Table II. Stability Constants of Hydroxouranyl and (Carbonato)uranyl Species

	this work		literature values		
species	$-\log {}^*\beta$	$\log \beta^a$	$-\log {}^*\beta$	$\log \beta^a$	ref
1,3,0	31.21 ± 0.05	21.81	...	21.57	3
1,2,0	19.19 ± 0.29	16.15	...	16.16	3
2,1,3	18.63 ± 0.08		...	...	
3,0,5	16.19 ± 0.16		16.2		16
2,0,2	5.89 ± 0.37		5.8		16

[a] Where $\log \beta_{130} = \log {}^*\beta_{130} - 3 \log ({}^*K_1K_2)$ and $\log \beta_{120} = \log {}^*\beta_{120} - 2 \log ({}^*K_1K_2)$. The K stands for the dissociation constants of H_2CO_3.

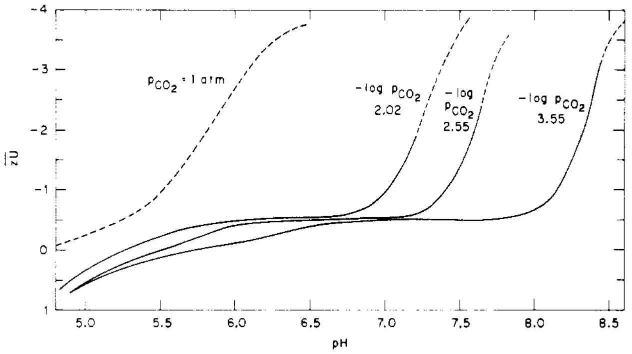

Figure 4. $\bar{z}(U)$ as a function of pH and p_{CO_2} at $a[U] = 0.001$ M. Solid lines describe conditions actually covered in this study. Dashed lines extend to calculated values.

range between complete complexation and complete hydrolysis. The values given by Tsymbal for the stability constants of these species are not consistent with the carbon content of uranium–carbonate solutions and the solubility data of β-$UO_3 \cdot H_2O$.[13]

Analysis of the data with the inclusion of additional hydrolytic species was also made. Testing a 4,0,7 species, proposed by Sylva et al.,[14] gave no improvement. On the other hand, the species 3,0,7 improved the fit slightly, but inclusion of this species in the model was considered to be unjustified because its contribution becomes important at pH values of relatively large uncertainties.

Finally, the consideration was given to the species 3,6,0 as an alternate to 1,2,0. This species was reported recently by Ciavatta et al.[15] on the basis of potentiometric and ^{13}C NMR data, but no stability constant was given. Its introduction produced large uncertainties on its stability constant. This is apparently a result of the minor contribution of this species to the total uranium concentration in the p_{CO_2} range covered in the present study.

The final fit of the data was made with the species 1,3,0, 1,2,0, 2,1,3, 3,0,5, and 2,0,2. The values found for the stability constants of these species are given in Table II.

Mass balance as a function of pH and p_{CO_2} were used to calculate species distribution under different conditions. These are presented in a condensed manner in Figure 4. The curves represent the average charge on the uranium species, $\bar{z}(U)$, as a function of pH and p_{CO_2}. The values of $\bar{z}(U)$ are obtained from the expression

$$\bar{z}(U) = \frac{\sum z[abx^z]}{[U_t]}$$

There is a similarity between the $\bar{z}(U)$ vs. pH plots presented here and the more familiar $\bar{n}$ vs. [L] plots, where $\bar{n}$ is the average ligand number and [L] is the ligand concentration. The similarity is not coincidental since $[CO_3^{2-}]$ is implicit by a combination of the pH and p_{CO_2} values.

Figure 4 shows a few relations that describe the system. The flat portion of the plots roughly defines the conditions of predominance of the hemicarbonate species. The pH range of existence of this species decreases as P_{CO_2} increases and becomes quite limited at 1 atm of CO_2. The steep rise in $\bar{z}(U)$ values occurring within a narrow pH range, particularly at low p_{CO_2}, is a reflection of the rather large difference, of the order of $10^{5.5}$, in the stability constants of the tricarbonate and dicarbonate complexes. The contribution of the hydrolytic species is evident in the pH range where the $\bar{z}(U)$ values approach zero and become positive.

Conclusions

The existence of a hydroxocarbonato species having a U/CO_3 mole ratio of 2.0 has been demonstrated by analytical, spectroscopic, and electrochemical means. The stoichiometry of the reactions leading to its formation from either UO_2^{2+} or $UO_2(CO_3)_3^{4-}$ and the data analyses of the potentiometric titrations indicate that this species is apparently $(UO_2)_2CO_3(OH)_3^-$.

The set of equilibrium constants derived from the fit of the data is in good agreement with values in the literature for those species that are known, therefore lending support to the reliability of the constant derived for the formation of the hemicarbonate species.

The hemicarbonate species is of importance under conditions similar to those found in natural waters, and it should be considered in speciation schemes of uranium(VI) in nature.

An integrated view of the carbonate complexation and hydrolysis of the uranyl ion as a function of pH and P_{CO_2} has been obtained.

Acknowledgment. I am very grateful to C. F. Baes, Jr., for help and guidance in the computer data analysis. The chemical analyses were performed by the Analytical Chemistry Division of Oak Ridge National Laboratory.

Registry No. U, 7440-61-1.

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Preparation and Characterization of (μ-Dichloroboryl)pentaborane(9)

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A variety of pentaborane(9) derivatives with the general formula $(\mu$-$X_nM)B_5H_8$ have been reported in the literature.[1,2] In these compounds the substituent group MX_n is located at a basal bridge position of the pyramidal pentaborane framework. Among those reported, (μ-dimethylboryl)pentaborane(9) ($[\mu$-$(CH_3)_2B]B_5H_8$) is unique in that the boron atom at the bridge position, or the B in the $B(CH_3)_2$ group, is sp^2 hybridized and the p_z orbital is left unused.[3]

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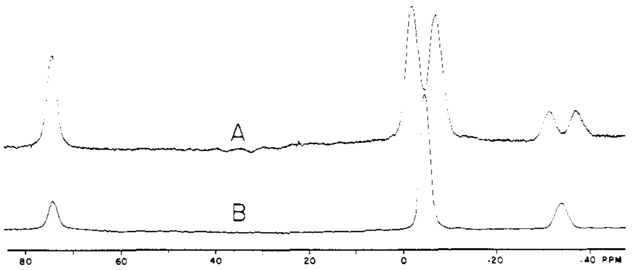

Figure 1. ^{11}B NMR spectra of (μ-Cl_2B)B_5H_8: (A) normal spectrum; (B) ^1H spin-decoupled spectrum.

Table I. ^{11}B and ^1H NMR Data for (μ-Cl_2B)B_5H_8[a]

^{11}B

shift,[b] ppm	J_{HB}, Hz	rel intens	assignt
74.8 (s)		1	B_μ
−4.5 (d)	160	4	B_{2-5}
−34.2 (d)	185	1	B_1

^1H

δ[c]	rel intens	assignt	δ[c]	rel intens	assignt
3.18	2	$H_{2,3}$ or $H_{4,5}$	−1.00	1	$H_{\mu 1}$
2.86	2	$H_{4,5}$ or $H_{2,3}$	−1.45	2	$H_{\mu 2}$
1.58	1	H_1			

[a] At 0 °C in CH_2Cl_2/CD_2Cl_2. [b] Relative to $BF_3 \cdot O(C_2H_5)_2$, low-field shifts being taken as positive. [c] Measured relative to CH_2Cl_2 (solvent), which was taken as δ 5.28.

During the course of our boron hydride reaction study involving the octahydropentaborate(1−) anion, a dichloroboryl derivative of pentaborane(9) was isolated. The preparation and characterization of the dichloro compound is reported in this note.

Results and Discussion

Treatment of potassium octahydropentaborate(1−) in dichloromethane with excess boron trichloride resulted in the formation of an extremely air-sensitive, liquid compound. The compound was characterized as (μ-dichloroboryl)pentaborane(9) by its mass, IR, and ^{11}B and ^1H NMR spectra:

$$KB_5H_8 + BCl_3 \rightarrow KCl + (\mu\text{-}Cl_2B)B_5H_8 \qquad (1)$$

The dichloroboryl compound appears stable below 0 °C in vacuo but slowly turns yellow upon standing at room temperature. It inflames spontaneously in air and is hydrolyzed readily by moisture, forming pentaborane(9) as the initial major product.

The ^{11}B NMR spectrum of the compound is shown in Figure 1, and the spectral data are summarized in Table I along with the ^1H NMR data. The large doublet signal at −4.5 ppm in the ^{11}B spectrum appears slightly dissymmetric due, presumably, to two overlapping doublets of equal intensity having slightly different shifts (no more than 0.5 ppm difference) and B–H coupling constants. The singlet signal at +74.8 ppm is attributed to the BCl_2 boron. The highly positive shift value of the signal suggests that the boron is sp^2 hybridized like that of the $B(CH_3)_2$ group in [μ-$(CH_3)_2B$]B_5H_8.[3] The doublet signal at −34.2 ppm is assigned to the apex boron atom. The structure shown in Figure 2 is consistent with the observed ^{11}B NMR spectrum and is analogous to that proposed for [μ-$(CH_3)_2B$]B_5H_8 in the literature.[3] The ^1H NMR spectrum is consistent also with the structure in the figure. The assignments for the ^1H signals were made by use of the single-frequency decoupling technique on boron spins. When the sample was irradiated with the frequency of the large doublet signal (−4.5 ppm), four of the five ^1H resonance signals became sharp. Two of them (δ −1.45 and −1.00) in an intensity ratio 2:1 were in the region of bridge hydrogen signals, and the other two signals (δ +2.86 and 3.16) were in a 2:2 intensity ratio and in the region of terminal hydrogen signals. These data indicate that the four boron atoms are not all equivalent and further support the earlier interpretation that the ^{11}B doublet at −4.5 ppm is an overlap of two doublet signals.

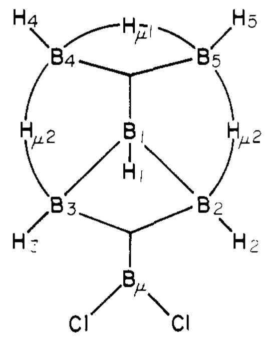

Figure 2. Structure proposed for (μ-Cl_2B)B_5H_8.

The mass spectrum of (μ-Cl_2B)B_5H_8 has the highest mass cutoff at m/e 148 as required for $^{11}B_6H_8{}^{37}Cl_2{}^+$. Intense peaks occur at m/e 80–85 and 52–62 for BCl_2^+ and $B_5H_n^+$, respectively. The facile dissociation of the μ-boryl substituent in the mass spectrometer was observed also for [μ-$(CH_3)_2B$]B_5H_8.[3]

The dichloroboryl compound reacted with diethyl ether, dimethyl ether, and tetrahydrofuran and gave addition compounds, $B_6H_8Cl_2 \cdot OR_2$, of the respective ethers. The ^{11}B NMR spectrum of the ether addition compound was not that expected for a simple adduct with the formula (μ-$Cl_2B \cdot OR_2$)B_5H_8. Furthermore, the chloroborane compound that was liberated by the treatment of the ether adducts with boron trifluoride was not the original (μ–Cl_2B)B_5H_8. Apparently, the boron framework of (μ-Cl_2B)B_5H_8 had undergone a rearrangement as the result of the ether treatment. Gaines and Iorns reported[3] that [μ-$(CH_3)_2B$]B_5H_8 isomerized to 4,5-dimethylhexaborane(10) when treated with diethyl ether. There seems to be a close resemblance between the behaviors of the two boryl compounds toward ethers. The more acidic character of the chloro compound is thought to be responsible for the formation of the ether adduct of the chloroborane compound. The detailed studies on the nature of the ether addition compounds and the supposed isomer of $B_6H_8Cl_2$ are under way in our laboratory, and the results will be reported at a later date.

Experimental Section

General Data. Conventional vacuum-line techniques were used for the handling of volatile compounds. Air- and moisture-sensitive solids were handled in glovebags filled with dry nitrogen. Boron trichloride, boron trifluoride, and dimethyl ether (Matheson Gas Products) were purified by fractional condensation on the vacuum line. Commercially obtained reagent grade diethyl ether and tetrahydrofuran were stored over $LiAlH_4$, and dichloromethane was stored over molecular sieves. These liquids were distilled directly into the reaction vessels.

The ^{11}B and ^1H NMR spectra were recorded on a Varian XL-100-15 spectrometer operating in the FT mode at 32.1 and 100 MHz, respectively. Chemical shifts were expressed with respect to $BF_3 \cdot O(C_2H_5)_2$ and tetramethylsilane. The mass spectra were obtained on a Hewlett-Packard HP-5933A mass spectrometer operating in the electron-impact mode at 70 eV.

Preparation of (μ-Cl_2B)B_5H_8. Potassium octahydropentaborate(1−) was prepared by the literature method[4] with use of dimethyl ether as the solvent. The solvent ether was pumped out at −45 °C from the reaction vessel. Dichloromethane and excess BCl_3 were then condensed in the vessel, and the mixture was stirred for 3 h at −80 °C. During this period of time the appearance of the reaction mixture changed from the original suspension of coarse solid (KB_5H_8) to a milky suspension of yellow-tinged, finely divided solid. After it was

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stirred further for 15 min at −45 °C and for 15 min at 0 °C, the reaction mixture was warmed to room temperature and the volatile components were distilled into a −197 °C trap until a yellow liquid and a white solid began to condense in the trap. Then, most of the solvent CH_2Cl_2 was pumped out from the cold trap at the temperatures below −60 °C. The remaining fraction was passed through −23 and −45 °C traps. The dichloroboryl compound was trapped in the −45 °C trap. Thus, treatment of 4.85 mmol of KB_5H_8 (estimated from the amount of hydrogen gas evolved in the reaction of KH with B_5H_9) with 14.6 mmol of BCl_3 in about 5 mL of dichloromethane yielded 3.04 mmol (0.437 g) of $(\mu\text{-}Cl_2B)B_5H_8$ (62.7% yield based on the $B_5H_8^-$ used). Anal. Calcd for $B_6H_8Cl_2$: Cl, 49.4%. Found: 49.1%. Infrared Spectrum (gas phase, 1 mm pressure, 100-mm path length cell, KBr windows, Beckman IR-20 spectrophotometer): 2608 (s), 2580 (m, sh), 1422 (m, br), 996 (w), 940 (w), 908 (s), 829 (m), 778 (m), 670 (w), 593 (w) cm^{-1}.

The product is extremely sensitive to moisture and air. The inner walls of the glassware need to be dried exhaustively before being brought into contact with the compound if the formation of a white solid deposit on the glass surface and the contamination of the compound with pentaborane(9) are to be avoided. Also, the compound is absorbed by Apiezon grease. The grease that is contaminated by the compound will catch fire when exposed to air. Extensive pumping is necessary before greased joints are disconnected.

Reactions of $(\mu\text{-}Cl_2B)B_5H_8$ with Ethers. When the dichloroboryl compound was treated with diethyl ether in dichloromethane at −80 °C a reaction occurred as evidenced by the appearance of a new set of ^{11}B NMR signals in the spectrum of the solution. The new signals were at +7.8 (br), −3.3 (br), −14.3 (d), and −52.3 (d) ppm in an approximately 1:1:3:1 intensity ratio. As long as the amount of the ether added was less than 1 mol/mol of the dichloroboryl compound, the signals of the dichloroboryl compound were still present in the spectrum even when the solution was warmed to room temperature. The product slowly decomposed at room temperature. The ^{11}B spectra of the products from the reactions with dimethyl ether and tetrahydrofuran were similar to that of the diethyl ether reaction product.

When a CH_2Cl_2 solution containing the ether addition compound was treated with excess boron trifluoride, the etherate of BF_3 and a compound that could be identified by a set of ^{11}B NMR signals were produced. The set of resonance signals was characterized by three doublets at −51, −12, and −8 ppm in an intensity ratio 1:~2:1 and a very broad signal centered at about +66 ppm and was independent of the kind of ethers in the orignal addition compound. It is noted that this set of signals could not be detected in the spectra of the room-temperature decomposition products of the $(\mu\text{-}Cl_2B)B_5H_8$ etherates.

Acknowledgment. The authors acknowledge support of this work by the U.S. Army Research Office. Thanks are due to Mr. Leonard H. Wojcik for undertaking the mass spectral measurements.

Registry No. $(\mu\text{-}Cl_2B)B_5H_8$, 81643-54-1; KB_5H_8, 56009-95-1; BCl_3, 10294-34-5; diethyl ether, 60-29-7.

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ESR Study of a Paramagnetic Titanium Methylene Complex and of Its Reactions with Olefins

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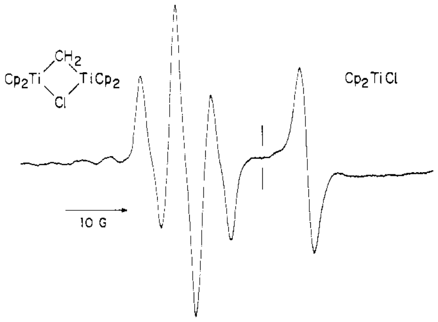

Figure 1. ESR spectrum (−50 °C) obtained by combining equal volumes of 0.02 M solutions of **1** and of THF in toluene at room temperature.

Transition-metal complexes of the simplest carbene, methylene, are of current interest because of their probable involvement in processes such as olefin metathesis[1] and Fischer–Tropsch[2] synthesis. The mononuclear complexes of this type, with one notable exception, $Cp_2(Me)Ta{=}CH_2$,[3] have all proven to be too reactive to be isolated as stable compounds. In several cases, however, the metal methylene complex could be stabilized by association with a suitable organometallic entity. This resulted in methylene groups that bridge two metal centers. Examples of such stabilization are found in the titanium methylene complex $Cp_2TiCH_2AlClMe_2$ (**1**),[4] which can be viewed as the union of Cp_2TiCH_2 and the diphilic $ClAlMe_2$, and the iron methylene complex $(\mu\text{-}CH_2)Fe_2(CO)_8$,[5] which can be viewed as $(CO)_4FeCH_2$ associated with the coordinatively unsaturated $Fe(CO)_4$ fragment. These complexes are diamagnetic as are the other known methylene complexes.[6] We wish to report now ESR evidence for a paramagnetic transition-metal methylene complex,[7] as well as ESR evidence that demonstrates, with the aid of appropriate isotopically labeled reagents, the facile exchange of the metal-bound CH_2 fragment with the CH_2 group of a terminal olefin, a step considered essential to the so-called degenerate metathesis reaction,[1] which exchanges methylene groups between terminal olefins of the type $CR_2{=}CH_2$ (eq 1).

$$CR_2{=}CH_2 + CR'_2{=}{}^*CH_2 \rightleftharpoons CR_2{=}{}^*CH_2 + CR'_2{=}CH_2 \qquad (1)$$

Experimental Section

General Considerations. All chemical manipulations were carried out in a glovebox (Vacuum Atmospheres Co.) under pure nitrogen. Toluene and THF were distilled from Na/benzophenone under nitrogen. The titanium methylene complex **1** was prepared according to a published procedure.[4] Careful recrystallizations from toluene are necessary to obtain **1** free of the paramagnetic impurity $Cp_2Ti(\mu\text{-}Cl)_2AlMe_2$ (**4**) (for ESR parameters see ref 16). Cp_2TiCl was obtained by degradative treatment of **1** with pyridine. The purified product was indistinguishable from Cp_2TiCl obtained by a more conventional method.[8] [^{13}C]Methylenecyclohexane, $^{13}CH_2{=}C_6H_{10}$, was purchased from Merck Sharp and Dohme Canada Ltd.

ESR spectra were obtained with a Bruker ER-420 spectrometer equipped with a field-tracking proton NMR gauss meter (B-NM 12) and a direct-reading microwave frequency counter. A field-frequency marking system interacting with a BNC 12 computer and a Teletype terminal allowed the precise measurement by computer of ESR splitting and *g* values with Bruker software.

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