Nuclear Magnetic Resonance Spectroscopic Study of Substituent Effect Transmission in Aryldimethylphosphane–Boranes

Joseph A. Albanese, Denise G. Kreider, and Charles D. Schaeffer, Jr.*

Department of Chemistry, Elizabethtown College, Elizabethtown, Pennsylvania 17022

Claude H. Yoder and Marjorie S. Samples

Department of Chemistry, Franklin & Marshall College, Lancaster, Pennsylvania 17604

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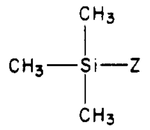
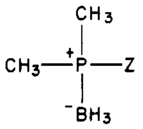
Proton, carbon-13, phosphorus-31, and boron-11 NMR coupling constants and chemical shifts are reported for seven meta- and para-substituted aryldimethylphosphane–boranes, $XC_6H_4P(CH_3)_2{\cdot}BH_3$. These data have been correlated with Hammett σ constants and with the substituent constants σ_I and $\sigma_R{}^\circ$. Parameters of the regression equations suggest that the $P(CH_3)_2BH_3$ substituent functions as an electron-withdrawing group and that in simple aromatic systems it is probably a better π acceptor than the isoelectronic $Si(CH_3)_3$ group. Values of C-4 ring carbon chemical shifts in p-XC_6H_4Y, where Y = $C(CH_3)_3$, $Si(CH_3)_3$, and $P(CH_3)_2BH_3$, are consistent with migration of π-electron density to the $P(CH_3)_2BH_3$ group, particularly when X can release electron density by resonance.

Introduction

Trimethylsilyl is without doubt the most ubiquitous substituent group in organosilicon chemistry, and it serves as the backbone of a vast number of stable compounds, many of which are of central industrial and commericial importance. The isoelectronic principle[1] suggests that dimethylphosphane–borane, $(H_3C)_2(H_3B)P$ (borane–dimethylphosphanyl), may display similar reactivity and stabilizing influence, although the increased polarity of the B–P bond suggested by the Lewis formula may forecast some differences in both physical and chemical properties between isoelectronic counterparts. For example, studies of dimethylphosphane–borane analogues of trimethylsilyl amides



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-Z$$



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle {}^-BH_3}{\overset{+}{P}}}-Z$$

reveal similar structure and rotational populations, although lower rotational barriers are detected for the formamide derivative of the phosphane–borane[2]. The chemistry of dimethylphosphane–borane, nevertheless, remains largely unexplored. Prior to the pioneering work of Schmidbaur[3,4] on the preparation of chlorodimethylphosphane–borane and related prototype derivatives, evidence for only two derivatives appeared in the literature.[5,6]

Our current investigations of the syntheses and NMR spectra of aryldimethylphosphane–boranes stem from our continued interest in the application of multinuclear magnetic resonance spectroscopy to the analysis of substituent effect transmission in aromatic systems.[7–18] The availability of NMR data for substituted aryltrimethylsilanes[9,19–28] affords a rare opportunity for the comparison of substituent effects in strictly isoelectronic aromatic systems.

Experimental Section

Compounds. Substituted aryldimethylphosphane–boranes were obtained in 50–75% yields by reaction of chlorodimethylphosphane–borane with the appropriate Grignard reagents (from aryl bromides) in anhydrous tetrahydrofuran (distilled under argon from calcium hydride) under an argon or nitrogen atmosphere, followed by hydrolysis, extraction of the aqueous phase with diethyl ether, and vacuum distillation or recrystallization from absolute ethanol. Vacuum distillations were performed on a 12-in. jacketed column packed with glass beads or helices and surmounted with an Ace Mini-Lab distillation head. Melting points were obtained on a Thomas-Hoover melting point apparatus and

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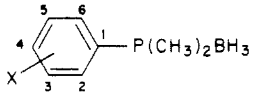
Table I. Proton, Boron-11, and Phosphorus-31 NMR Data[a]

X	^{1}H, P(CH$_3$)$_2$[b]	^{1}H, X(CH$_3$)$_n$[b]	^{11}B[c]	^{31}P[d]	$\vert ^2J(^{31}P–C–H)\vert$[e]	$\vert ^1J(^{11}B–^1H)\vert$[f]	$\vert ^1J(^{31}P–^{11}B)\vert$[g]
H	1.55		−39.4	+3.2	10.3	96.7	61.6
p-Cl	1.56		−39.4	+3.6	10.2	96.5	58.6
p-CH$_3$	1.55	2.39	−39.4	+2.1	10.3	95.0	61.6
p-OCH$_3$	1.54	3.84	−39.4	+1.3	10.4	93.8	61.5
p-N(CH$_3$)$_2$	1.50	3.00	−39.4	−0.5	10.4	93.8	64.5
p-*t*-C$_4$H$_9$	1.56	1.33	−39.4	+1.7	10.5	95.2	60.1
m-OCH$_3$	1.56	3.85	−39.4	+3.9	10.3	95.0	60.1

[a] Positive chemical shift values (δ) are to high frequency of the reference. [b] ^{1}H chemical shifts, 1% in CDCl$_3$, relative to internal Me$_4$Si (±0.01 ppm). [c] ^{11}B chemical shifts, 25% in CDCl$_3$, relative to external boron trifluoride etherate (±0.1 ppm). [d] ^{31}P chemical shifts, 25% in CDCl$_3$, relative to external 85% phosphoric acid (±0.1 ppm). [e] ±0.2 Hz; from ^{1}H spectra. [f] ±0.2 Hz; from proton-coupled ^{11}B spectra. [g] ±0.2 Hz; from proton-decoupled ^{11}B spectra.

Table II. Carbon-13 NMR Data[a]



X	C-1	C-2	C-3	C-4	C-5	C-6	P(CH$_3$)$_2$	other
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]	
p-Cl	129.5 (54.9)	132.3 (10.4)	129.1 (10.4)	137.7 (3.0)	129.1 (10.4)	132.3 (10.4)	12.9 (38.4) [130.6]	
p-CH$_3$	127.4 (56.8)	130.8 (9.8)	129.5 (10.4)	141.5 (2.4)	130.8 (9.8)	129.5 (10.4)	13.1 (39.1) [130.4]	CH$_3$, 21.4 [126.6]
p-OCH$_3$	121.6 (59.7)	132.6 (11.0)	114.4 (11.0)	162.0 (1.8)	114.4 (11.0)	132.6 (11.0)	13.3 (39.7) [130.1]	OCH$_3$, 55.3 [144.5]
p-N(CH$_3$)$_2$	114.7 (63.5)	132.1 (10.4)	111.8 (11.0)	152.1 (1.8)	111.8 (11.0)	132.1 (10.4)	13.6 (39.7) [130.3]	N(CH$_3$)$_2$, 40.0 [135.9]
p-*t*-C$_4$H$_9$	127.4 (56.8)	130.7 (9.8)	125.8 (10.4)	154.6 (2.4)	125.8 (10.4)	130.7 (9.8)	13.1 (39.1) [130.7]	C-α, 34.8; CH$_3$, 31.1 [125.7]
m-OCH$_3$	132.4 (54.3)	116.5 (11.6)	159.6 (12.2)	116.6 (2.4)	130.1 (11.6)	122.7 (8.5)	12.9 (39.1) [130.5]	OCH$_3$, 55.3

[a] Lead numbers are ^{13}C chemical shifts δ relative to internal Me$_4$Si, 25% in CDCl$_3$ (±0.1 ppm). Numbers in parentheses are $|J(^{31}P–^{13}C)|$ coupling constants (±0.2 Hz). Numbers in brackets are methyl $|^1J(^{13}C–^1H)|$ coupling constants (±0.2 Hz).

are uncorrected. Purity of all compounds probably exceeded 95%, as indicated by the absence of spurious signals in the proton and carbon-13 NMR spectra. Carbon and hydrogen combustion analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY 11377. Chlorodimethylphosphane–borane, prepared by the method of Schmidbaur,[3] was purchased as a 1.0 M solution in tetrahydrofuran from Strem Chemicals Inc., Newburyport, MA 01950, although on several occasions, we performed Schmidbaur's synthesis (from the highly pyrophoric chlorodimethylphosphine[29] and borane/tetrahydrofuran adduct). Boiling and melting points for the seven derivatives are as follows: H, bp 77–78 °C(0.03 mm); *p*-Cl, bp 118–120 °C (0.03 mm); *p*-CH$_3$, bp 124–126 °C (0.08 mm); *m*-OCH$_3$, bp 132–134 °C (0.03 mm); *p*-OCH$_3$, bp 135–137 °C (0.03 mm), mp 70–73 °C; *p*-*t*-C$_4$H$_9$, mp 101–103 °C; *p*-N(CH$_3$)$_2$, mp 111–113 °C. A representative preparation follows.

(4-*tert*-Butylphenyl)dimethylphosphane–borane was produced in 75% yield by reaction of *p*-bromo-*tert*-butylbenzene (21.4 g, 0.10 mol) with magnesium turnings (2.5 g, 0.10 mol) in anhydrous tetrahydrofuran in the presence of a catalytic amount of iodine (0.1 g), followed by a 1-h reflux period with constant magnetic stirring. The solution was cooled to ice water temperature, and a 1.0 M tetrahydrofuran solution of chlorodimethylphosphane–borane (114 mL, 0.10 mol) was added dropwise to the Grignard reagent during the next hour. The reaction mixture was heated to reflux for 2 h, and it then was hydrolyzed with ice water. After extraction (three portions of diethyl ether), the combined extracts were dried over anhydrous magnesium sulfate. Solvent was removed on a rotary evaporator, and the resulting oily pale yellow solid was recrystallized three times from absolute ethanol, to afford 15 g of white needles: mp 101–103 °C; ^{1}H NMR (CDCl$_3$, 60 MHz) δ 7.4–7.8 (m, 4 H, C$_6$H$_4$), 1.56 (d, 6 H, J_{HP} = 10.5 Hz, PMe$_2$), 1.33 (s, 9 H, *t*-C$_4$H$_9$), 1.30 (br qd, 3 H, J_{BH} = 95 Hz, J_{HP} = 12 Hz, BH$_3$). Anal. Calcd for C$_{12}$H$_{22}$BP: C, 69.26; H, 10.66. Found: C, 69.15; H, 10.94.

NMR Parameters. Proton spectra for compound identification were recorded in the continuous wave mode on a Varian EM-360A spectrometer, operating at 60 MHz. All other spectra were obtained in the Fourier transform mode on a JEOL FX90-Q spectrometer with Omniprobe and JEOL pulse and data system. Operating frequencies were 89.6 MHz (^{1}H), 22.5 MHz (^{13}C), 28.7 MHz (^{11}B), and 36.2 MHz (^{31}P). Samples were contained in 10-mm o.d. tubes. Spectra were normally recorded as 25% (w/v or v/v) solutions in CDCl$_3$ containing five drops of Me$_4$Si, while proton spectra used in the correlations were recorded for 1% solutions in CDCl$_3$. Sampling/spectral bandwidth combinations for fully proton-coupled and -decoupled conditions are as follows: ^{1}H, 16K/1000 Hz; ^{13}C, 16K/5000 Hz; ^{11}B, 8K/6000 Hz; ^{13}P, 16K/2800 Hz. Chemical shift reference for ^{11}B was boron trifluoride etherate and for ^{31}P was 85% phosphoric acid. The external reference materials for these two nuclei were contained in coaxial inner cells. Ambient probe temperature was 25 °C. The MINITAB program was used to perform all regression analyses of NMR data.

Results and Discussion

Table I presents proton, boron-11 and phosphorus-31 NMR chemical shifts and coupling constants for the seven

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Table III. Chemical Shift (δ) and Coupling Constant (Hz) Correlations[a]

parameter	ρ[c]	C[c]	r[d]
A. Correlations with σ[b]			
^1H, $P(CH_3)_2$	0.057	1.55	0.92
^{13}C, $P(CH_3)_2$	−0.73	13.0	0.96
^{13}C, C-1	16.7	129.0	0.93
^{31}P	4.33	2.88	0.97
$\lvert{}^1J(^{31}P-^{11}B)\rvert$	−4.8	60.4	0.90
$\lvert{}^1J(^{31}P-^{13}C)\rvert$, C-1	−9.0	55.9	0.96
B. Correlations with σ_I and $\sigma_R{}^\circ$[e]			
^{13}C, C-1	13.3, 31.8	131.2	0.99
^{13}C, C-2	3.5, −3.1	130.2	0.89
^{13}C, C-3	10.7, 41.2	132.2	0.95
^{13}C, C-4	−5.6, −50.1	132.6	0.88

[a] Coupling constants in Hz; chemical shifts in ppm. [b] Hammett σ constants were taken from ref 32. [c] Parameters of the equation: $\delta(J) = \rho\sigma + C$. [d] Correlation coefficient. [e] Substituent constants were taken from ref 33. The first ρ value is for σ_I; the second is for $\sigma_R{}^\circ$.

derivatives. Table II contains all carbon-13 NMR data and ring carbon assignments. Assignments of aromatic carbon resonances are based upon (1) additivity relationships among the ring carbon chemical shifts, (2) information obtained from off-resonance carbon-13 spectra, (3) relative magnitudes of $|J(^{31}P-^{13}C)|$ spin–spin coupling constants, and (4) comparison of shifts with data previously obtained for aromatic derivatives of main group 14 elements.[13,19] Data for monosubstituted benzene derivatives used for additivity calculations were taken from the literature.[30,31] Ring carbons in phenyldimethylphosphane–borane were assigned on the basis of phosphorus–carbon coupling constant magnitude and off-resonance spectral multiplicities. 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 similar magnitude of $|^2J(^{31}P-^{13}C)|$ and $|^3J(^{31}P-^{13}C)|$ in these systems (Table II). Also, it is well-known that $|^2J| < |^3J|$ in other aromatic compounds.[13,16,18] The substituent effects on the ring carbons of phenyldimethylphosphane–borane are as follows: C-1, +2.7; C-2,6, +2.4; C-3,5, +0.3; and C-4, +2.6 ppm, assuming a value of 128.5 ppm for the carbon-13 chemical shift of benzene. Agreement for additivity calculations (i.e., calculated vs. observed shifts) in these derivatives is frequently within ±2 ppm.

Correlations of all chemical shifts and spin–spin coupling constants with the substituent constants σ, σ_I, σ_R, σ^*, F, and R were attempted.[32,33] Table III contains the correlation parameters for those chemical shifts and coupling constants that correlate strongly ($r > 0.90$) with one or more of the substituent constants. The normal Hammett constants (σ_p, σ_m) correlated significantly more strongly than other constants, and two parameter (σ_I, σ_R and F, R) correlations are not significantly better. It is clear from Table III that the chemical shift and direct coupling constants involving the central atom of the $P(CH_3)_2BH_3$ group all correlate with σ. Other good correlations involve the carbon-13 and proton chemical shifts of the methyl groups attached to phosphorus and the C-1 ring carbon-13 chemical shifts. The ring carbon shifts were also correlated with Taft's σ_I and $\sigma_R{}^\circ$ values to allow comparison with *tert*-butyl and trimethylsilyl aromatics previously studied.[7,9,19] These correlations are also given in Table III. Similar correlations of ring and attached atom chemical shifts and coupling constants have been amply documented.[34–36]

Previously established correlations of $|^1J(^{13}C-^1H)|$ coupling constants and proton chemical shifts with Hammett σ constants in substituted *N,N*-dimethylanilines, anisoles, toluenes, and *tert*-butylbenzene[7] were used to determine σ constants for the $P(CH_3)_2BH_3$ group. When the least-squares parameters for the anisoles and *N,N*-dimethylanilines are used, the σ constants derived from both $\delta(^1H)$ and $|^1J(^{13}C-^1H)|$ correlations[7] vary from 0.7 to 1.1, with an average value of 0.8. This is comparable to the m-NO_2 substituent.[7] When substituted toluenes and *tert*-butylbenzenes are used to estimate σ, the values vary between 0.1 and 0.4, with an average of 0.3. Thus, the derived values of σ are dependent upon the nature of the group in the para position but are in all cases positive. It is reasonable to conclude, therefore, that the $P(CH_3)_2BH_3$ group is electron withdrawing and that resonance interactions (with systems containing substituents that release electron density by resonance) occur which increase the ability of the group to remove electron density from the aromatic ring. This resonance interaction must involve $\pi \rightarrow d$ interactions that are presumably enhanced by the formal positive charge on phosphorus.

Further evidence for the pronounced electron-withdrawing ability of the $P(CH_3)_2BH_3$ group comes from a comparison of para (C-4) carbon-13 chemical shifts in members of the series p-XC_6H_4Y, where Y = $C(CH_3)_3$, $Si(CH_3)_3$, $Ge(CH_3)_3$, $Sn(CH_3)_3$, and $P(CH_3)_2BH_3$. Although we illustrate this for two substituents, the chemical shift of the ring carbon atom attached directly to the substituent group X is greatest in the $P(CH_3)_2BH_3$ analogues in the cases examined. For example, when Z = p-OCH_3, the C-4 shifts for the five members of this series are 157.5, 160.5, 160.1, 160.3, and 162.0 ppm,[19] respectively. When X is p-CH_3, the C-4 shifts are 134.1, 137.9, 137.3, 137.3, and 141.5 ppm,[19,37] respectively. The shift of C-4 is known to be sensitive to the electronic effect of the substituent, and, since phosphorus has an electronegativity between that of carbon and silicon, the high-frequency shift of C-4 in the $P(CH_3)_2BH_3$ derivatives is probably a result of migration of π-electron density to the $P(CH_3)_2BH_3$ group. Moreover, this group is almost certainly a better π acceptor than the isoelectronic $Si(CH_3)_3$ group.

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Registry No. $PhP(CH_2)_2BH_3$, 35512-87-9; p-$ClC_6H_4P(CH_2)_2BH_3$, 96292-74-9; p-$CH_3C_6H_4P(CH_2)_2BH_3$, 96292-75-0; p-$OCH_3C_6H_4P(CH_2)_2BH_3$, 96292-76-1; p-$N(CH_3)_2C_6H_4P(CH_2)_2BH_3$, 96292-77-2; p-t-$C_4H_9C_6H_4P(CH_2)_2BH_3$, 96292-78-3; m-$OCH_3C_6H_4P(CH_2)_2BH_3$, 96292-79-4; PhBr, 108-86-1; p-ClC_6H_4Br, 106-39-8; p-$CH_3C_6H_4Br$, 106-38-7; p-$OCH_3C_6H_4Br$, 104-92-7; p-$N(CH_3)_2C_6H_4Br$, 586-77-6; p-t-$C_4H_9C_6H_4Br$, 3972-65-4; m-$OCH_3C_6H_4Br$, 2398-37-0; $Cl(CH_3)_2PBH_3$, 54220-72-3.

Comparison of the Ease of Thermolysis of Ortho-Substituted Phenyl Azides Having α,β or β,γ Imine Functions[1]

Peter A. S. Smith,* Gregory F. Budde, and Shang-Shing P. Chou

Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109

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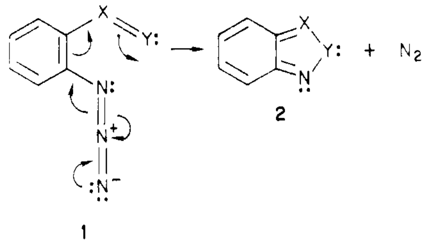
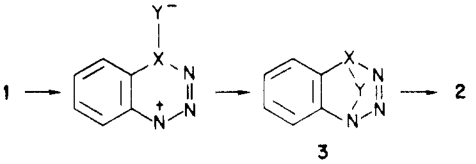
o-Azidobenzaldehyde benzylimine (**7**) thermolyzes 34 times faster than phenyl azide and 1.6 times faster than p-chlorobenzaldehyde o-azidoanil (**8**), whereas benzaldehyde (o-azidobenzyl)imine (**9**) and acetophenone (o-azidobenzyl)imines (**10a–e**) show little or no rate enhancement over phenyl azide. An electrocyclic mechanism can account for the rates of **7** and **8** relative to each other but not of **8** relative to phenyl azide; **9** and **10a–e** appear to thermolyze by nitrene formation, even though a mechanism through intramolecular cycloaddition may in principle be available. A mechanism based on electrostatic effects in a dipolar transition state can correlate the effects of different types of α,β-unsaturated ortho substituents.

Phenyl azides without ortho substituents decompose with unimolecular kinetics in the temperature range 140–180 °C to form nitrogen and products derived from further reactions of initially formed nitrene.[2–5] Activation energies are generally high (30–40 kcal/mol). The presence of almost any substituent in an ortho position causes some increase in rate of thermolysis (e.g., the ratio of rates for o-tolyl and phenyl azides is 1.27), but where the substituent is α,β-unsaturated, thermolysis is faster still and requires much lower temperatures[2–7] (50–110 °C) and activation energies are lower (ca. 22–27 kcal/mol). These facts were explained for o-nitrophenyl azide by the concept of a cyclic transition state for a concerted process in which the nitro group assists in the fragmentation of the azido group.[8–10] Dyall and Kemp[11] generalized this concept as shown in eq 1.



(1)

An alternative mechanism proposed by Hall, Behr, and Reed in 1974 consists of 1,3-cycloaddition of the azido group to the unsaturated ortho substitutent as a rate-limiting step, followed by extrusion of nitrogen from the resulting heterocycle (eq 2). These two mechanisms have engendered much experimentation and lively debate.[4,15–19]



(2)

A third mechanism has recently been proposed[18] in order to account for the sequence of accelerating effects with different ortho substituents, which has a pronounced gradient: ArN=N > O=N(O) > O=C(R) > R_2C=C(R). This mechanism assumes that conjugative charge separation contributes more to the structure of phenylnitrene than to the corresponding azide. Although it has a close relationship to the electrocyclic mechanism, it differs from it in an important respect, for in the latter mechanism, as viewed by Dyall,[4,14,16,19] "the driving force is provided by the delocalization energy of the new heterocycle which is partly formed in the transition state". In phenylnitrenes with an interactive substituent in the ortho position, a

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(1) Taken in part from the doctoral dissertation of S.-S.P.C. and in part from the Senior Honors thesis of G.F.B. Presented in part at the Second Chemical Congress on the North American Continent, Las Vegas, NV, Aug, 1980.

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