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Synthesis of $[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$: A Ligand Analogous to 1,2-Bis(diphenylphosphino)ethane with a "Built-in" Negative Charge

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Summary: An anionic diphosphinocarbaborane derivative with a two carbon atom spacer, 7,8-bis(diphenylphosphino)-7,8-dicarba-nido-undecaborate(1−), has been prepared. Copper complexes incorporating this ligand are presented and include the crystal structure data of $Cu\{PPh_3\}\{Me_2CO\}\{7,8\text{-}[PPh_2]_2\text{-}7,8\text{-}C_2B_9H_{10}\}$*: mol wt 885.7; space group* $P2_1/n$*;* $Z=4$*;* $a=11.028(1)$ *Å;* $b=35.300(10)$ *Å;* $c=12.330(1)$ *Å;* $\beta=102.10(2)°$*;* $R=0.066$ *for 5158 reflections having* $I > 3\sigma(I)$*.*

Our research on the coordination chemistry of macrocyclic derivatives of *exo*-dithiocarbaborane compounds[1] has shown the singularity of their chemistry. Their reactivity resembles that for complexes with diphosphinoalkane ligands and is determined by the presence of S and the length of the exocluster (S,S′) macrocyclic chain.[2] We have observed that the fewer the number of the macrocyclic links, the greater the possibility of a B(3)–M interaction. Some of the relevant features are the finding of a B(3)–Rh σ interaction in $[NMe_4][RhCl\{7,8\text{-}\mu\text{-}S(CH_2CH_2)S\text{-}C_2B_9H_{10}\}\{\sigma\text{-}7,8\text{-}\mu\text{-}S(CH_2CH_2)S\text{-}C_2B_9H_9\}]$[3] and a B(3)–H⇀Ru interaction in $[Ru(PPh_3)_2Cl\{7,8\text{-}\mu\text{-}S(CH_2CH_2)S\text{-}C_2B_9H_{10}\}]$.[4] All metal complex derivatives of these *exo*-dithiocarbaborane ligands contain the five-membered ring $S_a\text{–}M\text{–}S_b\text{–}C_c\text{–}C_c$ as a common feature where C_c indicates the carborane carbon atoms. To get further insight into the mutual influence of an electron rich element and the carbaborane cage, we have studied the reactivity of 7,8-bis(diphenylphosphino)-7,8-dicarba-*nido*-undecaborate(1−) $[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ compounds. Although complexes of 1,2-bis(diphenylphosphino)-*o*-carborane (1) with transition metals, such as nickel(II),[5] cobalt(II),[6] gold(I),[7] platinum(II),[8] palladium(II),[9] chromium, molybdenum, tungsten, iron,[10] and manganese,[11] have been reported, there is no previous report of a discreet complex that incorporates the anion $[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$. We report here the synthesis and characterization of copper complexes with $[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$: $Cu\{PPh_3\}\{7,8\text{-}[PPh_2]_2\text{-}7,8\text{-}C_2B_9H_{10}\}$ (2), $Cu\{PPh_3\}\{Me_2CO\}\{7,8\text{-}[PPh_2]_2\text{-}7,8\text{-}C_2B_9H_{10}\}$ (3), and $[NMe_4][Cu\{PPh_3\}Cl\{7,8\text{-}[PPh_2]_2\text{-}7,8\text{-}C_2B_9H_{10}\}]\cdot Me_2CO$ (4) as well as the molecular structure of 3, the first structurally authenticated example of a complex that incorporates the anion $[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$.

Experimental Section

Instrumentation. Elemental analyses were performed in our analytical laboratory using a Perkin-Elmer 240-B microanalyzer. IR spectra were obtained with KBr pellets on a Nicolet 710-FT spectrophotometer. The ^1H-NMR and ^{11}B-NMR spectra were obtained by using a Bruker AM 400WB instrument.

Materials. Before use, *o*-carborane (Dexsil Chemical Corp.) was sublimed under high vacuum; 1,2-bis(diphenylphosphino)-*o*-carborane (1) was prepared from *o*-carborane according to the literature.[12] A 1.7 M solution of *n*-butyllithium in hexane from Fluka was used as given. $Cu(PPh_3)_2Cl$ was synthesized according to the literature.[13] Ethanol was reagent grade.

Synthesis of $Cu\{PPh_3\}\{7,8\text{-}[PPh_2]_2\text{-}7,8\text{-}C_2B_9H_{10}\}$ (2). $Cu(PPh_3)_2Cl$ (248 mg, 0.398 mmol) was added to a deoxygenated ethanol suspension (50 mL) containing 0.2 g (0, 398 mmol) of $1,2\text{-}\{PPh_2\}_2\text{-}1,2\text{-}C_2B_{10}H_{10}$. The mixture was refluxed under N_2 for 3 h. The resulting white solid was removed by filtration and 117 mg (35.5%) of the analytically pure solid (2) were obtained. FTIR (KBr): ν [cm^{-1}] = 2512, 2520, 2538, 2575 (B–H). ^1H-FTNMR (400 MHz, CD_3COCD_3, 25 °C, TMS): δ −2.1 (s, br, BHB), 7.56, 7.47, 7.32, 7.2 (m, C_{aryl}–H). ^{11}B-FTNMR (128 MHz, CD_2Cl_2, 25 °C, $BF_3\cdot Et_2O$): $\delta = -6.5$ (d, $^1J(B,H) = 61$ Hz, 2B), −13.2 (d, $^1J(B,H) = 115$ Hz, 3B), −17.0 (d, $^1J(B,H) = 80$ Hz, 2B), −30.0 (d, $^1J(B,H) = 81$ Hz, 1B), −35.2 (d, $^1J(B,H) = 138$ Hz, 1B). Anal. Calcd for $C_{44}H_{45}B_9P_3Cu$: C, 63.86; H, 5.48. Found: C, 62.44; H, 5.46.

A colorless crystal suitable for X-ray analysis was grown from acetone (3).

Synthesis of $[NMe_4][Cu\{PPh_3\}Cl\{7,8\text{-}[PPH_2]_2\text{-}7,8\text{-}C_2B_9H_{10}\}]\cdot Me_2CO$ (4). NMe_4Cl was added to a hot deoxygenated methanol suspension (50 mL) containing 0.05 g (0,06 mmols) of 2. The mixture was refluxed under N_2 for 2 h. The mixture was kept at room temperature 15 h longer, and the solvent was evaporated under vacuum. After addition of water (25 mL) a white solid appeared which was removed by filtration. It was

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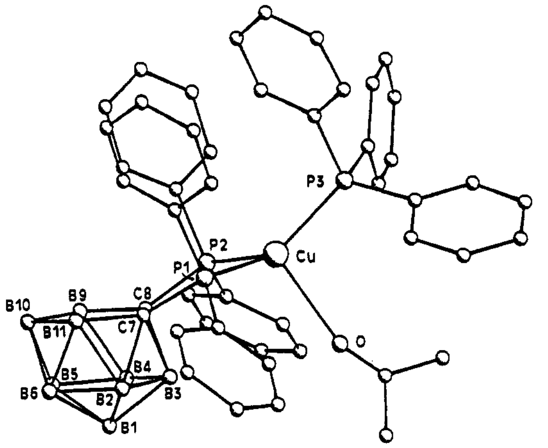

Figure 1. Structure of the Cu(I) complex Cu{PPh$_3$}{Me$_2$CO}{7,8-[PPh$_2$]$_2$-7,8-C$_2$B$_9$H$_{10}$} (**3**). Hydrogen atoms are omitted for clarity.

washed with water, ethanol, and ether. The white solid was recrystallized with acetone/dichloromethane/heptane yielding 40 mg (61%) of the analytically pure crystals (**4**). FTIR (KBr): ν [cm^{-1}] = 2563, 2528 (B–H). ^{1}H-FTNMR (400 MHz, CD$_3$COCD$_3$, 25 °C, TMS): δ -1.97 (s, br, BHB), 3.38 (s, 12, N(CH$_3$)$_4$), 6.85–6.95 (m, 20, C$_{aryl}$–H), 7.12–7.31 (m, 15, C$_{aryl}$–H). ^{11}B-FTNMR (128 MHz, CD$_2$Cl$_2$, 25 °C, BF$_3$·Et$_2$O): δ = -8.7 (s, br, 2B), -14.5 (d, ^1J(B,H) = 122 Hz, 3B), -17.0 (s, br, 2B), -30.8 (d, ^1J(B,H) = 86 Hz, 1B), -35.4 (d, ^1J(B,H) = 132 Hz, 1B). Anal. Calcd for C$_{44}$H$_{45}$B$_9$P$_3$Cu: C, 61.55; H, 6.38; N, 1.41. Found: C, 61.92; H, 6.88; N, 1.37.

Crystal structure data for 3: C$_{47}$H$_{51}$B$_9$OP$_3$Cu, mol wt = 885.7, monoclinic, space group $P2_1/n$, a = 11.028(1) Å, b = 35.300(10) Å, c = 12.330(1) Å, β = 102.10(2)°, Z = 4, d_{calcd} = 1.253 g·cm^{-3}, μ = 18.738 cm^{-1}, Cu Kα (λ = 1.5418 Å), graphite monochromated radiation, Philips PW4 diffractometer, 7565 measured reflections, 7410 independent reflections, 5158 observed reflections ($I > 3\sigma(I)$), empirical absorption correction (DIFABS) (Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158), solution by Patterson (Sheldrick G. M. SHELXS86. Program for crystal structure determination. University of Gottingen, Germany, 1986), anisotropic refinement (Stewart, J. M.; Machin P. A.; Dickinson, D. W.; Ammon, H. L.; Heck, H.; Flack, H. The XRAY76 system—version of January 1980. Computer Science Center, University of Maryland, College Park, MD) for all non-hydrogen atoms, H atoms localized on difference synthesis map and added as fixed isotropic contribution, final R = 0.066 (unit weight). Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, GB-Cambridge CB2 1EW, U.K., on quoting the full journal citation.

Results and Discussion

In order to compare the properties of 7,8-bis(dithio)-7,8-dicarba-*nido*-undecaborate(-1) derivatives with those of [7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$]$^-$, it was necessary to obtain this new nido species form. The reaction of **1** with alkoxide ion[14] does not produce the expected new nido species but yields 7,8-dicarba-*nido*-undecaborate(1–) by C–P cleavage. On the other hand, the reaction carried out in refluxing ethanol yielded **1** unaltered. Other attempts to produce the anion [7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$]$^-$ by using piperidine[15] were unsuccessful. Several other reactions were tested with bases of different strengths but did not yield the expected compound. However, in boiling water and HCO$_3^-$, we did have an indication of partial degradation with carborane–P retention, but this result is still to be fully confirmed. These results suggest why there has never been anything reported concerning the anion [7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$]$^-$ despite the fact that several papers dealing with metal complexes of the closo compound have been published.

Table I. Crystallographic Data

formula	C$_{47}$H$_{51}$B$_9$O$_1$P$_3$Cu$_1$
cryst size (mm)	0.13 × 0.16 × 0.50
symmetry	monoclinic $P2_1/n$
unit cell dimens: a (Å), b (Å), c (Å), α (deg), β (deg), γ (deg)	11.028, 35.300, 12.330, 90, 102.1, 90
packing: V (Å^3), Z, D_c (g.cm^{-1}), M, F(000), μ (cm^{-1})	4693.9, 4, 1.253, 885.7, 1840, 18.738
no. of reflexions:	
measd	7565
ind	7410
obsd	5158 (3σ(I) criterion)
range of hkl	0–12, 0–40, -14 to +14
value of R_{int}	0.066
max–min transm factors	0.864, 1.234
w scheme	unit weight
final R and R_w	0.066, 0.066

Table II. Fractional Atomic Coordinates (×10^4) and Their Estimated Standard Deviations[a]

atom	x	y	z
Cu	6953(1)	1343(2)	2156(7)
P1	8950(1)	1543(4)	2427(1)
P2	7131(1)	1045(4)	0574(1)
P3	6005(1)	1094(4)	3424(1)
O	5769(5)	1914(1)	1666(4)
B1	9227(7)	1872(2)	–0914(6)
B2	9908(7)	1901(2)	0491(6)
B3	8343(7)	1744(2)	0066(6)
B4	8249(7)	1481(2)	–1156(6)
B5	9721(8)	1439(2)	–1441(7)
B6	0783(7)	1705(2)	–0400(7)
B9	9157(7)	1064(2)	–0753(6)
B10	0774(7)	1204(2)	–0385(7)
B11	0797(8)	1479(2)	0889(6)
C7	9389(5)	1500(1)	1079(5)
C8	8457(5)	1257(2)	0139(4)
C401	5288(9)	2559(3)	1494(9)
C402	3746(9)	2086(3)	1813(11)
C403	5005(7)	2158(2)	1655(6)

[a] The coordinates of the phenolic ring carbon atoms are omitted and included as supplementary material.

Recent results obtained in our group have shown that the reaction of "electron rich" d^{10} metal ions Cu(I), Ag(I), and Au(I) with 1′,2′-(1,10-dithio-4,7-dioxadecane)-1′,2′-dicarba-*closo*-dodecaborane in degassed ethyl alcohol leads to partial degradation (removal of the carbon's adjacent boron atom) of the closo species. These results prompted us to pursue the search for the ligand [7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$]$^-$ by using a similar reaction.

When Cu(PPh$_3$)$_2$Cl was allowed to react with **1** in ethanol, a white solid (**2**) was obtained. The IR spectrum (main B–H stretching absorptions at 2538 cm^{-1}), the ^{11}B-NMR spectrum (which shows the characteristic pattern of 7,8-dicarba-*nido*-undecaborate(1–) derivatives (2:3:2:1:1), in the appropriate range of resonances (–6.5 → –35.2 ppm)), and the ^{1}H-NMR spectrum (B–H–B absorption at the range –1.9 → –2.1 ppm) proved the partially degraded nature of the new compound.

The crystal structure of the acetone adduct (**3**) is shown in Figure 1. Some details of the data collection and

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Table III. Selected Bond Distances (Å) and Angles (deg)

Cu–P1	2.270(2)	P3–C301	1.814(5)
Cu–P2	2.259(2)	P3–C307	1.810(7)
Cu–P3	2.234(2)	P3–C313	1.828(6)
Cu–O	2.407(5)	B3–C7	1.740(8)
P1–C7	1.832(6)	B3–C8	1.724(9)
P1–C101	1.825(6)	B9–B10	1.813(11)
P1–C107	1.820(5)	B9–C8	1.620(10)
P2–C8	1.821(6)	B10–B11	1.843(12)
P2–C201	1.820(5)	B11–C7	1.619(10)
P2–C207	1.826(6)	C7–C8	1.624(7)
P3–Cu–O	101.3(1)	B9–B10–B11	101.2(5)
P2–Cu–O	108.3(1)	B10–B11–C7	107.7(5)
P2–Cu–P3	123.9(1)	P1–C7–B3	110.4(4)
P1–Cu–O	103.5(1)	B11–C7–C8	110.8(5)
P1–Cu–P3	126.9(1)	P1–C7–C8	116.3(4)
P1–Cu–P2	90.9(1)	B9–C8–C7	112.7(5)
Cu–P1–C7	105.8(2)	P2–C8–C7	115.7(4)
Cu–P2–C8	106.5(2)	P2–C8–B3	111.8(4)

refinement are given in Table I. Important atom coordinates and isotropic thermal parameters are given in Table II. Important bond distances and angles are listed in Table III.

The single crystal X-ray structure analysis shows that each copper ion resides in a distorted tetrahedral environment provided by three phosphorus atoms (one from PPh_3 and two from the carbaborane moiety) and one oxygen atom (ketone). The three Cu–P distances are comparable (2.26 Å, Cu–P(carbaborane), vs 2.23, Cu–P(PPh_3)). In addition, the P–C(carbaborane) and P–C(aryl) distances are almost identical (1.82 Å). The carbaborane moiety is partially degraded, the vacant position being anti with regard to the acetone ligand. A striking feature is that the dihedral angle between planes $S–C_{carb}–C_{carb}–S$ and S–M–S (w angle)[16] has a value of 159.6°, very close to those found with *exo*-dithiocarbaborane compounds with open or long external chains.[2] This is another proof of the mentioned resemblance between the *exo*-sulfur and *exo*-phosphorus carbaborane compounds.

Consequently, it has been possible to incorporate the anionic ligand $[7,8\text{-}(PPh_2)_2\text{–}7,8\text{-}C_2B_9H_{10}]^-$ into a complex, starting from the corresponding closo ligand. Complex **2** is extremely stable, and the reactive location seems to be the fourth metal coordination. Thus, the acetone adduct (**3**) is obtained upon dissolution of **2** in acetone, or the anionic chloro complex (**4**) is obtained upon treatment of **2** with NMe_4Cl. In any case the CuP_3 moiety is preserved.

Even though we have not yet been able to produce the free ligand $[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$, the possibility of incorporating it into complexes is very high. As indicated, we initially suspected that only d^{10} electron rich complexes would accomplish the removal of B(3) in the closo compound (**1**); however recent results have indicated that, in alcohols, the partial degradation takes place even with non-d^{10} metal ions such as Rh(III) and Pd(II). This easy and straightforward general reaction for the synthesis of complexes containing the ligand $[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ contradicts the lack of data concerning this ligand.

In conclusion the new diphosphino ligand $[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ has been obtained, coordinated to metal complexes. It presents a coordination feature similar to that of the popular 1,2-bis(diphenylphosphino)ethane, but with the advantage of having a "built-in" negative charge which can be very useful in the design of interesting new organometallic compounds.

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Supplementary Material Available: Tables of atomic coordinates, bond distances, bond angles, and interatomic contacts (21 pages). Ordering information is given on any current masthead page.

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(16) Defined as the angle subtended by lines drawn from the midpoint of the S···S vector to the atom M and to the midpoint of the C(carb)···C(carb) vector, respectively.