

*Journal of Organometallic Chemistry*, 365 (1989) 23–35  
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands  
JOM 09561

## Multinuclear NMR spectroscopic studies of aryltrimethylsilanes and aryldimethylphosphaneboranes \*

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(Received July 18th, 1988)

### Abstract

Proton, boron-11, carbon-13, silicon-29, and phosphorus-31 NMR chemical shifts and coupling constants are reported for nine *ortho*- and 2,6-disubstituted aryltrimethylsilanes and five similarly substituted aryldimethylphosphaneboranes. Resonances in the natural-abundance carbon-13 NMR spectra for both sets of derivatives are assigned on the basis of additivity relationships, proton-coupled spectra, and relative magnitudes of  $|J(^{31}\text{P}-^{13}\text{C})|$  coupling constants. Carbon-13 chemical shifts and  $|^1J(^{13}\text{C}-^1\text{H})|$  coupling constants indicate that the  $\text{P}(\text{BH}_3)(\text{CH}_3)_2$  group is electron-withdrawing. The  $^{13}\text{C}$  chemical shifts of aryl C(5) carbons can be attributed to steric inhibition of resonance of about the same magnitude as that produced by *ortho*- $\text{Si}(\text{CH}_3)_3$ . Chemical shift and coupling constant data from previous work are expanded in terms of Taft's dual substituent constants  $\sigma_1$  and  $\sigma_{\text{R}}^0$ . Least squares solutions of these equations for aryldimethylphosphaneborane derivatives provide values of 0.41 for  $\sigma_1$  and 0.04 for  $\sigma_{\text{R}}^0$  for the  $\text{P}(\text{BH}_3)(\text{CH}_3)_2$  group. These constants produce reasonable agreement with observed  $^{13}\text{C}$  chemical shifts and coupling constants in the *ortho* derivatives.

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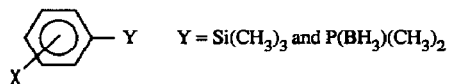
\* This paper is dedicated to the late Prof. J.J. Zuckerman in recognition of his important contributions to organometallic chemistry.

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## Introduction

The understanding of steric hindrance and electronic effects in organometallic compounds can be improved through the study of *ortho*-substituted aryl derivatives when careful comparisons are made with the corresponding *meta*- and *para*-substituted analogs. Previous studies of homologous aryl derivatives containing main-group element attachments to the aromatic ring have concentrated on *meta*- and *para*-substituted derivatives of Groups 13–15, with aryltrimethyl-silanes and -stannanes receiving the most scrutiny.

Our current investigations stem from our interest in the application of NMR spectroscopy to the analysis of substituent effects in aryltrimethylsilanes and germanes [1,2], -stannanes [2–8], aryl dimethyl-phosphines and -arsines [1], and in traditional aromatic systems, including toluenes, anisoles and *t*-butylbenzenes [2,9–11], and benzaldehydes [10–12]. The availability of NMR data for *meta*- and *para*-substituted aryl dimethylphosphaneboranes [13], and our present report of the



synthesis and NMR spectra of the *ortho* derivatives, afford a rare opportunity to assess the interplay of steric and electronic effects in the P(BH<sub>3</sub>)(CH<sub>3</sub>)<sub>2</sub> group. These effects can then be compared with those of the isoelectronic group Si(CH<sub>3</sub>)<sub>3</sub>.

## Experimental

### Compounds

All procedures were carried out under an argon or nitrogen atmosphere using oven-dried glassware and dry reagents. Commercial *n*-butyllithium (Aldrich Chemical Company) was purchased as a 2.5 *M* solution in hexanes. Solvents were normally removed under vacuum using a Büchi/Brinkmann Rotavapor-R rotary evaporation system. Vacuum distillations were performed on a 12-inch jacketed column packed with glass beads or helices and surmounted with an Ace Mini-Lab<sup>®</sup> distillation head. Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Purity of all compounds probably exceeded 95%, as indicated by elemental analysis and by the absence of spurious signals in the proton and carbon-13 spectra. Carbon and hydrogen combustion analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY 11377.

Substituted aryltrimethylsilanes were available from previous studies, or were prepared in 60–80% yields according to one of the following three methods: (1) reaction of trimethylchlorosilane with the appropriate Grignard reagent (G) (from magnesium turnings and commercially available substituted aryl bromides) in anhydrous tetrahydrofuran, followed by gravity filtration of magnesium salts through Celite<sup>®</sup>, hydrolysis with a saturated aqueous ammonium chloride solution, extraction of the aqueous phase with diethyl ether, drying of the organic layer over anhydrous magnesium sulfate; (2) reaction of trimethylchlorosilane with the appropriate organolithium reagent (L) (from lithium ribbon and aryl bromides), followed by filtration of lithium salts through Celite<sup>®</sup>; or 3) reaction of trimethyl-

chlorosilane with the organolithium reagent obtained from an exchange (E) between *n*-butyllithium and an aromatic compound containing an active hydrogen in a position *ortho* to the substituent. Solvents were removed under vacuum, and final products were isolated by vacuum distillation or by recrystallization from absolute ethanol. Methods of preparation and boiling points for the nine aryltrimethylsilane derivatives are as follows: H (G), b.p. 74°C/20 torr (lit. [1] b.p. 74°C/20 torr, lit. [14] b.p. 168°C, lit. [15] b.p. 168–169°C); *o*-CH<sub>3</sub> (G), b.p. 84–85°C/14 torr (lit. [16] b.p. 94°C/23 torr, lit. [17] b.p. 196°C, lit. [18] 198°C, lit. [19–20] 196–197°C, lit. [21] 95°C/25 torr, lit. [22] 195–196°C); 2,6-(CH<sub>3</sub>)<sub>2</sub> (G), b.p. 101°C/10 torr (lit. [22] 224–226°C, lit. [23] b.p. 61°C/1 torr); *o*-C<sub>2</sub>H<sub>5</sub> (G), b.p. 85–87°C/12–13 torr (lit. [21] 95–100°C/23 torr, lit. [24] b.p. 210–211°C); *o*-OCH<sub>3</sub> (G), b.p. 92–93°C/10 torr (lit. [25], b.p. 205–206°C, lit. [26] b.p. not given, lit. [27] b.p. 88–90°C/15 torr); 2,6-(OCH<sub>3</sub>)<sub>2</sub> (E), b.p. 78–80°C/0.5 torr (lit. [27] b.p. 51–52°C/0.1 torr); 2,6-(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> (E), m.p. 88–89°C; *o*-N(CH<sub>3</sub>)<sub>2</sub> (L), b.p. 80–83°C/0.03 torr, m.p. 88–89°C (lit. [28] b.p. 104°C/20 torr); *o*-Cl(G), b.p. 98°C/27 torr (lit. [17] b.p. 207–208°C, lit. [28] b.p. 95°C/18 torr, lit. [29] b.p. 89°C/15 torr).

Substituted aryl dimethylphosphaneboranes, which are clear colorless viscous liquids with foul odors or crystalline white solids, were available from previous studies [13], or were prepared in 40–60% yields according to the same three synthetic routes as the aryltrimethylsilanes. Dimethylchlorophosphaneborane, prepared by the method of Schmidbaur [30–32], was purchased as a 1.0 *M* solution in tetrahydrofuran from Strem Chemicals Inc., Newburyport, MA 01950; it was also prepared from pyrophoric dimethylchlorophosphine [33] and borane/tetrahydrofuran adduct. Methods of preparation, melting points, and boiling points for the five aryl dimethylphosphaneborane derivatives are as follows: H (G), b.p. 77–78°C/0.03 torr (lit. [34–35] b.p. not given); *o*-OCH<sub>3</sub> (G), b.p. 133–135°C/0.03 torr; 2,6-(OCH<sub>3</sub>)<sub>2</sub> (E), m.p. 72–74°C; 2,6-(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> (E), m.p. 91–93°C; *o*-N(CH<sub>3</sub>)<sub>2</sub> (L), b.p. 106–108°C/0.03 torr, m.p. 52–54°C. Two representative preparations follow.

2,6-Diethoxyphenyltrimethylsilane was prepared in 60% yield by the reaction of 1,3-diethoxybenzene (16.7, 0.10 mol) in 40 ml of ether with 42 ml (0.105 mol) of a 2.5 *M* solution of *n*-butyllithium in hexanes. The resulting pale yellow solution was heated at reflux for 1 h with vigorous magnetic stirring. The solution was cooled to room temperature, and trimethylchlorosilane (11.0 g, 0.101 mol) in 50 ml of ether was added dropwise. The cloudy reaction mixture was stirred at room temperature for 16 h, and then was filtered to remove lithium chloride. Solvent was removed under vacuum, and the resulting crude solid was recrystallized from absolute ethanol (m.p. 91–93°C) to yield colorless crystals. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 60 MHz) δ 7.4–6.4 (m, 3 H, C<sub>6</sub>H<sub>3</sub>), 3.89 (q, 4H, OCH<sub>2</sub>), 1.34 (t, 6 H, Me), 0.30 (s, 9 H, SiMe<sub>3</sub>). Anal. Found: C, 65.22; H, 9.46. C<sub>13</sub>H<sub>22</sub>O<sub>2</sub>Si calcd.: C, 65.50; H, 9.30%.

2,6-Diethoxyphenyldimethylphosphaneborane was secured in 40% yield from the reaction between 1,3-diethoxybenzene (16.7, 0.10 mol) in 50 ml of anhydrous diethyl ether and 42 ml (0.105 mol) of a 2.5 *M* solution of *n*-butyllithium in hexanes, followed by dropwise addition of 115 ml (0.1 mol) of a 1.0 *M* tetrahydrofuran solution of dimethylchlorophosphaneborane. Workup of the reaction mixture as above, followed by recrystallization of the crude product from absolute ethanol, afforded a white crystalline solid, m.p. 91–93°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 60 MHz) δ

6.3–7.4 (m, 3 H, C<sub>6</sub>H<sub>3</sub>), 3.97 (q, 4 H,  $^3J(^1\text{H}-^1\text{H})$  7.2 Hz, OCH<sub>2</sub>), 1.73 (d, 6 H,  $^2J(^{31}\text{P}-^1\text{H})$  10 Hz, PMe<sub>2</sub>), 1.48 (t, 6 H,  $^3J(^1\text{H}-^1\text{H})$  7.2 Hz, Me), 1.30 (br qd, 3 H,  $^1J(^{11}\text{B}-^1\text{H})$  95 Hz,  $^2J(^{31}\text{P}-^1\text{H})$  12 Hz, BH<sub>3</sub>). Anal. Found: C, 60.35; H, 9.47. C<sub>12</sub>H<sub>22</sub>BO<sub>2</sub>P calcd.: C, 60.03; H, 9.24%.

### *NMR parameters*

Proton spectra were recorded in the continuous wave mode on a Varian EM-360A spectrometer, operating at 60 MHz. Chemical shifts obtained in this way are believed accurate and reproducible to within  $\pm 0.005$  ppm, while coupling constants are reliable to  $\pm 0.2$  Hz. All other spectra were obtained in the Fourier transform mode on a JEOL FX90-Q spectrometer. Operating frequencies were 28.7 MHz (<sup>11</sup>B), 22.5 MHz (<sup>13</sup>C), 17.5 MHz (<sup>29</sup>Si), and 36.2 MHz (<sup>31</sup>P). Samples were contained in 10-mm o.d. tubes. Spectra were normally recorded as 25% (wt/vol or vol/vol) solutions in CDCl<sub>3</sub>, while proton spectra were recorded for 1% solutions in CDCl<sub>3</sub>. Sampling/spectral bandwidth combinations for proton-coupled and proton-decoupled conditions are as follows: <sup>11</sup>B, 16 K/6000 Hz; <sup>13</sup>C, 16 K/5000 Hz; <sup>29</sup>Si, 16 K/5000 Hz; <sup>31</sup>P, 16 K/3000 Hz. Data point resolution based on these sampling conditions indicates a maximum error of approximately  $\pm 0.6$  Hz in values obtained from <sup>11</sup>B, <sup>13</sup>C and <sup>29</sup>Si spectra, and  $\pm 0.4$  Hz in values derived from <sup>31</sup>P spectra, although multiple spectra of the same compound afforded a reproducibility approaching  $\pm 0.2$  Hz for chemical shifts and coupling constants (determined using standard deviation). Chemical shift reference compounds were internal tetramethylsilane (TMS) for <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si, external boron trifluoride etherate for <sup>11</sup>B, and external 85% phosphoric acid for <sup>31</sup>P. External reference materials were contained in coaxial inner cells. Ambient probe temperature was 25°C.

### *Regression analyses*

Regression analyses were performed on Macintosh personal computers using StatWorks and Cricket Graph software packages available from Cricket Software, Inc., Malvern, PA 19355.

## **Results**

Table 1 presents proton and silicon-29 NMR chemical shifts for nine aryltrimethylsilane derivatives. Table 2 contains proton, boron-11, and phosphorus-31 data for five aryl dimethylphosphaneboranes (determinations of  $|^2J(^{31}\text{P}-\text{B}-^1\text{H})|$  couplings, found to range between 11–13 Hz, are unreliable, owing to substantial line broadening caused by the quadrupole moment of boron-11 in both the proton and phosphorus-31 NMR spectra, and are not reported). Table 3 displays carbon-13 chemical shifts, coupling constants, and carbon assignments for both series. NMR data for several aryltrimethylsilanes [1,2,36–52] and aryl dimethylphosphaneboranes [13,34,53] included in this study have been reported previously, and our results are in excellent agreement for determinations in similar solvents. Assignments of aromatic carbon resonances are based upon (1) additivity relationships among the ring carbon chemical shifts, (2) the number of directly attached protons, obtained from off-resonance and DEPT carbon-13 spectra, (3) relative magnitudes of  $|J(^{31}\text{P}-^{13}\text{C})|$  spin–spin coupling constants in the phosphorus–boron compounds, and (4) comparison of chemical shift data with similar information previously

Table 1

Proton and silicon-29 NMR data for aryltrimethylsilanes<sup>a</sup>

X	$\delta$ ( <sup>1</sup> H), Si(CH <sub>3</sub> ) <sub>3</sub> <sup>b</sup>	$\delta$ ( <sup>1</sup> H), X(CH <sub>3</sub> ) <sub>n</sub> <sup>b</sup>	$\delta$ ( <sup>29</sup> Si) <sup>c</sup>
H	0.25 <sup>d</sup>	—	-5.10 <sup>e</sup>
<i>o</i> -CH <sub>3</sub>	0.34 <sup>f</sup>	2.46	-4.42 <sup>g</sup>
2,6-(CH <sub>3</sub> ) <sub>2</sub>	0.36	2.39	-5.31
<i>o</i> -C <sub>2</sub> H <sub>5</sub>	0.27	1.25 <sup>h</sup>	-4.87
<i>o</i> -OCH <sub>3</sub>	0.26 <sup>i</sup>	3.80 <sup>j</sup>	-5.10
2,6-(OCH <sub>3</sub> ) <sub>2</sub>	0.28 <sup>k</sup>	3.80 <sup>l</sup>	-5.10
2,6-(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	0.30	1.34 <sup>m</sup>	-6.75
<i>o</i> -N(CH <sub>3</sub> ) <sub>2</sub>	0.28	2.63	-6.99
<i>o</i> -Cl	0.37	—	-2.33

<sup>a</sup> Positive chemical shift values ( $\delta$ ) are to high frequency of the reference. <sup>b</sup> <sup>1</sup>H chemical shifts, 1% in CDCl<sub>3</sub>, relative to internal TMS ( $\pm 0.005$  ppm). <sup>c</sup> <sup>29</sup>Si chemical shifts, 25% in CDCl<sub>3</sub>, relative to internal TMS ( $\pm 0.03$  ppm). <sup>d</sup> Lit. [1]; lit. [38] -1.17 ppm from internal cyclohexane. <sup>e</sup> Lit. [37,40,45] -4.50 ppm, lit. [41-43,46,51] -5.1 ppm, lit. [49] -4.70 ppm, lit. [36] -4.20 ppm. <sup>f</sup> Lit. [39] 0.05 ppm to high frequency of C<sub>6</sub>H<sub>5</sub>SiMe<sub>3</sub>. <sup>g</sup> Lit. [49] -5.10 ppm, lit. [40] -4.75 ppm. <sup>h</sup>  $\delta$  (<sup>1</sup>H), CH<sub>2</sub> 2.68 ppm. <sup>i</sup> Lit. [27] 0.24 ppm. <sup>j</sup> Lit. [27] 3.7 ppm. <sup>k</sup> Lit. [27] 0.25 ppm. <sup>l</sup> Lit. [27] 3.68 ppm. <sup>m</sup>  $\delta$  (<sup>1</sup>H) OCH<sub>2</sub> 3.89 ppm.

obtained for aromatic derivatives of main group 14 elements. Some of these assignment techniques are illustrated in Figs. 1, 2, which show the proton-coupled <sup>13</sup>C spectrum with full nuclear Overhauser effect (NOE) for 2,6-diethoxyphenyltrimethylsilane, and the proton-decoupled <sup>13</sup>C spectrum for the isoelectronic phosphorus-boron analog. That the P(BH<sub>3</sub>)(CH<sub>3</sub>)<sub>2</sub> group remains intact during synthesis and workup is revealed by the characteristic "doublet of quartets" pattern observed in the proton-coupled boron-11 spectrum (Fig. 3). In general, caution must be exercised in making distinctions between carbon atoms two and three bonds distant from phosphorus solely on the basis of coupling constants, owing to the

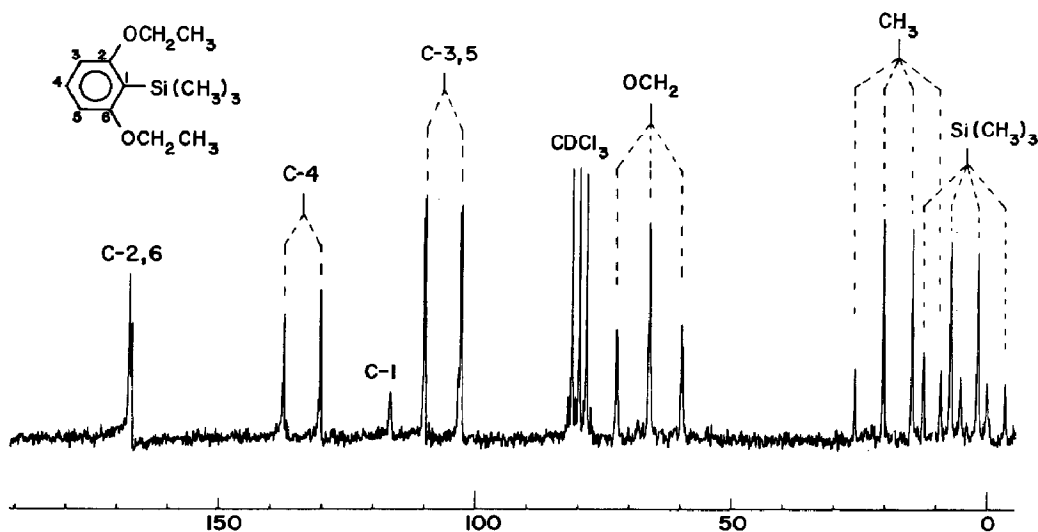


Fig. 1. Proton-coupled natural abundance carbon-13 NMR spectrum of 2,6-diethoxyphenyltrimethylsilane (25% wt/vol in CDCl<sub>3</sub>). This 16 K Fourier transform spectrum required 400 pulses over a 5000 Hz spectral bandwidth, and includes the full nuclear Overhauser effect.

Table 2

Proton, boron-11, and phosphorus-31 NMR data for aryltrimethylphosphaneboranes <sup>a</sup>

X	$\delta(^1\text{H}), \text{P}(\text{CH}_3)_2$ <sup>b</sup>	$\delta(^1\text{H}), \text{BH}_3$ <sup>b</sup>	$\delta(^1\text{H}), \text{X}(\text{CH}_3)_n$ <sup>b</sup>	$\delta(^{11}\text{B})$ <sup>c</sup>	$\delta(^{31}\text{P})$ <sup>d</sup>	$ ^2J(^{31}\text{P}-\text{C}-^1\text{H}) $ <sup>e</sup>	$ ^1J(^{11}\text{B}-^1\text{H}) $ <sup>f</sup>	$ ^1J(^{31}\text{P}-^{11}\text{B}) $ <sup>g</sup>
H	1.55 <sup>h</sup>	0.73 <sup>i</sup>	-	-39.4 <sup>i</sup>	+3.2 <sup>k</sup>	10.3 <sup>j</sup>	96.7 <sup>m</sup>	61.6 <sup>n</sup>
<i>o</i> -OCH <sub>3</sub>	1.59	0.77	3.93	-39.2	+1.4	10.0	95.2	64.5
2,6-(OCH <sub>3</sub> ) <sub>2</sub>	1.68	0.78	3.88	-35.9	-0.1	10.2	93.0	61.5
2,6-(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	1.73	0.78	1.48 <sup>o</sup>	-35.9	-0.3	10.1	95.2	60.1
<i>o</i> -N(CH <sub>3</sub> ) <sub>2</sub>	1.60	0.74	2.61	-37.7	+3.2	10.5	91.6	64.5

<sup>a</sup> Positive chemical shift values ( $\delta$ ) are to high frequency of the reference. <sup>b</sup> <sup>1</sup>H chemical shifts, 1% in CDCl<sub>3</sub>, relative to internal TMS ( $\pm 0.005$  ppm;  $\pm 0.05$  ppm for BH<sub>3</sub>, <sup>c</sup> <sup>11</sup>B chemical shifts, 25% in CDCl<sub>3</sub>, relative to external boron trifluoride etherate ( $\pm 0.02$  ppm). <sup>d</sup> <sup>31</sup>P chemical shifts, 25% in CDCl<sub>3</sub>, relative to external 85% phosphoric acid ( $\pm 0.01$  ppm). <sup>e</sup>  $\pm 0.2$  Hz; from <sup>1</sup>H spectra. <sup>f</sup>  $\pm 0.6$  Hz ( $\pm 1$  Hz for *o*-N(CH<sub>3</sub>)<sub>2</sub>; from proton-coupled <sup>11</sup>B spectra. <sup>g</sup>  $\pm 0.6$  Hz; from proton-decoupled <sup>11</sup>B spectra. <sup>h</sup> Lit. [34] 1.54 ppm (in methylene chloride relative to internal TMS). <sup>i</sup> Lit. [34] 0.73 ppm (in methylene chloride). <sup>j</sup> Lit. [34] 52.5  $\pm$  0.2 ppm (in methylene chloride, relative to external trimethylborate), lit. [35] 55.5 ppm (neat, relative to external trimethylborate). <sup>k</sup> Lit. [53] 3.90 ppm (in acetone-*d*<sub>6</sub>, relative to phosphoric acid). <sup>l</sup> Lit. [34] 10.5 Hz. <sup>m</sup> Lit. [34] 96 Hz and 93  $\pm$  5 Hz, lit. [35] 97 Hz. <sup>n</sup> Lit. [34] 53  $\pm$  5 Hz, lit. [35] 60 Hz. <sup>o</sup>  $\delta(^1\text{H}), \text{OCH}_2$  3.97 ppm.

Table 3

Carbon-13 NMR data <sup>a</sup>

X	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	Si(CH <sub>3</sub> ) <sub>3</sub>	Other
<i>A. Aryltrimethylsilylanes</i>								
H <sup>b</sup>	139.7	133.0	127.6	128.6	127.6	133.0	-0.5 [119.2]	
<i>o</i> -CH <sub>3</sub> <sup>c</sup>	138.4	143.6	129.9	129.3	125.0	134.4	+1.5 [119.0]	CH <sub>3</sub> , 23.0 [125.3]
2,6-(CH <sub>3</sub> ) <sub>2</sub>	136.0	144.0	128.1	128.7	128.1	144.0	+2.6 [119.3]	CH <sub>3</sub> , 24.8 [120.8]

<i>o</i> -OCH <sub>3</sub>	127.9	164.3	109.5	130.7	120.4	134.9	-1.0 [119.3]	OCH <sub>3</sub> , 54.9 [143.1]
2,6-(OCH <sub>3</sub> ) <sub>2</sub>	114.1	165.4	103.5	131.3	103.5	165.4	+1.4 [119.3]	OCH <sub>3</sub> , 55.0 [143.3]
2,6-(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	114.0	164.7	103.7	131.2	103.7	164.7	+1.8 [119.3]	OCH <sub>2</sub> , 63.4 [142.8], CH <sub>3</sub> , 14.8 [126.3]
<i>o</i> -N(CH <sub>3</sub> ) <sub>2</sub>	138.2	161.3	121.6	130.3	125.0	135.2	0.0 [118.8]	N(CH <sub>3</sub> ) <sub>2</sub> , 46.9 [133.7]
<i>o</i> -Cl	141.0	138.7	129.2	130.5	125.9	135.6	-0.8 [119.6]	CH <sub>2</sub> , 29.1 [124.2], CH <sub>3</sub> , 16.5 [121.5]
<i>o</i> -C <sub>2</sub> H <sub>5</sub>	137.6	149.9	128.0	129.3	125.0	134.4	+0.4 [118.1]	
<i>B. Aryldimethylphosphaneboranes</i>								
H	131.2 (55.4)	130.9 (14.0)	128.8 (9.8)	131.1 (1.8)	128.8 (9.8)	130.9 (14.0)	12.9 (39.1) [130.9]	
<i>o</i> -OCH <sub>3</sub>	117.4 (52.8)	161.6 (n.d.)	110.6 (3.6)	133.5 (1.8)	120.9 (12.2)	135.4 (15.8)	11.6 (40.8) [130.6]	OCH <sub>3</sub> , 55.4 [144.6]
2,6-(OCH <sub>3</sub> ) <sub>2</sub>	105.9 (59.8)	162.5 (n.d.)	104.6 (4.3)	133.1 (n.d.)	104.6 (4.3)	162.5 (n.d.)	14.8 (40.9) [131.5]	OCH <sub>3</sub> , 55.7 [144.7]
2,6-(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	105.7 (59.0)	161.8 (n.d.)	104.7 (4.9)	132.8 (n.d.)	104.7 (4.9)	161.8 (n.d.)	15.2 (41.5) [131.1]	OCH <sub>2</sub> , 64.5 [144.0], CH <sub>3</sub> , 14.6 [126.6]
<i>o</i> -N(CH <sub>3</sub> ) <sub>2</sub>	128.2 (54.9)	158.7 (n.d.)	123.7 (5.5)	133.4 (n.d.)	125.7 (11.6)	132.5 (1.8)	12.8 (41.5) [130.6]	N(CH <sub>3</sub> ) <sub>2</sub> , 46.7 [134.6]

<sup>a</sup> Lead numbers are <sup>13</sup>C chemical shifts (δ) relative to internal TMS, 25% in CDCl<sub>3</sub> (±0.03 ppm); positive values are to high frequency of the reference. Numbers in brackets are methyl |*J*(<sup>13</sup>C-<sup>1</sup>H)| coupling constants (±0.6 Hz). Numbers in parentheses are |*J*(<sup>31</sup>P-<sup>13</sup>C)| coupling constants (±0.6 Hz; n.d.: not detected (<1 Hz)). <sup>b</sup> Lit. [43] C(4) only, 128.3 ppm (neat), lit. [44] C(1), 140.4; C(2,6), 133.6; C(3,5), 128.0; C(4), 129.0 ppm (in 20% THF solution), lit. [46] C(1), 139.4; C(2,6), 132.8; C(3,5), 127.3; C(4), 128.3; Si(CH<sub>3</sub>)<sub>3</sub>, -1.0 ppm (neat), lit. [47] Si(CH<sub>3</sub>)<sub>3</sub> only, -0.58 ppm (neat), lit. [48,50] C(1), 140.33; C(2,6), 133.29; C(3,5), 127.77; C(4), 128.79 ppm (in CDCl<sub>3</sub>; these workers also investigated the solvent dependence of the carbon-13 phenyl resonances), lit. [49] C(1), 140.2; C(2,6), 133.6; C(3,5), 128.1; C(4), 129.2; Si(CH<sub>3</sub>)<sub>3</sub>, -0.5 ppm (neat). <sup>c</sup> Lit. [49] C(1), 138.0; C(2), 143.1; C(3), 129.5; C(4), 130.1; C(5), 125.4; C(6), 134.6; Si(CH<sub>3</sub>)<sub>3</sub>, 0.5; CH<sub>3</sub>, 23.4 ppm (neat).

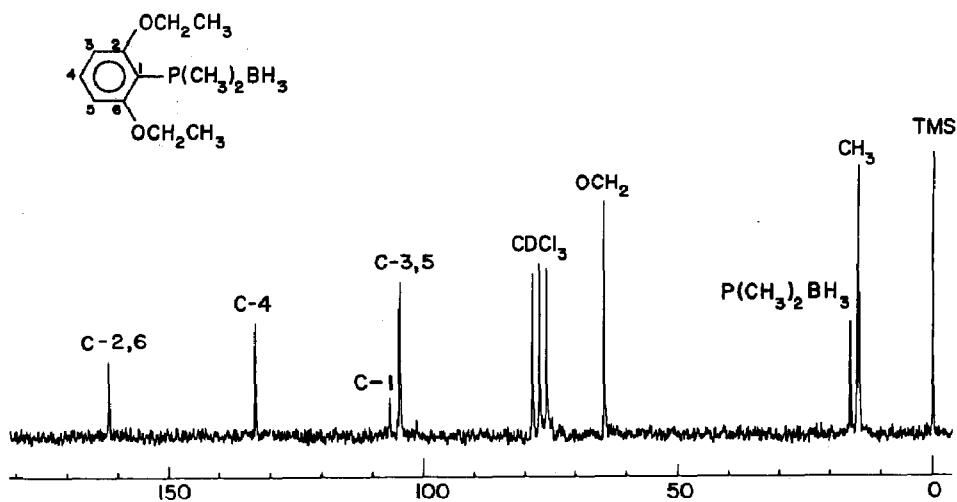


Fig. 2. Proton-decoupled natural abundance carbon-13 NMR spectrum of 2,6-diethoxyphenyldimethylphosphaneborane (25% wt/vol in  $\text{CDCl}_3$ ). This 16 K Fourier transform spectrum required 500 pulses over a 5000 Hz spectral bandwidth.

similar magnitude of  $|^2J(^{31}\text{P}-^{13}\text{C})|$  and  $|^3J(^{31}\text{P}-^{13}\text{C})|$  in these systems (Table 3). It is well-known that  $|^3J|$  is frequently greater than  $|^2J|$  for coupling constants involving carbon-13 in aromatic systems [54]. Additivity data for mono-substituted

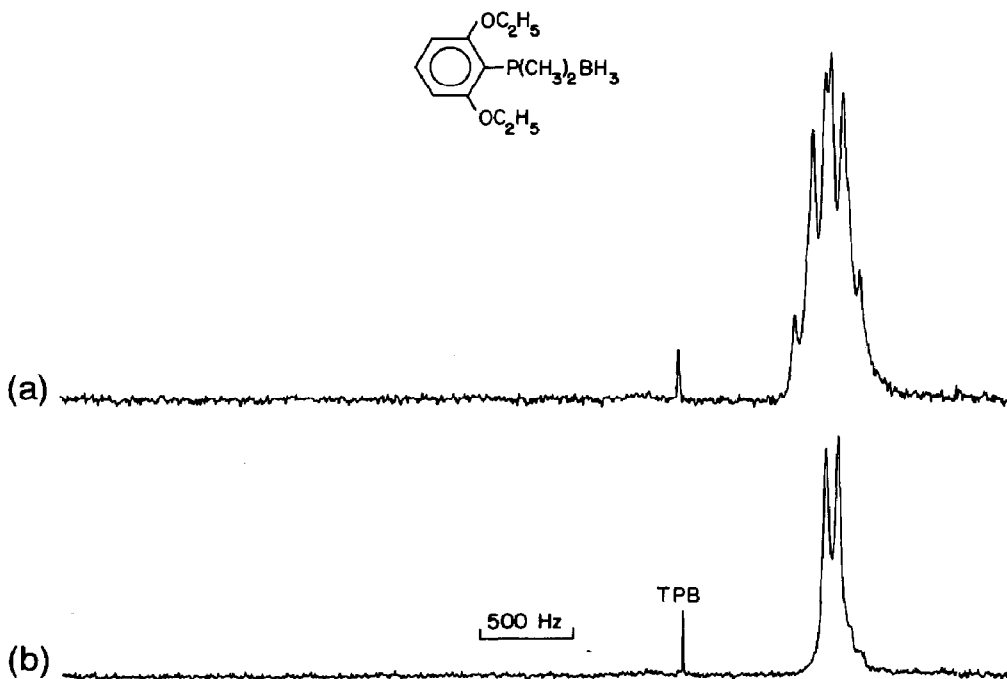


Fig. 3. Natural-abundance boron-11 NMR spectra of 2,6-diethoxyphenyldimethylphosphaneborane (25% wt/vol in  $\text{CDCl}_3$ ). Each 16 K Fourier transform spectrum required 500 pulses over a 6000 Hz bandwidth (TPB: sodium tetraphenylboron). (a) Proton-coupled spectrum with full NOE. (b) Proton-decoupled spectrum.



benzene derivatives used in additivity calculations were taken from the literature [55] and from our earlier studies [2,4,11]. Assignments of the ring carbon atoms in phenyldimethylphosphaneborane itself were made on the basis of phosphorus-carbon coupling constant magnitude, off-resonance and DEPT carbon-13 spectra; these values are: C(1) + 2.7; C(2,6) + 2.4; C(3,5) + 0.3; and C(4) + 2.6 ppm, assigning 128.5 ppm to the carbon-13 chemical shift of benzene. Benzene-based ring carbon chemical shifts for phenyltrimethylsilane, reported by us [2] and confirmed elsewhere [44,46,48–50], are: C(1) + 11.2; C(2,6) + 4.5; C(3,5) – 0.9; C(4) + 0.1 ppm. In contrast to early work on *ortho*- and poly-substituted aromatic systems in which additivity failed to predict shielding effects, there is good qualitative agreement (normally,  $\pm 1$ –4 ppm differences between calculated and observed shifts) in the two sets of derivatives reported here. Simple additivity has also afforded similar good qualitative agreement in assignments of ring carbons in *ortho*-substituted aryltrimethyltins [6], and in six additional series of *ortho*-substituted aromatic compounds [11].

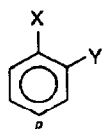
## Discussion

The preparation of the *ortho*- and 2,6-derivatives of both the aryltrimethylsilanes and dimethylphosphaneboranes proceeds smoothly, with higher yields for the former derivatives than for the latter. The previously observed [13] electron-withdrawing effect of the  $\text{P}(\text{BH}_3)(\text{CH}_3)_2$  group does not significantly affect the synthesis of these hindered derivatives.

In order to assess the electronic effect of the  $\text{P}(\text{BH}_3)(\text{CH}_3)_2$  in the *ortho* position, we examined the one-bond methyl  $|J(^{13}\text{C}-^1\text{H})|$  coupling constants of the  $\text{OCH}_3$  group in the anisoles. These coupling constants can be a more reliable indicator of electronic effects than  $^{13}\text{C}$  chemical shifts [11] and, moreover, the anisoles apparently do not suffer from steric inhibition of resonance [56]. The methyl  $|J(^{13}\text{C}-^1\text{H})|$  coupling constants for the *ortho*- and *para*-substituted [13] aryltrimethylphosphaneborane derivatives of anisole are 144.6 and 144.5 Hz, respectively. Thus, even though the  $\text{P}(\text{BH}_3)(\text{CH}_3)_2$  group is closer to the methoxy site in the *ortho* derivative, its overall electronic effect is essentially the same in both positions. Relative to  $|J(^{13}\text{C}-^1\text{H})|$  in anisole itself (143.0 Hz) [1,9,10], these values indicate overall relative electron withdrawal. Other electron-withdrawing groups display coupling constants that reflect similar *ortho* and *para* effects; for example, the methyl  $|J(^{13}\text{C}-^1\text{H})|$  coupling constants in *ortho*- [10] and *para*-nitroanisole [9] are 145.4 and 144.8 Hz, respectively.

The methyl  $|J(^{13}\text{C}-^1\text{H})|$  coupling constants for the  $\text{N}(\text{CH}_3)_2$  group in the dimethylphosphaneborane-substituted *N,N*-dimethylanilines are: *para*, 135.9 [13] and *ortho*, 134.6 Hz. The significantly smaller value for the *ortho* derivative is almost surely a result of steric inhibition of resonance which will decrease donation of electron density from the dimethylamino group into the aromatic ring. The consequent increase in electron density at the nitrogen, relative to the unhindered *para* derivative, produces a decrease in the coupling constant. In the trimethylsilyl-substituted *N,N*-dimethylanilines, there is a similar decrease in coupling constant from *para* (135.2 Hz) [1] to *ortho* (133.7 Hz). The magnitude of both changes suggests that steric inhibition of resonance occurs to approximately the same extent in both systems, and that the effective steric bulk of both  $\text{Si}(\text{CH}_3)_3$  and

Table 4

Carbon-13 chemical shift and  $|^1J(^{13}\text{C}-^1\text{H})|$  coupling constant comparisons

X	Y	$\delta$ (C(p)) (ppm) <sup>a</sup>	$ ^1J(^{13}\text{C}-^1\text{H}) $ (Hz) <sup>b</sup>
CH <sub>3</sub>	H	125.3	125.8
CH <sub>3</sub>	Si(CH <sub>3</sub> ) <sub>3</sub>	125.0	125.3
CH <sub>3</sub>	Sn(CH <sub>3</sub> ) <sub>3</sub>	125.1	125.3
OCH <sub>3</sub>	H	120.5	143.0
OCH <sub>3</sub>	Si(CH <sub>3</sub> ) <sub>3</sub>	120.4	143.1
OCH <sub>3</sub>	P(BH <sub>3</sub> )(CH <sub>3</sub> ) <sub>2</sub>	120.9	144.6
OCH <sub>3</sub>	Sn(CH <sub>3</sub> ) <sub>3</sub>	121.2	141.9
N(CH <sub>3</sub> ) <sub>2</sub>	H	116.7	134.5
N(CH <sub>3</sub> ) <sub>2</sub>	Si(CH <sub>3</sub> ) <sub>3</sub>	125.0	133.7
N(CH <sub>3</sub> ) <sub>2</sub>	P(BH <sub>3</sub> )(CH <sub>3</sub> ) <sub>2</sub>	125.7	134.6
N(CH <sub>3</sub> ) <sub>2</sub>	Sn(CH <sub>3</sub> ) <sub>3</sub>	125.3	133.6

<sup>a</sup> Carbon-13 chemical shifts for the monosubstituted benzenes are from ref. 11; data for aryltrimethylstannanes are from ref. 6. <sup>b</sup> Carbon-13 coupling constants to X-methyl protons. Data for the monosubstituted benzenes are from refs. 1, 9–11, 56; data for aryltrimethylstannanes are from ref. 6.

P(BH<sub>3</sub>)(CH<sub>3</sub>)<sub>2</sub> groups is similar. The trend in coupling constants in these same two *para*- and *ortho*-N(CH<sub>3</sub>)<sub>2</sub> derivatives is supported by the <sup>13</sup>C chemical shift of the C(5) ring carbon, a site *para* to the N(CH<sub>3</sub>)<sub>2</sub> substituent in the *ortho* derivative, and C(4), the corresponding site in the *para* derivative. C(5) in the *ortho* derivative is deshielded by 12.7 ppm relative to C(4), the analogous ring carbon in the *para* derivative, after taking into account the small effect (*ipso* + 2.7; *meta* + 0.3 ppm) of the P(BH<sub>3</sub>)(CH<sub>3</sub>)<sub>2</sub> group. For the anisoles, a similar comparison reveals only a modest 1.7 ppm deshielding of the analogous ring carbons, thereby indicating little or no steric inhibition of resonance. For the trimethylsilyl-substituted *N,N*-dimethylanilines, the deshielding of C(5) in the *ortho* derivative (125.0 ppm), relative to C(4) in the *para* (125.2 ppm) [2], after correcting for the Si(CH<sub>3</sub>)<sub>3</sub> group (*ipso* + 11.2; *meta* - 0.9 ppm), is 11.9 ppm.

Deshieldings in aromatic ring carbon atoms *para* to conjugating substituents have previously been interpreted in terms of steric inhibition of resonance. For substituted *N,N*-dimethylanilines [56–57] and nitrobenzenes [56,58], deshieldings for carbon C(5) relative to the carbon-13 shift of the corresponding position in *N,N*-dimethylaniline itself (i.e., C(4)) are consistent with a decrease in the contribution from the nearly planar hybrid structure expected in the unhindered case, and are shown in Table 4.

In order to assess the relative contributions of inductive and resonance effects to the overall electron-withdrawing nature of the P(BH<sub>3</sub>)(CH<sub>3</sub>)<sub>2</sub> group, we used the multiple regression equations for the dual substituent ( $\sigma_I$  and  $\sigma_R^0$ ) analysis of methyl  $|^1J(^{13}\text{C}-^1\text{H})|$  coupling constants and <sup>13</sup>C chemical shifts of C(1) ring carbons in *para*-substituted *t*-butylbenzenes [2], toluenes [11], anisoles [11], and benzenes [11,59], to obtain values for  $\sigma_I$  and  $\sigma_R^0$ . For example, for the ring carbon

atoms carrying the *t*-butyl group in a series of substituted *t*-butylbenzenes, the carbon-13 chemical shift correlation available from our previous study [2] is  $\delta(^{13}\text{C}(1)) = 7.58\sigma_{\text{I}} + 22.0\sigma_{\text{R}}^0 + 150.4$ . The three remaining equations are:  $|^1J(^{13}\text{C}-^1\text{H})| = 1.94\sigma_{\text{I}} + 1.30\sigma_{\text{R}}^0 + 125.8$ , from regression analysis of methyl  $|^1J(^{13}\text{C}-^1\text{H})|$  coupling constants in substituted toluenes [11];  $|^1J(^{13}\text{C}-^1\text{H})| = 1.73\sigma_{\text{I}} + 2.25\sigma_{\text{R}}^0 + 143.2$ , from regression analysis of methyl  $|^1J(^{13}\text{C}-^1\text{H})|$  coupling constants in substituted anisoles [11]; and  $\delta(^{13}\text{C}(1)) = 5.49\sigma_{\text{I}} + 20.4\sigma_{\text{R}}^0 + 127.8$ , from regression analysis of  $^{13}\text{C}$  chemical shifts of C(1) ring carbons in substituted benzenes [11,59]. These four equations are all of the form  $Z = A\sigma_{\text{I}} + B\sigma_{\text{R}}^0 + C$ , where  $Z = J$  or  $\delta$ , and can be solved simultaneously by multiple regression, to yield values of 0.41 for  $\sigma_{\text{I}}$  and 0.04 for  $\sigma_{\text{R}}^0$ . When these constants are used in the multiple regression equations for *ortho*-substituted anisoles [11], calculated values of 55.8 ppm for the  $^{13}\text{C}$  chemical shift and 144.4 Hz for the methyl  $|^1J(^{13}\text{C}-^1\text{H})|$  coupling constant of the  $\text{OCH}_3$  group are obtained for *ortho*-methoxyphenyldimethylphosphaneborane, numbers that are in good agreement with the experimental values of 55.4 ppm and 144.6 Hz determined in this study. The  $^{13}\text{C}$  chemical shift calculated for the ring carbon *para* to the  $\text{P}(\text{BH}_3)(\text{CH}_3)_2$  group in this same derivative is 132.4 ppm, which is also in good agreement with the 133.5 ppm value recorded for C(4) in this study. According to these  $\sigma$  constants, the  $\text{P}(\text{BH}_3)(\text{CH}_3)_2$  group acts primarily through the inductive effect, presumably owing to the formal positive charge on phosphorus, rather than by donation of  $\pi$ -electron density from the ring to  $3d$ -orbitals on phosphorus.

The trends in the chemical shifts and coupling constants for the two series of compounds, the aryltrimethylsilanes and aryldimethylphosphaneboranes, can also be compared by correlation analysis. When these values are correlated for the nine trimethylsilane derivatives, no correlations with correlation coefficients greater than 0.90 are obtained. For the five aryldimethylphosphaneboranes, however, there are several significant correlations and trends. A general trend in chemical shifts is revealed by comparing the 2,6-dialkoxy derivatives with the unsubstituted parent. This substitution decreases the C(1) carbon-13 and phosphorus-31 chemical shifts, but increases the boron-11 and carbon-13 chemical shifts of the  $\text{P}(\text{BH}_3)(\text{CH}_3)_2$  group. The decrease in C(1) carbon-13 and phosphorus-31 chemical shifts can be attributed to an increase in electron density at these sites due to the resonance effects of the alkoxy groups. The increase in the boron-11 and carbon-13 chemical shifts of the groups attached to phosphorus is consistent with the redistribution of electron density in adducts according to Gutmann's rules [60]. The correlation coefficient for the correlation of phosphorus-31 chemical shifts vs. C(1) carbon-13 chemical shifts is 0.99.

## Acknowledgements

We are indebted to the donors of the Petroleum Research Fund, administered by the American Chemical Society (C.D.S. and C.H.Y.), and the National Science Foundation (C.H.Y.) for partial support of this research. We also thank Strem Chemicals Inc. for preparing chlorodimethylphosphaneborane. Thomas A. Young assisted in preparing some of the compounds. This manuscript is dedicated to the memory of a teacher, scholar and friend to two of us, J.J. Zuckerman.

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