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Diethyl(di-*tert*-butylphosphino)borane and Related Compounds: The First Stable Monomeric Tetraalkyl Phosphinoborane

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Four new phosphinoborane compounds were prepared and characterized by ^1H, ^{13}C, ^{31}P, and ^{11}B NMR spectroscopy and elemental analysis. Monomeric $Et_2BP(t\text{-}Bu)_2$ was isolated as a volatile yellow liquid and $[Me_2BP(t\text{-}Bu)_2]_2$ as a colorless solid using salt elimination reactions. The colorless dimeric solids $[Me_2BP(SiMe_3)_2]_2$ and $[Et_2BP(SiMe_3)_2]_2$ were prepared via trimethylsilyl halide elimination reactions. The dimeric compounds dissociate in benzene or toluene at ambient temperature, and an equilibrium with the monomeric species is established. Variable-temperature ^1H NMR spectroscopy showed that $\Delta H = -93$ kJ/mol and $\Delta S = -285$ J/(mol·K) for the dimerization of $Me_2BP(t\text{-}Bu)_2$ and $\Delta H = -55 \pm 12$ kJ/mol and $\Delta S = -166 \pm 42$ J/(mol·K) for the dimerization of $Me_2BP(SiMe_3)_2$. Inverse 2D $^1H/^{13}C$ correlation studies were applied to monomer–dimer solutions and were vital to assignment of ^{13}C resonances. Solid-state ^{31}P NMR confirmed that $[Me_2BP(t\text{-}Bu)_2]_2$ and $[Me_2BP(SiMe_3)_2]_2$ are dimeric solids. The structure of $[Me_2BP(t\text{-}Bu)_2]_2$ was determined by single-crystal X-ray diffraction. Crystal data: triclinic, space group $P\bar{1}$, $a = 8.366(3)$ Å, $b = 8.0808(2)$ Å, $c = 9.311(2)$ Å, $\alpha = 74.98(2)°$, $\beta = 78.87(2)°$, $\gamma = 64.32(2)°$, $Z = 1$, and $R = 0.0628$.

Introduction

The structure and properties of monomeric phosphinoborane compounds ($R_2BPR'_2$) have been investigated primarily because of the insight they provide into the nature of π-bonding interactions between main-group atoms. The few examples of monomeric phosphinoborane compounds known and the extent of boron–phosphorus π-bonding interaction in them have been recently reviewed by Power.[1] In phosphinoborane compounds, as in the isoelectronic silenes and disilenes, formation of a double bond is much less favorable than two single bonds. As a result, the amphoteric phosphinoborane compounds form cyclic oligomers containing four-coordinate boron and phosphorus with B–P single bonds, unless stabilized by electronic or steric effects of the substituents.

Our interest in compounds containing a phosphorus–boron bond lies in their potential application as single-source precursors for the organometallic vapor phase epitaxy (OMVPE) of boron phosphide.[2] Ideally, the precursor compound should be a liquid with an appreciable vapor pressure at ambient temperature and have substituents that are easily and cleanly eliminated during pyrolysis. In this respect, monomeric phosphinoborane compounds are promising precursor candidates for OMVPE applications.

In general, monomeric phosphinoborane compounds are either kinetically stabilized compounds with sterically bulky substituents or electronically stabilized species, usually with amino substituents on the boron. In the amino-substituted compounds,[3] nitrogen reduces the electron deficiency at boron through π donation of electron density more efficiently than the phosphorus atom, thereby stabilizing the monomeric compounds. However, amino compounds were not considered viable precursor compounds, since pyrolysis of them might produce films containing boron nitride.

Useful kinetically stabilized phosphinoborane precursor compounds require substituents that are sufficiently bulky to prevent or minimize association yet have a low enough mass to provide a reasonable vapor pressure. In nearly all of the reported kinetically stabilized monomeric phosphinoboranes the boron atom is substituted with aryl groups. Consequently, the compounds are solids with very low vapor pressure, making them unsuitable as OMVPE precursor compounds. Additionally, a high percentage of carbon incorporation is usually found in films deposited using precursor compounds that contain aryl groups. Alkyl-substituted precursors generally produce cleaner films[4] where the alkyl groups can readily be lost during pyrolysis

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via a β-hydride elimination pathway. Prior to this report, di-*tert*-butyl(di-*tert*-butylphosphino)borane was the only reported example[5] of a tetraalkyl phosphinoborane. It was found to be unstable above −20 °C, undergoing β-hydride elimination of the boron *t*-Bu substituents and hydroboration of the resulting isobutene, ultimately forming the stable dimer $[i\text{-Bu(H)BP}(t\text{-Bu})_2]_2$.

The objective of this work is to determine the minimum steric bulk of the alkyl substituents necessary to stabilize a monomeric phosphinoborane compound and explore the electronic effect of the trimethylsilyl group attached to phosphorus. We report the preparation and characterization of the stable phosphinoborane compounds $Et_2BP(t\text{-Bu})_2$ (**1**), $[Me_2BP(t\text{-Bu})_2]_2$ (**2a**), $[Me_2BP(SiMe_3)_2]_2$ (**3a**), and $[Et_2BP(SiMe_3)_2]_2$ (**4a**) with alkyl substituents on the boron. Compounds **2a**–**4a** are dimeric as neat solids but are convenient sources of the monomeric phosphinoborane compounds $Me_2BP(t\text{-Bu})_2$ (**2b**), $Me_2BP(SiMe_3)_2$ (**3b**), and $Et_2BP(SiMe_3)_2$ (**4b**) in solution. Investigation of the monomer–dimer equilibrium in solution by variable-temperature ^{1}H NMR provides the first measure of the energy change for the dimerization.

Experimental Section

General Comments. All reactions and manipulations were carried out in dry, oxygen-free argon using standard Schlenkware or in a nitrogen-filled Vacuum Atmospheres drybox. Solvents were distilled from Na/benzophenone prior to use. Solid-state ^{31}P CP-MAS NMR spectra were recorded on a Bruker MSL200 spectrometer. Spinning rates were from 5.6 to 9.4 KHz for **2a** and at 6.3 KHz for **3a**, and chemical shifts were referenced externally to phosphoric acid. Unless otherwise stated, solution NMR spectra were recorded on a Bruker AMX-400 spectrometer and external references were used: phosphoric acid for ^{31}P spectra and $BF_3 \cdot Et_2O$ for ^{11}B spectra. The 80-MHz ^{1}H NMR spectra were obtained on a Bruker NR80 spectrometer. Microanalyses were performed by E + R Microanalytical Laboratory Inc., 96-34 Corona Ave., Corona NY 11368. Samples of Me_2BBr and $(TMS)_3P$ were purchased from Alrich Chemical Co. and used without further purification.

Calculations for Variable-Temperature ^{1}H NMR Experiments. For **2a** and **2b** the dimer to monomer exchange reaction in toluene-d_8 is slow on the ^{1}H NMR time scale at all temperatures examined. Values of the equilibrium constant were determined using the integrated areas of the methyl resonance for **2a** and **2b** from spectra obtained between 300 and 360 K using a 0.150 M solution (calculated as **2b** exclusively) in toluene-d_8. The mole fraction of monomer present, X_{2b}, was calculated using eq I.

$$X_{2b} = \frac{\text{monomer integral}}{\text{monomer integral} + 0.5(\text{dimer integral})} \qquad \text{(I)}$$

A variable-temperature ^{1}H NMR experiment was conducted using a toluene-d_8 solution of **3a** (0.101 M calculated as **3b**) from 223 to 383 K. Above 290 K, **3a** and **3b** are at fast exchange conditions on the ^{1}H NMR time scale. The observed shift for the methyl resonance (δ_{av}) is therefore the average of the signals from the monomeric and the dimeric species. The chemical shift of the average signal can be expressed using eq II, where F_{3b} is the fraction of methyl groups present in the monomer.

$$\delta_{av} = \delta_{3a} + F_{3b}(\delta_{3b} - \delta_{3a}) \qquad \text{(II)}$$

$$F_{3b} = \frac{[\mathbf{3b}]}{2[\mathbf{3a}] + [\mathbf{3b}]} = \frac{[\mathbf{3b}]}{0.101\ \text{M}}$$

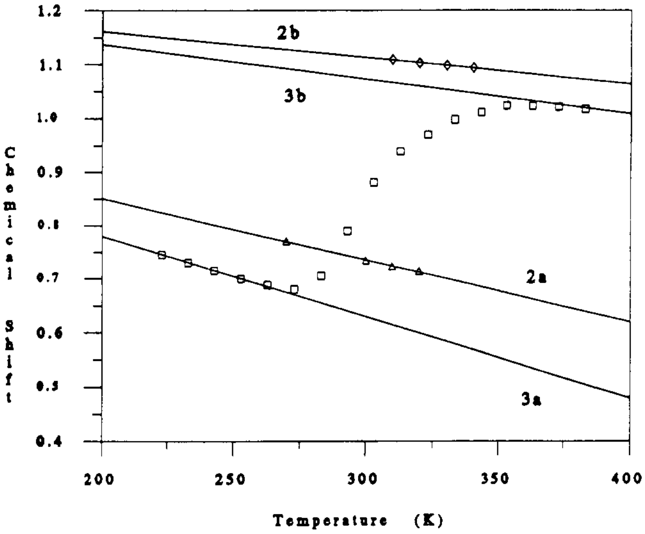

Figure 1. Plot of observed and extrapolated values for the chemical shift of the methyl resonance in **2a**, **2b**, **3a**, and **3b** versus temperature.

The concentration of monomer present could therefore be calculated from the observed chemical shift using eq III.

$$[\mathbf{3b}] = (0.101\ \text{M})\frac{\delta_{av} - \delta_{3a}}{\delta_{3b} - \delta_{3a}} \qquad \text{(III)}$$

The chemical shifts of the monomer and dimer methyl resonance (δ_{3a} and δ_{3b}) also have a temperature dependence which affects the chemical shift of the average signal that cannot be neglected in the calculations. The temperature effect on the chemical shift of **3a** ($\delta_{3a} = (1.50 \times 10^{-3})T + 1.080$) was obtained directly from the ^{1}H NMR spectra over the range 223–253 K, where the exchange rate is slow (Figure 1).

The presence of a small amount of dimer in the higher temperature spectra makes a significant contribution to changes in the observed chemical shift. Therefore, values used for δ_{3b} could not be extrapolated from the available data as plotted in Figure 1. However, it is reasonable to assume that the temperature effect will be similar to that for the methyl resonances of **2a**, **2b**, and **3a**, which show a linear dependence on the temperature (Figure 1), where $\delta_{2a} = (-1.15 \times 10^{-3})T + 1.080$ and $\delta_{2b} = (-4.88 \times 10^{-4})T + 1.259$. Thus, the slope for δ_{3b} was set at 42% of the slope for δ_{3a} (which is the ratio of the slope of $\delta_{2a}:\delta_{2b}$) and the constant was determined from the best fit of the ln K versus $1/T$ data to a straight line. The result, $\delta_{3b} = (-6.37 \times 10^{-4})T + 1.265$, was used to calculate the values of ln K plotted in Figure 5. The error limits were set by varying the slope for δ_{3b} between the extreme limits of -1.50×10^{-3}, the value for the slope of δ_{3a}, and −0.0002, obtained directly from the shift of **3b** at 373 and 383 K.

Synthesis of Et_2BCl. Et_2BCl was prepared using the general procedure for hydroboration.[6] Ethylene was slowly bubbled into a two-phase solution of 14.22 g of $H_2BCl \cdot SMe_2$ (85.39 mmol) and 100 mL of pentane with stirring at 20 °C. After 4$^1/_2$ h the solution was a single colorless phase, and it was apparent that no more ethylene was being consumed. The solution was frozen with liquid nitrogen, and 10.0 g of BCl_3 (85.39 mmol) was condensed into the flask. As the temperature was raised, $BCl_3 \cdot SMe_2$ formed as a white solid (identified by its singlet resonance in the 80-MHz ^{1}H NMR spectrum at 1.35 ppm in benzene-d_6). The volatile products and solvent were collected in a liquid-nitrogen trap at 10^{-2} Torr. The pentane was distilled off at 35 °C/1 atm; then the pressure was reduced to 200 mmHg, where about 2 mL of Et(H)BCl was collected at 30 °C/200 mmHg. The product, Et_2BCl (10.4 g, 90%

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[7] Brown, H. C.; Ravindran, N.; Kulkarni, S. U. *J. Org. Chem.* **1979**, *44*, 2417.

yield), was collected at 42 °C/200 mmHg, which compares with the reported[7] bp 78.7 °C at 760 mmHg. The 80-MHz ^{1}H NMR was a second-order spectrum consisting of a multiplet centered at 0.94 ppm, confirming that the product was free of all Me$_2$S.

Et$_2$BP(*t*-Bu)$_2$. A solution of 1.00 g of Et$_2$BCl (9.60 mmol) in 25 mL of benzene was slowly added to a slurry of 1.46 g of (*t*-Bu)$_2$PLi (9.60 mmol) in 50 mL of benzene at 20 °C with stirring. The reaction mixture was warmed slightly and turned light yellow as a white precipitate formed. After the mixture was stirred for 20 min, it was filtered through a fine-porosity frit to remove most of the LiCl. Stirring the suspension for longer periods decreased the yield of product and produced a mixture of unidentified compounds. Benzene was removed at 0 °C *in vacuo*, leaving about 2 mL of yellow liquid. This was transferred to an apparatus for a short-path distillation at 35 °C/10^{-2} Torr, the product being collected on a liquid-nitrogen-cooled probe. When the system was warmed to room temperature, 1.75 g (8.17 mmol, 85%) of the compound was collected as a light yellow liquid. Anal. Calcd for C$_{12}$H$_{28}$BP: C, 67.31; H, 13.18; P, 14.46; B, 5.05. Found: C, 67.25; H, 12.98; P, 14.28; B, 5.33.

[Me$_2$BP(*t*-Bu)$_2$]$_2$. A solution of 0.752 g of Me$_2$BBR (6.22 mmol) in 25 mL of benzene was slowly added to a slurry of 0.951 g of (*t*-Bu)$_2$PLi (6.25 mmol) in 50 mL of benzene at 20 °C with stirring. The reaction mixture warmed slightly and turned light yellow as a white precipitate formed. The mixture was stirred for 10 min and then filtered through a fine-porosity frit. The benzene solvent was removed *in vacuo*, leaving a colorless solid coated with a yellow oil. The crude product was dissolved in 50 mL of warm pentane and filtered through a fine-porosity frit. The solution was cooled to 0 °C and reduced to 5 mL *in vacuo*. The resulting colorless crystalline solid was collected, washed twice with 10 mL of cold pentane, and then dried *in vacuo* to give 0.512 g of **2a** (1.37 mmol, 44% yield, mp 122 °C, sublimes at 65 °C/10^{-2} Torr). Anal. Calcd for C$_{20}$H$_{48}$B$_2$P$_2$: C, 64.55; H, 13.00; P, 16.65; B, 5.81. Found: C, 64.56; H, 13.09; P, 16.80; B, 6.06.

[Me$_2$BP(TMS)$_2$]$_2$. A solution of 0.611 g of Me$_2$BBr (5.06 mmol) in 50 mL of benzene was slowly added to 1.267 g of P(TMS)$_3$ (5.06 mmol) in 50 mL of benzene with stirring at 20 °C. After 10 min a colorless solid formed, which slowly disappeared as the mixture was stirred for an additional 8 h. After the solvent was removed *in vacuo*, the colorless solid was recrystallized from pentane to give 0.805 g of **3a** (1.84 mmol, 72.9% yield, mp 105 °C, sublimes at 65 °C/10^{-2} Torr). Anal. Calcd for C$_{16}$H$_{48}$Si$_4$B$_2$P$_2$: C, 44.03; H, 11.08; P, 14.19; B, 4.95. Found: C, 43.96; H, 10.94; P, 14.23; B, 4.68.

[Et$_2$BP(TMS)$_2$]$_2$. A solution of 0.511 g of Et$_2$BCl (4.90 mmol) in 5 mL of toluene was added to 1.23 g of P(TMS)$_3$ (4.90 mmol) in 5 mL of toluene at 20 °C with stirring. The solution was heated to 90 °C for 10 h with stirring. The resulting light yellow solution was cooled to 20 °C, and all volatile materials were removed in vacuo. The light yellow solid remaining was dissolved in 20 mL of pentane. The volume of pentane was reduced to 5 mL and cooled to 0 °C. The crystallized product, **4a** (0.663 g, 1.35 mmol, 55% yield), was collected on a coarse frit as a colorless solid (mp 107 °C, sublimes at 65 °C/10^{-2} Torr). Anal. Calcd for C$_{20}$H$_{56}$Si$_4$B$_2$P$_2$: C, 48.77; H, 11.46; B, 4.39; P, 12.58. Found: C, 48.92; H, 11.04; B, 4.37; P, 12.47.

X-ray Structural Study of [Me$_2$BP(*t*-Bu)$_2$]$_2$. Suitable crystals were grown from a saturated benzene solution at room temperature as colorless cubes and mounted in thin-walled glass capillaries. The diffraction data were collected on a Siemens R3m/V diffractometer equipped with an incident-beam graphite monochromator using Cu Kα (λ = 1.541 78 Å) radiation. Space group determination was based on extinctions present and confirmed by the structure solution. The structure was determined by direct methods and refined with full-matrix least-squares methods using the Siemens SHELXTL PLUS (VMS) program. The function minimized was $\Sigma w(F_o - F_c)^2$ with the weighting scheme $w^{-1} = \sigma^2(F) + 0.0002F^2$ and the extinction correction $\chi = 0.020(5)$, where $F^* = F[1 + 0.002\chi F^2/(\sin 2\theta)]^{-1/4}$. The coordinates and anisotropic thermal parameters for the non-H atoms were refined. The isotropic thermal parameters for the hydrogen atoms were fixed and the positions calculated using a riding model. They were included in the structure factor calculations but not refined. Additional data collection and refinement parameters are listed in Table I.

Table I. Crystal and Refinement Data

formula	C$_{20}$H$_{48}$B$_2$P$_2$
cryst syst	triclinic
space group	$P\bar{1}$
cell constants	a = 8.366(3) Å, b = 8.808(2) Å, c = 9.311(2) Å, α = 74.98(2), β = 78.87(2)°, γ = 64.32(2)°
fw	372.1
v, Å^3	594.6(3)
Z	1
F(000)	208
d(calcd), g cm^{-3}	1.039
temp, °C	23
cryst dimens, mm	0.42 × 0.35 × 0.37
abs coeff, μ, mm^{-1}	1.638
2θ range, deg	3.5–114.0
ω scan speed, deg min^{-1}	constant, 9.01
2θ scan range, deg	1.10 plus Kα separation
data collected, *hkl*	–8 to 9, –8 to 9, 0–10
std rflns	3 std/97 rflns
no. of params refined	110
no. of rflns collected: indep, obsd	1530 (R_{int} = 0.00%), 1530 ($F > 3.0\sigma(F)$)
$R(F)$, $R(wF)$, GOF	0.0474, 0.0628, 2.89
Δ/σ (max)	0.058
$\Delta(\rho)$, e Å^{-3}	0.25

Results and Discussion

Stable Volatile Monomer. Our interest in the use of single-source precursor compounds for MOCVD as a means to control the composition of boron phosphide films motivated us to prepare a series of new volatile phosphinoborane compounds. We isolated 1, the first example of a stable monomeric tetraalkyl phosphinoborane, from reaction of (*t*-Bu)$_2$PLi with Et$_2$BCl in benzene (eq 1).

$$\mathrm{Et_2BCl} + \mathrm{LiP}(t\text{-Bu})_2 \rightarrow \underset{1}{\mathrm{Et_2BP}(t\text{-Bu})_2} + \mathrm{LiCl} \quad (1)$$

Diethyl(di-*tert*-butylphosphino)borane (1) is a volatile, light yellow liquid that remained unchanged after 4 months under an argon atmosphere at ambient temperature. The greater thermal stabilty of 1 over the previously reported (*t*-Bu)$_2$BP(*t*-Bu)$_2$ is likely the result of less facile retrohydroboration of the ethyl group.[5]

The compound was characterized by elemental analysis and multinuclear NMR, which is an extremely powerful technique for the characterization of these compounds since all nuclei have NMR-active isotopes. The shifts and coupling constants for the ^{1}H, ^{13}C, ^{31}P, and ^{11}B NMR spectra of 1 and all related compounds in toluene-d_8 are listed in Table II and discussed below.

The ^{1}H NMR spectrum of 1 in benzene-d_6 or toluene-d_8 is independent of concentration, and only a slight temperature dependence of the chemical shifts was observed. The proton signals of the ethyl substituents on the boron appear as a normal triplet and quartet with no splitting of the signals observed from three- and five-bond coupling to the phosphorus atom. A doublet at 1.34 ppm (^3J = 11.8 Hz) for the *t*-Bu substituents in the ^{1}H NMR spectrum of 1 is consistent with three-bond coupling to a single phosphorus atom in a monomeric species.

Two doublet signals were observed for the *t*-Bu carbon atoms in the ^{13}C spectrum of 1, which is also consistent

Table II. Chemical Shifts (ppm) of NMR Spectra in Toluene-d_8

$[R_2BPR'_2]_2$	^{31}P	^{11}B	$^1H(R)$	$^1H(R')$	$^{13}C(R)$	$^{13}C(R')$
$Et_2BP(t\text{-}Bu)_2$ (**1**)	43.0	73.20	1.02 (t, ^3J = 7.8 Hz, CH_3) 1.51 (q, ^3J = 7.8 Hz, CH_2)	1.34 (d, ^3J_P = 11.8 Hz)	9.42 (s, CH_3) 19.8 (br, CH_2)	34.73 (d, $^1J_{P-C}$ = 6.02 Hz, CMe_3) 33.87 (d, $^2J_{P-C}$ = 8.47 Hz, CH_3)
$[Me_2BP(t\text{-}Bu)_2]_2$ (**2a**)	27.6 (26.4)[a]	−3.99 (t, ^3J_P = 38 Hz)	0.73 (t, ^3J_P = 12.2 Hz)	1.40 (vt,[b] 5.4 Hz)	15.8 (br)	38.91 (vt,[b] 10.06 Hz, CMe_3) 33.57 (s, CH_3)
$Me_2BP(t\text{-}Bu)_2$ (**2b**)	51.6	84.44	1.14 (s)	1.35 (d, ^3J_P = 11.9 Hz)	18.2 (br)	34.57 (d, $^1J_{P-C}$ = 7.95 Hz, CMe_3) 33.91 (d, $^2J_{P-C}$ = 9.36 Hz, CH_3)
$[Me_2BP(SiMe_3)_2]_2$ (**3a**)	−148.1 (−149)[a]	−6.94	0.76 (t, ^3J_P = 14.9 Hz)	0.39 (vt,[b] 1.7 Hz)		
$Me_2BP(SiMe_3)_2$ (**3b**)	−142.5	85.88	1.01 (s)	0.32 (d, ^3J_P = 5.0 Hz)		
$[Et_2BP(SiMe_3)_2]_2$ (**4a**)	−162.3	−0.15	1.08 (t, ^3J = 6.7 Hz, CH_3) 1.16 (m, CH_2)	0.43 (vt,[b] 3.8 Hz)		
$Et_2BP(SiMe_3)_2$ (**4b**)	−143.3	85.87	1.01 (t, ^3J = 7.7 Hz, CH_3) 1.49 (q, ^3J = 6.6 Hz, CH_2)	0.34 (d, ^3J_P = 4.9 Hz)		

[a] Solid-state CP-MAS spectrum. [b] Virtual triplet, value given for $^3J_P + {}^5J_P$.

with one- and two-bond coupling to a single phosphorus atom in a monomeric compound. As in the ^1H spectrum, no coupling of the ethyl carbons to the phosphorus is observed through the three-coordinate boron atom. The ^{13}C signal for the methylene carbon attached to boron was very weak and broad, requiring a heteronuclear multiple quantum coherence (HMQC) NMR technique[8] for unambiguous identification.

The chemical shift of the ^{11}B resonance is very sensitive to the coordination number and, therefore, the best NMR probe to determine if the phosphinoborane compounds are monomeric in solution. The ^{11}B and ^{31}P NMR chemical shifts of **1** at 73.2 and 43.0 ppm, respectively, compare well with the reported values of 87.9 and 53.05 ppm for $(t\text{-}Bu)_2BP(t\text{-}Bu)_2$. These values are in the range expected for a monomeric compound, whereas a large upfield shift of both the ^{11}B and ^{31}P signals would be expected for four-coordinate centers in an oligomeric compound. Indeed, all NMR spectra of **1** are consistent with only the presence of a monomeric species in solution. On the basis of physical properties, including the higher vapor pressure of **1** compared to that of similar dimeric compounds (vide infra), we believe that the compound is also monomeric as a neat liquid.

Monomer–Dimer Equilibria. Decreasing the size of the boron substituents from ethyl to methyl allows the sterically less hindered compound to form a stable dimer. Thus, a colorless dimeric solid, bis[dimethyl(di-*tert*-butylphosphino)borane] (**2a**), was isolated from reaction of dimethylboron bromide with $(t\text{-}Bu)_2PLi$ in benzene (eq 2).

$$Me_2BBr + (t\text{-}Bu)_2PLi \rightarrow {}^1/_2[Me_2BP(t\text{-}Bu)_2]_2 + LiBr \quad (2)$$
$$\mathbf{2a}$$

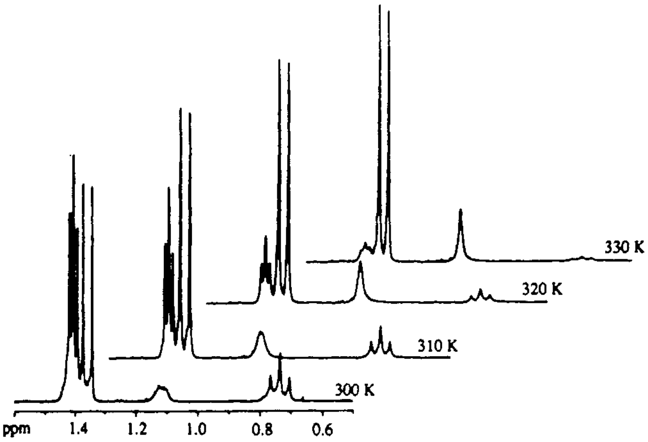
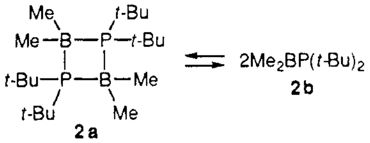


Figure 2. Variable-temperature ^1H NMR spectra of **2a** and **2b**.

In contrast to solutions of **1**, the ^1H NMR spectrum of **2a** in toluene-d_8 or benzene-d_6 is strikingly temperature and concentration-dependent (Figure 2). Two separate signals for the methyl protons and two sets of signals for the *t*-Bu protons were observed. This is consistent with of the presence of both a dimeric species (**2a**) and a monomeric species (**2b**) in solution with a very slow exchange rate occurring on the ^1H NMR time scale (eq 3).



2a ⇌ $2Me_2BP(t\text{-}Bu)_2$ **2b** (3)

The virtual triplet at 1.40 ppm in the ^1H NMR spectrum at 310 K (Figure 2) is assigned to the *t*-Bu protons in **2a** coupled to two phosphorus atoms which are chemically but not magnetically equivalent. The methyl resonance of **2a** at 0.73 ppm is split into a triplet by coupling to two equivalent phosphorus atoms in the symmetrical dimer. The remaining doublet at 1.35 ppm and singlet at 1.14 ppm in the spectrum are attributed to the monomeric species **2b**. Three-bond coupling of the *t*-Bu protons in **2b** to a single phosphorus atom produces a doublet, and the methyl signal appears as a singlet with no coupling through the three-coordinate boron to the phosphorus atom. Only a slight temperature dependence of the chemical shifts for the methyl (Figure 1) and *t*-Bu signals for **2a** and **2b** was observed. However, the relative intensities of the signals attributed to the monomeric species **2b** increase upon increasing the temperature (Figure 2) or decreasing the concentration, reflecting a shift in the equilibrium of eq 3.

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(8) Bax, A.; Subramanian, S. *J. Magn. Reson.* **1968**, *67*, 565.

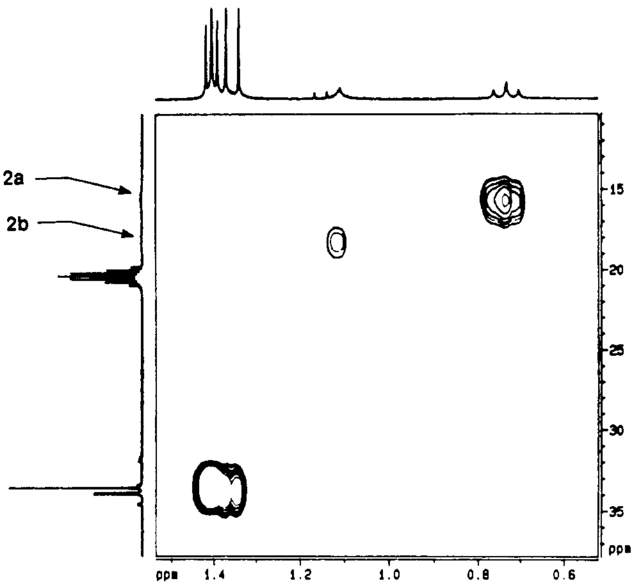

Figure 3. HMQC spectrum of **2a** and **2b** used to assign chemical shifts of carbon atoms α to the boron atom. Proton–carbon one-bond correlations are depicted.

The chemical shifts for the ^{13}C spectra of **2a** and **2b** are compiled in Table II. Assignments were made using a proton–carbon correlated HMQC NMR technique (Figure 3), which was essential in locating the resonance for carbons α to the boron atoms in **1**, **2a**, and **2b**. Note the very broad and weak peaks at 15.8 and 18.2 ppm in the ^{13}C spectrum shown in Figure 3. These could only be located and assigned to the methyl carbons in **2a** and **2b**, respectively, using this technique.

Two signals whose relative intensity was temperature-dependent were present in the ^{31}P spectrum of the compound, again indicative of an equilibrium between two species in solution. The monomer and dimer ^{31}P peak assignments were made by recording the spectrum at two temperatures and assigning the signal that increased in relative intensity at lower temperature to the dimer. The ^{31}P resonance for the monomer **2b**, at 51.6 ppm, is slightly upfield of the reported shift for $(t\text{-Bu})_2BP(t\text{-Bu})_2$ at 53.05 ppm and $Mes_2BP(t\text{-Bu})_2$ at 80.1 ppm.[9] As expected of a four-coordinate phosphorus center, the ^{31}P signal for the dimeric species **2a** at 27.6 ppm appears upfield of the three-coordinate monomer **2b**.

The ^{11}B signal of **2b** is a broad singlet at 84.44 ppm, in the range expected for three-coordinate boron. A large upfield shift is observed for the four-coordinate boron in the dimeric species **2a**, and coupling to both phosphorus atoms produces a broad triplet at −3.99 ppm. For comparison, Karsch et al. reported the ^{11}B shift of the $(t\text{-Bu})_2BP(t\text{-Bu})_2$ monomer at 87.9 ppm and the $[i\text{-Bu}(H)BP(t\text{-Bu})_2]_2$ dimer at −19.2 ppm.

X-ray Structure of $[Me_2BP(t\text{-Bu})_2]_2$. An X-ray diffraction study revealed that $[Me_2BP(t\text{-Bu})_2]_2$ (**2a**) is a centrosymmetric dimer in the solid state. The refinement data and atomic coordinates are listed in Tables I and III. A view of the molecule is shown in Figure 4, and bond lengths and selected angles are given in Table IV.

Table III. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3)

	x	*y*	*z*	*U*(eq)[a]
P	−193(1)	1225(1)	8603(1)	34(1)
C(1)	−1402(4)	2691(3)	11566(3)	56(1)
C(2)	1992(4)	1384(3)	10915(3)	54(1)
C(11)	−2368(3)	2988(3)	7854(3)	51(1)
C(12)	−3950(3)	2931(4)	8963(4)	65(1)
C(13)	−2434(5)	4779(4)	7684(6)	115(2)
C(14)	−2694(5)	2773(6)	6401(4)	120(3)
C(21)	1673(3)	1426(4)	7113(3)	49(1)
C(22)	3480(4)	65(5)	7569(4)	80(2)
C(23)	1800(5)	3153(5)	6946(6)	108(2)
C(24)	1472(5)	1211(7)	5612(4)	127(3)
B	175(4)	1228(3)	10751(3)	39(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

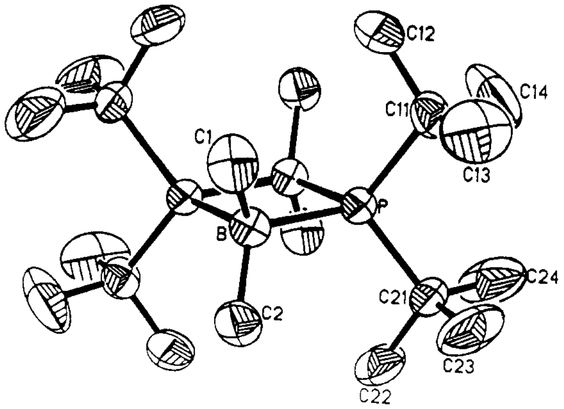

Figure 4. ORTEP diagram of $[Me_2BP(t\text{-Bu})_2]_2$ (**2a**).

Table IV. Selected Bond Distances (Å) and Angles (deg)

P–B	2.082(3)	C(21)–C(23)	1.537(6)
B–	2.081(3)	C(11)–C(13)	1.520(5)
P–	2.081(3)	C(21)–C(22)	1.522(4)
P–C(21)	1.916(3)	C(21)–C(24)	1.507(6)
P–C(11)	1.918(2)	C(1)–B	1.620(4)
C(11)–C(12)	1.520(4)	C(2)–B	1.623(5)
C(11)–C(14)	1.512(6)		
P–B–P	87.8(1)	C(12)–C(11)–C(13)	105.8(3)
B–P–B	92.2(1)	C(13)–C(11)–C(14)	109.4(3)
C(1)–B–C(2)	105.0(3)	C(12)–C(11)–C(14)	106.4(3)
C(11)–P–C(21)	105.9(1)	P–C(11)–C(14)	112.4(2)
C(21)–P–B	114.6(1)	P–B–C(1)	116.2(2)
P–C(11)–C(12)	110.3(2)	P–B–C(2)	115.6(2)
P–C(11)–C(13)	112.2(3)		

A noteworthy feature of the structure is the planar B_2P_2 ring with B–P distances of 2.082 Å, which is longer than the typical range of 1.94–2.0 Å found for the boron–phosphorus distances in such compounds.[1] This is the result of significant steric repulsion between the substituents in the dimer **2a** and is consistent with the observed dissociation of the compound in solution.

Dialkyl(bis(trimethylsilyl)phosphino)boranes. Analogs of **1** and **2a** with trimethylsilyl substituents on the phosphorus in place of the *t*-Bu groups were prepared using the trimethylsilyl halide elimination reaction[10] shown in eq 4. The purpose was to examine the effect of the trimethylsilyl group on the relative stability of the monomeric compounds.

$$R_2BX + P(SiMe_3)_3 \rightarrow$$

$$\tfrac{1}{2}[R_2BP(SiMe_3)_2]_2 + Me_3SiX \quad (4)$$

3a: R = Me, X = Br
4a: R = Et, X = Cl

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(9) Pestana, D. C.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 8426.

(10) Nöth, V. H.; Schrägle, W. *Z. Naturforsch.* **1961**, *16B*, 473.

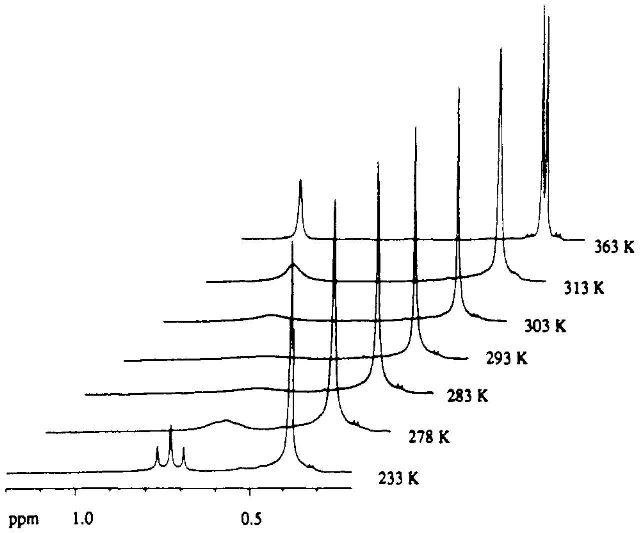

Figure 5. Variable-temperature ^1H NMR spectra of **3a** and **3b**.

Both **3a** and **4a** were isolated as colorless dimeric solids. The reaction of Me_2BBr occurred spontaneously at room temperature and was slightly exothermic. The reaction of Et_2BCl required heating, and the rate was very concentration dependent.

The NMR spectra of solutions of **3a** and **4a** are extremely temperature dependent and, like that of **2a**, characteristic of a monomer to dimer exchange process. Only resonances for the dimeric compound are observed in the ^1H NMR spectrum of **3a** at 233 K (Figure 5). The spectrum consists of a triplet for the methyl protons and a virtual triplet for the trimethylsilyl protons where both groups are coupled to two phosphorus atoms in a symmetrical dimer. Over the temperature range 300–325 K only two singlet signals were observed in the ^1H spectrum whose chemical shifts were temperature dependent. These spectra are consistent with an intermediate to fast exchange process on the ^1H NMR time scale occurring between **3a** and **3b** above 223 K. Above the coalescence temperature of 293 K, the observed signals are an average of the resonances of the monomer **3a** and the dimer **3b**. The observed chemical shift for the methyl groups above 293 K was used to calculate the equilibrium constant in the variable-temperature study below. The lifetime of the monomer is greater than that for the dimer at and above 325 K, and a doublet is observed for the trimethylsilyl group coupled to a single phosphorus atom.

The ^1H NMR spectra of **4a** show temperature effects similar to those of **3a** described above. At 260 K the spectrum consists of a virtual triplet for the trimethylsilyl groups and a triplet and multiplet for the ethyl substituents. At 340 K a doublet is observed for the trimethylsilyl groups and a normal triplet and quartet for the ethyl groups. In the intermediate-temperature spectra, the trimethylsilyl groups are a singlet and the ethyl groups are a broad multiplet with the methylene signal broader and more temperature dependent than the methyl resonance.

The ^{13}C spectra for **3a** and **3b** and for **4a** and **4b** were not resolved due to intermediate to fast exchange on the ^{13}C NMR time scale. Two ^{31}P signals were present in spectra of **3a**, and of **4a**, again indicative of two species in solution for all compounds prepared herein except 1. The trimethylsilyl substituents shift the ^{31}P signals approximately 100 ppm upflield of those for the *t*-Bu compounds, yet the three-coordinate monomeric compounds **3b** and **4b** still appear downfield of the four-coordinate dimeric species **3a** and **4a**.

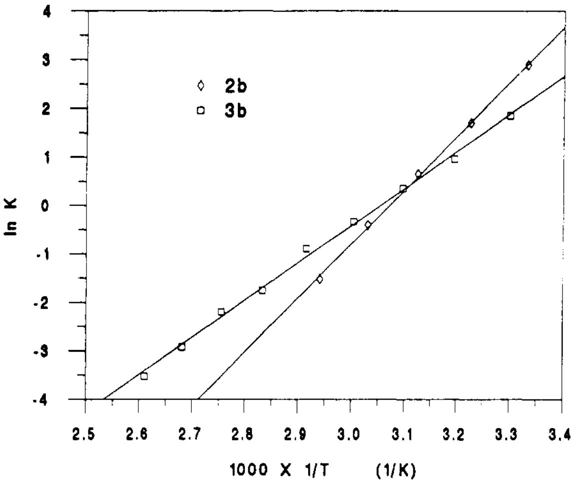

Figure 6. Plot of ln *K* versus 1/*T* for the dimerization of **2b** and **3b**.

The ^{11}B NMR spectrum of **3a** was obtained at 340 and 223 K. The spectrum at 340 K exhibited only one broad signal at 85.9 ppm, as expected for three-coordinate boron in the monomer **3b**. In the spectrum at 223 K a 93 ppm upfield shift to −7.0 ppm was observed for the four-coordinate boron in the dimeric compound **3a**. Two signals appeared in the ^{11}B spectrum of **4a** at 300 K, one at −0.15 ppm assigned to the dimer **4a** and a second resonance at 85.9 ppm from the monomer **4b**.

Solid-State ^{31}P NMR. A single resonance was observed in the solid-state ^{31}P CP-MAS spectrum of **2a** at 26.4 ppm and of **3a** at −149 ppm, both within approximately 1 ppm of the signal observed for the dimeric species in solution. This clearly establishes that the dimer-to-monomer equilibrium is a solution phenomenon and only the dimeric species exist in the solid. This also suggests that the dimeric species have the same structure in solution and in the solid state.

Exchange Process. Variable-temperature ^1H NMR experiments were carried out for toluene-d_8 solutions of **2a** and **2b** and of **3a** and **3b** to determine the equilibrium constants for the dimerization reaction (eq 5) and their temperature dependence.

$$\underset{\textbf{2a, 3a}}{2\,Me_2BPR_2} \rightleftarrows \underset{\textbf{2b, 3b}}{(Me_2BPR_2)_2} \qquad (5)$$

2a,b: R = *t*-Bu
3a,b: R = trimethylsilyl

The values for ΔH and ΔS for the dimerization of **2b** and **3b** were obtained from plots of ln *K* versus 1/*T* (Figure 6) according to the relationship $\ln K = -\Delta H/RT + \Delta S/R$. The result for the *t*-Bu-substituted compound **2b** is $\Delta H = -9.3$ kJ/mol and $\Delta S = -285$ J/(mol·K) and for the trimethylsilyl-substituted compound **3b** is $\Delta H = -55 \pm 12$ kJ/mol and $\Delta S = -166 \pm 42$ J/(mol·K). The uncertainty in the calculation of ΔH and ΔS is larger for the trimethylsilyl compounds since it was not possible to directly determine the temperature dependence of the chemical shift for the methyl resonance of **3b** directly from the ^1H NMR data.

There are offsetting electronic and steric influences to consider when comparing the $(t\text{-Bu})_2P$ and $(Me_3Si)_2P$ moieties in these examples. In general, electronic effects of the trimethylsilyl group on phosphorus are expected to favor formation of monomeric compounds. The trimethylsilyl substituents increase the electron density and lower the inversion barrier at phosphorus, effects which stabilize the multiply bonded monomer. A significant lowering of the inversion barrier has been reported for silylsubstituted phosphines,[11] and it is expected that the same effect would occur in the silyl-substituted phosphinoborane compounds. X-ray diffraction studies of silyl-substituted phosphinoboranes[9] indicate a greater degree of multiple boron–phosphorus bond character, which was attributed in part to the more electropositive nature of silicon and the lower barrier to trigonal-planar phosphorus required in the multiply bonded monomer. The value of ΔH found for the dimerization of **3b** is approximately 40 kJ/mol lower than that for **2b**, which can be attributed primarily to electronic effects of the trimethylsilyl substituents that stabilize the monomeric species.

More than offsetting this is the monomer destabilizing influence of the sterically less bulky trimethylsilyl group. The longer P–Si bond, typically 2.23–2.26 Å, compared to 1.8–1.9 Å for the P–C distance, reduces the steric bulk of the trimethylsilyl group.[9] This allows the trimethylsilyl-substituted monomers **3b** and **4b** to dimerize more easily than the *t*-Bu-substituted compounds **1** and **2b**. This steric effect likely accounts for the large difference in the values of ΔS found for the dimerization of **2b** and **3b**. The conclusion that the steric effect of the trimethylsilyl group is the dominant factor determining the stability of the monomers in this series of compounds is supported by the observation that **4a** is dimeric while **1** exists as a stable monomer.

Conclusions

From our results, it is clear that the thermal instability of $(t\text{-Bu})_2BP(t\text{-Bu})_2$ reported by Karsch et al. can be attributed to the facile retro-hydroboration reaction of the di-*tert*-butylborane moiety, rather than any inherent instability of tetraalkyl phosphinoborane compounds in general. The *t*-Bu substituents on phosphorus are sufficiently large to block dimerization of tetraalkyl phosphinoboranes with all but the smallest (methyl or hydride) substituted boron groups. This indicates that it should also be possible to isolate stable monomeric tetraalkyl phosphinoborane compounds using neopentyl or other alkyl substituents on boron, where β-hydride elimination is not possible or less favorable than for the *t*-Bu group. The fact that the value of ΔH measured for dimerization of **3b** is lower than that for **2b** indicates that electronic stabilizing effects are exerted on the monomer by the trimethylsilyl substituent. However, a lower kinetic stabilizing effect, due to its smaller steric bulk, allows the trimethylsilyl-substituted compounds to form more stable dimers. Comparison of the ^{31}P chemical shifts in solution and in the solid state allows us to unequivocally assign the higher field resonance to the dimeric species and demonstrates that solid-state NMR is a useful technique to probe the degree of association in neat samples of these compounds.

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Supplementary Material Available: Tables of anisotropic displacement coefficients of the non-H atoms, H atom coordinates, and isotropic displacement coefficients and unit cell packing diagrams for **2a** (7 pages). Ordering information is given on any current masthead page.

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[11] Baechler, R. D.; Mislow, K. *J. Am. Chem. Soc.* **1970**, *92*, 4758.