

Notes

Synthesis and Characterization of *o*-Carboranylmethyleneamine and *o*-Carboranylmethylenephosphine. Crystal Structure of $(\text{H}_3\text{B})(\text{NMe}_2\text{CH}_2\text{CCH})$ and $(\text{C}_2\text{B}_{10}\text{H}_{11})\text{CH}_2\text{PPh}_2$

Jinsoon Park, Sungjun Kim, Jaejung Ko*, Kwonil Park[†], Sungil Cho[‡],
Chai-Ho Lee[‡], Young-Haeng Lee[‡], and Sang Ook Kang*

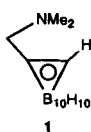
Department of Chemistry, Korea University, 208 Seochang, Chochiwon, Chungnam 339-700, Korea

[†]Department of Chemical Engineering, Junnong-dong 90, Seoul City University, Seoul 130-743, Korea

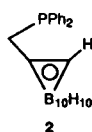
[‡]Department of Chemistry, Wonkwang University, Iksan 570-749, Korea

Received September 4, 1997

The preparation and coordination chemistry of *intra*-molecular coordination complexes have been an area of great interest for a number of years.¹ Our interest has been in the development of a potential ligand system in which the *o*-carborane nucleus functions as a ligand backbone.^{2,3} The carborane moiety, because of its unusual geometry and stability, is being extensively explored both from the standpoint of its own chemical reactivity as well as its function as a substituent. Previously, the syntheses of such ligand systems of the type 1⁴ and 2⁵ have been reported. However, the detailed preparation and characterization of such complexes have never been thoroughly studied. Thus, in the present work the formation of *o*-carboranylmethyleneamine **1** and *o*-carboranylmethylenephosphine **2** is now being studied in detail. Due to our interest in the formation of complexes **1** and **2**, a single crystal X-ray diffraction determination of **2** and (BH_3) -(propagyl amine) **5** was carried out to elucidate the nature of the reaction.



1



2

Experimental

Materials and instrumentation. Decaborane **4**, propargylbromide, and *N,N*-dimethylamino-2-propyne **3** were purchased from the Callery Chemical Co. and Aldrich, respectively, and used without purification. $\text{B}_{10}\text{H}_{12}(\text{SEt}_2)_2$ ⁶ and 1-(bromomethyl)-*o*-carborane⁴ were prepared by the literature methods. Proton, carbon-13, and boron-11 NMR spectra at 200.1, 50.3, and 64.2 MHz, respectively, were obtained using a Bruker WP-200 spectrometer. All boron-11 chemical shifts were referenced to $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ (0.0 ppm) with a negative sign indicating an upfield shift. All proton and carbon chemical shifts were measured relative to internal residual benzene from the lock solvent (99.5% C_6D_6) and then referenced to Me_4Si (0.00 ppm). High- and low-resolution mass spectra were obtained using a VG Micromass 7070H mass spectrometer. All melting points were uncorrected. Elemental analyses were obtained from Schwarzkopf

Laboratories, Woodside, NY, USA.

X-ray crystallography. Details of the crystal data and a summary of the intensity data collection parameters for **2** and **5** are given in Table 1. The crystals of **2** and **5** were grown from a hexane solution at -5°C . The crystals of **2** and **5** were mounted in thin-walled glass capillaries and seal-

Table 1. Crystallographic data for structural studies of compounds **2** and **5**

	2	5
Formula:	$\text{C}_{15}\text{H}_{23}\text{B}_{10}\text{P}$	$\text{C}_5\text{H}_{12}\text{BN}$
Formula Weight:	342.42	96.97
Crystal Class:	monoclinic	orthorhombic
Space group:	$P2_1/c$ (No. 14)	$Pnma$ (No. 62)
Z:	4	4
Cell constants:		
a, Å	10.819(1)	10.3860(8)
b, Å	13.9326(9)	8.021(1)
c, Å	13.2311(8)	8.355(1)
V, Å ³	1989.8(2)	696.1(1)
α , deg		
β , deg	93.929(8)	
γ , deg		
μ , cm^{-1}	0.133	0.052
crystal size, mm	$0.40 \times 0.20 \times 0.15$	$0.45 \times 0.15 \times 0.10$
D _{calcd} , g/cm^3	1.143	0.925
F(000)	12.00	216.00
Radiation:	Mo-K α ($\lambda=0.7170$)	Mo-K α ($\lambda=0.7170$)
Θ range, deg	2.0-27.0	2.0-27.0
h, k, l collected	+12, +15, ± 15	± 11 , ± 9 , +9
No. reflections measured:	3448	5400
No. unique reflections:	3286	693
No. reflections used in refinement	1019 [$F_o^2 > 3.0 \sigma(F_o^2)$]	531 [$F_o^2 > 3.0 \sigma(F_o^2)$]
No. parameters	236	67
Data/Parameter Ratio	4.3	7.9
² R_1 :	0.054	0.044
² R_w :	0.052	0.051
GOF:	1.457	2.945

$$^2R_1 = \frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2}^{1/2}; R_w = \frac{\sum w||F_o| - |F_c||}{\sum |F_o|}$$

ed under argon. The data sets of **2** and **5** were collected using a Rigaku diffractometer with an area detector employing graphite-monochromated Mo-K α radiation ($\lambda=0.7107$ Å) at a temperature of 253 K. X-ray data for **2** and **5** were processed, and the structure was solved and refined using the Molecular Structure Corporation teXan⁷ package on a Silicon Graphics Indigo R4000 computer. The intensity data were corrected for Lorentz and polarization effects. The structure was solved by a direct method (SIR88⁸). Re-

Table 2. Selected bond distances (Å) and Angles (°) for compound **2**

Bond Distances (Å)							
P1	C13	1.870(7)	P1	C14	1.837(8)		
P1	C20	1.832(8)	C1	C2	1.614(9)		
C1	C13	1.523(9)	C1	B3	1.73(1)		
C1	B4	1.71(1)	C1	B5	1.71(1)		
C1	B6	1.72(1)	C2	B3	1.72(1)		
C2	B6	1.70(1)	C2	B7	1.72(1)		
C2	B11	1.71(1)	C14	C15	1.37(1)		
C14	C19	1.37(1)	C15	C16	1.38(1)		
C16	C17	1.37(1)	C17	C18	1.35(1)		
C18	C19	1.40(1)	C20	C21	1.38(1)		
C20	C25	1.380(10)	C21	C22	1.38(1)		
C22	C23	1.37(1)	C23	C24	1.38(1)		
C24	C25	1.37(1)	B3	B4	1.77(1)		
B3	B7	1.78(1)	B4	B8	1.75(1)		
B4	B5	1.78(1)	B3	B8	1.78(1)		
B4	B9	1.79(1)	B5	B6	1.78(1)		
B5	B9	1.79(1)	B5	B10	1.78(1)		
B6	B10	1.75(1)	B6	B11	1.78(1)		
B7	B8	1.78(1)	B7	B11	1.79(1)		
B7	B12	1.78(1)	B8	B9	1.79(1)		
B8	B12	1.78(1)	B9	B10	1.78(1)		
B9	B12	1.77(1)	B10	B11	1.76(1)		
B10	B12	1.79(1)	B11	B12	1.76(1)		
Bond Angles (°)							
C13	P1	C14	97.6(3)	C13	P1	C20	103.7(4)
C14	P1	C20	101.6(3)	C2	C1	C13	119.5(6)
C2	C1	B3	61.9(5)	C2	C1	B4	110.6(6)
C2	C1	B5	110.4(6)	C2	C1	B6	61.1(5)
C13	C1	B3	120.2(6)	C13	C1	B4	122.1(6)
C13	C1	B5	118.4(6)	C13	C1	B6	114.3(6)
B3	C1	B4	61.8(5)	B3	C1	B5	113.7(6)
B3	C1	B6	114.4(6)	B4	C1	B5	62.7(5)
B4	C1	B6	114.1(6)	B5	C1	B6	62.3(5)
C1	C2	B3	62.3(5)	C1	C2	B6	62.7(5)
C1	C2	B7	112.8(6)	C1	C2	B11	112.8(6)
B3	C2	B6	116.1(6)	B3	C2	B7	62.1(5)
B3	C2	B11	114.4(6)	B6	C2	B7	116.0(6)
B6	C2	B11	63.0(5)	B7	C2	B11	62.9(5)
P1	C13	C1	115.5(5)	P1	C14	C15	124.6(7)
P1	C14	C19	116.7(8)	C15	C14	C19	118.8(8)
C14	C15	C16	120.8(9)	C15	C16	C17	119(1)
C16	C17	C18	121(1)	C17	C18	C19	118(1)
C14	C19	C18	120.8(9)	P1	C20	C21	115.9(7)
P1	C20	C25	125.7(6)	C21	C20	C25	118.4(7)
C20	C21	C22	120.9(8)	C21	C22	C23	120.6(9)
C22	C23	C24	118.3(9)	C23	C24	C25	121.3(9)
C20	C25	C24	120.4(8)				

finement was carried out using full-matrix least squares techniques based on F to minimize the quantity $\sum w(|F_o| - |F_c|)^2$ with $w=1/\sigma^2(F)$. Nonhydrogen atoms of **2** and **5** were anisotropically refined, and hydrogen atoms were isotropically refined for complex **5**. The refinement of **2** converged to $R_1=0.054$ and $R_{w2}=0.052$ and that of **5** converged to $R_1=0.044$ and $R_{w2}=0.051$. Selected bond distances and angles for **2** and **5** are given in Tables 2 and 3, respectively. The molecular structure of compounds **2** and **5** are given in Figures 1 and 2, respectively.

Reaction of B₁₀H₁₄ **4 with N,N-dimethylamino-2-propyne **3**.** A solution of 6.1 g (50 mmol) of decaborane **4** and 5.5 g (66 mmol) of propargylamine **3** in 50 mL of benzene was refluxed for 7.5 h. After cooling, the mixture was filtered and the filtrate was treated with dilute hydrochloric acid. The acid was neutralized and the amine, which is released, was recovered in ether. Isolation and recrystallization from pentane gave 3.6 g (18 mmol) of complex **1** as a waxy white solid. This corresponded to a 36% yield based on the consumed decaborane **4**. ¹¹B NMR (64.2 MHz, ppm, C₆D₆); -3.3 (d, 1B, $J_{BH}=140$ Hz), -5.5 (d, 1B, $J_{BH}=150$ Hz), -9.3 (d, 2B, $J_{BH}=160$ Hz), -11.9 (d, 2B, $J_{BH}=110$ Hz), -13.4 (d, 4B, $J_{BH}=120$ Hz); ¹H NMR (200.13 MHz, ppm, C₆D₆), 3.26 (s, 1H, CHCB₁₀H₁₀), 2.27 (s, 2H, CH₂), 1.66 (s, 6H, N-CH₃); ¹³C NMR (50.3 MHz, ppm, C₆D₆), 75.8 (s, 1C, CHCB₁₀H₁₀), 63.2 (s, 1C, CH₂), 58.8 (s, 1C, CHCB₁₀H₁₀), 46.7 (s, 2C, N-CH₃); exact mass calcd. for ¹¹B₁₀¹²C₅¹H₁₉¹⁴N 203.2448, found 203.2450; Anal. Calcd.: C, 29.83; H, 9.51; N, 6.96. Found: C, 30.01; H, 9.46; N, 6.89. Rf=0.96 by silica gel TLC analysis (benzene); Mp=4-5 °C; IR spectrum (KBr pellet, cm⁻¹) 3288 (w), 3066 (w, C-H), 2952 (w, C-H), 2832 (m, C-H), 2785 (s, C-H), 2572 (s, B-H), 2374 (w), 1455 (s), 1360 (w), 1268 (w), 1188 (m), 1094

Table 3. Selected bond distances (Å) and angles (°) for compound **5**

Bond Distances (Å)							
N2	C3	1.489(2)	N2	C6	1.487(2)		
N2	C6	1.487(2)	N2	B1	1.617(3)		
C3	C4	1.462(2)	C3	H3a	1.00(1)		
C3	H3a	1.00(1)	C4	C5	1.174(3)		
C5	H5	0.96(2)	C6	H6c	1.00(2)		
C6	H6a	1.01(2)	C6	H6b	1.03(2)		
B1	H1a	1.14(2)	B1	H1b	1.13(1)		
B1	H1b	1.13(1)					
Bond Angles (°)							
C3	N2	C6	109.7(1)	C3	N2	C6	109.7(1)
C3	N2	B1	107.9(1)	C6	N2	C6	109.2(2)
C6	N2	B1	110.1(1)	C6	N2	B1	110.1(1)
N2	C3	C4	114.5(2)	N2	C3	H3a	106.0(8)
N2	C3	H3a	106.0(8)	C4	C3	H3a	110.0(7)
C4	C3	H3a	110.0(7)	H3a	C3	H3a	110(1)
C3	C4	C5	179.1(2)	C4	C5	H5	179(1)
N2	C6	H6c	108.5(9)	N2	C6	H6a	109.8(9)
N2	C6	H6b	107.8(9)	H6c	C6	H6a	110(1)
H6c	C6	H6b	109(1)	H6a	C6	H6b	110(1)
N2	B1	H1a	106.2(9)	N2	B1	H1b	106.0(6)
N2	B1	H1b	106.0(6)	H1a	B1	H1b	113.0(8)
H1a	B1	H1b	113.0(8)	H1b	B1	H1b	111(1)

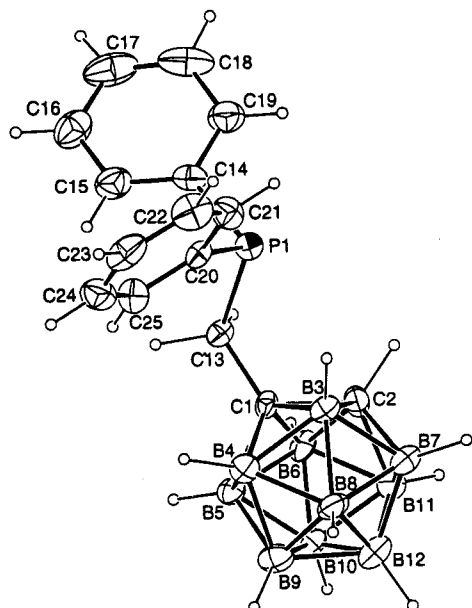


Figure 1. Molecular structure of **2**. The thermal ellipsoids are drawn at the 30% probability level.

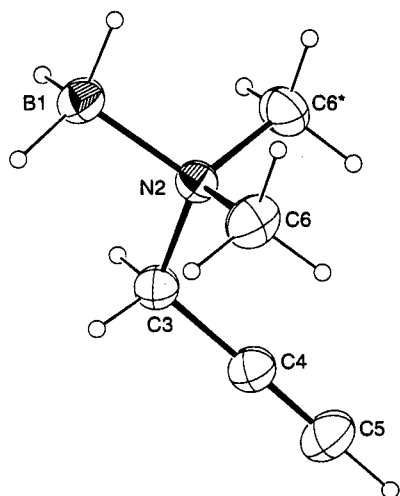


Figure 2. Molecular structure of **5**. The thermal ellipsoids are drawn at the 30% probability level.

(s), 1037 (s), 1014 (s), 913 (w), 862 (m), 807 (w), 722 (s), 675 (w), 577 (w), 570 (w), 552 (w), 517 (w).

Further extraction with diethyl ether followed by recrystallization at $-20\text{ }^{\circ}\text{C}$ gave the pure form of complex **5** (0.80 g, 8.2 mmol). ^{11}B NMR (64.2 MHz, ppm, C_6D_6); 9.8 (q, 1B, $J_{\text{BH}}=160$ Hz) ^1H NMR (200.13 MHz, ppm, C_6D_6) 3.10 (s, 1H, HCC), 2.63 (q, 3H, BH), 2.21 (s, 2H, CH_2), 1.73 (s, 6H, N- CH_3); ^{13}C NMR (50.3 MHz, ppm, C_6D_6) 188.8 (s, 1C, CHC), 120.1 (s, 1C, CHC), 64.7 (s, 1C, CH_2), 42.2 (s, 2C, N- CH_3); exact mass calcd. for $^{11}\text{B}^{12}\text{C}_5^{1}\text{H}_{12}^{14}\text{N}$ 97.1063, found 97.1069; Anal. Calcd.: C, 61.93; H, 12.47; N, 14.44. Found: C, 62.01; H, 12.40; N, 14.37. Mp= $2-4\text{ }^{\circ}\text{C}$; IR spectrum (KBr pellet, cm^{-1}) 3290 (s, C-H), 2950 (s, br, C-H), 2805 (s, C-H), 2424 (s, B-H), 2420 (s, B-H), 2400 (s, B-H) 2085 (w), 1510 (m, br), 1470 (s), 1375 (m), 1355 (m), 1325 (m), 1270 (m), 1170 (w), 1120 (m), 1040 (s), 1005

(m), 905 (w, br), 850 (m), 830 (w, br), 725 (w).

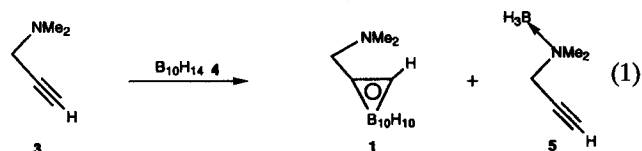
Reaction of $\text{B}_{10}\text{H}_{10}(\text{NCCH}_3)_2$ **6a with *N,N*-dimethylamino-2-propyne **3**.** Bis-(acetonitrile)decaborane **6a** was prepared by adding a solution of 7 mL of acetonitrile in 50 mL of dry toluene to an $80\text{ }^{\circ}\text{C}$ solution of 6.0 g (49 mmol) of decaborane **4** in 10 mL of dry toluene under a nitrogen atmosphere. After 2 h at $80\text{ }^{\circ}\text{C}$, a white solid precipitated. Propargylamine **3** (5.4 mL, 50 mmol in 50 mL of toluene) was added to the mixture over a 20 min period while the temperature was maintained at $80\text{ }^{\circ}\text{C}$. The resulting yellow solution was heated at $80-90\text{ }^{\circ}\text{C}$ for 12 h, followed by $100\text{ }^{\circ}\text{C}$ for 2 h. The residue was dissolved in methanol, and after gas evolution ceased, the solution was concentrated and the residue was extracted with hexane. The hexane was removed by vacuum evaporation, and the residue, a yellow oil, was purified by recrystallization in hexane at $-5\text{ }^{\circ}\text{C}$ to give 4.7 g (23 mmol, 47%) of waxy material **1**.

Reaction of $\text{B}_{10}\text{H}_{10}(\text{SEt}_2)_2$ **6b with *N,N*-dimethylamino-2-propyne **3**.** Propargylamine **3**, 50 mmol, was added to a refluxing solution of 50 mmol of $\text{B}_{10}\text{H}_{10}(\text{SEt}_2)_2$ **6b** in 100 mL toluene. After 18 h of refluxing, the reaction mixture was cooled and filtered, and the toluene was removed from the filtrate by distillation. The residue was dissolved in methanol, and after gas evolution ceased, the solution was concentrated and the residue was extracted with hexane. The hexane was removed by vacuum evaporation, and the residue, a yellow oil, was purified by recrystallization in hexane at $-5\text{ }^{\circ}\text{C}$ to give 4.0 g (20 mmol, 40%) of waxy material **1**.

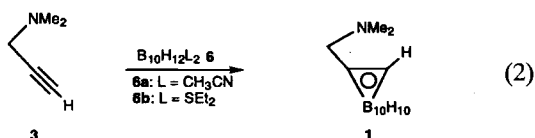
($\text{C}_2\text{B}_{10}\text{H}_{11}$) CH_2PPh_2 **2.** A solution of 4.6 g (21 mmol) of diphenylphosphorous chloride in 30 mL of dry ether was added dropwise to an ethereal solution of bromo(*o*-carboranyl-methyl)magnesium which was obtained from 5.0 g (21 mmol) of 1-(bromomethyl)-*o*-carborane and 1.0 g of magnesium at $5\text{ }^{\circ}\text{C}$. The mixture was refluxed for 2 h and cooled, and water was then added. The ether layer was separated and dried over CaCl_2 . After the removal of ether by vacuum, the residue was recrystallized from hexane. A 5.8 g (17 mmol, 81%) sample of complex **2** was obtained. ^{11}B NMR (64.2 MHz, ppm, C_6D_6); -2.3 (d, 1B, $J_{\text{BH}}=150$ Hz), -5.6 (d, 1B, $J_{\text{BH}}=130$ Hz), -9.3 (d, 2B, $J_{\text{BH}}=100$ Hz), -10.9 (d, 2B, $J_{\text{BH}}=120$ Hz), -12.8 (d, 4B, $J_{\text{BH}}=130$ Hz); ^1H NMR (200.13 MHz, ppm, C_6D_6), 7.21 (m, 3H, C_6H_5), 7.07 (d, 2H, C_6H_5), 3.21 (s, 1H, $\text{CHC}_2\text{B}_{10}\text{H}_{10}$), 2.67 (s, 2H, CH_2); exact mass calcd. for $^{11}\text{B}_{10}^{12}\text{C}_{15}^{1}\text{H}_{23}^{31}\text{P}$ 344.2468, found 344.2472; Anal. Calcd.: C, 52.61; H, 6.77. Found: C, 52.51; H, 6.99. Rf=0.96 by silica gel TLC analysis (benzene); Mp= $74-76\text{ }^{\circ}\text{C}$; IR spectrum (KBr pellet, cm^{-1}) 3067 (w, C-H), 2593 (s, B-H), 1439 (w, P-C), 1429 (w, P-C), 1250 (s, C=C), 1190 (w), 1125 (m), 1063 (m), 1017 (m), 1005 (w), 941 (w), 723 (s), 690 (w).

Results and Discussion

Previously, *o*-carboranylmethylamine **1** was prepared via the reaction of decaborane with propargylamine in benzene as shown in reaction 1.



We have noted that a compound such as propargyl amine preferentially led to the destruction of the decaborane to give borane·(propargyl amine) adducts as shown in reaction 1. Such degraded products include the $(\text{BH}_3)\cdot(\text{propargyl amine})$ 5, $(\text{B}_3\text{H}_7)\cdot(\text{propargyl amine})$, and $(\text{B}_9\text{H}_{12})\cdot(\text{propargyl amine})$ complexes. All of these species were characterized either by ^{11}B NMR or X-ray structural analysis. The low yield production of complex 1 can be explained in terms of the strong basicity of the propargyl amine. Therefore, we began to realize that the weakly coordinating Lewis base adducts $\text{B}_{10}\text{H}_{12}\text{L}_2$ 6 were needed to prevent unnecessary decomposition prior to the reaction with the acetylenic unit. Thus, the reactions of $\text{B}_{10}\text{H}_{12}\text{L}_2$ 6 with propargylamine 3 were investigated by employing a variety of conditions. The formation of a neutral entity 1 was first observed from the reactions of $\text{B}_{10}\text{H}_{12}\text{L}_2$ 6 with propargylamine 3 in refluxing toluene. The use of $\text{B}_{10}\text{H}_{12}\text{L}_2$ 6 has proven to be quite satisfactory for the synthesis of complex 1 since the activated form of decaborane $\text{B}_{10}\text{H}_{12}\text{L}_2$ 6 seems to afford good yields in a relatively short reaction period.



The composition of 1 was established by both elemental analysis and high resolution mass spectral analysis. Furthermore, the spectroscopic data (^1H , ^{13}C , and ^{11}B NMR) associated with complex 1 are also consistent with its assigned structure. The ^{11}B NMR spectrum of 1 consists of a set of overlapping doublets of relative intensities 1:1:2:2:4. The plane of symmetry indicated by the NMR data for complex 1 can be consistent only with substitution on the carborane at C(1) and C(2). The assignment of these resonances to the B(9), B(12), B(8, 10), B(4, 5), and B(7, 11, 3, 6) borons, respectively, is consistent with the assignments previously made by Todd for the spectrum of *closo*-3-Ph-1, 2- $\text{C}_2\text{B}_{10}\text{H}_{10}$.⁹ The ^1H NMR data are likewise in agreement with the proposed cage structure, thus confirming the presence of a cage C-H resonance (3.26 ppm) at the cage 2-position and one methylene (2.27 ppm) and two N-methyl (1.66 ppm) resonances of the amine substituent at the cage 1-position. The ^{13}C NMR spectrum contains cage carbon resonances at 75.8 and 58.8 ppm.

Similarly, the structure of 2 was easily established through spectroscopic (^1H , ^{13}C , and ^{11}B NMR) as well as analytical methods. The ^{11}B NMR spectrum of 2 shows five resonances of relative intensity 1:1:2:2:4 with the intensity four appearing to result from the overlap of 2 resonances of intensity 2. The plane of symmetry indicated by the NMR data can be consistent only with substitution of the carborane at C(1) and C(2). The ^1H and ^{13}C NMR data are likewise in agreement with the proposed cage structure and confirm the presence of a phosphine group at the cage 1-position. The ^1H NMR data contain a C-H resonance (3.21 ppm) for the cage 2-position and phenyl resonances (7.21 and 7.07 ppm) and a methylene resonance (2.67 ppm) for the diphenylphosphinomethane substituent.

Complexes 1 and 2 are structurally related. The molecular structure and atom-labeling scheme for complex 2 are

shown in Figure 1; whereas, selected bond distances (\AA) and angles ($^\circ$) are presented in Tables 2. The overall structure of 2 contains an diphenylphosphinomethane fragment connected to an *o*-carboranyl group. The drawing in Figure 1 illustrates how the diphenylphosphinomethane substituent effectively faces the large *o*-carborane from the side. The phosphorous atom P(1) is coplanar with a standard deviation of 0.19 \AA and with three atoms C(13), C(1), and C(2). The normal to this plane almost bisects the directions of the two orthogonal phenyl groups of the diphenylphosphine. The two carbon atoms of the two phenyl groups and one carbon atom of the methylene unit are bonded to a phosphorous atom in a pyramidal arrangement. The P-C bond lengths of 1.870(7)-1.837(8) \AA and C-P-C angles of 97.6(3)-103.7(4) $^\circ$ are similar to those in 1- PPh_2 -2-Me- $\text{C}_2\text{B}_{10}\text{H}_{10}$.¹⁰ The inter-cage boron-boron (1.75-1.79 \AA) and boron-carbon (1.70-1.73 \AA) distances are normal, and the carbon-carbon distance between the only adjacent carbons, C(1)-C(2) 1.614(9) \AA , is also in the range previously observed in other *o*-carborane cage systems.¹¹ The remaining carbon-carbon distances (1.35-1.40 \AA) on the phenyl groups of the two diphenylphosphines appear normal.

Complex 5 was only slightly soluble in diethylether and therefore precipitated during the reaction. Complex 5 has been crystallographically characterized (see Figure 2), and the spectroscopic data reported in the experimental section for 5 are consistent with their indicated formulation. The ^1H NMR spectrum of 5 confirms the presence of a propargyl amine group showing one acetylenic C-H resonance at 3.10 ppm, one methylene resonance at 2.21 ppm, and two N-methyl resonances at 1.73 ppm. Also, the ^1H NMR spectra confirm the presence of a BH_3 group showing a broad quartet with coupling of 160 Hz at 2.63 ppm. Indicative of the formation of a borane-base adduct derivative $(\text{BH}_3)\cdot(\text{propargyl amine})$ 5, strong B-H stretching absorptions at about 2420 cm^{-1} are observed. The conformation and atomic numbering scheme for 5 are shown in Figure 2; selected bond distances (\AA) and angles ($^\circ$) are listed in Tables 3. As shown in Figure 2, the structure of complex 5 consists of a BH_3 unit bonded to a propargylamine fragment. In this complex, the borane moiety is located in an *exo*-arrangement about the N(2)-C(3) bond with respect to the two methyl substituents on the nitrogen atom and one acetylenic group of the C(3) atom with C_s symmetry. The boron atom B(1), the atoms of the propargyl moiety [C(3), C(4), C(5)], and the nitrogen atom N(2) are essentially coplanar [average deviation from the mean plane of 0.008 \AA with a maximum deviation of 0.01 \AA associated with N(2)]. The B(1)-N(2) bond length of 1.617(3) \AA is similar to those found in other borane-amine adduct complexes such as $\text{H}_3\text{B}\cdot\text{NH}_3$, 1.672 \AA ;¹² $\text{H}_3\text{B}\cdot\text{NH}_3\cdot(18\text{-crown-6})$, 1.60 (6) \AA ;¹³ and $\text{H}_3\text{B}\cdot\text{NMe}_3$, 1.616 \AA .¹⁴

In conclusion, this report provides the detailed synthesis of *o*-carboranymethyleneamine 1. A combination of X-ray crystallographic and spectroscopic studies confirms the nature of this compound and reaction chemistry between decaborane 4 and propargylamine 3. Additionally, we report here the development of improved synthetic route to complex 1, starting with the readily available $\text{B}_{10}\text{H}_{10}\text{L}_2$ 6.

Acknowledgment. The present studies were supported by the Basic Science Research Institute program, Ministry of Education (BSRI-97-3407) and also by the Medicinal Re-

source Research Center sponsored by the Korea Science and Engineering Foundation (97-16-04-02-A-1). We thank Dr. Pat Carroll for his assistance in the X-ray crystallographic studies.

Supplementary Material Available. Tables of bond distances and bond angles, anisotropic thermal parameters, positional parameters for hydrogen atoms, and listings of observed and calculated structure factors. Supplementary materials are available from one of the authors (S. O. Kang) upon request.

References

- (a) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403. (b) Evans, D. W.; Baker, G. R.; Newkome, G. R. *Coord. Chem. Rev.* **1989**, *93*, 155. (c) Rothwell, I. P. *Acc. Chem. Res.* **1988**, *21*, 153. (d) Newkome, G. R.; Puckett, W. E.; Gupta, V. K.; Kiefer, G. E. *Chem. Rev.* **1986**, *86*, 451. (e) Rothwell, I. P. *Polyhedron* **1985**, *4*, 177. (f) Constable, E. C. *Polyhedron* **1984**, *3*, 1037. (g) Omae, I. *Chem. Rev.* **1979**, *79*, 287. (h) Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73. (i) Parshall, G. W. *Acc. Chem. Res.* **1970**, *3*, 139.
- Smith, Jr. H. D. *J. Am. Chem. Soc.* **1965**, *87*, 1878.
- (a) Smith, Jr. H. D.; Robinson, M. A.; Papetti, S. *Inorg. Chem.* **1967**, *6*, 1014. (b) Smith, Jr. H. D. *Inorg. Chem.* **1969**, *8*, 676.
- Heying, T. L.; Ager, Jr. J. W.; Clark, S. L.; Mangold, D. J.; Goldstein, H. L.; Hillman, M.; Polak, R. J.; Szymanski, J. W. *Inorg. Chem.* **1963**, *2*, 1089.
- Zakharkin, L. I.; Zhubekova, M. N.; Kazantsev, A. V. *Zh. Obsh. Khim.* **1972**, *42*, 1024.
- Graybill, B. M.; Ruff, J. K.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1961**, *83*, 2669.
- teXan: *Crystal Structure Analysis Package*, Molecular Structure Corporation (1985 & 1992).
- Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Polidori, G.; Spagna, R.; Viterbo, D. *J. Appl. Cryst.* **1989**, *72*, 389.
- Todd, L. J.; Siedle, A. R. *Progress in NMR Spectroscopy*, **1979**, *13*, 87.
- Kivekäs, R.; Sillanpää, R.; Teixidor, F.; Vinas, C.; Nunez, R. *Acta. Crystallogr. Scand.* **1994**, *C50*, 2027.
- Mastryukov, V. S.; Dorofeeva, O. V.; Vilkov, L. V. *Russ. Chem. Rev. (Engl. Transl.)* **1980**, *49*, 1181; *Usp. Khim.* **1980**, *49*, 2377.
- Shore, S. G.; Parry, R. W. *J. Am. Chem. Soc.* **1955**, *77*, 6084. (b) Huges, E. W. *J. Am. Chem. Soc.* **1956**, *78*, 502. (c) Lippert, E. L.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1958**, *80*, 503.
- Colquhoun, H. M.; Jones, G.; Maud, J. M.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc. Dalton Trans.* **1984**, 63.
- Bühl, M.; Steinke, T.; Schleyer, P. v. R.; Bose, R. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1160.

[1.1.1]Propellane: Reaction with Singlet Dihalocarbene

Woo Bung Lee*, Dong Won Oh, Mi Sook Park, and Chang Hyun Kim

Department of Chemistry, Kyungpook National University, Taegu 702-701, Korea

Received October 7, 1997

The [1.1.1]propellane has been extensively investigated in recent years and has provided important information on the very small ring hydrocarbon chemistry.^{1,2} The smallest propellane, [1.1.1]propellane, was first prepared by Wiberg in 1982.³ This compound has an inverted structure at the two bridgehead carbon atoms^{4,5} and the central C-C bond has sp² character, as well as the charge distribution has the high local charge density near the bridgehead carbon.^{5,6} This would suggest the possibility of relatively facile carbene addition across the bridgehead bond of [1.1.1]propellane. In a recent communication,⁷ we have reported the reaction of [1.1.1]propellane with carbenoid. The reaction of [1.1.1]propellane with phenylchlorocarbene had been studied previously by other workers.^{8,9} However, no example has been reported of the addition of singlet dihalocarbenes to [1.1.1]propellane.

In this paper, we have described the addition of singlet dihalocarbenes to [1.1.1]propellane and the reaction mechanism was discussed.

Experimental

General. Manipulations were performed under an inert atmosphere of nitrogen. Dry, oxygen-free solvents were employed throughout the reaction.

¹H and ¹³C NMR spectra were recorded at 300 MHz on a Varian unity plus spectrometer, GC-Mass were on a HP 5890 series II spectrometer and preparative GC separation was carried out in a Gow-Mac instrument with TCD detector and provided with a 5 ft packed column of 15% OV101.

Product yields were determined by analytical GC with bromoform as an internal standard and predetermined response factor for the products.

Reaction of [1.1.1]Propellane with dihalocarbene. [1.1.1]Propellane was prepared from 1,1-dibromo-2,2-bis-(chloromethyl)cyclopropane and methylolithium as described,¹⁰ and characterized by ¹H NMR (δ =2.04, s, 6H). Dihalocarbenes were generated from chloroform, bromoform and potassium-tert-butoxide at -30 °C.