ated XO_2^+ species of a pentavalent actinyl(V) element. However, with the exception of $KAmO_2F_2$, which had been known for some time,[2] no structure data had been given for any other fluoride containing an actinyl(V) species. The preparation of and lattice constants for several 1:1 rubidium (and one ammonium) actinyl(V) fluorides are described in the present note.

One recent publication[3] reported lattice constants for the series $KNpO_2CO_3$, $KPuO_2CO_3$, and $KAmO_2CO_3$. As a continuation of that work, similar data are given for $CsAmO_2CO_3$.

All pentavalent actinyl(V) species undergo disproportionation and are relatively easy to reduce. Therefore, considerable care must be exercised in the preparation of these compounds, especially those involving PuO_2^+, to maintain the actinyl(V) ion in its pentavalent state. The conditions described in the following section were found to be effective in preparing the actinyl(V) compounds in good yield.

Experimental

$CsAmO_2CO_3$.—Cesium americyl(V) carbonate was prepared by treating a slurry of pink $Am(OH)_3$ in *ca.* 0.5 *M* $CsHCO_3$ with ozone (5% O_3 in O_2) at 92° for 1 hr. The resulting tan precipitate was washed with small amounts of water, methyl alcohol, and acetone and air dried.

$RbNpO_2F_2$.—Rubidium neptunyl(V) fluoride was prepared by injecting a chilled solution of NpO_2^+ in ~0.1 *M* HNO_3 *into* a chilled saturated solution of rubidium fluoride (*ca.* 12 *M*) at 0°. The gray-green precipitate which formed was centrifuged rapidly, washed with small amounts of water, methyl alcohol, and acetone, and air dried. It was important to work as rapidly as possible during the precipitation step because of disproportionation of pentavalent neptunium.

$RbPuO_2F_2$.—Rubidium plutonyl(V) fluoride also required rapid manipulation for successful preparation. A solution of PuO_2^+ was injected into a solution of saturated rubidium fluoride at 0° at pH 6. The PuO_2^+ solution was prepared by addition of a 50% excess of hydrogen peroxide to a solution of PuO_2^{2+} according to the equation: $PuO_2^{2+} + {}^1/_2H_2O_2 \rightarrow PuO_2^+ + H^+ + {}^1/_2O_2$. This reduction is most conveniently carried out at pH 3 at 0°; the light green color of PuO_2^{2+} disappears within 5 min. with evolution of O_2. The reduction is quantitative and the absence of PuO_2^{2+} and Pu^{4+} was checked on a Cary spectrophotometer. The brilliant lavender-colored PuO_2^+ is reported stable up to 0.01 *M* PuO_2^+ at pH values of *ca.* 3.[4] Adjustment of the pH to 6 (with RbOH) was made *after* the reduction of PuO_2^{2+} to PuO_2^+. The PuO_2^+ solution was then combined rapidly with the RbF solution; the lavender precipitate was washed with a minimum amount of water, methyl alcohol, and acetone and air dried.

$NH_4PuO_2F_2$.—Ammonium plutonyl(V) fluoride was formed by adding solid NH_4F to a solution of PuO_2^+ at pH 6 prepared as above except that NH_4OH was used to adjust the pH. The addition of NH_4F was made at 0°. The lavender precipitate was treated in the same manner as the others.

$RbAmO_2F_2$.—Rubidium americyl(V) fluoride was made by addition of saturated RbF solution to AmO_2^+ in 0.01 *M* HCl. As with the other preparations, the precipitation was carried out at 0° although the rapid centrifugation and manipulations were not as necessary as with the neptunyl(V) and plutonyl(V) compounds. The tan rubidium americyl(V) precipitate was likewise washed with small amounts of water, methyl alcohol, and acetone and air dried.

X-Ray samples were prepared from the dried powders. The data from the X-ray films were treated as described elsewhere[3,5] to calculate lattice parameters and their standard deviations. Table I lists the lattice constants that were obtained for these compounds.

TABLE I

LATTICE DIMENSIONS OF ALKALI METAL ACTINYL(V) COMPOUNDS

Rhombohedral, Space Group $R\bar{3}m\text{-}D_{3d}^5$, $Z = 1$

			Hexagonal dimensions	
Compound	a_0, Å.	α, deg.	a_0, Å.	c_0, Å.
$RbNpO_2F_2$	6.814 ± 0.008	36.18	4.245 ± 0.005	19.07 ± 0.02
$RbPuO_2F_2$	6.796 ± 0.008	36.17	4.232 ± 0.005	19.02 ± 0.02
$RbAmO_2F_2$	6.789 ± 0.006	36.15	4.224 ± 0.004	19.00 ± 0.02
$NH_4PuO_2F_2$	6.817 ± 0.006	36.16	4.243 ± 0.004	19.08 ± 0.03

Hexagonal, Space Group $C6/mmc\text{-}D_{6h}^4$, $Z = 2$

Compound	a_0, Å.	c_0, Å.
$CsAmO_2CO_3$	5.123 ± 0.001	11.538 ± 0.007

Acknowledgment.—The author wishes to thank his colleague, Dr. F. H. Kruse, for setting up the computer programs involved in this work and for his advice concerning space group assignments, etc.

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[3] T. K. Keenan and F. H. Kruse, *Inorg. Chem.*, **3**, 1231 (1964).

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF OTTAWA, OTTAWA, CANADA

The Infrared Spectra of Some Compounds of Zirconium(IV) and Hafnium(IV) Tetrahalides and Ligands Containing Group V Donor Atoms

BY T. C. RAY AND A. D. WESTLAND

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Preparations of a number of complexes of zirconium(IV) halides and hafnium(IV) chloride have been reported previously together with studies of their infrared spectra in the 4000–650 cm.$^{-1}$ region. However, only one published work on the important 550–200 cm.$^{-1}$ region has appeared to date.[1] It is in this region that metal–ligand stretching frequencies should occur.

Pyridine and nitriles,[2] some secondary and tertiary amines,[3,4] and *o*-phenylenebisdimethylarsine[5] have been shown to form adducts with zirconium(IV) chloride and bromide. Infrared spectra have been recorded for some of the adducts,[4,6] but emphasis was placed upon investigation of the effect of coordination on the ligand modes themselves.

The present work deals with the preparation of complexes of ZrX_4 and HfX_4 (where X = Cl, Br) with donor molecules containing nitrogen, phosphorus, and arsenic and describes the effect of change of ligand and

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[2] H. J. Emeléus and G. S. Rao, *ibid.*, 4245 (1958).

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[4] G. W. A. Fowles and R. A. Walton, *J. Less-Common Metals*, **5**, 510 (1963).

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central metal atom on the metal–halogen stretching frequencies.

Experimental

Infrared spectra between 520 and 250 cm.$^{-1}$ were recorded using a Perkin-Elmer Model 13G spectrometer fitted with a grating blazed at 30 μ. Samples were mounted as Nujol mulls held between cesium iodide plates, whose edges were greased to prevent ingress of air. Instrument calibration was checked against the rotational spectrum of water vapor,[7] but the instrument was operated double-beam and was flushed continuously with a strong stream of nitrogen.

Analyses for metal in complexes containing nitrogen were carried out gravimetrically following preparation of the sample by Parr bomb combustion and precipitation with ammonia. Halogen was determined by Volhard titration. The procedure adopted for the diphosphine and diarsine complexes is described elsewhere[8] and involved precipitating the metals as their phosphates.

Zirconium(IV) chloride and hafnium(IV) chloride, supplied by A. D. Mackay, Inc., were both purified by sublimation in a sealed tube containing nitrogen, the former at a temperature of 280° and the latter at 275°.

Pyridine (Baker Analyzed Reagent) was dried over sodium hydroxide pellets before distillation and N,N′-tetramethylethylenediamine (temen) (Aldrich) was fractionally distilled under reduced pressure, the fraction boiling between 88 and 89° (50 mm.) being collected.

2,2′-Bipyridine (Fisher) was dried in a drying pistol for 3 hr. at 56° while 1,10-phenanthroline (Fisher) was sublimed under reduced pressure to yield a crystalline product, m.p. 118°.

The ligands 1,2-bis(diphenylphosphino)ethane and 1,2-bis-(diphenylarsino)ethane were prepared using a procedure described by Chatt and Hart.[9]

Zirconium(IV) Bromide.—Nuclear grade zirconium sponge (2 g.) was heated in an aluminum block furnace with bromine vapor at the vapor pressure of the liquid at room temperature for 48 hr. The temperature of the metal was kept such that sublimation of the product was maintained. Excess bromine present at the end of the reaction period was removed by pumping.

Anal. Calcd.: Zr, 22.20; Br, 77.78. Found: Zr, 22.01; Br, 76.20.

Preparation of Complexes.—All addition complexes were prepared using a procedure essentially the same as that described below.

Tetrachloro-2,2′-bipyridinezirconium(IV).—Carefully dried, sulfur-free benzene was distilled at reduced pressure from sodium metal into a Schlenk tube immersed in liquid nitrogen. The distillate (25 ml.) was allowed to attain room temperature, and dry nitrogen then was admitted. The content of an ampoule of zirconium(IV) chloride (1.50 g.) was introduced into the tube and to this suspension was added 2,2′-bipyridine (1.048 g., 1.04 mol. equiv.) dissolved in benzene (5 ml.). Vigorous stirring for 1.5 hr. produced a heavy white precipitate but stirring was continued for a further 24 hr. to ensure complete reaction. The solvent volume was then reduced by pumping to one-third before the solid material was separated in a filtering apparatus similar to that described by Fritz and co-workers.[10] The product was washed with two volumes of benzene before drying under vacuum at room temperature. As this compound, and the others in this series, was air-sensitive, all were stored in ampoules under nitrogen.

Results and Discussion

TABLE I

ANALYSIS FIGURES FOR COMPLEXES OF ZrX_4 (X = Cl, Br) AND $HfCl_4$

	Found, %		Calcd. %	
Compound[a]	Zr (Hf)	X	Zr (Hf)	X
$ZrCl_4 \cdot 3py$	19.35	30.15	19.87	30.6
$ZrCl_4 \cdot 2py$	22.87	35.70	23.32	36.25
$ZrBr_4 \cdot 2py$	16.03	56.19	15.80	55.97
$HfCl_4 \cdot 3py$	31.70	25.95	32.01	25.43
$HfCl_4 \cdot 2py$	36.84	29.35	37.30	29.64
$ZrCl_4 \cdot bipy$	23.44	36.43	22.75	35.75
$ZrBr_4 \cdot bipy$	15.90	55.91	16.09	56.37
$HfCl_4 \cdot bipy$	37.46	29.76	37.71	29.0
$ZrCl_4 \cdot phen$	22.05	34.33	22.0	33.62
$ZrBr_4 \cdot phen$	15.45	54.0	15.65	53.3
$HfCl_4 \cdot phen$	35.66	28.33	35.21	29.05
$ZrCl_4 \cdot temen$	26.12	40.61	26.55	41.0
$ZrBr_4 \cdot temen$	17.49	59.84	17.31	60.64
$HfCl_4 \cdot temen$	40.89	32.49	40.30	31.95
$ZrCl_4[(C_6H_5)_4P_2C_2H_4]$	14.44	22.46	13.94	22.16
$ZrBr_4[(C_6H_5)_4P_2C_2H_4]$	11.27	39.5	11.20	39.08
$HfCl_4[(C_6H_5)_4P_2C_2H_4]$	24.84	19.73	24.21	19.46
$ZrCl_4[(C_6H_5)_4As_2C_2H_4]$	12.68	19.71	12.36	19.30
$ZrBr_4[(C_6H_5)_4As_2C_2H_4]$	10.17	35.63	9.91	34.87
$HfCl_4[(C_6H_5)_4As_2C_2H_4]$	22.13	17.58	21.83	16.97

[a] temen = N,N′-tetramethylethylenediamine.

The complexes prepared are listed with analysis figures in Table I. Excess of ligand was present during preparation so that all the tetrahalide was consumed in the formation of the complexes. The ligands were soluble in benzene to some extent and thus the excess could be removed by washing. Under these conditions, the bidentate ligands all formed 1:1 adducts, but the reaction between pyridine and the tetrachlorides resulted in the isolation of a product which analyzed as $MCl_4 \cdot 3py$. Emeléus and Rao[2] reported the isolation of only a 1:2 adduct, but reaction in this case took place in excess ligand as solvent rather than in a lower boiling, inert solvent such as benzene, so that removal of excess solvent must have involved some heating with loss of pyridine from the complex. Heating of the 1:3 complexes reported here under vacuum at a temperature between 65 and 75° for 7 hr. did in fact result in removal of one molecule of pyridine. The infrared absorption bands in the region 350–270 cm.$^{-1}$ of both 1:2 and 1:3 adducts were very similar, however. Zirconium(IV) bromide formed only the 1:2 complex because, presumably, of steric hindrance of the bulky bromine atoms.

Complexes of the type MX_4Y_2, group C_{2v}, would be expected to show six infrared-active metal–ligand stretching vibrations. In the hypothetical case of no coupling between M–X stretching and any other modes, we may distinguish four modes, $2A_1$, B_1, and B_2, which consist mainly of stretching motions of the group MX_4 (C_{2v}). The two A_1 modes, probably strongly coupled, consist largely of (a) symmetric stretching of the halogen bonds *cis* to each other and (b) symmetric stretching of the halogen bonds *trans* to each other. One of the B modes contains antisymmetric stretching of the *cis* halogen bonds and the other contains the antisymmetric stretching of the *trans* bonds. The frequencies of these modes should be located in the broad range 400–250 cm.$^{-1}$. Band centers in this region have been measured for all except the

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(7) H. M. Randall, D. M. Dennison, N. Ginsburg, and L. R. Weber, *Phys. Rev.*, **52**, 160 (1937).

(8) W. F. Hillebrand, *et al.*, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1953.

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TABLE II

INFRARED ABSORPTION FREQUENCIES FOR TERTIARY AMINE COMPLEXES OF $ZrCl_4$, $ZrBr_4$, $HfCl_4$, AND $PtCl_4$ IN THE REGION 450–245 CM.$^{-1}$

$ZrCl_4$·3py	424m		343s	330.5s	303vs			
$ZrCl_4$·2py	424m		339vs	332vs	300vs			
$ZrBr_4$·2py	424m						246vs	
$HfCl_4$·3py	424m				305s	277vs		
$HfCl_4$·2py	424m		335m, b		303vs	283s		
$PtCl_4$·2py	424m		352vs	343vs	329vs			
Pyridine	406.5s							
$ZrCl_4$·bipy	417m		340vs	334vs	304m	288w		
$ZrBr_4$·bipy	416m						271vs	258vs
$HfCl_4$·bipy	419m		341s	314vs	305vs	279m		
$PtCl_4$·bipy	417m		346vs	340vs	330s	290w		
$ZrCl_4$·phen	426.5m	361s	348.5vs	343vs	303vs	282s		
$ZrBr_4$·phen							268s	259s
$HfCl_4$·phen	427m	347s	342.5s	331s	310vs	278.5m		
$PtCl_4$·phen			361s	348vs	324s			258vs
phenanthroline								258vs
$ZrCl_4$·temen			343vs	334vs	298m	276w		
$ZrBr_4$·temen							268vs	
$HfCl_4$·temen			340s	319s	307vs	279s		

Abbreviations: vs - very strong; s - strong; m - medium; w - weak; b - broad

TABLE III

INFRARED ABSORPTION FREQUENCIES OF DITERTIARY PHOSPHINE AND DITERTIARY ARSINE COMPLEXES OF ZrX_4, $HfCl_4$, AND PtX_4 ($X = Cl, Br$) IN THE REGION 460–250 CM.$^{-1}$

$ZrCl_4$(diph)	447.5w			414w			353s	345vs	301b	
$ZrBr_4$(diph)							257vs			
$HfCl_4$(diph)	415w						343s	324vs	303w	278s
$PtCl_4$(diph)		450m	433m	427m	394m	382w	345vs	289vs	272vs	
$PtBr_4$(diph)		458w	438w	419m	.391w	378w				
diph	443m			409m						
$ZrCl_4$(diar)	457m		335vs,b	316vs, b						
$ZrBr_4$(diar)				322w	301m		281m, b			
$HfCl_4$(diar)			340s, b			293vs, b				
$PtCl_4$(diar)	403m	393sh	344s	325m	310m	289vs	~283sh	270vs		
$PtBr_4$(diar)	401m	391m		323m	307m					
diar				326s	305s		284s			

diarsine complexes, for which spectral analysis was made impossible by the presence of strong arsine ligand modes which, superimposed on the metal–chlorine absorptions, gave broad bands with little structure.

Data on the frequency positions of metal–ligand stretching for ligands other than halide are sparse and only tentative assignments have been made. We have therefore attempted assignment of only the bands due to metal–halogen stretching at the present time.

Infrared data for the region 460–250 cm.$^{-1}$ are presented in Tables II and III; the tetrabromide complexes are included since they permit assignment of the metal–halogen modes indicated by underlining. These absorptions were extremely intense and often broad with relative intensities differing between the zirconium complexes and their hafnium analogs. Slight modifications of the ligand frequencies result from coordination, but these are easily identifiable and do not interfere (except in the case of the diarsine complexes) with any interpretation. Clark[11] has reported three metal–halogen absorptions between 390 and 290 cm.$^{-1}$ for the 2,2′-bipyridine and 1,10-phenanthroline complexes of titanium(IV) and vanadium(IV), but examination of Table II here reveals the existence of five strong peaks for MCl_4·phen and four for MCl_4·dipy. Their absence from the spectra of tetrabromide complexes leads to their assignment as ν(M–Cl). Four absorptions seem to be exhibited by the other tertiary amine and diphosphine complexes of zirconium and hafnium, but the lowest frequency recorded is of such variable intensity that it is too weak to be detected in some instances. Beattie and Webster[1] include far-infrared frequencies for pyridine and bipyridine complexes of the zirconium(IV) halides but, owing to their use of a prism rather than a grating instrument, they failed to resolve the two highest frequency metal–chlorine stretching bands. We suspect that in some cases certain of the higher frequency bands shown in Table III are not organic ligand internal modes but rather are metal–phosphorus stretching bands. We have insufficient data as yet to assign these definitely as such.

While maintaining the same central atom, there is little frequency displacement when changing the basicity of the amine ligand, although an additional band is observed for the 1,10-phenanthroline adducts and there are wide intensity variations. The additional M–Cl stretching mode in the phenanthroline complexes of zirconium and hafnium indicates a higher complexity than in complexes of the other amines. In the case of zirconium and hafnium, there is only a slight increase in the frequencies when nitrogen donors are replaced by phosphorus or arsenic donors. Two of the platinum–chlorine stretching frequencies are markedly lowered by such a replacement. This can be accounted for by the lower electronegativities of phosphorus and arsenic which should cause a *trans* bond loosening.[12] *trans*-Loosening would lower the frequencies of the A_1 and B_1 modes but leave B_2 scarcely affected as the motion in this last case is largely antisymmetric stretching of the chlorine atoms *cis* to the organic ligands.

As there is no comparable frequency shift with the zirconium and hafnium compounds, we conclude that the conditions which give rise to the *trans* effect in platinum chemistry are absent in the case of group IV metals. Adams, *et al.*,[12] have shown that the *trans* effect in platinum may have its origin either in π bonding or σ inductive phenomena. There is of course no question of π bonding by metal d electrons in the group IV metals, but we might have expected inductive effects to influence bond stretching. We suppose that even the inductive effects are inhibited by virtue of a much lower polarizability in the case of zirconium and hafnium than in the case of platinum. The larger number of electrons in the outer shell of platinum accounts for the difference.

The M–Cl stretching band of generally low but variable intensity cannot be associated with the B_1 mode since the bands in square-planar complexes of platinum analogous to B_1 here are very intense. The weak band is probably due to symmetric stretching of the

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[11] R. J. H. Clark, *J. Chem. Soc.*, 1377 (1963).

[12] D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *ibid.*, 734 (1964).

halogen bonds *cis* to the donor ligands. The intensity would be greater with greater coupling between the halogen stretching and the donor atom stretching.

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CONTRIBUTION FROM SPACE-GENERAL CORPORATION,
EL MONTE, CALIFORNIA

Hydrogen Exchange in the H_2O–$B_{10}H_{14}$–Cineole System. Suggested Structure for μ-$(C_2H_5O)B_{10}H_{13}$

BY ROBERT E. WILLIAMS

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The recent development of higher resolution n.m.r. equipment has made it possible to identify structurally several halogen derivatives of $B_{10}H_{14}$ which eluded interpretation with the older equipment.[1–3] The present note deals with additional chemistry of $B_{10}H_{14}$ as revealed by the B^{11} n.m.r. spectra at 64.2 Mc.

The 12.8-Mc. B^{11} n.m.r. spectrum of $B_{10}H_{14}$ dissolved in 1,8-cineole (an intramolecular ether) differed from the spectrum of $B_{10}H_{14}$ in the common ethers and other solvents[4,5]; in contrast, no differences are apparent in the B^{11} n.m.r. spectra of B_5H_9 alone, in cineole or in many other solvents. The $B_{10}H_{14}$ spectrum at 12.8 Mc. (in cineole) resembles partially deuterated decaborane more than $B_{10}H_{14}$. Since rapid hydrogen exchange could also cause such a "partially deuterated appearance," hydrogen exchange was assumed to take place[4] and was later confirmed.[5]

In a reinvestigation of $B_{10}H_{14}$–ether systems we obtained a 32.1-Mc. B^{11} n.m.r. spectrum of $B_{10}H_{14}$ in cineole and found, surprisingly, that it differed only slightly from that of $B_{10}H_{14}$ in other solvents. A more thorough investigation was planned for 32.1 Mc.; however, the Varian 64.2-Mc. experimental instrument,[6] utilizing a cryogenic magnet, became transiently available. Consequently, 64.2-Mc. spectra of $B_{10}H_{14}$ in dry cineole (4 months over calcium hydride) and in cineole saturated with water at room temperature were obtained. The results are shown in Figure 1. In the top spectrum, for comparison purposes, is the complete B^{11} n.m.r. assignment of $B_{10}H_{14}$ as determined by Schaeffer.[7] In the middle spectrum, $B_{10}H_{14}$ in dry cineole, it would seem that the 1,3 and 6,9 positions are less well-resolved than in other solvents, while in the water-saturated $B_{10}H_{14}$–cineole spectrum, the 5, 7, 8, and 10 doublet is collapsed and perhaps lessened in size due to hydrogen exchange.[4] Based on these spectra, several bits of data now fall into place. For one thing, H_2O (or another strong proton donor) must have been present in our original experiments at 12.8 Mc., since the spectrum of $B_{10}H_{14}$ has the appearance of a system undergoing tautomerism or hydrogen exchange. This phenomenon should not occur with B_5H_9 in moist cineole, since a water-free environment would automatically be created by the rapid reaction of B_5H_9 and H_2O.

Hawthorne and Miller carried out the original experiments[8] involving hydrogen exchange between $B_{10}H_{14}$ and D_2O in dioxane; they found that the four bridge hydrogens exchange first[8] (in minutes or seconds). In a subsequent investigation, we found that bridge hydrogen exchange was followed by the exchange of 6,9 terminal hydrogens (0–2 hr.), the 5, 7, 8, and 10 terminal hydrogens (0–2 hr.), and the 2,4 positions (partially) (3 hr.).[9] Alternatively, aging of bridge tetradeuteriodecaborane(14) in dioxane allows the bridge hydrogens and the 5, 7, 8, and 10 hydrogens to scramble (tens of hours).[4]

When cineole is substituted for dioxane, 6-benzyl-$B_{10}H_{13}$ exchanges the 13 boron-attached hydrogens much more rapidly.[5] When HCl is substituted for H_2O (*i.e.*, dioxane–$B_{10}H_{14}$–HCl), exchange also takes place,[10] but the rates are about 100-fold slower than in the dioxane–$B_{10}H_{14}$–H_2O system. Furthermore, the 1,3 and 2,4 positions are *not attacked* even after 400 hr. at room temperature. Quantitative recovery of $B_{10}H_{14}$ is obtained. Thus, both the substitution of H_2O for HCl and the substitution of cineole for dioxane promote exchange; cineole–$B_{10}H_{14}$–HCl, which may be the most interesting combination, has not been investigated.[11]

The reason why cineole promotes hydrogen exchange better than dioxane is probably related to the fact that cineole is a "ditertiary" intramolecular ether, especially noted for its capacity to add acid protons to form oxonium salts.[12] Perhaps it merely functions as a stronger Lewis base than dioxane (see eq. a in Figure 2) but more likely its activity is due to its greater propensity to form oxonium salts from H_2O and $B_{10}H_{14}$. If so, it would be expected to react reversibly with $B_{10}H_{14}$ to form $C_{10}H_{18}O{:}H^+$ and $B_{10}H_{13}^-$ (eq. b) and with H_2O to form $C_{10}H_{18}O{:}H^+$ and OH^-.

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(1) Specifically 1-$IB_{10}H_{13}$,[2] 1-$ClB_{10}H_{13}$,[3] and 2-$ClB_{10}H_{13}$[3] have been identified.

(2) R. E. Williams and T. P. Onak, *J. Am. Chem. Soc.*, **86**, 3159 (1964).

(3) R. E. Williams and E. Pier, *Inorg. Chem.*, **4**, 1357 (1965).

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(5) R. J. F. Palchak, J. H. Norman, and R. E. Williams, *J. Am. Chem. Soc.*, **83**, 3380 (1961).

(6) F. A. Nelson and H. E. Weaver, *Science*, **146**, 223 (1964).

(7) Professor Riley Schaeffer and co-workers have unambiguously assigned the skewed triplet at lowest field as the overlap of two doublets, representing the 1 and 3 boron nuclei (at lowest field) and the 6 and 9 doublet at higher field; private communication.

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(9) I. Shapiro, M. Lustig, and R. E. Williams, *ibid.*, **81**, 838 (1959).

(10) J. A. DuPont and M. F. Hawthorne, *ibid.*, **84**, 1804 (1962).

(11) An intermediate exchange rate and quantitative recovery of the $B_{10}H_{14}$ may be anticipated. Other boron hydrides would also become candidates for exchange. We have found that both B_5H_9 and B_6H_{10} seem to be stable indefinitely in solution with cineole at room temperature.

(12) P. Karrer, "Organic Chemistry," 3rd English Ed., Elsevier Publishing Co., New York, N. Y., 1947, p. 65.