Formation of N-B- and P-B-Bonded BH_3 Adducts of Me_2PNMe_2

Sir:

The basicity of the nitrogen atom adjacent to phosphorus in aminophosphines has been the subject of much discussion.[1-7] The consensus is that in acyclic aminophosphines the tricoordinate nitrogen atom assumes a planar configuration with respect to its substituents and thus demonstrates diminished basicity due to enhanced $N(p\pi)-P(d\pi)$ bonding.[2,4,7,8] Previous studies have indicated that acyclic aminophosphines behave as "P-donors only" in their reactions with diborane.[9-12] On the other hand, bis(borane) adducts are known to form with aminophosphines of the type $\overline{P(OCR_2CH_2)_2N}$ (R = H, Me).[8,13,14] Here the nitrogen atom in the constrained bicyclic structure possesses a pyramidal geometry, which presumably weakens the $p\pi-d\pi$ interaction and enables nitrogen to exhibit a more basic character.[8,13,14]

We have recently shown that both As-B and N-B adducts form when $BH_3{\cdot}THF$ reacts with acyclic aminoarsines, $R_2AsNR'_2$.[15,16] We were interested in extending our study to the aminophosphines, $R_2PNR'_2$, where the $p\pi-d\pi$ interaction and resulting configurational changes may influence the relative basicities of the P and N atoms. This report describes the unequivocal formation of $Me_2P\overline{NMe_2{\cdot}BH_3}$ (**1**), $Me_2\overline{PNMe_2{\cdot}BH_3}$ (**2**), and $Me_2PNMe_2{\cdot}2BH_3$ (**3**) in the reaction of Me_2PNMe_2 with $BH_3{\cdot}THF$. These results are significant as previous workers have excluded the possibility of the nitrogen atom as an active donor site in acyclic aminophosphines.[8-10,13,14] The formation of $Me_2P\overline{NMe_2{\cdot}BH_3}$ and synthesis of $Me_2PNMe_2{\cdot}2BH_3$ are conclusive evidences that the nitrogen atom as well as the phosphorus atom in acyclic aminophosphines exhibits a definite basicity toward borane. We note a decrease of ${}^1J_{P-B}$ in going from the mono(borane) adduct **2** (68.7 Hz) to the bis(borane) adduct **3** (49.4 Hz) (see Table I). Since ${}^1J_{P-B}$ values often permit a qualitative deduction pertaining to the extent of π-bonding, these data suggest that P-N π-bonding is significantly reduced in the bis(borane) adduct.

Only a P-B-bonded compound is obtained when (bis(trimethylsilyl)amino)dimethylphosphine, $Me_2PN(SiMe_3)_2$, reacts with $BH_3{\cdot}THF$ in a 1:3 mole ratio. The formation of $Me_2\overline{PN(SiMe_3)_2{\cdot}BH_3}$ (**4**) suggests that either the lower basicity of the N atom or the steric bulkiness of the two silyl groups or a combination of both factors favors the mono(borane) adduct. The π-acceptor property of the silyl group may significantly lower the basicity on nitrogen. The nucleophilicity of the phosphorus atom in $Me_2PN(SiMe_3)_2$ has been shown in a number of addition and complexation reactions.[17,18] For example its reaction with MeI readily gives $[(Me_3Si)_2NP^+Me_3]I^-$. The similarity in J values for **2** and **4** suggests that steric crowding inhibits the reactivity of nitrogen as a nucleophile in this case.

The appropriate amount of Me_2PNMe_2 was condensed at -196 °C onto a toluene-d_8 solution of $BH_3{\cdot}THF\text{-}d_8$[15,16] in a NMR tube equipped with a greaseless stopcock. The tube was sealed, agitated at -95 °C to assure mixing of the reactants, and inserted into the precooled (-90 °C) probe of the NMR spectrometer. The ${}^{11}B$, ${}^{13}C$, and ${}^{31}P$ NMR spectral data, collected as a function of temperature, are given in Table I.

The reaction of Me_2PNMe_2 with $BH_3{\cdot}THF$ has been investigated as a function of temperature and time for mole ratios of 1:0.5 to 1:3.0. In all cases at -90 °C, only small amounts of **1** and **3** are observed initially, suggesting that the formation of **2** is kinetically favored at low temperature. When a reaction is allowed to go to completion at a given temperature (mole ratios < 1:1, temperature -50 to 25 °C), only the presence of **2** and Me_2PNMe_2 is observed. When reactions with starting mole ratios greater than 1:1 go to completion, a mixture of **2** and **3** is obtained. The relative amounts of **2** and **3** obtained are dependent upon the initial mole ratio of the starting materials.

In a reaction with a 1:2 mole ratio of $Me_2PNMe_2{:}BH_3{\cdot}THF$ the reaction mixture initially contained 5.5%, 79%, 10%, and 5.5% of **1**, **2**, **3**, and Me_2PNMe_2, respectively, at -90 °C as determined from the ${}^{31}P$ NMR spectrum. The P-B coupling constants obtained from the ${}^{31}P$ and ${}^{11}B$ NMR spectra of **2** and **3** establish P-B bonding in these adducts. As the temperature is raised, the intensities of the peaks associated with the bis(borane) adduct increase at the expense of those of unreacted Me_2PNMe_2 and the

Table I. Multinuclear NMR Data for Borane Adducts of Acyclic Aminophosphines[a]

		chem shift, ppm				coupling const, Hz	
				${}^{13}C$			
compound	temp, °C	${}^{11}B$	${}^{31}P$	Me_2P	$-{}^{*}C-N-P$	${}^1J_{P-B}$	${}^1J_{P-C}$
Me_2PNMe_2	25		39.7	14.2 (d)	39.2 (d)		18.3
$Me_2P\overline{NMe_2{\cdot}BH_3}$ (1)	-70	-15.8	83.7	12.9 (d)	46.9 (d)		25.6
$Me_2\overline{PNMe_2{\cdot}BH_3}$ (2)	25	-38.3	63.7	11.8 (d)	37.3	68.7	40.6
$Me_2PNMe_2{\cdot}2BH_3$ (3)	25	-11.8 (B-N) -40.7 (B-P)	109.4	10.3 (d)	48.0 (d)	49.4	36.3
$Me_2PN(SiMe_3)_2$	25		32.6	19.4 (d)	4.7[c]		12.8
$Me_2\overline{PN(SiMe_3)_2{\cdot}BH_3}$ (4)	25	-34.5	51.1	19.9 (d)	5.5[c]	63.4	40.8

[a] ${}^{11}B$, ${}^{31}P$, and ${}^{13}C$ NMR spectra were recorded on a Nicolet 300-MHz multinuclear FT NMR spectrometer operating at 96.3, 121.5, and 75.4 MHz, respectively. $\delta({}^{11}B)$, $\delta({}^{31}P)$, and $\delta({}^{13}C)$ were measured relative to $BF_3{\cdot}OEt_2$, 85% H_3PO_4 and Me_4Si (internal) respectively. [b] Negative δ values indicate upfield shift from $BF_3{\cdot}OEt_2$. [c] C-Si-N, $\delta({}^{29}Si)$ = 9.9 (parent $\delta({}^{29}Si)$ = 6.5, ${}^2J_{Si-P}$ = 4.7 Hz).

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N-B **1** compound. At −10 °C there is a complete disappearance of the peaks assigned to $Me_2\overline{PNMe_2}\cdot BH_3$ and Me_2PNMe_2, and only the peaks due to **2** and **3** are observed. If the reaction mixture is maintained at −60 °C for 24 h, $Me_2PNMe_2\cdot 2BH_3$ is obtained in quantitative yields. The ^{11}B NMR spectrum now contains only two resonances of equal intensity associated with B–N and B–P coordination in **3** (See Table I). The NMR assignments for **2** have been confirmed by the synthesis of **2** and a comparison with the literature values.[10]

The bis(borane) adduct has been isolated by carrying out the reaction at −10 °C in a THF/toluene solvent mixture. Trap-to-trap fractionation at −10 °C gives a white solid, $Me_2PNMe_2\cdot 2BH_3$, in 85% yield. Satisfactory elemental analyses were obtained. This compound is quite stable thermally as indicated by its melting point (117 °C) and mass spectral data. The presence of a molecular ion (*m/e* 133) and the peaks corresponding to the fragmentation of the parent aminophosphine are noted in the mass spectrum.

Further work is in progress to determine the generality of such reactions and to study the steric and electronic factors that influence the relative basicities of these donor atoms.

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Articles

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Heat Capacity and Phase Transitions of the Mixed-Valence Compound $[Fe_3O(O_2CCH_3)_6(3\text{-Me-py})_3]\cdot 3\text{-Me-py}$[1]

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The heat capacity under constant pressure, C_p, of oxo-centered mixed-valence $[Fe_3O(O_2CCH_3)_6(3\text{-Me-py})_3]\cdot 3\text{-Me-py}$ has been measured with an adiabatic calorimeter between 12 and 350 K, where 3-Me-py is 3-methylpyridine. Four phase transitions were found to occur at 181, 263.5, 271.5, and 282.5 K. The cumulative enthalpy and entropy changes due to these four phase transitions were calculated to be $\Delta_{trs}H = 3410 \pm 130$ J mol^{-1} and $\Delta_{trs}S = 13.71 \pm 0.65$ J K^{-1} mol^{-1}, respectively. By comparison of the present results with the ^{57}Fe Mössbauer spectroscopy and the X-ray structural work already done for this complex, it is concluded that these phase transitions involve at various temperatures intramolecular electron transfer in the mixed-valence Fe_3O complexes and the order–disorder phenomenon of the pyridine solvate molecules jumping between two energetically equivalent positions in the solid state. The contributions from these two phenomena to the transition entropy are $R \ln 3$ and $R \ln 2$, respectively, and the sum is 14.90 J K^{-1} mol^{-1}. This accounts well for the observed value of 13.71 ± 0.65 J K^{-1} mol^{-1}. DTA thermograms for the solid solutions of $[Fe^{III}{}_2Fe^{II}{}_{1-x}Co^{II}{}_xO(O_2CCH_3)_6(3\text{-Me-py})_3]\cdot 3\text{-Me-py}$, where $x = 0$, 0.25, 0.5, 0.75, and 1.0, have been recorded between 80 and 350 K. The highest temperature phase transition found for the $x = 0.0$ compound is linearly shifted to a lower temperature with increasing x. The concentration dependence of the transition temperature, $T_C(x)$, is described by the linear equation $T_C(x)$ (K) $= 282.54 - 13.08x$. The lowest temperature phase transition at 181 K is easily undercooled. By comparison of the molar entropies of the undercooled and nonundercooled states at a common temperature (196.8395 K in the present case), it has been concluded that the undercooled phase has no residual entropy, that is, the molecules in this phase are in an ordered state at 0 K. A model for the observed phase transitions has been devised that accounts for all of the X-ray structural, spectroscopic, and heat capacity results for $[Fe_3O(O_2CCH_3)_6(3\text{-Me-py})_3]\cdot 3\text{-Me-py}$. Below 181 K all three iron ions are inequivalent and only one vibronic state of the Fe_3O complex is populated. At 181 K the thermal energy becomes comparable to intermolecular interactions and there is a phase transition such that the potential-energy diagram of the Fe_3O complex changes. At temperatures above 181 K two vibronic states (i.e., two minima in the potential-energy diagram) are populated. Finally, in the high-temperature phase transition which culminates at 282.5 K and has two anomalies at 263.5 and 271.5 K there is an onset of motion involving the 3-Me-py solvate molecule jumping between its two lattice sites. As a result the Fe_3O complex tends to become more equilateral than it is at low temperatures and all three vibronic states of the Fe_3O complex are populated to some degree.

Introduction

A recent exciting finding is that the rate of *intra*molecular electron transfer for a mixed-valence transition-metal complex in the solid state is significantly influenced by the onset of motion of ligands, solvate molecules, and/or counterions.[5-18] In the case of oxo-centered mixed-valence $[Fe_3O(O_2CCH_3)_6(py)_3]\cdot py$ (py = pyridine), for example, the orientational order–disorder phenom-

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