Crystal Structure of (η^2-Octahydropentaborano)bis(triphenylphosphine)-copper(I)

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The title compound, $[Cu(\eta^2-B_5H_8)(PPh_3)_2]$, crystallises as colourless needles in the monoclinic space group $P2_1/c$ with a = 14.393(2), b = 12.291(2), c = 20.194(3) Å, β = 105.50(1)°, and Z = 4. The structure was solved from diffractometer data on 1 998 independent reflections by use of Patterson and electron-density syntheses. Refinement by block-diagonal least-squares gave a final R of 0.0547. The molecular structure can be described as being derived from that of *nido*-B_5H_9 by replacing one of the basal bridging hydrogen atoms with a bridging Cu-$(PPh_3)_2$ group such that B(2)–Cu 2.209(13) and B(3)–Cu 2.236(13) Å. The dihedral angle between the planes B(1), B(2), B(3) and Cu,B(2), B(3) is 178.4°; the angle P(1)–Cu–P(2) is 123.4(1)°, and the mid-point between B(2) and B(3) is 0.20 Å from the CuP_2 plane. The copper atom is thus approximately trigonal planar and is formally a 16-electron species, being bonded to the pentaborane unit only *via* a three-centre bond between Cu, B(2), and B(3). All the borane hydrogen atoms were located and their positions preclude the possibility of bonding *via* Cu–H–B bonds.

THERE has been a growing recognition in recent years that boron hydrides and their anions can act as very effective ligands towards a wide variety of main-group metals and transition elements.[1] Various modes of attachment have been established, including simple two-electron, two-centre σ-bonding (B–M), two-electron, three-centre bonding (B–M–B), hydrogen-bridge bonding (B–H–M), and various degrees of polyhapto-bonding involving more than two boron atoms and more than two electrons. General principles have not yet emerged to enable confident prediction of the preferred type of bonding in a particular compound and it is therefore important to obtain unequivocal structural evidence for a variety of compounds in order that theoretical rationalizations and diagnostic rules can be developed. The *nido*-pentaborane anion, $[B_5H_8]^-$, is known to form a σ-bond to iridium in the octahedral complex $[Ir(B_5H_8)Br_2(CO)(PMe_3)_2]$,[2] whereas its 1-bromo-derivative, $B_5H_7Br^-$, forms a localized three-centre (η^2) bond in the trimethylsilyl derivative $[Si(B_5H_7Br)Me_3]$.[3] The recent report [4] of the copper complex $[Cu(B_5H_8)(PPh_3)_2]$ thus invited speculation as to its structure, particularly in view of the existence of copper–borane complexes which are known to bond *via* Cu–H–B bridge bonds, *e.g.* $[Cu(BH_4)(PPh_3)_2]$,[5] $[Cu(B_3H_8)(PPh_3)_2]$,[6] and $[\{Cu(PPh_3)_2\}_2(B_{10}H_{10})]\cdot CCl_3H$.[7] The structure of $[Cu(B_5H_8)(PPh_3)_2]$, to be described, establishes that it is not a member of this hydrogen bridge-bonded 18-electron series of copper(I) complexes but is the first example of a 16-electron copper(I)–borane complex featuring a three-centre bond between two adjacent basal boron atoms and the copper atom.

EXPERIMENTAL

The compound $[Cu(B_5H_8)(PPh_3)_2]$ was prepared according to Brice and Shore,[4] and recrystallised from dichloromethane–diethyl ether as needles.

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[5] S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, 1967, **6**, 2223.

[6] S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, 1969, **8**, 2755.

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Crystal Data.—$C_{36}H_{38}B_5CuP_2$, $M = 650.29$, Monoclinic, $a = 14.393(2)$, $b = 12.291(2)$, $c = 20.194(3)$ Å, $\beta = 105.50(1)°$, $U = 3\,442.4$ Å^3, $Z = 4$, $D_c = 1.255$ g cm^{-3}, $D_m = 1.24$ g cm^{-3}, $F(000) = 1\,352$. Space group $P2_1/c$. Cu-K_α radiation, $\lambda = 1.541\,8$ Å; μ(Cu-K_α) = 19.3 cm^{-1}.

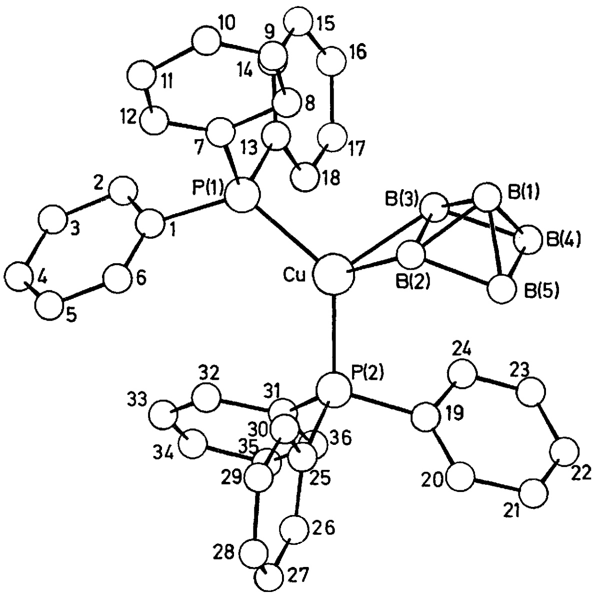

FIGURE 1 The molecular structure and atom-numbering for non-hydrogen atoms in $[Cu(\eta^2\text{-}B_5H_8)(PPh_3)_2]$

Structure Determination.—Cell dimensions were determined by a least-squares fit of setting angles for 12 reflections centred on a Hilger and Watts Y290 diffractometer, using Mo-K_α radiation ($\lambda = 0.710\,69$ Å). Intensities were recorded on a Nonius CAD 4 diffractometer, operated in the θ–2θ scan mode with a scintillation counter, pulse-height discrimination, and monochromatised Cu-K_α radiation. The crystal was of irregular shape with mean radius *ca.* 0.2 mm, and absorption corrections were not applied. The structure determination used the 1 998 independent reflections with $\theta < 70°$ and $I > 3\sigma(I)$, where $I = P - 2(B_1 + B_2)$ and $\sigma^2(I) = P + 4(B_1 + B_2) + (0.05I)^2$. The structure was solved by use of Patterson and electron-density syntheses and refined by block-diagonal least-squares. All hydrogen atoms appeared on a difference map computed at a late stage of the refinement. The phenyl hydrogen atoms were included in calculated positions, assuming C–H 1.0 Å; they were assigned isotropic temperature factors equivalent to those of the carbon atoms to which there were attached, but were not refined. The co-ordinates and isotropic temperature factors of the borane hydrogen atoms were refined, together with the co-ordinates and anisotropic temperature factors of the non-hydrogen atoms. Minimisation of $\Sigma w(F_o - |F_c|)^2$, with $w = 1/\sigma^2(F_o)$ derived from the expression for $\sigma^2(I)$, gave a final R of 5.47% and R' of 6.05%. Atomic scattering factors were taken from ref. 8. Final atomic co-ordinates and their estimated standard deviations (by inversion of the 9 × 9 and 4 × 4 block-diagonal least-squares matrix) are listed in Table 1.*

DISCUSSION

The molecular structure and atom numbering are shown in Figures 1 and 2, and bond lengths and angles with their estimated standard deviations are given in Table 2.

TABLE 1

Atomic co-ordinates with estimated standard deviations in parentheses

	x	y	z	
Cu(1)	0.256 3(1)	0.168 0(1)	0.242 6(1)	
P(1)	0.352 9(2)	0.079 7(2)	0.335 1(1)	
P(2)	0.164 8(2)	0.081 1(2)	0.148 8(1)	
B(1)	0.241 4(11)	0.450 9(10)	0.263 3(7)	
B(2)	0.282 6(9)	0.342 3(10)	0.228 0(7)	
B(3)	0.213 7(8)	0.323 8(9)	0.283 7(6)	
B(4)	0.125 6(11)	0.422 3(11)	0.238 2(7)	
B(5)	0.196 2(12)	0.439 5(9)	0.179 8(7)	
C(1)	0.387 9(6)	−0.064 0(7)	0.332 3(4)	
C(2)	0.371 9(7)	−0.138 3(8)	0.378 7(5)	
C(3)	0.393 1(8)	−0.249 1(9)	0.371 5(6)	
C(4)	0.428 6(8)	−0.282 9(10)	0.320 1(6)	
C(5)	0.447 3(7)	−0.207 9(10)	0.274 0(6)	
C(6)	0.426 1(7)	−0.097 1(9)	0.280 5(5)	
C(7)	0.465 4(7)	0.148 9(8)	0.376 8(4)	
C(8)	0.460 4(7)	0.261 8(8)	0.386 1(5)	
C(9)	0.544 8(8)	0.318 2(9)	0.415 4(5)	
C(10)	0.632 2(8)	0.269 3(10)	0.431 6(6)	
C(11)	0.636 6(7)	0.158 3(10)	0.421 1(6)	
C(12)	0.554 9(7)	0.099 1(9)	0.394 0(6)	
C(13)	0.282 8(6)	0.081 5(7)	0.398 2(5)	
C(14)	0.317 2(8)	0.110 4(9)	0.466 3(5)	
C(15)	0.257 0(9)	0.110 4(9)	0.508 5(6)	
C(16)	0.163 0(9)	0.077 1(9)	0.484 4(7)	
C(17)	0.126 3(8)	0.048 6(9)	0.417 7(6)	
C(18)	0.186 7(7)	0.049 9(8)	0.374 7(5)	
C(19)	0.053 5(6)	0.157 3(7)	0.113 5(4)	
C(20)	0.026 1(7)	0.199 2(8)	0.048 5(5)	
C(21)	−0.059 9(7)	0.258 5(8)	0.026 4(5)	
C(22)	−0.117 7(7)	0.271 3(8)	0.069 8(5)	
C(23)	−0.090 8(7)	0.232 1(9)	0.135 0(6)	
C(24)	−0.006 8(7)	0.172 6(8)	0.156 9(5)	
C(25)	0.222 9(6)	0.070 0(7)	0.080 2(5)	
C(26)	0.182 3(7)	0.014 7(8)	0.019 1(5)	
C(27)	0.228 7(7)	0.008 1(8)	−0.032 0(5)	
C(28)	0.316 7(7)	0.059 4(9)	−0.023 6(5)	
C(29)	0.358 7(7)	0.114 5(8)	0.035 4(5)	
C(30)	0.313 0(7)	0.120 3(8)	0.086 6(5)	
C(31)	0.123 9(6)	−0.057 5(7)	0.155 0(4)	
C(32)	0.195 6(7)	−0.136 5(8)	0.180 4(6)	
C(33)	0.170 9(8)	−0.243 8(8)	0.185 8(6)	
C(34)	0.077 2(8)	−0.275 1(8)	0.169 8(5)	
C(35)	0.006 7(7)	−0.199 9(8)	0.143 7(6)	
C(36)	0.031 1(7)	−0.091 7(7)	0.137 1(5)	
	x	y	z	U_{iso} *
H(1)	0.284(7)	0.532(8)	0.296(5)	114(36)
H(2)	0.362(6)	0.303(7)	0.227(4)	79(28)
H(3)	0.215(6)	0.306(7)	0.339(4)	70(27)
H(4)	0.068(6)	0.460(8)	0.246(4)	88(32)
H(5)	0.197(9)	0.498(11)	0.142(6)	166(54)
H(25)	0.215(5)	0.347(7)	0.162(4)	61(25)
H(34)	0.132(6)	0.304(8)	0.251(4)	96(32)
H(45)	0.096(6)	0.414(8)	0.170(4)	100(31)

* In the form $\exp[-2\pi^2 U_{iso}(2\sin\theta/\lambda)^2]$.

In the metallaborane framework (Figure 2) the copper atom replaces a bridge hydrogen of the parent B_5H_9 structure. The Cu–B distances (2.21 and 2.24 Å) are shorter than the Cu $\cdots$ H(2) and Cu $\cdots$ H(3) distances [2.33 and 2.76(9) Å]. In the corresponding $[BH_4]^-$ and $[B_3H_8]^-$ complexes in which the Cu–H–B bridge bonding

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* Observed and calculated structure-factor amplitudes and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 21882 (15 pp., 1 microfiche). See Notice to Authors No. 7, in *J.C.S. Dalton*, 1976, Index issue.

[8] 'International Tables for *X*-Ray Crystallography,' vol. IV, Kynoch Press, Birmingham, 1974.

seems clearly to be involved the Cu–H distances are substantially less than the Cu–B distances. Comparative Cu–H and Cu–B distances are: in [Cu(BH_4)($(PPh_3)_2$] 2.02(5) and 2.18(1),[5] in [Cu(B_3H_8)($(PPh_3)_2$] 1.84(5) and 2.30(1),[6] and in [{Cu($(PPh_3)_2$}$_2$($B_{10}H_{10}$)]·CCl_3H 1.88(6) and 2.08(7), and 2.30(2) Å.[7] The mode of attachment found here also contrasts with that in the iridium complex [Ir(B_5H_8)Br_2(CO)($(PMe_3)_2$] [2] in which the metal atom replaces a terminal hydrogen atom of the parent B_5H_9 molecule. In the present compound the position of the copper atom relative to the [B_5H_8]$^-$ unit is very similar to that found for the silicon atom in [Si(B_5H_7Br)Me_3] [3] where a quasi-tetrahedral silicon atom is bonded *via* a three-centre B–Si–B bond. However, the [Cu(B_5H_8)P_2] portion of the molecule (Figure 2) departs from ideal C_s symmetry, which is possessed by the $SiMe_3$ complex: the mid-point (X) between B(2) and B(3) is 0.20 Å from the P(1),Cu,P(2) plane (onto which Figure 2 is projected), and the B(2) · · · B(3) interatomic direction makes an angle of 16° with the normal to that plane. These distortions are probably the result of steric interactions with the triphenylphosphine ligands.

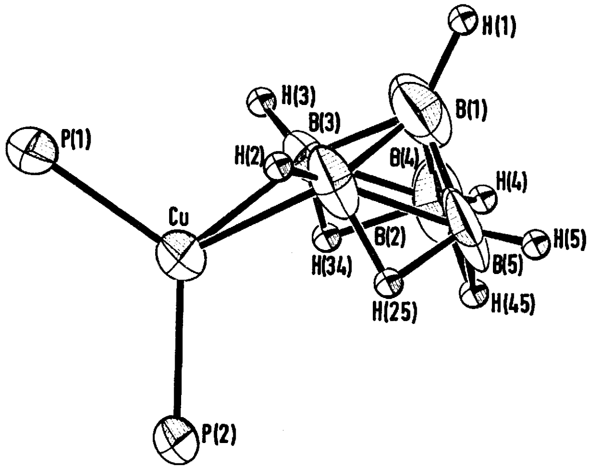

FIGURE 2 ORTEP drawing of the metallaborane framework and attached hydrogen atoms (which have been given artificial temperature factors of *B* 1.0 Å^2)

The dihedral angle between the planes B(1),B(2),B(3) and B(2),Cu,B(3) is 178.4° and the [B_5H_8]$^-$ group behaves as a two-electron donor to the copper(I) atom, which is thus formally a 16-electron species. The three-centre B(2)–Cu–B(3) bond, together with the two Cu–P bonds, forms an essentially trigonal-planar co-ordination about the copper atom: the angles subtended about the copper atom by phosphorus atoms and the point X midway between B(2) and B(3) are P(1)–Cu–X 114.0, P(2)–Cu–X 122.3, and P(1)–Cu–P(2) 123.4°, and the Cu–X direction is only 3.3° from the P(1),Cu,P(2) plane.

Since completing this work we have learned that similar structural conclusions have been drawn from n.m.r. and i.r. spectroscopic data,[9] though these were necessarily less detailed than the present precise determination of the positions of all the atoms in the structure.

TABLE 2

Bond lengths (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Distances			
Cu–P(1)	2.284(3)	B(1)–H(1)	1.25(10)
Cu–P(2)	2.266(3)	B(2)–H(2)	1.25(9)
Cu–B(2)	2.209(13)	B(3)–H(3)	1.14(8)
Cu–B(3)	2.236(13)	B(4)–H(4)	0.99(10)
B(1)–B(2)	1.69(2)	B(5)–H(5)	1.05(13)
B(1)–B(3)	1.69(2)	B(3)–H(34)	1.21(8)
B(1)–B(4)	1.65(2)	B(4)–H(34)	1.48(10)
B(1)–B(5)	1.64(2)	B(4)–H(45)	1.32(8)
B(2)–B(3)	1.70(2)	B(5)–H(45)	1.44(9)
B(3)–B(4)	1.81(2)	B(5)–H(25)	1.25(8)
B(4)–B(5)	1.76(3)	B(2)–H(25)	1.43(7)
B(5)–B(2)	1.81(2)		
P(1)–C(1)	1.84(1)	P(2)–C(31)	1.82(1)
P(1)–C(7)	1.82(1)	C–C(Ph)	1.340(19)— 1.412(15)
P(1)–C(13)	1.82(1)		
P(2)–C(19)	1.83(1)	Mean C–C(Ph)	1.379
P(2)–C(25)	1.80(1)		
(*b*) Angles			
P(1)–Cu–P(2)	123.4(1)	B(1)–B(3)–B(2)	60(1)
P(1)–Cu–B(2)	118.8(3)	B(1)–B(3)–B(4)	56(1)
P(1)–Cu–B(3)	105.7(3)	B(2)–B(3)–B(4)	92(1)
P(2)–Cu–B(2)	115.3(3)	B(1)–B(4)–B(3)	58(1)
P(2)–Cu–B(3)	123.9(3)	B(1)–B(4)–B(5)	58(1)
B(2)–Cu–B(3)	45.0(5)	B(3)–B(4)–B(5)	88(1)
B(2)–B(1)–B(3)	60(1)	B(1)–B(5)–B(2)	58(1)
B(2)–B(1)–B(5)	66(1)	B(1)–B(5)–B(4)	58(1)
B(3)–B(1)–B(4)	66(1)	B(2)–B(5)–B(4)	90(1)
B(4)–B(1)–B(5)	65(1)	Cu–P(1)–C(1)	122.9(3)
B(2)–B(1)–B(4)	98(1)	Cu–P(1)–C(7)	115.3(3)
B(3)–B(1)–B(5)	97(1)	Cu–P(1)–C(13)	103.6(3)
B(1)–B(2)–B(3)	60(1)	Cu–P(2)–C(19)	109.7(3)
B(1)–B(2)–B(5)	56(1)	Cu–P(2)–C(25)	113.1(3)
B(3)–B(2)–B(5)	90(1)	Cu–P(2)–C(31)	120.7(3)

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[9] G. G. Outterson, V. T. Brice, and S. G. Shore, *Inorg. Chem.*, 1976, **15**, 1456.