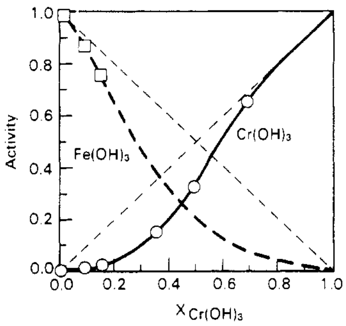

Figure 6. Activities of $Cr(OH)_3$ and $Fe(OH)_3$ in $Cr_xFe_{1-x}(OH)_3$. The solid curve was obtained by least-squares regression of the equilibrium $Cr(OH)_3$ activity coefficients (Table I) (circles) for the hypothetical standard state of $Cr(OH)_3$ (see eq 14). The corresponding activities of $Fe(OH)_3$ (dashed curve) were calculated by a Gibbs–Duhem equation; squares indicate the $Fe(OH)_3$ activities in Figure 2.

hypothetical state is not physically equivalent to freshly precipitated $Cr(OH)_3$. Activity coefficients for $Cr(OH)_3$ based on the hypothetical standard state ($\lambda^*_{Cr(OH)_3}$) are given by

$$\log \lambda^*_{Cr(OH)_3} = 0.28(1 - x)^2 - 1.79(1 - x)^3 \qquad (14)$$

The standard state of $Fe(OH)_3$ remains unchanged as the pure amorphous solid precipitated by the methods described earlier.

Activities of $Cr(OH)_3$ and $Fe(OH)_3$, based on eq 11 and 14, are shown in Figure 6. The shapes of the activity curves suggest that $Cr_xFe_{1-x}(OH)_3$ behaves like a typical solution that deviates negatively from an ideal mixture.

Conclusions

Solids containing different proportions of Cr(III) and Fe(III) were precipitated by $(C_2H_5)_4NOH$ or NaOH and equilibrated in 0.01 M perchlorate solutions between pH 2 and 6 in an N_2 atmosphere. Experiments were performed at different time periods and from under- and oversaturation and indicate that equilibrium was attained or could be estimated for solid compositions with less than about 70 mol % $Cr(OH)_3$.

In general, Cr contents in the 0.0018-μm filtrates decrease with a decrease in the mole fraction of $Cr(OH)_3$ in the solid (x). Activity coefficients for $Cr(OH)_3$ (solid) are much less than 1 at most of the investigated compositions ($x \leqslant 0.89$), indicating that mixing with $Fe(OH)_3$ is highly favorable. Activity coefficients for $Fe(OH)_3$ (solid) were calculated by using a Gibbs–Duhem equation and provide results that are consistent with the observed aqueous Fe activities in solutions contacting solids with values of $x \leqslant 0.15$. The results of these experiments support the hypothesis that coprecipitated $Cr(OH)_3$ and $Fe(OH)_3$ behave thermodynamically like solid solutions.

A composition-dependent solubility equation can be derived from the equations presented here and can be used to predict aqueous Cr concentrations in equilibrium with $Cr_xFe_{1-x}(OH)_3$. For $x \leqslant 0.69$ and for pH between 2 and 6, the following equation is valid:

$$\log (CrOH^{2+}) = -2pH + 4.18 + 0.28(1 - x)^2 - 1.79(1 - x)^3 + \log x \qquad (15)$$

Equation 15 is applicable to natural systems where the Fe(III)/Cr(III) ratio is high.

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Boron Nuclear Quadrupole Coupling in Trimethylphosphine–Borane

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The hyperfine splitting due to the boron nuclear electric quadrupole moment was measured in trimethylphospine–borane by Fourier transform microwave spectroscopy techniques. The coupling constant, eQq = 1.198 (20) MHz, was interpreted in terms of the fractional number of electrons donated from phosphorus to boron. A value of 0.61 was estimated. The results were compared with coupling constants for methylphosphine–borane and trifluorophosphine–borane.

The development of high-resolution Fourier transform microwave (FTMW) spectroscopy has led to the determination of boron nuclear quadrupole coupling constants in two phosphine–borane adducts, $PF_3 \cdot BH_3$[1] and $CH_3PH_2 \cdot BH_3$.[2] It is well-known that quadrupole coupling constants can give information about the electron distribution about boron.[3-5] This motivated us to undertake a similar analysis of $(CH_3)_3P \cdot BH_3$ in order to make comparisons among these systems. The microwave spectrum of $(CH_3)_3P \cdot BH_3$ had been previously investigated and structural parameters were determined, but the boron quadrupole splitting was not resolved.[6]

Experimental Section

The sample preparation has been described elsewhere.[6] The spectrum was observed with a FTMW spectrometer described in another report.[7] A heated pulsed supersonic nozzle was used to produce a molecular beam to minimize collisional broadening of the transitions. This was made by adding a small heated stainless-steel chamber containing a few tenths of a gram of solid to a modified Bosch fuel injector valve.[8] The carrier gas moving slowly through the chamber became saturated at the equilibrium

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Table I. Observed Frequencies ν_{obsd} (MHz) for the ^{11}B Hyperfine Components of Trimethylphosphine–Borane[a]

$J-J'$	K	$F-F'$	ν_{obsd}	ν_{calcd}	$\Delta\nu$
0–1	0	1.5–2.5	6 431.302	6 431.294	0.008
		1.5–1.5	6 431.590[b]	6 431.594	−0.004
		1.5–0.5	6 431.050	6 431.054	−0.004
1–2	0	2.5–3.5	12 862.682	12 682.671	0.011
		2.5–2.5	12 862.969	12 682.970	−0.001
		2.5–1.5		12 682.757	
		1.5–2.5	12 682.682	12 682.671	0.011
		1.5–1.5	12 862.456	12 862.458	−0.002
		1.5–0.5	12 862.145	12 862.157	−0.012
		0.5–1.5	12 863.000	12 862.996	0.004
		0.5–0.5	12 862.682	12 862.697	−0.015
1–2	1	2.5–3.5	12 862.632	12 862.610	0.022
		2.5–2.5	12 862.735	12 862.760	−0.025
		2.5–1.5		12 862.653	
		1.5–2.5	12 862.921	12 862.910	0.011
		1.5–1.5	12 862.785	12 862.803	−0.018
		1.5–0.5		12 862.653	
		0.5–1.5	12 862.532	12 862.533	−0.001
		0.5–0.5	12 862.395	12 862.384	0.011

[a] The values ν_{calcd} (MHz) were calculated with the parameters in Table III. $\Delta\nu = \nu_{obsd} - \nu_{calcd}$ (MHz). [b] Transition partially overlapped with an unassigned transition at 6431.632 MHz.

Table II. Observed Frequencies ν_{obsd} (MHz) for the ^{10}B Hyperfine Components of Trimethylphosphine–Borane[a]

$J-J'$	K	$F-F'$	ν_{obsd}	ν_{calcd}	$\Delta\nu$
0–1	0	3–4	6 596.034	6 596.031	0.003
		3–3	6 596.535	6 596.536	−0.001
		3–2	6 595.853	6 595.855	−0.002
1–2	0	4–5	13 192.248	13 192.254	−0.006
		4–4	13 192.700	13 192.704	−0.004
		4–3	13 192.632	13 192.632	0.000
		3–4	13 192.210	13 192.200	0.010
		3–3	13 192.144	13 192.128	0.016
		3–2	13 191.805	13 191.821	−0.016
		2–3	13 192.805	13 192.809	−0.004
		2–2	13 192.499	13 192.502	−0.003
		2–1	13 192.185	13 192.178	0.007
1–2	1	4–5	13 192.144	13 192.144	0.000
		4–4	13 192.375	13 192.369	0.006
		4–3	13 192.322	13 192.333	−0.011
		3–4	13 192.632	13 192.621	0.011
		3–3	13 192.580	13 192.585	−0.005
		3–2	13 192.421	13 192.432	−0.011
		2–3	13 192.247	13 192.245	0.002
		2–2	13 192.103	13 192.093	0.010
		2–1	13 191.928	13 191.930	−0.002

[a] The values ν_{calcd} (MHz) were calculated with the parameters in Table III. $\Delta\nu = \nu_{obsd} - \nu_{calcd}$ (MHz).

Table III. Rotational, Centrifugal, and Nuclear Quadrupole Coupling Constants for Trimethylphosphine–Borane

	^{11}B	^{10}B
B/MHz	3215.6780 (20)	3298.0793 (20)
B/MHz[6]	3215.63 (3)	3298.04 (3)
D_J/kHz	0.46 (10)	0.30 (10)
D_{JK}/kHz	3.50 (30)	2.70 (30)
eqQ/MHz[a]	1.198 (20)	2.521 (10)

[a] The hfs analysis is based on the $J = 0 \rightarrow 1$ transition. A global fit to all observed frequencies gives 1.199 (20) and 2.518 (10) MHz.

Table IV. Comparison of Observed P–B Bond Distances and ^{11}B Quadrupole Coupling Constants with n, the Fractional Number of Electrons Donated from P to B Estimated by Eq 4

	$eqQ(^{11}B)$/MHz	r(P–B)/Å	n	ref
$BH_3{\cdot}P(CH_3)_3$	1.198 (20)	1.901 (7)	0.61 (1)[a]	6
$BH_3{\cdot}PF_3$	1.478 (3)	1.835 (6)	0.57 (2)	1, 20
$BH_3{\cdot}PH_2CH_3$	1.600 (96)[b]	1.906 (6)	0.54 (2)	2, 6

[a] Uncertainty arising from eqQ and structural error limits. [b] Obtained by rotating the observed **eqQ** tensor onto the PB bond.

vapor pressure. With the valve pressurized to about 1 atm with Ar, the sample was pulsed into the microwave cavity. Although the ^{11}B species ground-state transitions could be detected at room temperature where the vapor pressure of $(CH_3)_3P{-}BH_3$ is about 0.5 Torr,[9] the intensity improved about 10-fold upon heating the valve head to 75 °C. The limiting resolution of the instrument is approximately 5–10 kHz.

Results and Discussion

The observed transitions for the ^{10}B and ^{11}B species are listed in Tables I and II. The accuracy of the line centers is $\leq$5 kHz. The observed spectral line widths were typically 20 kHz fwhm presumably due to unresolved magnetic hyperfine interactions from phosphorus and/or hydrogen and to residual Doppler broadening; experimental conditions were adjusted to minimize the Doppler splitting, which is common in this type of spectrometer,[10] and no such splitting could be clearly detected.

The spectra were assigned by using first-order quadrupole theory. The difference between the observed and calculated spectra are given in Tables I and II. The fit is considered satisfactory in view of the observed line widths. Also, the ratio of the $^{10}B/^{11}B$ coupling constants of 2.10 (5) is in reasonable agreement with values (2.08–2.19) observed in other studies.[1,11-14] The derived constants are given in Table III.

The quadrupole coupling constant was interpreted in terms of n, the number of electrons donated to boron by phosphorus, following the discussion of $PF_3{\cdot}BH_3$[1] and $CH_3PH_2{\cdot}BH_3$[2] (see also ref 15). Equation 1 was used, where eqQ is the measured coupling

$$eqQ = -(U_p)_z\left[\frac{eqQ_{210}}{1 + (n - 3i_\sigma)\epsilon}\right] \tag{1}$$

constant, $eqQ_{210}(^{11}B) = -5.39$ MHz[15] is the constant arising from a single $2p_z$ electron, $\epsilon = 0.5$[15] is the shielding constant for boron, $i_\sigma = 0.5|EN(H) - EN(B)|$ is the ionic character of the BH bond estimated from the electronegativities of H and B (2.15 and 2.00 respectively[15]), and $(U_p)_z$ is the unbalance in the p electrons in the z direction in the coupling atom defined in terms of the fractional number of electrons n_i in the p_x, p_y, and p_z orbitals:

$$(U_p)_z = \frac{n_x + n_y}{2} - n_z \tag{2}$$

With the z direction along the P–B bond axis and nominal sp^3 hybridization about the boron, the sp^3 hybrid in this direction can be described as follows, along with analogous equations for the other three hybrids:[15]

$$\psi_1 = (1 - 3a_s^2)^{1/2}\psi_s + (3a_s^2)^{1/2}\psi_{p_z} \tag{3}$$

a_s^2 can be estimated from the observed geometry,[6] $a_s^2 = \cos(\angle HBH)/(\cos(\angle HBH) - 1)$. This leads to eq 4, from which the

$$eqQ = \left[\frac{-3a_s^2(1 - i_\sigma - n)}{1 + (n - 3i_\sigma)\epsilon}\right]eqQ_{210} \tag{4}$$

population n of the ψ_1 hybrid can be estimated, i.e. the number

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of electrons donated from P to B.

The value obtained for *n*, which might also be considered the bond order of the adduct, is listed in Table IV along with the results for $PF_3{\cdot}BH_3$ and $CH_3PH_2{\cdot}BH_3$ computed by using the same values of i_σ, ϵ, and eqQ_{210}. In all three examples the small value of *n* indicates that considerably less than 1 electron is donated by the base to BH_3, consistent with the weak bonding in such adducts. The smaller *n* for $CH_3PH_2{\cdot}BH_3$ compared to $(CH_3)_3P{\cdot}BH_3$ is plausible based on various measurements (proton affinities,[16] UV–PES,[17] and adduct dissociation constants[18], which indicate that CH_3PH_2 is a less basic ligand than $(CH_3)_3P$. It is interesting that the coupling constants are sensitive to this basicity difference, while it is not so evident in their P–B distances (Table IV).

It is noted that $PF_3{\cdot}BH_3$ has a value of *n* between those of $(CH_3)_3P{\cdot}BH_3$ and $CH_3PH_2{\cdot}BH_3$ but a much shorter P–B distance. This is curious since $PF_3{\cdot}BH_3$ is partially dissociated in the gas phase with a ΔH of dissociation of 11 kcal[19,20] while $CH_3PH_2{\cdot}BH_3$ and $(CH_3)_3P{\cdot}BH_3$ are undissociated with $\Delta H_{diss} \geqslant 22$ kcal for $(CH_3)_3P{\cdot}BH_3$.[6] The stability differences might suggest that *n* should be somewhat smaller in $PF_3{\cdot}BH_3$ compared to *n* in the methylphosphine–borane adducts while the short bond distance might imply the opposite.

It is possible to reconcile these observations with the incorporation of π back-bonding from BH_3 to the PF_3. The proposal of back-donation as a supplement to σ donation from the phosphorus was made some years ago[21] although later ab initio calculations with a minimum basis set of Slater type orbitals indicated that the amount of π donation was small.[22] Back-donation was recently reintroduced to account for core binding energy data obtained from X-ray PE spectra.[23] The effect of π back-bonding can be illustrated by correcting eq 4 for some π bonding by using i_π to represent the fraction of the boron electrons in BH bonds transferred to PF_3. Since the boron p_x and p_y orbitals participate in the bonds to the hydrogens, the number of π electrons back-donated from the BH_3 group is given by $2(1 - i_\sigma)i_\pi$. This leads to

$$eqQ = \left[\frac{-3a_s^2(1 - n - i_\sigma) + i_\pi(1 - i_\sigma)}{1 + (n - 3i_\sigma - 2i_\pi - 2i_\pi i_\sigma)\epsilon}\right] eqQ_{210} \qquad (5)$$

If one assumes that the relationship between a_s^2 and the BH_3 geometry (eq 4) holds approximately even after the introduction of π bonding, then values of *n* can still be estimated as i_π is varied. This gives $n = 0.50$ for $i_\pi = 0.1$ and $n = 0.44$ for $i_\pi = 0.2$.[24] It is unclear how to partition the bonding between the two mechanisms, but values of i_π between 0.1 and 0.2 would seem appropriate. This would partition the bonding between approximately 2.7:1 and 1.2:1, respectively, among the σ and π mechanisms. Such amounts of π bonding, which presumably are energetically less effective than σ donation, should sufficiently increase the overall bond order to result in adduct formation at relatively short P–B distances while lowering the stability of $PF_3{\cdot}BH_3$ compared to the stability of the methylphosphine adducts. For comparison, in $H_3B{\cdot}CO$ where back-donation is also postulated,[21,23,25] Umeyawa and Morokuma estimated[26] that 0.32e of σ charge is transferred from CO to BH_3 and 0.20e of π charge is back-donated from BH_3 to CO. The earlier investigation of $PF_3{\cdot}BH_3$[22a] gave B–P overlap populations of 0.57 for the σ orbitals and 0.08 for π bonding, which is a somewhat smaller contribution from the π mechanism than proposed here from the quadrupole data. While the optimum partitioning between σ donation and π back-bonding cannot be settled by this study, it does appear that the inclusion of some back-bonding in $PF_3{\cdot}BH_3$ gives a more attractive interpretation of the quadrupole coupling constants when it is compared to the methylphosphines. A reinvestigation of $PF_3{\cdot}BH_3$ by ab initio techniques in the light of the quadrupole coupling constants and the recent X-ray PES results[23] should be helpful in interpreting these data.

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