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P versus C Protonation

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The Low Basicity of Phosphabenzenes: First Examples of Protonation, Alkylation, and Silylation Reactions**

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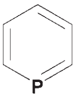
Dedicated to Professor Gottfried Märkl

Phosphabenzenes are dramatically weak bases and poor nucleophiles compared to N-aromatic compounds such as pyridine.[1] This situation reflects a much higher degree of *s* character in the heteroatom lone pair: 64 % on P in λ^3-phosphinine **1** versus 29 % on N in pyridine **2**.[2]



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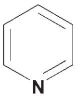

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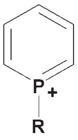

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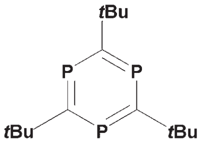
The gas-phase proton affinity of **1** (195.8 kcal. mol^{-1}) is closer to that of benzene (182.7 kcal mol^{-1}) than to pyridine (219.4 kcal mol^{-1}).[3] As a consequence, phosphabenzenes have not been protonated or electrophilically alkylated in condensed media, even though the anticipated cationic products of type **3** are known as stable entities. Ring-substituted examples of type **3** cations have been produced by halide abstraction from λ^5-aryl- or alkyl-halophosphinines with Lewis acids.[4,5] We now show that protonation, alkylation, and trialkylsilylation of phosphabenzenes can be achieved by exploiting the "strong yet gentle" characteristics of electrophilic reagents based on carborane anions.[6] The phosphabenzene of choice for this work is 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene **4** because of its solubility and synthetic accessibility.[7] We also report on the protonation chemistry of the structurally related 2,4,6-tri-*tert*-butyl-1-phosphabenzene **5**.



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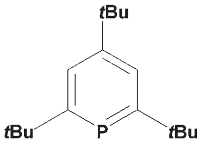

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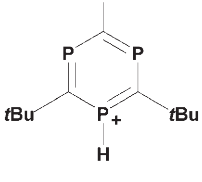
^{31}P NMR spectroscopy indicates that **4** ($\delta = 233.0$ ppm) undergoes immediate reaction with one equivalent of triflic acid in CD_2Cl_2. However, the product decomposes before it can be isolated and fully characterized.[8] Carborane acids, $H(CHB_{11}R_5X_6)$ (R = Me, Cl; X = Cl, Br, I), are stronger acids than triflic acid but, because carborane anions are less nucleophilic than triflate anion, they are a better choice for the protonation of delicate molecules.[6] When $H(CHB_{11}Me_5Br_6)$ is generated in situ by the reaction of $Et_3Si(CHB_{11}Me_5Br_6)$ with triflic acid and treated with **4** in benzene solution, a white precipitate forms immediately.[9] As discussed below, NMR spectroscopy and X-ray structural analysis show this to be the product of simple protonation at a phosphorus atom, forming $[H(P_3C_3tBu_3)][CHB_{11}Me_5Br_6]$ (**6**). Parallel results were obtained with $[CHB_{11}Cl_{11}]^-$ as the counterion.



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The protonation of **4** at P rather than C was anticipated by density functional theory (DFT) calculations which find protonation at phosphorus to be 40 kJ mol^{-1} more exothermic in spite of the ring π electrons forming the HOMO of **4**.[10] The identifying ^{31}P NMR characteristics of **6** are a doublet at $\delta = 304.4$ ppm ($^2J_{PP} = 49$ Hz) and a doublet of triplets at $\delta = 85.1$ ppm ($^2J_{PP} = 49$ Hz, $^1J_{PH} = 595$ Hz). In the ^{1}H NMR spectrum, the signal for the acidic proton appears appropriately downfield at $\delta = 9.46$ ppm with the same large $^1J_{PH}$ coupling constant (595 Hz) observed in the ^{31}P spectrum, confirming that the site of protonation is P.

The single-crystal X-ray structure of **6** confirms that a P atom is protonated (Figure 1).[11] Ion pairing of the cation with

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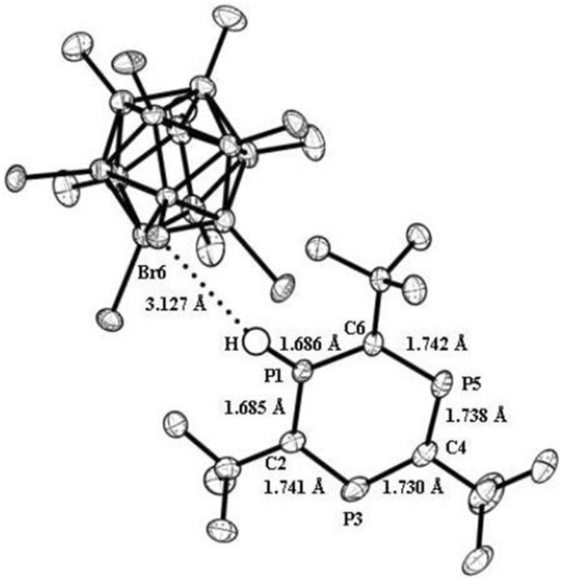
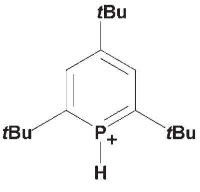


Figure 1. X-ray structure of [H(P$_3$C$_3$*t*Bu$_3$)][CHB$_{11}$Me$_5$Br$_6$] (**6**). Thermal ellipsoids are shown at 50% probability level.

the carborane anion through the acidic proton (H$^+\cdots$Br 3.13 Å) is observed, a feature common to carborane salts of highly acidic cations, such as arenium ions[12] and *tert*-butyl cation.[13] The major structural effect of protonation on the phosphabenzene is a shortening of the P–C bonds adjacent to the site of protonation, indicative of developing P^V character at the phosphininium center. The same effect was observed in the structurally related methyl phosphininium ion reported by Le Floch et al.[5] In **6** these two bonds average 1.686(2) Å; whereas those remote from the site of protonation average 1.738(3) Å, close to those in unprotonated **4** (1.727(8) Å;.[10] This bond shortening is accommodated by an equalization of the three nearest bond angles. The C–P–C bond angle at the site of protonation increases relative to **4** by approximately 13° to 122.4(1)° while the two adjacent P–C–P bond angles decrease by about 13° to an average of 122.5(1)°. The bond angles in the DFT-calculated cation coincide very closely with those determined by X-ray crystallography. No variance is $>2°$; most are $<1°$. The calculated P–C bond lengths are somewhat method dependent but all show the shortening of (0.5 ± 0.1 Å) at the protonated P atom relative to the remainder of the ring. With LDA, BP, and BLYP functionals, the average P–C bond length to the protonated P atom is 1.683, 1.700, and 1.707 Å, respectively, compared to 1.686(2) Å determined by X-ray, and the calculated remote P–C bonds average 1.731, 1.758, and 1.764 Å, respectively, compared to 1.738(3) Å in the X-ray structure. These comparisons suggest that the experimentally determined structure closely reflects the intrinsic structure and that the ring is not easily distorted by crystal-packing forces. The C$_3$P$_3$ ring remains effectively planar (max. deviation of any ring atom from the mean C$_3$P$_3$ plane is 0.02 Å), indicating that aromatic character is retained upon protonation. This result is consistent with calculations on protonated **1** that show only 6% loss of aromaticity upon protonation.[5]

Entirely analogous protonation chemistry occurs with the monophosphabenzene PC$_5$H$_2$*t*Bu$_3$ (**5**; ^{31}P NMR $\delta = 178.1$ ppm, s). Thus, a precipitate of [H(PC$_5$H$_2$*t*Bu$_3$)][CHB$_{11}$Me$_5$Cl$_6$] (**7**), is formed when **5** is treated in benzene with one equivalent of Et$_3$Si(CHB$_{11}$Me$_5$Cl$_6$) followed by triflic acid. The ^{31}P and ^{1}H NMR spectral data of **7** in CD$_2$Cl$_2$ show that protonation has occurred at the phosphorus atom (^{31}P $\delta = 60.2$ ppm, (dt, $^1J_{PH} = 625$ Hz, $^3J_{PH} = 36$ Hz); ^{1}H $\delta = 0.13$ (s, 15 H$_{Me}$), 1.48 (s, 9 H$_{But}$), 1.61 (s, 18 H$_{But}$), 8.45 (dd, 1 H, $^3J_{PH} = 36$, $^4J_{HH} = 4.6$ Hz), 9.32 ppm (dt, 1 H, $^4J_{HH} = 4.6$ Hz, $^1J_{PH} = 627$ Hz)).



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X-ray crystallography on a single crystal of **7** grown from CD$_2$Cl$_2$/hexanes confirms protonation at the phosphorus atom (Figure 2).[11] The C$_5$P ring is strictly planar (0.008 Å max. deviation of any ring atom from the mean C$_5$P plane) and the C–P bond lengths at the site of protonation (av 1.697(1) Å) are very close to those in **6** (av 1.686(2) Å).

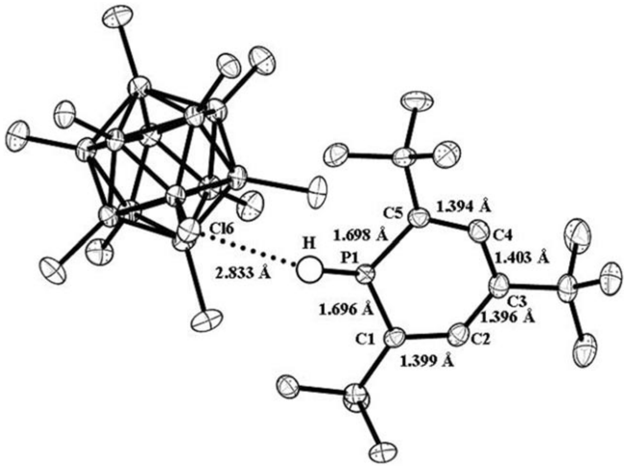

Figure 2. X-ray structure of [H(PC$_5$H$_2$*t*Bu$_3$)][CHB$_{11}$Me$_5$Cl$_6$] (**7**). Thermal ellipsoids are shown at 50% probability level.

To place the phosphabenzenes on a qualitative basicity scale with common arenes (mesitylene > C$_{60}$ > xylene > toluene > benzene),[6] bracketing experiments were carried out with arenium ion salts in CD$_2$Cl$_2$ solution. Treatment of phosphabenzenes **4** and **5** with the mesitylenium salt of the [CHB$_{11}$Me$_5$Cl$_6$]$^-$ ion gave homogeneous solutions that showed no evidence of protonation in the ^{31}P NMR spectrum. On the other hand, treatment of **4** and **5** with the corresponding toluenium ion salt led to formation of the [H(P$_3$C$_3$*t*Bu$_3$)]$^+$ and [H(PC$_5$H$_2$*t*Bu$_3$)]$^+$ ions, respectively. This places the basicities of **4** and **5** between those of mesitylene and toluene. The low solubility of the corresponding *o*-xylenium carborane salt, which did not form a homogeneous solution with **4** or **5**, thwarted further definitive placing of their basicities on the methylbenzene scale, although the lack of dissolution of the xylenium carborane in the presence of the phosphabenzenes does suggest that it is unable to protonate them. Overall, the

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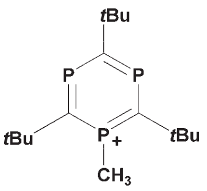
same behavior of **4** and **5** towards arenium ions indicates that the combination of intrinsic basicity and solvation energies that determines the basicities of these *tert*-butyl-phosphabenzenes in CH_2Cl_2 solution is not particularly dependent on the number of P atoms in the ring. They have about the same basicity as xylene.

Methyl triflate and $[Me_3O]^+$ are not strong enough methylating agents to alkylate phosphabenzenes.[5] By ^{31}P and ^1H NMR spectroscopy, we find there is no reaction when triphosphabenzene **4** is treated with MeOTf in benzene solution. On the other hand, alkyl carborane reagents are capable of alkylating a number of weakly nucleophilic molecules that are untouched by alkyl triflates.[14] Treatment of **4** with 1.1 equivalents of $Me(CHB_{11}Me_5Br_6)$ in CH_2Cl_2 at −80 °C followed by warming to room temperature, cleanly produced the desired methylation product $[Me(P_3C_3tBu_3)][CHB_{11}Me_5Br_6]$ (**8**). Low temperature is necessary to prevent reaction of the methyl carborane reagent with the solvent. The ^{31}P NMR spectrum of the product is consistent with alkylation at a phosphorus atom. A doublet is observed at $\delta = 302.6$ ppm ($^2J_{PP} = 52.0$ Hz), assigned to the two equivalent P atoms remote to the site of methylation, together with a doublet of quartets for the methylated P atom at $\delta = 133.8$ ppm with coupling constants of appropriate magnitude ($^2J_{PP} = 52.0$ Hz and $^2J_{PH} = 19.0$ Hz). As expected, these signals are in similar regions to those of the protonated cation $\mathbf{6}^+$. Compound **8** slowly decomposes to an oil over 24 h at room temperature without yielding crystals to date.



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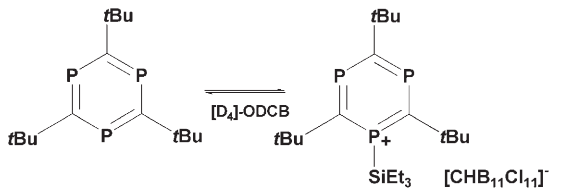
Finally, we have made a preliminary investigation of the nucleophilicity of compound **4** towards silylation. Trialkylsilylium carborane reagents, $R_3Si(CHB_{11}R_5X_6)$, are very potent sources of the $[R_3Si]^+$ electrophile.[15] For example, they are capable of silylating weak bases, such as phosphazenes (for example, *cyclo*-$N_3P_3Cl_6$, which is inert to boiling methyl triflate and trimethylsilyl triflate[16]). Somewhat surprisingly, however, treatment of **4** with one equivalent of $Et_3Si(CHB_{11}Me_5Br_6)$ in benzene solution at room temperature failed to show any reaction. The only signal in the ^{31}P NMR spectrum was that of **4** at $\delta = 233.0$ ppm. This result suggested that the use of a higher polarity solvent to favor ion formation and a more potent trialkysilylating reagent would be necessary to demonstrate nucleophilicity of **4** towards silicon. Thus, the solvent was changed to *o*-dichlorobenzene and the carborane anion was switched to the less basic[17] $[CHB_{11}Cl_{11}]^-$ ion. This approach has been used to achieve silylation of weak bases, such as *o*-dichlorobenzene and silanes.[18] Treatment of **4** with one equivalent of $Et_3Si(CHB_{11}Cl_{11})$ in $[D_4]$-*o*-dichlorobenzene ($[D_4]$-ODCB) showed partial reaction. In the ^{31}P NMR spectrum, the signal for the starting material was observed at $\delta = 232.8$ ppm but two additional signals consistent with formation of the anticipated P-silylated product appeared at $\delta = 268.95$ (d, 2 P) and 123.05 ppm (t, 1 P). The similarity of these chemical shifts to those of the methylated cation in **8** ($\delta = 302.6$ and 133.8 ppm) supports the formulation of $[Et_3Si(P_3C_3tBu_3)][CHB_{11}Cl_{11}]$ (**9**) according to equilibrium in Equation (1).



4 **9**

(1)

In summary, protonation, methylation, and partial silylation of phosphabenzenes has each been demonstrated. Overcoming the low basicity and weak nucleophilicity of phosphabenzenes requires the use of highly electrophilic reagents such as those based on CHB_{11}-type carborane anions. The H(carborane), Me(carborane), and R_3Si(carborane) reagents succeed where the corresponding triflate reagents fail. The success of this chemistry is not just because these reagents are more potent sources of H^+, Me^+, and $[R_3Si]^+$ electrophiles, they are also more gentle. The chemical inertness and extremely low nucleophilicity of carborane counterions slows down the decomposition of electrophile-activated cations, allowing them to be isolated. This opens a way to study their reactivity and since phosphininium cations have been implicated in a variety of reaction pathways and are potentially useful in synthesis, a situation which offers a promising direction for further research, particularly in transformations to new organophosphorus cations that are predicted[19] but have yet to be isolated and structurally characterized.

Experimental Section

All experiments were carried out under an inert atmosphere. Solvents were dried over Na and distilled prior to use. In a typical protonation reaction, freshly prepared Et_3Si(carborane)[12] (148 mg, 0.185 mmol) was combined with triphosphabenzene **4** (55.4 mg, 0.185 mmol) in a 5 mL vial with a stir bar. Benzene (approximately 1 mL) was added to give a pale yellow solution. Upon adding 2–3 drops (ca. 2 equiv) of triflic acid to this solution, a white powder precipitated. *n*-Hexane (ca. 2 mL) was added to complete the precipitation of the product which was collected by filtration, washed with *n*-hexane (ca. 2 mL) and dried under vacuum. The final product was dissolved in CD_2Cl_2 for NMR experiments and crystals for X-ray diffraction were grown by layering *n*-hexane over a CH_2Cl_2 solution. Further details and NMR spectra that establish compound purity are available as Supporting Information.

DFT calculations were carried out on $\mathbf{6}^+$ using ADF version ADF2006.01.[20] Triple zeta basis sets were employed with two added polarization functions on each atom (TZ2P). The geometry was optimized using a variety of functionals (LDA, BP, BLYP). The relative energy of the product when **4** is protonated at a carbon atom was estimated using the BP functional. In this case, the protonated C atom moves out of the plane of the ring.

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[8] Three signals in the initial ^{31}P NMR spectrum of this product ($\delta = 374.9$ (d, $J = 25$ Hz), 195.9 (br d, $J \approx 20$ Hz), 59.3 ppm (dd, $J = 20$, 25 Hz) and three separate *tert*-butyl signals in the ^{1}H NMR spectrum suggest a bicyclic structure, presumably from addition of triflic acid across a C=P bond.

[9] The rapid precipitation of the product as a carborane salt protects it from decomposition with any excess triflic acid that may be present.

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[11] Crystal data for **6**: $C_{21}H_{44}B_{11}Br_6P_3$, $M_r = 987.84$, monoclinic $P21/n$ (No. 14), $a = 15.0852(2)$, $b = 10.5889(2)$, $c = 24.8179(4)$ Å, $\beta = 103.1802(5)°$, $V = 3859.87(11)$ Å^3, $Z = 4$, $T = 100(2)$ K, $\mathrm{Mo}_{K\alpha}$, 115884 reflections collected (14715 independent) [R(int) = 0.0411], $R1 = 0.0347$ ($I > 2\sigma(I)$), $wR2$ (all data) = 0.0862. Crystal data for **7**: $C_{23}H_{46}B_{11}Cl_6P$, $M_r = 685.22$, monoclinic, $P21/n$ (No. 14), $a = 14.6953(4)$, $b = 10.6669(3)$, $c = 23.6576(7)$ Å, $\beta = 100.7892(4)°$, $V = 3642.85(18)$ Å^3, $Z = 4$, $T = 100(2)$ K, $\mathrm{Mo}_{K\alpha}$, 56110 reflections collected (11104 independent [R(int) = 0.0227], $R1 = 0.0295$ ($I > 2\sigma(I)$), $wR2$ (all data) = 0.0864. CCDC-679060 (**6**) and CCDC-679061 (**7**) contain the supplementary crystallographic data for this paper. These can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

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