Table III. Selected Interatomic Distances (Å) and Bond Angles (deg)[a]

S(1)-Pd	2.330 (1)	S(2)-Pd-S(1)	96.6 (0)
S(2)-Pd	2.328 (1)	S(3)-Pd-S(1)	82.7 (0)
S(3)···Pd	3.034 (1)	S(3)-Pd-S(2)	81.1 (0)

[a] Estimated standard deviations are given in parentheses.

Results and Discussion

The ion is square-planar (Figure 1) but shows significant axial interactions with the endodentate noncoordinated sulfur atoms. Fractional atomic coordinates and bond lengths and bond angles are given in Tables II and III. The mean Pd-S equatorial bond length is 2.329 (1) Å, longer than that found for the other isomer identified (2.27 Å)[17] but comparable with the $Pd(S_3)^{2+}$,[6,7] $Pd(18S_6)^{2+}$,[4,22] and other N_2S_4 ligand systems.[23] The axial sulfur atoms are located at 3.034 (1) Å from the metal center, considerably shorter than in isomer B (3.11 Å). The reason for the differences is provided in analysis of the spatial arrangements of the ligands. In isomer A, the sulfur atoms of the six-membered chelate ring are in the plane, while in isomer B it is the S donors of five-membered rings that are bonding. The bond distances reflect the increased binding strengths of the five-membered rings vis-a-vis the six in the boat configuration.

The equatorial bond angle S(1)-Pd-S(2) of 96.6 (0)° is larger than that in isomer B (88.8°) and also the corresponding $Pd([9]\text{-}aneS_3)^{2+}$ ion (88.63 (11)°) owing to the location of the six-membered chelate ring in the present complex. The presence of the five-membered "chelate" rings subtending the axial sites reduces the flexibility of the apical sulfur in its ability to be located in a position for coordination. This may be seen as resulting in a 12.2° angle between the normal to the PdS_4 plane and the Pd-S(3) vector, the value being somewhat larger than that in isomer B (9.9°) and $[Pd([9]\text{-}aneS_3)_2]^{2+}$ (7.80°).

Of interest is the cell packing for the complex (supplementary figure), where the Pd cations and the CH_3CN molecules lie in alternating planes, while the PF_6^- anions lie in a perpendicular plane. The position of the acetonitrile is such that the N atom is directed toward the palladium through the center of the pseudotrigonal face of a chelating ligand. As such, the solvent nitrogen may approach the Pd atom to a distance of ~6 Å. This feature has implications when considering the low-temperature ^{13}C NMR spectra. In the ^{13}C NMR spectrum at ambient temperatures a seven-line peak centered at δ 1.3 is seen due to the methyl group of the CD_3CN solvent (supplementary figure). A feature at δ 118.6 is seen due to the C atom of the nitrile. As the temperature is lowered, the solvent peaks are broadened, yielding two well-defined septets centered around δ 1.3 at -40 °C. Also two lines at δ 118.5 and 118.7 are distinctly seen from the carbon of the nitrile group. A third peak observed at δ 118.9 becomes more pronounced as the temperature is lowered due to a third type of CD_3CN molecule. The associated septet is just discernible at lower δ. Observation of three distinctive sets of solvent resonances implies that the solvent is partitioned into three magnetic environments, the first and second solvation spheres and the bulk solvent.

The Pd(II) complex is readily oxidized by NO^+ in acetonitrile to a Pd(III) ion, which $g_\parallel = 2.005$ and $g_\perp = 2.042$, characteristic of a tetragonally elongated octahedral complex ion. In addition to the reversible oxidation, there is electrochemical evidence for the formation of a Pd(I) ion under reducing conditions.

These g values compare well with those obtained for $[Pd([9]\text{-}aneS_3)_2]^{3+}$ and $[Pd([9]\text{-}aneN_3)_2]^{3+}$.[7,24] The axial S atoms in $[Pd([10]\text{-}aneS_3)_2]^{2+}$ are suitably disposed to promote octahedral stereochemistry around the d^7 metal ion. The unpaired electron occupies the d_{z^2} orbital as has been seen in the EPR spectra of other Pd(III) species.

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Supplementary Material Available: Table S1, listing experimental crystallographic data for the complex, Tables S2-S4, listing interatomic bond distances and angles, anisotropic temperature parameters, and selected intermolecular distances, Table S6, listing data on mean planes, and figures showing a diagram of the molecular packing, a ^1H NMR spectrum of the complex cation in CD_3NO_2, a ^{13}C NMR spectrum including the solvent region, and a representative ESR spectrum (17 pages); Table S5, listing calculated and observed structure factors (10 pages). Ordering information is given on any current masthead page.

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Synthesis and Solvolysis of Benzylamine-Boranes

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Introduction

The reactivity of donor base-borane addition compounds is highly sensitive to structural variations both in the donor portion of the molecule and in the coordination sphere of boron. Regarding amine-BH_3 adducts, it has been shown that solvolysis in water or mixed aqueous solvents occurs via two mechanisms, one presumed to involve rate-determining dissociative activation of the B-N bond (Scheme I) and the second involving electrophilic displacement of BH_3 through attack of the proton of a general acid at nitrogen (Scheme II).[1-8] Rates are sensitive to electronic and steric effects, and the nature of the amine largely determines whether the acid-independent or acid-dependent pathway will be dominant.[1] Substitution of one or more anionic ligands, e.g., halide, CN^-, and N_3^- for boron-bonded (hydridic) hydrogen, also has been shown to give rise to a change in hydrolysis mechanism with the reaction path dependent on the specific ligand.[9-12]

In this paper, we report the synthesis and hydrolytic reactivity of several substituted benzylamine-boranes and examine the influence of the intervening CH_2 group on effects of aryl substitution on reaction at the $\equiv N-BH_3$ site. Since the effectiveness of a donor-borane adduct as a hydridic reagent in aqueous media is dependent, in large measure, on the kinetic stability of the adduct toward hydrolytic decomposition, this study also has implications with respect to the utility of benzylamine-boranes as practical synthetic reagents.

Experimental Section

Materials. Amines, boron trifluoride-diethyl ether complex, tetrahydrofuran (THF), and *p*-dioxane were obtained from Aldrich. The $BF_3 \cdot Et_2O$ was distilled in vacuo prior to use. Sodium tetrahydridoborate was obtained from Aldrich or Morton International in 98% purity and dried in vacuo. The THF was boiled under reflux in a nitrogen atmosphere over CaH_2 for several hours and then collected by decantation and distilled from sodium and

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Scheme I

$$R_3N{\cdot}BH_3 \xrightarrow[\text{slow}]{k_1} [R_3N{\cdots}BH_3]^{\ddagger} \xrightarrow[\text{fast}]{H_2O} R_3N + B(OH)_3 + 3H_2$$

benzophenone. Dioxane was purified by refluxing with HCl to remove ketal and acetal impurities. The HCl was then neutralized with KOH and the dioxane refluxed over sodium/benzophenone and collected by distillation under N_2. Analytical reagent grade KIO_3, KI, and $Na_2S_2O_3$, used for iodometric determination of hydride in amine–borane hydrolysates, were obtained from Mallinckrodt, and Vitex Starch was obtained from GFS Chemicals.

Methods and Analyses. Elemental carbon and hydrogen analyses were performed by Schwartzkopf Microanalytical Laboratory. Melting points were taken on a Mel-Temp apparatus and are reported as uncorrected values. Ultraviolet–visible spectra were recorded on a Perkin-Elmer Model 552A spectrophotometer and infrared spectra on a Beckman IR-33 or Model 4250 spectrometer. The ^1H, ^{13}C, and ^{11}B NMR spectra were recorded in $CDCl_3$ solution on a Varian XL-300 spectrometer at 299.94, 75.43, and 96.23 MHz, respectively, using $(CH_3)_4Si$ as internal reference for ^1H and ^{13}C determinations and $BF_3{\cdot}Et_2O$ as external reference for ^{11}B spectra. Chemical shifts were reported assuming first-order spectra.

Syntheses. Amine–boranes were prepared via amine displacement of solvent from tetrahydrofuran–borane which was either obtained commercially from Aldrich or prepared in situ from $NaBH_4$ and $BF_3{\cdot}Et_2O$ by previously described methods developed at Morton International.[1,13] The specific synthesis of benzylamine–borane is described.

To a 500-mL three-neck round-bottom flask equipped with condenser, pressure-equalizing dropping funnel, and gas-inlet tube was added 5.70 g (150 mmol) of $NaBH_4$ and 50 mL of freshly purified THF. The suspension was cooled to near 0° and stirred while 2.8 mL (210 mmol) of $BF_3{\cdot}Et_2O$ was added dropwise over a 20-min period under a flow of dry N_2. A solution of 17.0 mL (155 mmol) of benzylamine in 50 mL of THF was added dropwise with continued stirring for 30 min. Sodium tetrafluoroborate was removed by filtration through a course fritted disk under N_2 and washed 3 times each with 15 mL of fresh THF. The clear filtrate was cooled and treated with hexane to induce crystallization. The solid product was collected by filtration and washed with cold hexane: yield, 8.9 g (49% theory); mp 57–58 °C. Anal. Found: C, 68.87; H, 10.31. Calcd for $C_7H_{12}NB$: C, 69.49; H, 10.00. An infrared spectrum obtained on a KBr wafer gave absorption bands due to ν_{B-H} at 2270, 2320, and 2395 cm^{-1}.

Kinetic Studies. Hydrolyses were carried out in 50% (v/v) aqueous dioxane at 25.0 °C. A weighed quantity of amine–borane was dissolved in 50 mL of dioxane in a 250-mL Erylenmeyer flask and the solution treated with 50 mL of water or aqueous HCl. Initial amine–borane concentrations were typically about 5 mM, with $[H^+]$ in the range 0.15–0.50 M. Constant ionic strength was maintained with KCl and the temperature controlled to ±0.05 °C with a Precision Scientific water bath. The concentration of amine–borane was determined at various times by a previously described iodometric procedure.[14] Some hydrolyses were carried out under pseudo-first-order conditions in excess $[H^+]$ and others in neutral dioxane–water solutions. Acid-independent and -dependent rate constants (k_1 and k_2) were obtained, respectively, from intercepts and slopes of lines arising from plots of pseudo-first-order rate constants vs $[H^+]$. In some cases, k_1 was obtained directly from rate studies in neutral aqueous dioxane. Temperature-dependent rate studies were carried out in the range 11.5–32.7 °C, circulating ice-water being used to obtain lower than ambient bath temperatures.

Results and Discussion

Solvolysis of benzyl- and substituted benzylamine–boranes proceeds via parallel reactions as previously described for the BH_3 adducts of substituted anilines[1] and quinolines[7] and as depicted in

Scheme II

$$R_3N{\cdot}BH_3 + HA \xrightarrow[\text{slow}]{k_2} \left[R_3N \begin{matrix} H{\cdot}{\cdot}A \\ BH_3 \end{matrix} \right]^{\ddagger} \xrightarrow[\text{fast}]{H_2O} R_3NH^+ + A^- + B(OH)_3 + 3H_2$$

$$-d[AB]/dt = [AB]\,(k_1 + k_2[H^+]) \qquad (1)$$

where AB denotes amine–borane. As seen in Table I, k_1 terms are smaller by factors of 10^2 to 10^4 than those for corresponding substituted aniline– and quinoline–boranes. This is undoubtedly the result of effective insulation by the methylene group of the electron-withdrawing effect of the aromatic ring system which otherwise tends to stabilize a transition-state configuration for dissociative activation of the B–N bond with accompanying dissipation of the $-^{\delta}B-N^{+\delta}-$ dipole (Scheme I). Nevertheless, the k_1 terms significantly exceed those observed for the hydrolysis of alkyl and nonaromatic heterocyclic amine–boranes in which reaction occurs virtually exclusively by the acid-dependent pathway.[1,2]

The effect of methoxy substitution is particularly noted. In aromatic systems, methoxy substituents are electron withdrawing by induction and electron donating by resonance with the resonance interaction usually dominating as reflected in the sign of the Hammett sigma parameters, $\sigma_{p\text{-}OCH_3} = -0.27$, $\sigma_{m\text{-}OCH_3} = +0.12$.[15] Such influences are displayed in aniline–borane hydrolysis where *p*-methoxy substitution results in retardation of the acid-independent rate (k_1) and enhancement of the acid-dependent reaction (k_2) where a full positive charge on nitrogen is being developed in the corresponding activated complex.[1] In benzylamine–borane, the $-CH_2$ spacer negates resonance effects of the 2- and 4-methoxy substituents. Consequently, only the inductive effect is seen and a measurable *increase* in k_1 occurs on methoxy substitution at either the 2, 3, or 4 position.

In terms of steric interactions, the intervening methylene may to a small degree also spatially insulate the 2-methoxy group from the reactive $N-BH_3$ function. In the aniline–borane series, an enhancement of k_1 with N-alkyl substitution is attributed to relief of steric strain in a transition state involving conversion of nitrogen from four to three coordination.[1] Here, similar relative effects are found in the transition from benzyl– to *N*-methylbenzyl– to *N,N*-dimethylbenzylamine–borane (1/1.5/6).

Not surprisingly, ring substitution in the benzylamine–boranes has a negligible effect on k_2. A change in the nature and position of a ring substituent in an aniline–borane has been shown to produce less of an effect on k_2 than on the k_1 term presumably because the transition from the $^{+\delta}N-B^{-\delta}$ dipole to a fully charged ammonium ion represents less change in polarity than dipole dissipation through dissociative activation. In the benzylamine–boranes, insertion of the methylene group appears to have essentially negated electronic ring substituent effects on the acid-dependent hydrolysis pathway. Trends in the k_2 term with N-alkyl substitution are probably due to effects of steric inhibition of cis attack by hydrogen ion. The effect here ($RNH_2BH_3/RNH(CH_3)BH_3/RN(CH_3)_2BH_3 \sim 3700/25/1$) is far more dramatic than that observed for the acid-independent reaction.

The temperature dependence of k_2 for benzylamine–borane is shown in Table II. Activation parameters ($\Delta H = 20.6$ kcal/mol; $\Delta S = 0.9$ eu) are similar to those previously reported for *p*-toluidine–borane solvolysis in 50% aqueous dioxane ($\Delta H = 21.7$ kcal/mol; $\Delta S = 0.6$ eu).

The increase in kinetic hydrolytic stability of benzylamine–boranes over the corresponding substituted aromatic amine adducts may signal their utility as hydridic reagents in aqueous organic solvent mixtures, and, in this regard, studies of benzylamine–borane reactivity toward oxyhalides and related substrates are

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Table I. Hydrolysis of Selected Amine–Boranes in 50% Aqueous Dioxane at 25.0 °C and I = 0.50 M

amine–borane	10^5k_1 (s^{-1})[a]	10^3k_2 (M^{-1} s^{-1})[a]
benzyl–	2.2	8.27
N-methylbenzyl–	3.5	0.328
N,*N*-dimethylbenzyl–	13	0.00224
2-methoxybenzyl–	8.6	11.3
3-methoxybenzyl–	4.9	9.13
4-methoxybenzyl–	15	
4-methylbenzyl–		10.7
4-chlorobenzyl–		7.82
aniline–[b]	1.9×10^4 [c]	1.74
4-methylaniline–[b]	8.3×10^3 [c]	2.71
4-methoxyaniline–[b]	4.7×10^3 [c]	3.02
quinoline–[d]	5.4×10^2 [c]	0.26
4-methylquinoline–[d]	2.8×10^2 [c]	0.74
isoquinoline–[d]	4.6×10^1 [c]	1.56

[a] $-d[AB]/dt = [AB](k_1 + k_2[H^+])$, AB = amine–borane. [b] Reference 1. [c] $I \simeq 0$. [d] Reference 7.

Table II. Temperature Dependence of Rate of Hydrolysis of Benzylamine–Borane in 50% Aqueous Dioxane

t (°C)	[HCl] (M)	10^3k_{obs}[a] (s^{-1})	10^3k_2[b] (M^{-1} s^{-1})
11.50	0.126	0.198	1.57
15.00	0.151	0.361	2.39
25.05	0.108	1.03	9.57
30.10	0.101	1.68	16.6
32.70	0.102	1.88	18.4

$\Delta H^\ddagger$ = 20.6 kcal/mol; $\Delta S^\ddagger$ = 0.912 cal/(mol K)

[a] From eq 1 where $k_{obs} = k_1 + k_2[H^+]$. [b] $k_2[H^+] \gg k_1$; thus $k_2 \simeq k_{obs}/[H^+]$.

being conducted. This is prompted, in part, by the fact that amine structure has been shown to influence the stoichiometry of reaction of amine–boranes with HOCl leading in some instances to hydride oxidation and in others to B-chlorination.[16,17]

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Supplementary Material Available: Details of preparative yields, analyses, and NMR spectral data (5 pages). Ordering information is given on any current masthead page.

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Comments on the Synthesis of Trisulfonated Triphenylphosphine: Reaction Monitoring by NMR Spectroscopy

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Introduction

There is widespread interest in the coordination chemistry of trisulfonated triphenylphosphine, TPPTS, owing to its utility in the hydroformylation reaction.[1-4] While the synthesis of TPPTS is straightforward, the reported workup procedures are cumbersome. Recently it has been shown that a complex mixture from a synthesis that contains 30% TPPTS and as many as four additional components can be separated by gel permeation chromatography.[5] As further noted by Herrmann et al.[5] analytical data not only for TPPTS itself but for complexes of TPPTS are remarkably sketchy; it appears to be the case that many compounds reported to be TPPTS derivatives most likely contain a mixture of mono-, di-, and trisulfonated triphenylphosphine. Sinou and Bakos et al.[6] have also shown that chromatography can be used to separate mono-, di-, tri-, and tetrasulfonated chiral diphosphines.[3] Kuntz reports that the synthesis of TPPTS yields a crude mixture that contains approximately 80% TPPTS and 20% TPPTS oxide after 20 h at 30 °C.[1] (We find that the reaction mixture contains significant disulfonated product after 30 h at 22 °C, vide infra.) Kuntz showed further that workup with butyl phosphate eliminates sodium sulfate and that formation of the barium salt yielded TPPTS in greater than 95% purity.[1] Although ^1H NMR data, in addition to ^{13}C and ^{31}P NMR data, are mentioned in several cases in the literature for TPPTS, nowhere does a detailed list of chemical shift data appear. Extensive ^{31}P NMR data are available for rhodium complexes of TPPTS,[7] and a reproduction of the ^1H NMR spectrum of TPPTS is reported in a dissertation; however, chemical shifts and coupling constants are not given.[8]

The ^1H NMR spectrum, in fact, is very sensitive to the extent of the sulfonation. Here we report the ^1H, ^{13}C, and ^{31}P NMR spectra of TPPTS and TPPTS oxide and give a detailed procedure for their use to monitor the extent of sulfonation of triphenylphosphine. Additionally the mass spectra for TPPTS and TPPTS oxide, recorded using fast atom bombardment, are reported.

Experimental Section

All manipulations were performed under nitrogen by standard Schlenk techniques. Fuming sulfuric acid was obtained from Aldrich. Triphenylphosphine was purchased from either Aldrich or Strem Chemical Co. and used without further purification. NMR solvents, methanol-d_4, THF-d_8, and D_2O were obtained from Aldrich.

Routine NMR measurements were done on a Bruker 200-MHz spectrometer, at an observation frequency of 200.133 MHz for ^1H and 81.015 MHz for ^{31}P. High-field ^1H, ^{13}C, and ^{31}P NMR data were obtained on a Varian RU400 NMR spectrometer at 399.052, 100.577, and 161.903 MHz, respectively. The FAB mass spectra[9] were recorded on a VG 7070E-HF spectrometer. The samples were vaporized and ionized with 8-kV Ar atoms from a glycerol matrix. The accelerating voltage was 4 kV, and the spectrum was scanned from 50 to 750 amu. Summaries of the fragmentation patterns for TPPTS and TPPTS oxide are given in Tables I and II.

Sufonation of Triphenylphosphine (TPP). With minor changes the procedure reported by Kuntz was followed for the sulfonation of TPP.[1] A 10-g sample of TPP was added slowly to 100 mL of 20% fuming sulfuric acid at 0 °C.; efficient cooling is necessary to prevent local overheating. The mixture was allowed to reach room temperature (22 °C) and the reaction continued for up to ca. 150 h to give complete sulfonation.

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