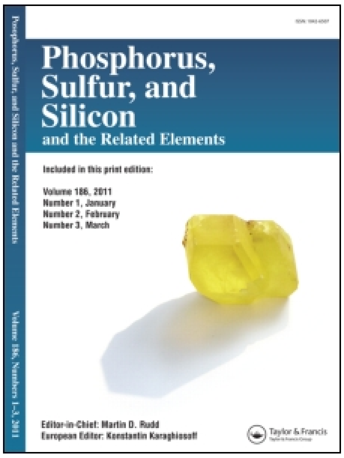
This article was downloaded by:
On: *29 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS AND CHARACTERIZATION OF THE FIRST BORANE ADDUCTS AND BORON CATIONS OF SOME N-ALKYL AND N-AMINOTRIPHENYLPHOSPHORANIMINES

William K. Holley[a]; George E. Ryschkewitsch[a]
[a] Department of Chemistry, University of Florida, Gainesville, FL, U.S.A.

To cite this Article Holley, William K. and Ryschkewitsch, George E.(1990) 'SYNTHESIS AND CHARACTERIZATION OF THE FIRST BORANE ADDUCTS AND BORON CATIONS OF SOME N-ALKYL AND N-AMINOTRIPHENYLPHOSPHORANIMINES', Phosphorus, Sulfur, and Silicon and the Related Elements, 53: 1, 271 — 284
To link to this Article: DOI: 10.1080/10426509008038036
URL: http://dx.doi.org/10.1080/10426509008038036

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus, Sulfur, and Silicon, 1990, Vol. 53, pp. 271-284
© 1990 Gordon and Breach Science Publishers S.A.
Reprints available directly from the publisher
Printed in the United Kingdom
Photocopying permitted by license only

SYNTHESIS AND CHARACTERIZATION OF THE FIRST BORANE ADDUCTS AND BORON CATIONS OF SOME *N*-ALKYL AND *N*-AMINOTRIPHENYLPHOSPHORANIMINES

WILLIAM K. HOLLEY† and GEORGE E. RYSCHKEWITSCH
Department of Chemistry, University of Florida, Gainesville, FL 32610 (U.S.A.)

(Received January 19, 1990)

The first borane adducts of *N*-alkyl and *N*-aminotriphenylphosphoranimines, $Ph_3P{=}N{-}R$, were prepared by two different general synthetic methods. The first method involved displacement of THF (tetrahydofuran) from THF-borane by the free imines, and the second employed the reaction of $LiBH_4$ with iminium bromides, $Ph_3P{=}N(R)HBr$, in diethyl ether. Imine boranes, $Ph_3P{=}N(R)BH_3$, were synthesized where R = methyl, ethyl, *n*-propyl, isopropyl, isobutyl, t-butyl, dimethylamino, phenylamino, and methyl, phenylamino as the nitrogen attached groups. Symmetrical boron cations, $(Ph_3P{=}NR)_2BH_2^+$, where R = methyl, ethyl, and *n*-propyl, were synthesized by displacement of iodide from in-situ generated iodoborane adducts, $Ph_3P{=}N(R)BH_2I$, by the free imines. An attempt to form an unsymmetrical boron cation from $(CH_3)_3NBH_2I$ and $Ph_3P{=}N(n\text{-}C_3H_7)$ resulted only in a mixture of the corresponding symmetrical boron cations. Physical, chemical and spectral properties of the borane adducts and boron cations, namely thermal and hydrolytic stabilities, infrared and NMR data are presented. Oxidative and reductive stabilities of the boron cations were studied. The borane adducts can be chlorinated with either HCl or Ph_3CCl. Relative base strengths of some imines were determined by following the exchange of BH_3 between borane adducts of $(CH_3)_3N$ or $4\text{-}(CH_3)C_5H_4N$ and the imines via NMR.

Key words: Phosphoranimine, borane, synthesis, characterization, boron, cation.

Downloaded At: 16:51 29 January 2011

INTRODUCTION

Triphenylphosphoranimines, $Ph_3P{=}N{-}R$, represent an important class of reactive intermediates in organic synthesis. A number of such compounds, with different groups attached to the nitrogen, have been synthesized by others using different methods.[1-6] Although several BF_3 adducts of triphenylphosphoranimines have been reported,[7,8] the only BH_3 adduct mentioned is that of $Ph_3P{=}NH$.[7] We report here the synthesis and characterization of the first BH_3 adducts of triphenylphosphoranimines having *N*-alkyl or *N*-amino groups. The syntheses were accomplished by two different general synthetic methods both applied to the *N*-alkyl and *N*-amino substituted imines. The first method involved displacement of THF (tetrahydrofuran) from THF-borane by the free imines (Equation (1)).[9,10]

$$Ph_3P{=}N{-}R + (THF)BH_3 \Rightarrow Ph_3P{=}N(R)BH_3 + THF \qquad (1)$$

where R = CH_3, C_2H_5, $n\text{-}C_3H_7$, $i\text{-}C_3H_7$, $i\text{-}C_4H_9$, $t\text{-}C_4H_9$, $N(CH_3)_2$, N(H)Ph $N(CH_3)Ph$.

---

† Author to whom all correspondence should be addressed.

The second method utilized the reaction of iminium bromides with ethereal solutions of $LiBH_4$ (Equation (2)).[11]

$$Ph_3P{=}N(R)HBr + LiBH_4 \Rightarrow Ph_3P{=}N(R)BH_3 + LiBr + H_2 \qquad (2)$$

where $R = CH_3$, $N(CH_3)_2$. Investigation of some chemical properties of the borane adducts led to the first reaction between a borane adduct and Ph_3CCl which gave the monochloroborane adduct, $Ph_3P{=}N(CH_3)BH_2Cl$.

In order to compare the chemistry of these adducts with amine boranes, we report here the synthesis of symmetrical boron cations of the type $(Ph_3P{=}NR)_2BH_2^+$. Boron cations have been easily prepared by displacement of iodide from amine iodoboranes by neutral bases.[12-16] Thus, the synthesis of our symmetrical boron cations was accomplished by reaction of in-situ generated imine iodoboranes with the corresponding imines (Equations (3) and (4)).

$$2Ph_3P{=}N(R)BH_3 + I_2 \Rightarrow 2Ph_3P{=}N(R)BH_2I + H_2 \qquad (3)$$

$$Ph_3P{=}N(R)BH_2I + Ph_3P{=}NR \Rightarrow (Ph_3P{=}NR)_2BH_2^+I^- \qquad (4)$$

where $R = CH_3$, C_2H_5, n-C_3H_7. We also report the attempted synthesis of an unsymmetrical boron cation by reaction of $(CH_3)_3NBH_2I$ with $Ph_3P{=}N(n\text{-}C_3H_7)$.

The borane adducts and boron cations were characterized by elemental analysis, and by their NMR and IR spectra. We report reactivities of our cations toward Ag^+, BH_4^-, anhydrous and aqueous HCl, NaOH, and neutral water and compare results with reactivities of bis(amine) boron cations.

Phosphoranimines have been shown to be basic materials.[1,2,5,7,8,17-19] We report relative basicities of *N*-alkyltriphenylphosphoranimines toward BH_3 by measuring the extent of exchange of BH_3[20] between the imines and borane adducts of $(CH_3)_3N$ and $4\text{-}(CH_3)C_5H_4N$ (4-picoline) via NMR data. Information on the ^1H and ^{31}P NMR spectra of triphenylphosphoranimines is scant.[4,21]. Therefore, we report NMR spectra on all the imines used and discuss spectral trends upon BH_3 and BH_2^+ complexation.

Downloaded At: 16:51 29 January 2011

EXPERIMENTAL

General Comments

Borane-THF complex was obtained from Aldrich Chemical Company and was used without further purification. Trimethylamine borane was purchased from Callery Chemical Company, and 4-picoline borane was synthesized from 4-picoline and THF-borane. Both were sublimed prior to use. Lithium borohydride was obtained from Metal Hydrides, Inc. Amines and 4-picoline were purchased from various commercial sources and were distilled prior to use. Trimethylamine iodoborane was prepared by the published procedure[22] and sublimed prior to use. Tetra(n-butyl)-ammonium borohydride was purchased from Aldrich Chemical Company and was recrystallized from ethyl acetate. Imines were prepared by dehydrobromination of the corresponding iminium bromides by sodamide in liquid NH_3[3,4] and were recrystallized from heptane or heptane-THF. The synthesis of $Ph_2PNNH(Ph)$ (**1**) is representative of the procedure used. Iminium bromides were prepared by the published procedures.[3-5] Triphenylchloromethane was purchased from Fisher Scientific and was recrystallized from heptane. Solvents were distilled from sodium benzophenone ketyl or P_2O_5 under N_2. All other chemicals were reagent grade and were used without further purification. All manipulations were carried out under an atmosphere of dry N_2 in a Vacuum/Atmospheres Dri-Lab or in standard Schlenk Apparatus. All evaporations were done at 25°C under a steady stream of dry N_2. Melting points were obtained in sealed tubes on a Thomas Hoover Melting Point Apparatus and were uncorrected. Constant temperatures for basicity studies were attained in a Haake FJ constant temperature bath. Elemental analyses were performed by the Microanalysis Service of the University of Florida.

^1H NMR spectra were taken in CD_2Cl_2 with a JEOL FX-100 or a Nicolet NT-300 instrument with $(CH_3)_4Si$ as an internal reference. $^{31}P\{^1H\}$ and ^{11}B NMR spectra were recorded with a Varian XL200 or the Nicolet NT-300 instrument. $^{31}P\{^1H\}$ spectra were obtained in C_6H_6 for the borane adducts and in CD_2Cl_2 for the boron cations at 80.984 or 121.477 MHz with 85% H_3PO_4 as the external reference. ^{11}B spectra were taken in CD_2Cl_2 at 64.184 or 96.270 MHz with $(CH_3O)_3B$ as the external reference. ^{31}P and ^{11}B shifts are reported with negative ppm downfield from the corresponding references. All IR spectra were recorded under N_2 in KBr disks using a Nicolet 5DXB FTIR spectrometer.

Preparation of $Ph_3PNNH(Ph)$ (**1**). The apparatus consisted of a nitrogen-flushed 500 mL three neck flask immersed in a dry ice acetone bath. The flask was fitted with a thimble, a dry ice condenser and a gas addition tube which was connected to an ammonia cylinder. To $[Ph_3PN(H)NH(Ph)]Br$ (22.466 g, 49.999 mmoles) in 300 mL of anhydrous liquid NH_3, sodamide (2.148 g, 55.06 mmoles) was added via the thimble. Stirring the yellow mixture for 1 h, followed by evaporation of the NH_3, afforded a light yellow solid. Extraction of the solid with 300 mL of THF left a white solid (NaBr). Evaporation of the yellow extract gave a yellow solid (14.790 g, 80% yield), which was recrystallized from THF-heptane affording **1** as yellow crystals (9.789 g, 66% yield) mp 132-133°C (Found: C, 78.05; H, 5.61; N, 7.41%. $C_{24}H_{21}N_2P$ calcd.: C, 78.24; H, 5.75; N, 7.60%). NMR data on the imines and reference numbers are presented in Table I.

TABLE I

^1H and $^{31}P\{^1H\}$ NMR data of imines*

Imine	^1H resonances δ, ppm and coupling constants J, Hz				$^{31}P\{^1H\}$
	δ_1	δ_2	δ_3	Aromatics	δ, ppm
$Ph_3PNNH(Ph)$	(**1**) 5.54 $J_{P-H} = 4.15$			7.38–7.94 6.57–7.20	−18.93
$Ph_3PNNCH_3(Ph)^4$	(**2**) 3.06 $J_{P-H} = 0.49$			7.38–7.98 6.61–7.33	−14.62
$Ph_3PNN(CH_3)_2^{4,21}$	(**3**) 2.33			7.38–7.82	−15.57
$Ph_3PN(CH_3)^{3,21}$	(**4**) 2.90 $J_{P-H} = 24.54$			7.41–7.77	−7.95
$Ph_3PN(C_2H_5)^3$	(**5**) 3.15 $J_{1-2} = 7.04$ $J_{P-H} = 19.54$	1.17 $J_{2-1} = 7.04$ $J_{P-H} = 1.54$		7.36–7.76	−3.56
$Ph_3PN(n\text{-}C_3H_7)^3$	(**6**) 3.04 $J_{1-2} = 7.08$ $J_{P-H} = 17.01$	1.50 $J_{2-1} = 7.08$ $J_{2-3} = 7.14$	0.88 $J_{3-2} = 7.14$	7.40–7.75	−3.67
$Ph_3PN(i\text{-}C_3H_7)^3$	(**7**) 3.36 $J_{1-2} = 6.16$ $J_{P-H} = 19.84$	1.08 $J_{2-1} = 6.16$ $J_{P-H} = 1.04$		7.38–7.78	0.52
$Ph_3PN(i\text{-}C_4H_9)^3$	(**8**) 2.87 $J_{1-2} = 6.47$ $J_{P-H} = 15.39$	1.59 $J_{2-1} = 6.47$ $J_{2-3} = 6.59$	0.90 $J_{3-2} = 6.59$	7.40–7.76	−3.50
$Ph_3PN(t\text{-}C_4H_9)^{3,21}$	(**9**) 1.16 $J_{P-H} = 1.22$			7.38–7.87	14.05

*All the δ values represent the centers of the resolvable or complex multiplets; ^1H spectra were run in CD_2Cl_2 with $(CH_3)_4Si$ as an internal reference; $^{31}P\{^1H\}$ spectra were recorded in C_6H_6 with negative shifts being downfield from 85% H_3PO_4 as external reference.

Syntheses of N-alkyl and N-aminotriphenylphosphoranimine Boranes from THF-borane and Imines. In a typical experiment, twice the stoichiometric amount of THF-borane was added to a stirred saturated solution of an imine in THF. The yields and melting points of the crude and recrystallized materials and reference numbers are given in Table II. Analytical data are listed in Table III. NMR data are given in Tables IV and V. The general workup of this preparative method is represented by the synthesis of $Ph_3PN(CH_3)BH_3$ (**10**).

Downloaded At: 16:51 29 January 2011

TABLE II

Yields and melting points of imine boranes and bis(imine) boronium iodides[a]

Compound		Yield % of crude product	mp °C of crude product	mp °C of recrystallized product
$Ph_3PN(CH_3)BH_3$	**(10)**	90	184–186	190–191
$Ph_3PN(C_2H_5)BH_3$	**(11)**	92	176–180	182–183
$Ph_3PN(n\text{-}C_3H_7)BH_3$	**(12)**	91	168–169	169–170
$Ph_3PN(i\text{-}C_3H_7)BH_3$	**(13)**	90	171–176	186–187
$Ph_3PN(i\text{-}C_4H_9)BH_3$	**(14)**	72	150–153	158–159
$Ph_3PN(t\text{-}C_4H_9)BH_3$	**(15)**	94	183–187	193–194
$Ph_3PNNH(CH_3)_2BH_3$	**(16)**	83	125–126	b
$Ph_3PNNH(Ph)BH_3$	**(17)**	72	126–127	130–131
$Ph_3PNN(CH_3)(Ph)BH_3$	**(18)**	92	140–141	141–142
$[Ph_3PN(CH_3)]_2BH_2^+I^-$	**(20)**	93	164–168	215–217
$[Ph_3PN(C_2H_5)]_2BH_2^+I^-$	**(21)**	73	186–190	197–199
$[Ph_3PN(n\text{-}C_3H_7)]_2BH_2^+I^-$	**(22)**	91	190–194	200–202

[a] All the imine boranes decompose at their melting points.

[b] The crude product precipitated as white needles which gave a satisfactory elemental analysis.

Downloaded At: 16:51 29 January 2011

TABLE III

Analyses of imine boranes and bis(imine) boronium iodides

Compound		%C	%H	%N
10	Calcd.	74.78	6.94	4.59
	Found	75.00	7.09	4.54
11	Calcd.	75.26	7.26	4.39
	Found	75.15	7.31	4.26
12	Calcd.	75.69	7.56	4.20
	Found	75.22	7.86	4.15
13	Calcd.	75.69	7.56	4.20
	Found	75.63	7.68	4.10
14	Calcd.	76.09	7.84	4.03
	Found	76.13	8.09	3.83
15	Calcd.	76.09	7.84	4.03
	Found	76.02	8.04	3.91
16	Calcd.	71.88	7.24	8.38
	Found	71.63	7.38	8.10
17	Calcd.	75.41	6.33	7.33
	Found	75.31	6.42	7.10
18	Calcd.	75.77	6.61	7.07
	Found	75.49	6.69	6.85
19	Calcd.	67.93	6.27	3.96
	Found	67.82	6.52	3.76
20	Calcd.	63.18	5.30	3.88
	Found	62.82	5.22	3.73
21	Calcd.	64.02	5.64	3.73
	Found	63.34	5.61	3.56
22	Calcd.	64.80	5.96	3.60
	Found	64.51	6.01	3.41

Downloaded At: 16:51 29 January 2011

TABLE IV

^1H and $^{31}P\{^1H\}$ NMR data of imine boranes and bis(imine) boronium iodides[a]

Compound	^1H resonances δ, ppm and coupling constats J, Hz δ_1	 δ_2	 δ_3	Aromatics	$^{31}P\{^1H\}$ δ, ppm
10	2.63 $J_{P-H} = 15.26$			7.35–7.89	−36.10
11	2.90 $J_{1-2} = 7.00$ $J_{P-H} = 18.09$	1.09 $J_{2-1} = 7.00$		7.36–7.90	−34.69
12[b]	2.78 $J_{AB} = J_{AB'} = 7.57$ $J_{AA'} = 0.89$ $J_{P-H} = 16.73$	1.64 $J_{BA} = J_{BA'} = 7.57$ $J_{BB'} = 0.89$ $J_{2-3} = 7.38$	0.652 $J_{3-2} = 7.38$	7.36–7.91	−34.91
13	3.03 $J_{1-2} = 6.50$ $J_{P-H} = 15.30$	1.26 $J_{2-1} = 6.50$		7.42–7.89	−32.45
14[b]	2.62 $J_{1-2} = 7.10$ $J_{P-H} = 12.77$	2.28 $J_{2-1} = 7.10$ $J_{2-3} = 6.68$	0.69 $J_{3-2} = 6.68$	7.41–7.88	−35.24
15	1.20 $J_{P-H} = 0.49$			7.37–7.91	−23.01
16	2.44			7.36–7.81	−36.41
17	5.08 $J_{P-H} = 2.93$			7.33–7.93 6.68–7.18	−40.24[c]
18	3.13			7.41–7.93 6.61–7.22	−41.12
19	3.09 $J_{1-2} = 7.08$ $J_{P-H} = 18.80$	1.06 $J_{2-1} = 7.08$		7.35–7.89	−42.67[c]
21	2.43 $J_{P-H} = 14.77$			7.54–7.75	−43.35[c]
22	2.81 $J_{1-2} = 6.98$ $J_{P-H} = 21.36$	0.50 $J_{2-1} = 6.98$		7.26–7.83	−41.54[c]
23	2.62 $J_{AB} = J_{AB'} = 8.39$ $J_{AA'} = 1.70$ $J_{P-H} = 21.07$	0.95 $J_{BA} = J_{BA'} = 8.39$ $J_{BB'} = 1.70$ $J_{2-3} = 7.26$	0.32 $J_{3-2} = 7.26$	7.25–8.08	−41.73[c]

[a] All the δ values represent the centers of the resolvable or complex multiplets; ^1H spectra were run in CD_2Cl_2 with $(CH_3)_4Si$ as an internal reference; $^{31}P\{^1H\}$ spectra were recorded in C_6H_6 for borane adducts and in CD_2Cl_2 for bis(imine) boronium iodides with negative shifts being downfield from 85% H_3PO_4 as external reference.

[b] ^1H spectrum obtained at 300 MHz.

[c] ^{31}P spectra obtained at 80.984 MHz.

Preparation of $Ph_3PN(CH_3)BH_3$ (**10**). To **4** (1.381 g, 4.740 mmoles) in 6 mL of THF, THF-borane (8.00 mL of 1.00 M, 8.00 mmoles of BH_3) was added. Stirring the mixture for 1.5 h at 25°C, followed by addition of 150 mL of heptane gave a white solid which was filtered and washed with four 40 mL portions of heptane. The solid, dried in vacuo, weighed 1.309 g (90% yield) mp 184–186°C dec. Recrystallization of a portion of the solid (0.296 g) from benzene-heptane afforded **10** as colorless crystals (0.170 g, 63% yield) mp 190–191°C dec.

Syntheses of Imine Boranes from $LiBH_4$ and Iminium Bromides. Two experiments were carried out to demonstrate the usefulness of this experimental method toward *N*-alkyl and *N*-aminotriphenylphosphoraniminium bromides. The apparatus consisted of a nitrogen-flushed 100 mL three neck flask equipped with a pressure compensated addition funnel, a reflux condenser, and a nitrogen inlet tube connected to a mercury bubbler. The top of the condenser was also connected to a mercury bubbler.

TABLE V

^{11}B NMR data of imine boranes and bis(imine) boronium iodides[a]

Compound	Chemical shift, δ, ppm	Multiplicity	Coupling constant, $J_{B—H}$, Hz
10	33.98	4	88.53
11	35.52	4	84.59
12	35.10	4	84.74
13	39.50	4	82.76
14	35.79	4	86.49
15	35.14	4	88.54
16	44.17	4	91.74
17[b]	35.47	4	66.24
18	40.30	1	c
19[b]	23.95	1	c
20[b]	25.84	1	c
21[b]	29.72	1	c
22[b]	27.51	1	c

[a] All the δ values represent the proton decoupled peaks; spectra were run in CD_2Cl_2 with positive shifts being upfield from $(CH_3O)_3B$ as external reference.

[b] Spectra obtained at 64.184 MHz.

[c] Coupling in these peaks was absent due to quadrupole relaxation.

Downloaded At: 16:51 29 January 2011

Preparation of **10**. To $Ph_3P{=}N(CH_3)HBr$ (1.893 g, 5.085 mmoles), a solution of $LiBH_4$ (0.147 g, 6.75 mmoles) in 20 mL of Et_2O was added via the funnel. After the mixture was stirred for 1 h evolving H_2, Et_2O (20 mL) was added. The funnel and inlet tube were replaced by stoppers, and the inlet tube was connected to the top of the condenser. Heating the mixture to reflux for 4 h, followed by cooling to 25°C and evaporation of the solvent gave a white solid. Extraction of the solid with two 80 mL portions of C_6H_6, followed by evaporation of the combined extracts afforded a white solid (0.916 g, 59% yield). Recrystallization of a portion of the solid (0.307 g) from benzene-heptane gave **10** as colorless crystals (0.189 g, 62% yield). The mp, ^1H and ^{11}B NMR spectra of the crystals were identical to an authentic sample of **10**. In the same manner, **16** was prepared in a 66% crude yield.

Chlorination of Imine Boranes with Ph_3CCl. The reactivity of imine boranes with Ph_3CCl is demonstrated in the synthesis of $Ph_3PN(C_2H_5)BH_2Cl$ (**19**).

Preparation of $Ph_3PN(C_2H_5)BH_2Cl$ (**19**). To **11** (0.601 g, 1.88 mmoles) in 25 ml of CH_2Cl_2, Ph_3CCl (0.526 g, 1.89 mmoles) was added. ^{31}P and ^{11}B NMR spectra recorded on an aliquot removed after 3 h of stirring showed only one peak each, indicating quantitative monochlorination. Stirring the solution for 4 h at 25°C, followed by additon of 200 mL of heptane afforded a white solid, which was filtered and washed with 30 mL of heptane. The solid, dried in vacuo, weighed 0.658 g (99% yield). Recrystallization of a portion of the solid (0.610 g) from C_6H_6 gave **19** as colorless crystals (0.310 g, 51% yield) mp 185–186°C dec. Analytical data are listed in Table III. NMR data are given in Tables IV and V.

Synthesis of Bis(N-alkyltriphenylphosphoranimine) Boronium Iodides. In a typical boron cation synthesis, a stoichiometric amount of I_2 was added to a C_6H_6 solution of the imine borane. After all the I_2 had reacted, a stoichiometric quantity of the imine was added, and the product was isolated. The crude yields and the melting points of the crude and reprecipitated boron cations and reference numbers are given in Table II. Analytical data are listed in Table III. NMR data are given in Tables IV and V. The general workup of this preparative method is represented by the synthesis of $[Ph_3PN(CH_3)]_2BH_2^+I^-$ (**20**).

Preparation of $[Ph_3PN(CH_3)]_2BH_2^+I^-$ (**20**). To **10**, (0.341 g, 1.12 mmoles) in 60 mL of C_6H_6, I_2 (0.124 g, 0.487 mmoles) was added with stirring causing evolution of H_2. The I_2 color disappeared after 10 min. Addition of **4** (0.292 g, 1.00 mmoles) to the colorless solution, followed by stirring of the mixture for 1.5 h, gave a white solid which was filtered and washed with 100 mL of C_6H_6. The solid, dried in vacuo, weighed 0.669 g (93% yield) mp 164–168°C. A solution of a portion of the crude solid (0.282 g) in a minimum amount of CH_2Cl_2 was filtered. Addition of Et_2O to the filtrate afforded **20** as a white powder (0.275 g, 98% yield) mp 215–217°C.

Attempted synthesis of $\{[Ph_3PN(n\text{-}C_3H_7)]BH_2[N(CH_3)_3]\}^+I^-$ (**23**). To $(CH_3)_3NBH_2I$ (1.001 g, 5.035 mmoles) in 100 mL of C_6H_6, **6** (1.617 g, 5.062 mmoles) was added. Stirring the mixture for 14 h gave a white solid which was filtered and washed with 100 mL of C_6H_6. The solid, dried in vacuo, weighed 1.903 g (73% yield). A ^1H NMR spectrum of the solid in CD_2Cl_2 was recorded and showed only a set of peaks and a singlet ($\delta = 3.00$ ppm) corresponding to **22** and $[(CH_3)_3N]_2BH_2^+I^-$, respectively, in the same solvent. The ratio of the integrated areas under the peaks was consistent with an equimolar mixture of both products.

Addition of 50 mL of water to a portion of the solid (1.467 g) formed a slurry which was stirred for 10 min and then filtered. The filtered solid, dried in vacuo, weighed 1.202 g. A ^1H NMR spectrum of the solid in CD_2Cl was recorded and showed only two sets of peaks corresponding to **22** and $Ph_3PN(n\text{-}C_3H_7)H^+$ (**24**)[23] in the same solvent. Addition of 30 mL of a saturated aqueous solution of NH_4PF_6 to the aqueous filtrate formed a white precipitate, which was filtered and dried in vacuo (0.370 g, 95% yield). A ^1H NMR spectrum of the precipitate in CD_2Cl_2 was recorded and showed only a singlet ($\delta = 2.50$ ppm) corresponding to $[(CH_3)_3N]_2BH_2^+PF_6^-$.[24]

Hydrolytic Stability. Mixtures of **22** (0.627 g, 0.476 g, and 0.453 g) in 50 mL each of 1M HCl, neutral, and 1M NaOH solutions, respectively were prepared and vigorously stirred for 15 min. The solids were rapidly filtered and then dried in vacuo over P_2O_5. ^1H and ^{31}P NMR spectra of the recovered solids were recorded in CD_2Cl_2. Spectra of the acid treated solid showed only peaks corresponding to $(C_6H_5)_3PO$ in the same solvent. Spectra of the neutral water treated solid showed two sets of peaks corresponding to **22** and **24**[23] in a 3:1 mole ratio from the integrated ^{31}P spectrum. Spectra of the base treated solid showed only peaks corresponding to **22**.

Relative Basicities of N-alkyltriphenylphosphoranimines. Experiments were performed to measure the relative base strengths of imines **4–9** in sealed 5 mm NMR tubes employing solutions of trimethylamine borane or 4-picoline borane with each imine. The reactions are summarized in equations 5 and 6.

$$\text{Imine} + (CH_3)_3NBH_3 \Leftrightarrow \text{ImineBH}_3 + (CH_3)_3N \tag{5}$$

$$\text{Imine} + 4\text{-}(CH_3)C_5H_4NBH_3 \Leftrightarrow \text{ImineBH}_3 + 4\text{-}(CH_3)C_5H_4N \tag{6}$$

The approximate starting concentration of each reactant was 0.1 M. ^1H or ^{11}B NMR spectra of each sample were recorded after 7 d at 25°C to determine if exchange had occurred. In those experiments where exchange did occur at 25°C, the corresponding samples were then kept at 25°C until chemical equilibrium was attained. The samples were then kept at 50°C until chemical equilibrium had been reached. Relative base strengths were measured by recording ^1H or a combination of $^{11}B\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra and converting integrated areas under the peaks of interest into mole ratios of products to reactants.[25] The mole ratios are expressed as R_t = [(moles of ImineBH$_3$)(moles of $(CH_3)_3N$)]/[(moles of Imine)(moles of $(CH_3)_3NBH_3$)], and R_p = [(moles of ImineBH$_3$)(moles of 4-$(CH_3)C_5H_4N$)]/[moles of Imine)(moles of 4-$(CH_3)C_5H_4NBH_3$)]. Chemical equilibrium was inferred when the ratios in each experiment became constant over time. The ratios are presented in Table VI.

In order to establish that the two sets of ratios are consistent, a separate exchange experiment was performed using $(CH_3)_3NBH_3$ and 4-picoline approximately 0.1 M in each in C_6H_6. The reaction is described in Equation (7).

$$(CH_3)_3NBH_3 + 4\text{-}(CH_3)C_5H_4N \Leftrightarrow (CH_3)_3N + 4\text{-}(CH_3)C_5H_4NBH_3 \tag{7}$$

The equilibrium mole ratios of products to reactants at 25°C and 50°C were measured as previously described using ^1H NMR spectra and are 0.014 and 0.024 respectively. Calculated ratios for this system as R_t/R_p for each imine are presented in Table VI.

RESULTS

General Properties

The imine boranes are white crystalline solids which are soluble in CH_2Cl_2, C_6H_6, THF, and $CHCl_3$ and insoluble in heptane and H_2O. The boron cations are white

Downloaded At: 16:51 29 January 2011

TABLE VI

Basicities of imines[a]

Imine	Temperature, °C	Mole ratios of products to reactants[b] R_t	R_p	R_t/R_p
4	25	0.055	4.2	0.013
	50	0.81	33	0.025
5	25	0.0015	0.10	0.014
	50	0.15	6.0	0.025
6	50	0.050	2.0	0.025
7	50	0.0056	0.22	0.025
8	50	0.016	0.68	0.023
9	25	no reaction	no reaction	
	50	no reaction	no reaction	

[a] Basicities were measured relative to exchange of BH_3 between imines and borane adducts of trimethylamine and 4-picoline as described in Equations (3) and (4).

[b] The mole ratios are expressed as $R_t = [(\text{moles of ImineBH}_3)(\text{moles of }(CH_3)_3N)]/[(\text{moles of Imine})(\text{moles of }(CH_3)_3NBH_3)]$, and $R_p = [(\text{moles of ImineBH}_3)(\text{moles of 4-}(CH_3)C_5H_4N)]/[(\text{moles of Imine})(\text{moles of 4-}(CH_3)C_5H_4NBH_3)]$.

Downloaded At: 16:51 29 January 2011

powders which are very soluble in CH_2Cl_2 and $CHCl_3$, but are insoluble in C_6H_6, Et_2O, heptane, and H_2O.

Thermal Stability

The imine boranes are stable at 25°C but decompose with evolution of H_2 at their melting points. A $^{31}P\{^1H\}$ NMR C_6H_6 solution spectrum of the solid obtained by heating a sample of **12** to 190°C for 20 min showed only major and minor resonances corresponding to Ph_3P and Ph_3PBH_3 respectively. A $^{11}B\{^1H\}$ NMR spectrum, on the same solution showed peaks corresponding to Ph_3PBH_3 and two broad signals in the region 0 to −30 ppm indicating sp^2 bonded borons.[26] The solid bis(imine) boron cations are indefinitely stable at 25°C.

Hydrolytic Stability

The imine boranes are not stable toward hydrolysis but react slowly with H_2O. In contact with moist air, **19** decomposes producing $Ph_3P{=}N(C_2H_5)H^+$.[27] The bis(imine) boron cations are decomposed by acidic and neutral aqueous solutions producing $(C_6H_5)_3PO$ (88% yield) and the corresponding iminium salts, respectively (Equations (8) and (9)). No evidence for formation of $(C_6H_5)_3PO$ via decomposition in neutral

$$\underset{(\mathbf{22})}{[Ph_3PN(R)]_2BH_2^+} + H_3O^+ \Rightarrow Ph_3PO + \text{other products} \tag{8}$$

$$\underset{(\mathbf{22})}{[Ph_3PN(R)]_2BH_2^+} + H_2O \Rightarrow \underset{(\mathbf{24})}{Ph_3PN(R)H^+} + \text{other products} \tag{9}$$

$$R = n\text{-}C_3H_7$$

solution was found. The bis(imine) boron cations are stable when mixed with cold aqueous NaOH for short periods of time.

Reaction with Anhydrous HCl

Solutions of **11** and **21** in CH_2Cl_2 reacted stepwise with portions of an anhydrous solution of HCl in CH_2Cl_2 producing first **19** and finally $Ph_3P{=}N(C_2H_5)H^{+}$[27] along with H_2 (Equations (10) and (11)). The reactions were followed via ^{31}P NMR spectra of aliquots removed after each HCl addition.

$$\underset{\textbf{(21)}}{[Ph_3PN(R)]_2BH_2^+} + HCl \Rightarrow Ph_3PN(R)H^+ + \underset{\textbf{(19)}}{Ph_3PN(R)BH_2Cl} \tag{10}$$

$$\underset{\textbf{(19)}}{Ph_3PN(R)BH_2Cl} + 3HCl \Rightarrow Ph_3PN(R)H^+ + 2H_2 + BCl_4^- \tag{11}$$

where $R = C_2H_5$.

Downloaded At: 16:51 29 January 2011

Stability Towards Ag$^+$

A solution of **21** in CH_2Cl_2 reacted with excess $AgPF_6$ causing rapid H_2 evolution and forming a black solid. The solid dissolved in 15M HNO_3 causing evolution of NO_2, and the resulting solution gave a white precipitate with addition of HCl.

Reaction with I_2

The imine boranes reacted with stoichiometric quantities of I_2 for monoiodination in C_6H_6 evolving H_2 and completely decolorizing the I_2. Attempts to isolate and identify monoiodinated products were unsuccessful.

Stability Towards BH_4^-

In general, solutions of **20**, **21**, and **22** in CH_2Cl_2 were treated with stoichiometric amounts of $(n\text{-}C_4H_9)_4NBH_4$. The solutions were stirred, and aliquots were removed periodically over 7 d. ^{11}B and ^{31}P NMR spectra were recorded on the aliquots immediately after removal and showed that the boron cations reacted slowly with BH_4^- forming the corresponding borane adducts exclusively and quantitatively.

Relative Base Strengths

In general, for the reactions described by equations 5 and 6, it was found that $(CH_3)_3NBH_3$ and $4\text{-}(CH_3)C_5H_4NBH_3$ transferred BH_3 to **4** and **5** at 25°C and to imines **4–8** at 50°, but not to **9** at either temperature. In order to determine if observations with **9** were consequences of slow kinetics or unfavorable thermodynamics, equilibrium was approached from the opposite direction in both systems. At 50°C BH_3 exchanged quantitatively from **15** to both $(CH_3)_3N$ and 4-picoline, but no exchange occurred at 25°C. The exchange reactions attained chemical equilibrium slowly, but the $(CH_3)_3NBH_3$ systems were faster than corresponding 4-$(CH_3)C_5H_4NBH_3$ systems. For example, it took 41 days for the reaction between $(CH_3)_3NBH_3$ and **4** to reach equilibrium, and 70 days for the reaction between 4-$(CH_3)C_5H_4NBH_3$ and **4** to reach equilibrium, both at 25°C. Using the ratios as a measure of relative Lewis basicity, we find that $(CH_3)_3N$ is a stronger base than imines **4**, **5**, and 4-picoline at both 25° and 50°C. At 50°C, $(CH_3)_3N$ is a stronger base than imines **6–9**. At 25°C, 4-picoline is a stronger base than **5** and a weaker base than **4**. At 50°C, 4-picoline is a stronger base than imines **7–9** but a weaker base tham imines **4–6**.

Infrared Spectra

The assignments of the various bands were made by straightforward comparisons between the spectra of the coordinated and free imines. All the imines have similar IR spectra except for the expected differences caused by the R groups attached to nitrogen. Characteristic absorptions include P–C and C–N stretching vibrations found in the regions 1432–1440 and 1105–1311 cm^{-1} respectively.[28,29]. Both vibrations do not change significantly upon complexation by BH_3. In addition, a broad band in the region 879–1335 cm^{-1}, which shifts to lower wavenumbers upon complexation by BH_3, was assigned as the P═N stretch.[5,30] The stretching vibrations and deformation modes for the BH_3 groups are both doublets found in the regions 2232–2302 and 1071–1164 cm^{-1} respectively. The stretching vibrations and deformation modes for the BH_2 groups appear as doublets and singlets respectively in the regions 2274–2329 and 1185–1210 cm^{-1}, respectively. An additional broad band, assigned to the B—N stretch, appears in the borane adduct and boron cation spectra between 882 and 936 cm^{-1}. The P═N and B—N stretching vibrations in the boron cation spectra are not significantly different than those found in the corresponding borane adducts.

NMR Spectra

The chemical shifts, δ, in ppm of the ^1H and $^{31}P\{^1H\}$ resonances and coupling constants, J, in Hz, of the ^1H resonances for the imines, imine boranes, and bis(imine) boronium iodides are reported in Tables I, IV, and IV respectively. The chemical shifts, δ, in ppm and coupling constants, J, in Hz of the ^{11}B resonances are reported in Table V. The integrated intensities of the ^1H spectra agreed well with the expected values. The coupling patterns of the alkyl groups are what is expected for their corresponding structures. In addition, long range coupling to the α and β protons by the phosphorus atom is observed.[21] ^1H spectra of some imines have been reported previously by others,[21] and our results agree well with theirs.

In general, for the imines, the ^1H resonances δ_1, δ_2, δ_3, and the ^{31}P resonances show definite chemical shifts upfield, downfield, upfield, and downfield, respectively, upon coordination by BH_3. A general decrease in $J_{P—H}$ is also observed upon BH_3 and BH_2^+ complexation of the imines. The ^{31}P and ^{11}B resonances of **19** both show shifts downfield relative to those of **11** as expected.[31,32] The ^{11}B resonances are quartets, with varying degrees of

Downloaded At: 16:51 29 January 2011

quadrupole relaxation, for all the BH_3 adducts as expected. The ^{11}B resonances of the bis(imine) boronium cations are extremely broad and show no multiplicity due to quadrupole relaxation of the expected triplets. The broad peaks do not change significantly when the protons are decoupled. The $^{31}P\{^1H\}$ resonances are sharp well resolved singlets. There are definite upfield chemical shifts in all the alkyl ^1H resonances and downfield chemical shifts in the $^{31}P\{^1H\}$ resonances of the imines upon coordination by a BH_2^+ group. Protons attached to boron could not be resolved, due to quadrupole relaxation, but were observed in integrated area ratios.

DISCUSSION

Two different general synthetic methods were used to produce borane adducts. The first procedure employed displacement of a donor (THF) coordinated to BH_3[9,10] by free imines (Equation (1)). The second method used reactions of iminium bromides with $LiBH_4$ in Et_2O (Equation (2)), demonstrating analogous behaviour with ammonium ions.[11] Both synthetic methods are convenient and rapid at room temperature and produce borane adducts with good purity. The first procedure gives essentially quantitative yields. The second has the advantage of not using isolated imines, which are difficult and time consuming to prepare, making it the preferred route to borane adducts of imines. The reactivities of the imine boranes toward anhydrous HCl, and I_2 are similar to those reported for amine boranes.[32–35] The reaction of **11** with Ph_3CCl (1:1 mole ratio) producing **19**, quantitatively, is noteworthy, since this reaction demonstrates a new and simple pathway to haloborane adducts.

The *N*-aminotriphenylphosphoranimines, $Ph_3P{=}N{-}N(R)R'$, have two lone pairs of electrons available for BH_3 complexation, but elemental analyses show that only one BH_3 unit per molecule was added. Steric and electronic factors explain why a second BH_3 unit does not add to the molecule. Steric hindrance by the attached BH_3 may shield the lone pair from attack. The positive formal charge on the coordinated nitrogen would create a larger Z_{eff} on the uncoordinated nitrogen, reducing the basicity by contraction of the lone pair. NMR data are consistent with mono-addition of BH_3 at the α-nitrogen atom, $Ph_3P{=}N(BH_3)N(R)R'$, demonstrating parallel behavior with alkylation of imines.[4] Coordination of only the β-nitrogen, $Ph_3P{=}NN(BH_3)(R)R'$, would not be expected to change the ^{31}P NMR chemical shift significantly from that of the free imine. Coordination of the α-nitrogen is expected to cause a substantial shift downfield in the ^{31}P NMR resonance relative to the free imine, as observed. The groups $(CH_3)_2N$ and $(CH_3)_2C$ are structurally similar. Coordination of the α-nitrogen of **3** is expected to show a shift in the CH_3 ^1H resonance similar to that seen in **7** upon coordination by BH_3, as observed. Coordination of the β-nitrogen of **3** is expected to produce a substantial broadening of the CH_3 ^1H resonance from the boron quadrupole moment. It was observed that the linewidth of the CH_3 ^1H resonance of **16** is not substantially different from that of **3**. Resonance stabilization of the positive formal charge formed upon coordination of the α-nitrogen explains why monoaddition at this position occurs preferentially.

Downloaded At: 16:51 29 January 2011

Downloaded At: 16:51 29 January 2011

The slow exchange reactions (Equations (5), (6), and (7)) may be attributed to repulsion between the nucleophile lone pair and the negative formal charge of the coordinated boron in an Sn2 mechanism. Since $(CH_3)_3N$ is a stronger base than 4-picoline toward BH_3, an Sn1 mechanism contradicts the observed kinetics. In general, as the alkyl group becomes larger, the basicity of the corresponding imine decreases as expected from steric considerations. This observation was also made in studies of BF_3 adducts of imines.[8] All of the R_t/R_p values in Table VI are close to the directly determined experimental values indicating good consistency between individual exchange experiments and that equilibrium was attained in each system. Others have reported[10] that when $(CH_3)_3N$ and $C_5H_5NBH_3$ exchange BH_3 in the gas phase, the equilibrium product to reactant ratio is 32.1, which correlates well with our analogous system using 4-picoline.

The reactivities of **22** toward cold aqueous acidic, neutral and basic solutions (Equations (8) and (9)) contrast those seen in bis(amine) boron cations in which acid retards and base accelerates hydrolysis.[13–16,36] Thus, the mode of hydrolysis of bis(imine) boron cations must be different than in bis(amine) boron cations. The stability of **22** to cold aqueous NaOH implies that loss of imine (**6**) from **22** does not occur and that attack at the P atoms of **22** is hindered by shielding from the $p\pi - d\pi$ electrons of the P=N bond. Production of $(C_6H_5)_3PO$ by reaction of **22** with aqueous HCl (Equation (8)) is not unexpected, since some phosphoranimies undergo hydrolysis to the corresponding amines and $(C_6H_5)_3PO$.[3,4,6,18,37] This may occur in two steps, the first being protonation of the $p\pi$-$d\pi$ electron pair on a N atom to form a dication, $\{[Ph_3P{-}N(R)H]BH_2[(R)N{=}PPh_3]\}^{2+}$, followed by cleavage of the P–N bond by attack of a water molecule on the positively charged P atom through a vacant d orbital. The reaction of **22** with neutral water, producing **24** (Equation (9)) and no $(C_6H_5)_3PO$, must proceed by a different route than the reaction of **22** with aqueous HCl (Equation (8)) does. The reaction of **21** with anhydrous HCl (Equations (10) and (11)) may occur via loss of imine (**5**) from the cation (**21**) followed by protonation of **5** or via protonation of the $p\pi - d\pi$ electron pair on a N atom in **21** forming the dication $\{[Ph_3P{-}N(R)H]BH_2[(R)N{=}PPh_3)\}^{2+}$, which could then cleave with displacement by Cl^-.

The bis(imine) boron cations reduce Ag^+ forming Ag and H_2. This process probably occurs through formation of an imine haloborane adduct, since bis(amine) boron cations do not undergo oxidation readily. The reactions of the bis(imine) boron cations with BH_4^-, forming the corresponding borane adducts slowly and quantitatively, imply that the mixtures are less thermodynamically stable than the corresponding borane adducts. This result is interesting, since few bis(alkylamine) boron cations have been shown to react similarly.[38,39] These reactions are expected to occur via loss of imine from the boron cation.

The synthesis of the new cations proceeded rapidly with reproducibly high yields. The in situ generated iodoborane, $Ph_3P{=}N(n\text{-}C_3H_7)BH_2I$, reacted faster with imine (**6**) than $(CH_3)_3NBH_2I$ did. The difference between the reactivities of the two iodoboranes can be attributed to steric and electronic factors governing an Sn2 mechanism.[24]

Only one attempt was made to prepare an unsymmetrical boron cation (**23**) with the products being a mixture of the symmetrical boron cations (**22**) and

$[(CH_3)_3N]_2BH_2^+I^-$) in equimolar proportions. No evidence for the production of **23** was observed. This result is interesting, since previously reported syntheses of unsymmetrical boron cations, employing alkylamines and substituted pyridines as ligands, did not give any symmetrical boron cations.[16] Since equimolar amounts of **22** and $[(CH_3)_3N]_2BH_2^+I^-$ were produced, any mechanism explaining this phenomenon must include cleavage of a B—N bond producing free $(CH_3)_3N$. Normally iodide displacement is the expected pattern of a nucleophilic substitution reaction on coordinated iodoboranes.[16] Displacement of $(CH_3)_3N$ by transamination can occur only if a base stronger than $(CH_3)_3N$ is used. Since **6** is a weaker base than $(CH_3)_3N$, mechanistic steps employing transamination are not expected in our reaction. Production of **23** by iodide displacement as the first step (Equation (12)), followed by displacement of $(CH_3)_3N$ by I^- to give the imine iodoborane (Equation (13)), would produce free $(CH_3)_3N$. The corresponding iodoboranes could then react with $(CH_3)_3N$ and **6** forming the observed products, $[(CH_3)_3N]_2BH_2^+I^-$ and **22**, respectively.

$$\underset{(\mathbf{6})}{Ph_3P{=}NR} + (CH_3)_3NBH_2I \Rightarrow \underset{(\mathbf{23})}{\{[Ph_3PNR]BH_2[N(CH_3)_3]\}^+I^-} \tag{12}$$

$$\underset{(\mathbf{23})}{\{[Ph_3PNR]BH_2[N(CH_3)_3]\}^+I^-} \Rightarrow Ph_3P{=}N(R)BH_2I + (CH_3)_3N \tag{13}$$

where $R = n\text{-}C_3H_7$.

Downloaded At: 16:51 29 January 2011

ACKNOWLEDGEMENTS

The authors express their appreciation to the University of Florida for support of this work and to the Instrument Program, Chemistry Division, National Science Foundation for assistance in the purchase of the Nicolet NT-300 NMR spectrometer. We also thank Professor Wallace Brey, University of Florida, for recording NMR spectra on the Nicolet NT-300.

REFERENCES AND NOTES

1. H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2,** 635 (1919).
2. H. Staudinger and E. Hauser, *Helv. Chim. Acta.*, **4,** 861 (1921).
3. H. Zimmer and G. Singh, *J. Org. Chem.*, **28,** 483 (1963).
4. H. Zimmer and G. Singh, *J. Org. Chem.*, **29,** 1579 (1964).
5. L. Horner and H. Oediger, *Liebigs Ann. Chem.*, **627,** 142 (1959).
6. H. Zimmer, M. Jayawant and P. Gutsch, *J. Org. Chem.*, **35,** 2826 (1970).
7. R. Appel and F. Vogt, *Chem. Ber.*, **95,** 2225 (1962).
8. H. Zimmer and G. Singh, *J. Org. Chem.*, **29,** 3412 (1964).
9. A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, **59,** 780 (1937).
10. H. C. Brown, H. I. Schlesinger and S. Z. Cardon, *J. Am. Chem. Soc.*, **64,** 325 (1942).
11. G. W. Schaeffer and E. R. Anderson, *J. Am. Chem. Soc.*, **71,** 2143 (1949).
12. J. E. Douglas, *J. Am. Chem. Soc.*, **86,** 5431 (1964).
13. G. E. Ryschkewitsch, *J. Am. Chem. Soc.*, **89,** 3145 (1967).
14. G. E. Ryschkewitsch and J. M. Garrett, *J. Am. Chem. Soc.*, **89,** 4240 (1967).
15. K. C. Nainan and G. E. Ryschkewitsch, *Inorg. Chem.*, **7,** 1316 (1968).
16. K. C. Nainan and G. E. Ryschkewitsch, *J. Am. Chem. Soc.*, **91,** 330 (1969).
17. G. Singh, Dissertation, University of Cincinnati, 1964.
18. G. Singh, Main Group Elements and Their Compounds, Methodicum Chemicum, (Academic Press, New York, 1978), **7B,** p. 529.
19. A. W. Johnson and S. C. K. Wong, *Can. J. Chem.*, **44,** 2793 (1966).

20. W. A. G. Graham and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **3**, 164 (1956).
21. F. Kaplan, G. Singh, and H. Zimmer, *J. Phys. Chem.*, **67**, 2509 (1963).
22. G. E. Ryschkewitsch and J. W. Wiggins, *Inorg. Synth.*, **12**, 120 (1970).
23. $(C_6H_5)_3PN(n\text{-}C_3H_7)HBr$; ^1H NMR (CD_2Cl_2, 100 MHz): δ_1 2.95 ($J_{1-2} = 7.51$, $J_{P-H} = 10.38$, $J_{1-(NH)} = 6.60$ Hz), δ_2 1.58 ($J_{2-1} = 7.51$, $J_{2-3} = 7.26$ Hz), δ_3 0.74 ($J_{3-2} = 7.26$ Hz), δ_4 (aromatics and N-H) 7.51-7.95; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 80.984 MHz): $\delta = -38.33$.
24. K. C. Nainan, Dissertation, University of Florida, 1969.
25. For a complete description of experimental methods used and data treatment, see: W. K. Holley, Dissertation, University of Florida, 1986.
26. K. Niedenzu and J. W. Dawson, Boron Nitrogen Compounds, (Academic Press, New York, 1965), pp. 154–158.
27. $(C_6H_5)_3PN(C_2H_5)HBr$; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.48 MHz), $\delta = -38.06$ ppm.
28. L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).
29. N. B. Colthup, *J. Optical Soc. Am.*, **40**, 397 (1950).
30. H. R. Allcock, Phosphorus-Nitrogen Compounds, (Academic Press, New York, 1972), p. 48.
31. J. H. Letcher and J. R. Van Wazer, P^{31} Nuclear Magnetic Resonance, Topics in Phosphorus Chemistry, (Interscience Publishers, New York, 1967), **5**, pp. 75–225.
32. J. W. Wiggins and G. E. Ryschkewitsch, *Inorg. Chim. Acta*, **4**, 33 (1969).
33. G. E. Ryschkewitsch and J. W. Wiggins, *Inorg. Synth.*, **12**, 116 (1970).
34. H. Noeth and H. Beyer, *Chem. Ber.*, **93**, 2251 (1960).
35. W. H. Myers, G. E. Ryschkewitsch, M. A. Mathur, and R. W. King, *Inorg. Chem.*, **14**, 2874 (1975).
36. N. E. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 1033 (1964).
37. R. Appel and A. Hauss, *Chem. Ber.*, **93**, 405 (1960).
38. M. Inoue and G. Kodama, *Inorg. Chem.*, **7**, 430 (1968).
39. H. Noeth, H. Beyer and H. Vetter, *Chem. Ber.*, **97**, 110 (1964).

Downloaded At: 16:51 29 January 2011