for  $\text{H}_3\text{Nb}(\text{C}_5\text{H}_5)_2$ , Nb-ring(centroid) = 2.059 Å, Nb-C(av) = 2.375 Å, ring-Nb-ring bending angle = 141.6°; for  $\text{H}_3\text{Ta}(\text{C}_5\text{H}_5)_2$ , Ta-ring = 2.065 Å, Ta-C(av) = 2.393 Å, ring-Ta-ring bending angle = 139.9°. The structure of the isoelectronic compound  $[\text{H}_3\text{W}(\text{C}_5\text{H}_5)_2]^+\text{Cl}^-$  has also been examined, and found to be similar to that of  $\text{H}_3\text{Nb}(\text{C}_5\text{H}_5)_2$  and  $\text{H}_3\text{Ta}(\text{C}_5\text{H}_5)_2$ . Crystallographic details: for  $\text{H}_3\text{Nb}(\text{C}_5\text{H}_5)_2$ , space group  $P4_12_12$ ,  $a = 11.012$  (5) Å,  $c = 14.960$  (5) Å,  $V = 1814.1$  Å<sup>3</sup>,  $Z = 8$ ; for  $\text{H}_3\text{Ta}(\text{C}_5\text{H}_5)_2$ , space group  $P4_12_12$ ,  $a = 10.965$  (5) Å,  $c = 14.817$  (7) Å,  $V = 1781.6$  Å<sup>3</sup>,  $Z = 8$ . Final agreement factors (based on  $F$ ) for data with  $I > 3\sigma$ : in  $\text{H}_3\text{Nb}(\text{C}_5\text{H}_5)_2$ ,  $R_F = 0.035$  and  $R_{wF} = 0.043$  for 1530 reflections (x-ray data collected at room temperature); in  $\text{H}_3\text{Ta}(\text{C}_5\text{H}_5)_2$ ,  $R_F = 0.069$  and  $R_{wF} = 0.051$  for 841 reflections (neutron data collected at 90 K).

The bonding in bent metal sandwich complexes has been an actively discussed subject in recent years.<sup>4-7</sup> The original model proposed by Ballhausen and Dahl in 1961<sup>4</sup> involved three hybrid orbitals directed as shown in I, while an alternative model, proposed by Alcock in 1967,<sup>5</sup> essentially replaced the central orbital in the Ballhausen-Dahl scheme ( $\psi_3$  in I) by a two-lobed orbital perpendicular to it ( $\psi_3'$  in II).



It is now fairly clear that in complexes of the type  $(\text{C}_5\text{H}_5)_2\text{ML}_2$  the Alcock model is preferred. Recent x-ray crystallographic<sup>5,6</sup> and EPR studies<sup>7a,b</sup> by Green, Prout, Dahl, and their co-workers have shown that for the series of compounds  $(\text{C}_5\text{H}_5)_2\text{ML}_2$  ( $L = \text{CH}_3, \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{SC}_6\text{H}_5$ ), the observed structural features are best explained by the presence or absence of nonbonding electrons in a  $\psi_3'$ -type orbital (II). Lauher and Hoffmann recently have systematically studied

the bonding in such complexes, within the framework of extended Hückel (EH) MO theory.<sup>7c</sup> Their EH treatment delineates three frontier orbitals available to bond to the ligands L, quite similar to those deduced on qualitative grounds by Green et al.<sup>6a</sup> and clarifies the relationship between the contrasting hybridization schemes of Ballhausen and Dahl and Alcock models. They point out that these latter schemes are equivalent to taking different linear combinations of the frontier orbitals. In this paper, as part of our continuing investigations of the structures of metal hydride complexes,<sup>8</sup> we report the crystal structure determinations of two of the simplest complexes of the  $(\text{C}_5\text{H}_5)_2\text{ML}_3$  type:  $(\text{C}_5\text{H}_5)_2\text{NbH}_3$  and  $(\text{C}_5\text{H}_5)_2\text{TaH}_3$ .

$\text{H}_3\text{Ta}(\text{C}_5\text{H}_5)_2$  was first prepared by Wilkinson and co-workers in 1961 by the reaction of  $\text{TaCl}_5$ ,  $\text{NaC}_5\text{H}_5$ , and  $\text{NaBH}_4$  in tetrahydrofuran.<sup>9</sup> On the basis of NMR data (which showed an  $A_2B$  pattern of signals in the hydridic region) and other spectral evidence, a bent-sandwich structure with three M-H bonds arranged along orbitals  $\psi_1$ - $\psi_3$  in I was proposed. Recent photoelectron studies of the compound support this model by showing three peaks attributable to Ta-H bonding electrons.<sup>6c</sup>

Interest in  $\text{H}_3\text{Ta}(\text{C}_5\text{H}_5)_2$  was heightened in 1970 when Barefield, Parshall, and Tebbe discovered a remarkable  $\text{H}_2/\text{D}_2$  exchange reaction catalyzed by it: when a  $\text{C}_6\text{D}_6$  solution of  $\text{H}_3\text{Ta}(\text{C}_5\text{H}_5)_2$  is heated under a hydrogen atmosphere, HD and  $\text{D}_2$  can be detected in the vapor phase.<sup>10</sup> This exchange reaction, which was also found to take place with other polyhydrido