between the mean-squared displacements of the meta and ortho C atoms was restrained to 0 along their bond. While the anisotropic thermal parameters for these carbon atoms, as well as those of the chlorine atoms of the methylene chloride, model the actual electron density rather well, their magnitudes and extreme anisotropies suggest unresolved disorder rather than normal thermal motion. The disorder of the phenyl group involves different rotational conformations about the P(1)–C(21) bond. More complex models were considered.

The hydrogen atoms were, in general, placed in calculated positions, and the shifts of their coordinates during least-squares refinement were linked to those of the carbon atoms to which they were bonded. The one exception to this was H(1) (bonded to N), which was refined independently. A single isotropic thermal parameter was refined for the two H atoms of the methylene bridge in the chelate (H(2) and H(3)), another for the H atom sites of the methylene chloride (H(4)–H(7)), and one for all the H atoms of the phenyl groups. The root mean square |shift/esd| was 0.01, while the largest |shift/esd| was 0.08, for the final full-matrix least-squares refinement of 215 parameters for 2296 observations ($F_o \leq 5.0\sigma(F_o)$) and 32 restraints. The largest peak in the final difference map was 0.4 (4) e Å^{-3}. With unit weights, $w(|F_o| - |F_c|)^2$ was near constant as a function of both $|F_o|$ and $(\sin\theta)/\lambda$.

Complex scattering factors for neutral atoms[21] were used in the calculation of structure factors. The programs used for data reduction, structure solution and refinement were from ref 22. The program suite CRYSTALS[23] was employed in the final stages of refinement involving the use of restraints. Diagrams were generated with the program SNOOPI.[24] All computations were carried out on a MicroVAX-II computer.

Listings of full experimental details, coordinates and temperature factors for the hydrogen atoms, other than H(1), anisotropic temperature

factors, and observed and calculated structure factors are deposited as supplementary material.

Summary and Conclusion

One phosphorus atom of bis(diphenylphosphino)methane and its ethane homologue can be cleanly oxidized with trimethylsilyl or trimethylgermyl azide. As prepared, the resultant methylene-bridged phosphoranimine phosphines appear to exist as conformational isomers in the case of the Me₃Si and Me₃Ge derivatives, but only one form was shown by the fluoroaromatic derivative (readily obtained from the reaction of the silyl or germyl precursors with an activated fluoroaromatic) and the free imine (obtained by mild hydrolysis of the original silyl and germyl ligands). These new ligands readily formed P,N chelate complexes with Pd(II), and regardless of the conformational complexity of the ligand, only one complex was formed. Conducting the complexation reaction in water (or hydrolysis of the Me₃Si- or Me₃Ge-containing complexes of Pd(II)) gives the Pd(II) complex of the parent imine. The structural characterization of this complex showed a chelate with normal bonding features.

This work demonstrates that the heterodifunctional ligand system formed by controlled oxidation of the one phosphorus center in a diphosphine readily forms stable chelate complexes with the prototypical late-transition-metal Pd(II) center. A variety of substitutional changes can be made to the ligand that allow basicity at nitrogen to be modified. In addition, parallel chemistry can be developed by the higher homologue and by the related phosphoranimine arsine. Further extensions to the chemistry of this versatile system are in progress.

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Syntheses and Properties of [Cu{B₂H₄·2P(CH₃)₃}₂]X (X = Cl, I) and X-ray Crystal Structure of the Iodide

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Chloride and iodide salts of bis{bis(trimethylphosphine)tetrahydrodiboron-*H¹,H²*}copper(I), [Cu{B₂H₄·2P(CH₃)₃}₂]X (X = Cl, I), were prepared by the reactions of B₂H₄·2P(CH₃)₃ with the copper(I) halides. X-ray crystal structure analysis of the iodide shows that each ligand is coordinated to the copper atom through two vicinal hydrogen atoms and the copper atom is ligated with four hydrogen atoms tetrahedrally. Crystal data: monoclinic with the space group *I2/a*, $a = 13.003$ (1) Å, $b = 16.257$ (2) Å, $c = 12.974$ (3) Å, $\beta = 92.63$ (1)°, $V = 2739.7$ (8) Å³, $Z = 4$, and $R(F_o) = 0.057$ for 1676 reflections with $|F_o| > 3\sigma(F_o)$.

Introduction

Although quite a large number of metallaboranes or metal complexes of boron hydrides have been reported,[1-4] most of them are neutral or anionic, and only a small number of cationic boron hydride complexes are known, i.e. [Fe(CO)₃(B₅H₁₀)]⁺,[5] [Co-

(CO)₃(B₅H₉)]⁺,[5] [Cu₂(PPh₃)₄(BH₄)]⁺,[6] and [NiL(BH₄)]⁺ (L = cyclic tetramine or noncyclic quadridentate Schiff base).[7] This is due to the fact that only anionic boron hydrides are known to be good ligands and is parallel to the scarcity of cationic boron hydrides[8] in contrast to the abundance of neutral and anionic boron hydrides.

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Bis(trimethylphosphine)–diborane(4) is the first neutral borane Lewis base adduct that coordinates to metals[9] as a bidentate ligand. Hence it is a good candidate as a ligand to form cationic metal complexes of borane. All the complexes with $B_2H_4\cdot2P(CH_3)_3$ as a ligand so far reported are neutral mixed-ligand complexes: $ZnCl_2\{B_2H_4\cdot2P(CH_3)_3\}$,[9,10] $CuX(PPh_3)\{B_2H_4\cdot2P(CH_3)_3\}$,[9,10] $CuX\{B_2H_4\cdot2P(CH_3)_3\}$,[10] and $Ni(CO)_2\{B_2H_4\cdot2P(CH_3)_3\}$.[10,11] The $Cu\{B_2H_4\cdot2P(CH_3)_3\}^+$ moiety is isolobal with BH_2^+ as well as CuL_2^+ (L = Lewis base such as trialkylphosphine), which is a versatile chemical moiety to form various metallaboranes.[1,4] The triboron cation $B_3H_6\cdot2P(CH_3)_3^+$, which is formed by the reactions of $B_2H_4\cdot2P(CH_3)_3$ with B_2H_6 or B_4H_{10}, is considered to be the result of the coordination of $B_2H_4\cdot2P(CH_3)_3$ to the cationic species BH_2^+.[12] This formalism showed us the possibility of allowing $Cu\{B_2H_4\cdot2P(CH_3)_3\}^+$ to react with another $B_2H_4\cdot2P(CH_3)_3$. We now report that $B_2H_4\cdot2P(CH_3)_3$ reacts with copper(I) halides to form the first homoleptic cationic complexes $[Cu\{B_2H_4\cdot2P-(CH_3)_3\}_2]X$ (X = Cl, I).

This complex can be regarded as a commo-class metallapentaborane derivative. Since no commo-class lower borane has been reported, the complex is important as a model compound for such commo-class boranes. Furthermore the complex is notable as the first example of monomeric copper(I) complex that is coordinated tetrahedrally only by hydrogen atoms.

Experimental Section

A. General Procedures and Equipment. Conventional vacuum-line techniques were used for handling volatile compounds. Air- and moisture-sensitive solids were handled in a glovebox or in clear plastic bags filled with dry nitrogen. All solvents were purified by distillation over appropriate drying agents under nitrogen. $B_2H_4\cdot2P(CH_3)_3$ was prepared by the reaction of laboratory stock B_5H_9 and excess $P(CH_3)_3$.[13] Copper(I) chloride was purified according to the method reported in ref 14. Copper(I) iodide was dried in a high vacuum at about 400 °C. Infrared spectra were recorded as KBr disks on a JASCO IR-810 infrared spectrometer. The ¹H, ¹¹B, and ³¹P NMR spectra were recorded on Varian XL-200 and JEOL FX-90Q instruments. The chemical shifts for ¹¹B and ³¹P were expressed with respect to $BF_3\cdot O(C_2H_5)_2$ and 85% orthophosphoric acid; positive values indicate downfield shifts.

B. Synthesis of [Cu{B₂H₄·2P(CH₃)₃}₂]I. To a mixture of 101 mg (0.56 mmol) of $B_2H_4\cdot2P(CH_3)_3$ and 54 mg (0.28 mmol) of copper(I) iodide was added 20 mL of dichloromethane by vacuum distillation. The mixture was stirred magnetically at 0 °C in the dark for 4 h. Insoluble copper(I) iodide gradually dissolved, and the solution became clear. After evaporation of the solvent, the colorless residue was extracted with 6 mL of dichloromethane. Removal of solvent afforded the desired product in almost quantitative yield. Anal. Calcd for $C_{12}H_{44}B_4CuIP_4$: C, 26.39; H, 8.12. Found: C, 27.17; H, 8.71. IR (KBr), cm⁻¹: ν(BH) 2340 (s), ν(BHCu) 1938 (m, br). ¹H NMR (200 MHz, CD₂Cl₂): δ 1.29 (t, 36 H, CH₃), –0.1 (br d, 8 H, BH). ¹¹B{¹H} NMR (28.8 MHz, CD₂Cl₂): δ –44.5 (br d). ³¹P{¹H} NMR (36.3 MHz, CD₂Cl₂): δ 2.1 (br d).

[Cu{B₂H₄·2P(CH₃)₃}₂]I was also obtained by slow diffusion of pentane into a dichloromethane solution of $CuI(PPh_3)\{B_2H_4\cdot2P(CH_3)_3\}$. The $CuI(PPh_3)\{B_2H_4\cdot2P(CH_3)_3\}$ used here was prepared by the method of Snow.[10]

C. Synthesis of [Cu{B₂H₄·2P(CH₃)₃}₂]Cl. The complex chloride was prepared from copper(I) chloride and $B_2H_4\cdot2P(CH_3)_3$ by almost the same method as that used for the iodide. Anal. Calcd for $C_{12}H_{44}B_4ClCuP_4$: C, 31.70; H, 9.76; Cl, 7.80. Found: C, 31.06; H, 10.01; Cl, 7.06. IR (KBr), cm⁻¹: ν(BH) 2330 (s), ν(BHCu) 1940 (m, br). ¹H NMR (200 MHz, CD₂Cl₂): δ 1.27 (t, 36 H, CH₃), –0.1 (br d, 8 H, BH). ¹¹B{¹H} NMR (28.8 MHz, CD₂Cl₂): δ –43.1 (br s). ³¹P{¹H} NMR (36.3 MHz, CD₂Cl₂): δ –0.4 (br d).

D. X-ray Crystal Structure Determination of [Cu{B₂H₄·2P(CH₃)₃}₂]I. Octahedral crystals of [Cu{B₂H₄·2P(CH₃)₃}₂]I used for the X-ray structure analysis were obtained by slow diffusion of diethyl ether into a dichloromethane solution of the compound. Most of the crystals obtained were twinned and were not suitable for X-ray diffraction study. A crystal with the dimensions 0.3 × 0.2 × 0.1 mm was selected by

Table I. Crystallographic Data for [Cu{B₂H₄·2P(CH₃)₃}₂]I

| chem formula:	space group:
$C_{12}H_{44}B_4CuIP_4$	$I2/a$ (variant of No. 15)
fw = 546.07	T = 20 °C
a = 13.003 (1) Å	λ = 0.710 73 Å
b = 16.257 (2) Å	ρ_{calcd} = 1.32 g cm⁻³
c = 12.974 (3) Å	μ = 21.4 cm⁻¹
β = 92.63 (1)°	$R(F_o)$ = 0.057
V = 2739.7 (8) Å³	$R_w(F_o)$ = 0.076
Z = 4	

examination under a polarized microscope, and was jam-fit into a thin-wall glass capillary under nitrogen. Diffraction measurements were made on a Rigaku AFC-6A automated four-circle diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Crystallographic and experimental data are listed in Table I. The reflection data were corrected for Lorentz and polarization factors but not for absorption. The structure was solved by the heavy-atom method. The positions of copper, iodine, and two phosphorus atoms were deduced from the Patterson function and refined by the block-diagonal least-squares method. Positions of other non-hydrogen atoms were deduced from successive Fourier syntheses. Anisotropic temperature factors were applied for non-hydrogen atoms. Positions of hydrogen atoms attached to boron atoms were deduced from difference Fourier synthesis and refined with isotropic temperature factors. No hydrogen atoms bonded to carbon atoms were found. Atomic scattering factors for non-hydrogen atoms and hydrogen atoms were taken from ref 15 and 16, respectively. The calculations were performed on a Nippon Electric Co. ACOS-2000 computer at the Computer Center of Tohoku University using the Universal Program System UNICSIII.[17]

Results and Discussion

A. Syntheses of Bis{bis(trimethylphosphine)tetrahydrodiboron-H^1,H^2}copper(I) Iodide and Chloride. Reaction of 1 mol of copper(I) iodide with 2 mol of $B_2H_4\cdot2P(CH_3)_3$ in dichloromethane gave colorless crystals of [Cu{B₂H₄·2P(CH₃)₃}₂]I almost quantitatively. The preparation of the chloride was also carried out by a procedure similar to that for the iodide.

$$CuX + 2B_2H_4\cdot2P(CH_3)_3 \rightarrow [Cu\{B_2H_4\cdot2P(CH_3)_3\}_2]X$$
$$X = Cl, I$$
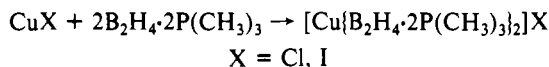
The iodide was also formed during the recrystallization of $CuI(PPh_3)\{B_2H_4\cdot2P(CH_3)_3\}$ in a dichloromethane/pentane solution. This finding indicates the occurrence of the following reaction:

$$2CuI(PPh_3)\{B_2H_4\cdot2P(CH_3)_3\} \rightarrow$$
$$[Cu\{B_2H_4\cdot2P(CH_3)_3\}_2]I + CuI(PPh_3)_n$$
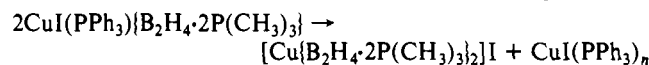
$CuI(PPh_3)_n$ was isolated as white powder and characterized by its infrared spectrum. Further investigation of this compound has not been made.[18]

The chloride is less stable than the iodide and decomposes gradually to give metallic copper under a nitrogen atmosphere even in the solid state. Both complexes decompose to deposit copper more rapidly in solution than in the solid state.

B. Structure of [Cu{B₂H₄·2P(CH₃)₃}₂]I. The infrared spectrum of [Cu{B₂H₄·2P(CH₃)₃}₂]I showed a strong absorption at 2340 cm⁻¹ and a broad peak with the maximum at 1938 cm⁻¹. These absorptions are assigned to the stretching modes of B–H$_{terminal}$ and B–H–Cu bonds, respectively. No absorption due to δ(BH₂) around 1120 cm⁻¹ was observed. This spectral pattern is quite similar to that of $ZnCl_2\{B_2H_4\cdot2P(CH_3)_3\}$,[9,10] whose structure was ascertained by single-crystal X-ray analysis, and shows that $B_2H_4\cdot2P(CH_3)_3$ functions as a bidentate ligand coordinated to the metal through two vicinal hydrogen atoms.

The molecular structure was determined by a single-crystal X-ray diffraction study. Table II shows the final atomic coor-

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Table II. Final Atomic Parameters for $[Cu\{B_2H_4 \cdot 2P(CH_3)_3\}_2]I^a$

atom	x	y	z	$B_{eqv}/Å^{2\,b}$
I	2500	3743.8 (5)	0	5.1
Cu	2500	8730.5 (9)	0	4.8
P(1)	4160 (2)	7054 (1)	489 (2)	4.1
P(2)	1969 (2)	10423 (1)	1596 (2)	3.9
B(1)	2835 (9)	7507 (6)	624 (7)	4.1
B(2)	1865 (7)	9950 (6)	259 (7)	3.9
C(1)	4944 (8)	6972 (6)	1688 (7)	6.4
C(2)	4953 (8)	7641 (6)	-386 (8)	6.0
C(3)	4156 (8)	5997 (6)	2 (9)	6.1
C(4)	2796 (8)	9844 (5)	2495 (7)	5.1
C(5)	2472 (8)	11481 (5)	1647 (8)	5.7
C(6)	749 (8)	10494 (7)	2237 (9)	6.5

atom	x	y	z	$B_{iso}/Å^2$
H(B1a)	242 (5)	716 (4)	121 (5)	2.9 (14)
H(B1b)	296 (5)	797 (4)	110 (5)	2.8 (14)
H(B2a)	126 (5)	1023 (3)	-17 (4)	2.2 (13)
H(B2b)	140 (5)	941 (4)	43 (6)	4.3 (17)

^{a} Coordinates for non-hydrogen atoms are multiplied by 10^4 and those for hydrogen atoms by 10^3. ^{b} The equivalent isotropic temperature factors for non-hydrogen atoms were computed by using the following expression: $B_{eqv} = {}^4/_3(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{12}ab \cos \gamma + B_{13}ac \cos \beta + B_{23}bc \cos \alpha)$. The B_{ij}'s are defined by: $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23})]$.

Table III. Interatomic Distances (Å) for $[Cu\{B_2H_4 \cdot 2P(CH_3)_3\}_2]I$

Cu–H(B1b)	1.96 (7)	Cu–H(B2b)	1.91 (7)
Cu···B(1)	2.184 (10)	Cu···B(2)	2.179 (9)
B(1)–H(B1a)	1.11 (7)	B(2)–H(B2a)	1.05 (6)
B(1)–H(B1b)	0.98 (7)	B(2)–H(B2b)	1.09 (7)
B(1)–B(1')	1.80 (2)	B(2)–B(2')	1.81 (2)
B(1)–P(1)	1.889 (12)	B(2)–P(2)	1.897 (13)
P(1)–C(1)	1.825 (13)	P(2)–C(4)	1.814 (10)
P(1)–C(2)	1.832 (12)	P(2)–C(5)	1.840 (9)
P(1)–C(3)	1.832 (10)	P(2)–C(6)	1.829 (12)

Table IV. Bond Angles (deg) for $[Cu\{B_2H_4 \cdot 2P(CH_3)_3\}_2]I$

H(B1b)–Cu–H(B1b')	102 (3)	H(B2b)–Cu–H(B2b')	109 (3)
H(B1b)–Cu–H(B2b)	111 (3)	H(B1b)–Cu–H(B2b')	112 (3)
B(1)···Cu···B(1')	48.8 (4)	B(2)···Cu···B(2')	49.1 (4)
Cu–H(B1b)–B(1)	89 (5)	Cu–H(B2b)–B(2)	89 (5)
B(1')–B(1)–H(B1a)	113 (4)	B(2')–B(2)–H(B2a)	118 (4)
B(1')–B(1)–H(B1b)	129 (4)	B(2')–B(2)–H(B2b)	127 (4)
B(1')–B(1)–P(1)	108.8 (7)	B(2')–B(2)–P(2)	108.2 (6)
P(1)–B(1)–H(B1a)	110 (4)	P(2)–B(2)–H(B2a)	110 (4)
P(1)–B(1)–H(B1b)	104 (4)	P(2)–B(2)–H(B2b)	99 (4)
H(B1a)–B(1)–H(B1b)	92 (6)	H(B2a)–B(2)–H(B2b)	93 (5)
B(1)–P(1)–C(1)	115.2 (5)	B(2)–P(2)–C(4)	113.1 (5)
B(1)–P(1)–C(2)	113.3 (5)	B(2)–P(2)–C(5)	115.0 (5)
B(1)–P(1)–C(3)	114.1 (5)	B(2)–P(2)–C(6)	114.5 (5)
C(1)–P(1)–C(2)	105.0 (5)	C(4)–P(2)–C(5)	105.3 (4)
C(1)–P(1)–C(3)	102.6 (5)	C(4)–P(2)–C(6)	104.0 (5)
C(2)–P(1)–C(3)	105.5 (5)	C(5)–P(2)–C(6)	103.9 (5)

dinates and equivalent isotropic temperature factors. Interatomic distances and bond angles are given in Tables III and IV. Figure 1 shows the ORTEP diagram of the cation, and Figure 2 shows the packing diagram.

The crystal is composed of $[Cu\{B_2H_4 \cdot 2P(CH_3)_3\}_2]^+$ cations and iodide ions. The cation as well as the iodide ion resides on the crystallographic 2-fold axis, which passes through the midpoints of the B–B bonds. The copper atom is ligated by two $B_2H_4 \cdot 2P(CH_3)_3$ molecules. Each $B_2H_4 \cdot 2P(CH_3)_3$ is coordinated to the copper atom through two vicinal hydrogen atoms, respectively. The coordination geometry around the copper atom is almost tetrahedral as shown by H–Cu–H angles in Table IV. Bridging hydrogen atoms deviate from the planes defined by Cu–B(1)–B(1') and Cu–B(2)–B(2') only by 0.16 and 0.02 Å (for H(B1b) and H(B2b)), respectively. The conformation of the ligand is eclipsed and quite similar to that of $ZnCl_2\{B_2H_4 \cdot 2P(CH_3)_3\}$.[9] The dihedral angle between the Cu–B(1)–B(1') plane and the Cu–B(2)–B(2')
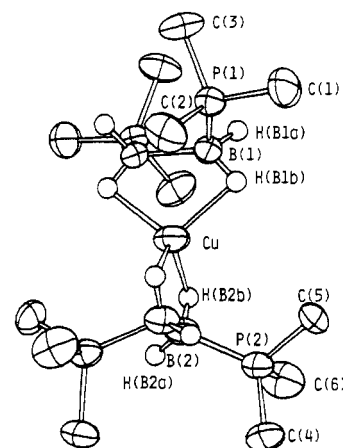
Figure 1. ORTEP diagram of $[Cu\{B_2H_4 \cdot 2P(CH_3)_3\}_2]^+$ with atomic numbering scheme.
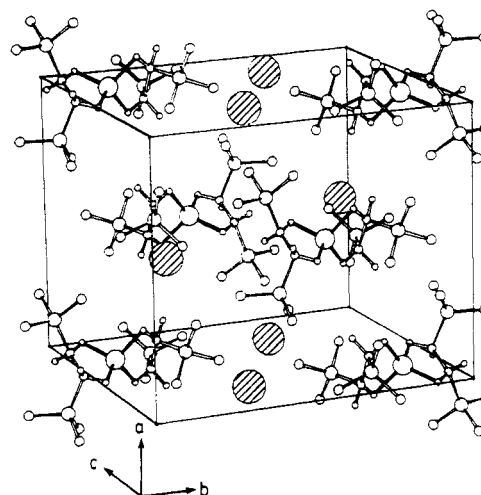
Figure 2. Packing diagram for $[Cu\{B_2H_4 \cdot 2P(CH_3)_3\}_2]I$. Iodine atoms are hatched.

plane is almost orthogonal: 94.5°.

Cu–H bond lengths (1.91 (7), 1.96 (7) Å) are comparable with those for $[(PPh_3)_2Cu(B_3H_8)]$ (1.83 (5), 1.85 (5) Å)[19] and $[\{(PPh_3)_2Cu\}_2(B_{10}H_{10})]$ (1.84 (6)–2.09 (7) Å),[20] where each borane chelates to Cu(I) through two vicinal hydrogen atoms. But Cu···B distances (2.179 (9), 2.184 (10) Å) are shorter than those for $[(PPh_3)_2Cu(B_3H_8)]$ (2.30 (1) Å)[19] and $[\{(PPh_3)_2Cu\}_2(B_{10}H_{10})]$ (2.28 (1)–2.32 (1) Å)[20] by 0.10–0.14 Å, and also shorter than those for $ZnCl_2\{B_2H_4 \cdot 2P(CH_3)_3\}$ by 0.09 Å[9] although ionic radii of Cu(I) and Zn(II) are the same.[21] The Cu···B distances for the present complex are even shorter than those for $[(PPh_3)_2Cu(B_5H_8)]$ (2.209 (13), 2.236 (13) Å) where direct Cu–B bonds are observed.[22] This might be due to some direct interaction between Cu···B as is proposed in the case of $Cu(PMePh_2)_3(BH_4)$.[23] B–B distances (1.80 (2), 1.81 (2) Å) are comparable with those in $ZnCl_2\{B_2H_4 \cdot 2P(CH_3)_3\}$ (1.814 (6) Å),[9] but longer than free $B_2H_4 \cdot 2P(CH_3)_3$ (1.740 (7) Å)[24] as well as other bis(Lewis base)diborane(4)'s, $B_2H_4 \cdot 2PPh_3$ (1.76 (2) Å),[25] and $B_2H_4 \cdot 2CO$ (1.78 (1) Å).[26,27]

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The complex prepared in this work is a new member of the series of cationic metal borane complexes and is the first monomeric copper(I) complex in which the central metal is bound tetrahedrally to four hydrogen atoms. In connection with this, copper atom in polymeric $Cu_2(B_{10}H_{10})$ is bound tetrahedrally to adjacent $B_{10}H_{10}^{2-}$ ions through four vicinal hydrogen atoms.[28]

Although the complex is a 1:1 ionic salt, the packing in the crystal is, interestingly, rather complex as shown in Figure 2. A cation is surrounded by four cations (Cu···Cu = 6.622 (3)–7.701 (2) Å) tetrahedrally and six anions (Cu···I = 7.645 (1)–8.180 (2) Å), four of which surround the cation tetrahedrally and the rest of which lie in capping positions of the hexahedron made of four anions and four cations. An anion is surrounded by six cations and four anions (I···I = 7.644 (1)–7.678 (1) Å), inversely.

C. NMR Spectra. ^1H, $^{11}B\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of the iodide and the chloride in CD_2Cl_2 at room temperature are almost the same, suggesting that these complexes take the same structure in solution.

The ^1H NMR spectrum (200 MHz) of $[Cu\{B_2H_4\cdot 2P(CH_3)_3\}_2]^+$ consists of two signals in a 36:8 ratio. The intense low-field one at +1.29 ppm was assigned to the methyl protons of trimethylphosphine groups. This appears as a triplet with a peak separation

of 5.3 Hz due to the virtual coupling to ^{31}P.[29] The high-field signal is a broad doublet ranging from +0.7 to −1.0 ppm with the center at −0.1 ppm and is assigned to the eight hydrogens connected to boron atoms. The signal shows temperature dependence with a 90-MHz instrument. It is featureless at room temperature but appears as a single peak at −90 °C. This phenomenon is due to quadrupole-induced ^{10}B and ^{11}B spin relaxation ("thermal" decoupling), which is general among boranes.[30] The area of this peak shows that $B_2H_4\cdot 2P(CH_3)_3$ ligands are fluxional and the bridging and terminal hydrogens are equivalent on an NMR time scale even at −90 °C.[31] The chemical shift of ^{11}B for the present complex is smaller than that of free $B_2H_4\cdot 2P(CH_3)_3$ by about 7.1 ppm,[29] but is comparable with that of $ZnCl_2\{B_2H_4\cdot 2P(CH_3)_3\}$.[9]

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Reaction of Dimethyl Sulfide–Triborane(7) with Dimethyl Sulfide. A Formation Reaction of Pentaborane(9)

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The triborane(7) adduct of dimethyl sulfide was isolated as a liquid at room temperature. The adduct reacted with additional dimethyl sulfide to give pentaborane(9) and dimethyl sulfide–borane(3). This conversion of triborane(7) to pentaborane(9) was interpreted in terms of borane framework expansion involving diborane(4) adducts that had been established in this laboratory.

Introduction

Some years ago, studies of the reaction chemistry of boron hydride compounds with trimethylphosphine were initiated in our laboratory. The purpose of the studies was to find stable products and definable reactions of these compounds by taking advantage of the strongly basic character of $P(CH_3)_3$. Because of the strong "$(CH_3)_3P\rightarrow borane$" dative bond, secondary reactions, which are often caused by the dissociative instability of borane adducts, were suppressed, and thus definable reactions could be identified in reaction systems that would be intractable otherwise. A summary of the results has been described elsewhere.[1]

Some successful results having been obtained in the above studies, efforts were then directed to borane reactions involving other Lewis bases, including weaker bases. New observations, particularly those involving weaker bases such as $N(CH_3)_3$,[2] were then interpreted in the light of knowledge acquired from the earlier studies. Recently, we extended the same line of study to the reactions between lower borane compounds and alkyl sulfides. In this report, the behavior of $B_3H_7\cdot S(CH_3)_2$ toward $S(CH_3)_2$ is described and interpreted.

Results

A. Isolation of $B_3H_7\cdot S(CH_3)_2$. The reaction of tetraborane(10) with dimethyl sulfide gives dimethyl sulfide adducts of triborane(7) and borane(3).[3] The triborane(7) adduct $B_3H_7\cdot S(CH_3)_2$, was separated from its coproduct $BH_3\cdot S(CH_3)_2$ by fractional condensation as a stable liquid that could be handled at room temperature without decomposition. A dichloromethane solution of the compound remained unchanged for several hours at room temperature. Similarly, the diethyl sulfide adduct of triborane(7) was isolated. Dimethyl sulfide–triborane(7) could also be prepared by treating $B_3H_7\cdot THF$ with $S(CH_3)_2$. This latter method has an advantage over the other of not having $BH_3\cdot S(CH_3)_2$ in the products; the time-consuming fractionation can be avoided if the compound has to be separated in a pure form. The ^{11}B NMR

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