proportional to the concentration of MeOH supporting an S_N2 mechanism (see Scheme II, pathway "A"). Pathway "B" invokes an S_N1 mechanism where the rate of formation of $[(Co_2(CO)_6(CH{\equiv}CCH_2OMe)]$ (**4**) is dependent on the equilibrium constant K_{eq} and not on the methanol concentration. These results suggest that the route in which preliminary decomplexation of the sulfide ligand occurs to give the propargylic cation complex, which then reacts with methanol, is less favored.

Further reactivity studies with these organometallic species are currently under investigation, including reactions with other types of bases and nucleophiles.

Conclusion

The presence of heteroatoms, such as S, N, or P, has increased the stability of the propargylic cationic complex, while its reactivity toward nucleophiles may be selectively modified, as shown with the pyridinium complex compared to the sulfonium complexes. Moreover the reactivity of these latter complexes is attributed to the sulfide derivatives and not to the propargylic cation complex $[(Co_2(CO)_6(CH{\equiv}CCH_2)]BF_4$. These substituted propargylic cationic compounds therefore have the potential for selective tuning toward nucleophilic attack, and further investigations of this reactivity are in progress.

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Supplementary Material Available: For **2a**, tables listing crystal data, bond distances and angles, and anisotropic thermal parameters (4 pages); a listing of observed and calculated structure factors for **2a** (8 pages). Ordering information is given on any current masthead page.

Notes

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Synthesis and Structural Characterization of New Boron-Substituted Monocarbon Carborane Adducts: *nido*-8-L-7-$CB_{10}H_{12}$ (L = SMe_2, PPh_3)

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Introduction

Synthetic pathways have previously been reported for the formation of the carbon-substituted members of the *nido*-7-L-$CB_{10}H_{12}$ family of monocarbon carboranes.[1-5] Although two B-substituted analogues, *nido*-9-L-7-$[((CH_3)_3Si)_2CH]CB_{10}H_{11}$[6,7] (L = $(CH_3)_2S$ or $(C_6H_5)_3P$) and *nido*-2-$(CH_3)_2S$-9-C_6H_{11}-7-$[NH(t\text{-}C_4H_9)]CB_{10}H_{10}$[8] have been reported, no general procedures have been developed for the production of the parent B-substituted compounds. We report herein a simple synthesis of *nido*-8-$(CH_3)_2S$-7-$CB_{10}H_{12}$ (I), the structural characterization of its triphenylphosphine analogue *nido*-8-$(C_6H_5)_3P$-7-$CB_{10}H_{12}$ (II), and some initial chemical studies of I which indicate that it may serve as a useful starting material for the construction of a variety of monocarbon carborane clusters.

Experimental Section

The $CB_{10}H_{13}^-$ anion was prepared according to the published procedure.[4] Dimethyl sulfide, sodium hydride, and triphenylphosphine were purchased from Aldrich Chemicals and used as received. Cyclopentadienylnickel carbonyl dimer was obtained from Alfa Products/Ventron Division. Toluene and concentrated sulfuric acid were obtained from Baker Chemical Co. All reaction solvents were reagent grade and dried according to literature methods.

Proton NMR spectra at 200 MHz were obtained on a Bruker WP-200 Fourier transform spectrometer. Boron-11 NMR spectra at 160.5 MHz were obtained on a Bruker AM-500 Fourier transform spectrometer. All boron-11 chemical shifts are referenced to $BF_3{\cdot}O(C_2H_5)_2$ (0.0 ppm) with a negative sign indicating an upfield shift. All proton chemical shifts were measured relative to internal residual solvent from the lock solvents used and are referenced to tetramethylsilane (0.0 ppm) with positive values indicating downfield shifts. Two-dimensional ^{11}B–^{11}B NMR experiments were conducted as described previously.[9]

High- and low-resolution mass spectra were obtained on a Hitachi Perkin-Elmer RMH-2 mass spectrometer and/or a VG Micromass 7070H mass spectrometer. Infrared spectra were obtained on a Perkin-Elmer 1430 spectrophotometer.

8-$(CH_3)_2S$-7-$CB_{10}H_{12}$ (I). In a 200-mL Erlenmeyer flask were placed 0.5 g (2.4 mmol) of $[NMe_4]^+[CB_{10}H_{13}]^-$ and 60 mL of anhydrous dimethyl sulfide. To the resulting suspension was quickly added 10 mL of concentrated sulfuric acid, and the resulting two-phase solution stirred at room temperature for 2 h. The dimethyl sulfide layer was then extracted with methylene chloride. The oily solid that was obtained upon evaporation of the methylene chloride was washed with three 15-mL portions of cold water, filtered, and dried under vacuum at 60 °C for 12 h. The resulting white solid (0.33 g, 1.7 mmol, 71% yield) was identified as 8-$(CH_3)_2S$-7-$CB_{10}H_{12}$, mp 110–112 °C. Exact mass for $^{12}C_3{}^1H_{18}{}^{11}B_{10}{}^{32}S$: calcd, 196.206; found 196.206. ^{11}B NMR (160.5 MHz, C_6D_6 (*J*, assignment)): δ 0.32 (142 Hz, B5), −4.72 (s, B8), −8.37 (155 Hz, B3), −10.29 (100 Hz, B2 or B11), −10.97 (140 Hz, B2 or B11), −17.01 (129 Hz, B9), −23.46 (143 Hz, B1), −25.74 (122 Hz, B10), −29.00 (142 Hz, B4,6). ^1H NMR (200-MHz boron spin-decoupled, C_6D_6, d (intensity, assignment)): δ 3.21 (1, BH), 2.71 (2, BH), 2.26 (3, BH), 1.83 (1, CH), 1.61 (1, BH), 1.38 (3, CH_3S), 1.32 (3, CH_3S), −2.87 (1, BHB), −3.35 (1, BHB). IR (KBr pellet, cm^{-1}): 3020 s, 2925 m, 2560 sh, 2537 s, 1980 w, 1420 s, 1340 m, 1105 m, 1080 m, 1050 m, 1040 m, 1010 m, 980 s, br, 920 m, 880 w, 810 sh, 750 m, 710 m, 670 w, 629 m.

8-PPh_3-7-$CB_{10}H_{12}$ (II). In a one-piece 100-mL reaction flask equipped with a high-vacuum stopcock adapter, were placed 0.30 g (1.5 mmol) of I, 0.40 g (1.5 mmol) of triphenylphosphine, and 30 mL of dry benzene. The resulting solution was then heated in vacuo at reflux for 18 h with periodic degassings. The volatile components of the reaction were then removed in vacuo, and the resulting yellow solid was extracted with 5 mL of dry methylene chloride. Pentane (5 mL) was added and the solution cooled to −5 °C, which resulted in the precipitation of white crystals of 8-$(C_6H_5)_3P$-7-$CB_{10}H_{12}$ (II) [0.37 g (0.94 mmol), 63% yield; mp 233–234 °C]. Exact mass measurements for $^{12}C_{19}{}^1H_{27}{}^{11}B_{10}{}^{31}P$, $(P-2)^+$: calcd, 394.2624; found, 394.2688 (the parent ion was not observed). ^{11}B NMR (160.5 MHz, C_6D_6 (*J*, intensity)): δ 0.85 (139 Hz, 1), −8.05 (150 Hz, 2), −10.37 (130 Hz, 1), −11.99 (154 Hz, 1), −18.87 (135 Hz, 1), −21.03 (s, 1), −22.50 (121 Hz, 1), −25.22 (128 Hz, 1), −28.57 (146 Hz, 1). ^1H NMR (200 MHz, C_6D_6, d (intensity, assignment)): δ 7.57 (15, Ph), 1.83 (1, CH), −3.21 (2, BHB). IR (KBr, cm^{-1}): 3020 w, 2980 w, 2960 w, 2550 s, 1420 s, 1330 w, 1260 s, 1190 w, 1110 m, 1050 sh, 1020 w, 990 sh, 910 w, 890 w, 870 w, 850 w, 800 s, 750 m, 730 s, 700 m, 680 w, 650 m, 630 m, 610 m, 530 s, 500 sh, 480 m, 440 m, 400 s.

Thermolysis of 8-$(CH_3)_2S$-7-$CB_{10}H_{12}$. In a 100-mL one-neck round-bottom flask equipped with a high-vacuum stopcock adapter were placed 0.10 g (0.52 mmol) of I and 25 mL of dry toluene. The solution was heated at reflux for 25 h in vacuo with periodic removal of noncon-

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densable gas at −196 °C. The toluene was removed in vacuo and the resulting oily material extracted with methylene chloride. Addition of 10 mL of cold pentane resulted in the precipitation of white *closo*-4-$(CH_3)_2S$-2-$CB_{10}H_{10}$ (III) (0.08 g, 0.42 mmol, 80% yield); mp 108–109 °C. Exact mass for $^{12}C_3{}^1H_{16}{}^{11}B_{10}{}^{32}S$: calcd, 194.1903; found, 194.1918. ^{11}B NMR (160.5 MHz, C_6D_6 (*J*, assignment)): δ 1.53 (143 Hz, 1), −7.63 (139 Hz, 1), −10.90 (146 Hz, 2), −19.03 (168 Hz, 2), −23.91 (141 Hz, 1) −27.81 (s, 1), −29.10 (148 Hz, 2). ^1H NMR (200 MHz, C_6D_6, d (intensity, assignment)): 2.32 (1, CH), 1.46 (6, Me_2S).

Solid samples that were thermolyzed at 160 °C in sealed tubes in vacuo also gave *closo*-8-$(CH_3)_2S$-7-$CB_{10}H_{12}$, although in lower yields (60%) than the solution reactions.

[*closo*-2-$CB_{10}H_{11}$]$^-$ (IVa). In a one-piece 100-mL reaction flask were placed 0.40 g (2.1 mmol) of 8-$(CH_3)_2S$-7-$CB_{10}H_{12}$ and 0.8 g (0.33 mmol) of NaH (97% active) under argon. The flask was transferred to a high-vacuum line and evacuated and 30 mL of dry THF added. The resulting solution was heated at reflux for 24 h, with periodic degassing at −196 °C to remove evolved hydrogen. Removal of the THF in vacuo left an oily solid, which was treated with methanol under an argon atmosphere to destroy the excess NaH. The solution was then concentrated in a rotary evaporator and 10 mL of water added. The pH of the solution was adjusted to 7 and aqueous tetramethylammonium chloride added, resulting in the precipitation of 0.33 g (1.6 mmol, 77% yield) of $[NMe_4]^+[CB_{10}H_{11}]^-$ (IV), which was identified by comparison of its ^{11}B NMR spectrum with that of the published spectrum.[1,2,10]

Analogous reactions of I with either KOH or TMEDA also resulted in the formation of IVa, but in lower yields (60% and 30%).

Reaction of 8-$(CH_3)_2S$-7-$CB_{10}H_{12}$ (I) and $[(\eta\text{-}C_5H_5)Ni(CO)]_2$. In a one-piece 100-mL flask equipped with a high-vacuum stopcock were placed 0.10 g (0.52 mmol) of I and 0.15 g (0.50 mmol) of cyclopentadienylnickel carbonyl dimer. The flask was evacuated and 25 mL of dry benzene added in vacuo. The reaction mixture was then heated at reflux for 6 h. The solution was then concentrated and separated by column chromatography to give 2-$(\eta\text{-}C_5H_5)$-2,1-$NiCB_{10}H_{11}$ [0.09 g (0.34 mmol), 68% yield], which was identified by comparison of its spectral data with the published values.[11]

***closo*-$[CB_{11}H_{12}]^-$.** In a greaseless 100-mL round-bottom flask equipped with a high-vacuum stopcock adapter were placed 0.10 g (0.52 mmol) of I and 3 mL of $(n\text{-}C_4H_9)_3P{\cdot}BH_3$. The flask was frozen at −196 °C and evacuated. The resulting solution was heated at 180 °C for a period of 24 h, with periodic removal of noncondensable gas. After H_2 evolution ceased, the flask was cooled to room temperature and 20 mL of cold pentane added, resulting in the precipitation of a white solid. The solid was filtered and washed with six 20-mL portions of cold pentane to remove excess base borane. The filtrate was left to stand, resulting in the precipitation of additional product. The total weight of the combined solids of $[HP(n\text{-}C_4H_9)_3]^+[CB_{11}H_{12}]^-$ (VI) was 0.14 g (0.40 mmol) for a yield of 78%. The compound was identified by its ^{11}B NMR spectrum, which is identical with the published spectrum.[1,2,10,12]

Crystallographic Data for 8-PPh_3-7-$CB_{10}H_{12}$. Single crystals were grown over several days by slow evaporation in air of cold methylene chloride/pentane solutions. A suitably sized crystal was mounted and transferred to the diffractometer. Refined cell dimensions and their standard deviations were obtained from least-squares refinement of 25 accurately centered reflections.

Collection and Reduction of the Data. Diffraction data (Table I) were collected at 295 K on an Enraf-Nonius four-circle CAD-4 diffractometer employing Mo Kα radiation from a highly oriented graphite-crystal monochromator. The intensities of three standard reflections measured at intervals of 100 reflections showed no systematic change during data collection. The raw intensities were corrected for Lorentz and polarization effects by using the Enraf-Nonius program START.

Solution and Refinement of the Structure. All calculations were performed on a VAX 11/750 computer using the Enraf-Nonius structure package.[13] The full-matrix least-square refinement was based on *F*, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights (w) were taken as $4F_o^2/(\sigma(F_o^2))^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The neutral-atom scattering factors and complex anomalous dispersion corrections were those stored in the SDP package. Agreement factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

Table I. Data Collection and Structure Refinement Information for 8-$(C_6H_5)_3P$-7-$CB_{10}H_{12}$

space group	$P\bar{1}$
a, Å	10.221
b, Å	14.661
c, Å	7.962
α, deg	94.45
β, deg	104.47
γ, deg	84.76
V, Å^3	1148.6
Z	2
ρ(calcd) g cm^{-3}	1.138
cryst dimens, mm	0.10 × 0.10 × 0.08
mol formula	$C_{19}H_{27}B_{10}P$
mol wt	393.50
scanning range, deg	$4 \le 2\theta \le 50$
h,k,l collcd	±12, ±17, −9
no. of measured I's	4370
no. of $F_o^2 > 3\sigma(F_o^2)$	2646
no. of variables	364
abs coeff (μ), cm^{-1}	1.19
transm coeff, %	98.7
max, %; min, %	98.5; 98.9
R	0.052
R_w	0.062

Direct methods (Multan) yielded the locations of all non-hydrogen atoms. Anisotropic refinements followed by difference Fourier syntheses resulted in the location of all hydrogens. All hydrogens were refined and included in the structure factor calculations. A regular icosahedron, from which this compound is derived, possesses 3-fold symmetry. II was found to be disordered by a 3-fold rotational axis passing through the phosphorus atom, B8 and B6. Rotation about this axis disordered B8, B6, and C7. The disorder problem was treated by assigning C7 in one of its equivalent positions for 70% of the time and into the other configuration for 30% of the time. The final refinement included a numerical absorption correction along with anisotropic thermal parameters for non-hydrogen atoms and fixed isotropic thermal parameters for the hydrogen atoms (6 Å^2). A final difference Fourier was featureless with the final peak being 0.29 e/Å^3. Final positional parameters are given in Table II, and selected intramolecular bond distances are presented in Table III.

Results and Discussion

The reaction of $[NMe_4]^+[CB_{10}H_{13}]^-$ with dimethyl sulfide and concentrated sulfuric acid was found to produce *nido*-8-SMe_2-7-$CB_{10}H_{12}$ (I) in 71% yield.

$$CB_{10}H_{13}^- + SMe_2 + H^+ \rightarrow 8\text{-}SMe_2\text{-}7\text{-}CB_{10}H_{12} + H_2 \quad (1)$$

The ^{11}B NMR spectrum of I at 160.5 MHz consists of nine resonances with relative intensities 1:1:1:1:1:1:1:1:2, indicating the absence of mirror symmetry. The singlet observed at −4.72 ppm is consistent with the presence of a boron-substituted dimethyl sulfide group. The spectrum is sufficiently different from that observed for the silylated compound *nido*-9-SMe_2-7-$(Me_3Si)_2CH$-$CB_{10}H_{11}$[6] to suggest that the exopolyhedral dimethyl sulfide groups are substituted at different boron sites in the two compounds. The ^1H NMR spectrum of I consists of a cage C–H resonance, appearing as a broad singlet at 1.83 ppm, separate bridge hydrogens resonances at −2.87 and −3.35 ppm, and two singlets of intensity 3 at 1.38 and 1.32 ppm, respectively, attributed to the inequivalent methyl resonances of the dimethyl sulfide group. The spectral data are thus consistent with an 11-vertex open-cage geometry containing two bridging hydrogens on the open face.

Reaction of I with triphenylphosphine resulted in the displacement of the dimethyl sulfide and formation of *nido*-8-PPh_3-7-$CB_{10}H_{12}$ (II) in 63% yield.

$$8\text{-}Me_2S\text{-}7\text{-}CB_{10}H_{12} + PPh_3 \rightarrow 8\text{-}PPh_3\text{-}7\text{-}CB_{10}H_{12} + Me_2S \quad (2)$$

Both the one- and two-dimensional ^{11}B NMR spectra of II are similar to those of I, indicating that the triphenylphosphine in II and the dimethyl sulfide in I are bound at the same boron position. A single-crystal X-ray study of II demonstrated that the compound, consistent with its nido skeletal electron count, adopts the structure shown in Figure 1 based on an icosahedron missing one vertex. The carbon atom is located on the open pentagonal face

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Table II. Atomic Positional Parameters and Their Estimated Standard Deviations for 8-PPh_3-7-$CB_{10}H_{12}$

atom	*x*	*y*	*z*	*B*,[a] Å^2
P	0.71755 (8)	0.25173 (6)	0.3341 (1)	3.25 (2)
B1	0.2579 (4)	0.2922 (4)	0.3087 (6)	6.2 (1)
B2	0.3194 (5)	0.3937 (4)	0.4110 (7)	6.1 (1)
B3	0.3988 (5)	0.3295 (4)	0.2616 (6)	6.1 (1)
B4	0.3990 (4)	0.2151 (3)	0.2901 (6)	5.7 (1)
B5	0.3092 (4)	0.2057 (4)	0.4517 (7)	7.0 (1)
B6	0.2629 (4)	0.3176 (3)	0.5303 (6)	5.0 (1)
C7	0.4911 (5)	0.3705 (3)	0.4553 (7)	4.5 (1)
C7′	0.534 (1)	0.281 (1)	0.603 (1)	5.2 (3)
B8	0.5447 (4)	0.2712 (3)	0.3979 (5)	3.34 (8)
B9	0.4846 (5)	0.1815 (3)	0.5017 (6)	6.2 (1)
B10	0.3976 (5)	0.2505 (4)	0.6535 (6)	6.4 (1)
B11	0.4178 (5)	0.3677 (4)	0.6224 (6)	5.8 (1)
C11	0.7578 (3)	0.3498 (2)	0.2388 (4)	3.34 (7)
C12	0.6698 (3)	0.3813 (2)	0.0850 (4)	4.26 (8)
C13	0.7007 (4)	0.4537 (3)	0.0078 (5)	4.76 (9)
C14	0.8164 (4)	0.4973 (2)	0.0788 (5)	4.98 (9)
C15	0.9045 (4)	0.4660 (3)	0.2270 (5)	5.09 (9)
C16	0.8758 (3)	0.3928 (2)	0.3071 (4)	4.18 (8)
C17	0.7267 (3)	0.1543 (2)	0.1825 (4)	3.60 (7)
C18	0.7492 (5)	0.1589 (3)	0.0557 (5)	7.4 (1)
C19	0.8021 (6)	0.0850 (3)	−0.0597 (6)	10.1 (1)
C20	0.7455 (5)	0.0074 (3)	−0.0503 (5)	6.6 (1)
C21	0.6788 (4)	0.0006 (2)	0.0760 (5)	5.2 (1)
C22	0.6690 (3)	0.0744 (2)	0.1936 (5)	4.50 (9)
C23	0.8506 (3)	0.2325 (2)	0.5268 (4)	3.47 (7)
C24	0.8588 (4)	0.2948 (2)	0.6697 (4)	4.44 (8)
C25	0.9645 (4)	0.2836 (3)	0.8167 (4)	4.98 (9)
C26	1.0591 (4)	0.2117 (3)	0.8213 (5)	5.9 (1)
C27	1.0510 (4)	0.1490 (3)	0.6831 (5)	5.9 (1)
C28	0.9480 (3)	0.1592 (3)	0.5336 (4)	4.56 (9)
HB1	0.163 (4)	0.295 (3)	0.212 (5)	
HB2	0.272 (4)	0.466 (3)	0.388 (5)	
HB3	0.405 (4)	0.351 (3)	0.125 (5)	
HB4	0.396 (4)	0.162 (3)	0.187 (5)	
HB5	0.245 (5)	0.146 (3)	0.458 (5)	
HB6	0.169 (4)	0.333 (3)	0.575 (5)	
HC7	0.528 (6)	0.410 (4)	0.438 (7)	
HC7′	0.64 (1)	0.281 (9)	0.72 (2)	
HB9	0.544 (4)	0.112 (3)	0.532 (5)	
HB10	0.391 (4)	0.224 (3)	0.774 (5)	
HB11	0.421 (4)	0.422 (3)	0.716 (5)	
HB56	0.585 (4)	0.230 (4)	0.554 (5)	
HB910	0.502 (4)	0.307 (3)	0.683 (5)	
HC12	0.589 (4)	0.348 (3)	0.035 (5)	
HC13	0.637 (4)	0.479 (3)	−0.092 (5)	
HC14	0.839 (4)	0.552 (3)	0.033 (5)	
HC15	0.980 (4)	0.493 (3)	0.269 (5)	
HC16	0.936 (4)	0.369 (3)	0.401 (5)	
HC18	0.825 (4)	0.214 (3)	0.047 (5)	
HC19	0.844 (4)	0.094 (3)	−0.136 (5)	
HC20	0.752 (4)	−0.045 (3)	−0.132 (5)	
HC21	0.641 (4)	−0.056 (3)	0.090 (5)	
HC22	0.621 (4)	0.073 (3)	0.286 (5)	
HC24	0.787 (4)	0.351 (3)	0.667 (5)	
HC25	0.966 (4)	0.330 (3)	0.906 (5)	
HC26	1.131 (4)	0.204 (3)	0.918 (5)	
HC27	1.121 (4)	0.092 (3)	0.673 (5)	
HC28	0.932 (4)	0.116 (3)	0.435 (5)	

[a] Hydrogen atoms were refined isotropically, with artificial thermal parameters of 6.0 Å^2.

Table III. Interatomic Distances (Å) for 8-PPh_3-7-$CB_{10}H_{12}$

P–B8	1.948 (4)	C7–B8	1.583 (6)
P–C11	1.801 (3)	C7–B11	1.687 (8)
P–C17	1.808 (3)	B8–B9	1.832 (7)
P–C23	1.799 (3)	B9–B10	1.859 (7)
B1–B2	1.732 (7)	B10–B11	1.792 (8)
B1–B3	1.721 (8)	C11–C12	1.408 (4)
B1–B4	1.779 (7)	C11–C16	1.380 (4)
B1–B5	1.728 (8)	C12–C13	1.365 (5)
B1–B6	1.764 (6)	C13–C14	1.369 (5)
B2–B3	1.769 (7)	C14–C15	1.375 (5)
B2–B6	1.743 (8)	C15–C16	1.379 (5)
B2–C7	1.709 (7)	C17–C18	1.366 (6)
B2–B11	1.781 (6)	C17–C22	1.377 (5)
B3–B4	1.710 (8)	C18–C19	1.375 (6)
B3–C7	1.692 (6)	C19–C20	1.337 (7)
B3–B8	1.799 (6)	C20–C21	1.363 (7)
B4–B5	1.777 (8)	C21–C22	1.388 (5)
B4–B8	1.763 (6)	C23–C24	1.393 (4)
B4–B9	1.777 (7)	C23–C28	1.392 (5)
B5–B6	1.777 (7)	C24–C25	1.389 (4)
B5–B9	1.746 (6)	C25–C26	1.361 (5)
B5–B10	1.746 (7)	C26–C27	1.369 (6)
B6–B10	1.748 (6)	C27–C28	1.385 (5)
B6–B11	1.769 (6)		

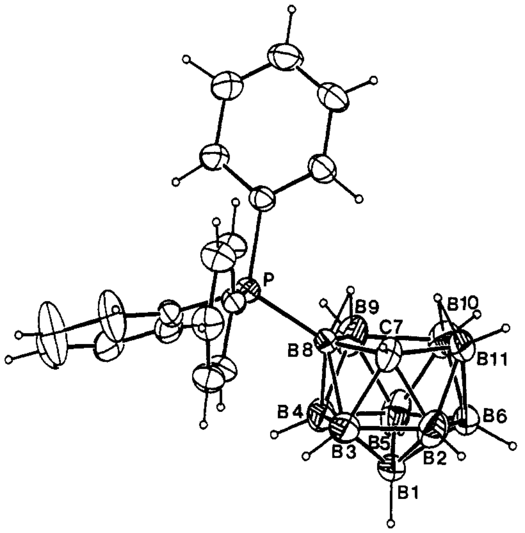

Figure 1. ORTEP drawing of the molecular structure of *nido*-8-$(C_6H_5)_3P$-7-$CB_{10}H_{12}$ (II).

and the triphenylphosphine is substituted at an adjacent boron atom (B8). The B–P distance in I (1.948 (4) Å) is similar to the B–P distance (1.928 (5) Å) observed in *nido*-9-PPh_3-7-$(Me_3Si)_2CHCB_{10}H_{11}$[7]. Two bridge hydrogens were found bridging the B8–B9 and B10–B11 edges. The remaining cage distances (Table III) and angles are similar to those observed for both *nido*-9-PPh_3-7-$(Me_3Si)_2CHCB_{10}H_{11}$[7] and for *nido*-2-$(CH_3)_2S$-9-$C_6H_5$-7-[NH(*t*-$C_4H_9$)]$CB_{10}H_{11}$[8].

Since the $CB_{10}H_{13}^-$ anion cannot accommodate an additional bridging hydrogen upon reaction with acid, the reaction sequence leading to the formation of I probably involves the initial formation of an unstable $CB_{10}H_{14}$ intermediate, which is similar to the reactive $B_{11}H_{15}$ species that is observed upon protonation of the isoelectronic $B_{11}H_{14}^-$ anion,[14a] that rapidly decomposes with elimination of H_2.

$$CB_{10}H_{13}^- + H^+ \rightarrow [CB_{10}H_{14}] \quad (3)$$

$$[CB_{10}H_{14}] \rightarrow [CB_{10}H_{12}] + H_2 \quad (4)$$

$$[CB_{10}H_{12}] + SMe_2 \rightarrow 8\text{-}SMe_2\text{-}7\text{-}CB_{10}H_{12} \quad (5)$$

The resulting acidic $CB_{10}H_{12}$ fragment, containing a vacant orbital on the open face, could then react with the nucleophilic dimethyl sulfide to yield the final product in which the base is substituted at a terminal site on B8. Similar reaction sequences have been proposed for the reaction of $B_{11}H_{14}^-$ with acid in dimethyl sulfide solution[14] and for the reaction of 7,8-$C_2B_9H_{12}^-$ with sulfuric acid in the presence of DMSO,[15] resulting in the production of $B_{11}H_{13}{\cdot}SMe_2$ and 9-SMe_2-7,8-$C_2B_9H_{12}$, respectively. Substitution occurs in both 9-SMe_2-7,8-$C_2B_9H_{12}$ and I at a boron atom on the open face that is adjacent to a cage carbon.

I was found to undergo a variety of reactions, suggesting that it may serve as a useful starting material for the generation of

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a range of monocarbon carborane cage systems. In particular, I was found to undergo cage closure and cage capping reactions similar to those that had previously been observed for 9-SMe_2-7-$[(Me_3Si)_2CH]CB_{10}H_{11}$.[6,7]

Thus, reaction of I with NaH results in hydrogen loss, dimethyl sulfide dissociation, and cage closure to yield the known *closo*-$CB_{10}H_{11}^-$ anion IVa. Likewise, thermolysis of I was found to result in hydrogen loss to yield a single product, *closo*-4-SMe_2-2-$CB_{10}H_{10}$ (III) in high yield. On the basis of the similarity of its spectral data with that obtained for *closo*-4-SMe_2-2-$[(Me_3Si)_2CH]$-$CB_{10}H_{10}$, III is proposed to adopt a structure based on a dodecahedron in which the dimethyl sulfide is bound at the 4-boron position.

$$\textit{nido}\text{-8-}Me_2S\text{-7-}CB_{10}H_{12} + NaH \rightarrow \textit{closo}\text{-2-}CB_{10}H_{11}^- + H_2 + SMe_2 \tag{6}$$

$$\textit{nido}\text{-8-}Me_2S\text{-7-}CB_{10}H_{12} \xrightarrow{\Delta} \textit{closo}\text{-4-}SMe_2\text{-2-}CB_{10}H_{11} + H_2 \tag{7}$$

In a reaction related to that previously found for 7-Me_3N-7-$CB_{10}H_{12}$,[12a] the dehydro capping of the open face of I was accomplished by reacting the carborane with tributylphosphine–borane to yield the known closo anion $CB_{11}H_{12}^-$ in 80% yield (eq 8). Likewise, the reaction (eq 9) of I with cyclopentadienylnickel

$$8\text{-}SMe_2\text{-7-}CB_{10}H_{12} + (n\text{-}C_4H_9)_3P\cdot BH_3 \rightarrow [LH]^+[CB_{11}H_{12}]^- + H_2 + SMe_2 \tag{8}$$

$$8\text{-}SMe_2\text{-7-}CB_{10}H_{12} + \tfrac{1}{2}[(\eta\text{-}C_5H_5)NiCO]_2 \rightarrow 2\text{-}(\eta\text{-}C_5H_5)\text{-2,1-}NiCB_{10}H_{11} + CO + \tfrac{1}{2}H_2 + SMe_2 \tag{9}$$

carbonyl dimer resulted in the formation of the known[11] metallacarborane 2-(η-C_5H_5)-2,1-$NiCB_{10}H_{11}$.

The formation of V may be envisioned via a dehydro insertion of the (η-C_5H_5)Ni onto the open face of carborane I, followed by dissociation of the dimethyl sulfide bound to the cage, to produce the formal $RCB_{10}H_{10}^{3-}$ ligand.

Acknowledgment. We thank the National Science Foundation for the support of this work. We also thank Drs. George Furst and Pat Carrol for their assistance in obtaining the NMR and X-ray crystallographic data.

Supplementary Material Available: Tables of anisotropic temperature factors, bond angles, and least-squares planes (6 pages); a listing of observed and calculated structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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Influence of Electronic Configuration on the Structure and Optical Properties of $KSnOPO_4$

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Introduction

Potassium titanyl phosphate ($KTiOPO_4$, or KTP) has become the material of choice for second-harmonic generation (SHG) from Nd:YAG laser light at 1.064 μm and has also demonstrated considerable utility for nonlinear optical (NLO) and electrooptical (EO) applications such as sum and difference frequency mixing (SFG), optical parametric oscillation (OPO), and electrooptic switching.[1] The KTP structures is acentric and consists of one-dimensional chains of TiO_6 octahedra linked by phosphate tetrahedra to give a three-dimensional network. The cations lie in channels parallel to the [001] direction. In the chain, the TiO_6 groups share corners to link up alternately as cis and trans with respect to the central Ti atom. These Ti–O bonds are alternately short (<1.75 Å) and long (>2.10 Å) through the chain, and each short Ti–O bond is trans to a long bond.[2] The long–short nature of the bridging Ti–O bonds leads to a picture of the TiO_6 unit as a distorted octahedron in which the Ti atom has been displaced from the geometric center. Several theories point to distortion of the MO_6 unit from perfect octahedral symmetry as the source of second-order nonlinearity in KTP and other metal oxide systems with distorted octahedral geometries such as perovskites, $LiNbO_3$, and tungsten bronzes. In all models, the degree of distortion of the MO_6 group strongly influences NLO susceptibility.[3]

In a study of phase-matching properties of crystals with the general formula $KTi_{1-x}Sn_xOPO_4$, Jarman and Grubb determined that $KSnOPO_4$ has no measurable SHG intensity.[4] It was postulated that the "second-order Jahn–Teller" effect responsible for MO_6 distortion in KTP is weakened or nullified by the d^{10} electronic configuration of tin(IV), eliminating any net contribution to the bulk susceptibility tensor $\chi(2)_{ijk}$ from the Sn–O bonds.[4] However, it is not immediately apparent whether this electronic influence should merely result in a loss of short M–O bonds, as is the case in the compound $KGaPO_4F_{0.7}(OH)_{0.3}$,[5] or if substitution results in crystallization in a centric space group, as is the case in the high-temperature ($T > T_c$) form of $TlTiOPO_4$.[6]

In this work, the effects of d^{10} metal substitution on the electronic and structural properties of KTP are examined by using X-ray crystallography, SHG intensities, and UV spectral data. Changes in band energies and in the degree of mixing of bonding (valence band) and antibonding (charge-transfer band) MOs are used to explain the resulting structural and optical properties.

Experimental Section

Synthesis. Crystals of $KSnOPO_4$ were grown from a phosphate flux with a K:P ratio of 1.33:1, prepared by fusing 0.067 mol of KH_2PO_4 (Fisher) and 0.033 mol of $K_2HPO_4\cdot 3H_2O$ (Mallinckrodt). To this was added 0.010 mol of SnO_2 (Alfa), and the mixture was heated at 1125 °C in a Pt crucible. The SnO_2 reacted swiftly with the phosphate flux to yield $KSnOPO_4$, which was allowed to remain in contact with the flux for 10 days to ensure its saturation. The resulting melt was poured off from the undissolved $KSnOPO_4$, reheated to 1125 °C and then cooled to 750 °C over 24 h. Small $KSnOPO_4$ crystals precipitated from the melt. After the flux was poured off, the crystals were washed with hot water and recovered by filtration. The crystals were colorless pinacoidal prisms, typically 0.2–0.5 mm on edge. Many crystals contained flux inclusions; yield was 0.028 g. $KSnOPO_4$ that had not dissolved in the initial melt was worked up in identical fashion, resulting in powder consisting of white grains approximately 50 μm in diameter.

A finer grained $KSnOPO_4$ powder was obtained via a gel synthesis technique in which 1.00 g of K_2SnCl_6[7] was treated with 2.74 g of $K_2HPO_4\cdot 3H_2O$ in 5.0 mL of H_2O to form a hydrogel, which was sealed in a Teflon bag and autoclaved at 200 °C at autogenous pressure for 5 days. After cooling, the resulting suspension was filtered and air-dried. $KSnOPO_4$ powder was obtained in quantitative yield. This material consisted of tetragonal microcrystals approximately 4 μm long and 2 μm wide, both as individual pieces and in clusters.

Structure Solution. A single crystal devoid of inclusions with approximate dimensions 0.5 × 0.4 × 0.15 mm was mounted on a glass fiber with epoxy prior to data collection on an automated Huber four-circle X-ray diffractometer (graphite-monochromated Mo Kα radiation, λ =

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