a considerable contrast with the anation rate of the aquohydroxo complex by phosphate,[4] where the water-exchange rate exceeds the ligand-interchange rate by a factor of between 10 and 20. Our K_{IP} value of only about 6 at 25° is somewhat lower than expected, since the corresponding constant for the $\mathrm{Co(en)_2(H_2O)_2}^{3+}$–$\mathrm{HC_2O_4}^-$ system is about 120 (40°) and for the $\mathrm{Co(en)_2(H_2O)(OH)}^{2+}$–$\mathrm{HPO_4}^{2-}$ system about 60 (22.5°). This may be related to the fact that the anions in the latter two systems are protonated, enabling a type of multiple H bonding not possible in the present system. It is of interest that the pseudo-second-order rate constants, $(k_0(\mathrm{cor}))K_{\mathrm{IP}}$, for oxalate and phosphate anation at low anion concentration are almost identical (5.2×10^{-3} M^{-1} sec^{-1} at 25° for $\mathrm{C_2O_4}^{2-}$, 4.6×10^{-3} M^{-1} sec^{-1} at 22.5° for $\mathrm{HPO_4}^{2-}$).

A study was next made of the rate of disappearance of the uncharged intermediate $\mathrm{Co(en)_2(OH)(C_2O_4)}$, using freshly prepared solutions of the latter (0.004 M) in the presence of 0.05 M $\mathrm{Na_2C_2O_4}$ at a total ionic strength of 0.37 M, temperatures of 40, 45, and 50°, and pH's of 7.8, 8.1, and 9.9. The rate constants k' (for $\mathrm{Co(en)_2C_2O_4}^+$ formation by ring closure) and k'' (for oxalate displacement by OH^-) are derived by apportioning the observed pseudo-first-order rate constant between the products[16] according to the relative amounts of each (see Table II). The constant k_2 is derived from k' on the assumption that *all* ring closure is according to reaction 5, whence $k_2 = k'f'$, where f' is the fraction[17] of unidentate oxalato complex in the form $\mathrm{Co(en)_2(H_2O)(C_2O_4)}^+$. To calculate k_3, it is assumed that oxalate displacement is first order in base concentration, so $k_3 = k''/[\mathrm{OH}^-]$.

TABLE II

RATE OF DISAPPEARANCE OF $\mathrm{Co(en)_2(OH)(C_2O_4)}$ AT IONIC STRENGTH 0.37 M AND VARIOUS TEMPERATURES AND ACIDITIES

pH	$10^5k'$, sec^{-1}	$10^5k''$, sec^{-1}	10^3k_2, sec^{-1}	k_3, M^{-1} sec^{-1}
		40°		
7.8	2.3	0.1	0.5	0.4
8.1	1.4	0.15	0.6	0.3
9.9	...	7.9	...	0.3
		45°		
7.8	4.1	0.2	0.9	0.8
8.1	2.6	0.3	1.1	0.6
9.9	...	15.3	...	0.5
		50°		
7.8	7.2	0.4	1.5	1.6
8.1	4.5	0.6	1.9	1.2
9.9	...	30.0	...	1.0

It is seen that the various k_2 and k_3 values at a given temperature are reasonably in agreement, considering the uncertainties inherent in the estimates. The respective temperature parameters are $\Delta H_2^{\ddagger} = 23.0 \pm 0.5$ kcal/mol, $\Delta S_2^{\ddagger} = -6.5 \pm 1.0$ cal deg^{-1} mol^{-1}, $\Delta H_3^{\ddagger} = 27 \pm 1$ kcal/mol, and $\Delta S_3^{\ddagger} = 8 \pm 2$ cal deg^{-1} mol^{-1}. Extrapolation of k_2 to 25° suggests a value of around 10^{-4} sec^{-1} for this constant at the lower temperature, consistent with our preliminary estimate of a half-time for ring closure of the aquooxalato species of 2.5 hr. An extrapolation of k_3 to 71° yields a value of 15 M^{-1} sec^{-1} so that it is easily understandable that no evidence for intermediate formation of unidentate oxalato species was discernible in our study[6] of the base-catalyzed hydrolysis of $\mathrm{Co(en)_2C_2O_4}^+$. The rate constant for the first step of this reaction, the reverse of reaction 3, is 2.7×10^{-2} M^{-1} sec^{-1} at 71°, less than 0.002 as rapid as the second step defined by k_3.

Finally, some remarks need to be made concerning the stereochemistry of the various processes which have been considered. We are unable to deduce from our evidence whether it is the cis or trans form of the aquohydroxo complex which is involved in reactions 1 and 2. However, this is of little concern in the evaluation of our constants, since the two forms are present in approximately equal amounts (the cis/trans ratio is 1.4 over a wide temperature range[4]) and the rate of equilibration of these stereoisomers is much more rapid than those of any of the other reactions under consideration (equilibration half-time is 2.3 min[9] at 25°). Also, as already pointed out, the water-exchange rates of the two forms are almost identical,[5] so one would expect them to be equally reactive in dissociative interchange. As to the geometry of the product $\mathrm{Co(en)_2(OH)(C_2O_4)}$, one can argue that it is nearly all in the cis configuration since ring closure to give $\mathrm{Co(en)_2C_2O_4}^+$ is essentially complete up to pH 8.1, a reaction which is impossible for the trans isomer. The spectral data also tend to favor the cis configuration as the major constituent, since the molar extinction coefficient of $\mathrm{Co(en)_2(OH)(C_2O_4)}$ at the maximum in the 500-nm region (83) is not far from that of *cis*-$\mathrm{Co(en)_2(OH)_2}^+$ (93) but differs substantially from that of the trans analog (41). However, the cis–trans isomerization of the $\mathrm{Co(en)_2(OH)(C_2O_4)}$ complex may be as rapid (through its protonated aquooxalato form) as is the corresponding reaction of the aquohydroxy species. In this event, the ring-closure reaction could always occur through the cis isomer without any limitation by the rate of the trans to cis conversion.

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[16] At the lower pH's, the concentration ratio of the products in any given run is constant with time, indicating a parallel first-order reaction system. At pH 9.9, reaction 6 is the only observable process, and k'' is derived by treating the data as belonging to a pseudo-first-order equilibration.

[17] For the purposes of this calculation, the value of pK_a is estimated to be about 6.5 in the 40–50° range (using a ΔH value of 4 kcal/mol as suggested by Lincoln and Stranks[4] for this type of acid–base equilibrium).

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Novel Synthesis of Difluorophosphine Oxide, $\mathrm{F_2HPO}$

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Difluorophosphine oxide, $\mathrm{F_2HPO}$, was first characterized and reported by Treichel, Goodrich, and Pierce[1]

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[1] P. M. Treichel, R. A. Goodrich, and S. B. Pierce, *J. Amer. Chem. Soc.*, **89**, 2017 (1967).

as a decomposition product of the fluorophosphorane HPF_4. Charlton and Cavell[2] have shown that hydrogen iodide cleaves dimethylaminophosphoryl difluoride, $(CH_3)_2NP(O)F_2$, to F_2HPO, while Parry and Centofanti[3] have described preparation of F_2HPO by the reaction of μ-oxo-bis(difluorophosphine), F_2POPF_2, with hydrogen bromide. We wish to report a very simple synthesis of F_2HPO which is based upon the fluorination of phosphorous acid using ZnF_2 in the presence of PBr_3. Yields were 60-80%.

While attempting to fluorinate phosphorus tribromide with anhydrous zinc fluoride at 80°, it was found that only traces of phosphorus trifluoride and silicon tetrafluoride were produced. Duplication of the same reaction using moist zinc fluoride, however, produced PF_3, SiF_4, HBr, and F_2HPO, with yields dependent upon the water content of the system. These reactions suggested that the moist ZnF_2 had initially hydrolyzed the PBr_3 to H_3PO_3; the resulting H_3PO_3 was then fluorinated to F_2HPO. To check this suggestion, partially hydrolyzed PBr_3 (formed by direct addition of water) was fluorinated at 55°, to give a 70% yield of F_2HPO and a small amount of PF_3 and SiF_4. The yield was calculated by assuming that the added water was converted to H_3PO_3 and subsequently fluorinated to F_2HPO. When deuterium oxide was substituted for water, F_2DPO was formed. When H_3PO_3 was added directly to PBr_3 and then mixed with ZnF_2 at 55°, F_2HPO was obtained in 80% yield, based on the H_3PO_3 added.

The role of the PBr_3 in the fluorination process is not yet known, but in its absence, fluorination of H_3PO_3 will not proceed. Higher yields of F_2HPO are obtained when the PBr_3 concentrations are large compared to the ZnF_2 and H_3PO_3 concentrations. The PBr_3 may well serve as a dispersion medium and may increase the stirring efficiency of the mixture.[4] Thus when an excess of PBr_3 is used, the viscosity of the resulting ZnF_3–PBr_3–H_3PO_3 slurry does not rapidly increase and efficient stirring can be maintained.

Since anhydrous PBr_3 was not noticeably fluorinated by ZnF_2 under the conditions used, PF_3 formation, observed in the F_2HPO preparation, was probably due to decomposition to the F_2HPO as previously noted.[2]

Experimental Section

Apparatus and General Procedure.—Standard vacuum procedures were used. The fluorination setup consisted of a 250-ml, two-necked, round-bottomed flask fitted with a powder addition tube and a water-cooled condenser which was connected to a vacuum line and manometer. With a combination heater and magnetic stirrer, the contents of the fluorination flask were heated through a water bath and continuously mixed by a Teflon-coated stirring bar.

Preparation of F_2HPO by Hydrolytically Produced H_3PO_3.—In a typical reaction, 11 ml of PBr_3 was transferred by a syringe into the reaction flask to which 1 ml of H_2O was added. After consumption of the H_2O and removal of HBr (system flashed with dry nitrogen), the ZnF_2 addition tube was inserted and the reactor evacuated. The water bath was warmed to 55° and a 4-g quantity of ZnF_2 was slowly added to the stirred PBr_3–H_3PO_3 solution.[4] Volatiles were removed into vacuum line traps thus maintaining the pressure in the reactor at 20 mm. After addition of the ZnF_2, the reaction was allowed to continue until the pressure no longer exceeded 20 mm. Fractionation of the collected volatiles through a series of U traps cooled to −35, −95, and −196° resulted in SiF_4 and PF_3 being retained in the −196° trap and a 1.1-g recovery of F_2HPO (69%) in the −95° trap. In a similar reaction, deuterium oxide was substituted for water and deuterated difluorophosphine oxide was produced (evidenced by a P–D infrared band at 1825 cm^{-1}).[5]

Preparation of F_2HPO by Direct Addition of H_3PO_3.—To 20 ml of PBr_3, 1.3 g of anhydrous H_3PO_3 was added and fluorinated as described above with 6 g of ZnF_2. The temperature was 55° and pressure was maintained at 15 mm by removing volatiles into the vacuum system. Fractionation of the products, as before, gave an 80% yield of F_2HPO.

Acknowledgment.—This work was conducted during tenure of a National Aeronautics and Space Administration traineeship held by E. A. D. which is gratefully acknowledged.

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[2] T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, **6**, 2204 (1967).

[3] R. W. Parry and L. F. Centofanti, *ibid.*, **7**, 1005 (1968).

[4] H_3PO_3 is not soluble in PBr_3 but forms an oily layer on the PBr_3.

[5] K. Nakomato, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963.

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Difunctional Lewis Acids.[1] IV. *cis*-1,2-Bis(dihaloboryl)cyclohexanes

By Michael J. Biallas

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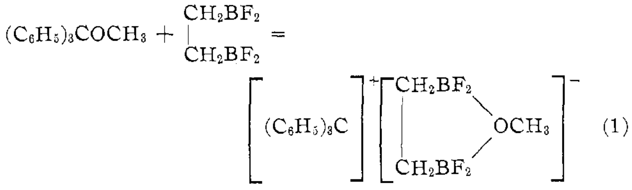
Chelate adducts of difunctional Lewis acids have been prepared only as anions,[1] *e.g.*



$$(C_6H_5)_3COCH_3 + \begin{array}{l}CH_2BF_2\\ | \\ CH_2BF_2\end{array} = \left[(C_6H_5)_3C\right]^+\left[\begin{array}{l}CH_2BF_2\\ | \qquad\quad OCH_3\\ CH_2BF_2\end{array}\right]^- \qquad (1)$$

Attempts to prepare uncharged Lewis acid chelates presumably have failed since the 1,2-bis(dihaloboryl)ethanes assume a predominantly trans conformation in the liquid state[2] (Figure 1a). Apparently the rotational energy barrier about the C–C bond is overcome by the stronger donor–acceptor interaction of the three-coordinate anion donor, whereas the weaker interaction

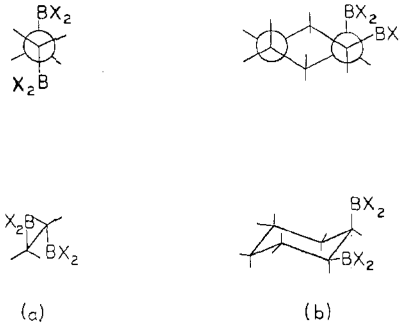


Figure 1.—Trans and gauche conformations of (a) 1,2-bis(dihaloboryl)ethane and (b) *cis*-1,2-bis(dihaloboryl)cyclohexane.

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[1] (a) Part III: M. J. Biallas, *J. Amer. Chem. Soc.*, **91**, 7290 (1969); (b) D. F. Shriver and M. J. Biallas, *ibid.*, **89**, 1078 (1967); (c) M. J. Biallas and D. F. Shriver, *ibid.*, **88**, 375 (1966).

[2] D. F. Shriver, J. F. Jackovitz, and M. J. Biallas, *Spectrochim. Acta*, *Part A*, **24**, 1469 (1968).