

AD-A181 979

CUPRACARBORANES CONTAINING A CLOS0-CU(I)C2B9 GEOMETRY
SYNTHESIS AND STRUC (U) CALIFORNIA UNIV LOS ANGELES
DEPT OF CHEMISTRY AND BIOCHEMISTR V DO ET AL
15 JUN 87 TR-128 N00014-85-K-0772 F/G 7/3

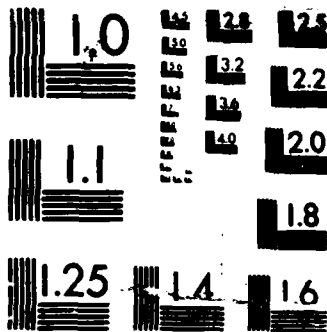
1/1

UNCLASSIFIED

NL



END
8-87
DTIC



MICROCOPY RESOLUTION TEST CHART

AD-A181 979

12

OFFICE OF NAVAL RESEARCH

DTIC FILE COPY

Contract N00014-85-K-0772

Work Unit No. 4326-808

TECHNICAL REPORT NO. 128

Cupracarboranes Containing a *closo*-Cu(I)C₂B₉ Geometry.
Synthesis and Structure of [(PPh₃)CuC₂B₉H₁₁]⁻ and [(PPh₃)₂Cu₂(μ-H)₂C₂B₉H₉].

by

Youngkyu Do, Han Chyul Kang, Carolyn B. Knobler and M. Frederick Hawthorne*

Prepared for Publication

in

Inorganic Chemistry

University of California at Los Angeles
Department of Chemistry and Biochemistry
Los Angeles, California 90024

June, 1987

DTIC
ELECTE
JUN 25 1987
S D
E

Reproduction in whole or in part is permitted for
any purpose of the United States Government

This document has been approved for public release and sale;
its distribution is unlimited

87 6 24 062

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Distribution list enclosed	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE		4. PERFORMING ORGANIZATION REPORT NUMBER(S) 128	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) 128		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION UCLA Dept. of Chem. & Biochem.	6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research	
6c. ADDRESS (City, State, and ZIP Code) 6115 Young Hall 405 Hilgard Avenue Los Angeles, CA 90024		7b. ADDRESS (City, State, and ZIP Code) Department of the Navy Arlington, VA 22217	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-85-K-0772/RNT Code: 4135004	
8c. ADDRESS (City, State, and ZIP Code)		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO.	TASK NO.
		PROJECT NO.	WORK UNIT ACCESSION NO. 4326-808
11. TITLE (Include Security Classification) Cupracarboranes Containing a <i>closo</i> -Cu(I) ₂ B ₉ Geometry. Synthesis and Structure of [(PPh ₃) ₂ Cu ₂ (μ-H) ₂ C ₂ B ₉ H ₉] ⁻ and [(PPh ₃) ₂ Cu ₂ (μ-H) ₂ C ₂ B ₉ H ₉].			
12. PERSONAL AUTHOR(S) Youngkyu Do, Han Chyul Kang, Carolyn B. Knobler and M. Frederick Hawthorne*			
13a. TYPE OF REPORT Technical Report	13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Year, Month, Day) 06/15/87	15. PAGE COUNT
16. SUPPLEMENTARY NOTATION To be published in <u>Inorganic Chemistry</u>			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	metallacarborane; cupracarborane; bridging boron-hydride; bimettalacarborane <u>Carborane</u>
19. ABSTRACT (Continue on reverse if necessary and identify by block number) The reaction chemistry of [nido-7,8-C ₂ B ₉ H ₁₁] ₂ with copper(I) has been examined to provide anaerobic synthetic routes to two novel phosphinocupracarboranes, [(PPh ₃) ₂ Cu ₂ (μ-H) ₂ C ₂ B ₉ H ₉] ⁻ and [(PPh ₃) ₂ Cu ₂ (μ-H) ₂ C ₂ B ₉ H ₉]. The structural analysis reveals that both cupracarboranes adopt a <i>closo</i> geometry for the d ¹⁰ MC ₂ B ₉ icosahedra. Two copper(I) centers of the homodinuclear complex are incorporated into one carborane cage via the open pentagonal C ₂ B ₃ face and two B-H-Cu bridges. Both bridging BH units stem from the upper pentagonal belt resulting in the interatomic Cu(I)-Cu(I) distance of 2.576(1) Å. The relatively close Cu(I)-Cu(I) proximity can be ascribed to a metal-metal interaction and the dinuclear cupracarborane can be viewed as a zwitterionic salt which upon dissolution remains intact while exhibiting fluxional behavior. The nature of these fluxional processes has been explored by variable temperature multinuclear FTNMR spectroscopy. Key words: Crystallization [(PPh ₃) ₂ Cu ₂ (μ-H) ₂ C ₂ B ₉ H ₉] crystallizes in the monoclinic space group P2 ₁ /n, with a = 10.005(2), b = 20.693(4), c = 18.998(3) Å, β = 92.664(6)°, Z = 4. PPN[(PPh ₃) ₂ Cu ₂ B ₉ H ₁₁] →			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL M. F. Hawthorne		22b. TELEPHONE (Include Area Code) (213)825-7378	22c. OFFICE SYMBOL

crystallizes in the monoclinic space group $P2_1/n$, with $\underline{a} = 11.507(1)$, $\underline{b} = 14.772(1)$,
 $\underline{c} = 30.751(2)$ Å, $\beta = 90.284(2)^\circ$, $Z = 4$.

**Cupracarboranes Containing a *closo*-Cu(I)C₂B₉ Geometry.
 Synthesis and Structure of
 [(PPh₃)CuC₂B₉H₁₁]⁻ and [(PPh₃)₂Cu₂(μ-H)₂C₂B₉H₉].**



Youngkyu Do, Han Chyul Kang, Carolyn B. Knobler
 and M. Frederick Hawthorne*

Department of Chemistry and Biochemistry
 University of California, Los Angeles
 Los Angeles, California 90024

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

Abstract

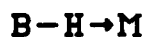
The reaction chemistry of [*nido*-7,8-C₂B₉H₁₁]²⁻ with copper(I) has been examined to provide anaerobic synthetic routes to two novel phosphinocupracarboranes, [(PPh₃)CuC₂B₉H₁₁]⁻ and [(PPh₃)₂Cu₂(μ-H)₂C₂B₉H₉]. The structural analysis reveals that both cupracarboranes adopt a *closo* geometry for the d¹⁰ MC₂B₉ icosahedra. Two copper(I) centers of the homodinuclear complex are incorporated into one carborane cage via the open pentagonal C₂B₃ face and two B-H-Cu bridges. Both bridging BH units stem from the upper pentagonal belt resulting in the interatomic Cu(I)-Cu(I) distance of 2.576(1) Å. The relatively close Cu(I)-Cu(I) proximity can be ascribed to a metal-metal interaction and the dinuclear cupracarborane can be viewed as a zwitterionic salt which upon dissolution remains intact while exhibiting fluxional behavior. The nature of these fluxional processes has been explored by variable temperature multinuclei FTNMR spectroscopy.

[(PPh₃)₂Cu₂(μ-H)₂C₂B₉H₉] crystallizes in the monoclinic space group *P*2₁/*n*, with *a* = 10.005(2), *b* = 20.693(4), *c* = 18.998(3) Å, β = 92.664(6)°, *Z* = 4. PPN[(PPh₃)CuC₂B₉H₁₁]⁻ crystallizes in the monoclinic space group *P*2₁/*n*, with *a* = 11.507(1), *b* = 14.772(1), *c* = 30.751(2) Å, β = 90.284(2)°, *Z* = 4.

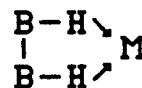
Cupracarboranes Containing a *closo*-Cu(I)C₂B₉ Geometry. Synthesis and Structure of [(PPh₃)CuC₂B₉H₁₁]⁻ and [(PPh₃)₂Cu₂(μ-H)₂C₂B₉H₉].

Sir:

An additional manifestation of the versatile electron donor ability of [*nido*-7,8-C₂B₉H₁₁]²⁻ (**1**)¹ in metallacarborane chemistry has recently appeared in the form of polynuclear metallacarboranes involving exopolyhedral boron-hydride-metal three-center, two-electron linkages.^{2,3} While the bridge bonding mode **I** is the most usual pattern encountered in polynuclear metal complexes of **1**, the unit **II** has only been realized in the bimetallic aluminacarborane, *commo*-3,3'-Al[(*exo*-8,9-(μ-H)₂Al(C₂H₅)₂-3,1,2-AlC₂B₉H₉)-(3',1',2'-AlC₂B₉H₁₁)] (**2**),^{3c,4} in which the bridging BH units stem from the upper and



I



II

lower pentagonal belts of one dicarbollide cage. As part of the investigation into the extended use of **1** in the synthesis of novel metallacarboranes containing metal-hydride-boron bridge bonds, the reaction chemistry of **1** with copper(I) has been examined.⁵

Routes to two novel phosphinocupracarboranes have recently been discovered. Depending on the absence or presence of (PPN)⁺Cl⁻ (PPN⁺ = *bis*(triphenylphosphoranylidene)ammonium cation), the dithallium salt⁶ of **1** reacts with triphenylphosphine-substituted

copper(I) chlorides (L_nCuCl , $n = 1,2$) to form either dinuclear *closo*-[*exo*-4,8-(μ -H) $_2$ Cu-(PPh $_3$)-3-(PPh $_3$)-3,1,2-Cu $_2$ B $_9$ H $_9$] (**3**; white; 79%) or mononuclear (PPN)[*closo*-3-(PPh $_3$)-3,1,2-Cu $_2$ B $_9$ H $_9$] [(PPN)-**4**; off-white; 84%]. Both compounds were characterized by single-crystal X-ray analyses⁷ as well as other means.⁸

The crystal structure of **3** consists of two enantiomers related by an inversion center to form the racemic system. The structure of **3**, shown in Figure 1, contains two copper(I) centers

[Figure 1]

which are incorporated into one carborane cage via the open pentagonal C $_2$ B $_3$ face and two B-H-Cu bridges as in mode II. Both bridging BH units originate from the upper pentagonal belt, in contrast to **2**, such that the plane of Cu(01)-B(04)-B(08) forms a dihedral angle of 40.9° with the pentagonal C $_2$ B $_3$ plane (± 0.016 Å) and the interatomic distance between two copper(I) ions of formal d¹⁰ configuration is 2.576(1) Å. This structural situation raises at least two engaging questions as to the geometry of the polyhedral framework of the Cu(03)C $_2$ B $_9$ fragment and the extent of Cu(I)-Cu(I) interaction.

The structure of metallacarboranes containing electron-rich late transition metal ions has been described in terms of molecular distortions such as the slipping,^{9,10} folding¹⁰ and tilting^{5,11} distortions. The parameters which are associated with these molecular distortions remain useful for descriptive purposes, but do not always delineate the electron count of the polyhedral framework of the MC $_2$ B $_9$ cages. Nevertheless, the structural analysis favors *closo* geometry for the Cu(03)C $_2$ B $_9$ cage of **3**. In **3**, the lower B $_5$ plane is nearly planar (± 0.004 Å) while the upper C $_2$ B $_3$ plane experiences a minor distortion with 2.3° and 1.1° for the folding parameters¹⁰ θ and ϕ , respectively. The displacement of Cu(03) from the perpendicular passing through the centroid of the lower B $_5$ plane, known as the slipping parameter Δ ,¹⁰ is calculated to be 0.25 Å. These values for the distortion parameters fall into the range observed in *closo* icosahedral metallacarboranes¹² rather than slipped metallacarboranes.¹³ The interaction of copper with the cage via the open C $_2$ B $_3$ face in **3** is typical of *closo*-MC $_2$ B $_9$ complexes so far

structurally characterized,^{14,15} with a mean M-C/M-B distance ratio (1.06) close to unity. The anionic *closo*-[LCuC₂B₉H₁₁]⁻ fragment of **3** can be synthesized as a separate, isolated entity. The compound (PPN)·**4** is such an example and the structure of **4**, as displayed in Figure 2, also

[Figure 2]

adopts *closo* geometry.¹⁶ The *closo* geometry for the d¹⁰ MC₂B₉ icosahedra, in both **3** and **4**, seems to be unusual since a progressive opening of the MC₂B₉ metallacarborane cage has been pointed out⁵ as a trend in the structural changes for the isoelectronic 18-electron series [Re(CO)₃-C₂B₉H₁₁]⁻,^{12a} [Au(S₂CNEt₂)C₂B₉H₁₁],^{11,13c} [Hg(PPh₃)C₂B₉H₁₁],^{5,17} and [Tl-C₂B₉H₁₁]⁻.^{17,18} However this geometry has been anticipated as a possible structure for (PPh₃)CuC₂B₉H₁₀(C₅H₅N)⁵ by analogy with the known η⁵ structure of (PPh₃)Cu(C₅H₅)¹⁹

A range of Cu-Cu distances from 2.35 Å to about 3.6 Å is found in polynuclear copper(I) compounds.²⁰ MO analyses performed with Cu_nⁿ⁺ (n = 2,4) at the extended Hückel level of approximation supports the existence of a soft and attractive Cu(I)-Cu(I) interaction, overlaid upon the requirements of the bridging ligand set.^{20b} In [Cu₂(tmen)₂(μ-CO)(μ-PhCO₂)]⁺ the bridging ligand stereochemistry dominates, resulting in the very short Cu(I)-Cu(I) distance of 2.419(2) Å,^{20c} whereas in **3** the stereochemical requirements of the bridging ligand (**1**) are likely to be minimal since the elevation angles of the hydrogen substituents in the MC₂B₉H₁₁ cages are not restricted to that of a regular icosahedron.^{10b} Thus the relatively close Cu(I)-Cu(I) proximity in **3** can be considered to be a consequence of a metal-metal interaction similar to that found in Fe₂(CO)₆C₄(CH₃)₂(OH)₂²¹ and its homologues.²²

Although the isolation of the anionic compound **4** supports the zwitterionic nature of **3**, (PPN)·**4** does not convert to **3** in the presence of LCuCl. The dinuclear structural integrity of **3** remains intact upon dissolution although fluxional motions become operative above 253 K since coalescence occurs at this temperature as observed by variable temperature ³¹P{¹H} FTNMR spectroscopy.^{8a} At 203 K, the two phosphorus nuclei of **3** are distinguishable while the two

CH hydrogens of the carborane cage remain indistinguishable in ^1H NMR, indicating that at least one kind of fluxional motion is still present at this temperature. The evidence at hand does not unequivocally reveal the nature of the fluxional processes.

Acknowledgment. The authors gratefully acknowledge the support of this work by the Office of Naval Research. We also would like to thank Dr. A. Varadarajan for informative discussions.

Supplementary Material Available: Details of crystallographic data collection, tables of positional and thermal parameters and interatomic distances and angles (15 pages). Ordering information is given on any current masthead page.

References and Footnotes

1. Hawthorne, M. F.; Young, D. C.; Andrews, T. D.; Howe, D. V.; Pilling, R. L.; Pitts, A. D.; Reintjer, M.; Warren, Jr., L. F.; Wegner, P. A. *J. Am. Chem. Soc.* 1968, 90, 879.
2. Green, M.; Howard, J. A. K.; James, A. P.; Jelfs, A. N. de M.; Nunn, C. M.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* 1985, 1778.
3. a) Baker, R. T.; King, III, R. E.; Knobler, C. B.; O'Con, C. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* 1978, 100, 8266. b) Behnken, P. E.; Marder, T. B.; Baker, R. T.; Knobler, C. B.; Thompson, M. R.; Hawthorne, M. F. *J. Am. Chem. Soc.* 1985, 107, 932. c) Rees, Jr., W. S.; Schubert, D. M.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* 1986, 108, 5367. d) Do, Y.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* 1987, 109, 1853.
4. The bridging unit II is not uncommon in metallaboranes or in mononuclear metallocarboranes. Examples include the following: (a) $\text{Cu}_2(\text{PPh}_3)_4(\text{B}_{10}\text{H}_{10})$; Gill, J. T.; Lippard, S. J. *Inorg. Chem.* 1975, 14, 751. (b) $\text{HMn}_3(\text{CO})_{10}(\text{BH}_3)_2$; Kaesz, H. D.; Fellman, W.; Wilkes, G. R.; Dahl, L. F. *J. Am. Chem. Soc.* 1965, 87, 2753. (c) *exo-nido*-Phosphinerhodacarboranes; Knobler, C. B.; Marder, T. B.; Mizusawa, E. A.; Teller, R. G.; Long, J. A.; Behnken, P. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* 1984, 106, 2990.
5. The derivative chemistry of **1** with Cu(I) has remained virtually unexplored. The only compound reported to date is $[(\text{PPh}_3)\text{CuC}_2\text{B}_9\text{H}_{10}(\text{NC}_5\text{H}_5)]$ for which X-ray structural data are not available: Colquhoun, H. M.; Greenhough, T. J.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* 1979, 619.
6. Spencer, J. L.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* 1972, 1178.

7. a) Suitable crystals of **3** and (PPN) **4** were grown from dichloromethane/ether. Diffraction data on both compounds were collected at 25 °C on a locally built automated diffractometer, using Mo K α radiation, to a maximum 2 θ of 50°. The structures were solved by a combination of conventional Patterson, Fourier and least-squares techniques.
- b) Crystallographic data for **3** [(PPN) **4**]: $a = 10.005(2)$ [11.507(1)] Å, $b = 20.693(4)$ [14.772(1)] Å, $c = 18.998(3)$ [30.751(2)] Å, $\beta = 92.664(6)$ [90.284(2)] °, $V = 3924$ [5227] Å³; space group, $P2_1/n$ [$P2_1/n$]; unique data ($I > 3 \sigma(I)$), 5071 [4831]; R (R_w), 4.5 (6.1) [6.4 (7.5)] %. All calculations were performed on the DEC VAX 750 of the J. D. McCullough Crystallography Laboratory using the UCLA Crystallography Package.
8. (a) Data for **3**: Anal. Calcd. (Found): C, 58.21 (57.94); H, 5.27 (5.10); B, 12.41 (11.79); Cu, 16.21 (16.11); P, 7.90 (7.44). IR spectrum (KBr): $\nu_{\text{BH}} = 2559, 2498$; $\nu_{\text{BHCu}} = 2327$ (weak and broad) cm⁻¹. Chemical shifts upfield of the reference are designated as negative. ¹¹B{¹H} NMR (160.463 MHz) in dichloromethane, referenced to external BF₃·OEt₂ in C₆D₆: -17.4, -19.7, -22.5, -24.2, -29.7, -31.2 ppm. ¹H NMR (200.133 MHz) in CD₂Cl₂ (referenced to residual solvent protons = 5.32 ppm): 2.01 (carborane CH). ³¹P{¹H} NMR (81.02 MHz) (CD₂Cl₂; referenced to 85% H₃PO₄): 7.9 (above 253 K); 4.7 and 10.1 ppm (at 203 K). (b) Data for **4**: Anal. Calcd. (Found): C, 67.48 (67.44); H, 5.66 (5.75); B, 9.76 (9.57); Cu, 6.37 (6.26); N, 1.41 (1.36); P, 9.32 (9.39). IR spectrum (KBr): $\nu_{\text{BH}} = 2571, 2537, 2488, 2418$ cm⁻¹. ¹¹B{¹H} NMR (CH₂Cl₂): -17.2, -20.2, -22.1, -23.0, -24.9, -34.9 ppm. ¹H NMR in CD₂Cl₂: 1.57 ppm (carborane CH). ³¹P{¹H} NMR (CD₂Cl₂): 20.6 (PPN), 7.8 (PPh₃) ppm.
9. a) Warren, Jr., L. F.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1968**, *90*, 4823; **1970**, *92*, 1157. b) Wing, R. M. *J. Am. Chem. Soc.* **1967**, *89*, 5599; **1968**, *90*, 4828.
10. a) Mingos, D. M. P.; Forsyth, M. I. *J. Chem. Soc., Chem. Commun.* **1977**, 605. b) Mingos, D. M. P.; Forsyth, M. I. *J. Chem. Soc., Dalton Trans.* **1978**, 1363.

11. Colquhoun, H. M.; Greenhough, T. J.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* **1978**, 303.
12. a) $\theta = 1.4^\circ$, $\phi = 1.2^\circ$, $\Delta = 0.05 \text{ \AA}$ for $[\text{Re}(\text{CO})_3\text{C}_2\text{B}_9\text{H}_{11}]^-$. Zalkin, A.; Hopkins, T. E.; Templeton, D. H. *Inorg. Chem.* **1966**, *5*, 1189. b) $\Delta = 0.05 \text{ \AA}$ for $[(\text{PPh}_3)_2\text{RhC}_2\text{B}_9\text{H}_{11}]^-$. Walker, J. A.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1985**, *24*, 2688. c) $\theta + \phi = 9.7^\circ$, $\Delta = 0.26 \text{ \AA}$ for $(\text{PMe}_3)_2\text{PdC}_2\text{B}_9\text{H}_{11}$. Colquhoun, H. M.; Greenhough, T. J.; Wallbridge, M. G. H. *J. Chem. Soc., Chem. Commun.* **1978**, 322.
13. a) $\theta + \phi = 14.5^\circ$, $\Delta = 0.52 \text{ \AA}$ for $[\text{C}_2\text{H}_4(\text{NMe}_2)_2]\text{PdC}_2\text{B}_9\text{H}_{11}$. Reference 12c. b) $\theta = 4.7^\circ$, $\phi = 4.4^\circ$, $\Delta = 0.42 \text{ \AA}$ for $(\text{PEt}_3)_2\text{PtC}_2\text{B}_9\text{H}_{11}$. Reference 10. c) $\theta = 7.7^\circ$, $\phi = 9.5^\circ$, $\Delta = 0.5 \text{ \AA}$ for $(\text{S}_2\text{CNEt}_2)\text{AuC}_2\text{B}_9\text{H}_{11}$. Reference 11 and Colquhoun, H. M.; Greenhough, T. J.; Wallbridge, M. G. H. *J. Chem. Soc., Chem. Commun.* **1976**, 1019.
14. The mean M-C/M-B distances ratio for the *closo* icosahedral metallocarboranes excluding the *commo* systems: a) 0.97 in $(\text{PPh}_3)_2(\text{HSO}_4)\text{RhC}_2\text{B}_9\text{H}_{11}$. Kalb, W. C.; Teller, R. G.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1979**, *101*, 5417. b) 0.99 in $(\text{PPh}_3)(\text{Br}_2)\text{RhC}_2\text{B}_9\text{H}_{11}$. Zheng, L.; Baker, R. T.; Knobler, C. B.; Walker, J. A.; Hawthorne, M. F. *Inorg. Chem.* **1983**, *22*, 3350. c) 0.99 in $[\text{Re}(\text{CO})_3\text{C}_2\text{B}_9\text{H}_{11}]^-$. Reference 12a. d) 0.99 in $(\text{PPh}_3)_2\text{HRhC}_2\text{B}_9\text{H}_{11}$. Hardy, G. E.; Callahan, K. P.; Strouse, C. E.; Hawthorne, M. F. *Acta Cryst.* **1976**, *B32*, 264. e) 1.0 in $(\text{PPh}_3)(\text{NO}_3)\text{RhC}_2\text{B}_9\text{H}_{11}$. Demidowicz, Z.; Teller R. G.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1979**, 831. f) 1.01 in $[(\text{PPh}_3)_2\text{RhC}_2\text{B}_9\text{H}_{11}]^-$. Reference 12b. g) 1.02 in $(\text{PPh}_3)(\text{CO})\text{RhC}_2\text{B}_9\text{H}_{10}(\text{C}_5\text{H}_5\text{N})$. Teller, R. G.; Wilczynski, J.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1979**, 472. h) 1.02 and 1.03 in $[(\text{PPh}_3)\text{RhC}_2\text{B}_9\text{H}_{11}]_2$. Reference 3a,b. i) 1.08 in $(\text{PMe}_3)_2\text{PdC}_2\text{B}_9\text{H}_{11}$. Reference 12c.

15. The mean M-C/M-B distances ratio for the slipped icosahedral metallocarboranes excluding the *commo* systems: a) 1.13 in $(\text{PEt}_3)_2\text{PtC}_2\text{B}_9\text{H}_{11}$. Reference 13b. b) 1.20 in $[\text{C}_2\text{H}_4(\text{NMe}_2)_2]\text{PdC}_2\text{B}_9\text{H}_{11}$. Reference 13a. c) 1.26 in $(\text{S}_2\text{CNEt}_2)\text{AuC}_2\text{B}_9\text{H}_{11}$. References 11 and 13c.
16. For **4**, the values of θ , ϕ , Δ and the M-C/M-B ratio are 2.4° , 1.6° , 0.21 \AA and 1.07, respectively.
17. Colquhoun, H. M.; Greenhough, T. J.; Wallbridge, M. G. H. *J. Chem. Soc., Chem. Commun.* **1977**, 737.
18. Colquhoun, H. M.; Greenhough, T. J.; Wallbridge, M. G. H. *Acta Cryst.* **1978**, B34, 2373.
19. Cotton, F. A.; Takats, J. *J. Am. Chem. Soc.* **1970**, 92, 2353.
20. a) Reference 3d and references cited therein. b) Mehrotra, P. K.; Hoffmann, R. *Inorg. Chem.* **1978**, 17, 2187 and references cited therein. c) Pasquali, M.; Floriani, C.; Gaetani-Maufredotti, A.; Guastini, C. *J. Am. Chem. Soc.* **1981**, 103, 185.
21. Hock, A. A.; Mills, O. S. *Acta Cryst.* **1961**, 14, 139.
22. a) Chin, H. B.; Bau, R. *J. Am. Chem. Soc.* **1973**, 95, 5068. b) Dettlaf, G.; Weiss, E. *J. Organometal. Chem.* **1976**, 108, 213.

Department of Chemistry and Biochemistry
University of California, Los Angeles
Los Angeles, California 90024

Youngkyu Do
Han Chyul Kang
Carolyn B. Knobler
M. Frederick Hawthorne*

Figure Captions

Figure 1. Structure of $[(PPh_3)_2Cu_2(\mu-H)_2C_2B_9H_9]$ (3) showing atom-labeling scheme. Labeling of phenyl rings and all hydrogen atoms except the bridging hydrides have been omitted for clarity. Selected values of interatomic distances (Å) and angles (deg): Cu(01)-Cu(03), 2.576(1); Cu(01)-P(02), 2.197(1); Cu(03)-P(01), 2.164(1); Cu(03)-C(C₂B₃ face), 2.331(4), 2.280(4); Cu(03)-B(C₂B₃ face), 2.226(5), 2.164(5), 2.140(5); Cu(01)-B(C₂B₃ face), 2.173(5), 2.210(4); P(01)-Cu(03)-B(10), 162.5(1).

Figure 2. Structure of $[(PPh_3)CuC_2B_9H_{11}]^-$ (4) showing atom-labeling scheme. Selected values of interatomic distances (Å) and angles (deg): Cu(03)-P(01), 2.147(2); Cu(03)-C(C₂B₃ face), 2.316(6), 2.317(6); Cu(03)-B(C₂B₃ face), 2.181(7), 2.167(7), 2.116(7); P(01)-Cu(03)-B(10), 162.9(1).

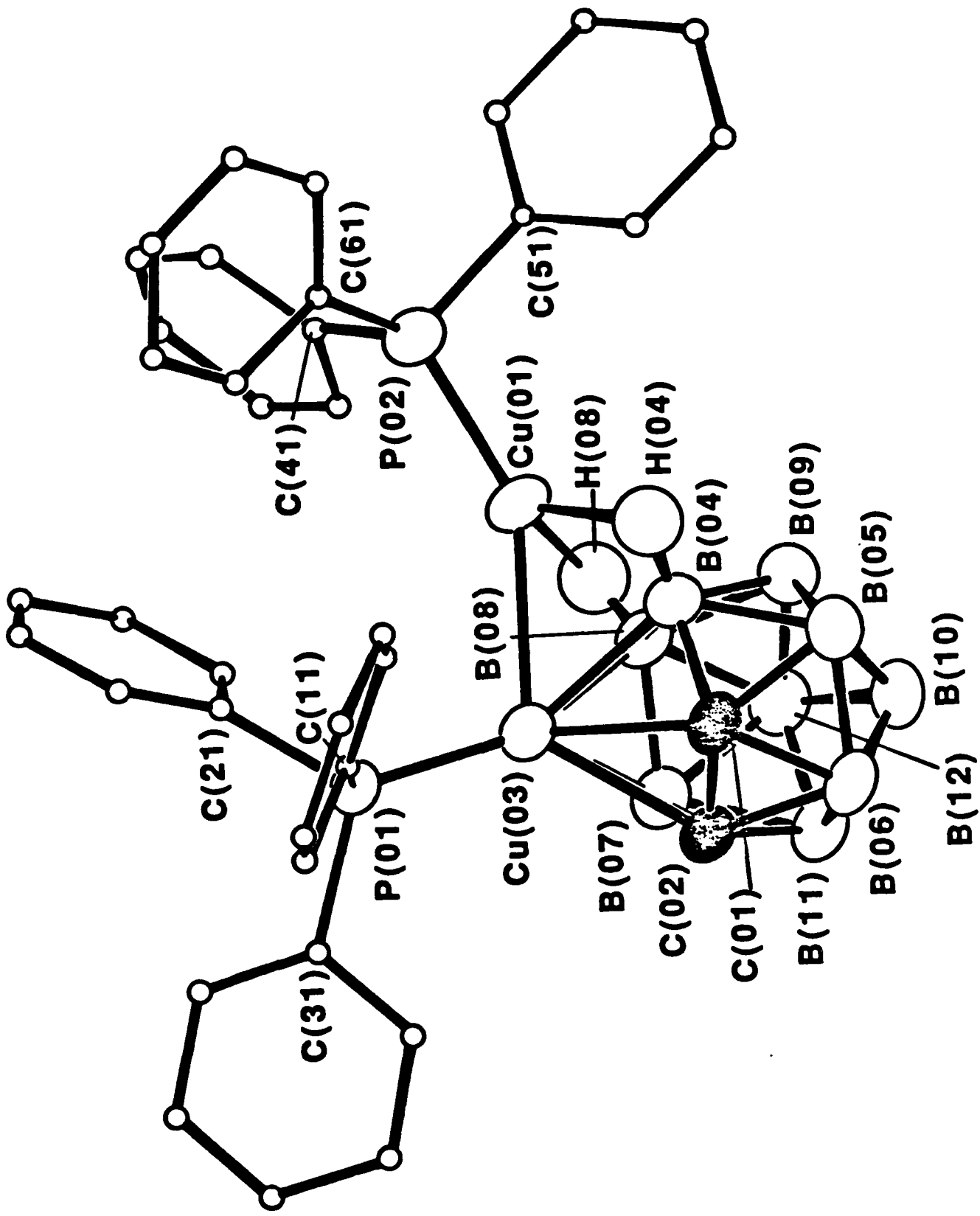
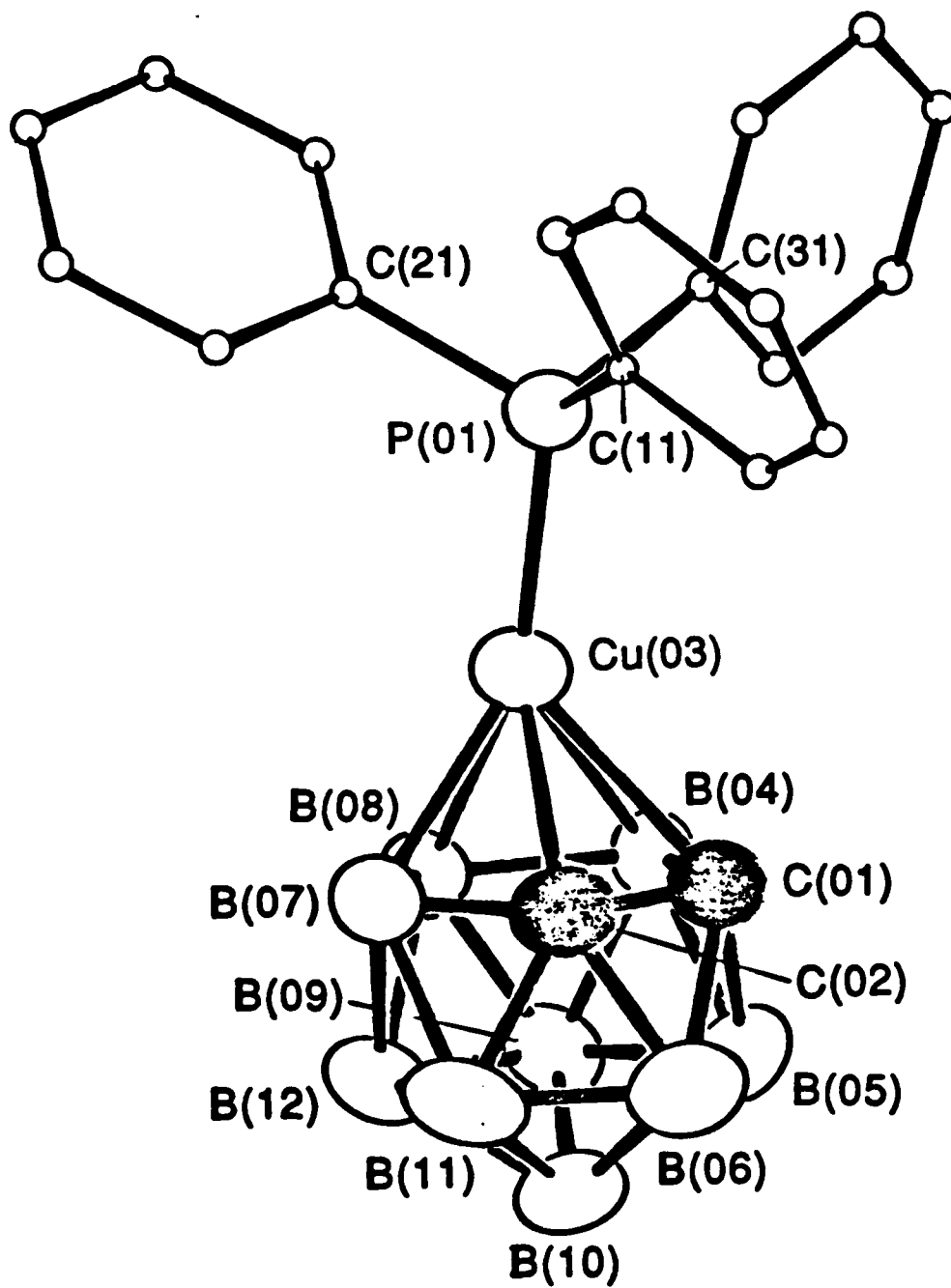


Fig #2



TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 1113 800 N. Quincy Street Arlington, Virginia 22217-5000	2	Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Dr. Bernard Douda Naval Weapons Support Center Code 50C Crane, Indiana 47522-5050	1	Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko, Code L52 Port Hueneme, California 93401	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12 high quality	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
DTNSRDC Attn: Dr. H. Singerman Applied Chemistry Division Annapolis, Maryland 21401	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1

END

8-87

DTIC