$$\{\text{triol}\}(\text{ClO}_4)_3\text{:}\quad |J\ (P)| = |J_0| + (0.7 \pm 0.1\ \text{cm}^{-1}\ \text{kbar}^{-1}\ P)$$

$$\{\text{rhodo}\}\text{Cl}_5\cdot\text{H}_2\text{O}\text{:}\quad |J\ (P)| = |J_0| + (0.15 \pm 0.02\ \text{cm}^{-1}\ \text{kbar}^{-1}\ P)$$

The zero subscript refers to ambient pressure. The biquadratic parameter j is pressure-independent for both complexes within the experimental accuracy of our measurements. Considering that J_0 is −64 and −15.2 cm^{-1} for {triol}$(ClO_4)_3$ and {rhodo}$Cl_5{\cdot}H_2O$, respectively, the relative increase of $|J|$ with pressure is practically the same for the two complexes.

We can estimate the pressure dependence of the molecular structure, i.e. the local compressibility from the observed shift of the spin-allowed $^4A_2 \rightarrow {}^4T_2$ band in the crystal absorption spectrum under applied pressure. Approximating the ligands as point charges and assuming an isotropic compression, we can calculate the compressibility of the complex with volume V, which is defined as

$$\chi = -(1/V)\mathrm{d}V/\mathrm{d}P \qquad (2)$$

We obtain 10×10^{-4} and 6×10^{-4} kbar^{-1} for {triol}$^{3+}$ and {rhodo}$^{5+}$, respectively. The {triol}$^{3+}$ complex appears to be significantly more compressible than the {rhodo}$^{5+}$ complex. The relative increase of the exchange parameter with decreasing volume is given by

$$-(V/J)(\mathrm{d}J/\mathrm{d}V) = (1/\chi J)(\mathrm{d}J/\mathrm{d}P) \qquad (3)$$

Insertion of the experimental values of χ, J, and $\mathrm{d}J/\mathrm{d}P$ leads to the following relative volume dependences: 10.9 and 16.4 for {triol}$^{3+}$ and {rhodo}$^{5+}$, respectively.

The antiferromagnetic part of the exchange parameter J can be interpreted as "kinetic exchange",[6] and as such it is related to one-electron-transfer integrals which can be estimated by a molecular orbital calculation.[7] For a chromium(III) pair we have[8]

$$J = -\frac{1}{18U}\sum_{i=1}^{3}(e_i^- - e_i^+)^2 \qquad (4)$$

where i numbers the singly occupied t_2 orbitals on a single chromium(III) center. e_i^- and e_i^+ are the energies of MO's built from the minus and plus combinations of the magnetic orbitals i. U is the electron-transfer energy, a slowly varying quantity as a function of distortions. We performed extended Hückel MO calculations[9] for both complexes in their ambient and compressed geometries and obtained the following values for the relative volume dependence ($-(V/J)(\mathrm{d}J/\mathrm{d}V)$): 3.1 and 6.3 for {triol}$^{3+}$ and {rhodo}$^{5+}$, respectively. Both these values are approximately a factor of 3 smaller than those dedudced experimentally, 10.9 and 16.4, respectively. Part of this discrepancy may be due to our assumption of an isotropic local compressibility. But it is clear that the extended Hückel technique is not able to reproduce the pressure dependence quantitatively. However, it is significant that the greater relative volume dependence of J in the {rhodo}$^{5+}$ complex is correctly obtained in the calculation.

Acknowledgment. We are indebted to P. Chaudhuri and K. Wieghardt from the University of Bochum for providing {triol}$(ClO_4)_3$. Financial support by the Swiss National Science Foundation is acknowledged.

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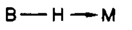
Cupracarboranes Containing a *closo*-$Cu^IC_2B_9$ Geometry. Synthesis and Structure of $[(PPh_3)CuC_2B_9H_{11}]^-$ and $[(PPh_3)_2Cu_2(\mu\text{-}H)_2C_2B_9H_9]$

Sir:

An additional manifestation of the versatile electron-donor ability of $[nido\text{-}7,8\text{-}C_2B_9H_{11}]^{2-}$ (**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)$_2$Al(C_2H_5)$_2$-3,1,2-$AlC_2B_9H_9$)(3′,1′,2′-$AlC_2B_9H_{11}$)] (**2**),[3c,4] in which the bridging BH units stem from the upper and 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]



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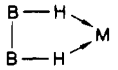

II

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 salt[6] 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-$CuC_2B_9H_9$] (**3**; white; 79%) or mononuclear (PPN)[*closo*-3-(PPh_3)-3,1,2-$CuC_2B_9H_{11}$] ((PPN)**4**; off-white; 84%). Both compounds were characterized by single-crystal X-ray analyses[7] as well as other means.[8]

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(4) The bridging unit II is not uncommon in metallaboranes or in mononuclear metallacarboranes. Examples include the following. (a) $Cu_2(PPh_3)_4(B_{10}H_{10})$: Gill, J. T.; Lippard, S. J. *Inorg. Chem.* **1975**, *14*, 751. (b) $HMn_3(CO)_{10}(BH_3)_2$: Kaesz, H. D.; Fellman, W.; Wilkes, G. R.; Dahl, L. F. *J. Am. Chem. Soc.* **1965**, *87*, 2753. (c) *exo-nido*-(Phosphine)rhodacarboranes: 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 $[(PPh_3)CuC_2B_9H_{10}(NC_5H_5)]$, 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.

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(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 Kα radiation, to a maximum 2θ value 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; β = 92.664 (6) [90.284 (2)]°; V = 3924 [5227] Å^3; 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 computer of the J. D. McCullough Crystallography Laboratory using the UCLA Crystallography Package.

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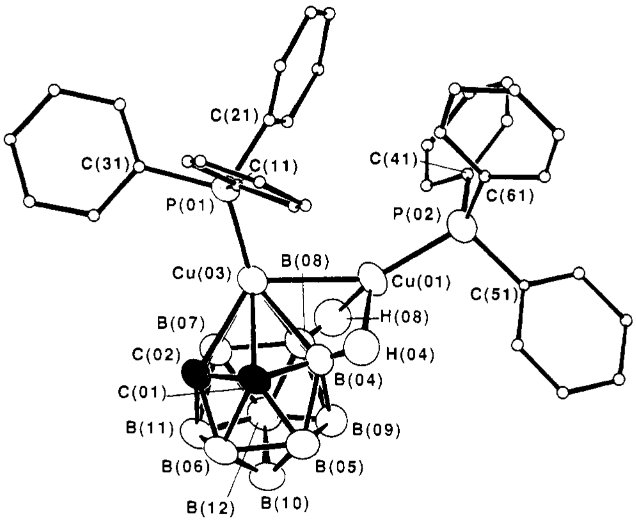

Figure 1. Structure of $[(PPh_3)_2Cu_2(\mu\text{-}H)_2C_2B_9H_9]$ (**3**) showing atom-labeling scheme. Labeling of phenyl rings and all hydrogen atoms except the bridging hydrides have been omitted for clarity. Selected values of interatomic distances (Å) and angles (deg): Cu(01)–Cu(03), 2.576 (1); Cu(01)–P(02), 2.197 (1); Cu(03)–P(01), 2.164 (1); Cu(03)–C(C_2B_3 face), 2.331 (4), 2.280 (4); Cu(03)–B(C_2B_3 face), 2.226 (5), 2.164 (5), 2.140 (5); Cu(01)–B(C_2B_3 face), 2.173 (5), 2.210 (4); P(01)–Cu(03)–B(10), 162.5 (1).

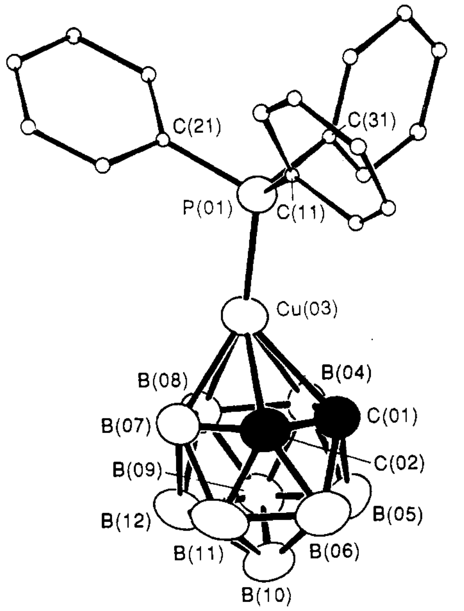

Figure 2. Structure of $[(PPh_3)CuC_2B_9H_{11}]^-$ (**4**) showing atom-labeling scheme. Selected values of interatomic distances (Å) and angles (deg): Cu(03)–P(01), 2.147 (2); Cu(03)–C(C_2B_3 face), 2.316 (6), 2.317 (6); Cu(03)–B(C_2B_3 face), 2.181 (7), 2.167 (7), 2.116 (7); P(01)–Cu(03)–B(10), 162.9 (1).

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 that are incorporated into one carborane cage via the open pentagonal C_2B_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 the case for **2**, such that the plane of Cu(01)–B(04)–B(08) forms a dihedral angle of 40.9° with the pentagonal C_2B_3 plane (±0.016 Å) and the interatomic distance between two copper(I) ions of formal d^{10} 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 $Cu(03)C_2B_9$ 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] folding,[10] and tilting[5,11] distortions. The parameters that 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_2B_9 cages. Nevertheless, the structural analysis favors closo geometry for the $Cu(03)C_2B_9$ cage of **3**. In **3**, the lower B_5 plane is nearly planar (±0.004 Å) while the upper C_2B_3 plane experiences a minor distortion with 2.3 and 1.1° for the folding parameters[10] 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 metallacarboranes[12] rather than slipped metallacarboranes.[13] The interaction of copper with the cage via the open C_2B_3 face in **3** is typical of *closo*-MC_2B_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*-$[LCuC_2B_9H_{11}]^-$ 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 adopts closo geometry.[16] The closo geometry for the d^{10} MC_2B_9 icosahedra, in both **3** and **4**, seems to be unusual since a progressive

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(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): ν_{BH} = 2559, 2498 cm^{-1}; ν_{BHCu} = 2327 (weak and broad) cm^{-1}. Chemical shifts upfield of the reference are designated as negative. $^{11}B\{^1H\}$ NMR (160.463 MHz, in dichloromethane, referenced to external $BF_3 \cdot OEt_2$ in C_6D_6): −17.4, −19.7, −22.5, −24.2, −29.7, −31.2 ppm. ^1H NMR (200.133 MHz, in CD_2Cl_2, referenced to residual solvent protons at 5.32 ppm): 2.01 ppm (carborane CH). $^{31}P\{^1H\}$ NMR (81.02 MHz, CD_2Cl_2, referenced to 85% H_3PO_4): 7.9 ppm (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): ν_{BH} = 2571, 2537, 2488, 2418 cm^{-1}. $^{11}B\{^1H\}$ NMR (CH_2Cl_2): −17.2, −20.2, −22.1, −23.0, −24.9, −34.9 ppm. ^1H NMR (in CD_2Cl_2): 1.57 ppm (carborane CH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 20.6 (PPN), 7.8 ppm (PPh_3).

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(12) (a) θ = 1.4°, ϕ = 1.2°, and Δ = 0.05 Å for $[Re(CO)_3C_2B_9H_{11}]^-$: Zalkin, A.; Hopkins, T. E.; Templeton, D. H. *Inorg. Chem.* **1966**, *5*, 1189. (b) Δ = 0.05 Å for $[(PPh_3)_2RhC_2B_9H_{11}]^-$: Walker, J. A.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1985**, *24*, 2688. (c) $\theta + \phi$ = 9.7° and Δ = 0.26 Å for $(PMe_3)_2PdC_2B_9H_{11}$: Colquhoun, H. M.; Greenhough, T. J.; Wallbridge, M. G. H. *J. Chem. Soc., Chem. Commun.* **1978**, 322.

(13) (a) $\theta + \phi$ = 14.5° and Δ = 0.52 Å for $[C_2H_4(NMe_2)_2]PdC_2B_9H_{11}$: Reference 12c. (b) θ = 4.7°, ϕ = 4.4°, and Δ = 0.42 Å for $(PEt_3)_2PtC_2B_9H_{11}$: Reference 10. (c) θ = 7.7°, ϕ = 9.5°, and Δ = 0.5 Å for $(S_2CNEt_2)AuC_2B_9H_{11}$: Reference 11. Colquhoun, H. M.; Greenhough, T. J.; Wallbridge, M. G. H. *J. Chem. Soc., Chem. Commun.* **1976**, 1019.

(14) The mean M–C/M–B distance ratio for the closo icosahedral metallacarboranes excluding the commo systems are as follows: (a) 0.97 in $(PPh_3)_2(HSO_4)RhC_2B_9H_{11}$: Kalb, W. C.; Teller, R. G.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1979**, *101*, 5417. (b) 0.99 in $(PPh_3)(Br_2)RhC_2B_9H_{11}$: Zheng, L.; Baker, R. T.; Knobler, C. B.; Walker, J. A.; Hawthorne, M. F. *Inorg. Chem.* **1983**, *22*, 3350. (c) 0.99 in $[Re(CO)_3C_2B_9H_{11}]^-$: Reference 12a. (d) 0.99 in $(PPh_3)_2HRhC_2B_9H_{11}$: Hardy, G. E.; Callahan, K. P.; Strouse, C. E.; Hawthorne, M. F. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 264. (e) 1.0 in $(PPh_3)(NO_3)RhC_2B_9H_{11}$: Demidowicz, Z.; Teller, R. G.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1979**, 831. (f) 1.01 in $[(PPh_3)_2RhC_2B_9H_{11}]^-$: Reference 12b. (g) 1.02 in $(PPh_3)(CO)RhC_2B_9H_{10}(C_5H_5N)$: Teller, R. G.; Wilczynski, J.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1979**, 472. (h) 1.02 and 1.03 in $[(PPh_3)RhC_2B_9H_{11}]_2$: Reference 3a,b. (i) 1.08 in $(PMe_3)_2PdC_2B_9H_{11}$: Reference 12c.

(15) The mean M–C/M–B distance ratios for the slipped icosahedral metallacarboranes excluding the commo systems are as follows: (a) 1.13 in $(PEt_3)_2PtC_2B_9H_{11}$: Reference 13b. (b) 1.20 in $[C_2H_4(NMe_2)_2]PdC_2B_9H_{11}$: Reference 13a. (c) 1.26 in $(S_2CNEt_2)AuC_2B_9H_{11}$: 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 Å, and 1.07, respectively.

opening of the MC_2B_9 metallacarborane cage has been pointed out[5] as a trend in the structural changes for the isoelectronic 18-electron series $[Re(CO)_3C_2B_9H_{11}]^-$,[12a] $[Au(S_2CNEt_2)C_2B_9H_{11}]$,[11,13c] $[Hg(PPh_3)C_2B_9H_{11}]$,[5,17] and $[TlC_2B_9H_{11}]^-$.[17,18] However, this geometry has been anticipated as a possible structure for $(PPh_3)CuC_2B_9H_{10}(C_5H_5N)$[5] by analogy with the known η^5 structure of $(PPh_3)Cu(C_5H_5)$.[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_n^{n+} (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 $[Cu_2(tmen)_2(\mu\text{-}CO)(\mu\text{-}PhCO_2)]^+$ 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 $MC_2B_9H_{11}$ 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 $Fe_2(CO)_6C_4(CH_3)_2(OH)_2$[21] 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 $^{31}P\{^1H\}$ 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. We gratefully acknowledge the support of this work by the Office of Naval Research. We also thank Dr. A. Varadarajan for informative discussions.

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

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Articles

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Charge Density and Bonding in Bis(dihydrodi-1-pyrazolylborato)nickel(II): $X - X_{HO}$, Multipolar Analysis, and ab Initio Calculation

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Bis(dihydrodi-1-pyrazolylborato)nickel(II), $[H_2B(C_3N_2H_3)_2]_2Ni^{II}$, crystallized in the orthorhombic space group *Pbca* with a = 17.484 (4) Å, b = 14.534 (3) Å, c = 6.324 (2) Å (room temperature parameters), and Z = 4. The valence electron distribution in this complex has been studied by experimental and theoretical methods. The experimental density distribution was investigated by using two sets of accurate diffraction data collected at 183 and 150 K and analyzed with the atomic multipole technique. Electron density is in excess along the diagonal of the Ni–N directions and along the axis perpendicular to the molecular NiN_4 plane; other deformation density features are observed in the pyrazolyl ring and in the nitrogen lone-pair region. Atomic charge densities (in electrons) are as follows: Ni, +1.06; N(1), −0.32; N(2), −0.26; B, +0.45; C(3), +0.03; C(4), −0.24; C(5), −0.13. Ab initio theoretical calculations are in agreement with the experimental results although atomic charges are predicted to be slightly smaller (in absolute value).

Introduction

Highly accurate, low-temperature, very high angle X-ray diffraction has become a widely used technique to obtain information on the mechanism of bond formation in rather large molecules which are difficult to handle with ab initio methods. Moreover, this technique can supply information on atomic charges and electron densities that is difficult to obtain with other techniques. However, in order to have reliable information, particular attention must be paid to the experimental part: automatic diffractometer, cooling device, and intense-radiation source. These instruments are now generally available, but not everywhere; nevertheless, this is an organization problem and not a scientific one. Moreover, the least-squares refinements with multipole density functions, describing the atomic deformations upon bond formation, produce enhanced Fourier maps virtually free from random noise. The electronic structure of NiN_4 square-planar complexes has been studied extensively not only by theoretical calculations ranging from extended Hückel[1] to CNDO/INDO[2] methods but also by experimental techniques.[3] X-ray diffraction

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