1095 (w), 1080 (s), 1006 (m), 966 (s), 921 (w), 910 (m), 885 (m), 746 (m), 734 (w), and 721 (m) cm^{-1}.

(c) **$(C_2H_5)_4N[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Pd$ (7).** A mixture of 0.361 g (0.571 mmole) of $[(C_2H_5)_4N]_2$-**5** and 0.215 g (0.580 mmole) of **6** was stirred in 30 ml of dichloromethane for 2 min. The solution, which became deep red, was filtered, hexane was added until crystallization was initiated, and, upon standing for 10 min, 0.373 g (0.744 mmoles, 65%) of $(C_2H_5)_4N$-**7** separated as lustrous brown leaflets. *Anal.* Calcd for $(C_2H_5)_4NPd(B_9C_2H_{11})_2$: Pd, 21.22; B, 38.81; C, 28.74; H, 8.44; N, 2.79. Found: Pd, 22.02; B, 37.96; C, 26.35; H, 8.62; N, 2.18. The compound was very air and moisture sensitive, both in the solid state and in solution. The infrared spectrum (Nujol mull) of $(C_2H_5)_4N$-**7** contained absorptions at 3050 (w), 2533 (s), 1300 (w), 1218 (w), 1181 (m), 1143 (w), 1079 (s), 1031 (w), 1011 (m), 970 (s), 915 (m), 861 (m), 790 (m), 745 (m), and 721 (w) cm^{-1}.

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Carborane Analogs of π-Allyls. The Crystal and Molecular Structure of Triphenylmethylphosphonium Bis((3)-1,2-dicarbollyl)cuprate(III)[1]

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Abstract: The crystal structure of $[(C_6H_5)_3PCH_3]Cu(C_2B_9H_{11})_2$ has been determined from a single-crystal X-ray diffraction study. The triclinic cell $I\bar{1}$ with $a_0 = 11.74$ Å, $b_0 = 15.30$ Å, $c_0 = 19.96$ Å, $\alpha = 97.9°$, $\beta = 94.2°$, and $\gamma = 99.0°$ contains four formula units. The carbametallic anion $Cu(C_2B_9H_{11})_2^-$ (isostructural with the corresponding Cu(I)) is distorted from a π-sandwich configuration by a slippage of the carborane moieties parallel to one another so that the primary coordination sphere of copper is six borons, three from each carborane cage. The molecular symmetry of the anion is C_{2h}, and the copper–boron stereochemistry has a striking likeness to bis(π-allyl)nickel(II). This similarity lends further support to the description of the bonding in the electron-rich carbametallics as π-allylic. Also the bisdicarbollyls of Au(III), Ni(II), and Ni(III) have been shown to be isomorphous with the Cu(III), Cu(II), and Co(III) compounds, respectively. Thus for the 3d metallo bisdicarbollyls, it has been established that the d^8 and d^9 complexes have suffered a slip distortion, while those with seven or less d electrons are symmetrical π sandwiches.

Copper forms a series of electron-rich bisdicarbollyls. These compounds are related by one-electron changes in oxidation state, the formal metal valence ranging from one to three.[2]

A very unusual and interesting stereochemistry was revealed in the structure of the middle member of this series,[3] in which a severe slip distortion from the geometry of a π-sandwich compound was extant. From considerations of the molecular geometry, single-crystal visible dichroism, and single-crystal electron spin resonance, a description of the molecule as a carborane analog of a bis(π-allyl) was formulated.

Preliminary molecular orbital calculations indicate that tendencies toward distortion lie in a delicate balance of two factors, the electron-rich nature of the system and the heterocyclic character of the ligand.[4]

Because of the unusual structure observed for the blue copper(II) species, and the possibility of a molecular geometry change in going to Cu(III), as well as the unusual oxidation state for copper (unknown in organometallic chemistry), it was decided to determine the crystal structure of the copper(III) dicarbollide when it became available.

An added attraction was the fact that the copper(III) species is formally isoelectronic with the fully characterized diamagnetic bis(π-allyl)nickel(II),[5] in the same manner that the iron carbametallics are isoelectronic with ferrocene and ferrocenium ion.[6,7]

Experimental Section

Dark blood red needles of the triphenylmethylphosphonium salt of $Cu(C_2B_9H_{11})_2^-$ were provided by Professor M. F. Hawthorne and Mr. L. F. Warren of this department.

Using a polarizing microscope, a very small single crystal (0.4 × 0.04 × 0.01 mm) was selected and mounted in a borosilicate capillary. The crystals are dichroic, changing in color from dark red to orange. This dichroism was surveyed using a Donnay optical analyzer, and its relationship to the structure will be discussed below.

Precession (Mo Kα) and Weissenberg (Cu Kα) photographs indicated that the crystal was triclinic with $a_0 = 11.74$ Å, $b_0 = 15.30$ Å, $c_0 = 19.96$ Å, $\alpha = 97.9°$, $\beta = 94.2°$, $\gamma = 99.0°$. Systematic absences for $h + k + l = 2n + 1$ indicated a body-centered unit cell. A Delaunay reduction failed to reveal any hidden symmetry, so the centered triclinic cell was retained as this was the most con-

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[1] Supported by an intramural grant of the University of California, and in part by the National Science Foundation under Grant GP-8055.

[2] (a) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling. A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *J. Am. Chem. Soc.*, **90**, 879 (1968); (b) L. F. Warren. Jr., and M. F. Hawthorne, *ibid.*, **90**, 4823 (1968).

[3] R. M. Wing, *ibid.*, **89**, 5599 (1967).

[4] R. M. Wing. R. Keyes, and M. Rettig, unpublished results.

[5] H. Dietrich and R. Uttech, *Z. Krist.*, **122**, 60 (1965).

[6] M. F. Hawthorne. D. C. Young, and P. A. Wegner. *J. Am. Chem. Soc.*. **87**, 1818 (1965).

[7] A. Zalkin, D. H. Templeton, and T. E. Hopkins. *ibid.*, **87**. 3988 (1965).

venient setting. The space group finally proved to be $I\bar{1}$ with the general fourfold position $\pm(X, Y, Z\colon \frac{1}{2} + X, \frac{1}{2} + Y, \frac{1}{2} + Z)$.

Owing to the instability and limited amount of the compound, no analysis was available. However, from the unit cell volume, measured density (ρ = 1.22 g/cc by flotation in CS_2–C_6H_5Cl), and the assumption of four formula units per cell, a molecular/weight of 632 amu was calculated, indicating $[(C_6H_5)_3PCH_3]Cu(C_2B_9H_{11})_2$ (mol wt = 627 amu) as the most reasonable composition.

Reflections were collected for $0kl$ through $7kl$ out to $\sin\theta = 0.7$ (Cu Kα radiation) on a Nonius integrating Weissenberg camera, using a multiple-film technique. Their intensities were estimated visually, by comparison with a set of time exposures of a single reflection prepared previously during the copper(II) carborane structure determination. The data were corrected for Lorentz polarization but not for absorption ($\mu r \sim 0.01$), and the layers were scaled individually during refinement.

All calculations were performed on an IBM 7040 computer having a 32K memory. The Fourier program was a local modification of that developed at the UCLA Crystallographic Laboratories.[8]

The Busing–Martin–Levy ORFLS[9] crystallographic least-squares program as modified by Dahl, Doedens, and Blount for rigid groups and Stucky for anomalous dispersion was used in the refinement. The function $\Sigma w(|F_o| - |F_c|)^2$ was minimized.

The atomic scattering power of copper was corrected for the real part of the anomalous dispersion by −2.1 e and the imaginary part by 0.7 e. Corrections of 0.2 e and 0.5 e were similarly made for P.[10] The atomic scattering powers of Cu(1) and neutral P, C, B, and H were taken from standard tables.[11]

In the last six cycles of refinement, the data were weighted as follows: $F_o \leq 40.0$, $w = 1.0$; $F_o > 40.0$, $w = 40.0/F_o$.[12]

A single crystal of the red complex $(C_6H_5)_3PCH_3Au(C_2B_9H_{11})_2$ upon X-ray examination gave the following cell constants: a_0 = 11.66 Å, b_0 = 15.34 Å, c_0 = 20.06 Å, α = 96.0°, β = 94.5°, γ = 99.2°. Space group $I\bar{1}$ or I1.

The crystal data for the green $(Et_4N)_2Ni^{II}(C_2B_9H_{11})_2$ compound (a_0 = 12.94 Å, b_0 = 9.01 Å, c_0 = 8.60 Å, α = 93.8°, β = 90.8°, and γ = 116.0°) are in accord with that of the bis(dicarbollyl) of copper(II).[3]

Because the Ni(II) structure is of critical importance in the scheme of things, intensity data were collected for the $[h0l]$ zone on the Weissenberg camera, and for $[hk0]$ and $[0kl]$ zones on a precession camera. These data show no differences from those reported previously for the Cu(II) structure.

Single-crystal X-ray diffraction experiments on the triphenylmethylphosphonium salts of the Co(III) and Ni(III) bis((3)-1,2-dicarbollyls) show that they are isomorphous.

$(C_6H_5)_3PCH_3Co(C_2B_9H_{11})_2$: orthorhombic Pbca, a_0 = 19.90 Å, b_0 = 13.51 Å, c_0 = 24.30 Å.

$(C_6H_5)_3PCH_3Ni(C_2B_9H_{11})_2$: orthorhombic Pbca, a_0 = 20.04 Å, b_0 = 13.51 Å, c_0 = 24.48 Å.

Solution of the Structure

Two potential solutions for the Cu and P atom coordinates were derived from a three-dimensional Patterson map.

The first, with all atoms in the general fourfold positions, gave Cu at (0, $\frac{1}{4}$, 0) and P at (0.03, 0.52, 0.59), would not refine below an R value of 0.35, and resulted in a cation–cation contact which was unreasonably close. This solution was therefore discarded in favor of the second, in which two independent coppers occupy the special twofold $\bar{1}$ sites, one at 0, 0, 0 and the other at 0, $\frac{1}{2}$, 0, and P was placed at 0.03, 0.27, and 0.59.

Two cycles of refinement of the eight film scale factors, the copper isotropic temperature factors, and the phosphorus positional and temperature factors were made at which point the disagreement factor R was 0.49.

A three-dimensional electron density map based on the Cu and P phases revealed all 44 independent nonhydrogen atoms.

Since treatment of all these atoms in a least-squares refinement represents a very large number of parameters, and because the quality of the data does not justify refinement of the benzene rings, the atoms were placed into rigid groups as follows: the phenyl carbons were to be arranged in D_{6h} symmetry with C–C = 1.397 Å, and the carborane cages were assumed to have icosahedral symmetry with B–B = 1.79 Å. Thus at this stage the refinement was for four individual atoms, Cu(1), Cu(2), P, and the methyl C, and five groups.

Seven parameters were assigned to each group. These were three positional coordinates and three rotational parameters ϕ, θ, and ρ defined as successive rotations about Z, X', and Y'' where Z is the original Z axis, X' is the transformed X after the ϕ rotation, and Y'' is the new Y after successive ϕ and θ rotations.[13] An isotropic temperature factor was the seventh group parameter.

Four cycles of refinement lowered the residual to 0.20. Then the group restriction was lifted from the cage atoms and two cycles on their individual positional and temperature factors lowered the residual to 0.17.

The intracage distances were observed to fall into three classes with (for each cage) one short (~1.52 Å), six intermediate (~1.70 Å), and 18 long (~1.80 Å) distances. This enabled us to chose the two carbon atoms from among the 11 atoms of each icosahedron. The temperature parameters were of little value in making this distinction, although they were in agreement.

A difference Fourier map was computed at this point, and all the phenyl hydrogens as well as many of the cage hydrogens were clearly evident at magnitudes of about 0.6 e/Å^3.

The phenyl hydrogens were included with the phenyl groups (*vide supra*), maintaining the symmetry and using C–H = 1.08 Å.

We reverted to group refinement of the cages primarily as a device to place all the cage hydrogens. The groups were reconstructed to have C_s symmetry with C–C = 1.54 Å, C–B = 1.70 Å, and B–B = 1.80 Å, and the hydrogens were radially directed with C–H = 1.1 Å and B–H = 1.2 Å. Individual temperature factors were allowed for the nonhydrogen cage atoms.

Two cycles of refinement depressed the disagreement factor to 0.14.

The group restriction was again lifted from the cage heavy atoms and the residual after four cycles of refinement reached a final value of 0.125. The weighted R is 0.17 and the standard error 7.88. In these final cycles of refinement storage limitations forced separate refinement of organic cation and inorganic anion. The phenyl carbons were assigned individual temperature factors, and the hydrogens were given the temperature factor of the corresponding carbon. Cage hydrogens were not refined and only the coppers and phosphorus were given anisotropic temperature factors.

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(8) P. Gantzel and H. Hope, unpublished.

(9) W. R. Busing, K. O. Martin, and H. A. Levy, ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn.

(10) D. H. Templeton in "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 214, Table 3.3.2B.

(11) J. A. Ibers, ref 10, p 202, Table 3.3.1A.

(12) E. W. Hughes, *J. Am. Chem. Soc.*, 63, 1737 (1941).

(13) C. Scheringer, *Acta Cryst.*, 16, 546 (1963).

Table I. Final Positional and Thermal Parameters for $(C_6H_5)_3PCH_3Cu(C_2B_9H_{11})_2$

Atom	X/A^a	Y/B	Z/C	B (iso)^b
		First Icosahedron		
Cu	0.0	0.0	0.0	...
C(2)	0.1344 (21)	−0.1104 (15)	−0.0205 (11)	4.4 (5)
C(3)	0.0177 (19)	−0.1605 (14)	−0.0358 (10)	3.3 (5)
B(4)	−0.0789 (23)	−0.1031 (17)	−0.0836 (13)	3.4 (6)
B(5)	0.0253 (24)	−0.0096 (17)	−0.1063 (13)	3.5 (6)
B(6)	0.1427 (24)	−0.0055 (17)	−0.0531 (13)	3.6 (6)
B(7)	0.1147 (28)	−0.2051 (20)	−0.0773 (15)	5.2 (7)
B(8)	−0.0155 (27)	−0.1972 (19)	−0.1191 (15)	4.7 (7)
B(9)	−0.0082 (22)	−0.1071 (15)	−0.1622 (12)	2.4 (5)
B(10)	0.1246 (24)	−0.0453 (17)	−0.1480 (13)	3.6 (6)
B(11)	0.2141 (26)	−0.1000 (19)	−0.0892 (15)	4.5 (7)
B(12)	0.1095 (25)	−0.1608 (18)	−0.1611 (13)	3.9 (6)
		Second Icosahedron		
Cu*	0.0	0.5	0.0	...
C(2)*	−0.0467 (19)	0.4519 (14)	−0.1286 (11)	3.3 (5)
C(3)*	0.0618 (19)	0.5233 (14)	−0.1144 (11)	3.5 (5)
B(4)*	0.1559 (29)	0.5106 (21)	−0.0469 (17)	5.7 (8)
B(5)*	0.0969 (23)	0.4023 (16)	−0.0228 (13)	3.3 (6)
B(6)*	−0.0387 (26)	0.3738 (19)	−0.0691 (15)	4.7 (7)
B(7)*	0.0381 (28)	0.4519 (20)	−0.1884 (16)	5.2 (7)
B(8)*	0.1830 (27)	0.4881 (19)	−0.1374 (15)	4.7 (7)
B(9)*	0.2086 (23)	0.4061 (16)	−0.0863 (12)	3.1 (6)
B(10)*	0.0826 (29)	0.3207 (21)	−0.0985 (16)	5.8 (8)
B(11)*	−0.0188 (28)	0.3502 (21)	−0.1581 (16)	5.5 (7)
B(12)*	0.1384 (34)	0.3730 (26)	−0.1683 (20)	7.9 (10)
		Cation		
P	0.0331 (5)	0.2719 (3)	0.5881 (3)	...
Meth	0.1742 (20)	0.3148 (14)	0.6304 (11)	3.9 (5)

	Groups					
	X/A	Y/B	Z/C	ϕ^d	θ	ρ
Phen 1	−0.0452 (9)	0.0873 (7)	0.6430 (6)	2.38 (2)	1.97 (1)	−1.02 (2)
Phen 2	−0.1319 (9)	0.4128 (7)	0.6328 (5)	−0.63 (1)	−0.38 (1)	0.31 (1)
Phen 3	0.0312 (9)	0.2424 (6)	0.4268 (4)	−1.57 (1)	0.08 (1)	−1.57 (1)

[a] Estimated standard deviation of last significant figures in parentheses. [b] Cu, Cu,* and P temperature factors were refined anisotropically, and are given below.[c]

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	3.8 (3)	3.6 (2)	2.8 (2)	1.1 (2)	0.61 (2)	1.0 (2)
Cu*	4.0 (3)	3.3 (2)	3.8 (2)	1.0 (2)	0.2 (2)	−0.6 (2)
P	2.5 (4)	2.4 (2)	2.8 (3)	1.2 (2)	0.6 (2)	0.3 (2)

All temperature factors in units of (Å)^2, with $B_{ij} = 4b_{ij}/a_i{}^*a_j{}^*$ and $Tr = \exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{13} + 2klb_{23})]$. [c] The anisotropic thermal parameters will be inaccurate owing to strong correlation with the layer scale factors. [d] Angles in radians.

Table II. Derived Parameters for Phenyl Group Carbons

	X/A	Y/B	Z/C	B, Å^2
		Phenyl 1		
1	−0.0114	0.1685	0.6196	3.6 (5)
2	0.0132	0.1616	0.6880	5.2 (6)
3	−0.0207	0.0804	0.7114	5.6 (6)
4	−0.0791	0.0062	0.6664	5.6 (6)
5	−0.1036	0.0131	0.5980	6.9 (7)
6	−0.0697	0.0943	0.5746	5.4 (6)
		Phenyl 2		
1	−0.0641	0.3484	0.6124	3.6 (6)
2	−0.0330	0.4363	0.6000	4.9 (6)
3	−0.1008	0.5006	0.6204	6.1 (7)
4	−0.1997	0.4772	0.6532	5.6 (6)
5	−0.2308	0.3894	0.6656	6.6 (7)
6	−0.1631	0.3250	0.6452	5.4 (6)
		Phenyl 3		
1	0.0329	0.2561	0.4975	3.0 (5)
2	0.1357	0.2507	0.4673	3.4 (5)
3	0.1340	0.2370	0.3965	5.0 (6)
4	0.0296	0.2287	0.3560	3.8 (5)
5	−0.0732	0.2342	0.3863	3.8 (5)
6	−0.0716	0.2479	0.4570	2.6 (4)

The parameter shifts in the last cycle were a maximum of one-tenth of their estimated errors.

The final atom coordinates and temperature factors are given in Tables I and II. Table III is a listing of the observed and calculated structure factors.

The bond lengths, angles, and some best least-square planes are listed in Tables IV–VI. Standard deviations of the atom parameters were estimated from the diagonal elements of the inverted normal equation matrix in the usual way. Errors in derived quantities were calculated according to Cruickshank's method.[14] The atom labeling is the same for the tables and figures, except that on occasion a label is asteriated to symbolize the second chemically equivalent but crystallographically independent anion.

Discussion

There are no significant structural differences between this red bisdicarbollyl of copper(III) and the blue bisdicarbollyl of copper(II).[3]

Previously reported magnetic resonance data leave little doubt that the blue compound is formally copper-

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(14) D. W. J. Cruickshank and A. P. Robertson, *Acta Cryst.*, 6, 698 (1953).

Table III. Observed and Calculated Structure Amplitudes (× 2.52) for $(C_6H_5)_3PCH_3Cu(C_2B_9H_{11})_2$

K	L	FOBS	FCAL
****	H=	0	*****
2	0	206	205
4	0	480	489
6	0	168	137
8	0	315	348
10	0	117	121
12	0	159	184
-7	1	142	149
-5	1	179	164
-3	1	427	395
1	1	202	226
3	1	90	73
5	1	57	37
7	1	70	65
9	1	69	26
11	1	80	57
-12	2	227	246
-8	2	351	376
-6	2	129	140
-4	2	462	501
-2	2	429	379
0	2	799	649
2	2	232	230
4	2	195	185
6	2	177	184
8	2	178	182
10	2	189	205
-9	3	68	34
-7	3	44	52
-5	3	184	184
-3	3	78	72
-1	3	36	92
3	3	134	105
7	3	73	48
11	3	87	70
-12	4	173	198
-8	4	92	90
-6	4	133	124
-4	4	48	53
-2	4	232	233
0	4	595	572
2	4	100	103
6	4	110	148
8	4	156	169
10	4	104	124
-7	5	163	178
-5	5	138	126
-3	5	33	46
-1	5	30	27
1	5	221	203
5	5	61	95
9	5	93	79
11	5	84	33
-12	6	65	44
-8	6	79	81
-6	6	264	274
-2	6	470	453
0	6	188	181
4	6	143	175
6	6	247	252
8	6	166	164
-9	7	77	41
-7	7	69	75
-3	7	125	131
-1	7	230	212
5	7	82	95
9	7	87	97
11	7	114	109
-10	8	124	132
-8	8	111	108
-6	8	186	214
-4	8	264	254
-2	8	131	151
0	8	269	280
2	8	115	136
4	8	317	297
6	8	144	151
-9	9	101	109
-5	9	129	129
-3	9	100	97
-1	9	184	176
1	9	158	170
3	9	68	65
5	9	99	94
9	9	84	33
-12	10	67	36
-10	10	108	101
-8	10	90	77
-6	10	68	80
-4	10	189	179
0	10	260	240
2	10	128	137
4	10	144	159
8	10	91	90
10	10	87	63
-11	11	94	34
-9	11	153	176
-7	11	154	148
-3	11	65	44
5	11	77	54
-10	12	85	74
-8	12	166	154
-4	12	54	35
-2	12	109	109
0	12	157	174
2	12	104	79
4	12	84	92
8	12	114	106
-3	13	57	53
1	13	57	58
5	13	64	67
-6	14	81	49
-2	14	133	148
6	14	103	119
-3	15	88	90
3	15	92	36
-6	16	85	112
-4	16	146	159
-2	16	145	152
-2	18	115	116
****	H=	1	*****
-2	-17	98	93
4	-17	155	159
-3	-16	89	34
3	-16	87	79
5	-16	96	98
7	-16	69	86
-4	-15	183	195
-2	-15	86	90
0	-15	92	81
2	-15	110	113
4	-15	146	166
6	-15	125	110
8	-15	89	72
-5	-14	139	146
1	-14	115	83
7	-14	103	81
-8	-13	142	127
-6	-13	126	111
-4	-13	82	72
0	-13	109	112
2	-13	188	199
4	-13	60	85
6	-13	154	154
-1	-12	72	18
1	-12	71	74
3	-12	114	116
5	-12	99	95
7	-12	68	104
11	-12	90	76
-8	-11	105	91
-6	-11	107	125
-2	-11	121	115
2	-11	116	122
4	-11	92	102
6	-11	129	112
8	-11	62	35
-9	-10	88	15
-5	-10	160	162
-3	-10	68	43
-1	-10	110	118
1	-10	98	116
3	-10	145	154
5	-10	108	108
7	-10	155	172
9	-10	82	18
11	-10	106	78
-10	-9	166	174
-6	-9	166	180
-4	-9	179	179
-2	-9	174	172
2	-9	193	200
4	-9	224	236
6	-9	74	69
8	-9	120	133
12	-9	69	77
-11	-8	68	54
-9	-8	91	71
-7	-8	124	134
-5	-8	134	152
-3	-8	149	155
-1	-8	105	96
1	-8	255	236
3	-8	89	88
5	-8	107	92
7	-8	76	54
9	-8	78	48
-10	-7	111	91
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-8	8	138	134
-6	8	164	169
-4	8	165	144
0	8	103	124
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5	9	136	133
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-6	10	125	124
-4	10	90	96
-2	10	139	147
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3	11	87	71
5	11	92	43
7	11	113	108
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-8	12	175	182
-4	12	158	170
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0	12	160	193
2	12	152	152
4	12	92	106
6	12	104	88
-9	13	85	47
-7	13	92	70
-5	13	89	79
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-1	13	151	169
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3	13	83	104
-8	14	104	114
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2	14	124	115
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3	-14	84	111
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2	-13	96	115
6	-13	103	102
-1	-12	76	22
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-6	-11	90	98
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2	-11	114	118
4	-11	83	84
6	-11	97	110
8	-11	94	88
-9	-10	87	47
-3	-10	93	90
-1	-10	74	67
1	-10	52	58
5	-10	58	23
7	-10	108	122
-10	-9	118	125
-6	-9	145	175
-4	-9	275	279
-2	-9	122	120
0	-9	224	209
2	-9	146	142
4	-9	151	150
6	-9	83	88
8	-9	144	161
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-7	-8	102	101
-3	-8	82	63
-1	-8	58	47
1	-8	45	15
3	-8	90	83
9	-8	93	78
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-8	-7	226	249
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-4	-7	307	315
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0	-7	208	196
2	-7	140	133
4	-7	187	143
6	-7	86	79
8	-7	139	115
10	-7	150	146
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3	-6	61	38
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-10	-5	101	71
-6	-5	131	126
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-2	-5	214	197
2	-5	178	144
6	-5	203	208
8	-5	78	41
10	-5	136	118
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-5	-4	68	88
-3	-4	275	245
1	-4	103	86
3	-4	218	178
5	-4	67	41
11	-4	88	70
-12	-3	67	65
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-5	-2	20	15
-3	-2	83	101
-1	-2	75	108
1	-2	154	147
3	-2	68	49
7	-2	75	64
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-10	-1	164	168
-8	-1	128	113
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-2	-1	299	424
0	-1	148	232
2	-1	249	267
4	-1	102	102
6	-1	136	139
8	-1	160	149
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-9	0	104	91
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-5	0	39	4
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1	0	48	64
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4	1	200	206
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8	1	196	214
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4	3	177	192
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-1	4	131	129
1	4	29	5
9	4	66	48
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0	5	189	198
4	5	151	167
6	5	158	146
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-5	6	95	26
-1	6	31	13
1	6	44	9
3	6	116	134
7	6	79	59
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2	7	114	110
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6	7	112	113
8	7	67	65
-11	8	87	70
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1	8	73	61
3	8	43	43
7	8	79	89
-10	9	103	102
-8	9	95	97
-6	9	219	208
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4	9	116	108
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-1	10	125	117
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3	10	73	78
-10	11	140	151
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-6	11	139	150
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0	11	112	122
2	11	204	200
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-5	-9	83	79
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6	-6	113	103
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-7	-5	96	77
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3	-5	52	25
5	-5	169	148
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0	-4	227	247
2	-4	113	90
4	-4	269	254
6	-4	72	79
8	-4	224	271
-9	-3	77	75
-7	-3	66	78
-5	-3	54	47
-3	-3	221	214
-12	-2	67	76
-8	-2	146	139
-6	-2	190	167
-4	-2	351	337
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6	-2	93	84
8	-2	155	137
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-12	0	126	129
-10	0	73	64
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-6	0	183	145
-4	0	214	193
0	0	211	223
4	0	78	75
6	0	164	175
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-1	1	37	49
1	1	87	110
3	1	63	56
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-10	2	105	103
-8	2	142	161
-6	2	107	121
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6	2	175	195
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-10	4	67	78
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-11	5	60	54
-7	5	128	127
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-6	6	114	135
-4	6	49	42
-2	6	170	186
0	6	135	151
4	6	98	76
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-9	7	73	39
-7	7	51	58
-3	7	62	51
-1	7	62	35
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0	8	119	105
2	8	52	65
4	8	106	110
-7	9	113	130
-8	10	121	140
-6	10	79	63
-4	10	120	110
0	10	70	83
4	10	78	106
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-3	13	103	114
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1	-12	84	96
3	-12	79	48
5	-12	89	91
-6	-11	62	53
-2	-11	81	115
2	-11	58	47
4	-11	112	123
-7	-10	81	24
-3	-10	125	124
1	-10	54	20
3	-10	73	62
-8	-9	81	52
-6	-9	109	87
-4	-9	111	113
0	-9	109	94
2	-9	81	64
4	-9	126	129
-5	-8	86	50
-3	-8	49	67
1	-8	62	85
-8	-7	184	207
-4	-7	141	159
-2	-7	57	71
0	-7	222	201
2	-7	137	144
8	-7	81	78
-9	-6	78	12
-5	-6	71	43
-3	-6	55	32
1	-6	41	45
7	-6	77	51
-10	-5	115	112
-8	-5	114	113
-4	-5	146	164
-2	-5	203	189
0	-5	176	104
2	-5	192	179
6	-5	115	133
8	-5	80	85
-5	-4	119	99
-3	-4	86	93
-1	-4	100	114
-10	-3	84	66
-8	-3	48	26
-6	-3	157	131
-2	-3	80	113
0	-3	69	62
2	-3	131	132
6	-3	135	126
-11	-2	72	69
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-7	-2	74	9
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5	-2	65	33
7	-2	100	106
-10	-1	109	90
-6	-1	177	169
0	-1	106	153
2	-1	56	63
4	-1	79	84
6	-1	94	93
8	-1	87	105
-11	0	72	91
-7	0	54	15
-5	0	116	101
-3	0	150	168
3	0	86	97
-10	1	206	196
-8	1	135	117
-6	1	262	227
-4	1	145	155
-2	1	172	211
0	1	158	170
2	1	101	114
4	1	169	207
6	1	73	81
8	1	97	171
-11	2	79	57
-5	2	84	86
-3	2	104	158
-1	2	35	41
1	2	60	64
-10	3	131	139
-8	3	138	129
-6	3	384	157
-4	3	289	242
-2	3	49	37
0	3	177	161
2	3	106	99
4	3	135	148
6	3	58	46
-9	4	95	89
-3	4	47	93
-1	4	83	87
3	4	57	52
-8	5	148	180
-4	5	104	175
-2	5	74	59
0	5	196	196
2	5	86	86
4	5	55	30
6	5	86	102
-9	6	52	64
-5	6	158	128
-3	6	98	81
3	6	69	83
5	6	53	51
-10	7	55	24
-8	7	73	87
-4	7	43	93
-2	7	218	200
0	7	91	91
6	7	106	104
-9	8	55	35
-5	8	82	55
-1	8	46	26
-6	9	152	144
-2	9	144	127
0	9	50	66
4	9	86	38
-9	10	56	57
-5	10	67	93
-1	10	80	83
1	10	55	29
-6	11	148	151
-4	11	53	32
-2	11	69	53
0	11	54	51
-1	12	72	44

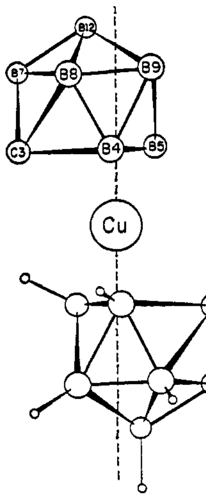

Figure 1. The $Cu(C_2B_9H_{11})_2^-$ anion viewed down its molecular twofold axis.

Table IV. Distances in $(C_6H_5)_3PCH_3Cu(C_2B_9H_{11})_2$

Cu–C(2)	2.50 (2)	Cu*–C(2)*	2.56 (2)
Cu–C(3)	2.51 (2)	Cu*–C(3)*	2.50 (2)
⟨Cu–C⟩ = 2.52			
Cu–B(4)	2.17 (3)	Cu*–B(4)*	2.11 (3)
Cu–B(5)	2.15 (3)	Cu*–B(5)*	2.04 (3)
Cu–B(6)	2.05 (3)	Cu*–B(6)*	2.18 (3)
⟨Cu–B⟩ = 2.11			
C(2)–C(3)	1.45 (3)	C(2)*–C(3)*	1.52 (3)
C(2)–B(6)	1.80 (3)	C(2)*–B(6)*	1.80 (4)
C(2)–B(7)	1.69 (4)	C(2)*–B(7)*	1.61 (4)
C(2)–B(11)	1.73 (4)	C(2)*–B(11)*	1.68 (4)
C(3)–B(4)	1.83 (3)	C(3)*–B(4)*	1.73 (4)
C(3)–B(7)	1.64 (4)	C(3)*–B(7)*	1.69 (4)
C(3)–B(8)	1.68 (4)	C(3)*–B(8)*	1.67 (4)
⟨C–B⟩ = 1.71			
B(4)–B(5)	1.86 (4)	B(4)*–B(5)*	1.83 (4)
B(4)–B(8)	1.81 (4)	B(4)*–B(8)*	1.85 (4)
B(4)–B(9)	1.83 (4)	B(4)*–B(9)*	1.90 (4)
B(5)–B(6)	1.67 (4)	B(5)*–B(6)*	1.74 (4)
B(5)–B(9)	1.71 (3)	B(5)*–B(9)*	1.89 (4)
B(5)–B(10)	1.60 (4)	B(5)*–B(10)*	1.80 (4)
B(6)–B(10)	1.89 (4)	B(6)*–B(10)*	1.84 (4)
B(6)–B(11)	1.87 (4)	B(6)*–B(11)*	1.80 (4)
B(7)–B(8)	1.72 (4)	B(7)*–B(8)*	1.88 (4)
B(7)–B(11)	1.89 (4)	B(7)*–B(11)*	1.80 (4)
B(7)–B(12)	1.89 (4)	B(7)*–B(12)*	1.88 (5)
B(8)–B(9)	1.72 (4)	B(8)*–B(9)*	1.77 (4)
B(8)–B(12)	1.79 (4)	B(8)*–B(12)*	1.77 (5)
B(9)–B(10)	1.67 (4)	B(9)*–B(10)*	1.79 (4)
B(9)–B(12)	1.72 (4)	B(9)*–B(12)*	1.75 (5)
B(10)–B(11)	1.88 (4)	B(10)*–B(11)*	1.77 (5)
B(10)–B(12)	1.73 (4)	B(10)*–B(12)*	1.81 (5)
B(11)–B(12)	1.86 (4)	B(11)*–B(12)*	1.85 (5)
⟨B–B⟩ = 1.80			
P–meth	1.79 (2)	P–phen-1	1.80 (2)
P–phen-2	1.80 (2)	P--phen-3	1.79 (2)

(II).[3] The diamagnetism of the red compound can only be explained on the basis of its containing copper(III). Although a very light atom could certainly have been missed in the present study, the presence of a proton or other singlet cation would lead to the wrong magnetic properties.

The $Cu(C_2B_9H_{11})_2^-$ ions have C_{2h} symmetry by virtue of a slip distortion (Figure 1) which places the copper closer to the ligand borons (2.11 Å) than carbons (2.52 Å).

Table V. Selected Bond Angles in $(C_6H_5)_3PCH_3Cu(C_2B_9H_{11})_2$

Anion					
Angle	Degrees Cage 1	Degrees Cage 2	Angle	Degrees Cage 1	Degrees Cage 2
C(2)–B(7)–B(11)	57	59	B(11)–B(10)–B(6)	59	60
B(7)–B(11)–C(2)	55	55	B(10)–B(6)–B(11)	60	58
B(11)–C(2)–B(7)	67	66	B(6)–C(2)–B(11)	64	62
C(2)–B(7)–C(3)	52	55	C(2)–B(11)–B(6)	60	62
B(7)–C(3)–C(2)	66	60	B(11)–B(6)–C(2)	56	55
C(3)–C(2)–B(7)	62	65	B(7)–B(8)–B(12)	65	62
C(3)–B(8)–B(7)	58	56	B(8)–B(12)–B(7)	55	62
C(8)–B(7)–C(3)	60	56	B(12)–B(7)–B(8)	59	56
B(7)–C(3)–B(8)	62	68	B(8)–B(9)–B(12)	63	60
C(3)–B(4)–B(8)	55	55	B(9)–B(12)–B(8)	59	60
B(4)–B(8)–C(3)	63	59	B(12)–B(8)–B(9)	58	59
B(8)–C(3)–B(4)	62	66	B(9)–B(10)–B(12)	61	58
B(4)–B(9)–B(8)	61	61	B(10)–B(12)–B(9)	58	60
B(9)–B(8)–B(4)	62	63	B(12)–B(9)–B(10)	61	62
B(8)–B(4)–B(9)	56	56	B(10)–B(11)–B(12)	55	60
B(4)–B(5)–B(9)	61	61	B(11)–B(12)–B(10)	63	58
B(5)–B(9)–B(4)	63	58	B(12)–B(10)–B(11)	62	62
B(9)–B(4)–B(5)	55	61	B(11)–B(7)–B(12)	59	61
B(5)–B(10)–B(9)	63	63	B(7)–B(12)–B(11)	60	58
B(10)–B(9)–B(5)	57	59	B(12)–B(11)–B(7)	61	62
B(9)–B(5)–B(10)	61	58	C(2)–Cu C(3)	34	35
B(5)–B(6)–B(10)	53	60	C(3) Cu B(4)	45	43
B(6)–B(10)–B(5)	56	57	B(4) Cu B(5)	51	52
B(10)–B(5)–B(6)	71	63	B(5) Cu B(6)	47	49
B(6)–B(11)–B(10)	61	62	B(6) Cu C(2)	45	44

Cation			
Angle	Degrees	Angle	Degrees
Meth–P C(11)	105	C(11)–P–C(21)	109
Meth–P C(21)	109	C(11)–P–C(31)	112
Meth–P C(31)	112	C(21)–P–C(31)	109

Table VI. Some Best Least-Squares Planes in the $Cu_2(C_2B_9H_{11})_2^-$ Ion. Orthogonal Coordinates[a]

Atom	Distance from plane, Å	Atom	Distance from plane, Å
Plane 1		Plane 2	
(Cu, B(5), B(7), B(12))		(Cu*, B(5)*, B(7)*, B(12)*)	
Cu	0.000	Cu*	0.003
B(5)	0.000	B(5)*	−0.044
B(7)	0.000	B(7)*	−0.054
B(12)	0.000	B(12)*	0.081
C(2)	0.77	C(2)*	−0.77
C(3)	−0.68	C(3)*	0.75
B(4)	−1.46	B(4)*	1.40
B(6)	1.31	B(6)*	−1.41
B(9)	−0.92	B(9)*	0.93
B(10)	0.74	B(10)*	−0.96
B(8)	−1.35	B(8)*	1.45
B(11)	1.49	B(11)*	−1.43
Plane 3		Plane 4	
(C(2), C(3), B(4), B(5), B(6))		(C(2)*, C(3)*, B(4)*, B(5)*, B(6)*)	
C(2)	−0.039	C(2)*	−0.020
C(3)	−0.029	C(3)*	−0.028
B(4)	0.100	B(4)*	0.072
B(5)	−0.146	B(5)*	−0.075
B(6)	0.122	B(6)*	0.056
Cu	1.705	Cu*	1.681
B(7)	−1.47	B(7)*	−1.38
B(8)	−1.41	B(8)*	−1.46
B(9)	−1.51	B(9)*	−1.64
B(10)	−1.54	B(10)*	−1.60
B(11)	−1.44	B(11)*	−1.41
B(12)	−2.45	B(12)*	−2.46

[a] Plane 1: $0.918X + 0.320Y + 0.233Z = 0.000$. Plane 2: $0.806X + 0.573Y + 0.145Z = 4.382$. Plane 3: $-0.364Z + 0.443Y + 0.820Z = 1.705$. Plane 4: $-0.522Z + 0.524Y + 0.672Z = 2.332$.

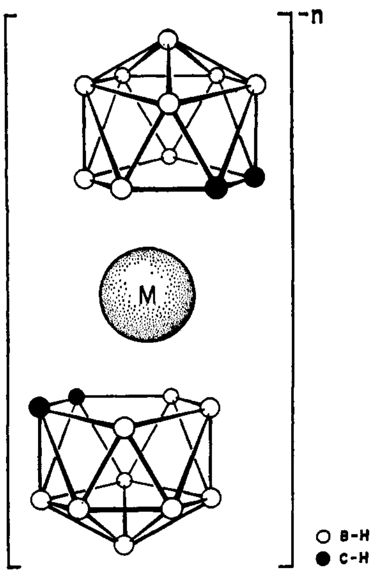

Figure 2. An idealized drawing of the "π-allyl-like" metallobis(dicarbollyls): M = Cu(II), n = 2; M = Cu(III), n = 1; M = Ni(II), n = 2; M = Au(III), n = 1.

Again the shrinkage of the dicarborane C–C bond from that observed in the symmetrical sandwich compounds is evident. We have gathered in Table VII some of the critical bond lengths determined for several transition metal carboranes. The symmetrical π-sandwich compounds are characterized by a reasonably constant distance from the five carborane face atoms to the metal and a C–C (carborane) bond length of *ca.* 1.6 Å.

Table VII. Some Selected Bond Lengths in Transition Metal Carbollyls

	Distance, Å			
Compound	M–cage ⊥	⟨M–C⟩[f]	⟨M–B⟩[g]	C–C
$C_5H_5FeC_2B_9H_{11}$[a]	1.47	2.04	2.09	1.58
$(CO)_3ReC_2B_9H_{11}^-$[b]	. . .	2.31	2.34	1.61
$Co(C_2B_9H_{11})_2^-$[c] disorder	1.47	(2.07)		. . .
$Cu(C_2B_9H_{11})_2^{2-}$[d]	1.79	2.57	2.20	1.53
$Cu(C_2B_9H_{11})_2^-$[e]	1.70	2.52	2.11	1.49[g]

[a] Reference 7. [b] A. Zalkin, T. E. Hopkins, and D. H. Templeton, *Inorg. Chem.*, **5**, 1189 (1966). [c] A. Zalkin, T. E. Hopkins, and D. H. Templeton, *ibid.*, **6**, 1911 (1967). [d] Reference 3. [e] This study. [f] Average of three distances. [g] Average of two distances.

Upon distortion the metal–boron distances shrink, and the metal–carbon distances rise accordingly with a concomitant shortening in the carborane C–C bond to *ca.* 1.5 Å.

In this study we have shown that Cu(III) forms a highly distorted bis (π-allylic) type sandwich compound with the dicarbollyl dianion and that the Au(III) compound is isomorphous. In addition $(Et_4N)_2Ni(C_2B_9H_{11})_2$ is isomorphous with the previously characterized Cu(II) bisdicarbollyl complex. Thus we now know of four examples of the slip-distorted structure as depicted in Figure 2.

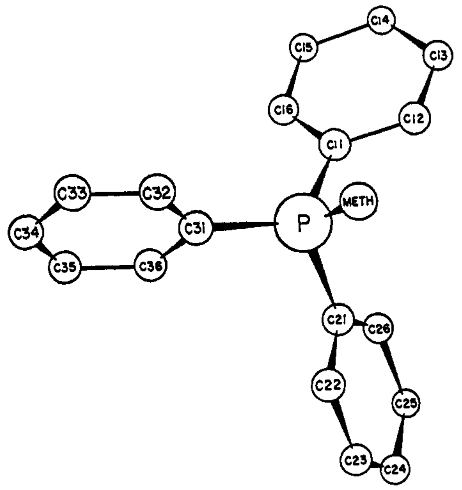

Figure 3. The triphenylmethylphosphonium ion viewed approximately down its threefold axis.

It has also been established that the Ni(III) bis((3)-1,2-dicarbollyl) assumes the symmetrical π-sandwich configuration.[15]

In the dark colored, red Au(III) and Cu(III) and blue Cu(II) compounds the optical dichroism is such that maximum absorption occurs with the electric vector perpendicular to the twofold axis of the idealized C_{2h} anion, and the absorption is zero or very small when the electric vector is lined up parallel to the twofold axis. This, plus the large molar extinction coefficients for these absorptions (~5000 for the blue Cu(II)),[2b,16] imply that they are charge-transfer bands. The light green paramagnetic Ni(II) compound has its maximum absorption with the light polarized parallel to the molecular twofold axis.

The triphenylmethylphosphonium ion is very nearly a perfect tetrahedron with ⟨P–C⟩ = 1.795 Å and all C–P–C angles within two standard deviations (4°) of being tetrahedral. The over-all symmetry is approximately C_{3v} with the phenyl rings being oriented in the expected propellor-like arrangement (Figure 3).

There are 14 contacts between the separate ions of about 3.85 Å, all other packing contacts being in excess of 4.0 Å. These distances are commensurate with the van der Waals radii of the atoms involved, so there is no reason to suspect packing forces as the origin of the observed distortion of the carbametallic anion.

Summary and Conclusions

Bisdicarbollyls have been synthesized and characterized now for most of the oxidation states of the first-row transition metals. The known compounds are arranged in Table VIII according to their metal d electronic configurations.

We define as electron-rich metalloaromatics those compounds in which the metal (in its formal valence state) has electrons beyond the d^6 configuration. With the exception of Ni(III), the characterized compounds of

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(15) (a) Private communication from Professor Galen Stucky, University of Illinois. (b) Also this salt has been shown to be isomorphous with the corresponding Co(III) compound which, as the cesium salt, was established to be a symmetrical π sandwich: A. Zalkin, T. E. Hopkins, and D. H. Templeton, *Inorg. Chem.*, **6**, 1911 (1967).

(16) L. F. Warren, private communication.

Table VIII. Bis((3)-1,2 dicarbollyl)s of the 3d Transition Metals[a]

Symmetrical π sandwich			Distorted π-allyls	
d^5	d^6	d^7	d^8	d^9
	Fe^{II}	Co^{II}	Ni^{II}	Cu^{II}
Fe^{III}	Co^{III}	Ni^{III}	Cu^{III}	
	Ni^{IV}			

[a] Italicized ions form bis(dicarbollyl)s of unknown structure.

this classification are distorted *via* a slip deformation (*vide supra*). Further, all the characterized complexes with six or less metal d electrons are symmetrical π sandwiches.

This slip distortion is not observed for the analogous metallocenes, all of which are symmetrical,[17] but we feel it is to be expected for the "*ortho*" or (3)-1,2-dicarbollyls as a consequence of the heterocyclic nature of the ligand.

Thus experimentally we have seen the qualitative boundary beyond which distortion takes place and observe that both electron richness plus ligand asymmetry are required.

A noncarborane example of a slip-distorted, electron-rich metalloaromatic is the bridged naphthalene (10 π electron) complex of chromium tricarbonyl.[18] The aromatic ligand is quite unsymmetrical, possessing only a mirror plane. It is slipped within this mirror such that only one of its two equivalent benzenoid-like ends is associated with the chromium tricarbonyl moiety.

Another way in which metalloaromatics can be forced to distort is by introducing the asymmetry directly onto the metal atom. Situations of this sort have been discussed by Mason, *et al.*,[19,20] We are presently investigating this phenomenon further, both experimentally and theoretically, in an effort to find the thresholds for, and the energetics of, distortion in electron-rich metalloaromatics.

Acknowledgments. I wish to thank Professor M. Frederick Hawthorne for providing the metallocarborane crystals and for stimulating conversations regarding the properties and chemistry of these interesting materials. Thanks are due to Mr. L. F. Warren for his contributions, material and intellectual, and especially for his persistence in crystallizing and recrystallizing the many compounds used in this study. Mr. H. P. Calhoun aided by collecting the crystal data for $(C_6H_5)_3PCH_3Co(C_2B_9H_{11})_2$. The computation center at Riverside generously made available many hours of time on the IBM 7040.

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(17) E. Weiss and E. O. Fisher, *Z. Anorg. Allgem. Chem.*, **278**, 219 (1955).

(18) P. E. Baikie and O. S. Mills, *Chem. Commun.*, 683 (1966).

(19) M. J. Bennett, M. R. Churchill, M. Gerloch, and R. Mason' *Nature*, **201**, 1318 (1964).

(20) R. Mason and G. B. Robertson in "Advances in Structure Research by Diffraction Methods," Vol. 2, Interscience Publishers, New York, N. Y., 1966, pp 35–74.