the phenyl ring is perpendicular to the ethylenic plane, H_B is closer to the shielding region due to the phenyl ring anisotropy than H_C, and this may bring about part of the upfield shift for H_B in the free ligand.

Finally it is to be noted that only the dimeric complexes of platinum show broad ethylenic proton resonance signals. Of several possible mechanisms[13] for the broadening, exchange and reorientation of the styrene group are likely. The exchange mechanism can be excluded by the following observation. In contrast to the ethylenic proton resonance, the phenyl proton resonance is narrow. If the exchange mechanism were responsible, the latter would be expected to be as broad as the former, because shift differences between the free ligands and complexes are of the same order of magnitude for both proton groups.

It is apparent from Figure 2 that the reorientation mechanism can be responsible for the line broadening in the dimeric complexes. In the orientation (I), H_A and H_C are closer to the terminal chlorine atoms, while H_B is closer to the bridge chlorine atoms, and in (II) the situation is reversed. The terminal and bridge chlorine atoms must have spatially[3] and electronically different characters, and hence each proton should experience different magnetic fields in (I) and (II). If the reorientation rate with the coordination bond as axis is comparable to the shift difference in (I) and (II), which may be probably of the order of 10 Hz, line broadening will be observed. This may be considered to be the case with styreneplatinum(II) chlorides; the phenyl proton signals remain narrow, since their shifts are presumably unaffected by reorientation, those protons being significantly remote from the chlorine atoms. For the same reason such broadening was observed also for the proton resonance of the dimer of Zeise's salt in acetonitrile and acetone solutions, which indicates also that the broadening is not due to specific solvent interactions.

On the other hand, styrenepalladium(II) chlorides give narrow proton resonance signals. It can be understood if we consider that the reorientation rate of the styrene groups is faster in the palladium complexes owing to the weaker coordination bonds discussed above. The proton resonance signals of Zeise's salt and its homologs are also narrow. In the case of these monomeric forms, each proton does not experience nonequivalence by reorientation. Thus no line broadening could occur irrespective of the reorientation rate, and nmr spectra are of no direct use in studying this rate process. However, it is felt that the reorientation rate may actually be slower for the monomers in view of their probably stronger coordinative bonding.

Because of their limited solubilities at low temperatures and instabilities at high temperatures, variable-temperature experiments could not be performed to confirm the above discussions on the reorientation of ethylene groups in these complexes. So an attempt has been made to prepare a sterically hindered complex. Di-μ-chloro-dichlorobis(2,3,5,6-tetramethylstyrene)diplatinum(II) provides such an example. Reorientation of the styrene group in the molecule would be difficult due to the bulky substituents on the phenyl ring, and narrow absorption lines are expected if the above views are valid. Indeed such a spectrum has been observed, enabling us to detect ^{195}Pt satellites with $J(\text{Pt–H}_A) = 62$ Hz, $J(\text{Pt–H}_B) = 70$ Hz, and $J(\text{Pt–H}_C) = 74$ Hz. Although the dimeric complex of 2,3,4,5-tetramethylstyrene with a substituent at only one ortho position was also prepared, its low solubility did not allow an nmr observation.

Acknowledgment.—We are indebted to Dr. T. Shingu and Miss M. Okawa for measurements on a Varian A-60 spectrometer.

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Studies in Boron Hydrides. VIII. Substituent Effects in Boron Hydrides. Pentaborane(9) and Phenylboronic Acid

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We have become interested in using nuclear magnetic resonance techniques to study the magnitude and nature of substituent effects in various boron hydride derivatives. Boron-11 nmr spectroscopy, long recognized for its utility in obtaining structural information,[2] has received far less use as a method for examining substituent effects. Beachell and Beistel[3] observed a linear correlation between the boron-11 nmr chemical shifts in a series of para-substituted phenylboronic acids relative to phenylboronic acid and the Hammett σ value of the substituent. Onak and coworkers[4] studied the boron-11 nmr spectra of methyl- and halogen-substituted pentaboranes and accounted for the observed chemical shifts in terms of six parameters for the CH_3, Cl, and Br groups. These parameters are singular owing to the geometry of the pentaborane(9) molecule and may not be readily compared with substituent parameters employed in the treatment of more conventional derivatives, *e.g.*, benzene. Furthermore, no separation of the effects of CH_3, Cl, or Br into resonance and inductive effects was made by these workers. We have reexamined extant boron-11 nmr chemical shift data for these systems and attempted to rationalize these shifts in terms of familiar substituent effects which have proved to be so useful in organic chemistry.

Experimental Section

The treatment which we have adopted is based upon the substituent constants derived by Swain and Lupton.[5] The change in the chemical shift of the nucleus of interest in the substituted derivative relative to that of the unsubstituted derivative, $\int_{\mathrm{H}}^{\mathrm{X}}$, is factored into inductive (or field) and resonance effects as shown in eq 1, where F and R are the field and resonance constants of

$$\int_{\mathrm{H}}^{\mathrm{X}} = fF + rR \qquad (1)$$

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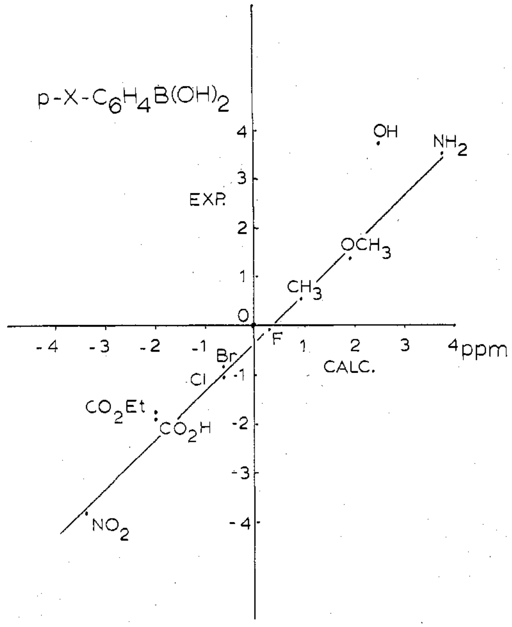

Figure 1.—The experimental *vs.* calculated ^{11}B nmr chemical shifts for para-substituted phenylboronic acids.

the substituent as tabulated in ref 5 and f and r are empirically determined weighting parameters. Optimal values for f and r are then calculated by a χ^2 minimization of the difference between the experimental chemical shift and that calculated on the basis of eq 1.[6]

Results and Discussion

As the basis for evaluating the applicability of this technique for the study of substituent effects in boron hydrides we examined the published data of Beachell, *et al.*,[3] for the boron-11 nmr chemical shifts of para-substituted phenylboronic acids. A graph of calculated *vs.* experimental chemical shift is shown in Figure 1. The χ^2 analysis yields optimal values of $f = -2.26$, $r = -5.65$, $\% f = 28.6$ and $\% r = 71.4$, with a linear correlation coefficient, $\bar{r}$, of 97.5%.

These data reveal two major implications: first, the boron-11 nmr chemical shift of a sterically isolated boron atom can be separated into a resonance and an inductive effect and, second, the susceptibility of the boron-11 nmr chemical shift to resonance effects is very large; in fact almost as large as that of the para C in monosubstituted benzenes as measured by ^{13}C nmr.[7]

Chemical shifts for 1-XB_5H_8 were taken from a recent compilation by Onak, *et al.*,[4] for X = H, CH_3, Cl, Br, I, and C_2H_5. For 2-substituted derivatives, 2-XB_5H_8, where X = H, CH_3, Cl, Br, I, and C_2H_5, values in ref 4 were used along with other literature values for X = OCH_3,[8] $(CH_3)_3Si$,[9] F[10], and C_2H_5.[11] The values obtained for f and r, along with the linear correlation coefficient, $\bar{r}$, are shown in Table I for the various positions in 1- and 2-substituted pentaboranes.

TABLE I

CORRELATION OF ^{11}B NMR CHEMICAL SHIFTS IN SUBSTITUTED PENTABORANES

Position	f	r	$\% f$[a]	$\% r$[a]	$\bar{r}$
		1-XB_5H_8			
B(1)	−6.34	47.23	11.8	88.2	41.8
B(2,3,4,5)	−2.24	−1.14	66.4	33.6	91.8
		2-XB_5H_8			
B(1)	−0.41	−2.93	12.2	87.8	65.5
B(2)	6.75	71.55	8.6	91.4	89.3
B(3,5)	−0.12	−7.14	1.7	98.3	80.9
B(4)	5.94	−35.12	14.5	85.5	92.1

[a] Absolute values of f and r are normalized so that their sum equals 100.0.

Two features can be readily distinguished. First, the agreement between calculated and experimental chemical shifts as measured by the linear correlation coefficient is both significant and gratifying. This is especially true when one considers the inherent errors in measuring boron-11 nmr chemical shifts in different laboratories and on different instruments. Second, the importance of resonance interactions in determining the chemical shifts of the basal borons is very large—as large as or larger than that encountered in simple benzene analogs.[7]

The resonance contribution to the chemical shift of the basal borons in 1-substituted derivatives is seen to be significantly smaller than at any position in the 2-substituted derivatives. This may be taken to imply that the apical boron in pentaborane(9) is "insulated" with respect to resonance in that this mechanism is not dominant in transmitting substituent perturbations from apical to basal positions.

The correlations for the B(1) positions are unsatisfactory and inclusion of factors other than those discussed herein appear to be necessary in order to explain the chemical shifts of the apical borons for either the 1- or 2-substituted derivatives.

We have applied the Swain–Lupton treatment to the ^1H nmr chemical shifts for 1- and 2-substituted XB_5B_8 (X = H, CH_3, Cl, Br, C_2H_5), measured by Onak, *et al.*,[4] and the results of these calculations are shown in Table II. The internal consistency of these shifts is greater than those of the boron-11 nmr spectra and the correlation coefficients are very large.

TABLE II

CORRELATIONS OF PROTON CHEMICAL SHIFTS IN SUBSTITUTED PENTABORANES

Position	f	r	$\% f$	$\% r$	$\bar{r}$
		1-XB_5H_8			
H(μ)	0.53	−1.81	22.6	77.4	99.8
H(2,3,4,5)	−0.29	0.57	33.5	66.5	98.9
		2-XB_5H_8			
Hμ(2,5)	1.45	−3.66	28.4	71.6	97.2
Hμ(3,4)	0.27	−1.07	2.5	97.5	99.7
H(4)	−0.14	−1.35	9.4	90.6	89.6
H(3,5)	−0.18	−1.34	12.1	87.9	97.4
H(1)	0.14	−0.53	20.9	79.1	99.1

We conclude therefore that, in favorable cases, boron-11 nmr spectroscopy can be used as a technique for evaluating substituent effects in the nominally electron deficient boron hydrides and that these effects may be

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(6) The χ^2 minimization was done on a CDC 6400 computer using the STEPIT subroutine, copyright 1965, by J. P. Chandler, available through the Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, Ind. 47401.

(7) A similar analysis of the para carbon carbon-13 nmr chemical shift of a series of monosubstituted benzenes yields $\% f = 13.5$, $\% r = 85.6$, and $\bar{r} = 98.0\%$: G. M. Bodner, to be submitted for publication.

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accounted for by an appropriate combination of field and resonance contributions. Additional work, to appear elsewhere, will extend our analyses to carboranes and polyhedral boranes.

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Sorption of Gaseous Bromine Trifluoride on Sodium Fluoride

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The interaction between gaseous bromine trifluoride (BrF_3) and sodium fluoride (NaF) was studied for the following purposes.

(i) In the author's laboratory, a study has been made on the fluoride volatility process for reprocessing of nuclear fuels. Gaseous BrF_3 may be used as the fluorinating reagent, and NaF has been used as the chemical trap to separate uranium and plutonium from the fission products. It is therefore necessary to check the interaction between BrF_3 and NaF.

(ii) BrF_3 seems to be more reactive to uranium compounds than elemental fluorine, though more stable thermodynamically.[1] With gaseous BrF_3, the materials can be fluorinated at lower temperatures and lower concentrations of the reacting gas than with F_2.[2-5] Why this is so, has not been made clear yet; however, it may be due to the adsorption of BrF_3 on the materials. The present study was carried out to obtain information on the reactivity of BrF_3.

Experimental Section

Reagent grade sodium fluoride in powder of purity greater than 99% was used, after outgassing overnight at 350° under vacuum.[6,7] Particle size ranged from 1 to 5 μ, and the surface area as determined by krypton adsorption was 0.2 m^2/g.

Commercial grade bromine trifluoride, from the Matheson Co., was purified by vacuum distillation, as reported previously.[8]

All valves and tubing in the apparatus in contact with bromine trifluoride were made of Monel or Teflon. The weight increase of samples caused by sorption of the BrF_3 was obtained with a thermobalance, details of which were given in the previous work.[5] About 100 mg of the sodium fluoride was placed in the reaction tube. After outgassing the sample powder, the reaction tube was raised to a specific temperature and filled immediately with helium gas at atmospheric pressure. Gaseous BrF_3 of a given partial pressure in helium as the carrier gas was then allowed to pass through the reaction tube at a constant flow rate. A continuous record of the weight change of the sample with the time was obtained with a recording potentiometer.

Results and Discussion

The weight change of sample with the time is shown in Figure 1. In this experiment, gaseous BrF_3 of partial pressure 15 mm was passed over the sample at 110°. The weight increased rapidly in the first 50 min and then very slowly. The shape of sorption curve is similar to that of UF_6 on NaF reported by other workers.[6] About 120 min after the start, the supply of BrF_3 was stopped, and the reaction tube was evacuated (10^{-2} mm) to observe any change in weight. Since no change was caused, the sample was then heated under vacuum. At 140°, the weight started to decrease because of the desorption of BrF_3, returning gradually to its initial weight; unlike a physically adsorbed layer, the sorbed BrF_3 was not removed by reducing the pressure. The weight increase obtained during the 120 min was 57 mg, which was some 10^3 times the amount of BrF_3 expected for its physical or chemical adsorption on the sodium fluoride; it was therefore indicated that the sorbed BrF_3 diffused into the sodium fluoride crystal.

In some experiments, the temperature of sorption was varied, with the BrF_3 partial pressure being kept constant at 15 mm. The results of experiments are shown in Figure 2. The rate of the sorption decreased with increase of the temperature, and no weight increase was observed at temperatures over 180°. The sorption was therefore found to be a nonactivated one.

A fluorine-18-exchange reaction was examined between BrF_3 and NaF. The nuclide ^{18}F was prepared by irradiation of the sodium fluoride in the 20-MeV linear accelerator of Japan Atomic Energy Research Institute by the reaction $^{19}F(\gamma,n)^{18}F$. The radioactive sodium fluoride (NaF*) was then treated with gaseous BrF_3 in the same way as in Figure 1; the BrF_3 desorbed from the NaF* was collected in a counting tube. Consequently, a fluorine-exchange reaction was noticed between sodium fluoride and the sorbed bromine trifluoride; the percentage exchange, calculated by Gens' equation,[9] was 19%. It was considered that fluorine atoms were exchanged through complex formation.[10,11]

In the experiments, it was found that the repeated sorption and desorption of BrF_3 on sodium fluoride increases the rate of sorption. In Figure 3, curve I is the sorption curve for the original NaF at 110° and BrF_3 partial pressure 15 mm. The sorbed BrF_3 was then desorbed from the material by heating to 150° under vacuum. The sodium fluoride obtained was treated again with gaseous BrF_3 under the same conditions as in the first sorption. Curve II shows the second sorption, which proceeds much more rapidly up to a point (P) which corresponds to the final point in the first sorption; it then proceeds slowly. In the third treatment, the sorption rate is further increased, as shown in the figure. These results indicate that an irreversible change in the sample occurred in the course of the sorption and desorption process. Micro-

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