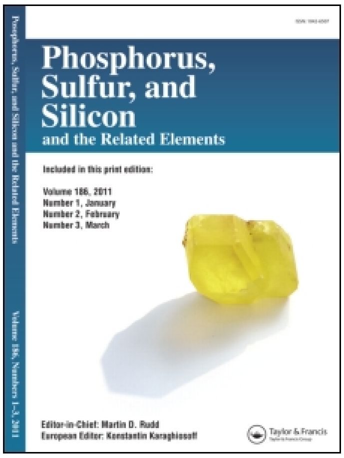

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THE PREPARATION, CHARACTERIZATION AND REACTION CHEMISTRY OF SMALL BRIDGING PHOSPHABORANE SYSTEMS PREPARED FROM THE REACTION OF [(2,2-DIMETHYL-1-(TRIMETHYLSILOXY)PROPYLIDENE)-TRIMETHYLSILYLPHOSPHINE] WITH PENTABORANE(9)

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Communication

THE PREPARATION, CHARACTERIZATION AND REACTION CHEMISTRY OF SMALL BRIDGING PHOSPHABORANE SYSTEMS PREPARED FROM THE REACTION OF [(2,2-DIMETHYL-1-(TRIMETHYLSILOXY)PROPYLIDENE)-TRIMETHYLSILYLPHOSPHINE] WITH PENTABORANE(9)

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The reaction of [(2,2-dimethyl-1-(trimethylsiloxy)propylidene)-trimethylsilylphosphine], **1**, with pentaborane(9) under mild conditions produced the bridged phosphinopentaborane cluster $((^tBu)(Me_3SiO)HCP(SiMe_3))B_5H_8$, **2**, in high yield. This phosphaborane reacts readily with water to quantitatively produce the corresponding P—H substituted cage compound $((^tBu)(Me_3SiO)HCP(H))B_5H_8$, **3**, via an electrophilic exopolyhedral substitution reaction at the phosphorus atom. All new compounds have been characterized by a variety of spectroscopic methods including ^1H, ^{13}C, ^{11}B, ^{31}P NMR, FT-IR and mass spectroscopic analysis.

Key words: Phosphaborane; boron hydrides; borane cluster; deprotonation; MNDO; ^{11}B NMR.

INTRODUCTION

An understanding of the synthetic and reaction chemistry of small heteroborane cluster species provides insight into the chemistry of a variety of molecular polyhedral species. Of particular interest are the relationships between cage geometry, electronic structure and chemical reactivity in these clusters. The small phosphaborane cluster compounds, with fewer than nine-vertex atoms, provide convenient systems in which to probe these relationships since theoretical and experimental tools are readily available for their study.[1,2] Although the first phosphinopentaborane synthesis was reported by Burg[3–5] over twenty years ago, very little is known about the chemistry of these systems, including their complete spectroscopic characterization. In this paper we report the first reaction of a low coordinate phosphorous compound with a neutral borane cluster system. This reaction provides a clean, high yield route to a variety of bridging phosphinopentaborane species. This phosphinopentaborane compound was found to readily undergo an electrophilic

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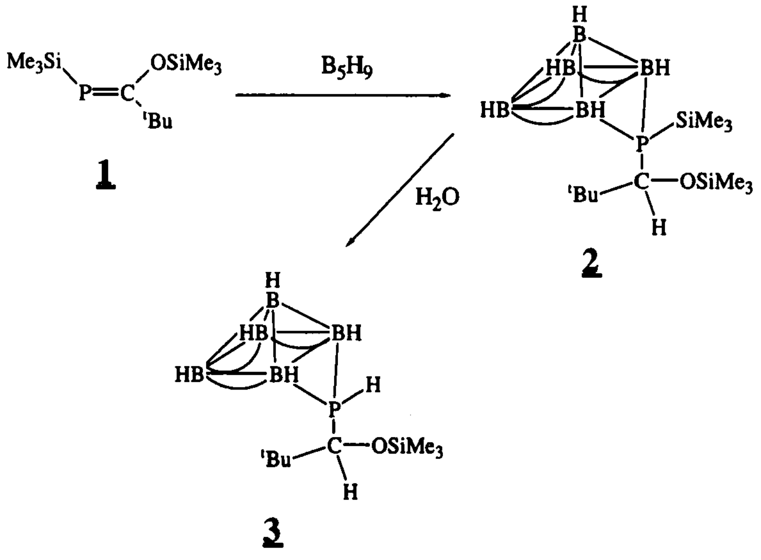
substitution reaction with water to eliminate trimethylsilyl alcohol thus forming the corresponding P—H substituted cage compound.

RESULTS AND DISCUSSION

The phosphaalkene ((^{t}Bu)(Me$_3$SiO)C=P(SiMe$_3$), **1**, prepared previously by Becker[6] and Cowley,[7] was found to react readily with pentaborane(9) to yield the bridging small phosphaborane compound, ((^{t}Bu)(Me$_3$SiO)HCP(SiMe$_3$))B$_5$H$_8$, **2**. This reaction pathway is shown in Scheme I. The reaction mixture was stirred at room temperature for two days and the very small amount of unreacted B$_5$H$_9$ which remained was removed under vacuum by a trap-to-trap distillation at −196°C. ^{11}B NMR analysis of the reaction product indicated the presence of only the new product, **2**. The slightly air-sensitive and moderately moisture-sensitive, light orange-yellow, oily liquid thus obtained was found to be soluble in a wide variety of both polar and non-polar organic solvents. The yield of pure **2** was 82% (4.74 g, 14.6 mmol, based on the final weight of the pure product obtained).

The minimum energy MNDO[1] calculated geometry for compound **2** is shown in Figure 1. The structure consists of a distorted square pyramid of boron atoms bridged by a P(SiMe$_3$)(CH(OSiMe$_3$)^{t}Bu) group. This structure can be thought of as being derived from the pentaborane(9) framework through the substitution of a bridging hydrogen atom for a bridging phosphine fragment. Since it is believed that the phosphino-group is bonded to the cage by two 2-center-2-electron interactions[2–5,8] instead of a 3-center-2-electron interaction as in B—H—B bonding, the B(2)—B(3) distances has lengthened significantly (from 1.86 Å in B$_5$H$_9$[1] to a 2.36 Å calculated distance in **2**). The phosphorus atom is calculated to be displaced from the basal plane of the cage by 49.6°. The chemistry and proposed structure of compound **2** is very different from the proposed phosphorus cage-inserted com-



SCHEME I The synthesis and reaction with water of small bridging phosphaborane systems. [⌣ indicates bridging hydrogen atom].

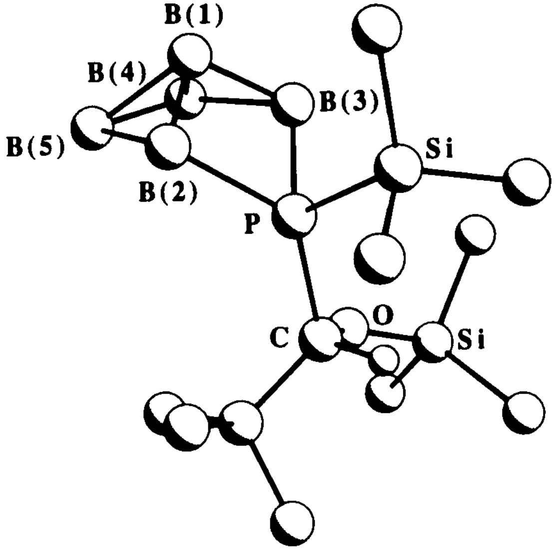


FIGURE 1 MNDO calculated minimum energy geometry for one isomer of compound **2**. The protons on the borane cage and methyl groups have been omitted for clarity.

pound, $(Me_3Si)_2C{=}PB_5H_8$, isolated from the reaction of $(Me_3Si)_2C{=}PCl$ with the pentaborane(9) anion, as previously reported by Gaines.[8]

The ^{11}B NMR spectrum of **2**, shown in Figure 2, exhibits three singlet boron resonances in the ^1H decoupled spectrum at −2.2, −19.6 and −48.6 ppm (relative to BF_3-Et_2O) with a 2:2:1 relative intensity. The two downfield resonances correspond to the two sets of equivalent basal boron atoms, B(2,3) and B(4,5), and appear as broad unresolved peaks in the ^1H decoupled spectrum. In the ^1H coupled ^{11}B spectrum, the upfield boron resonance corresponding to the apical boron atom resolves into a well defined $B{-}H_{terminal}$ coupled doublet (J_{BH} = 152 Hz). The resonances for the basal boron atoms, however, become significantly broader with no apparent B—H or P—H coupling resolution. This failure to resolve basal boron resonances in small phosphaborane systems has been observed previously.[2,4] The ^{31}P NMR shows a single broad resonance at −124.5 ppm. ^1H and ^{13}C NMR data also support the structural assignment of **2** as a bridging phosphinopentaborane system.[8] The FT-IR spectrum of **2** shows four BH vibrations in the range of 2365 to 2580 cm^{-1}.

Compound **2** readily reacted with water to produce $((^tBu)(Me_3SiO)HCPH)B_5H_8$, **3**, as shown in Scheme 1. The ^1H decoupled ^{11}B NMR spectrum of **3**, shown in Figure 1, is qualitatively similar to that observed for **2** and consists of three resonances with a 2:2:1 relative intensity. In the decoupled spectrum of **3**, however, the basal boron atoms bonded to the phosphino-group are resolved into a well defined B—P coupled doublet (J_{BP} = 82 Hz). In the ^1H coupled spectrum, the resonance for these phosphorus-bridged boron atoms appears as a poorly resolved triplet arising from the overlap of $B{-}H_{terminal}$ and $B{-}P_{bridged}$ coupled resonances. The unique apical boron atom and the two remaining basal boron atoms, B(4,5), are each split into $B{-}H_{terminal}$ coupled doublets as expected. Verification of the substitution of the trimethylsilyl group on phosphorus by a proton was provided

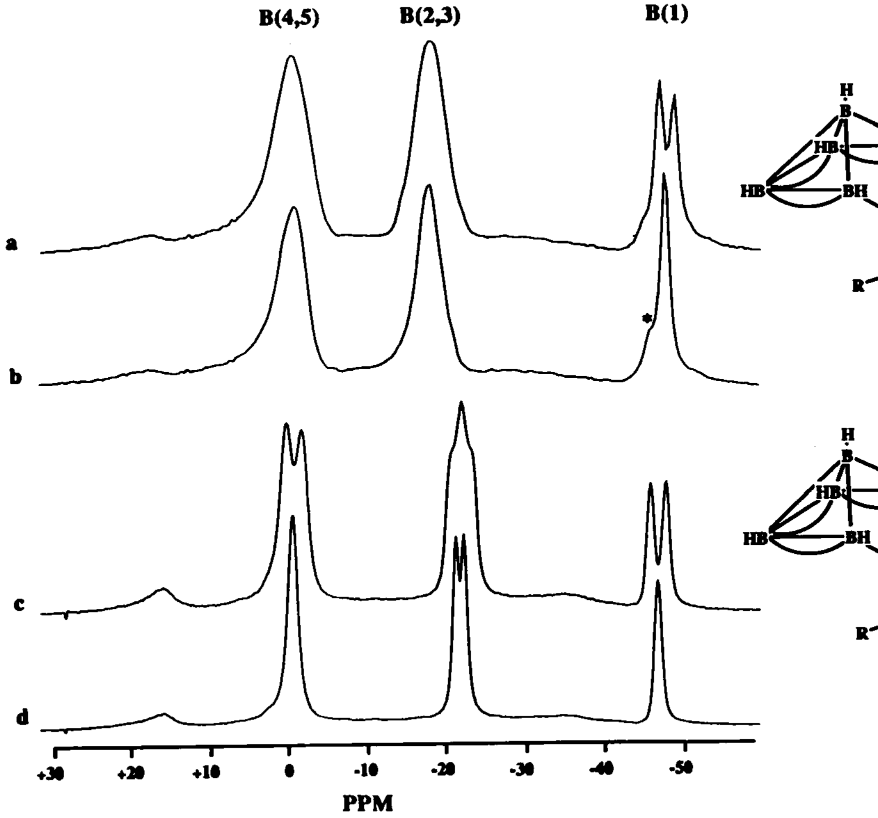


FIGURE 2 80-HMz ^{11}B NMR spectrum for μ-((^{t}Bu)(Me$_3$SiO)HCP(SiMe$_3$))B$_5$H$_8$, ((^{t}Bu)(Me$_3$SiO)HCPH)B$_5$H$_8$, 3, in CDCl$_3$ relative to BBr$_3$ (40.0 ppm). (a) ^{1}H coupled ^{11}B trum of 2, (b) {^{1}H}-decoupled ^{11}B NMR spectrum of 2 (asterisk indicates a small impurity in (c) ^{1}H coupled ^{11}B NMR spectrum of 3 (basal boron atoms B(4,5) and the unique apica show simple B—H$_{terminal}$ doublets while the phosphorus bridged borons (B(2,3)) show doublets pattern (which decouples to a phosphorous coupled doublet in the {^{1}H}-decoupl J_{BP} = 82 Hz, J_{BH} = 80 Hz)), (d) {^{1}H}-decoupled ^{11}B NMR spectrum of 3.

by ^1H NMR and FT—IR spectroscopy. The ^1H NMR spectrum of **3** shows the absence of the phosphorus trimethylsilyl resonance previously observed for compound **2** at 0.49 ppm and the appearance of both a P—H resonance at 5.27 ppm (J_{PH} = 410 Hz) and a HPCH vicinal proton-proton coupling (J_{HPCH} = 3.0 Hz). The ^{31}P NMR spectrum also shows a resonance at −97.5 ppm with the same P—H coupling resolved. The magnitude of the PH coupling is consistent with other P—H coupling constants reported previously.[9,10] Finally, a P—H stretch at 2400 cm^{-1} was clearly observed in the FT—IR spectrum of **3**.[11]

In summary, the reaction of a phosphaalkene with pentaborane(9) provided a convenient and high yield synthesis of a small bridged phosphaborane cluster system. This phosphinoborane cluster reacts cleanly and rapidly with water to substitute a proton on the phosphorus center. These reactions provide a general access route to the exopolyhedral organometallic chemistry of these species.[2]

EXPERIMENTAL

Preparation and characterization for **1**. The starting phosphaalkene $(Me_3Si)P{=}C(^tBu)(OSiMe_3)$, **1**, was prepared according to literature procedures.[6]

Preparation and characterization for **2**. In a 500 mL round bottom reaction flask was placed 17.8 mmol of dried and degassed phosphaalkene **1**. Into this flask was condensed 17.8 mmol of pentaborane(9) at − 196°C and the reaction mixture was slowly warmed to room temperature and stirred at this temperature for an additional two days. The unreacted B_5H_9 was removed under vacuum by trap-to-trap distillation. The slightly air-sensitive and moderately moisture-sensitive light orange-yellow oil was obtained in an 82% yield. ^{11}B NMR ($CDCl_3$) δ −2.2 (s, B(4,5)), −19.6 (s, B(2,3)), −48.6 (d, B(1), J_{BH} = 152 Hz); ^1H NMR ($CDCl_3$) δ −1.75 (s, 3H, bridging H), −0.37 (q, 1H, B(1)H, J_{BH} = 150.3 Hz), 0.17 (s, 9H, $OSi(C\underline{H}_3)_3$), 0.49 (d, 9H, $PSi(C\underline{H}_3)_3$), J_{PH} = 5.4 Hz), 0.92 (s, 9H, $C(C\underline{H}_3)_3$), 3.49 (d, 1H, $PC\underline{H}$, J_{PH} = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 0.11 (d, $PSi(\underline{C}H_3)_3$, J_{CP} = 9.2 Hz), 0.93 (s, $OSi(\underline{C}H_3)_3$), 26.99 (d $C(\underline{C}H_3)_3$, J_{CP} = 4.3 Hz), 37.31 (d, $\underline{C}(CH_3)_3$, J_{CP} = 3.6 Hz), 78.24 (d, $P\underline{C}$, J_{CP} = 10.5 Hz); ^{31}P ($CDCl_3$) δ −124.5 (s); FT—IR (KCl plates) 2956 (s, ν_{CH}), 2899 (m, ν_{CH}), 2868 (m, ν_{CH}), 2580 (s, ν_{BH}), 2533 (sh, ν_{BH}), 2519 (s, ν_{BH}), 2365 (w, ν_{BH}) cm^{-1}; Mass Spec. (Relative intensities are given with the largest peak in the envelope normalized to 100.0%. The calculated values are based on natural abundances and normalized to the most intense peak in the envelope) 329 (Calcd 1.2, Found 1.1; P^+ envelope), 328 (Calcd 7.9, Found 5.6; P^+ envelope), 327 (Calcd 25.1, Found 20.9; P^+ envelope), 326 (Calcd 95.8, Found 94.5, $^{12}C_{11}{}^1H_{36}{}^{11}B_5{}^{16}O^{31}P^{28}Si_2$; P^+ envelope), 325 (Calcd 100.0, Found 100.0; P^+ envelope), 324 (Calcd 47.4, Found 45.5; P^+ envelope), 323 (Calcd 11.0, Found 8.9; P^+ envelope), 322 (Calcd 1.2, Found 1.0; P^+ envelope), 168 (Calcd 2.8, Found 4.5, $P^+ - R$ envelope), 167 (Calcd 21.0, Found 38.7, $^{12}C_3{}^1H_{17}{}^{11}B_5{}^{31}P^{28}Si_1$; $P^+ - R$ envelope), 166 (Calcd 44.9, Found 44.9, $P^+ - R$ envelope), 165 (Calcd 38.7, Found 22.0, $P^+ - R$ envelope), 164 (Calcd 16.9, Found 5.3, $P^+ - R$ envelope), 163 (Calcd 4.1, Found 0.5, $P^+ - R$ envelope), 159 (100.0, $C(OSiMe_3)(^tBu)H^+$).

Preparation and characterization for **3**. Using standard inert atmosphere techniques,[2] 0.68 mmol of **2** was dissolved in 5 mL of dry THF. To this solution was added 0.7 mmol of water. After several minutes, the solvent was removed *in vacuo* to leave an off-white solid. The product was further purified employing either standard column chromatographic or HPLC chromatographic procedures (HPLC parameters; 2.5 × 10 cm 15μ porasil column eluted with 100% methylene chloride with a flow rate of 7 mL/min., **3** eluted from the column in 5.6 min.). The final product was obtained as a white, relatively air-stable oil in near quantitative conversion from **2** (0.16 g, 93.4% yield). ^{11}B NMR ($CDCl_3$) δ −1.6 (d, B(4,5), J_{BH} = 156 Hz), −22.0 (t, B(2,3), J_{BP} = 82 Hz, J_{BH} = 80 Hz), −47.5 (d, B(1), J_{BH} = 152 Hz); ^1H NMR ($CDCl_3$) δ −1.80 (br s, 2H, bridging H), −1.40 (br s, 1H, bridging H), −0.04 (q, 1H, B(1)H, J_{BH} = 152.3 Hz), 0.17 (s, 9H, $OSi(C\underline{H}_3)_3$), 1.00 (s, 9H, $C(C\underline{H}_3)_3$), 3.33 (dd, 1H, $PC\underline{H}$, J_{PH} = 7.2 Hz, J_{HH} = 3.0 Hz), 5.27 (d, 1H, PH, J_{PH} = 410 Hz); ^{13}C NMR ($CDCl_3$) δ 0.76 (s, $OSi(\underline{C}H_3)_3$), 26.57 (d, $C(\underline{C}H_3)_3$, J_{CP} = 4.8 Hz), 37.24 (s, $\underline{C}(CH_3)_3$, 79.64 (s, $P\underline{C}$); ^{31}P NMR ($CDCl_3$) δ −97.5 (d, J_{PH} = 410 Hz); FT—IR (KCl plates) 2956 (s, ν_{CH}), 2900 (br, ν_{CH}), 2867 (m, ν_{CH}), 2587 (m, ν_{BH}), 2541 (m, ν_{BH}), 2400 (w, ν_{PH}) cm^{-1}. Mass Spec. (Relative intensities are given with the largest peak in the envelope normalized to 100.0%. The calculated values are based on natural abundances and normalized to the most intense peak in the envelope) 256 (Calcd 3.6, Found 2.5; P^+ envelope), 255 (Calcd 14.7, Found

12.6; P^+ envelope), 254 (Calcd 89.7, Found 86.2, $^{12}C_8{}^1H_{28}{}^{11}B_5{}^{16}O^{31}P^{28}Si$; P^+ envelope), 253 (Calcd 100.0, Found 100.0; P^+ envelope), 252 (Calcd 48.1, Found 47.4; P^+ envelope), 251 (Calcd 11.8, Found 10.7; P^+ envelope), 250 (Calcd 1.5, Found 1.0; P^+ envelope), 161 (Calcd 4.4, Found 3.9; $C(OSiMe_3)({}^tBu)H^+$), 160 (Calcd 14.3, Found 12.9; $C(OSiMe_3)({}^tBu)H^+$), 159 (Calcd 100.0, Found 100.0; $C(OSiMe_3)({}^tBu)H^+$, $^{12}C_8{}^1H_{19}{}^{16}O^{28}Si$).

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