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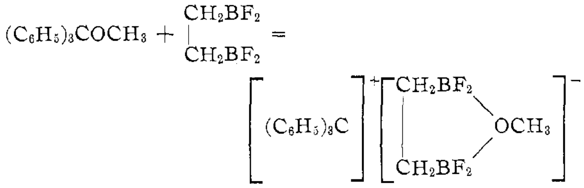
Difunctional Lewis Acids.[1] IV. *cis*-1,2-Bis(dihaloboryl)cyclohexanes

By Michael J. Biallas

Received October 29, 1970

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



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

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

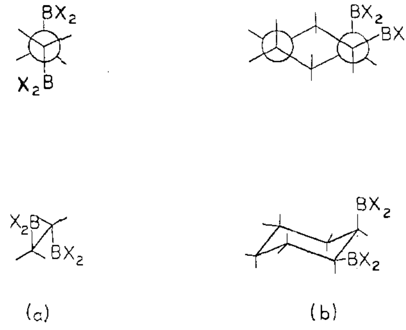


Figure 1.—Trans and gauche conformations of (a) 1,2-bis(dihaloboryl)ethane and (b) *cis*-1,2-bis(dihaloboryl)cyclohexane.

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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).

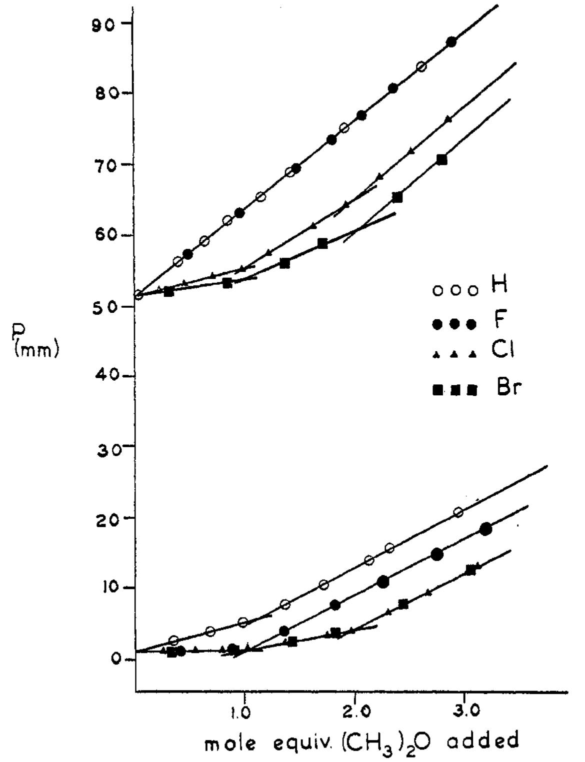


Figure 2.—Normalized tensimetric titration curves for reaction in hexane of *cis*-1,2-bis(dihaloboryl)cyclohexanes, $C_6H_{10}B_2X_4$, with $(CH_3)_2O$. Data for the upper curve were obtained at 0° and for the lower curve at −45°. Letter denotes acid substitutent, X.

of the uncharged four-coordinate donor is insufficient to overcome this barrier. This paper describes further efforts to prepare uncharged chelate adducts by utilizing the favorable steric arrangement found in the cis-1,2-disubstituted cyclohexanes.[3] This gauche arrangement (Figure 1b) places the two acid sites in an optimal position for coordination to a single donor atom. (This is the same orientation found in the conventional chelates of many common difunctional Lewis bases, *e.g.*, ethylenediamine.[4])

Experimental Section

Techniques.—Since the compounds used in these studies were air and/or moisture sensitive, all manipulations were carried out on a vacuum line or in a nitrogen-filled glove bag. The tensimetric titration technique has been described previously.[1b] Molecular weights were obtained cryoscopically in carbon tetrachloride solution in conjunction with a Dymec Model 2801 A quartz thermometer. A low-temperature Hornig-type cell was used to obtain ir spectra at −45° on a Beckman IR-12 instrument. A Varian A-60 spectrometer was used for nmr measurements. Raman spectra of samples prepared directly in capillary tubes were obtained on an instrument equipped with a SPEX 1400-11 double monochromator and 6328-Å He–Ne laser excitation.

Materials.—*cis*-1,2-Bis(dichloroboryl)cyclohexane (I) was prepared by direct reaction of diboron tetrachloride with cyclohexene. Fractionation through a 0° trap separated the products from unreacted materials and a tarry, involatile residue in the reaction vessel; yield 83%. *Anal.* Calcd: Cl, 57.7. Found: Cl, 57.7. Molecular weight: calcd, 245.6; found, 244. The ir spectrum matched the published spectrum.[5]

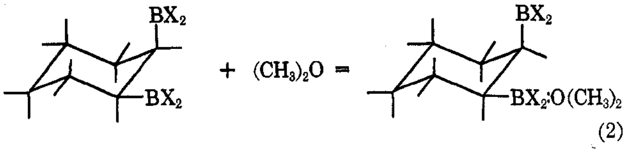
cis-1,3-Bis(difluoroboryl)cyclohexane (II) was prepared from I by treatment with freshly sublimed antimony trifluoride. Fractionation through a traps at 0, −45, and −196° allowed separation of the product from starting material and the principal side product, BF_3; yield 43%. Molecular weight: calcd, 179.8; found, 177. Product purity was demonstrated by exhibition of a constant vapor pressure (4.7 mm at 0°) by all fractions of a sample. The ir spectrum was free of the characteristic B–Cl absorption at 940 cm^{-1}.

cis-1,2-Bis(dibromoboryl)cyclohexane (III) was prepared quantitatively from I or II by successive equilibrations with fresh samples of boron tribromide until the ir spectrum of the product showed an absence of the characteristic B–Cl or B–F stretching vibration at 940 and 1390 cm^{-1}, respectively. *Anal.* Calcd: Br, 75.5. Found: Br, 77.0. Molecular weight: calcd, 423.4; found, 414.

cis-1,2-Bis(dihydridoboryl)cyclohexane (IV) was prepared from I by treatment with lithium borohydride. The reaction was more facile if just enough ethyl ether to wet the lithium borohydride was added. Fractionation through 0, −63, and −196° traps allowed separation of starting material, product, and solvent; yield 3–5%. Molecular weight: calcd, 107.8; found, 110.6. Compound purity was verified by nmr (two complex, unresolved multiplets in a 2:5 ratio). A hydrogen-bridged structure for this compound was suggested by its ir spectrum. Peaks at 2523 and 1491 cm^{-1} are indicative of terminal and bridged B–H bonds, respectively.[6–8] This point is under further investigation.

Results and Discussion

Tensimetric titrations showed that dimethyl ether reacted with all of the acids to give white, solid adducts at −45° (Figure 2)[8]



(2)

Unfortunately, the 1:1 adducts were not true chelated adducts, as was shown by the ir and Raman spectra of the adduct of II.[9] Absorption peaks at 1386 and 1030 cm^{-1} indicated the presence of both trigonal and tetrahedral B–F moieties in the adduct.[1c,10] Acids I and III also gave 2:1 adducts as shown in eq 3.

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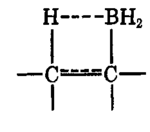
(3) (a) M. Zeldin, A. R. Gatti, and T. Wartik, *J. Amer. Chem. Soc.*, **89**, 4217 (1967); (b) R. W. Rudolph, *ibid.*, **89**, 4216 (1967); (c) T. D. Coyle and J. J. Ritter, *ibid.*, **89**, 5739 (1967).

(4) K. Nakamoto and P. J. McCarthy, "Spectroscopy and Structure of Metal Chelate Compounds," Wiley, New York, N. Y., 1968.

(5) M. Zeldin, Ph.D. Dissertation, Pennsylvania State University, June 1966; University Microfilms, Ann Arbor, Mich.

(6) H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962.

(7) In retrospect, it seems that a bridged structure is necessary to maintain molecular integrity. Otherwise, free rotation about the B–C axis would allow the molecule to assume the four-center configuration occurring in dehydroboration reactions, *e.g.*

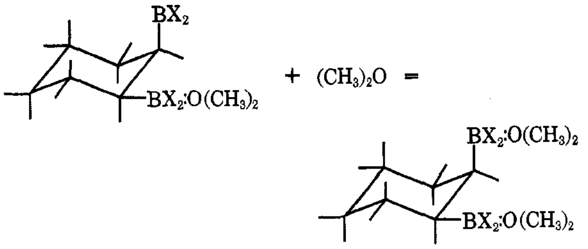


(See ref 6.) The formation of unwanted by-products is probably the cause of the very small yields. The presence of the ether seems to disfavor the side reaction, even though it does not appear to prevent it completely. (See footnote 8.)

(8) The reaction of dimethyl ether with IV exhibited a slight hysteresis in the titration curve if the reaction vessel was allowed to warm to room temperature between incremental additions. This may be due to a side reaction of the acid. (See footnote 7.)

(9) Adducts of I and III fluoresced under Raman excitation, and the low volatility of these acids precluded the use of the low-temperature ir cell to obtain satisfactory spectra. The adduct of acid IV was, of course, dissociated at −45° (See Figure 2.)

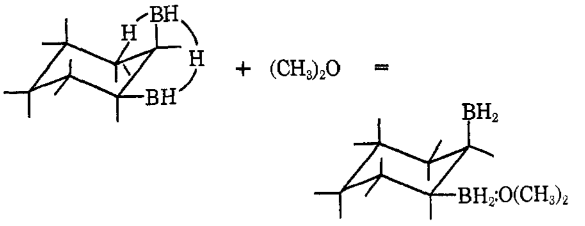
(10) It is possible that the donor "hops" between the 1,2-cis acid sites at the same rate as the ring flexes. This would allow the donor molecule to maintain association with the more accessible equatorial site. However, as this would not be a true chelate adduct anyway, the possibility was not investigated any further.



(3)

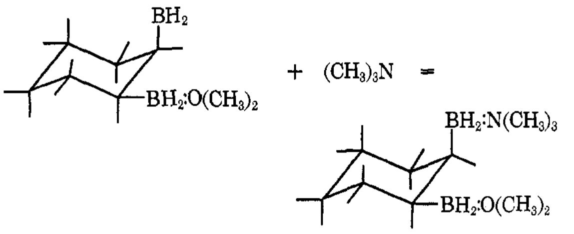
The relative degree of dissociation was indicated by the slope of the titration curves. It is seen that, for dimethyl ether, acid strength[11] is more important than steric requirements in determining the extent of donor–acceptor bond formation. With the bulkier Lewis base trimethylamine, an optimum balance of these two factors is achieved with II (Figure 3). The adducts of the more bulky acid I and the weaker acid IV are each more highly dissociated.

Quantitative displacement of coordinated ether can be effected by reaction of the adducts with the stronger amine base (Figure 4). In the titration curve, the first level portion and the inflection point showed formation of the 1:1 ether adduct



(4)

After the break, trimethylamine was added incrementally to the adduct solution. The second plateau indicated that the first mole equivalent of trimethylamine occupied the unused second acid site



(5)

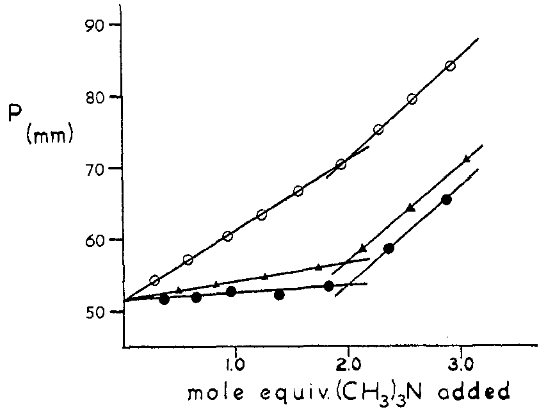


Figure 3.—Normalized tensimetric titration curve for reaction in hexane of *cis*-1,2-bis(dihaloboryl)cyclohexanes, $C_6H_{10}B_2X_4$, with $(CH_3)_3N$. Reaction temperature was 0°.

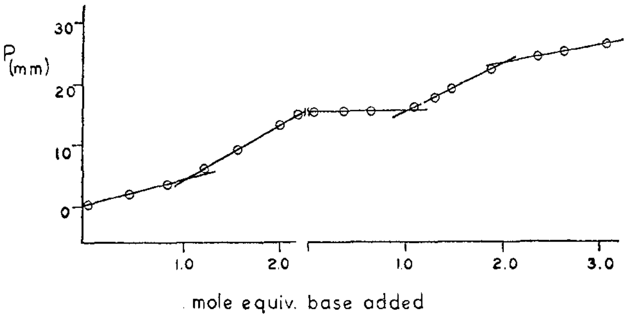
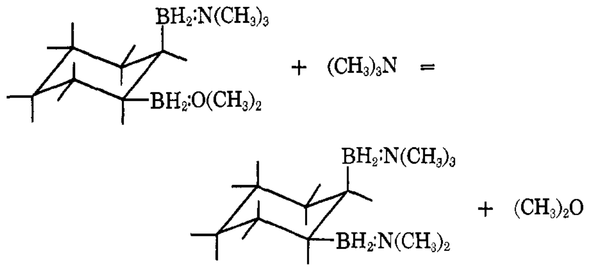


Figure 4.—Tensimetric titration curve for reaction in hexane of *cis*-1,2-bis(dihydridoboryl)cyclohexane, $C_6H_{10}B_2H_4$, with $(CH_3)_2O$ and subsequent displacement reaction with $(CH_3)_3N$. Reaction temperature was −45°.

The second rising portion of the curve occurred as the coordinated ether was displaced from the adduct



(6)

The last inflection point was observed as the formation of the 2:1 amine–acid adduct was completed.

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[11] P. H. Clippard and R. C. Taylor, *Inorg. Chem.*, **8**, 2802 (1969).

Correspondence

Factors Influencing the Stereochemistry of Four-Coordinate Copper(I)-Phosphine Complexes

Sir:

The structures of $((C_6H_5)_3P)_2CuX$ compounds, where X is a bidentate monoanion, were recently determined, primarily to elucidate the bonding between the X group and the copper atom.[1–4] A feature common to these complexes was the surprisingly large P–Cu–P angles, ranging from 120 to 131°. In order to evaluate plausible explanations[3,4] for the size and variation of the P–Cu–P angles and Cu–P bond lengths, a program of

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[1] S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, **6**, 2223 (1967).

[2] M. Bartlett and G. J. Palenik, *Acta Crystallogr., Sect. A*, **25**, S173 (1969).

[3] G. G. Messmer and G. J. Palenik, *Inorg. Chem.*, **8**, 2750 (1969).

[4] S. J. Lippard and K. M. Melmed, *ibid.*, **8**, 2755 (1969).