Contribution of the *nido*-[7,8-$C_2B_9H_{10}$]$^-$ Anion to the Chemical Stability, Basicity, and ^{31}P NMR Chemical Shift in *nido*-*o*-Carboranylmonophosphines

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Received August 1, 2000

The icosahedral dicarboranes and their decapitated anion, 1-R′-1,2-$C_2B_{10}H_{10}$ (*closo*) and [7-R′-7,8-$C_2B_9H_{10}$]$^-$ (*nido*), exert a distict influence at the α position of substituents attached to the cage carbon atom. The *closo* fragment is electron-withdrawing while the *nido* anion is electron-releasing. These effects are studied by ^{31}P NMR, phosphorus oxidation, and phosphorus protonation in [7-PR_2-8-R′-7,8-$C_2B_9H_{10}$]$^-$ species. The ^{31}P NMR chemical shift dependence is related to the R alkyl or aryl nature of [7-PR_2-8-R′-7,8-$C_2B_9H_{10}$]$^-$. No direct relationship to the nature of the R substituent on the *nido*-carboranylmonphosphine toward oxidation has been found. The basicity of the *nido*-alkylcarboranylmonophosphines is the highest while the lowest corresponds to the *nido*-arylcarboranylmonophosphines. Interpretation can be carried out qualitatively by considering the electronic properties of the cluster and the nature of the R groups. The influence of R′ is less relevant. Confirmation of the molecular structure of the oxidated and protonated *nido*-carboranylmonophosphine compounds was obtained by X-ray diffraction analysis of [NBu_4][7-P(O)Ph_2-8-Ph-7,8-$C_2B_9H_{10}$] and [7-PH(^{i}Pr)$_2$-8-Me-7,8-$C_2B_9H_{10}$].

Introduction

Tertiary phosphines are among the most important ligands in inorganic chemistry. This comes as a result of their electronic and steric properties that make them very valuable in coordination chemistry and catalysis. Their nucleophilicity, in general, increases with increasing pK_a, although within a given series of phosphines it is modified by steric hindrance.[1] In general, tertiary phosphines are very sensitive species[2] showing weakly basic properties and are readily oxidized by air to produce even more weakly basic molecules such as phosphine oxides. Oxidation and protonation reactions are of particular importance in understanding the activity of phosphines.[3]

We reported earlier[4] the synthesis and structural characterization of several monosubstituted 1,2-dicarba-*closo*-dodecaborane derivatives which incorporate a phosphorus atom bonded to one of the cluster carbon atoms. These *closo*-carboranylmonophosphines are less basic than similar organophosphorus compounds and less reactive toward oxygen, acids, and metal ions due to the influence of the carborane cluster on the P atom. On the contrary, their *nido*-derivatives are very reactive toward metals ions.[5]

It is important to point out that the deboronation process from *closo*-carboranylmonophosphines to *nido*-carboranylmonophosphines is not easy to deal with. If deboronation is attempted with alkoxide,[6] the expected *nido* species is not produced, due to the cleavage of the $C_{cluster}$−P bond. If it is attempted with piperidine−toluene[7] in a 1:4 ratio (*closo*-carboranylmonophosphines:piperidine) at 20 °C, the *closo* precursor is left unaltered. Better results were obtained in toluene for a *closo*-carboranylmonophosphine/piperidine ratio of 1:50 or in ethanol with a ratio of 1:25.[8]

The *nido*-cluster strongly influences the phosphorus atom response, not only in the easily observable shielding chemical shift in ^{31}P NMR but in their chemical properties. In this paper, we report on the preparation of new *nido*-carboranylmonophosphines, the contribution of the *nido* cluster to the ^{31}P chemical shift in the NMR spectra, and their reactivity toward oxygen and acids. The crystal structures of [NBu_4][7-P(O)Ph_2-8-Ph-7,8-$C_2B_9H_{10}$] and [7-PH(^{i}Pr)$_2$-8-Me-7,8-$C_2B_9H_{10}$] are also reported.

Experimental Section

Instrumentation. Microanalyses were performed in our analytical laboratory using a Carlo Erba EA1108 microanalyzer. IR spectra were recorded with KBr pellets on a Nicolet 710-FT spectrophotometer. The ^{1}H NMR (300.13 MHz), ^{11}B NMR (96.29 MHz), ^{31}P and ^{31}P{^{1}H} NMR (121.48 MHz), and ^{13}C{^{1}H} (75.47 MHz) spectra were obtained on Bruker ARX 300 instruments. All NMR measurements were performed in deuterated solvents at 22 °C. The ^{11}B NMR chemical shifts are referenced to external BF_3·OEt_2, while the ^{1}H and ^{13}C data are referenced to $SiMe_4$. The ^{31}P data are referenced to external 85% H_3PO_4. Chemical shifts are reported in units of parts per million (ppm), and all coupling constants are reported in hertz (Hz). The B−H(bridge) coupling, corresponding to the B(10) observed at ca. −30 ppm, is not indicated in the ^{11}B NMR data. In most of the cases, these couplings just broaden the doublet, thus making the calculation difficult and inaccurate; however, they can be estimated to be ca. 40 Hz. Positive values of the shifts, according to the IUPAC convention, are to high frequency.

Materials. The *closo*-carboranylmonophosphines [1-PEt_2-2-Ph-1,2-$C_2B_{10}H_{10}$] and [1-P(^{i}Pr)$_2$-2-Ph-1,2-$C_2B_{10}H_{10}$] and *nido*-carboranylmonophosphines [NBu_4][7-PPh_2-8-Ph-7,8-$C_2B_9H_{10}$], [NMe_4][7-PPh_2-8-Me-

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10.1021/ic000858p CCC: $20.00
Published on Web 04/24/2001

7,8-$C_2B_9H_{10}$], [NBu_4][7-P(^{i}Pr)$_2$-8-Me-7,8-$C_2B_9H_{10}$], [NBu_4][7-PEt_2-8-Me-7,8-$C_2B_9H_{10}$] ,and [NMe_4][7-PPh_2-7,8-$C_2B_9H_{11}$] were prepared according to the literature.[4,8] Piperidine, toluene, and ethanol were of reagent quality. The solvents were dried from sodium and deoxygenated. CH_3NO_2 (HPLC grade) was purchased from LAB-SCAN, $(CD_3)_2CO$ and CD_3OD from SDS, and 70% $HClO_4$ from Panreac. Unless mentioned elsewhere, the reactions were carried out under a dinitrogen atmosphere.

Preparation of [NBu_4][7-PEt_2-8-Ph-7,8-$C_2B_9H_{10}$]. To a three-necked round-bottom flask (250 mL) fitted with a dinitrogen inlet/outlet, containing piperidine (1.38 g, 16.22 mmol) and 1-diethylphosphino-2-phenyl-1,2-dicarba-*closo*-dodecaborane (0.20 g, 0.65 mmol), was added deoxygenated ethanol (20 mL). The mixture was degassed again. The solution was refluxed for 16 h, and once cooled, the solvent was evaporated. The residue was again dissolved in ethanol (10 mL), and a solution of an excess of tetrabutylammonium bromide in water (10 mL) was added dropwise while a dinitrogen stream was bubbled through the solution. A white solid was precipitated, filtered off, and washed with water (5 mL) and dried (194 mg, 56%). Anal. Calcd for $C_{28}H_{61}B_9NP$: C, 62.31; H, 11.31; N, 2.60. Found: C, 62.95; H, 11.65; N, 2,66. IR, ν (cm^{-1}): 2966, 2875 (C−H); 2523 (B−H). ^{1}H NMR ($(CD_3)_2CO$), δ: −2.15 (br s, 1 H, B−H−B), 0.89 (m, 6 H, CH_3), 0.99 (t, 12 H, CH_3, ^3J(H,H) = 7), 1.45 (hex, 8 H, CH_2, ^3J(H,H) = 7), 1.83 (q, 8 H, CH_2, ^3J(H,H) = 8), 2.23 (m, 4 H, CH_2), 3.44 (t, 8 H, NCH_2, ^3J(H,H) = 9), 7.04−7.35 (m, 5 H, C_6H_5). ^{11}B NMR ($(CD_3)_2CO$), δ: −7.2 (d, 1B, ^1J(B,H) = 130), −10.6 (d, 1B, ^1J(B,H) = 152), −13.2 (d, 1B, ^1J(B,H) = 111), −14.1 (d, 1B, ^1J(B,H) = 132), −17.9 (d, 2B, ^1J(B,H) = 129), −19.0 (d, 1B, ^1J(B,H) = 133), −32.3 (d, 1B, ^1J(B,H) = 129), −35.1 (d, 1B, ^1J(B,H) = 139). ^{31}P{^{1}H} NMR ($(CD_3)_2CO$), δ: −5.43 (s, PEt_2). ^{13}C{^{1}H} NMR ($(CD_3)_2CO$), δ: 10.66 (d, J(P,C) = 8), 11.02 (d, J(P,C) = 7), 12.99 (s), 19.47 (s), 21.20 (d, J(P,C) = 15), 22.53 (d, J(P,C) = 15), 23.51 (s), 58.56 (s), 125.10 (s), 126.22 (s), 126.61 (s), 132.77 (s).

Preparation of [NBu_4][7-P(^{i}Pr)$_2$-8-Ph-7,8-$C_2B_9H_{10}$]. To a three-necked round-bottom flask (250 mL) fitted with a dinitrogen inlet/outlet, containing piperidine (1.18 g, 13.82 mmol) and 1-diisopropylphosphino-2-phenyl-1,2-dicarba-*closo*-dodecaborane (0.20 g, 0.55 mmol), was added deoxygenated ethanol (20 mL). The mixture was degassed again. The solution was refluxed for 17 h, and once cooled, the solvent was evaporated. The residue was again dissolved in ethanol (10 mL), and a solution of an excess of tetrabutylammonium bromide in water (10 mL) was added dropwise while a dinitrogen stream was bubbled through the solution. A white solid was precipitated, filtered off, washed with water (10 mL), and dried (100 mg, 32%). Anal. Calcd for $C_{30}H_{65}B_9NP$: C, 63.47; H, 11.46; N, 2.46. Found: C, 64.10; H, 11.85; N, 2.23. IR, ν (cm^{-1}): 2965, 2874 (C−H); 2523 (B−H). ^{1}H NMR ($(CD_3)_2CO$), δ: −2.30 (br s, 1 H, B−H−B), 1.04 (t, 12 H, CH_3, ^3J(H,H) = 7), 1.00 (m, 12 H, CH_3), 1.48 (hex, 8 H, CH_2, ^3J(H,H) = 7), 1.83 (q, 8 H, CH_2, ^3J(H,H) = 7), 2.15 (m, 2 H, CH), 3.44 (t, 8 H, NCH_2, ^3J(H,H) = 8), 6.95−7.60 (m, 5 H, C_6H_5). ^{11}B NMR ($(CD_3)_2CO$), δ: −7.9 (d, 1B, ^1J(B,H) = 115), −9.0 (d, 1B, ^1J(B,H) = 152), −13.5 (d, 1B,^1J(B,H) = 144), −15.1 (d, 1B, ^1J(B,H) = 192), −17.2 (d, 2B, ^1J(B,H) = 154), −18.7 (d, 1B,^1J(B,H) = 154), −31.8 (d, 1B, ^1J(B,H) = 134), −34.4 (d, 1B, ^1J(B,H) = 144). ^{31}P{^{1}H} NMR ($(CD_3)_2CO$), δ: 16.86 (s, P(^{i}Pr)$_2$). ^{13}C{^{1}H} NMR ($(CD_3)_2CO$), δ: 12.99 (s), 17.02 (s), 19.48 (s), 19.92 (d, J(P,C) = 23), 21.94 (d, J(P,C) = 17), 22.57 (d, J(P,C) = 19), 23.54 (s), 24.74 (d, J(P,C) = 17), 25.21 (d, J(P,C) = 21), 58.49 (s), 124.96 (s), 126.02 (s), 126.9 (s), 133.54 (s).

Preparation of [NBu_4][7-P(O)R_2-8-R′-7,8-$C_2B_9H_{10}$]. General Procedure. The *nido* species were oxidized by their reaction in a 1:0.5 molar ratio with a 0.1163 M solution of H_2O_2 in acetone. For the following preparation only the reagents are indicated.

Preparation of [NMe_4][7-P(O)Ph_2-8-Me-7,8-$C_2B_9H_{10}$]. [NMe_4][7-PPh_2-8-Me-7,8-$C_2B_9H_{10}$] (50 mg, 0.12 mmol), H_2O_2 (0.50 mL), and acetone (5 mL) afforded [NMe_4][7-P(O)Ph_2-8-Me-7,8-$C_2B_9H_{10}$]. Anal. Calcd for $C_{19}H_{35}B_9NOP$: C, 54.11; H, 8.36; N, 3.32. Found: C, 54.97; H, 8.30; N, 3.23. ^{1}H NMR ($(CD_3)_2CO$), δ: −2.17 (br s, 1 H, B−H−B), 1.38 (s, 3 H, CH_3), 3.45 (s, 12 H, CH_3), 7.28−8.11 (m, 10 H, C_6H_5).^{11}B NMR ($(CD_3)_2CO$), δ: −7.2 (d, 2B, ^1J(B,H) = 186), −11.1 (d, 1B, ^1J(B,H) = 139), −12.5 (d, 1B, ^1J(B,H) = 146), −14.5 (d, 1B, ^1J(B,H) = 178), −16.0 (d, 1B, ^1J(B,H) = 145), −21.6 (d, 1B, ^1J(B,H) = 151), −33.2 (d, 1B, ^1J(B,H) = 135), −35.2 (d, 1B, ^1J(B,H) = 146). ^{31}P{^{1}H} NMR ($(CD_3)_2CO$), δ: 31.75 (s, P(O)Ph_2). ^{13}C{^{1}H} NMR ($(CD_3)_2CO$), δ: 23.29 (s), 55.07 (s), 126.59 (d, J(P,C) = 9), 128.15 (d, J(P,C) = 11), 130.05 (s), 130.78 (s), 132.26 (d, J(P,C) = 7), 132.82 (d, J(P,C) = 8).

Preparation of [NMe_4][7-P(O)Ph_2-7,8-$C_2B_9H_{11}$]. [NMe_4][7-PPh_2-7,8-$C_2B_9H_{11}$] (50 mg, 0.13 mmol), H_2O_2 (0.55 mL), and acetone (5 mL) afforded [NBu_4][7-P(O)Ph_2-7,8-$C_2B_9H_{11}$]. Anal. Calcd for $C_{18}H_{33}B_9NOP$: C, 53.02; H, 8.16; N, 3.44. Found: C, 52.98; H, 8.06; N, 3.38. ^{1}H NMR ($(CD_3)_2CO$), δ: −2.25 (br s, 1 H, B−H−B), 3.45 (s, 12 H, CH_3), 7.15−7.75 (m, 10 H, C_6H_5). ^{11}B NMR ($(CD_3)_2CO$), δ: −7.9 (d, 1B, ^1J(B,H) = 144), −9.5 (d, 1B, ^1J(B,H) = 144), −12.5 (d, 2B, ^1J(B,H) = 166), −14.7 (d, 2B, ^1J(B,H) = 144), −19.3 (1B), −33.0 (d, 1B, ^1J(B,H) = 125), −35.1 (d, 1B, ^1J(B,H) = 144). ^{31}P{^{1}H} NMR ($(CD_3)_2CO$), δ: 39.27 (s, P(O)Ph_2).^{13}C{^{1}H} NMR ($(CD_3)_2CO$), δ: 55.25 (s), 127.42−134.58 (m).

Preparation of [NBu_4][7-P(O)Ph_2-8-Ph-7,8-$C_2B_9H_{10}$]. [NBu_4][7-PPh_2-8-Ph-7,8-$C_2B_9H_{10}$] (50 mg, 0.08 mmol), H_2O_2 (0.34 mL), and acetone (5 mL) afforded [NBu_4][7-P(O)Ph_2-8-Ph-7,8-$C_2B_9H_{10}$]. Anal. Calcd for $C_{36}H_{61}B_9NOP$: C, 66.30; H, 9.43; N, 2.15. Found: C, 65.40; H, 9.24; N, 2.16. ^{1}H NMR ($(CD_3)_2CO$), δ: −1.83 (br s, 1 H, B−H−B), 1.09 (t, 12 H, CH_3, ^3J(H,H) = 7), 1.59 (hex, 8 H, CH_2, ^3J(H,H) = 7), 1.94 (q, 8 H, CH_2, ^3J(H,H) = 7), 3.55 (t, 8 H, NCH_2, ^3J(H,H) = 8), 6.69−8.09 (m, 15 H, C_6H_5).^{11}B NMR ($(CD_3)_2CO$), δ: −6.8 (d, 2B, ^1J(B,H) = 146), −11.8 (d, 1B, ^1J(B,H) = 144), −13.7 (d, 1B, ^1J(B,H) = 156), −15.6 (d, 2B, ^1J(B,H) = 136), −22.4 (1B), −32.9 (d, 1B, ^1J(B,H) = 130), −34.9 (d, 1B, ^1J(B,H) = 144). ^{31}P NMR ($(CD_3)_2CO$), δ: 26.26 (s, P(O)Ph_2).^{13}C{^{1}H} NMR ($(CD_3)_2CO$), δ: 12.96 (s, CH_3), 19.47 (s, CH_2), 23.49 (s, CH_2), 58.47 (s, NCH_2), 124.79−139.84 (m).

Preparation of [NBu_4][7-P(O)(^{i}Pr)$_2$-8-Me-7,8-$C_2B_9H_{10}$]. [NBu_4][7-P(^{i}Pr)$_2$-8-Me-7,8-$C_2B_9H_{10}$] (50 mg, 0.1 mmol), H_2O_2 (0.45 mL), and acetone (5 mL) afforded [NBu_4][7-P(O)(^{i}Pr)$_2$-8-Me-7,8-$C_2B_9H_{10}$]. Anal. Calcd for $C_{25}H_{63}B_9NOP$: C, 57.52; H, 12.16; N, 2.68. Found: C, 57.31; H, 12.38; N, 2.47. ^{1}H NMR ($(CD_3)_2CO$), δ: −2.30 (br s, 1 H, B−H−B), 0.97 (t, 12 H, CH_3, ^3J(H,H) = 7), 1.19 (m, 6 H, CH_3), 1.30 (m, 6 H, CH_3), 1.44 (hex, 8 H, CH_2, ^3J(H,H) = 7), 1.76 (s, 3 H, CH_3), 1.82 (q, 8 H, CH_2, ^3J(H,H) = 7), 2.14 (m, 1 H, CH), 2.43 (m, 1 H, CH), 3.43 (t, 8 H, NCH_2, ^3J(H,H) = 8).^{11}B NMR ($(CD_3)_2CO$), δ: −7.9 (1B), −8.3 (1B), −12.7 (d, 2B, ^1J(B,H) = 156), −15.23 (d, 2B, ^1J(B,H) = 144), −20.1 (d, 1B, ^1J(B,H) = 135), −32.8 (d, 1B, ^1J(B,H) = 132 Hz), −35.1 (d, 1B, ^1J(B,H) = 144 Hz). ^{31}P{^{1}H} NMR ($(CD_3)_2CO$), δ: 55.10 (s, P(O)(^{i}Pr)$_2$). ^{13}C{^{1}H} NMR ($(CD_3)_2CO$), δ: 12.99 (s, CH_3), 14.96 (s), 16.39 (d, J(P,C) = 19), 17.12 (d, J(P,C) = 26), 19.47 (s, CH_2), 23.51 (s, CH_2), 24.83 (s), 58.43 (s, NCH_2).

Preparation of [NBu_4][7-*P(O)*(^{i}Pr)$_2$-8-Ph-7,8-$C_2B_9H_{10}$]. [NBu_4][7-P(^{i}Pr)$_2$-8-Ph-7,8-$C_2B_9H_{10}$] (50 mg, 0.09 mmol), H_2O_2 (0.38 mL), and acetone (5 mL) afforded [NBu_4][7-P(O)(^{i}Pr)$_2$-8-Ph-7,8-$C_2B_9H_{10}$]. Anal. Calcd for $C_{30}H_{65}B_9NOP$: C, 61.69; H, 11.22; N, 2.40. Found: C, 61.35; H, 11.01; N, 2.29. ^{1}H NMR ($(CD_3)_2CO$), δ: −2.35 (br s, 1 H, B−H−B), 0.85 (t, 12 H, CH_3, ^3J(H,H) = 7), 0.90 (m, 12 H, CH_3), 1.25 (hex,

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8 H, CH_2, ^3J(H,H) = 7), 1.72 (q, 8 H, CH_2, ^3J(H,H) = 7), 1.95 (m, 2 H, CH), 3.40 (t, 8 H, NCH_2, ^3J(H,H) = 8), 6.85−7.45 (m, 5 H, C_6H_5). ^{11}B NMR ($(CD_3)_2CO$), δ: −7.3 (d, 2B, ^1J(B,H) = 145), −14.2 (d, 3B, ^1J(B,H) = 138), −16.5 (1B), −20.8 (d, 1B, ^1J(B,H) = 165), −32.5 (d, 1B, ^1J(B,H) = 130), −34.6 (d, 1B, ^1J(B,H) = 149). ^{31}P{^{1}H} NMR ($(CD_3)_2CO$), δ: 56.89 (s, P(O)(^{i}Pr)$_2$). ^{13}C{^{1}H} NMR ($(CD_3)_2CO$), δ: 12.99 (s, CH_3), 16.90 (d, J(P,C) = 15), 18.16 (s), 19.48 (s, CH_2), 23.53 (s, CH_2), 27.94(s), 58.44 (s, NCH_2), 125.42 (s), 126.04 (s), 133.58 (s).

Preparation of [NBu_4][7-P(O)Et_2-8-Me-7,8-$C_2B_9H_{10}$]. [NBu_4][7-PEt_2-8-Me-7,8-$C_2B_9H_{10}$] (50 mg, 0.10 mmol), H_2O_2 (0.45 mL), and acetone (5 mL) afforded [NBu_4][7-P(O)Et_2-8-Ph-7,8-$C_2B_9H_{10}$]. Anal. Calcd for $C_{23}H_{59}B_9NOP$: C, 55.92; H, 12.04; N, 2.84. Found: C, 55.65; H, 11.85; N, 2.68. ^{1}H NMR ($(CD_3)_2CO$), δ: −2.44 (br s, 1 H, B−H−B), 1.08 (t, 12 H, CH_3, ^3J(H,H) = 7), 1.27 (m, 6 H, CH_3), 1.49 (hex, 8 H, CH_2, ^3J(H,H) = 7), 1.78 (s), 1.89 (q, 8 H, CH_2, ^3J(H,H) = 8), 2.12 (m, 4 H, CH_2), 3.04 (t, 8 H, NCH_2, ^3J(H,H) = 8). ^{11}B NMR ($(CD_3)_2CO$), δ: −7.7 (1B), −8.2 (2B), −12.2 (1B), −15.3 (d, 2B, ^1J(B,H) = 158), −18.6 (1B), −33.4 (d, 1B, ^1J(B,H) = 132), −35.7 (d, 1B, ^1J(B,H) = 101). ^{31}P{^{1}H} NMR ($(CD_3)_2CO$), δ: 50.52 (s, P(O)-Et_2). ^{13}C{^{1}H} NMR ($(CD_3)_2CO$), δ: 5.64(s), 6.95(s), 13.03 (s, CH_3), 19.53 (s, CH_2), 21.70 (d, J(P, C) = 17), 22.91 (s, CH_2), 23.54 (s), 24.96-(s), 58.45 (s, NCH_2).

Preparation of [7-PHEt_2-8-Ph-7,8-$C_2B_9H_{10}$]. To a three-necked round-bottom flask (250 mL) fitted with a dinitrogen inlet/outlet, containing piperidine (1.77 g, 20.27 mmol) and 1-diethylphosphino-2-phenyl-1,2-dicarba-*closo*-dodecaborane (0.25 g, 0.81 mmol),was added deoxygenated ethanol (25 mL). The mixture was degassed again. The solution was refluxed for 24 h, and once cooled, the solvent was evaporated. When ethanol (15 mL) was added to the residue, a crystalline white solid precipitated. The solid was filtered off, washed with ethanol (5 mL), and air-dried (115 mg, 48%). Anal. Calcd for $C_{12}H_{26}B_9P$: C, 48.27; H, 8.78. Found: C, 48.38; H, 8.31. IR, ν (cm^{-1}): 2980, 2938 (C−H); 2530, 2432 (B−H). ^{1}H{^{11}B} NMR ($(CD_3)_2CO$), δ: −2.01 (br s, 1 H, B−H−B), 1.23 (m, 6 H, CH_3), 2.24 (m, 4 H, CH_2), 5.44 (br d, 1 H, P−H, ^1J(P, H) = 476), 7.33−7.57 (m, 5 H, C_6H_5). ^{11}B NMR ($(CD_3)_2CO$), δ: −6.9 (d, 2B, ^1J(B,H) = 134), −10.9 (d, 1B, ^1J(B,H) = 144), −13.6 (d, 1B, ^1J(B,H) = 163), −15.2 (d, 2B, ^1J(B,H) = 144), −22.3 (d, 1B, ^1J(B,H) = 154), −30.6 (d, 1B, ^1J(B,H) = 96), −34.1 (d, 1B, ^1J(B,H) = 144). ^{31}P NMR ($(CD_3)_2CO$), δ: 24.50 (d, PHEt_2, ^1J(P,H) = 476). ^{13}C{^{1}H} NMR ($(CD_3)_2CO$), δ: 7.15 (d, J(P,C) = 8), 7.25 (d, J(P,C) = 8), 13.15 (d, J(P,C) = 53), 14.05 (d, J(P,C) = 53), 128.1 (s), 128.5 (s), 132.3 (s), 137.8 (d, J(P,C) = 8).

Preparation of [7-P(^{i}Pr)$_2$-8-Ph-7,8-$C_2B_9H_{10}$]. To a three-necked round-bottom flask (250 mL) fitted with a dinitrogen inlet/outlet, containing piperidine (1.27 g, 14.88 mmol) and 1-diisopropylphosphino-2-phenyl-1,2-dicarba-*closo*-dodecaborane (0.20 g, 0.60 mmol), was added deoxygenated ethanol (20 mL). The mixture was degassed again. The solution was refluxed for 24 h, cooled to room temperature, and kept for 24 h at these conditions without stirring. After, the solvent was evaporated under vacuum and the water (15 mL) was added, the mixture was stirred at room temperature for 5 h, giving a white solid. The solid was filtered off, washed twice with water (10 mL), and air-dried. The addition of a HCl (1 M) solution (1 mL) dropwise to the solution increased the yield (150 mg, 77%). Anal. Calcd for $C_{14}H_{30}B_9P$: C, 51.48; H, 9.26. Found: C, 51.45; H, 8.88. IR, ν (cm^{-1}): 2982,2932 (C−H); 2569,2535,2521 (B−H). ^{1}H NMR ($(CD_3)_2CO$), δ: −2.20 (br s, 1 H, B−H−B), 1.16 (m, 12 H, CH_3), 2.67 (m, 2 H, CH), 5.08 (br d, 1 H, P−H, ^1J(P,H) = 459), 7.33 (m, 5 H, C_6H_5). ^{11}B NMR ($(CD_3)_2CO$), δ: −6.8 (d, 1B, ^1J(B,H) = 143), −8.0 (d, 1B, ^1J(B,H) = 150), −10.4 (d, 1B, ^1J(B,H) = 139), −14.7 (d, 2B, ^1J(B,H) = 173), −16.3 (d, 1B, ^1J(B,H) = 176), −22.9 (d, 1B, ^1J(B,H) = 151), −30.8 (d, 1B, ^1J(B,H) = 136), −34.3 (d, 1B, ^1J(B,H) = 144). ^{31}P NMR ($(CD_3)_2CO$), δ: 36.20 (d, P(^{i}Pr)$_2$, ^1J(P,H) = 459). ^{13}C{^{1}H} NMR ($(CD_3)_2CO$), δ: 16.50 (d, J(P,C) = 15), 17.98 (s), 18.79 (s), 22.73 (s), 23.37 (s), 24.09 (d, J(P,C) = 19), 128.1 (s), 128.5 (s), 133.0 (s), 134.7 (s).

Preparation of [7-P(^{i}Pr)$_2$-8-Me-7,8-$C_2B_9H_{10}$]. The degradation procedure used was that described in the literature for [NBu_4][7-P$^i Pr_2$-8-Me-7,8-$C_2B_9H_{10}$].[8] After the ethanol was eliminated under vacuum, the residue was dissolved in water (10 mL) and a HCl (1 M) solution was added dropwise, giving a white precipitate. The solid was filtered off, washed twice with water (5 mL), and air-dried (30 mg, 63%). Anal. Calcd for $C_9H_{28}B_9P$: C, 40.85; H, 10.67. Found: C, 41.29; H, 10.75. IR, ν (cm^{-1}): 2973, 2917, 2875 (C−H); 2544, 2509 (B−H). ^{1}H NMR ($CDCl_3$), δ: −2.70 (br s, 1 H, B−H−B), 1.49 (m, 12 H, CH_3), 1.65 (s, 3 H, CH_3), 2.72 (m, 2, CH), 5.46 (dm, 1 H, P−H, ^1J(P,H) = 444). ^{11}B NMR ($CDCl_3$), δ: −6.0 (d, 1B, ^1J(B,H) = 144), −8.4 (d, 1B, ^1J(B,H) = 163), −10.1 (d, 2B, ^1J(B,H) = 144), −12.7 (d, 1B, ^1J(B,H) = 173), −16.6 (d, 1B, ^1J(B,H) = 134), −22.0 (d, 1B, ^1J(B,H) = 144), −30.6 (d, 1 B, ^1J(B,H) = 115), −34.0 (d, 1B, ^1J(B,H) = 144). ^{31}P NMR ($CDCl_3$), δ: 37.03 (d, PH(^{i}Pr)$_2$, ^1J(P,H) = 444). ^{13}C{^{1}H} NMR ($CDCl_3$), δ: 17.17 (s), 18.04 (s), 18.75 (d, J(P,C) = 19), 23.02 (s), 23.59 (s), 24.16 (d, J(P,C) = 10), 24.82 (s).

Preparation of [7-PHPh_2-8-Ph-7,8-$C_2B_9H_{10}$]. To a three-necked round-bottom flask (250 mL) fitted with a dinitrogen inlet/outlet, containing piperidine (4.2 g, 49.6 mmol) and 1-diphenylphosphino-2-phenyl-1,2-dicarba-*closo*-dodecaborane (0.4 g, 0.99 mmol), was added dried and deoxygenated toluene (40 mL). The mixture was degassed again. The solution was refluxed for 26 h, cooled to room temperature, and kept for 24 h at these conditions without stirring. After the solvent was evaporated under vacuum, the residue was again dissolved in ethanol (15 mL) and a solution of HCl (1 M) in water was added dropwise to precipitate a white solid. The solid was filtered off, washed twice with water (10 mL), and air-dried (200 mg, 51%). It was not possible to get a good analysis, since piperidine was present as an impurity. Anal. Calcd for $C_{20}H_{26}B_9P$: C, 60.86; H, 7.64. Found: C, 60.32; H, 7.56. IR, ν (cm^{-1}): 2959,2924,2853 (C−H); 2544 (B−H). ^{1}H NMR ($(CD_3)_2CO$), δ: −1.85 (br s, 1 H, B−H−B), 7.25 (d, 1 H, P−H, ^1J(P, H) = 507), 7.39 (m, 15 H, C_6H_5). ^{11}B NMR ($(CD_3)_2CO$) δ: −7.10 (d, 2B, ^1J(B,H) = 126), −8.69 (1B), −13.54 (2B), −16.95 (d, 1B, ^1J(B,H) = 139), −22.78 (d, 1B, ^1J(B,H) = 140), −30.89 (d, 1B, ^1J(B,H) = 113), −34.85 (d, 1B, ^1J(B,H) = 143). ^{31}P NMR ($(CD_3)_2$-CO), δ: 15.74 (d, PHPh_2, ^1J(P,H) = 507).

Autoxidation Studies. The *nido*-carboranylmonophosphines (15 mg) were dissolved in 0.5 mL of deuterated acetone or methanol. Their autoxidation was carried out in NMR tubes at room temperature (22 °C) and followed by ^{31}P NMR spectroscopy at various time intervals. The NMR tubes were evacuated, refilled with normal air, and partially filled with the solution of the *nido*-carboranylmonophosphines to be studied. Estimations of the relative concentrations of species were made from peak heights.

Titrations. Suitable amounts of *nido*-carboranylmonophosphines were dissolved in CH_3NO_2 and titrated with 0.100 M $HClO_4$ solutions. All titrations were followed by using a CRISON micropH 2000 with a glass electrode. Following Berners-Price,[3] PPh_3 was used as a standard. Aqueous pK_a values were calculated using the formula of Streuli[9] modified by Allman and Goel:[10]

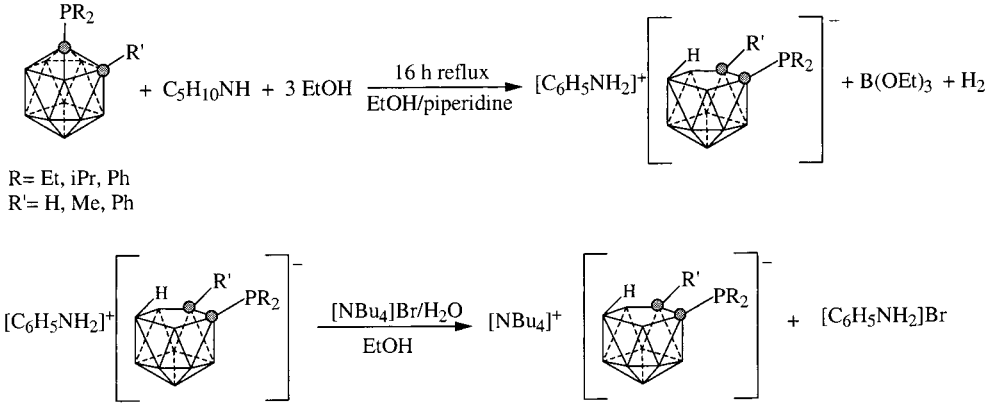
$$pK_a = 10.12 - 0.0129(\Delta HNP + 573)$$

where ΔHNP = [HNP(PPh_3) − HNP(*nido*-carboranylmonophosphines)].

X-ray Structure Determination of [NBu_4][7-P(O)Ph_2-8-Ph-7,8-$C_2B_9H_{10}$] and [7-PH(^{i}Pr)$_2$-8-Me-7,8-$C_2B_9H_{10}$]. The unit cell parameters and single-crystal data collections for both compounds were performed at ambient temperature on a Rigaku AFC5S diffractometer using graphite-monochromatized Mo Kα radiation. Data obtained were corrected for Lorentz and polarization effects but not for absorption. A total of 3929 and 2964 unique reflections were collected by the $\omega/2\theta$ scan mode ($2\theta_{max} = 50°$) for [NBu_4][7-P(O)Ph_2-8-Ph-7,8-$C_2B_9H_{10}$] and [7-PH(^{i}Pr)$_2$-8-Me-7,8-$C_2B_9H_{10}$], respectively. Although the data collection speed for the former was 2°/min, the data set contained only 1246 reflections greater than $3\sigma(I)$ (31.5%).

The structure of [NBu_4][7-P(O)Ph_2-8-Ph-7,8-$C_2B_9H_{10}$] was solved by direct methods and refined by full-matrix least-squares by using the SHELX-97 program system.[11] In the $[NBu_4]^+$ ion, terminal part of one butyl group is disordered with the carbon atoms C44 and C45 occupying two positions, the site occupancies being 0.64(2) for C44A and C45A and 0.36(2) for C44B and C45B. P, O, N, and fully occupied C atoms were refined with anisotropic displacement parameters. Boron atoms and disordered carbon atoms were refined with isotropic

Scheme 1. Partial Degradation of *closo*-Carboranylmonophosphines to *nido*-Carboranylmonophosphines



displacement parameters. Hydrogen atoms were included in the calculations at the fixed distances from their host atoms or rotating groups (CH_3) and treated as riding atoms using the SHELX-97 default parameters.

The structure of [7-PH(^{i}Pr)$_2$-8-Me-7,8-$C_2B_9H_{10}$] was solved by direct methods and refined by SHELX-97. All non-hydrogen atoms were refined with anisotropic diplacement parameters. Hydrogen atoms bonded to the carborane cage and that connected to P were refined isotropically, but rest of the H atoms were included in the calculations at the fixed distances from their host atoms and treated as riding atoms or rotating groups using the SHELX-97 default parameters.

Results and Discussion

I. Partial Degradation or Deboronation of the *closo*-Carboranylmonophosphines. The reaction of *closo*-carboranylmonophosphines 1-PR_2-2-R′-1,2-$C_2B_{10}H_{10}$ (R = Ph, Et, ^{i}Pr; R′ = Me) with piperidine using a 1:25 ratio in ethanol for 16 h produces in high yield the respective *nido*-carboranylmonophosphines [7-PR_2-8-R′-7,8-$C_2B_9H_{10}$]$^-$.[8] The general reaction is shown in Scheme 1. It has been known for years that the partial degradation reaction on *o*-carborane is driven by a nucleophilic attack which can remove one of their BH units (B(3) or B(6)), formally as BH^{2+}, leaving *nido*-shaped [7,8-$C_2B_9H_{12}$]$^-$ or [7,8-$C_2B_9H_{11}$]$^{2-}$ anions. Several nucleophiles such as alkoxides,[6] amines,[7] fluorides,[12] and phosphanes[13] have been used. The partial degradation of *closo*-carboranylmonophosphines using the well-established procedure[6a] with KOH in ethanol was unsuccessful because the $C_{cluster}$−P bond was hydrolyzed, and only the *nido* [7,8-$C_2B_9H_{12}$]$^-$ was obtained. In contrast, the degradation process with piperidine in toluene[7] in a 1:4 molar ratio of *closo*-carboranylmonophosphines to piperidine at 20 °C did not give the desired *nido* species, and the starting *closo* compounds were recovered.

To discern on the identification of the removed BH unit using piperidine in ethanol, the partial degradation reaction was carried out at reflux temperature for 16 h on 1-P^{i}Pr$_2$-2-Ph-1,2-$C_2B_9H_{10}$. ^{11}B, ^{11}B{^{1}H}, ^{31}P{^{1}H}, and ^{31}P spectra of the reaction crude were recorded. The ^{31}P{^{1}H} and ^{31}P spectra show a single resonance at 16.86 ppm that confirms the presence of the *nido* [7-P^{i}Pr$_2$-8-Ph-1,2-$C_2B_9H_{10}$]$^-$ anion. The ^{11}B{^{1}H} spectrum displays the pattern 1:1:1:1:2:1:1:1 in the range between −8.51 and −35.41 ppm characteristic of the *nido* [7-P^{i}Pr$_2$-8-Ph-1,2-$C_2B_9H_{10}$]$^-$ species.[8] An extra resonance at + 17.02 ppm is always present. The ^{11}B spectrum clearly shows that this resonance corresponds to a boron atom with no B−H bond. Since this the only extra resonance observed, it most likely corresponds to the removed BH vertex. According to the literature,[14] the chemical shift for ethyl borate appears at +17.2,[15] 17.6,[16] and 18.1 ppm.[17] It is known that borate esters produce azeotropes with their respective alcohols.[18] The $B(OEt)_3$·7.75EtOH azeotrope lowers the $B(OEt)_3$ boiling point from 117−119 °C to 76.6 °C. [18] Considering that the removed boron vertex had been converted to $B(OEt)_3$, the reaction mixture was evaporated at 0.1 mm and volatiles were trapped at −78 °C. The ^{11}B spectrum of the remaining mother liquor shows only the pattern for the *nido* [7-P^{i}Pr$_2$-8-Ph-1,2-$C_2B_9H_{10}$]$^-$ anion. The ^{11}B spectrum of the trapped solution showed only the complementary resonance at + 17.02 ppm. Once the fate of the removed BH^{2+} is known, the question of how this $B(OEt)_3$ is produced remains. Our explanation of why the partial degradation reaction of *closo*-carboranylmonophosphines with piperidine in ethanol is successful is based on the fact that piperidine is a secondary amine, a possible nucleophile and a base,[19] that establishes an acid/base equilibrium with ethanol. Piperidinium ethoxide is present in a minor amount in the reaction medium, much less than is required for a quick degradation but sufficient enough amount to slowly and smoothly produce $B(OEt)_3$. The low $[EtO]^-$ concentration produces mild conditions that prevent the $C_{cluster}$−P hydrolysis.

Our conclusion is that the partial degradation of *closo*-carboranylmonophosphines is greatly dependent on the presence of the phosphorus atom bonded to the cluster carbon atom. This modifies the electronic distribution in the *closo* cluster and the B(3)/B(6) atoms become less electrophilic than in 1,2-R,R′-1,2-$C_2B_9H_{10}$ derivatives (R,R′ = alkyl or aryl groups). This would explain that the partial degradation reaction[7] with piperidine in toluene does not proceed. In contrast, the strong partial degradation conditions using alkoxides[6] are too aggresive and lead to alkaline hydrolysis of the $C_{cluster}$−P bond. The low constant concentration of alkoxides reported here permits the combination of the nucleophilicity of the $[EtO]^-$ with the mild conditions required to preserve the $C_{cluster}$−P bond.

For comparison purposes, two new *nido*-carboranylmonophosphines, [NBu_4][7-PEt_2-8-Ph-7,8-$C_2B_9H_{10}$] and [NBu_4][7-P(^{i}Pr)$_2$-8-Ph-7,8-$C_2B_9H_{10}$], have been prepared by following this procedure. These compounds were characterized by IR andNMR spectroscopy and elemental analysis, which corroborate the formation of the *nido* species.

Two experimental observations, during the *nido*-carboranylmonophosphines characterization, motivated us to further study the influence of the *nido*-[7,8-$C_2B_9H_{12}$]$^-$ anion on the phosphorus oxidation and basicity. The first observation was the result of extending the deboronation refluxing time from 16 to 21 h. In this case, the ^{31}P{^{1}H} NMR of the solution displayed two different resonances, one corresponding to the *nido* species and a second one, which was split into a doublet in the ^{31}P

Scheme 2. Oxidation of *nido*-Carboranylmonophosphines

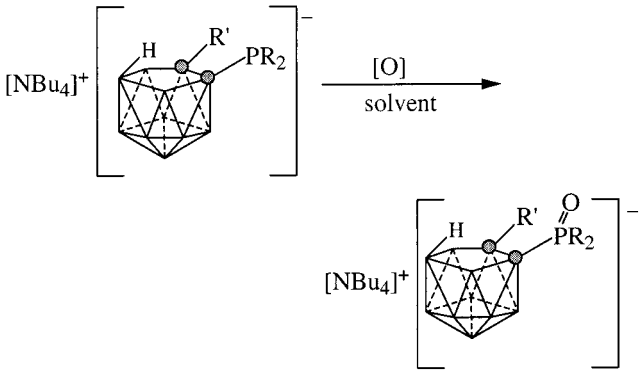


Table 1. Difference between the $^{31}P\{^1H\}$ NMR (ppm) of *nido*-Carboranylmonophosphines Containing a P(III) and the Corresponding Oxides Containing a P(V)

		δ ^{31}P *nido*		
R	R′	P(III)	P(V)	Δ
Et	Me	−8.29	50.52	58.81
Et	Ph	−5.43	44.30	49.73
^{i}Pr	Me	15.43	55.10	39.67
^{i}Pr	Ph	16.86	56.89	40.03
Ph	Me	12.79	31.75	18.96
Ph	H	19.53	39.27	19.74
Ph	Ph	10.50	26.26	15.76

NMR spectrum, with a high coupling constant. This fact led us to think that a new species containing a P−H bond had been formed.

The second observation came about as a result of allowing the former solution to stand for 3 days in the air. The $^{31}P\{^1H\}$ NMR spectrum showed that the *nido* species resonance disappeared and a new resonance at a lower field was observed. The new signal indicated that the *nido* species was oxidized in solution. On the contrary, the ^{31}P NMR spectrum evidenced that a species containing a P−H bond was stable under air.

Forced Oxidation of *nido*-Carboranylmonophosphines. We have forced the oxidation of *nido*-carboranylmonophosphines to their corresponding phosphine oxides using hydrogen peroxide in acetone[20] (Scheme 2). The new oxidized species were not isolated, but their spectroscopic characterization was followed in solution by ^{31}P and ^{11}B NMR. In all cases, only one peak at a lower field with regard to the starting *nido* species was observed in the $^{31}P\{^1H\}$ NMR spectra. These resonances did not split in the ^{31}P NMR. The ^{11}B NMR of the new phosphine oxides showed just minor differences with regard to the *nido* precursor.

In the oxidized species the negative charge of the *nido* cluster is maintained while the phosphorus oxidation state has changed from P(III) to P(V). This is clearly reflected in the $^{31}P\{^1H\}$-NMR spectra (Table 1) where it can be observed that the chemical shifts for the oxidized species have shifted to lower field as much as 58.81 ppm.

The formation of the oxide was corroborated when attempting to grow crystals of [NBu_4][7-PPh_2-8-Ph-7,8-$C_2B_9H_{10}$]. After the slow evaporation of a solution of this compound in acetone in the air, crystals suitable for X-ray diffraction were obtained. The *nido* compound had reacted with O_2 to produce the corresponding phosphine oxide [NBu_4][7-P(O)Ph_2-8-Ph-7,8-$C_2B_9H_{10}$]. The molecular structure is described at the end of this section (Figure 1).

Forced Protonation of the *nido*-Carboranylmonophosphines. The protonation of these *nido*-carboranylmonophosphines was forced by increasing the refluxing time in the deboronation process or by reacting with an acid (see Scheme 3). As is well-known, phosphines react with perchloric acid in ethanol to give the tertiary phosphonium salts.[21] When *nido*-carboranylmonophosphines are reacted with an aqueous solution of hydrochloric acid in ethanol, a white solid immediately precipitates in a very good yield. The spectroscopic data of the compound confirmed the formation of the expected protonated zwitterionic species.

These phosphonium salts of general formulas [7-PHR_2-8-R′-7,8-$C_2B_9H_{10}$] were characterized by spectroscopic data and elemental analysis, which were consistent with the proposed formulas. The ^{1}H NMR spectra displayed broad resonances at ca. −2.05 ppm (B−H−B) and broad doublets between 5.0 and 7.5 ppm with a coupling constant ^1J(P,H) between 450 and 500 Hz, indicating the P−H bond formation in the compounds (see Table 2). As a general trend, the $^{31}P\{^1H\}$ NMR resonances of these phosphonium salts appear at lower field than those observed for the respective nonprotonated *nido*-species. As a

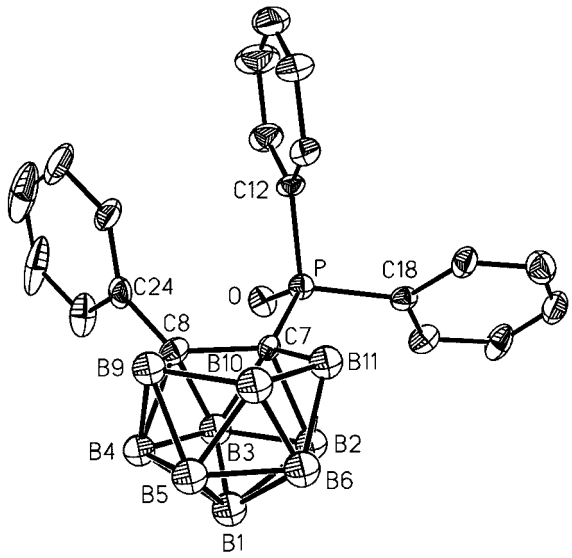


Figure 1. Perspective view of the anion of [NBu_4][7-P(O)Ph_2-8-Ph-7,8-$C_2B_9H_{10}$] showing 20% displacement ellipsoids. Hydrogen atoms are omitted for clarity.

Scheme 3. Forced Protonation of *nido*-Carboranylmonophosphines To Form the Zwitterionic Species

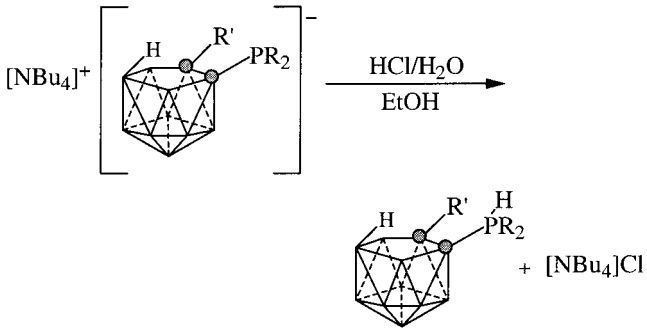


Table 2. ^{1}H and $^{31}P\{^1H\}$ Chemical Shifts (in ppm) and Coupling Constants between the P and H Atoms in Absolute Values (in hertz)

compounds	δ ^{1}H	δ $^{31}P\{^1H\}$	^1J(P,H)
[7-$PHEt_2$-8-Ph-7,8-$C_2B_9H_{10}$]	5.44	24.50	476
[7-PH(^{i}Pr)$_2$-8-Ph-7,8-$C_2B_9H_{10}$]	5.08	36.20	459
[7-PH(^{i}Pr)$_2$-8-Me-7,8-$C_2B_9H_{10}$]	5.46	37.03	444
[7-$PHPh_2$-8-Ph-7,8-$C_2B_9H_{10}$]	7.25	15.74	507

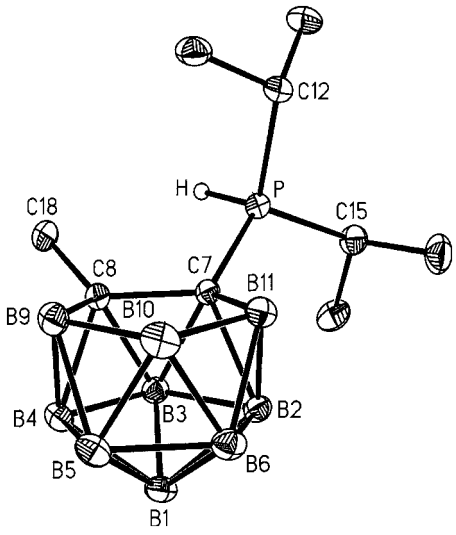


Figure 2. Perspective view of [7-PH(^{i}Pr)$_2$-8-Me-7,8-$C_2B_9H_{10}$] showing 20% displacement ellipsoids. Hydrogen atoms, except that bonded to phosphorus, are omitted for clarity.

Table 3. Crystallographic Data for [NBu_4][7-P(O)Ph_2-8-Ph-7,8-$C_2B_9H_{10}$] and [7-PH(^{i}Pr)$_2$-8-Me 7,8-$C_2B_9H_{10}$

	[NBu_4][7-P(O)Ph_2-8-Ph-7,8-$C_2B_9H_{10}$]	[7-PH(^{i}Pr)$_2$-8-Me-7,8-$C_2B_9H_{10}$]
chem formula	$C_{36}H_{61}B_9NOP$	$C_9H_{28}B_9P$
fw	652.12	264.57
a (Å)	13.884(7)	11.1860(9)
b (Å)	21.485(4)	9.3633(10)
c (Å)	13.404(7)	16.1673(11)
β (deg)	90	93.090(7)
V (Å^3)	3998(3)	1690.9(3)
Z	4	4
space group	$P2_12_12_1$ (No. 19)	$P2_1/c$ (No. 14)
T (°C)	21	21
λ (Å)	0.710 69	0.710 69
ρ (g cm^{-3})	1.083	1.039
μ (cm^{-1})	0.97	1.40
R1[a] [$I > 2\sigma(I)$]	0.0752	0.0390
wR2[b] [$I > 2\sigma(I)$]	0.1478	0.0990

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.

confirmation, in the ^{31}P NMR these resonances are split into a doublet with the same coupling constant as those observed in the corresponding ^{1}H NMR. The ^{11}B{^{1}H} NMR spectra of the protonated compounds and their *nido* precursors are very similar. This proves that the reaction takes place on the *exo*-cluster phosphorus atom. Besides, a good crystal of [7-PH(^{i}Pr)$_2$-8-Me-$C_2B_9H_{10}$] (Figure 2) has been grown which has enabled elucidation of its molecular structure.

Crystal Structure of [NBu_4][7-P(O)Ph_2-8-Ph-7,8-$C_2B_9H_{10}$]. The structure of the compound consists of well-separated cations and anions without any close contact between them. A view of the anionic part is shown in Figure 1, crystal data are listed in Table 3, and selected interatomic distances and angles are reported in Table 4. Crystal structure analysis confirmed the *nido* geometry of the carborane cage and the phosphine oxide formation. Fairly large esd's of the geometrical parameters limit a detailed discussion of the bond lengths and angles. However, some observations have been made. The C(7)−C(8) distance of 1.592(11) Å falls in the range found for the *nido* carboranes, and the P−C(7)−C(8)−C(24) torsion angle of −7.6(11)° is normal for a carborane cluster bearing bulky substituents at the cluster carbons. The angles around the C(7) and C(8) atoms do not indicate any considerable repulsion between the cluster carbon substituents. However, comparison of the C−P bond distances in the present anion and those of [7-PPh_2-8-S^{i}Pr-7,8-$C_2B_9H_{10}$]$^-$ [22] reveals that the P−C(7) bond of 1.811(7) Å in [7-P(O)Ph_2-8-Ph-7,8-$C_2B_9H_{10}$]$^-$ is significantly shorter than the bond of 1.855(3) Å in the compared anion.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for [7-P(O)Ph_2-8-Ph-7,8-$C_2B_9H_{10}$]$^-$

P−O	1.484(5)	C7−B11	1.608(12)
P−C7	1.811(7)	C8−C24	1.533(11)
P−C12	1.795(8)	C8−B9	1.600(13)
P−C18	1.812(9)	B9−B10	1.804(15)
C7−C8	1.592(11)	B10−B11	1.784(14)
O−P−C12	111.3(4)	B11−C7−P	122.5(6)
O−P−C7	115.4(3)	B3−C7−P	113.7(6)
C12−P−C7	106.8(4)	B2−C7−P	117.6(6)
O−P−C18	109.4(4)	C24−C8−C7	118.9(6)
C12−P−C18	104.6(4)	C24−C8−B9	116.0(8)
C7−P−C18	108.8(4)	C24−C8−B3	120.0(8)
C8−C7−P	118.7(5)	C24−C8−B4	120.5(7)

Table 5. Selected Bond Lengths (Å) and Angles (deg) for [7-PH(^{i}Pr)$_2$-8-Me-7,8-$C_2B_9H_{10}$]

P−C7	1.788(2)	C7−B11	1.631(3)
P−C12	1.817(2)	C8−C18	1.526(2)
P−C15	1.820(2)	C8−B9	1.617(3)
P−H	1.30 (2)	B9−B10	1.846(3)
C7−C8	1.598(2)	B10−B11	1.825(3)
C7−P−C12	110.78(8)	B11−C7−P	116.41(12)
C7−P−C15	117.94(9)	B3−C7−P	118.72(12)
C12−P−C15	109.33(9)	B2−C7−P	120.89(12)
C7−P−H	106.6(8)	C18−C8−C7	121.41(15)
C12−P−H	106.5(8)	C18−C8−B9	119.56(15)
C15−P−H	104.9(8)	C18−C8−B4	117.40(15)
C8−C7−P	117.81(12)	C18−C8−B3	114.67(15)

Crystal Structure of [7-PH(^{i}Pr)$_2$-8-Me-$C_2B_9H_{10}$]. A drawing of the zwitterionic molecule is illustrated in Figure 2, crystal data are given in Table 3, and selected interatomic distances and angles are listed in Table 5. Structure analysis confirmed the *nido* nature of the carborane cluster and protonation of the PPh_2 group. The C(7)−C(8) distance (1.598(2) Å) and the P−C(7)−C(8)−C(12) torsion angle (6.1(2)°) agree with the corresponding values of [7-P(O)Ph_2-8-Ph-7,8-$C_2B_9H_{10}$]$^-$. Further comparison of [NBu_4][7-P(O)Ph_2-8-Ph-7,8-$C_2B_9H_{10}$] and [7-PH(^{i}Pr)$_2$-8-Me-7,8-$C_2B_9H_{10}$] reveals that the carborane's open face, C_2B_3 belt, of the former compound is slightly shorter than the corresponding one in the latter. The reason for that can be such that the negative charge in the former compound is concentrated at the oxygen atom of the P═O group, while in the later compound it is located on the upper belt of the carborane cage.

II. Contribution of the *nido*-Carboranylmonophosphines to the ^{31}P Chemical Shift. It has been stablished that *closo*-carboranyl groups have a strong-acceptor effect[23] on the carbon substituent. On the contrary, the anionic *nido* cluster releases part of its electron density toward the carbon substituent.[24] The electron-acceptor character of the *closo* cluster was observed for the *closo*-carboranylmonophosphines[4e] and it was calculated from the contribution of the *closo*-carboranyl fragment to the ^{31}P NMR chemical shift, as had been done with organic phosphines.[25] Table 6 contains the ^{31}P{^{1}H} NMR chemical shifts of *closo*-carboranylmonophosphines[4e] and their respective *nido* derivatives. The phosphorus chemical shift of the *nido*-alkylcarboranylmonophosphine species has shifted to higher field with respect to the *closo* precursors. This difference is not observed for the *nido*-arylcarboranylmonophosphines. This different behavior between aryl- and alkylcarboranylmonophos-

Table 6. $^{31}P\{^1H\}$ Chemical Shift (in ppm) for *nido*-[7-PR_2-8-R′-7,8-$C_2B_9H_{10}$]$^-$ and *closo*-Carboranylmonophosphines [1-PR_2-2-R′-1,2-$C_2B_{10}H_{10}$][4e]

		δ $^{31}P\{^1H\}$		
R	R′	nido	closo	Δ (δ ^{31}P)
Et	Me	−8.29	5.37	−13.66
Et	Ph	−5.43	9.93	−15.36
^{i}Pr	Me	15.73	33.82	−18.09
^{i}Pr	Ph	16.86	38.50	−21.64
Ph	Me	12.79	10.97	+1.82
Ph	H	19.53	25.58	−6.05
Ph	Ph	10.50	13.40	−2.90

phines will also be found later, when discussing the *nido*-carboranylmonophosphines basicity. The difference of chemical shifts between the *closo* and *nido* species shall be attributed to the cluster influence and this shall also permit us to calculate the contribution of the *nido*-carboranyl anion to the ^{31}P NMR.

It has been reported[25] that eq 1 reproduces quite well the contributions of fragments to the ^{31}P NMR chemical shifts for phosphorus compounds. Recently, we reported[4e] the contribution of the *o*-carboranyl fragment to be + 57.2 ppm, while the phenyl-*o*-carboranyl contribution is +43.3 ppm and the methyl-*o*-carboranyl is +38.7 ppm. We considered that it would be possible to calculate the *nido* cluster contribution, applying the same eq 1.

$$\delta_P = -62 + \Sigma(\sigma^P)_R \qquad (1)$$

Table 7 contains the $(\sigma^P)_{nido}$ calculated values for the cluster contribution. A quick look indicates a great dispersion of the $(\sigma^P)_{nido}$ values, and one could easily be induced to believe that it is unrealistic to give a specific value to $(\sigma^P)_{nido}$. However, we believe that this dispersion is motivated by the existence of the aryl groups on the phosphorus. If the [7-PR_2-8-Me-7,8-$C_2B_9H_{10}$]$^-$ (R = Et, ^{i}Pr) set is considered, the $(\sigma^P)_{nido}$ contribution should be (25.71 + 23.73)/2 = 24.72 ppm, and when the [7-PR_2-8-Ph-7,8-$C_2B_9H_{10}$]$^-$ (R = Et, ^{i}Pr) set is considered, the contribution should be (28.57 + 24.86)/2 = 26.71 ppm, not far one from the other. Thus, the $(\sigma^P)_{nido}$ contribution will be close to 25.7, as no major modulation by the substitution at C(8) is found (24.72 vs 26.71).

Table 7. Contribution of the *nido* Cluster to the ^{31}P Chemical Shift, $(\sigma^P)_{nido}$ Calculated from eq 1

nido	R	$(\sigma^P)_R$	$(\sigma^P)_{nido}$
[7-PEt_2-8-Me-7,8-$C_2B_9H_{10}$][a]	Et	14	25.71
[7-P(^{i}Pr)$_2$-8-Me-7,8-$C_2B_9H_{10}$][a]	^{i}Pr	27	23.73
[7-PPh_2-8-Me-7,8-$C_2B_9H_{10}$][b]	Ph	18	38.79
[7-PEt_2-8-Ph-7,8-$C_2B_9H_{10}$][a]	Et	14	28.57
[7-P(^{i}Pr)$_2$-8-Ph-7,8-$C_2B_9H_{10}$][a]	^{i}Pr	27	24.86
[7-PPh_2-8-Ph-7,8-$C_2B_9H_{10}$][a]	Ph	18	36.50

[a] Cation = $[NBu_4]^+$. [b] Cation = $[NMe_4]^+$.

Table 8. Oxidation of *nido*-Carboranylmonophosphines

	% oxide		
nido	1 day	2 days	3 days
[7-PEt_2-8-Me-7,8-$C_2B_9H_{10}$]$^-$	100		
[7-PEt_2-8-Ph-7,8-$C_2B_9H_{10}$]$^-$	6	20	30
[7-P(^{i}Pr)$_2$-8-Me-7,8-$C_2B_9H_{10}$]$^-$	32	36	50
[7-P(^{i}Pr)$_2$-8-Ph-7,8-$C_2B_9H_{10}$]$^-$	5	50	75
[7-PPh_2-8-Me-7,8-$C_2B_9H_{10}$]$^-$	36	36	36
[7-PPh_2-8-Ph-7,8-$C_2B_9H_{10}$]$^-$	22	40	53
[7-PPh_2-7,8-$C_2B_9H_{10}$]$^-$	0	0	2[a]

[a] In MeOH.

III. Nucleophilicity and Basicity of the *nido*-Carboranylmonophosphines. The cluster influence on the phosphorus atom is not only observed in the ^{31}P NMR chemical shift but also in its chemical properties. While the *closo*-carboranylmonophosphines are stable in solution, their *nido* derivatives are readily oxidized, yielding the corresponding oxide, or are protonated, producing their phosphonium salts as zwitterionic species.

Autoxidation of the *nido*-Carboranylmonophosphines. The autoxidation process of *nido*-carboranylmonophosphines was studied in acetone and MeOH and followed by ^{31}P NMR spectroscopy (see Experimental Section). Clearly from Table 8 the rate of oxidation in these phosphines depends more on the R′ bonded to the C(8) in the cluster than on the R group at the phosphorus atom.

No great differences were observed when the oxidation reactions were carried out in MeOH; thus the disparity of values shown above seem to suggest that the stability toward oxidation is more of a kinetic nature than due to electronic effects.

pK_a of the *nido*-Carboranylmonophosphines. The *nido*-carboranylmonophosphines basicity has been tested by measuring its pK_a values. The low solubility of these *nido*-carboranylmonophosphines in H_2O precluded directly calculating the pK_a of these species. However, this can be overcome by using the approach of Streuli[9] modified by Allman and Goel.[10] In this method, a known solution of phosphine in CH_3NO_2 is titrated with $HClO_4$. Results are then compared to those of a phosphine of known pK_a by applying an experimental equation. The pK_a values for the various *nido*-carboranylmonophosphines are listed in Table 9. As a reference, pK_a values of known and similar tertiary phosphines are also included in the table.

Keeping in mind that errors may arise due to the approximation of converting E values into pK_a values, the pK_a results obtained seem very reasonable and allow interesting conclusions. The more basic *nido*-carboranylmonophosphines are those that incorporate donating groups, Et and ^{i}Pr fragments, bonded to the phosphorus. Also, the substituents on the C(8) position modify the pK_a value. In this case the results are also logical as the more donating group (Me) produce the phosphines with the highest pK_a while the more electron-withdrawing group (Ph)

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Table 9. pK_a Values for *nido*-Carboranylmonophosphines and Tertiary Phosphines[9]

compound	pK_a	Δ(pK_a) R′ = Me, R′ = Ph
PEt_3	8.69	
[7-PEt_2-8-Me-7,8-$C_2B_9H_{10}$]$^-$	9.49	
[7-PEt_2-8-Ph-7,8-$C_2B_9H_{10}$]$^-$	8.88	0.61
$P(nPr)_3$	8.64	
[7-$P(^iPr)_2$-8-Me-7,8-$C_2B_9H_{10}$]$^-$	9.39	
[7-$P(^iPr)_2$-8-Ph-7,8-$C_2B_9H_{10}$]$^-$	8.76	0.63
PPh_3	2.73	
[7-PPh_2-8-Me-7,8-$C_2B_9H_{10}$]$^-$	5.91	
[7-PPh_2-8-Ph-7,8-$C_2B_9H_{10}$]$^-$	5.86	0.05

the lowest pK_a. The pK_a difference between 8-Me- and 8-Ph is 0.6. Interestingly, the pK_a values of these *nido*-carboranylmonophosphines are comparable to the pK_a values of neutral organic tertiary phosphines. The situation changes considerably when the arylcarboranylphosphines [7-PPh_2-8-Me-7,8-$C_2B_9H_{10}$]$^-$ and [7-PPh_2-8-Ph-7,8-$C_2B_9H_{10}$]$^-$ are considered. These carboranylmonophosphines are distinctly more basic than PPh_3, which can be considered its organic analogue. In addition, the existence of a donating or electron-withdrawing group (Me or Ph) on the cluster C(8) position does not alter the pK_a significantly.

As mentioned, in the $^{31}P\{^1H\}$ NMR chemical shifts there was also a gap between aryl- and alkylcarboranylphosphines. All produce a shift to higher field, although the shift was definitively smaller for the arylphosphines. Considering the pK_a's values found, all *nido*-carboranylmonophosphines are more basic than their organic analogues, but the *nido*-arylcarboranylphosphines are more basic with regard to their equivalent organic analogues than the alkyl ones.

Thus, while the influence of the *closo* moiety, 1,2-$C_2B_{10}H_{12}$, on the *exo*-cluster lone pair containing substituent is related to its electron-acceptor character, producing low coordinating ligands, the high reactivity of the corresponding *nido* derivatives is due to the electron-donor capacity of the *nido*-[7,8-$C_2B_9H_{10}$]$^-$ anion.

The *nido* cluster dissipates electron density on the phosphorus atom, increasing the pK_a and thus facilitating the capture of a proton from the reaction environment. So, after the deboronation reaction has taken place, the possibility of oxidation and protonation of the phosphorus atoms is very high. The capture of a proton in dialkyl derivatives is very favorable, providing a route to produce a neutral zwitterionic compound. The distinct character of the *closo* C_2B_{10} cluster vs the *nido* $[C_2B_9]^-$ species is equally well shown in the $^{31}P\{^1H\}$ NMR spectra. This can be easily understood simply considering the shielding or deshielding effect of the cluster on the phosphorus atom. The electron-withdrawing *closo* C_2B_{10} cluster pulls electron density out of the P, deshielding the nucleus and causing a downfield shift. On the contrary, the anionic *nido* $[C_2B_9]^-$ cluster dissipates electron density into the phosphorus, consequently shielding it and shifting the phosphorus resonance to higher field.

The Case for the Benzocarborane. We feel that a similar explanation could be given to the distinct reactivity of benzocarborane[26] (*closo* species) and its *nido* derivative. These two

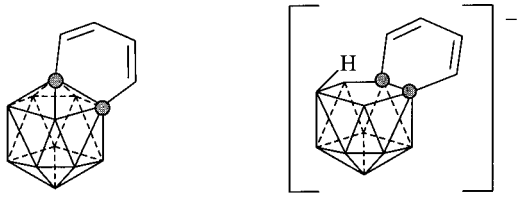

Figure 3. *closo*-Benzocarborane and *nido*-benzocarborane.

compounds are represented in Figure 3. Wade and co-workers[27] clearly established by X-ray structural analysis that benzocarborane was nonaromatic as the C−C bond lengths in the C_6 ring shows alternating values consistent with the localized single and double bonds. They also observed that benzocarborane did not undergo a Diels−Alder reaction with malic anhydride, despite its diene character, while with the analogous *nido*-benzocarborane the Diels−Alder reaction proceeded. Their interpretation was that the difference in reactivity was attributable to a combination of steric and electronic factors.[28]

Our view of the system is that the cluster influence, either *closo* or *nido*, is very strong on the cluster's carbon α substituent.[4a] We invoked a $p_\pi-p_\pi$ interaction between the α carbon and the cluster carbon. The relevant point, however, is that the cluster influence is of distinct sign, whether it is *closo* or *nido*. The *closo* and *nido* clusters exhibit, respectively, a $-I$ and $+I$ effect (I = inductive effect). Thus, the diene in the *closo*-benzocarborane is a poor base while the diene in the *nido*-benzocarborane is a strong base, ready to search for the LUMO of the dienophile. The higher basicity of the *nido*-benzocarborane is enlarged, considering that the cluster's negative charge is distributed mostly on the open face and not so much on the rest of the cluster. This also explains why B−H's on the open face coordinate to metal quite readily, while other B−H's behave more as spectators,[29] and certainly explains why *nido*-carboranylthioethers and *nido*-carboranylphosphines are such good coordinating ligands.

Acknowledgment. This work was supported, in part, by CIRIT (Project QFN95-4721) and by CICYT (Project MAT98-0921). R. K. thanks the Academy of Finland (Project 41519).

Supporting Information Available: X-ray crystallographic files, in CIF format, for [NBu_4][7-$P(O)Ph_2$-8-Ph-7,8-$C_2B_9H_{10}$] and [7-$PH(^iPr)_2$-8-Me-7,8-$C_2B_9H_{10}$]. This material is available free of charge via the Internet at http://pubs/acs/org.

IC000858P

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