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Thermochemical Investigation into the Lewis Acidity of the Boron Atom in Some Triaryloxyboranes

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Thermochemical measurements have shown that the Lewis acidity of the boron atom in a series of eight substituted triaryloxyboranes $B(OC_6H_4X)_3$ varies according to the electronic properties and position of the substituent. This is attributed to a variation in the basicity of the *internal* oxygen bases which participate in the intramolecular Lewis acid–base π interaction with the boron atom. For the systems studied the maximum variation amounts to 60 kJ mol^{-1} between the para-substituted cyano and methoxy compounds.

Introduction

The relative acidity of the boron atom in BL_3 compounds (L = H, halogen, alkyl, aryl, OR, or NR_2) has been of interest for some time. In these compounds the *internal* base in L participates in an intramolecular Lewis acid–base reaction and donates electron density into the empty p orbital of the boron atom by a $p\pi$–$p\pi$ mechanism. In the past this π stabilization or vertical reorganization energy[1] has been considered in thermodynamic cycles as a fixed quantity, characteristic of the acid and independent of the base.[2]

Drago[3] has shown that this concept of a constant reorganization energy for each Lewis acid is incorrect and that the extent of rearrangement of the acid is variable depending upon the strength of the bond formed with the *external* base and suggests that there is residual π bonding in the adducts. The mass spectral data of Lanthier and Millar on trimethylamine adducts of the boron halides support the idea of residual π bonding in the boron–halogen bonds in donor–acceptor complexes.[4] Shriver and Swanson[5] have obtained data, from B–N bond lengths and force constants in boron trifluoride and trichloride adducts of acetonitrile, that question the traditional idea of reorganization energies. It has also been shown, from a theoretical investigation into the mechanism of adduct formation of boron trifluoride and borane complexes, that these reactions can proceed without activation energy.[6]

In a real situation, therefore, the boron atom acidity is satisfied by electron donation from the *external* and *internal* bases. In this situation, where π bonds already exist and the possibility of σ-bond formation arises, it is to be expected that the energy of the π bonds will diminish as the molecule distorts to facilitate the σ-bond formation. This process will continue until maximum stabilization (minimum energy) of the whole system is achieved. The strength of the σ bond and the extent of the acid reorganization will depend on the basicity of the *external* base relative to the *internal* bases. Data on the magnitude of the interaction between boron Lewis acids and several *external* bases are available.[2b] In addition there are several theoretical calculations of π reorganization energies which for the boron halides give the order $BF_3 > BCl_3 > BBr_3 > BI_3$.[7] These values must now be considered to represent a maximum value for the intramolecular acid–base interaction. Lappert et al.[8] have shown, from extended Hückel calculations based on mass spectral data, that in the boron halides the π charge transfer from halogen to boron follows the order $BI_3 > BBr_3 > BCl_3 > BF_3$ and that the overall boron–halogen bond polarity is dominated by the σ charge drift from the boron to halogen. These two sequences are not incompatible. The results of other calculations agree with both sequences with the exception of BI_3.[1]

It would be of interest therefore to see to what extent the intramolecular π stabilization energy can be modified by manipulating the π basicity of the *internal* bases while keeping the *external* base constant. This will allow conclusions to be drawn about the importance of π stabilization energies in such systems. To do this requires a system where such variables as $B \rightarrow L$ σ charge drift, due to the different electronegativities of L, and steric and/or nonbonded electron repulsions, which may come into operation on adduct formation, are minimized. The only major variable has to be the π electron density on the internal bases. These criteria cannot be achieved when there is a total change of L in BL_3. If, however, the $p\pi$ electron basicity of the *internal* bases can be manipulated over a reasonable range without any major alteration to the system, it should be possible to obtain quantitative data that can be identified with the variation in π stabilization energy of the acid system under investigation. Furthermore some idea about the magnitude of the variation in reorganization energies of the acid in the general acid–base reaction (eq 1) is to be

$$\text{base} + BL_3 \rightarrow \text{base}\cdot BL_3 \qquad (1)$$

expected; here the basicity of the base varies over a wide range (amines, ethers, halide ions, etc.) as the acid is kept constant.

Table I. Enthalpy Changes at 25°[a]

Substituent X	$-\Delta H_1$	ΔH_2	$-\Delta H_3$	ΔH_4
H	86.45 ± 0.58	31.05 ± 0.56	162.1 ± 1.5	0
m-Me	86.13 ± 0.64	42.61 ± 0.92	166.0 ± 2.5	+3.9 ± 2.9
m-Cl	108.37 ± 0.88	41.31 ± 0.60	162.0 ± 1.9	−0.1 ± 2.4
m-OMe	98.49 ± 1.22	43.53 ± 0.42	158.1 ± 2.7	−4.0 ± 3.1
p-Me	81.61 ± 1.08	37.62 ± 1.14	165.4 ± 2.3	+3.3 ± 2.8
p-Cl	89.32 ± 0.80	28.11 ± 0.78	137.1 ± 1.4	−25.0 ± 2.1
p-OMe	81.02 ± 1.28	45.34 ± 0.64	123.4 ± 2.8	−38.7 ± 3.2
p-CN	114.48 ± 0.60	23.40 ± 0.48	182.6 ± 2.1	+20.5 ± 2.6

[a] (i) A(l) + B(l) → AB(s), ΔH_1; (ii) solution of AB(s) in benzene, ΔH_2; (iii) A(g) + B(g) → AB(benzene), ΔH_3; (iv) the displacement reaction A(g) + A′B(solvated) → AB(solvated) + A′(g), ΔH_4. All values in kJ mol^{-1}.

Substituted triaryloxyboranes $B(OC_6H_4X)_3$ appeared to be amenable to quantitative study. In these systems the suitably substituted phenyl rings are in competition with the boron atom for the electron density of the oxygen atoms. This paper reports the enthalpies of adduct formation between triaryloxyboranes and the reference base 4-methylpyridine. This quantity monitors the differences in the intramolecular interaction of the oxygen atoms within the acids.

Results and Discussion

The enthalpy change, ΔH_1, for the reaction

$$\mathrm{A(l) + B(l) \rightarrow AB(s)} \quad \Delta H_1$$

where A is one of eight substituted triaryloxyboranes, B is 4-methylpyridine, and AB is the corresponding adduct, is given in Table I. They were computed from the enthalpy changes for the reaction of the acids, base, and adducts with excess of the same solvent, in most cases 1.0 *M* sodium hydroxide solution. Because of the hydrolytic stability of some of the adducts and hence their very slow reaction times with 1.0 *M* sodium hydroxide solution two other solvent systems were used. These are described in the Experimental Section. This scheme assumes negligible enthalpies of mixing between the hydrolysis products. Determination of the enthalpy of solution of pure boric acid and 4-methylpyridine in solvents containing the stoichiometric amount of the other reaction products showed no detectable differences from the values obtained for the pure solvents. The assumption is therefore valid. Partial conversion to the gas-phase enthalpies of adduct formation, which permits true comparisons to be made, is possible since the enthalpy of sublimation of the acids[9] and the enthalpy of vaporization of 4-methylpyridine,[10] $\Delta H = 45.33 \pm 0.01$ kJ mol^{-1}, are available. Unfortunately, as for many such systems, it proved impossible to measure the enthalpy of sublimation of the adducts. Therefore recourse had to be made to the use of an inert solvent in order to obtain data for each system that would permit realistic comparisons to be made. Drago[11] has shown that cyclohexane, carbon tetrachloride, and benzene possess the necessary properties required for such studies with benzene being the least desirable. In this study benzene was the only solvent of the three in which the adducts showed appreciable solubility. The enthalpies of solution of the adducts in benzene ΔH_2 are given in Table I. These permit the calculation of the enthalpy changes ΔH_3 for the hypothetical reaction

$$\mathrm{A(g) + B(g) \rightarrow AB(benzene\ solution)} \quad \Delta H_3$$

for each system. The values are given in Table I. In order to observe the substituent effect, relative to hydrogen, on the magnitude of the intramolecular interaction energy and allow realistic comparisons to be made, values for the enthalpy of the displacement reaction, ΔH_4, have been calculated (Table I); here the reference acid A is taken as $B(OPh)_3$. It is assumed that because of the close chemical and structural similarity of the adducts, their solvation energies in benzene will cancel. The values for the displacement reactions confirm expectations in the sense that the π inductive effects of the para-substituted rings serve to modify the oxygen π electron basicity whereas this basicity remains insensitive to meta substitution. The range of 60 kJ mol^{-1} provides the first quantitative empirical data on the kind of variation to be expected in the π stabilization energy of an acid in its acid–base reactions.

$$\mathrm{A(g) + A'B(solvated) \rightarrow AB(solvated) + A'(g)} \quad \Delta H_4$$

It has been established that the boron alkoxides are very weak Lewis acids, only forming complexes with the strongly basic alkoxide anions.[12] This indicates that the magnitude of the π stabilization energies in these compounds are much greater than in the aryl oxides and that the spread of 60 kJ mol^{-1} observed here for a closely related system is at the lower end of the range that can be expected in the systems $B(OR)_3$ (R = alkyl or aryl).

Experimental Section

Preparation of the Compounds. The preparation and characterization of the acids have been reported.[9] The adducts were made by allowing stoichiometric amounts of acid and base to react, in the absence of moisture, in a special all-glass apparatus which permitted fractional crystallization of the product. All were white crystalline solids with the exception of the *p*-cyano derivative which was a glass at room temperature. Satisfactory analyses for boron and 4-methylpyridine in these compounds were obtained. Their melting points and analyses are available as supplementary material.

4-Methylpyridine was dried by refluxing over potassium hydroxide pellets and then fractionally distilled and stored under vacuum.

Calorimeter. The calorimeter and experimental procedures have been described.[9] The calorimetric data for the enthalpy of reaction of the acids, base, and adducts with one of the hydrolysis solvents are available as supplementary material. Errors in these data are quoted as twice the standard deviation of the mean.

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Registry No. $B(OC_6H_5)_3$, 1095-03-0; $B(OC_6H_4\text{-}m\text{-}Me)_3$, 14750-98-2; $B(OC_6H_4\text{-}m\text{-}Cl)_3$, 42080-72-8; $B(OC_6H_4\text{-}m\text{-}OMe)_3$, 42080-76-2; $B(OC_6H_4\text{-}p\text{-}Me)_3$, 14643-62-0; $B(OC_6H_4\text{-}p\text{-}Cl)_3$, 7359-58-2; $B(OC_6H_4\text{-}p\text{-}OMe)_3$, 42080-75-1; $B(OC_6H_4\text{-}p\text{-}CN)_3$, 42080-77-3; $4\text{-}MeC_5H_4N$, 108-89-4; $4\text{-}MeC_5H_4N{\cdot}B(OC_6H_5)_3$, 20340-65-2; $4\text{-}MeC_5H_4N{\cdot}B(OC_6H_4\text{-}m\text{-}Me)_3$, 34332-61-1; $4\text{-}MeC_5H_4N{\cdot}B(OC_6H_4\text{-}m\text{-}Cl)_3$, 54699-06-8; $4\text{-}MeC_5H_4N{\cdot}B(OC_6H_4\text{-}m\text{-}OMe)_3$, 54699-07-9; $4\text{-}MeC_5H_4N{\cdot}B(OC_6H_4\text{-}p\text{-}Me)_3$, 34330-45-5; $4\text{-}MeC_5H_4N{\cdot}B(OC_6H_4\text{-}p\text{-}Cl)_3$, 54699-08-0; $4\text{-}MeC_5H_4N{\cdot}B(OC_6H_4\text{-}p\text{-}OMe)_3$, 54699-09-1; $4\text{-}MeC_5H_4N{\cdot}B(OC_6H_4\text{-}p\text{-}CN)_3$, 54699-10-4.

Supplementary Material Available. Tables listing the melting points and analyses of the adducts and the enthalpies of reaction of the acids, base, and adducts will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number AIC40664W.

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nido-Metalloboranes Derived from $B_{10}H_{10}{}^{2-}$

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Anhydrous $K_2B_{10}H_{10}$ was found to react with $LLPtCl_2$ complexes where L = triphenylphosphine or LL = 1,2-bis(diphenylphosphino)ethane, diphos, in ethanolic chloroform to form isomeric ethoxy-substituted *nido*-metalloboranes, $LLPtB_{10}H_{11}OC_2H_5$. These complexes are derivatives of the $LLPtB_{10}H_{12}$ metalloboranes and arise from the polyhedral expansion of the *closo*-borane anion. This reaction is one of the few examples in which the $B_{10}H_{10}{}^{2-}$ skeleton is radically altered.

Introduction

The polyhedral borane anion, $B_{10}H_{10}{}^{2-}$, is prominent among the $B_nH_n{}^{2-}$ *closo*-borane dianions because of its extreme thermal, hydrolytic, and oxidative stability[1] coupled with its wide scope of derivative chemistry.[1] In the vast majority of its reactions, the boron framework of $B_{10}H_{10}{}^{2-}$ remains intact, and a formal hydride (H^-) is merely replaced by a substitutent. Prior to the chemistry reported here, only three reactions had been discovered in which the *closo*-$B_{10}H_{10}{}^{2-}$ framework was altered. Protonation of $B_{10}H_{10}{}^{2-}$ in acetonitrile with CF_3CO_2H resulted in the apparent formation of a *nido*-$B_{10}H_{11}{}^-$ ion as inferred from ^{11}B NMR spectroscopy.[2] Muetterties has reported[3] that upon careful dehydration of $(H_3O^+)_2B_{10}H_{10}{}^{2-}$, irreproducible yields of a volatile species, formulated as $B_{10}H_{12}OH_2$, were obtained. Finally, Marshall and coworkers[4] disclosed the important discovery that $B_{10}H_{10}{}^{2-}$ reacted with anhydrous HCl in diethyl sulfide solvent to produce the decaborane derivative, $B_{10}H_{12}[S(C_2H_5)_2]_2$.[5]

We now report the reaction of $B_{10}H_{10}{}^{2-}$ with two group 8c metal complexes which resulted in the expansion of this *closo*-borane dianion to form an 11-particle icosahedral fragment.

Discussion

Synthesis and Characterization. Reaction of *cis*-$(PPh_3)_2PtCl_2$ with $B_{10}H_{10}{}^{2-}$ in hot alcoholic chloroform resulted in the production of two isomeric complexes, Ia and Ib, formulated as $(PPh_3)_2PtB_{10}H_{11}(OC_2H_5)$. The same reaction utilizing $(diphos)PtCl_2$ yielded three isomers, IIa–c, formulated as $(diphos)PtB_{10}H_{11}(OC_2H_5)$. The reaction is depicted in Figure 1. Attempts to extend this chemistry to include the two remaining members of this triad (Ni, Pd) proved fruitless. These compounds contain an ethoxy-substituted $B_{10}H_{12}{}^{2-}$ ligand; the unsubstituted parent borane, $B_{10}H_{12}{}^{2-}$, has been reportedly isolated by Wilks and Carter[6] from the extended treatment of decaborane, $B_{10}H_{14}$, with sodium hydride. The parent complex $LLPtB_{10}H_{12}$[7] (L = triphenylphosphine, LL = diphos), III, was first prepared by reaction of the $B_{10}H_{13}{}^-$ ion with $(PPh_3)_2PtCl_2$. An X-ray diffraction study[8] of $[(B_{10}H_{12})_2Ni]^{2-}$, which contains two $B_{10}H_{12}{}^{2-}$ ligands fused through the transition metal atom, proved the heavy-atom arrangement of the $\{B_{10}H_{12}\}$ moiety to be that depicted in Figure 1.

The infrared spectra of Ia and b and IIa–c exhibited absorptions characteristic of terminal B–H vibrations, absorptions characteristic of the phenyl moiety, and strong and broad absorptions located at ca. 1250 cm^{-1} which were assigned to B–O stretching modes. Complete infrared data are presented in the Experimental Section.

The proton NMR spectra[9] (60, 100, or 251 MHz) of Ia and Ib displayed a complex pattern of resonances which were attributed to the phosphine ligands, in addition to resonances assigned to the ethoxy methylene protons and a triplet assigned to the ethoxy methyl protons. Integration of these spectra established the ratio of triphenylphosphine:ethoxy moieties as 2:1, thus supporting the analytical data.

The methylene protons always appeared as the AB portion of an ABX_3 pattern.[10] Evidently, the nonequivalence of the methylene protons was due to stereoelectronic influences exerted by the close proximity of the platinum–phosphine vertex and the open face of the icosahedral fragment such that one rotational configuration about the C–O bond is preferred over other configurations.[10] The 251-MHz proton NMR spectrum of Ia identified a resonance at τ 12.9 (B–H–B bridge proton region) and Ib exhibited a similar broad resonance at τ 12.7. The integral of these resonances was not considered to be accurate enough to establish the number of protons (i.e., 1 or 2) associated with this resonance.

The proton NMR spectra[9] of IIa–c contained resonances assigned to the diphosphine ligand, and similar to the spectra of Ia and b, resonances attributed to an ethoxy substituent were observed. Again, the methylene protons of the ethoxy group appeared as the AB portion of an ABX_3 system,[10] and the 251-MHz PMR spectra of all three isomers exhibited resonances attributable to B–H–B bridge protons. One B–H–B bridge proton resonance was located at τ 12.2 for IIa, while IIc exhibited a bridge proton resonance at τ 10.2. In contrast, IIb was the only complex to exhibit two identifiable bridge protons (τ 10.9 and 12.1).

The proton-decoupled 80.5-MHz ^{11}B NMR spectra of Ia and b and IIa–c are shown in Figure 2. Although the ^{11}B spectrum of III at 32 MHz was poorly resolved,[7] the proton-decoupled spectrum at 80.5 MHz was much more resolved and is included in Figure 2. Figure 1 suggests four unique boron atom pairs and two unique boron atom environments for III, and the spectrum of III is consistent with this prediction.

The ^{11}B spectra of Ia and b and IIa display eight unique resonances, whereas IIb and c displayed six or seven unique resonances and therefore established the absence of molecular symmetry in these metalloboranes. Ten unique boron environments exist in all five cases and resonances with integrals greater than 1 are the result of coincidental overlap. The possible positions of substitution in Ia and b and IIa–c,