A Route to *exo*-Heterodisubstituted and Monosubstituted *o*-Carborane Derivatives

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Received August 8, 1996

Introduction

To synthesize new *o*-carborane-derived materials such as asymmetric macrocycles, compounds for boron−neutron capture therapy,[1] and asymmetric catalysts, monosubstituted precursors are required. According to Kahl and co-workers,[2] heterofunctional polyhedral carboranes appeared to be logical synthetic targets in investigations of compounds for BNCT. Unfortunately there are not many methods available to prepare such compounds as has recently been stressed.[3,4] The reaction of terminal alkynes with $B_{10}H_{12}L_2$ suffers from the scarcity of appropriate alkynes, and monolithiation of 1,2-$C_2B_{10}H_{12}$ at carbon competes unfavorably with dilithiation, which leads to complex mixtures.

This problem has recently been solved by blocking one of the C_c positions in *o*-carborane with a $-Si(Me)_2CMe_3$ (TBDMS) group; effecting the desired reaction in the other C_c position; and subsequently deprotecting the C_c-$Si(Me)_2CMe_3$ position with $N(Bu)_4F$.[2] A second procedure consists of producing the lithiation reaction in dimethoxyethane.[5] Monosubstituted *o*-carborane derivatives can be synthesized by the reaction of *o*-carborane with 1 equiv of BuLi and the appropriate electrophile in dimethoxyethane. The 1,2-Li_2-1,2-$C_2B_{10}H_{10}$ compound, which would lead to the disubstituted species, is most probably avoided due to the bulkiness of the first Li(dimethoxyethane) moiety which blocks the entering of the second group. By using this second procedure it was possible to produce 1-SH-1,2-$C_2B_{10}H_{11}$ almost quantitatively, which then provided a route to heterodisubstituted compounds. Our group has been concerned with the synthesis of dithioether (1,2-$(SR)_2$-1,2-$C_2B_{10}H_{10}$),[6] monothioether (1-SR-2-R′-1,2-$C_2B_{10}H_{10}$),[7] diphosphino (1,2-$(PR_2)_2$-1,2-$C_2B_{10}H_{10}$),[8] and monophosphino compounds (1-PR_2-2-R′-1,2-$C_2B_{10}H_{10}$).[8f,9] So, disubstitution was achieved either with two sulfur or two phosphorus elements bonded to the cluster. One way to lower the symmetry of the disubstituted species while maintaining their electron-rich chelating capacity consists of producing heterodisubstituted S,P compounds. This paper discusses a synthetic path to heterodisubstituted 1-PPh_2-2-SR-1,2-$C_2B_{10}H_{10}$ compounds from 1,2-$C_2B_{10}H_{12}$ and their partial degradation to get the [7-PPh_2-8-SR-7,8-$C_2B_9H_{10}$]$^-$ anions. The $-PPh_2$ group was chosen over other $-PR_2$ moieties because of considerably better stability.

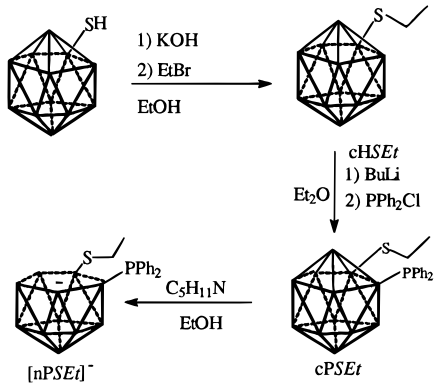

Figure 1. Synthetic path to *closo*-heterodisubstituted *o*-carborane derivatives and their partial degradation.

Results and Discussion

Two strategies were possible to produce the desired 1-PPh_2-2-SR-1,2-$C_2B_{10}H_{10}$ compounds: (i) to produce first 1-PPh_2-$C_2B_{10}H_{11}$ and later derivatize the second C_c−H, or (ii) to initially produce 1-SR-1,2-$C_2B_{10}H_{11}$ followed by derivatization of the second C_c−H. However the stability of 1-PPh_2-1,2-$C_2B_{10}H_{11}$ toward BuLi in diethyl ether was not as good as expected, since a high proportion of 1,2-$C_2B_{10}H_{12}$ was obtained. Thus 1-SH-1,2-$C_2B_{10}H_{11}$ was chosen as the starting material. The overall procedure for the synthesis of 1-PPh_2-2-SEt-1,2-$C_2B_{10}H_{10}$ is indicated in Figure 1.

Starting from 1-SH-1,2-$C_2B_{10}H_{11}$ the derivatives 1-SR-1,2-$C_2B_{10}H_{11}$ were obtained after deprotonation with KOH in ethanol followed by alkylation with the appropriate alkyl bromide (R = Et, Bz). For R = ^{i}Pr and Bu the deprotonation was done with KOH in ethanol but the alkylation was in THF, since in ethanol C_c−S bond breaking did take place. Compounds with R = Et, Bz, ^{i}Pr, and ^{n}Bu have been obtained, which are named cH*SEt*, cH*SBz*, cH*S^{i}Pr*, and cH*SBu*, respectively. The c stands for *closo* cluster 1,2-$C_2B_{10}H_{10}$ and the remaining letters indicate the carbon atoms' substituents. For cH*SEt*, it means that one cluster carbon atom forms a C_c−H bond while the second forms C_c−*SEt*. Yields have been found in the range 65−95%. The introduction of the $-PPh_2$ group requires one

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S0020-1669(96)00971-8 CCC: $14.00

to perform the reaction in dry diethyl ether at low temperature (−42 °C). We have noticed that higher temperatures lower the yield and produce more impure products. Reaction of the cHS*R* compounds with BuLi followed by addition of 1 equiv of $ClPPh_2$ produced the chemicals cPS*Et*, cPS*Bz*, cPS^i*Pr*, and cPS*Bu* in approximately 75% yields. In this nomenclature P denotes one PPh_2 group on one cluster carbon.

Partial degradation or the formal removal of a B^+ of the cHS*R* compounds to the *nido* species [nHS*R*]$^-$ was readily accomplished by KOH in ethanol for compounds [nHS*Et*]$^-$, [nHS^i*Pr*]$^-$ and [nHS*Bu*]$^-$. The n stands for *nido* cluster 7,8-$C_2B_9H_{10}$ and the remaining letters indicate, as before, the carbon atoms' substituents. For [nHS*Bz*]$^-$ a second method based on piperidine in ethanol[6c,6d] was required. Salts were prepared from aqueous solutions with $[NBu_4]^+$ for [nHS*Et*]$^-$ and $[NMe_4]^+$ for [nHS*Bz*]$^-$, [nHS^i*Pr*]$^-$, and [nHS*Bu*]$^-$. Conditions for the partial degradation of the heterodisubstituted compounds cPS*R* were more critical than for cHS*R* compounds since, as we reported earlier, this C_c−P bond[8] is susceptible to nucleophiles. In KOH/ethanol total breaking of the C_c−P bond was observed. Piperidine in ethanol in the molar ratio of substrate/piperidine of 1/10 has been found to be the best procedure. Under these conditions yields of 90% for [nPS*R*]$^-$ compounds have been obtained.

Characterization. *Closo* Species. *Closo* monosubstituted and heterodisubstituted *o*-carborane derivatives have been characterized by elemental analyses and IR and NMR techniques. The IR spectra show the typical ν(B−H) absorption at frequencies above 2550 cm^{-1}, characteristic of *closo*-1-R-2-R′-1,2-$C_2B_{10}H_{10}$ derivatives. The $^{11}B\{^1H\}$ NMR of cHS*R* compounds present spectral data in the typical range for 1-R-2-R′-1,2-$C_2B_{10}H_{10}$ compounds between −1 and −13 ppm. The nature of the R alkyl group does not greatly influence the $^{11}B\{^1H\}$ NMR spectrum, and they show 1:1:4:4 (cHS*Et*, cHS*Bz*, cHS*Bu*), or 1:1:4:2:2 (cHS^i*Pr*) patterns. The $^{11}B\{^1H\}$ NMR spectra of the heterodisubstituted *closo* species cPS*R* are even more compressed than those of the cHS*R* and appear in the range between 0 and −10 ppm. The observed patterns are 1:1:2:2:4 (cPS*Et*) and 1:1:4:4 (cPS*Bz*, cPS^i*Pr*, cPS*Bu*). As observed neither for cHS*R* nor for cPS*R*, the $^{11}B\{^1H\}$ NMR pattern at 96.3 MHz reflects the structural asymmetry of both type of compounds. The $^{31}P\{^1H\}$ NMR spectra for cPS*R* compounds show a resonance close to 10 ppm, corresponding to the unit $-PPh_2$. The lack of correspondence between the expected number of resonances in the $^{11}B\{^1H\}$ NMR spectra and the expected structures led us to grow crystals of the compound cPS^i*Pr*, which will be described later.

***Nido* Species.** The *nido* species have been characterized by elemental analyses and IR and NMR techniques. For both [nHS*R*]$^-$ and [nPS*R*]$^-$ *nido* species, strong IR ν(B−H) resonances close to 2520 cm^{-1} have been found. The $^{11}B\{^1H\}$ NMR of [nHS*R*]$^-$ species are consistent with the asymmetry of the molecules, and patterns 1:1:1:2:1:1:1:1 have been found for all of them in the range between −9 and −37 ppm, which is in agreement with [7-R-8-R′-7,8-$C_2B_9H_{10}$]$^-$ derivatives. For [nPS*R*]$^-$ species the $^{11}B\{^1H\}$ NMR data are also in the same range of the spectrum, and this is fully consistent with the compounds' asymmetry producing 1:1:1:1:1:1:1:1:1 patterns. The $^{31}P\{^1H\}$ NMR spectra show only one signal close to 10 ppm, a position very similar to the one found for the cPS*R* compounds. In order to ascertain the *nido* geometry of these species, the crystal structure of $[NMe_4]$[nPS^i*Pr*] was determined.

X-ray Molecular Descriptions. In the solid state the C_c-substituents of 1-PPh_2-2-S^{i}Pr-1,2-$C_2B_{10}H_{10}$ (cPS^i*Pr*) and [7-PPh_2-8-S^{i}Pr-7,8-$C_2B_9H_{10}$]$^-$ ([nPS^i*Pr*]$^-$) are orientated in a manner that is not suitable for bidentate S,P coordination to one metal atom. (Figures 2 and 3). In [7-PPh_2-8-S^{i}Pr-7,8-$C_2B_9H_{10}$]$^-$ the S−C bond lengths do not deviate significantly from the values of the corresponding *closo* compound, and the difference between the P−C_c and P−C_{arom} distances is barely significant and smaller than that in the *closo* compound. The P−C_c−C_c−S torsion angles in *nido* [9.0(3) Å] and *closo* [−11.0(4)°] compounds are comparable. As expected, the most important difference between the bond parameters of the two compound is in the C_c−C_c distances, the distance being considerable shorter in the *nido* [1.607(4) Å] than in the *closo* compound [1.747(5) Å]. As reported earlier,[10] the cluster C_c−C_c distance in 1,2-dicarba-*closo*-dodecaboranes increases with increasing number of substituents connected to the cluster C atoms, and in compounds substituted with sulfur, the distance is longer than in the nonsubstituted compounds or in compounds substituted with carbon or phosphorus. Thus the observed C_c−C_c distance in the *closo* compound is as expected, being longer than that in 1-PPh_2-2-Me-1,2-$C_2B_{10}H_{10}$ [10d] but shorter than that in 1,2-S,S'-$C_2B_{10}H_{10}$ compounds.[6c,d]

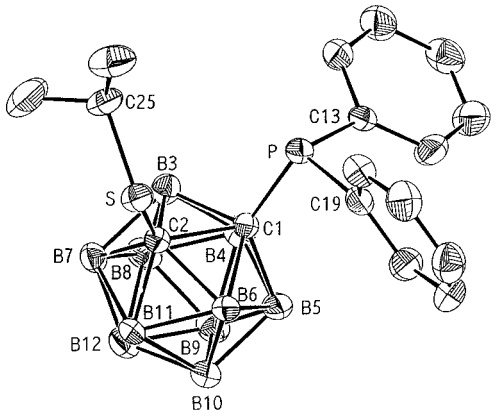

Figure 2. ORTEP plot of 1-PPh_2-2-S^{i}Pr-1,2-$C_2B_{10}H_{10}$, showing 30% displacement ellipsoids. Hydrogen atoms are omitted for clarity.

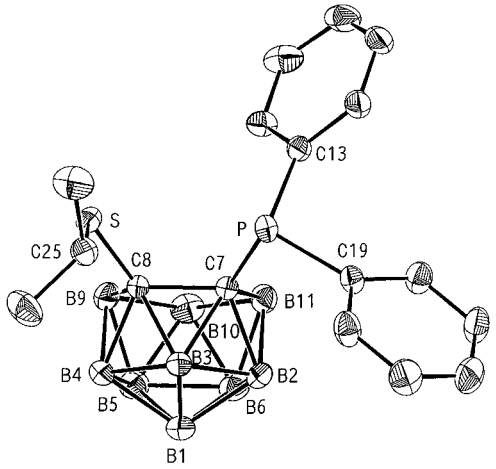

Figure 3. ORTEP plot of [7-PPh_2-8-S^{i}Pr-7,8-$C_2B_9H_{10}$]$^-$ showing 30% displacement ellipsoids. Hydrogen atoms are omitted for clarity.

It is interesting to notice that in *closo* compound the P−C_c bond is *ca*. 0.06 Å longer than the P−C_{arom} bonds, but the S-C_c distance, on the contrary, is *ca*. 0.07 Å shorter than the S−C_{alif} bond. Thus it seems that sulfur and phosphorus substituents

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both have different contributions to the lengthening of C_c-C_c bond and an opposite influence on the bond lengths of the two atoms.

Discussion. The synthesis of *closo* and *nido* C_c-heterodisubstituted compounds derivatives of 1-PPh_2-2-SR-1,2-$C_2B_{10}H_{10}$ has been conducted. They contain both C_c-P and C_c-S bonds in the same carborane cluster. This is the first time that such species are reported, and it is the result of advances in the development of easy routes to monosubstituted *o*-carborane compounds. The existence of an available cluster C_c-H unit allows the introduction of a second and different functional group. This type of compound complements the 1,2-$(SR)_2$-1,2-$C_2B_{10}H_{10}$[11] and 1,2-$(PR_2)_2$-1,2-$C_2B_{10}H_{10}$[12] families and permits access to chelating S,P heterodisubstituted *o*-carborane derivatives. The chelating properties of 1,2-$(PR_2)_2$-1,2-$C_2B_{10}H_{10}$ have been shown as well as those of 1,2-$(SR)_2$-1,2-$C_2B_{10}H_{10}$ but not those of 1-PR_2-2-SR-1,2-$C_2B_{10}H_{10}$. The chelating asymmetry of these ligands shall be of interest in coordination and organometallic chemistry. Moreover the rigid all pseudoplanar $R-C_c-C_c-R'$ moiety shall confer to these *o*-carborane derivatives distinct coordinating properties with regard to their sp^3 organic analogs. The chemistry of their [7-PPh_2-8-SR-7,8-$C_2B_9H_{10}]^-$ *nido* derivatives seems to be even more promising. The cluster's negative charge shall facilitate the formation of a chelating anionic ligand, whose negative moiety will be seldom involved in coordination to metal though it will strongly influence the coordinating capacity of the chelating unit. These characteristics are highly uncommon with conventional organic ligands, and their implications are as yet unknown.

Experimental Section

Materials and Methods. Commercial *o*-carborane was sublimed under high vacuum at 0.01 mmHg prior to use. 1-Thio-*o*-carborane was synthesized according to the literature.[4] A 1.6 M solution of *n*-butyllithium in hexane was used as purchased. Reaction solvents were reagent grade and were distilled from appropriate drying agents under dinitrogen prior to use. All organic and inorganic salts were analytical reagent grade and were used as received. All reactions were carried out under a dinitrogen atmosphere employing Schlenk techniques. Microanalyses were performed by using a Perkin-Elmer 240 B microanalyser. IR spectra were obtained as KBr pellets on a Nicolet 710-FT spectrophotometer. The ^{1}H NMR (300 MHz), ^{11}B NMR (96.3 MHz), and ^{31}P{^{1}H} NMR (121.5 MHz) spectra were recorded on a Bruker ARX 300WB spectometer. Chemical shift values for ^{1}H NMR spectra were referenced to an internal standard of $SiMe_4$ in deuterated solvents. Chemical shift values for ^{11}B NMR spectra were referenced relative to external $BF_3{\cdot}OEt_2$. Chemical shift values for ^{31}P NMR spectra were referenced relative to external 85% H_3PO_4.

1. Synthesis of *Closo* Species. 1.1. Monosubstituted Species. 1-(Thioethyl)-1,2-dicarba-*closo*-dodecaborane (cHS*Et*). To a two-necked round-bottom flask (25 mL) fitted with a dinitrogen inlet/outlet, containing deoxygenated ethanol (10 mL), was added KOH (37 mg, 0.567 mmol). After this was stirred for 15 min, cHS*H* (100 mg, 0.567 mmol) and ethylbromide (100 mg, 0.917 mmol) were added to the solution. The mixture was refluxed for 2 h, and the solvent was evaporated in a vacuum. To the residue were added diethyl ether (10 mL) and aqueous 0.5 M KOH (10 mL). The layers were separated, and the organic extracts were washed with aqueous 0.5 M KOH (3 × 10 mL), dried, and evaporated in a vacuum to yield a yellow oil (111 mg, 95%). Anal. Calcd for $C_4H_{16}B_{10}S$: C, 23.51; H, 7.89; S, 15.69. Found: C, 23.89; H, 8.09; S, 15.14. FTIR (KBr): ν (cm^{-1}) = 3064 (C−H), 2600, 2579 (B−H). ^{1}H NMR ($(CD_3)_2CO$): δ = 1.26 (t, ^1J(H,H) = 7.4 Hz, 3H, −C**H**$_3$), 3.05 (q, ^1J(H,H) = 7.4 Hz, 2H, −S−C**H**$_2$−), 4.75 (b, 1H, BC−**H**). ^{11}B NMR ($(CD_3)_2CO$): δ = −1.8 (d, ^1J(B,H) = 153.2 Hz, 1B), −5.2 (d, ^1J(B,H) = 172.8 Hz, 1B), −9.3 (d, ^1J(B,H) = 153.6 Hz, 4B), −12.2 (d, ^1J(B,H) = 153.6 Hz, 4B).

1-(Thiobenzyl)-1,2-dicarba-*closo*-dodecaborane (cHS*Bz*). The procedure was similar to that described for cHS*Et* using cHS*H* (100 mg, 0.567 mmol) and benzylbromide (171 mg, 0.999 mmol) to yield an yellow oil (120 mg, 80%). Anal. Calcd for $C_9H_{18}B_{10}S$: C, 40.58; H, 6.81; S, 12.04. Found: C, 40.90; H, 6.48; S, 11.64. FTIR (KBr): ν (cm^{-1}) = 3064 (C−H), 2600 (B−H). ^{1}H NMR ($(CD_3)_2CO$): δ = 4.33 (s, 2H, S−C**H**$_2$), 4.84 (b, 1H, BC−**H**), 7.32−7.48 (m, 5H, −C_6**H**$_5$). ^{11}B NMR ($(CD_3)_2CO$): δ = −1.8 (d, ^1J(B,H) = 153.6 Hz, 1B), −5.1-(d, ^1J(B,H) = 153.6 Hz, 1B), −9.2 (d, ^1J(B,H) = 172.8 Hz, 4B), −12.2 (d, ^1J(B,H) = 163.6 Hz, 4B).

1-(Thioisopropyl)-1,2-dicarba-*closo*-dodecaborane (cHS^i*Pr*). To a two necked round bottom flask (25 mL) fitted with a dinitrogen inlet/outlet, containing deoxygenated ethanol (10 mL), was added KOH (38 mg, 0.567 mmol). After this was stirred for 15 min, cHS*H* (100 mg, 0.567 mmol) was added, and the resulting mixture was allowed to stir for 1 h. The solvent was evaporated in a vacuum, and the resulting residue was dissolved in dry THF (10 mL). Isopropylbromide (139 mg, 1.13 mmol) was added to the solution. The mixture was refluxed for 2 h and the solvent was evaporated in a vacuum. Diethyl ether (10 mL) and aqueous 0.5 M KOH (10 mL) were added to the residue. The layers were separated and the organic extracts were washed with aqueous 0.5 M KOH (3 × 10 mL), dried and evaporated in a vacuum to yield an yellow oil (80 mg, 65%). Anal. Calcd for $C_5H_{18}B_{10}S$: C, 27.50; H, 8.31; S, 14.68. Found: C, 27.88; H, 8.51; S, 14.98. FTIR (KBr): ν (cm^{-1}) = 3064 (C−H), 2600 (B−H). ^{1}H NMR ($(CD_3)_2$-CO): δ = 1.34 (d, ^1J(H,H) = 6.9 Hz, 6H, −C**H**$_3$), 3.45 (h, ^1J(H,H) = 6.9 Hz, 1H, −C**H**<), 4.74 (b, 1H, BC−**H**). ^{11}B NMR ($(CD_3)_2CO$): δ = −1.7 (d, ^1J(B,H) = 144.0 Hz, 1B), −5.1 (d, ^1J(B,H) = 153.6 Hz, 1B), −9.3 (d, ^1J(B,H) = 172.8 Hz, 4B), −11.5 (d, ^1J(B,H) = 105.6 Hz, 2B), −12.2 (d, ^1J(B,H) = 57.6 Hz, 2B).

1-(Thiobutyl)-1,2-dicarba-*closo*-dodecaborane (cHS*Bu*). The procedure was analogous to that described for cHS^i*Pr* using cHS*H* (100 mg, 0.567 mmol) and butyl chloride (80 mg, 1.16 mmol) to yield an yellow oil (80 mg, 70%). Anal. Calcd for $C_6H_{20}B_{10}S$: C, 38.01; H, 8.67; S, 13.80. Found: C, 39.00; H, 8.70; S, 13.67. FTIR (KBr): ν (cm^{-1}) = 3064 (C−H), 2600 (B−H). ^{1}H NMR ($(CD_3)_2CO$): δ = 0.93 (t, ^1J(H,H) = 7.26 Hz, 3H, −C**H**$_3$), 1.41 (h, ^1J(H,H) = 7.26 Hz, 2H, −C**H**$_2$−CH_3), 1.57 (q, ^1J(H,H) = 7.26 Hz, 2H, −C**H**$_2$−CH_2−), 3.03 (t, ^1J(H,H) = 7.26 Hz, 2H, −S−C**H**$_2$−), 4.75 (b, 1H, BC−**H**). ^{11}B NMR ($(CD_3)_2CO$): δ = −1.8 (d, ^1J(B,H) = 144.0 Hz, 1B), −5.3 (d, ^1J(B,H) = 144.0 Hz, 1B), −9.2 (d, ^1J(B,H) = 163.2 Hz, 4B), −12.2 (d, ^1J(B,H) = 163.2 Hz, 4B).

1.2. Heterodisubstituted Species. 1-(Diphenylphosphino)-2-(thioethyl)-1,2-dicarba-*closo*-dodecaborane (cPS*Et*). To a solution of 118 mg (0.567 mmol) of cHS*Et* in 10 mL of dry diethyl ether at −42 °C contained in a three-necked round bottom flask, fitted with a dinitrogen inlet/outlet, was added 0.7 mL (0.57 mmol) of *n*-butyllithium dropwise with stirring. The mixture was stirred at this temperature for 1 h. Then 127 mg (0.578 mmol) of chlorodiphenylphosphine was added, and the suspension was kept stirring at this temperature for 1 h. While being warmed to ambient temperature, the mixture was quenched with 10 mL of water and transferred to a separatory funnel and the layers separated. The organic layer was washed with 0.5 M of Na_2-CO_3 (3 × 10 mL) and the aqueous layer was extracted with diethyl ether (10 mL). The combined extracts were then dried over $MgSO_4$. The evaporation of the solvent in a vacuum followed by crystallization of the residue from diethyl ether /light petroleum (1:1) gave white crystals (168 mg, 75%). Anal. Calcd for $C_{16}H_{25}B_{10}PS$: C, 49.46; H, 6.49; S, 8.25. Found: C, 49.56; H, 6.34; S, 7.85. FTIR (KBr): ν (cm^{-1}) = 2607, 2579, 2586, 2558 (B−H). ^{1}H NMR ($(CD_3)_2CO$): δ = 1.29 (t, ^1J(H,H) = 7.5 Hz, 3H, −C**H**$_3$), 3.03 (q, ^1J(H,H) = 7.5Hz, 2H, −C**H**$_2$−CH_3), 7.54−8.02 (m, 10 H, C_6**H**$_5$). ^{11}B NMR ($(CD_3)_2$-CO): δ = −0.7 (d, ^1J(B,H) = 124.8 Hz, 1B), −3.5 (d, ^1J(B,H) = 153.6 Hz, 1B), −8.0 (d, ^1J(B,H) = 163.2 Hz, 2B), −8.9 (2B), −9.9 (d, ^1J(B,H) = 163.2 Hz, 4B). ^{31}P{^{1}H} NMR ($(CD_3)_2CO$): δ = 9.4 (s, **P**(C_6H_5)).

1-(Diphenylphosphino)-2-(thiobenzyl)-1,2-dicarba-*closo*-dodecaborane (cPS*Bz*). The method was as described for cPS*Et* using

(11) Teixidor, F.; Viñas, C.; Sillanpää, R.; Kivekäs, R.; Casabó, J. *Inorg. Chem.* **1994**, *33*, 2645.
(12) Teixidor, F.; Viñas, C.; Abad, M.; Kivekäs, R.; Sillanpää, R. *J. Organomet. Chem.* **1996**, *509*, 139.

cH*SBz* (110 mg, 0.413 mmol) to give white crystals. Yield: 132 mg, 72%. Anal. Calcd for $C_{21}H_{27}B_{10}PS$: C, 55.98; H, 6.04; S, 7.12. Found: C, 56.09; H, 5.65; S, 6.90. FTIR (KBr): ν (cm^{-1}) = 2635, 2614, 2593, 2572 (B−H). ^{1}H NMR ($(CD_3)_2CO$): δ = 4.3 (s, 2H, -S−C**H**$_2$), 7.4 (m, 5 H, −CH_2C_6**H**$_5$), 7.60−8.05 (m, 10H, P(C_6**H**$_5$)). ^{11}B NMR ($(CD_3)_2CO$): δ = −0.7 (d, ^1J(B,H) = 147.8 Hz, 1B), −3.5 (d, ^1J(B,H) = 147.8 Hz, 1B), −8.8 (4B), −9.9 (d, ^1J(B,H) = 112.3 Hz, 4B). ^{31}P{^{1}H} NMR ($(CD_3)_2CO$): δ = 11.17 (s, **P**(C_6H_5)).

1-(Diphenylphosphino)-2-(thioisopropyl)-1,2-dicarba-*closo*-dodecaborane (cP*S*^{i}*Pr*). The method was analogous to the preparation of cP*SEt*, but used cH*Si*^{i}*Pr* (110 mg, 0.504 mmol) to give white crystals. Yield: 150 mg, 75%. Anal. Calcd for $C_{17}H_{27}B_{10}PS$: C, 50.72; H, 6.76; S, 7.91 Found: C, 51.00; H, 6.56; S, 7.53. FTIR (KBr): ν (cm^{-1}) = 2607, 2579, 2551 (B−H). ^{1}H NMR ($(CD_3)_2CO$): δ = 1.43 (d, ^1J(H,H) = 6.6 Hz, 6H, −C**H**$_3$), 3.57 (h, ^1J(H,H) = 6.6 Hz, 1H, −C**H**<), 7.51−8.01 (m, 10 H, C_6**H**$_5$). ^{11}B NMR ($(CD_3)_2CO$): δ = −0.4 (d, ^1J(B,H) = 144.0 Hz, 1B), −3.5 (d, ^1J(B,H) = 153.6 Hz, 1B), −8.8 (4B), −9.6 (d, ^1J(B,H) = 163.2 Hz, 4B). ^{31}P{^{1}H} NMR ($(CD_3)_2CO$): 10.46 (s, **P**(C_6H_5)).

1-(Diphenylphosphino)-2-(thiobutyl)-1,2-dicarba-*closo*-dodecaborane (cP*SBu*). The procedure was anologous to that described for cP*SEt*, using cH*SBu* (100 mg, 0.430 mmol) to give a crystalline product. Yield: 140 mg, 78%. Anal. Calcd for $C_{18}H_{29}B_{10}PS$: C, 51.90; H, 7.02; S, 7.72. Found: C, 52.16; H, 6.86; S, 7.37. FTIR (KBr): ν (cm^{-1}) = 2607, 2579 (B−H). ^{1}H NMR ($(CD_3)_2CO$): δ = 0.97 (t, ^1J(H,H) = 7.2 Hz, 3H, −C**H**$_3$), 1.49 (h, ^1J(H,H) = 7.2 Hz, 2H, −C**H**$_2$−CH_3), 1.66 (q, ^1J(H,H) = 7.2 Hz, 2H, −CH_2−C**H**$_2$−), 2.98 (t, ^1J(H,H) = 7.2 Hz, 2H, −S−C**H**$_2$−), 7.54−8.01 (m, 10 H, C_6**H**$_5$). ^{11}B NMR ($(CD_3)_2CO$): δ = −0.7 (d, ^1J(B,H) = 124.8 Hz, 1B), −3.5 (d, ^1J(B,H) = 153.6 Hz, 1B), −8.8 (4B), −9.6 (d, ^1J(B,H) = 115.2 Hz, 4B). ^{31}P{^{1}H} NMR ($(CD_3)_2CO$): 10.71 (s, **P**(C_6H_5)).

2. Synthesis of *Nido* Species. 2.1. Monosubstituted Species. Synthesis of Tetrabutylammonium 7-(Thioethyl)-7,8-dicarba-*nido*-undecaborate(1−) ([NBu$_4$][nH*SEt*]). To a two-necked round-bottom flask (25 mL) fitted with a dinitrogen inlet/outlet, containing deoxygenated ethanol (10 mL), was added KOH (158 mg, 2.81 mmol). After this was stirred for 30 min at room temperature, a solution of cH*SEt* (90 mg, 0.44 mmol) in 6 mL of deoxygenated ethanol was added . The mixture was allowed to stir for 4 h. Once the mixture cooled, the solvent was evaporated under vacuum. Water (6 mL) was added to the residue. While N_2 was bubbled into the solution, an excess of tetrabutylammonium chloride in water (5 mL) was added and a solid precipitated. After the suspension stood for 30 min, the solid was collected by filtration, washed with water (5 × 2 mL) and diethyl ether, and dried under vacuum to get a white solid (158 mg, 83%). Anal. Calcd for $C_{20}H_{52}B_9NS$: C, 55.10; H, 12.02; N, 3.21; S, 7.35. Found: C, 55.33; H, 11.60; N, 3.00; S, 7.16. FTIR (KBr): ν (cm^{-1}) = 2521 (B−H). ^{1}H NMR ($(CD_3)_2CO$): δ = −2.61 (b, 1H, B**H**B), 1.00 (t, ^1J(H,H) = 9.0 Hz, 12H, −CH_2C**H**$_3$), 1.21(t, ^1J(H,H) = 6.0 Hz, 3H, −C**H**$_3$), 1.41 (h, ^1J(H,H) = 9.0 Hz, 8H, CH_2C**H**$_2$$CH_3$), 1.83 (m, 8H, −$CH_2$C**H**$_2$$CH_2$−), 2.50 (m, 1H, S−C**H**$_2$−), 2.87 (m, 1H, −S−C**H**$_2$−), 3.45 (t, ^1J(H,H) = 9.0 Hz, 8H, NC**H**$_2$). ^{11}B NMR ($(CD_3)_2CO$): δ = −9.7 (d, ^1J(B,H) = 41.4 Hz, 1B), −10.1 (d, ^1J(B,H) = 34.7 Hz, 1B), −14.5 (d, ^1J(B,H) = 179.1 Hz, 1B), −16.6 (d, ^1J(B,H) = 146.7 Hz, 2B), −17.6 (d, ^1J(B,H) = 105.9 Hz, 1B), −21.9 (d, ^1J(B,H) = 148.3 Hz, 1B), −32.7 (d, ^1J(B,H) = 98.7 Hz, 1B), −36.4 (d, ^1J(B,H) = 137.6 Hz, 1B).

Synthesis of Tetramethylammonium 7-(Thioisopropyl)-7,8-dicarba-*nido*-undecaborate(1−) ([NMe$_4$][nHS^i*Pr*]). The procedure was similar to that described for [NBu$_4$][nH*SEt*], using cHS^i*Pr* (100 mg, 0.458 mmol). Yield: 90 mg, 70%. Anal. Calcd for $C_9H_{30}B_9NS$: C, 38.37; H, 10.73; N, 4.95; S, 11.38. Found: C, 38.63; H, 10.31; N, 4.90; S, 10.98. FTIR (KBr): ν (cm^{-1}) = 2518 (B−H). ^{1}H NMR ($(CD_3)_2CO$): δ = −2.64 (b, 1H, B**H**B), 1.08 (d, ^1J(H,H) = 6.0 Hz, 3H, −C**H**$_3$), 1.28(d, ^1J(H,H) = 6.0 Hz, 3H, −C**H**$_3$), 3.27 (m, 1H, −S−C**H**<), 3.46 (s, 12H, N(C**H**$_3$)$_4$). ^{11}B NMR ($(CD_3)_2CO$): δ = −9.5 (d, ^1J(B,H) = 69.3 Hz, 1B), −10.2 (d, ^1J(B,H) = 65.5 Hz, 1B), −14.7 (1B), −16.2 (2B), −17.5 (1B), −21.7 (d, ^1J(B,H) = 151.2 Hz, 1B), −32.5 (d, ^1J(B,H) = 127.1 Hz, 1B), −36.4 (d, ^1J(B,H) = 142.1 Hz, 1B).

Synthesis of Tetramethylammonium 7-(Thiobutyl)-7,8-dicarba-*nido*-undecaborate(1−) ([NMe$_4$][nH*SBu*]). The method was analogous to the preparation of [NBu$_4$][nH*SEt*], but using cH*SBu* (40 mg, 0.172 mmol) to yield a white solid (34 mg, 70%). Anal. Calcd for $C_{10}H_{32}B_9NS\cdot{}^1/_6C_6H_{14}$: C, 42.61; H, 11.16; N, 4.52; S, 10.34. Found: C, 42.05; H, 10.74; N, 4.47; S, 9.94. FTIR (KBr): ν (cm^{-1}) = 2523 (B−H). ^{1}H NMR ($(CD_3)_2CO$): δ = −2.57 (b, 1H, B**H**B), 0.93 (t, ^1J(H,H) = 6.0 Hz, 3H, −C**H**$_3$), 1.40 (m, 2H, −C**H**$_2$$CH_3$), 1.51(m, 2H, −$CH_2$C**H**$_2$$CH_2$−), 2.49 (m, 2H, −S−C**H**$_2$−), 3.46 (s, 12H, N(C**H**$_3$)$_4$). ^{11}B NMR ($(CD_3)_2CO$): δ = −9.6 (d, ^1J(B,H) = 45.5 Hz, 1B), −10.1 (d, ^1J(B,H) = 52.0 Hz, 1B), −14.6 (d, ^1J(B,H) = 188.7 Hz, 1B), −17.57 (d, ^1J(B,H) = 107.1 Hz, 1B), −18.6 (d, ^1J(B,H) = 140.0 Hz, 2B), −22.1 (d, ^1J(B,H) = 148.4 Hz, 1B), −32.7 (d, ^1J(B,H) = 130.4 Hz, 1B), −36.4 (d, ^1J(B,H) = 142.4 Hz, 1B).

Synthesis of Tetramethylammonium 7-(Thiobenzyl)-7,8-dicarba-*nido*-undecaborate(1−) ([NMe$_4$][nH*SBz*]). Under a dinitrogen atmosphere, cH*SBz* (84 mg, 0.315 mmol) was dissolved in 10 mL of degassed absolute ethanol. Piperidine (0.31 mL, 3.15 mmol) was added dropwise with stirring, and the system was brought to reflux for 4 h and 30 min. Ethanol was eliminated and the residue was dissolved in water. Upon the addition of tetramethylammonium chloride, a gelatinous solid was obtained which was filtered and washed with hexane to yield a white solid (52 mg, 50%). Anal. Calcd for $C_{13}H_{30}B_9NS$: C, 47.35; H, 9.17; N, 4.25; S, 9.72. Found: C, 46.48; H, 8.79; N, 4.65; S, 9.62. FTIR (KBr): ν (cm^{-1}) = 2516(B−H). ^{1}H NMR ($(CD_3)_2CO$): δ = −2.53 (b, 1H, B**H**B), 3.45 (s, 12 H, N(C**H**$_3$)$_4$), 3.9 (d, ^1J(H,H) = 12.0 Hz, 1H, −S−C**H**$_2$), 4.0 (d, ^1J(H,H) = 12.0 Hz, 1H, −S−C**H**$_2$), 7.25−7.30 (m, 5H, C_6**H**$_5$). ^{11}B NMR ($(CD_3)_2CO$): δ = −10.0 (d, ^1J(B,H) = 127.1 Hz, 1B), −11.3 (d, ^1J(B,H) = 127.1 Hz, 1B), −15.3 (1B), −18.0 (d, ^1J(B,H) = 130.0 Hz, 3B), −22.5 (d, ^1J(B,H) = 148.3 Hz, 1B), −33.8 (d, ^1J(B,H) = 84.7 Hz, 1B), −37.7 (d, ^1J(B,H) = 138.3 Hz, 1B).

2.2. Heterodisubstituted Species. Synthesis of Tetramethylammonium 7-(Diphenylphosphino)-8-(thioethyl)-7,8-dicarba-*nido*-undecaborate(1−) ([NMe$_4$][nP*SEt*]). Under a dinitrogen atmosphere, cP*SEt* (141 mg, 0.363 mmol) was dissolved in 30 mL of degassed absolute ethanol. Piperidine (0.36 mL, 3.63 mmol) was added dropwise with stirring, and the system was brought to reflux for 16 h. The ethanol was eliminated, and the residue was disolved in 4 mL of ethanol, upon the addition of an aqueous solution of tetramethylammonium chloride. As a result a gelatinous solid was obtained which was filtered and washed with water and hexane to yield a white solid (162 mg, 98%). Anal. Calcd for $C_{20}H_{37}B_9NPS$: C, 52.94; H, 8.23; N, 3.09; S, 7.05. Found: C, 53.32; H, 7.96; N, 3.36; S, 6.75. FTIR(KBr): ν (cm^{-1}) = 2544, 2510 (B−H). ^{1}H NMR (CD_2Cl_2): δ = −2.18 (b, 1H, B**H**B), 1.14 (t, ^1J(H,H) = 9.0 Hz, 3H, −C**H**$_3$), 2.26 (m, 1H, −S−C**H**$_2$), 2.65 (m, 1H, −S−C**H**$_2$), 3.24 (s, 12 H, N(C**H**$_3$)$_4$), 7.25−7.40 (m, 10H, C_6**H**$_5$). ^{11}B NMR (CD_2Cl_2): δ = −8.9 (d, ^1J(B,H) = 81.8 Hz, 2B), −12.9 (1B), −21.0 (1B), −16.7 (d, ^1J(B,H) = 121.1 Hz, 3B), −34.0 (d, ^1J(B,H) = 158.9 Hz, 1B), −36.0 (d, ^1J(B,H) = 141.8 Hz, 1B). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = 9.4 (s, **P**(C_6H_5)).

Synthesis of Tetramethylammonium 7-(Diphenylphosphino)-8-(Thiobenzyl)-7,8-dicarba-*nido*-undecaborate(−1) ([NMe$_4$][nP*SBz*]). The preparation of this compound was analogous to that reported for [NMe$_4$][nP*SEt*], using cP*SBz* (100 mg, 0.222 mmol) to yield a white solid, (91 mg, 80%). Anal. Calcd for $C_{25}H_{39}B_9NPS$: C, 58.43; H, 7.65; N, 2.73; S, 6.24. Found: C, 58.10; H, 7.26; N, 3.10; S, 5.94. FTIR (KBr): ν (cm^{-1}) = 2517 (B−H). ^{1}H NMR (CD_2Cl_2): δ = −2.11 (b, 1H, B**H**B), 3.24 (s, 12 H, N(C**H**$_3$)$_4$), 3.45 (d, ^1J(H,H) = 9.0 Hz, 1H, −S−C**H**$_2$−), 3.95 (d, ^1J(H,H) = 9.0 Hz, 1H, −S−C**H**$_2$−), 6.76−7.2 (m , 10H, C_6**H**$_5$). ^{11}B NMR (CD_2Cl_2): δ = −8.4 (2B), −13.1 (1B), −16.5 (d, ^1J(B,H) = 180.0 Hz, 3B), −21.0 (1B), −33.8 (d, ^1J(B,H) = 159.2 Hz, 1B), −35.8 (d, ^1J(B,H) = 153.1 Hz, 1B). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = 9.1 (s, **P**(C_6H_5)).

Synthesis of Tetramethylammonium 7-(Diphenylphosphino)-8-(thioisopropyl)-7,8-dicarba-*nido*-undecaborate(−1) ([NMe$_4$][nP*S*^{i}*Pr*]). The preparation was done in a manner similar to that described for [NMe$_4$][nP*SEt*], using cP*S*^{i}*Pr* (285 mg, 0.706 mmol). Yield: 300 mg, 91%. FTIR (KBr): ν (cm^{-1}) = 2558, 2530, 2509 (B−H). Anal. Calcd for $C_{21}H_{39}B_9NPS$: C, 54.14; H, 8.44; N, 3.01; S, 6.88. Found: C, 54.20; H, 9.03; N, 2.76; S, 6.70. FTIR (KBr): ν (cm^{-1}) = 2558, 2530, 2509 (B−H). ^{1}H NMR ($(CD_3)_2CO$): δ = −2.08 (b, 1H, B**H**B), 1.03 (d, ^1J(H,H) = 6.0 Hz, 3H,−C**H**$_3$), 1.06 (d, ^1J(H,H) = 6.0 Hz, 3H, −C**H**$_3$), 3.24 (m, 1H, −S−C**H**<), 3.49 (s, 12H, N(C**H**$_3$)$_4$), 6.76−7.2 (m , 10H, C_6**H**$_5$). ^{11}B NMR ($(CD_3)_2CO$): δ = −7.0 (d, ^1J(B,H) =

Table 1. Crystallographic Data for 1-PPh_2-2-S^{i}Pr-1,2-$C_2B_{10}H_{10}$ (cPS^i*Pr*) and [NMe_4][7-PPh_2-8-S^{i}Pr-7,8-$C_2B_9H_{10}$] ([NMe_4][nPS^i*Pr*])

	cPS^i*Pr*	[NMe_4][nPS^i*Pr*]
chem formula	$C_{17}H_{27}B_{10}PS$	$C_{21}H_{39}B_9NPS$
fw	402.54	465.87
a, Å	10.657(2)	9.665(2)
b, Å	12.709(4)	18.235(2)
c, Å	17.444(3)	15.900(2)
β, deg	105.07(2)	95.84(1)
V, Å^3	2281.4(9)	2787.7(7)
Z	4	4
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
T, °C	21	21
λ, Å	0.710 69	0.710 69
D_{calcd}, g cm^{-3}	1.172	1.110
μ, mm^{-1}	0.21	0.18
R^a	0.058	0.047
$R_w{}^b$	0.056	0.040

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table 2. Selected Atomic Coordinates and Equivalent Displacement Parameters for 1-PPh_2-2-S^{i}Pr-1,2-$C_2B_{10}H_{10}$ (cPS^i*Pr*)

	x	*y*	*z*	U_{eq},^{a} Å^2
S	1.0526(1)	0.55831(9)	0.73908(7)	0.0512(5)
P	0.7733(1)	0.6719(1)	0.65450(6)	0.0448(4)
C(1)	0.8239(4)	0.6780(3)	0.7663(2)	0.040(2)
C(2)	0.9798(4)	0.6272(3)	0.8051(2)	0.041(2)
B(3)	0.9575(5)	0.7603(4)	0.8001(3)	0.049(2)
B(4)	0.8050(5)	0.7851(4)	0.8216(3)	0.053(2)
B(5)	0.7345(5)	0.6627(5)	0.8334(3)	0.051(2)
B(6)	0.8446(5)	0.5621(4)	0.8186(3)	0.045(2)
B(7)	1.0610(5)	0.6986(4)	0.8857(3)	0.049(2)
B(8)	0.9523(6)	0.7965(4)	0.8975(3)	0.060(2)
B(9)	0.8145(6)	0.7356(5)	0.9180(3)	0.061(2)
B(10)	0.8372(5)	0.5970(5)	0.9156(3)	0.053(2)
B(11)	0.9897(5)	0.5749(4)	0.8959(3)	0.047(2)
B(12)	0.9706(5)	0.6811(5)	0.9567(3)	0.056(2)
C(13)	0.6576(4)	0.7814(4)	0.6338(2)	0.045(2)
C(19)	0.6779(4)	0.5516(4)	0.6305(2)	0.048(2)
C(25)	1.1315(5)	0.6572(4)	0.6900(3)	0.062(2)

^{a} $U_{eq} = {}^1/_3\sum_i\sum_j \mathbf{U}_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 1-PPh_2-2-S^{i}Pr-1,2-$C_2B_{10}H_{10}$ (cPS^i*Pr*)

S−C(2)	1.777(5)	C(1)−C(2)	1.747(5)
S−C(25)	1.843(6)	P−C(13)	1.832(5)
P−C(1)	1.884(4)	P−C(19)	1.822(5)
C(2)−S−C(25)	107.1(2)	C(1)−P−C(13)	99.7(2)
S−C(2)−B(3)	122.3(3)	C(1)−P−C(19)	105.4(2)
S−C(2)−B(6)	111.8(3)	S−C(2)−B(7)	125.6(3)
S−C(2)−C(1)	117.5(3)	P−C(1)−C(2)	112.0(3)
S−C(2)−B(11)	118.7(3)	P−C(1)−B(3)	111.4(3)
P−C(1)−B(4)	124.9(3)	P−C(1)−B(5)	130.2(3)
P−C(1)−B(6)	118.5(3)		

63.5 Hz, 1B), −7.8 (d, ^1J(B,H) = 121.8 Hz, 1B), −12.4 (d, ^1J(B,H) = 144.5 Hz, 1B), −14.7 (d, ^1J(B,H) = 134.8 Hz, 1B), −15.9 (d, ^1J(B,H) = 118.5 Hz, 2B), −19.9 (d, ^1J(B,H) = 159.4 Hz, 1B), −33.0 (d, ^1J(B,H) = 114.9 Hz, 1B), −34.5 (d, ^1J(B,H) = 142.5 Hz, 1B). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ = 10.83 (s, **P**(C_6H_5)).

X-ray Studies. X-ray measurements for 1-PPh_2-2-S^{i}Pr-1,2-$C_2B_{10}H_{10}$ and [$N(Me)_4$][7-PPh_2-8-S^{i}Pr-7,8-$C_2B_9H_{10}$] were made on a Rigaku AFC5S diffractometer using monochromatized Mo Kα radiation (λ = 0.710 69 Å). The unit cell parameters were determined by least-squares refinements of 25 carefully centered reflections. The data were collected using the $\omega-2\theta$ scan technique to a maximum 2θ value of 50°. Both data were corrected for Lorentz and polarization effects.

The structures were solved by direct methods using SHELXS86 program.[13] Least-squares refinement and all subsequent calculations for 1-PPh_2-2-S^{i}Pr-1,2-$C_2B_{10}H_{10}$ were performed using the XTAL[14] program package. The non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were placed at their calculated positions [C−H = 0.95 Å, B−H = 1.10 Å and *U*(H) = 1.2U_{eq}(host atom)]. The refinement of [$N(Me)_4$][7-PPh_2-8-S^{i}Pr-7,8-$C_2B_9H_{10}$] was performed with TEXSAN,[15] refining the non-hydrogen atoms with anisotropic displacement parameters and H(B) atoms with fixed isotropic displacement parameters. The H(C) atoms were placed at their calculated positions. For both structures the minimized function was $\sum w(\Delta F)^2$, where $1/w = \sigma^2(F_o)$ and neutral atomic scattering factors were those included in the programs.

Crystallographic data are presented in Table 1; atomic coordinates in Tables 2 and 4 and selected bond distances and angles in Tables 3 and 5.

Table 4. Selected Atomic Coordinates and Equivalent Displacement Parameters for [NMe_4][7-PPh_2-8-S^{i}Pr-7,8-$C_2B_9H_{10}$] ([NMe_4][nPS^i*Pr*])

	x	*y*	*z*	B_{eq},^{a} Å
S	0.22269(9)	0.66589(4)	0.57049(5)	3.35(4)
P	0.11676(8)	0.58994(5)	0.73648(5)	2.93(3)
B(1)	0.5474(4)	0.5246(2)	0.7001(2)	3.8(2)
B(2)	0.4220(4)	0.5289(2)	0.7718(2)	3.6(2)
B(3)	0.3705(4)	0.5345(2)	0.6624(2)	3.2(2)
B(4)	0.5008(4)	0.5845(2)	0.6161(2)	3.6(2)
B(5)	0.6260(4)	0.6132(2)	0.6957(3)	4.1(2)
B(6)	0.5770(4)	0.5782(2)	0.7952(3)	4.1(2)
C(7)	0.3076(3)	0.5957(2)	0.7326(2)	2.6(1)
C(8)	0.3536(3)	0.6277(2)	0.6455(2)	2.7(1)
B(9)	0.4956(4)	0.6747(2)	0.6576(2)	3.6(2)
B(10)	0.5582(4)	0.6720(2)	0.7703(3)	4.1(2)
B(11)	0.4181(4)	0.6197(2)	0.8128(2)	3.5(2)
C(13)	0.0832(3)	0.6697(2)	0.8018(2)	3.0(1)
C(19)	0.1062(3)	0.5115(2)	0.8084(2)	3.0(1)
C(25)	0.1258(3)	0.5915(2)	0.5132(2)	3.7(2)

^{a} $B_{eq} = ({}^3/_4)\sum_i\sum_j b_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for [NMe_4][7-PPh_2-8-S^{i}Pr-7,8-$C_2B_9H_{10}$] ([NMe_4][nPS^i*Pr*])

S−C(8)	1.789(3)	S−C(25)	1.837(3)
C(7)−B(11)	1.637(4)	P−C(7)	1.855(3)
P−C(13)	1.835(3)	C(8)−B(9)	1.613(5)
P−C(19)	1.840(3)	B(9)−B(10)	1.833(6)
C(7)−C(8)	1.607(4)	B(10)−B(11)	1.839(6)
C(8)−S−C(25)	109.5(1)	P−C(7)−B(3)	113.6(2)
C(7)−P−C(13)	102.0(1)	P−C(7)−B(11)	124.2(2)
C(7)−P−C(19)	100.5(1)	S−C(8)−C(7)	118.5(2)
S−C(8)−B(3)	122.5(2)	P−C(7)−C(8)	114.4(2)
S−C(8)−B(4)	122.8(2)	P−C(7)−B(2)	123.6(2)
S−C(8)−B(9)	114.1(2)		

Acknowledgment. The authors are grateful to the CIRIT for financial support (Grant QFN95-4721), and to Spanish Ministerio de Educación y Ciencia (Grants AP 93 and SAB95-0249).

Supporting Information Available: Tables X-ray of experimental details, hydrogen atom positional parameters and thermal parameters, anisotropic thermal parameters, interatomic distances and angles for cPS^i*Pr* and nPS^i*Pr* (23 pages). Ordering information is given on any current masthead page.

IC9609719

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