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Novel *exo-nido*-Cupracarborane with an Unusual Solution Fluxionality. Synthesis and Structure of [9,10-*exo*-{Cu(PPh$_3$)$_2$}-9,10-(μ-H)$_2$-7,8-*nido*-C$_2$B$_9$H$_{10}$]

Young-Whan PARK, Jinkwon KIM, Sangsoo KIM,[†] and Youngkyu DO[*]
Department of Chemistry and Center for Molecular Science, KAIST,
373-1 Kusung-dong, Taejon 305-701, Korea
[†]Lucky Central Research Institute, Taejon 302-343, Korea

Synthetic routes to [9,10-*exo* -{Cu(PPh$_3$)$_2$}-9,10-(μ-H)$_2$-7,8-*nido*-C$_2$B$_9$H$_{10}$] which displays an unusual solution dynamic property have been devised. The molecular structure and composition of the novel d^{10} *exo-nido*-cupracarborane, established by single-crystal X-ray analysis and ^{11}B NMR spectroscopy, reveal the η^2-hapticity of *nido*-C$_2$B$_9$ cage toward an *exo*-Cu(PPh$_3$)$_2$ moiety as well as the presence of the 12th H atom.

In recent years, the use of dicarbollide cluster has been directed toward the biomedical application$^{1)}$ as well as the synthesis of unique main group,$^{2)}$ lanthanide and alkaline-earth metallacarboranes,$^{3)}$ and metallacarborands.$^{4)}$ Particularly, developments of the heterodicarborane chemistry of the main group elements have proceeded largely in the form of π-complexes,$^{2a,5-8)}$ resulting in the paucity of recent work on the σ-coordination dicarborane chemistry. Prompted by this and recent demonstration$^{9)}$ on the use of d^{10} *endo*-auracarborane,$^{10)}$ we have directed part of our efforts toward the synthesis of new σ-bonded metallacarboranes of d^{10} group 11 metals and heavier group 14 atoms in the formal +4 state, leading to the observations of *exo*-σ-bonded dimeric argentacarboranes [9,9'-*exo*-{Ag(EPh$_3$)$_2$}$_2$-4,9,4',9'-(μ-H)$_4$-7,8,7',8'-*nido*-(C$_2$B$_9$H$_{10}$)$_2$] (E = As; Sb)$^{11)}$ and *endo*-σ-bonded group 14 heterodicarboranes [10-*endo*-(MPh$_3$)-10-μ-H-7,8-*nido*-C$_2$B$_9$H$_{10}$]$^-$ (M = Ge; Sn).$^{12)}$ Described herein are brief accounts of synthesis, structure and solution fluxionality of *exo*-η^2-bonded cupracarborane [9,10-*exo*-{Cu(PPh$_3$)$_2$}-9,10-(μ-H)$_2$-7,8-*nido*-C$_2$B$_9$H$_{10}$] (**1**).

The neutral compound **1** can be prepared via two reaction routes outlined in Scheme 1. The path **A** and

$$\mathrm{Tl_2C_2B_9H_{11}}\ \underset{\textbf{A}}{\xrightarrow[\mathrm{THF}]{\mathrm{Mn(CO)_5Br}}\ \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{CuCl(PPh_3)_3}}}\ \mathbf{1}\ \underset{\textbf{B}}{\xleftarrow{\mathrm{FeCl_2}}\ \xleftarrow[\mathrm{THF}]{\mathrm{CuCl(PPh_3)_3}}}\ \mathrm{Tl_2C_2B_9H_{11}}$$

Scheme 1 .

B afforded analytically pure$^{13)}$ **1** in the yields of 33 and 19%, respectively. In a typical anaerobic run for the path **A**, an orange solution generated by stirring the equimolar slurry of $Tl_2C_2B_9H_{11}$ (0.5 mmol) and $Mn(CO)_5Br$ in 20 mL of THF for 12 h at room temperature was added to a slurry of $CuCl(PPh_3)_3$ (0.5 mmol) in 10 mL of CH_2Cl_2, resulting in the immediate color change to greenish yellow and the formation of grey precipitate. After the reaction mixture was stirred for 5 h at ambient temperature, blue-grey solid was removed and the concentrated filtrate was treated with Et_2O. The resulting pale greenish yellow crystalline solids were collected, washed with Et_2O and recrystallized from CH_2Cl_2–Et_2O, affording 120 mg of white crystalline **1**.

The crystal structure$^{14)}$ of **1** consists of two enantiomers related by an inversion center to form a racemic system. The molecular structure of **1**, shown in Fig. 1, contains a cationic $[Cu(PPh_3)_2]^+$ unit that is incorporated into the carborane cage via two Cu–B interactions and two B–H–Cu bridge bonds. The asymmetric dihapticity of the boron atoms of the carborane ligand, illustrated in Fig. 2, is manifested as varying Cu–B distances (2.233 and 2.413 Å) and Cu–H distances (1.869 and 2.364 Å), resulting in C_1 symmetry nature. It is noteworthy that boron atoms involved in both B–H–Cu bridge bonds stem from the open pentagonal C_2B_3 plane of the carborane cage. The metal-to-carborane cage bonding pattern observed in **1** is similar to those observed in [9,10-*exo*-{(μ-H)$_2$AlEt$_2$}-7,8-*nido*-$C_2B_9H_{10}$],$^{15)}$ [*closo*-*exo*-4,8-{(μ-H)$_2$Cu(PPh$_3$)}-3-(PPh$_3$)-3,1,2-CuC$_2$B$_9$H$_9$],$^{16)}$ and [*exo*-*nido*-9,10-{W(CO)$_2$(η-C$_5$Me$_5$)}-9,10-(μ-H)$_2$-7,8-C$_2$B$_9$H$_8$-7,8-Me$_2$],$^{17)}$ but is quite different from those observed in its heavier congener argentacarboranes.$^{11)}$ The charge neutrality imposed by the crystal structure of **1** indicates the presence of the 12th H atom in the carborane cage and although the identity of this H atom was not confirmed by X-ray analysis, the coupling pattern of the signal at –32.5 ppm in ^{11}B NMR spectra

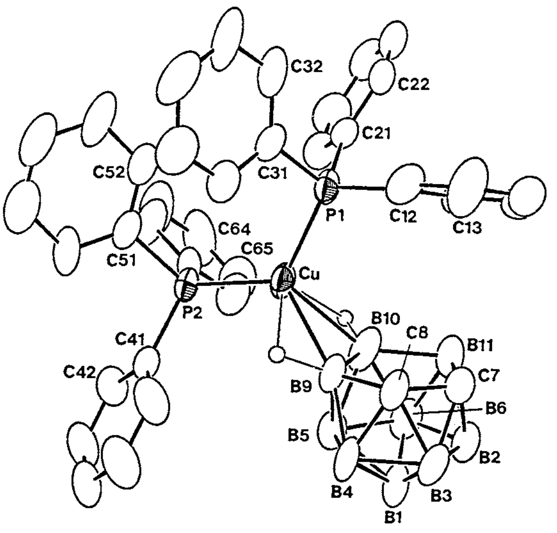


Fig. 1. The molecular structure of [9,10-*exo*-{Cu(PPh$_3$)$_2$}-9,10-(μ-H)$_2$-7,8-*nido*-$C_2B_9H_{10}$] (**1**). The position of the 12th H atom has not been located.

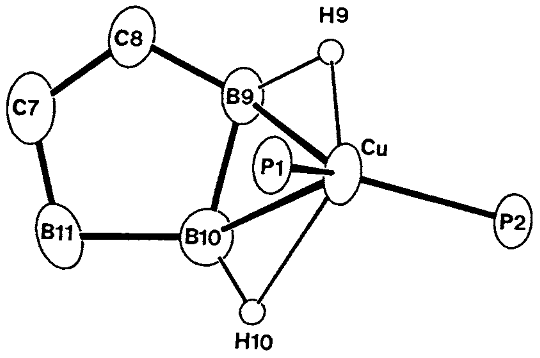
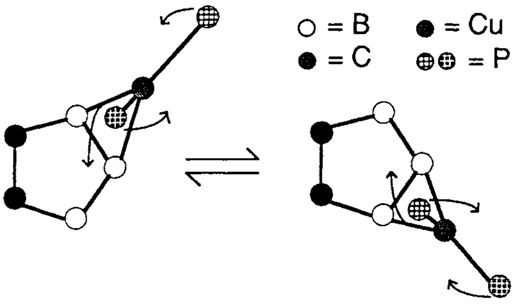


Fig. 2. Projection of CuP_2 fragment of **1** onto the open pentagonal C_2B_3 plane. Dimensions: Cu-P1 2.264(1), Cu-P2 2.271(1), Cu-B9 2.233(4), Cu-B10 2.413(5), Cu-H9 1.869, Cu-H10 2.364, B9-B10 1.788(6), B10-B11 1.843(8), B9-C8 1.562(6), B11-C7 1.638(7), C7-C8 1.548(6) Å; P1-Cu-P2 123.3(1), B9-Cu-B10 45.0(2)°.

(Fig. 3) is clearly in support of its presence.[18)]

The 96.3 MHz $^{11}B\{^{1}H\}$ NMR spectrum of **1** consisting of five distinct resonances is not consistent with the prediction derived from the C_1 solid symmetry of **1**, indicating the presence of a sort of solution dynamic process so that the symmetry of the C_2B_9 cage in solution approaches C_s. The observation of one carboranyl CH proton resonance even at 203 K supports the same solution fluxionality is operative as low as 203 K. In addition, the single appearance of $^{31}P\{^{1}H\}$ NMR resonances at 1.14 ppm as low as 203 K suggests the concomitant occurrence of an another type of fluxional motion which renders two distinguishable phosphorus atoms magnetically equivalent. The foregoing solution spectroscopic properties can be best ascribed to a fluxional pathway consisting of a wigwag fluxional motion and a concurrent position exchange of two PPh_3 groups as shown in Scheme 2.



Scheme 2. A Possible fluxional pathway of **1** in solution.

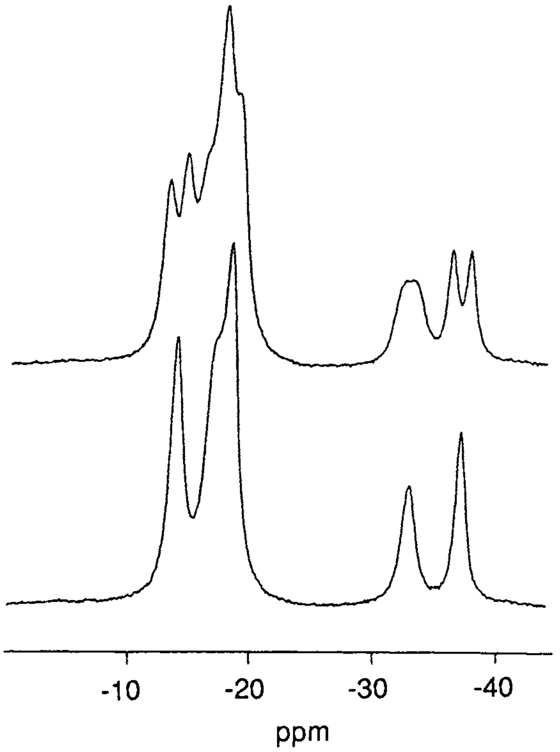


Fig. 3. 96.3 MHz ^{11}B (top) and $^{11}B\{^{1}H\}$ (bottom) NMR spectra of **1** in CH_2Cl_2 at ambient temperature. The shape of the resonance at –32.5 ppm in the top spectrum is indicative of the presence of the 12th H atom on the carborane cage.

Currently, the reactivity of **1** toward replacement of the 12th H atom by its isolobal analogues is under investigation. Support of this work by the Korea Science and Engineering Foundation is gratefully acknowledged.

References

1) M. F. Hawthorne, A. Varadarajan, C. B. Knobler, S. Chakrabarti, R. J. Paxton, B. G. Beatty, and F. L. Curtis, *J. Am. Chem. Soc.*, **112**, 5365 (1990).

2) M. J. Manning, C. B. Knobler, M. F. Hawthorne, and Y. Do, *Inorg. Chem.*, **30**, 3591 (1991); P. Jutzi, D. Wegener, and M. B. Hursthouse, *Chem. Ber.*, **124**, 295 (1991); P. Jutzi, D. Wegener, and M. B.

Hursthouse, *J. Organomet. Chem.*, **418**, 277 (1991).

3) R. Khattar, C. B. Knobler, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **112**, 4962 (1990); *Inorg. Chem.*, **29**, 2191 (1990).

4) X. Yang, C. B. Knobler, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **114**, 380 (1992); *Angew. Chem., Int. Ed. Engl.*, **30**, 1509 (1991).

5) N. S. Hosmane and J. A. Maguire, "Advances in Boron and the Boranes," ed by J. F. Liebman, A. Greenberg and R. E. Williams, VCH Publishers(1988), pp. 297-328.

6) P. Jutzi and P. Galow, *J. Organomet. Chem.*, **319**, 139 (1987); P. Jutzi, *Pure Appl. Chem.*, **62**, 1035 (1990).

7) D. M. Schubert, M. C. Bandman, W. S. Rees, Jr., C. B. Knobler, P. Lu, W. Nam, and M. F. Hawthorne, *Organometallics*, **9**, 2046 (1990); D. M. Schubert, W. S. Rees, Jr., C. B. Knobler, and M. F. Hawthorne, *ibid.*, **9**, 2938 (1990).

8) P. Jutzi, D. Wegener, and M. B. Hursthouse, *Chem. Ber.*, **124**, 295 (1991); *J. Organomet. Chem.*, **418**, 277 (1991).

9) J. A. K. Howard, J. C. Jeffrey, P. A. Jelliss, T. Sommerfeld, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, **1991**, 1664.

10) E. J. M. Hamilton and A. J. Welch, *Polyhedron*, **9**, 2407 (1990).

11) Y.-W. Park, J. Kim, and Y. Do, *J. Chem. Soc., Chem. Commun.*, submitted for publication.

12) J. Kim, S. Kim, and Y. Do, *J. Chem. Soc., Chem. Commun.*, **1992**, 938.

13) Satisfactory elemental analyses for C and H were obtained. Data for **1**: IR (KBr, cm^{-1}, ν_{BH} 2562(s), 2553(s), 2531(s), 2516(s), 2486(s), 2466(s) and ν_{BHCu} 2266(weak and broad); ^{1}H NMR (CDCl$_3$, ppm), 7.43, 7.29, 7.27 (m, phenyl H), 1.77(s, carboranyl CH) and –3.56(s, bridging BH); ^{11}B{^{1}H} NMR (CH$_2$Cl$_2$–10% CDCl$_3$, referenced to external BF$_3$·OEt$_2$, ppm), –13.5, –16.7, –19.0, –32.5 and –36.7; ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$–10% CDCl$_3$, ppm), 1.14.

14) Crystallographic data for **1**: $C_{38}H_{42}B_9CuP_2$, FW = 721.5, triclinic, $P\overline{1}$, a = 11.026(4), b = 13.864(5), c = 13.897(5) Å, α = 92.58(2), β = 106.06(2), γ = 105.70(2)°, V = 1948.7 Å^3, Z = 2, D_c = 1.23 g cm^{-3}, R (R_w) = 0.070(0.080) for 5665 observed data [$F > 6\sigma(F)$]. The diffraction data were collected on Enraf-Nonius CAD4 diffractometer at 293 K in the ω-2θ scan mode using Mo-Kα radiation to a maximum 2θ value of 50° and corrected for Lorentz and polarization effects. The structure were solved with use of heavy atom method (SHELXS 86) and full-matrix least-squares procedures (SHELX 76) on the CRAY-2S/4-128 supercomputer.

15) M. R. Churchill, A. H. Reis, Jr., D. A. T. Young, G. R. Willey, and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, **1971**, 298.

16) Y. Do, H. C. Kang, C. B. Knobler, and M. F. Hawthorne, *Inorg. Chem.*, **26**, 2348 (1987); H. C. Kang, Y. Do, C. B. Knobler, and M. F. Hawthorne, *ibid.*, **27**, 1716 (1988).

17) S. A. Brew, J. C. Jeffrey, M. D. Mortimer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, **1992**, 1365.

18) J. Buchanan, E. J. M. Hamilton, D. Reed, and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, **1990**, 677.

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