procedure was the same as that utilized for the corresponding Co(III) complex. As in the case of Cr(III), both antipodes were isolated. When the double complex was cleaved with potassium iodide, $(-)_{5461}K_3[Rh(C_2O_4)_3]$ was obtained. The specific rotations were $[\alpha]_D$ 0° and $[\alpha]_{5461}$ −66° for a 0.1% solution. This material was dissolved in the minimum amount of cold water, the solution was filtered, and sufficient 95% alcohol was added just to induce precipitation. The cloudy solution was cooled in ice for 15 min before the product was collected by filtration, washed with acetone, and air dried. The specific rotations were $[\alpha]_D$ 0° and $[\alpha]_{5461}$ − 74° for a 0.1% solution. Further recrystallization did not raise the angle of rotation.

Instrumentation.—Optical rotations were determined either on a Bendix-Ericson U.K. Ltd. Type 143 A ETL-NPL automatic polarimeter or on a Durrum-Jasco ORD/UV-5 optical rotatory dispersion recorder.

Discussion

The (+)- or (−)-tris(ethylenediamine)cobalt(III) ion can be used as a resolving agent for the rapid resolution of the tris(oxalato) complexes of Cr(III), Co(III), and Rh(III). When $(-)Co(en)_3^{3+}$ is used to effect the resolution, the least soluble diastereoisomters formed are $(-)[Co(en)_3](-)[Cr(C_2O_4)_3]$, $(-)[Co(en)_3](+)_{5461}[Co(C_2O_4)_3]$, and $(-)[Co(en)_3](-)_{5461}[Rh(C_2O_4)_3]$.

The solubility rule of Werner[10,11] when applied to these diastereoisomers indicated that $(-)Cr(C_2O_4)_3^{3-}$, $(+)_{5461}Co(C_2O_4)_3^{3-}$, and $(-)_{5461}Rh(C_2O_4)_3^{3-}$ all have the same configuration. This is in agreement with the optical rotatory dispersion data which indicate all of the anions in the least soluble diastereoisomers to have the same configuration. The absolute configurations of the anions in the diasterioisomer are L when compared to $D\text{-}Co(en)_3^{3+}$.

A comparison of the results using the $(-)Co(en)_3^{3+}$ ion as the resolving agent for the tris(oxalato) complexes of Cr(III), Co(III), and Rh(III) with those obtained by other investigators with other resolving agents is shown in Table I.

TABLE I

Complex anion	$[\alpha]_D$, deg: Lit.	$[\alpha]_D$, deg: This work
$Cr(C_2O_4)_3^{3-}$	±1640[a]	+1550–1600, −1680[b]
$Co(C_2O_4)_3^{3-}$	±4050[a,c]	
	±1940[d,e]	−1850, +1875[e]
	±1375[a,f]	−1425[f]
$Rh(C_2O_4)_3^{3-}$	±85[a]	−74[g]
	0[h]	0

[a] F. P. Dwyer and A. M. Sargeson, *J. Phys. Chem.*, **60**, 1331 (1956). [b] A 0.02% solution at room temperature. [c] A 0.016% solution at 20°. [d] G. B. Kauffman, L. T. Takahashi, and N. Sugisaka, *Inorg. Syn.*, **8**, 207 (1966). [e] A 0.032% solution at 5°; see discussion. [f] A 0.04% solution at 20° and λ 5461 Å. [g] A 0.1% solution at room temperature at λ 5461 Å. [h] A. Werner, *Ber.*, **45**, 1229 (1912).

In the case of $(-)[Co(en)_3](+)_{5461}[Co(C_2O_4)_3]$ the double complex was so insoluble in water that the diastereoisomer could not be conveniently cleaved by grinding with a saturated solution of potassium iodide. If both antipodes of the anion are desired, the best way to obtain them is to carry out two separate resolutions using $(+)Co(en)_3^{3+}$ and $(-)Co(en)_3^{3+}$ as the resolving agents and isolate the desired optical form from the filtrate after removal of the diastereoisomer.

It is not necessary to resort to this method in the case of the Cr(III) and Rh(III) complexes since the diastereoisomer can be rather easily cleaved by grinding with potassium iodide.

The (+)- or $(-)Co(en)_3^{3+}$ ion can be used to resolve the $(\pm)Co(C_2O_4)_3^{3-}$ ion, and the separation using (+)- or $(-)Co(en)_3^{3+}$ would appear to be equal to that obtained by the use of the $(+)Ni(phen)_3^{2+}$ ion as the resolving agent.

Acknowledgment.—We thank the National Science Foundation for a matching equipment grant for the purchase of the spectropolarimeter.

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[11] A. Werner, *Ber.*, **45**, 1228 (1912).

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Amine–Borane Hydrolysis at Bridgehead Nitrogen

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Received December 27, 1968

In a previous study,[1] it was suggested that the acid-catalyzed hydrolysis of BH_3 adducts of a series of alkyl, aryl, and heterocyclic amines proceeded by a rate-determining electrophilic displacement of BH_3 from nitrogen by the proton of a general acid, followed by rapid hydrolysis of the borane fragment. A comparable mechanism has been suggested by Ryschkewitsch for the acid hydrolysis of methylamine–boranes.[2,3] No implications have been made as to the geometry of transition states for such displacements, although models of transition states for electrophilic substitution at saturated carbon, based on numerous reactions of aliphatic substrates, are described in the literature.[4–6]

In relation to this question, we chose to study the rates of hydrolysis of triethylamine–borane and quinuclidine–borane in aqueous dioxane in the region 25–60°. Since electronic inductive effects should be quite similar for these substrates, it was felt that a comparison of rates should provide an indication of the effect of the rigidity of nitrogen at the bridgehead position on the ease of formation of the activated complex. The similarity in rate, as well as enthalpy and entropy of activation for these substrates (Table I), strongly suggests

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[1] H. C. Kelly, F. R. Marchelli, and M. B. Giusto, *Inorg. Chem.*, **3**, 431 (1964).

[2] G. E. Ryschkewitsch, *J. Am. Chem. Soc.*, **82**, 3290 (1960).

[3] G. E. Ryschkewitsch, "Boron–Nitrogen Chemistry," Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964.

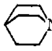
[4] J. March, "Advances in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1968, Chapter 12, and pertinent references therein.

[5] D. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965.

[6] H. B. Charman, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2523 2530 (1959).

TABLE I

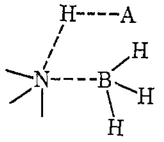
RATES OF HYDROLYSIS OF TRIETHYLAMINE–BORANE AND QUINUCLIDINE–BORANE IN 50% AQUEOUS DIOXANE ($\mu = 0.5$)

Temp, °C	$[H^+]$, M	10^4k_2, M^{-1} sec^{-1}	
		$(C_2H_5)_3NBH_3$	NBH$_3$
22.5	0.0906	0.174	0.186
	0.204		0.197
	0.306	0.160	
26.5	0.204	0.341	0.378
	0.306	0.286	0.340
	0.413	0.287	0.352
39.4	0.0906	1.57	1.92
	0.189	1.62	1.99
	0.306	1.62	2.08
52.3	0.0906		12.3
	0.204	8.70	11.4
	0.306	9.02	
$\Delta H^{\ddagger}$, kcal/mol		24.3[a]	25.3[a]
$\Delta S^{\ddagger}$, eu		+2.0	+5.6

[a] Obtained by linear regression analysis of data using the average of tabulated values taken at each temperature.

that their hydrolyses proceed by the same mechanism, and precludes a back-side attack of the electrophile accompanied by inversion at nitrogen. It seems reasonable to conclude that attack by hydrogen ion occurs from the same side of the nitrogen atom as that from which the leaving group (BH_3) departs.

A crude sketch of such a transition state is represented in I for attack by a general acid, HA, and is



I

formally similar to transition-state models proposed for SE2 reactions at saturated carbon which lead to retention of configuration such as found, for example, in the mercury exchange between mercury(II) halides and optically active dialkylmercury substrates[6] and in acid solvolysis at bridgehead carbon in organomercury compounds.[7] The question as to whether some degree of bond formation occurs between boron of the leaving group and A (*e.g.*, H_2O when the attacking electrophile is hydronium ion) is not answered from the available data, but if such were the case, the mechanistic classification for the reaction would be SE*i*[4,6] and the transition state would probably best be considered a four-center type. Alternatively, the departure of BH_3 may be assisted by a solvent molecule other than one coordinated to the entering electrophile (H^+). It seems more attractive to presume that any finite existence of borane as an intermediate in aqueous solution is that of a hydrated form perhaps such as H_2OBH_3, rather than free BH_3, but the extent to which a solvent oxygen may be coordinating to boron in the transition state is only speculative at this point.

Experimental Section

Materials.—Quinuclidine hydrochloride was obtained from Aldrich Chemical Co. and triethylamine from Eastman. Lithium and sodium tetrahydroborates and lithium tetrahydroaluminate were obtained from Ventron Corp. Diethyl ether (Mallinckrodt) was boiled under reflux with $LiAlH_4$ and distilled prior to use. Tetrahydrofuran (Baker) was heated with potassium hydroxide pellets for several hours, cooled, decanted onto $LiAlH_4$, and heated under reflux for over 12 hr before being collected by fractional distillation from this reagent (bp 65°). *This solvent should be peroxide free before undertaking this treatment since serious explosions have been reported on treatment of impure THF with solid or aqueous KOH.*[8] Commercial *p*-dioxane (Eastman or Matheson Coleman and Bell) was heated with aqueous hydrochloric acid under streaming nitrogen and then treated with solid KOH to separate the aqueous layer. The wet dioxane was then boiled for several hours and collected by fractional distillation (bp 101°). Boron trifluoride–diethyl ether complex (Eastman or MCB) was distilled *in vacuo* prior to use, bp 25° (~2 mm).

About 0.5–1.0 M ethereal solutions of lithium tetrahydroborate, used for the preparation of quinuclidine–borane, were prepared as follows. Commercial $LiBH_4$ was dissolved in dry diethyl ether and small quantities of insoluble material were collected by filtration under dry N_2. A 10-ml sample of clear filtrate was drawn and the ether evaporated *in vacuo* to give a white solid residue. The concentration of $LiBH_4$ in the solution was calculated from the weight of residue assuming it to be the pure hydride.

Solvents for kinetic studies were prepared by dilution of a standard solution of aqueous hydrochloric acid with an equal volume of *p*-dioxane. The ionic strength of all solutions was maintained essentially constant by adding sufficient reagent grade potassium chloride to make the total concentration of 1:1 electrolyte equal to 0.5 M.

Triethylamine–Borane.—The method of preparation is similar to that described for the synthesis of arylamine–boranes.[1] A solution of tetrahydrofuran–borane was generated by the addition of 33 g (0.23 mol) of boron trifluoride–diethyl ether complex in 80 ml of tetrahydrofuran to a stirred suspension of 7.7 g of 95% sodium tetrahydroborate (0.19 mol) in about 200 ml of tetrahydrofuran at 0°. This solution was treated dropwise with a solution of 19.0 g (0.19 mol) of triethylamine in about 55 ml of tetrahydrofuran with stirring at the same temperature. The suspension was warmed to room temperature. Solids were collected by filtration under pressure of N_2 and washed with fresh portions of solvent. The oily product was recovered from the filtrate by evaporation of solvent *in vacuo*. Subsequent vacuum distillation gave 14.1 g (65% theory) of a colorless fraction, bp 47–48° (3 mm). *Anal.* Calcd for $C_6H_{18}NB$ (mol wt, 115.03): H (hydridic), 2.63; B, 9.41. Found: H (hydridic), 2.65, 2.65; B, 9.51, 9.49.

Quinuclidine–Borane.—This compound was prepared by a method similar to that of Schaeffer and Anderson,[9] involving dropwise addition of 120 ml of a 1.0 M solution of $LiBH_4$ in ether to a stirred suspension of 10.34 g (0.07 mol) of quinuclidine hydrochloride in 400 ml of ether at room temperature. Solids were collected by filtration under dry nitrogen and washed with fresh portions of ether, and the crude solid product was recovered by evaporation of solvent *in vacuo* from the combined filtrate and washings; crude yield, 9.9 g. The product was washed in cold (~5°) water until the washings were neutral toward litmus paper and was subsequently dried *in vacuo*. A white crystalline solid was obtained; mp 161–162°; yield, 6.5 g (73% of theory). *Anal.* Calcd for $C_7H_{16}NB$ (mol wt, 125.03): C, 67.25; H, 12.90; N, 11.21; B, 8.65; H (hydridic), 2.42. Found: C, 66.97; H, 13.05; N, 11.21; B, 8.63; H (hydridic), 2.34.

In a subsequent preparation a 7.01-g yield (90% of theory) of

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[7] S. Winstein and T. G. Traylor, *J. Am. Chem. Soc.*, **78**, 2597 (1956).

[8] *Org. Syn.*, **46**, 105 (1966).

[9] G. W. Schaeffer and E. R. Anderson, *J. Am. Chem. Soc.*, **71**, 2143 (1949).

quinuclidine–borane (mp 159–161°) was obtained from 2.2 g of $LiBH_4$ and 9.2 g of quinuclidine hydrochloride. *Anal.* Calcd for $C_7H_{16}NB$: H (hydridic), 2.42. Found: H (hydridic), 2.42.

Kinetic Measurements.—Temperatures at which rate studies were carried out were maintained within ±0.04° by use of a Wilkins-Anderson constant-temperature bath. At t_0, a weighed sample (usually about 40–80 mg) of amine–borane was treated with an appropriate volume of solvent which had been equilibrated at the appropriate temperature, and the rate of disappearance of amine–borane was then followed by iodometric determination of soluble hydride at various intervals of time. Usually large batches of solvent were prepared and separate samples of a given batch (about 100 ml) were used for studies of the rates of hydrolyses of both amine–boranes at the same time. Initial concentrations of amine–borane ranged from about 0.004 to 0.008 *M*. Hydrogen ion was always present in large excess (0.09–0.41 *M*). For a given run, a "pseudo-first-order" rate constant was obtained from the slope of the line obtained by plotting the logarithm of the amine–borane concentration against time. The second-order rate constant, defined as

$$k_2 = \frac{-\mathrm{d}[\mathrm{AB}]}{\mathrm{d}t} \Big/ [\mathrm{AB}][\mathrm{H_3O^+}]$$

where [AB] is the concentration of amine-borane, was obtained by dividing the pseudo-first-order constants by the value of $[H_3O^+]$ for that particular run.

Acknowledgments.—This research was supported by The Robert A. Welch Foundation and the Texas Christian University Research Foundation. The authors wish to acknowledge Dr. Donald Noyce of The University of California, Berkeley, Calif., for helpful discussions.

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Far-Infrared Spectra of Tetrakis(triethyl phosphite) Complexes of Nickel(0), Palladium(0), and Platinum(0)

BY VICTOR G. MYERS, FRED BASOLO, AND KAZUO NAKAMOTO

Received November 20, 1968

Recently, a number of investigations have been made on far-infrared spectra of metal complexes containing various phosphines.[1–12] Table I summarizes some metal–phosphorus stretching frequencies assigned by these investigators. It is seen that these frequencies scatter over a wide frequency region from 460 to 90 cm^{-1}. Several investigators[10,12] have suggested that this scattering of frequencies may be due to the differences in the nature (1) of the metals (oxidation state, electronic configuration, etc.), (2) of the phosphine ligands PR_3, where R is CH_3, C_2H_5, or C_6H_5, and (3) in the structure of the complex (stereochemistry, coordination number, etc). If this is the case, a meaningful comparison of metal–phosphorus stretching frequencies can only be made for a series of metal complexes in which the three factors mentioned above are kept constant. However, such a series is very rare. This paper reports the far-infrared spectra and band assignments for a series of compounds of the type $M[P(OC_2H_5)_3]_4$ (M = Ni(0), Pd(0), or Pt(0)), all of which presumably have tetrahedral or nearly tetrahedral structures.

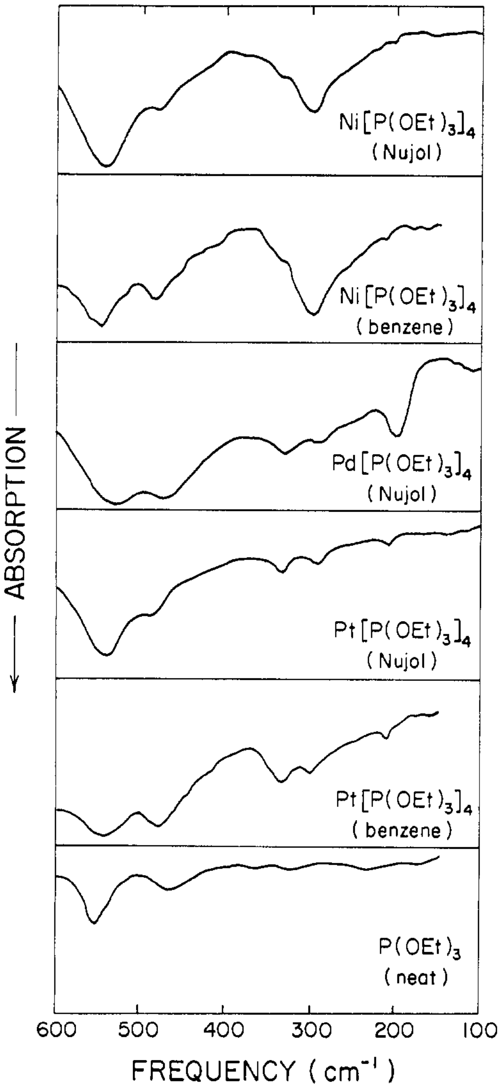

Figure 1.—Infrared spectra of tetrakis(triethyl phosphite) complexes of Ni(0), Pd(0), and Pt(0) obtained in Nujol mull or in benzene solution.

Experimental Section

Samples of the white tetrakis(triethyl phosphite) complexes of nickel(0), palladium(0), and platinum(0) used in the present spectroscopic investigation were gifts from Dr. M. Meier, who

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