

in a stream of nitrogen. It was then dissolved in the minimum volume of dichloromethane (~3 ml) and treated with methanol (15 ml). On cooling overnight at 0° yellow crystals separated; these were washed with methanol and dried *in vacuo* (0.19 g, 95% based on VII). VIII could also be prepared by heating Ru(CO)₂(SP)₂ (V) in *n*-nonane for 5 hr or by heating the σ -bonded complex VI in *n*-nonane for 20–30 hr. Ir spectroscopy showed that VII was an intermediate in both cases (see text).

Preparation of Dihalocarbonylbis-1,4-[*o*-(diphenylphosphino)phenyl]-*cis*-2-buteneruthenium(II) Complexes, RuX₂(CO){*o*-(C₆H₅)₂PC₆H₄CH₂CH=CHCH₂C₆H₄P(C₆H₅)₂-*o*} [X = Cl (IX(i) and IX(ii)) or X = Br (X(i) and X(ii))] by Hydrogen Halide Addition to VIII. (i) A solution of VIII (0.1 g) in dichloromethane (5 ml) was degassed by passing nitrogen through it for several minutes and then treated with dry hydrogen chloride gas. The color changed from deep yellow to almost colorless over a period of 2 min, after which time the solution was again flushed with nitrogen. Solvent was removed under reduced pressure, and the residue was recrystallized from dichloromethane–methanol (1:4) to give colorless crystals IX(ii) (ν (CO) 1990 cm⁻¹ (Nujol)) which were washed with methanol

and dried *in vacuo* (yield, ~90%). On standing for several days the mother liquor deposited a mixture of colorless and yellow crystals, identified by their ν (CO) bands at 1990 and 2015 cm⁻¹ as IX(ii) and IX(i), respectively. These could not be separated owing to the ease with which IX(i) isomerized to IX(ii).

(ii) The procedure described above was repeated using hydrogen bromide in place of hydrogen chloride. The orange-brown complex initially isolated was X(i) (ν (CO) 2010 cm⁻¹ (Nujol)) (~90% yield). This isomerized at room temperature over a period of 3 weeks in dichloromethane to the more stable X(ii) (ν (CO) 1989 cm⁻¹), as shown by nmr spectroscopy. The same process occurred more rapidly on three successive recrystallizations of X(i) from dichloromethane–methanol (1:4).

Acknowledgments. We thank Dr. R. Bramley for the CAT program for ³¹P nmr spectra, and Johnson Matthey Co. (UK) for a loan of ruthenium trichloride. We also thank Mr. C. Arandjelovic for running some of the proton nmr spectra.

Transition Metal Hydroborate Complexes. VI.¹ The Solid-State Structure of μ -Bis(cyanotrihydroborato)-tetrakis(triphenylphosphine)dicopper(I)

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Abstract: The structure of μ -bis(cyanotrihydroborato)-tetrakis(triphenylphosphine)dicopper(I) has been determined in a single-crystal X-ray diffraction study. The compound crystallizes in the space group *P*2₁/*n* of the monoclinic system with four dimeric molecules per unit cell. The lattice parameters are *a* = 18.100 (1) Å, *b* = 27.407 (5) Å, *c* = 13.615 (1) Å, and β = 104.43 (1)°, with ρ_{obsd} = 1.28 (3) and ρ_{calcd} = 1.27 g cm⁻³. From 2921 independent observed reflections collected by diffractometer the structure was solved and refined with the phenyl rings constrained as rigid bodies to a final value for the discrepancy index *R*₁ of 0.060. No crystallographic symmetry is imposed on the molecule. The H₃BCN⁻ ligands bridge the two copper atoms forming a ten-membered nonplanar ring, with a Cu···Cu distance of 5.637 (2) Å. Each quasitetrahedral copper atom is bonded to two triphenylphosphine ligands and to a hydrogen and a nitrogen atom from the different cyanotrihydroborate groups. The Cu–N distances are 1.96 (1) and 2.01 (1) Å. The average Cu–H distance of 1.86 ± 0.1 Å is similar to those found in related bis(triphenylphosphine)copper(I) hydroborate complexes. The structure is a rare example of a hydroborate ligand bonded by only one of its hydrogen atoms to a metal atom. The Cu–P distances are 2.262 (3), 2.242 (3), 2.272 (3), and 2.280 (3) Å, and the P–Cu–P angles are 124.8 (1) and 122.1 (1)°. The geometry of the coordinated H₃BCN ligand, determined for the first time, compares favorably to that of H₃CCN in related complexes. The local site symmetry at the boron atoms of the two cyanotrihydroborate ligands is distinctly different and can account for the appearance of two CN stretching bands in the infrared spectrum.

The cyanotrihydroborate anion, H₃BCN⁻, was first isolated as the lithium salt in 1951,² and its utility as a selective organic reducing agent was later reported.^{3,4} Although the M–CNBH₃ linkage had been obtained from a solution of dicyanobis(*o*-phenanthroline)iron(II) that was allowed to react with diborane,⁵ complexes containing M–NCBH₃ bonds were unknown until recently.^{6–8}

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As discussed in a previous paper,⁹ interest in the title compound was initially generated from its infrared spectrum which strongly suggested the presence of both Cu–NCBH₃ and Cu–HBH₂CN type linkages. In particular, two possible dimeric structures were considered, and the present X-ray diffraction study was undertaken to determine which (if either) was the correct one. Additional incentive for this investigation was derived from the need to (1) test the remote possibility that the ligand had isomerized to form M–CNBH₃ bonds, (2) elucidate the nature of the copper–hydroborate attachment, and (3) determine the detailed molecular geometry of the cyanotrihydroborate anion, especially in its role as a bridging ligand. Also it was felt that structural information might help to assess the effect of the cyanide group on the coordinat-

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Table I. Final Positional, Group, and Thermal Parameters of the Atoms for $[(C_6H_5)_3P]_2Cu(NCBH_2)_2^{a,b}$

Atom	x	y	z	B, Å ²
Cu1	0.25204 (9)	0.24630 (6)	0.1183 (1)	
P1	0.2362 (1)	0.2416 (1)	0.2778 (2)	
P2	0.2755 (1)	0.3152 (1)	0.0428 (2)	
Cu2	0.25948 (8)	0.06927 (5)	-0.0897 (1)	
P3	0.2354 (1)	0.0780 (1)	-0.2607 (2)	
P4	0.2754 (1)	-0.0053 (1)	-0.0133 (2)	
N1	0.1849 (5)	0.1975 (4)	0.0355 (7)	
C1	0.1612 (7)	0.1600 (5)	0.004 (1)	
B1	0.133 (1)	0.1088 (6)	-0.032 (1)	
N2	0.3299 (5)	0.1214 (3)	-0.0156 (8)	
C2	0.3561 (6)	0.1481 (5)	0.047 (1)	
B2	0.3908 (9)	0.1827 (6)	0.140 (1)	
H1	0.072 (6)	0.101 (4)	-0.050 (7)	5.5
H2	0.163 (5)	0.080 (4)	0.044 (8)	6.5
H3	0.168 (6)	0.095 (3)	-0.080 (7)	6.5
H4	0.347 (5)	0.214 (3)	0.135 (6)	4.5
H5	0.392 (5)	0.157 (4)	0.205 (7)	5.5
H6	0.440 (6)	0.197 (4)	0.134 (7)	5.5
CA1 ^c	0.1910 (5)	0.1841 (2)	0.2980 (6)	4.0 (2)
CB1	0.1169 (4)	0.1819 (2)	0.3096 (6)	6.1 (3)
CC1	0.0830 (3)	0.1368 (3)	0.3166 (6)	7.7 (3)
CD1	0.1233 (5)	0.0940 (2)	0.3120 (7)	6.6 (3)
CE1	0.1975 (5)	0.0962 (2)	0.3004 (7)	8.2 (3)
CF1	0.2313 (3)	0.1412 (3)	0.2934 (6)	6.9 (3)
CA2	0.3240 (3)	0.2443 (4)	0.3796 (5)	3.8 (2)
CB2	0.3844 (4)	0.2695 (3)	0.3571 (4)	4.8 (2)
CC2	0.4530 (4)	0.2745 (3)	0.4304 (6)	5.6 (3)
CD2	0.4611 (3)	0.2542 (5)	0.5262 (5)	6.1 (3)
CE2	0.4007 (4)	0.2289 (3)	0.5487 (4)	6.4 (3)
CF2	0.3321 (4)	0.2240 (3)	0.4754 (6)	5.1 (2)
CA3	0.1717 (8)	0.2864 (7)	0.3101 (6)	3.6 (2)
CB3	0.1173 (5)	0.3062 (3)	0.2292 (4)	5.0 (2)
CC3	0.0598 (6)	0.3360 (5)	0.2473 (5)	5.9 (3)
CD3	0.0567 (8)	0.3460 (7)	0.3464 (7)	6.3 (3)
CE3	0.1111 (5)	0.3262 (3)	0.4273 (4)	5.8 (3)
CF3	0.1686 (6)	0.2965 (5)	0.4092 (5)	5.1 (2)
CA4	0.3385 (4)	0.3568 (3)	0.1296 (5)	3.5 (2)
CB4	0.4152 (4)	0.3601 (2)	0.1296 (5)	5.3 (2)
CC4	0.4639 (3)	0.3900 (3)	0.2000 (6)	7.2 (3)
CD4	0.4358 (4)	0.4164 (3)	0.2700 (6)	6.1 (3)
CE4	0.3591 (5)	0.4130 (2)	0.2700 (5)	5.8 (3)
CF4	0.3104 (3)	0.3832 (3)	0.1997 (5)	4.2 (2)
CA5	0.1902 (3)	0.3511 (2)	-0.0099 (5)	3.9 (2)
CB5	0.1227 (4)	0.3254 (2)	-0.0465 (6)	5.6 (3)
CC5	0.0553 (3)	0.3504 (3)	-0.0892 (6)	6.8 (3)
CD5	0.0555 (3)	0.4010 (3)	-0.0952 (6)	6.6 (3)
CE5	0.1231 (5)	0.4268 (2)	-0.0585 (6)	5.9 (3)
CF5	0.1904 (3)	0.4018 (2)	-0.0159 (5)	4.8 (2)
CA6	0.3192 (4)	0.3099 (3)	-0.0631 (5)	4.0 (2)
CB6	0.3552 (4)	0.2662 (2)	-0.0754 (6)	7.3 (3)
CC6	0.3912 (5)	0.2612 (2)	-0.1541 (7)	9.6 (4)
CD6	0.3912 (5)	0.2999 (3)	-0.2203 (6)	7.2 (3)
CE6	0.3553 (4)	0.3435 (3)	-0.2080 (5)	7.0 (3)
CF6	0.3193 (4)	0.3485 (2)	-0.1293 (6)	5.2 (3)
CA7	0.1888 (8)	0.1354 (3)	-0.3072 (5)	4.1 (2)
CB7	0.1333 (6)	0.1404 (2)	-0.3979 (5)	6.0 (3)
CC7	0.0983 (4)	0.1854 (4)	-0.4247 (5)	7.5 (3)
CD7	0.1188 (8)	0.2253 (3)	-0.3607 (7)	8.5 (4)
CE7	0.1743 (7)	0.2203 (3)	-0.2699 (7)	11.5 (5)
CF7	0.2093 (5)	0.1754 (4)	-0.2432 (5)	8.6 (4)
CA8	0.3194 (3)	0.0763 (3)	-0.3127 (5)	3.5 (2)
CB8	0.3802 (4)	0.0472 (2)	-0.2630 (4)	4.5 (2)
CC8	0.4435 (4)	0.0417 (3)	-0.3028 (5)	4.3 (2)
CD8	0.4460 (3)	0.0654 (4)	-0.3923 (5)	4.8 (2)
CE8	0.3852 (4)	0.0945 (2)	-0.4420 (4)	4.9 (2)
CF8	0.3219 (4)	0.1000 (3)	-0.4022 (5)	5.0 (2)
CA9	0.1736 (9)	0.0318 (5)	-0.3351 (7)	3.9 (2)
CB9	0.1184 (6)	0.0125 (2)	-0.2910 (5)	5.3 (2)
CC9	0.0679 (6)	-0.0227 (5)	-0.3420 (7)	7.2 (3)
CD9	0.0727 (9)	-0.0388 (6)	-0.4372 (8)	6.4 (3)
CE9	0.1279 (6)	-0.0196 (2)	-0.4814 (5)	6.6 (3)
CF9	0.1783 (5)	0.0157 (5)	-0.4303 (6)	5.2 (2)
CA10	0.3438 (4)	-0.0420 (3)	-0.0595 (5)	3.0 (2)
CB10	0.4204 (4)	-0.0433 (2)	-0.0070 (4)	4.2 (2)
CC10	0.4725 (2)	-0.0696 (3)	-0.0459 (5)	5.3 (2)
CD10	0.4481 (4)	-0.0946 (3)	-0.1371 (5)	5.0 (2)

Table I (Continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²		
CE10	0.3716 (4)	-0.0933 (2)	-0.1896 (4)	5.0 (2)		
CF10	0.3194 (3)	-0.0670 (3)	-0.1508 (5)	4.3 (2)		
CA11	0.1925 (3)	-0.0458 (2)	-0.0285 (5)	3.4 (2)		
CB11	0.1207 (4)	-0.0246 (1)	-0.0423 (5)	4.2 (2)		
CC11	0.0565 (3)	-0.0539 (2)	-0.0530 (5)	4.6 (2)		
CD11	0.0639 (3)	-0.1045 (2)	-0.0498 (5)	4.7 (2)		
CE11	0.1356 (4)	-0.1257 (1)	-0.0360 (5)	4.5 (2)		
CF11	0.1999 (3)	-0.0964 (2)	-0.0253 (5)	3.9 (2)		
CA12	0.3144 (3)	-0.0047 (2)	0.1241 (3)	3.0 (2)		
CB12	0.3327 (4)	0.0402 (2)	0.1712 (5)	4.6 (2)		
CC12	0.3613 (4)	0.0427 (2)	0.2759 (5)	4.7 (2)		
CD12	0.3715 (3)	0.0001 (3)	0.3336 (3)	4.6 (2)		
CE12	0.3532 (4)	-0.0448 (2)	0.2865 (5)	4.5 (2)		
CF12	0.3246 (4)	-0.0473 (2)	0.1818 (5)	4.4 (2)		
Group	<i>X</i> ₀ ^d	<i>Y</i> ₀	<i>Z</i> ₀	<i>φ</i>	<i>θ</i>	<i>ρ</i>
1	0.1572 (3)	0.1390 (2)	0.3050 (3)	-2.077 (5)	2.831 (5)	-2.953 (5)
2	0.3925 (3)	0.2492 (1)	0.4528 (4)	2.508 (7)	-2.268 (4)	-0.878 (7)
3	0.1142 (3)	0.3162 (1)	0.3282 (4)	-1.85 (1)	-1.970 (4)	-1.20 (1)
4	0.3871 (3)	0.3866 (1)	0.1998 (3)	1.239 (5)	-2.508 (4)	-2.425 (5)
5	0.1229 (3)	0.3761 (2)	-0.0525 (3)	-0.515 (4)	3.187 (4)	0.200 (4)
6	0.3552 (2)	0.3049 (2)	-0.1417 (4)	0.272 (5)	2.902 (5)	1.993 (5)
7	0.1538 (3)	0.1804 (2)	-0.3339 (4)	-0.947 (8)	-2.320 (5)	0.219 (8)
8	0.3827 (2)	0.0709 (1)	-0.3525 (3)	0.615 (6)	2.397 (4)	2.200 (6)
9	0.1231 (2)	-0.0035 (1)	-0.3862 (4)	-1.48 (1)	2.023 (5)	2.26 (1)
10	0.3960 (2)	-0.0683 (1)	-0.0983 (3)	1.923 (5)	2.468 (4)	0.777 (5)
11	0.1281 (2)	-0.0751 (1)	-0.0391 (3)	-2.527 (4)	3.089 (4)	-3.037 (4)
12	0.3430 (2)	-0.0022 (1)	0.2288 (3)	3.082 (4)	-3.066 (4)	-1.206 (4)
Atom	<i>β</i> ₁₁ ^e	<i>β</i> ₂₂	<i>β</i> ₃₃	<i>β</i> ₁₂	<i>β</i> ₁₃	<i>β</i> ₂₃
Cu1	4.08 (7)	1.16 (3)	5.7 (1)	-0.21 (4)	1.28 (7)	-0.02 (5)
P1	3.6 (1)	1.01 (5)	5.5 (2)	-0.20 (7)	1.0 (1)	0.11 (9)
P2	3.2 (1)	1.03 (5)	4.7 (2)	0.10 (7)	1.3 (1)	0.21 (9)
Cu2	3.60 (7)	1.09 (2)	5.7 (1)	0.04 (3)	1.52 (7)	0.09 (5)
P3	3.4 (1)	1.10 (5)	5.4 (2)	0.09 (7)	1.5 (1)	0.14 (9)
P4	2.8 (1)	1.04 (5)	4.6 (2)	0.00 (6)	1.3 (1)	0.00 (9)
N2	3.1 (4)	1.1 (2)	6.8 (9)	-0.2 (2)	0.4 (5)	-0.1 (3)
C2	2.1 (5)	1.2 (2)	7 (1)	0.1 (3)	0.9 (6)	-0.0 (4)
B2	2.9 (7)	1.3 (3)	11 (1)	0.4 (4)	0.8 (9)	-0.2 (6)
N1	4.2 (5)	1.6 (2)	7.5 (9)	0.1 (2)	1.9 (5)	0.0 (3)
C1	3.3 (5)	1.2 (3)	8 (1)	0.0 (3)	1.2 (6)	0.0 (4)
B2	4.1 (8)	1.1 (3)	16 (2)	-0.5 (4)	4 (1)	-1.3 (6)

^a Atoms are labeled as indicated in Figures 1 and 2. ^b Standard deviations, in parentheses, occur in the last significant figure for each parameter. ^c In this table, CA1, for example, refers to carbon atom A of phenyl ring 1. ^d *X*₀, *Y*₀, and *Z*₀ are the fractional coordinates of the center of gravity of the rigid-body constrained phenyl rings, and *φ*, *θ*, and *ρ* are the orientational angles given in radians. These parameters are defined in ref 18. ^e *β*'s are defined in the text; values reported here are $\times 10^3$.

ing ability of the RBH₃⁻ anion since the structure of a related BH₄⁻ derivative, tetrahydroboratobis(triphenylphosphine)copper(I), is known.¹⁰ Finally of interest was to learn whether the values of the Cu-P bond length and P-Cu-P angle correlated with expectations based upon a recent analysis of the factors influencing the stereochemistry of four-coordinate copper(I) phosphine complexes,¹¹ a subject of recent investigation in our laboratory.¹²

Experimental Procedure

Collection and Reduction of the Data. The compound was prepared as described previously⁹ (we thank Dr. P. S. Welcker for supplying crystals suitable for X-ray diffraction work), and a suitable multifaceted crystal was mounted with nail polish along the *b** axis on the end of a glass fiber. After an approximate alignment on the optical goniometer, the crystal was transferred to the precession camera where unit cell and space group information were obtained using Ni-filtered Cu K α radiation (λ 1.5418 Å). The observed extinctions, *h*0*l*, *h* + *l* \neq 2*n*, and 0*k*0, *k* \neq 2*n*, uniquely suggested the space group to be *P*2₁/*n*, an unconventional setting of

*P*2₁/*c*¹³ having the general equivalent positions (*x*, *y*, *z*), (-*x*, -*y*, -*z*), ($1/2 + x$, $1/2 - y$, $1/2 + z$), and ($1/2 - x$, $1/2 + y$, $1/2 - z$). This choice was later proved correct by the successful refinement of the structure.

A crystal of approximate dimensions 0.2 \times 0.1 \times 0.1 mm was mounted along (601) in a glass capillary (for convenience only) and transferred to a Picker FACS-I-DOS diffractometer for data collection. Several open counter ω scans showed the mosaic spread to be \sim 0.07-0.10°, which is acceptably low. Lattice parameters *a* = 18.100 \pm 0.001 Å, *b* = 27.407 \pm 0.005 Å, *c* = 13.615 \pm 0.001 Å, and β = 104.426 \pm 0.007° were determined at 23° by a least-squares refinement of the setting angles for 12 reflections which were carefully centered on the Cu K α line (λ 1.54051 Å). The calculated density, assuming eight [(C₆H₅)₃P]₂Cu(NCBH₃) formulas per unit cell, is 1.27 g/cm³. The average density measured by flotation in aqueous KI solutions is 1.28 \pm 0.03 g/cm³, in agreement with the observed value.

Intensity data were obtained with Cu K α radiation using a symmetric scan range of 1.25° in 2θ plus the K α ₁-K α ₂ difference. The takeoff angle at the X-ray tube was 2.0°, and an aperture of 4.0 \times 4.0 mm was placed in front of the scintillation counter at a distance of about 31 cm from the crystal. Stationary crystal, stationary counter background counts of 10 sec were taken at the beginning and end of the scan range. Aluminum foil attenuators of various thickness were automatically inserted in front of the counter aperture whenever the counting rate exceeded 10,000 cps in order to eliminate saturation of the counter circuit. Three standards were

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(13) "International Tables for X-Ray Crystallography," Vol. I, 3rd ed, Kynock Press, Birmingham, England, 1969, p 99.

collected every 97 reflections and showed no crystal or electronic instability. A total of 4372 data were collected out to $2\theta < 80^\circ$. After 273 equivalent $hk0$ reflections were averaged with an agreement factor of 0.041, 2921 data were judged to be observed by the criterion $F^2 > 3\sigma(F^2)$. The value for $\sigma(F^2)$ was obtained from the expression¹⁴

$$\sigma(F^2) = (Lp)^{-1}[E + (t_c/2t_b)^2(B_1 + B_2) + (\epsilon I)^2]^{1/2}$$

where E is the total integrated counts, $(t_c/2t_b)$ is the ratio of the time spent counting the integrated peak intensity to the total background counting time, B_1 and B_2 are the individual background counts, ϵ is the "ignorance factor" set equal to 0.04 in this case, $I = E - (t_c/2t_b)(B_1 + B_2)$, and $(Lp)^{-1}$ is the Lorentz-polarization factor. The intensities, I , were corrected for Lp effects but not absorption. The transmission coefficients were estimated to range from 0.775 to 0.816,¹⁵ a relatively small variation due to the low linear absorption coefficient (20.6 cm^{-1}) and small, fairly uniform crystal dimensions.

The scattering factors used were for the neutral atoms.¹⁶ Corrections for anomalous dispersion effects for the Cu and P atoms were taken from the compilations of Cromer¹⁷ and applied to the calculated structure factor amplitudes. The data were placed on an approximately absolute scale through a modification of Wilson's method¹⁸ which produced an estimated mean B of 3.98 \AA^2 and scale factor of 0.333.

Determination and Refinement of the Structure. Using the corrected data, an origin removed, sharpened Patterson map was computed. It was immediately evident that the compound was a dimer as the structure formed by the Cu and P atoms could be clearly seen on the $X = 0.0$ section of the vector map. The Cu-Cu distance was approximately 5.8 \AA , and the $(P_2Cu)_2$ unit was approximately parallel to the YZ plane.

The initial difficulty due to inadequate phasing in the X direction was eliminated upon the location of several carbon atoms from a difference Fourier map based on phases assigned after a least-squares refinement of the two copper and four phosphorus atom positional and thermal parameters. Successive cycles of least-squares refinements of the scale factor, positional parameters, and isotropic temperature factor and subsequent difference Fourier syntheses revealed all but three of the carbon atoms in the 12 crystallographically independent phenyl rings. The resulting values of 0.139 and 0.188 were calculated for the discrepancy factors $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ and $R_2 = (\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2)^{1/2}$, respectively, where $w = 4F_o^2 / \sigma^2(F_o^2)$. The function $\sum w(|F_o| - |F_c|)^2$ was minimized.

At this stage the 12 crystallographically independent phenyl rings were treated as rigid body contributions to the structure, with C-C distances of 1.39 \AA . There are 150 atoms (including H) in the asymmetric unit, and, if conventional full-matrix least-squares techniques were employed, it would have required the refinement of 631 parameters, assigning anisotropic temperature factors to the copper and phosphorus atoms and isotropic B 's to all other atoms. Such a refinement would overextend the approximately 2900 observed data points. The program BUGLS¹⁵ allows the simultaneous refinement of individual atoms and of groups of atoms and has the capability of including the fixed hydrogen atom contributions to A and B parts of the structure factor.¹⁸ The total number of parameters in the final refinement (see below) was thereby reduced to 277 including the scale factor.

In order to verify that the copper atoms were indeed bonded to nitrogen atoms, and that no structural rearrangement had

occurred which would result in the existence of M-CN BH_3 linkages (as proposed for $Fe(phen)_2(CNBH_3)_2$),⁵ the scattering factors for carbon and nitrogen atoms were interchanged, and a least-squares refinement was run, with variation of positional and isotropic thermal parameters of the N and C ligand atoms. The temperature factors for the pseudonitrogen atoms decreased in value to 0.8 and 2.1 (from 3.1 and 4.3, respectively) while those for the pseudocarbon atoms increased to 7.2 and 7.4 (from 3.6 and 4.3, respectively). The original model therefore is presumed to be the correct one.

Examination of a difference Fourier map following isotropic rigid body refinement of the phenyl rings and individual Cu, P, and light atoms of the cyanotrihydroborate group showed residual electron density near the $(P_2CuNCB)_2$ atoms. Thus, in subsequent refinements, anisotropic thermal parameters of the form $exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ were assigned to these atoms.

After refinement of the parameters so that the change in the positional coordinates was at most 0.01 that of the standard deviation of these values, a fixed contribution was computed for the phenyl ring H atoms and used in the structure factor calculations (the C-H distances were set equal to 1.08 \AA). A difference Fourier map at this stage clearly showed the six hydrogen atoms of the two BH_3 groups. The positional parameters of these atoms were varied to convergence on subsequent refinement cycles. Their isotropic thermal parameters were assigned values to reflect the thermal motion of the boron atom to which they are attached as well as their structural function as a bridging or terminal atom. In the final refinement stages a modification of the weighting scheme was introduced to improve the constancy of the function $w\Delta^2$ for the various classes of reflections.¹⁹ The empirical function used set $w = (26.0 - 0.402F + 0.00283F^2)^{-1}$. In the last refinement cycles the parameters varied by no more than 0.5% of their estimated standard deviations and the discrepancy indices converged at $R_1 = 0.060$ and $R_2 = 0.072$. The value of the function¹⁹ $[(\sum w\Delta^2)/(m - n)]^{1/2}$ was 1.206, compared to the ideal value of 1.0. A final difference map showed only slight residual electron density of $\sim 0.4 \text{ e/\AA}^3$ near the phenyl rings, and the structure was thus considered to be complete.²⁰

Table I contains the final atomic positional and thermal parameters for all atoms, with their standard deviations derived from the inverse matrix of the last-least-squares refinement cycle. A summary of the geometry of all nonphenyl atoms is included in Table II, and Table III lists short intramolecular interactions of phenyl ring hydrogens with other atoms in the structure. Table IV lists the root-mean-square amplitudes of vibration for the atoms refined anisotropically. The size and orientation of the anisotropic ellipsoids are shown along with the atom labeling scheme in Figures 1 and 2.

Discussion

The molecular configuration of $[(C_6H_5)_3P]_2Cu_2(NCBH_3)_2$ consists of dimeric units (Figures 1 and 2). Each copper atom is four-coordinate. The coordination geometry is that of a distorted tetrahedron defined by two phosphorus atoms and a nitrogen and hydrogen atom from two different ligands. The two bidentate bridging cyanotrihydroborate anions and the two copper atoms form a nonplanar, ten-membered ring. To our knowledge there is only one other reported structure²¹ in which a single hydrogen atom of a hydroborate group is bonded to a metal atom, although singly bridged three-center B-H-Mn bonds occur in solid $HMn_3(CO)_{10}(BH_3)_2$.²²

Unlike the approximately planar configuration found for the copper atoms and bridging ligands in $[(C_6H_5)_2-$

(14) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(15) Calculations were performed on an IBM 360-91 computer using the following programs: ACAC, a revised version of the Prewitt absorption correction program; XDATA, the Brookhaven Wilson Plot and scaling program; FORDAP, the Zalkin Fourier program; BUGLS, the Brown University version of the Busing-Martin-Levy structure factor calculation and least-squares refinement program (ORFLS) modified by Ibers and Doedens for rigid-body refinement; ORFFE, the Busing-Martin-Levy molecular geometry and error function program; and ORTEP, the Johnson thermal ellipsoid plotting program, in addition to various local data processing programs.

(16) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).

(17) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(18) For further discussion and definition of the group parameters, see S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, **18**, 511 (1965). The assignment of individual isotropic thermal parameters to ring carbon atoms was added at a later date.¹⁵

(19) D. W. J. Cruickshank in "Computing Methods of Crystallography," J. S. Rollett, Ed., Pergamon Press, New York, N. Y., 1965, pp 112-115.

(20) See paragraph at end of paper regarding supplementary material.

(21) (a) F. A. Cotton, J. L. Calderon, M. Jeremic, and A. Shaver, *J. Chem. Soc., Chem. Commun.*, 777 (1972); (b) F. A. Cotton, M. Jeremic, and A. Shaver, *Inorg. Chim. Acta*, **6**, 543 (1972).

(22) H. D. Kaesz, W. Fellmann, G. R. Wilkes, and L. F. Dahl, *J. Amer. Chem. Soc.*, **87**, 2753 (1965).

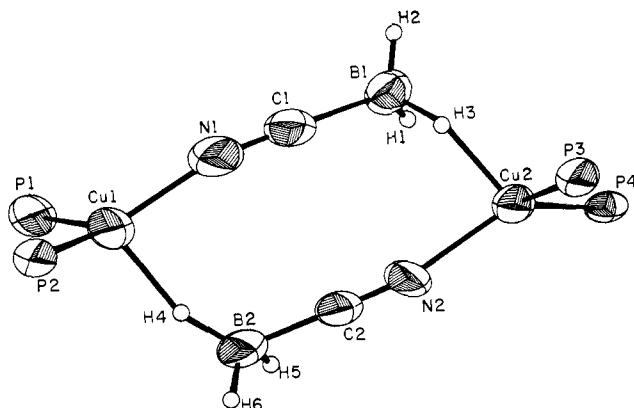


Figure 1. The ten-membered ring and its bonded atoms in $[((\text{C}_6\text{H}_5)_3\text{P})_2\text{Cu}(\text{NCBH}_3)]_2$ showing the atom designations. The 50% probability thermal ellipsoids are depicted.

Table II. Molecular Geometry for $[((\text{C}_6\text{H}_5)_3\text{P})_2\text{Cu}(\text{NCBH}_3)]_2^a$

Intramolecular Bond Distances (Å)			
Cu1-P1	2.262 (3)	Cu2-P3	2.272 (3)
Cu1-P2	2.242 (3)	Cu2-P4	2.280 (3)
Cu1-H4	1.90 (10)	Cu2-H3	1.83 (11)
Cu1-N1	1.96 (1)	Cu2-N2	2.01 (1)
Cu1-B2	3.01 (2)	Cu2-B1	2.81 (1)
N1-C1	1.15 (1)	N2-C2	1.13 (1)
C1-B1	1.53 (2)	C2-B2	1.59 (2)
B1-H1	1.08 (11)	B2-H4	1.17 (10)
B1-H2	1.29 (11)	B2-H5	1.12 (10)
B1-H3	1.09 (10)	B2-H6	1.00 (10)
P1-CA1	1.830 (8)	P3-CA7	1.822 (10)
P1-CA2	1.831 (7)	P3-CA8	1.831 (7)
P1-CA3	1.822 (17)	P3-CA9	1.821 (16)
P2-CA4	1.823 (9)	P4-CA10	1.823 (8)
P2-CA5	1.821 (7)	P4-CA11	1.837 (7)
P2-CA6	1.815 (7)	P4-CA12	1.829 (6)
Cu1...Cu2	5.637 (2)		
Selected Intramolecular Bond Angles (in Degrees)			
P1-Cu1-P2	124.8 (1)	P3-Cu2-P4	122.1 (1)
H4-Cu1-N1	100 (3)	H3-Cu2-N2	99 (3)
H4-Cu1-P1	101 (3)	H3-Cu2-P3	95 (3)
H4-Cu1-P2	100 (3)	H3-Cu2-P4	110 (3)
N1-Cu1-B2	92.6 (4)	N2-Cu2-B1	92.6 (5)
N1-Cu1-P1	107.8 (3)	N2-Cu2-P3	112.0 (3)
N1-Cu1-P2	118.1 (3)	N2-Cu2-P4	114.6 (3)
C2-B2-H4	106 (5)	C1-B1-H1	119 (6)
C2-B2-H5	101 (5)	C1-B1-H2	104 (5)
C2-B2-H6	110 (6)	C1-B1-H3	107 (6)
H4-B2-H5	114 (7)	H1-B1-H2	106 (8)
H4-B2-H6	108 (8)	H1-B1-H3	121 (8)
H5-B2-H6	117 (8)	H2-B1-H3	95 (7)
Cu1-H4-B2	158 (7)	Cu2-H3-B1	148 (8)
Cu1-N1-C1	160 (1)	Cu2-N2-C2	158 (1)
N1-C1-B1	176 (1)	N2-C2-B2	176 (1)
Cu1-P1-CA1	111.2 (2)	Cu2-P3-CA7	113.6 (3)
Cu1-P1-CA2	115.5 (3)	Cu2-P3-CA8	115.3 (3)
Cu1-P1-CA3	115.8 (4)	Cu2-P3-CA9	115.5 (4)
Cu1-P2-CA4	112.8 (2)	Cu2-P4-CA10	110.9 (3)
Cu1-P2-CA5	113.4 (2)	Cu2-P4-CA11	118.9 (2)
Cu1-P2-CA6	117.8 (3)	Cu2-P4-CA12	115.6 (3)
CA1-P1-CA2	104.8 (4)	CA7-P3-CA8	104.1 (5)
CA1-P1-CA3	102.0 (5)	CA7-P3-CA9	103.9 (6)
CA2-P1-CA3	106.1 (5)	CA8-P3-CA9	102.8 (5)
CA4-P2-CA5	104.4 (4)	CA10-P4-CA11	103.6 (4)
CA4-P2-CA6	103.9 (4)	CA10-P4-CA12	103.6 (4)
CA5-P2-CA6	103.0 (4)	CA11-P4-CA12	102.5 (3)

^a See footnotes *a* and *b*, Table I.

$\text{CH}_3)_2\text{PCu}(\text{NCS})_2$,²³ the ten-membered ring in $[((\text{C}_6\text{H}_5)_3\text{P})_2\text{Cu}(\text{NCBH}_3)]_2$ is considerably distorted. A similar

(23) A. P. Gaughan, R. F. Ziolo, and Z. Dori, *Inorg. Chim. Acta*, **4**, 640 (1970).

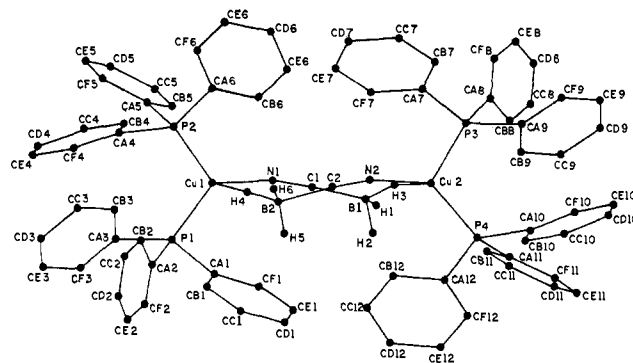


Figure 2. An ORTEP produced diagram of the molecule showing the atom labeling scheme.

Table III. Short (3.0 Å) Intramolecular Phenyl Ring Hydrogen Atom Contacts in $[((\text{C}_6\text{H}_5)_3\text{P})_2\text{Cu}(\text{NCBH}_3)]_2^a$

Cu1-HB2	2.98	Cu2-HB12	2.89
Cu1-HB3	2.93	P3-HF7	2.81
Cu1-HB5	2.98	P3-HB8	2.86
P1-HB1	2.98	P3-HF8	2.98
P1-HF1	2.87	P3-HB9	2.82
P1-HB2	2.82	P4-HB10	2.94
P1-HB3	2.84	P4-HF10	2.90
P2-HB4	2.92	P4-HB11	2.89
P2-HF4	2.92	P4-HF11	2.96
P2-HB5	2.85	P4-HB12	2.87
P2-HF5	2.99	P4-HF12	2.97
P2-HB6	2.88	C2-HB6	2.60
P2-HF6	2.95	B2-HB6	2.62
N1-HB5	2.78	N2-HF7	2.63
B1-HB11	2.60	N2-HB12	2.36
H1-HB11	2.49	C2-HB12	2.45
H2-HB11	2.23	H4-HB2	2.76
H2-HB12	2.87	H4-HB6	2.29
H3-HB9	2.71	H4-HC12	2.69
H3-HB11	2.52	H5-HF1	2.41
H6-HB6	2.56	H5-HB12	2.70

^a In this table, HB1, for example, refers to a phenyl hydrogen atom bonded to carbon atom B of phenyl ring 1.

Table IV. Root-Mean-Square Amplitudes of Vibration (in Å)^{a,b}

Atom	Min	Int	Max
Cu1	0.207 (3)	0.223 (2)	0.255 (2)
Cu2	0.203 (2)	0.215 (2)	0.240 (2)
P1	0.191 (5)	0.221 (4)	0.243 (4)
P2	0.190 (5)	0.201 (5)	0.228 (5)
P3	0.201 (6)	0.207 (5)	0.237 (4)
P4	0.188 (5)	0.199 (5)	0.216 (4)
N1	0.23 (1)	0.25 (1)	0.27 (1)
C1	0.21 (2)	0.22 (2)	0.27 (2)
B1	0.19 (3)	0.22 (2)	0.39 (2)
N2	0.19 (2)	0.22 (1)	0.26 (1)
C2	0.17 (2)	0.22 (2)	0.26 (2)
B2	0.19 (3)	0.24 (2)	0.32 (2)

^a Taken along the principal axes of the thermal ellipsoids. The orientation of these axes may be seen from Figure 1. ^b See footnotes *a* and *b*, Table I.

distortion was reported for $[((\text{C}_6\text{H}_5)_3\text{P})_2\text{Cu}(\text{N}_3)]_2$.²⁴ This difference is not surprising when one considers the intramolecular steric interactions present in these molecules. The diphenylmethylphosphine ligand suffers much less overall steric hindrance than triphenylphosphine in these compounds, and the interactions of the

(24) R. F. Ziolo, A. P. Gaughan, Z. Dori, C. G. Pierpont, and R. Eisenberg, *J. Amer. Chem. Soc.*, **92**, 738 (1970); *Inorg. Chem.*, **10**, 1289 (1971).

phenyl rings with the bridging ligands are therefore smaller. Indeed, an examination of the perspective view of the molecular structure of the thiocyanate dimer²³ shows the methyl carbons to be orientated in the direction of the bridging ligand atoms, which would alleviate the possible steric interactions. Similar results have also been found in the structural analysis of other copper(I) complexes containing $(C_6H_5)_2(CH_3)Y$ or $(C_6H_5)(CH_3)_2Y$ ligands ($Y = P, As$).^{12b}

The nonbonded Cu–Cu distance of 5.637 (2) Å is longer than that found in the thiocyanate bridged dimer²³ where a value of 5.30 ± 0.02 Å was reported. The greater distance in the present structure may be attributed to the combined effects of the increased steric interactions of the triphenylphosphine compared to the diphenylmethylphosphine ligand as well as the general increase in the number of bridging atoms.

The Cu–H bond distances of 1.83 (11) and 1.90 (10) Å compare favorably with the values of 1.84 (5) and 1.85 (5) Å in $[(C_6H_5)_3P]_2Cu(B_3H_8)$.²⁵ Apparently the electron-withdrawing cyanide group has little effect on the coordinating ability of the BH_3CN^- hydrogen atoms. The essential constancy of the refined Cu–H bond distances in the $[L_2Cu(NCBH_3)_2]_2$ and $L_2Cu(B_3H_8)$ complexes led us to reexamine the refinement of the $L_2Cu(BH_4)$ structure. Here the Cu–H bond length of 1.89 Å obtained from a difference Fourier synthesis refined to a value of 2.02 (5) Å^{1,10} which, at the time, was not recognized to be unusually long. In the original refinement of the structure,¹⁰ the weighting scheme used was that written into the 1967 version of Prewitt's absorption correction program ACAC. This scheme, which was only used for the $[(C_6H_5)_3P]_2Cu(BH_4)$ structure, assigned more excessive weights to the strong reflections than does the expression¹⁴ defined in the Experimental Section. Analysis of the function $w\Delta^2$ for the various classes of reflections¹⁹ in the original refinement revealed serious deficiencies, and empirical weights, $w = (10.68 - 0.74F + 0.020F^2)^{-1}$, were introduced. This new refinement had little effect on the heavy-atom parameters. Except for slight adjustments in the phenyl ring parameters, which made their geometry slightly more regular, all changes were less than one standard deviation. The boron hydrogen atom coordinates were substantially modified, however. The new results for the copper borohydride structure are summarized in Table V along with selected features of the copper-coordination spheres of the present compound and the octahydrotriborate analog. The value of 1.75 (3) Å for the Cu–H distance in the borohydride complex is now in closer agreement with results for the other two compounds, demonstrating the pronounced effect that the weighting scheme can have on the refinement of hydrogen atoms. The greater reliability of hydrogen atom positional parameters obtained from difference Fourier maps rather than from the weighting scheme has been noted previously.²⁶

The mean Cu–H distance of 1.82 Å for the three structures (Table V) is compatible with results for other first-row transition metals with bridging hydrogen atoms.²⁷ The Cu···B distances and Cu–H–B angles

(25) S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, **8**, 2755 (1969).

(26) See, for example, D. M. Collins, W. R. Scheidt, and J. L. Hoard, *J. Amer. Chem. Soc.*, **94**, 6689 (1972).

(27) B. A. Frenz and J. A. Ibers in "Transition Metal Hydrides," E. L. Muetterties, Ed., Marcell Dekker, New York, N. Y., 1971, p 42.

Table V. Comparison of Selected Bond Distances and Angles of the Copper Coordination Spheres of Three $[(C_6H_5)_3P]_2CuX$ Complexes^a

Distance	Value, Å	Angle	Value, deg
$X = NCBH_3^b$			
Cu1–H4	1.90 (10)	Cu1–H4–B2	158 (7)
Cu2–H3	1.83 (11)	Cu2–H3–B1	148 (8)
Cu2···B1	2.81 (1)		
Cu1···B2	3.01 (2)		
$X = BH_4^c$			
Cu–H _b	1.75 (3)	H _b –Cu–H _b '	61 (2)
Cu···B	2.196 (6)	Cu–H _b –B	95 (2)
$X = B_3H_8^d$			
Cu–H5	1.84 (5)	H5–Cu–H6	103 (2)
Cu–H6	1.85 (5)	Cu–H5–B2	100 (3)
Cu···B2	2.30 (1)	Cu–H6–B3	98 (3)
Cu···B3	2.30 (1)		

^a Numbers given in parentheses refer to the standard deviation in the last significant figures used. ^b See Figure 1 for labeling scheme. ^c See ref 10 for labeling scheme. The new refined hydrogen atoms positional parameters (see text) are H_b ($x = 0.006$ (1), $y = 0.284$ (3), $z = 0.201$ (2)) and H_t ($x = 0.042$ (2), $y = 0.431$ (5), $z = 0.287$ (3)). These parameters produce the following bond distances (Å) and angles (deg): B–H_b, 1.08 (2); B–H_t, 1.15 (4); P–Cu–H_b, 107.3 (7); P–Cu–H_b', 122.4 (7); H_b–B–H_b', 103 (3); H_b–B–H_t', 110 (4); H_b–B–H_t, 109 (3); H_b–B–H_t', 113 (2). ^d See ref 25 for labeling scheme.

are substantially larger in the cyanotrihydroborate dimer than in the other two compounds (Table V). This result is not surprising in view of the bridging nature of the cyanotrihydroborate group and the insensitivity of the bonding 1s orbital on a bridging hydrogen atom to the angle at that atom. The average B–H distance of 1.13 (10) Å for the cyanotrihydroborate complex is slightly shorter than anticipated from a neutron diffraction study of uranium borohydride (mean value 1.25 Å),²⁸ a displacement expected on theoretical grounds.²⁹

As seen in Figure 1, there are two different conformational orientations of the boron terminal hydrogen atoms with respect to the NCB axes. The two terminal hydrogen atoms on B2 straddle the approximate plane formed by N2, C2, B2, and C1, whereas these hydrogens on B1 lie on one side only of the plane formed by N1, C1, B1, and C2.³⁰ In the latter case, the result is a displacement of boron atom B1 toward the copper atom (Tables II and V). The local site symmetries of the two cyanotrihydroborate ligands are thus seen to be distinctly different, a result which accounts for the observed 15-cm^{-1} separation of the $C\equiv N$ stretching frequencies in the solid mull infrared spectrum of $[(C_6H_5)_3P]_2Cu(NCBH_3)_2$.⁹ The difference in attachment of the BH_3CN groups probably occurs to minimize the nonbonded steric interactions with the phenyl ring ortho hydrogen atoms (labeled HB and HF, Table III).

The Cu–N distances of 1.96 (1) and 2.01 (1) Å are comparable to the value of 2.02 (2) Å reported in the structure of $[(C_6H_5)_2CH_3P]_2Cu(NSC)_2$.²³ The observed Cu–N–C angles are 160 (1) and 158 (1)°. These

(28) E. R. Bernstein, W. C. Hamilton, T. A. Keiderling, S. J. La Placa, S. J. Lippard, and J. J. Mayerle, *Inorg. Chem.*, **11**, 3009 (1972).

(29) T. A. Halgren, R. J. Anderson, D. S. Jones, and W. N. Lipscomb, *Chem. Phys. Lett.*, **8**, 547 (1971).

(30) Calculations give the following displacements from the best mean planes: through N1, C1, B1, and C2 N1, -0.01 Å; C1, 0.02 Å; B1, -0.01 Å; C2, 0.00 Å; H1, -0.03 Å; H2, -1.13 Å and through N2, C2, B2, and C1 N2, -0.02 Å; C2, 0.03 Å; B2, -0.01 Å; C1, 0.00 Å; H5, -1.11 Å; H6, 0.51 Å.

values suggest that, as in $\text{Cu}_2\text{Cl}_4(\text{CH}_3\text{CN})_2$ and $\text{Cu}_3\text{Cl}_6(\text{CH}_3\text{CN})_2$ (where values of 165 (4) and 159 (1) $^\circ$ are reported³¹), the nitrogen atoms do not use pure sp hybrid orbitals but have partial sp^2 character. The average N-C bond distance of 1.14 (1) Å is reasonable and compares favorably with a recent value of 1.17 (3) Å found in the crystal structure of $\text{VO}(\text{NO}_3)_3 \cdot \text{CH}_3\text{CN}$, which contains the ligand NCCH_3 bonded through the nitrogen atom to the vanadyl ion.³² In the structures of $\text{VO}(\text{NO}_3)_3 \cdot \text{CH}_3\text{CN}$ ³² and $\text{B}_{20}\text{H}_{16}(\text{NCCH}_3)_2 \cdot \text{CH}_3\text{CN}$,³³ distances of 1.46 (4) Å, and an average distance of 1.47 (1) Å, respectively, were found for the C-C bonds in the NCCH_3 ligands, values smaller than the mean C-B bond length of 1.56 (3) Å in the present structure. This result is expected from the smaller covalent radius of 0.77 Å for tetrahedral carbon compared with 0.88 Å for tetrahedral boron.³⁴

The geometry of the bis(triphenylphosphine)copper(I) attachment (Table II) in the present determination is in general agreement with a recent analysis of the factors influencing the stereochemistry of four-coordinate copper(I) phosphine complexes.¹¹ The P-Cu-P angle is typically large (124.8 $^\circ$). It may be seen from Table II that there is one short Cu-P bond length of 2.242 (3) Å in the cyanotrihydroborate dimer. Two other structures recently determined also show one such short Cu-P bond, *viz.*, (a) 2.24 (1) Å *vs.* the average of 2.271 (1) Å in the thiocyanate bridged dimer²³ and (b) 2.250 (3) Å *vs.* 2.271 (4) Å in the azide bridged dimer,²⁴ the two values in each instance given for phosphorus atoms bonded to the same copper atom. Although no concrete conclusions may be reached at this time to explain why these bond lengths should be significantly shorter than the other Cu-P lengths in the same structures, two factors are important to mention.

(31) R. D. Willett and R. E. Rundle, *J. Chem. Phys.*, **40**, 838 (1964).

(32) F. W. B. Epstein, E. Enwall, D. M. Morris, and D. Sutton, *Inorg. Chem.*, **10**, 678 (1971).

(33) J. H. Enemark, L. B. Friedman, and W. M. Lipscomb, *Inorg. Chem.*, **5**, 2165 (1966).

(34) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 246.

First, since a difference in bond lengths does occur for phosphorus atoms attached to the same copper atom, one must question the validity of the assumption used earlier¹¹ that the amount of s character in a given P-Cu bond may be deduced from the value of the P-Cu-P angle. If this were the case, one would expect the amount of s character in both Cu-P bonds to be the same with resultant equal values for the bond distances. This is clearly not the case, as is shown in the three dimeric structures just cited. Second, the fact that this phenomenon occurs in both diphenylmethylphosphine and triphenylphosphine compounds suggests that intramolecular interactions are not responsible for the deviations. Obviously, the structural analysis of more copper compounds of this type must be determined before a definitive explanation of these anomalies may be presented.

The average P-C distance of 1.82 ± 0.01 Å and other geometric parameters of the triphenylphosphine ligands are in close agreement with results found in the structure determinations for related compounds.^{1, 25}

Acknowledgments. We are grateful to the National Science Foundation for support of this work under Grant GP 27239 and to the Alfred P. Sloan Foundation for a Research Fellowship to S. J. L. We also wish to thank Dr. C. G. Pierpont and Mr. D. Barton for their valuable assistance with the computations. A teacher-scholar grant to S. J. L. from the Camille and Henry Dreyfuss Foundation, applied to the purchase of the automated diffractometer, is also gratefully acknowledged.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-69.